**A Nonaqueous Organic Redox Flow Battery Using Multi-electron Quinone Molecules**

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**Abstract**

Organic redox flow batteries are promising energy storage devices due to their moderately low-cost and scalability. This paper introduces a new multi-electron redox active material, tetra-amino[anthraquinone](https://en.wikipedia.org/wiki/Anthraquinone) (DB-1) that is capable of forming cations with an oxidation state of 4+, yielding one of the highest electrode potentials (up to 4.4 V *vs*. Li) and the largest multi-electron transfer (*ca.* 4 e). Computational calculations using density functional theory reveal that the DB-1 molecule has narrower HOMO-LUMO band gaps (< 3 eV) than similar molecules (> 3.9 eV). Stable charge-discharge cycling performance of this organic molecule is observed with high energy efficiencies (*ca.* 71 %) at a relatively high current density of 20 mA cm2 over 50 cycles, demonstrating the marked potential of DB-1 for future redox flow battery applications.

**Keywords:** energy storage device; multi-electron quinone molecule; organic redox flow battery; nonaqueous redox flow battery

**1. Introduction**

Renewable energy sources such as wind and solar are gradually replacing fossil fuels for electricity generation but the intermittency of wind and solar generation limits the mainstream adoption of these energy sources for power generation [1–6]. Redox flow batteries are a promising technology for grid scale stationary energy storage to complement renewable energy systems and have attracted interest from academic research and industrial development [7–9,10]. Unlike other energy storage technologies, RFBs offer a long life-time, decoupled energy (arbitrarily large storage volume and concentration) and power (electrode area), high round-trip efficiency, scalability and design flexibility, fast response, and low environmental impacts [4,11–19].

Since energy is stored in the active species contained in the electrolytes, the battery performance is strongly influenced by the properties of these redox-active components such as solubility, redox potential, chemical stability and cost [2,20]. The electrolyte cost per unit energy stored can be enhanced by maximizing the number of electron-transfers per molecule, the open circuit cell voltage (OCV), and the concentration of redox active material [2,12,21,22]. New redox species, having a higher solubility and electrode potential are being explored, but some are restricted in aqueous electrolytes due to the electrolysis of water [23,24]. In contrast, non-aqueous electrolytes enable higher energy density batteries by offering a wider potential window. Side reactions caused by electrolyte decomposition can be minimized and the use of high-energy active materials (e.g. metallic lithium) becomes possible for both electrode reactions. Replacing water with non-aqueous solvents may also improve the solubility of active materials and enable reactions with a higher number of electron-transfers [4,14,25–29].

In recent years, organic redox-active materials have received significant attention as they are abundant in nature, environmentally friendly, may offer the possibility of recycling, and can offer competitive electrochemical characteristics [2,6,26,30–33]. Quinones are among the most studied molecules in non-aqueous systems and several have been synthesized [10,14,15,32,34–39]. Their use in battery electrolytes has focused on achieving a high electrode potential and good solubility [26,33,36]. Most quinones undergo a 2e reduction to form anions (Scheme II) and the reduction route limits the electrode potentials to less than 3.0 V *vs*. Li in non-aqueous electrolytes [33,40–42].

Here, we introduce a quinone molecule for RFBs that presents multi-electron reactions at highly positive electrode potentials (> 3.0 V *vs*. Li). Unlike typical quinone molecules, the proposed aminoanthraquinone dye (Disperse Blue 1 (DB-1)) contains 4 amine groups in the side rings that enable the molecule to be positively charged by forming cations with an oxidation state of up to 4+ [43]. Density functional theory (DFT) calculations were used to better understand the electrochemical behavior of the active quinone molecules at different oxidation states. Voltammetric studies and DFT calculations demonstrated that this molecule was capable of forming both anions and cations at electrode potentials ranging from 1.7 to 4.4 V *vs*. Li, involving up to 6 electron-transfers. The proposed quinone chemistry in this work showed high energy efficiency (ca. 71 %) at high current density (20 mA cm-2) with nearly 100% capacity retention.

**2. Materials and methods**

**2.1. Materials**

Disperse blue-1 (DB-1) (Mw: 268.27 g mol-1), Bis(trifluoromethane) sulfonimide lithium (LiTFSI) (Mw: 287.1 g mol-1), b[enzoquinone](https://en.wikipedia.org/wiki/1,4-Benzoquinone) (BQ) (Mw: 108.09 g mol-1), [naphthoquinone](https://en.wikipedia.org/wiki/1,4-Naphthoquinone) (NQ) (Mw: 158.15 g mol-1), [anthraquinone](https://en.wikipedia.org/wiki/Anthraquinone) (AQ) (Mw: 208.22 g mol-1), tetramethyl piperidinyloxyl (TEMPO) (Mw: 156.25 g mol-1), phenylenediamine (PD) (Mw: 108.14 g mol-1), dimethyl sulfoxide (DMSO) (Mw: 78.13 g mol-1) and acetonitrile (Mw: 41.05 g mol-1) were supplied by Sigma Aldrich. Deionized (DI) water was obtained from a Zuez water purification system (specific resistance, 18.2 MΩ-cm).

**2.2. Density functional theory (DFT) calculations**

The molecular geometry optimization and excited state determination (reduced/oxidized) for various quinone-type molecules were performed by means of DFT calculations incorporating the Becke three-parameter Lee–Yang–Parr exchange correlation (B3LYP), hybrid functional and the 6-31+ G (d, p) basis set [43] in DMSO solvent. All DFT calculations were performed with the Gaussian09.

**2.3. Electrochemical characterizations**

Cyclic voltammetry was used to evaluate the electrochemical behavior of soluble active molecules in different electrolytes (DMSO and acetonitrile) using a potentiostat (PGSTAT302N, Metrohm AG) at potential sweep rates between 50 and 700 mV s-1. A three-electrode glass cell with 20 mL volume was used, where working electrodes were either platinum or glassy carbon. Counter and reference electrodes were platinum and silver, respectively. Potential measurements were transformed relative to the lithium electrode potential by adding 3.2 V to the reference electrode readings. This conversion was determined experimentally in DMSO solvent.

**2.4. Flow-cell charge-discharge experiments**

Acetonitrile and DMSO were evaluated as solvent for DB-1 based on the solubility and electrochemical properties. The solubility of DB-1 in DMSO was found to be around 1 M, however further work is needed to determine the solubility of the oxidized forms of DB-1. Qiao *et al.* [44] have been reported that *ca*. 3.9 M of the LiTFSI salt can be dissolved in DMSO, close to the 4 M that would be required in order to achieve full 4-electron charging of 1 M DB-1. In addition, DMSO is more stable than acetonitrile in the voltage window of CV experiments, as shown in Figures S5 and S6. For battery experiments (Figure S13), the cell was assembled in an Ar-filled glovebox. Two platinized titanium plates (Ti-shop Ltd., UK) were used as current collector. Graphite felt and Li foil (0.6 mm thickness, MTI, USA) were used as the working and counter electrodes, respectively, with a Nafion 115 membrane. A separated lithium foil was used as the reference electrode for the potential measurements of the half-cell. The battery was galvanostatically charged and discharged at a current density of 20 mA cm2 (2.5 cm2) at room temperature (22±1 oC) using a potentiostat (PGSTAT302N, Metrohm AG). The oxidized structure of the DB-1 molecule in the electrolyte were confirmed by nuclear magnetic resonance spectra (1H NMR) using a Bruker AVANCE 400 MHz spectrometer by dissolved the dried powders (vacuum-drying of charged electrolytes) in deuterated acetone. The N+= bond was determined by FTIR spectra using a FTS 3500 spectrometer.

**3. Results and discussion**

The oxidation routes of aminoanthraquinones (2e) have been demonstrated elsewhere(i.e. Disperse Violet-1 (DV-1) [45], Disperse Blue-134 (DB-134) [46,47]) and shown more positive electrode potentials (> 3.5 V *vs*. Li) than most quinone molecules. When the 4e oxidation processes (Q → Q4+, Scheme I) are considered, the proposed molecule has one of the most positive electrode potentials (*ca.* 4.0 V *vs*. Li) and theoretical charge capacity (*ca.* 399.6 mA h g1) reported to date (Figure 1a). Together with the typical 2e carbonyl reduction route of quinones (Q → Q2 , Scheme II), the DB-1 molecule could involve up to 6e transfers (proposed as Scheme I and II, detailed version available in Figure S1) resulting in a very high theoretical specific capacity of *ca.* 599 mA h g1.

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Scheme I. The oxidation of DB-1: Formation of a radical cation and divalent cation through the oxidation of the DB-1.

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Scheme II. The reduction of DB-1: formation of a radical anion and divalent anion through the reduction of DB-1.

Since metallic lithium has the most negative electrode potential (−3.0 V *vs*. SHE) and the highest specific capacity (*ca.* 3,842 mA h g1), it would be advantageous to combine these high-energy electrode reactions together to form a lithium-organic hybrid flow battery. This battery concept takes advantage of the scale-up characteristics of RFBs and the high energy density of Li-ion batteries [32,48–51],[52]. In reported hybrid systems of this type, excess lithium metal was often used and underwent lithium electrodeposition-dissolution, while liquid phase (or sometimes semi-solid) active electrolytes based on organic species were used as the positive electrode reactions [32,40,48,51].

The electrochemical properties and feasibility of DB-1 at several oxidation states were evaluated using DFT calculations and compared with other similar organic molecules, such as BQ, NQ, AQ, TEMPO, and PD. For both experiments and mathematical calculations, DMSO was selected as a solvent due to its relatively high dielectric constant (*εr* = 46.7), which is beneficial to both solubility of the redox species and ionic conductivity of the electrolyte. Higher concentrations of DB-1 (*ca.* 1.0 M) could be dissolved in DMSO compared to other non-aqueous solvents (e.g. acetonitrile: < 0.1 M). In the recent work of Brushett and co-workers[14], DMSO was reported to have superior ionic conductivities to conventional carbonate electrolytes (e.g. propylene carbonate), including both supporting liquid electrolytes and ion-exchange membranes.

Through DFT calculations, the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) of the above molecules were calculated in DMSO, as shown in Figure 1b. The energy values of these orbitals calculated for other organic molecules are similar to those reported in the literature [40,46,53]. These HOMO and LUMO contours predict the favoured oxidation and reduction sites within the molecular structures, respectively. It can be seen that DB-1 remained stable at oxidation states of up to 4+ before further oxidation is expected on the peripheral amino substituents. A small HOMO-LUMO gap reveals a smaller energy required for the oxidation and reduction processes, which are often associated with faster reaction kinetics and thus smaller electrode overpotentials. At various oxidation states, DB-1 shows a narrower HOMO-LUMO gap (< 3 eV) than other similar molecules (> 3.9 eV), indicating its suitability for use as an active material for battery applications.

The electrode potentials of these molecules can be further validated with the LUMO energy levels, which have been shown to have a linear correlation with electrode potential for molecules with similar reaction mechanisms (Figure 1c) [40,46].The electrode potential of the DB-14+/DB-12+ redox couple was calculated to be 4.4 V *vs*. Li (Figure 1c), which is even more positive than those for molecules containing electropositive nitrogen centre cations, e.g. TEMPO+ and PD2+. The typical electrode potential of ‘quinone’ reaction of DB-1/DB-12 was more negative than most quinone molecules, i.e. BQ, NQ and AQ, due to the incorporations of amino groups and the high degree of aromaticity [40,43,45,52].

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| Figure 1. | a) Comparison of the upper potential limit of redox active materials versus theoretical capacity (Ah/kg) for reported organic batteries (RFBs and Li-ion batteries). The molecular orbital energy levels of DB-1 and other similar organic molecules obtained by DFT calculations in DMSO solvent; b) HOMO and LUMO energy levels; c) LUMO energy as a function of the electrode potential for molecules (Qn-2/ Qn, 0 ≤ n ≤ 4) where reduction is occurring on O= or N+= groups. HOMO and LUMO distributions of DB-1 for the oxidation and reduction sites are available in Figure S2. |

In general, the electrode potentials of DB-1 (or other molecules) tended to increase with its (or their) oxidation states. The total charge of these atoms was equal to the overall oxidation state of the molecule or ion. The charge distributions (Mulliken calculations) of DB-1 molecules at oxidation states from 2− to 4+ are presented in Figure 2a. When the DB-1 was oxidized to cationic forms, the highest positive charge density is concentrated in the carbon atoms of the central ring, rather than those adjacent to the nitrogen atom as reported in DB-134 [46]. The other atoms were only slightly more positive than those at lower oxidation states.

Electrostatic potential (ESP) was used to rationalize the likely interactions of the DB-1 molecule with the electrolyte counter ions in the oxidation (TFSI) or reduction (Li+) processes. ESP itself corresponds to the attraction / repulsion of protons by the concentrated electron density in the molecules. Consistent with Mulliken charge distribution, the ESP contour mapping (Figure 2b) showed that the regions close to the centre of the molecule had more negative and positive ESPs upon reduction and oxidation, respectively. The calculated charge and ESP were even more positive than those regions adjacent to the N+ atoms in the oxidation reaction (scheme I). The positive regions (surface) tended to interact with Li+ and bis(trifluoromethane) sulfonimide (TFSI) ions in the DMSO electrolyte. The magnitudes of these intermolecular attractive forces increased significantly with the oxidation state, and eventually reached up to +0.55 a.u. at the oxidation state of 4+. The resulting structure of the oxidized DB-1 molecule with TFSI salt was confirmed experimentally by 1H NMR spectroscopy in deuterated acetone (Figure 2c). The chemical shift of protons within the amine groups (from 2.68 to 3.21 ppm) indicated the reduced electron density in the hydrogen orbital, suggesting more positive charges in those regions. The formation of the N= group of the oxidized molecule was also confirmed by Fourier transform infrared (FT-IR) spectra, with an adsorption band at *ca.* 1690 cm−1 (Figure S15).

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| Figure 2. | a) Mulliken charge distribution and b) Electrostatic potential (ESP) distribution for the DB-1 molecule in the reduced, neutral, and oxidized states obtained by DFT calculations in DMSO. Enlarged figures of Mulliken charge distribution of DB-1 are available in Figure S14. c) 1H NMR spectra of the neutral DB-1 and the oxidized DB dissolved in deuterated acetone with LiTFSI salt. |

Once the oxidation route of the DB-1 molecule (Q → Q4+) had been confirmed by the mathematical DFT calculations (Table S1), the electrochemical properties of DB-1 were evaluated by cyclic voltammetry and compared with other organic molecules in DMSO (Figure 3a). For the typical 2e reduction processes (Q → Q2-) attributed to the two carbonyl groups, two quasi-reversible peaks were observed. The electrode potentials shifted towards more negative values with the number of aromatic rings (from BQ to AQ) and the incorporation of amine groups [40,43,46], as discussed earlier in the DFT study. However, the amine group containing a nitrogen atom also enables the molecule to be oxidized, providing a positive charge. As shown in Figure 3b, the number of quasi-reversible peaks observed at more positive electrode potentials (> 3.2 V *vs*. Li) was related to the number of nitrogen atom within the selected molecules (TEMPO and PD) [40,45,46]. For the hypothesized oxidation route of the DB-1 molecule (Q → Q2+→ Q4+), a number of overlapping quasi-reversible peaks were observed, indicating multi-electron transfers of at least 3 electron-transfers at highly positive electrode potentials from 3.2 up to 4.4 V *vs*. Li.

In these potential regions, the reduction and oxidation processes of the DB-1 molecule were also evaluated individually at various scan rates between 50 and 700 mV s1, as shown in Figure 3c. From this data, linear relationships between the peak current and the square root of the scan rate were observed (Figures S3 and S4), indicating that reactions were controlled by the diffusion of DB-1 molecule in the electrolyte [40,46]. The proposed multiple oxidation states of the DB-1 molecule were further demonstrated by sweeping the electrode potentials from the open-circuit potential (3.5 V *vs*. Li) to a wide range of electrode potentials (1.7 to 4.7 V *vs*. Li) spanning the reduction and oxidation processes. It can be seen that the DB-1 molecule exhibited more than 5 electron-transfers as characterized by a number of distinct peaks observed in Figure 4c, consistent with our hypothesis (Scheme I) and the DFT calculations. This voltammogram obtained using a DMSO solvent and glassy carbon electrode had superior electrochemical behaviour to those using acetonitrile (Figure S6) and a platinum electrode (Figure S7). For example, faster kinetics and more reversible reactions were observed in DMSO than in acetonitrile solvent, while platinum had a tendency to oxidize the electrolyte at highly positive electrode potentials (*ca.* 4.0 V *vs*. Li).

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| Figure 3. | a) Cyclic voltammograms of quinone molecules containing two carbonyl groups in the negative electrode potential at 100 mV s1 scan rate. b) Cyclic voltammograms of organic molecules contain amine group in the positive electrode potential at 100 mV s1 scan rate. c) Cyclic voltammograms of DB-1 for lower (left side), higher (right side) voltage ranges, at scan rates of 50 – 700 mV s1, and for a wide voltage window of 1.7 – 4.7 V *vs.* Li at a 100 mV s1 scan rate (bottom). Experimental conditions: 10.0 mM of each organic molecules in DMSO and 1.0 M LiTFSI, glassy carbon working electrode, platinum wire counter electrode, and an Ag wire reference electrode (+3.2 V *vs*. Li). |

Although fast, reversible electrochemical kinetics were not observed in the CV data, the multiple electron transfers and potential range indicate that DB-1 is a promising redox species with relatively high charge and energy storage capacity. To exploit the energy content of the DB-1 molecule and obtain a high cell voltage, the galvanostatic charge-discharge performance of a DB-1 positive half-cell was evaluated in a divided cell architecture with a lithium metal anode (Figure 4a), using a DB-1 concentration of 80 mM in the highly positive potential region (> 2.0 V *vs*. Li). This study focuses on this positive electrode potential region, aiming to achieve a high mean cell voltage in discharge trials [32,49–51]. The experiments were conducted at a constant current of 50 mA through a 2.5 cm2  area electrode in this highly positive potential region to assess the 4 electron-transfer per molecule at very positive electrode potentials (Figure 4b). The Li|DB-1 hybrid battery showed an open-circuit voltage of 3.5 V and delivered a stable discharge capacity (*ca.* 111 mA h) over 50 cycles at a current density of 20 mA cm2. The current density was higher than most non-aqueous systems (< 20 mA cm2) [12,14,29,53] ,with active species concentration comparable to recent systems (Table S2)[8,12,32,40,48,51,55,56].

In spite of the relatively poor kinetics observed from the CV with a glassy carbon electrode, the battery performance suggests that fast electrochemical kinetics were obtained for the 4-electron transfers for DB-1 during charge-discharge cyclings, which used a high-surface-area electrode graphite felt electrodes. Electrochemical kinetics are very sensitive to the electrode material, and the battery test results suggest that the graphite felt was able to achieve fast, reversible kinetics for the DB-1 redox reactions. Over 50 cycles, the efficiencies remained steady with an average coulombic efficiency of *ca.* 99 %, voltage efficiency of *ca.* 71 %, and energy efficiency of *ca.* 71 %, as shown in Figure 4c. Despite the relatively high current density (20 mA cm2), these efficiencies were similar to those of other non-aqueous RFB systems. Capacity retention was nearly 100% (Figure 4d), demonstrating superiority over many other non-aqueous systems that showed continuous capacity fading during prolonged cycling [2,4,51]. The resulting energy density was *ca*. 22 W h L1 (80 mM DB-1) and could be further increased at higher DB-1 concentrations. Considering a 6 electron-transfer and a molar mass of 268.27 g mol1, the theoretical capacity was estimated as 599.6 mA h g1. About 62% of this value has been achieved, which was equivalent to almost a 4-electron transfer, as reflected by the selected potential range (2.6 to 4.35 V *vs*. Li) identified in the voltammogram (Figure 3c). Comparison of the cell performance with other recent non-aqueous systems has been summarized in Table S3.

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| Figure 4. | a) Schematic illustration of Li-organic RFB. b) Representative charge-discharge voltage and current curves versus time (at 80 mM DB-1, 14-15 mL). c) Plot of battery performance: coulombic efficiency, voltage efficiency, and energy efficiency versus cycling numbers d) Charge-discharge capacity and capacity retention versus cycling number. Supporting electrolyte: 1.0 M LiTFSI in DMSO; Nafion 115 cation membrane; current density: 20 mA cm-2 (50 mA) |

**4. Conclusions**

In summary, this study describes a systematic evaluation of DB-1 as a redox active material for energy storage applications by means of electronic structures, electrochemical properties, and flow cell studies. Computational modeling using DFT-based calculations revealed that the incorporated amine and carbonyl groups in DB-1 can be oxidized and reduced to multiple cationic and anionic forms. Voltammetric studies and DFT calculations (in DMSO solvent) demonstrated that this molecule (theoretical specific energy: 1,858 W h kg-1) was capable of forming both anions and cations at electrode potentials ranging from 1.7 to 4.4 V *vs.* Li, involving up to 6 electron-transfers and exhibiting one of the highest electrode potentials (up to 4.4 V *vs.* Li) in the literature. Since these quinone derivatives can be extracted from organic raw materials, the proposed organic RFB system provides an environmental friendly and more sustainable option for grid-scale energy storage applications compared to metal based redox systems. By assessing the 4 electron-transfer per molecule at highly positive electrode potential regions (2.0 – 4.4 V vs. Li), the proposed chemistry in this work showed average high energy efficiency (*ca.* 71 %) at high current density (20 mA cm2) with nearly 100% capacity retention. These results reveal that DB-1 is a promising redox active material for RFBs applications.

**Supporting Information**

The Supporting Information provides numerical modeling and DFT calculation details, experimental methods, electrochemical analysis, and characterization figures, tables for additional electrochemical and structural analyses (PDF).

**Notes**

The authors declare no competing financial interest.

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