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Prediction of cathodic $E^1_{1/2}$ and $E^2_{1/2}$ values for viologen-containing conjugated unimers and dimers from calculated pK_b values of the aromatic substituents

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ABSTRACT

A library of 18 conjugated, rod-like compounds with either one or two viologen residues were synthesized and characterized electrochemically. Containing up to 8 aromatic/heterocyclic rings in conjugation, the members of the library differ in the substitution pattern of electron-withdrawing or -donating groups on the aromatic substituents of the viologen units. The first and second half-wave potentials of each member were found to be linearly correlated with the calculated pK_b values of the aromatic end-groups. This relationship will enable the half-wave potentials of related, novel, substituted viologen species to be predicted using a simple, empirical formula.

Introduction

Viologens are disubstituted 4,4′-bipyridinium ions that undergo two sequential one-electron transfer reactions to form firstly a radical cation and secondly a neutral quinoidal species.[1] The electron-deficient nature and reversible redox behavior of substituted viologens has seen them become ubiquitous entities in a wide range of research fields including supramolecular chemistry,[2] electrochromic displays,[3] photovoltaic cells,[4] sensors,[5] electron-transfer photosensitizers[6] and catalytic hydrogen generation.[7] They are also emerging as key components of functional metal organic frameworks including those used for carbon sequestering.[8] Very recently, synthetic and analytical studies of conjugated rod-like viologen containing compounds by ourselves[9] and the groups of Zhao[10] and Wang[11] have shown them to exhibit unique redox properties and self-assembly characteristics.[12]

The reversible redox properties of the viologen are generally key to the functionality of the system, and so knowledge of the precise half-wave potential ($E_{1/2}$) of the viologen is of vital importance. Within the extensive number of viologen species reported to date, there has been some attempt to investigate how the structure of the *N*-substituent affects the redox properties of the viologen.[13,14] However, for viologen containing compounds it is clear that $E_{1/2}$ is also dependent on the solvent, counterion and counter-electrode.[15] The non-uniformity of conditions used during electrochemical analysis by different research groups thus hinders direct comparison of data from these sources. Indeed, until the present work, there has been no systematic structure/property investigation of aromatic *N,N*′-substituted viologens under directly comparable conditions.

Herein, we report the use of previously optimised[9,16] Zincke-type[17] reaction conditions in a modular synthesis to produce a library of 18 π-conjugated unimers (**1a–i**) and dimers (**2a–i**) containing either one or two viologen residues, respectively. The members of each series differ in the substitution patterns on the non-viologen, aromatic rings. The redox properties of the members of this series were compared so as to correlate the effect of the structure of the substituents on the half-wave reduction ($E_{1/2}$) potentials of the viologen residue.

Results and discussion

The synthesis of aryl-substituted viologen unimers was achieved by reaction of the appropriate aryl amine (**3a–i**, for structures see Table 1) with the well known di-Zincke salt **4** (Scheme 1).[16,18] The aromatic end-groups were selected to fall into

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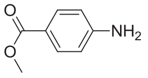
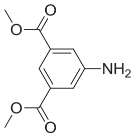
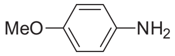
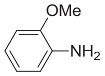
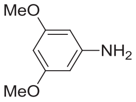
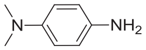
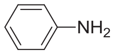
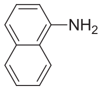
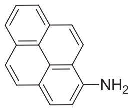
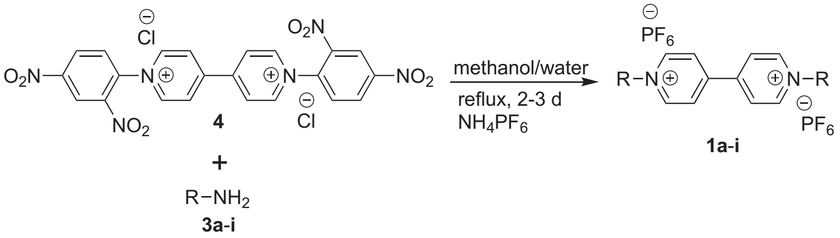
Table 1
Reaction yields, calculated pK_b values and experimentally determined $E_{1/2}$ values for the unimeric and dimeric viologens synthesized in this work.

Aromatic mono-amine	Unimeric viologen series				Dimeric viologen series			
	Compound (Yield)	Calc.[a] pK_b	$E^{1}_{1/2}$ (V)[b]	$E^{2}_{1/2}$ (V)[b]	Compound (Yield)	Mean Calc.[c] pK_b	$E^{1}_{1/2}$ (V)[b]	$E^{2}_{1/2}$ (V)[b]
 **3a**	**1a**[21] (93%)	2.7	−0.583	−0.794	**2a** (95%)	3.55	−0.619	−0.900
 **3b**	**1b**[9] (93%)	1.3	−0.609	−0.830	**2b**[9] (77%)	2.85	−0.629	−0.921
 **3c**	**1c**[22] (95%)	5.1	−0.705	−1.026	**2c** (n.d.)			
 **3d**	**1d** (92%)	4.4	−0.689	−1.041	**2d** (85%)	4.4	−0.669	−1.046
 **3e**	**1e** (79%)	3.5	−0.654	−0.931	**2e** (90%)	3.95	−0.660	−0.976
 **3f**	**1f** (81%)	6.1	−0.770	−1.107	**2f** (n.d.)			
 **3g**	**1g**[23] (96%)	4.6	−0.664	−0.946	**2g** (87%)	4.5	−0.679	−0.996
 **3h**	**1h**[20] (87%)	4.1	−0.664	−0.991	**2h** (92%)	4.25	−0.664	−1.007
 **3i**	**1i** (85%)	4	−0.664	−0.981	**2i** (95%)	4.2	−0.659	−0.996

[a] Calculated using software that can be accessed from Ref. 24.
[b] Solutions in anhydrous DMF at a glassy carbon disc electrode ($d = 2$ mm) at $v = 500$ mV s^{-1}. The $E_{1/2}$ values are given versus the standard ferrocene/ferrocenium (Fc/Fc^{+}) couple used as an internal reference. For voltammograms see the ESI.
[c] Average pK_b for the amine on **5** (calculated[24] $pK_b = 4.3$) and the appropriate mono-amine (**3a**–**i**).



Scheme 1. Synthesis of mono-viologen species **1a**–**h**. For the structures of amines **3a**–**i** see Table 1.

one of three structural types, having either electron withdrawing substituents (**3a**, **3b**) or electron donating substituents (**3c**–**f**), or else containing varying numbers of fused aromatic rings (**3g**–**i**). During the synthesis of the unimers, each double substitution reaction proceeded cleanly under identical conditions to give the target compounds in high and reproducible yields (>80%).[19]

Synthesis of the dimeric series of compounds started with double addition of Zincke salt **5**[20] to 3,3′-dimethoxybenzidine (**6**, Scheme 2), which has been previously shown to be a good partner in the Zincke reaction.[9] Addition of 1-chloro-2,4-dinitrobezene to intermediate **7** resulted in the formation of di-Zincke salt **8** that was the common intermediate for the synthesis of the series of di-viologen conjugated systems **2a**–**h**. As can be seen from Table 1, the target di-viologen compounds (**2a**–**i**) were mostly isolated in good yields, although **2c** and **2f** could not be isolated cleanly under these general reaction conditions.