Towards developing efficient metalloporphyrin-based hybrid photocatalysts for CO₂ reduction; an ab initio study

Ostovan, Azar; Papior, Nick Rübner; Zahedi, Mansour; Moshfegh, Alireza Z.

Published in:
Physical Chemistry Chemical Physics

Link to article, DOI:
[10.1039/d0cp03279d](https://doi.org/10.1039/d0cp03279d)

Publication date:
2020

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Ostovan, A., Papior, N. R., Zahedi, M., & Moshfegh, A. Z. (2020). Towards developing efficient metalloporphyrin-based hybrid photocatalysts for CO₂ reduction; an ab initio study. *Physical Chemistry Chemical Physics*, 22(40), 23128-23140. <https://doi.org/10.1039/d0cp03279d>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

PCCP

Physical Chemistry Chemical Physics

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: A. Ostovan, N. Papior, M. Zahedi and A. Z. Moshfegh, *Phys. Chem. Chem. Phys.*, 2020, DOI: 10.1039/D0CP03279D.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

Cite this: DOI: 00.0000/xxxxxxxxxx

Towards Developing Efficient Metalloporphyrin-Based Hybrid Photocatalysts for CO₂ Reduction; An Ab Initio Study†Azar Ostovan,^a Nick R. Papior,^b Mansour Zahedi^c and Alireza Z. Moshfegh ^{*a,d}Received Date
Accepted Date

DOI: 00.0000/xxxxxxxxxx

A series of thiophene-based donor-acceptor-donor (D–A–D) oligomer substituted metalloporphyrins (MPors) with different 3d central metal-ions (M=Co, Ni, Cu, and Zn) were systematically investigated to screen efficient hybrid photocatalysts for CO₂ reduction based on density functional theory (DFT) and time-dependent DFT simulations. Compared with based MPors, the newly designed hybrid photocatalysts have a lower bandgap energy, stronger and broader absorption spectra, enhanced intermolecular charge transfer, exciton lifetime, and light-harvesting efficiency. Then, the introduction of the D–A–D electron donor (ED) groups into the meso-positions of MPors can act as a promising method for the construction of efficient photocatalysts. According to calculated adsorption distance, adsorption energy, Hirshfeld charge as well as electrostatic potential analysis, it was revealed that the CO₂ physically adsorbed on the designed photocatalyst surface. In addition, among the studied model systems the ZnPor(ED)₄ catalyst with four D–A–D electron donors exhibits the best photocatalytic performance due to its broadest absorption spectra with $\lambda_{max} = 500.12$ nm and the largest value for adsorption energy obtained around 26 kJ·mol^{−1}. Finally, the sensor ability of the ZnPor(ED)₄-based multi-terminal molecular junction for CO₂ gas detection is determined by the aid of Green's function methods. The transmission plot of considered molecular junction due to physical adsorption of CO₂ on the molecule surface are barely perturbed, leading to low sensitivity for this device. We believe that such theoretical design can provide a general approach for further experimental and computational studies of photocatalysts used in CO₂ reduction process.

1 Introduction

In recent years, fast growth of population, urbanization, industrialization and improving people's living standards lead to growth of fossil fuels consumption.¹ Global dependence on fossil fuels not only speeds up the depletion of the non-renewable natural energy resources but also leads to a massive growth of carbon dioxide (CO₂) emissions in the atmosphere. Meanwhile, the high concentration of CO₂ in the atmosphere is regarded as the main contributor in the greenhouse gas effect causing global warming, climate changes, and other environmental problems.² The negative impact of CO₂ emission on our planet is one of the current major challenges which motivated a future scenario heavily relying on fossil fuel replacement by other renewable energy sources.³

Thus, recommending inexhaustible green energy resources and control, then reducing the volume of CO₂ emissions become a serious issue related to the life quality. There are three main approaches for CO₂ removal/capture technologies which are classified as: (1) direct lowering down of CO₂ concentration, (2) CO₂ capture and storage (CCS), and (3) CO₂ consumption and trans-formation.^{4,5} As compared, the associated costs of direct reduction, gas storage and transport for abundant volume of CO₂ make the feasibility of such approaches still limited.⁶ The third approach, transformation of CO₂ molecule by the aid of innovative catalyst materials is more appealing, which can also alleviate the negative effects of CO₂ gas and provide valuable products such as methane, methanol, ethanol, etc., which can be used as promising alternative fuels.⁷ Use of solar energy (photochemical) and electricity driven from sunlight (electrochemical) to transform CO₂ into fuels or more value-added products are the most promising technological solutions to addressing CO₂ elimination.⁸ The photochemical model using photocatalysts and solar energy as simulates natural photosynthesis process has been employed as one of the most promising, compelling, and challenging protocols for CO₂ reduction, namely CO₂ photoreduction which acts without producing secondary pollution.⁹ To date, various types of active and robust photocatalysts compounds including titanium

^a Department of Physics, Sharif University of Technology, Tehran, Iran^b DTU Computing Center, Department of Applied Mathematics and Computer Science, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark.^c Department of Chemical and Petroleum Sciences, Shahid Beheshti University G.C., P.O. Box 19839-63113, Evin, Tehran 19839, Iran^d Institute for Nanoscience and Nanotechnology, Sharif University of Technology, Tehran, Iran

E-mail: moshfegh@sharif.edu

† Electronic Supplementary Information (ESI) available. See DOI: 10.1039/cXCP00000x/

dioxides,¹⁰ zinc oxides,¹¹ metal chalcogenides,¹² inorganic perovskite halides,¹³ and etc., has been designed and fabricated to utilize as catalysts for the CO₂ conversion process. Even though fast-growing of such photocatalysts, a number of obvious drawbacks still exist including their high prices, high recombination of electron-hole pairs, and susceptibility to gas poisoning which might limit these materials for reduction applications.^{6,14} From this point of view, there is a necessity to fabricate alternative and innovative CO₂ photoreduction catalysts.

Porphyrin (Por), a four pyrrolic subunits interconnected via methine bridges, owing to its unique extended π -conjugated network, high chemical and thermal stability, large ratio series, easy synthesis, low price, adjust ability¹⁵ etc., is one of the most fascinating and innovative catalyst which can be tuned to boost its applications for photocatalyst fabrication. Furthermore, the diversity of reaction positions (i.e. four meso and eight β -coordination sites) in Por-based materials is also a benefit to efficient functionalization by finely tuning the electronic, optical and photochemical properties through molecular level design.¹⁶ Por-based materials are widely used in dye-sensitized solar cells (DSSCs),¹⁷ sensors,¹⁸ and field effect transistors (FETs) manufacturing,¹⁹ etc. According to recent research,²⁰ metalloporphyrins (MPors) derivatives are potential materials for both photochemical and photoelectrochemical reduction of CO₂. So, constructions of MPor-based photocatalysts systems are in the center of attention and are expected to be increasingly applied in the near future. The solar irradiation (AM1.5G) composed of 0.04 ultraviolet (UV) rays ($\lambda < 400$ nm), 0.53 visible (Vis) light ($400 < \lambda < 800$ nm) and 0.43 near-infrared (NIR) light ($\lambda > 800$ nm).¹⁶ However, MPor-based materials due to the ligand-to-metal charge transfer (LMCT) absorption band which lies in the shorter wavelength region, are mainly photoactive in the UV light region ($\lambda = 200\text{--}400$ nm) limiting their applications in photoreduction process.^{21,22} Therefore, to extend the spectral responsive range of MPor-based materials various strategies such as functionalized with visible light active organic ligands, constructing semiconductor heterojunctions, and photosensitizing with dyes were reported^{23,24} providing an alternative strategy to enhance the MPors visible light absorption. Especially, the hybrids MPor-based photocatalysts have been extensively studied, as they can adopt a range of capability for photocatalytic, photocurrent, and photovoltaic applications.²⁵ Although there have been many previous studies on the capacity of MPor-based materials as photochemical and (or) electrochemical catalysts in CO₂ reduction,^{26,27} comparatively little attention has been given to the use of narrow bandgap thiophene-based oligomer to achieve a molecular-level control for MPor UV–Vis light active component in CO₂ photoreduction. MPor-based compounds possess donor-acceptor-donor (D–A–D) structures could accelerate the electron injection and postpone the recombination of an electron-hole pairs in result of the push–pull effect.¹⁷ The light-harvesting ability and energy levels of MPors can be modulated using such electron donors (EDs). The expanded D–A–D low bandgap (LBG) oligomers were developed to possess broad and strong optical absorption, which can capture the solar irradiation as much as possible.²⁸ We envisaged a novel MPor-based catalysts which serve a D–A–D thiophene-based LBG oligomer, 4,7-

Bis(thiophene-2-yl)-2,1,3-benzothiadiazole,²⁹ as an ED. Considering D–A–D molecular architecture concept as the most versatile point of view in affording improved electronic and spectral properties of organic electronics,³⁰ here we take D–A–D oligomer to theoretically design a new series of MPor-based catalysts to solve the energy mismatch between MPor photocatalysts and solar radiation spectrum. These hybrid photocatalysts, would be of benefit for both adsorbing CO₂ on the photocatalyst active site and light harvesting at EDs during reduction process. Previous experimental studies,^{31,32} have demonstrated CO₂ photoreduction of MPor-based structures UV–Vis light in the gas phase. Motivated by these findings and by knowing that MPor frameworks in the nature have the ability to coordinate 3d metal-ions, in this research we tested the photoactivity of D–A–D thiophene-based oligomer substituted MPors with different central metal-ions (M=Co, Ni, Cu and Zn). Then, the application of designed catalyst in an attempt for CO₂ detection were calculated. In single molecular junction, it is possible that the central molecule electronic levels can be altered by gas adsorption³³ and this will affect the conductance values. This kind of MPor-based nanoscale gas sensors have gained increased attention in the theoretical and experimental works due to high sensitivity and chemical selectivity.^{34,35}

It has been shown that the computational studies as low-cost and reliable methods provide scientists a beneficial insight to find out photocatalyst trends, and then providing a rational model for designing and development of enhanced photocatalysts. In the following, we employ ab-initio methods to computationally design and improve hybrid MPor-based photocatalysts for two technological purposes, namely the CO₂ photoreduction and the CO₂ sensor device. The electronic properties, absorption spectra, electron density difference (EDD) and charge transition (CT) characteristics, electrostatic potential surface (EPS) and transmission spectra as the key factors affecting the performance of photocatalysts for CO₂ adsorbing and sensing were investigated. The calculated key factors and the procedure of study are shown in Fig. 1. The main goal of this report is to enhance the photocatalytic properties of MPors with different 3d central metal-ions using narrow bandgap EDs in CO₂ adsorption process. Then, the sensor ability of the best optimized photocatalyst in CO₂ adsorption will be further studied.

2 Method

2.1 Studied Model Systems and Nomenclature

In this study, the metal (M)-porphyrin (Por) complexes (MPors) (Fig. S1 of ESI†) are used in the hybrid model system as the catalyst active sites, where the electron donor (ED) is a thiophene-based LBG oligomer (Fig. S2 of ESI†). Four 3d transition metals (M=Co, Ni, Cu and Zn) were studied for the analysis of their potential in CO₂ photoreduction. Here, the direct connection of the ED to meso-position of catalyst active site leads to a non-planar structure after relaxation (Fig. S3 of ESI†). The planarity is particularly important because it affects photocatalyst degree of conjugation, which further influences on catalytic performance. For instance, to control the planarity of hybrid catalyst, ethynyl (C≡C)

Fig. 1 The procedure and calculated key factors to investigate the performance of investigated photocatalysts.

group was employed as the π -spacer, which is beneficial for the formation of chemical interaction, charge transfer between ED and MPor, and resulted in a strongly coupled Por-based architectures.³⁶ As shown in Fig. S4 (ESI[†]), the optimized structures of photocatalysts for the four investigated 3d transition metals exhibit good planarity. The dihedral angle formed between active site and EDs is close to 180° for all structures. For convenience, the studied hybrid model system which is composed of MPor, π -spacer and ED was named by its sequence combination abbreviation, as well as the number of the EDs. For example, the CoPor(ED)₄ is the one using for the system which has the cobalt ion as the central metal of porphyrin ring and four electron donors bind to its meso-positions.

2.2 Photocatalysts model and calculations

Initially the level of theory tested for the isolated ED and MPor, to serve as a precursor for the calculation of the newly designed photocatalyst structures. Ground state unrestricted density functional theory (UDFT) calculations have been carried out by employing the well-known Becke three-parameter hybrid method with the nonlocal correlation provided by the Lee–Yang–Parr (B3LYP).^{37,38} This functional has been widely used as comparatively accurate functional for the calculation of the geometrical properties of MPor-based complexes, providing data that are comparable to experimental results.^{16,28,39} A mixture of basis sets: LANL2DZ⁴⁰ for 3d metal-ions and 6-31+G(d,p) basis set was set for the rest of atoms. Then the ED and MPors geometries are fully optimized as needed in our study. The validity of the B3LYP functional was evaluated by comparison with structural parameters that obtained from the five other unrestricted functionals. The functionals can be classified into three types (1) standard hybrid: OPBE⁴¹ and PBE0,⁴² (2) hybrid meta: M06⁴³ and (3) long-range corrected hybrid: CAM-B3LYP⁴⁴ and ω B97XD⁴⁵ functionals which are among the popular functionals in simulation of transition metal complexes. All the hybrid DFT functionals show

consistent results with B3LYP for all MPors and also there was little difference between experimental and calculated ground state values (see Tables S1 to S4 of ESI[†]). The root mean square error (RMSE) values for considered hybrid functionals were found to be $\approx 0.01 - 0.04/\text{\AA}$. Considering a slightly better performance of M06 than B3LYP functional for all MPors, but a meaningful computational time difference between B3LYP and M06 (Table S5 of ESI[†]), to balance between computational resources and accuracy, the hybrid photocatalyst related computations are conducted by the aid of B3LYP functional. At the next step, by using the B3LYP functional, the validity of employed basis sets was evaluated with large mixed basis sets: LACV3P for metal-ions and 6-31++G(d,p) for the rest of atoms. The obtained data by the introduced extended basis sets are consistent with those of the small basis sets (Table S6 to S9 of ESI[†]). As the second diffuse function of 6-31++G(d,p) basis set may have less effect on the calculated structural parameters the improvement is seen using LACV3P/6-31++G(d,p) can be attributed to the implementation of LACV3P basis set on the metal-ions. To balance between computational time and accuracy, the LANL2DZ/6-31+G(d,p) basis set in combination with B3LYP functional is employed for geometry relaxation. The validity of the considered level of theory was also reported in other similar MPor-based systems.⁴⁶ Frontier molecular orbital (FMO) energy levels and HOMO–LUMO energy gaps were obtained utilizing the same level of theory. The spin-considered excitations of the ED and MPor were computed by the linear-response time-dependent DFT (TDDFT) on the corresponding optimized geometries. The theoretical electronic spectra were computed by Franck–Condon type singlet–singlet vertical transitions considering fifty lowest energy excited states for MPor and ED. Herein, we evaluated the quality of TDDFT functionals by comparison among all maximum absorption wavelength (λ_{max}) of calculated UV–Vis spectra. In previous studies,^{47,48} the long-range corrected functionals such as CAM-B3LYP,⁴⁴ ω B97XD,⁴⁵ and LC- ω PBE⁴⁹ have been identified to be accurate function-

als for the description of time-dependent properties of donor-acceptor-donor EDs. Tables S9 to S13 of ESI† show a comparison between available experimental λ_{max} of the studied MPors and ED and also our calculated values using the three long-range corrected functionals and BHandHLYP³⁷ hybrid functional. As it can be seen, the calculated values using BHandHLYP are shown a blue shift with respect to the other functionals and also displays a bigger difference as compared with experimental results.⁵⁰ Since CAM-B3LYP functional provides the best λ_{max} values for both ED and MPors in accordance with experimental data (see Tables S9 to S13 of ESI†), it was adopted to analyze λ_{max} , and its related description expressed by oscillator strength (f), light harvesting efficiency (LHE) and exciton life time (τ).

To model the hybrid photocatalyst, we simulated a special structure in which the ED is connected to meso-position of the MPor through the ethynyl spacer. The aforementioned level of theory has been successfully applied for the calculation of the ground state and excited states of isolated ED and photocatalyst active site in the following steps. Coordination of different number of ED to meso-positions of catalyst active site were tested to find how many number(s) of ED(s) are needed for simulation of a hybrid photocatalyst which has a λ_{max} is analogous well with maximum irradiation wavelength (λ_{Ir}) of solar spectrum in visible region at around 500 nm. As Fig. S5 and Table S15 of ESI† represent the photocatalysts λ_{max} matches well with the solar λ_{Ir} when the maximum capacity of MPor meso-positions are used for catalyst construction. Vibrational frequency calculations were also performed on all optimized photocatalysts to verified that the geometries of ground state reached a true minimum point on the potential energy surfaces. To explore the adsorption energy (E_{ads}) of CO₂ on a catalyst surface, the E_{ads} is defined as:

$$E_{ads} = E_{MPor(ED)_4-CO_2} - E_{MPor(ED)_4} - E_{CO_2} \quad (1)$$

where $E_{MPor(ED)_4-CO_2}$ is the total energy of CO₂-adsorbed photocatalyst, $E_{MPor(ED)_4}$ is the energy of the pristine photocatalyst and E_{CO_2} is the energy of the CO₂ molecule. According to equation 1, a negative value of E_{ads} is analogous to an energetically favored adsorption. Population analysis was conducted using Hirshfeld⁵¹ charge analysis on the optimized $E_{MPor(ED)_4-CO_2}$ structures. The molecular electrostatic potential (ESP) analysis was performed to understand the CO₂ adsorption details. ESP is fundamentally defined as the interaction energy of positive point charge with a molecule.⁵² ESP in terms of atomic orbitals (AO) that form the basis set is expressed by the following formula:

$$V_{ESP} = \sum_A \frac{Z_A}{|R_A - r|} - \sum_{\mu} \sum_{\nu} P_{\mu\nu} \int \frac{\Phi_{\mu}(r') \Phi_{\nu}(r')}{|r' - r|} dr', \quad (2)$$

where $P_{\mu\nu}$ are the density matrix elements. Charge density difference (CDD) plots were visualized using GaussView 6.0 in conjunction with Gaussian cube generator. All the calculations for the ground and excited states of hybrid photocatalyst at molecular level were carried out using the Gaussian 09, revision B.01

software.⁵³

2.3 Gas Sensor Model and calculation

In order to gain more details regarding the CO₂ sensor ability of the hybrid model system studied in this work, we carried out electron transport calculations for the most stable CO₂ adsorbed configuration. Our model systems are shown in Fig. 2 and Fig. S6 of ESI†. As it can be seen, the model device are divided into three parts: (1) four gold nanowire (GNW) electrodes, (2) the central region, and (3) buffer regions. The electrodes are composed of four optimized Au unit cells. The lattice constant is obtained 2.88 Å which is in well agreement with available theoretical and experimental values.^{54,55} The central region includes hybrid structure before and after CO₂ adsorption bonded to several layers of GNW unit cells using sulfur linkage, in which the screen effect is taken into account. We extended the GNW electrodes using buffer regions, the region behind each electrode in Fig. 2 and Fig. S6 of ESI†. The buffer atoms act as additional screening region and serve to obtain a bulk electrode potential profile.

Fig. 2 Structure of four-terminal ZnPor(ED)₄ devices after CO₂ adsorption. The boxed regions indicated four semi-infinite GNW electrodes. The μ_1 , μ_2 , μ_3 , and μ_4 represent the electrode chemical potential. A buffer region is located behind each electrode acts as additional screening region when calculating the initial NEGF guess.

Geometric relaxation are based on DFT as implemented in the SIESTA package,⁵⁶ and the electronic transport properties are performed using DFT in combination with fully self-consistent non-equilibrium Green's function (NEGF) formalism, which is implemented by TranSIESTA package,⁵⁷ extended with a implemented N-terminals capability following Saha et al.⁵⁸ In the weakly bonded systems such as gas adsorption, it is a necessity to consider an additional functional to correctly describe weak interactions like the Van der Waals (vdW) interactions. For this purpose, we em-

played a vdW correction to the generalized gradient approximation (GGA) of Perdew and co-workers (PBE)⁴¹ to describe efficiently the exchange-correlation functional. The long-range vdW dispersion correction approach is performed by method of Grimme,⁵⁹ in order to evaluate the device electronic structure. The core electrons are modeled with Troullier–Martins nonlocal pseudopotential,⁶⁰ and valence electrons are described by the double- ζ plus polarization (DZP) basis set.⁵⁶ The 200 Ry cut-off energy and the 100k-points mesh in the Brillouin zone sampling along the periodic direction were considered. A level broadening of $\eta = 10^{-6}$ eV was used in the electrodes calculations. The self-consistency cycle criterion for density matrix is chosen as 10^{-4} . Before computation of the transport properties, the central region before and after gas adsorption were relaxed by minimizing the atomic force to be smaller than 0.02 eV/Å. The current flowing out of the electrode j to other electrodes $j' \neq j$, driven by the bias V , is obtained from the multi-terminal Landauer-Buttiker formula:⁶¹

$$I_j = \frac{2e}{h} \sum_{j' \neq j} \int_{-\infty}^{+\infty} dE \text{Tr}[A_j \Gamma_{j'} (f_j - f_{j'})], \quad (3)$$

where

$$A_j = G^r \Gamma_j G^{r\dagger} \quad (4)$$

is the j th electrode spectral function. In this equation, G^r and $G^{r\dagger}$ are the retarded and advanced Green's functions of the scattering region and Γ_j , the level-width function, is defined as follows:

$$\Gamma_j = i[\Sigma_j^r - (\Sigma_j^r)^\dagger] \quad (5)$$

Σ_j^r is the j th electrode retarded self-energy.

3 Results and discussion

3.1 Structural and electronic properties

Initially, first three spin-states of catalysts active site are calculated in order to determine the favourable spin-states relative stability energies. Table S16 of ESI† suggesting that the low spin-states (doublet spin-state for the CoPor and CuPor and singlet spin-state for the NiPor and ZnPor catalyst active site) are energetically favorable than the higher spin-states. Complexes in Fig. S4 of ESI† show the relaxed geometric structures of MPor(ED)₄. The

Fig. 3 Electronic structures and selected MOs of (a) CoPor(ED)₄, (b) NiPor(ED)₄, (c) CuPor(ED)₄, and (d) ZnPor(ED)₄ photocatalysts. HOMO, SOMO, and LUMO are represented as H, S, and L, respectively. Blue and red lines indicate the α - and β -electrons related MOs.

related electronic structures with the selected visualized FMOs are given in Fig. 3 to investigate electron occupancy and predict photocatalytic activity; the expanded figures on the FMOs and sub-FMOs could be found in Figs. S7 to S10 of ESI†. Here, SOMO, HOMO and LUMO are stand for singly occupied MO, highest-occupied MO, and lowest-unoccupied MO, respectively. Due to the spin-unrestricted formalism, the MOs were calculated as α and β spin-orbitals. Here, all the filled molecular orbitals spaces in all catalyst, SOMO- N (with $N = 0$ to 5), i.e. the HOMOs(α) and HOMOs(β) were localized on the EDs and Por moieties with the π -orbital characteristic. Then, the high-lying filled MOs are mainly composed of the π -orbital characteristic from the EDs and Por ligand. The MOs with central metal-ion contribution were visualized on the deeper HOMO energy levels (HOMO-6(α) and HOMO-7(β) for CoPor(ED)₄, HOMO-6($\alpha(\beta)$) for NiPor(ED)₄, HOMO-6(α) and HOMO-7(β) for CuPor(ED)₄ and HOMO-11($\alpha(\beta)$) for ZnPor(ED)₄ see Fig. S11 of ESI†). In the unfilled molecular spaces, on the other hand, the distribution of molecular orbitals is dependent on the type of the central metal-ion. The LUMO($\alpha(\beta)$) and LUMO($\alpha(\beta) + 1$) of CoPor(ED)₄ and NiPor(ED)₄ photocatalysts are disturbed on the metal d_{xz} orbital and the π^* -orbital of EDs and Por ring. The Cu metal-ion shares its d_{yz} orbital from LUMO($\alpha(\beta) + 4$) and only the π^* wave function of EDs and Por ring were participated in the LUMO($\alpha(\beta)$) to LUMO($\alpha(\beta) + 5$) of the ZnPor(ED)₄. Thus different central metal-ions leading to different FMOs contribution and then different electron transfer behaviour. The site of electron transfer through a photocatalytic reaction can be recognized based on the HOMO and LUMO distribution.⁶² In all above cases, the unstable HOMOs lie on the EDs and Por ring, mostly EDs, so the non-metal centered electron transfer occurs for all photocatalysts. In other words, during the electron transfer Por and EDs could serve as the electron donors, and the electron acceptor could be the central metal-ions, Por and EDs. The delocalized wave functions over photocatalysts due to enhance the overlap integral ($c \int \Psi_i \Psi_j$, where Ψ_i and Ψ_j refer to the ground and excited eigenstate) between ground eigenstate and excited eigenstate can increase the probability of electron transition.⁶³ The contribution of the EDs to the HOMOs and LUMOs of catalyst indicates that the photogenerated electrons can transfer to the nearby active site unit, conveniently along the ethynyl spacer groups. It is predictable due to the $\pi - \pi^*$ nature of transition for the ZnPor(ED)₄, excited electrons can be more efficiently transferred from Por skeleton to the CO₂ molecule than the others, which is beneficial for the photoexcited electron injection from the ZnPor(ED)₄ excited state into CO₂ gas and can be helpful in reduction process.

The computed HOMO-LUMO gap (E_g) of the MPor(ED)₄ photocatalysts with M=Co, Ni, Cu, and Zn central ions exhibits a decrease in values with the following order CoPor(ED)₄ (1.74 eV) < NiPor(ED)₄ (1.71 eV) < CuPor(ED)₄ (1.66 eV) < ZnPor(ED)₄ (1.63 eV), see Table S17 of ESI†. With the addition of EDs to meso-positions of the photocatalysts active site the E_g is reduced in comparison with that of its corresponding base MPors (compare Tables S16 and S17 of ESI†). It is well known that a semiconductor with narrow E_g , can harvest a wide range of solar energy and electrons are more expected to transit from HOMOs to

LUMOs and its UV-Vis absorption spectra is more red-shifted. So, the low bandgap EDs have ability to enhance charge transfer of photocatalysts and then the efficiency for photoreduction of CO₂ will also be improved.⁶² Here all studied photocatalysts have shown an E_g below the 1.8 eV, thus under solar irradiation can demonstrate a high photocatalytic activity.

3.2 Optical properties

Fig. 4 depicts the calculated absorption profile of four different photocatalysts and Table 1 lists the λ_{max} corresponding spectral data that are obtained using long range corrected CAM-B3LYP as TDDFT functional. The MPors UV-Vis absorption spectra can be divided into two main absorption bands: the intense absorption band at around 400 nm, called Soret-band, and some less intensive absorption bands at around 500 – 650 nm, called Q-bands.⁶⁴ As it is expected from the strong electronic coupling between the EDs and photocatalyst active site, computations show that the absorption spectra of the MPor(ED)₄ photocatalyst are different from a mere sum of the spectra of the constituent sub-units. The calculated absorption spectra of photocatalysts demonstrate another type of absorption band, called charge transfer (CT), a high intensity broad absorption band in the UV-Vis-NIR region at around 300 – 1200 nm that is neither exist in the absorption spectra of the isolated EDs nor MPor active site. The smaller E_g of photocatalysts rather based MPors (compare Tables S16 and S17 of ESI†) and CT band, implies effective electronic interaction existing between EDs and MPor molecular orbitals across the catalyst framework which plays a crucial role in the interfacial charge transfer process for the CO₂ photoreduction.²⁸ The more fluent electron transport in the extended π -conjugated network

Fig. 4 UV-Vis-NIR absorption spectra of CoPor(ED)₄ (blue line), NiPor(ED)₄ (red line), CuPor(ED)₄ (green line), and ZnPor(ED)₄ (magenta line) photocatalysts.

Table 1 Calculated maximum absorption wavelength (λ_{max} , nm), transition energy (TE, eV), oscillator strengths (f), light harvesting efficiency (LHE), lifetime (τ , ns), and nature of transitions of MPor(ED)₄ photocatalysts.

CoPor(ED) ₄	NiPor(ED) ₄	CuPor(ED) ₄	ZnPor(ED) ₄
λ_{max} = 492.67 nm	λ_{max} = 495.97 nm	λ_{max} = 497.26 nm	λ_{max} = 500.12 nm
TE = 2.52 eV	TE = 2.50 eV	TE = 2.49 eV	TE = 2.48 eV
f = 0.92	f = 0.97	f = 0.97	f = 0.98
LHE = 0.88	LHE = 0.89	LHE = 0.89	LHE = 0.90
τ = 5.23 ns	τ = 5.23 ns	τ = 5.38 ns	τ = 5.60 ns
MO(421 β) $\rightarrow$ MO(426 β) (11%)	MO(422 α) $\rightarrow$ MO(428 α) (10%)	MO(422 β) $\rightarrow$ MO(428 β) (11%)	MO(423 α) $\rightarrow$ MO(429 α) (12%)
MO(422 α) $\rightarrow$ MO(427 α) (10%)	MO(422 β) $\rightarrow$ MO(428 β) (10%)	MO(423 α) $\rightarrow$ MO(429 α) (11%)	MO(423 β) $\rightarrow$ MO(429 β) (12%)
MO(421 α) $\rightarrow$ MO(423 α) (8%)	MO(421 α) $\rightarrow$ MO(423 α) (9%)	MO(421 β) $\rightarrow$ MO(423 β) (9%)	MO(422 α) $\rightarrow$ MO(424 α) (8%)
MO(420 β) $\rightarrow$ MO(423 β) (8%)	MO(421 β) $\rightarrow$ MO(423 β) (9%)	MO(422 α) $\rightarrow$ MO(425 α) (8%)	MO(422 β) $\rightarrow$ MO(424 β) (8%)

in comparison with that of the MPor would be the main reason for the smaller bandgap followed by red-shift in the λ_{max} absorption band of the MPor(ED)₄ photocatalysts compared to MPor macrocycles (compare Table 1 and Tables S10 to S13 of ESI†). As shown in Fig. 4, the relative intensity of CT band of all photocatalysts show approximately close intensity with a bit more intense peak for the ZnPor(ED)₄ photocatalysts. Due to the same effect of EDs for all the reactors, this different absorption characteristics exactly comes from the contribution of the central metal-ion of the active site which affects the distribution of the FMOs.¹⁶ As can be seen from Fig. 4, the overall shapes of absorption spectra of the investigated photocatalysts are similar with a slightly red-shifted λ_{max} for the ZnPor(ED)₄ compared to those of Ni, Co, and Cu-based model systems (see Table 1). This is in well correspondence with FMOs analysis (section 1.1) and indicates that in the present photocatalysts the light harvesting occurs mainly in the EDs where the central metal-ions have less effect during the electronic excitation. The UV–Vis–NIR spectra indicate that the pull-push EDs can extend the spectral absorption wavelength of MPors, which only absorb light with $\lambda < 400$ nm because of their relatively wide bandgap energy. These results demonstrate that the photocatalyst properties of MPors can be improved and tuned by introduction the ED groups in meso-positions. Albeit the improved absorption properties of Por-based catalysts have been reported in the previous studies,^{17,26,28} the absorption strength were rather lower than those of the MPor(ED)₄ photocatalysts, and their absorption band is not broad in comparison with those of MPor(ED)₄. Thus, for the MPors as the catalyst active site due to the manifestation of a intense CT band at around 300 to 1200 nm. This matches closely with the strongest irradiation band of the solar spectrum, using low bandgap EDs as an efficient way for improving the light-harvesting properties through the photocatalytic reaction. Then, two intrinsic drawbacks of Pors which have limited their photoconversion efficiency can be solved by ED groups. First, the absorption vacancy in the region between Soret and Q bands and second, the limited absorption in the NIR region of solar spectra which both reduce the light harvesting ability.¹⁷

Table 1 summarizes the main characteristic absorption properties of MPor(ED)₄ photocatalysts obtained for the λ_{max} , in terms of the excitation wavelength (λ_{max} , nm), transition energy (TE, eV), oscillator strength (f), light harvesting efficiency (LHE), and exciton lifetime (τ). The electronic transition composition with regard to the molecular orbital fragments is also collected in Tables S19 to S22 of ESI†. Comparing Tables S10 to S13 of ESI† and Ta-

ble 1, the λ_{max} value of MPor(ED)₄, shows an obvious red-shifting with respect to that of its base MPor; which exactly results from the contribution of EDs units. The λ_{max} value centered at 492.67 nm for CoPor(ED)₄, 495.97 nm for NiPor(ED)₄, 497.26 nm for CuPor(ED)₄ and 500.12 nm for ZnPor(ED)₄, respectively. Upon weaker interaction between Por and Zn²⁺ metal-ion with complete 3d-shell than between Por and incomplete 3d-shell (Co: 3d⁷, Ni: 3d⁸ and Cu: 3d⁹), a more red shifted λ_{max} absorption peak is observed in case of the ZnPor(ED)₄.²⁴ The full width at half maximum (FWHM) of the investigated photocatalysts using the Gaussian fit for the UV–Vis–NIR spectra are obtained 304.90, 325.90, 353.93, and 406.58 nm for the CoPor(ED)₄, NiPor(ED)₄, CuPor(ED)₄, and ZnPor(ED)₄, respectively. The increasing trend in the FWHM is consistent with increasing 3d electron density of the corresponding metal used in the MPor photocatalysts. LHE is an important factor in photocatalyst systems. The photocatalytic process begins with the absorption of sunlight on photocatalyst surface, and then transfer of excitons to the catalyst active site.⁶⁵ So, the improved capture of sunlight is a basis for the photoconversion of CO₂ molecule. The LHE can be obtained from the calculated oscillator strength as described below:⁶⁶

$$LHE : 1 - 10^{-f} \quad (6)$$

A considerable value of LHE owing to the incorporation of EDs has been obtained for all the investigated photocatalysts, which can gradually improve their activity in CO₂ adsorption. The exciton lifetime of MPors is also increased from 0.10 – 0.15 to around 5.23 – 5.60 ns. τ -enhancement at around 37 to 52 times was achieved upon ED coordination (see Tables 1 and Table S23 of ESI†). Thus introduction of ED groups into the meso-position of MPors gives rise to the significant changes in the photoexcitation properties, including a red-shift in λ_{max} with the value around of 150 nm as well as an increase in the exciton lifetime and light harvesting efficiency. This is in consistent with experimental reports using the ZnPor and different types of electron donors in meso-positions.^{67,68}

Based on the electronic configuration (see Tables S19 to S22 of ESI†), the λ_{max} absorption band of MPor(ED)₄ model systems were attributed to the mixed characteristic of HOMO–5 $\alpha(\beta)$ $\rightarrow$ LUMO+5 $\alpha(\beta)$ with the major contribution of HOMO(β) $\rightarrow$ LUMO+4(β), HOMO(β) $\rightarrow$ LUMO+4(β), HOMO(β) $\rightarrow$ LUMO+5(β) and HOMO($\alpha(\beta)$) $\rightarrow$ LUMO+5($\alpha(\beta)$) for CoPor(ED)₄, NiPor(ED)₄, CuPor(ED)₄ and ZnPor(ED)₄, respectively. As mentioned above,

Fig. 5 Electron density difference (EDD) map of (a) CoPor(ED)₄, (b) NiPor(ED)₄, (c) CuPor(ED)₄, and (d) ZnPor(ED)₄ photocatalysts. The contour isovalue is 0.006. The purple and yellow represent the positive and negative electron density, respectively.

the λ_{max} band of photocatalysts involving the π (EDs or (and) Por) to π^* (EDs or Por) and π (EDs or (and) Por) to π^* (EDs or por) and d (central metal) transitions, which can be classified according to $\pi - \pi^*$ and ligand-to-metal charge transition (LMCT). Consequently, the λ_{max} transition characteristics of photocatalysts has $\pi - \pi^*$ and LMCT nature of transitions. Fig. 5 represents the visualization of electron density difference (EDD) between the intended excited state (S_n) and the fundamental state (S_0) in a transition gives rise to the λ_{max} absorption. The purple region indicates where the difference density is positive, meaning that the EDD in the excited state is larger than that in the fundamental state; otherwise the yellow region indicates where the difference density is negative, meaning that the EDD in the excited state is smaller than that in the fundamental state. Moreover, the yellow region represents where the electrons are coming from, and the purple region represents where the electrons are going when moving from the S_0 to the S_n . Photocatalysts EDDs reveal that the electron-hole pairs disturb over both EDs and MPors units, but the distribution size and shape depend on the central metal-ion. For the ZnPor(ED)₄, most of the electron density goes into the two of EDs and Por ring. This is true for the CoPor(ED)₄, NiPor(ED)₄, and CuPor(ED)₄ photocatalysts as well, but they also gain electron density in the metal $3d$ orbitals. The positive value of electron density in the metal $3d$ orbitals for Co, Ni and Cu centered photocatalysts, demonstrates their electron acceptor property during transition. For the Zn centered catalyst, the electron density moves into the EDs and Por ring, in result of filled $3d$ sub-shell. From the above discussion, the EDs has ability to enhance charge transfer through the catalyst skeleton and have a

considerable contribution to change their electronic structure. As it can be seen, the λ_{max} electronic transition is delocally excited. This property provides charge delocalized states which are more reactive and so represent a narrower HOMO–LUMO gap.³⁰

3.3 CO₂ adsorption on photocatalysts

Here, we have investigated the adsorption of CO₂ gas on photocatalyst frameworks as the key step in the photoreduction process. Carbon (C-mode, Figs. 6a and 6b) and oxygen (O-mode, Figs. 6c and 6d) coordination of CO₂ molecule to the central metal-ion were taken into account. Two possible configurations schemes for gas adsorption with respect to the catalyst active site were considered. In the first configuration, the gas molecule were located along the one pyrrole ring (A-configuration, Figs. 6a and 6c) and in the second configuration, the gas molecule were located between two pyrrole rings (B-configuration, Figs. 6b and 6d). Gas initial distance from the central metal was set to 2.5, 3.0,

Fig. 6 Different CO₂ adsorption states (a) The CO₂ gas is placed along the two pyrrole rings and is coordinated through the carbon atom: CA-configuration. The initial bond length between carbon and active site is set as 2.5, 3.0, and 3.5 Å: CA_{2.5}, CA_{3.0}, and CA_{3.5}, (b) The CO₂ gas is placed between the two pyrrole rings and is coordinated through the carbon atom: CB-configuration. The initial bond length between carbon and active site is set as 2.5, 3.0, and 3.5 Å: CB_{2.5}, CB_{3.0}, and CB_{3.5}, (c) The CO₂ gas is placed along the two pyrrole rings and is coordinated through the oxygen atom: OA-configuration. The initial bond length between oxygen and active site is set as 2.5, 3.0 and 3.5 Å: OA_{2.5}, OA_{3.0}, and OA_{3.5}, (d) The CO₂ gas is placed between the two pyrrole rings and is coordinated through the oxygen atom: OB-configuration. The initial bond length between oxygen and active site is set as 2.5, 3.0, and 3.5 Å: OB_{2.5}, OB_{3.0}, and OB_{3.5}.

Table 2 Calculated M–O–C–O bond length (d , Å), CO₂ binding energy (E_b , kJ·mol^{−1}), Hirshfeld charge (q_H), and C=O bond length of CO₂ ($d_{C=O}$, Å).

photocatalyst	d	E_b	q_H	$d_{C=O}$
CoPor(ED) ₄	2.61	20.11	−0.125	1.189
NiPor(ED) ₄	3.19	12.24	−0.166	1.188
CuPor(ED) ₄	3.13	13.13	−0.170	1.188
ZnPor(ED) ₄	2.54	26.31	−0.150	1.189

and 3.5 Å. Considering modes, configurations and bond distances twelve different states of CO₂ adsorption were calculated for each photocatalyst. For example, for CA form of adsorption or equally when CO₂ binds through carbon (C) atom and it is positioned along one pyrrole ring (A) (Figs. 6a and 6b); three bond distances (2.5, 3.0, and 3.5 Å) considered as CA_{2.5}, CA_{3.0}, and CA_{3.5}. Similarly, for CB, OA, and OB form of adsorption all bonding distances were computed, by summing up all the considered states together, we get twelve different states for each catalyst. No dependency to the type of central metal-ion, we have found that CO₂ binds linearly and with adsorption bond angle deviated from 180° to all photocatalysts after geometric relaxation. There are two final modes of CO₂ adsorption: binding through the oxygen atom (M–O–C–O) and binding through the carbon atom (M–CO₂). The mode of coordination is depend on the type of central metal-ion. Ni and Cu can bind using two modes (carbon and oxygen atom) while Co and Zn coordinate only through the oxygen coordination mode. In the later case, during the C-mode relaxation the gas molecule rotates and finally oxygen atom sits on the top of metal-ions (Co and Zn) and binds to the metal 3d orbital. Considering the importance of stability, the relative energy difference between the final adsorption states were collected in Table S24 of ESI†. The character in the parentheses beside each relative stability energy is the final state of adsorption after geometry relaxation. As mentioned above, since the transformation of CA- and CB-states to OA- and OB-states, there are just two final states with specific M–O–C–O bond distance for the CoPor(ED)₄ and ZnPor(ED)₄ catalysts. The obtained results show that the O-coordination mode has the lower energy than the C-coordination mode and also the B-configuration of CO₂ with respect to the photocatalyst framework is more stable than the A-configuration; thus the most stable state for all simulated photocatalysts is OB-state. The difference in the calculated final energy of two similar states with different starting states in Table S24 of ESI†, for example CA- and OA-states relaxed to OA-states can be attributed to the numerical accuracy of calculations. In the following, we just discuss the most stable state for each photocatalyst, when the gas binds with OB-configuration to the catalyst framework. The relaxed geometry of the most stable states are shown in Fig. S12 of ESI† and the adsorption bond length ($d_{M-O-C-O}$), the binding energy (E_b), of OB state of adsorption (the most stable states) are tabulated in the Table 2. The adsorption bond length is defined as the optimized distance between central metal-ion and CO₂. The obtained results for the CoPor(ED)₄, NiPor(ED)₄, CuPor(ED)₄, and ZnPor(ED)₄ indicate that the adsorption distances are 2.61, 3.19, 3.13, and 2.54 Å, respectively. Theses values show that no chemical bond forms since the calculated bond lengths are significantly larger than the

sum of the covalent atomic radii of atoms (see Table S25 of ESI†). Thus, no chemical bonds is expected to form by CO₂ adsorption on such photocatalysts. The binding energy (second column of Table 2) for CO₂ adsorption on catalyst frameworks is not overly strong; the calculated adsorption energies is below 50 kJ/mol for all catalysts which fall in the range of physical adsorption energy (1–100 kJ/mol) of gas molecules. It was found that the increasing trend of E_b follows: CuPor(ED)₄–CO₂ < NiPor(ED)₄–CO₂ < CoPor(ED)₄–CO₂ < ZnPor(ED)₄–CO₂ which has the opposite trend as that of decreasing d values of bond distance. The smaller values of d result in a stronger interaction and thus a more negative E_b .⁶⁹ The Hirshfeld charge of the oxygen atoms in isolated CO₂ is −0.182 where that of oxygen in Co–O, Ni–O, Cu–O, and Zn–O is −0.125, −0.166, −0.170 and −0.150, respectively. One can see that charge difference ($\Delta\rho$) before and after adsorption of CO₂ molecule on CoPor(ED)₄–CO₂, NiPor(ED)₄–CO₂, CuPor(ED)₄–CO₂, and ZnPor(ED)₄–CO₂ framework is 0.057, 0.016, 0.012, and 0.032 respectively. Small values of $\Delta\rho$ indicate the CO₂ gas physically adsorb on catalyst surface.⁷⁰ The reason behind more value of $\Delta\rho$ for the CoPor(ED)₄ is tendency to d^6 low-spin configuration of cobalt metal-ion. By charge transfer to new axial ligand (CO₂), the d^7 configuration of Co(II) can gain more stability by approaching to low-spin d^6 configuration. As shown in the last column of Table 2, the C–O bond length of the gas molecule is almost remain unchanged. This distance for the isolated gas is 1.88 Å compared with determined by calculated value of 1.88 Å for NiPor(ED)₄–CO₂ and CuPor(ED)₄–CO₂ and 1.89 for CoPor(ED)₄–CO₂ and ZnPor(ED)₄–CO₂. Linear bonding of CO₂ molecule, low values of adsorption energy and no evident alternation of bond length and electronic charge of CO₂ before and after adsorption were observed in all cases advocates the physisorption of CO₂ molecule. The physisorption of CO₂ gas on the MPor-based photocatalysts were reported recently elsewhere.⁶²

The reason why each catalyst select special mode of adsorption (O- or C- and O-mode), why oxygen coordination mode is more stable and why CO₂ binds with the angle deviated from 180° to the photocatalysts surfaces, can be well characterized by the electrostatic potential (ESP) analysis.⁷¹ ESP is a graphical analysis and due to its relation to electron density can be used in understanding electrophilic and nucleophilic attacks in a reaction.⁷² Thus, when a negative charge moving toward a molecule, it will avoid areas with negative potential, electron-rich site, and prefer positive areas or electron-deficient site and vice versa for positive charge. Van der Waals intramolecular interactions which are known as the main interaction in physical adsorption are also reflected in ESP surface analysis and can be used to understand the interactions between CO₂ and photocatalysts.⁵² Fig. 7a depicts the ESP isosurface of the photocatalyst before and after CO₂

Fig. 7 Electrostatic potential analysis (ESP) of (a) the MPor(ED)₄ photocatalysts and (b) their CO₂ adsorbed structures.

adsorption. In this projection the potential increases in the order of red < orange < yellow < green < blue; the blue region appear for the nucleophilic region and the red region appear for the electrophilic region. The two oxygen atoms and carbon atom of gas molecule shows nucleophilic (red) and electrophilic (blue) area. The end oxygens can be easily adsorbed on the central metal-ion. Here, the visualized EPSs clearly exhibit strong positive area (blue) for the CoPor(ED)₄ and ZnPor(ED)₄ embedded by the π -conjugated system (Por, spacers and EDs) leaving a electrophilic region (orange to red) around the metal-ions. The strong nucleophilic region provide a reactive site for adsorption of the electrophilic oxygen atom of the gas while its carbon atom is unfavorable. On the other hand, for the NiPor(ED)₄ and CuPor(ED)₄ the central metal-ions represent light blue to green regions which demonstrate natural site for gas adsorption. Thus there is no special preference for catalyst to bind through the carbon or oxygen

atom and we had seen both mode of adsorptions in these photocatalysts. The negative area (yellow to orange) exists on the surface of the Por ring and spacer force the other negative area, the other hand oxygen atom (non-adsorbed one) to move far away due to the repulsion effect. So, CO₂ molecule will be adsorbed with special angle with respect to the catalyst plane. In the following, EPS analysis were conducted to investigate the effects of CO₂ adsorption on the electronic properties of catalysts; visual

representation of EPS for CO₂ adsorbed catalysts were exhibited in Fig. 7b. The EPS analysis reveal the charge density are locally changed on the central metal-ion due to the CO₂ adsorption and demonstrate uniformity on the surface in comparison with that of pristine catalysts. Consequently, the physical adsorption model can be confirmed because the catalyst and CO₂ adsorbed system appear complementarily based on our EPS analysis. Based on what discussed above, we obtained a similar improvement on MPor-based frameworks via the LBG electron donor substitution while CO₂ tends to bind more strongly to the ZnPor-based catalyst. Thus, more preference for the CO₂ absorbing. Enhanced applications of the ZnPor-based materials as CO₂ capturing catalysts were also reported in previous literatures.^{73,74}

In order to explore the CO₂ sensing ability of the ZnPor(ED)₄, we carried out the calculation of the conductance spectra before and after the gas adsorption at zero voltage. A four-probe model, where four semi-infinite GNWs electrodes are in contact with the central scattering region was used to calculate the electron transport properties of studied model systems, as shown in Fig. 2 and Fig. S6 of ESI†. Fig. 8, shows the transmission spectrum of the ZnPor(ED)₄ (blue plots) and CO₂-adsorbed ZnPor(ED)₄ (green plots) setups. Transmission spectra are plotted between electrode one, the nearest electrode to the gas molecule, and the three other electrodes for better understanding the effect of CO₂ adsorption

Fig. 8 Transmission spectrum of four-terminal ZnPor(ED)₄ device before (blue curves) and after (green curves) CO₂ adsorption at zero bias voltage. Transmission spectra is plotted between (a) electrode 1 and electrode 2, (b) electrode 1 and electrode 3, and (c) electrode 1 and electrode 4.

on conductance value. The Fermi level is shifted to zero in all the plots. Since the leading roles of conductance are close to the Fermi level, we focus on these energies. After CO₂ adsorption, the device conductance is almost unchanged between all electrodes (electrode 1 to electrode 2, electrode 1 to electrode 3, and electrode 1 to electrode 4) compared to the ZnPor(ED)₄ device (compare blue and green plots in Fig. 8). The negligible reduced conductance values reflects weak vdW interaction which does not affect conduction channels in the ZnPor(ED)₄ molecular junction. Equivalently, the adsorption of CO₂ does not alter the electronic structure of central molecule. This is due to physical adsorption of the gas on catalyst surface in which the electronic structure of the central complex is barely perturbed by adsorption.⁷⁵ This means a low sensitivity for this device, which limits its application as a sensor of CO₂ molecule. One idea to improve the efficiency of the simulated molecular junction in CO₂ detection might be to investigate the effect of the axial ligand on the CO₂ adsorption related properties and also conductance values. As suggested by other groups,⁷⁶ the reactivity of the MPors can be tuned by the axial ligand coordination. In this respect, it is of importance to see how axial ligand (nature and state) can affect both catalytic and CO₂ detection performance.

4 Conclusions

In summary, a systematic computational study has been carried out towards exploring the potential of MPors (M = Co, Ni, Cu, and Zn) complexes tuned narrow bandgap EDs as CO₂ photoreduction catalyst. The calculated bandgap, frontier molecular orbital, maximum absorption wavelength, exciton lifetime, and light harvesting efficiency have clarified that these hybrid catalysts are quite practical in this regard and the ZnPor(ED)₄ holds the best catalytic performance. In addition, investigation of CO₂ adsorption over the catalyst active site reveals that the mode of gas adsorption depends on the type of central metal. physisorption of CO₂

have been clarified by detailed study of adsorption energy, Hirshfeld charge, and bond length analysis of CO₂, electrostatic potential surface, and transmission spectra of hybrid catalysts. We hope that this newly studied hybrid catalysts can be helpful towards design and fabrication the new CO₂ photocatalysts which need molecular-level engineering in both computational and experimental researches.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors thank Research and Technology Council of Sharif University of Technology for partial assistance. Financial support of the Iran National Science Foundation (INSF) through Research Project No 97021720 is highly appreciated. The support and resources from the Cluster Center for High Performance Computing at Chemistry Department of Shahid Beheshti University of Iran are gratefully acknowledged.

References

- 1 M. L. Grasso, J. Puszkil, L. F. Albanesi, M. Dornheim, C. Pistidda and F. C. Gennari, *Phys. Chem. Chem. Phys.*, 2019, **21**, 19825–19834.
- 2 M. López, L. Broderick, J. J. Carey, F. Vines, M. Nolan and F. Illas, *Phys. Chem. Chem. Phys.*, 2018, **20**, 22179–22186.
- 3 M. Faraji, M. Yousefi, S. Yousefzadeh, M. Zirak, N. Naseri, T. H. Jeon, W. Choi and A. Z. Moshfegh, *Energy Environ. Sci.*, 2019, **12**, 59–95.
- 4 A. A. Khan and M. Tahir, *J. CO₂ Util.*, 2019, **29**, 205–239.
- 5 J. Kothandaraman and D. J. Heldebrant, *Green Chem.*, 2020, **22**, 828–834.
- 6 H. Shen, T. Peppel, J. Stunk and Z. Sun, *Sol. RRL*, 2020, DOI:10.1002/solr.201900546.
- 7 D. J. Fermin and F. Marken, *Electrochemical Reduction of Carbon Dioxide: Overcoming the Limitations of Photosynthesis*, The Royal Society of Chemistry, Cambridge, 2018.
- 8 L. Collado, A. Reynal, F. Fresno, M. Barawi, C. Escudero, V. Perez-Dieste, J. M. Coronado, D. P. Serrano, J. R. Durrant, A. Víctor *et al.*, *Nat. Commun.*, 2018, **9**, 1–10.
- 9 S. Zhu and D. Wang, *Adv. Energy Mater.*, 2017, **7**, 1700841–1700865.
- 10 S. Sorcar, S. Yoriya, H. Lee, C. Grimes and S. Feng, *Mater. Today Chem.*, 2020, DOI:10.1016/j.mtchem.2020.100264.
- 11 M. Samadi, M. Zirak, A. Naseri, E. Khorashadizade and A. Z. Moshfegh, *Thin Solid Films*, 2016, **605**, 2–19.
- 12 H. Pang, X. Meng, H. Song, W. Zhou, G. Yang, H. Zhang, Y. Izumi, T. Takei, W. Jewasuwana, N. Fukata *et al.*, *Appl. Catal. B*, 2019, **244**, 1013–1020.
- 13 S. Matavos-Aramyan, S. Soukhakian, M. H. Jazebizadeh, M. Moussavi and M. R. Hojjati, *Appl. Mater. Today*, 2020, DOI:10.1016/j.apmt.2019.100499.
- 14 A. Erdemir, G. Ramirez, O. L. Eryilmaz, B. Narayanan, Y. Liao, G. Kamath and S. K. Sankaranarayanan, *Nature*, 2016, **536**, 67–71.

- 15 J. M. Park, J. H. Lee and W.-D. Jang, *Coord. Chem. Rev.*, 2020, **407**, 213157.
- 16 J. Wang, D. Liu, Q. Liu, T. Peng, R. Li and S. Zhou, *Appl. Surf. Sci.*, 2019, **464**, 255–261.
- 17 Y. Gao, W. Guan, L.-K. Yan and Y. Xu, *Phys. Chem. Chem. Phys.*, 2019, **21**, 3822–3831.
- 18 M. Mone, S. Tang, P. Murto, B. A. Abdulahi, C. Larsen, J. Wang, W. Mammo, L. Edman and E. Wang, *Chem. Mater.*, 2019, **31**, 9721–9728.
- 19 S. Zhou, C. Li, J. Zhang, Y. Yu, A. Zhang, Y. Wu and W. Li, *Chem. Asian J.*, 2017, **12**, 1861–1864.
- 20 Y. Zheng, J. Wang, J. Zhang, T. Peng and R. Li, *Dalton Trans.*, 2017, **46**, 8219–8228.
- 21 R. Urzúa-Leiva, R. Pino-Rios and G. Cárdenas-Jirón, *Phys. Chem. Chem. Phys.*, 2019, **21**, 4339–4348.
- 22 G. Zhao, H. Pang, G. Liu, P. Li, H. Liu, H. Zhang, L. Shi and J. Ye, *Appl. Catal. B*, 2017, **200**, 141–149.
- 23 M. Zalas, B. Gierczyk, A. Bossi, P. R. Mussini, M. Klein, R. Pankiewicz, M. Makowska-Janusik, Ł. Popena and W. Stampor, *Dyes Pigm.*, 2018, **150**, 335–346.
- 24 C. Wang, X. Chen, H. Pan, D. Qi and J. Jiang, *J. Catal.*, 2019, **373**, 75–80.
- 25 Y. Zhu, Y. Huang, Q. Li, D. Zang, J. Gu, Y. Tang and Y. Wei, *Inorg. Chem.*, 2020, **59**, 2575–2583.
- 26 L. Lin, C. Hou, X. Zhang, Y. Wang, Y. Chen and T. He, *Appl. Catal. B*, 2018, **221**, 312–319.
- 27 C. Long, X. Li, J. Guo, Y. Shi, S. Liu and Z. Tang, *Small Methods*, 2019, **3**, 1800369.
- 28 J. Jiang, S. Guo, X. Wang, L. Xu, Q. Li and X. Zhang, *R. Soc. Open Sci.*, 2019, **6**, 181199.
- 29 P. Ledwon, N. Thomson, E. Angioni, N. J. Findlay, P. J. Skabara and W. Domagala, *RSC Adv.*, 2015, **5**, 77303–77315.
- 30 A. Ostovan, Z. Mahdaviifar and M. Bamdad, *Polymer*, 2017, **126**, 162–176.
- 31 N. Sadeghi, S. Sharifnia and M. S. Arabi, *J. CO₂ Util.*, 2016, **16**, 450–457.
- 32 X. Li, J. Yu, M. Jaroniec and X. Chen, *Chem. Rev.*, 2019, **119**, 3962–4179.
- 33 D. Zou, W. Zhao, B. Cui, D. Li and D. Liu, *Phys. Chem. Chem. Phys.*, 2018, **20**, 2048–2056.
- 34 M. H. Chang, N.-Y. Kim, Y. H. Chang, Y. Lee, U. S. Jeon, H. Kim, Y.-H. Kim and S.-J. Kahng, *Nanoscale*, 2019, **11**, 8510–8517.
- 35 M. H. Chang, Y. H. Chang, N.-Y. Kim, H. Kim, S.-H. Lee, M.-S. Choi, Y.-H. Kim and S.-J. Kahng, *Phys. Rev. B*, 2019, **100**, 245406.
- 36 G. Reddy, R. Katakam, K. Devulapally, L. A. Jones, E. Della Gaspera, H. M. Upadhyaya, N. Islavath and L. Giribabu, *J. Mater. Chem. C*, 2019, **7**, 4702–4708.
- 37 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372–1377.
- 38 C. Lee, W. Yang and F. Parr, *Phys. Rev. B*, 1988, **37**, 785.
- 39 M. Xie, F.-Q. Bai, J. Wang, Y.-Q. Zheng and Z. Lin, *Phys. Chem. Chem. Phys.*, 2018, **20**, 3741–3751.
- 40 L. E. Roy, P. J. Hay and R. L. Martin, *J. Chem. Theory Comput.*, 2008, **4**, 1029–1031.
- 41 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.
- 42 C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158–6170.
- 43 Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215–241.
- 44 T. Yanai, D. P. Tew and N. C. Handy, *Chem. Phys. Lett.*, 2004, **393**, 51–57.
- 45 J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615–6620.
- 46 L. Yang, F. Wang, J. Gao and Y. Wang, *Phys. Chem. Chem. Phys.*, 2019, **21**, 1271–1276.
- 47 L. Liu, P. Eisenbrandt, T. Roland, M. Polkehn, P.-O. Schwartz, K. Bruchlos, B. Omiecienski, S. Ludwigs, N. Leclerc, E. Zaborova *et al.*, *Phys. Chem. Chem. Phys.*, 2016, **18**, 18536–18548.
- 48 L. Kara Zaitri and S. M. Mekelleche, *Mol. Phys.*, 2020, **118**, 1–10.
- 49 O. A. Vydrov and G. E. Scuseria, *J. Chem. Phys.*, 2006, **125**, 234109.
- 50 M. B. M. Krishna, N. Venkatramaiah and D. N. Rao, *J. Opt.*, 2013, **16**, 015205.
- 51 F. L. Hirshfeld, *Theor. Chim. Acta*, 1977, **44**, 129–138.
- 52 V. Gupta, *Principles and applications of quantum chemistry*, Academic Press, Cambridge, 2015.
- 53 R. A. Gaussian09, Inc., Wallingford CT, 2009, **121**, 150–166.
- 54 C. Zhu, J.-X. Liang and G. Wei, *Phys. Chem. Chem. Phys.*, 2016, **18**, 12338–12343.
- 55 J. Li, X. Li, H.-J. Zhai and L.-S. Wang, *Science*, 2003, **299**, 864–867.
- 56 J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón and D. Sánchez-Portal, *J. Phys. Condens. Matter*, 2002, **14**, 2745–2779.
- 57 N. Papior, N. Lorente, T. Frederiksen, A. García and M. Brandbyge, *Comput. Phys. Commun.*, 2017, **212**, 8–24.
- 58 K. K. Saha, W. Lu, J. Bernholc and V. Meunier, *J. Chem. Phys.*, 2009, **131**, 164105.
- 59 S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787–1799.
- 60 N. Troullier and J. Martins, *Solid State Commun.*, 1990, **74**, 613–616.
- 61 M. Büttiker, *Phys. Rev. Lett.*, 1986, **57**, 1761–1764.
- 62 C. Chen, C. Tang, W. Xu, Y. Li and L. Xu, *Phys. Chem. Chem. Phys.*, 2018, **20**, 9536–9542.
- 63 A. Masunov, S. Tretiak, J. W. Hong, B. Liu and G. C. Bazan, *J. Chem. Phys.*, 2005, **122**, 224505.
- 64 Y.-d. Zhao, J.-j. Fu, H.-b. Li, H. Dong and Y. Liao, *Chem. Res. Chin. Univ.*, 2013, **29**, 974–981.
- 65 Z. Lian, M. Jiang, F. Qiao, Z. Yuan, M.-N. Chen, R.-Z. Wang, T. Zhang, L.-P. Xu, H. Yan, S. Zhuo *et al.*, *Dyes Pigm.*, 2019, **162**, 475–480.
- 66 W. Li, J. Wang, J. Chen, F.-Q. Bai and H.-X. Zhang, *Phys. Chem. Chem. Phys.*, 2014, **16**, 9458–9468.

- 67 S. H. Kang, M. J. Jeong, Y. K. Eom, I. T. Choi, S. M. Kwon, Y. Yoo, J. Kim, J. Kwon, J. H. Park and H. K. Kim, *Adv. Energy Mater.*, 2017, **7**, 1602117.
- 68 M. Adineh, P. Tahay, W.-K. Huang, H.-P. Wu, E. W.-G. Diau and N. Safari, *RSC Adv.*, 2016, **6**, 102979–102983.
- 69 F. Safari, M. Moradinasab, M. Fathipour and H. Kosina, *Appl. Surf. Sci.*, 2019, **464**, 153–161.
- 70 S. Yang, G. Lei, H. Xu, B. Xu, H. Li, Z. Lan, Z. Wang and H. Gu, *Appl. Surf. Sci.*, 2019, **480**, 205–211.
- 71 P. Politzer and J. S. Murray, *Theor. Chem. Acc.*, 2002, **108**, 134–142.
- 72 V. Gupta, P. Thul, S. Mishra, R. Pratap and V. J. Ram, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, 2009, **72**, 82–101.
- 73 J. Liang, Y.-Q. Xie, Q. Wu, X.-Y. Wang, T.-T. Liu, H.-F. Li, Y.-B. Huang and R. Cao, *Inorg. Chem.*, 2018, **57**, 2584–2593.
- 74 Y. Kuramochi, Y. Fujisawa and A. Satake, *J. Am. Chem. Soc.*, 2020, **142**, 705–709.
- 75 K. Oura, V. Lifshits, A. Saranin, A. Zotov and M. Katayama, *Surface science: an introduction*, Springer Science & Business Media, Cambridge, 2013.
- 76 K. C. Christoforidis, D. A. Pantazis, L. L. Bonilla, E. Bletsas, M. Louloudi and Y. Deligiannakis, *J. Catal.*, 2016, **344**, 768–777.

A table of contents entry

A series of metalloporphyrin-based hybrid photocatalysts were theoretically design for efficient CO₂ reduction.