An Organic Super-Electron-Donor as a High Energy Density Negative Electrolyte for Nonaqueous Flow Batteries

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An Organic Super-Electron-Donor as a High Energy Density Negative Electrolyte for Nonaqueous Flow Batteries

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A highly reducing diquat-type molecule was explored as a negative electrolyte for nonaqueous redox flow batteries. The molecule displays a highly negative 2+/0 reduction potential of -1.67 V (vs. ferrocene), a low mass per electron transferred, and good solubility in CH_3CN in both redox states. Moderate capacity retention is observed during electrochemical charge-discharge cycling. A pathway for decomposition during electrochemical cycling is elucidated, and this provides a clear path forward for enhancing stability.

The deployment of wind and solar power as a significant fraction of the energy supplied to the electrical grid will require energy storage on a very large scale, and redox flow batteries (RFBs) are a promising technology for inexpensive large-scale stationary storage.[1–3] Current commercial RFBs are based on aqueous solutions containing inorganic redox species such as vanadium, zinc-bromine, and iron.[4] In contrast to these inorganic species, organic molecules afford the opportunity to modify molecular structure to tune redox potential, stability, and solubility.[5,6] Herein we explore the RFB-relevant properties and electrochemical cycling behaviour of an “organic super-electron-donor” first reported by Murphy and coworkers.[7]

Methyl viologen (Fig. 1) is a redox-active organic molecule that undergoes reversible reduction in two single-electron steps from the dication to the neutral molecule.[8] Methyl viologen and its analogues have been extensively explored as negative electrolytes, or “negolytes” (the redox-active materials for the negative electrode), in both aqueous and non-aqueous redox flow batteries.[9–14] The related molecule diquat (Fig. 1) is based on 2,2′-bipyridine rather than 4,4′-bipyridine, and it too has been studied as a flow battery negoltye.[15] Finally there is a known molecule related to diquat with an extra methylene group bridging the nitrogen atoms (diquat′ in Fig. 1). All three of these molecules undergo two single-electron reductions at the following reported potentials ($E_{1/2}$ in acetonitrile vs. ferrocene$^{+/0}$): methyl viologen, -0.83 V and -1.25 V[8]; diquat, -0.75 V and -1.24 V[16]; diquat′, -0.95 V and -1.26 V.[17] The presence of two reversible redox events is highly desirable for application in RFBs, as this enables the storage of two electrons per molecule, thus facilitating the creation of high energy density batteries. However, the application of these molecules in RFBs is limited by three factors. First, their redox potentials are relatively high compared to state-of-the-art negolytes, which have potentials as low as -2.34 V vs. ferrocene$^{+/0}$.[18] Thus, viologen derivatives with lower redox potentials would be highly desirable. Second, the separation between the two redox potentials is relatively large, which results in a ~ 0.4 V step-down in voltage during battery discharge when both redox events are utilized. The ideal RFB negolyte would undergo multi-electron reduction at the same redox potential. Finally, it is necessary that all oxidation states of a redox couple have high solubility in the solvent/electrolyte system used in a flow battery, and this is limited for the viologens and diquat. For example, experiments in our laboratory have shown that the radical cation methyl viologen$^{\cdot+}$ PF_6^- has a solubility of less than 0.05 M in CH_3CN/$[NBu_4][PF_6]$.

We hypothesized that the bis(dimethylamino) derivative of diquat′, **M**$^{2+}$/**M** (Fig. 1), could potentially address all three of these issues, and thus serve as an attractive RFB negolyte. Compound **M** was originally designed by Murphy and coworkers as a reducing agent for synthetic organic reactions.[7,19,20] The strongly electron-donating dimethylamino groups shift the reduction potential to -1.69 V (in DMF, vs. ferrocene$^{+/0}$).[7] Furthermore, reduction occurs in a single, two-electron step from the dication directly to the neutral molecule. While the solubility of **M**$^{2+}$/**M** has not been reported, we hypothesized that the dimethylamino substituents could significantly enhance solubility relative to methyl viologen and diquat. We report here a detailed exploration of the solubility, cyclic

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Electronic Supplementary Information (ESI) available: Experimental details, charge-discharge curves, post-cycling CV and NMR spectrum, NMR spectra after stability tests. See DOI: 10.1039/x0xx00000x

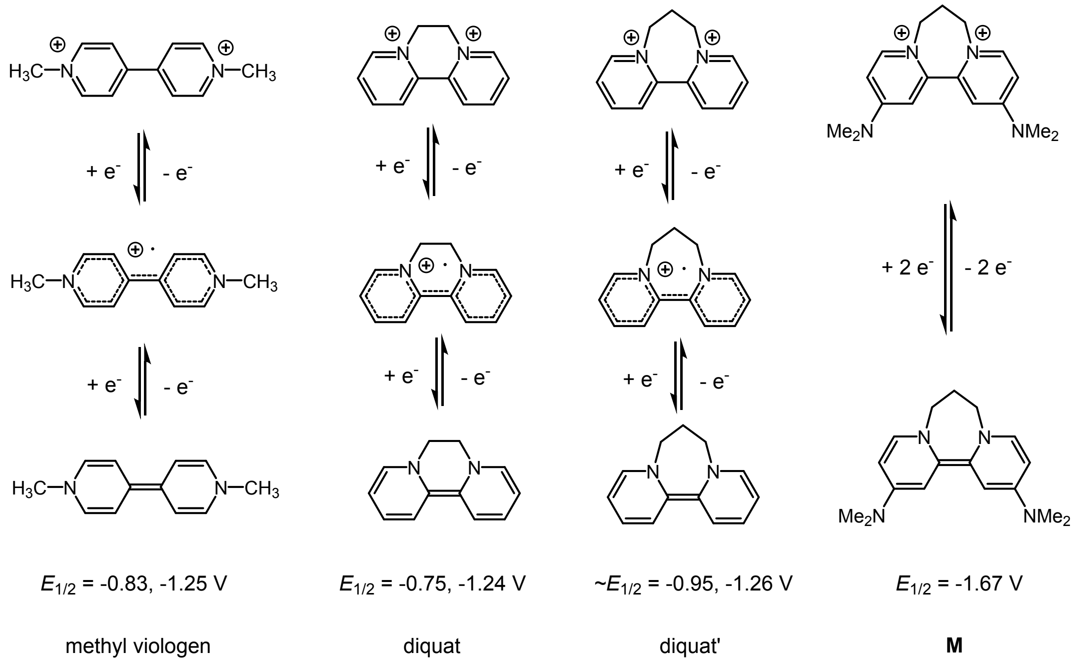
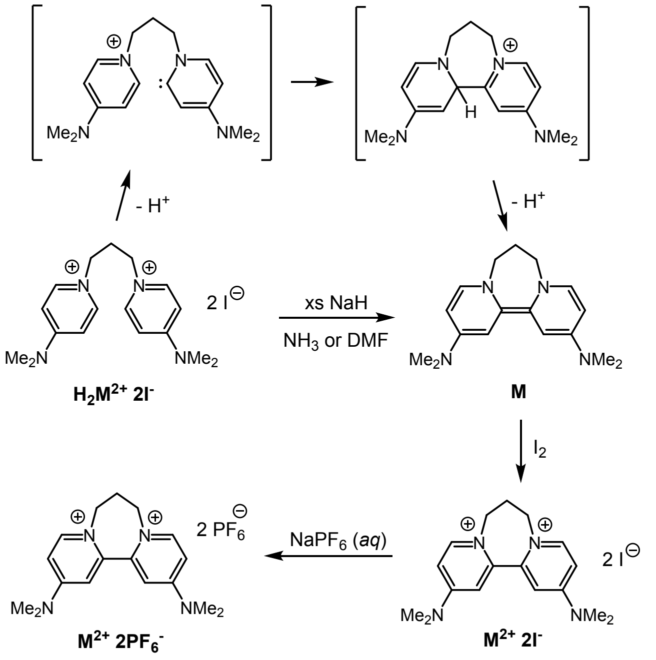


Fig. 1 Redox processes of methyl viologen, diquat, diquat′, and **M**, with their respective redox potentials in CH_3CN (vs. $Fc^{0/+}$).

voltammetry, and charge-discharge cycling of $\mathbf{M^{2+}/M}$ to assess its suitability as an negolyte for RFBs.‡



Scheme 1 Synthesis of **M** and $\mathbf{M^{2+}}$, including the mechanism of the formation of **M**.

Compound **M** and $\mathbf{M^{2+}[PF_6]_2}$ were synthesized using literature procedures.[7,21] As summarized in Scheme 1, this involves the deprotonation of the open-chain dication $\mathbf{H_2M^{2+}\,2I^-}$ with NaH to afford a transient carbene intermediate, which then undergoes a cyclization and second deprotonation to afford **M**.[7,19] The dication $\mathbf{M^{2+}}$ is then accessed via the oxidation of **M** with I_2 (to form $\mathbf{M^{2+}\,2I^-}$), followed by ion exchange with $NaPF_6$ to yield $\mathbf{M^{2+}[PF_6]_2}$.[21]

We first evaluated the solubility of **M** and $\mathbf{M^{2+}[PF_6]_2}$ in acetonitrile, the most common solvent for non-aqueous RFBs. Solubility tests of **M** were carried out in a nitrogen-filled glovebox, while those of $\mathbf{M^{2+}[PF_6]_2}$ were conducted under ambient atmosphere. Calibrated volumes of saturated solutions were evaporated to dryness, and the mass of the residue was measured to determine solubility. These experiments revealed solubilities in CH_3CN of 0.70 M for **M** and 0.60 M for $\mathbf{M^{2+}[PF_6]_2}$. Because $\mathbf{M^{2+/0}}$ can serve as a two-electron couple, the limiting solubility of 0.60 M for $\mathbf{M^{2+}[PF_6]_2}$ in CH_3CN corresponds to a maximum theoretical Faradaic concentration of 1.20 M and a capacity of over 32 Ah·L^{-1}, which is comparable to recently reported high-concentration organic active materials in nonaqueous flow batteries.[18,22–24]

Cyclic voltammetry (CV) experiments were conducted on $\mathbf{M/M^{2+}}$ in the RFB-relevant medium of 0.5 M NBu_4PF_6 in CH_3CN. The experiments used a 5 mM solution of $\mathbf{M^{2+}[PF_6]_2}$ with a glassy carbon working electrode and a scan rate of 100 mV/s. Under these conditions, $\mathbf{M^{2+}[PF_6]_2}$ shows a single reversible two-electron reduction to **M** at $E_{1/2}$ = -1.67 V vs. ferrocene$^{+/0}$, which is very similar to that reported for $\mathbf{M^{2+}[PF_6]_2}$ in DMF ($E_{1/2}$ = -1.69 V).[21] To preliminarily assess the electrochemical stability of $\mathbf{M^{2+}[PF_6]_2}$, CV cycling through the $\mathbf{M^{2+/0}}$ couple was repeated 10 times. As shown in Fig. 2, no significant change in current was observed from cycle 2 to 10, indicating good stability on the CV timescale.

Electrochemical cycling of $\mathbf{M/M^{2+}}$ was next examined in a flow cell containing graphite charge-collecting plates with an interdigitated flow field, in combination with 400 µm thick carbon-felt electrodes and a Celgard separator. A 50 mM solution of a 1:1 mixture of **M** and **M^{2+}[PF_6]$_2$** in 0.5 M NBu_4PF_6 in MeCN was flowed through the cell at 10 mL/min. The material was cycled to a cutoff voltage of +0.5 V and the polarity of the electrodes reversed and it was cycled to -0.5 V and the polarity reversed again to complete the cycle (this is a two-electrode system with no reference electrode). A schematic of the flow cell with the electrochemical reactions of one half-cycle are shown in Fig. 3. The resulting capacity and coulombic efficiency versus cycle number are shown in Fig. 4. (Charge-discharge curves are given in the ESI as Fig. S1.) The first full cycle captured 60% of the theoretical capacity of the battery solution. Over the first 20 cycles, 20% of capacity was lost. Over cycles 20-100, the rate of capacity loss was much lower, with an additional 12% of capacity loss over those 80 cycles. (The 100 cycles occurred over a period of 45 h.) Coulombic efficiency was well over 99% for all cycles after the first several. Cycling was stopped after 177 charge-discharge cycles, and the solutions from both reservoirs were combined. A portion of this solution was examined by CV (Fig. S2), which showed a reversible wave at the potential of **M/ M^{2+}**, but also a small additional reversible wave at approximately -1.92 V (vs. $Fc^{+/0}$) and an irreversible oxidation at +0.4 V, both due to unidentified species. Collectively, this data suggest that the observed capacity fade is largely due to decomposition during electrochemical cycling.

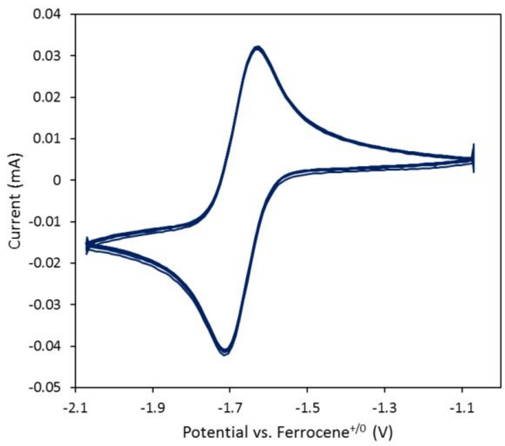


Fig. 2 Cycles 2-10 of repeated CVs of **M^{2+}[PF_6]$_2$** in CH_3CN-[NBu_4][PF_6].

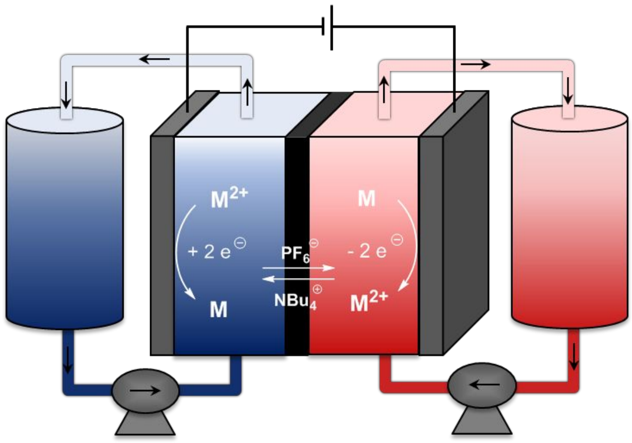


Fig. 3 A schematic diagram of the flow cell with the electrochemical reactions of one half-cycle for **M^{2+}/M**.

We next sought to identify the decomposition products. The post-cycling solution was treated with I_2 to convert **M** and any other reduced species to their oxidized state. The volatiles were removed under vacuum, and a sample of the solid residue was dissolved in d_6-DMSO and analysed via ^{1}H NMR spectroscopy (Fig. S3). In addition to **M^{2+}** (which derives from both the **M^{2+}** present in the original post-cycling solution, as well as **M** that is oxidized by I_2), the other major species observed by NMR spectroscopy is the open-chain dication **H_2M^{2+}** (in an approximate 2.2:1 molar ratio of **M** to **H_2M^{2+}**). The identity of **H_2M^{2+}** was further confirmed via electrospray ionization mass spectrometry. **H_2M^{2+}** is likely formed via the protonation of **M** during cycling, which is simply the reverse of the deprotonation of **H_2M^{2+}** in the synthesis of **M** shown in Scheme 1.

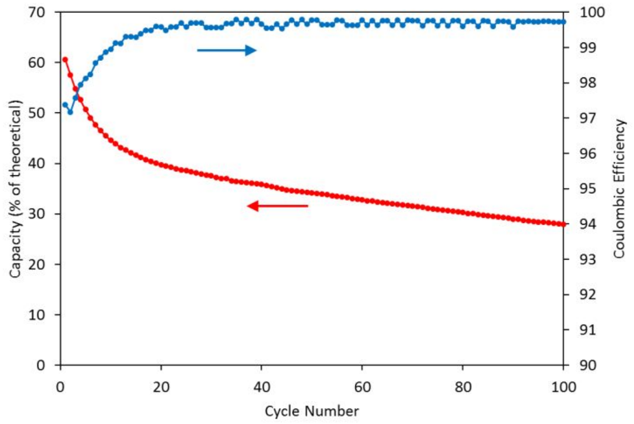
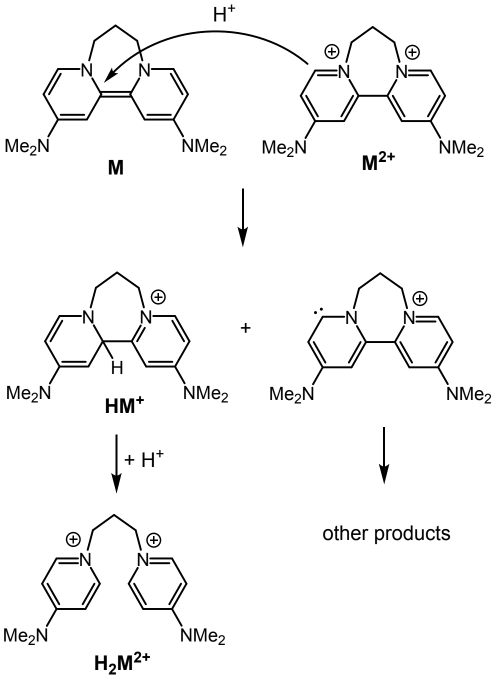


Fig. 4 Capacity and coulombic efficiency vs cycle number for **M^{2+}/M** in CH_3CN-[NBu_4][PF_6] in a flow battery system.

We note that **M^{2+}** and **M** are both stable on their own for days in MeCN/NBu_4PF_6 solutions, but that relatively fast decomposition to **H_2M^{2+}** occurs during electrochemical cycling. This led us to hypothesize that decomposition results from the presence of mixture of **M^{2+}** and **M** during electrochemical cycling, with **M^{2+}** serving as the source of protons for the formation of **H_2M^{2+}**. More specifically, we reasoned that the deprotonation of **H_2M^{2+}** to **M** (Scheme 1) can be considered as a reversible reaction $\mathbf{M} + 2\,H^+ \rightleftharpoons \mathbf{H_2M^{2+}}$. The hydrogen atoms on the 6-position of **M^{2+}** are expected to have a pK_a similar to that of the 6-position hydrogens on **H_2M^{2+}**, which means that **M** is a strong enough base to deprotonate **M^{2+}**. This would generate a transient carbene that can then react with solvent or other species to irreversibly form decomposition products (Scheme 2). The **HM^+** can then be protonated a second time (by **M^{2+}** or another source) to form the observed **H_2M^{2+}**.

To test this proposed decomposition pathway, we compared the stability of an acetonitrile solution of **M** to that of a mixture of **M** and **M^{2+}[PF_6]$_2$**. A 50 mM solution of **M** was held for 16 h at 22 °C in dry CH_3CN in a glovebox, and a second solution that was 50 mM in **M** and 50 mM in **M^{2+}[PF_6]$_2$** was held for 16 h under identical conditions. Both solutions were then quenched with I_2, concentrated under vacuum, and the solid residue was dissolved in d_6-DMSO and analysed via ^{1}H NMR spectroscopy (Fig. S4). The product from the solution of **M** is mainly $\mathbf{M^{2+}}$, with only traces (~5%) of unidentified impurities. Most importantly, no $\mathbf{H_2M^{2+}}$ is identifiable in the ^{1}H NMR spectrum. This is consistent with minimal decomposition of neat **M** in CH_3CN. In contrast, the ^{1}H NMR spectrum of the residue of the I_2-quenched $\mathbf{M/M^{2+}[PF_6]_2}$ solution shows the presence of 0.2 equivalents of $\mathbf{H_2M^{2+}}$ for every equivalent of $\mathbf{M^{2+}}$ present, in addition to other unidentified impurities. These observations are consistent with the proton transfer-initiated decomposition reaction proposed in Scheme 2.



Scheme 2 Reaction of **M** with $\mathbf{M^{2+}}$, leading to $\mathbf{H_2M^{2+}}$ and decomposition products.

In conclusion, while $\mathbf{M^{2+/0}}$ has many desirable characteristics for an organic negolyte for nonaqueous flow batteries (high solubility in CH_3CN, a low redox potential, two electrons transferred at that low potential), its long-term stability is ultimately limited by the reaction between **M** and $\mathbf{M^{2+}}$ when both are present in solution. In a flow battery it is unavoidable that both redox states of a given negolyte will be present in the same solution for extended periods of time. (Notably, this has not been a hindrance to the extensive use of **M** as a synthetic reagent, where **M** and $\mathbf{M^{2+}}$ are both present in the same solution for relatively short times.[7,19–21]) We are currently investigating the synthesis of derivatives of **M** that are substituted at the 6-pyridyl position to prevent the reactions shown in Scheme 2 and increase their stability and suitability for flow batteries.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ Since the first report of **M**, Murphy and Dyker have both reported molecules with even more negative reduction potentials.[25–27] However, several other factors (relative ease of synthesis, low molecular weight, good solubility) led us to identify **M** as an ideal candidate for exploration as a nonaqueous flow battery negolyte.

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An organic "super-electron-donor" has several properties that are desirable in a negative electrolyte for nonaqueous redox flow batteries, including a highly negative $2^+/0$ reduction potential, a low mass per electron transferred, and good solubility in CH_3CN in both redox states.