Molecular Engineering Strategies for Symmetric
Aqueous Organic Redox Flow Batteries

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

TOC GRAPHICS
Redox flow batteries (RFB) have the potential to become a long-lasting, low-cost, easily scalable and safe energy storage technology. RFBs based on metal ions are already commercially available but have some drawbacks including highly volatile cost of the active material. All-organic aqueous RFBs, where both active materials are organic molecules, are under intense investigation since they hold promise to reduce the cost and the environmental footprint of RFBs. A major challenge for their development is the identification of suitable candidates for the redox-active molecules, which need to have suitable redox potentials, good solubility, long-term chemical stability and low crossover through the separator membrane. Computational studies have been used extensively to explore the chemical space of redox-active molecules for RFBs. One promising strategy is finding redox molecules which have two redox processes, which could be employed in symmetric RFBs (SRFBs). The main advantage of this concept, as described in details by Potash et al., is that the same species is dissolved in both tanks thereby minimizing the detrimental effects of membrane crossover. Moreover, in the discharged state, the two tanks contain solutions with identical composition, resulting in the absence of any chemical and electrochemical potentials across the cell. A few candidates for aqueous and non-aqueous symmetric RFB electrolytes have been proposed recently, but no systematic study of structure-property relationships has been reported to date. The common feature of molecules with two redox processes is the presence of (at least) two redox units. If one defines an SRFB as a device with the same composition of the tanks in the discharged state, one could think of a design where two different types of electroactive molecules are dissolved in both tanks. Then, one molecule acts as a posolyte and the other as a negolyte, while half of the material remains inactive. It is not immediately clear whether combining multiple redox units in the same molecule has advantages over such a trivial SRFB. This would be the case if there was a synergy between the redox units.
either in terms of voltage or solubility. In this contribution, we aim to answer this question by performing a systematic computational investigation of a class of three-ring candidate molecules for aqueous SRFBs. This choice gives us enough flexibility for the exploration of different multi-redox chemistries, while keeping the size of the molecules practically small. Although long-term chemical stability is one of the main challenges in the design of molecules for aqueous RFBs, here we restrict the discussion to electrochemical properties and solubility in water. Our central hypothesis is that the electronic interaction between redox units offers an extra degree of freedom that can be exploited to tune the cell voltage of an SRFB. We will assess the magnitude of this interaction by comparing the potentials of molecules with multiple redox units to those of analogous molecules with a single redox unit.

We build a set of molecules based on an exemplary anthracene-like backbone, a popular template in many state-of-the-art electrolytes.\textsuperscript{3,6,7,28,29} We consider a range of prototypical template redox units (1,2-quinone, 1,4-quinone, pyrazine and pyridazine) and build each molecule by introducing two redox units on two of the aromatic rings. Additionally, we consider substitution of two aromatic carbons in the ring without redox-active groups with the oxygen, nitrogen and sulfur heteroatoms. When the heteroatom is nitrogen, this ring becomes a pyrazine, so the molecule effectively has three redox unit. The molecules with three redox units will be discussed separately.

The resulting structures and their indexes are listed in Chart 1. On a selected subset of these molecules (see ensuing discussion), we take one step further by adding electron-donating and electron-withdrawing substituents and discuss the impact on redox potentials and solubility.
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 (AH$_6$). We assume that all redox processes are concerted two-electron, two-proton reactions, as is the case for most quinone-like species.$^{3,11,11,19}$ 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 $\Delta U = U_1 - U_2$ ($\Delta U_{\text{max}} = U_1 - U_3$ 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 $AH_2$ 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 $AH_2$, corresponding to the largest possible $\Delta U$. We follow the same approach for the TR molecules (28-35) and choose the most stable of the three isomers of the species $AH_2$ and $AH_4$.

For each molecule shown in Chart 1, the values of $U_1$, $U_2$ and $\Delta U$ 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. Alizarin and a substituted quinizarin (molecules 1 and 4) have been recently reported to be good candidates for symmetric aqueous batteries;\textsuperscript{19} the calculated potentials and $\Delta U$ of 1 and 4 are consistent with the
reported experimental values of alizarin and 2,3-dimethyl-quinizarin. To understand how $\Delta U$ depends on the interaction between the two redox units on a small molecule, we computed for each molecule the redox potentials of two single redox (SR) reference molecules, which have only one of the redox units, while the other redox-active ring is just benzenic. For example, the SR references of molecule 8 are shown in Chart S1 (Supporting Information) and the difference between their redox potentials is $\Delta U_{SR}$.

In molecules 1-8, where the redox units are both quinones, $\Delta U$ is considerably larger than $\Delta U_{SR}$. This can be interpreted as being due to the electronic interaction between the two non-equivalent quinone redox units when they are located on the same molecule. In molecule 1, for example, $\Delta U_{SR} = 0.25$ V and $\Delta U = 1.36$ V. However, we note that in molecules 1-8, the increase of $\Delta U$ with respect to $\Delta U_{SR}$ is predominantly due to $U_1$ shifting to higher potential rather than $U_2$ shifting to lower potential. In other words, the reduced species $\text{AH}_2$ and $\text{AH}_4$ are stabilized more than the oxidized species $\text{A}$ with respect to the SR references. One reason for this stabilization is the electronic interaction between the (hydro)quinone units, which may be stronger in the more aromatic $\text{AH}_2$ and $\text{AH}_4$ than in the ‘quinonic’ A. Additionally, we find that a significant component of the stabilization of the reduced species is the intramolecular $\text{O-H-O}$ hydrogen bonding; an effect previously reported in literature. To estimate how much of the stabilization is due to hydrogen bonding, we compute for molecule 1 the energies of the conformers of $\text{AH}_2$ and $\text{AH}_4$ with the hydroxyl hydrogens pointing away from the oxygens, i.e. the less stable conformers without hydrogen bonding. As shown in the top panel of Figure 2, the stabilization of $\text{AH}_2$ and $\text{AH}_4$ with respect to their less stable conformers is indeed rather large, which results in a +0.3 V shift of $U_1$ and a +0.4 V increase of $\Delta U$ with respect to its conformer without hydrogen bonding (see bottom panel of Figure 2).
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 $G_{gas}^{corr}$ and the solvation energy of the protons $n\Delta G_{sol}(H^+)$ where $n = 4, 2, 0$ for (A, AH$_2$, AH$_4$). For the reduced species AH$_2$ and AH$_4$, the most stable conformer is in black and the conformer without intramolecular hydrogen bonds is in light blue. Bottom: Redox potentials of the conformers shown in the top panel (SR references in gray).

The remaining difference between $\Delta U_{SR}$ (gray) and $\Delta U$, without the effect of hydrogen bonds, can be attributed to the electronic interaction between quinones. This effect is observed mainly in molecules where two quinone units are on adjacent rings, where the electronic interaction is stronger and hydrogen bonding between quinone units is possible.

When the two redox units are different (molecules 7-21), the interactions between them appear in general to be weaker. In molecules 7-12, where the redox units are not on adjacent rings, the
values of $U_1$, $U_2$ and $\Delta U$ are very similar to those of their SR references, which in 8-12 already have large $\Delta U_{\text{SR}}$ values. In molecules 13-15 and 17-21, the significant ~0.2 V positive shift of $U_1$ with respect to the SR references is due to the electronic interaction between adjacent redox units; additionally, a weak O–H---N hydrogen bond may contribute to the stabilization of AH$_2$. It is interesting to compare molecules 13 and 16 which are isomers and differ only by the location of the benzene ring: in molecule 16, $\Delta U = 0.05$ V is smaller than $\Delta U_{\text{SR}} = 0.11$ V; in contrast, there is a large relative gain in $\Delta U$ for molecule 13 (from 0.01 V to 0.31 V). This observation should serve as a warning that the interaction between redox units depends strongly on the electronic structure of the whole molecule and cannot always be guessed from the outset. Therefore, an accurate calculation of redox potentials should be included in molecular design workflows for electrochemical applications. In molecules 22-24, the quinone units are not on adjacent units, thereby weakening the interaction and preventing intramolecular hydrogen bonding. The $\Delta U$ values are around 0.2 V for the fully aromatic 22 (due to purely electronic interaction) and closer to 0 V for 23 and 24 where the aromaticity is interrupted by the heteroatoms, switching off also the electronic interaction between the redox units. The same pattern is observed in the group 25-27, where the aromatic 25 has large $\Delta U$ while in 26 and 27 $\Delta U \sim 0$ V.

We discuss next the redox potentials of molecules 28-35 which have three redox units. The results, shown in Figure 3, are consistent with the observations made so far: multiple redox units which are part of the same aromatic system can interact strongly and increase the maximum $\Delta U$. All molecules present a large positive shift of $U_1$ with respect to the SR reference, which indicates stabilization of the species AH$_2$ with one of the quinone unit reduced as discussed before. $U_3$, which is due to the reduction of the pyrazine unit, is always shifted to lower potentials, with the only exceptions being molecules 31 and 33, where it is due to the pyridazine unit. Overall, the
triple redox (TR) design strategy seems another promising way of tweaking the potentials and increasing the theoretical voltage of symmetric RFBs.

Figure 3. Redox potentials $U_1$ (purple), $U_2$ (green) and $U_3$ (blue) of molecules 28-35. $\Delta U_{\text{max}} = U_1 - U_3$ 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, which is much stronger when they are on adjacent rings; ii) intramolecular hydrogen bonding between adjacent units. These effects are strongest in the double quinones 1-6 which can achieve $\Delta U$ in the range 0.85-1.36 V compared to $\Delta U_{\text{SR}}$ of 0.04-0.16 V. When there are two different redox units, the gain with respect to the SR
reference is smaller but can still be of significant magnitude. The interaction between three redox units can also yield significant gains in $\Delta U$.

Another crucial property for RFB electrolytes is the solubility. Although an accurate prediction of solubility is not in the scope of this letter, we are interested how it is affected by the presence of multiple redox units. The solvation free energy $\Delta G_{\text{sol}}$ (see Computational Methods) is used as a qualitative indicator of its solubility, as demonstrated in previous studies.\(^7\) We report in Figure 4 the values of $\Delta G_{\text{sol}}$ of molecules 1-35 and of their SR references in the fully oxidized form, which is usually less soluble,\(^7\) so it is limiting.

![Figure 4. Free energies of solvation in water computed with the C-PCM model\(^{32,32,33}\) (see Computational Section) of double and triple redox molecules (DR, TR) and of their single redox (SR) reference structures, all in the fully oxidized form. Structures shown in Chart 1.](image)

The results unequivocally suggest that multiple redox units should always improve solubility with respect to single redox molecules. This observation constitutes another strong advantage stemming from the proposed design rule of multiple redox units on the same aromatic backbone.

We investigate next the effects of adding electron-donating and electron-withdrawing substituents to a subset of the structures in Chart 1. We focus on molecules 1, 8, 31 and 35 because they have large $\Delta U$ and are representative of the variety of structures considered. We choose as
representative substituents the electron-donating methoxy group (OMe) and the electron-withdrawing sulfonic acid group (SO$_3$H), whose effects on redox potentials of quinones are roughly the same but with opposite signs.\textsuperscript{7} To assess the substituent effect, we consider first single substitution at all available aromatic carbons, then double substitutions at selected positions (see subsequent discussion). The resulting structures are shown in Chart S2 (Supporting Information). The redox potentials and $\Delta U$ of the singly substituted molecules are shown in Figure S1 (Supporting Information). In general, OMe tends to shift potentials down and SO$_3$H tends to shift the potentials up with respect to the unsubstituted molecule, in accordance with previous computational studies on quinones.\textsuperscript{7} In particular, we observe that in molecule 8, where the redox units are different and are electronically isolated by the oxygen heteroatoms, the substituent effect is easier to rationalize. OMe has a very small effect when attached to the quinone unit (8a), but shifts $U_2$ down when attached to the pyrazine unit (8b). SO$_3$H instead has a greater effect and shifts $U_1$ up when attached to the quinone unit (8c) and $U_2$ up when attached to the pyridazine unit (8d). Molecule 1, however, is an exception to this tendency as $\Delta U$ becomes smaller with OMe in position 5 and with SO$_3$H in any position. In the TR molecules (31 and 35), all potentials are in general shifted to lower values. The maximum $\Delta U$ is increased in some cases (8b, 8c, 31b, 31c, 35a). In summary, the effect of substituents on the redox potentials is easy to predict when the redox units do not interact strongly.

Since substituents are expected to affect the solubility, we report in Figure S2 (Supporting Information) the solvation free energies $\Delta G_{\text{sol}}$ of the substituted and unsubstituted compounds in the oxidized form. While OMe substitution has little effect on $\Delta G_{\text{sol}}$, SO$_3$H consistently yields a significant increase of $-\Delta G_{\text{sol}}$, which is not surprising since a hydrophilic group is expected to increase solubility in water.\textsuperscript{7}
With these considerations in mind, one can try to combine one electron-withdrawing and one electron-donating substituent (*push-pull* design strategy) on the same molecule with the goal of increasing \( \Delta U \) (and therefore the theoretical voltage) while also improving solubility. To this end, we select molecules 8, 31 and 35. In molecules 8 and 31, we add \( \text{SO}_3\text{H} \) to the quinone unit, which we expect to shift \( U_1 \) higher, and OMe to the other available redox unit, which should push \( U_2 \) lower, thereby obtaining an even larger \( \Delta U \). In molecule 35, we adopt the same strategy. We consider both combinations of substitution positions and obtain the molecules 8e, 8f, 31e, 31f, 35c and 35d, as shown in **Chart S2** (Supporting Information). The redox potentials and \( \Delta U \) of these push-pull doubly substituted molecules are reported in **Figure S2** (Supporting Information). The proposed substitution design strategy proved successful in increasing the \( \Delta U \) of molecule 8 from 1.11 V (unsubstituted) to 1.23 V (singly substituted with either OMe or \( \text{SO}_3\text{H} \), 8b or 8c) and 1.33 V (doubly substituted with OMe and \( \text{SO}_3\text{H} \), 8d and 8f). The predictability of this effect is due to the fact that the two redox units are connected by two oxygen atoms which interrupt the aromatic system and thereby prevent electronic interaction between the redox units. Therefore, the potentials \( U_1 \) and \( U_2 \) of molecule 8 are individually tunable. In molecules 31 and 35, where the backbone is fully aromatic, the push-pull substitutions did not increase \( \Delta U \) with respect to single substitutions. Finally, the double substitution did not significantly affect the solvation free energies compared to single \( \text{SO}_3\text{H} \) substitution (see **Figure S3**, Supporting Information).

By computing the redox potentials and solvation free energies of a representative set of molecules with two and three redox units, we have understood how the interactions between redox units on the same molecule affect the redox potentials and the difference between them. The electronic interaction plays the biggest role in increasing the difference between the redox potentials, and it can be switched off by interrupting the aromatic system between the redox units.
Intramolecular hydrogen bonds between redox units on neighboring rings tend to push the more positive potential to even higher values. The solubility of molecules with multiple redox units is found to be better than their single redox counterparts. Finally, by adding substituents one can fine-tune one or both potentials when the redox units are electronically separated, but substitution effects can be more unpredictable when they are part of the same aromatic system. In this letter we have outlined some fundamental structure-property relationships which enable us to establish guidelines for the design of organic electrolytes for aqueous SRFBs. A complete set of design rules should incorporate tuning of reduction potential, solubility, stability, and synthetic accessibility. In this work we primarily have addressed the first, and to some extent the second, of these properties. The target for the reduction potential is to achieve as high cell voltage as possible while observing stability limits of the molecule itself and of the aqueous medium in contact with the carbon electrodes and the active materials. In practice this likely limits the cell voltage to < 1.5 V. A symmetric electrolyte with large $\Delta U$ and improved solubility can be built in two ways: i) incorporating two or more equivalent redox units on the same aromatic backbone; ii) assembling two or more different redox units which already have a given $\Delta U_{SR}$ when on separate molecules. In the latter case, the units can be electronically connected or isolated if the $\Delta U_{SR}$ needs to be increased or preserved. The choice of redox units also determines the absolute positions of the potentials: for example, the double quinone motif is likely to push the more positive potential further up. The potentials may then be tuned further by substitution, keeping in mind the considerations outlined above. The set of design rules outlined here forms a solid basis for future investigations with the goal of finding ideal organic electrolytes for symmetric aqueous redox flow batteries.

COMPUTATIONAL METHODS
All energies are computed at the B3LYP/6-311G(d,p) level of theory with the Q-Chem 5.0 software.\textsuperscript{34} The energies in solution are computed with the conductor-like polarizable continuum model (C-PCM)\textsuperscript{32,33,35} using a dielectric constant of 78.39 (water). The reduction potential (in V) for the generic reaction \( A + 2H^+ + 2e^- \rightarrow AH_2 \) is calculated with the direct approach:\textsuperscript{36}

\[
U = -\frac{1}{ne} \left( \Delta E_{\text{sol}} + \Delta G_{\text{gas}}^{\text{corr}} + n\Delta G_{\text{sol}}(H^+) \right) - V_{\text{SHE}}
\]

where \( n = 2 \) is the number of electrons and protons transferred, \( e \) is the elementary charge and the energy differences are expressed in eV. \( \Delta E_{\text{sol}} = E_{\text{sol}}(AH_2) - E_{\text{sol}}(A) \) is the reaction energy computed as the energy difference between the solvated species at the gas phase geometry. \( \Delta G_{\text{gas}}^{\text{corr}} = \Delta H_{\text{gas}} - T\Delta S_{\text{gas}} \) is the thermal correction to the reaction free energy (\( \Delta H_{\text{gas}} \) includes zero-point energy and vibrational enthalpy and \( -T\Delta S_{\text{gas}} \) is the entropy contribution) computed from vibrational frequency calculations in gas phase at 298 K. The solvation free energy of the proton \( \Delta G_{\text{sol}}(H^+) \) and the standard hydrogen electrode potential \( V_{\text{SHE}} \) are set to values consistent with the C-PCM solvation model (\(-11.335\) eV and 4.47 V respectively).\textsuperscript{37} The solvation free energy is computed as \( \Delta G_{\text{sol}} = E_{\text{sol}} - E_{\text{gas}} \) at the gas phase geometry.

ASSOCIATED CONTENT

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

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Notes

The authors declare no competing financial interest.

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