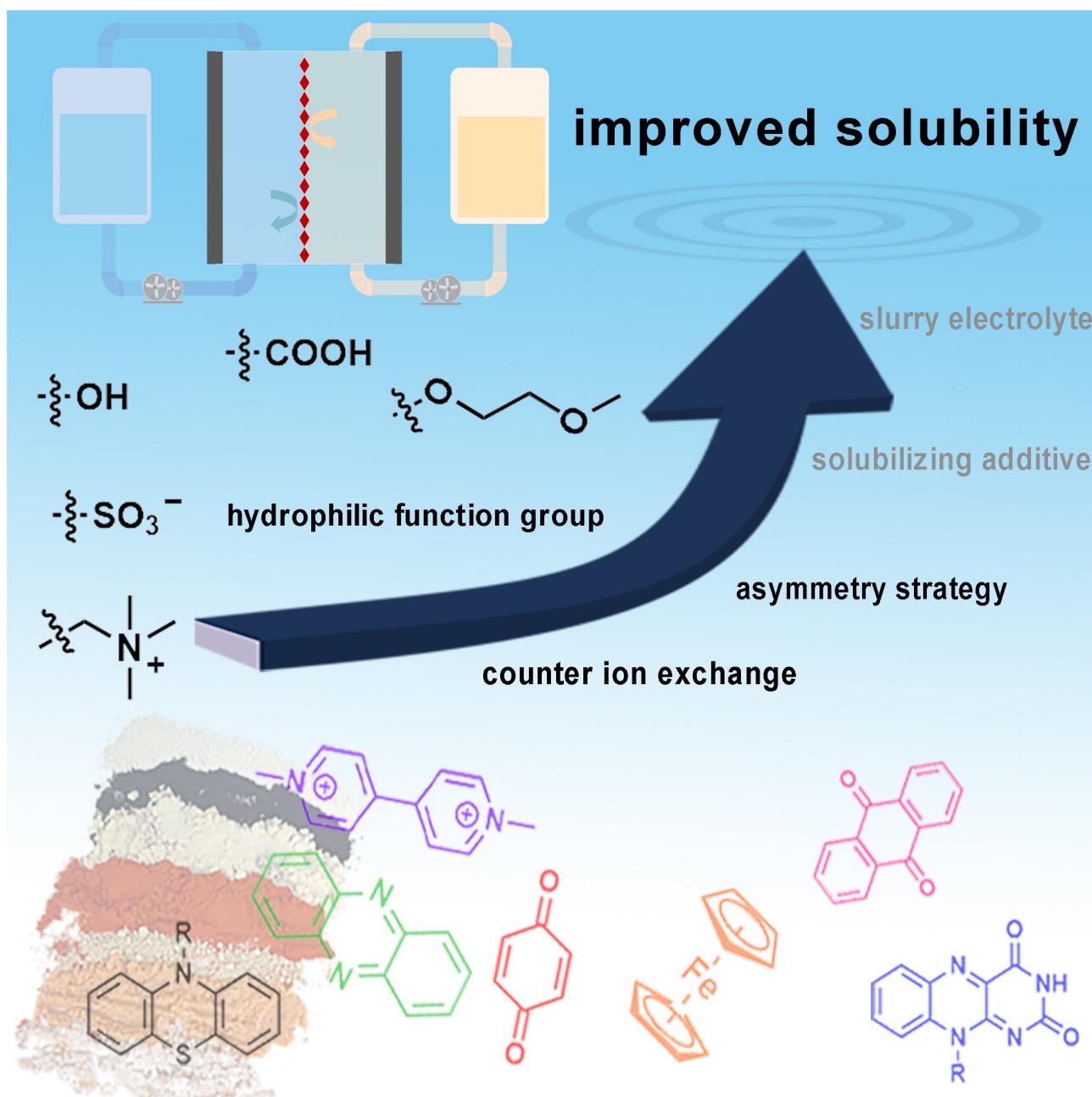


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Strategies for Improving Solubility of Redox-Active Organic Species in Aqueous Redox Flow Batteries: A Review

Xiao Wang,^[a] Rajeev K. Gautam,^[a] and Jianbing "Jimmy" Jiang^{*[a]}

Redox flow batteries (RFB) have emerged as one of the most promising technologies for large-scale energy storage owing to their high safety, long operation life, and decoupled design of energy and power. However, the problems of high cost and low energy density restrict their further development. The cost merit and tunable structure of organic redox-active materials have prompted the development of organic RFBs. The solubility of the redoxmer is recognized as a parameter that contributes directly to the energy density. Herein, we focus on strategies for

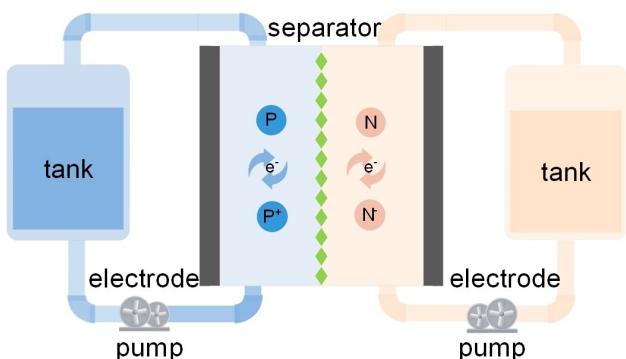
enhancing the solubility of organic redoxmers in aqueous RFBs. The effects of incorporating different hydrophilic functional groups on the solubility of the redoxmer and its effect on the performance of other batteries are systematically and exhaustively described. Other strategies, such as molecular symmetry tuning and employing more soluble counterions and cosolvents, are also summarized. The development trends and prospects for organic RFBs are also discussed.

1. Introduction

The conflict between the rapidly increasing energy consumption and environmental pollution caused by fossil fuels has prompted the utilization of environmentally friendly clean energy sources. However, despite their advantages, renewable energy sources, such as wind and solar energy, supply energy intermittently, as a major disadvantage. Large-scale energy storage technology can effectively realize smooth regulation of the power peak of the grid by stocking excess energy during peak power generation and utilizing the stored energy to offset power shortages when power generation is low or inaccessible.^[1] Redox flow batteries (RFBs) show bright prospects as candidates for large-scale energy storage.^[2] In RFBs, the active materials for energy storage and the electrodes for redox reactions are spatially separated, which not only enables decoupling of the power and energy, but also facilitates modular design and replacement of battery components.^[3] An electrochemical cell is usually composed of electrode materials, separator, and the redoxmer solution that flows through. Electrode materials are required to be electrochemically passive porous structures with large specific surface areas, such as carbon felt, carbon paper, metal foam, etc.^[4] The functions of the separator are to: (1) inhibit the crossover of redoxmer; (2) maintain the balance of the positive and negative charge of the battery via allowing for supporting ion transportation through the membrane; (3) avoid the internal short circuit of the battery.^[5] Positive and negative redoxmers dissolved in electrolytes are defined as catholyte and anolyte, respectively. These electrolytes are stored in the external tanks and driven by a peristaltic pump to electrochemical cells where the battery reaction occurs. During charging, oxidization reaction occurs on the catholyte. Meanwhile, the anolyte obtains electrons and become reduced. The reacted electrolytes then flow back to the tanks to complete the energy storage process (Scheme 1).^[6] The separate storage of positive and negative electrolytes also minimizes self-discharging during off-working times.^[7] The solution-based active materials used in RFBs significantly reduce the risk of detrimental dendrite growth on the electro-

des, and the flowing electrolytes dissipate the heat generated during the charging/discharging process to alleviate the safety concerns caused by the accumulation of heat.^[8] Compared with lead-acid and lithium-ion batteries, another exclusive feature of flow batteries is the high recyclability of the liquid electrolytes, which is conducive to offsetting the high cost and the environmental impact of future energy storage technologies.^[9]

In 1949, the concept of utilizing redox-active material solutions to store energy was first proposed in patents.^[10] Owing to the urgent demand for energy storage technologies on spacecraft, the National Aeronautics and Space Administration (NASA) explored a series of redox systems such as Fe–Cr, Br⁻/Br₃⁻, V²⁺/V³⁺, and V⁴⁺/V⁵⁺ in the 1970s; these systems now form the basis for various flow-battery systems.^[11] However, because of the serious lag in the development of ion exchange membranes, it was not until the 1980s that modern all-vanadium-based (VRFB) flow batteries were extensively studied and developed.^[12] VRFBs are considered the most competitive large-scale energy storage systems as they are generally fundamental understood and have a long lifetime, high efficiency, and lower risk of cross-contamination.^[13] Despite these advantages, VRFBs also suffer from drawbacks such as high cost (especially the vanadium electrolyte, which accounts for over 40% of the total cost), corrosion due to the strongly acidic electrolyte, and low energy density.^[14] Other RFB systems, such as iron-chromium, iron-titanium, vanadium-bromine, and polysulfide-bromine, have also been proposed and studied for decades; however, limitations such as poor reversibility, slow reaction rates, and crossover preclude their further application.^[14b,15] To alleviate these issues, organic redox



Scheme 1. Schematic view of a RFB system.

[a] X. Wang, R. K. Gautam, J. "Jiang

Department of Chemistry, University of Cincinnati
P.O. Box 210172, Cincinnati, Ohio 45221-0172, United States
E-mail: jianbing.jiang@uc.edu

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compounds have been proposed as alternatives to traditional inorganic electrolytes.^[1b,c,2c,16] Organic redox-active materials are potent candidates for flow battery electrodes, featuring high structural diversity and tunability, accessibility, and cost-effectiveness.^[17] Attempts have been made to break the electrochemical window of water by utilizing non-aqueous flow batteries employing organic solutions as electrolytes to achieve higher energy densities; however, the high cost, low ion conductivity, and safety issues associated with flammable organic solvents restrict their practical application.^[18] Compared to non-aqueous systems, water is non-flammable, inexpensive, and has a high dielectric constant and large dipole moment, leading to greater safety, cost-effectiveness, and high ionic conductivity of batteries in which it is used as a solvent.^[19]

The energy density of batteries is directly correlated with the battery voltage (V), electrolyte concentration (C), and number of electrons (n) involved in the reaction^[20] according to the well-accepted formula (energy density = $nCFV$, where F is Faraday's constant). To obtain a higher energy density, remarkable attention has been paid to molecular engineering strategies for improving the solubility of the redoxmer by introducing various solubilizing functional groups into the molecular framework.^[21] The effect of introducing solubilizing functional groups into the redox cores on the solubility of the redoxmer is phenomenal.^[22] For example, incorporating water-soluble groups such as NH_4^+ or SO_4^{2-} enhanced the solubility of anthraquinones (from $<0.03\text{ M}$ to $>1.9\text{ M}$) at neutral pH.^[22b,23]

Although the solubility aspect of redoxmers has been included in several review articles,^[4,20,22b,24] a comprehensive discussion and summary is still lacking. Herein, we review the effect of the solubility of redox species on redox flow batteries. First, the effects of various hydrophilic units on the solubility are discussed, after which other techniques for solubility enhancement, including intramolecular hydrogen bonding, ion-symmetry-breaking strategy, and optimization of counterions

are introduced. Perspectives for improving the solubility of redox materials while maintaining a high energy density and long cyclability in RFBs are then presented.

2. Incorporation of hydrophilic substituents

One of the most efficient ways to enhance the overall energy density of batteries is to increase the concentration of the redox species, where the concentration adjustment does not affect the cost of other battery components, such as the electrode, or the reservoir size.^[25] Thermodynamically, the dissolution of a substance can be regarded as a reaction, and the spontaneity of the reaction depends on the Gibbs free energy change of the process.^[26] According to the Gibbs free energy equation: $G=U - TS + pV=H - TS$, where U is the internal energy of the system, T is the temperature (K), S is the entropy, p is the pressure, V is the volume, and H is the enthalpy, the factors that affect the solubility are temperature, pressure, volume, the degree of disorder of the system (entropy), and the internal energy of the system itself.^[27] In terms of temperature, increasing the temperature reduces the Gibbs free energy, promoting dissolution. On the other hand, since the dissolution process of most solid solutes is endothermic (depends on the energy difference between endothermic (e.g., hydrate process) and exothermic (e.g., diffusion) process during dissolution), thus, in most cases, elevated temperature can be considered as a favorable condition for the dissolution process, according to Le Chatelier principle.^[28] While the effect of pressure on the solubility of gases is very significant, the relatively packed arrangement of molecules of solid or liquid solutes renders pressure less effective in dissolution. From the perspective of intramolecular energy, when the molecular interactions (including hydrogen bonding, ionic bonding, ion-induced dipole forces, ion-dipole forces, and Van der Waals



Xiao Wang received his Master's degree at Qingdao University of Science and Technology. He is now a Ph.D. candidate under the supervision of Professor Jianbing "Jimmy" Jiang at University of Cincinnati. His research mainly focuses on redox flow batteries.



Rajeev K. Gautam completed his Ph.D. from the Indian Institute of Technology Kanpur in Materials Science, where his focus was on the development of nanostructured materials for PEM Fuel Cells. Dr. Gautam received SERB-DST Young scientist fellowship in 2017 to conduct his research on vanadium redox flow batteries. Currently, he is working as a postdoctoral fellow in Dr. Jiang's group at the Department of Chemistry, University of Cincinnati and his research interests include aqueous and non-aqueous redox flow batteries, slurry batteries, and membrane-free biphasic batteries.



Jianbing "Jimmy" Jiang is currently an Assistant Professor in the Department of Chemistry at the University of Cincinnati. Dr. Jiang earned his B.S. from Jiangnan University in 2007 and M.S. from East China University of Science and Technology in 2010, working with Dr. He Tian. He obtained his Ph.D. from North Carolina State University (advisor: Jonathan Lindsey) working on tetrapyrrole compounds for energy applications. In 2015, he joined Yale University as a Postdoctoral Associate and then an Associate Research Scientist in the Department of Chemistry and Yale Energy Sciences Institute, working with Professors Gary Brudvig and Robert Crabtree on organometallic materials for small molecule activation and energy storage.

dispersion forces) in the solid state are weaker than the interactions between the solute and the solvent, high solubility can be achieved.^[22b,29] In addition, other physical properties such as polarity and dielectric constant also affect the solubility of compounds. Given the high polarity of water and the principle of "like dissolves like", polar molecules should be readily soluble in aqueous media.^[30] Essentially, polarity originates from the inhomogeneity of the net charge distribution; the greater the inhomogeneity, the higher the polarity. Completely uniform distribution renders no polarity. Dipole moment is the most commonly used indicator to measure the polarity of molecules, and its essence is the separation of positive and negative charge centers in the system. However, influenced by the symmetry of the molecule, in many cases, the dipole moment cannot accurately reflect the polarity of the molecule.^[31] For example, the pyrazine molecule composed of two carbon-carbon double bonds has small dipole moment due to the high symmetry, yet the net charge distribution on the molecular surface is actually non-uniform. However, it is the local non-uniformity, known as "local polarity", that endows pyrazine with high water solubility.^[32] The introduction of polar groups through chemical grafting can improve the overall water solubility of the compound. The high dielectric constant of water (80.1 F/m at 20°C) is another important property of water, which characterizes the strong ability of water to solvate solute molecules and separate ions.^[34] Because of the hydrophobic nature of organic compounds, the majority of unmodified redoxmers exhibit inferior solubility in aqueous media, thus incorporating a hydrophilic group increases the affinity of redox molecules and water, resulting in high solubility.^[4,14b,35] The discussion in this section is organized around different hydrophilic functional groups.

2.1. Sulfonate

The use of sulfonate to enhance the solubility of materials in water represents a common strategy in the design of new compounds.^[33b,36] Bentien et al. investigated the effect of different numbers of sulfonate units on the solubility of anthraquinone (AQ) (single substituent: AQS, double substituent: AQDS, Figure 1).^[22b] The general conclusion of that study is that greater sulfonation results in higher solubility in all pH ranges. The solubility changed from < 1 mM for underivatized anthraquinone to approximately 1 M for sulfonated anthraquinone. Notably, the number of sulfonic groups was not the only factor affecting the solubility. The solubility of anthraquinone is also affected by other properties such as the substitution site and counter ion. For example, AQS(2) (with a single sulfonic group) showed higher solubility than AQDS(1,8) and AQDS(1,5) (bearing two sulfonic groups). Systematic studies on sulfonate-modified anthraquinones were carried out by Aziz et al., and a similar conclusion was drawn, that is, introducing sulfonate groups increased the solubility of anthraquinones to approximately 1 M in acidic solution.^[1b,37] Due to the small size of the sulfonate unit, modification of the molecules had a negligible effect on the kinetic parameters (e.g., $3.81 \times 10^{-6} \text{ cm}^2/\text{s}$).^[1b,38]

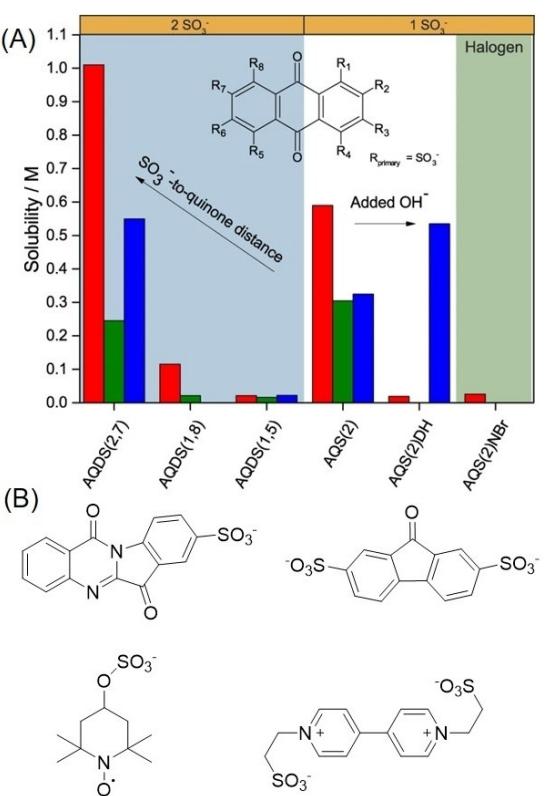


Figure 1. A) Solubility of sulfonated AQs. Solubility < 10 mM is denoted as zero. Numbering sequence of the substitution sites are indicated in the structures in the figure. Adapted from Ref. [22b]. Copyright (2016) The Author(s). Published by Springer Nature. B) Sulfonated redoxmers.

High electrochemical stability is another key aspect for ensuring satisfactory battery performance. Kosek et al. proposed and developed a method for evaluating the stability of batteries based on a combination of flow electrolysis cells and double half-cells, which enabled the electrochemical stability of the catholyte or anolyte to be independently explored at different states of charge (SOCs), and concluded that the sulfonated AQ electrolyte demonstrated excellent electrochemical stability at various SOC during battery cycling.^[39]

The solubility of other redox-active organic molecules can also be enhanced by incorporating sulfonate units.^[33a,c,d,36a-c,40] Examples include fluorenone (1.5 M in 2 M NaOH), tryptanthrin (1.28 M in 1.0 M KCl), viologen (1.1 M in 1 M KCl), and 2,2,6,6-tetramethylpiperidine-N-oxyl (1.0 M in 2 M ZnCl₂, Figure 1B).^[33] Owing to the relative stability of sulfonates, flow batteries adopting sulfonated redoxmers show high Coulombic efficiency and better cycle stability. Notably, the electron-donating nature of sulfonate shifts the potential of the redoxmer towards the positive direction. Thus, for negative electrode materials, introducing sulfonates results in potential loss.

2.2. Carboxylate

Carboxylate is the deprotonated form of carboxylic acid, and has a pKa of ~4.5,^[41] and presents high polarity, high ionization

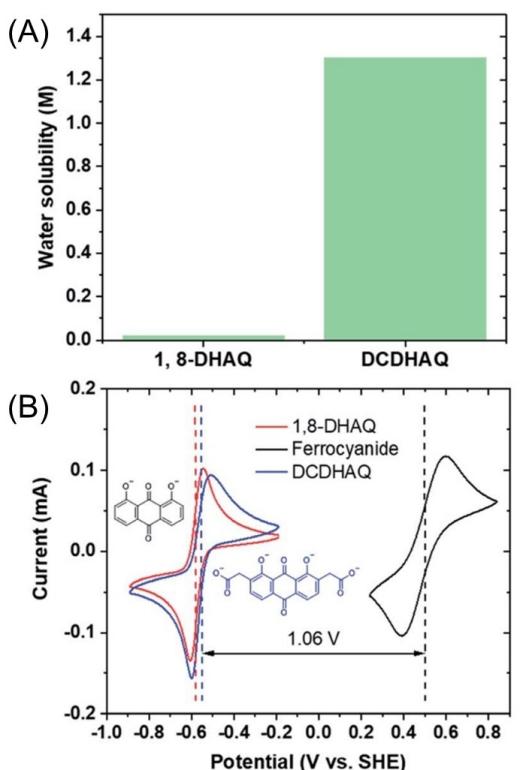


Figure 2. A) Comparison of solubility of 1,8-DHAQ and DCDHAQ in 1 M KOH. B) Cyclic voltammograms of 5 mM 1,8-DHAQ, 5 mM DCDHAQ, and 10 mM potassium ferrocyanide at pH 14 at a scan rate of 100 mV/s. Adapted with permission from Ref. [43]. Copyright (2021) Royal Society of Chemistry.

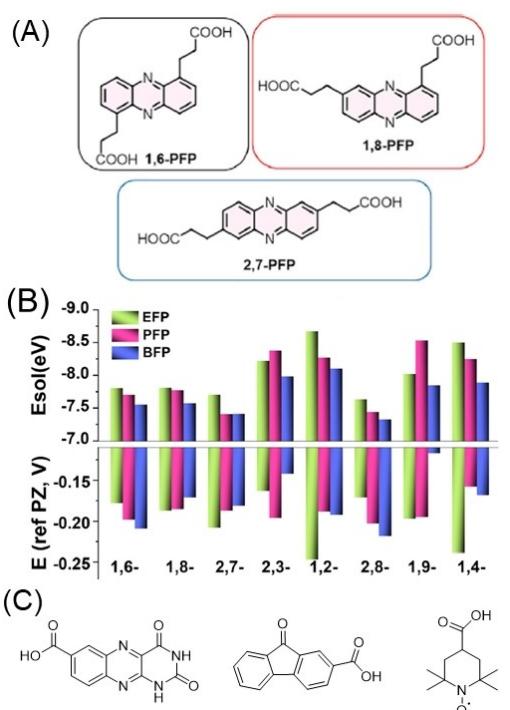


Figure 3. A) Structure of PFPs. B) Density functional theory (DFT)-calculated reduction potentials and solvation energies of phenazines. Adapted with permission from Ref. [44]. Copyright (2018) Elsevier Inc. C) Carboxylated redoxmers.^[47]

tendency, and ease of hydrogen-bond formation.^[42] Aziz and coworkers proposed dual carboxylate-modified 1,8-dihydroxyanthraquinone (DCDHAQ) to improve the redoxmer solubility and suppress the disproportionation reaction.^[43] The solubility of DCDHAQ increased by more than two orders of magnitude (from <0.02 M (1,8-DHAQ) to 1.3 M) in 1 M KOH (Figure 2A). Similar to sulfonate, the electron-withdrawing nature of carboxylate shifted the redox potential of the compound in the positive direction by ~20 mV (Figure 2B). The kinetic parameters of DCDHAQ (diffusion: 1.7×10^{-6} cm²/s, electron transfer rate constant: 7.4×10^{-4} cm/s, and charge transfer coefficient: 0.54) indicated that introducing carboxylate does not affect the redox kinetics of this compound. The resulting DCDHAQ-based battery had a low capacity fade rate of 0.03 % per day.

Phenazine has also been carboxylate-modified to enhance its solubility.^[44] Underivatized phenazine shows limited solubility in water and excellent redox electrochemical performance,^[45] and thus could be a promising RFB candidate if its solubility can be improved.^[46] Ji et al. prepared three phenazine compounds bearing two carboxylate units at different positions: 1,6-PFP, 2,7-PFP, and 1,8-PFP (Figure 3A). The solubility of the PFPs was evaluated using UV-visible spectroscopy. 1,6-PFP exhibits a solubility of 1.01 M in 1.0 M KOH at 25 °C, 1.20 M in 1.0 M KOH at 45 °C, and 1.02 M in water at pH 12 at 25 °C. 2,7-PFP affords a solubility of 0.84 M in 1.0 M KOH at 25 °C, 0.97 M in 1.0 M KOH at 45 °C, and 0.79 M in water at pH 12 at 25 °C. 1,8-PFP has the highest solubility of ~1.5 M in 1.0 M KOH at 25 °C, 2.05 M in 1.0 M KOH at 45 °C, and 1.09 M in water at pH 12 at 25 °C. Compared to unmodified PFP, carboxylation affords considerably higher solubility at different temperatures and pH. PFPs also exhibit excellent low permeabilities (10^{-13} cm²/s), fast kinetics (diffusion of the order 10^{-6} cm²/s, electron transfer rate constant of the order 10^{-4} cm/s), and negligible cell capacity fading (no capacity decay at 25 °C for over forty days). Theoretical simulations were employed to predict the redox potentials and solubility of the phenazine species, where the data were consistent with the experimental results (Figure 3B).

In addition to the extensive research on AQ and phenazine,^[38b,43,44,48] other organic compounds have been successfully carboxylated, including alloxazine,^[47a,b] fluorenone,^[47c] TEMPO,^[47d] and naphthoquinone,^[47e] which all demonstrate improved solubility and excellent chemical and battery performance (Figure 3C). Overall, due to the high polarity and strong solvation ability of carboxylate, the water solubility of carboxyl-substituted compounds is significantly improved.

2.3. Hydroxy

Owing to the high electronegativity of the oxygen atom, the single bond between oxygen and hydrogen is highly polar, promoting hydrogen bond formation and consequent enhancement of the water solubility.^[49] Hydroxyl groups are prone to dissociation in aqueous solutions, especially for phenolic hydroxy units under alkaline conditions. The applica-

tion of hydroxyl groups as water-solubilizing moieties in flow battery electrode materials has proven to be effective.^[2c,50] Wang et al. systematically studied the stability and solubility of various hydroxylated phenazine compounds.^[36d] All dihydroxyphenazine (DHP) regioisomers presented poor solubility in neutral water, but demonstrated improved solubility in an alkaline aqueous solution (Figure 4A). Hydroxylation of DHP at different sites resulted in different solubility properties in 1 M NaOH (Figure 4B). The solubility of 1,6-, 1,9-, and 2,7-DHPs was <0.10 M, whereas 1,3- and 1,4-DHP showed high solubility, with values of 0.28 M and 0.36 M, respectively. More surprisingly, 1,8- and 2,3-DHP showed high solubility (1.84 M and 1.60 M, respectively). The solubility of 1,3- and 1,6-DHP was significantly improved (moving from 0.28 to 1.61 M and 0.07 to 0.60 M, respectively) by changing the base from NaOH to KOH. In addition, all DHPs also exhibited excellent kinetics (diffusion on the order of 10^{-5} cm²/s order, electron transfer rate constant of 10^{-3} cm/s) and superb stability of the cell capacity.^[36d] Hydroxyl units can significantly increase the solubility of organic compounds under basic conditions, but their water-solubilizing capability is not as high under acidic or neutral conditions.^[22b] Consequently, instead of existing as a single substituent, hydroxyl is more often used in combination with other polar groups, such as quaternized amine,^[51] sulfate,^[2c] or carboxylate^[38b] to achieve high solubility.

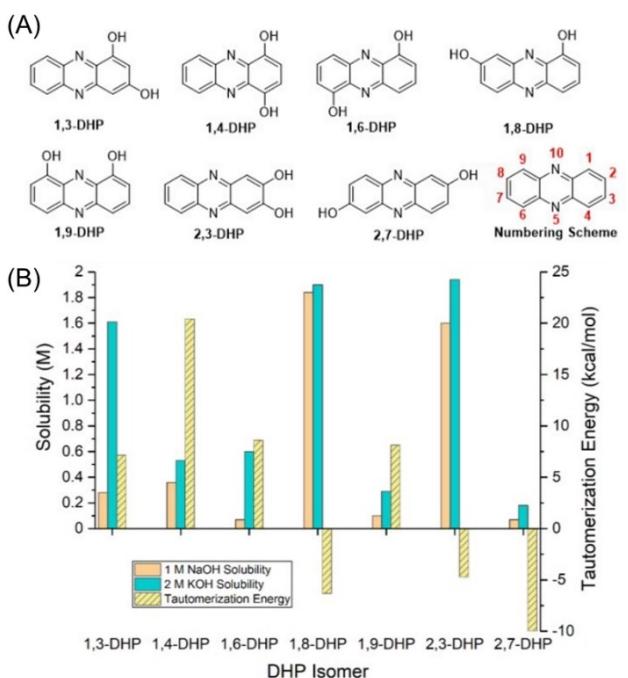


Figure 4. A) DHP isomers and numbering scheme of phenazine core. B) Solubility data for DHP isomers in 1 M NaOH and 2 M KOH, and tautomerization energy of 3,4-dihydro isomer (1,2-dihydro for 1,3-DHP and 6,7-dihydro for 1,8-DHP). Relative free energies of ring hydrogenated isomers (3,4-dihydro) are reported in comparison with that of 5,10-dihydro isomer. Adapted with permission from Ref. [36d]. Copyright (2021) Royal Society of Chemistry.

2.4. Phosphate

Compared with the ability to achieve high solubility under acidic or alkaline conditions, solubility enhancement under near-neutral conditions is highly challenging. Phosphate units can remain in their ionic state over a wide pH range, making phosphate an ideal pH-insensitive, water-solubilizing unit. In addition, the molecular polarity of phosphate is high, rendering phosphate one of the few bifunctional substituents.^[48a,50] Aziz et al. introduced phosphoric acid groups into anthraquinone and viologen molecules, and boosted the solubility of anthraquinone and viologen to 0.75 M and 1.23 M, respectively, in a slightly alkaline environment ($\text{pH}=9$).^[52] Both phosphate redoxmers exhibited similar kinetic parameters before and after modification (diffusion: 10^{-6} cm²/s for both electron redox processes, electron transfer rate constant: 10^{-3} cm/s for both electron redox processes). Owing to the mild aqueous conditions for battery cycling, the battery performance was greatly improved. With the use of phosphate anthraquinone, 97% of the theoretical capacity was maintained over 480 cycles, corresponding to an average capacity retention of 99.99964% per cycle.^[52] Nevertheless, the solubilizing effect of phosphate is inferior to that of other polar groups, such as sulfonic acid groups, carboxyl, and other strong polar groups.^[1b,38b,47b,48a,50] The pH buffering effect enables the phosphate-modified redoxmer to remain in a relatively neutral environment, which significantly reduces the corrosiveness of the electrolyte and improves the safety of the battery.

2.5. Poly(ethylene glycol)

As a non-ionic, polar, water-miscible solvent, ethylene glycol is highly hydrophilic because of its strong polarity (dipole moment >0.7) and high dielectric constant (37).^[53] Because of these characteristics, poly(ethylene glycol) (PEG), the polymeric form of ethylene glycol, exhibits strong affinity for water, which has led to the long-term use of PEG groups as solubilizing groups for drugs.^[54] Unlike most other strongly polar groups, the PEG chain, although extremely polar, does not dissociate in water (regardless of the PEG chain end group), enabling the use of neutral pH and less corrosive conditions for aqueous batteries. Jin et al. synthesized and evaluated a series of PEG-modified AQs with different substituent sites (Figure 5A). The solubility of the PEGAQs varied from 0.001 M to 1.2 M (Figure 5B): 1,4- and 1,8-PEGAQ are miscible with water; solubilities of ~ 0.5 M were observed for both 1,5- and 2,7-PEGAQ, whereas poor solubility of less than 1 mM was found for 1,2- and 2,6-PEGAQ under neutral conditions. The large solubility increase for 1,4-PEGAQ may be due to destruction of the molecular symmetry.^[55] 1,8-PEGAQ has high solubility (1.2 M in 1 M KCl), excellent redox reversibility, and fast kinetics (diffusion of 2.6×10^{-6} cm²/s).^[56] In a parallel study, Jiang et al. presented a series of AQ compounds with different PEG lengths: 3 (PEG3-AQ), 12 (PEG12-AQ), and 45 (PEG45-AQ) ethylene glycol units at the same substitution site (Figure 5c).^[17a] The solubility of these three analogous compounds differs. PEG3-AQ is the least

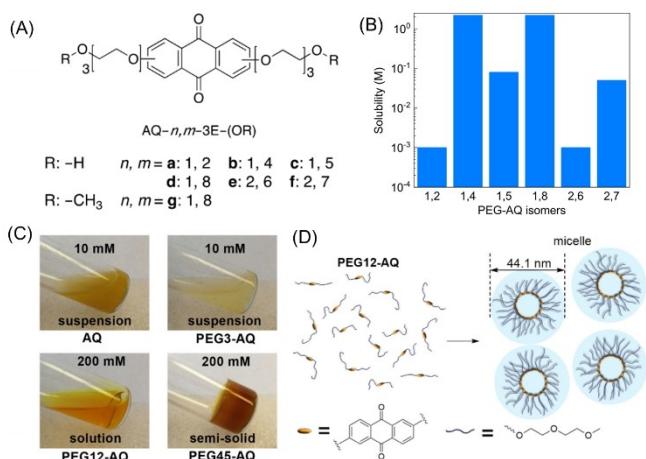


Figure 5. A) Structure of AQs with different substituent sites. B) Solubility of AQs with different substituent sites. Adapted with permission from Ref. [56]. Copyright (2019) American Chemical Society. C) Solubility of AQ, PEG3-AQ, PEG12-AQ, and PEG45-AQ in water. D) Micelle structure of PEG12-AQ with aqueous electrolytes. Adapted with permission from Ref. [17a]. Copyright (2020) Wiley-VCH.

soluble in water (less than 10 mM) due to the few polar PEG segments, whereas PEG12-AQ and PEG45-AQ are completely miscible with water under neutral conditions. However, longer PEG units also induced higher viscosity (Figure 5C), which could result in slow electrochemical kinetics and high pump loss.^[3b,57]

As one of the few neutral solubilizing groups, PEG units exhibit remarkable water-solubilizing capability. The flexible PEG chain also enables high tailorability of the redoxmer, increases the molecular size, which inhibits crossover, and forms colloids, thereby inhibiting decomposition of the compound (Figure 5D).^[58] The downside of introducing PEG units into the redoxmer is the increased electrolyte viscosity.

2.6. Quaternary amine

Isoelectronic with sodium ions, ammonium ions exhibit metallic properties similar to those of sodium ions, such as high dissociation in water, which benefits the water solubility.^[59] Hydrogen bonds between ammonium ions and water improve the affinity of each component for the other.^[60] Because of these properties, quaternary amines can dissociate in water and are compatible with organic frameworks, thus affording high water solubility and synthetic utility.^[61] Beh et al. adopted this strategy in studying bis(3-trimethylammonio)propyl viologen tetrachloride (BTMAP-Vi) as the anolyte and bis((3-trimethylammonio)propyl)-ferrocene dichloride as the catholyte (BTMAP-Fc) in aqueous RFBs (Figure 6A).^[62] The two positively charged quaternary ammonium groups exhibit extremely high water solubility. For instance, BTMAP-Fc has a solubility of 1.9 M in water at 20 °C, compared to the completely insoluble unmodified ferrocene (Fc). BTMAP-Vi has a similar solubility (2.0 M in water). Introducing quaternary ammonium groups not only maintains the fast kinetics of the redox reactions, but also improves the electrochemical stability of the redoxmers, as

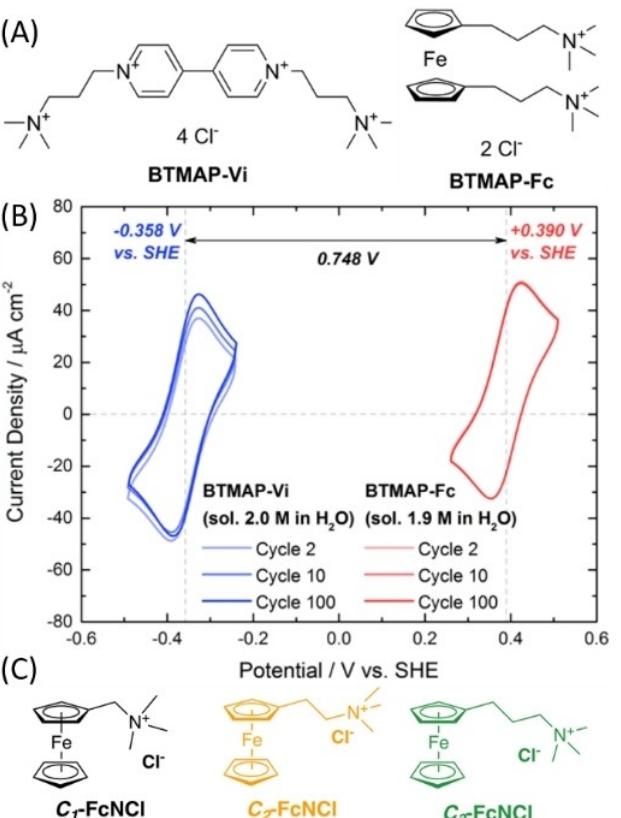


Figure 6. A) Structures of BTMAP-Vi and BTMAP-Fc. B) Cyclic voltammograms of BTMAP-Vi (blue trace) and BTMAP-Fc (red trace). Conditions: 1.0 mM in 0.5 M NaCl, 10 mV s⁻¹ sweep rate. The 2nd, 10th, and 100th cycles are superimposed. Adapted with permission from Ref. [62]. Copyright (2017) American Chemical Society. C) Structures of the Fc derivatives.^[63]

confirmed by long-term cyclic voltammetry (CV) tests (Figure 6B). In a separate study, Liu et al. systematically studied the effects of the linker length on the physicochemical properties, battery performance, and degradation mechanisms using the ferrocene molecular platform: (ferrocenylmethyl)trimethylammonium chloride (C1-FcNCl), (2-ferrocenyl-ethyl)trimethylammonium chloride (C2-FcNCl), and (3-ferrocenylpropyl)trimethylammonium chloride (C3-FcNCl) (Figure 6C). As the linker length increased, the water solubility decreased from 4.0 M for C1-FcNCl to 2.60 M for C2-FcNCl and 2.30 M for C3-FcNCl at room temperature.^[63] As a commonly used solubilizing group for redoxmers in flow batteries, quaternary ammonium groups have been successfully applied in a series of redoxmers, including viologen,^[62,64] bridged bipyridine,^[65] ferrocene,^[17b,62] TEMPO,^[16,64b,d] and anthraquinone.^[66] Substitution with the quaternary ammonium salt group enables adjustability and confers stable chemical and electrochemical properties, and low pH-dependence to the redoxmers.^[64a,c,d]

2.7. Other polar groups

In addition to the strongly polar substituents mentioned above, other substituents have also been explored for solubility enhancement.^[67] Song et al. introduced imidazole amidated TEMPO, where a huge solubility enhancement (from 0.3 M to 2.3 M) was achieved by introducing the methylimidazole group into acylamino TEMPO.^[68] The resulting conjugated structure also inhibited the ring-opening reaction of TEMPO, leading to enhanced battery performance. Yu et al. introduced amine groups into phenothiazine to achieve 1.5 M solubility in a mixture of acetic acid and sulfuric acid.^[21b] Similar to amino groups, most of these low-polar and non-ionized substituents are introduced as solubility regulators, as well as redox potential tuning units.^[21b, 67–69]

3. Counterion Effect

Distinct from the direct introduction of hydrophilic groups, the replacement of counter ions is an effective way to improve the solubility of ionic redoxmers. ^[23,70] A striking example is the use of ferrocyanide. The low solubility of $K_4[Fe(CN)_6]$ (~0.8 M in pH=7, ~0.40 M in pH=14) and $Na_4[Fe(CN)_6]$ (0.56 M in water) is a known hindrance to their applications.^[71] However, a mix $Na/K_4[Fe(CN)_6]$ solution has been investigated, leading to a higher concentration of ~1.5 M in pure H₂O and 1.0 M in alkaline medium. Nevertheless, such a design is not conducive to the stability of the battery, because the dynamic cation ratio

of Na/K during battery cycling affects the solubility.^[72] Luo et al. studied the same ferrocyanide system using a cation modulation method. The solubility of ferricyanide changes dramatically in the presence of other cations (NH_4^+ , K⁺, Na⁺). $(NH_4)_3[Fe(CN)_6]$ and $(NH_4)_4[Fe(CN)_6]$ show higher solubility of 1.6 M and 1.92 M, respectively, in aqueous solutions than the corresponding $Na_3[Fe(CN)_6]/Na_4[Fe(CN)_6]$ (0.56 M/1.2 M) and $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (0.72 M/1.31 M) counterions (Figure 7). When paired with a viologen anolyte, the battery exhibited nearly 100% capacity retention and 62.6% average energy efficiency over 1,000 cycles.^[71]

Other counter ion strategies, such as mixing metal ions or organic cations, have also been adopted in flow battery systems.^[36a,73] Theoretically, the solubility of most ionizable compounds can be improved by employing hydrophilic ions.^[23,66, 70]

4. Molecular Asymmetry

According to Carnelley's rule,^[74] the solubility of a molecule can be improved by reducing the symmetry of the entire molecule, for example, by introducing substituents at the asymmetric sites of the compounds.^[75] Following this symmetry reduction method, Li et al. dramatically increased the solubility of highly symmetric molecular $M_4[Fe^{II}(Dcbpy)_3]$ ($M=Na$ or K) to 1.22 M by introducing a second ligand, cyanide (Figure 8).^[75] In another study from the same research group, the same asymmetric strategy was also used to synthesize and evaluate highly soluble fluorenone compounds.^[33d] Yang et al. also found that for regioisomers, centrosymmetric molecules exhibit reduced solubility compared to their asymmetric counterparts.^[36d, 55, 56, 76] Except for the above-mentioned papers, there is a lack of systematic research on the effect of asymmetry on solubility, however, both theoretical calculations and actual measured results prove that asymmetric molecules have an advantage in solubility than symmetric ones.^[22a, 77] Therefore, the principle of asymmetry has important guiding significance for the synthesis of redoxmer, especially the substitution position of substituents or complexes.

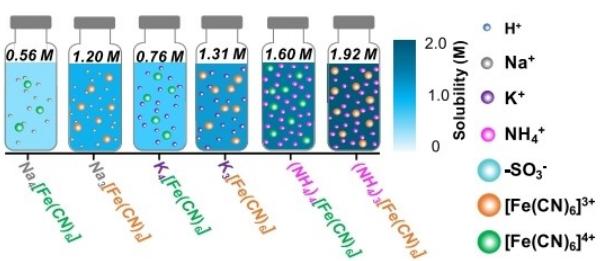


Figure 7. Diagrammatic representation of water solubility of ferrocyanide and ferricyanide salts. Adapted with permission from Ref. [71]. Copyright (2019) Elsevier.

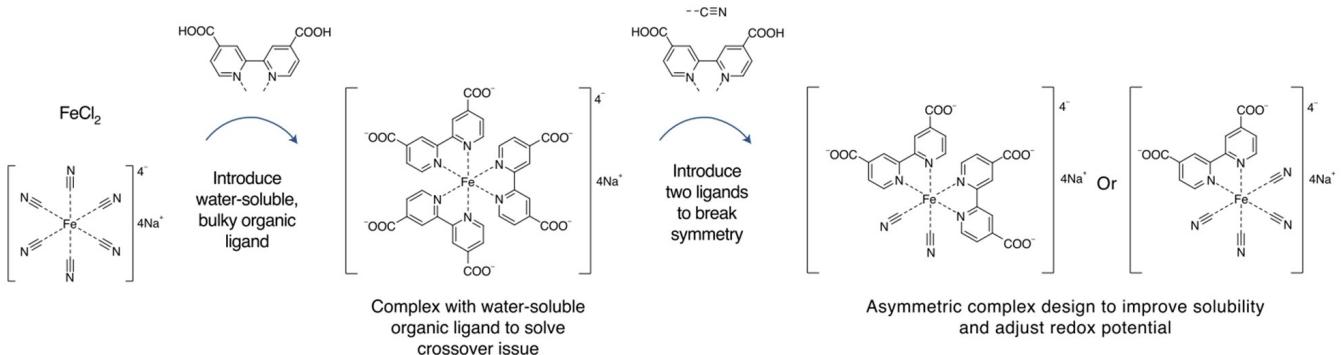


Figure 8. Strategy for rational design of asymmetric iron complex. Adapted with permission from Ref. [75]. Copyright (2021) Springer Nature

Table 1. Summary of different solubilizing strategies.

Strategies	Advantages	Disadvantages	Notes about vanadium flow battery
Incorporation of hydrophilic substituents	Tunability in redoxmer potential and pH environment; adjustable molecular size to suppress crossover	Additional synthetic efforts; increased viscosity caused by poly(ethylene glycol) chains	The introduction of hydrophilic groups is unlikely to occur in inorganic vanadium flow batteries; molecular tunability is one of the biggest advantages of organic RFBs.
Molecular asymmetry	Can be combined with other strategies	Additional synthetic efforts	
Counterion effect	Simple ion replacement; can be combined with other strategies	Not applicable for non-ionic compounds	Constrained by different valences of vanadium ions, counter ion replacement in VFB is limited to chloride and sulfate ions, which have little effect on solubility. ^[78]
Temperature	Easy to operate	Limited application	Solubilities of V ^{II} , V ^{III} , and V ^{IV} species increase under higher temperature. However, V ^V shows opposite trends. ^[79]
Additives	Low cost; easy to operate	Unclear mechanism	Organic or inorganic additives (ammonium, phosphate, hydrogen phosphate ^[80]) can be complexed with V ^V to act as a precipitation inhibitor to increase solubility

5. Summary and Perspective

Different strategies and concepts for improving the solubility of various redox organic species in aqueous media, including: (1) incorporating polar substituents, (2) enhancing molecule dissociation, (3) breaking the central symmetry of the molecule, and (4) employing hydrophilic counterions were summarized. Comparison of the advantages and disadvantages of various solubilization strategies benchmarking against commercial VFB is summarized in Table 1. The dominant strategy for solubility improvement is still the incorporation of hydrophilic ionizable groups. Owing to the individuality of redoxmer cores, solubility optimization typically involves tedious organic synthesis. The solubility can also be improved with the aid of additives. For example, the solubility of 2,7-AQDS increases from ~0.3 M to 0.8 M upon adding ethylene glycol (EG) and polyvinylpyrrolidone (PVP) to the electrolyte, facilitated by bond formation.^[81] Battery additives are widely utilized in several energy storage technologies (vanadium flow batteries,^[82] lead-acid batteries,^[83] and lithium-ion batteries^[84]), where their presence promotes battery performance without affecting battery reactions. Solubilizing additives build a bridge between the aqueous solution and the compound through amphiphilic molecules. While this strategy has a relatively low cost, one disadvantage of utilizing additives is the vague mechanism for performance enhancement. Currently, there is no in-depth research on solubilizing additives, whereas surfactants and amphiphilic and electrochemically stable organic solvents have great potential. Physical methods can also be used to improve the solubility of redox materials. As mentioned in Section 2, the main physical factors affecting the solubility are temperature and pressure. For RFB applications, most solutes are solid or liquid, thus the effect of pressure on solubility is insignificant. Temperature does have non-negligible influence on solubility. Ji et al. explored the solubility of phenazines at different temperatures, and found that at an elevated temperature (45 °C) the solubility of all phenazines increases.^[44] Schubert et al. also explored the stability of tailor-made ferrocene copolymer redoxmer at a high temperature of 60 °C,^[85] pioneering the study of wide-range-

temperature AORFB. For future development, theoretical calculations are required to pre-screen the target molecules.^[77,86] On the other hand, poorly soluble materials can also be utilized for slurry-based flow batteries, which has been successfully studied.^[87] In summary, to develop practical, high-concentration redox materials for RFBs, interdisciplinary research, including organic synthesis, material science, and computation, is urgently needed.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords: redox chemistry · redox flow battery · solubilizing · synthetic methods · water solubility

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