

Surface engineering and photophysics of InP/ZnS quantum dots for photocatalytic application

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Surface engineering and photophysics of InP/ZnS quantum dots for photocatalytic application

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Ph.D. Thesis Department of Chemistry Technical University of Denmark February 2023

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Ph.D. Thesis

February 28th, 2023

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Preface and acknowledgment

My life as a Ph.D. student is coming to the end, all the experience full of happiness, distress, and surprise, during the project is visible before my eyes. After recalling three years of study at Chemistry department, Technical University of Denmark (DTU), it has been meaningful and eventful for me that I will never forget in my whole life.

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The end is another beginning of life, I will keep going with loves from who I love and who loves me.

Qian Zhao

February 2023, Lyngby Denmark.

Contributions during PhD project

The thesis is mainly based on the following papers.

I. Inorganic ligands-mediated hole attraction and surface structural reorganization in InP/ZnS QD photocatalysts studied via ultrafast visible and midinfrared spectroscopies (Chapter 3)

Yang Liu, Ying Zhou, Mohamed Abdellah, Weihua Lin, Jie Meng, <u>Qian Zhao</u>, Shan Yu, Zhanghui Xie, Qinying Pan, Fengying Zhang, Tonu Pullerits and Kaibo Zheng.

Sci China Mater 2022, 65(9): 2529-2539

II. Multi-electron Donation Promotes the Photocatalytic Conversion of Carbon Dioxide to Methane in a Covalent Bonded Metal-complex/Quantum Dots Hybrid Catalyst. (Chapter 4)

<u>Qian Zhao</u>, Mohamed Abdellah, Yang Liu, Jie Meng, Xianshao Zou, Kasper Enemark-Rasmussen, Yuehan Cao, Yijiang Chen, Ying Zhou, Tonu Pullerits, Sophie E. Canton, Hong Xu, and Kaibo Zheng.

Manuscript to be submitted.

III. Size-dependent Multi-electron Donation in Metal-complex Quantum Dots Hybrid

Catalyst for Photocatalytic conversion of Methane. (Chapter 5)

<u>Qian Zhao</u>, Mohamed Abdellah, Yuehan Cao, Jie Meng, Xianshao Zou, Kasper Enemark-Rasmussen, Yijiang Chen, Hengli Duan, Qinyin Pan, Ying Zhou, Yuran Niu, Tonu Pullerits, Sophie E. Canton, and Kaibo Zheng.

Manuscript to be submitted.

My contribution to the papers

My works in chapter 3 mainly focus on the literature review and sample synthesis, while in chapters 4 and 5, I performed the photocatalytic system design, sample synthesis, structural characterizations, supervised spectroscopy experiments and data analysis, manuscript writing.

Other Publications not included in this thesis

(1) Mingli Liang, Weihua Lin, Qian Zhao, Jun Li, Lin Zhu, Brice Sarpi, Alexei Zakharov, Ivan G Scheblykin, Tönu Pullerits, Yuran Niu, Sophie E Canton, Kaibo Zheng. Spatially Resolved Local Electronic Properties of 2D Lead Halide Perovskite Single Crystals Studied by X - Ray Photoemission Electron Microscopy. Sol. RRL 2023, 7, 2200795.

(2) Sol Laura Gutierrez Alvarez, Christina Basse Riel, Mahtab Madani, Mohamed Abdellah, Qian Zhao, Xianshao Zou, Tonu Pullerits, Kaibo Zheng. Morphology-Dependent One- and Two-Photon Absorption Properties in Blue Emitting CsPbBr₃ Nanocrystals. J. Phys. Chem. Lett. 2022, 13, 22, 4897–4904.

(3) A Goyal, E Andrioti, Y Tang, Q Zhao, K Zheng, KD Newell, P Schall. Mechanochemical synthesis of stable, quantum-confined CsPbBr₃ perovskite nanocrystals with blue-green emission and high PLQY. J. Phys. Mater. 2022, 5 024005.

(4) Mingli Liang, Weihua Lin, Zhenyun Lan, Jie Meng, Qian Zhao, Xianshao Zou, Ivano E Castelli, Tonu Pullerits, Sophie E Canton, Kaibo Zheng. Electronic structure and trap states of two-dimensional ruddlesden-popper perovskites with the relaxed Goldschmidt tolerance factor. ACS Appl. Electron. Mater. 2020, 2, 5, 1402–1412.

(5) Qinying Pan, Mohamed Abdellah, Yuehan Cao, Weihua Lin, Yang Liu, Jie Meng, Quan Zhou, Qian Zhao, Xiaomei Yan, Zonglong Li, Hao Cui, Huili Cao, Wenting Fang, David Ackland Tanner, Mahmoud Abdel-Hafiez, Ying Zhou, Tonu Pullerits, Sophie E Canton, Hong Xu, Kaibo Zheng. Ultrafast charge transfer dynamics in 2D covalent organic frameworks/Re-complex hybrid photocatalyst. Nat Commun 2022, 13, 845.

(6) Jie Meng, Zhenyun Lan, Weihua Lin, Mingli Liang, Xianshao Zou, Qian Zhao, Huifang Geng, Ivano E Castelli, Sophie E Canton, Tönu Pullerits, Kaibo Zheng. Optimizing the quasi-equilibrium state of hot carriers in all-inorganic lead halide perovskite nanocrystals through Mn doping: fundamental dynamics and device perspectives Chem. Sci., 2022, 13, 1734-1745.

(7) Shuang Yu, Jie Meng, Qinying Pan, Qian Zhao, Tõnu Pullerits, Yingguo Yang, Kaibo Zheng, Ziqi Liang. Imidazole additives in 2D halide perovskites: impacts of –CN versus – CH_3 substituents reveal the mediation of crystal growth by phase bufferingEnergy Environ. Sci., 2022, 15, 3321-3330.

(8) Weihua Lin, Mingli Liang, Yuran Niu, Zhesheng Chen, Marie Cherasse, Jie Meng, Xianshao Zou, Qian Zhao, Huifang Geng, Evangelos Papalazarou, Marino Marsi, Luca Perfetti, Sophie E Canton, Kaibo Zheng, Tönu Pullerits. Combining two-photon photoemission and transient absorption spectroscopy to resolve hot carrier cooling in 2D perovskite single crystals: the effect of surface layer. J. Mater. Chem. C, 2022, 10, 16751-16760.

(9) Mingli Liang, Weihua Lin, Qian Zhao, Xianshao Zou, Zhenyun Lan, Jie Meng, Qi Shi, Ivano E Castelli, Sophie E Canton, Tonu Pullerits, Kaibo Zheng. Free carriers versus selftrapped excitons at different facets of ruddlesden–popper two-dimensional lead halide perovskite single crystals. J. Phys. Chem. Lett. 2021, 12, 20, 4965–4971.

Abstract

Photocatalytic H₂ evolution from water splitting by using quantum dots is an encouraging way to tackle the energy shortage. On the other hand, conversion of CO₂ to chemical fuels by photocatalytic approach is also regarded as a promising solution to simultaneously address both energy crisis and environmental issues, high-efficient photocatalytic materials are therefore developed and investigated. Among them, $Re(bpy)(CO)_{3}L$ (bpy = 2.2'-bipyridine, L = halogen atom) and their derivative attract tremendous attention on photocatalytic reduction CO_2 applications due to 1) ultralong lifetime of excited triplet metal-to-ligand charge transfer (³MLCT)state allows photoinduced electrons transfer to catalytic site efficiently, 2) transition metal center can fix CO_2 molecule onto itself easily, 3) band alignment can be tuned by modification of bpy moiety where can also store oneelectron-reduced species. However, transition metal complex photocatalyst suffers from insufficient visible light absorption and difficult multi-electron accumulation due to inevitable triplet-triplet annihilation. In this case, we employed heavy-metal free colloidal quantum dot InP/ZnS as photosensitizer to achieve robust light absorption at the visible range, multi-electron transfer process, finally realized photocatalytic conversion of CO₂ to 8-electron product methane. In this context, surface engineering and typical photophysical properties affected by the introduction of InP/ZnS QDs for photocatalytic applications were systematically investigated in this thesis for understanding the excited dynamics of heterostructure photocatalytic systems involving InP/ZnS QDs.

In the first work of thesis, we studied the photoinduced charge carriers dynamics in InP/ZnS QDs engineered by a series of inorganic ligands (S^{2^-} , Cl^- , and $PO4^{3^-}$) and organic ligand (oleylamine) by time-resolved spectroscopies (transient absorption (TA) spectroscopy, time-resolved midinfrared (TRIR) spectroscopy and time-resolved photoluminescence (TRPL)) Complementary with TA and TRPL, we confirmed the ultrafast hole transfer from InP/ZnS to surface ligand. Strikingly, QDs capped with S^{2^-} exhibited fast hole injection time and long-lived hole lifetime at S^{2^-} determined to be 4.2 ps and >4.5 ns respectively. S^{2^-} ligand also can remove electrostatically attached surfactants (NMF) to compensate for the spatial charge redistribution and balance the ionic radii and net charge to create an optimal condition for charge transfer. Such conditions are beneficial to prohibit excellent photocatalytic H₂ evolution (213 µmol/mg

within 10 h), which elucidates the crucial role of surface ligand in the photocatalytic activities of colloidal QDs.

In the second work, we introduced InP/ZnS as photosensitizer and linked with $Re(bpy)(CO)_3Br$ photocatalyst by covalent bond. Possible multi-electron donation within the specific QD/transition metal complex hybrid photocatalyst system was confirmed when multiple photocatalysts were attached to one QD. After basic structural characterization, the time-dependent density functional theory (TD-DFT) calculation presented an unconventional electronic structure, photoexcited electrons directly resided on the bpy moiety of Re-catalyst, and exhibited efficient exciton delocalization and separation. Transient absorption and infrared spectroscopy revealed the ultrafast multi-electron transfer on two-attachment mode to be shorter than one picosecond, while excited holes were delocalized on QD with an ultralong lifetime, which guaranteed excellent multi-electron donation during photocatalytic reactions. Accordingly, such multiple photocatalyst attachment exhibited significant catalytic activity on photocatalytic reduction of CO_2 to 8-electron product methane. This work provides a new strategy to control photocatalytic products via multi-electron donation pathway tuned by attached molecules.

In the last work, we employed the same QD/transition metal complex structure but modified the multi-electron transfer driving force by tuning the band alignment of QDs, Re-catalyst covalently tethered to QDs with three different sizes were therefore prepared due to the electronic structure of QDs is size-tunable. Similar to the second work, after basic characterization, transient absorption demonstrated the smallest QDs exhibited efficient multi-electron transfer to be short than one picosecond due to the large electron transfer driving force, ultrafast multi-electron injection prevented the Auger recombination and annihilation process. Finally, photocatalytic reduction of CO_2 to methane can only be achieved by the smallest QDs with two catalysts attachment mode. This work demonstrated that the driving force dominates the multi-electron transfer process and consider as a guidance for engineering the photocatalytic performance of CO_2 reduction, as well as the product selectivity.

Abstract-Danish

Fotokatalytisk H₂-udvikling fra vandspaltning ved brug af kvanteprikker er en opmuntrende måde at tackle energimanglen på. På den anden side betragtes konvertering af CO₂ til kemiske brændstoffer ved fotokatalytisk tilgang også som en lovende løsning til samtidig at løse både energikrise og miljøproblemer, højeffektive fotokatalytiske materialer udvikles og undersøges derfor. Blandt dem tiltrækker $\operatorname{Re}(bpy)(CO)_{3L}$ (bpy = 2,2'-bipyridin, L = halogenatom) og deres derivat enorm opmærksomhed på fotokatalytisk reduktion af CO₂ på grund af 1) ultralang levetid for exciteret triplet metal-til- ligand ladningsoverførsel (3MLCT) tilstand tillader fotoinduceret elektronoverførsel til katalytisk sted effektivt, 2) overgangsmetalcenter kan nemt fiksere CO₂-molekyle på sig selv, 3) båndjustering kan indstilles ved modifikation af bpy-del, hvor der også kan lagre en-elektron-reduceret arter. Overgangsmetalkompleks fotokatalysator lider imidlertid af utilstrækkelig absorption af synligt lys og vanskelig multielektronakkumulering på grund af uundgåelig triplet-triplet udslettelse. I dette vi tungmetalfri kolloid kvantepunkt InP/ZnS tilfælde brugte som fotosensibilisator for at opnå robust lysabsorption i det synlige område, multielektronoverførselsproces, endelig realiseret fotokatalytisk omdannelse af CO₂ til 8-elektronproduktmetan. I denne sammenhæng blev overfladeteknik og typiske fotofysiske egenskaber påvirket af introduktionen af InP/ZnS QD'er til fotokatalytiske applikationer systematisk undersøgt i denne afhandling for at forstå den exciterede dynamik af heterostrukturfotokatalytiske systemer, der involverer InP/ZnS QD'er.

I det første afhandlingsarbejde undersøgte vi den fotoinducerede ladningsbærers dynamik i InP/ZnS QD'er konstrueret af en række uorganiske ligander (S²⁻, Cl⁻ og PO4³⁻) og organisk ligand (oleylamin) ved tidsopløste spektroskopier (transient absorption (TA) spektroskopi, tidsopløst midinfrarød (TRIR) spektroskopi og tidsopløst fotoluminescens (TRPL)) Komplementært med TA og TRPL bekræftede vi den ultrahurtige huloverførsel fra InP/ZnS til overfladeligand. Påfaldende nok udviste QD'er, der var dækket med S²⁻, hurtig hulindsprøjtningstid og langtidsholdbar hullevetid ved S²⁻ bestemt til at være henholdsvis 4.2 ps og >4,5 ns. S²⁻ ligand kan også fjerne elektrostatisk vedhæftede overfladeaktive stoffer (NMF) for at kompensere for den rumlige ladningsomfordeling og balancere de ioniske radier og nettoladningen for at

Х

skabe en optimal betingelse for ladningsoverførsel. Sådanne forhold er gavnlige til at forhindre fremragende fotokatalytisk H₂-udvikling (213 μmol/mg inden for 10 timer), hvilket belyser overfladeligandens afgørende rolle i de fotokatalytiske aktiviteter af kolloide QD'er.

I det andet arbejde introducerede vi InP/ZnS som fotosensibilisator og forbundet med Re(bpy)(CO)₃Br fotokatalysator ved kovalent binding. Mulig multielektrondonation inden for det specifikke QD/overgangsmetalkomplekshybridfotokatalysatorsystem blev bekræftet, når flere fotokatalysatorer blev knyttet til en QD. Efter grundlæggende strukturel karakterisering præsenterede den tidsafhængige densitetsfunktionelle teori (TD-DFT) beregning en ukonventionel elektronisk struktur, fotoexciterede elektroner befandt sig direkte på bpy-delen af Re-katalysator og udviste effektiv exciton-delokalisering og separation. Forbigående absorption og infrarød spektroskopi afslørede, at den ultrahurtige multi-elektronoverførsel på tovedhæftningstilstand var kortere end et picosekund, mens exciterede huller blev delokaliseret på QD med en ultralang levetid, hvilket garanterede fremragende multi-elektrondonation under fotokatalytiske reaktioner. Følgelig udviste en sådan multipel fotokatalysatorvedhæftning betydelig katalytisk aktivitet på fotokatalytisk reduktion af CO2 til 8-elektronproduktmethan. Dette arbejde giver en ny strategi til at kontrollere fotokatalytiske produkter via multielektrondonationsvej tunet af vedhæftede molekyler.

I det sidste arbejde brugte vi den samme QD/overgangsmetalkompleksstruktur, men modificerede multi-elektronoverførselsdrivkraften ved at indstille båndjusteringen af QD'er, Re-katalysator kovalent bundet til QD'er med tre forskellige størrelser blev derfor forberedt på grund af den elektroniske strukturen af QD'er er størrelsesjusterbar. I lighed med det andet arbejde, efter grundlæggende karakterisering, viste transient absorption, at de mindste QD'er udviste effektiv multi-elektronoverførsel til at være kortere end et picosekund på grund af den store elektronoverførselsdrivkraft, ultrahurtig multielektroninjektion forhindrede Auger-rekombinations- og annihilationsprocessen. Endelig kan fotokatalytisk reduktion af CO_2 til metan kun opnås med de mindste QD'er med to katalysatorer vedhæftningstilstand. Dette arbejde demonstrerede, at drivkraften dominerer multi-elektronoverførselsprocessen og betragter som en vejledning til konstruktion af den fotokatalytiske ydeevne af CO_2 -reduktion, såvel som produktselektiviteten.

Abbreviations

PS. Photosensitizer QD: quantum dot MLCT: Metal to ligand charge trasnfer ISC: Intersystem crossing HOMO: Highest occupied molecular orbital DFT: Density functional theory **TEOA:** Triethanolamine ACN: Acetonitrile DMF: Dimethylformamide SCE: Standard calomel electrode **OER:** One-electron-reduction TOF: turnover frequency **KIE**: Kinetic isotope effects TTA: Triplet-triplet annihilation MOFs: Metal-organic frameworks COFs: Covalent organic frameworks **CB**: Conduction band UV: ultraviolet PET: photoinduced electron transfer LUMO: Lowest unoccupied molecular orbital TA: transient absorption PL: photoluminescence IQE: Internal quantum efficiency AugR: Auger recombination MV: Methyl viologen TRIR: Time-resloved infrared absorption spectroscopy NMR: Nuclear magnetic resonance XPS: X-ray photoelectron spectroscopy XII

UPS: Ultraviolet photoelectron spectroscopy

GC: Gas chromatograph

CCD: Charge-coupled device

OPA: Optical parametric amplifier

HWP: half-wave plate

GSB: Ground state bleach

ESA: Excited state absorption

PIA: Photoinduced absorption

IR: Infrared

RF: Radiofrequency

BE: binding energy

KE: Kinetic energy

VBM: Valence band maximum

CBM: Conduction band minimum

CTS: Charge transfer state

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Chapter 1 Introduction

Deforestation, excessive consumption of fossil fuels, industrial revolution and other human activity have significantly disorganized the natural carbon cycle on our planet due to substantial amounts of CO₂ released into the atmosphere. With the increasing concentration of atmospheric CO₂ (increased with an average growth of 2 ppm per year, already exceeding 419 ppm in January 2023) ^{1,2}, the influence of these kinds of greenhouse gas cannot be ignored currently. A series of environment issues including climate changes and ocean acidification ^{3,4} has caused severe global warming. In addition, seeking efficient and sustainable energy supplements is also one of the biggest challenges for human beings due to 4.58×10^{20} J of global annual energy consumption. Unfortunately, around 85% of demanding energy has been obtained from fossil fuels, As an enormous energy source, the sun provides an average intensity of 4.93 MJ/m² for the earth with the usable energy of 3×10^{24} J per year, which exceeds more than 10000 times of global energy demanding^{1,5}. In this scenario, capturing the abundant CO₂ from atmosphere and converting them to chemical fuels as storage of solar energy may is an ideal scenario to combat both crises of energy and environment.

Photocatalyst, a kind of material that can absorb light to trigger the catalytic reaction, has been considered a 'green' way to achieve the conversion of solar energy to chemical energy. Among various photocatalysts, metals, and semiconductors exhibit good stability and activity but suffer from poor product selectivity. Conversely, enzymes show excellent turnover efficiency and product selectivity, but their poor stability and restricted operative conditions limited their large-scale applications. The transition metal complexes occurred as another promising type of photocatalysts. The richness of 6d-orbital on transition metal enables complexes to easily capture gas molecule surrounding them, while its organic ligands are convenient to tune the electronic state structure of the complex. Re(bpy)CO₃L ((bpy = 2,2'-bipyridine), L = halogen atoms) is an emerging transition metal complex photocatalyst, which often displays extraordinary product

selectivity good stability and activity^{6,7}, however, inefficient light absorption at visible range restrains photocatalytic performance⁸.In order to tackle the above bottleneck, employing photosensitizer (PS) as electron donor or reservoir to Re(bpy) is a promising approach^{9,10}. The photoinduced electron transfer (single electron or multi-electron transfer) from PS to Re(Bpy) therefore dominates the photocatalytic reactions performance. Therefore, investigation and understanding of detailed information on the electron transfer process are also necessary for the high-efficient photocatalytic system design and applications.

In this chapter, the advantages of Re(bpy) in photocatalytic reduction of CO_2 are discussed. Besides that, the fundamentals of critical excited state dynamics for photocatalytic CO_2 reduction including electron transfer and the multi-electron accumulation dynamics are also briefly introduced.

1.1 Re(bpy) complex for photocatalytic application

Since fac-Re(bpy)(CO)₃Cl (bpy = 2,2'-bipyridine) catalyst was first reported by Lehn⁹ and coworkers in 1985, they represented an unusual process of artificial photosynthesis and solar energy storage and conversion. Moreover, this kind of transition metal organometallic complex plays a vital role in photocatalytic reduction of CO₂ applications as both photocatalyst and photosensitizer (PS), thus it attracts tremendous attention for the development of a novel homogeneous or hybrid photocatalytic system, and highefficient photocatalyst by modification of bipyridine ligand^{11,12} and halogen atom¹³, even the changes of transition metal center¹². Various hybrid catalytic structures involving Re(bpy) complexes as building blocks with versatile photochemical or photophysical characteristics have been reported^{14–19}. In the following sections, the merits and drawbacks of Re(bpy) in photocatalytic applications as well as their detailed photophysical features will be briefly introduced.

1.1.1 Advantages of Re(bpy) for photocatalytic application

The photoactivated rhenium bipyridyl family such as Re(bpy)(CO)_{3L} (L = halogen atoms) and their derivatives have been widely investigated due to versatile photophysical and photochemical properties for photocatalytic applications as photocatalyst or redox photosensitizer^{9,20}. The lowest excited state lifetime of Re(bpy) base complex is sufficient 2 long to allow electron or energy transfer to nearby components if proper energetic or electronic conditions are satisfied. In general, Re(bpy) complex will first be excited to singlet metal to ligand charge transfer (¹MLCT) or ligand to ligand charge transfer (¹LLCT) state, then crosses to triplet MLCT (³MLCT) state owing to rapid intersystem crossing (ISC) from the upper vibrational energy level (tens of femtosecond). Afterward, the hot electron vibrational cools to the lowest ³MLCT within 20 ps and survives for about 60 ns before depopulating to the ground state via triplet emissions, which is depicted in Figure 1.1. It should be noted that the lowest excited state of Re(bpy) complex may switch from MLCT (M→bpy) to LLCT (halogen atom→bpy) character if halogen atom is a strong donor such as Br or I (Cl has also been shown this character recently²¹), and can provide suitable highest occupied molecular orbital (HOMO) for the complex. Therefore, Re(bpy)(CO)₃X low-lying single and triplet excited state has MLCT characters but unlike other Re complex derivatives like [Ru(im)(CO)₃(phen)] ((im = imidazole, phen = 1,10-phenanthroline) with a halide to bpy LLCT contribution.



Nuclear coordination

Figure 1.1 Schematic illustration of potential surfaces and time scales related to ¹MLCT photoexcitation of Re catalyst followed by efficient ISC process and relaxed to ³MLCT state.

Transition metal complexes are widely used for photocatalytic reduction of CO_2 due to 1) the rich electron at the d-orbital of metal center²² can interact with the frontier molecule orbital of CO_2 ; 2) transition metal is able to provide vacant orbital for oxygen atom in CO_2 molecule, it is therefore easy to achieve the fixation of CO_2 . Even though CO_2 is a kinetically stable gas with no net dipole, it can still be activated to both nucleophilic character at carbon atom and electrophilic character at oxygen $atom^{23}$. Thus transition metal in high reduction state typically binds CO₂ to the carbon atom while predominantly interacting with oxygen atoms when at a high oxidation state. Reactions or fixation processes between CO2 and transition metal have been investigated during the past decades^{5,24,25}, and the basic coordination mode of CO₂ with transition metal has also been identified with five modes^{5,24}, which is of great importance to understand and further design the catalytic process. As shown in schematic 1.1, CO₂ can coordinate with transition metal by (1) electron donation from transition metal to carbon orbital with the formation of metallo-acid derivative, (2) π -complex formation via C=O double bond, (3) weak donation of π electrons to the metal, (4) donation of oxygen lone electron pair to the vacant orbital of transition metal, (5) oxygen atom in CO_2 chelating to the metal center^{24,26}. Transition metal catalyst would be inactive in mode IV or V where the oxygen atom in CO_2 chelates to the metal center, which affords a stable complex. In this context, in order to well explain the detailed mechanism of photocatalytic process especially the photocatalytic reduction of CO₂, 1, 2, and 3 coordination mode²⁶ are mainly employed. Schneider et al. investigated the detailed mechanism of photocatalytic reduction of CO_2 by Re(bpy)(CO)₃Cl via ¹³C kinetic isotope effect and density functional theory (DFT) calculation method in ACN and DMF solvent²⁷. In the schematic illustration (Figure 1.2), the initial species is one-electron-reduced Re(bpy)(CO)₃Cl intermediate, 17-electron [Re⁰(bpy)CO₃] complex generated by quenching of excited ³MLCT state of Re(bpy)(CO)₃Cl by triethanolamine (TEOA). All possible interactions between Re(bpy)(CO)₃Cl intermediates and TEOA after CO₂ molecule insertation and corresponding free-energy (ΔG), activation free-energy (ΔG^{\ddagger}) changes and reduction potential are summeried according to DFT calculation results. Their work displayed the CO_2 bind to Re metal center mainly through coordination mode 1, which is owing to the richness of electron for Re(bpy)(CO)₃Cl complex.



Schematic 1.1. Possible coordination mode between CO2 molecule and transition metal.



Figure 1.2 Schematic illustration of reaction mechanism of CO_2 reduction by $Re(bpy)(CO)_3Cl$ catalyst in the solvent ACN (a) and DMF (b) obtained at M06 level of DFT calculation. The free energy changes (ΔG) and activation free energies (ΔG^{\ddagger}) are reported

in units of kcal/mol and reduction potentials (E) in units of volts vs SCE. Figure is reproduced from ref 27^{27} with permission.

For Re(bpy) based organometallic complex, the nature of easy synthesis and the facile modification of diimine ligand makes it easy to etune their electronic properties and photocatalytic performance ²⁸.

In general, the photocatalytic CO_2 reduction performance is strongly determined by the excited state dynamics of Re(bpy). As mentioned above, the excited state of Re(bpy) will quickly evolve to the lowest ³MLCT state after rapid intersystem crossing and hot ³MLCT state cooling down after excitation. Such ³MLCT state undergoes reductive quenching with sacrificial electron donor and further forms a one-electron-reduced species (OER). Interestingly, the negative charge in OER species resides on bipyridine ligand as previous literature reported¹. Thus, the OER species become super stable and further enhance the photocatalytic reduction of CO_2 owing to the capability of further donating electrons ¹⁰. Clark and co-workers¹¹ also demonstrated that the excited state dynamics highly rely on the configuration of bipyridine ligands. First, the configuration of ligand determines the reduction potential level, and consequently the driving force for the single or multiple electron donation⁷. On the other hand, Talukdar ²⁹ and co-workers investigated a series of aniline-based hydrogen-bond donors decorated at bipyridyl ligand Re complexes for enhancement of electrochemical CO_2 reduction activity. They claimed that the metasubstituted aniline complex showed the highest turnover frequency (TOF) owing to the hydrogen-bonding interactions organization around the active site in DMF solvent, which efficiently increased local concentration of protons and further enhance the catalytic activity (Figure 1.3), corresponding reductive potential changes is displayed at table 1.1. Therefore, the bipyridine ligand plays a vital role in ultimate lowest triplet excited state or reduction potential determination and OER storage, as well as the catalytic performance. Additionally, various excited state also depends on the relative energy levels of the metal and ligand orbitals, as well as the extent of interaction between them³⁰.



Figure 1.3 Development of catalytic performance by modification of bipyridyl ligand skeleton. Figure is reproduced from ref. 29²⁹ with permission.

Table 1.1 Reductive potentials (versus $Fc^{+/0}$) and diffusion coefficients (D) of 1-Re, 2-Re, 3-Re, and ReBpy from cyclic voltammetry measurement in anhydrous CH₃CN/0.1 M Bu₄NPF₆ solutions under N₂ atmosphere. Table is reproduced from ref. 29²⁹ with permission.

catalyst	$E_{\rm p1,c}$ (V)	$E_{\rm p2,c}$ (V)	$D (cm^2 s^{-1})$
1-Re	-1.81	-2.22	1.31×10^{-5}
2-Re	-1.73	-2.14	1.18×10^{-5}
3-Re	-1.84	-2.24	1.36×10^{-5}
ReBpy	-1.79	-2.15	1.72×10^{-5}

1.1.2 Photocatalytic mechanism of Re(bpy) organometallic complex

The mechanism of photocatalytic CO₂ reduction by Re(bpy) including the reaction pathway and kinetics has been extensively studied, especially via ¹³C kinetic isotope effects (KIE) measurement complement with DFT calculations. As summarized in schematic 1.2. Re(bpy)(CO)₃L catalyst is excited to ¹MLCT state after absorbing around 400 nm UV light and then relaxes through rapid ISC to ³MLCT state. Reduction by electron from sacrificial donor or photosensitizer formed OER species and induced the halogen atom loss. OER species of complex here played important role 1) capturing the CO_2 molecule after the loss of ligand L (e.g. halogen atoms) and 2) donating the second electron to the CO_2 adduct. Then the solvent or sacrificial donor (such as TEOA) coordinates to metal center following the CO_2 molecule to replace the solvent or sacrificial donor or insert between donor and Re metal to form CO_2 adduct. Donation of electron from other OER species facilitated the cleavage of C–O bond and release of reduction product^{13,31}.

Modification of bipyridine skeleton and the changes of halogen atom may affect the reduction potential, and accumulation of photoinduced electron^{13,32}, determining the driving force of reduction process, while the exist of electron donor such as TEOA³³ or solvent exchange^{31,34} indeed change the details of photocatalytic mechanism owing to the coordination between transition metal center and solvent molecule or TEOA. ²⁷.



Schematic 1.2 Illustration of the mechanism of photocatalytic reduction of CO_2 for Re(bpy) complex.

1.1.3 Photoinduced electron accumulation on Re(bpy) catalyst

As introduced above, photocatalytic reduction of CO_2 requires multiple electrons to convert CO_2 to short-chain hydrocarbon chemical fuels (table 1.2), therefore the capability of multi-electron accumulation or stage is crucial for the catalysts. For Re(bpy) complex, the unique characters including high energy level of excited state, long excited state lifetime⁹ may facilitate multi-electron accumulation. The diimine in the Bpy ligand is also well-known as electron pool¹. However, efficient triplet-triplet annihilation (TTA) due to efficient ISC process and long-lived triplet excited state severely limited the electron accumulation on Re(bpy) complex. Such problem could be solved by engineering multinuclear configuration in the complex. Ishitani et al.²⁰ reported ring-shaped Re(I) multinuclear complexes, tetranuclear and hexanuclear complexes, to accumulate 2.9–3.6 and 4.4 electrons in one molecule, respectively.

Alternatively, this hurdle could be overcome by exploring promising photosensitizers as excellent electron pool or sacrificial multi-electron donor, which will be introduced in the following section Recently, A novel triazole-linked ruthenium photosensitizer and a rhenium catalyst were reported by Philipp Gotico³³ to investigate the photoinduced charge accumulation towards photoreduction reaction of CO₂. The first reduction process indicated the photoinduced electron resides on the extended triazole ligand and the using of sacrificial agent stabilized the electron. However, the first electron recombined with the hole generated by the second photoinduced electron immediately, which lead to only one electron located on the bridging ligand.

Table	1.	2	Different	products	of	CO_2	corresponding	to	the	standar	d e	lectroc	hemica	ιl
potenti	als	in	aqueous	solution (p	Η	= 7, 2	25°C).							

CO2 reduction reactions	Standard electrode potential vs NHE (V)
$\rm CO_2+e^- \rightarrow \rm CO_2^{}$	-1.900
$\rm CO_2+2H^++2e^- \rightarrow \rm HCOOH$	-0.610
$\rm CO_2+2H^++2e^- \rightarrow \rm CO+H_2O$	-0.530
$CO_2+4H^++4e^- \rightarrow HCHO+H_2O$	-0.480
$\rm CO_2+6H^++6e^- \rightarrow CH_3OH+H_2O$	-0.380

$CO_2+8H^++8e^- \rightarrow CH_4+2H_2O$	-0.240
$2CO_2+12H^++12e^- \rightarrow C_2H_4+4H_2O$	-0.349
$2\mathrm{CO}_2\text{+}12\mathrm{H}^+\text{+}12\mathrm{e}^- \rightarrow \mathrm{C}_2\mathrm{H}_5\mathrm{OH}\text{+}3\mathrm{H}_2\mathrm{O}$	-0.329
$2CO_2+14H^++14e^- \rightarrow C_2H_6+4H_2O$	-0.270
$3\mathrm{CO}_2$ +18H ⁺ +18e ⁻ \rightarrow C3H ₇ OH+5H ₂ O	-0.310

1.2 Photosensitizer employed in Photocatalytic system

In terms of single-component photocatalytic systems based on Re(bpy) complexes, even though they can work as both photosensitizer and photocatalyst, insufficient visible light absorption and difficulty of multi-electron accumulation limit their photocatalytic applications, in particular the capability of generating multi-electron product. and in CO_2 photoreduction, multi-electron reaction is required because one electron reduction is highly endothermic reaction. Applying another PS to Re(Bpy) to serve as efficient electron donors has been proved to be a promising solution. Here we will briefly introduce how PS function to improve the catalytic CO_2 reduction performance in a hybrid catalyst system. In general, photosensitizers harvest light and are excited to generate electrons, the photogenerated electrons are transferred to photocatalysts to reduce CO_2 and release reduction products.

Photosensitizers for CO_2 photoreduction are required^{35,36} to have sufficient long excited state lifetime which allows photoinduced electron transfer to photocatalyst; strong absorption at excitation wavelength and wide absorption range at visible light region because of the efficient utilization of solar light; strong oxidation power in the exited state that can capture electron from electron donor or provide electrons by itself; good electron pool achieving coherent multi-electron accumulation and good stability of OER species during the photoreduction reactions. Diverse PS have been widely explored to enhance the photocatalytic reduction of CO_2 performance. Those PS include transition metal complexes^{37–42}, metal-oxide semiconductors typically $TiO_2^{7,43}$, colloidal quantum dots $(QDs)^{6,44-47}$, photoactive porous coordination polymers including metal–organic frameworks (MOFs)^{48–52} and covalent organic frameworks (COFs)^{53–56}. TiO_2 is widely used as PS because TiO_2 can work as both electron transport and reservoir so that catalysts susceptibly obtain on-demand multi-electron supply from TiO_2 promoting the photoreduction of CO_2 process. On the other hand, metal-oxide semiconductors as an effective PS improve the catalytic durability and enhance the performance by smooth electron supply, however, it may require another molecule assist to broaden the absorption range of visible light⁵⁷ owing to the band gap (3.2 eV) of pristine TiO_2 being active only at UV light.

Porous coordination polymers, also known as MOF or COF, have extensive attraction on photocatalytic applications as PS due to extremely large surface area and tunable porous which is benefit not only for CO₂ adsorption and separation^{58,59}, also provide abundant photocatalytic active sites for CO₂ reduction⁴⁹. In addition, excitons excited at MOF or COF photosensitizer undergo efficient charge separation process^{60–62} owing to the rapid electron migration to attached catalytic species, as a result, enhances the photocatalytic performance. The majority of MOF and COF suffer from relatively lower molar absorption coefficient^{63–66} than other conventional photosensitisers, their electric conductivity is also highly restricted by the inadequate level alignment and mismatch between organic ligand orbital and metal orbitals⁴⁹.



Figure 1.4 Various PS employed in photocatalytic reduction of CO₂ system including COF materials, CulnS₂ colloidal QD, TiO₂ and transition metal complex Ru(II)bpy. Figures are reproduced from ref. 53^{53} , ref. 67^{67} , ref. 10^{10} and ref. 42^{42} respectively with permission.

Among those PS, Quantum dots attracted increasing attention for their unconventional photophysical and photochemical properties. Size tunable band gap energy lead to super broad absorption range at visible region (Figure 1.5), high absorption coefficient (10⁵ M⁻¹cm⁻¹ at least)⁶⁸, and long excited state lifetime^{69–75} make QDs an excellent candidate as light harvester and photoinduced electron supplement. However, most QDs with outstanding optical properties consist of heavy metal or poor thermal stability⁷⁶ limiting their applications. While their heavy metal-free substations such as InP QDs suffer from the super low quantum yield and short excited state lifetime due to the deep gap states induced by the surface dangling bond or the defects the produced by inevitable oxidation reaction of P atom⁷⁷, which makes it difficult for the charge separation.

As discussed above, transition metal complex (e.g. Ru(bpy)) faces challenges in CO2 photocatalytic reduction because of the triplet-triplet annihilation, thus the second electron donation generally from OER; Combining PS such as COF and MOF materials have been reported to achieve charge accumulation via efficient electron delocalization, extended conjugated system enable COF and MOF accumulate more charges over entire plane⁷⁸; while TiO₂ and QDs can also realize the charge accumulation on their conduction band (CB) due to semiconductor itself can work as good electron pool for charge accumulation⁷⁹.



Figure 1.5 Colloidal perovskite CsPbX₃ QDs exhibit size- and composite- tunable band gap energies covering the entire visible spectra region with narrow and bright emission. Colloidal solutions under UV light irradiation ($\lambda = 365$ nm) (a) and their photoluminescence spectra ($\lambda_{exc} = 400$ nm for all but 350 nm for CsPbCl₃ samples) (b). Figure is reproduced from ref. 74⁷⁴ with permission.

Electrons participating in photocatalytic reactions come from the photon absorption at particular wavelength with a certain energy to excite the PS to excited state, thus photoinduced electron transfer process and their determining factor in photocatalytic system is highly critical. We next briefly talk about photoinduced electron transfer including single electron or multi-electron transfer processes.

1.3 Photoinduced electron transfer process

Generally, most photoinduced electron transfer (PET) occurs in a binary system comprising an electron donor and an electron acceptor, referring to the process of electron transfer from the electron donor to the electron acceptor after light excitation at a specific wavelength. When electron donor and electron accepter coexist in one molecule, the process is known as intramolecule PET process. While in intermolecule PET process, charge transfer occurs between different molecules or semiconductors. When electron donor is excited via light illumination with suitable excitation wavelength, electron populate to the lowest unoccupied molecular orbital (LUMO) or conduction band (CB) of the donor after fast intraband vibrational relaxation. This photoinduced electron will move from the LUMO or CB of the electron donor to the LUMO or CB of the acceptor, as shown in Figure 1.6.



Figure 1.6 Schematic of PET mechanism in dyes (a) and in colloidal CdSe quantum dot with different sizes (b). Figures are reproduced from ref 80 ⁸⁰ and 81⁸¹ with permission.

Fundamental dynamics of intermolecule PET process were first identified by Marcus and Weller in 1940s and 1980s^{82,83}, respectively. PET plays a critical role in converting solar energy to chemical energy in nature, also in many fields such as photo-synthesis⁸⁴, photocatalytic materials⁶², photovoltaics⁸⁵, photo-switches^{86–88}, and photochromic materials⁸⁹ and photo-sensors⁹⁰ However, PET usually competes with other excited state depopulation processes such as radiative or nonradiative recombination, and the electron or hole trapping process. PET rate for electron transfer from electron donor to electron acceptor can be modeled by the Marcus equation and Rehm-Weller equation for molecular system⁹¹, in which PET rate is primarily determined by the oxidation potential of the donor and reduction potential of the acceptor, as well as the dielectric constant of solvent. Therefore, electron transfer rate is tuned by the differential of potential between them via ligand modification⁹² or other unit adding⁹³, or lower the electron-tunneling potential through the morphology changes⁹⁴, respectively.

To identify the detailed PET pathway and its dynamics in molecular systems, the detection of radical ions by time-resolved spectroscopies has been considered as a robust tool⁸². For example, laser flash photolysis experiments can measure the transient

absorption of radical anion and cation species to probe charge separation and recombination, also electron spin resonance and infrared spectroscopies and timeresolved resonance Raman can provide detailed information related to charge separation and recombination. In terms of semiconductor materials, transient absorption (TA) spectroscopy⁹⁵ and time-resolved PL spectroscopy ⁹⁶ are often used to probe the excited state depopulation in donor and population in acceptor materials to establish the PET pathway. In addition, PET process can also be visualized via fluorescence quenching phenomenon ^{97–99}. In this section, we mainly discuss the PET process on heterogeneous hybrid systems in the field of photocatalytic applications (e.g. photocatalytic H₂ evolution or photocatalytic reduction of CO₂). Besides, PET process in a heterogeneous system is mainly discussed in two scenarios, single electron transfer, and multi-electron transfer. Next, we talk about the single electron process firstly.

1.3.1 Single electron transfer process

The general heterogeneous hybrid catalytic system involves photocatalysts and photosensitors as light harvesters, electron pools, and supplements. With the light excitation above the bandgap, semiconductor undergoes photon absorption, exciton generation, exciton dissociation, photoinduced electron transfers to LUMO of photocatalyst followed by those electrons participating in the photocatalytic reaction eventually as shown in Figure 1.7. Photoinduced holes, however, are consumed in photocatalytic oxidation reaction which we don't discuss in this section.



Figure 1.7 Mechanism illustration and PET process for semiconductor/molecule hybrid system for photocatalytic reduction of CO_2 . Figure reproduced from ref. 100^{100} with permission.

The kinetics of photoinduced electron transfer k_{ET} in heterogeneous hybrid system¹⁰¹ can also be determined by Marcus equation as mentioned above:

$$k_{ET} = \frac{2\pi}{\hbar} \bullet V^2 \bullet \left(\frac{1}{4\pi\lambda k_B T}\right)^{\frac{1}{2}} exp\left[-\frac{(\lambda + \Delta G^{\circ})^2}{4\lambda k_B T}\right]$$
(1)

where \hbar is the reduced Plank constant, k_B is the Boltzmann constant, T is the temperature, λ is the reorganization energy, ΔG° is the driving force for the electron transfer, often obtained as the differential between the value of LUMO of catalyst and CB of semiconductor, V is the electron coupling strength. Moreover, V usually expressed by the function of donor and acceptor interspacing, d:

$$V = V_0 e^{-\beta d} \tag{2}$$

where V_0 is a constant and β is a damping factor. Thus, the energy band alignment^{101–103} and the distance of semiconductor and molecule^{96,104–106} govern PET rate.



Figure 1.8 Schematic illustration of electron transfer timescale related to the driving force ΔG° determined by the off-sets between CB of QD concerning LUMO of co-catalyst Pt cluster (a). The dependence of H₂ efficiency (IQE) and electron transfer rates on the off-sets (b). With the driving force decrease, electron transfer to co-catalyst become slower. Schematic illustration of CdS QDs with different lengths of ligand (c) and corresponding to the transient current responses (d). Transient photocurrent response showed a decreased photocurrent response with an increase in the length of ligands suggesting the increase of the length of ligands lead to harder migration of photoinduced charge carriers. Figures reproduced from ref. 103¹⁰³ and ref. 105¹⁰⁵ with permission.

On the other hand, besides the photoinduced electron transfer to LUMO of catalyst, the excited electrons can also either recombine with hole radiatively or non-radiatively, or can be trapped by trap state produced by vacancy of defect inside the semiconductor or on the surface. Trap state resides below the original CB edge of semiconductor with low energy level compared with initial excited state, therefore electrons are easily trapped leading to the decrease of excited state lifetime¹⁰⁷. In most cases, time scale of PET is generally close to or longer than the electron trapping¹⁰⁸ (less than ten picosecond for electron trapping, tens or hundreds of picoseconds for PET), therefore the presence of trap state could inevitably suppress PET process¹⁰⁹. To prolong the excited state lifetime, semiconductors such as QDs needed passivated¹¹⁰ by ZnS or ZnSe whose bandgap is slightly larger than QD, since electrons can be localized at excited state of core QDs.

1.3.2 Multi-electron transfer process

Conventional electron transfer process in photocatalytic application mostly refer to a single electron transfer scenario, namely, only one electron-hole pair is created after light irradiation following mitigating to catalyst, while the process of photoinduced electron transfers to reduction object (CO_2 or water) refer as electron donation. However, single electron transfer process also involves the case that only one photoinduced electron transfers to catalyst even if multiple electron-hole pairs are generated due to most electrons undergoing intrinsic or fast Auger recombination (AugR) or annihilation (trion or biexciton AugR) before transfer. In general, it is more convenient to track the electron transfer process, due to the absence of other higher-order excited state depopulation dynamics such as its Auger recombination or annihilation 95 . Secondly, even though versatile PS is employed in

heterostructure photocatalytic systems, part of them suffer from low absorption coefficient leading to a lack of capability of multi-electron generation under visible light irradiation with high intensity. However, photocatalytic conversion of CO₂ to chemical fuels and H₂ evolution is two-electron reaction¹¹¹, which means two electrons are required at least to achieve photocatalytic reactions. Therefore, many photocatalytic reactions demand the good stability of OER as another electron donation¹³ comes from OER, in particular, in the case of transition metal complex as PS. For multi-electron product producing, e.g. HCHO, CH₃OH and CH₄, TiO₂ is a good electron sink for multi-electron storage, supplement and electrons transport $ability^{10,112}$, it is a promising candidate for photoinduced multi-electron transfer process, however, as electron acceptor^{113,114}. COF and MOF co-catalyst for photocatalytic reduction of CO_2 to multi-electron products were widely reported, while multi-electron products evolution attribute to large amount of catalytic site, fast electron-hole pair separation and electron delocalization^{115,116}, hurdle of photoinduced multi-electron transfer⁶³ remain. QDs is also an excellent candidate for photoinduced multi-electron transfer owing to sufficient molar absorption coefficient^{117,118} which is also size-tunable as shown in Figure 1.9, if Auger recombination and annihilation of multi-electron smoothly overcome, as well as the fast electron-hole recombination.



Figure 1.9 Molar absorption coefficient of $CuInS_2$ quantum dot at 400 nm wavelength increase with the diameter changes. Figure reproduced from ref. 117^{117} with permission.

Therefore, the majority of heterostructure photocatalytic systems achieve multi-electron product evolution via multi-electron donation process even single electron-hole pair created from PS. It should be noted that PET process provides the possibility of electron donation to catalyst, electron transfer determines the process of electron mitigate to catalyst, while electron donation means the electron is captured by CO_2 adduct or CO_2 molecule.

In photoinduced multi-electron transfer, more than one electron-hole pair generation simultaneous and transfer to electron acceptor overall are satisfied. Taking semiconductor QD as example, once multiexciton is created, small volume of QDs enhances the biexciton recombination and annihilation process. Electron-hole pairs in QD recombine non-radiatively by transferring their energy to another carrier in such process. Auger recombination for biexciton in QDs occurs in general 10-100 ps time scale and features size-dependent⁹⁵, which compete with multi-electron extraction process and following photocatalytic reactions. On the other hand, electron-hole pair recombination process become more exacerbated when the number of exciton increase since 1) amplitudes of electron and hole wavefunction are enhanced which speed up the charge separation and recombination process and 2) equivalent acceptors (holes) created once first electron migrates to acceptor, the presence of first charge exhibit strong Coulombic force to subsequent electron^{119,120}. Therefore, enhanced Auger recombination and biexciton annihilation, as well as separated charges recombination hinder the multielectron transfer process in the field of photocatalytic applications (Figure 1.10).



Figure 1.10 Competition of multi-exiton separation, multi-electron transfer with Auger annihilation and charge recombination process in QD-catalyst system. Figure reproduced from ref. 119¹¹⁹ with permission.

Photoinduced multi-electron transfer process seems can be achieved by fast electron injection time (less than 10 ps) and extension of charge recombination process. Young et. al. ¹²¹ realized two-electron transfer process with PbS acting as multi-electron donor

whilst viologen-derivative served as multi-electron acceptor. Due to the cyclophane binds on the surface of QDs and sharing the electron with viologen units, the specific QDmolecule system exhibited ultrafast electron transfer rate and long lifetime of molecular excited state shown in Figure 1.11. For two-electron transfer process, the second electron transfer rate was calculated to be 5 ps, slower than first electron transfer rate attributing to the existence of first excited hole slightly alert reduction potential, which increases the Columbic interaction between electrons and holes.



Figure 1.11 Schematic illustration of photoinduced single and multi-electron transfer in the electrostatically bound complex CdS:ExBox⁴⁺. Figure reproduced from ref. 121¹²¹ with permission.

The same phenomenon was also observed in CdSe–ZnO system⁹⁵. Another scenario in this valuable work that has been discussed is the trion and biexciton AugR occurred during the multiexciton generation. Biexciton AugR reduces the electron-hole pair efficiently which results in only single electron transfer can occur, while long-lived lifetime of trion (~140 ps in this work) facilitate the efficient second electron injection which takes place at the timescale of tens of picosecond. It suggests that trion AugR competes with second electron injection and trion AugR significantly affects the multi-electron transfer process. (Figure 1.12) Moreover, CdSe/CdS core-shell QDs delivered up to 19 electrons to methyl viologen (MV²⁺) indicating the efficient photoinduced multi-electron transfer process for QD–molecule system¹¹⁹.



Figure 1.12 Multi-electroninjection and AugR processes present in biexciton generated CdSe QDs attached to ZnO. Figure is reproduced from ref. 95^{95}
Reference

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Chapter 2 Methodology

A brief introduction of all the main techniques employed in this thesis will be presented in this chapter. These techniques are utilized to analyze the excited state dynamics of QD-molecule systems for photocatalytic application including transient absorption (TA) spectroscopy and time-resolved mid-infrared absorption spectroscopy (TRIR). For structural characterization of QD-molecule system, nuclear magnetic resonance (NMR) was used to identify the binding mode of Re-catalyst to InP/ZnS QDs, X-ray photoelectron spectroscopy (XPS) analyzed the composition of QD-molecule system and disentangled the number of Re-catalyst attaching to per QD. Band alignment of QD-molecule systems with different sizes was confirmed by ultraviolet photoelectron spectroscopy (UPS). Finally, photocatalytic performance evaluation of all samples was performed by gas chromatography (GC).

2.1 Ultrafast spectroscopies

During the photocatalytic reactions, processes like charge separation, transfer and recombination in every step occur in femtosecond to microsecond time scales approximately, which can only probe by time-resolved pump-probe setups. TA and TRIR are therefore utilized in this work.

2.1.1 Transient absorption spectroscopy (TA)

Conventional TA setup mainly comprises of Ti:Sapphire laser generator, optical parametric amplifier, delay stage, charge-coupled device (CCD) camera detector and other optics to modify the laser path and its optical properties as shown in Figure 2.1. Briefly, an 800 nm laser pulse that is between 80 and 100 fs in duration depending on the resolution is produced from Ti:Sapphire laser generator and then split into two paths in general. The first beam called pump light goes into optical parametric amplifier (OPA) which can convert 800 nm beam light to expected excitation wavelength. This beam is

reflected by a retroreflector and then goes to delay stage, where adjusts delay time range from 100 fs to 6 ns. Afterward, beam is focused into the sample through a chopper wheel. Chopper wheel here is used to block every other beam and effectively drops the repetition rate of pump pulse from 500 Hz to 2k Hz. Fluence of pump beam is modulated by a natural density filter when specific number of photon absorption is needed. The second beam from Ti:Sapphire termed probe light is attenuated by half-wave plate (HWP) and polarizing filter, then focuses on sapphire or calcium fluoride crystal to generate a continuum white light range from ultraviolet to infrared region. Eventually, the probe pulse is focused into sample then goes to CCD camera directly. The pump and probe beams overlap noncolinearly in space at magic angle of 54.7 degrees to minimize the polarization artifacts.



Figure 2.1 Schematic diagram of femtosecond transient absorption measurement.

Then we talk about the TA spectra collection and experiment proceeding. A weak pump pulse (a pulse with super low intensity to avoid multiphoton absorption/multi-electron transfer process) is focused on the sample with delay time t concerning probe pulse. Difference of absorption spectrum (ΔA) is then calculated by the absorption spectra at excited state minus those at ground state². By changing different delay times between pump and probe pulse, the spectra record a ΔA at each delay time, so ΔA profile as function of delay time t and wavelength λ , $\Delta A(\lambda,t)$ is therefore obtained, and calculated by the equation followed:

$$\Delta A(\lambda, t) = A_t(\lambda, t) - A_0(\lambda, t)$$
(2.1)

where A_0 is the absorption of sample at ground state and A_t is the absorption at delay time t. Figure 2.2 shows the simple case of sample with ground state (G) and excited state (S₁ and S₂). In the absence of pump pulse, only probe pulse hits on the sample, and most of electron on the ground state, even though a certain electron is excited then undergoes a fast depopulation process. At t < 0, the detector observes the intensity of ground state (G) absorption in spectrum. Then, the pump pulse reaches at sample at t = 0 creating a high, non-equilibrium population in the excited state S1. At t > 0, the intensity in spectrum contributes to the reduction of absorption at ground state G \rightarrow S1 and new component due to excited state absorption S1 \rightarrow S2 appeared. The decrease in absorption calculated by equation (2.1) forms a negative signal in transient absorption spectra known as ground state bleach (GSB), and the new component exhibits a positive signal called excited state absorption (ESA, also refer as photoinduced absorption, PIA). Transient absorption spectra ΔA record the difference between A_0 and A_t indicating the absorption changes affected by pump pulse, thus ΔA reach to zero depicts sample depopulating entirely.



Figure 2.2 Schematic diagram of transient absorption experiment proceeding.

2.1.2 Time-resolved mid-infrared spectroscopy (TRIR)

Time-resolved mid-infrared spectroscopy in principle is the same as TA on the measurement and experimental proceeding³ but the probe pulse records the timedependent changes in mid-infrared spectrum (Figure 2.3). Molecules absorb IR light at resonance to their intrinsic vibrational frequency corresponding to special chemical structures. Moreover, vibrational frequency and width of functional groups in organic molecules are often quite sensitive to micro-environment changes. Therefore TRIR with visible light pump and IR probe can be used to deduce the excited dynamics of molecule or their interaction with surrounding environment. Decay and rise in intensity of a particular vibrational band over time gives the information on decay of reactants and formation of products. New bands appear in the spectra and their decay depict the formation dynamics of intermediate. Finally, transient change in spectra lineshape can provide the information including solvent interaction, environmental changes and redistribution of photogenerated charges can be recorded by TRIR spectroscopy.



Figure 2.3 Schematic diagram of TRIR measurement with pump-probe pulse and delay time between them.

Moreover, TRIR also is a powerful technique to probe free charge carriers directly and trapped charge carriers indirectly in the presence of nanocrystal semiconductors. In such case, a positive drift of whole spectra ($\Delta A > 0$) regardless of wavenumber can be observed clearly, which may indicate the charge carriers are excited into a continuous band rather than to discrete band after IR photons absorption⁴. The following transition could be either within high energy level of CB or trapped by midgap trap states. (Figure 2.4) On the other hand, interband transition of free charge carriers can be interpreted via TRIR

spectra, in which the increased absorption upon decreasing of wavenumber can be noticed⁵. This phenomenon is attributed to interband transition requiring tight electronphonon to conserve momentum. However, in our work, TRIR was used to probe the free charge carriers transition from QDs to Re-catalyst, no interband transition occurred inside QD, and TRIR spectra were therefore reflected the free carrier relaxation.



Figure 2.4 IR absorption mechanism for UV excited semiconductor leading to structurefree up-shift of the whole IR spectrum (left) and corresponding to the changes in TRIR spectra (right). The dashed trace (A) represents the pre-excitation spectrum, whereas traces B, C, and D represent the spectra at increasing relaxation times. Figures reproduced from ref 4⁴ with permission.

2.2 Structural characterization

2.2.1 Nuclear magnetic resonance (NMR)

The chemical structure and composition of substance can be determined by nuclei of atoms with specific magnetic properties, nuclear magnetic resonance (NMR) is therefore widely used to confirm the detailed chemical structures of chemicals. Basic NMR spectrometer mainly consists of magnet, magnetic field, radiofrequency (RF) transmitter, detector and sample tube⁶ (Figure 2.5a). Therein, RF transmitter is a radio frequency electromagnetic field generator that creates and absorbs the frequency range of 10 to 800 MHz to excite protons in the imaging field. This electromagnetic radiation makes electrically charged nucleus promote to higher energy level (E₂) from lower energy level (E₁), the difference between them is termed ΔE , which depends on the strength of magnetic field and the nuclear field moment size. According to Planck's Law, ΔE is proportional to its frequency (v):

$$\Delta E = h \nu \tag{2.1}$$

When electromagnetic radiation disappears, charged nucleus relaxes to low energy (E₁) and releases energy which can be recorded in the form of spectra, and these spectra are exclusive for every nucleus and are equivalent to ΔE (Figure 2.5b).



Figure 2.5 Schematic illustration of typical NMR spectrometer (a) and signal in NMR spectrum related to the difference between two energy (b). Figures reproduced from ref. 4⁴ with permission.

The Quantum mechanically subatomic including electrons, neutrons and protons have spin, and the protons and neutrons exhibit paired spin in some atoms such as ¹²C, ¹⁴N, ¹⁶O, and ³²S. In some cases, they cancel each other leading to the overall spin disappeared⁷. While their isotopic element ¹³C, ¹⁵N, ¹⁹F, ³¹P as well as ¹H does possess the overall spin due to the unpaired protons and neutrons. The spin of protons and neutrons creates a magnetic moment that will align with external applied magnetic field B₀ in only 2I+1 ways, either towards the magnetic field or away from it. For single nucleus with I=1/2, only one transition is possible between E₁ and E₂. Energetically preferred orientation has the lower energy whose magnetic moment aligned parallel with applied field (spin m = +1/2) donated as α , while the higher energy aligns anti-parallel (spin m = -1/2) referred to as β . Only nuclei with spin can absorb the energy (electromagnetic radiation) and be promoted to the less favorable higher energy state. Thus, many types of NMR spectroscopy are utilized for various structure identification as significant analytical techniques

2.2.2 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a powerful surface analysis technique for element analysis of thin film less than 10 nm as well as chemical state, hybridization and chemical environment. Briefly, X-ray with certain energies bombard the surface of thin film and kinetic energy of escaped photoelectrons from atom core level is measured (Figure 2.6). The energy of X-ray can be expressed⁸ by the equation followed:

$$i\nu = BE + KE + \varphi_{WF} \tag{2.2}$$

BE is the binding energy of electrons which represents the tightness of electrons binding to atoms or orbitals, KE is the kinetic energy of emitted electrons and φ_{WF} is the spectroscopy work function which is a constant. KE and φ_{WF} can be measured by XPS, then BE can calculate by equation 2.2. It should be noted that the binding energy of materials to the fermi level because of the φ_{WF} included. Photoelectron peaks position in XPS spectra recorded by the element and which orbital they ejected, and the binding energy of electrons is intrinsic properties of material, therefore we can deduce the elements and their chemical state from the binding energy, that is the peak position from XPS spectra. In addition, the peak intensity, *I*, is proportional to the number of elements⁹ within the sampled region, *n*, on the thin surface, then *n* can be determined by the equation as followed:

$$\frac{n_A}{n_B} = \frac{l_A/s_A}{l_B/s_B} = (l_A/l_B)(s_A/s_B)$$
(2.3)

where *s* is the relative sensitivity factor of element which is mostly set in the analytical software of commercial instruments, thus we can confirm the atomic ratio of elements or the molar ratio of different chemical bonding by the peak areas directly if the thin film is uniform and the thickness is less than 10 nm.



Figure 2.6 Schematic diagram of principle and simple case for XPS measurement.

2.2.3 Ultraviolet photoelectron spectroscopy (UPS)

Measurement of ultraviolet photoelectron spectroscopy is similar to XPS, however, the excitation source is changed to Helium ultraviolet which interacts with the valence electron of materials (Figure 2.7) because of the lower beam energy compared with X-ray (The most commonly used X-ray sources in XPS are MgKa (1253.6 eV) and AlKa (1486.6 eV)¹⁰, while the energy of He^I radiation is 80 eV for UPS measurement in this work). Accordingly, UPS provides the information state density of particular valence level as function of binding energy and confirms the energy level on an absolute value. In this project, band alignment of quantum dot semiconductors with different size was studied by UPS spectroscopy. The work function can be calculated by the equation as followed:

$$\varphi_{WF} = hv - KE \tag{2.4}$$

where hv is the radiation energy, *KE* is the kinetic energy of photoelectrons which can also be obtained from XPS spectra. In addition, energetic difference between valence band maximum (VBM) and fermi-level energy E_f are elucidated by UPS, which further illustrates the dopant density and doping type of semiconductors (n-type or p-type). Complementary with Tauc plot transformed from UV-vis absorption spectra of materials reveals the band gap energy of materials, the position of conduction band minimum (CBM) is therefore identified. UPS and UV-vis absorption spectra depict the semiconductor band alignment on an absolute value.



Figure 2.7 Schematic of the principle of ultraviolet photoelectron spectroscopy (UPS)

2.2.4 Gas chromatograph (GC)

For the evaluation of photocatalytic performance, gas chromatograph is regarded as a powerful and widely used technique to separate complex mixtures and quantify the photocatalytic products. In this project, the precise amount of H₂, CO, and CH₄ evolution was determined by GC. Typical components of GC are shown in Figure 2.11a, where carry gas supply provides a continuous flow of mobile phase that transports the solutes through the column. Ultrapure helium, hydrogen or nitrogen are used as carry gas which supplies from high-pressure gas cylinders with two-stage pressure. Photocatalytic product is introduced through injector onto the head of column, then detector records the gas upon living the column. An amplified electric signal is produced here, data are sent to computer for analysis.

GC can quantitively analyze gas mixtures thanks to its chromatographic gas separation process. In simple terms chromatography could be regarded as a series of discontinuous equilibrium steps occurred during the separation process. In a very small segment of column, equilibrium is formed between solutes in mobile phase and stationary phase, which can be defined by solute-specific distribution constant K:

$$K = c_s / c_m \tag{2.5}$$

where c_s is concentration of component in the stationary phase, c_m is concentration of component in the mobile phase. Therefore, successful separation is only taken place when the distribution constant is different. The portion of solute that remains in mobile phase is continually transported to the next segment of column and another equilibrium is established similar to previous case. The bigger K, the longer stay the component in the stationary phase and the slower is overall migration rate through the column, the later signal peak appears in the spectra.

On the other hand, the distribution constant K is also affected by the vapor pressure of solutes and polarity of the stationary phase, the higher vapor pressure or the lower polarity of the stationary phase the higher is its potion in mobile phase, and the faster is it transported through column. However, multiple transfer reactions including multiple solution/vaporization and adsorption/desorption take place during the solutes transportation. It results in the different retention times of individual components in the stationary phase, then each component is recorded by the detector one by one producing an amplified signal and stored for further analysis (Figure 2.11b).



- $t_{\rm R}$ Total retention time
- t'_{R} Adjusted retention time

Figure 2.8 Scheme of typical gas chromatograph (a) and Hypothetical gas chromatogram for two components 1 and 2 (b). Figures reproduced from ref 11^{11} with permission.

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Chapter 3 Inorganic ligands-mediated hole attraction on H₂ evolution

Generally, fast electron transfer efficiency has been considered as crucial factor to promote the photocatalytic reduction performance (e.g. H₂ evolution or CO₂ reduction). However, electron transfer leads to corresponding hole accumulation as electron usually possess a faster transfer rate than holes, which also play a critical efficiency-limiting step. Quantum dots surface modification by various surface ligand is regarded as a promising way to extract photoinduced charges and further enhance the photocatalytic performance. Therefore, in this work, different types of ligands including organic long-chain molecules (oleylamine) and inorganic ligands (S²⁻, PO4³⁻, and Cl⁻) attached at InP/ZnS QDs were employed to investigate the dynamics of photogenerated holes towards photocatalytic H_2 evolution. Ultrafast holes transfer process from InP/ZnS QDs to ligand was revealed by time-resolved photoluminescence and femtosecond transient absorption spectroscopy Complementary with midinfrared spectroscopy, the fastest hole transfer time of InP/ZnS capped by S^2 was determined to be 4.2 ps. Moreover, after 0.8 ns of electron and trapped hole dissociation time, long-lived injected holes at S²⁻ removed electrostatically attached surfactants to alert the spatial charge redistribution. Other inorganic ligands (PO4³⁻ and S^{2-} , Cl⁻, and PO4³⁻) capped QDs exhibit fast hole injection time than S^{2-} , however, the short dissociation time of charge transfer state (CTS) diminishes the lifetime of holes at ligand due to strong Coulombic force between photoinduced holes and electrons resided on surfactant. Instead, S²⁻ ligand ensured highest efficiency of hole attraction due to the optimal balance between surface electrostatic force and ionic radii. Such observations rationalized the excellent photocatalytic H_2 evolution (213.6 μ mol/g within 10 h) in InP/ZnS QDs capped with $S^{2^{-}}$ ligand and elucidates the excited state dynamics of holes affected by the different surface ligands.

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Inorganic ligands-mediated hole attraction and surface structural reorganization in InP/ZnS QD photocatalysts studied *via* ultrafast visible and midinfrared spectroscopies

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ABSTRACT Photoinduced carrier dynamical processes dominate the optical excitation properties of photocatalysts and further determine the photocatalytic performance. In addition, as the electrons generally possess a faster transfer rate than holes, hole transfer and accumulation are critical, and they play the key efficiency-limiting step during the photocatalytic process. Therefore, a comprehensive understanding of the dynamics of photogenerated holes and their determining factors in the photocatalytic system is highly essential to rationalize the full catalytic mechanism and develop highly efficient photocatalysts, which have not yet been revealed. In this work, the photoinduced charge carrier dynamics in InP/ZnS quantum dots (QDs) capped with longchain L-typed ligands (oleylamine) and inorganic ligands (sulfide ion (S²⁻)) were explored. Time-resolved photoluminescence and femtosecond transient-absorption spectroscopy unambiguously confirmed the ultrafast hole transfer from the InP core to S²⁻ ligands. Moreover, by probing the bleach of vibrational stretching of the ligands with transient midinfrared absorption spectroscopy, the hole transfer time was determined to be 4.2 ps. The injected holes are long-lived at the S^{2-} ligands (>4.5 ns), and they can remove electrostatically attached surfactants to compensate for the spatial charge redistribution. Finally, compared with other inorganic ligands such as Cl^- and PO_4^{3-} , S^{2-} balances the ionic radii and net charge to ensure the optimal condition for charge transfer. Such observation rationalizes the excellent photocatalytic H₂ evolution (213.6 µmol mg⁻¹ within 10 h) in InP/ZnS QDs capped with S^{2-} compared with those capped with other ligands and elucidates the role of surface ligands in the photocatalytic activity of colloidal QDs.

Keywords: InP/ZnS QD photocatalysts, surface ligands, ultrafast visible spectroscopies, midinfrared spectroscopies, hole transfer

INTRODUCTION

Photocatalytic hydrogen evolution (PHE) has aroused broad

interest because of the increasing demand for clean and sustainable energy sources [1-3]. However, the catalytic performance of most state-of-the-art photocatalysts is hindered by some photophysical bottlenecks among which the inefficient charge carrier separation after photoexcitation is frequently reported [4-7]. For addressing this issue, numerous important studies have focused on electron collection, which directly triggers proton reduction for H_2 evolution [8,9]. However, as the electrons generally possess a faster transfer rate than holes, the hole transfer is critical for the whole catalytic process, and the severe charge recombination caused by hole accumulation is a key efficiency-limiting step for photocatalytic H₂ evolution in many cases [10-12]. Therefore, a comprehensive understanding of the dynamics of photogenerated holes and their determining factors in the photocatalytic system is highly essential to rationalize the full catalytic mechanism and develop highly efficient photocatalysts.

Recent studies suggest that the surface chemistry engineering of various photocatalysts plays a role in controlling the photoinduced dynamics of electrons and holes. For example, surface ligands engineering can significantly modulate the charge carrier transfer in semiconductor colloidal quantum dots (QDs) [13-19]. Surface ligands of QDs usually anchor to the surface uncoordinated atoms and passivate the surface trap states, avoiding the random recombination of charge carriers and ensuring the sufficiently long excited-state lifetime to drive proton reduction [20-22]. Furthermore, when the molecular orbitals of surface ligands fall into the bandgap of the QDs, they could act as donors or acceptors to selectively induce photogenerated charge carrier transfer in QDs [23-33]. Nevertheless, surface ligands can also form dielectric energy barriers against the crystalline core of QDs to prevent photogenerated charges from tunneling toward the outside environment randomly [23]. Therefore, optimizing such photophysical tradeoff remains a highly demanding task to comprehensively understand charge carrier transfer dynamics and finally develop efficient QD photocatalysts. Moreover, compared with conventional organic/ inorganic surface ligands (such as oleylamine (OLA), carboxyl,

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mercapto, hydroxyl, and amino group) for QDs, inorganic chalcogenide ligands usually possess lone pair electrons, and they can selectively capture photogenerated holes by Coulombic attraction, which provides a perfect hole sacrificial agent to induce hydrogen generation [26,34-37]. For example, Ohmori et al. [37] found that S^{2-} in the solution could capture holes to enhance photocatalytic performance. Furthermore, we revealed that the S^{2-} ligands can serve as a hole-trap state to capture holes and drastically improve the PHE efficiency of InP/ZnS QDs and CdSe QDs [33,38]. However, the assumed inorganic ligandsmediated hole attraction has not been rigorously verified. The detailed pathways of hole transfer could also be different from that of QDs with conventional organic ligands, as the anchoring of those inorganic surface ligands relies on the electrostatic forces rather than covalent bonds. Therefore, an in-depth investigation of photoinduced hole dynamics of QDs capped with inorganic ligands is essential to manifest their superior photocatalytic performance. It is also crucial for the rational design of advanced photocatalysts.

Therefore, InP/ZnS QDs with different surface ligands (OLA, Cl⁻, S²⁻, and PO₄³⁻) were targeted as a benchmark system. The photoinduced hole transfer dynamics from QDs to surface ligands has been initially explored via the complementary studies of time-resolved photoluminescence (TRPL), femtosecond (fs) transient visible absorption (fs-TA), and fs-time resolved infrared (fs-TRIR) absorption spectroscopies. TRPL and fs-TA probe the depopulation of excited holes at InP QDs, whereas fs-TRIR confirms the population of transferred holes at surface ligands concurrently. We have demonstrated that the holes would transfer to the surface S²⁻ ligand within 4.2 ps, form a charge transfer state (CTS) with a lifetime of 900 ps, and stay at the ligands for more than 4.5 ns. This ligands-mediated hole transfer substantially retards the recombination of electron-hole pairs. In addition, fs-TRIR reveals for the first time the structural reorganization of surface ligands after hole injection induced by the decoupling of counterions and the redistribution of surface electrostatic force at ultra-long timescale. Such a phenomenon only occurs with the S²⁻ ligands because of the large electrostatic driving force to dissociate the CTS; thus, the H₂ evolution efficiency from H₂S splitting has been enhanced 3.74 and 11.3 times than those of other inorganic ligands (e.g., Cl^{-} and PO_{4}^{3-}). Our results indicate that S²⁻ surface ligands-mediated hole scavenging during the photocatalytic activity is combined with the fast charge transfer and slow structural dynamics of the surface ligands, which unveils the importance of dynamics over hole transfer in artificial photosynthesis.

EXPERIMENTAL SECTION

Sample preparation

All the InP and InP/ZnS QDs were synthesized by hot injection methods identical to our previous published work, and the detailed synthesis procedures can be found in the references [20,34]. The S^{2-} capping agents were attached to QDs by the ligand exchange process with details described in the reference [34].

Time-resolved visible spectroscopies

The fs-TA measurements were performed using a standard femtosecond pump-probe setup. Spitfire XP Pro regenerative amplifier seeded by Mai Tai SP femtosecond oscillator generates

the laser pulses with 800 nm wavelength and 80 fs pulse-length under 1 kHz repetition rate (all techniques from Spectra-Physics). TRPL measurements were carried out *via* a time-correlated single photon counting setup (TCSPC) utilizing a pulsed diode laser. Moreover, TA data were analyzed by the singular value decomposition (SVD).

fs-TRIR spectroscopies

The fs-TRIR measurement with 1 kHz Ti: sapphire amplifier (1 mJ, 45 fs output, Spitfire Pro, Spectra Physics) was performed using a commercial integration device, which split into two separate optical parametric amplifiers (TOPAS-C, Light Conversion), generating the visible pump at 400 nm and the mid-IR probe (1850–2200 cm⁻¹) pulses. The instrument response function for the experiments was approximately 100 fs.

Photocatalytic H₂ generation from H₂S

The photocatalytic H₂ generation from saturated H₂S over InP/ ZnS QDs with different surface ligands was achieved *via* a homemade off-line system. Firstly, H₂S gas was bubbled into a threeneck flask containing 50 mL DI water with Na₂S (0.1 mol L⁻¹) and Na₂SO₃ as the hole sacrificial agents to obtain H₂S absorbent. Secondly, 1 mg QDs together with 5 mL H₂S absorbent were added into the Pyrex tube. Before reaction, the Pryex tube was de-aerated with Ar gas for 15 min to remove impurity air and then injected with 0.5 mL CH₄ as the standard reference gas for quantitative analysis. At last, monochromatic light-emitting diode light (440 nm, 84 mW cm⁻²) was used as the light source to illuminate InP QDs and gas chromatograph (TM GC-2010 Plus, China, Ar carrier gas, molecular sieve 5 Å, TCD detector) was used to monitor the amount of evolved H₂.

RESULTS AND DISCUSSION

Photocatalytic H_2 evolution of InP/ZnS QDs capped with different ligands

In our work, photocatalytic H₂ evolution from H₂S absorbent aqueous solution with Na₂S/Na₂SO₃ as the hole sacrificial agent was selected as a reference reaction to elucidate the role of surface ligands in photocatalytic reaction. Millions of tons of H_2S (>4 × 10⁷ t) are widely produced from oil and gas extraction every year with high-density hydrogen energy [39,40]. As shown in Fig. 1a, evident photocatalytic activities only occur in QDs with PO⁴⁻, Cl⁻, and S²⁻ ligands under light illumination. The negligible activity in InP/ZnS capped with OLA ligands (namely InP/ZnS-OLA) should be attributed to the electrical barrier effect of insulator carbon chains. In addition, InP/ZnS capped with S²⁻ ligands (namely InP/ZnS-S) exhibits the highest H₂ evolution efficiency (213.6 µmol mg⁻¹) in 10 h and the highest apparent quantum yield (AQY, 19.3% at 440 nm, the detailed calculation can be seen in the Supplementary information). Moreover, as shown in Fig. 1b, the H₂ evolution of InP/ZnS-S is stable up to 10 h, whereas the catalytic reaction ceases after 3 h in a sample capped with phosphate (PO_4^{3-}) and chloride ion (Cl⁻) ligands (namely, InP/ZnS-PO₄ and InP/ZnS-Cl, respectively). In the following section, we will rationalize the superior photocatalytic performance of QDs capped with S²⁻ by investigating the excited-state dynamics, particularly the photoinduced hole transfer, which has been dominated by the surface ligands in the QD system [40-42].



Figure 1 Hydrogen (a) and long-time hydrogen (b) evolutions of InP/ZnS QDs capped with different surface ligands.



Figure 2 Steady-state absorption and photoluminescence spectra of InP QDs and InP/ZnS QDs capped with (a, b) OLA ligands and (d, e) S^{2-} ligands; (c, f) structure illustration of QDs covered with different ligands.

Structure and steady-state spectroscopies

QDs capped with S²⁻ exhibited the highest H₂ evolution efficiency and catalytic stability among all QDs. Accordingly, we conducted detailed photophysical studies on this sample using QDs capped with conventional organic OLA as the control reference. A series of InP/ZnS QDs with different ZnS growth times (0-120 min) were synthesized following the hot injection protocols, and inorganic S²⁻ ligands were introduced to replace the original organic OLA ligands attached on the QD surface as evidenced by Fourier transform infrared (FT-IR) spectra (Fig. S1). Those samples were then named by InP-OLA, InP/ ZnS-OLA, InP/ZnS-OLA (30 min), InP/ZnS-OLA (60 min), InP/ZnS-OLA (120 min) for OLA-capped QDs, while InP-S, InP/ZnS-S (30 min), InP/ZnS-S (60 min), InP/ZnS-S (120 min) for S^{2–}-capped QDs. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images (Fig. S2) of QD samples with OLA and S²⁻ ligands exhibited homogeneous particles with an average size of 2-3 nm. Lattice spacing was calculated to be 0.33 nm following literature data along (111) facets of InP [20,34]. Moreover, energy dispersive X-ray spectroscopy (EDX) analysis (Table S1) revealed the gradually increased elemental composition of zinc and sulfur after introducing the ZnS layer on InP QDs. Powder X-ray diffraction (PXRD) patterns (Fig. S3) also confirmed the retainment of the intrinsic zinc blende structure in QDs during the ZnS growth and ligand exchange. However, no clear heterojunction boundary between ZnS and InP was observed from the HRTEM images (Fig. S2), implying a potential gradient or alloy structures for our InP/ZnS QDs [20,34,38,43,44]. Fig. 2 illustrates the steady-state absorption and PL spectra of the as-prepared neat InP and InP/ZnS QDs with a typical absorption (emission) peak located at 525 nm (580 nm), which should be ascribed to the absorption and emission of 1S excitons, respectively [34,45-48]. The unchanged absorption band edges and emission peaks during the ZnS layer growth and S^{2-} ligand exchange exclude the direct contribution of the ZnS layer or the S²⁻ ligand to the optical transition. On the contrary, the PL quantum yield (PLQY) of InP QDs is modulated by ZnS growth and ligand exchange. The PLQY of OLA-capped QDs significantly increases from 7.5% to 55% with the increase of ZnS growing time because of the passivation of surface trap states [34,47-51]. Nevertheless, the PLQY of QDs capped with S²⁻ shrunk drastically below 2% and became less dependent on ZnS growth, which indicated that S²⁻ ligands introduced an extra nonradiative charge carrier recombination channel [35,36,52,53]. For rationalizing additional quenching, we first characterized the electronic structures of InP/ZnS QDs to demonstrate the possible depopulation pathway of the excited species. The valence band maximum (VBM) position could be confirmed by the X-ray photoelectron spectroscopy (XPS) valance band spectra of QDs (Fig. S4), while the conduction band minimum (CBM) was further determined by adding up the optical band gap extracted from the absorption spectra (Fig. 2), which is consistent with other reports [48]. The energy level of S²⁻ ligands at -0.48 eV vs. normal hydrogen electrode (NHE) calculated by electrochemistry is higher than the VBM of InP, providing sufficient driving force for photoinduced hole injection [30]. The lone pair electrons of S^{2-} ligands have Coulombic attraction with the photogenerated holes at the VBM of the InP, reducing the potential barrier of the ZnS layer and consequently making the hole transfer more thermodynamically feasible [51,54-57].

fs-TA absorption and TRPL spectroscopy

We first measured the fs-TA for all the as-prepared InP QDs and InP/ZnS QDs to elucidate photophysics and charge transfer dynamics (Figs S5 and S6). The typical TA spectra of InP/ZnS QD (30 min) samples capped with OLA and S^{2–} ligands show a characteristic band-edge ground-state bleaching (GSB) signal at approximately 530 nm (Fig. 3a, c), which is attributed to the state filling of 1S exciton states [34,50,58–60]. The SVD fitting of fs-TA data generates four excited-state decay components

(Fig. 3b, d and Table 1). The fast components with lifetime (τ_1) of 0.2-0.4 ps for QDs capped with OLA and S²⁻ ligands are fingerprints of the cooling of hot electrons from a higher vibration level to CBM (blue curves), which are featured as the negative GSB signal at a higher energy level than band-edge bleach. The board positive bands from 500 to 600 nm represent the population of the band-edge state resulting from hot-carrier cooling. The subpicosecond lifetimes (0.2–0.4 ps) also resemble the conventional hot-carrier cooling time in semiconductor QDs [45,46]. The slowest component with a lifetime longer than the TA time-delay ($\tau > 10$ ns) of OLA-capped QDs (Fig. 3b) exhibits a typical Gaussian GSB band. It overlapped perfectly with the ground-state absorption band edge (depicted as GSA). In addition, such a long lifetime is consistent with the PL lifetime shown in Fig. 4. This finding should be ascribed to the radiative recombination of electrons and holes at the band edge [56]. Compared with component τ_4 , the other two components τ_2 (5.8 ps) and τ_3 (1.24 ns) show slightly blue-shifted GSB with an additional positive band at the red side of the bleach. In component τ_2 , such positive band is narrower from 590 to 610 nm. It reflects a typical biexciton Stark effect in QDs after pump excitation, which can be mimicked by the differential spectrum between ground-state absorption and a red-shifted (20 nm) version of it (dashed green line in Fig. 3b) [47,61,62]. Moreover, we found that the PLQY and the lifetime of τ_2 component in InP/ZnS samples increase synchronously with the increase of ZnS growing time, whereas lifetimes (τ_1 , τ_3 , and τ_4) of other components remain constant (Table 1). This finding indicates that the τ_2 component should be more surface-related. In this scenario, the τ_2 component can be attributed to the fast-surface trapping of the photo-excited electrons in some of the QDs, whereas the remaining pool of QDs does not show this trapping channel. Component τ_3 (1.24 ns) shows a pronounced and broad



Figure 3 Transient-absorption spectra and respective SVD fittings of InP/ZnS QDs (30 min) samples capped with (a, b) OLA and (c, d) S²⁻ ligands; lifetimes of τ_2 (e) and τ_3 (f) components vs. ZnS growing time of InP/ZnS QDs capped with OLA and S²⁻ ligands.

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Figure 4 TCSPC kinetics of InP/ZnS QDs (30 min) with (a) OLA and (b) S²⁻ ligands, respectively.

Table 1	SVD fitting lifetime	of each component	of all InP and InP/ZnS QD)s
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Commis	Lifetime				
Sample	τ_1 (ps)	$ au_2$ (ps)	$ au_3$ (ns)	$ au_4$ (ns)	
InP-OLA	0.4	4.5	0.9	>10	
InP/ZnS-OLA (30 min)	0.3	5.7	1.2	>10	
InP/ZnS-OLA (60 min)	0.2	8.7	1.1	>10	
InP/ZnS-OLA (120 min)	0.2	12.8	1.2	>10	
InP-S	0.2	4.9	0.9	>10	
InP/ZnS-S (30 min)	0.1	7.0	0.8	>10	
InP/ZnS-S (60 min)	0.2	9.0	0.8	>10	
InP/ZnS-S (120 min)	0.2	10.4	0.9	>10	

positive absorption band from 560 to 900 nm. Different possibilities are identified to interpret this component: (1) Auger recombination, (2) electron depopulation, or (3) hole depopulation in QDs. Considering that the average excitation density per OD <N> << 1, the possibility of Auger recombination can be excluded (for detailed calculation, see the Supplementary information and Fig. S7). On the contrary, TA signals are not sensitive to the hole dynamics in strongly confined QDs, where the close-packed states and flat band distribution make the state filling at VB less detectable in GSB [58,59,63]. Therefore, component τ_3 can only be attributed to excited electron depopulation. The SVD components of QDs capped with S²⁻ are summarized in Fig. 3d. The spectral feature and lifetime for τ_1 and τ_2 are similar to those in OLA-capped QDs, manifesting the same processes (i.e., hot-carrier cooling and surface electron trapping). The τ_3 component of QDs capped with S²⁻ still represents electron depopulation but with a shorter lifetime. The τ_4 component exhibits extra featureless positive absorption from 580 to 900 nm in addition to the GSB of the band-edge excitation.

We also conducted TRPL measurement of all samples using TCSPC to obtain an insight into the excited-state dynamics, where the decay dynamics of excited electrons and holes can be retraced [36]. The PL kinetics can also be well fitted using a multiexponential decay equation [57,64]:

 $f(t_N) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + \dots + A_N e^{-t/\tau_N},$

where τ is the lifetime of the different components, *N* is the number of components in charge recombination, and *A* is the contribution ratio of each component to the total decay. Fig. 3a,

b illustrate the PL decay dynamics of QDs capped with OLA and S²⁻ excited at 438 nm. The PL lifetimes of QDs capped with OLA increase with ZnS addition, and the PL decays can be globally fitted by using three components with analogous lifetime sets $(\tau_1, \tau_2, \text{ and } \tau_3)$ but with varying amplitude (Table 2). Component τ_1 in TRPL exhibits the identical lifetime as TA decay component τ_3 (1.2 ns), reflecting the same electron depopulation. The gradual shrinkage in the amplitude of component τ_1 with the increment of ZnS addition follows the trend of PLQY (Fig. 1b). This finding indicates that such electron depopulation is also a primary nonradiative process that quenches the emission of QDs [36]. As the surface passivation by ZnS strongly determines the PLQY, such electron depopulation should also be related to surface trapping but should be originated differently from the fast ps timescale electron trapping described by TA decay component τ_2 . Therefore, components τ_2 and τ_3 with long lifetimes can be assigned to all radiative recombination of photogenerated species. When the surface of QDs is replaced with S²⁻ ligands, the PL kinetics remains the same regardless of ZnS coating (Fig. 3). We can fit the kinetics by one fast component with a lifetime of 0.8 ns (τ_1) and one slow component with a lifetime of approximately 10 ns (τ_2). The fast component resembles the lifetime of τ_3 in TA dynamics, which should be attributed to the abovementioned electron depopulation in QDs. Moreover, such a process dominates the PL kinetics, and it is insensitive to surface passivation, indicating that it is irrelevant to any surface trapping.

fs-TRIR absorption spectroscopy

To date, the possible hole transfer to the S^{2-} ligands still cannot

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Table 2 TRPL lifetimes and the respective amplitudes of all InP and InP/ZnS QDs

Comula	Lifetime (ns)			
Sample	$ au_1$	$ au_2$	$ au_3$	
InP-OLA	1.2 (81%)	20 (14%)	135 (5%)	
InP/ZnS-OLA (30 min)	1.2 (18%)	25 (54%)	105 (28%)	
InP/ZnS-OLA (60 min)	1.2 (10%)	25 (53%)	107 (37%)	
InP/ZnS-OLA (120 min)	1.2 (19%)	25 (50%)	114 (31%)	
InP-S	0.8 (86%)	10 (14%)	_	
InP/ZnS-S (30 min)	0.8 (94%)	14 (6%)	_	
InP/ZnS-S (60 min)	0.8 (92%)	11 (8%)	-	
InP/ZnS-S (120 min)	0.8 (88%)	11 (12%)	-	



Figure 5 (a) Schematic illustration of hole transfer; (b) FTIR and corresponding TRIR spectra under different decay times of InP/ZnS-S QDs (inset is schematic of vibration mode); (c) TRIR kinetic traces at different probe wavelengths and (d) differential kinetic trace up to 4500 ps delay after photoexcitation of InP/ZnS QD sample capped with S^{2-} ligands (30 min).

be confirmed merely by probing the excited-state depopulation in QDs. Therefore, time-resolved mid-IR spectroscopy was used. It can monitor the transient change of vibrational modes in the molecules during radical species formation after external charging [65,66]. In general, S^{2-} or other inorganic ionic ligands can bond to the surface of QDs either by electrostatic attraction with uncoordinated surface atoms (e.g., Zn) or X-type bonding. The surface residual charges are responsible for the dispersion of the QDs in the polar solvent [65]. On the contrary, the surface charges can also be balanced by protonated free amines in the solution to form bounded ion pairs [67–70]. Based on our synthesis methods, sulfur was dissolved into *N*-methylformamide (NMF) to link with InP/ZnS QDs, and it finally formed S^{2–} ligands coated on the surface of QDs. Therefore, S^{2–} ions should also electrostatically adsorb NMF *via* their protonated amino groups (Fig. 5a). Steady-state FTIR clearly shows the extra peak in QDs capped with S^{2–} corresponding to the vibration modes of the attached NMF (Fig. 5b and Fig. S1) [67]. This finding indicates an electrostatically balanced bilayer on the surface of our QDs (Fig. 5a). If a hole is injected into the S^{2–} ligands, the extra donated charge would break the electrostatic balance and change the vibration strength of adsorbed NMF (Fig. 5a). Consequently, the characteristic C=O stretching band of NMF can be utilized to identify the hole injection process. Here we used the IR laser pulse as a probe to measure fs-TRIR spectra with wavelengths covering the C=O stretching band (i.e., $5100-6200 \text{ nm or } 1610-1960 \text{ cm}^{-1}$) and trace the corresponding kinetics. As shown in Fig. 5b and Fig. S8b, the TRIR spectra of QDs capped with S²⁻ initially show a typical derivative transient signal with a negative peak at 5950 nm (i.e., 1695 cm^{-1}) and a positive peak at 5650 nm (i.e., 1770 cm⁻¹) up to 600 ps. At longer delay times, a negative bleaching band at 5950 nm dominates the transient derivative signal, demonstrating the blue shift of the C=O stretching band, because the population of extra holes in the S²⁻ ligands diminishes the Coulombic interaction toward NMF, thereby enhancing the vibrational motion of the C=O bonds. In addition, a featureless positive signal all over the wavelength region at early time scale can be observed, corresponding to the intraband transition of photogenerated free charge carriers^[63]. In our case, the photoexcited electron-hole pairs in InP QDs formed excitons spontaneously because of the strong quantum confinement. The hole transfer to the S2ligands leads to the dissociation of an exciton and consequently releases free electrons in the conduction band of QDs. On the contrary, the excited species in OLA-capped QDs is purely exciton; therefore, no clear transient signal could be observed in TRIR (Fig. S8). Furthermore, we compared the kinetic traces at 5500 and 5950 nm (Fig. 5c), where the former represents the pure dynamics of free charges as the decay returns to zero at a long delay time and the latter is a combination between the absorption of free charges and bleaching of C=O stretching. The differential kinetic trace (Fig. 5d and Fig. S9) could reveal the pure kinetics of the C=O stretching mode bleaching. It displayed an ultrafast increase within 4.2 ps, followed by a flat plateau up to 900 ps, and ended with a slow rise of the kinetics at long time delay. The ultrafast component should represent the initial hole injection from VB of the QDs to the S²⁻ ligands. The second period of 900 ps flat plateau shares a similar lifetime to that of the middle component observed in TA and PL decays. One of the possible interpretations of the process is the geminate recombination between excited electrons in the CB of QDs and injected holes in the S²⁻ ligands. However, we should observe fast quenching in PL decay corresponding to the hole injection time (i.e., 5 ps), whereas the following geminate recombination should be invisible after the quenching of emission. Alternatively, we attributed this process to the formation and dissociation of an intermediate CTS that consists of the injected holes in S²⁻ and left-over electrons in the CB of QDs with strong Coulombic interaction. We observed the same CTS in our previous studies for CdSe QDs after photoinduced electron injection to the ZnO acceptors [39]. Within this model, the injected holes can hop back and forth between the S²⁻ ligands and the VB of the QDs and exhibit an equilibrium hole population at the ligands. Consequently, the TRIR kinetics remains constant. On the contrary, as the hole, which can hop back, can also recombine with the electrons radiatively, the PL emission would only be completely quenched after the dissociation of such a CTS state. Therefore, the time-resolved quenching in PL decay is equal to the CTS dissociation time extracted in TRIR and fs-TA in this study (i.e., 900 ps).

After the CTS dissociation, a slow increase of the C=O bleach could be observed in TRIR kinetics. As the electronic states should be constant after hole injection and CTS dissociation, the

following modification on the vibration mode of the surface ligands can only be induced by the slow structural dynamics of the ligands. Besides direct evidence from structural characterization, we can still provide some possible scenarios. First, the existence of an extra hole at the S²⁻ ligands would significantly diminish its electrostatic attraction to NMF and lead to the detachment of one or even both anchored NMF (Fig. 5a). This scenario may cause the spatial reorientation of surface ligands to minimize the surface energy and neutralize the electrostatic charges. This process would change the local C=O stretching strength in NMF but in a slower manner compared with the electronic dynamics [66,71–73]. Second, the spectral feature of TA component τ_3 in OLA-capped QDs is the same as that of the abovementioned component with a lifetime of 800 ps in QDs capped with S²⁻. This scenario indicates a similar excited-state scheme between the two cases; that is, the hole is depopulated from the VB with electrons staying at the CB. As no hole injection to the ligands is expected in OLA-capped QDs, the only possibility is the trapping of holes from the surface hole traps. Here the 1.2 ns lifetime refers to the nonradiative recombination between electrons and trapped holes on the surface.

Fig. 6 summarizes all the photoinduced processes in the two types of QDs with different surface ligands. In OLA-capped QDs, one portion of the QDs (pool A) undergoes fast-surface electron trapping after excitation within 4-10 ps. By contrast, the other portion of the QDs (pool B) undergoes hole trapping, followed by the geminate recombination with excited electron within 1.2 ns. Electron and hole trapping represent the main nonradiative loss of the excited states, which can be efficiently diminished by surface passivation via ZnS. The radiative recombination in QDs, except for trapping, exhibits a lifetime longer than 10 ns. In QDs capped with S²⁻, the hole injection entirely suppresses hole trapping to the surface S²⁻ ligands within the picosecond timescale. The injected holes are still bounded with residual electrons in the QDs to form the intermediate CTS state within 0.8-0.9 ns dissociation time. After CTS dissociation, the injected holes can stay long at the S²⁻ ligands, facilitating the photocatalytic reaction. However, they will trigger the removal of electrostatic absorption surfactant NMF and lead to the slow geometrical reorganization of the surface ligands, which modify the vibration mode of the counterions in the colloidal solution.

The abovementioned analysis of charge transfer dynamics indicates that surface-anchored S²⁻ ligands efficiently dissociate the CTS state, which improves photogenerated hole transfer, thereby achieving excellent photocatalytic H₂ evolution efficiency compared with InP/ZnS QDs capped with OLA ligands. Moreover, as shown in Fig. 1a, other InP/ZnS QDs capped with inorganic surface ligands exhibited good photocatalytic H₂ evolution efficiency. Thus, we measured the TRIR of InP/ZnS QDs capped with various inorganic ligands, including Cl-, PO4³⁻, and S²⁻, to rationalize the relationship between hole injection dynamics of different inorganic ligands and photocatalytic performance systematically. Photoinduced bleaches of C=O vibration in NMF have been observed in all the three samples, indicating the abovementioned hole injection to the surface ligands (for detailed TRIR spectra, see Figs S10 and S11). The deferential TRIR kinetics shown in Fig. 7 illustrated faster hole injection to the Cl⁻ and PO₄³⁻ ligands (<1 ps) compared with S²⁻. However, no NMF removal processes are observed as



Figure 6 Schematic illustration of the photophysical pathways of different components after photoexcitation of QDs capped with (a) OLA and (b) S²⁻.



Figure 7 TRIR differential kinetic trace (6000–5580 nm) of QDs capped with various ligands (i.e., OLA, Cl^- , PO_4^{3-} , and S^{2-}) and corresponding schematic of the hole injection dynamics.

the bleaches constantly delay over time, which can be attributed to the backward recombination of injected holes with the residual electrons in QDs. The absence of NMF removal probably indicates that the injected holes are still bounded in the CTS states without dissociation. The underlying reason needs further exploration, but we can provide some assumptions here. The overall Coulombic energy between injected holes and electrons at ODs dominates the dissociation of CTS states, which is screened by the electrostatic force created from the surface ligands. Such electrostatic force is increased with the net charges of the surface ligands (i.e., $PO_4^{3-} > S^{2-} > Cl^-$) and decreased with their ionic radii (i.e., PO_4^{3-} (238 pm) < S^{2-} (184 pm) < Cl^{-} (181 pm)). S²⁻ ligands can be optimal in those two tradeoff factors and may possess the largest electrostatic force to dissociate the CTS states. Consequently, photogenerated electrons are free to diffuse to the surface reduction sites, whereas NMF removal would ensure the direct intact between the catalysts and reagents in the photocatalytic reaction; thus, InP/ZnS-S exhibits excellent H₂ evolution performance.

Based on the abovementioned observation, we can rationalize the underlying mechanism behind the superior photocatalytic performance of QDs capped with S²⁻: (1) the S²⁻ ligands function as an intermediate state to direct the hole transfer toward the surface of the QDs, thereby diminishing charge recombination and facilitating the reduction of proton hydrogen; (2) thorough hole transfer and surface structure reorganization ensure the efficient hole scavenge in the medium and prevent the spatial charge accumulation, which is the main origin of photodegradation during the catalytic reaction [74-76]; (3) photocatalytic H₂ evolution from H₂S splitting in our system occurs under sulfur-rich aqueous condition; therefore, the S²⁻ ligand is more stable than other inorganic ligands. These mechanisms should account for the superior photocatalytic performance of QDs capped with the S²⁻ ligands to QDs with other inorganic ligands [34].

CONCLUSION

We systematically explored the photogenerated charge carrier dynamics of InP/ZnS QD photocatalysts with different surface ligands by TRPL, ultrafast fs-TA, and TRIR spectroscopies. Complementary studies from TRPL and fs-TA unambiguously confirmed ultrafast hole transfer from InP QDs to surface S²⁻ ligands. TRIR further characterized the hole transfer time to be 4.2 ps and identified the formation of CTS after hole injection with the dissociation time of 0.8–0.9 ns. The injected holes were long lived at the S^{2-} ligands (>4.5 ns), and they removed the electrostatically attached surfactants on the ligands. Those observations rationalized the enhanced photocatalytic performance in InP/ZnS QDs capped with S²⁻ compared with QDs capped with other inorganic and organic ligands. Furthermore, our results demonstrated a dynamically modified surface chemistry during the photocatalytic reaction associated with the charge transfer to the surface ligands. We hypothesized that our understanding of the role of surface ligands in the photocatalytic process of colloidal QDs opens a new avenue for designing and engineering QD-based photocatalysts.

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Author contributions Zhou Y and Zheng K conceived the research and designed the experiments. Liu Y designed the synthesis. Liu Y, Xie Z and Zhao Q performed the synthesis. Abdellah M performed ultrafast mid-IR spectroscopy. Lin W performed ultrafast visible spectroscopy. Liu Y and Meng J performed the TEM and HRTEM characterizations. Liu Y wrote the manuscript with support from Zhou Y and Zheng K. Yu S, Pan Q, Zhang F and Pullerits T revised the manuscript. All authors discussed the results and commented on the manuscript.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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通过瞬态可见和瞬态中红外光谱研究InP/ZnS QDs 无机配体诱导的表面空穴转移和构型调整过程

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摘要 光生载流子动力学过程可以显著影响材料光催化活性.通常,光 生电子的转移速率远高于光生空穴的,致使空穴的转移和累积成为影 响光催化效率的关键因素.因此,深入探究光生空穴转移过程和动力学 可以极大地帮助我们认识和理解光催化机理,但该工作鲜有人关注研 究.本工作中,时间分辨荧光光谱(TRPL)和飞秒瞬态可见吸收光谱(fs-TA)表明空穴会从InP转移至表面S²⁻配体.此外,瞬态中红外光谱 (TRIR)中S²⁻配体伸缩振动信号表明该空穴转移时间为4.2 ps.转移至 S²⁻配体的空穴具有明显的长寿命特征(>4.5 ns)并且会导致表面活性物 的静电解离和构型重组.最后,通过与其他无机配体(Cl⁻、PO₄³⁻)比较, 我们发现S²⁻配体具有最合适平衡的离子半径和净电荷,因此带有该配 体的InP/ZnS量子点(InP/ZnS QDs)光催化集具有最高的光解硫化氢产 氢活性(213.6 μmol mg⁻¹).本文的研究结果为理解InP QDs光催化过程 和机理提供了有价值的见解.

Inorganic ligands-mediated hole attraction and surface structural reorganization in InP/ZnS QD photocatalysts studied *via* ultrafast visible and midinfrared spectroscopies

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1 Experimental Procedures

Materials: All the chemical reagents were purchased from Sigma-Aldrich & VWR in analytical grade and without any further purification during the experiment.

Sample preparation: All the InP and InP/ZnS QDs was synthesized by hot injection methods identical to our previous published work, and the detailed synthesis procedures can be found in reference [1-3]. The S²⁻ capping agents are attached to QDs by ligands exchange process with details described in reference [2].

Structure characterization: Powder X-ray diffraction (PXRD) was performed with a PANalytical X'pert diffractometer operated at 40 kV and 40 mA using Cu Kα radiation. The high-resolution transmission electron microscopy (HRTEM) images were recorded on FEI Tecnai G2 20 microscope operated at 200 kV. Energy dispersive X-ray spectroscopy (EDX) was performed with a Quanta FEG 250 analytical ESEM spectrometer.

Steady-state spectroscopies: Agilent 8453 UV-Vis spectrometer spectrophotometer has been carried out to do UV-Vis diffuse reflection spectra measurement (UV-DRS). Fourier transform infrared spectra (FTIR) was performed on a Nicolet 6700 spectrometer. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific XPS spectrometer, with Al Kα radiation (1486 eV) as the excitation X-ray source. Photoluminescence (PL) was performed via SPEX Fluorolog 1681 standard spectrofluorometer.

Time-resolved visible spectroscopies: Femtosecond transient absorption spectroscopy (fs-TA) measurements were performed using a standard femtosecond pump-probe setup [4-5]. Spitfire XP Pro regenerative amplifier, which seeded by Mai Tai SP femtosecond oscillator generates the laser pulses with 800 nm wavelength and 80 fs pulse-length under 1 kHz repetition rate (All techniques from Spectra-Physics). Here, we select 400 nm pump pulses generated by a BBO crystal as a second harmonic of the laser in our experiment and the supercontinuum generation from a thin CaF₂ plate for the probe. A Berek compensator was used in the pump beam to get magic angle (54.7°) mutual polarization between the pump and probe beams. The sample was moved to a new spot after each time delay point in order to avoid photodamage. Time resolved photoluminescence (TRPL) measurements were carried out via time-correlated single photon counting setup (TCSPC) utilizing a pulsed diode laser. The frequency of the laser was triggered externally at 5 kHz by a square wave generator with 40 ps pulse duration, all samples were excited at 438 nm, light intensity was set to 0.1 µW to fully exclude multi-excitation with excitation beam size of 2×10⁻³ cm². The emitted photons were detected by a fast avalanche photodiode (SPAD, Micro Photon Device) with response time less than 50 ps after passing through a 450 nm long band-pass filter. Moreover, TA data was analyzed by the singular value decomposition (SVD). The two-dimensional (2D) transient absorption data is an n×m matrix composed of time points (n) and wavelengths (m). The principle of the SVD fitting is to 58

obtain several main spectral components from the original data through mathematical processing, and then obtain the spectrum and time dynamics curves of transient species by analyzing several principal components

Time-resolved mid-IR spectroscopies: Ultrafast transient mid-IR absorption spectroscopy measurement with 1 kHz Ti: sapphire amplifier (1 mJ, 45 fs output, Spitfire Pro, Spectra Physics) was performed using commercial integration device, which split into two separate optical parametric amplifiers (TOPAS-C, Light Conversion) and generate the visible pump at 400 nm and the mid-IR probe (1850-2200 cm⁻¹) pulses. Before the pulse reaching the sample, the wedged ZnSe window can split the probe beam into equal intensity probe as well as reference beams. Only one probe beam can interact with the photoexcited volume of the sample, although both beams pass through the sample. Here, a single f =10 cm off axis parabolic mirror was used to focus all the beam into an ~70 μ m spot size in the sample (sample was mounted in a Harrick flow cell), which makes pump intensity attenuate to 650 μ W. The probe and reference beams were dispersed by a commercial monochromator (Triax 190, HORIBA Jobin Yvon) equipped with a 75 groove/mm grating and detected on a dual array, 2×64 -pixel mercury cadmium telluride detector (InfraRed Associated, Inc.). The instrument response function for the experiments was approximately 100 fs [6-7]

Photo-catalytic H₂ generation from H₂S and isotope experiment: The photocatalytic H₂ generation from saturated H₂S over InP/ZnS QDs with different surface ligands was achieved via home-made off-line system ^[8]. Firstly, H₂S gas was bubbled into a three-necks flask which containing 50 mL DI water with Na₂S (0.1 M) and Na₂SO₃ as hole sacrificial agent to obtain H₂S absorbent. Secondly, 1 mg of QDs together with 5 mL H₂S absorbent was added into Pyrex tube. Before reaction, the Pryex tube was de-aerated with Ar gas for 15 minutes to remove impurity air and then injected with 0.5 mL CH4 as standard reference gas for quantitative analysis. At last, monochromatic LED light (440 nm, 84 mW/cm²) was carried out as light source to illuminate InP QDs and gas chromatograph (TM GC-2010 Plus, China, Ar carrier gas, molecular sieve 5 Å, TCD detector) was used to monitor amount of evolved H₂. The apparent quantum yield (AQY) of InP/ZnS QDs was calculated sing Eq below:

 $AQY(\%) = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\%$

 $= \frac{\text{number of hydrogen molecules} \times 100\%}{\text{number of incident photons}} \times 100\%$

In addition, in order to trace the source of hydrogen in as-prepared system, deuterium oxide was introduced as H2S absorbent with all same other conditions. The mass spectrometer (OMNIStar GSD 320 O1, PFEIFFER VACUUM) has been selected to analyze H₂, HD and D₂ qualitatively and quantitatively.

Results and Discussion

2.1 FT-IR spectra





2.2 High-resolution TEM image



Figure S2. TEM and HRTEN images of InP/ZnS QDs (30 min) samples with (a, b) OLA and (c, d) S²⁻ ligands

2.3 Powder X-ray diffraction (PXRD) spectra



Figure S3. PXRD patterns of InP and InP/ZnS QDs (30 min) samples with OLA and S²⁻ ligands.



Figure S4. XPS valence band spectra and corresponding energy gap of InP and InP/ZnS QDs with (a) OLA and (b) S²⁻ ligands.

2.5 Transient absorption (TA) spectra and singular value decomposition (SVD) fitting of of InP and

InP/ZnS QDs with OLA ligands



Figure S5. Transient absorption spectra and the respective SVD fittings of (a, b) InP QDs, (c, d) InP/ZnS QDs (60 min) and (e, f) InP/ZnS QDs (120 min) samples with OLA ligands

2.6 Transient absorption (TA) spectra and singular value decomposition (SVD) fitting of InP and InP/ZnS





Figure S6. Transient absorption spectra and the respective SVD fittings of (a, b) InP QDs, (c, d) InP/ZnS QDs (60 min) and (e, f) InP/ZnS QDs (120 min) samples with S²⁻ ligands.

2.7 Transient Infrared absorption (TR-IR) spectra of InP and InP/ZnS QDs with OLA and S²⁻ ligands



Figure S7. Two-dimensional transient infrared absorption (TR-IR) spectra of InP/ZnS QDs (30 min) samples with (a) OLA and (b) S²⁻ ligands.

2.8 Transient Infrared absorption (TR-IR) kinetic trace InP and InP/ZnS QDs with OLA and S²⁻ ligands



Figure S8. Transient infrared absorption (TR-IR) kinetic traces at different probe wavelength up to 4500 ps delay after photoexcitation for InP/ZnS QDs (30 min) samples with (a) OLA and (b) S²⁻ ligands

2.9 Transient Infrared absorption (TR-IR) spectra of InP and InP/ZnS QDs with Cl⁻ and PO₄³⁻ ligands



Figure S9. Two-dimensional transient infrared absorption (TR-IR) spectra of InP/ZnS QDs (30 min) samples with (a) Cl⁻ and (b) PO_4^{3-} ligands.

2.10 Transient Infrared absorption (TR-IR) kinetic trace InP and InP/ZnS QDs with Cl⁻ and PO₄³⁻ ligands



Figure S10. Transient infrared absorption (TR-IR) kinetic traces at different probe wavelength up to 4500 ps delay after photoexcitation for InP/ZnS QDs (30 min) samples with (a) Cl⁻ and (b) PO₄³⁻ ligands;

2.11 EDX results

Sample	Element content (At%)							
	Р	In	Zn	S				
InP-OLA	25.2	17.5	3.9	0.3				
InP/ZnS-OLA (30 min)	22.6	19.4	7.5	5.7				
InP/ZnS-OLA (60 min)	26.0	20.3	11.7	10.8				
InP/ZnS-OLA (120 min)	24.2	17.4	12.4	11.1				
InP-S	10.3	12.2	3.2	7.4				
InP/ZnS-S (30 min)	10.6	10.4	9.6	10.3				
InP/ZnS-S (60 min)	10.7	13.2	10.2	13.5				
InP/ZnS-S (120 min)	12.2	10.8	9.9	12.4				

Table S1. EDX results of InP and InP/ZnS QDs samples with OLA and $S^{2\text{-}}$ ligands

2.12 Calculation of excitation intensity per quantum dots

S1. Photoluminescence quantum yield (PLQY) calculation

In this regard, the PLQY (n) could be evaluated as the fraction of radiative recombination among all the recombination processes of the charge carrier as:

$$\eta = \frac{\sum_{i} A_{i} k_{rad}^{i}}{\sum_{i} A_{i} k_{rad}^{i} + \sum_{j} A_{j} k_{nonrad}^{j}}$$
(eq. S1)

where k_{rad} and k_{nonrad} refer to the rates of the radiative and non-radiative recombination processes, respectively, and A_{i,j} represents the amplitude of each decay component

S2. Excitation intensity per quantum dot calculation

Usually, InP QDs can be excited to higher multiple excitons states under high excitation intensity and the initial multiple exciton population was followed Poisson distribution.

$$P_{N} = \frac{e^{(N)} * \langle N \rangle^{N}}{N!}$$
(eq. S2)
where $\langle N \rangle$ is the average number of excitons per QDs, N is the number of excitons, and P_N is the fraction of QDs with N excitons.

Moreover, we can also use equation S3 to present the average number of excitons per QDs, where $\sigma^{(1)}$ means the cross-section in one-photon absorption at excitation wavelength and / is the excitation intensity in units of the number of photons per pulse per cm⁻².

$$\langle N \rangle = \sigma^{(1)} * I$$
 (eq. S3)

Both considering eq S2 and eq S3, we can calculate the fraction of excited QDs, P_{exc} , as such equation S5:

$$P_{exc} = \sum_{N=1}^{\infty} P_N = 1 - P_0 = 1 - e^{-\langle N \rangle} = 1 - e^{-\sigma^{(1)} * \mathbf{I}}$$
(eq. S4)

If we know P_{exc} , we can calculate $\sigma^{(1)}$, $\langle N \rangle$ and know the suitable excitation intensity of pump. On the other hand, long time component signal in GSB kinetic curve is more related to radiative recombination and reflect the real photo-physical dynamic information in QDs sample. Therefore, we measured excitation intensity depended TA and got the ΔA_0 at t=0, which we call it $\Delta A_0(I)$ by fitting the long-time component signal in GSB kinetic curve (figure S9a). Then, we set excitation intensity (I, photons per pulse per cm⁻²) and $\Delta A_0(I)$ signal as X and Y axis, respectively. Lastly, fitting these data via equation S5, where C is constant and then we can calculate the value of $\langle N \rangle_0$ and one-photon absorption cross-section ($\sigma^{(1)} = 0.217 * 10^{-13}$) cause $\Delta A_0(I)$ is proportional to P_{exc} .

$$\Delta A_0(I) = \frac{\Delta A(I)}{e^{-t/\tau}} = C * \left(1 - e^{-\binom{I}{I_0} * \langle N \rangle_0}\right)$$
(eq. S5)

2.13 Fitting results of excitation intensity per quantum dots



Figure S11 (a) Excitation intensity depended TA kinetics for InP QDs probed at 400 nm, I_0 = photons/cm² per pulse. (b) TA signal $\Delta A_0(I)$ rescaled from long-time component (Figure S11a) as a function of excitation intensity for InP QDs probed at 400 nm, fit according to equation S5

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Author Contributions

Ying Zhou and Kaibo Zheng conceived the research and designed the experiments. Yang Liu designed the synthesis. Yang Liu, Zhanghui Xie and Qian Zhao performed the synthesis. Mohamed Abdella performed ultrafast mid-IR spectroscopy. Weihua Lin performed ultrafast visible spectroscopy. Yang Liu and Jie Meng performed characterization. Yang Liu wrote the manuscript with support from Ying Zhou and Kaibo Zheng. Shan Yu, Fengying Zhang and Tonu Pullerits revised the manuscript. All authors discussed the results and commented on the manuscript

Chapter 4 Multi-electron donation on photocatalytic CH₄ evolution

Multi-electron donation plays a crucial role in the photocatalytic reduction of CO₂ to shortchain chemical fuels, particularly in the conversion of multi-electron products such as formic acid, methane, and methanol, which is sustainable and promising solution to mitigate the CO₂ concentration in the atmosphere and global warming. Multi-electron mediated reduction process not only lowers required redox potentials of corresponding products but can also enhance photocatalytic conversion efficiency. However, it remains a challenge for achieving multi-electron donation as many demanding requirements must be satisfied, for instance, sufficiently long-lived lifetime of excited state and stable intermediate species, as well as efficient electron transfer to suppress the competition with Auger recombination and annihilation which usually occurred in multi-electron donation process. On the other hand, inspired by reported study in other catalytic system, multi-electron donation can be achived by introducing multiple accessible catalytic sites in the catalysts. Thus, in this chapter, we introduce InP/ZnS quantum dot tethered by Recatalyst for photocatalytic reduction of CO₂ reactions. We identified the binding type between Re-catalyst and QDs by ³¹P NMR measurement firstly, ensuring Re-catalyst linked to the surface of QDs via covalent bond due to strong bonding enabling efficient electron transfer process has been reported. Moreover, the specific configuration exhibits unconventional electronic structure, exciton extended their band to bpy moiety of Recatalyst, the significant exciton delocalization due to the evident frontier orbital overlapping promoted the electron separation process further enhanced electron transfer from QDs to Re-catalyst.

In this work, we highlighted the fact thatconcentration of Re-catalyst attached to each QD camengineer the electron transfer process and even more precisely control the photocatalytic reaction pathway. Therefore, we confirmed the number of Re-catalyst per

QD by XPS measurement and corresponding to excited state dynamics by transient absorption spectroscopy (TA) complementary with time-resolved infrared (TRIR) measurement. Two attached Re-catalyst mode achieved sufficient multi-electron donation process with ultrafast electron injection time less than one picosecond and the capability of photocatalytic conversion of CO_2 to CH_4 . While one attached mode can only achieve CO evolution due to the lack of capability of multiple electron donation, which presented extraordinary product selectivity.

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This article is given below.

Multi-electron Donation Promotes the Photocatalytic Conversion of Carbon Dioxide to Methane in a Covalent Bonded Metal-complex/Quantum Dots Hybrid Catalyst

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Abstract

Multi-electron donation remains a challenge for photocatalytic conversion of CO₂ to multielectron products (e.g., CH4, CH3OH, and CH3COOH) due to the efficient Auger recombination or annihilation at multiple excitation conditions for conventional molecules or semiconductor photocatalysts. In this paper, we demonstrated possible multi-electron donation within a quantum dot (QD)/metal complex hybrid photocatalyst system when multiple metal complexes are attached to one OD. Structural characterization first confirmed the number of catalysts attached per QD. The time-dependent density functional theory (TD-DFT) calculation identified that photoexcited electrons directly resided on the ligand of the metal complexes. Combining the studies from transient visible and infrared spectroscopies, we reveal that the efficient multi-electron transfer from one excited QD can be achieved when two metal complexes are anchored to one QDs with an electron injection time shorter than one ps. The transferred electrons are localized at the metal centers while the holes are delocalized in QD with an ultralong lifetime. This can guarantee efficient multi-electron donation during the photocatalytic reactions. Consequently, such multiple catalysts attachment facilitates the CO₂ photocatalytic reduction, where an unconventional methane production involving the donation of eight electrons has been significantly enhanced. This work establishes a strategy to control CO₂ reduction products via tuning the multi-electron donation pathways through molecular engineering.

Introduction:

Tremendous fossil fuel consumption and the consequent CO₂ emission have caused both energy crises and environmental issues such as climate change and global warming. The solar-driven photocatalytic reduction of CO2, which reduces CO2 into CO or other short-chain hydrocarbon chemical fuels, is attracting extensive attention as a promising solution. However, due to the high energy of the C=O bond in CO₂ molecules, one electron-mediated reduction of CO₂ is highly endergonic.¹ Alternatively, if more electrons can be utilized, the redox potentials of the corresponding products can be much lower, making the reaction energetics favorable in practice.² To achieve such a multi-electron-mediated reaction, the optimal catalysts should have excited states with sufficiently long lifetimes.³ In addition, their intermediate reduced states should still be stable and reductive to complete the multi-electron donation. Finally, the bonding between the CO₂ adsorbent and the catalytic site should be strong regardless of the reduction states.¹ Such requirement is demanding for most traditional semiconductors or molecular photocatalysts; since the excited states suffer from fast annihilation or Auger recombination when multiple electrons are generated. Moreover, the intermediate radical products usually don't have sufficiently low overpotential to donate the additional electrons.⁴ The above challenge is exacerbated when more electrons are required to generate multi-electron reduction products (e.g., CH₄, CH₃OH) compared with conventional two-electron reduction products (e.g., CO and formate).

Among the state-of-the-art photocatalysts, Re(I)-complexes have been considered as potential candidates to tackle the above issues. First, the d⁶ transition metal center provides an ultrafast long-lived lowest triplet excited state and an efficient intersystem crossing channel.³ Metal ions can also stably fix the CO₂ adsorbent. Most importantly, their oneelectron reduced intermediates are still stable in solution and have enough negative overpotential to trigger the second electron donation.⁵ Therefore, efficient CO₂ photocatalytic reduction to CO has been widely reported.⁶ The catalytic performance can be further enhanced when the complex is anchored to various photosensitizers to extend the capability for light absorption. However, severe annihilation still prohibits the efficient donation of multi-electrons from individual catalytic molecules⁷. To stabilize the excited electron accumulation at the catalytic sites prior to the catalytic reaction, one could bridge multiple Re(I) moieties to form multi-nucleus complexes where each metal center can store one excited electron.⁸ Alternatively, we recently demonstrated that Re-complexes could be immobilized into covalent organic frameworks (COF), where photogeneration of electrons delocalized within the frameworks can serve as electron reservoirs complementing the electron localized at the metal center for multi-electron donation.⁷

Inspired by the above results, here we have developed a new design that attached a fixed number of multiple Re-complexes (Re-bpy) onto InP/ZnS semiconductor quantum dots (ODs) with tightly covalent bonding. InP ODs ensure broad light absorption with a high extinction coefficient. TD-DFT calculations confirm that the covalent bonding induces a direct electronic transition from the QD surface to the Re-complex moieties due to significant frontier orbital overlapping. Complementary investigations from transient visible absorption (TA) and transient IR absorption spectroscopies (TRIR) reveal that two electrons can efficiently transfer to each metal center when two complexes are attached to one OD. In addition. TRIR characterization indicates that the final excited state, where the multiple electrons reside at the metal center and multiple holes are delocalized, exhibits a long lifetime (>> 5 ns). As a result, we observed a higher CO₂ photocatalytic reduction activity, and to our surprise, enhanced methane production in samples with two attached Re-bpy catalysts. We attributed this phenomenon to the long-lived photo-generated electron accumulation at the multiple Re(I) centers on individual OD, which promotes multi-electron donation. Our work establishes efficient photocatalysts for multi-electron CO₂ reduction products. It also provides a strategy to precisely control the photocatalytic CO₂ reduction pathway by quantitatively controlling the number of available electrons that can be donated.

Results and discussion

Structural Characterization:

InP/ZnS colloidal quantum dots (InP/ZnS), 2-mercaptoethanol capped QDs (InP/ZnS -ME), and InP/ZnS QDs attached with Re- photocatalysts with two different concentrations were synthesized according to literature protocol with slight modification.^{9–12} Here, InP/ZnS-ReCat(0.5) and InP/ZnS-ReCat(2) were used to define the two samples to be investigated here as representatives of one and two catalysts attached, which will be confirmed later. In short, InP/ZnS QDs were synthesized via the hot injection method, and oleylamine was replaced with 2-mercaptoethanol by ligand exchange. Finally, Re-photocatalyst was covalently linked to QD through an esterification reaction between the hydroxyl and the phosphate groups. (For details of the synthesis procedure, see S.I.). The absorption band edges of these samples are almost identical except for a subtle blue shift from 510 nm in InP/ZnS QDs to 500 nm in InP/ZnS-ReCat(2) (Fig 1a). Likewise, the emission peak of these QDs occurred at 560 nm with narrow full width at half maximum (FWHM) around 60 nm (Fig 1b). The above characterization indicates that both the average size and the size distribution of the QDs did not change during the ligand exchange and the photocatalyst attachment.



Fig 1. Optical and NMR characterization. Normalized UV-vis absorption (Fig. 1a) and steady-state photoluminescence spectra (Fig. 1b) excited at 365 nm of InP/ZnS, InP/ZnS-ME and InP/ZnS-ReCat dissolved in hexane and DMF respectively. ³¹P NMR spectra (Fig. 1c) of Re photocatalyst, InP/ZnS-ReCat.

Since the photo-induced charge transfer process is significantly influenced by the coordination between the QDs and the catalysts in the hybrid structure, we first characterize the interfacial bonding mode by both Fourier-transform infrared spectroscopy (FTIR) and phosphorus-31 nuclear magnetic resonance (³¹P NMR) spectrum to ensure that the Re

photocatalyst was covalently anchored to InP/ZnS QDs. The C=O stretching bonds (2025 and 1887 cm⁻¹) and the C–N peak (1213 cm⁻¹) for the bpy moiety are preserved in InP/ZnS–ReCat but the C=O stretching vibration of Re(CO)₃Cl moiety at 2025 and 1887 cm⁻¹ is invisible (Fig. S1), which may be due to the small amount of Re photocatalyst attached. ³¹P NMR characterization further confirmed the binding mode between the catalyst and the QDs, as shown in Fig. 1c. The peak broadening of the P signal in the phosphate ligand for QD-ReCat compared with pristine ReCat suggested the substantial cross-ligand electron transfer from quantum dots to Re photocatalyst, illustrating that the photocatalyst is indeed covalently linked to the QD. It should be noted that the signal for P atoms within InP QDs located within entirely different regions around -178 ppm.¹³



Fig 2. Quantitative evaluation of the photocatalyst tethered to InP/ZnS quantum dot. High-resolution XPS spectra of InP/ZnS-ReCat (0.5) (Fig 2a) and InP/ZnS-ReCat(2) (Fig. 2b) for Re 4f and In 3d with atomic ratio of Re and In, the corresponding structure was inserted.

In order to quantify the amount of photocatalyst attached per quantum dot, elemental analysis of InP/ZnS-ReCat was carried out by X-ray photoelectron spectroscopy (XPS) to calculate the precise atomic ratio between Re and In atoms since they are the main elements in the photocatalyst and quantum dots, respectively. Fig. 2 shows the Re 4f (42.18 eV and 44.28 eV) and In 3d (452.58 eV and 444.98 eV) core level emission spectra of InP/ZnS-ReCat(0.5) and InP/ZnS-ReCat(2) samples, respectively. The binding energies of those core level emissions are consistent with the value observed in pure Re photocatalyst and InP/ZnS QDs (see Fig. S2), suggesting that the Re photocatalysts are anchored to InP/ZnS QDs. The

atom ratios of Re and In are calculated to be 0.04: 10.45 and 0.07: 8.83, corresponding to one photocatalyst per InP/ZnS QD and two photocatalysts per InP/ZnS QD, respectively. (For detailed calculation methods, see S.I.).



Fig 3. TD-DFT calculation of the samples. UV-vis spectra of (a) InP/ZnS-ReCat(0.5) and (b) InP/ZnS-ReCat(2) compared with TD-DFT calculated fragment, corresponding to electron transition from HOMO to LUMO level illustration of (c) InP/ZnS-ReCat(0.5) and (d) InP/ZnS-ReCat(2), respectively.

Excited state structures:

In general, the QDs and the outer-shell molecules in the hybrid structure can be considered to form heterojunctions. However, since the Re-complexes are strongly coupled with the QDs surface via covalent bonds, the excited state of QDs can also be modified due to surface ligand-induced exciton delocalization.^{14–16} In order to confirm the excited state structure of the samples, we conducted TD-DFT calculations as shown in Fig. 3. The organic-inorganic hybrid structure, InP/ZnS cluster covalently linked to one or two Re photocatalyst via 2-mercaptoethanol as a linker, were used to model the photocatalytic systems. GGA-PBE, 82

DNP-4.4 level of theory has been employed to calculate the electronic structure and the electronic transition under COSMO-model. Fig 3a and 3b display the calculated excitation spectra (blue curves) of InP/ZnS-ReCat(0.5) and InP/ZnS-ReCat(2), which are in agreement with the experimental absorption spectra (red curves). For InP/ZnS-ReCat(0.5), the calculated spectra mainly consist of two electronic bands at 567 nm (S1) and 418 nm (S2). The low-energy band S1 is dominated by the electronic transition from the HOMO (within InP/ZnS cluster) to the LUMO (on the bpy moiety of Re photocatalyst) level as shown in Fig 3c, which suggests that the band edge optical transition occurs directly from InP/ZnS to the bpy moiety of the Re-photocatalyst. Such a scenario also applies to the high-energy band S2, which is dominated by the electronic transition from the HOMO-1 to the LUMO+1 and from the HOMO-2 to the LUMO+2. When two catalysts are tethered to the QDs in InP/ZnS-ReCat(2), the band edge optical transition (S1, 577 nm) is also dominated by the electronic transition from the surface of the OD to the bpy moiety of the Re photocatalyst and the highenergy band (S2, 562 nm) indicating a high-energy optical transition from the surface of the OD to the bpy moiety of one of the Re photocatalyst (HOMO-1 to LUMO+1) and further to the bpy moiety of another Re photocatalyst (HOMO-2 to LUMO+2).

The TD-DFT calculations of both samples clearly confirm the hybridization between the frontier orbitals of the QDs and the attached metal complexes, where the LUMO orbitals are already located at the moiety of Re-catalyst. As a result, the photo-induced charge transfer from the QDs to the metal complexes should be replaced by exciton dissociation and intra-molecular charge transfer from bpy moiety to Re(I) center, which is unconventional in other QDs-molecules complexes system.^{17–19} We attribute this fact to the strong covalent bonding between the complexes and the QD surface.

Excited state dynamics:

In order to rationalize the detailed mechanism of the photocatalytic reaction for the QDscomplex systems, it is necessary to clarify the excited state dynamics, especially the pathway and timescale for the photo-induced charge transfer process. Therefore, studies with transient absorption (TA) spectroscopy and time-resolved infrared (TRIR) spectroscopy were implemented. We started with the low excitation intensity with the fluence of 8.5×10^{11} ph/cm⁻². Under such conditions, the average excitation per QD $\langle N \rangle$ can be estimated to be 0.32, which means that only one electron can be generated per excitation pulse for a photocatalytic reaction from QDs (For details in excitation density $\langle N \rangle$ calculation, see S.I.). Fig. 4a exhibits a TA absorption spectrogram of InP/ZnS-ReCat(2) with 450 nm excitation. A broad negative band from 475 nm to 520 nm was clearly observed. It can be attributed to the band-edge ground state bleach (GSB) corresponding to the population of the lowest excited state.²⁰ The TA kinetics at the minimum of the GSB represent the depopulation dynamics of the lowest excited state S1. It also should be noted that the band edge TA GB of II-VI ODs (e.g CdSe, PbS) is only predominantly contributed by the electron population at the CB due to the much larger DOS and degeneracy of the VB edge states.²¹ In order to disentangle the electron transfer process, we compared the TA kinetics of InP/ZnS, InP/ZnS-ME, InP/ZnS-ReCat(0.5) and InP/ZnS-ReCat(2) as shown in Fig. 4b. TA kinetics of InP/ZnS-ME exhibit faster decay on the early time scale over 10 ps compared with pristine InP/ZnS ODs. This is widely observed in other semiconductor ODs due to charge trapping introduced by dangling bonds after ligand exchange.²¹ The trapping time varies from tens of ps to hundreds of ps depending on the energy alignment between the excited state and the trap states. Furthermore, when the QDs are linked to the catalysts, the GSBs decay even faster, which indicates that additional excitation depopulation pathways have been introduced by the Re-catalyst attachment. This is most probably due to the photo-induced charge transfer to the Re-catalyst. In particular, the TD-DFT calculation above confirms that the S1 of InP/ZnS-ReCat consists of the electron being located at the bpy moiety, which means that photo-excited electrons should already reside at the Re-catalyst after cooling from the initial excited high energy level. Therefore, the charge transfer pathway can only be from bpy to the Re(I) center.



Fig 4. Transient absorption (TA) and time-resolved infrared (TRIR) study. TA (a) and TRIR (b) spectra of InP/ZnS-ReCat under 450 nm excitation at the fluence of 8.5×10^{11} ph/cm⁻². Comparison of the TA (b) and TRIR (e) kinetics for all samples. Comparison

of the TA kinetics after deducting between InP/ZnS-ME and InP/ZnS-ReCat and TRIR kinetics for InP/ZnS-ReCat(0.5) (c) and InP/ZnS-ReCat(2) (f).

In order to further characterize the charge transfer dynamics, TRIR was employed to probe the location of the transferred electrons. In our previous studies on a similar Re-catalyst linked to a covalent organic framework, clear transient bleach of vibrational mode of C=O was observed as a fingerprint of the photo-induced electron injection to the Re(I) center due to the formation of Re(I) radical.⁷ However, such transient signals could not be observed in the present QD-catalyst system, as shown in Fig. 4d, probably due to the low concentration of the Re-catalyst attached to each QDs. Nevertheless, we observed a broad featureless positive TRIR signal in InP/ZnS-ReCat covering all the wavenumber ranges as shown in Fig. 4d. This is the fingerprint of interband transition of excited free carriers in semiconductors.²² Such positive TRIR signals, however, are absent in the InP/ZnS quantum dots and InP/ZnS-ME as shown in Fig. S3, where the major photoexcited species in neat QDs are excitons due to high exciton binding energy.²³⁻²⁵ Fig. 4e shows the integrated TRIR kinetics of all the samples. The fast rise of the positive signal in InP/ZnS-ReCat indicates the fast exciton dissociation to free carriers after excitation. According to the TD-DFT calculations above, the photo-generated electrons and holes should be located at the bpy moiety and in the ODs, respectively, with spatial separation. We can then conclude that such exciton dissociation should be attributed to the charge transfer from bpy to Re(I) center, which further separates the electrons from the excited holes. In addition, since the electrons residing at the Recomplex side should be localized, the free carrier signal in TRIR spectra should only be contributed by the mobile holes remaining in QDs. In addition, the TRIR decay of two InP/ZnS-ReCat samples (i.e. InP/ZnS-ReCat(0.5), InP/ZnS-ReCat(2)) exhibit similar decay kinetics (Fig. 4e) which means that the depopulation of excited holes is not affected by the concentration of surface catalysts when $\langle N \rangle < 1$.

Comparison between the TA and TRIR kinetics can provide an overview of the depopulation dynamics of excited electrons and holes from the initial excited states, as depicted in Fig. 4c and f. Before that, it is necessary to extract the TA kinetics only from InP/ZnS-ReCat since there remain QDs not attached to Re-cat even with the average number of ligands per QD above 1. We achieve that by subtracting the TA kinetics of InP/ZnS-ReCat by that of InP/ZnS-ME after normalization of the amplitude at long time decay at 2 ns as shown in the Fig. S7. This is based on the assumption that the excited electrons in InP/ZnS-ReCat should almost be entirely depopulated from their initial excited states after such long time scale due to the fast charge transfer processes. The remaining long-lived GSB should then only be contributed by the residual QDs without catalysts in the samples. The resultant differential TA kinetics

are plotted in Fig. 4c and 4f, and compared with the TRIR kinetics. In general, the TA and TRIR kinetics of both samples exhibit similar decay rates at a long time scale > 10 ps. Since TRIR only probes the excited hole dynamics as discussed above, we believe that the electron-hole geminate recombination should be dominant at this time scale. At an early time scale < 10 ps, the TA kinetics decay much faster than TRIR kinetics indicating the additional fast electron transfer process from the initial excited states.

We have fitted all the TA and TRIR kinetics with multi-exponential decay functions, as summarized in table 1. First, we found that the fast rising of TRIR kinetics exhibit the same rates with early time-scale decay of the TA kinetics with a lifetime of 0.6 ps as shown in Fig. 4c. As discussed above, this is the fingerprint of electron transfer from bpy to Re(I), leading to the dissociation of excitons to free carriers. This charge transfer rate is much higher than other hybrid catalyst systems where similar Re-complexes were involved.⁷ This can be rationalized based on the fact that it features as inter-unit transfer within the Re-bpy moieties instead of an interfacial charge transfer process from QDs to Re-bpy.^{5,7,26} In addition, a picosecond component (2.6 ps for TRIR, 8 ps in TA) and a sub-ns component (230 ps in TRIR, 203 ps in TA) can be concurrently observed from the two measurements. As mentioned above, those processes should be correlated to the depopulation of the dissociated holes in ODs, which can only be probed in TRIR signals. The former picosecond component is close to the hole-trapping time at the surface of thiol-capped QDs.²¹ The latter can be assigned to the electron-hole recombination within those ODs that charge transfer to Re(I) center doesn't happen since the ultrafast electron injection would overwhelm the excited electron depopulation in TA kinetics within those QDs. In the TRIR kinetics, one additional ultrafast long-lived component (3.2 ns) can also be observed but is absent in the TA kinetics. We believe this is contributed by the free holes dissociated from the initial exciton and delocalized within ODs, which cannot be probed in TA as mentioned above. In this scenario, the excited holes that finally populated at the VB edge of InP/ZnS QDs should also contribute minorly to the GB, which explains the absence of the nanosecond long-lived components. This means that the transferred electrons at Re(I) centers as well as the residual holes in the QDs will be long-lived (>> 5 ns) before they recombine together, which is favorable for the photocatalytic reactions.

	<n></n>	A_1	t1 (ps)	A ₂	t ₂ (ps)	A ₃	t ₃ (ns)
TRIR							
InP/ZnS-ReCat(0.5)	< 1	0.43	2.6	0.17	230	0.40	3.2
InP/ZnS-ReCat(2)	< 1	0.30	1.0	0.24	40	0.46	5.5
TA							
InP/ZnS-ReCat(0.5)	< 1	0.35	0.7	0.31	8	0.34	0.2
InP/ZnS-ReCat(2)	< 1	0.36	0.3	0.30	4	0.34	0.2
InP/ZnS-ReCat(0.5)	> 1	0.22	0.7	0.25	9	0.53	0.2
InP/ZnS-ReCat(2)	> 1	0.31	0.3	0.20	4	0.49	0.2

Table 1. Multiexponential Fitting Parameters of TA and TRIR kinetics

When two catalysts have been attached to one QD, we find both the TRIR and the TA kinetics of the InP/ZnS-ReCat(2) samples are almost identical to those of InP/ZnS-ReCat(0.5) as shown in Fig. 4f, except for the slightly faster decay at early timescale in TA kinetics, which will be discussed in the following section. This indicates that the increased number of attached catalysts does not significantly modulate the charge transfer and recombination dynamics when only one excitation is implemented per QD (i.e. (<N><1)).



Fig. 5. TA kinetic comparison of single electron donation and multielectron donation for sample InP/ZnS-ReCat(0.5) (A) and InP/ZnS-ReCat(2) (B).

As the photocatalytic CO_2 reduction process features a multielectron reaction,²⁷ next we study the dynamics of photo-induced charge transfer when multiple electrons are generated in the system. In this regard, we do the same analysis of TA dynamics with the $\langle N \rangle$ larger than 1, allowing two electrons to be excited simultaneously within one OD. Interestingly, the TA spectra of multielectron excitation are similar to single electron excitation, but the kinetics are different, indicating different excited state depopulation pathways. We can also subtract the TA kinetics of InP/ZnS-ReCat with InP/ZnS-Me under multielectron excitation conditions after normalization at the long time delay to extract the additional excitation depopulation pathway induced by charge transfer. Fig. 5 compares the differential TA kinetics taken under the single and multiple excitation conditions for OD with only one catalyst attached (InP/ZnS-ReCat(0.5), Fig. 5a) as well as two catalysts attached (InP/ZnS-ReCat(0.5), Fig. 5b). We also fit all the kinetics with multiexponential decay functions as summarized in table 1. A noticeable difference shown in Fig. 5 is that the TA GB kinetics decays much faster under multi-excitation conditions compared with single excitation at one catalyst attachment mode (Fig. 5a). On the other hand, these two kinetics look similar in two catalysts' attachment mode (Fig. 5b). This can be quantitatively reflected by the decrease of the fast decay component (0.7 ps) amplitude from 35% to 22%. It indicates it is difficult for a second excited electron to be transferred to the Re(I) frontier orbital after it is already populated by one electron. However, when two catalysts are attached to one QDs, first, the charge transfer time is shortened by a factor of two from 0.7 ps to 0.3 ps, which can be understood as the doubling of the density of states of the acceptor'. Second, the charge transfer channel is not blocked when two electrons are excited, resulting in identical TA kinetics (Fig. 5b). Obviously, the multielectron donation should be more efficient in multicatalyst attachment based on the above comparison owing to higher charge transfer efficiency. In this scenario, more available carriers can be provided in this system for photocatalytic reactions.

Photocatalytic performance:

In the last step, we conduct photocatalytic CO₂ reduction of the InP/ZnS-ReCats to confirm the influence of excited state dynamics on the catalytic performance. Fig 6a shows there is a rapid production of CO for InP/ZnS-ReCat(2) within the first 2 hours of CO₂RR (from 1.36 mmol g⁻¹ at 1 hour to 2.13 mmol g⁻¹ at 2 hour) with the highest apparent quantum yield (AQY) to be 18%. The production is saturated after 2 hours, where the concentration of CO remained unchanged and the overall AQY decreased. However, when there is less than one catalyst attached at QDs (i.e. InP/ZnS-ReCat(0.5)), the CO production rates are significantly diminished to be less than 0.15 mmol g⁻¹ h⁻¹ with the calculated AQY negligible compared with InP/ZnS-ReCat(2) case. The enhancement of the CO production with multi-catalyst attachment is expected due to the promoted multi-electron donation, as concluded above. Two-electron-mediated CO₂ reduction to CO is easier to achieve in this case. It should be noted that the reduction products were confirmed to be converted from the CO₂ reduction instead of the decomposition of a reactant or sacrificial agent from the control experiment in the absence of CO₂ (For details, see Fig. S8).



Fig 6. Photocatalytic CO₂ reduction performance. Photocatalytic evaluations of CO (a), CH₄ (b) and selectivity of CH₄ towards CO (c) by InP/ZnS-ReCat(0.5) (referred to as single catalyst) and InP/ZnS-ReCat(2) (referred to as multi-catalyst).

To our surprise, we observed the additional reduction products of CH₄ besides CO as shown in Fig. 6b. The CH₄ production rate for the multi-catalyst is about 0.13 mmol g^{-1} h⁻¹, with the AQY calculated to be 1.7 %. The production of CH₄ is usually challenging in CO₂ reduction since it is an 8-electron mediated process therefore, it is seldom realized. Apparently, the enhanced production of CH4, in InP/ZnS-ReCat(2) should be attributed here to the efficient multi-electron donation. More importantly, the CH₄ generation keeps stable even after the saturation of CO generation after 2h, as shown in Fig. 6b. This accounts for the change of production selectivity of CH₄ towards CO over time, as illustrated in Fig. 6c for InP/ZnS-ReCat(2). In the first 2h, the yield of CH4 remains relatively time-independent due to the constant production rates of both CO and CH₄. After 2h, the saturation of CO production increases the selectivity of CH₄ production. Such a concurrent production of CO and CH₄ suggests there could be a conversion from CO to CH₄ with the participation of other intermediate products (e.g. H₂) in the system, which is also observed in other catalysts systems:^{27,28} In that case, CO can be considered the intermediate for the CO₂-to-CH₄ conversion, which should exhibit saturation in concentration when the generation and decomposition reach equilibrium. In addition, the CH₄ production selectivity of the multicatalyst sample is much higher than that of the single catalyst in our system, as shown in Fig. 6c. This indicates that the promotion of multi-electron donation not only facilitates the

efficiency of multi-electron mediated reduction process but also determines the final products. The detailed photocatalytic pathways can be manipulated accordingly, as illustrated in Schematics 1.



Schematic 1. Pathways for photocatalytic CO₂ reduction to be implemented when single (left) and multiple (right) ReBpy complexes are attached to one QD.

Conclusion:

In conclusion, multi-electron donation via attaching multiple Re catalysts onto InP/ZnS QDs to enhance the CO₂ photoreduction approach has been demonstrated. TD-DFT calculations reveal the high overlap between the QD conduction band and the frontier orbital of the Re-catalyst due to strong covalent bonding, which results in a direct electronic transition from QD surface to the Re-Complex moieties. Complementary TA and TRIR demonstrated ultrafast charge transfer from the QD to the metal centers. The number of catalysts attached to the QD significantly affects the charge transfer process. Multi-electron can be efficiently transferred to the metal center within 0.3 ps when two catalysts have been attached per QD. Such an efficient charge transfer suppresses possible Auger recombination or annihilation process. Moreover, the final excited state, where multiple electrons reside at metal centers and multiple holes are delocalized in the QD exhibit a long lifetime. This facilitates the multi-electron mediated CO_2 photocatalytic reduction, where an unconventional 8-electron involved methane production has been significantly enhanced. This work establishes a strategy to control CO_2 reduction products via tuning the multi-electron donation pathways through molecular engineering.

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Ethics declarations

Submission of a competing interests statement is required for all content of the journal.
Supplementary Information

Supplementary Information: should be combined and supplied as a separate file, preferably in PDF format.

Supplementary Information

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Materials and methods

The photocatalyst (Re(bpy)(CO)3Br) was prepared according to previous literature procedures.¹ Indium(III) chloride (98%, Sigma-Aldrich), zinc(II) chloride (98%, Sigma-Aldrich), zinc(II) iodide (98%, Sigma-Aldrich), oleylamine (technical grade, 70%, Sigma-Aldrich), tris(diethylamino)phosphine (98%, Sigma-Aldrich), sulfur powder (99.98%, Sigma-Aldrich), trioctylphosphine (TOP, 97%, Sigma-Aldrich), 2-mercaptoethanol (ME, 99%, Sigma-Aldrich), chloroform (99.5%, Sigma-Aldrich), ethanol (EtOH, for HPLC, VWR Chemicals), hexane (HEX, for HPLC, VWR Chemicals), dimethylformamide (DMF, for HPLC, VWR Chemicals), toluene (for HPLC, VWR Chemicals).

Synthesis of 510 nm InP/ZnS ODs. The process of synthesis InP/ZnS quantum dot was prepared by previous literature² with a little modification. Briefly, the mixture of 111 mg (0.5)mmol) of indium(III) chloride as indium precursor, 160 mg (0.5 mmol) zinc(II) iodide and 204 mg (1.5 mmol) of zinc(II) chloride as zinc precursor was dissolved into 5 mL (15 mmol) of oleylamine, then evacuated by Schlenk techniques and kept under vacuum at 120 °C for 1 h. Afterward, the reaction system was heated to 180 °C under an Argon atmosphere. 0.5 mL (1.8 mmol) of tris(diethylamino)phosphine (phosphorous:indium ratio = 3.6:1) was quickly injected into the mixture. The system was kept at 180 °C for 30 min to drive the growth of InP quantum dot to completion and was further heated to 260 °C and slowly added 1 mL of TOP-S (2M) solution at the rate of 0.2 mL/min. TOP-S solution was prepared by dissolving 0.128 g of sulfur powder in 2 mL of TOP under an inert atmosphere. The system was kept at 260 °C for 3 h to passivate the InP ODs. Finally, the system was cooled down to room temperature. To purify InP/ZnS QDs, about 10 mL of EtOH were added for the precipitation of QDs. After centrifugation, the supernatant was discarded and the precipitated QDs was further dissolved into HEX subsequent centrifugation. Then the precipitation was discard, keep the supernatant and precipitation in 15 mL of EtOH. Following centrifugation, the QDs were again dispersed into 20 mL HEX and centrifuged to remove the insoluble impurities. The prepared QDs were kept well in solution at 2-6 °C.

Synthesis of InP/ZnS-ME QDs. InP/ZnS-ME was prepared by ligand exchange method according to the previous literature ² with slight modification. Briefly, most of the solvent (HEX) in the as-prepared InP/ZnS QDs solution was first removed by the rotary evaporation approach. Then about 2500 times molar excess of ME was added to the reaction system. The mixture was heated to 90 °C under a vacuum to remove the rest of HEX. Afterward, the reaction mixture was kept at 90 °C under Argon atmosphere for approximately 1 h or less until the solution became clear. After cooling down to room temperature, chloroform was added to precipitate the resulting ME-decorated InP/ZnS QDs (ME-capped QDs, InP/ZnS-

ME). Centrifugation at 5000 rpm for about 5 min yielded the targeted products and easily dispersed into DMF. The prepared InP/ZnS-ME were kept well in solution at 2-6 °C.

Synthesis of InP/ZnS-ReCat QDs. The mixture of different molar mass ratio of InP/ZnS-ME and Re(bpy)(CO)₃Br was evacuated and injected argon gas by Schlenk techniques three times, then the system was heated to 100 °C under argon atmosphere for 3 hours. Following cooling down to room temperature, toluene was added for precipitation of InP/ZnS-ReCat QDs, and centrifugation at 5000 rpm for about 5 min was used to purify the products. Finally, the precipitation was easily dispersed into DMF and kept the solution at 2-6 °C in dark place for further measurement.

The different molar mass ratio of InP/ZnS-ME and Re(bpy)(CO)₃Br was used to control the average amount of Re(bpy)(CO)₃Br molecules covalently tethered to the surface of per QD, which was confirmed by XPS measurement. The molar mass ratio of InP/ZnS-ME and Re(bpy)(CO)₃Br was 1: 0.5 means one photocatalyst covalently tethered to per QD, refer to InP/ZnS-ReCat(0.5) in this work. Similarly, the molar mass was 1:2 means two photocatalysts covalently tethered to per QD, refer to InP/ZnS-ReCat(2).

Photocatalytic Reduction of CO2

The method of photocatalytic reduction of CO₂ was carried out according to literature methods with a little modification. 0.35 mg of InP/ZnS-ReCat was dispersed in 5 mL of CH₃CN, and 0.5 mL of TEOA (triethanolamine) in 10 mL septum-sealed glass vials. The mixture was purged with Ar for 10 min and CO₂ for 15 min to wipe out air, and then irradiated by a LED lamp with 440 wavelengths (light intensity: 83.8 mW/cm²; irradiation area: 0.25 cm²) for 6 h and kept stirring during the photocatalytic reaction. The amount of CO and CH₄ generated was quantified every 1 hour by using Shimadzu gas chromatography (GC-2010) by analyzing 500 μ L of the headspace. The control experiment was also carried out only in the absence of CO₂.

Computational methods

To investigate the relationship of the optical properties with molecular structures and electronic structures, we constructed InP/ZnS-ReCat(0.5) (Supplementary Table 1 and 3) and InP/ZnS-ReCat(2) (Supplementary Table 2 and 4) to represent one quantum dot connected with one and two Re-catalytic centers. An implicit solvent model was used to reflect the solvation environment and implemented using SMD solvation model³ in Gaussian 16 package⁴. PBE0⁵⁻⁷ was selected as the exchange-correlation functional; def2-SVP^{8,9} was selected as the basis set for DFT calculations. Acetonitrile parameters were used to represent

the solvents in the SMD models¹⁰. Time-dependent density functional theory (TD-DFT) calculations were also performed using these parameters. The UV-vis absorption spectra and electron excitations were analyzed using the Multiwfn program¹¹.

Characterization

Fourier-Transformed Infrared Spectroscopy (FT-IR) data were obtained by using ALPHA P FT-IR spectrometer (Bruker). The sample material just has to be brought into contact with the measurement interface. Samples was prepared in DMF solution. X-ray Photoelectron Spectroscopy (XPS) data were got by using XPS-Thermo Scientific with Al K α (1486 eV) as the excitation X-ray source. The pressure of the analysis chamber was maintained at $2\times10-10$ mbar during measurement. The sample material was prepared by dispersing it in DMF and then dripping it onto a silicon wafer then dried in air. The peak of C 1s at about 284.8 eV was used to calibrate the energy scale. The XPS data were performed to precisely quantify the number of Re-catalyst tether to one quantum dot by integrating the area of atom peaks. The absorption spectra were measured in a UV-vis absorption spectrophotometer from Agilent Technologies (Santa Clara, USA). Photoluminescence (PL) was performed via Spex Fluorolog 1681 standard spectrofluorometer. Transmission electron microscopy (TEM) images were obtained with a Tecnai G2 T20 TEM.

Nuclear magnetic resonance (NMR) measurement. All presented NMR spectra were either measured on a Bruker Avance IIIHD spectrometer operating at a ³¹P frequency of 242.93 MHz (14.1 T) equipped with a 5mm Bruker BBFO probe, or a Bruker Avance III Nanobay operating at a ³¹P frequency of 161.97 MHz (9.4 T) equipped with a 5 mm CryoProdigy probe. For the quantum dots with attached photo catalyst 65-75k scans were accumulated with an interscan delay of 1.5 seconds, 30° flip-angle and ¹H power-gated decoupling. For the free photo catalyst 16 scans were accumulated with an interscan delay of 2.5 seconds, 90° flip-angle and ¹H power-gated decoupling. The samples were measured "asprepared" adding only 5 vol% of DMF-d7 for lock and shimming. Chemical shifts are reported relative to H_3PO_4 using the lock signal from DMF-d7.

Transient absorption (TA) spectroscopy measurements. The transient absorption (TA) measurements were carried out by laser-base pump-probe spectroscopy with the laser power intensity equating to less than one phonon and two phonons absorption per quantum dot. Laser pulse (800 nm, 40 fs pulse length, 2 KHz repetition rate) were generated by a femtosecond oscillator (Mai Tai SP, both Spectra Physics). Excitation pulse at the wavelength of 450 nm to ensure the pulse only exciting the light harvester (quantum dots) not

photocatalyst, which generated an optical parametric amplifier (Topas C, Light Conversion). For the probe, a broad supercontinuum spectrum was generated from a thin sapphire crystal and split by a beam splitter into a probe pulse and a reference pulse. The probe pulse and the reference pulse were dispersed in a spectrograph and detected by a diode array (Pascher Instruments). A Berek compensator in the pump beam was placed to set the mutual polarization between pump and probe beams to magic angle (54.7°). Excitation power intensity and spot size were necessary for the calculation of excitation fluence, and further determined the average number of excitons $\langle N \rangle$ per QDs.

Transient Mid-IR Absorption Spectroscopy. A frequency doubled Q-switched Nd:YAG laser (Quanta-Ray ProSeries, Spectra-Physics) was employed to obtain 450 nm pump light, 10 mJ/pulse with a fwhm of 10 ns. The 450 nm pump light was used through the MOPO crystal to pump the sample. Probing was done with the continuous wave quantum cascade (QC) IR laser with a tuning capability between 1893 and 2300 cm⁻¹ (Daylight Solutions). For IR detection, a liquid nitrogen-cooled mercury cadmium-telluride (MCT) detector (KMPV10–1J2, Kolmar Technologies, Inc.) was used. The IR probe light was overlapped with the pump beam in a quasi-co-linear arrangement at 25° angle. Transient absorption traces were acquired with a Tektronix TDS 3052 500 MHz (5 GS/s) oscilloscope in connection with the L900 software (Edinburgh Instruments) and processed using Origin 2021 software. Samples were kept in a modified Omni cell (Specac) with O-ring sealed CaF₂ windows and a path length of 1 mm. All samples were re-prepared to keep fresh before measurement, and DMF was used as solvent in all experiments.

Absorption cross section determination. High excitation fluence could excite QDs to multiple exciton states. With a usual assumption, the initially generated multiple exciton population follows the Poissonian distribution

$$P_N = \frac{e^{-\langle N \rangle} \cdot \langle N \rangle^N}{N!} \qquad (1)$$

where $\langle N \rangle$ is the average number of excitons per QDs, N is the number of excitons and P_N is the fraction of NCs with N excitons. We can use $\langle N \rangle = \sigma \cdot I$ to present the average number of excitons per NCs, where σ is the absorption cross-section at the excitation wavelength and I is the excitation intensity in units of the number of photons per pulse per excitation area. From equation (1), we can calculate the fraction of excited NCs, P_{exc} , as:

$$P_{exc} = \sum_{N=1}^{\infty} P_N = 1 - P_0 = 1 - e^{-\langle N \rangle} = 1 - e^{-\sigma \cdot I}$$
(2)

If we know P_{exc} , σ can be calculated from (2). We obtain P_{exc} by measuring the excitation intensity dependence of the late-time region signal ($t \ge 1 ns$), which corresponds to the last remaining exciton after the Auger process. Due to multiple excitations generated at high pump intensity excitation in NCs is rapidly lost via Auger process leaving only one excitation at latetime region ($t \ge 1 ns$). The signal $\Delta A_0(I, t\ge 1 ns)$ intensity can be rescaled to the corresponding signal at t = 0, which we call $\Delta A_0(I)$. We use the lowest excitation intensity as reference excitation intensity and corresponding average number of excitons per NCs, $\langle N \rangle_{0}$.as reference number of excitons per QDs.

$$\Delta A_0(I) = \frac{\Delta A0(I, t \ge 1 \text{ ns})}{e^{-\frac{t}{\tau}}} = \Delta A_0 \cdot \left(1 - e^{-(I \cdot I_0 \cdot \langle N \rangle_0)}\right)$$
(3)

 ΔA_0 , denotes the largest possible single-exciton signal rescaled to t = 0.

Based on the rescaled signal $\Delta A_0(I)$, we perform exponential fit to equation (3). From the fitting, we get the value of $\langle N \rangle_0$, and absorption cross-section σ of InP/ZnS QDs at 400 nm (3.1 eV) were calculated. The absorption cross-section σ at 450 nm was calculated based on the values of σ at 400 nm and absorption spectra. The calculated result is shown at Figure S5.

InP/ZnS QDs, InP/ZnS-ME and InP/ZnS-ReCat concentration calculation. All samples including InP/ZnS QDs, InP/ZnS-ME and InP/ZnS-ReCat can be considered as InP based quantum dots. InP based quantum dots concentration was determined by Beer–Lambert law

$$A = \varepsilon c l \qquad (4)$$

where A is the absorption of the sample, ε is the molar extinction coefficient, c is the concentration of InP based quantum dots, l is the optic path length in cm. If we know ε , c can be calculated from (4). ε can be obtained by the empirical formula reported by previous literature¹²:

$$\varepsilon_{410} = (1.29 \pm 0.06) \times 10^4 d_{0D}^3 \tag{5}$$

where ε_{410} is the molar extinction coefficient of samples at 410 nm excitation wavelength, d_{QD} is the size of InP based quantum dots confirmed by TEM measurement (Figure S3 and S4). It should be note that A is the absorption of samples at 410 nm.

Determination of the number of Re-catalysts attached to per InP/ZnS quantum dot. For InP based quantum dots, their lattice parameter value a is 0.5861 nm and 4 indium atoms in 100

complete unit cell, which reported by previous literature¹³. The Volume of InP/ZnS is calculated by equation followed:

$$V = \frac{4}{3}\pi d_{QD}^3 \qquad (6)$$

where d_{QD} is the size of InP based quantum dots. The number of unit cell of InP for per InP/ZnS QD is easy to abtain to be 52 and 208 indium atoms for per InP/ZnS QD. Then the number of In and Re atom in sample could be calculated by the ratio of indium and rhenium in XPS spectra, we also comfirm the number of Re-catalsyt via the number of Re atom as only one Re atom is located per Re-cataslyt. The calculated results of two samples in this work is followed:

Sample	Size	Unit	Ratio of	Ratio of	The	The
name	(diameter)	cell in	In atom	Re atom	number of	number of
		one QD			In atoms in	catalyst
					one QD	linked to
						one QD
InP/ZnS-			10.12	0.04		0.82(1)
ReCat(0.5)	27.000	52	10.15	0.04	208	0.82 (1)
InP/ZnS-	2.7 1111	52	8.2	0.07	208	1.75 (2)
ReCat(2)			0.3	0.07		1.75(2)

Calculation details of the apparent quantum yield (AQY)

The energy of one photon (E_{photon}) with the wavelength of λ_{inc} (nm) is calculated by the following eauation:

$$E_{photon} = \frac{hc}{\lambda_{inc}} \qquad (6)$$

where $h(J \cdot s)$ is Planck's constant, $c(m \cdot s^{-1})$ is the speed of light and $\lambda_{inc}(m)$ is the wavelength of the incident monochromatic light.

The total energy of the incident monochromatic light (E_{total}) is calculated by the following equation:

$$E_{total} = I_{inc}St \qquad (7)$$

where I_{inc} (W·m⁻²) is the power density of the incident monochromatic light, S (m²) is the irradiation area and t (s) is the the duration of the incident light exposure.

According to the Beer-Lambert law:

$$A = \log_{10} \frac{I_{inc}}{I_{tra}} = \varepsilon cL \qquad (8)$$

Where A is the measured absorbance, I_{inc} (W·m⁻²) is the intensity of the incident light at a given wavelength, I_{tra} (W·m⁻²) is the transmitted intensity, L (m) the path length through the sample, and c (mol·L⁻¹) the concentration of the absorbing species.

Then the power density of absorbed monochromatic light (Ia) by catalysts is:

$$I_a = I_{inc} - I_{tra} \tag{9}$$

Then the power density of absorbed monochromatic light (I_a) by catalysts is:

$$E_a = E_{total} - E_{tra} = (I_{inc} - I_{tra})St$$
(10)

The number of absorbed photons (N_{photon}) by catalysts can be obtained through the following equation:

$$N_{photon} = \frac{E_a}{E_{photon}} = \frac{(I_{inc} - I_{tra})St\lambda_{inc}}{hc}$$
(11)

The moles of incident photons (n_{photon}) absorbed by catalysts can be obtained through the following equation:

$$n_{photon} = \frac{N_{photon}}{N_A} = \frac{(I_{inc} - I_{tra})St\lambda_{inc}}{hcN_A}$$
(12)

Where N_A (mol⁻¹) is the Avogadro constant.

Finally, The AQY is calculated by the number of molecules Nmol undergoing an event (conversion of reactants or formation of products) relative to the number of photon Nph absorbed by the photocatalyst in the following expression:

$$\varphi_{AQY} = \frac{n_{mol}(mol \, s^{-1})}{n_{ph}(einstein \, s^{-1})} \tag{13}$$

Supplementary Figures



Supplementary Figure 1: FTIR spectra of Free Re-catalsyt, InP/ZnS-ReCat(0.5) and InP/ZnS-ReCat(2) in DMF



Supplementary Figure 2: XPS spectra of indium atom for pure InP/ZnS QDs and rhenium atom for pure Re-catalyst.



Supplementary Figure 3: TRIR 2D spectra of InP/ZnS quantum dot and InP/ZnS-ME.



Supplementary Figure 4: HR-TEM images for InP/ZnS quantum dots.



Supplementary Figure 5: Size distribution of InP/ZnS quantum dots



Supplementary Figure 6: Cross section calculation for InP/ZnS quantum dots



Supplementary Figure 7: Illustration of subtracting the TA kinetics of InP/ZnS-ReCat by that of InP/ZnS-ME after normalization of the amplitude at long time decay.



Supplementary Figure 8: Production of CO in the photocatalytic conversion of CO_2 with or without CO_2 for InP/ZnS-ReCat(2).

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Orbital Name	Orbital Number	Energy (eV)	iso-surface images
LUMO+5	443	0.126	
LUMO+4	442	-0.155	
LUMO+3	441	-0.360	
LUMO+2	440	-1.306	

Supplementary Table 1: Calculated DFT energy levels of InP/ZnS-ReCat(0.5).

LUMO+1	439	-1.403	
LUMO	438	-2.385	
НОМО	437	-4.186	
HOMO-1	436	-4.277	
НОМО-2	435	-4.333	

НОМО-3	434	-4.402	
HOMO-4	433	-4.511	
НОМО-5	432	-4.629	

Orbital Name	Orbital Number	Energy (eV)	iso-surface images
LUMO+5	577	-1.35218	
LUMO+4	576	-1.40482	
LUMO+3	575	-1.42781	
LUMO+2	574	-1.46343	

Supplementary Table 2: Calculated DFT energy levels of InP/ZnS-ReCat(2).

LUMO+1	573	-2.42064	
LUMO	572	-2.42849	
НОМО	571	-4.53557	
HOMO-1	570	-4.60462	
НОМО-2	569	-4.7289	

НОМО-3	568	-4.90555	
НОМО-4	567	-4.93767	
НОМО-5	566	-5.06226	

Atom	x (Å)	y (Å)	z (Å)
Zn	4.59366	9.20262	-1.76651
Zn	6.75649	9.24671	0.09142
Zn	1.37652	5.62850	2.06041
Zn	2.92974	6.70791	4.16387
Zn	2.98842	10.93166	0.69110
Zn	1.86140	9.62804	2.94792
Zn	6.34925	6.07979	-0.22852
Zn	4.12431	4.46605	1.15284
Zn	1.34805	8.50934	-0.95405
Zn	2.24498	5.86944	-1.15509
Zn	5.02860	9.26971	3.82259
Zn	6.79026	7.25241	2.73953
Р	4.43219	6.84236	-1.33619
Р	5.02170	10.00030	1.55723
Р	1.29778	7.92212	1.37695
Р	4.79336	5.94689	2.83882
In	3.87044	7.71764	1.10245
S	1.98084	4.03326	0.34744
S	2.96396	8.95554	4.95435
S	2.56755	10.44247	-1.60047
S	8.08033	7.30955	0.74484
S	1.51765	11.77998	2.23278
S	6.08767	3.66128	-0.07798
S	0.56689	6.85808	-2.35583
S	7.08106	8.50907	4.66612
S	6.70252	10.07629	-2.03871
S	1.24180	5.16361	4.30380
С	7.06957	3.08822	1.35173
С	8.55184	3.28235	1.12511
Н	6.85849	2.01815	1.50435
Н	8.79618	4.35636	1.06439
Н	8.87085	2.80678	0.18567
0	9.29290	2.63876	2.17177

Supplementary Table 3: Atomistic coordinates of InP/ZnS-ReCat(0.5).

С	11.20867	4.48901	2.77033
С	11.08568	5.87589	2.74408
С	12.13608	6.64541	2.23476
Ν	13.25339	6.06553	1.74899
С	13.37435	4.73270	1.77968
С	12.38424	3.90718	2.28837
С	12.11037	8.11940	2.19663
С	11.06627	8.88164	2.72464
С	11.13048	10.27260	2.66209
С	12.24899	10.86051	2.06922
С	13.25268	10.04219	1.57261
N	13.18887	8.70745	1.63582
Р	9.93367	3.39113	3.43685
0	10.43164	2.40854	4.42708
0	8.84991	4.46630	3.94687
Р	9.74901	11.28913	3.26792
0	9.19479	10.53485	4.53060
0	10.56224	12.54448	3.88754
0	8.79373	11.67427	2.19227
Re	14.75901	7.38817	0.84785
С	15.95164	6.05330	0.14817
Br	13.24038	7.24817	-1.30791
С	15.80000	7.49205	2.44599
С	15.87777	8.71497	0.02185
0	16.65413	5.23978	-0.27427
0	16.44568	7.55524	3.40580
0	16.53490	9.52272	-0.47711
Н	10.17660	6.35261	3.10759
Н	14.29989	4.31168	1.38408
Н	12.54051	2.82668	2.30085
Н	10.20777	8.39848	3.19227
Н	12.35560	11.94438	2.00095
Н	14.14417	10.47155	1.11253
Н	8.14242	4.07994	4.49192
Н	8.39516	9.85212	4.44728

Н	10.06640	13.36836	3.74936
Н	6.74536	3.63286	2.25325

Atom	x (Å)	y (Å)	z (Å)
Zn	5.53893	2.19627	4.62771
Zn	8.25295	3.01775	4.17104
Zn	4.33674	7.61227	7.31254
Zn	6.53083	8.71289	5.86101
Zn	4.91954	4.53924	2.58742
Zn	4.86517	7.52243	3.41295
Zn	8.10504	3.49979	7.33106
Zn	6.73838	5.92401	8.65326
Zn	2.97796	4.25667	5.25799
Zn	4.10064	4.28821	7.92034
Zn	8.12270	7.06471	3.37995
Zn	9.53250	5.83072	5.57775
Р	5.85293	3.10687	6.82925
Р	7.17825	4.90229	3.13752
Р	3.79043	6.51014	5.24711
Р	7.79220	6.91438	6.81362
In	6.15298	5.34533	5.50014
S	4.50174	6.17886	9.27824
S	6.70866	8.96539	3.47392
S	3.53858	2.86226	3.42077
S	9.92883	3.52276	5.85642
S	4.29919	6.48487	1.26923
S	8.17836	4.21671	9.65654
S	2.06094	3.45547	7.23273
S	10.38464	7.18921	3.90831
S	7.27851	0.98420	3.75670
S	5.08332	9.79826	7.24633
С	9.71890	5.18019	9.84007
С	10.93799	4.29886	9.67426
Н	9.72236	5.62781	10.84611
Н	11.00338	3.92011	8.64005
Н	10.88898	3.43319	10.35142
0	12.12189	5.02254	10.03718

Supplementary Table 4: Atomistic coordinates of InP/ZnS-ReCat(2).

С	13.85143	4.41222	8.00973
С	13.60910	4.25402	6.64773
С	14.27136	3.24124	5.94818
N	15.12797	2.40640	6.57182
С	15.35897	2.55591	7.88198
С	14.74954	3.54504	8.63809
С	14.09654	3.02012	4.50131
С	13.27944	3.81975	3.70040
С	13.17383	3.54744	2.33768
С	13.90587	2.48032	1.81451
С	14.70669	1.73484	2.66733
N	14.80044	1.99472	3.97632
Р	13.11017	5.73843	8.99392
0	14.08944	6.59175	9.70590
0	12.18577	6.45576	7.88731
Р	12.03920	4.51273	1.29610
0	12.11021	5.98617	1.84918
0	12.89558	4.56798	-0.07464
0	10.69665	3.88526	1.15099
Re	16.02554	0.80506	5.35939
С	16.94183	-0.16200	6.74569
Br	13.78452	-0.49959	5.85387
С	17.60989	1.81029	5.00088
С	16.60417	-0.55851	4.13541
0	17.48135	-0.74365	7.58481
0	18.57960	2.40619	4.78496
0	16.93670	-1.37466	3.38922
Н	12.90701	4.90986	6.13531
Н	16.06264	1.86039	8.34162
Н	14.98541	3.62648	9.70092
Н	12.72899	4.65548	4.13369
Н	13.86931	2.22882	0.75336
Н	15.29807	0.90048	2.28682
Н	11.87507	7.33645	8.15910
Н	11.41377	6.30065	2.56243

Н	12.31042	4.65264	-0.84556
Н	9.72809	5.99640	9.10035
С	2.48443	6.70065	1.27238
С	1.77383	5.50938	0.65866
Н	2.26412	7.59611	0.67015
Н	1.72405	4.66608	1.36839
Н	2.31075	5.16560	-0.23713
0	0.46463	5.86031	0.19176
С	-1.23716	4.42403	1.79702
С	-1.31674	4.23530	3.17304
С	-1.74873	3.00543	3.67501
Ν	-2.08792	1.99485	2.84947
С	-1.98658	2.16567	1.52476
С	-1.56845	3.35882	0.95443
С	-1.88797	2.73920	5.11715
С	-1.52047	3.66291	6.09466
С	-1.67091	3.33775	7.44089
С	-2.19475	2.08741	7.76616
С	-2.54567	1.21843	6.74050
Ν	-2.39415	1.53160	5.44895
Р	-0.86065	6.04041	1.07477
0	-1.95639	6.60721	0.25426
0	-0.45000	6.87431	2.39269
Р	-1.19522	4.50713	8.75567
0	-0.00042	5.34873	8.16534
0	-2.35085	5.64134	8.73551
0	-1.05379	3.80953	10.06259
Re	-2.82715	0.14681	3.79135
С	-3.01192	-0.92758	2.20920
Br	-0.29171	-0.54062	4.02707
С	-4.64950	0.69920	3.63943
С	-3.37057	-1.39236	4.80648
0	-3.10739	-1.56378	1.25025
0	-5.75945	1.01691	3.54261
0	-3.68893	-2.31662	5.42093

Н	-1.06338	5.05014	3.84916
Н	-2.26353	1.31796	0.89614
Н	-1.52342	3.44460	-0.13310
Н	-1.09476	4.62531	5.81246
Н	-2.31818	1.78156	8.80655
Н	-2.95808	0.23309	6.96326
Н	-0.50521	7.83589	2.25310
Н	0.78942	4.74552	7.83008
Н	-3.05317	5.41659	9.36659
Н	2.13619	6.88507	2.29917

Supplementary Table 5: Molecular orbital transitions and their contributions to each excited state in InP/ZnS-ReCat(0.5), including excitation energy (in eV), wavelength (in nm), oscillator strength (f) and orbital contributions (in %).

1 1.4273 eV 868.66 nm f= 0.00000 Spin multiplicity= 1:

H -> L 82.1%, H-2 -> L 15.8%

- # 2 1.5416 eV 804.26 nm f= 0.00020 Spin multiplicity= 1:
 H-2 -> L 69.1%, H-1 -> L 13.3%, H -> L 12.4%
- # 3 1.5616 eV 793.96 nm f= 0.00040 Spin multiplicity= 1: H-1 -> L 84.0%, H-2 -> L 10.8%
- # 4 1.6314 eV 759.99 nm f= 0.00000 Spin multiplicity= 1: H-3 -> L 88.3%
- # 5 1.7282 eV 717.42 nm f= 0.00010 Spin multiplicity= 1: H-4 -> L 91.8%, H-3 -> L 5.2%
- # 6 1.8535 eV 668.92 nm f= 0.00000 Spin multiplicity= 1: H-5 -> L 86.7%, H-6 -> L 11.1%
- # 7 1.9136 eV 647.91 nm f= 0.00000 Spin multiplicity= 1:
 H-6 -> L 85.3%, H-5 -> L 10.9%
- # 8 2.0864 eV 594.25 nm f= 0.00100 Spin multiplicity= 1: H-7 -> L 80.8%, H-8 -> L 13.6%
- # 9 2.1408 eV 579.15 nm f= 0.00130 Spin multiplicity=1:
 H-8 -> L 82.8%, H-7 -> L 14.5%
- # 10 2.2561 eV 549.55 nm f= 0.00010 Spin multiplicity= 1: H-9 -> L 91.7%
- # 11 2.3564 eV 526.16 nm f= 0.00000 Spin multiplicity= 1: H-10 -> L 88.3%, H-11 -> L 6.9%
- # 12 2.4096 eV 514.54 nm f= 0.00000 Spin multiplicity= 1: H-11 -> L 85.2%, H-10 -> L 5.9%
- # 13 2.4123 eV 513.97 nm f= 0.00240 Spin multiplicity= 1: H -> L+1 85.1%, H-2 -> L+1 12.3%
- # 14 2.4288 eV 510.48 nm f= 0.00000 Spin multiplicity= 1:

H-12 -> L 86.6%, H-13 -> L 6.1%

- # 15 2.4695 eV 502.06 nm f= 0.00020 Spin multiplicity= 1: H -> L+2 75.4%, H-2 -> L+2 20.7%
- # 16 2.4807 eV 499.80 nm f= 0.00080 Spin multiplicity= 1: H-13 -> L 82.1%, H-12 -> L 5.1%
- # 17 2.5209 eV 491.83 nm f= 0.00040 Spin multiplicity= 1: H-1 -> L+1 58.5%, H-2 -> L+1 28.9%, H-3 -> L+1 7.4%
- # 18 2.5328 eV 489.51 nm f= 0.00180 Spin multiplicity= 1: H-2 -> L+1 53.3%, H-1 -> L+1 35.1%, H -> L+1 10.4%
- # 19 2.5448 eV 487.21 nm f= 0.00220 Spin multiplicity= 1:
 H-17 -> L 93.5%, H-18 -> L 5.4%
- # 20 2.5795 eV 480.65 nm f= 0.00000 Spin multiplicity= 1: H-14 -> L 94.6%
- # 21 2.5859 eV 479.46 nm f= 0.00130 Spin multiplicity= 1: H-2 -> L+2 68.1%, H -> L+2 17.6%, H-1 -> L+2 8.6%
- # 22 2.6026 eV 476.39 nm f= 0.00320 Spin multiplicity= 1: H-3 -> L+1 83.7%
- # 23 2.6301 eV 471.40 nm f= 0.00000 Spin multiplicity= 1: H-1 -> L+2 88.4%, H-2 -> L+2 5.4%
- # 24 2.6457 eV 468.63 nm f= 0.00450 Spin multiplicity= 1: H-15 -> L 87.8%
- # 25 2.6800 eV 462.63 nm f= 0.05800 Spin multiplicity= 1: H-20 -> L 91.6%
- # 26 2.6870 eV 461.42 nm f= 0.00020 Spin multiplicity= 1: H-3 -> L+2 83.3%, H-4 -> L+2 7.0%
- # 27 2.6994 eV 459.30 nm f= 0.00220 Spin multiplicity= 1: H-4 -> L+1 90.5%, H-3 -> L+1 5.3%
- # 28 2.7796 eV 446.05 nm f= 0.00040 Spin multiplicity= 1: H-4 -> L+2 87.5%, H-3 -> L+2 7.4%
- # 29 2.8254 eV 438.82 nm f= 0.00120 Spin multiplicity= 1: H-5 -> L+1 88.0%, H-6 -> L+1 9.1%

- # 30 2.8869 eV 429.47 nm f= 0.00000 Spin multiplicity= 1: H-6 -> L+1 87.8%, H-5 -> L+1 8.5%
- # 31 2.9039 eV 426.96 nm f= 0.00170 Spin multiplicity= 1: H-5 -> L+2 83.2%, H-6 -> L+2 13.5%
- # 32 2.9626 eV 418.50 nm f= 0.00020 Spin multiplicity= 1: H-16 -> L 90.2%
- # 33 2.9738 eV 416.92 nm f= 0.00000 Spin multiplicity= 1: H-6 -> L+2 79.3%, H-5 -> L+2 13.5%
- # 34 3.0618 eV 404.94 nm f= 0.00000 Spin multiplicity= 1: H-7 -> L+1 78.8%, H-8 -> L+1 15.4%
- # 35 3.0831 eV 402.14 nm f= 0.00000 Spin multiplicity= 1: H-18 -> L 83.7%
- # 36 3.1086 eV 398.84 nm f= 0.00000 Spin multiplicity= 1: H-8 -> L+1 73.4%, H-7 -> L+1 15.9%, H-19 -> L 6.7%
- # 37 3.1245 eV 396.81 nm f= 0.00480 Spin multiplicity= 1: H-7 -> L+2 64.7%, H-8 -> L+2 18.4%, H-19 -> L 7.5%
- # 38 3.1283 eV 396.33 nm f= 0.00090 Spin multiplicity= 1:
 H-19 -> L 79.2%, H-7 -> L+2 7.7%, H-8 -> L+1 5.9%
- # 39 3.1914 eV 388.49 nm f= 0.00040 Spin multiplicity= 1: H-21 -> L 87.5%, H-24 -> L 5.6%
- # 40 3.1957 eV 387.97 nm f= 0.00150 Spin multiplicity= 1: H-8 -> L+2 75.2%, H-7 -> L+2 19.5%
- # 41 3.2285 eV 384.03 nm f= 0.00170 Spin multiplicity= 1: H-9 -> L+1 90.5%
- # 42 3.2845 eV 377.48 nm f= 0.00000 Spin multiplicity= 1: H-30 -> L 96.4%
- # 43 3.3025 eV 375.43 nm f= 0.00030 Spin multiplicity= 1: H-23 -> L 46.7%, H-24 -> L 24.9%, H-9 -> L+2 10.0%
- # 44 3.3106 eV 374.51 nm f= 0.00060 Spin multiplicity= 1: H-9 -> L+2 79.2%, H-23 -> L 6.4%
- # 45 3.3240 eV 373.00 nm f= 0.00620 Spin multiplicity=1:

- H-10 -> L+1 78.3%, H-11 -> L+1 14.1%
- # 46 3.3495 eV 370.16 nm f= 0.00030 Spin multiplicity= 1: H-22 -> L 80.5%, H-23 -> L 5.5%
- # 47 3.3820 eV 366.60 nm f= 0.00000 Spin multiplicity=1:

H-11 -> L+1 73.7%, H-10 -> L+1 11.6%, H-13 -> L+1 7.5%

- # 48 3.3964 eV 365.05 nm f= 0.00010 Spin multiplicity=1:
- H-12 -> L+1 67.4%, H-24 -> L 6.8%, H-26 -> L 5.4%
- # 49 3.4032 eV 364.32 nm f= 0.00060 Spin multiplicity=1:
- H-24 -> L 31.3%, H-26 -> L 21.4%, H-23 -> L 19.9%, H-12 -> L+1 17.0%
- # 50 3.4128 eV 363.29 nm f= 0.00460 Spin multiplicity=1:

H-10 -> L+2 90.9%

- # 51 3.4467 eV 359.72 nm f= 0.00010 Spin multiplicity=1:
- H-26 -> L 52.3%, H-24 -> L 15.1%, H-22 -> L 8.7%, H-27 -> L 8.1%, H-23 -> L 5.5%
- # 52 3.4547 eV 358.89 nm f= 0.00080 Spin multiplicity= 1:

H-13 -> L+1 76.1%, H-12 -> L+1 5.9%

- # 53 3.4689 eV 357.42 nm f= 0.00010 Spin multiplicity=1:
- H-11 -> L+2 79.9%, H-12 -> L+2 10.3%
- # 54 3.4730 eV 356.99 nm f= 0.00010 Spin multiplicity= 1:

H-25 -> L 85.2%, H-26 -> L 6.5%

- # 55 3.4835 eV 355.92 nm f= 0.00060 Spin multiplicity=1:
- H-12 -> L+2 70.4%, H-13 -> L+2 13.5%, H-11 -> L+2 7.6%
- # 56 3.5198 eV 352.25 nm f= 0.00300 Spin multiplicity= 1:
- H-13 -> L+2 52.3%, H-27 -> L 21.1%, H-15 -> L+2 5.5%, H-11 -> L+2 5.3%
- # 57 3.5262 eV 351.61 nm f= 0.00010 Spin multiplicity=1:
- H-27 -> L 56.9%, H-13 -> L+2 17.8%
- # 58 3.5339 eV 350.84 nm f= 0.00000 Spin multiplicity= 1:

H -> L+3 89.4%, H-2 -> L+3 9.6%

- # 59 3.5450 eV 349.74 nm f= 0.00210 Spin multiplicity=1: H-14 -> L+1 87.1%
- # 60 3.5584 eV 348.43 nm f= 0.04200 Spin multiplicity= 1:
- H -> L+5 76.3%, H -> L+6 17.7%

- # 61 3.6136 eV 343.10 nm f= 0.00100 Spin multiplicity= 1: H-15 -> L+1 58.7%, H-17 -> L+1 32.7%
- # 62 3.6201 eV 342.49 nm f= 0.00590 Spin multiplicity= 1:
- H-17 -> L+1 57.5%, H-15 -> L+1 31.7%, H-18 -> L+1 5.5%
- # 63 3.6391 eV 340.70 nm f= 0.02700 Spin multiplicity= 1: H-1 -> L+5 73.8%, H-1 -> L+6 17.4%
- # 64 3.6458 eV 340.07 nm f= 0.00450 Spin multiplicity= 1: H-14 -> L+2 83.3%, H-28 -> L 6.4%, H-29 -> L 5.1%
- # 65 3.6493 eV 339.75 nm f= 0.00000 Spin multiplicity= 1: H-2 -> L+3 74.5%, H-1 -> L+3 15.4%, H -> L+3 7.8%
- # 66 3.6521 eV 339.49 nm f= 0.00180 Spin multiplicity= 1:
- H-29 -> L 39.1%, H-28 -> L 32.9%, H-14 -> L+2 11.7%, H-15 -> L+2 6.8%
- # 67 3.6558 eV 339.14 nm f= 0.00000 Spin multiplicity= 1:
- H-1 -> L+3 84.0%, H-2 -> L+3 13.2%
- # 68 3.6748 eV 337.39 nm f= 0.00100 Spin multiplicity= 1: H-15 -> L+2 75.3%, H-13 -> L+2 5.4%
- # 69 3.6854 eV 336.42 nm f= 0.00460 Spin multiplicity= 1: H-20 -> L+1 93.5%
- # 70 3.7078 eV 334.39 nm f= 0.01050 Spin multiplicity= 1: H-17 -> L+2 70.5%, H-2 -> L+5 13.5%
- # 71 3.7082 eV 334.35 nm f= 0.04100 Spin multiplicity= 1: H-2 -> L+5 59.5%, H-17 -> L+2 16.1%, H-2 -> L+6 13.1%
- # 72 3.7387 eV 331.62 nm f= 0.00010 Spin multiplicity= 1: H -> L+4 89.3%, H-2 -> L+4 9.3%
- # 73 3.7483 eV 330.77 nm f= 0.00000 Spin multiplicity= 1: H-3 -> L+3 95.0%
- # 74 3.7745 eV 328.48 nm f= 0.00040 Spin multiplicity= 1:
 H-29 -> L 25.8%, H-33 -> L 25.5%, H-28 -> L 24.9%, H-32 -> L 20.6%
- # 75 3.7761 eV 328.34 nm f= 0.00720 Spin multiplicity= 1:
- H-20 -> L+2 40.1%, H-32 -> L 21.5%, H-28 -> L 17.5%, H-29 -> L 11.5%, H-33 -> L 5.6%
- # 76 3.7846 eV 327.60 nm f= 0.00630 Spin multiplicity=1:
- 128

H-20 -> L+2 52.5%, H-33 -> L 18.1%, H-32 -> L 9.8%, H-28 -> L 8.5%, H-29 -> L 8.2%

- # 77 3.7888 eV 327.24 nm f= 0.16210 Spin multiplicity= 1: H-3 -> L+5 74.0%, H-3 -> L+6 16.9%
- # 78 3.8465 eV 322.33 nm f= 0.15250 Spin multiplicity= 1:
 H-33 -> L 42.6%, H-32 -> L 39.7%
- # 79 3.8475 eV 322.25 nm f= 0.00650 Spin multiplicity= 1: H-4 -> L+3 93.7%
- # 80 3.8536 eV 321.74 nm f= 0.00010 Spin multiplicity= 1: H-2 -> L+4 72.1%, H-1 -> L+4 18.5%, H -> L+4 7.2%
- # 81 3.8601 eV 321.19 nm f= 0.00000 Spin multiplicity= 1: H-1 -> L+4 80.9%, H-2 -> L+4 15.9%
- # 82 3.8725 eV 320.17 nm f= 0.11560 Spin multiplicity= 1: H-4 -> L+5 77.4%, H-4 -> L+6 17.3%
- # 83 3.9353 eV 315.06 nm f= 0.00040 Spin multiplicity= 1: H-16 -> L+1 91.9%
- # 84 3.9520 eV 313.73 nm f= 0.00020 Spin multiplicity= 1: H-3 -> L+4 93.7%
- # 85 3.9581 eV 313.24 nm f= 0.00230 Spin multiplicity= 1: H -> L+6 62.9%, H -> L+5 14.9%, H-2 -> L+6 12.5%
- # 86 3.9668 eV 312.55 nm f= 0.08660 Spin multiplicity= 1: H-5 -> L+5 66.7%, H-5 -> L+6 15.9%, H-6 -> L+5 5.0%
- # 87 3.9710 eV 312.22 nm f= 0.00050 Spin multiplicity= 1: H-5 -> L+3 89.4%, H-6 -> L+3 9.0%
- # 88 3.9899 eV 310.75 nm f= 0.02750 Spin multiplicity= 1: H-6 -> L+5 66.4%, H-6 -> L+6 15.4%
- # 89 4.0144 eV 308.85 nm f= 0.00120 Spin multiplicity= 1: H-16 -> L+2 85.6%, H-18 -> L+2 5.6%
- # 90 4.0154 eV 308.77 nm f= 0.00000 Spin multiplicity= 1: H-6 -> L+3 88.1%, H-5 -> L+3 8.8%
- # 91 4.0511 eV 306.05 nm f= 0.00000 Spin multiplicity= 1: H-4 -> L+4 95.5%
- # 92 4.0536 eV 305.86 nm f= 0.00210 Spin multiplicity=1: H-18 -> L+1 82.5%
- # 93 4.0725 eV 304.44 nm f= 0.00020 Spin multiplicity=1:
- H-2 -> L+6 56.7%, H-2 -> L+5 12.6%, H-1 -> L+6 10.3%, H -> L+6 9.8%
- # 94 4.0939 eV 302.85 nm f= 0.00030 Spin multiplicity=1:

H-1 -> L+6 67.3%, H-1 -> L+5 16.2%, H-2 -> L+6 8.3%

- # 95 4.1054 eV 302.00 nm f= 0.00110 Spin multiplicity= 1: H-19 -> L+1 93.0%
- # 96 4.1176 eV 301.11 nm f= 0.00010 Spin multiplicity= 1:
 H-31 -> L 87.4%, H-18 -> L+2 6.6%
- # 97 4.1324 eV 300.03 nm f= 0.00490 Spin multiplicity= 1:
 H -> L+8 64.1%, H-18 -> L+2 11.1%, H -> L+9 8.5%
- # 98 4.1348 eV 299.86 nm f= 0.00090 Spin multiplicity= 1:
 H-18 -> L+2 59.9%, H -> L+8 12.2%, H-31 -> L 6.9%
- # 99 4.1601 eV 298.03 nm f= 0.00240 Spin multiplicity= 1: H-21 -> L+1 75.1%, H-3 -> L+6 8.6%, H-24 -> L+1 6.0%
- # 100 4.1641 eV 297.75 nm f= 0.00030 Spin multiplicity= 1: H-3 -> L+6 60.3%, H-3 -> L+5 14.3%, H-21 -> L+1 11.2%
- # 101 4.1748 eV 296.98 nm f= 0.00000 Spin multiplicity= 1: H-5 -> L+4 89.8%, H-6 -> L+4 8.7%
- # 102 4.1779 eV 296.76 nm f= 0.00130 Spin multiplicity= 1: H-19 -> L+2 89.1%
- # 103 4.2038 eV 294.93 nm f= 0.00400 Spin multiplicity= 1: H-1 -> L+8 58.6%, H-7 -> L+5 20.7%
- # 104 4.2095 eV 294.53 nm f= 0.01110 Spin multiplicity= 1:
- H-20 -> L+3 40.0%, H-7 -> L+3 27.1%, H-17 -> L+3 16.9%
- # 105 4.2191 eV 293.86 nm f= 0.01550 Spin multiplicity= 1:

H-7 -> L+3 37.0%, H-6 -> L+4 14.1%, H-20 -> L+3 10.3%, H-7 -> L+5 8.1%, H-1 -> L+8 7.7%

106 4.2195 eV 293.84 nm f= 0.00390 Spin multiplicity= 1:

H-6 -> L+4 71.0%, H-7 -> L+3 14.1%, H-5 -> L+4 6.9%

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107 4.2210 eV 293.73 nm f= 0.00090 Spin multiplicity= 1:

H-7 -> L+5 23.2%, H-1 -> L+8 17.8%, H-7 -> L+3 15.7%, H -> L+10 11.2%, H-7 -> L+6 5.5%

108 4.2252 eV 293.44 nm f= 0.02790 Spin multiplicity= 1:

H-17 -> L+3 56.1%, H-20 -> L+3 17.1%, H-20 -> L+4 5.7%

109 4.2321 eV 292.96 nm f= 0.20290 Spin multiplicity= 1:

H-34 -> L 26.1%, H-36 -> L 26.0%, H-20 -> L+3 14.9%, H-35 -> L 11.5%

110 4.2455 eV 292.04 nm f= 0.00780 Spin multiplicity= 1:

- H-21 -> L+2 72.4%, H-24 -> L+2 5.7%
- # 111 4.2467 eV 291.95 nm f= 0.00140 Spin multiplicity= 1:
- H -> L+10 33.4%, H-7 -> L+5 14.6%, H-21 -> L+2 10.5%, H-8 -> L+5 8.7%
- # 112 4.2574 eV 291.22 nm f= 0.00640 Spin multiplicity= 1:

H-2 -> L+8 21.6%, H-8 -> L+5 21.0%, H -> L+9 14.2%, H-2 -> L+9 13.6%

113 4.2609 eV 290.98 nm f= 0.00570 Spin multiplicity= 1:

H-4 -> L+6 70.5%, H-4 -> L+5 15.7%

114 4.2645 eV 290.74 nm f= 0.00050 Spin multiplicity= 1:

H-8 -> L+3 93.1%

115 4.2740 eV 290.09 nm f= 0.01020 Spin multiplicity= 1:

H-23 -> L+1 53.7%, H-24 -> L+1 26.7%, H-18 -> L+1 5.8%

116 4.2859 eV 289.28 nm f = 0.02350 Spin multiplicity = 1:

H-8 -> L+5 27.1%, H-2 -> L+8 16.7%, H -> L+10 16.7%, H-1 -> L+9 6.3%, H-8 -> L+6 6.1%

117 4.2915 eV 288.91 nm f = 0.00850 Spin multiplicity = 1:

H -> L+9 26.2%, H -> L+12 14.4%, H-3 -> L+8 12.8%, H-2 -> L+8 10.2%, H-1 -> L+9 5.0%

118 4.3150 eV 287.33 nm f= 0.01040 Spin multiplicity= 1:

H-3 -> L+8 36.4%, H -> L+12 14.1%, H-9 -> L+5 5.5%, H -> L+14 5.4%

119 4.3192 eV 287.05 nm f = 0.00100 Spin multiplicity = 1:

H-1 -> L+9 21.8%, H-2 -> L+8 17.2%, H -> L+12 13.6%, H -> L+9 7.7%, H-1 -> L+12 6.8%

120 4.3235 eV 286.77 nm f = 0.00150 Spin multiplicity = 1:

H-22 -> L+1 80.5%, H-25 -> L+1 5.3%

- # 121 4.3396 eV 285.70 nm f= 0.00230 Spin multiplicity= 1:
- H-17 -> L+4 80.7%, H-30 -> L+3 6.7%
- # 122 4.3411 eV 285.61 nm f= 0.00690 Spin multiplicity= 1:
- H-1 -> L+10 42.6%, H-3 -> L+9 10.6%, H -> L+10 6.8%, H-1 -> L+15 5.7%
- # 123 4.3478 eV 285.17 nm f= 0.00050 Spin multiplicity= 1:
- H-23 -> L+2 51.3%, H-24 -> L+2 27.7%, H-18 -> L+2 5.8%
- # 124 4.3553 eV 284.67 nm f= 0.00310 Spin multiplicity= 1:
- H-9 -> L+5 18.3%, H-1 -> L+9 13.4%, H-1 -> L+10 12.4%, H-4 -> L+8 6.8%, H-3 -> L+8 5.6%
- # 125 4.3690 eV 283.78 nm f= 0.00060 Spin multiplicity= 1:

H-9 -> L+3 30.9%, H-9 -> L+5 14.6%, H-24 -> L+1 8.1%, H-26 -> L+1 6.8%, H-30 -> L+1 5.6%

126 4.3696 eV 283.74 nm f= 0.00240 Spin multiplicity= 1:

H-9 -> L+3 33.9%, H-24 -> L+1 16.7%, H-30 -> L+1 16.2%, H-26 -> L+1 14.1%, H-23 -> L+1 10.9%

- # 127 4.3701 eV 283.71 nm f= 0.00040 Spin multiplicity= 1:
- H-9 -> L+3 30.7%, H-9 -> L+5 22.3%, H -> L+12 6.1%, H-9 -> L+6 5.6%, H-1 -> L+9 5.1%
- # 128 4.3744 eV 283.43 nm f= 0.00090 Spin multiplicity= 1:
- H-30 -> L+1 67.2%, H-24 -> L+1 12.0%, H-26 -> L+1 5.9%, H-23 -> L+1 5.9%
- # 129 4.3852 eV 282.73 nm f= 0.00020 Spin multiplicity= 1:
- H-5 -> L+6 67.9%, H-5 -> L+5 15.6%, H-6 -> L+6 9.2%
- # 130 4.3887 eV 282.51 nm f= 0.00720 Spin multiplicity= 1:
- H-4 -> L+8 36.4%, H-2 -> L+10 30.5%
- # 131 4.3969 eV 281.98 nm f= 0.00100 Spin multiplicity= 1:
- H-4 -> L+8 22.7%, H-2 -> L+10 20.6%, H -> L+15 8.1%, H-3 -> L+10 6.1%
- # 132 4.3999 eV 281.79 nm f= 0.00090 Spin multiplicity= 1:
- H-22 -> L+2 71.8%, H-26 -> L+2 8.3%, H-25 -> L+2 5.5%
- # 133 4.4173 eV 280.68 nm f= 0.00010 Spin multiplicity= 1:
- H-26 -> L+1 50.2%, H-24 -> L+1 14.3%, H-27 -> L+1 13.0%, H-22 -> L+1 10.1%, H-23 -> L+1 5.2%
- # 134 4.4198 eV 280.52 nm f= 0.00020 Spin multiplicity= 1:
- 132

H-7 -> L+4 85.8%

135 4.4240 eV 280.25 nm f= 0.00240 Spin multiplicity= 1:

H-2 -> L+9 25.2%, H-2 -> L+12 20.8%, H-2 -> L+10 8.5%, H-7 -> L+4 6.5%, H-2 -> L+8 5.2%

136 4.4406 eV 279.21 nm f= 0.00270 Spin multiplicity= 1:

H-25 -> L+1 74.5%

137 4.4430 eV 279.06 nm f= 0.00490 Spin multiplicity= 1:

H-6 -> L+6 17.5%, H-3 -> L+9 11.7%, H-3 -> L+10 8.9%, H-6 -> L+5 7.5%, H-25 -> L+1 6.3%, H-1 -> L+12 5.6%

138 4.4467 eV 278.82 nm f= 0.00140 Spin multiplicity= 1:

H-6 -> L+6 48.6%, H-6 -> L+5 8.6%, H-5 -> L+6 5.6%

- # 139 4.4494 eV 278.65 nm f= 0.00550 Spin multiplicity= 1: H-38 -> L 82.5%
- # 140 4.4522 eV 278.48 nm f= 0.00190 Spin multiplicity= 1:
- H-26 -> L+2 39.2%, H-24 -> L+2 21.5%, H-23 -> L+2 15.0%
- # 141 4.4670 eV 277.56 nm f= 0.00130 Spin multiplicity= 1: H-8 -> L+4 87.8%
- # 142 4.4696 eV 277.39 nm f= 0.00340 Spin multiplicity= 1:

H-30 -> L+2 74.9%, H-10 -> L+5 6.8%

143 4.4703 eV 277.35 nm f= 0.00770 Spin multiplicity= 1:

H-10 -> L+5 37.5%, H-30 -> L+2 11.3%, H-10 -> L+6 8.7%, H-8 -> L+4 5.7%

144 4.4731 eV 277.18 nm f= 0.00030 Spin multiplicity= 1:

H-10 -> L+3 93.0%

145 4.4792 eV 276.80 nm f= 0.00990 Spin multiplicity= 1:

H-11 -> L+5 37.8%, H-3 -> L+9 11.2%, H-11 -> L+6 8.8%, H-2 -> L+9 6.8%, H-2 -> L+12 5.2%

146 4.4820 eV 276.63 nm f= 0.00170 Spin multiplicity= 1:

H-27 -> L+1 71.2%, H-26 -> L+1 8.4%, H-23 -> L+1 6.1%

147 4.4906 eV 276.10 nm f= 0.00750 Spin multiplicity= 1:

H-2 -> L+12 14.1%, H-2 -> L+9 11.6%, H-3 -> L+10 6.9%, H-2 -> L+8 6.7%, H -> L+12 6.1%, H-12 -> L+5 5.8%, H -> L+14 5.5%

148 4.4968 eV 275.72 nm f= 0.00050 Spin multiplicity= 1:

H-26 -> L+2 33.3%, H-24 -> L+2 25.2%, H-27 -> L+2 13.6%, H-23 -> L+2 10.5%, H-22 -> L+2 9.4%

149 4.5096 eV 274.93 nm f= 0.00260 Spin multiplicity= 1:

H-3 -> L+10 23.6%, H-11 -> L+5 11.7%, H-4 -> L+9 10.5%, H-4 -> L+10 6.6%, H -> L+15 6.6%

150 4.5144 eV 274.64 nm f= 0.00270 Spin multiplicity= 1:

H-11 -> L+3 41.9%, H-4 -> L+9 8.6%, H-3 -> L+9 7.6%

151 4.5153 eV 274.59 nm f= 0.00300 Spin multiplicity= 1:

H-11 -> L+3 50.2%, H-4 -> L+9 7.4%, H-3 -> L+9 6.2%

152 4.5253 eV 273.98 nm f= 0.00010 Spin multiplicity= 1:

H -> L+7 90.6%, H-2 -> L+7 7.4%

153 4.5316 eV 273.60 nm f= 0.00730 Spin multiplicity= 1:

H-12 -> L+5 26.5%, H-5 -> L+8 17.6%, H-2 -> L+12 10.0%, H-12 -> L+6 6.2%, H -> L+13 5.6%

154 4.5354 eV 273.37 nm f= 0.00130 Spin multiplicity= 1:

H-25 -> L+2 52.5%, H-34 -> L 17.7%, H-36 -> L 8.0%

- # 155 4.5422 eV 272.96 nm f= 0.00140 Spin multiplicity= 1:
- H-34 -> L 34.3%, H-25 -> L+2 26.0%, H-36 -> L 13.7%, H-35 -> L 8.8%
- # 156 4.5448 eV 272.80 nm f= 0.00050 Spin multiplicity= 1:
- H-12 -> L+3 86.9%

157 4.5487 eV 272.57 nm f= 0.00340 Spin multiplicity= 1:

H-5 -> L+8 39.4%, H-12 -> L+5 9.7%, H-4 -> L+9 8.1%, H-12 -> L+3 6.8%

158 4.5518 eV 272.38 nm f= 0.00110 Spin multiplicity= 1:

H-1 -> L+12 15.6%, H-2 -> L+12 11.3%, H-5 -> L+8 8.2%, H-3 -> L+12 7.1%, H -> L+13 5.6%

159 4.5625 eV 271.75 nm f= 0.00410 Spin multiplicity= 1:

H-4 -> L+9 22.6%, H-1 -> L+12 17.6%, H-3 -> L+10 7.1%, H-3 -> L+12 7.0%

160 4.5709 eV 271.25 nm f= 0.00030 Spin multiplicity= 1:

H-27 -> L+2 63.1%, H-23 -> L+2 10.3%, H-25 -> L+2 7.4%, H-26 -> L+2 7.0%

161 4.5737 eV 271.08 nm f= 0.00010 Spin multiplicity= 1:

H-9 -> L+4 94.0%

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# 162 4.5819 eV 270.60 nm f= 0.00300 Spin multiplicity= 1:
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H-4 -> L+10 24.6%, H-1 -> L+14 11.4%

163 4.5977 eV 269.67 nm f= 0.00220 Spin multiplicity= 1:

H-29 -> L+1 34.2%, H-28 -> L+1 27.7%, H-35 -> L 14.4%, H-37 -> L 8.4%

164 4.5997 eV 269.55 nm f= 0.00400 Spin multiplicity= 1:

H-4 -> L+10 18.6%, H-1 -> L+14 14.6%, H -> L+14 10.6%, H-1 -> L+13 9.3%, H-2 -> L+13 6.0%

165 4.6063 eV 269.16 nm f= 0.00340 Spin multiplicity= 1:

H-35 -> L 33.9%, H-36 -> L 23.2%, H-28 -> L+1 12.7%, H-29 -> L+1 10.6%

166 4.6082 eV 269.05 nm f = 0.00730 Spin multiplicity = 1:

H -> L+13 19.3%, H-3 -> L+12 14.9%, H-1 -> L+14 6.0%, H-3 -> L+10 5.3%

167 4.6133 eV 268.75 nm f= 0.00000 Spin multiplicity= 1:

H-13 -> L+3 92.2%

168 4.6166 eV 268.56 nm f= 0.00370 Spin multiplicity= 1:

H -> L+15 30.1%, H -> L+13 6.1%, H-6 -> L+8 5.8%, H-4 -> L+10 5.1%

169 4.6181 eV 268.47 nm f= 0.00050 Spin multiplicity= 1:

H-7 -> L+6 52.5%, H-7 -> L+5 10.1%, H-8 -> L+6 8.8%

170 4.6236 eV 268.16 nm f= 0.00220 Spin multiplicity= 1:

H-3 -> L+12 12.5%, H -> L+14 11.8%, H-2 -> L+13 11.0%, H-2 -> L+14 6.4%, H -> L+15 5.8%

171 4.6369 eV 267.39 nm f= 0.00910 Spin multiplicity= 1:

H-13 -> L+5 27.8%, H-6 -> L+8 7.7%, H-1 -> L+14 6.2%, H-13 -> L+6 6.1%, H-5 -> L+9 5.1%

172 4.6395 eV 267.24 nm f= 0.00170 Spin multiplicity= 1:

H-1 -> L+7 49.1%, H-2 -> L+7 30.7%, H-6 -> L+8 7.5%

173 4.6416 eV 267.12 nm f= 0.00830 Spin multiplicity= 1:

H-6 -> L+8 24.5%, H-2 -> L+7 16.3%, H-13 -> L+5 15.7%, H-1 -> L+14 5.7%, H-6 -> L+9 5.5%

174 4.6445 eV 266.95 nm f= 0.00030 Spin multiplicity= 1:

H-1 -> L+7 45.1%, H-2 -> L+7 37.5%

175 4.6450 eV 266.92 nm f= 0.00630 Spin multiplicity= 1:

H-41 -> L 42.0%, H-37 -> L 20.7%, H-35 -> L 8.4%, H-36 -> L 5.8%

176 4.6495 eV 266.66 nm f= 0.00330 Spin multiplicity= 1:

H-14 -> L+5 13.8%, H-2 -> L+13 13.1%, H-4 -> L+10 8.7%, H-5 -> L+10 5.8%, H-3 -> L+14 5.5%

- # 177 4.6612 eV 265.99 nm f= 0.00300 Spin multiplicity= 1:
- H-4 -> L+12 23.9%, H-14 -> L+5 11.8%, H-37 -> L 8.8%
- # 178 4.6643 eV 265.82 nm f= 0.00280 Spin multiplicity= 1:
- H-37 -> L 38.1%, H-41 -> L 24.0%, H-4 -> L+12 6.8%
- # 179 4.6695 eV 265.52 nm f= 0.01530 Spin multiplicity= 1:
- H-1 -> L+15 20.2%, H-13 -> L+5 14.8%, H-4 -> L+12 6.8%, H-3 -> L+12 5.8%
- # 180 4.6732 eV 265.31 nm f= 0.00130 Spin multiplicity= 1:

H-8 -> L+6 20.6%, H-5 -> L+9 13.2%, H-5 -> L+10 12.9%, H-2 -> L+14 6.1%, H-8 -> L+5 5.4%

181 4.6760 eV 265.15 nm f= 0.00280 Spin multiplicity= 1:

H-8 -> L+6 35.5%, H-5 -> L+9 7.2%, H-8 -> L+5 6.6%, H-5 -> L+10 6.2%, H-7 -> L+6 6.2%, H-2 -> L+14 6.2%, H-10 -> L+4 5.1%

182 4.6763 eV 265.13 nm f = 0.00440 Spin multiplicity = 1:

H-10 -> L+4 76.7%, H-8 -> L+6 5.3%

- # 183 4.6845 eV 264.67 nm f= 0.02570 Spin multiplicity= 1:
- H-20 -> L+4 54.9%, H-10 -> L+4 10.7%, H-17 -> L+7 9.0%
- # 184 4.6915 eV 264.27 nm f= 0.01390 Spin multiplicity= 1:
- H-1 -> L+13 13.4%, H-2 -> L+13 10.6%, H-5 -> L+10 5.3%
- # 185 4.6951 eV 264.07 nm f= 0.00000 Spin multiplicity= 1:
- H-14 -> L+3 98.2%
- # 186 4.7005 eV 263.77 nm f= 0.01150 Spin multiplicity= 1:
- H-2 -> L+14 8.8%, H-14 -> L+5 8.6%, H-4 -> L+12 8.4%, H-6 -> L+8 7.6%, H-1 -> L+13
- 7.5%, H-6 -> L+10 7.4%, H-2 -> L+15 7.2%, H-3 -> L+13 6.1%, H-1 -> L+14 5.5%
- # 187 4.7080 eV 263.35 nm f = 0.01490 Spin multiplicity = 1:
- H-5 -> L+9 18.3%, H-3 -> L+13 14.1%, H-3 -> L+14 12.3%, H-14 -> L+5 5.8%
- # 188 4.7166 eV 262.87 nm f= 0.00710 Spin multiplicity= 1:

H-1 -> L+13 13.0%, H-2 -> L+15 7.3%, H-5 -> L+10 6.1%, H-1 -> L+14 5.5%, H-29 -> L+2 5.0%

189 4.7178 eV 262.80 nm f = 0.00040 Spin multiplicity = 1:

H-28 -> L+1 26.8%, H-29 -> L+1 19.2%, H-29 -> L+2 14.3%, H-28 -> L+2 9.3%, H-11 - > L+4 5.2%

190 4.7192 eV 262.72 nm f= 0.00040 Spin multiplicity= 1:

H-11 -> L+4 79.9%, H-28 -> L+1 5.1%

191 4.7216 eV 262.59 nm f= 0.00130 Spin multiplicity= 1:

H-1 -> L+13 10.6%, H -> L+17 9.8%, H-3 -> L+14 9.1%, H-1 -> L+15 7.8%, H-2 -> L+14 6.8%

192 4.7230 eV 262.51 nm f= 0.01280 Spin multiplicity= 1:

H-29 -> L+2 28.0%, H-28 -> L+2 26.1%, H-29 -> L+1 18.4%, H-28 -> L+1 15.7%

193 4.7369 eV 261.74 nm f= 0.00220 Spin multiplicity= 1:

H-3 -> L+7 35.1%, H-2 -> L+15 6.5%, H-6 -> L+9 6.4%

194 4.7394 eV 261.60 nm f= 0.00090 Spin multiplicity= 1:

H-3 -> L+7 49.3%, H-3 -> L+14 8.8%, H-2 -> L+15 5.0%

195 4.7427 eV 261.42 nm f= 0.00250 Spin multiplicity= 1:

H-3 -> L+15 15.5%, H-3 -> L+7 10.4%, H-2 -> L+14 8.7%, H-4 -> L+15 7.2%, H-3 -> L+13 6.7%, H -> L+17 6.3%

196 4.7487 eV 261.09 nm f = 0.00010 Spin multiplicity = 1:

H-12 -> L+4 94.2%

197 4.7621 eV 260.36 nm f= 0.00780 Spin multiplicity= 1:

H-6 -> L+9 10.8%, H-3 -> L+13 8.7%, H-5 -> L+10 7.8%, H-3 -> L+15 7.2%, H-2 -> L+15 6.3%

198 4.7732 eV 259.75 nm f= 0.01940 Spin multiplicity= 1:

H -> L+17 21.7%, H-2 -> L+14 8.4%, H-5 -> L+10 7.9%, H-42 -> L 7.7%, H-2 -> L+13 5.6%

199 4.7759 eV 259.60 nm f = 0.00670 Spin multiplicity = 1:

H-42 -> L 41.2%, H-43 -> L 20.5%, H-39 -> L 8.1%

200 4.7848 eV 259.12 nm f= 0.00370 Spin multiplicity= 1:

H-2 -> L+15 24.7%, H-4 -> L+14 11.1%, H-4 -> L+13 8.0%, H-8 -> L+8 7.3%, H-3 -> L+15 5.8%

201 4.7891 eV 258.89 nm f= 0.00020 Spin multiplicity= 1:

H-9 -> L+6 71.5%, H-9 -> L+5 15.8%

202 4.7970 eV 258.46 nm f= 0.00070 Spin multiplicity= 1:

H-7 -> L+8 16.3%, H -> L+19 11.4%, H-4 -> L+14 11.1%, H-7 -> L+9 6.9%

203 4.8006 eV 258.27 nm f= 0.00840 Spin multiplicity= 1:

H-3 -> L+15 14.8%, H-3 -> L+13 6.9%, H-6 -> L+12 6.7%, H-6 -> L+10 6.2%, H -> L+19 6.1%

204 4.8144 eV 257.53 nm f= 0.00200 Spin multiplicity= 1:

H-7 -> L+8 20.0%, H-6 -> L+10 11.1%, H-3 -> L+13 8.1%, H-4 -> L+13 7.1%, H-3 -> L+14 5.3%

205 4.8167 eV 257.40 nm f= 0.00030 Spin multiplicity= 1:

H-13 -> L+4 84.6%, H-15 -> L+3 9.8%

206 4.8174 eV 257.37 nm f= 0.00020 Spin multiplicity= 1:

H-15 -> L+3 84.0%, H-13 -> L+4 9.6%

207 4.8226 eV 257.09 nm f= 0.04990 Spin multiplicity= 1:

H-32 -> L+1 55.6%, H-33 -> L+1 17.3%

- # 208 4.8245 eV 256.99 nm f= 0.00090 Spin multiplicity= 1:
- H -> L+11 39.0%, H-4 -> L+15 10.8%, H-5 -> L+12 9.7%, H-32 -> L+1 6.2%
- # 209 4.8302 eV 256.69 nm f= 0.00140 Spin multiplicity= 1:

H -> L+11 17.8%, H-8 -> L+8 16.7%, H-4 -> L+15 16.0%

210 4.8340 eV 256.48 nm f= 0.02370 Spin multiplicity= 1:

H-2 -> L+17 10.9%, H-6 -> L+10 10.2%, H-4 -> L+13 7.0%, H -> L+19 6.9%, H-4 -> L+14 6.2%

- # 211 4.8381 eV 256.27 nm f= 0.00040 Spin multiplicity= 1:
- H-4 -> L+7 93.3%
- # 212 4.8400 eV 256.17 nm f= 0.01100 Spin multiplicity= 1:
- H-5 -> L+12 25.1%, H -> L+19 12.4%, H -> L+11 11.1%, H-1 -> L+17 6.9%
- # 213 4.8470 eV 255.80 nm f= 0.08300 Spin multiplicity= 1:

H-33 -> L+1 59.0%, H-32 -> L+1 27.0%

214 4.8586 eV 255.19 nm f= 0.00460 Spin multiplicity= 1:

H-8 -> L+8 18.5%, H-5 -> L+14 14.3%, H-5 -> L+13 11.2%, H-2 -> L+17 7.7%, H-4 -> L+14 5.8%, H-1 -> L+17 5.4%

215 4.8613 eV 255.04 nm f= 0.01390 Spin multiplicity= 1:

H-4 -> L+15 23.0%, H-8 -> L+8 15.3%, H-7 -> L+8 8.6%

216 4.8665 eV 254.77 nm f= 0.00680 Spin multiplicity= 1:

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- H-5 -> L+14 21.8%, H-2 -> L+17 13.4%, H-5 -> L+13 7.1%, H-4 -> L+13 6.4%
- # 217 4.8708 eV 254.55 nm f= 0.00580 Spin multiplicity= 1:
- H-1 -> L+17 25.1%, H-2 -> L+17 18.4%
- # 218 4.8733 eV 254.42 nm f= 0.00430 Spin multiplicity= 1:
- H-28 -> L+2 50.4%, H-29 -> L+2 41.7%
- # 219 4.8774 eV 254.20 nm f= 0.03230 Spin multiplicity= 1:

H-4 -> L+14 11.8%, H-15 -> L+5 11.4%, H-2 -> L+17 9.5%, H-1 -> L+19 5.7%, H-4 -> L+13 5.1%, H-7 -> L+9 5.0%, H-1 -> L+17 5.0%

- # 220 4.8894 eV 253.58 nm f= 0.00020 Spin multiplicity= 1:
- H-10 -> L+6 68.9%, H-10 -> L+5 16.5%
- # 221 4.8934 eV 253.37 nm f= 0.01680 Spin multiplicity= 1:

H-3 -> L+17 23.0%, H -> L+20 9.5%, H-1 -> L+17 7.1%, H-1 -> L+19 6.9%, H-5 -> L+13 5.1%

- # 222 4.8989 eV 253.09 nm f= 0.00120 Spin multiplicity= 1:
- H-14 -> L+4 94.6%
- # 223 4.9020 eV 252.93 nm f= 0.06050 Spin multiplicity= 1:
- H-32 -> L+2 52.8%, H-30 -> L+3 15.9%
- # 224 4.9115 eV 252.44 nm f= 0.00660 Spin multiplicity= 1:
- H-15 -> L+5 10.2%, H-1 -> L+17 8.7%, H-1 -> L+19 8.0%, H-4 -> L+13 6.3%
- # 225 4.9128 eV 252.37 nm f= 0.00220 Spin multiplicity= 1:
- H-39 -> L 55.9%, H-40 -> L 12.4%, H-42 -> L 8.2%
- # 226 4.9212 eV 251.94 nm f= 0.00490 Spin multiplicity= 1:
- H-15 -> L+5 20.5%, H-4 -> L+13 14.2%, H-3 -> L+17 10.8%
- # 227 4.9224 eV 251.88 nm f= 0.00860 Spin multiplicity= 1:

H-6 -> L+12 27.5%, H-3 -> L+17 8.7%

- # 228 4.9357 eV 251.20 nm f= 0.00850 Spin multiplicity= 1:
- H-2 -> L+11 42.8%, H-2 -> L+19 7.9%, H -> L+11 5.8%
- # 229 4.9406 eV 250.95 nm f= 0.01350 Spin multiplicity= 1:

H-33 -> L+2 75.8%, H-45 -> L 6.6%

- # 230 4.9422 eV 250.87 nm f= 0.00200 Spin multiplicity= 1:
- H-11 -> L+6 67.1%, H-11 -> L+5 15.7%

- # 231 4.9442 eV 250.77 nm f= 0.00030 Spin multiplicity= 1:
- H-1 -> L+11 26.9%, H-9 -> L+8 19.7%, H -> L+20 8.3%
- # 232 4.9505 eV 250.45 nm f= 0.00740 Spin multiplicity= 1:
- H-1 -> L+11 47.9%, H-9 -> L+8 17.9%
- # 233 4.9526 eV 250.34 nm f= 0.00750 Spin multiplicity= 1:

H-2 -> L+11 26.2%, H-2 -> L+19 9.6%, H-1 -> L+11 8.9%, H -> L+20 7.8%, H-3 -> L+19 7.5%

234 4.9572 eV 250.11 nm f= 0.02520 Spin multiplicity= 1:

H-6 -> L+13 12.2%, H-5 -> L+15 8.2%, H-5 -> L+7 8.0%, H-7 -> L+9 6.2%, H-12 -> L+6 5.8%, H-5 -> L+14 5.6%, H-6 -> L+14 5.1%

235 4.9606 eV 249.94 nm f= 0.00010 Spin multiplicity= 1:

H-5 -> L+7 45.4%, H-12 -> L+6 33.7%, H-12 -> L+5 7.9%

236 4.9627 eV 249.83 nm f= 0.00860 Spin multiplicity= 1:

H-30 -> L+4 87.6%

- # 237 4.9639 eV 249.77 nm f= 0.00520 Spin multiplicity= 1:
- H-5 -> L+7 35.7%, H-12 -> L+6 27.9%, H-12 -> L+5 6.1%
- # 238 4.9796 eV 248.98 nm f= 0.00350 Spin multiplicity= 1:

H-5 -> L+15 20.2%, H-6 -> L+15 8.3%, H-6 -> L+14 7.7%, H-8 -> L+9 7.1%, H-11 -> L+8 5.2%

239 4.9821 eV 248.86 nm f= 0.00150 Spin multiplicity= 1:

H-8 -> L+9 24.1%, H-7 -> L+9 12.3%, H-4 -> L+17 10.2%, H-1 -> L+20 5.2%

240 4.9873 eV 248.60 nm f = 0.01420 Spin multiplicity = 1:

H-40 -> L 24.8%, H-45 -> L 22.3%, H-39 -> L 10.1%, H-33 -> L+2 9.1%

241 4.9883 eV 248.55 nm f= 0.01160 Spin multiplicity= 1:

H-6 -> L+15 11.0%, H -> L+20 7.6%, H-2 -> L+19 6.9%, H-6 -> L+13 6.5%, H-5 -> L+13 6.2%

242 4.9924 eV 248.35 nm f= 0.00360 Spin multiplicity= 1:

 $\label{eq:H-2} \begin{array}{l} H \rightarrow L+20 \ 9.3\%, H-7 \rightarrow L+10 \ 8.4\%, H-3 \rightarrow L+17 \ 7.3\%, H-2 \rightarrow L+19 \ 6.8\%, H-5 \rightarrow L+15 \\ 6.5\%, H-5 \rightarrow L+17 \ 6.0\%, H-40 \rightarrow L \ 5.8\%, H-6 \rightarrow L+15 \ 5.6\% \end{array}$

243 4.9941 eV 248.26 nm f= 0.00120 Spin multiplicity= 1:

H-4 -> L+17 20.9%, H-6 -> L+13 8.1%, H-6 -> L+14 6.4%

- # 244 4.9979 eV 248.07 nm f= 0.02180 Spin multiplicity= 1:
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H-40 -> L 29.5%, H-45 -> L 21.5%, H-43 -> L 9.1%, H-39 -> L 8.7%

- # 245 5.0048 eV 247.73 nm f= 0.00070 Spin multiplicity= 1:
- H-6 -> L+7 73.6%, H-5 -> L+7 6.3%
- # 246 5.0049 eV 247.73 nm f= 0.00430 Spin multiplicity= 1:

H-3 -> L+19 15.7%, H-6 -> L+7 13.4%, H-4 -> L+17 6.1%, H-8 -> L+9 5.8%, H-2 -> L+19 5.1%

247 5.0103 eV 247.46 nm f= 0.00530 Spin multiplicity= 1:

H-7 -> L+10 21.9%, H-8 -> L+9 10.4%, H-7 -> L+9 8.3%, H-5 -> L+15 5.3%

248 5.0130 eV 247.33 nm f= 0.00170 Spin multiplicity= 1:

H-13 -> L+6 62.8%, H-13 -> L+5 14.2%

249 5.0173 eV 247.11 nm f= 0.04420 Spin multiplicity= 1:

H-30 -> L+3 15.5%, H-32 -> L+2 7.4%, H-5 -> L+13 6.9%, H-20 -> L+7 6.7%, H-15 -> L+4 6.1%

250 5.0186 eV 247.05 nm f= 0.06400 Spin multiplicity= 1:

H-30 -> L+3 9.8%, H-5 -> L+13 8.2%, H-15 -> L+4 6.4%, H-32 -> L+2 5.0%

251 5.0203 eV 246.97 nm f= 0.01520 Spin multiplicity= 1:

H-15 -> L+4 79.6%

252 5.0272 eV 246.63 nm f= 0.01020 Spin multiplicity= 1:

H-9 -> L+8 13.8%, H-6 -> L+15 12.7%, H-7 -> L+10 8.3%

253 5.0374 eV 246.13 nm f= 0.00320 Spin multiplicity= 1:

H-3 -> L+11 43.8%, H-6 -> L+14 11.2%, H-6 -> L+13 5.4%

254 5.0460 eV 245.71 nm f= 0.00540 Spin multiplicity= 1:

H-3 -> L+11 33.7%, H-8 -> L+10 16.2%, H-6 -> L+14 5.7%

255 5.0525 eV 245.39 nm f= 0.00220 Spin multiplicity= 1:

H-1 -> L+20 18.2%, H-8 -> L+10 13.0%, H-4 -> L+17 10.7%

256 5.0621 eV 244.93 nm f= 0.00490 Spin multiplicity= 1:

H-43 -> L 43.7%, H-42 -> L 18.1%, H-44 -> L 6.9%, H-45 -> L 6.3%

257 5.0631 eV 244.88 nm f= 0.00850 Spin multiplicity= 1:

H-1 -> L+20 9.6%, H-4 -> L+19 7.3%, H-11 -> L+8 5.8%, H-3 -> L+19 5.2%, H-6 -> L+13 5.1%

258 5.0728 eV 244.41 nm f= 0.01520 Spin multiplicity= 1:

H -> L+21 23.5%, H-7 -> L+12 16.3%, H-10 -> L+8 5.1%

259 5.0776 eV 244.18 nm f= 0.00100 Spin multiplicity= 1:

H-16 -> L+3 56.4%, H -> L+21 10.4%, H-16 -> L+5 6.3%

260 5.0780 eV 244.16 nm f= 0.00400 Spin multiplicity= 1:

H-16 -> L+3 39.5%, H -> L+21 15.9%, H-16 -> L+5 7.0%

261 5.0848 eV 243.83 nm f= 0.01820 Spin multiplicity= 1:

H-7 -> L+12 14.1%, H-10 -> L+8 7.6%, H-4 -> L+19 7.2%, H-11 -> L+8 6.3%, H -> L+20 5.3%

#262 5.0857 eV 243.79 nm f = 0.00220 Spin multiplicity = 1:

H-31 -> L+1 91.2%

263 5.0870 eV 243.73 nm f= 0.00710 Spin multiplicity= 1:

H-7 -> L+12 13.1%, H-16 -> L+5 10.4%, H-10 -> L+8 9.0%, H-4 -> L+19 8.2%, H-3 -> L+20 6.2%, H-8 -> L+9 5.2%

264 5.0934 eV 243.42 nm f= 0.00740 Spin multiplicity= 1:

H-2 -> L+20 26.2%, H-10 -> L+8 14.3%, H-12 -> L+8 6.0%

#265 5.1059 eV 242.83 nm f = 0.02350 Spin multiplicity = 1:

H-16 -> L+5 9.0%, H-9 -> L+9 8.3%, H-8 -> L+10 6.9%, H-12 -> L+8 6.7%

266 5.1098 eV 242.64 nm f= 0.00110 Spin multiplicity= 1:

H-9 -> L+9 10.9%, H-8 -> L+10 8.8%, H-6 -> L+13 7.5%, H -> L+22 6.7%, H-1 -> L+21 5.3%

#267 5.1135 eV 242.46 nm f = 0.00220 Spin multiplicity = 1:

H-14 -> L+6 73.2%, H-14 -> L+5 17.1%

268 5.1213 eV 242.10 nm f= 0.00560 Spin multiplicity= 1:

H-5 -> L+17 22.1%, H-9 -> L+10 17.2%, H-1 -> L+20 5.5%, H-11 -> L+8 5.3%

269 5.1240 eV 241.97 nm f= 0.00200 Spin multiplicity= 1:

H-3 -> L+20 23.1%, H-12 -> L+8 11.0%, H-5 -> L+19 6.9%, H-11 -> L+8 5.8%, H-10 -> L+8 5.2%

#270 5.1367 eV 241.37 nm f = 0.01680 Spin multiplicity = 1:

H-16 -> L+5 10.1%, H-11 -> L+8 8.3%, H-2 -> L+20 7.8%, H-9 -> L+9 6.7%, H-3 -> L+20 5.6%

#271 5.1382 eV 241.30 nm f = 0.01040 Spin multiplicity = 1:

H-8 -> L+12 20.5%, H-17 -> L+6 16.0%, H-4 -> L+11 13.4%, H-10 -> L+9 5.1%

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- # 272 5.1390 eV 241.26 nm f= 0.00290 Spin multiplicity= 1:
- H-4 -> L+11 42.2%, H-17 -> L+6 23.2%, H-17 -> L+5 7.5%
- # 273 5.1407 eV 241.18 nm f= 0.00240 Spin multiplicity= 1:

H-4 -> L+11 20.1%, H-8 -> L+12 15.6%, H-17 -> L+6 13.6%, H-1 -> L+21 6.5%, H-17 -> L+5 5.1%

- # 274 5.1475 eV 240.86 nm f= 0.01570 Spin multiplicity= 1:
- H-12 -> L+8 16.5%, H -> L+22 12.7%
- # 275 5.1509 eV 240.70 nm f= 0.01950 Spin multiplicity= 1:
- H-9 -> L+10 23.7%, H-1 -> L+21 7.0%
- # 276 5.1637 eV 240.11 nm f= 0.01730 Spin multiplicity= 1:
- H-8 -> L+12 14.0%, H-3 -> L+20 11.1%, H-5 -> L+17 5.9%, H-10 -> L+9 5.5%
- # 277 5.1702 eV 239.81 nm f= 0.00320 Spin multiplicity= 1:
- H-3 -> L+20 14.0%, H-9 -> L+9 10.1%, H-5 -> L+19 7.9%
- # 278 5.1731 eV 239.67 nm f= 0.00480 Spin multiplicity= 1:
- H-31 -> L+2 71.9%, H-15 -> L+6 5.1%
- # 279 5.1762 eV 239.53 nm f= 0.00020 Spin multiplicity= 1:
- H -> L+16 69.1%, H-2 -> L+16 7.2%
- # 280 5.1777 eV 239.46 nm f= 0.00740 Spin multiplicity= 1:
- H-18 -> L+5 11.9%, H-31 -> L+2 6.5%, H-10 -> L+9 5.7%, H-12 -> L+8 5.6%

281 5.1796 eV 239.37 nm f= 0.00030 Spin multiplicity= 1:

H-15 -> L+6 58.6%, H-15 -> L+5 12.3%, H-31 -> L+2 8.8%

282 5.1878 eV 238.99 nm f= 0.02240 Spin multiplicity= 1:

H -> L+22 21.9%, H-3 -> L+21 6.0%, H-7 -> L+12 5.9%

283 5.1953 eV 238.65 nm f= 0.00740 Spin multiplicity= 1:

H-20 -> L+6 29.4%, H-36 -> L+1 10.3%, H-34 -> L+1 9.4%, H-20 -> L+5 8.9%, H-17 -> L+6 5.4%

#284 5.1964 eV 238.60 nm f = 0.00260 Spin multiplicity = 1:

H-1 -> L+21 14.3%, H-14 -> L+8 6.7%, H-2 -> L+21 6.7%, H-8 -> L+13 5.9%, H-12 -> L+9 5.2%

285 5.2030 eV 238.29 nm f = 0.00930 Spin multiplicity = 1:

H-11 -> L+10 7.1%, H-13 -> L+8 6.5%, H-4 -> L+20 6.0%, H -> L+22 6.0%, H-10 -> L+10 5.6%

- # 286 5.2052 eV 238.19 nm f= 0.00020 Spin multiplicity= 1: H-18 -> L+3 88.8%, H-17 -> L+3 5.3%
- # 287 5.2080 eV 238.06 nm f= 0.00090 Spin multiplicity= 1: H-7 -> L+7 86.3%
- # 288 5.2104 eV 237.96 nm f= 0.00460 Spin multiplicity= 1:
- H-4 -> L+20 28.2%, H-7 -> L+13 8.4%, H-13 -> L+8 6.4%, H-6 -> L+17 6.3%
- # 289 5.2181 eV 237.60 nm f= 0.00720 Spin multiplicity= 1:
- H-6 -> L+19 9.3%, H-1 -> L+21 8.6%, H-8 -> L+13 7.3%, H-1 -> L+22 7.0%, H-7 ->
- L+14 7.0%, H-7 -> L+13 5.8%, H-13 -> L+8 5.2%, H-7 -> L+15 5.1%
- # 290 5.2247 eV 237.30 nm f= 0.03980 Spin multiplicity= 1:
- H-20 -> L+6 15.0%, H-36 -> L+1 9.2%, H-34 -> L+1 8.5%, H-17 -> L+6 7.0%
- # 291 5.2305 eV 237.04 nm f= 0.02780 Spin multiplicity= 1:
- H-7 -> L+13 9.9%, H-6 -> L+17 8.0%, H-1 -> L+22 7.7%, H-11 -> L+9 5.9%
- # 292 5.2328 eV 236.94 nm f= 0.01300 Spin multiplicity= 1:
- H-19 -> L+3 24.4%, H-9 -> L+12 7.7%
- # 293 5.2339 eV 236.89 nm f= 0.00270 Spin multiplicity= 1:
- H-19 -> L+3 70.1%
- # 294 5.2389 eV 236.66 nm f= 0.03230 Spin multiplicity= 1:
- H-9 -> L+12 15.5%, H-4 -> L+20 15.2%, H-13 -> L+8 14.1%, H-7 -> L+14 5.9%
- # 295 5.2406 eV 236.58 nm f= 0.00720 Spin multiplicity= 1:
- H-49 -> L 41.7%, H-44 -> L 28.3%, H-45 -> L 6.5%, H-43 -> L 5.8%
- # 296 5.2436 eV 236.45 nm f= 0.00190 Spin multiplicity= 1:
- H-2 -> L+21 9.8%, H-8 -> L+15 9.3%, H-8 -> L+13 7.4%, H-13 -> L+9 6.7%, H-7 -> L+15 6.0%
- #297 5.2444 eV 236.41 nm f= 0.00770 Spin multiplicity= 1:
- H-7 -> L+15 13.4%, H-7 -> L+14 12.2%, H-9 -> L+12 10.4%, H-10 -> L+9 6.3%
- # 298 5.2543 eV 235.97 nm f= 0.00190 Spin multiplicity= 1:
- H-5 -> L+11 11.1%, H-19 -> L+5 8.5%, H-1 -> L+22 8.0%, H-8 -> L+14 5.3%
- # 299 5.2553 eV 235.92 nm f= 0.00160 Spin multiplicity= 1:
- H-8 -> L+7 89.6%
- # 300 5.2579 eV 235.81 nm f= 0.01070 Spin multiplicity= 1:

H-14 -> L+8 12.3%, H-8 -> L+15 8.4%, H-10 -> L+12 5.9%

Supplementary Table 6: Molecular orbital transitions and their contributions to each excited state in InP/ZnS-ReCat(2), including excitation energy (in eV), wavelength (in nm), oscillator strength (f) and orbital contributions (in %).

1 1.6697 eV 742.55 nm f= 0.00000 Spin multiplicity= 1:

H -> L+1 90.0%, H-1 -> L+1 9.7%

- # 2 1.7259 eV 718.37 nm f= 0.00020 Spin multiplicity= 1: H -> L 98.3%
- # 3 1.8080 eV 685.75 nm f= 0.00010 Spin multiplicity= 1: H-1 -> L 89.5%, H-2 -> L 7.8%
- # 4 1.8100 eV 685.00 nm f= 0.00060 Spin multiplicity= 1: H-1 -> L+1 78.2%, H-2 -> L+1 11.8%, H -> L+1 8.7%
- # 5 1.8956 eV 654.06 nm f= 0.00020 Spin multiplicity= 1:
 H-2 -> L 89.1%, H-1 -> L 8.4%
- # 6 1.9143 eV 647.67 nm f= 0.00000 Spin multiplicity= 1: H-2 -> L+1 86.4%, H-1 -> L+1 11.3%
- # 7 2.0558 eV 603.09 nm f= 0.00510 Spin multiplicity= 1: H-3 -> L 96.1%
- # 8 2.0633 eV 600.90 nm f= 0.00000 Spin multiplicity= 1: H-3 -> L+1 98.6%
- # 9 2.1063 eV 588.64 nm f= 0.00000 Spin multiplicity= 1: H-4 -> L 95.7%
- # 10 2.1093 eV 587.80 nm f= 0.00000 Spin multiplicity= 1: H-4 -> L+1 98.7%
- # 11 2.1963 eV 564.51 nm f= 0.00030 Spin multiplicity= 1: H-5 -> L 80.5%, H-7 -> L 11.1%
- # 12 2.2061 eV 562.01 nm f= 0.00190 Spin multiplicity= 1:
 H-5 -> L+1 89.5%, H-7 -> L+1 6.7%
- # 13 2.3590 eV 525.58 nm f= 0.00370 Spin multiplicity= 1: H-6 -> L 75.7%, H-7 -> L 14.6%, H-5 -> L 5.5%
- # 14 2.3760 eV 521.82 nm f= 0.00030 Spin multiplicity= 1:

H-6 -> L+1 97.7%

- # 15 2.4085 eV 514.78 nm f= 0.00010 Spin multiplicity= 1: H-7 -> L 67.1%, H-6 -> L 19.8%, H-5 -> L 8.0%
- # 16 2.4148 eV 513.43 nm f= 0.00090 Spin multiplicity= 1: H-7 -> L+1 87.7%, H-5 -> L+1 5.8%
- # 17 2.5166 eV 492.67 nm f= 0.00250 Spin multiplicity= 1: H-15 -> L 98.0%
- # 18 2.5322 eV 489.63 nm f= 0.00210 Spin multiplicity= 1: H-16 -> L+1 99.2%
- # 19 2.5588 eV 484.54 nm f= 0.00160 Spin multiplicity= 1: H-8 -> L 92.9%
- # 20 2.5689 eV 482.64 nm f= 0.00000 Spin multiplicity= 1: H-8 -> L+1 93.0%
- # 21 2.6128 eV 474.53 nm f= 0.00630 Spin multiplicity= 1: H-9 -> L 73.2%, H-10 -> L 21.4%
- # 22 2.6172 eV 473.73 nm f= 0.00070 Spin multiplicity= 1: H-9 -> L+1 88.5%, H-10 -> L+1 6.2%
- # 23 2.6438 eV 468.96 nm f= 0.04750 Spin multiplicity= 1: H-17 -> L 91.4%
- # 24 2.6664 eV 464.99 nm f= 0.04270 Spin multiplicity= 1: H-18 -> L+1 50.3%, H -> L+3 40.6%
- # 25 2.6705 eV 464.27 nm f= 0.01810 Spin multiplicity=1: H -> L+3 46.8%, H-18 -> L+1 45.5%
- # 26 2.6811 eV 462.44 nm f= 0.00010 Spin multiplicity= 1: H -> L+2 93.0%
- # 27 2.6893 eV 461.03 nm f= 0.00090 Spin multiplicity=1:
- H-10 -> L 56.1%, H-9 -> L 18.4%, H-11 -> L 15.2%, H-17 -> L 5.7%
- # 28 2.6908 eV 460.77 nm f= 0.00220 Spin multiplicity= 1:

H-10 -> L+1 58.8%, H -> L+5 17.4%, H-11 -> L+1 9.0%

- # 29 2.6980 eV 459.54 nm f= 0.00020 Spin multiplicity= 1:
- H -> L+5 68.9%, H-10 -> L+1 16.5%, H-1 -> L+5 9.1%

- # 30 2.7217 eV 455.54 nm f= 0.00020 Spin multiplicity= 1: H-11 -> L+1 78.1%, H-10 -> L+1 7.7%
- # 31 2.7270 eV 454.65 nm f= 0.00060 Spin multiplicity= 1: H-11 -> L 72.8%, H-10 -> L 13.3%
- # 32 2.7488 eV 451.05 nm f= 0.00000 Spin multiplicity= 1: H -> L+4 98.8%
- # 33 2.7610 eV 449.06 nm f= 0.00010 Spin multiplicity= 1: H-1 -> L+2 87.8%, H-2 -> L+2 7.7%
- # 34 2.7779 eV 446.32 nm f= 0.00010 Spin multiplicity= 1:
- H-12 -> L+1 34.2%, H-1 -> L+3 32.8%, H-13 -> L+1 20.4%, H-2 -> L+3 5.0%
- # 35 2.7815 eV 445.75 nm f= 0.00050 Spin multiplicity=1:
- H-1 -> L+3 47.3%, H-12 -> L+1 25.8%, H-13 -> L+1 12.4%, H-2 -> L+3 5.8%
- # 36 2.7887 eV 444.59 nm f= 0.00000 Spin multiplicity=1:
- H-12 -> L 60.7%, H-14 -> L 22.7%, H-13 -> L 6.6%
- # 37 2.8101 eV 441.21 nm f= 0.00100 Spin multiplicity=1:
- H-1 -> L+4 73.0%, H-12 -> L 10.7%, H-2 -> L+4 10.5%
- # 38 2.8202 eV 439.63 nm f= 0.00050 Spin multiplicity=1:
- H-14 -> L 45.9%, H-12 -> L 24.3%, H-13 -> L 9.9%, H-1 -> L+4 8.0%
- # 39 2.8404 eV 436.50 nm f= 0.00000 Spin multiplicity=1:
- H-13 -> L+1 49.9%, H-12 -> L+1 32.9%, H-11 -> L+1 5.4%, H-10 -> L+1 5.3%
- # 40 2.8501 eV 435.02 nm f= 0.00040 Spin multiplicity=1:
- H-2 -> L+2 88.1%, H-1 -> L+2 7.5%
- # 41 2.8634 eV 433.00 nm f= 0.00210 Spin multiplicity=1:
- H-1 -> L+5 68.3%, H-2 -> L+5 18.4%, H -> L+5 10.4%
- # 42 2.8962 eV 428.09 nm f= 0.00020 Spin multiplicity=1: H-2 -> L+3 87.1%, H-1 -> L+3 10.4%
- # 43 2.9033 eV 427.05 nm f= 0.00030 Spin multiplicity= 1: H-2 -> L+4 80.9%, H-1 -> L+4 13.6%
- # 44 2.9613 eV 418.68 nm f= 0.00010 Spin multiplicity= 1: H-2 -> L+5 78.3%, H-1 -> L+5 18.1%
- # 45 2.9732 eV 417.01 nm f= 0.00010 Spin multiplicity=1:

- H-13 -> L 77.8%, H-14 -> L 17.7%
- # 46 3.0104 eV 411.85 nm f= 0.00590 Spin multiplicity= 1: H-3 -> L+2 92.7%
- # 47 3.0365 eV 408.31 nm f= 0.00000 Spin multiplicity= 1: H-14 -> L+1 91.5%
- # 48 3.0380 eV 408.11 nm f= 0.00440 Spin multiplicity= 1: H-3 -> L+3 96.7%
- # 49 3.0489 eV 406.65 nm f= 0.00000 Spin multiplicity= 1: H-3 -> L+4 93.3%
- # 50 3.0561 eV 405.69 nm f= 0.00040 Spin multiplicity= 1: H-4 -> L+2 94.2%
- # 51 3.0864 eV 401.71 nm f= 0.00330 Spin multiplicity= 1: H-4 -> L+3 97.7%
- # 52 3.1042 eV 399.41 nm f= 0.00240 Spin multiplicity= 1: H-3 -> L+5 96.7%
- # 53 3.1161 eV 397.88 nm f= 0.00020 Spin multiplicity= 1: H-4 -> L+4 85.8%, H-5 -> L+4 6.4%
- # 54 3.1566 eV 392.78 nm f= 0.00090 Spin multiplicity= 1: H-4 -> L+5 96.9%
- # 55 3.1626 eV 392.03 nm f= 0.00130 Spin multiplicity= 1: H-5 -> L+2 59.5%, H-5 -> L+4 17.6%, H-7 -> L+2 5.6%
- # 56 3.1699 eV 391.13 nm f= 0.00110 Spin multiplicity= 1: H-19 -> L 95.3%
- # 57 3.1715 eV 390.93 nm f= 0.00030 Spin multiplicity= 1:
- H-5 -> L+4 41.7%, H-5 -> L+2 25.7%, H-7 -> L+4 11.4%, H-4 -> L+4 6.6%
- # 58 3.1728 eV 390.77 nm f= 0.00090 Spin multiplicity=1:
- H-19 -> L+1 83.6%, H-5 -> L+3 7.4%
- # 59 3.1893 eV 388.75 nm f= 0.00170 Spin multiplicity= 1: H-5 -> L+3 81.4%, H-19 -> L+1 7.8%, H-7 -> L+3 6.2%
- # 60 3.2304 eV 383.80 nm f= 0.00160 Spin multiplicity= 1:
- H-5 -> L+5 82.4%, H-7 -> L+5 9.7%

- # 61 3.2341 eV 383.37 nm f= 0.00000 Spin multiplicity= 1: H-15 -> L+1 99.1%
- # 62 3.2487 eV 381.64 nm f= 0.00000 Spin multiplicity= 1: H-16 -> L 100.0%
- # 63 3.2739 eV 378.70 nm f= 0.00040 Spin multiplicity= 1: H-29 -> L 98.6%
- # 64 3.2742 eV 378.67 nm f= 0.00000 Spin multiplicity=1: H-28 -> L+1 98.5%
- # 65 3.2976 eV 375.98 nm f= 0.00000 Spin multiplicity= 1: H-17 -> L+1 99.5%
- # 66 3.3162 eV 373.87 nm f= 0.00150 Spin multiplicity= 1:
- H-6 -> L+2 53.7%, H-18 -> L 24.0%, H-7 -> L+2 10.1%, H-20 -> L 5.1%
- # 67 3.3171 eV 373.77 nm f= 0.00040 Spin multiplicity= 1:

H-18 -> L 75.0%, H-6 -> L+2 17.8%

- # 68 3.3394 eV 371.28 nm f= 0.00060 Spin multiplicity= 1:
- H-20 -> L 53.6%, H-21 -> L 14.3%, H-6 -> L+2 9.7%, H-6 -> L+4 6.0%, H-22 -> L 5.4%
- # 69 3.3548 eV 369.57 nm f= 0.00100 Spin multiplicity=1: H-6 -> L+3 93.3%
- # 70 3.3575 eV 369.28 nm f= 0.00050 Spin multiplicity=1:
- H-22 -> L+1 51.8%, H-20 -> L+1 29.7%, H-21 -> L+1 9.7%
- # 71 3.3581 eV 369.21 nm f= 0.00080 Spin multiplicity= 1:
- H-6 -> L+4 57.7%, H-7 -> L+4 11.4%, H-5 -> L+4 11.2%
- # 72 3.3690 eV 368.01 nm f= 0.00020 Spin multiplicity= 1:
- H-7 -> L+2 70.5%, H-6 -> L+2 12.1%, H-5 -> L+2 6.5%
- # 73 3.3980 eV 364.87 nm f= 0.00150 Spin multiplicity= 1: H-7 -> L+3 86.5%, H-5 -> L+3 5.9%
- # 74 3.4123 eV 363.34 nm f= 0.00250 Spin multiplicity= 1: H-7 -> L+4 56.5%, H-6 -> L+4 23.0%, H-5 -> L+4 11.7%
- # 75 3.4225 eV 362.26 nm f= 0.00030 Spin multiplicity= 1: H-6 -> L+5 90.9%
- # 76 3.4378 eV 360.65 nm f= 0.00120 Spin multiplicity=1:
- 150

H-20 -> L+1 42.5%, H-22 -> L+1 38.7%, H-21 -> L+1 6.6%, H-6 -> L+5 5.1%

- # 77 3.4470 eV 359.69 nm f= 0.00150 Spin multiplicity= 1:
- H-22 -> L 47.3%, H-21 -> L 29.4%, H-24 -> L 13.6%
- # 78 3.4484 eV 359.54 nm f= 0.00860 Spin multiplicity= 1: H-7 -> L+5 78.7%, H-5 -> L+5 8.6%
- # 79 3.4972 eV 354.52 nm f= 0.00010 Spin multiplicity=1:
- H-21 -> L 36.4%, H-22 -> L 34.5%, H-20 -> L 25.7%
- # 80 3.5078 eV 353.45 nm f= 0.00010 Spin multiplicity= 1: H-21 -> L+1 75.1%, H-20 -> L+1 18.8%
- # 81 3.5178 eV 352.45 nm f= 0.00060 Spin multiplicity= 1: H-8 -> L+2 90.6%
- # 82 3.5419 eV 350.05 nm f= 0.00040 Spin multiplicity= 1: H-8 -> L+3 91.5%
- # 83 3.5539 eV 348.87 nm f= 0.00120 Spin multiplicity= 1: H-8 -> L+4 81.1%, H-14 -> L+4 6.7%
- # 84 3.5637 eV 347.91 nm f= 0.00360 Spin multiplicity= 1:
- H-9 -> L+2 60.6%, H-10 -> L+2 13.6%, H-24 -> L 9.3%, H-15 -> L+2 6.4%
- # 85 3.5736 eV 346.94 nm f= 0.00490 Spin multiplicity=1:

H-15 -> L+2 81.2%, H-24 -> L 9.3%

- # 86 3.5842 eV 345.92 nm f= 0.00210 Spin multiplicity=1:
- H-24 -> L 51.2%, H-9 -> L+2 15.2%, H-21 -> L 8.6%, H-15 -> L+2 8.2%
- # 87 3.5968 eV 344.71 nm f= 0.00270 Spin multiplicity=1:
- H-9 -> L+3 77.3%, H-23 -> L+1 7.4%, H-10 -> L+3 6.6%
- # 88 3.6050 eV 343.92 nm f= 0.00030 Spin multiplicity= 1:
 H-23 -> L+1 61.2%, H-25 -> L+1 15.5%, H-9 -> L+3 9.6%
- # 89 3.6102 eV 343.43 nm f= 0.00290 Spin multiplicity= 1:
- H-9 -> L+4 54.1%, H-10 -> L+4 27.6%
- # 90 3.6142 eV 343.05 nm f= 0.00020 Spin multiplicity= 1: H-8 -> L+5 81.2%, H-9 -> L+5 5.1%
- # 91 3.6158 eV 342.90 nm f= 0.00770 Spin multiplicity= 1: H-16 -> L+3 93.8%

- # 92 3.6252 eV 342.01 nm f= 0.00240 Spin multiplicity= 1:
- H-15 -> L+4 79.9%
- # 93 3.6289 eV 341.66 nm f= 0.00200 Spin multiplicity= 1:
- H-10 -> L+2 34.3%, H-17 -> L+2 31.9%, H-11 -> L+2 9.8%, H-15 -> L+4 9.8%, H-9 -> L+2 7.6%
- # 94 3.6482 eV 339.85 nm f= 0.00290 Spin multiplicity=1:
- H-17 -> L+2 58.9%, H-10 -> L+2 22.8%, H-11 -> L+2 8.8%
- # 95 3.6533 eV 339.38 nm f= 0.00980 Spin multiplicity= 1:
- H-9 -> L+5 45.9%, H-25 -> L+1 11.4%, H-10 -> L+3 8.9%, H-23 -> L+1 7.7%
- # 96 3.6563 eV 339.10 nm f= 0.00150 Spin multiplicity= 1:
- H-10 -> L+3 35.1%, H-9 -> L+5 26.7%, H-11 -> L+3 10.5%
- # 97 3.6638 eV 338.40 nm f= 0.00050 Spin multiplicity= 1:
- H -> L+10 84.0%, H-1 -> L+10 5.3%
- # 98 3.6649 eV 338.30 nm f= 0.00180 Spin multiplicity=1:
- H-25 -> L+1 29.4%, H-10 -> L+3 21.2%, H-23 -> L+1 15.5%, H-27 -> L+1 9.2%, H-9 -> L+5 7.2%
- # 99 3.6809 eV 336.83 nm f= 0.00120 Spin multiplicity= 1:
- H-11 -> L+2 23.4%, H-17 -> L+4 18.1%, H-27 -> L 17.7%, H-25 -> L 9.7%, H-23 -> L 8.8%
- # 100 3.6836 eV 336.58 nm f= 0.00210 Spin multiplicity= 1:
- H-16 -> L+5 90.4%
- # 101 3.6865 eV 336.32 nm f= 0.00460 Spin multiplicity= 1:
- H-18 -> L+3 91.5%
- # 102 3.6891 eV 336.08 nm f= 0.00460 Spin multiplicity= 1:
- H-17 -> L+4 41.6%, H-11 -> L+2 21.4%, H-10 -> L+4 9.3%, H-9 -> L+4 7.5%, H-10 -> L+2 6.6%
- # 103 3.6988 eV 335.20 nm f= 0.00310 Spin multiplicity= 1:
- H-23 -> L 25.4%, H-11 -> L+2 24.8%, H-27 -> L 12.8%, H-25 -> L 9.3%
- $\# 104 \ 3.7082 \text{ eV} \ 334.35 \text{ nm} \text{ f} = 0.00150 \text{ Spin multiplicity} = 1:$
- H-10 -> L+4 39.3%, H-17 -> L+4 26.7%, H-9 -> L+4 22.2%
- # 105 3.7088 eV 334.30 nm f= 0.00090 Spin multiplicity= 1:
- H-11 -> L+3 70.1%, H-10 -> L+3 15.2%
- 152

106 3.7241 eV 332.92 nm f= 0.00350 Spin multiplicity= 1: H-26 -> L+1 49.7%, H-31 -> L+1 14.6%, H-24 -> L+1 10.8% # 107 3.7255 eV 332.80 nm f= 0.00040 Spin multiplicity= 1: H-11 -> L+4 48.6%, H-23 -> L 24.6%, H-14 -> L+4 8.3%, H-7 -> L+4 5.6% # 108 3.7342 eV 332.02 nm f= 0.00680 Spin multiplicity= 1: H-23 -> L 22.1%, H-12 -> L+2 21.2%, H-27 -> L 15.7%, H-11 -> L+4 14.5% # 109 3.7389 eV 331.61 nm f= 0.00130 Spin multiplicity= 1: H-10 -> L+5 70.0%, H-13 -> L+5 14.2% # 110 3.7422 eV 331.31 nm f= 0.00270 Spin multiplicity= 1: H-12 -> L+2 40.0%, H-27 -> L 11.5%, H-26 -> L 9.1%, H-25 -> L 7.6%, H-14 -> L+2 7.2% # 111 3.7467 eV 330.92 nm f= 0.06780 Spin multiplicity= 1: H-1 -> L+10 78.4% # 112 3.7522 eV 330.43 nm f= 0.00300 Spin multiplicity= 1: H-12 -> L+3 55.8%, H-13 -> L+3 26.9% # 113 3.7578 eV 329.94 nm f= 0.00010 Spin multiplicity= 1: H-26 -> L 44.6%, H-12 -> L+2 17.3%, H-30 -> L 7.5%, H-14 -> L+4 5.4% # 114 3.7581 eV 329.91 nm f= 0.00140 Spin multiplicity= 1: H-18 -> L+5 57.0%, H-11 -> L+5 27.6%, H-33 -> L+1 5.7% # 115 3.7627 eV 329.51 nm f= 0.00140 Spin multiplicity= 1: H-11 -> L+5 53.7%, H-18 -> L+5 23.7%, H-33 -> L+1 5.3% # 116 3.7707 eV 328.81 nm f= 0.00350 Spin multiplicity= 1: H-33 -> L+1 45.1%, H-35 -> L+1 41.0%, H-18 -> L+5 10.5% $\# 117 \quad 3.7732 \text{ eV} \quad 328.59 \text{ nm} \quad f= 0.00180 \quad \text{Spin multiplicity}= 1:$ H-34 -> L 50.5%, H-36 -> L 43.7% # 118 3.7782 eV 328.16 nm f= 0.00460 Spin multiplicity= 1: H-14 -> L+4 43.5%, H-11 -> L+4 11.2%, H-13 -> L+4 9.8%, H-8 -> L+4 7.6%, H-26 -> L 7.6%, H-12 -> L+2 5.1% # 119 3.7894 eV 327.19 nm f= 0.00000 Spin multiplicity= 1: H-24 -> L+1 78.2%, H-26 -> L+1 11.5% # 120 3.7991 eV 326.35 nm f= 0.00000 Spin multiplicity= 1:

H -> L+7 92.1%, H-1 -> L+7 7.7%

- # 121 3.8024 eV 326.07 nm f= 0.00080 Spin multiplicity= 1:
- H-14 -> L+2 59.4%, H-13 -> L+2 13.9%, H-12 -> L+2 8.2%, H-26 -> L 5.2%
- # 122 3.8137 eV 325.10 nm f= 0.00350 Spin multiplicity= 1:
- H-12 -> L+4 63.2%, H-30 -> L 12.6%, H-25 -> L 11.5%
- # 123 3.8197 eV 324.59 nm f= 0.00030 Spin multiplicity= 1:

H -> L+6 94.9%

- # 124 3.8202 eV 324.55 nm f= 0.02100 Spin multiplicity= 1:
- H-12 -> L+4 27.4%, H-25 -> L 22.7%, H-30 -> L 20.6%
- # 125 3.8215 eV 324.44 nm f= 0.00250 Spin multiplicity= 1:
- H-13 -> L+5 38.6%, H-12 -> L+5 36.7%, H-10 -> L+5 6.7%
- # 126 3.8242 eV 324.21 nm f= 0.00040 Spin multiplicity= 1:
- H-13 -> L+3 50.6%, H-12 -> L+3 28.0%, H-10 -> L+3 5.1%
- # 127 3.8328 eV 323.48 nm f= 0.11210 Spin multiplicity= 1:
- H-35 -> L+1 30.7%, H-33 -> L+1 20.2%, H-27 -> L+1 19.1%, H-26 -> L+1 6.1%
- # 128 3.8479 eV 322.21 nm f= 0.08810 Spin multiplicity= 1:
- H-36 -> L 42.5%, H-34 -> L 29.5%, H-27 -> L 5.7%
- # 129 3.8503 eV 322.01 nm f= 0.07020 Spin multiplicity= 1:
- H-27 -> L+1 47.7%, H-35 -> L+1 15.7%, H-33 -> L+1 12.3%, H-25 -> L+1 12.0%
- # 130 3.8795 eV 319.59 nm f= 0.00020 Spin multiplicity= 1:
- H-12 -> L+5 49.9%, H-13 -> L+5 25.1%, H-11 -> L+5 7.7%, H-10 -> L+5 5.5%
- # 131 3.8814 eV 319.43 nm f= 0.17950 Spin multiplicity= 1:
- H-2 -> L+10 90.1%
- # 132 3.8844 eV 319.18 nm f= 0.00030 Spin multiplicity= 1:
- H-30 -> L 39.2%, H-25 -> L 25.6%, H-27 -> L 18.9%, H-26 -> L 13.3%
- # 133 3.8882 eV 318.87 nm f= 0.00260 Spin multiplicity= 1:
- H-30 -> L+1 40.6%, H-31 -> L+1 26.8%, H-26 -> L+1 11.9%, H-25 -> L+1 5.5%
- # 134 3.9250 eV 315.88 nm f= 0.00010 Spin multiplicity= 1:
- H-13 -> L+2 76.4%, H-14 -> L+2 18.3%
- # 135 3.9303 eV 315.46 nm f = 0.00000 Spin multiplicity = 1:

H-1 -> L+6 94.0%

136 3.9405 eV 314.64 nm f= 0.00000 Spin multiplicity= 1: H-1 -> L+7 88.2%, H -> L+7 7.2% # 137 3.9835 eV 311.24 nm f= 0.00010 Spin multiplicity= 1: H-31 -> L+1 47.7%, H-30 -> L+1 46.4% # 138 3.9984 eV 310.08 nm f= 0.00010 Spin multiplicity= 1: H-13 -> L+4 78.6%, H-14 -> L+4 16.6% # 139 4.0021 eV 309.80 nm f= 0.00010 Spin multiplicity= 1: H -> L+9 46.0%, H -> L+8 45.3% # 140 4.0164 eV 308.69 nm f= 0.00000 Spin multiplicity= 1: H-2 -> L+6 96.8% # 141 4.0178 eV 308.59 nm f= 0.00040 Spin multiplicity= 1: H-31 -> L 85.3%, H-30 -> L 7.4% # 142 4.0185 eV 308.53 nm f= 0.00130 Spin multiplicity= 1: H-14 -> L+3 91.5% # 143 4.0300 eV 307.65 nm f= 0.08850 Spin multiplicity= 1: H-3 -> L+10 55.7%, H-32 -> L 12.7%, H -> L+9 9.8%, H -> L+8 8.2% # 144 4.0304 eV 307.62 nm f= 0.09080 Spin multiplicity= 1: H-3 -> L+10 23.9%, H-4 -> L+10 23.2%, H -> L+9 22.8%, H -> L+8 20.3% # 145 4.0335 eV 307.39 nm f= 0.01920 Spin multiplicity= 1: H-32 -> L 73.6%, H-3 -> L+10 8.2% # 146 4.0353 eV 307.25 nm f= 0.06390 Spin multiplicity= 1: H-4 -> L+10 59.1%, H -> L+8 11.5%, H -> L+9 9.7%, H-32 -> L 5.1% # 147 4.0380 eV 307.04 nm f= 0.00060 Spin multiplicity= 1: $H-2 \rightarrow L+7 94.2\%$ # 148 4.0429 eV 306.67 nm f= 0.00030 Spin multiplicity= 1: H-32 -> L+1 93.6% # 149 4.0630 eV 305.15 nm f= 0.00000 Spin multiplicity= 1: H-28 -> L 98.7% # 150 4.0695 eV 304.67 nm f= 0.00000 Spin multiplicity= 1: H-29 -> L+1 99.2% # 151 4.0925 eV 302.95 nm f= 0.00010 Spin multiplicity= 1:

H-14 -> L+5 88.5%

- # 152 4.1241 eV 300.63 nm f= 0.00000 Spin multiplicity= 1: H-19 -> L+2 95.4%
- # 153 4.1400 eV 299.48 nm f= 0.00060 Spin multiplicity= 1: H-1 -> L+9 56.9%, H-1 -> L+8 32.1%
- # 154 4.1420 eV 299.33 nm f= 0.00010 Spin multiplicity= 1: H-1 -> L+8 55.2%, H-1 -> L+9 32.3%
- # 155 4.1536 eV 298.50 nm f= 0.00010 Spin multiplicity= 1: H-19 -> L+3 92.7%
- # 156 4.1619 eV 297.90 nm f= 0.00680 Spin multiplicity= 1: H-5 -> L+10 78.1%
- # 157 4.1784 eV 296.73 nm f= 0.00160 Spin multiplicity= 1: H-19 -> L+4 93.9%
- # 158 4.1876 eV 296.07 nm f= 0.00080 Spin multiplicity= 1: H-3 -> L+6 86.7%, H-15 -> L+6 7.9%
- # 159 4.1965 eV 295.45 nm f= 0.00350 Spin multiplicity= 1: H-17 -> L+6 63.5%, H-15 -> L+6 18.1%, H-3 -> L+6 9.1%
- # 160 4.1978 eV 295.36 nm f= 0.00440 Spin multiplicity= 1: H -> L+12 74.1%, H -> L+13 10.5%, H-1 -> L+12 7.8%
- # 161 4.2062 eV 294.77 nm f= 0.00000 Spin multiplicity= 1: H-3 -> L+7 96.7%
- # 162 4.2078 eV 294.65 nm f= 0.00760 Spin multiplicity= 1: H-15 -> L+6 56.9%, H-17 -> L+6 23.9%
- # 163 4.2132 eV 294.28 nm f= 0.00010 Spin multiplicity= 1: H-16 -> L+2 99.5%
- # 164 4.2152 eV 294.14 nm f= 0.02600 Spin multiplicity= 1: H-18 -> L+7 47.5%, H-16 -> L+7 26.8%, H-38 -> L+1 9.1%
- # 165 4.2187 eV 293.89 nm f= 0.00680 Spin multiplicity= 1: H-19 -> L+5 75.5%, H-16 -> L+7 5.9%
- # 166 4.2235 eV 293.56 nm f= 0.01460 Spin multiplicity= 1: H-16 -> L+7 50.2%, H-18 -> L+7 26.9%

- # 167 4.2259 eV 293.39 nm f= 0.01400 Spin multiplicity= 1: H -> L+13 57.9%, H -> L+11 12.3%, H -> L+12 10.6%, H-39 -> L 8.1%
 # 168 4.2272 eV 293.30 nm f= 0.00160 Spin multiplicity= 1:
- H-2 -> L+9 49.0%, H-2 -> L+8 40.8%
- # 169 4.2281 eV 293.24 nm f= 0.00010 Spin multiplicity= 1: H-15 -> L+3 99.0%
- # 170 4.2301 eV 293.10 nm f= 0.00020 Spin multiplicity= 1: H-4 -> L+6 98.5%
- # 171 4.2323 eV 292.95 nm f= 0.02870 Spin multiplicity= 1: H-38 -> L+1 43.6%, H-39 -> L 24.2%, H-18 -> L+7 10.1%
- # 172 4.2362 eV 292.68 nm f= 0.47790 Spin multiplicity= 1: H-39 -> L 50.9%, H-38 -> L+1 23.8%
- # 173 4.2401 eV 292.41 nm f= 0.00120 Spin multiplicity= 1: H-2 -> L+8 49.9%, H-2 -> L+9 43.8%
- # 174 4.2433 eV 292.19 nm f= 0.00120 Spin multiplicity= 1: H-4 -> L+7 98.2%
- # 175 4.2670 eV 290.57 nm f= 0.00080 Spin multiplicity= 1: H -> L+11 79.0%, H -> L+13 11.9%
- # 176 4.2713 eV 290.27 nm f= 0.00000 Spin multiplicity= 1: H-16 -> L+4 99.9%
- # 177 4.2791 eV 289.74 nm f= 0.00570 Spin multiplicity= 1: H-1 -> L+13 74.3%, H-2 -> L+13 6.3%, H-1 -> L+11 5.9%
- # 178 4.2814 eV 289.59 nm f= 0.00000 Spin multiplicity= 1: H-18 -> L+2 98.8%
- # 179 4.2915 eV 288.91 nm f= 0.00020 Spin multiplicity= 1: H-17 -> L+3 99.0%
- # 180 4.2943 eV 288.72 nm f= 0.00000 Spin multiplicity= 1: H-15 -> L+5 99.4%
- # 181 4.3044 eV 288.04 nm f= 0.00190 Spin multiplicity= 1: H-6 -> L+10 40.7%, H-20 -> L+2 30.2%, H-21 -> L+2 7.0%
- # 182 4.3065 eV 287.90 nm f= 0.00070 Spin multiplicity= 1:

H-6 -> L+10 39.2%, H-20 -> L+2 32.7%, H-21 -> L+2 8.3%

- # 183 4.3229 eV 286.81 nm f= 0.00760 Spin multiplicity= 1: H-20 -> L+4 57.6%, H-21 -> L+4 19.6%
- # 184 4.3285 eV 286.44 nm f= 0.00490 Spin multiplicity= 1:

H-2 -> L+13 63.4%, H-1 -> L+11 14.2%, H-2 -> L+11 7.8%

- # 185 4.3294 eV 286.38 nm f= 0.01210 Spin multiplicity= 1:
- H-22 -> L+3 49.6%, H-20 -> L+3 31.2%, H-21 -> L+3 9.9%
- # 186 4.3308 eV 286.28 nm f= 0.00330 Spin multiplicity= 1:
- H-15 -> L+9 42.7%, H-15 -> L+8 38.8%, H-29 -> L+6 6.6%
- # 187 4.3370 eV 285.88 nm f= 0.00300 Spin multiplicity= 1:
- H-16 -> L+8 43.9%, H-16 -> L+9 41.3%, H-28 -> L+7 6.7%
- # 188 4.3395 eV 285.71 nm f= 0.00000 Spin multiplicity= 1: H-18 -> L+4 98.9%
- # 189 4.3409 eV 285.62 nm f= 0.00000 Spin multiplicity= 1: H-5 -> L+6 93.5%
- # 190 4.3438 eV 285.43 nm f= 0.00340 Spin multiplicity= 1:
- H-1 -> L+12 27.3%, H-7 -> L+10 24.6%, H-1 -> L+11 23.1%, H-2 -> L+13 7.5%
- # 191 4.3439 eV 285.42 nm f= 0.00050 Spin multiplicity= 1:
- H-29 -> L+2 85.0%, H-29 -> L+4 11.3%
- # 192 4.3473 eV 285.20 nm f= 0.00170 Spin multiplicity= 1:
- H-1 -> L+12 45.6%, H-7 -> L+10 21.9%, H-2 -> L+12 8.1%, H-1 -> L+11 6.2%, H -> L+12 5.0%
- # 193 4.3504 eV 284.99 nm f= 0.00250 Spin multiplicity= 1:

H-7 -> L+10 33.0%, H-1 -> L+11 30.8%, H-1 -> L+13 6.7%, H-2 -> L+13 5.6%, H-1 -> L+17 5.0%

- # 194 4.3576 eV 284.52 nm f= 0.00000 Spin multiplicity= 1:
- H-17 -> L+5 99.2%
- # 195 4.3583 eV 284.48 nm f= 0.00010 Spin multiplicity= 1:

H-5 -> L+7 94.3%

196 4.3710 eV 283.65 nm f= 0.00020 Spin multiplicity= 1:

H-28 -> L+3 89.0%, H-28 -> L+5 7.8%

197 4.3863 eV 282.66 nm f= 0.00040 Spin multiplicity= 1:

H -> L+17 40.0%, H-1 -> L+16 13.2%

198 4.3874 eV 282.59 nm f= 0.00440 Spin multiplicity= 1:

H-22 -> L+5 15.2%, H -> L+16 11.8%, H-1 -> L+17 11.0%, H -> L+17 10.7%, H-20 -> L+5 8.3%, H -> L+24 5.3%

199 4.3897 eV 282.44 nm f= 0.00010 Spin multiplicity= 1:

H-22 -> L+5 32.3%, H-20 -> L+5 18.4%, H-21 -> L+5 6.6%, H -> L+16 6.5%, H-1 -> L+17 5.1%

200 4.3990 eV 281.85 nm f= 0.00140 Spin multiplicity= 1:

H-3 -> L+9 29.1%, H-3 -> L+8 22.9%, H-22 -> L+2 19.4%, H-21 -> L+2 12.8%, H-24 -> L+2 6.2%

201 4.4006 eV 281.74 nm f= 0.00060 Spin multiplicity= 1:

H-22 -> L+2 27.6%, H-3 -> L+9 22.1%, H-3 -> L+8 17.9%, H-21 -> L+2 17.1%, H-24 -> L+2 7.8%

 $\# 202 \quad 4.4072 \text{ eV} \quad 281.32 \text{ nm} \quad \text{f}= 0.00110 \quad \text{Spin multiplicity}= 1:$

H-29 -> L+4 49.4%, H-3 -> L+8 19.3%, H-3 -> L+9 10.2%, H-29 -> L+2 6.3%, H-37 -> L 5.7%

203 4.4072 eV 281.32 nm f = 0.00100 Spin multiplicity = 1:

H-3 -> L+9 29.2%, H-3 -> L+8 27.0%, H-29 -> L+4 25.9%, H-37 -> L+1 7.2%

204 4.4125 eV 280.98 nm f= 0.00300 Spin multiplicity= 1:

H-37 -> L 69.5%, H-29 -> L+4 9.8%

205 4.4130 eV 280.95 nm f= 0.00060 Spin multiplicity= 1:

H-37 -> L+1 59.1%, H-3 -> L+8 6.7%, H-22 -> L+3 6.4%, H-34 -> L+1 5.3%, H-3 -> L+9 5.2%

#206 4.4143 eV 280.87 nm = 0.00340 Spin multiplicity=1:

H-20 -> L+3 35.7%, H-22 -> L+3 33.1%, H-37 -> L+1 9.2%, H-21 -> L+3 7.9%

#207 4.4237 eV 280.27 nm f = 0.00210 Spin multiplicity = 1:

H -> L+18 31.0%, H -> L+16 20.9%, H -> L+14 7.6%, H-1 -> L+17 5.6%, H-1 -> L+18 5.5%

208 4.4316 eV 279.77 nm f= 0.00160 Spin multiplicity= 1:

H-2 -> L+11 74.6%, H-1 -> L+11 6.7%

209 4.4329 eV 279.69 nm f= 0.00330 Spin multiplicity= 1:

H-1 -> L+17 34.6%, H-1 -> L+16 15.7%, H -> L+24 5.6%, H-1 -> L+11 5.3%, H-1 -> L+24 5.3%

- # 210 4.4383 eV 279.35 nm f= 0.00810 Spin multiplicity= 1: H-41 -> L 78.4%
- # 211 4.4404 eV 279.22 nm f= 0.00540 Spin multiplicity= 1: H-42 -> L+1 71.5%, H-28 -> L+5 10.9%
- # 212 4.4405 eV 279.21 nm f= 0.00100 Spin multiplicity= 1: H-4 -> L+9 55.3%, H-4 -> L+8 36.1%
- # 213 4.4451 eV 278.92 nm f= 0.00010 Spin multiplicity= 1: H-4 -> L+8 55.6%, H-4 -> L+9 40.8%
- # 214 4.4492 eV 278.67 nm f= 0.00040 Spin multiplicity= 1:
- H-21 -> L+2 30.0%, H-22 -> L+2 25.3%, H-20 -> L+2 22.1%, H-2 -> L+12 14.2%
- # 215 4.4494 eV 278.65 nm f= 0.00010 Spin multiplicity= 1:
- H-2 -> L+12 63.4%, H-1 -> L+12 8.5%, H-21 -> L+2 7.2%, H-22 -> L+2 5.3%
- # 216 4.4502 eV 278.60 nm f= 0.00140 Spin multiplicity= 1:
- H-28 -> L+5 77.7%, H-42 -> L+1 9.9%, H-28 -> L+3 6.9%
- # 217 4.4553 eV 278.28 nm f= 0.00100 Spin multiplicity= 1:
- H-22 -> L+4 38.1%, H-21 -> L+4 30.9%, H-24 -> L+4 15.3%, H-20 -> L+4 6.4%
- # 218 4.4630 eV 277.80 nm f= 0.00010 Spin multiplicity= 1:
- H-33 -> L 95.5%
- # 219 4.4726 eV 277.21 nm f= 0.00000 Spin multiplicity= 1: H-34 -> L+1 91.5%, H-37 -> L+1 7.5%
- # 220 4.4745 eV 277.09 nm f= 0.00170 Spin multiplicity= 1: H-8 -> L+10 74.4%
- # 221 4.4791 eV 276.81 nm f= 0.00030 Spin multiplicity= 1: H-20 -> L+5 40.3%, H-22 -> L+5 39.8%, H-21 -> L+5 8.5%
- # 222 4.4850 eV 276.44 nm f= 0.00010 Spin multiplicity= 1: H-21 -> L+3 71.2%, H-20 -> L+3 21.8%
- # 223 4.4888 eV 276.21 nm f= 0.00000 Spin multiplicity= 1: H-35 -> L 98.2%
- # 224 4.4899 eV 276.14 nm f= 0.00000 Spin multiplicity= 1:
- 160

H-6 -> L+6 93.8%

- # 225 4.4973 eV 275.69 nm f= 0.01150 Spin multiplicity= 1:
- H-2 -> L+16 36.3%, H-2 -> L+14 12.4%, H-4 -> L+13 7.5%, H-2 -> L+15 6.4%
- # 226 4.4980 eV 275.64 nm f= 0.00000 Spin multiplicity= 1:

H-36 -> L+1 98.7%

227 4.5052 eV 275.20 nm f= 0.00000 Spin multiplicity= 1:

H-6 -> L+7 98.4%

228 4.5108 eV 274.86 nm f= 0.00130 Spin multiplicity= 1:

H-3 -> L+13 76.8%

- # 229 4.5196 eV 274.33 nm f= 0.00010 Spin multiplicity= 1:
- H-22 -> L+4 43.8%, H-21 -> L+4 28.3%, H-20 -> L+4 23.6%
- # 230 4.5279 eV 273.82 nm f= 0.00310 Spin multiplicity= 1:
- H -> L+18 27.9%, H -> L+16 11.5%, H-1 -> L+16 5.9%, H-2 -> L+16 5.0%, H-1 -> L+18 5.0%
- # 231 4.5314 eV 273.61 nm f= 0.00180 Spin multiplicity= 1:

H-24 -> L+2 74.2%, H-21 -> L+2 13.2%

232 4.5322 eV 273.56 nm f= 0.00000 Spin multiplicity= 1:

H-7 -> L+6 89.0%

233 4.5489 eV 272.56 nm f= 0.00380 Spin multiplicity= 1:

H-4 -> L+13 58.7%, H-2 -> L+16 5.3%

234 4.5515 eV 272.40 nm f= 0.00040 Spin multiplicity= 1:

H-5 -> L+9 47.6%, H-5 -> L+8 35.4%

235 4.5565 eV 272.10 nm f= 0.00020 Spin multiplicity= 1:

H-7 -> L+7 95.3%

236 4.5584 eV 271.99 nm f= 0.00050 Spin multiplicity= 1:

H-5 -> L+8 48.9%, H-5 -> L+9 35.8%

- # 237 4.5610 eV 271.84 nm f= 0.01360 Spin multiplicity= 1:
- H-9 -> L+10 28.4%, H-2 -> L+17 20.6%, H-21 -> L+5 8.5%
- # 238 4.5612 eV 271.82 nm f= 0.00590 Spin multiplicity= 1:
- H-21 -> L+5 52.4%, H-20 -> L+5 18.8%, H-9 -> L+10 7.4%, H-25 -> L+5 5.4%
- # 239 4.5659 eV 271.54 nm f= 0.02940 Spin multiplicity= 1:

H-2 -> L+17 42.8%, H-9 -> L+10 30.3%

- # 240 4.5752 eV 270.99 nm f= 0.00040 Spin multiplicity= 1:
- H-23 -> L+3 53.8%, H-25 -> L+3 24.5%
- # 241 4.5810 eV 270.65 nm f= 0.00130 Spin multiplicity= 1:
- H-24 -> L+4 63.0%, H-21 -> L+4 13.9%, H-3 -> L+11 8.0%, H-22 -> L+4 5.2%
- # 242 4.5886 eV 270.20 nm f= 0.00640 Spin multiplicity= 1:
- H-3 -> L+11 21.5%, H -> L+19 20.0%, H-3 -> L+12 11.5%
- # 243 4.5917 eV 270.02 nm f= 0.00730 Spin multiplicity= 1:
- H-3 -> L+11 44.1%, H -> L+19 14.2%, H-24 -> L+4 6.1%, H -> L+20 5.7%
- # 244 4.5991 eV 269.58 nm f= 0.00030 Spin multiplicity= 1:
- H-3 -> L+12 78.7%, H-3 -> L+11 9.1%
- # 245 4.6153 eV 268.64 nm f= 0.00430 Spin multiplicity= 1:
- H-10 -> L+10 34.4%, H -> L+20 24.4%, H-1 -> L+19 6.5%
- # 246 4.6293 eV 267.82 nm f= 0.00040 Spin multiplicity= 1:
- H-10 -> L+10 27.6%, H-4 -> L+11 15.1%, H-1 -> L+19 12.2%, H -> L+20 8.1%, H-1 -> L+18 5.3%
- # 247 4.6314 eV 267.70 nm f= 0.00050 Spin multiplicity= 1:
- H-23 -> L+5 66.0%, H-25 -> L+5 9.6%, H-23 -> L+3 5.2%
- # 248 4.6356 eV 267.46 nm f= 0.00040 Spin multiplicity= 1:
- H-25 -> L+3 21.9%, H-23 -> L+3 20.0%, H-27 -> L+3 8.3%, H-4 -> L+11 7.0%
- # 249 4.6369 eV 267.39 nm f= 0.00100 Spin multiplicity= 1:
- H-4 -> L+11 20.2%, H-25 -> L+3 11.4%, H-23 -> L+3 10.5%, H-4 -> L+12 9.5%, H-23 -> L+5 6.5%, H-10 -> L+10 5.2%
- # 250 4.6418 eV 267.10 nm f= 0.00600 Spin multiplicity= 1:
- H-4 -> L+12 31.4%, H-11 -> L+10 25.9%, H-12 -> L+10 5.9%
- # 251 4.6464 eV 266.84 nm f= 0.00270 Spin multiplicity= 1:
- H-4 -> L+12 41.7%, H-11 -> L+10 16.3%, H-4 -> L+11 10.4%, H-12 -> L+10 5.5%
- # 252 4.6529 eV 266.47 nm f= 0.00080 Spin multiplicity= 1:
- H-23 -> L+2 49.9%, H-25 -> L+2 11.0%, H-27 -> L+2 9.2%
- # 253 4.6545 eV 266.37 nm f= 0.00090 Spin multiplicity= 1:

H-4 -> L+11 22.4%, H -> L+19 10.3%, H-23 -> L+2 9.8%, H-2 -> L+18 9.4%, H-1 -> L+18 8.8%

254 4.6604 eV 266.04 nm f= 0.00410 Spin multiplicity= 1:

H-3 -> L+16 12.9%, H-1 -> L+19 10.2%, H-11 -> L+10 8.0%, H-4 -> L+16 7.6%, H-2 -> L+19 6.8%, H-1 -> L+20 6.5%

255 4.6642 eV 265.82 nm f= 0.00600 Spin multiplicity= 1:

H-12 -> L+10 20.4%, H-3 -> L+16 14.7%, H-11 -> L+10 11.4%, H-3 -> L+14 5.1%

256 4.6690 eV 265.55 nm f= 0.02360 Spin multiplicity= 1:

H-17 -> L+9 27.1%, H-17 -> L+8 24.7%, H-15 -> L+14 7.0%, H-27 -> L+4 6.2%

257 4.6732 eV 265.31 nm f= 0.00670 Spin multiplicity= 1:

H-45 -> L+1 55.8%, H-18 -> L+8 11.1%, H-18 -> L+9 10.4%

258 4.6734 eV 265.30 nm f= 0.01110 Spin multiplicity= 1:

H-27 -> L+4 43.4%, H-25 -> L+4 18.7%, H-23 -> L+4 8.6%, H-17 -> L+9 5.2%

259 4.6821 eV 264.80 nm f= 0.00540 Spin multiplicity= 1:

H-26 -> L+3 28.4%, H-31 -> L+3 10.9%, H-1 -> L+18 7.4%, H-18 -> L+8 6.2%, H-18 -> L+9 5.8%, H-12 -> L+10 5.3%

#260 4.6825 eV 264.78 nm f = 0.00450 Spin multiplicity = 1:

H-1 -> L+18 17.6%, H-12 -> L+10 13.7%, H-26 -> L+3 11.1%, H-1 -> L+19 5.9%

#261 4.6862 eV 264.57 nm f = 0.00040 Spin multiplicity = 1:

H-8 -> L+6 94.6%

#262 4.6870 eV 264.53 nm f = 0.01950 Spin multiplicity = 1:

H-45 -> L+1 13.1%, H-18 -> L+8 9.5%, H-18 -> L+9 8.9%, H-26 -> L+3 5.5%, H-2 -> L+18 5.0%

#263 4.6878 eV 264.48 nm = 0.01120 Spin multiplicity = 1:

H-3 -> L+16 7.3%, H-4 -> L+16 7.3%, H-45 -> L+1 6.5%, H-2 -> L+18 5.5%, H-18 -> L+8 5.1%

#264 4.6882 eV 264.46 nm f = 0.00380 Spin multiplicity = 1:

H-26 -> L+2 29.2%, H-27 -> L+2 18.9%, H-23 -> L+2 15.0%

265 4.6929 eV 264.20 nm f= 0.00240 Spin multiplicity= 1:

H-26 -> L+2 26.9%, H-27 -> L+2 24.8%, H-25 -> L+2 16.7%, H-30 -> L+2 10.9%

#266 4.6944 eV 264.11 nm f = 0.00220 Spin multiplicity = 1:

H-25 -> L+5 29.1%, H-23 -> L+5 11.0%, H-27 -> L+5 9.4%, H-21 -> L+5 6.1%

- # 267 4.6960 eV 264.02 nm f= 0.00550 Spin multiplicity= 1:
- H-25 -> L+5 14.9%, H-2 -> L+18 9.3%, H-1 -> L+19 6.8%, H-2 -> L+19 5.7%, H-23 -> L+5 5.6%, H-3 -> L+16 5.3%
- # 268 4.7017 eV 263.70 nm f= 0.00050 Spin multiplicity= 1:

H-6 -> L+9 47.5%, H-6 -> L+8 36.1%

269 4.7050 eV 263.52 nm f= 0.00000 Spin multiplicity= 1:

H-8 -> L+7 96.7%

270 4.7072 eV 263.39 nm f= 0.00020 Spin multiplicity= 1:

H-6 -> L+8 51.6%, H-6 -> L+9 43.2%

271 4.7139 eV 263.02 nm f= 0.00090 Spin multiplicity= 1:

H-1 -> L+18 14.8%, H-1 -> L+20 13.6%, H-1 -> L+23 6.5%, H-3 -> L+17 6.2%, H-2 -> L+18 5.7%

- # 272 4.7191 eV 262.73 nm f= 0.00610 Spin multiplicity= 1:
- H-47 -> L 70.7%, H-48 -> L 15.1%
- # 273 4.7217 eV 262.58 nm f= 0.00650 Spin multiplicity= 1:

H-5 -> L+11 32.8%, H-5 -> L+13 10.0%, H -> L+21 7.5%, H-3 -> L+17 6.4%

274 4.7271 eV 262.28 nm f= 0.00420 Spin multiplicity= 1:

H -> L+21 19.0%, H-3 -> L+17 17.4%, H-5 -> L+11 12.1%, H-1 -> L+20 9.4%, H -> L+22 6.3%

- # 275 4.7375 eV 261.71 nm f= 0.00710 Spin multiplicity= 1:
- H-5 -> L+12 57.2%, H-5 -> L+11 6.3%

276 4.7420 eV 261.46 nm f= 0.01520 Spin multiplicity= 1:

H-7 -> L+9 11.6%, H-5 -> L+12 11.1%, H-3 -> L+17 9.7%, H-7 -> L+8 9.4%, H -> L+24 9.4%

277 4.7449 eV 261.30 nm f= 0.00370 Spin multiplicity= 1:

H-7 -> L+9 31.9%, H-7 -> L+8 27.6%

278 4.7473 eV 261.17 nm f= 0.00000 Spin multiplicity= 1:

H-9 -> L+6 89.0%, H-10 -> L+6 8.4%

#279 4.7505 eV 260.99 nm f= 0.01760 Spin multiplicity= 1:

H-38 -> L 24.3%, H-40 -> L 16.1%, H -> L+24 10.6%, H-3 -> L+17 9.8%

280 4.7508 eV 260.98 nm f= 0.01280 Spin multiplicity= 1:

H-38 -> L 26.5%, H-40 -> L 17.3%, H -> L+24 11.2%, H-3 -> L+17 9.9% 164 # 281 4.7529 eV 260.86 nm f= 0.00170 Spin multiplicity= 1:

H-40 -> L+1 31.4%, H-23 -> L+4 20.3%, H-46 -> L+1 9.4%, H-30 -> L+2 7.2%, H-25 -> L+2 5.2%

282 4.7531 eV 260.85 nm f= 0.00250 Spin multiplicity= 1:

H-23 -> L+4 27.1%, H-40 -> L+1 26.5%, H-46 -> L+1 7.9%, H-30 -> L+2 7.1%

283 4.7547 eV 260.76 nm f= 0.00430 Spin multiplicity= 1:

H-23 -> L+4 29.5%, H-30 -> L+2 22.4%, H-25 -> L+2 12.7%, H-38 -> L 5.6%

284 4.7566 eV 260.66 nm f= 0.00060 Spin multiplicity= 1:

H-5 -> L+13 18.0%, H-2 -> L+19 16.6%, H-5 -> L+11 10.9%, H-7 -> L+9 8.9%, H-5 -> L+12 7.3%

285 4.7584 eV 260.56 nm f= 0.00070 Spin multiplicity= 1:

H-7 -> L+8 45.1%, H-7 -> L+9 35.1%

286 4.7602 eV 260.46 nm f= 0.00000 Spin multiplicity= 1:

H-9 -> L+7 94.5%

287 4.7705 eV 259.90 nm f= 0.01620 Spin multiplicity= 1:

H-2 -> L+19 26.2%, H-5 -> L+13 20.7%, H-2 -> L+18 9.1%

288 4.7728 eV 259.77 nm f= 0.00010 Spin multiplicity= 1:

H-24 -> L+3 78.0%, H-26 -> L+3 10.8%

289 4.7816 eV 259.29 nm f= 0.00410 Spin multiplicity= 1:

H-26 -> L+5 45.7%, H-31 -> L+5 14.6%, H-24 -> L+5 14.0%, H-39 -> L+1 5.9%, H-30 -> L+5 5.0%

290 4.7870 eV 259.00 nm f= 0.00020 Spin multiplicity= 1:

H-40 -> L 46.2%, H-38 -> L 38.3%, H-43 -> L 10.0%

291 4.7889 eV 258.90 nm f= 0.01140 Spin multiplicity= 1:

H-1 -> L+21 16.8%, H-39 -> L+1 9.7%, H-2 -> L+20 8.7%, H-1 -> L+22 6.5%, H-1 -> L+24 5.4%

#292 4.7894 eV 258.87 nm f= 0.00170 Spin multiplicity= 1:

H-39 -> L+1 74.0%

293 4.7957 eV 258.53 nm f= 0.00100 Spin multiplicity= 1:

H -> L+15 31.0%, H -> L+16 9.6%, H-4 -> L+17 8.8%, H-2 -> L+24 8.6%, H-1 -> L+21 7.2%

294 4.7972 eV 258.45 nm f= 0.00050 Spin multiplicity= 1:
H-26 -> L+4 58.4%, H -> L+15 15.5%

295 4.7980 eV 258.41 nm f= 0.00000 Spin multiplicity= 1:

H -> L+15 26.6%, H-26 -> L+4 13.8%, H-2 -> L+24 11.1%, H-4 -> L+17 6.0%, H-1 -> L+21 5.9%

296 4.8011 eV 258.24 nm f= 0.02350 Spin multiplicity= 1:

H-34 -> L+2 53.6%, H-36 -> L+2 7.6%, H-34 -> L+4 5.8%

297 4.8026 eV 258.16 nm f= 0.00130 Spin multiplicity= 1:

H-3 -> L+18 20.6%, H-7 -> L+13 8.7%, H-34 -> L+2 6.6%, H-2 -> L+20 5.5%

298 4.8048 eV 258.04 nm f= 0.01640 Spin multiplicity= 1:

H-6 -> L+13 23.5%, H-2 -> L+24 11.0%, H-4 -> L+17 10.1%, H-2 -> L+21 5.4%

299 4.8073 eV 257.91 nm f= 0.02060 Spin multiplicity= 1:

H-27 -> L+3 20.4%, H-33 -> L+3 14.3%, H-35 -> L+3 7.8%, H-31 -> L+3 6.7%, H-6 -> L+13 6.1%, H-26 -> L+3 5.8%

- # 300 4.8126 eV 257.62 nm f= 0.02550 Spin multiplicity= 1:
- H-2 -> L+20 27.4%, H-2 -> L+23 7.6%, H-1 -> L+21 6.4%

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Chapter 5 Size-dependent multi-electron donation on CH₄ evolution

The energetic alignment between conduction band minimum of quantum dots and lowest unoccupied molecular orbital of catalyst refers as driving force dominates the electron transfer rate on QD-molecule hybrid photocatalytic system according to Marcus equation. As the previous chapter reported, the special configuration of QD-molecule hybrid photocatalyst we designed achieved efficient multi-electron donation process during the photocatalytic conversion of CO₂ to CH₄ due to the unconventional electronic structure as well as the existence of multiple catalytic sites. On the other hand, QDs are famous for their size-tunable band structures, which opens up a new view for engineering the multielectron donation process by alerting the QDs size. Thus, in this chapter, we optimized band alignment of QDs-molecule catalyst by exploring the size-dependent photoinduced electron transfer dynamics and further photocatalytic reduction of CO₂ performance. After basic characterization of samples, we confirmed the detailed band alignment via UPS measurement complementary with corresponding UV-vis spectra. Transient absorption spectroscopy revealed their excited state dynamics and rationalized the QDs with smallest size within QD-molecule catalyst achieving photoinduced multi-electron transfer process and CH₄ evolution. We attributed this phenomenon to large driving force between CB of InP/ZnS QDs and redox level of Re-catalyst and efficient multi-electron accumulation on the Re-catalyst. Besides, the photoinduced hole-trapping process was found as a limit factor on the photocatalytic conversion of CO_2 to CO. This work provides a new strategy for improving product selectivity of photocatalytic reduction of CO2 via modulation of QDs size.

This chapter is a prepared article: Size - dependent Multi-electron Donation in Metalcomplex Quantum Dots Hybrid Catalyst for Photocatalytic conversion of Methane with authors of Qian Zhao, Mohamed Abdellah, Yuehan Cao, Jie Meng, Xianshao Zou, Weihua Lin, Kasper Enemark-Rasmussen, Yijiang Chen, Hengli Duan, Qinyin Pan, Ying Zhou, Tonu Pullerits, Sophie E. Canton, Yuran Niu, and Kaibo Zheng. This article is given below.

Size-dependent Multi-electron Donation in Metalcomplex Quantum Dots Hybrid Catalyst for Photocatalytic conversion of Methane.

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Abstract

Multi-electron donation plays a vital role upon light-driven conversion of CO_2 to add-value chemical fuels. Its efficiency was reported strongly depends on the energy alignment bewteen the excited state of donor and acceptor . In this paper, we demonstrated the band alignment of QD significantly affect the multi-electron transfer process and further alter photocatalytic conversion of methane in a InP/ZnS QDs-Re-complexes hybrid catalyst system. TEM, XPS and UPS charaterization identified the size of QDs, the number of catalyst attached to per QD and the band alignment of hybrid catalyst respectively. Transient absorption spectroscopy reveals the fast multi-electron transfer from QD to Re-catalyst can only be achieved within Re-2.3 nm due to the sufficient driving force, where electron injection time was shorter than one picosecond. Fast electron injection process guaranteed the efficient multi-electron donation to CO_2 species supressing the competition of Auger recombination of multi-electrons. Subsequently, photocatalytic conversion of CO_2 to CH_4 process enhanced by Re-2.3 nm. This work demonstrated QDs size dominated the multi-electron transfer by electronic band alignment and can be considered as a guidance for engineering product selectivity and efficiency in the photocatalytic CO_2 reduction.

Introduction

Conversion of CO₂ to add-value products (short-chain chemical fuels or materials) by photocatalytic reduction is regarded as a promising approach to address issues of increasingly severe energy shortage and consequent greenhouse gas emission that leads to global warming¹. Unlike the photocatalytic H₂ evolution, one electron mediated reduction of CO₂ is a highly endothermic reaction due to much more stable C = O bond in CO₂ molecule^{2,3}. In contrast, multiple electrons mediated production is generally more energetic favorable with reduced redox overpotential corresponding products. However, in order to donate Multi-electron s after excitation, photocatalysts are required to have long-lived excited states, stable intermediate of one-electron-reduction (OER) species and strong bonds between CO₂ molecule and catalytic sites⁴. Compared with photocatalytic evolution of CO and formic acid (i.e. 2-electron reduction product), this requirement is more demanding for multi-electron reduction products (e.g. CH₄ or methanol) evolution^{5,6}. Therefore, seeking suitable catalysts with efficient Multi-electron donation capability becomes the critical issue to be tackled for the CO₂ photocatalytic reduction application.

Transition metal complex especially Re(I) complex has been regarded as one of the promising candidates to achieve Multi-electron donations for CO₂ catalytic reduction since 1) their lowest triplet excited state lifetime is sufficiently long enough to ensure efficient photo-induced electron transfer to catalytic sites; 2) rich electrons at d-orbital interact with C atom or transition metal provide vacant d-orbital for O atom in CO₂ molecule, which means transition metal is easy to fix CO₂ molecule onto itself by strong bond^{7,8}; 3) their OER species are stable in solution with low overpotential facilitating the subsequent electron transfer to CO₂ adducts. However, most of the Re(I) complexes featured narrow absorption bands in the visible region 9, and fast triple-triple annihilation (TTA) prohibits Multi-electron accumulation on single molecule 6. According to recent reports, the absorption response of Re(I) complexes can be extended by attaching photosensitizers to form hybrid catalysts ¹⁰⁻¹³, which fast annihilation can be solved by employing multi-Re(I) nuclear configuration to enlarge the spatial distance of the excited electrons in the reservoir pools before donated to CO₂ adducts^{14,15}. Recently, we demonstrated a novel hybrid catalysts tructure with InP/ZnS quantum dot (QDs) covalently attached by multiple Re-catalysts to tackle these two problems

concurrently. On one hand, QDs featured board absorption band and high absorption coefficient complimentary to the Re(I) complexes. On the other hand, strong covalent bonding resulted in efficient QD-to-surface ligand exciton delocalization, and multiple catalyst attachments enabled efficient injection of multiple photo-excited electrons from one QD with transferred electrons separated within individual surface catalyst with long lifetime (manuscript 2).

In this paper, we further optimized these structures by investigating the QD size dependence on the photo-induced charge transfer dynamic as well as the catalytic performance of CO_2 photoreduction. This was inspired by the common belief that the electronic structure of QD is significantly tuned by size within a strong quantum confinement regime. Consequently, the driving force for Multi-electron transfer should also be QD size dependent. We prepared three InP/ZnS-Re complex catalyst with different QD size for conversion of CO_2 to CO_2RR by photocatalytic approach. As a result, only QD-Re catalyst with the smallest size of InP/ZnS achieved photo-induced multi-electron transfer process producing CH_4 evolution. We attributed this phenomenon to large driving force between CB of QDs and Re(I) redox level and efficient photo-generated multi-electron accumulation on Re(I) center. Moreover, we also found photoinduced hole trapping limited conversion of CO_2 to CO process. This work provide a new strategy for multi-electron transfer control and fundamental method for optimal photocatalytic product selectivity and efficiency.

Results and Discussion:



Figure 1. Basic characterization of each sample. UV-vis spectra (a), photoluminescence spectra (b), and 31P NMR spectra (c) of each sample. TEM characterization and histograms of size distribution insert for Re-2.3 nm (d), Re-3.3 nm (e) and Re-3.8 nm (f) respectively. XPS spectra for the amount of Re-catalyst determination, Re-2.3 nm (g), Re-3.3 nm (h) and Re-3.8nm (i).

InP/ZnS colloidal quantum dot (InP/ZnS) with different sizes were obtained according to the previous literature protocol with slight modifications¹⁶. After 2-mercaptoethanol (ME) capped the InP/ZnS QDs (InP/ZnS-ME) were prepared via ligand exchange method, Rephotocatalyst was covalently linked to InP/ZnS QDs by simple esterification reaction between hydroxyl and phosphate group. Size control of InP/ZnS QDs was generally achieved by tuning the concentration ratio of ZnCl₂ and ZnI₂ precursors as well as the growth temperature of InP core. (For detailed synthesis procedure, see supporting information). Here, quantum dot/complex hybrid photocatalyst with different size of QDs were synthesized and defined by Re-2.3 nm, Re-3.3 nm and Re-3.8 nm according to their average sizes confirmed by TEM characterization (Fig. 1d, 1f, 1e). The absorption band edge and photoluminescence peak of the QDs shift to the longer wavelength with increasing sizes as shown in Fig 1a and Fig 1b, respectively, which is consistent with a previous study16. Interestingly, absorption spectra of QD/molecule complexes system show clear blue shift of the band edge diminishing of exciton band compared with their corresponding pristine quantum dots (Figure S1), which indicates delocalization of the charges from exciton and modification of the QDs electronic states via molecule attachment.

In order to reveal the coordination mode between Re-complexes and QDs, phosphorus-31 nuclear magnetic resonance (³¹P NMR) spectrum was first employed to identify the bonding type between QDs and Re-catalyst. As shown in Fig 1c, the significant broadening P peak at 5.5 ppm in the phosphate group for Re-2.3 nm, Re-3.3 nm and Re-3.8 nm comparing with pristine Re-catalyst illustrated that a substantial electron transfer process occurred between QDs and Re-catalyst. This confirmed Re-catalyst is covalently linked to the InP/ZnS quantum dot. Note that the P signal for P element in InP/ZnS QD in ³¹P NMR spectrum located in entirely different regions around -178 ppm¹⁷.

The amount of Re-photocatalysts attached to per InP/ZnS QD was quantified by X-ray photoelectron spectroscopy (XPS) measurement and calculated via precise atomic ratio between Re and In atoms, since In atoms and Re atoms are the main elements and only exist in quantum dots and catalysts, respectively. Figure 1 shows Re 4f (42.18 eV and 44.28 eV) and In 3d (452.58 eV and 444.98 eV) core level emission spectra of Re-2.3 nm (Fig. 1g), Re-3.3 nm (Fig. 1h) and Re-3.8 nm (Fig. 1i), respectively. The atomic ratios bewteen Re and In are calculated to be 0.08: 8.24, 0.06: 12.28, 0.04: 13.96, leading to approximate two Recatalsyts attached to per I study, we confirmed the amount of Re-photocatalyst on each QD determine the dynamics CO_2 photoreduction. Multiple catalyst attached to one QD can facilitated the multiexciton donation and further controlled the photocatalytic product. Inspired by that, in this work we ensured two Re-catalyst attachement for each sample.



Figure 2. Energetic level of each samples determination. UPS spectra of each samples and gold reference (a) and Tauc plot of absorption spectra (b). Energy level schematic for illustration the relative energy difference between each samples and Re-catalyst.

In order to reveal the QD size dependence on the charge transfer process, we first investigated the excited state structure of the specific hybrid system. In our previous study (manuscript 2), the excited state structure of Re-QDs with size of 2.7 nm has been confirmed through TD-DFT calculation. We observed that covalently coupled Re-Bpy exhibit strong frontier orbitals hybridization with QDs, in which the LUMO orbitals of the hybrid system already reside on the bipyridine moiety of Re-catalsyt, while the HOMO orbitals are dominantly contributed by the QDs (manuscript 2). Therefore, compared with pristine QDs where the excited exciton localized in the QDs volume, excited electrons in Re-QDs undergoes delocalization extending to bpy fragment. In this regard, efficient hybridization between frontier orbitals of Re-Bpy catalyst and QDs conduction band reduce the hybrid excited state level and facilitate exciton delocalization process, which lead to the slight blue shift and diminish of exciton band on absorption spectra compared with pristine QDs.

In general, the optical band gap of InP QDs are size tuneable due to the change of quantum confinement, where we confirm the energy state of each sample by ultraviolet photoemission spectra (UPS) and steady state absorption measurement. As shown in Figure 2a, the valence

band (VB) edge of each sample is almost the same in UPS spectra, with 0.5 eV of binding energy verses Fermi level. We also obtained the work function of them to be 5.6 eV with the 80 eV photon energy (Fig S2). The absolute value of valence band maximum (VBM) could then be calculated to be -5.1 eV. Afterward, the optical band gap (Eg) of each sample was determined from Tauc plot of the absorption spectra to be 2.35 eV, 2.02 eV and 1.94 eV for Re-2.3 nm, Re-3.3 nm and Re-3.8 nm respectively (Figure 2b). The conduction band minimum of each sample was then deducted by adding the Eg to VBM to be -2.75 eV, -3.08 eV and -3.16 eV for Re-2.3 nm, Re-3.3 nm and Re-3.8 nm respectively. Since the excited electrons in QDs are expected to be injected to Re(I) center. We also placed the redox level of Re(I) in ReBpy charaterizated via electrochemical measurement in our previous paper to be -3.11 eV. The final energy band alignment of each sample were displayed in Figure 2c. It is clear that the conduction band (CB) levels Re-2.3 nm and Re-3.8 nm are higher than Re(I) level enabling the electron injection. In contrast, the excited electron in Re-3.8 nm may be difficult to transfer to Re(I) center since its energetic unfavorable.



Figure 3. TA spectra and kinetics purify. 2D TA spectra of Re-2.3 nm (a), Re-3.3 nm (b) and Re-3.8 nm (c) with 470 nm excitation wavelength. TA kinetics subtraction process illustration for Re-2.3 nm (d), Re-3.3 nm (e) and Re-3.8 nm (f).

To rationalize the detailed mechanism of photocatalytic reactions for Re-QDs hybrid system, excited state dynamics of each sample were studied by transient absorption (TA) spectroscopy with 470 nm excitation wavelength in order to avoid the direct excitation of Re-Bpy catalyst. Since CO₂ photoreduction is typically mediated by multi-electron donation, a comparison of excited state dynamics under single-excitation and multi-excitation on QDs would help to rationalize the catalytic performance. In this scenario, we utilized two excitation intensities to control the excitation density in each OD $\langle N \rangle$ ensuring only one electron or two electrons can be generated per excitation pulse for photocatalytic reactions (For details in excitation density calculation, see supporting information). Figure 3a - c exhibit typical 2D TA spectra of Re-QDs of different sizes with <N>=0.50. All of the spectra feature a broad negative band at different position corresponding to their absorption band edge as shown in Fig. 1a, which can be attributed to band-edge ground state bleach (GSB). Positive excited state absorption (ESA) in the red regions can also be observed. Those features indicate quick population of the band edge lowest excited state after excitation. The excited state dynamics was then studied by analysing the kinetics of the GSB minimum which represent the depopulation dynamics of the lowest excited state. Before the study, it is indispensable to purify the TA kinetics of each sample since unattached QDs by Re-catalyst remains in the pool of QDs. As depicted in Figure 3d, e and f, we achieve that via subtracting kinetics of Re-ODs by that of InP/ZnS-ME (i.e. ODs without catalyst attachment) after normalizing the amplitude at long time decay (after 2 ns). We assume that the excited state of Re-ODs was depopulated entirely after such long time decay due to the fast charge transfer process, the long-lived remaining GSB should be only contributed by residual QDs without Re-catalsyt attachment.



Figure 4. Single electron donation analysis. TA kinetics extracted from minimum GSB for all samples (a) and corresponding excited state schematic diagram of lifetime and electron transfer pathway (b).

The resultant differential TA kinetics of three samples after subtraction process are shown in Fig. 4a. GSB decay of Re-2.3 nm is much faster than that of Re-3.3 nm indicating the fast electron transfer process from initial excited state compared with Re-3.3 nm at early time scale <1 ps. In contrast, no differeiental kinetics of Re-3.8 nm can be observed after substration owing to identical GSB decay Re-3.8 nm and pristine QDs (Fig 3f), which suggested excited state depopulation pathway has been not changed after Re-Bpy attachment in this sample. For Re-2.3 nm QDs, TA kinetic can be fitted by three exponential decay component with lifetimes of 0.3 ps (21%), 8.0 ps (52%) and 367 ps (27%). This results were consistent with previous studies where excited state dynamics of Re-QDs with similar size was analyzed by the complementary measurement between TA and time-resolved infrared spectroscopy (TRIR) (manuscript 2). The subpicosecond component (0.3 ps) to ultrafast can be assigned to electron transfer QDs to Re(I) center resulting the dissolation of the exited excition and generation of free holes in QDs that can be fingerprinted in TRIR in our previous study. In addition, we confirmed via TD-DFT calculation that in our OD-Re system the LUMO level is dominantly contributed by the Bpy orbital, indicating the excited electrons would already reside at Bpy moiety. Therefore, such a component refers to the fast electron injection from Bpy directly to Re(I) center. The 8.0 ps component can be attributed to hole trapping by trap state produced by thiol ligand (manuscript 2) which is commonly observed in thiol-capped QDs system with similar trapping time¹⁸. Finally, the 367 ps component 180

should be correlated to the recombination Re center between the transferred electrons in Re(I) and residual holes in QDs.

In contrast, the excited state depopulation in Re-3.3 nm is much slower as shown in Fig. 4a. We can also fitted the decay by three exponential component. The lifetime of fastest component (4 ps) is similar to the hole trapping process in Re-2.3 nm mentioned above. More importantly, the amplitude ratios of this component are also identical in two samples (i.e. 55% for Re-3.3 nm and 52% for Re-2.3 nm). This indicates it should also be attributed to similar surface hole trapping process. The Longest component of 1.7 ns for Re-3.3 nm is close to the intrinsic exciton recombination time in InP QDs¹⁹, i.e. depopulation of the excited electrons the CB of the QDs to the ground state. The middle component (51 ps) may correspond to the slow charge transfer to Re(I) due to the low driving force of the charge transfer comparable to the thermal energy kBT as shown in Fig. 4b.

We can rationalize such different excited state dynamics of three samples from their energy band alignment between the band edge states and energy level of Re(I) center as displayed in Fig 4b. The large driving force of electron transfer (i.e. Ecb-ERe(I) =0.36 eV) and short transfer distance²⁰ (i.e. distance between Bpy and Re(I) to be 0.208 nm) garantee the efficient electron transfer rate for Re-2.3 nm. While the driving force is only 0.03 eV for Re-3.3 nm, which is comparable to the thermal energy kBT (0.026 eV). This means the excited electrons will most probably spatially delocalized between QDs and Re(I) center during thermal fluctuation, and finally depopulate to the ground state from CB of QDs. Reversely, CB of Re-3.8 nm is lower than Re(I) means electron injection is suppressing, similarly, no hole trapping is available may because larger QDs have less surface traps during the Re attachment and the driving force for hole traps in large QDs is low.



Figure 5. Multi-electron donation analysis. TA kinetics extracted from minimum GSB for all samples (a) and corresponding excited state schematic diagram of lifetime and electron transfer pathway (b).

Multi-electron donation plays a crucial in photocatalytic CO₂ reduction. Subsequently we studied the photo-induced charge transfer dynamics of three samples with <N> 1 to monitor whether multiple electrons excited in QDs can be efficiently injected to the Re(I) for the CO_2 reduction. We implement the same subtraction operation as single electron donation analysis to remove the contribution from pristine QDs, and the result is shown in Fig. 5a. All the kinetics can also be fitted by the multiexponential decay function. The fitted component of Re-2.3 nm is similar to single electron excitation condition (i.e. subpicosecond electron injection, picosecond hole trapping, as 100 ps electron-hole recombination). This indicates efficient electron transfer retained when multiple electrons are excited in QDs since two catalysts have been attached per QDs ensuring an independent charge transfer channel for each electron as we also explained before in our previous report(manuscript 2). However, the excited depopulation process for Re-3.3 nm in this case is much slower as shown in Fig. 5a. In that sample, we found lifetime of ps decay component remains indicating the retaining hole trapping process in Re-3.3 nm QD. The longest component of 2.7 ns can also be attributed to the single electron-hole recombination time identical to the single excitation case. The middle component with lifetime of 70 ps refers to Auger recombination of multiple exciton instead of multi-electron injection to Re(I) since the kinetics decay exhibit second order recombination feature (For details see supporting information). This means no efficient multi-electron transfer to Re(I) can be achieved for Re-3.3 nm sample. As clarified above,

low driving force (0.03 eV) limit the electron transfer process. Secondly, subsequent electrons require overcome more Coulombic force from the first hole in QDs even if the first electron complete its' transfer.²¹

In terms of Re-3.8 nm QD, we start to see differentials signal different from single electron excitation scenario since the Auger process may be different between QDs and Re-QDs due to different dielectron screening effect of the surface ligand^{22–24}. Therefore, the obtained 100 ps decay component should be attribute to the Auger recombination of multi-exciton in Re-3.8nm, while 1.1 ns component is close to intrinsic single exciton lifetime in pristine QDs. Note the surface hole trapping process is still absent in Re-3.8 nm sample in this case. The overall charge transfer pathway and corresponding lifetime are summarized in Fig 5b.



Figure 6. Photocatalytic reduction CO₂ performance. Photocatalytic evolution of CO (a) and CH₄ (b) for three samples. Schematic illustration of pathways for photocatalytic reduction of CO₂ with two Re-catalyst attachment (c).Light pink region in Re-3.3 show the electron transfer reversely to Re(I) center, dotted line means electrons hardly participate in the photocatalytic reduction of CO₂ reactions.

We finally investigated photocatalytic CO₂ reduction performance of the three Re-QDs. All the Re-QD samples were dispersed into CH₃CN and 10% triethanolamine (TEOA) as a sacrificial donor. To guarantee only QDs were excited, the mixture was irradiated by an LED lamp with 440 excitation wavelength for 6 h after purging with Argon for 10 minutes. As shown in Fig 6a, Re-2.3 nm exhibit excellent photocatalytic performance with the CO photoreduction yield of 2.1 mmol/g , much higher than 0.19 mmol/g for Re-3.8 nm and 0.30 mmol/g for Re.3.3 nm, and respectively.

According to the above discussion, both single electron donation and Multi-electron donation are efficient in Re 3.3 nm facilitating the CO₂ reduction. Note that even though the surface hole trapping occurred in Re-2.3 nm, there still remains 50% QDs in the QD pool free from the hole trapping where the excited holes can be scavenged by the electron donated from sacrificial agent TEOA. In contrast, both Re-3.3 nm and Re-3.8 nm suffered from inefficient electron transfer to Re(I). In this scenario, excited electron resided in bpy moiety of Re-catalyst according to the DFT calculation are still feasible to participant in CO₂ reduction in the media but with much less efficiency than transferred electron at Re(I) due to 1) much shorter lifetime, and 2) longer distance with the absorbent CO₂ species. As a result, the CO production yield is much less. The slightly higher CO production in Re-3.8 nm than Re-3.3 nm can be attributed to the reduced hole trapping process as illustrated in Fig. 5b.

More importantly, efficient multi-electron donation in Re-2.3 nm facilitated 8-electron meditated photocatalytic production of CH_4 as shown in Fig 6b, which has also been clarified in our previous work(manuscript 2). As illustrated in Fig. 6c, excited QD in Re-2.3 nm undergoes effective excition delocalization due to unconventional electronic structure, photoinduced holes accepted electrons from TEOA which promoted charge separation. Eventually, fast electron transfer process occurs simultaneously on two catalysts as depicted in Fig 6c, efficient multi-electron donation enables photocatalytic CH_4 evolution. On the other hand, Re-3.3 nm and Re-3.8 nm QDs have excited electrons either limited distributed between Re(I) center and Bpy or entirely localized within initial excitons, preventing the electron donation for the CO_2 reduction, explaining their inferior CO and absent CH_4 production.

In summary, we prepared three InP/ZnS colloidal quantum dot with different size and successfully attached two Re-catalysts onto each QDs via covalent bond. The characterization on their electronic structure revealed that the energy alignment bewteen CB of the QDs and LUMO level of Re-catalysts is strongly QD size dependent, where the CB level of Re-2.3 nm QDs is higher than the ReBpy level while 3.3 nm and 3.8 nm QDs have 184

CB level close and lower than the Re level, respectively. As a result, Re-2.3 nm exhibit excellent electron injection from QDs to Re-catalyst. Such injection is valid at both single excitation and multiple excitation mode for each QDs due to the two Re-catalysts attachment. In contrast, Re-3.3 nm and Re-3.8 nm QDs showed inefficient electron transfer processes due to insufficient driving force. Therefore only Re-2.3 nm exhibited CO_2 reduction efficiency where both two-electron mediated product CO and 8-electron mediated product CH_4 can be obtained. This work demonstrates the critical effect of QDs size on the electronic band alignment in QD-catalyst hybrid structures and consequently dominates the efficiency of multi-electron donation for catalytic CO_2 reduction. This can be considered as guidance for future material engineering on photocatalysts for CO_2 photocatalytic reduction with optimal efficiency and selectivity.

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Ethics declarations

Submission of a competing interests statement is required for all content of the journal.

Supplementary Information

Supplementary Information: should be combined and supplied as a separate file, preferably in PDF format.

Supplementary Information

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Materials and methods

The photocatalyst (Re(bpy)(CO)3Br) was prepared according to previous literature procedures.¹ Indium(III) chloride (98%, Sigma-Aldrich), zinc(II) chloride (98%, Sigma-Aldrich), zinc(II) iodide (98%, Sigma-Aldrich), oleylamine (technical grade, 70%, Sigma-Aldrich), tris(diethylamino)phosphine (98%, Sigma-Aldrich), sulfur powder (99.98%, Sigma-Aldrich), trioctylphosphine (TOP, 97%, Sigma-Aldrich), 2-mercaptoethanol (ME, 99%, Sigma-Aldrich), chloroform (99.5%, Sigma-Aldrich), ethanol (EtOH, for HPLC, VWR Chemicals), hexane (HEX, for HPLC, VWR Chemicals), dimethylformamide (DMF, for HPLC, VWR Chemicals), toluene (for HPLC, VWR Chemicals).

Synthesis of InP/ZnS ODs with the size of 2.3 nm. The process of synthesis InP/ZnS quantum dot was prepared by previous literature² with a little modification. Briefly, the mixture of 111 mg (0.5 mmol) of indium(III) chloride as indium precursor, 320 mg (1.0 mmol) zinc(II) iodide and 136 mg (1.0 mmol) of zinc(II) chloride as zinc precursor was dissolved into 5 mL (15 mmol) of oleylamine, then evacuated by Schlenk techniques and kept under vacuum at 120 °C for 1 h. Afterward, the reaction system was heated to 180 °C under an Argon atmosphere. 0.5 mL (1.8 mmol) of tris(diethylamino)phosphine (phosphorous:indium ratio = 3.6:1) was quickly injected into the mixture. The system was kept at 180 °C for 30 min to drive the growth of InP quantum dot to completion and was further heated to 260 °C and slowly added 1 mL of TOP-S (2M) solution at the rate of 0.2 mL/min. TOP-S solution was prepared by dissolving 0.128 g of sulfur powder in 2 mL of TOP under an inert atmosphere. The system was kept at 260 °C for 3 h to passivate the InP QDs. Finally, the system was cooled down to room temperature. To purify InP/ZnS QDs, about 10 mL of EtOH were added for the precipitation of QDs. After centrifugation, the supernatant was discarded and the precipitated QDs was further dissolved into HEX subsequent centrifugation. Then the precipitation was discard, keep the supernatant and precipitation in 15 mL of EtOH. Following centrifugation, the ODs were again dispersed into 20 mL HEX and centrifuged to remove the insoluble impurities. The prepared QDs were kept well in solution at 2-6 °C.

Synthesis of InP/ZnS QDs with the different size. Size of InP/ZnS QDs was modulated by the different concentration ratio of zinc(II) iodide and zinc(II) chloride precursers and the InP core growth temperature. The main process of synthesis is decribed above. In summary, when 306 mg (2.25 mmol) of zinc(II) chloride was added, 3.3 nm of InP/ZnS was obtained; when added 306 mg (2.25 mmol) of zinc(II) chloride and the temperature of InP core growth increased to 260 °C from 180 °C, 3.8 nm of InP/ZnS was obtained.

Synthesis of InP/ZnS-ME QDs. InP/ZnS-ME was prepared by ligand exchange method according to the previous literature ² with slight modification. Briefly, most of the solvent

(HEX) in the as-prepared InP/ZnS QDs solution was first removed by the rotary evaporation approach. Then about 2500 times molar excess of ME was added to the reaction system. The mixture was heated to 90 °C under a vacuum to remove the rest of HEX. Afterward, the reaction mixture was kept at 90 °C under Argon atmosphere for approximately 1 h or less until the solution became clear. After cooling down to room temperature, chloroform was added to precipitate the resulting ME-decorated InP/ZnS QDs (ME-capped QDs , InP/ZnS-ME). Centrifugation at 5000 rpm for about 5 min yielded the targeted products and easily dispersed into DMF. The prepared InP/ZnS-ME were kept well in solution at 2-6 °C.

Synthesis of Re-2.3 nm, Re-3.3 nm and Re-3.8 nm. The mixture of 1: 2 molar mass ratio of InP/ZnS-ME and Re(bpy)(CO)₃Br was evacuated and injected argon gas by Schlenk techniques three times, then the system was heated to 100 °C under argon atmosphere for 3 hours. Following cooling down to room temperature, toluene was added for precipitation of Re-QDs, and centrifugation at 5000 rpm for about 5 min was used to purify the products. Finally, the precipitation was easily dispersed into DMF and kept the solution at 2-6 °C in dark place for further measurement.

Photocatalytic Reduction of CO₂.

The method of photocatalytic reduction of CO_2 was carried out according to literature methods with a little modification. Around 0.45 mg of InP/ZnS-ReCat was dispersed in 5 mL of CH₃CN, and 0.5 mL of TEOA (triethanolamine) in 10 mL septum-sealed glass vials. The mixture was purged with Ar for 10 min and CO_2 for 15 min to wipe out air, and then irradiated by a LED lamp with 440 wavelengths (light intensity: 83.8 mW/cm²; irradiation area: 0.25 cm²) for 6 h and kept stirring during the photocatalytic reaction. The amount of CO and CH₄ generated was quantified every 1 hour by using Shimadzu gas chromatography (GC-2010) by analyzing 500 µL of the headspace. The control experiment was also carried out only in the absence of CO_2 .

Characterization

Fourier-Transformed Infrared Spectroscopy (FT-IR) data were obtained by using ALPHA P FT-IR spectrometer (Bruker). The sample material just has to be brought into contact with the measurement interface. Samples was prepared in DMF solution. X-ray Photoelectron Spectroscopy (XPS) data were got by using XPS-Thermo Scientific with Al K α (1486 eV) as the excitation X-ray source. The pressure of the analysis chamber was maintained at $2\times10-10$ mbar during measurement. The sample material was prepared by dispersing it in DMF and then dripping it onto a silicon wafer then dried in air. The peak of C 1s at about 284.8 eV was used to calibrate the energy scale. The XPS data were performed to precisely quantify the number of Re-catalyst tether to one quantum dot by integrating the area of atom peaks. The absorption spectra were measured in a UV-vis absorption spectrophotometer from

Agilent Technologies (Santa Clara, USA). Photoluminescence (PL) was performed via Spex Fluorolog 1681 standard spectrofluorometer. Transmission electron microscopy (TEM) images were obtained with a Tecnai G2 T20 TEM.

Nuclear magnetic resonance (NMR) measurement. All presented NMR spectra were either measured on a Bruker Avance IIIHD spectrometer operating at a ³¹P frequency of 242.93 MHz (14.1 T) equipped with a 5mm Bruker BBFO probe, or a Bruker Avance III Nanobay operating at a ³¹P frequency of 161.97 MHz (9.4 T) equipped with a 5 mm CryoProdigy probe. For the quantum dots with attached photo catalyst 65-75k scans were accumulated with an interscan delay of 1.5 seconds, 30° flip-angle and ¹H power-gated decoupling. For the free photo catalyst 16 scans were accumulated with an interscan delay of 2.5 seconds, 90° flip-angle and ¹H power-gated decoupling. The samples were measured "asprepared" adding only 5 vol% of DMF-d⁷ for lock and shimming. Chemical shifts are reported relative to H_3PO_4 using the lock signal from DMF-d⁷.

Transient absorption (TA) spectroscopy measurements. The transient absorption (TA) measurements were carried out by laser-base pump-probe spectroscopy with the laser power intensity equating to less than one phonon and two phonons absorption per quantum dot. Laser pulse (800 nm, 40 fs pulse length, 2 KHz repetition rate) were generated by a femtosecond oscillator (Mai Tai SP, both Spectra Physics). Excitation pulse at the wavelength of 450 nm to ensure the pulse only exciting the light harvester (quantum dots) not photocatalyst, which generated an optical parametric amplifier (Topas C, Light Conversion). For the probe, a broad supercontinuum spectrum was generated from a thin sapphire crystal and split by a beam splitter into a probe pulse and a reference pulse. The probe pulse and the reference pulse were dispersed in a spectrograph and detected by a diode array (Pascher Instruments). A Berek compensator in the pump beam was placed to set the mutual polarization between pump and probe beams to magic angle (54.7°). Excitation power intensity and spot size were necessary for the calculation of excitation fluence, and further determined the average number of excitons $\langle N \rangle$ per QDs.

Ultraviolet Photoelectron Spectroscopy (UPS). The UPS measurements were carried out using the PEEM endstation of the MAXPEEM beamline at MAX IV laboratory in Lund, Sweden. We utilized the micro-spot XPS mode of the PEEM instrument to measure the local XPS from a spot with a size of 5 μ m on the sample. This enabled us to mount multiple samples on a single substrate and measure them simultaneously. During sample preparation, dispersion drops containing quantum dots in four different sizes were deposited on a single Au-plated Si wafer using a pipette. After drying in a desiccator, the drops turned into coffee-

ring shapes with an average diameter of 1 mm. These drops were spaced apart from each other to facilitate independent measurements on each of them, as well as on the bare Au area between the samples. This method allowed all UPS measurements from different samples to be automatically aligned on the energy scale, without the need for further calibration, as all the samples were electrically connected through the Au substrate. The substrate with samples was loaded into the PEEM chamber and measured under ultra-high vacuum (UHV) conditions with a base pressure better than 1x10-10 torr. To ensure that the UPS data collected from the samples did not contain contributions from the Au substrate, we selected thick areas where no Au 4f signals could be detected. The energy resolution of the instrument in this operation mode is approximately 100 meV, and the photon energy used in the measurement was 80 eV.

Absorption cross section determination. High excitation fluence could excite QDs to multiple exciton states. With a usual assumption, the initially generated multiple exciton population follows the Poissonian distribution

$$P_N = \frac{e^{-\langle N \rangle} \cdot \langle N \rangle^N}{N!} \qquad (1)$$

where $\langle N \rangle$ is the average number of excitons per QDs, N is the number of excitons and P_N is the fraction of NCs with N excitons. We can use $\langle N \rangle = \sigma \cdot I$ to present the average number of excitons per NCs, where σ is the absorption cross-section at the excitation wavelength and I is the excitation intensity in units of the number of photons per pulse per excitation area. From equation (1), we can calculate the fraction of excited NCs, P_{exc} , as:

$$P_{exc} = \sum_{N=1}^{\infty} P_N = 1 - P_0 = 1 - e^{-\langle N \rangle} = 1 - e^{-\sigma \cdot I}$$
(2)

If we know P_{exc} , σ can be calculated from (2). We obtain P_{exc} by measuring the excitation intensity dependence of the late-time region signal ($t \ge 1 ns$), which corresponds to the last remaining exciton after the Auger process. Due to multiple excitations generated at high pump intensity excitation in NCs is rapidly lost via Auger process leaving only one excitation at latetime region ($t \ge 1 ns$). The signal $\Delta A_0(I, t\ge 1 ns)$ intensity can be rescaled to the corresponding signal at t = 0, which we call $\Delta A_0(I)$. We use the lowest excitation intensity as reference excitation intensity and corresponding average number of excitons per NCs, $\langle N \rangle_{0}$.as reference number of excitons per QDs.

$$\Delta A_0(I) = \frac{\Delta A0(I, t \ge 1 \text{ ns})}{e^{-\frac{t}{\tau}}} = \Delta A_0 \cdot \left(1 - e^{-(I \cdot I_0 \cdot \langle N \rangle_0)}\right)$$
(3)

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 ΔA_0 , denotes the largest possible single-exciton signal rescaled to t = 0.

Based on the rescaled signal $\Delta A_0(I)$, we perform exponential fit to equation (3). From the fitting, we get the value of $\langle N \rangle_0$, and absorption cross-section σ of InP/ZnS QDs at 400 nm (3.1 eV) were calculated. The absorption cross-section σ at 450 nm was calculated based on the values of σ at 400 nm and absorption spectra. The calculated result is shown at Figure S3.

InP/ZnS QDs, InP/ZnS-ME and Re-QDs concentration calculation. All samples including InP/ZnS QDs, InP/ZnS-ME and Re-QDs can be considered as InP based quantum dots. InP based quantum dots concentration was determined by Beer–Lambert law

$$A = \varepsilon c l \qquad (4)$$

where A is the absorption of the sample, ε is the molar extinction coefficient, *c* is the concentration of InP based quantum dots, *l* is the optic path length in cm. If we know ε , c can be calculated from (4). ε can be obtained by the empirical formula reported by previous literature³:

$$\varepsilon_{410} = (1.29 \pm 0.06) \times 10^4 d_{0D}^3 \tag{5}$$

where ε_{410} is the molar extinction coefficient of samples at 410 nm excitation wavelength, d_{QD} is the size of InP based quantum dots confirmed by TEM. It should be note that A is the absorption of samples at 410 nm.

Determination of the number of Re-catalyst attaching to per InP/ZnS quantum dot. For InP based quantum dots, their lattice parameter value a is 0.5861 nm and 4 indium atoms in complete unit cell, which reported by previous literature⁴. The Volume of InP/ZnS is calculated by equation followed:

$$V = \frac{4}{3}\pi d_{QD}^3 \qquad (6)$$

where d_{QD} is the size of InP based quantum dots. The number of unit cell of InP for per InP/ZnS QD is easy to abtain to be 32 and 128 indium atoms for per InP/ZnS QD. Then the number of In and Re atom in sample could be calculated by the ratio of indium and rhenium in XPS spectra, we also comfirm the number of Re-catalsyt via the number of Re atom as only one Re atom is located per Re-cataslyt. The calculated results of three samples in this work is followed:

Sample name	Size (diameter)	Unit cell in one QD	Ratio of In atom	Ratio of Re atom	The number of In atoms in one QD	The number of catalyst linked to one QD
Re-2.3 nm	2.3 nm	32	8.24	0.11	128	1.70
Re-3.3 nm	3.3 nm	94	12.28	0.06	376	1.83
Re-3.8 nm	3.8 nm	143	13.96	0.04	572	1.64

Supplementary Figures



Supplementary Figure 1: Absorption spectra for comparison of InP/ZnS QDs with 2.3 nm (a), 3.3 nm (b) and 3.8 nm (c) and corresponding to their QD/molecule complexes system.



Supplementary Figure 2: UPS kinetic energy spectrum of QD/molecule complexes with different QD size.



Supplementary Figure 3: Cross section calculation for InP/ZnS quantum dots with the size of 2.3 nm (a), 3.3 nm (b) and 3.8 nm (c) respectively.

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