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Published in:
ACS Materials Letters

Link to article, DOI:
[10.1021/acsmaterialslett.0c00028](https://doi.org/10.1021/acsmaterialslett.0c00028)

Publication date:
2020

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Fornari, R. P., Mesta, M., Hjelm, J., Vegge, T., & de Silva, P. (2020). Molecular Engineering Strategies for Symmetric Aqueous Organic Redox Flow Batteries. *ACS Materials Letters*, 2(3), 239-246.
<https://doi.org/10.1021/acsmaterialslett.0c00028>

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ACS Materials Lett., **Just Accepted Manuscript** • DOI: 10.1021/acsmaterialslett.0c00028 • Publication Date (Web): 07 Feb 2020

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Molecular Engineering Strategies for Symmetric Aqueous Organic Redox Flow Batteries

Rocco Peter Fornari*, Murat Mesta, Johan Hjelm, Tejs Vegge,
Piotr de Silva*

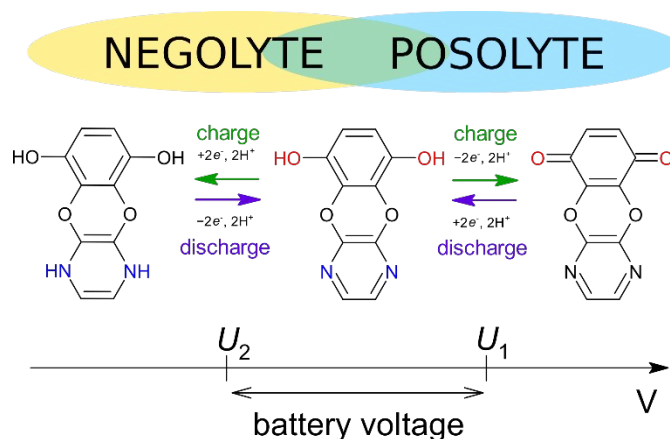
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3 ABSTRACT: Symmetric aqueous organic redox flow batteries (RFBs)
4 are potentially a cheap, durable and safe energy storage
5 technology. Unlike normal asymmetric flow batteries, they are
6 based on electrolytes that exist in at least three oxidation states
7 and can undergo a minimum of two distinct redox processes. We
8 compute the redox potentials of selected electrolytes intending to
9 understand how the interaction between the redox units affects the
10 potentials. We find that electronic interaction between redox
11 units and intramolecular hydrogen bonding can both be exploited to
12 tune the difference between the redox potentials, i.e. the
13 theoretical voltage of the battery. The redox potentials can be
14 further fine-tuned in either direction by adding substituents.
15 Starting from these observations we formulate a set of rules which
16 will help finding ideal candidates for symmetric RFBs.
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TOC GRAPHICS



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3 Redox flow batteries (RFB) have the potential to become a long-
4 lasting, low-cost, easily scalable and safe energy storage
5 technology.¹ RFBs based on metal ions are already commercially
6 available but have some drawbacks including highly volatile cost
7 of the active material.¹ Many alternative RFB concepts² and active
8 materials^{2,3} are currently being developed. All-organic aqueous
9 RFBs, where both active materials are organic molecules, are under
10 intense investigation^{4,5} since they hold promise to reduce the cost
11 and the environmental footprint of RFBs. A major challenge for
12 their development is the identification of suitable candidates for
13 the redox-active molecules, which need to have suitable redox
14 potentials, good solubility, long-term chemical stability and low
15 crossover through the separator membrane.^{1,6} Computational studies
16 have been used extensively to explore the chemical space of redox-
17 active molecules for RFBs.⁷⁻¹⁷ One promising strategy is finding
18 redox molecules which have two redox processes, which could be
19 employed in symmetric RFBs (SRFBs). The main advantage of this
20 concept, as described in details by Potash et al.¹⁸, is that the
21 same species is dissolved in both tanks thereby minimizing the
22 detrimental effects of membrane crossover. Moreover, in the
23 discharged state, the two tanks contain solutions with identical
24 composition, resulting in the absence of any chemical and
25 electrochemical potentials across the cell.¹⁸ A few candidates for
26 aqueous¹⁹⁻²⁴ and non-aqueous^{18,25-31} symmetric RFB electrolytes have
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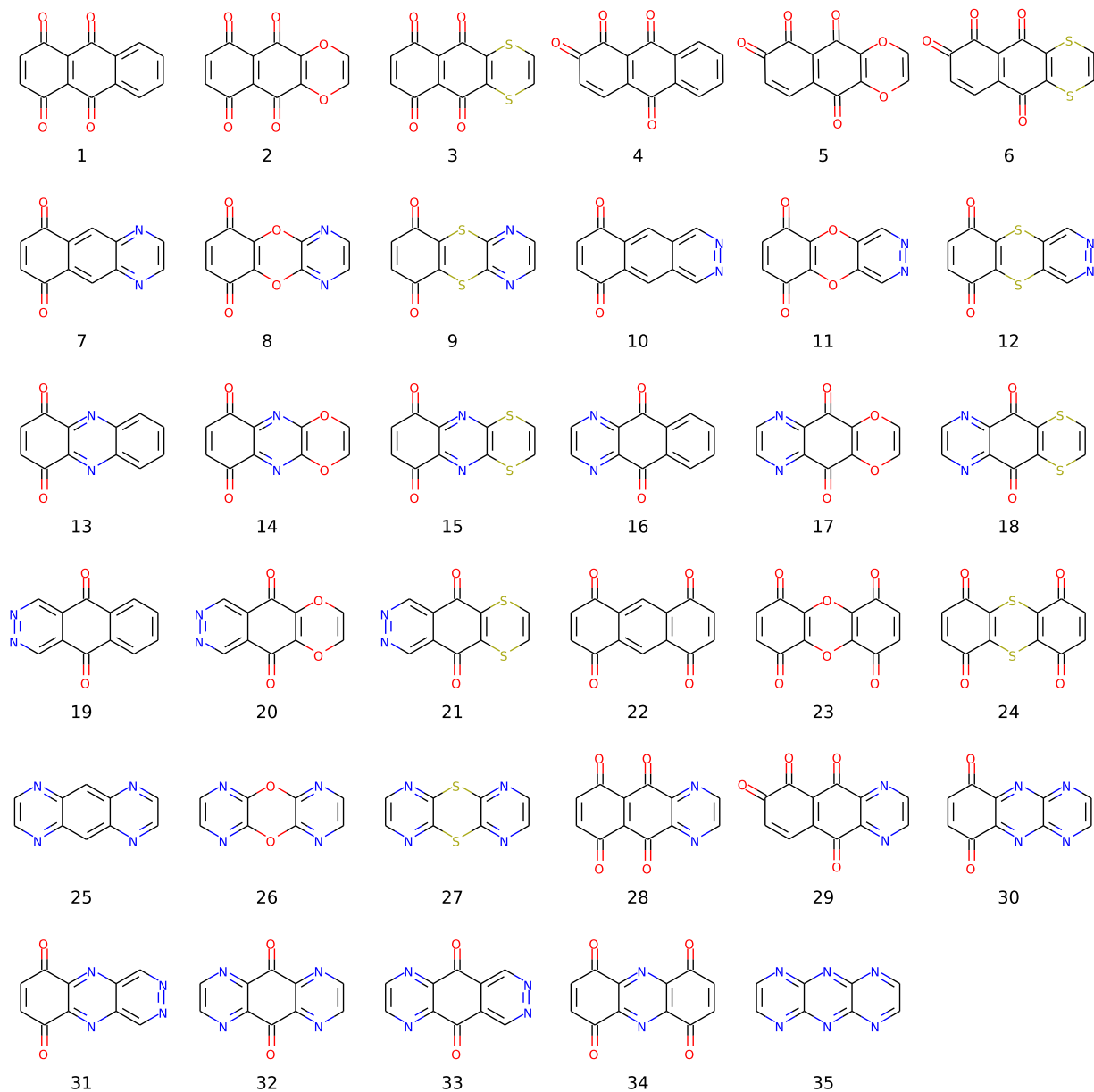
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3 been proposed recently, but no systematic study of structure-
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5 property relationships has been reported to date. The common
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7 feature of molecules with two redox processes is the presence of
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9 (at least) two redox units. If one defines an SRFB as a device
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11 with the same composition of the tanks in the discharged state,
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13 one could think of a design where two different types of
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15 electroactive molecules are dissolved in both tanks. Then, one
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17 molecule acts as a posolyte and the other as a negolyte, while
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19 half of the material remains inactive. It is not immediately clear
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21 whether combining multiple redox units in the same molecule has
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23 advantages over such a trivial SRFB. This would be the case if
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25 there was a synergy between the redox units either in terms of
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27 voltage or solubility. The latter has been explored in combi
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29 molecules, where distinct posolyte and anolyte molecules have been
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31 covalently connected through solubility-enhancing linkers.^{19,21,23}
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33 In this contribution, we aim to answer the question whether
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35 installing multiple redox moieties on a compact molecular core can
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37 lead to additional synergies compared to directly mixing two types
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39 of electrolytes or combining them into one molecule through a
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41 linker. This is achieved by performing a systematic computational
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43 investigation of a class of three-ring candidate molecules for
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45 aqueous SRFBs and comparing the results with a judiciously chosen
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47 reference system composed of two molecules with just one redox
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49 moiety each (vide infra and **Chart S1** in the Supporting
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3 Information). This choice gives us enough flexibility for the
4 exploration of different multi-redox chemistries, while keeping
5 the size of the molecules practically small. The objective of this
6 study is to elucidate new structure-property relationships for
7 bipolar SRFB materials and guide the subsequent experimental
8 molecular design rather than propose a specific new material.
9 Although long-term chemical stability is one of the main challenges
10 in the design of molecules for aqueous RFBs, here we restrict the
11 discussion to electrochemical properties and solubility in water.
12 Our central hypothesis is that the electronic interaction between
13 redox units offers an extra degree of freedom that can be exploited
14 to tune the cell voltage of an SRFB. We will assess the magnitude
15 of this interaction by comparing the potentials of molecules with
16 multiple redox units to those of analogous molecules with a single
17 redox unit.

18
19 We build a set of molecules based on an exemplary anthracene-
20 like backbone, a popular template in many state-of-the-art
21 electrolytes.^{6,9,10,32,33} We consider a range of prototypical template
22 redox units (1,2-quinone, 1,4-quinone, pyrazine and pyridazine)
23 and build each molecule by introducing two redox units on two of
24 the aromatic rings. Additionally, we consider substitution of two
25 aromatic carbons in the ring without redox-active groups with the
26 oxygen, nitrogen and sulfur heteroatoms. When the heteroatom is
27 nitrogen, this ring becomes a pyrazine, so the molecule effectively

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3 has three redox unit. The molecules with three redox units will be
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5 discussed separately. The resulting structures and their indexes
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7 are listed in **Chart 1**. On a selected subset of these molecules
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9 (see ensuing discussion), we take one step further by adding
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11 electron-donating and electron-withdrawing substituents and
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13 discuss the impact on redox potentials and solubility.
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Chart 1. Structures of the considered electrolytes in their fully oxidized forms.



The molecules with two redox units (1-27) are named *double redox* (DR) and can exist in three forms: fully oxidized (A), partially reduced (AH_2) and fully reduced (AH_4). Those with three redox units (28-35) are named *triple redox* (TR) have one further stable state

(AH₆). We assume that all redox processes are concerted two-electron, two-proton reactions, as is the case for most quinone-like species.^{6,14,14,22} We evaluate the potentials in water at pH=0, i.e. we consider all species fully protonated to avoid the computation of anions with charge -2, -4 and -6 which can be unreliable with density functional theory (DFT) and implicit solvation models. The redox potentials for the processes $A + 2H^+ + 2e^- \rightarrow AH_2$, $AH_2 + 2H^+ + 2e^- \rightarrow AH_4$ and $AH_4 + 2H^+ + 2e^- \rightarrow AH_6$ are named U_1 , U_2 and U_3 respectively, and the difference $\Delta U = U_1 - U_2$ ($\Delta U_{\max} = U_1 - U_3$ in TR molecules) is the maximum theoretical voltage of the battery. When the positions of the redox units are not equivalent (molecules 1-21), two different isomers of AH₂ are possible, depending on which redox unit is reduced first. The energy differences between the two isomers are in the range 0.08-2.30 eV for molecules 1-21; when it is small, it should be expected that a mixture of the two isomers can be produced when discharging the battery. For simplicity, we report the potential values determined by the more stable isomer of AH₂, corresponding to the largest possible ΔU . We follow the same approach for the TR molecules (28-35) and choose the most stable of the three isomers of the species AH₂ and AH₄.

For each molecule shown in **Chart 1**, the values of U_1 , U_2 and ΔU are reported in **Figure 1**.

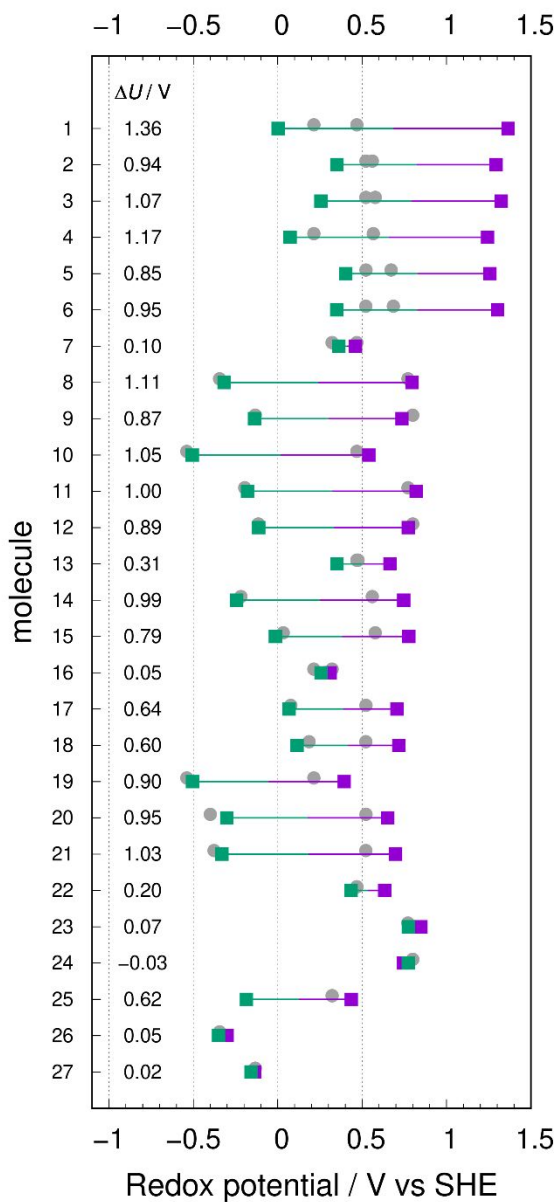


Figure 1. Redox potentials U_1 (purple) and U_2 (green) of molecules 1-27. $\Delta U = U_1 - U_2$ values are listed on the left. The potentials of the single redox (SR) references of each molecule are represented by grey dots.

Some of the considered structures have been already proposed as RFB electrolytes. Derivatives of alizarin and quinizarin

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3 (molecules 1 and 4) have been recently reported to be good
4 candidates for symmetric aqueous batteries;^{20,22} the calculated
5 potentials and ΔU of 1 and 4 are consistent with the reported
6 experimental values of alizarin and quinizarin derivatives.^{20,22} To
7 understand how ΔU depends on the interaction between the two redox
8 units on a small molecule, we computed for each molecule the redox
9 potentials of two *single redox* (SR) reference molecules, which
10 have only one of the redox units, while the other redox-active
11 ring is just benzenic. For example, the SR references of molecule
12 8 are shown in **Chart S1** (Supporting Information) and the difference
13 between their redox potentials is ΔU_{SR} . This choice of the reference
14 structures is to a large extent arbitrary as stripping the quinone
15 groups or replacing heteroatoms with carbons not only switches off
16 the redox functionality but also induces global changes in the
17 electronic structure of conjugated rings. Nevertheless, it is the
18 conceptually simplest way to gauge the interactions between
19 multiple redox units on the same molecule. Because the objective
20 of this work is to understand the advantages of merging multiple
21 redox moieties in a single compact molecular core, the choice of
22 reference molecules with the same size of the core is the most
23 natural for such comparisons.

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51 In molecules 1-8, where the redox units are both quinones, ΔU is
52 considerably larger than ΔU_{SR} . This can be interpreted as being due
53 to the electronic interaction between the two non-equivalent
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3 quinone redox units when they are located on the same molecule. In
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5 molecule 1, for example, $\Delta U_{\text{SR}} = 0.25$ V and $\Delta U = 1.36$ V. However,
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8 we note that in molecules 1-8, the increase of ΔU with respect to
9
10 ΔU_{SR} is predominantly due to U_1 shifting to higher potential rather
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12 than U_2 shifting to lower potential. In other words, the reduced
13
14 species AH_2 and AH_4 are stabilized more than the oxidized species
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16 A with respect to the SR references. One reason for this
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18 stabilization is the electronic interaction between the
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20 (hydro)quinone units, which may be stronger in the more aromatic
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22 AH_2 and AH_4 than in the 'quinonic' A. Additionally, we find that a
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24 significant component of the stabilization of the reduced species
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26 is the intramolecular O-H---O hydrogen bonding; an effect
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28 previously reported in literature.³⁴ To estimate how much of the
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30 stabilization is due to hydrogen bonding, we compute for molecule
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32 1 the energies of the conformers of AH_2 and AH_4 with the hydroxyl
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34 hydrogens pointing away from the oxygens, i.e. the less stable
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36 conformers without hydrogen bonding. As shown in the top panel of
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38 **Figure 2**, the stabilization of AH_2 and AH_4 with respect to their
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40 less stable conformers is indeed rather large, which results in a
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42 +0.3 V shift of U_1 and a +0.4 V increase of ΔU with respect to its
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44 conformer without hydrogen bonding (see bottom panel of **Figure 2**).
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46 Stabilization of the conformers is likely to be due to a
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48 combination of hydrogen bonding and reduced steric repulsion with
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50 neighboring hydrogens. A non-negligible conformer stabilization
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effect was found to be relevant in a few other molecules, for which comparisons analogous to **Figure 2** are reported in **Figure S4** (Supporting Information).

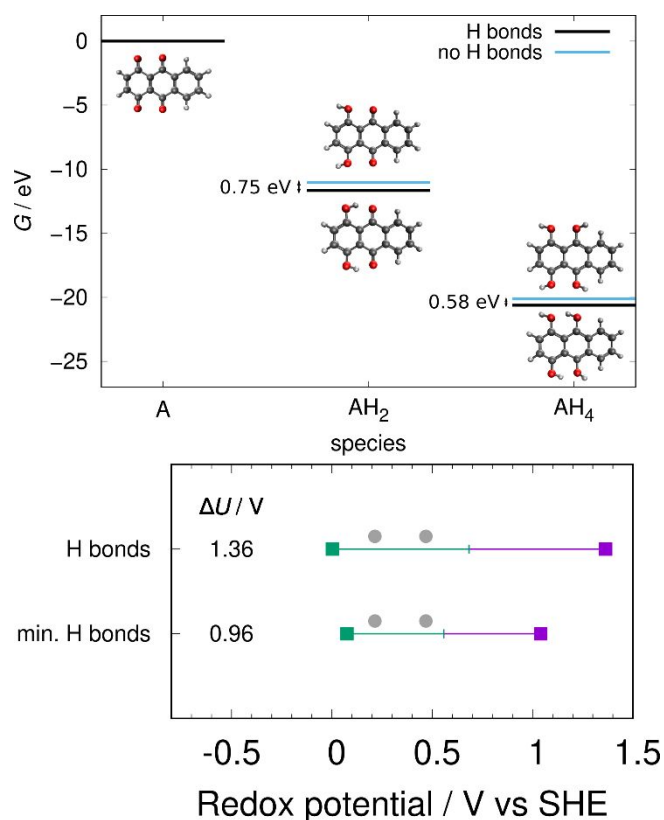


Figure 2. Top: Free energies (relative to the species A) and structures of the solvated reduced forms of molecule 1. Free energies include the thermal correction $G_{\text{gas}}^{\text{corr}}$ and the solvation energy of the protons $n\Delta G_{\text{sol}}(\text{H}^+)$ where $n = 4, 2, 0$ for (A, AH₂, AH₄). For the reduced species AH₂ and AH₄, the most stable conformer is in black and the conformer with the minimum number of intramolecular hydrogen bonds is in light blue. Bottom: Redox potentials of the conformers shown in the top panel (SR references in gray).

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3 The remaining difference between ΔU_{SR} (gray) and ΔU , without the
4 effect of hydrogen bonds, can be attributed to the electronic
5 interaction between quinones. This effect is observed mainly in
6 molecules where two quinone units are on adjacent rings, where the
7 electronic interaction is stronger and hydrogen bonding between
8 quinone units is possible.
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11 When the two redox units are different (molecules 7-21), the
12 interactions between them appear in general to be weaker. In
13 molecules 7-12, where the redox units are not on adjacent rings,
14 the values of U_1 , U_2 and ΔU are very similar to those of their SR
15 references, which in 8-12 already have large ΔU_{SR} values. In
16 molecules 13-15 and 17-21, the significant ~ 0.2 V positive shift
17 of U_1 with respect to the SR references is due to the electronic
18 interaction between adjacent redox units; additionally, a weak
19 O-H---N hydrogen bond may contribute to the stabilization of AH_2
20 in molecule 18 (see **Figure S4**, Supporting Information). It is
21 interesting to compare molecules 13 and 16 which are isomers and
22 differ only by the location of the benzene ring: in molecule 16,
23 $\Delta U = 0.05$ V is smaller than $\Delta U_{\text{SR}} = 0.11$ V; in contrast, there is a
24 large relative gain in ΔU for molecule 13 (from 0.01 V to 0.31 V).
25 This observation should serve as a warning that the interaction
26 between redox units depends strongly on the electronic structure
27 of the whole molecule and cannot always be guessed from the outset.
28 In general, in the case of multiple redox moieties, the
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3 substituents can strongly interact with all of them, making
4 building intuition harder. Therefore, in such cases accurate
5 calculations of redox potentials should be included in molecular
6 design workflows.
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11 The changes in charge distribution and aromaticity in different
12 redox states for a representative subset of molecules and their
13 associated SR reference structures are shown in **Figure S5**
14 (Supporting Information) in the form of electrostatic potential
15 (ESP) maps and nucleus-independent chemical shifts (NICS) which is
16 a widely accepted measure of aromaticity.³⁵ Since aromaticity is
17 only one of the components of electronic stabilization energy
18 (which in turn determines the redox potentials), we limit this
19 analysis to qualitative considerations following a recent
20 example.²⁴ In general, quinone units are non-aromatic and become
21 aromatic when reduced, while pyrazine units are aromatic and become
22 slightly anti-aromatic upon reduction. In molecule 1 the strong
23 interaction between the quinone units is evidenced by the smaller
24 change in aromaticity of the outer redox unit compared to its
25 reference SR₂: when going from A to AH₂, instead of becoming fully
26 aromatic as in SR₂, this hydroquinone shares some electronic
27 density and quinone character with the middle quinone unit. Only
28 when the latter is also reduced to AH₄, the NICS values become more
29 similar to those of the reduced SR references. In molecules 13 and
30 17 the interaction between the quinone and pyrazine redox units is
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3 evidenced by weaker aromatic and anti-aromatic character in the
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5 AH₄ form compared to the SR references. In molecule 8, instead,
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7 the oxygen atoms make the middle ring slightly antiaromatic and
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9 there is no interaction between the redox units: here the ESP maps
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11 and NICS values are very similar to those of the SR reference
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13 structures.
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17 In molecules 22-24, the quinone units are not on adjacent units,
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19 thereby weakening the interaction and preventing intramolecular
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21 hydrogen bonding. The ΔU values are around 0.2 V for the fully
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23 aromatic 22 (due to purely electronic interaction) and closer to
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25 0 V for 23 and 24 where the aromaticity is interrupted by the
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27 heteroatoms, switching off also the electronic interaction between
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29 the redox units. The same pattern is observed in the group 25-27,
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31 where the aromatic 25 has large ΔU while in 26 and 27 $\Delta U \sim 0$ V.
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35 We discuss next the redox potentials of molecules 28-35 which
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37 have three redox units. The results, shown in **Figure 3**, are
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39 consistent with the observations made so far: multiple redox units
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41 which are part of the same aromatic system can interact strongly
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43 and increase the maximum ΔU . All molecules present a large positive
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45 shift of U_1 with respect to the SR reference, which indicates
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47 stabilization of the species AH₂ with one of the quinone unit
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49 reduced as discussed before. U_3 , which is due to the reduction of
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51 the pyrazine unit, is always shifted to lower potentials, with the
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53 only exceptions being molecules 31 and 33, where it is due to the
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3 pyridazine unit. Overall, the triple redox (TR) design strategy
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5 seems another promising way of tweaking the potentials and
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7 increasing the theoretical voltage of symmetric RFBs. It should be
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9 noted, however, that such a four-state battery, operating between
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11 potentials U_1 and U_3 , would not be truly symmetric as the tanks
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13 would contain different species in the discharged state (AH_2 and
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15 AH_4). Such even-state electrolytes may have certain disadvantages
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17 for SRFBs as noted by Potash et al.¹⁸ Nevertheless, it has to be
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19 noted that this situation is completely analogous to the Vanadium
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21 RFB, in which the vanadium ions are oxidized/reduced between the
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23 V^{2+}/V^{3+} and VO^{2+}/VO_2^+ redox pairs. Despite not being completely
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25 symmetric, VRFB enables electrolyte rebalancing strategies that
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27 can be used to mitigate the membrane cross-over.
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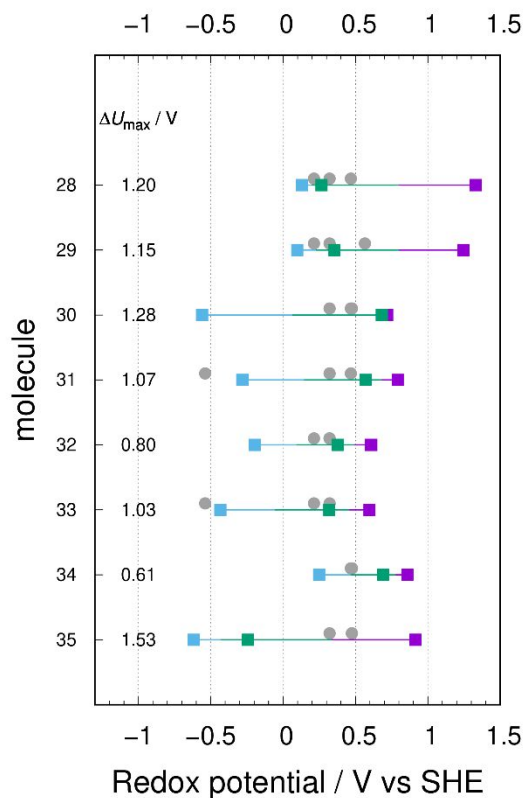
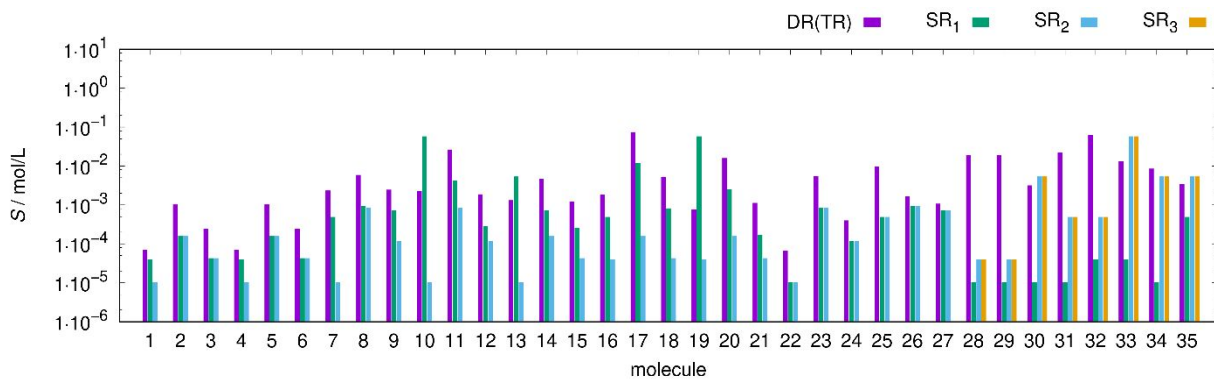


Figure 3. Redox potentials U_1 (purple), U_2 (green) and U_3 (blue) of molecules 28-35. $\Delta U_{\max} = U_1 - U_3$ values are listed on the left. The potentials of the single redox (SR) references of each molecule are represented by grey dots.

In summary, we have identified two effects responsible for the increased theoretical voltage of a flow battery based on molecules with multiple redox units compared to the same units on separate molecules: i) electronic interaction between the redox units; ii) intramolecular hydrogen bonding between adjacent units. These effects are strongest in the double quinones 1-6 which can achieve ΔU in the range 0.85-1.36 V compared to ΔU_{SR} of 0.04-0.16 V. When

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3 there are two different redox units, the gain with respect to the
4 SR reference is smaller but can still be of significant magnitude.
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6 SR reference is smaller but can still be of significant magnitude.
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8 The interaction between three redox units can also yield
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10 significant gains in ΔU .

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12 Another crucial property for RFB electrolytes is the solubility.
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14 Although an accurate prediction of solubility is not in the scope
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16 of this letter, we are interested how it is affected by the
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18 presence of multiple redox units. We report in **Figure 4** the
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20 solubilities (predicted with the ChemAxon Solubility Plugin³⁶) of
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22 molecules 1-35 and of their SR references in the solubility-
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24 limiting redox form, which was chosen for each structure as the
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26 form with the lowest solubility.
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43 **Figure 4.** Solubility in water at pH = 0 computed with the ChemAxon
44 Solubility Plugin³⁶ of double and triple redox molecules (DR, TR)
45 and of their single redox (SR) reference structures. Structures
46 shown in **Chart 1**.
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53 The results show that multiple redox units often improve
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55 solubility with respect to molecules of the same size but with a
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3 single redox unit. This should be seen as a positive collateral
4 effect stemming from the proposed design rule of multiple redox
5 units on the same molecular core, whose primary goal is realizing
6 symmetric electrolytes with high potential difference. Once a
7 suitable compound has been found, various strategies can be
8 employed to improve solubility: adding hydrophilic
9 substituents,^{4,10} decreasing the melting point by discouraging
10 crystal packing³⁷ and altering the composition of the electrolyte
11 e.g. by adding chloride salts³⁸ or exchanging sodium ions with
12 larger hydrophilic organic cations.²⁰
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25 We investigate next the effects on the redox potentials of adding
26 electron-donating and electron-withdrawing substituents to a
27 subset of the structures in **Chart 1**. We focus on molecules 1, 8,
28 31 and 35 because they have large ΔU and are representative of the
29 variety of structures considered. We choose as representative
30 substituents the electron-donating methoxy group (OMe) and the
31 electron-withdrawing sulfonic acid group (SO₃H), whose effects on
32 redox potentials of quinones are roughly the same but with opposite
33 signs.¹⁰ To assess the substituent effect, we consider first single
34 substitution at all available aromatic carbons, then double
35 substitutions at selected positions (see subsequent discussion).
36 The resulting structures are shown in **Chart S2** (Supporting
37 Information). The redox potentials and ΔU of the singly substituted
38 molecules are shown in **Figure S1** (Supporting Information). In
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3 general, OMe tends to shift potentials down and SO₃H tends to shift
4 the potentials up with respect to the unsubstituted molecule, in
5 accordance with previous computational studies on quinones.¹⁰ In
6 particular, we observe that in molecule 8, where the redox units
7 are different and are electronically isolated by the oxygen
8 heteroatoms, the substituent effect is easier to rationalize. OMe
9 has a very small effect when attached to the quinone unit (8a) but
10 shifts U_2 down when attached to the pyrazine unit (8b). SO₃H instead
11 has a greater effect and shifts U_1 up when attached to the quinone
12 unit (8c) and U_2 up when attached to the pyridazine unit (8d).
13 Molecule 1, however, is an exception to this tendency as ΔU becomes
14 smaller with OMe in position 5 and with SO₃H in any position. In
15 the TR molecules (31 and 35), all potentials are in general shifted
16 to lower values. The maximum ΔU is increased in some cases (8b,
17 8c, 31b, 31c, 35a). In summary, the effect of substituents on the
18 redox potentials is easy to predict when the redox units do not
19 interact strongly.

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22 Since substituents are expected to affect the solubility, we
23 report in **Figure S3** (Supporting Information) the predicted
24 solubilities of the substituted and unsubstituted compounds,
25 each in the solubility-limiting redox form. While in most cases
26 OMe substitution has little effect on solubility, SO₃H mostly
27 yields a significant increase of solubility which is not
28 surprising since it is a hydrophilic group.

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3 With these considerations in mind, one can try to combine one
4 electron-withdrawing and one electron-donating substituent (*push-*
5 *pull* design strategy) on the same molecule with the goal of
6 increasing ΔU (and therefore the theoretical voltage) while also
7 improving solubility. To this end, we select molecules 8, 31 and
8 35. In molecules 8 and 31, we add SO_3H to the quinone unit, which
9 we expect to shift U_1 higher, and OMe to the other available redox
10 unit, which should push U_2 lower, thereby obtaining an even larger
11 ΔU . In molecule 35, we adopt the same strategy. We consider both
12 combinations of substitution positions and obtain the molecules
13 8e, 8f, 31e, 31f, 35c and 35d, as shown in **Chart S2** (Supporting
14 Information). The redox potentials and ΔU of these push-pull doubly
15 substituted molecules are reported in **Figure S2** (Supporting
16 Information). The proposed substitution design strategy proved
17 successful in increasing the ΔU of molecule 8 from 1.11 V
18 (unsubstituted) to 1.23 V (singly substituted with either OMe or
19 SO_3H , 8b or 8c) and 1.33 V (doubly substituted with OMe and SO_3H ,
20 8d and 8f). The predictability of this effect is due to the fact
21 that the two redox units are connected by two oxygen atoms which
22 interrupt the aromatic system and thereby prevent electronic
23 interaction between the redox units. Therefore, the potentials U_1
24 and U_2 of molecule 8 are individually tunable. In molecules 31 and
25 35, where the backbone is fully aromatic, the push-pull
26 substitutions did not increase ΔU with respect to single
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3 substitutions. Finally, the double substitution did not
4 significantly affect the solubility compared to single SO₃H
5 substitution (see **Figure S3**, Supporting Information).
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10 Although the goal of this paper is elucidating structure-property
11 relationships and proposing design rules rather than viable
12 candidates for SRFBs, we report in **Tables S1** and **S2** (Supporting
13 Information) the synthetic accessibility (SA) score computed with
14 the RDKit-based implementation³⁹ of the method described in ref.⁴⁰
15 for all structures considered in all redox forms. A general trend
16 is that molecules with multiple redox units are expected to be
17 more difficult to synthesize than their SR counterparts. Those
18 with more varied heteroatoms are predicted to be less accessible.
19 Among the molecules with $\Delta U > 0.8$ V, those easier to synthesize
20 (with SA score of at least one of the redox forms below 2.6) are
21 1, 4, 19, 28, 29, 32, 34 and 1a-f, where molecules 1 and 4 have
22 already been synthesized and characterized in an SRFB setup.^{20,22}
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39 By computing the redox potentials and solubilities of a
40 representative set of molecules with two and three redox units, we
41 have understood how the interactions between redox units on the
42 same molecule affect the redox potentials and the difference
43 between them. The electronic interaction plays the biggest role in
44 increasing the difference between the redox potentials, and it can
45 be switched off by interrupting the aromatic system between the
46 redox units. Intramolecular hydrogen bonds between redox units on
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3 neighboring rings tend to push the more positive potential to even
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5 higher values. The solubility of molecules with multiple redox
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7 units is found to be better than their single redox counterparts.
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9 Finally, by adding substituents one can fine-tune one or both
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11 potentials when the redox units are electronically separated, but
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13 substitution effects can be more unpredictable when they are part
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15 of the same aromatic system. In this letter we have outlined some
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17 fundamental structure-property relationships which enable us to
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19 establish guidelines for the design of organic electrolytes for
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21 aqueous SRFBs. A complete set of design rules should incorporate
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23 tuning of reduction potential, solubility, synthetic accessibility
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25 and stability. In this work we primarily have addressed the first,
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27 and to some extent the second and third, of these properties. The
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29 target for the reduction potential is to achieve as high cell
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31 voltage as possible while observing stability limits of the
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33 molecule itself and of the aqueous medium in contact with the
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35 carbon electrodes and the active materials. In practice this likely
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37 limits the cell voltage to < 1.5 V. A symmetric electrolyte with
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39 large ΔU and improved solubility can be built in two ways: i)
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41 incorporating two or more equivalent redox units on the same
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43 aromatic backbone; ii) assembling two or more different redox units
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45 which already have a given ΔU_{SR} when on separate molecules. In the
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47 latter case, the units can be electronically connected or isolated
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49 if the ΔU_{SR} needs to be increased or preserved. The choice of redox
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3 units also determines the absolute positions of the potentials:
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5 for example, the double quinone motif is likely to push the more
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7 positive potential further up. The potentials may then be tuned
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9 further by substitution, keeping in mind the considerations
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11 outlined above. The set of design rules outlined here forms a solid
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13 basis for future investigations with the goal of finding ideal
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15 organic electrolytes for symmetric aqueous redox flow batteries.
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18 COMPUTATIONAL METHODS

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20 All energies are computed at the B3LYP/6-311G(d,p) level of
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22 theory with the Q-Chem 5.0 software.⁴¹ The energies in solution are
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24 computed with the conductor-like polarizable continuum model (C-
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26 PCM)⁴²⁻⁴⁴ using a dielectric constant of 78.39 (water). The reduction
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28 potential (in V) for the generic reaction $A + 2H^+ + 2e^- \rightarrow AH_2$ is
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30 calculated with the direct approach:⁴⁵
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$$34 \quad U = -\frac{1}{ne}(\Delta E_{\text{sol}} + \Delta G_{\text{gas}}^{\text{corr}} + n\Delta G_{\text{sol}}(\text{H}^+)) - U_{\text{SHE}}$$

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36 where $n=2$ is the number of electrons and protons transferred, e
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38 is the elementary charge and the energy differences are expressed
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40 in eV. $\Delta E_{\text{sol}} = E_{\text{sol}}(\text{AH}_2) - E_{\text{sol}}(\text{A})$ is the reaction energy computed as the
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42 energy difference between the solvated species at the gas phase
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44 geometry. $\Delta G_{\text{gas}}^{\text{corr}} = \Delta H_{\text{gas}} - T\Delta S_{\text{gas}}$ is the thermal correction to the
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46 reaction free energy (ΔH_{gas} includes zero-point energy and
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48 vibrational enthalpy and $-T\Delta S_{\text{gas}}$ is the entropy contribution)
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50 computed from vibrational frequency calculations in gas phase at
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3 298 K. The solvation free energy of the proton $\Delta G_{\text{sol}}(\text{H}^+)$ and the
4 standard hydrogen electrode potential U_{SHE} are set to values
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6 consistent with the C-PCM solvation model (-11.335 eV and 4.47 V
7
8 respectively).⁴⁶ The solvation free energy is computed as $\Delta G_{\text{sol}} = E_{\text{sol}}$
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13 $-E_{\text{gas}}$ at the gas phase geometry.

14 15 ASSOCIATED CONTENT

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18 **Supporting Information.** Chart explaining the concept of single
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20 redox reference structures, structures of molecules with
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22 electron-donating and electron-withdrawing substituents, redox
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24 potentials and solvation free energies of substituted molecules.
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37 Notes

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39 The authors declare no competing financial interest.
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42 43 ACKNOWLEDGMENTS

44
45 This work was financially supported through an investment by
46
47 Innovation Fund Denmark via the Grand Solutions project "ORBATS"
48
49 file nr. 7046-00018B.
50

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