

A Novel Hydroxylated Tetracationic Viologen for Aqueous Flow Batteries: [(DMAE-Pr)₂-Vi]

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Introduction

Molecular engineering on viologens, formally 4,4'-bipyridilium salt, for flow batteries applications has brought to light the positive effect of substituents bearing hydroxyl and ammonium groups.^{1,3} The presence of hydroxyl groups alters not only the HOMO-LUMO levels, i.e., the electronic structure, but also the dihedral angle of the radical cation with an effect on the dimerization of the latter.² With this in mind, we rationally designed a new viologen bearing both hydroxyl- and positively charged groups, i.e., ammonium groups, in order to achieve superior solubility and battery performance. This new viologen, [(DMAE-Pr)₂-Vi], is here presented (Fig.1):

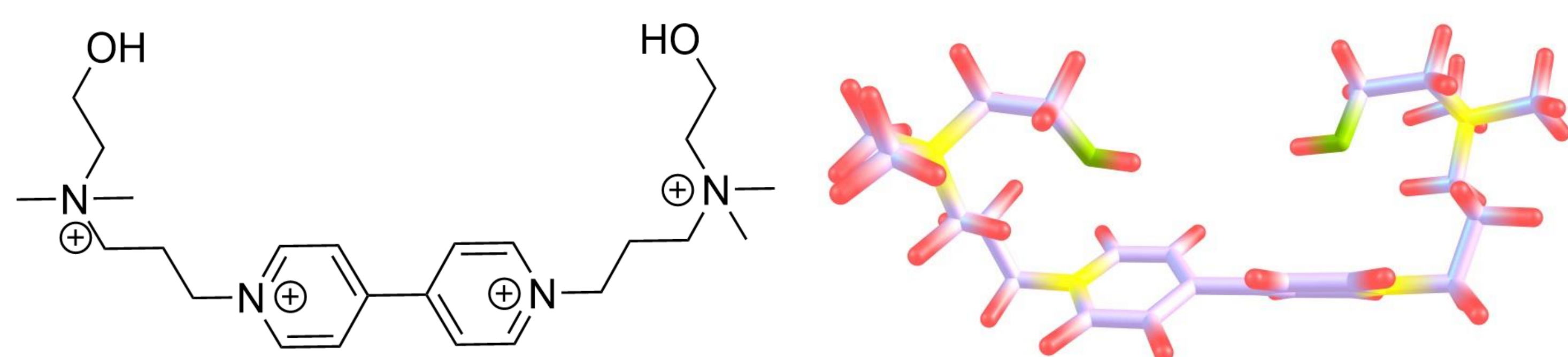


Fig. 1: [(DMAE-Pr)₂-Vi] and its optimized ground state (right).

Molecular design

The use of the bifunctional compound dimethylaminoethanol (DMAE) allowed the easy and reproducible preparation of the new hydroxylated tetracationic viologen by means of two successive S_N2 reactions (i.e., Menshutkin reaction) up to 17 g scale (Fig. 2).

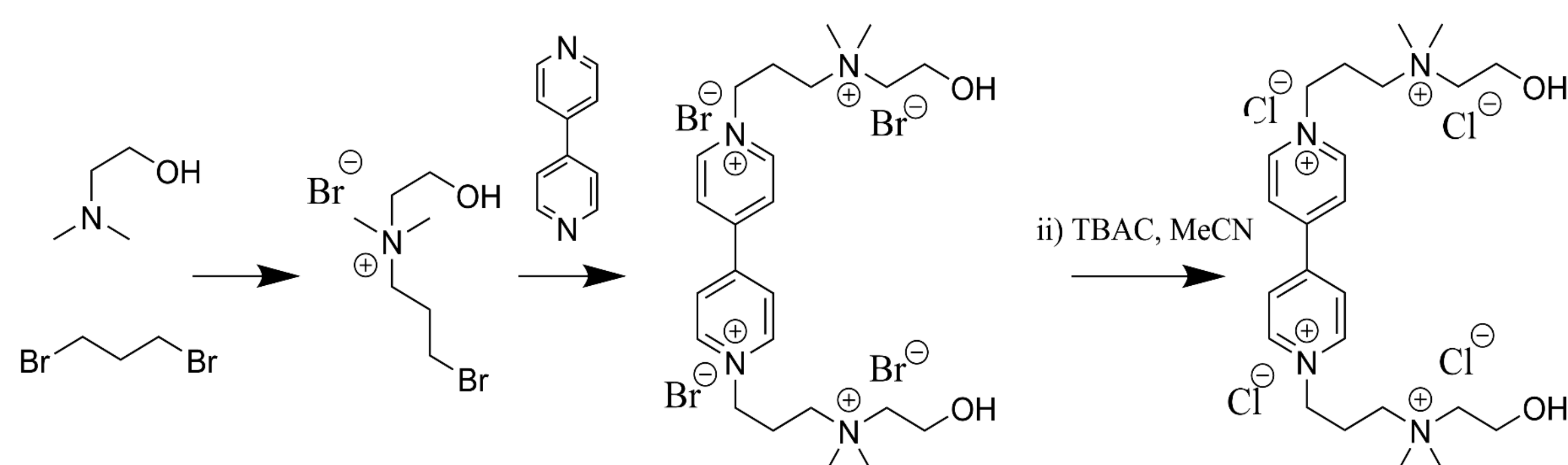


Fig. 2: Synthetic pathway for [(DMAE-Pr)₂-Vi].

The terminal primary alcohol moiety increased its solubility of 30% (2.7 vs 2.0 M) compared to the pristine BTMAP-Vi.⁴ Interestingly, as can be seen from Fig. 4, the hydroxyl groups point either at the bipyridinium rings, i.e., the redox centre, or at the newly formed double bond for the doubly reduced species.

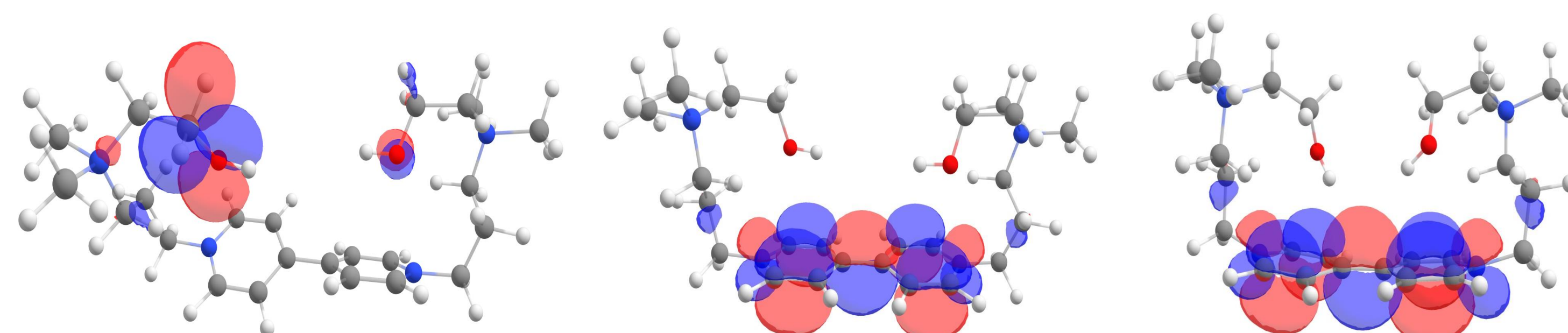


Fig. 3: Three redox states for [(DMAE-Pr)₂-Vi] including molecular orbitals: tetracation (left, HOMO), trication (middle, SOMO) dication (right, HOMO).

Characterization

The dihedral angle was calculated and compared to some analogues (Fig. 4, left). Cyclic voltammetry - with KCl as supporting electrolyte - was used to assess the formal potentials and the effect of the concentration on the shape of the voltammograms (Fig. 4, right).^{4,5}

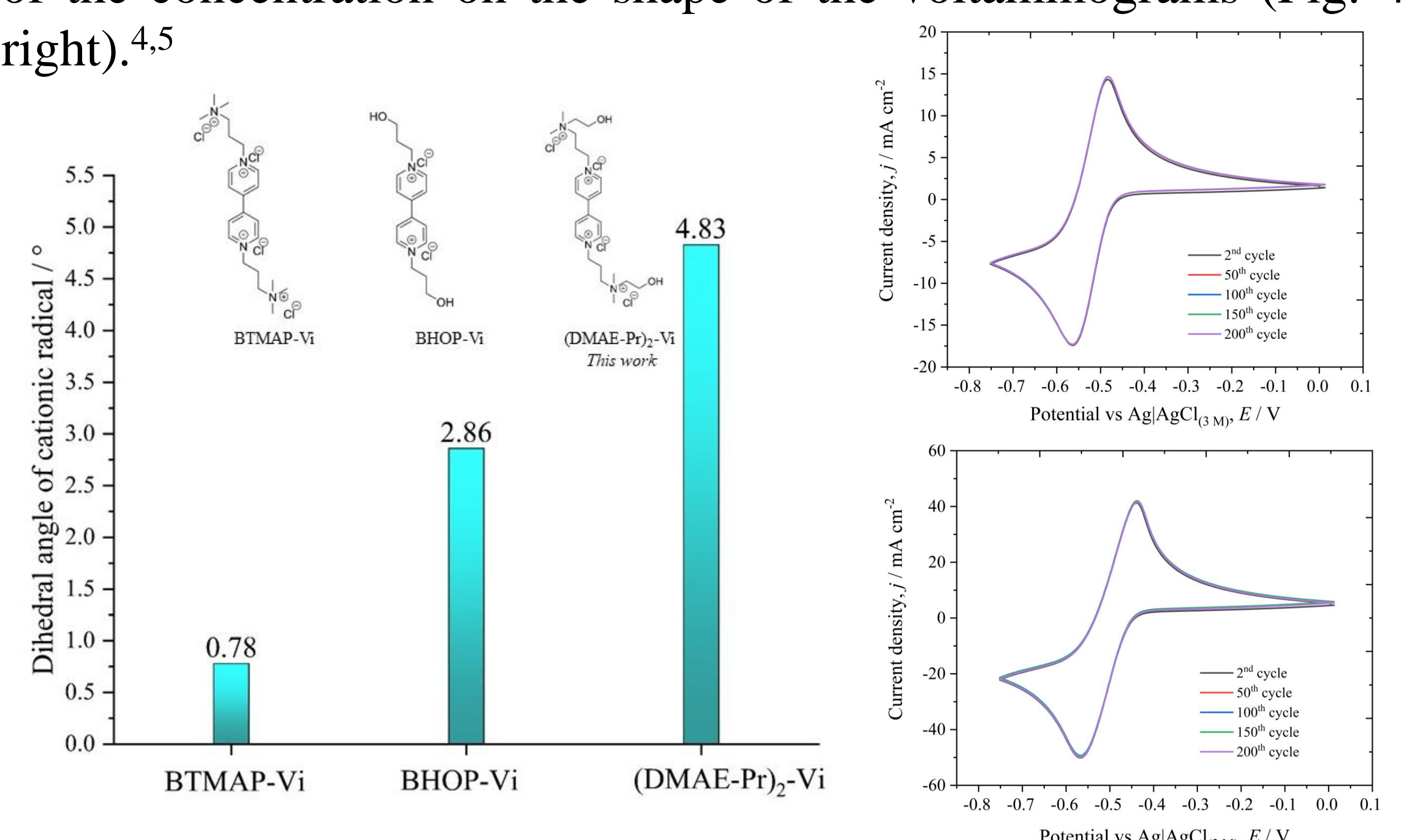


Fig. 4: Dihedral angle plot (left), CVs at 0.1 M (right-top) and 0.5 M (right) for [(DMAE-Pr)₂-Vi].

Flow battery

Flow battery tests have been carried out by pairing [(DMAE-Pr)₂-Vi] with two different and easily accessible posolytes, namely TEMPOL and FcNCl, using KCl as supporting electrolyte, and FAS-30 as anion exchange membrane (Fig. 5).⁵

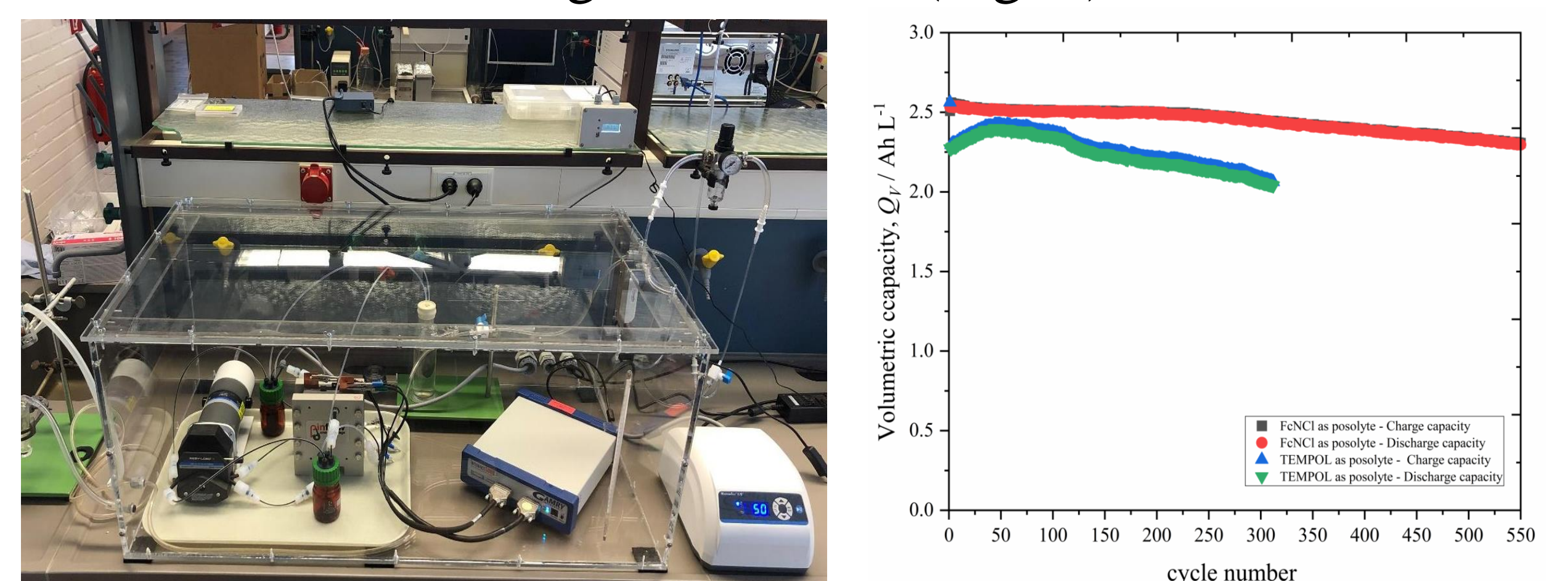


Fig. 5: Experimental setup (left), Q_v vs cycle (TEMPOL vs FcNCl) (right).

Outlook

The novel hydroxylated tetracationic viologen showed high solubility and promising performance as negolyte. Capacity retention was limited by crossover of posolyte species and solvent. The ferrocene derivative allowed for lower capacity fade rate.

Future work will further improve capacity retention by: Using new membranes and synthesizing less permeable posolyte molecules.

References

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Acknowledgements

The authors thank the support of TU Clausthal and the Research Center Energy Storage Technologies (EST). LFA is grateful to the Alexander von Humboldt Foundation for sponsoring a research fellowship.