Synthesis and Characterization of New Conjugation-extended Viologens Involving a Central Aromatic Linking Group

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New viologens, in which two pyridinium moieties are linked by a central five-membered heteroaromatic or phenylene framework, giving stable radical cations on single electron reduction and showing an intense fluorescence emission are efficiently synthesized and characterized.

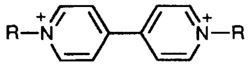
Viologens represented in the general formula **1** are the most important redox reagents used widely not only for the basic study of electrochemical[1] and photoelectrochemical[2] processes but also for electrochromic materials,[3] for electron transfer mediators in the conversion of photoenergy into chemical energy,[4] and for functional elements of molecular devices,[5] because of their easy and reversible single electron-accepting ability producing stable and coloured radical cations. So far some vinylogous viologens **2**[6] have been synthesized in prospect of developing a new or superior function to **1**. Unfortunately the butadienylene- (**2**: $n = 2$) and higher polyethenylene-extended ones (**2**: $n > 2$) tend to be reduced to the unstable radical cations,[6] so that they are unfavourable for developing some of the above mentioned performance.

Therefore, new viologens having different skeletal structures from traditional ones and giving stable radical cations are of current interest. In the course of our study on the creation of multi-stage redox systems[7] we have now designed and synthesized new conjugation-extended viologens in which two pyridinium moieties are linked by a central five-membered heteroaromatic framework, **3** and **4**, together with the benzologue **5** and have proved that **3** and **4** afford very stable and intensely coloured radical cations in one-electron reduction and moreover they display a fluorescence emission with a very high quantum yield in the visible region.

The viologens **3**–**5** have been synthesized by the *N*-methylation of hitherto unknown 2,5-bis(4-pyridyl)-thiophene **6**, -furan **7** and 1,4-bis(4-pyridyl)benzene **8** which are efficiently prepared by a one-pot synthesis through the palladium-mediated cross-coupling reaction between 4-trimethylstannylpyridine[8] and the corresponding 2,5-dibromoheteroaromatics or 1,4-dibromobenzene in 50–60% yields.†

The heterocyclic three-ring assembling viologens, **3** and **4**, undergo reversible two-stage one-electron reduction in cyclic voltammetry (Fig. 1), indicating the formation of stable radical cations **3**$^{+\bullet}$ and **4**$^{+\bullet}$ as well as the corresponding neutral species, without causing conformational changes through the redox process. These properties of **3** and **4** are quite notable since **5** and **2** ($n \geqslant 2$) undergo one-stage two-electron reduction, even though their pyridinium moieties are separated out by the same four sp^2 carbons as those of **3** and **4**. From the X-ray structural analysis, **3** is shown to be in a nearly coplanar conformation in which the dihedral angles of the pyridinium rings with respect to the central thiophene ring are 7.2 and 6.1°.‡ Therefore, the thermodynamic stability of **3**$^{+\bullet}$ and **4**$^{+\bullet}$ should be ascribed to the rigid and coplanar conformations of **3** and **4**, in addition to the enhanced conjugative interaction among the one weak electron-donating five-membered ring and two electron-attracting pyridinium moieties.

Electrochemical reduction of **3**, using tetra-n-butylammonium perchlorate as supporting electrolyte, produced the radical cation **3**$^{+\bullet}$ exhibiting a strong EPR signal ($g = 2.0038$) with rather complicated hyperfine splittings. An essentially identical spectrum was also obtained by the one-electron reduction with 3% Na–Hg in degassed acetonitrile, which persisted with undiminished intensity for a couple of weeks at room temperature. We could measure the complete absorption spectra of **3**$^{+\bullet}$ and **4**$^{+\bullet}$ formed by the Na–Hg reduction of **3** and **4** in acetonitrile (Fig. 2). Both of these spectra are similar in band shapes to that of **1**$^{+\bullet}$ (R = Me), but the low-energy A band (n–π* transition at 1047–1124 nm) and the higher-energy B band (π–π* transition at 568–561 nm) showed substantial bathochromic shifts by 440–517 and 171–164 nm, respectively, from the corresponding bands of **1**$^{+\bullet}$[1b,9] Thus, it should be possible to use **3** and **4** as novel electrochromic display systems in which colouration is brought about by the



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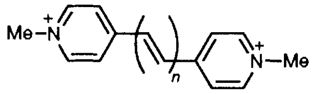

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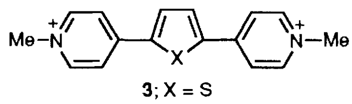
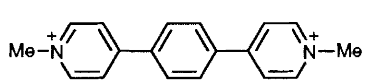


3; X = S
4; X = O



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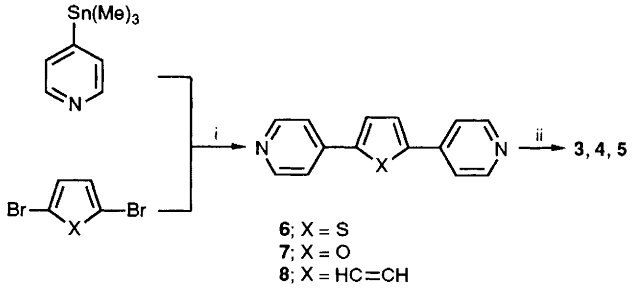
† Satisfactory elemental analyses and spectroscopic data were obtained for all new compounds. *Selected physical data* for **3** ($2BF_4^-$ salt): pale yellow needles, m.p. (decomp.) >285 °C; ^{1}H NMR (200 MHz, CF_3CO_2D), δ 4.47 (6H, s, NMe), 8.13 (2H, s, ThiH-3,4), 8.32 (4H, d, *J* 6.0 Hz, PyH-3,5), 8.72 (4H, d, *J* 6.0 Hz, PyH-2,6); ^{13}C NMR (50.3 MHz, CF_3CO_2D), δ 49.5 (NMe), 125.8 (PyC-3,5), 135.0 (ThiC-3,4), 145.0 (PyC-4), 147.4 (PyC-2,6), 151.1 (ThiC-2,5); UV (MeCN) λ_{max}/nm (log ε) 243 (3.95), 281 (3.84), 369 (4.61), 385sh (4.54); **4** ($2BF_4^-$ salt): pale yellow needles, m.p. >300 °C; ^{1}H NMR (200 MHz, CF_3CO_2D), δ 4.11 (6H, s, NMe), 7.39 (2H, s, ThiH-3,4), 8.08 (4H, d, *J* 7.0 Hz, PyH-3,5), 8.38 (4H, d, *J* 7.0 Hz, PyH-2,6); ^{13}C NMR (50.3 MHz, CF_3CO_2D), δ 49.5 (NMe), 121.2 (ThiC-3,4), 124.4 (PyC-3,5), 145.8 (PyC-4), 147.4 (PyC-2,6), 154.3 (ThiC-2,5); UV (MeCN) λ_{max}/nm (log ε) 243 (4.12), 304 (3.76), 368 (4.61), 384 (4.65); **5** ($2BF_4^-$ salt): colourless needles, m.p. >300 °C; ^{1}H NMR (200 MHz, CD_3CN), δ 4.32 (6H, s, NMe), 8.14 (4H, s, PhH-2,3,5,6), 8.33 (4H, d, *J* 7.0 Hz, PyH-3,5), 8.70 (4H, d, *J* 7.0 Hz, PyH-2,6); ^{13}C NMR (50.3 MHz, CF_3CO_2D), δ 49.6 (NMe), 128.0 (PyC-3,5), 131.4 (PhC-2,3,5,6), 139.5 (PhC-1,4), 147.3 (PyC-2,6), 158.7 (PyC-4); UV (MeCN) λ_{max}/nm (log ε) 316 (4.56) (Py = pyridine, Thi = thiophene).

‡ *Crystal data* for **3** ($2BF_4^-$ salt): $C_{16}H_{16}B_2F_8N_2S$, $M = 442.02$, monoclinic, space group $P2_1/n$, $a = 18.453(3)$, $b = 9.919(1)$, $c = 10.836(3)$ Å, $\beta = 99.30(1)°$, $V = 1957.1$ Å^3, $Z = 4$, $D_c = 1.500$ g cm^{-3}. The final R value = 0.055 and R_w = 0.090 for 2004 observed reflections. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 1 *Reagents and conditions*: i, $Pd[P(Ph)_3]_4$, toluene, reflux; ii, MeI, MeCN, reflux, or Me_3OBF_4, MeCN, 90 °C, or MeBr, MeCN, 40–45 °C

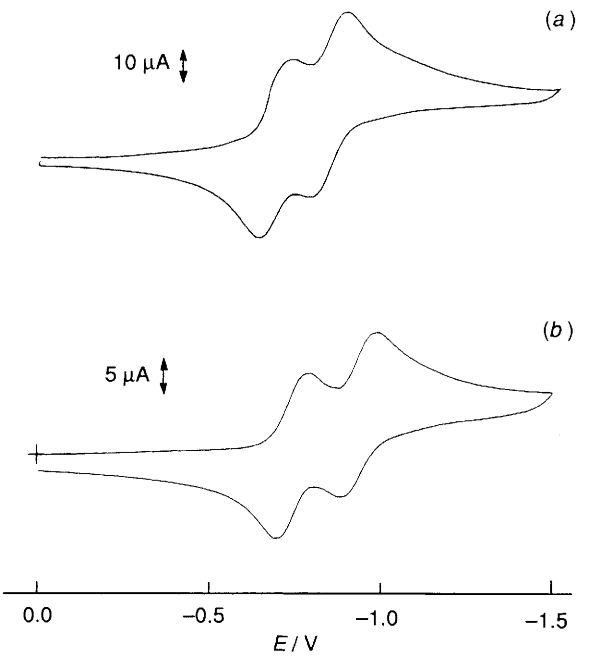


Fig. 1 Cyclic voltammograms of (*a*) **3** and (*b*) **4**, 0.1 mmol dm^{-3} in MeCN with 0.1 mol dm^{-3} Et_4NClO_4 at room temperature [scan rate: 50 mV s^{-1}; reference electrode: saturated calomel electrode (SCE)]

most intense B band in the visible region or sensitive to the semiconductor laser light owing to the A band in the near infrared region. The half-wave reduction potentials (E_1^{red}) of **3** and **4** are more negative by about 0.26–0.31 V than that of **1** (R = Me), but these values can be easily made more positive by introducing slightly more electron-withdrawing substituents§ such as cyanomethyl groups on the N-atoms as shown in Table 1.

The viologens **3**, **4** and **5** showed fluorescence emission spectra upon photoexcitation at room temperature. The photophysical data are summarized in Table 2. Neither **1** nor **2** are fluorescent. The bipyridines **6**, **7** and **8** also showed fluorescence emission, but quite noticeably, the intensities of the fluorescence spectra were drastically increased in the viologens **3**, **4** and **5** compared with the bipyridines **6**, **7** and **8**. The fluorescence maxima at the shortest wavelength corresponding to the 0–0 transition were shifted to a longer wavelength region on going from **5** to **3** or **4**. The experimentally determined fluorescence quantum yields (Φ_f)¶ are very high in **3** and **4** and relatively low in **5**. The radiative (K_r) and non-radiative (K_{nr}) rate constants estimated from the Φ_f and the observed lifetimes (τ_f) are relatively small and almost the same in **3** and **4** within experimental error, but are significantly large in **5**. The Frank–Condon factors between the ground (S_0)

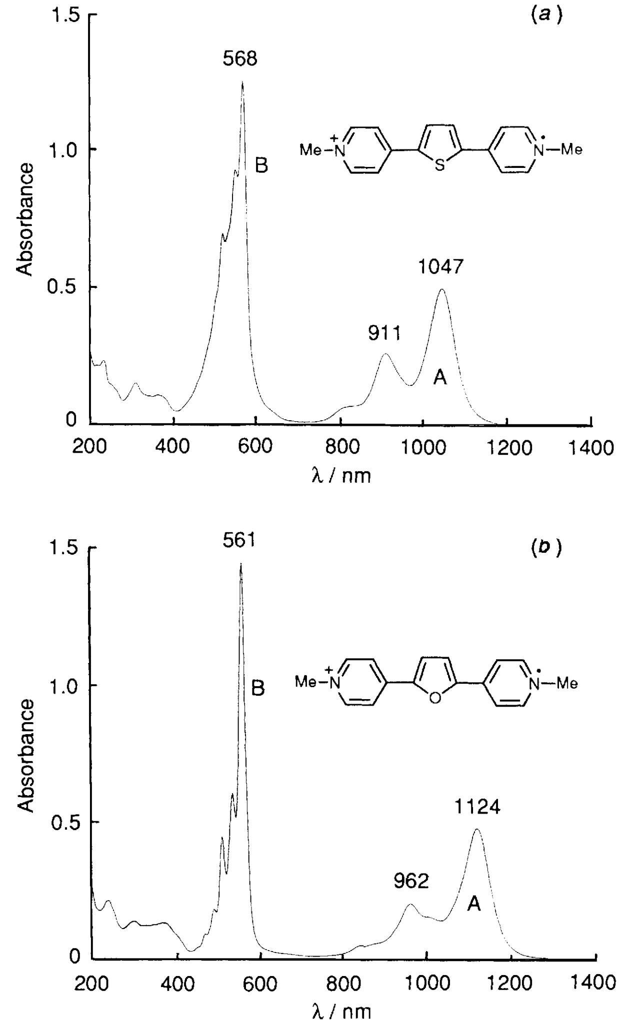


Fig. 2 Electronic spectra of radical cations of conjugation-extended viologens, (*a*) $\mathbf{3}^{+\bullet}$ and (*b*) $\mathbf{4}^{+\bullet}$, in MeCN

Table 1 Electrochemical properties[a] of conjugation-extended viologens, **3**, **4**, **5** and reference compounds **1** and **2** in MeCN

Compound	E_1^{red}	E_2^{red}	ΔE	$\log K_{sem}$
1 (R = Me)	−0.43	−0.85	0.42	7.12
3	−0.69	−0.84	0.15	2.54
3 (N^+CH_2CN)	−0.43	−0.55	0.12	2.03
4	−0.74	−0.93	0.19	3.22
5	−0.91 (2e)		0	—
2 (*n* = 2)	−0.59 (2e)		0	—

[a] Obtained by cyclic voltammetry operated under the conditions given in the caption to Fig. 1. E_1^{red} and E_2^{red} values are the average of peak potentials of the reversible anodic and cathodic segments of the cycle.

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§ The bisquaternary salts of **6** substituted with Et, $PhCH_2$, $MeSCH_2$, and $NCCH_2$ groups on the N atoms have also been synthesized, in which both of the reduction potentials E_1^{red} and E_2^{red} are in linear correlations (r_{E1} = 0.9958, r_{E2} = 0.9917) with the sum of Taft's σ^*-constant, $\Sigma\sigma^*$.

¶ The fluorescence quantum yields (Φ_f) were determined by the comparison of the integrated emission area across the band of the samples with that of perylene in benzene (Φ_f = 0.99).[10]

Table 2 Photophysical properties of conjugation-extended viologens, **3**, **4** and **5**, in MeCN

Compound	Excitation λ_{max}/nm	Fluorescence λ_{max}/nm	Lifetime τ_f/ns	Quantum yield Φ_f	k_r/s^{-1} $\times 10^{-8}$	k_{nr}/s^{-1} $\times 10^{-8}$
4	368, 384	412, 426	1.71	0.84	4.92	0.94
3	369, 385sh	417, 427	1.55	0.75	4.85	1.61
5	318	375	1.17	0.69	5.92	2.66

and the excited singlet state (S_1) in **3** as well as **4** may be small enough to evaluate the high quantum yields since **3** is proved to be in nearly coplanar conformation from the X-ray crystal analysis as mentioned above. The degradation of the quantum yield in **5** may be ascribed to the relatively large Frank–Condon factor which results from the enhanced torsional oscillation of the twisted intercyclic phenyl–pyridinium bonds. These findings will open a new extension for using these heterocyclic three-ring assembling viologens for valuable water soluble lasing dyes.[11]

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