Communications

Predicting Redox Behavior of Methyl Viologen and Analogues in Water using Density Functional Theory

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Redox flow batteries (RFBs) are gaining attraction as promising energy storage devices.[1] While aqueous RFBs (ARFBs) exhibit lower voltages due to the limited potential window of water, they offer advantages in terms of safety. Despite some commercialization of ARFBs, ongoing research endeavors strive to improve their performance. Alkyl viologens, structurally similar to **a1** in Figure 1 have been widely investigated as ARFB anolytes.[2]

To enhance their performance, modifications have been explored in two key directions: 1. Improving solubility: Alkyl groups at the 1,1' positions were substituted with charged functional groups such as 3-(trimethylammonio) propyl, 3-sulfonatopropyl, and 3-carboxypropyl. This strategy effectively increases solubility, crucial for high concentration electrolytes and enhanced energy density.[3,4] 2. Suppressing dimerization: Upon single-electron reduction, viologen radical cations can form dimers, hindering battery performance. Introducing conjugated ring systems like phenylene, furandiyl, or thiophenediyl between the pyridinium rings of viologen (compounds **a2**, **a3**, and **a4** in *Fig.* 1) hinders dimerization. Notably, these extended molecules exhibit lower reduction potentials (RPs) compared to their parent compound. This suggests potentially higher cell voltages, improved reversibility of redox reactions, and ultimately, enhanced battery performance.[5]

Seeking further performance enhancements, the author investigated modifications beyond altering the viologen backbone. This strategy involved changing the connection position of the pyridine rings in molecules **a1-a4**, resulting in the isomeric compounds **b1-b4** (*Fig.* 1). Notably, while sharing the same chemical formula as their counterparts, these isomers possess distinct arrangements of atoms. To evaluate the impact of this structural variation, density functional theory (DFT) calculations were employed to determine the reduction potentials (RPs) of both the original compounds (**a1-a4**) and their newly generated isomers (**b1-b4**) in water.

All calculations were performed using the Gaussian 09 software.[6] The RPs were determined employing the thermodynamic cycle represented in *Scheme* 1. In the cycle, "Ox" and "Red" denoted oxidized and reduced species, respectively. Gas and solution states are indicated using "(g)" and "(s)", respectively. The Gibbs free energy of the gas-phase electron, following the electron convention with Fermi-Dirac statistics, was set to −3.632 kJ/mol.[7] The solution-phase Gibbs free energy difference, ΔG_s°, is
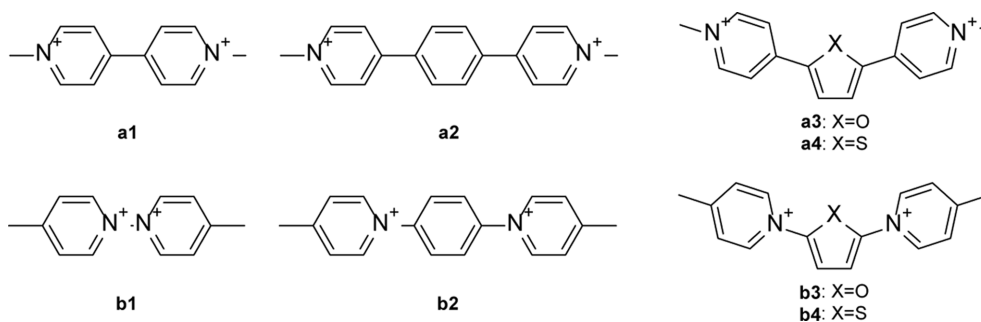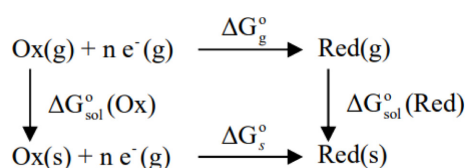

Figure 1. The molecular structures of methyl viologen (**a1**) and its extended molecules (**a2**, **a3** and **a4**) and their isomers obtained by changing the linking positions of pyridines.

Scheme 1. Born-Haber cycle.

determined by two factors: Gas-phase Gibbs free energy difference, ΔG_g° and the solvation-free energy difference, $\Delta\Delta G_{sol}^{\circ} = \Delta G_{sol}^{\circ}$ (Red) $- \Delta G_{sol}^{\circ}$ (Ox). The RP relative to the standard hydrogen electrode (SHE) can be evaluated using the equation, $E_{1/2}$ vs $SHE = -\Delta G_s^{\circ}/nF - 4.281$, where n is the number of electrons transferred in the reduction reaction and F is Faraday's constant. This equation was first reported by Isse and Gennaro.[8]

All DFT calculations employed the M06-2X functional, which is recognized as one of the most accurate hybrid functionals for organic compounds.[9] Geometry optimization for both dicationic and radical cationic forms of the studied molecules was performed using the 6-311++G(d,p) basis set. The unrestricted method was employed for open-shell species. Frequency calculations at the same theoretical level ensured that optimized structures corresponded to true minima on the potential energy surface. Solvation-free energies were computed using the SMD model,[10] a universal continuum solvation model based on the solute electron density, to incorporate solvent effects on energetics. The accuracy of the proposed method was assessed using compounds **a1-a4**. The mean absolute deviation (MAD) between calculated and experimental RPs in acetonitrile was 0.003 V, with the root mean square (RMS) deviation of 0.036 V (see *Table* S1 in supporting information). This excellent agreement shows that the method is reliable, at least for predicting RPs for molecules studied in this work.

Table 1 summarizes the calculated adiabatic electron affinities (AEAs) corrected with zero-point energies and the RPs of the studied compounds. The calculated RP of methyl viologen (−0.40 V) closely matches with the exper-

imental value[11] (−0.45 V), demonstrating the high accuracy of the employed computational method. Replacing the **a1-a4** compounds with their corresponding structural isomers, **b1-b4,** leads to a significant decrease in their RPs. Specifically, the RPs drop by −0.46 V, −0.45 V, −0.34 V, and −0.45 V, averaging a reduction of −0.42 V. This suggest that the **b1-b4** isomers hold great premise as superior anolytes in ARFB, due to their enhanced ease of oxidation, potentially leading to higher energy output. Furthermore, **b1-b4** isomers exhibit lower AEAs compared to **a1-a4** (−0.06, −0.08, 0.01, and −0.17 eV; average of −0.08 eV). This along with the corresponding decrease in RPs gives the resulting reductions in $\Delta\Delta G_{sol}^{\circ}$ for **b1-b4** isomers (−0.40, −0.37, −0.35, and −0.27 eV, average of −0.35 eV). The decrease in $\Delta\Delta G_{sol}^{\circ}$ contributes four times as much to the reduction of RPs of **b1-b4** isomers as the decrease in AEAs compared to **a1-a4** isomers. This indicates that optimizing solvation properties could be a viable strategy for further enhancing the performance of ARFB anolytes.

CONCLUSION

This study employed computational method to investigate the RPs of methyl viologen and several extended molecules, and their structural isomers. Comparison with reported experimental values revealed excellent agreement, with a mean absolute deviation of 0.003 V. Notably, the calculated RPs of the **b1-b4** isomers were consistently lower than those of their corresponding **a1-a4** counterparts. This suggests that the **b1-b4** compounds, due to their enhanced ease of oxidation, hold promise as potentially superior anolytes for ARFBs. Further research focused on experimental validation and detailed analysis of the factors contributing to the observed RP differences is warranted to definitively confirm their potential in ARFB applications.

Supporting Information. *Table* S1 presents the calculated and experimental reduction potentials of **a1-a4** in acetonitrile.

Table 1. Calculated adiabatic electron affinities (AEA, eV) and reduction potentials vs SHE ($E_{1/2}$, V) for methyl viologen and analogues

Species	AEA	$E_{1/2}$	Species	AEA	$E_{1/2}$
a1	9.00	−0.40	**b1**	8.94	−0.85
a2	7.67	−0.83	**b2**	7.58	−1.28
a3	8.10	−0.65	**b3**	8.11	−0.99
a4	8.07	−0.56	**b4**	7.90	−1.01

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