JOURNAL OF APPLIED ELECTROCHEMISTRY **24** (1994) 1213–1221

Studies of tetra-(bipyridilium) salts as possible polyelectrochromic materials

D. R. ROSSEINSKY, P. M. S. MONK*

Department of Chemistry, The University, Exeter EX4 4QD, Great Britain

Received 17 March 1994; revised 14 May 1994

A polybipyridilium species has been prepared with four diquaternised bipyridine moieties around a durene core; mixed halide (bromide with iodide or with chloride) as well as single-anion (chloride) salts were studied, and their electrochemistry investigated. Three reduction processes are inferred producing a pink (di-reduced) species, a purple (tetra-reduced) species and a beige-coloured fully-reduced product. Mixed anion effects, in conjunction with dimer association and comproportionation, led to more complicated anodic electrochemistry than when only chloride anions were involved.

1. Introduction

Electrochromic species – those which change colour on electron transfer – are currently the focus of scientific and technological interest [1]. This property both facilitates spectroelectrochemistry, and finds an application in electrochromic devices (ECDs), of possible use in displays or light attenuation in optical shutters and ‘curtains’. Bipyridilium (bipm) salts are often cited for ECD use since they may typically possess three colours, one for each oxidation state (structures (**1**)–(**3**)), although the dication (**1**) in solution is invariably colourless or only feebly tinted. A species comprising *n* bipyridilium units might thus, in principle, exhibit $2n+1$ colours, excluding charge combinations of 2+ and 0 on bipyridilium units, because of intramolecular comproportionation.

There are two electrode reactions for each bipyridilium unit in an electrochromic system (scheme 1): reduction of the dication (**1**) to form a radical cation

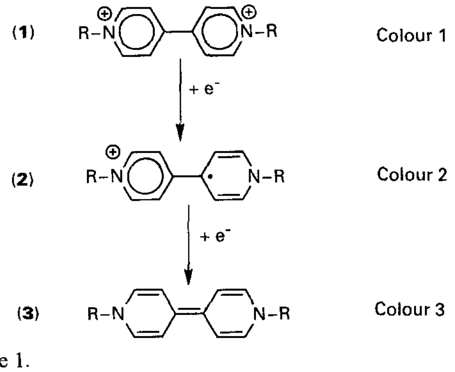
$$\mathrm{bipm}^{2+} + \mathrm{e}^- \longrightarrow \mathrm{bipm}^{+\cdot} \qquad (1)$$

((**1**), colour 1) ((**2**), colour 2)

and further reduction to yield a di-reduced species (**3**).

$$\mathrm{bipm}^{+} + \mathrm{e}^- \longrightarrow \mathrm{bipm}^{0} \qquad (2)$$

((**2**), colour 2) ((**3**), colour 3)

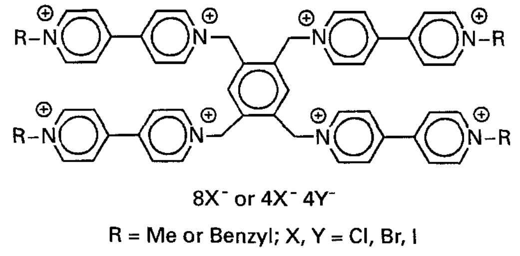


Scheme 1.

The majority of electrochromic display devices containing bipyridilium salts have employed heptyl viologen (1,1′-diheptyl-4,4′-bipyridilium) bromide [2–15] as the active component evincing colour. For this system, the effect of the anions [9, 10], electrode substrate [9, 11–13] and the potential used for deposition [13–16] have been investigated thoroughly. A few studies have also been made of different bipyridilium species in solution [13, 16–20], for example Bruinink [17] used a salt in which the two pyridinium rings were separated by several methylene linkages. Salts with alkyl groups other than heptyl, both symmetrical [12, 15, 18] and unsymmetrical [16, 18], have also been investigated, as have nuclear-substituted species [19, 20] having substituents attached directly to the aromatic pyridilium rings. Also, aryl-substituted bipyridilium salts have been studied for inclusion within ECDs [21–24].

Multiply linked bipyridilium systems offer the prospect of multistep varied colouration. To date, however, few species containing more than one bipyridilium unit have been considered for electrochromic used [25, 26]. Thus Hünig *et al.* [25] reported electrochrome chains containing two or three bipyridilium units separated by alkyl chains of various lengths and, in common with Harriman *et al.* [26], have prepared polyelectrochromic species in which the two bipyridilium units are connected via a xylyl link.

Here, novel species having four bipyridyl units around a central durene core (**4**) are studied electrochemically and spectroelectrochemically. Because of



$8X^-$ or $4X^-\ 4Y^-$

R = Me or Benzyl; X, Y = Cl, Br, I

(**4**)

---

* Present address: Department of Chemistry, Manchester Metropolitan University, Chester Street, Manchester M1 5GD, Great Britain.

the huge (8+) nominal cationic charge on the reactant, water with its high permittivity was chosen as solvent in order to minimise ion pairing with the anions. Mixed bromide–iodide, bromide–chloride, and solely chloride salts were studied. The methyl species (**4**) we call 'methyl-8+' and so on.

2. Experimental details

Syntheses of the bipyridilium multiredox species are detailed in the Appendix (roman numerals identify Appendix species): the anion compositions are determined by the halogens present in the starting reagents, or by ion exchange. Methylviologen MV^{2+} is reduced to $MV^{+\cdot}$ by Zn dust [27] or room-temperature aqueous sodium dithionite solution [30], and further reduced to MV° by warm (50 °C) sodium dithionite solution [31]; these procedures with methyl-8+ gave respectively a pink product, a purple product and a beige product; likewise with benzyl-8+, but the first product here was maroon-red, not pink. These three products could be generated electrochemically by reduction at the appropriate potentials (see Sections 3 and 4); for comparison with the chemically reduced products spectra of the electrogenerated species were obtained in a spectroelectrochemical cell of 1 cm pathlength with an ITO glass working electrode against one optical face, small frit-ended tubes being inserted (away from the light-beam) for reference and counter electrode solution contacts. In separate experiments, potentials corresponding to the three major cathodic peaks were applied and the corresponding colours were observed to grow out from the ITO surface. These were then scanned spectrophotometrically.

All the electrochemistry was performed at 20 °C on an Oxford Electrodes potentiostat. The working electrode was either 2 mm Pt wire, 0.1 mm diameter (cleaned electrolytically by ±0.7 V excursions in 0.1 M H_2SO_4 ending with $-0.7 \rightarrow 0$ V), an 8 mm diameter glassy carbon disc (prescoured with diamond paste then rinsed with acetone and then water) or indium tin oxide (ITO)-coated glass (Coates). A platinum counter electrode and a saturated calomel electrode as reference, completed the cells. Voltammetry solutions (containing 1 mM tetrabipyridyl and 0.2 M aqueous KCl) were purged with nitrogen. The CV's depicted proceed clockwise from 0.0 V.

U.v.–vis. spectroscopy of solutions was performed in a Hewlett Packard 8452A diode array spectrophotometer connected to an HP 9000-300 computer.

3. Results

3.1. *General*

Despite the use of aqueous media, specific anion effects were still marked: Br^- and I^- produced insoluble products on reduction, while Cl^- as sole counter-anion gave soluble product. Despite dissolution of the Br^-/I^- and Br^-/Cl^- species in excess (0.2 M) KCl, the retention of distinct spectra and voltammetry in connection with the particular counteranion of the specific electroactive material taken, indicates that the original counteranion remains associated with the cation and even the neutral throughout the measurements, and a rather wide study would be required to establish the individual equilibria involved. Here we present an overall survey of the main features of the different systems, particularly with a view to their application in electrochromism. The inferred sequence of association $I^- > Br^- > Cl^-$ would follow if, as is probable, weaker X^- hydration permits stronger association. The difference in proton n.m.r. for compounds (i) and (ii) in the appendix indicates a stronger specific interaction of I^- with the unreduced ring: the identical 4H of the chloride (ii) become distinguishable as 2H plus 2H in the iodide (i), and indeed *all* $bipm^{2+}$ iodides are coloured, but not the chlorides. Likewise, the n.m.r. of the final methyl-8+ species shows I^- in compound (iv) to influence all bipm protons equivalently, whereas in compounds (v) and (vi) the $4Br^-4Cl^-$ and $8Cl^-$ bipm protons are differentiated, which implies I^- symmetrically located on the bipm, and less intimate dispositions of the anions in (v) and (vi).

3.2. *Methyl-8+ 4Br⁻ 4I⁻*

Only two redox peaks were obtained in the CV of methyl-8+ bromide–iodide (**4**) when dissolved in aqueous potassium chloride electrolyte, with platinum as the working electrode. If formal electrode potentials E^0 are taken as the mid-point between respective cathodic and anodic CV peaks, then $E^0_{(1)} = -0.485$ V ($\Delta E_p = 60$ mV) and $E^0_{(2)} = -0.820$ V ($\Delta E_p = 60$ mV). At potentials more negative than $E^0_{(1)}$, the material deposited on the cathode was pink, while a purple species appeared at potentials negative of $E^0_{(2)}$. The reduction products on platinum gave rise to a hazy colouration (possibly indicating colloid or micellar species) around the electrode surface: with a transparent (ITO) electrode, product appeared to be a solid which partially adhered to the electrode, with applied potentials not exceeding −0.90 V vs SCE.

Glassy carbon working electrodes allowed access to more negative potentials which evoked more peaks in the CV of methyl-8+ $4Br^-4I^-$. The number of peaks, peak potentials (Table 1), and the respective peak

Table 1. Peak potentials and colours of the reduction products for methyl-8+ 4Br⁻ 4I⁻ (Fig. 1)

E_{pc}/V	E_{pa}/V	ΔE_p/mV	*Product colour*
−0.550	−0.480	70 (reductive limit taken as −0.7 V)	Pink
−0.780	−0.720	60	Purple
−1.210	−0.770	440 (peaks 3 and 3′a)	Beige
	−0.840	270 (peaks 3 and 3′b)	

The potential of *pa*(1) varied from −0.430 to −0.515 V, the value depending on E_λ.

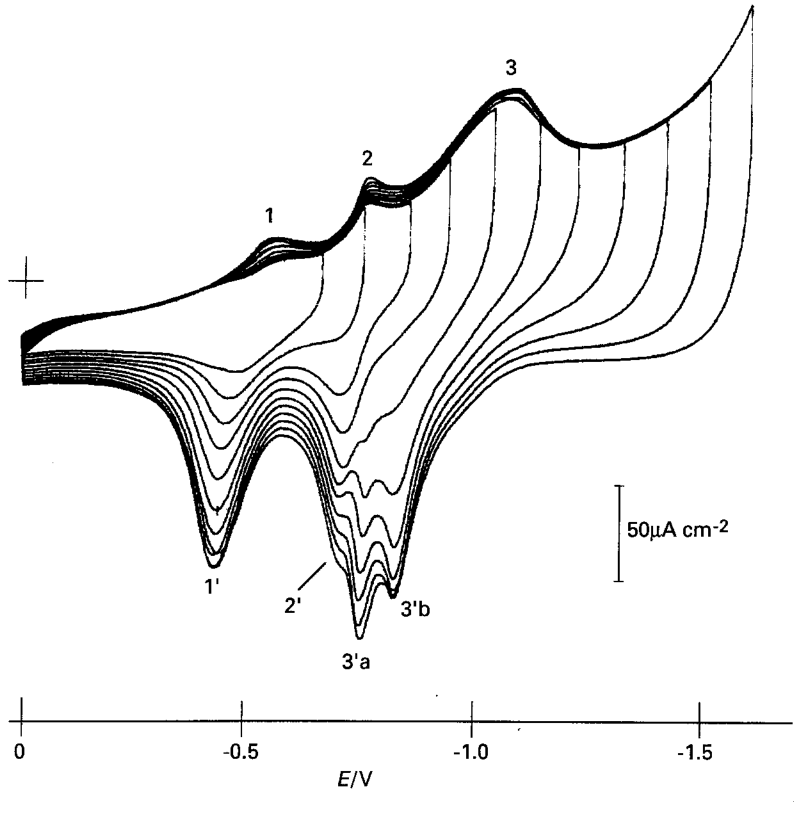


Fig. 1. CV on glassy carbon of 1 mM methyl-8+ $4Br^-4I^-$ in aqueous 0.2 M KCl, recorded as a function of switch potential E_λ. Scan rate $\nu = 50\,mV\,s^{-1}$. (All CVs start at 0 V and proceed clockwise.)

currents were dependent upon the scanning limit employed (Fig. 1).

CVs with scanning limits 0.0 V and −1.2 V were obtained over a range of scan rates ν, (Figs 2 and 3). Up to five cathodic peaks were evident, but complexity does ensue with colloid formation [21] favoured by slow scans, which were thus not used on the other samples. In the reverse, anodic, limbs, with slow scan rates, peak 1′ increased in size with respect to the other peaks, and a new oxidative peak appeared at −0.5 V. With single bipyridiliums, the comproportionation $bipm^{2+} + bipm^0 \rightarrow 2bipm^+$ enhances the concentration of $bipm^+$; here the corresponding peak 1′ was hence probably enlarged as a consequence of an *intermolecular* (not intramolecular) comproportionation, since CVs of the dilute methyl-8+ solutions (e.g. 0.1 mM) did not evince peak 1′. Peak 1′ was just evident when the concentration of methyl-8+ was low, but as the concentration of electroactive species was increased to say 0.5 mM, peak 1 increased and peak 1′ became obvious. CVs of dilute solutions did not show peak 1′, even with scan rates of only $1\,mV\,s^{-1}$. If the negative scan limit E_λ was extended from −1.1 to −1.3 V, (Fig. 3), the peak 1′ (now large at low ν) developed a minor post-peak (Fig. 3), and diminution of the other (−1 to −0.5 V) peaks. Colloidal complication could again be responsible for the reverse-limb divergences, but these largely disappear on the recathodising limbs, which approximately superimpose (Fig. 1).

U.v.–vis. spectra of the coloured reduction products of methyl-8+ $4Br^-4I^-$ are identical, whether of chemical or electrochemical origin. Table 2 lists approximate extinction coefficients ϵ for the former, approximate because, for example, some zinc is consumed in side reactions or present as ZnO neglected in stoichiometry calculations, while Fig. 4 shows spectroelectrochemical (potential dependent) traces for layers (of unknown concentration) of electroreduced species abutting the ITO electrode in the optical cell. The spectra are very similar to those of an *o*-xylyl compound prepared by Harriman *et al.* [26] (analogous to half the durene-8+ compound, see Section 4), but there are also some similarities to the spectra for the dimers of the radical cation of benzyl viologen [26], (Table 3). Accordingly, 1-methyl-1′-benzyl viologen (Me–Bz–V) was

Table 2. Spectroscopic data for aqueous methyl-8+ $4Br^-4I^-$ and chemical reduction products (ca. 50 μM, 20 °C, 2 mm cells)

Species	λ_{max}/nm	$\epsilon/dm^3\,cm^{-1}\,mol^{-1}$
Parent compound	410 (slight; CT with I^- anion?)	ca. 100
Pink	540 (sh at 395, 512, 628)	ca. 40 000
Purple	512, 542	ca. 35 000
Beige	495	ca. 9000

Table 3. Spectroscopic wavelength maxima for radical cation monomers and dimers of methyl benzyl viologen (Me–Bz–V) bromide/chloride and for benzyl viologen (BzV) chloride in water

Species	λ_{max}/nm	*Concentration*/μM	*Ref.*
Me–Bz–V^+	598, 395, (sh, 555, 660)	12	
$(Me\text{–}Bz\text{–}V)_2^{2+}$	545, 366, (sh 384, 395 596)	120	
BzV^+	604, 400	6.64	[25]
$(BzV)_2^{2+}$	540, 360	664	[25]

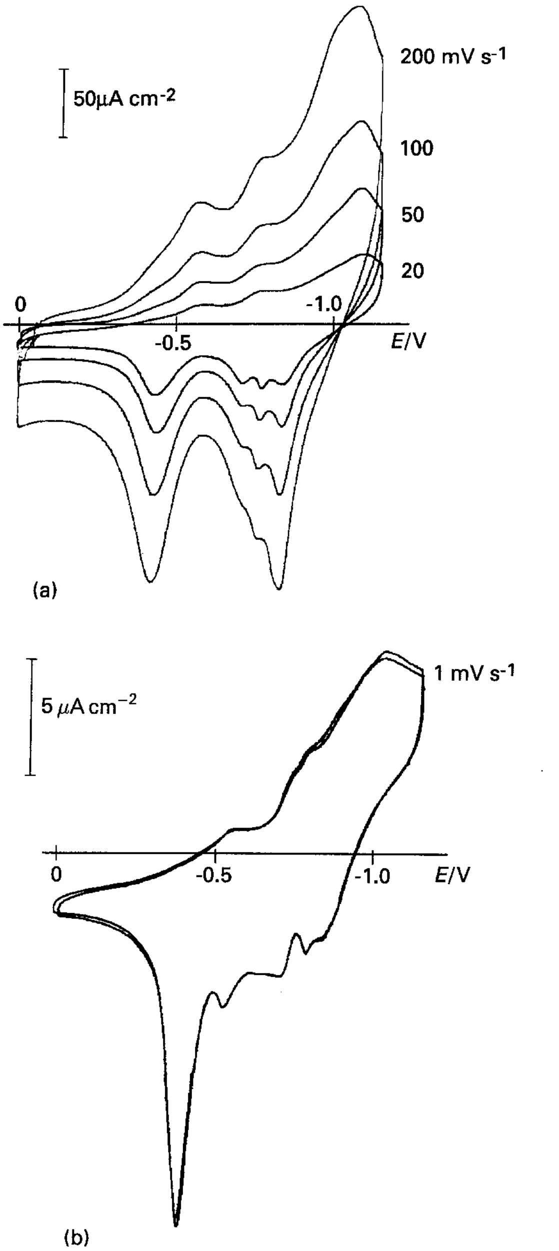


Fig. 2. The CV on glassy carbon of 1 mM methyl-8+ $4Br^{-}4I^{-}$ in aqueous 0.2 M KCl, taken as a function of scan rate. (a) $\nu = 20$–$200\,mVs^{-1}$ and (b) $\nu = 1\,mVs^{-1}$.

prepared as a close analogue to the chromophore within (4), and its u.v.–vis. spectrum investigated (Table 3). The concentrations cited in Table 3 are upper limits (equal to those of the fully oxidized species before reduction). ZnO is a strong adsorbent, hence some of the radical cation will undoubtedly have been adsorbed into this solid on the surface of the zinc dust used in reduction. The higher concentration peaks are ascribed to dimerised radicals, as follows.

Spectra of concentrated aqueous solutions of alkyl substituted bipyridilium radical cations are different from the spectra of dilute solutions, because of radical cation dimerisation [28, 30]. In organic solvents, dimerisation is inhibited by ion pair formation of the monomeric radical cation with its counter ion [32]; therefore in low dielectric solvents favouring ion pair formation, the spectrum was expected to

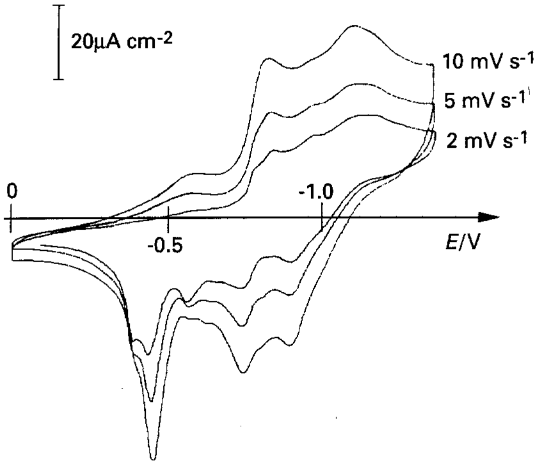


Fig. 3. The CV on glassy carbon 1 mM methyl-8+ $4Br^{-}4I^{-}$ in aqueous 0.2 M KCl, and with scan limits 0.0 and −1.3 V, as a function of scan rate ν.

show predominantly radical cation monomer. Accordingly, the methyl–benzyl viologen radical cation studied in methanolic solution had wavelength maxima at 396 nm, 610 nm and in addition 725 nm (close to aqueous monomer values, Table 3), indicating that the Me–Bz–V^{+} exists solely as monomer in methanolic solution at room temperature. Similarly, the methyl viologen radical cation MV^{+} in acetonitrile solution only exhibits spectroscopic bands attributable to unassociated (monomeric) MV^{+} [33].

3.3. *Methyl-8+ $4Br^{-}4Cl^{-}$*

With this compound in which Cl^{-} replaces I^{-}, the products of the electrode reaction were apparently more soluble in water than was the bromide-iodide salt, and its CV on glassy carbon was less complicated with but two reductive peaks (Fig. 5). The formal electrode potential of the first couple was −0.700 V ($\Delta E_p = 70\,mV$). Anodic (reverse limb) CV peaks occurred at −1.2 V, at −1.05, −0.84 and −0.75 V with a strong dependence of CV peak structure on scan rate again. Spectroscopic data for coloured reduction products are listed in Table 4.

3.4. *Methyl-8+ $8Cl^{-}$*

The methyl-8+ $8Cl^{-}$ salt was prepared by ion exchange in low yield (see Appendix). The salt was extremely water soluble in all its redox forms. The u.v.–vis. spectrum of the first reduction product have wavelength maxima at $\lambda_{max} = (510\,nm\ sh)$, 537, 353 and 830 nm (contrast Table 2 for the $4Br^{-}4I^{-}$ salt). The final product appeared purple.

Table 4. Absorbance maxima of aqueous methyl-8+ $4Cl^{-}4Br^{-}$ and chemical reduction products ca. 10^{-4} M

Species	λ_{max}/nm
Parent compound	402
Red/maroon	556
Purple	540

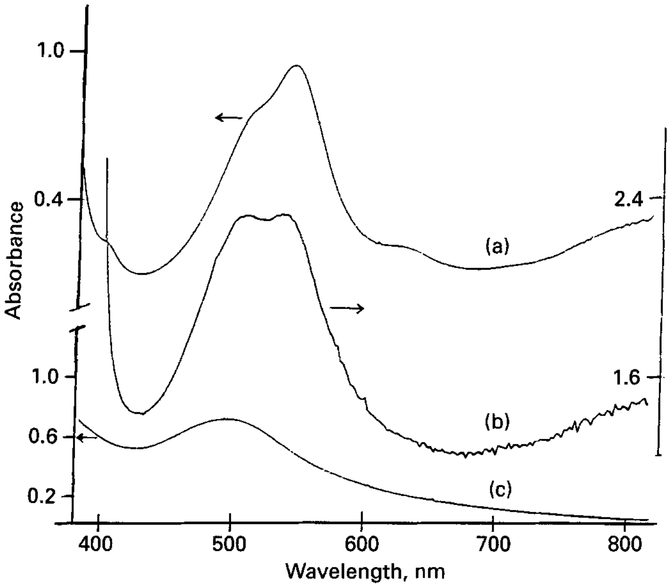


Fig. 4. U.v.–vis. spectra of the (a) pink (−0.5 V), (b) purple (−0.8 V) and (c) beige (−1.05 V) electrochemical reduction products of methyl-8+ $4Br^{-}4I^{-}$, originally ca. 50 μM.

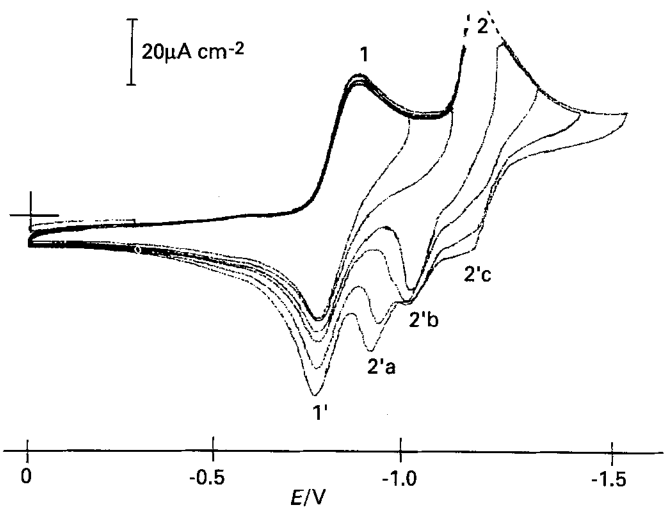


Fig. 5. CV on a glassy carbon of 1 mM methyl-8+ $4Br^{-}4Cl^{-}$ in aqueous 0.2 M KCl, as a function of E_{λ}. $\nu = 50\,mV\,s^{-1}$.

Apart from the incremental current behaviour (below; also see Section 4) the CV on glassy carbon in aqueous solution was relatively uncomplicated (Fig. 6), showing only two redox couples in the potential range 0 to −0.17 V giving $E_{pc(1)} = -0.430\,V$ and $E_{pa(1)} = -0.320\,V$ for the first peak and its reverse, and $E_{pc(2)} = -1.020\,V$ with $E_{pa(2)} = -0.830\,V$. When the switch potential, E_{λ}, was insufficiently negative for a second reduction reaction to occur, reproduced traces occurred, and the peak pa(1) was sharp, falling at a potential independent of the scan rate employed. However, when E_{λ} was sufficiently negative for a second electron transfer reaction to occur, at about −1.0 V, the peak pa(1), while still present, largely subsided: presumably product formed at pa(2) reacts with other reduction products, by comproportionation, disproportionation or adduct formation, to form longer-lived redox species (see Section 4).

3.5. *Benzyl-8+ $4Cl^{-}4Br^{-}$*

The species like methyl-8+, in which benzyl substituents were used instead of methyl, has properties similar to those of the methyl-8+ $4I^{-}4Br^{-}$ compound both in terms of its electrochemistry and its

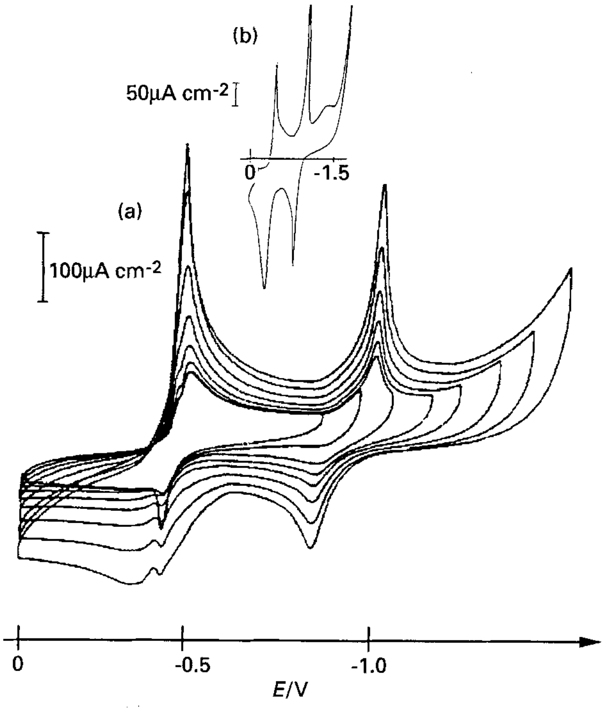


Fig. 6. CV on a glassy carbon of 1 mM methyl-8+ $8Cl^{-}$ in aqueous 0.2 M KCl. $\nu = 50\,mV\,s^{-1}$. (a) CV as a function of scan limit; (b) a preliminary scan (peak at E_{λ}, H_2 evolution; at −1.4 V, oxygen trace).

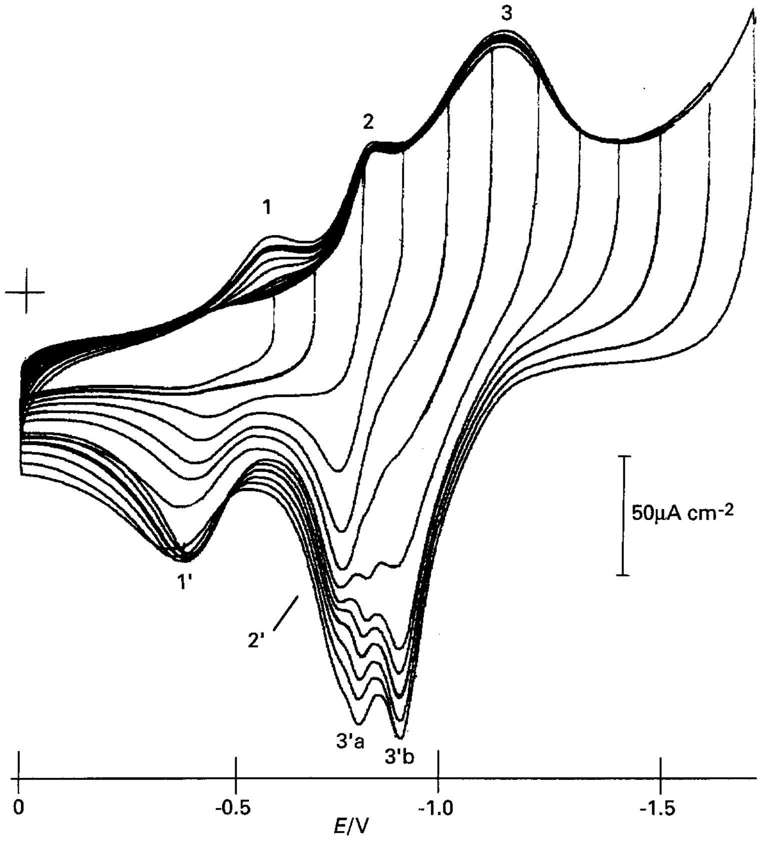


Fig. 7. CV on a glassy carbon of 1 mM benzyl-8 + $4Br^{-}4Cl^{-}$ in aqueous 0.2 M KCl, as a function of E_{λ}. $\nu = 50\,mV\,s^{-1}$.

spectroelectrochemistry (Table 5). With platinum as working electrode, the following peak potentials were obtained: $E_{pc(1)} = -0.515\,V$, $E_{pa(1)} = -0.350\,V$ (red/maroon product), and $E_{pc(2)} = -0.935\,V$, $E_{pa(2)} = -0.740\,V$ (purple product). On glassy carbon with more negative scanning limits accessible, more complicated CVs were obtained (Fig. 7): Table 5 lists peak potentials. Cathodic peak 1 grew on cycling, from insignificance, in contrast with otherwise similar Me-8 + Br^{-}/I^{-} CVs. A dependence was observed of CV peak structure on scan rate similar to that for the methyl-8 + iodide/bromide compound.

4. Discussion

Voltammetry (Figs 1 and 7) shows Me-8 + Br^{-}/I^{-} and Bz-8 + Cl^{-}/Br^{-} to undergo three reductive steps labelled 1, 2, 3, which from peak magnitudes and spectra (below) are assigned as $8+ \rightarrow 6+$, $6+ \rightarrow 4+$ and $4+ \rightarrow 0$, respectively. The Me-8 + Cl^{-}/Br^{-} and Me-8 + $8Cl^{-}$ (Figs 5 and 6) fail to achieve the final step before solvent breakdown. The complexities of the anodic limbs with all but Me-8 + $8Cl^{-}$ are ascribed to aggregation and possible colloidal interference, which is largely cancelled on return to the start potential 0 V. Me-8 + $8Cl^{-}$ shows simple anodic behaviour but continuously incremental currents on continuous cycling. Here oligomers (dimer, trimer, ...) of soluble nature are presumed to grow without cancellation, and to be of such geometry that any diminution of diffusion coefficient has less effect than the associated enhancement of transferable charge, so giving the current increases; the minimal peak-potential shifts are, however, notable. The specificity of anion influence is in accord with our general view (final paragraph of Section 4), and the intermediate CV behaviour of the Br^{-}/Cl^{-} cf. the Br^{-}/I^{-} and Cl^{-}-only species, in the Me-8 + series, is approximately as expected.

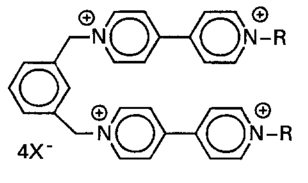
The u.v.–vis. spectra of alkyl bipyridilium radical cations in (dilute) aqueous solution typically show [30] a broad band at ca. 600 nm, shifting in more concentrated solutions to lower wavelengths, with a new band appearing at ca. 900 nm which is attributable to dimer [30], formed by Reaction 3

$$2bipm^{+} = (bipm)_2^{2+} \tag{3}$$

Harriman [26] prepared the *ortho* and the *meta*

Table 5. Peak potentials and colours of the chemical reduction products of benzyl-8 + 4Cl⁻4Br⁻

E_{pc}/V	E_{pa}/V	ΔE_p/mV	*Product colour*
−0.560	−0.480	70	Red/maroon
−0.745	−0.695	50	Purple
−1.150	−0.750	400 (from peaks 3 and 3′a)	Beige
	−0.830	320 (from peaks 3 and 3′b)	



R = Me; X = Cl

(5)

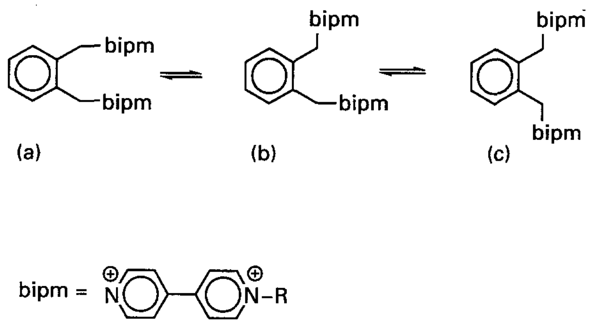


Fig. 8. Spatial configuration of the bis-bipyridyl compound with (a) bipm planes perpendicular to the benzene ring plane and possibly intramolecularly associated; (b) and (c) with no intramolecular association between bipm moieties.

bis(bipyridyl) species (**5**) which contains two bipyridine units. Following reduction, a species was formed with intramolecular radical association (overlap of bipyridilium π orbitals), Fig. 8(a). Fig. 8(b) and (c) show other molecular orientations possible which do not involve internal radical association, i.e., where coulombic repulsions are minimised. The methyl-8+ compound (**4**) (comprising four bipyridine units) is structurally similar to the species (**5**) [26] comprising two bipyridyl units. The species (**4**) may also assume several conformational isomers (Fig. 9), one of which has the planes of the two bipyridine units parallel in space and approximately perpendicular to the plane of the benzene bridge (Fig. 9). The intramolecular association in reduced forms of (**4**) involves pairing of the odd π electrons on the two bipyridine moieties. Since molecular movement about benzylic methylene linkages is free and unrestricted, the benzene ring in (**4**) acts merely as part of a flexible bridge between the two bipyridilium units.

In the spectra of the three reduction products of the methyl-8+ species (Fig. 4), the pink reduced species has a peak at 535 nm, whereas the purple product has two close optical bands, perhaps ascribable to chromophores of very similar structure, but somewhat different energy. The much lower extinction coefficient of the beige product implies, as expected, the absence of the optical charge transfer that confers intense colouration: since di-reduced *single*-bipyridilium species are commonly virtually colourless, with low extinction coefficients [32], the beige material is surely the zero-charge fully-reduced material. The pink species is thus deemed to be an intramolecularly associated radical cation pair (Fig. 9(a)), with the two bipyridyl moieties not involved in the interaction remaining dicationic and unassociated; the purple species possibly comprises two dimerised chromophores, Fig. 9(b).

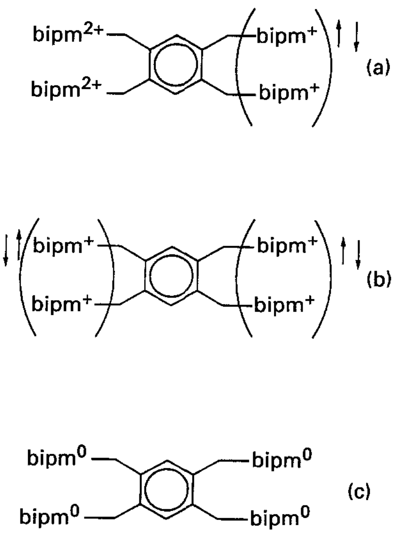


Fig. 9. Proposed structures of (a) pink species, (b) purple species and (c) beige species. Opposed arrows represent possibly paired electron spins of the odd electrons of half-reduced bipm moieties.

Table 6. Apparent diffusion coefficients D of aqueous methyl-8+ with counter-anion calculated from $i_{pc(1)}$ at $E_{pc(1)}$ assuming $n = 2$
For 8Cl⁻ species, first cycle

Anions	*$10^6 D$/cm^2 s^{-1}*
$4Br^-4I^-$	1.79 ± 0.2
$4Br^-4Cl^-$	2.25 ± 0.5
$8Cl^-$	2.85 ± 0.1

Since completion of this work, studies of double-bipyridilium and triple-bipyridilium species, in acetonitrile and dimethylformamide, respectively [35, 36] have appeared. The diminished complexity of the interactions here, resulting from having few bipyridiliums per molecule, has allowed more detailed analysis to be made, but questions do arise concerning anion participation, since even perchlorate, in low permittivity solvents, will associate with 4+ and 6+ cations; however, such solvents apparently do not cause insolubility of products [35, 36].

If it is assumed that the same number, n, of electrons are transferred at $E_{pc(1)}$ for the chloride and mixed-anion methyl-8+ species, then approximate diffusion coefficients, D, may be determined using the Randles–Sevcik equation [34] (approximate, since CVs are not exactly reversible). With n taken as 2, the values of D in Table 6 were obtained. Since all salts were dissolved in 0.2 M KCl, this is additional evidence for strong specific retentive ion association with the particular halides present in the preparation. The sequence implies least cation-anion association with Cl⁻.

5. Conclusion

Specific anion effects, intramolecular association, and comproportionation, lead to complicated electrochemistry, which is markedly different in chloride-only systems. Three major reductions are inferred, to give (pink or red) di-reduced species, (purple) tetra-reduced species and with two materials, (beige) fully-reduced product. The range of colouration is less than expected, and the colours in the pink-red-purple range are comparable with single-bipyridilium intensities.

Acknowledgements

We thank ICI Ltd and SERC for a CASE studentship for P.M.S.M.

References

[1] 'Electronic Materials for Displays Initiative'. Science and Engineering Research Council Meeting, Royal Institution, London, 26 Oct. 1993.

[2] C. J. Schoot, J. J. Ponjée, H. T. van Dam, R. A. van Doorn and P. T. Bolwijn, *Appl. Phys. Lett.* **23** (1973) 64.

[3] H. T. van Dam and J. J. Ponjée, *J. Electrochem. Soc.* **121** (1974) 1555.

[4] K. Belinko, *Appl. Phys. Lett.* **29** (1976) 363.

[5] J. Bruinink and C. G. A. Kregting, *J. Electrochem. Soc.* **125** (1978) 1397.

[6] S. Fletcher, L. Duff and R. G. Barradas, *J. Electroanal. Chem.* **100** (1979) 759.

[7] D. J. Barclay, B. F. Bowden, A. C. Lowe and J. C. Wood, *Appl. Phys. Lett.* **42** (1983) 911.

[8] A. Golden and J. Przyluski, *Electrochim. Acta* **30** (1985) 1231.

[9] R. J. Jasinski, *J. Electrochem. Soc.* **124** (1977) 637.

[10] A. Yasuda, H. Mori, Y. Takehana and A. Ohkoshi, *J. Appl. Electrochem.* **14** (1984) 323.

[11] R. J. Jasinski, *J. Electrochem. Soc.* **125** (1978) 1619.

[12] R. C. Ceislinski and N. R. Armstrong, *ibid.* **127** (1980) 2605.

[13] B. Scharifker and C. Wehrmann, *J. Electroanal. Chem.* **185** (1985) 93.

[14] J. Bruinink and P. van Zenten, *J. Electrochem. Soc.* **124** (1977) 1232.

[15] G. S. Ostrom and D. A. Buttry, *J. Electroanal. Chem.* **256** (1988) 411.

[16] A. Bewick, D. W. Cunningham and A. C. Lowe, *Makromol. Chem. Macromol. Symp.* **8** (1987) 355.

[17] J. Bruinink, J. J. Ponjée and C. G. A. Kregting, *J. Electrochem. Soc.* **124** (1977) 1854.

[18] M. Lapkowski and W. Szulbinski, *J. Electroanal. Chem.* **300** (1991) 159.

[19] N. J. Goddard, A. C. Jackson and M. G. Thomas, *ibid.* **159** (1983) 325.

[20] J. A. Barltrop and A. C. Jackson, *J. Chem. Soc., Perkin II* (1984) 367.

[21] D.R. Rosseinsky, P. M. S. Monk and R. A. Hann, *Electrochim. Acta* **35** (1990) 1113.

[22] J. G. Kenworthy, ICI Ltd., *British Patent 1314049* (1973).

[23] H. Mori, *Jpn. J. Appl. Phys.* **26** (1987) 1356.

[24] A. Yasuda and J. Seto, *J. Appl. Electrochem.* **18** (1988) 333.

[25] W. Geuder, S. Hünig and A. Suchy, *Tetrahedron* **42** (1986) 1665.

[26] P. Neta, M-C. Richoux and A. Harriman, *J. Chem. Soc., Faraday Trans. II* **81** (1985) 1427.

[27] S. G. Mayhew and F. Muller, *Biochem. Soc. Trans.* **10** (1982) 176.

[28] W. Schwartz, Ph.D. thesis, University of Wisconsin, 1962, quoted in [29].

[29] A. G. Evans, J. C. Evans and M. W. Baker, *J. Chem. Soc., Perkin Trans. II* (1977) 1797.

[30] E. Kosower and J. L. Cotter, *J. Am. Chem. Soc.* **86** (1964) 5524.

[31] J. E. Carey, J. E. Cairns and J. E. Colchester, *J. Chem. Soc., Chem. Comm* (1969) 1280.

[32] C. L. Bird and A. T. Kuhn, *Chem. Soc. Rev.* **10** (1981) 49.

[33] S. H. R. Brienne, R. P. Cooney and G. A. Bowmaker, *J. Chem. Soc., Faraday Trans.* **87** (1991) 1355.

[34] A. J. Bard and L. R. Faulkner, 'Electrochemical Methods', Wiley, New York (1980).

[35] M. Mohammed, *Electrochim. Acta* **33** (1988) 417.

[36] S. Imabayashi, N. Kitamura, S. Tazuke and K. Tokuda, *J. Electroanal. Chem.* **243** (1988) 143.

[37] J. E. Sutton, P. M. Sutton and H. Taube, *Inorg. Chem.* **18** (1979) 1017.

[38] (Assignment of NMR peaks for bipyridilium compounds) G. G. Barna and J. G. Fish, *J. Electrochem. Soc.* **128** (1981) 1290.

Appendix

1,2,4,5-tetrakis(1-bromomethyl)-benzene (tetrabromodurene) from Aldrich, was recrystallised from ethanol and water. Drying in a vacuum oven at 60 °C produced white crystals. 4,4′-bipyridine was purified by conversion to the diacetate salt and alkaline displacement, as literature [37]. All samples were vacuum dried at 60 °C.

(i) *1-methyl-4-(4′-pyridine)-pyridinium iodide*

To bipyridine (5.5 g, 28.6 mmol) dissolved in 50 ml of ethyl acetate, methyl iodide was added in vast excess and allowed to stand overnight. Excess MeI was removed from filtered brilliant-yellow crystalline product by washing thoroughly with ether. Recrystallisation from cold MeOH and ether was followed by drying in a vacuum oven. IR: 3026 cm^{-1}, s, (C–H); 1648 cm^{-1}, s, 1588 cm^{-1}, 1549 cm^{-1}, mult. (C=C, C=N, conj); 1416 cm^{-1}, s, (C=C arom); 811 cm^{-1}, s, (*o*-phenylene H). ^{1}H-NMR: (D_2O, SSD) peaks at 5.02 ppm, s, (3H), methyl; 8.30 ppm, d, (2H), 8.73 ppm, d, (2H), 9.22 ppm, t, (4H), pyridyl + pyridine [38].

(ii) *1-methyl-4-(4′-pyridine)-pyridinium chloride*

Aqueous 1-methyl-4-(4′-pyridine)-pyridinium iodide was converted to the chloride salt by ion-exchange using Duolite A101D resin (BDH) in concentrated sodium chloride solution. Solution was passed three times through a tube packed with the Duolite resin, recharged with NaCl following each passage. After rotary evaporation to dryness *in vacuo*, the product was solvent extracted with hot methanol, then recrystallized three times from methanol and ether to yield a pure white powder. IR: 3017 cm^{-1}, mult. (C–H); 1702 cm^{-1}, s, 1663 cm^{-1}, s, 1620 cm^{-1}, s, (C=C, C=N conj); 814 cm^{-1}, (*o*-phenylene H). ^{1}H-NMR: (D_2O, SSD) peaks at 4.50 ppm, s, (3H), methyl: 8.37 ppm, mult. (4H), 8.98 ppm, d, (4H), pyridyl + pyridine.

(iii) *1-methyl-1′-benzyl-4,4′-bipyridilium iodide chloride*

1-Methyl-4-(4′-pyridine)-pyridinium iodide (1 g, 3.16 mmol) dissolved in 25 ml of methanol was refluxed very strongly for 1 h with 25 ml of benzyl chloride (27.5 g, 0.21 mole). After partial solvent removal by vacuum, then cooling in an ice bath, ether was added slowly to effect precipitation. Two recrystallisations from MeOH and ether followed. IR: 3218 cm^{-1}, s, (C–H), 1620 cm^{-1}, mult. (C=C, C=N conj); 810 cm^{-1}, s, (*o*-phenylene H). ^{1}H-NMR: (D_2O, SSD) peaks at 2.25 ppm, s, (3H), methyl; 5.97 ppm, s, (2H), benzylic H; 7.59 ppm, s, (5H), phenyl H; 8.54 ppm, d, (4H), 9.10 ppm, d, (4H), pyridyl + pyridyl.

(iv) *methyl-8+* $4Br^{-}4I^{-}$

Tetrabromodurene (0.25 g, 0.56 mmol) dissolved in 10 ml of methanol was added slowly to a refluxing ethanolic solution of 1-methyl-4-(4′-pyridine)-pyridinium iodide (0.95 g, 3 mmol, excess) over a half-hour period and refluxed for 2 h. After cooling, the brown precipitate was collected by Buchner filtration, washed copiously with ether, and recrystallised from MeOH and ether. IR: 3036 cm^{-1}, mult. (C–H); 1639 cm^{-1}, s, (C=C, C=N conj); 1410 cm^{-1}, s, (arom C=C); 813 cm^{-1}, s, (*o*-phenylene H).

^{1}H-NMR: (D_2O, SSD) peaks at 4.59 ppm, s, (12H), methyl; 4.66 ppm, s, (8H), benzylic; 7.80 ppm, s, (2H), phenyl; 8.03 and 8.05 ppm, d of d, (16H), 8.86 and 8.88 ppm, d of d, (16H), bipyridyl.

(v) *Methyl-8+ 4Br⁻4Cl⁻*

Tetrabromodurene and excess 1-methyl-4-(4′-pyridine)-pyridinium chloride mixed in ethanol, were refluxed strongly for 2 h, and recrystallized as in (iv). IR: 2951 cm^{-1}, mult, (C–H); 1634 cm^{-1}, s, 1557 cm^{-1}, s, 1500 cm^{-1}, s, (C=C, C=N conj); 807 cm^{-1}, s, (*o*-phenylene H). ^{1}H-NMR: D_2O, SSD) peaks at 3.51 ppm, s, (12H), methyl; 6.25 ppm, s, (8H), benzyl; 7.91 and 8.45 ppm, d of d, (8H each), 8.75 ppm and 9.05 ppm, d of d, (8H each), bipyridyl.

(vi) *Methyl-8+ 8Cl⁻*

Methyl-8+ tetrabromide tetrachloride dissolved in concentration aqueous NaCl solution was passed through an ion-exchange column, as in (ii). After three elutions and water removal by rotary evaporation *in vacuo*, the product was extracted with hot methanol, and recystallized twice from cold MeOH and ether. IR: 2935 cm^{-1}, mult, (C–H); 1638 cm^{-1}, s, 1560 cm^{-1}, s, (C=C, C=N, conj); 828 cm^{-1}, s, (*o*-phenylene H). ^{1}H-NMR: (D_2O, SSD) peaks at 3.68 ppm, s, (12H), methyl; 6.26 ppm, s, (2H), phenyl; 6.47 ppm, s, (8H), benzyl; 7.96 and 8.41 ppm, d, of d, (8H each), 8.56 and 8.80 ppm, d of d, (8H each), bipyridyl.

(vii) *1-Benzyl-4-(4′-pyridine)-pyridinium chloride*

Bipyridine (5 g, 26 mmol), dissolved in toluene, was gently refluxed with excess benzyl chloride (25 ml, 27.5 g, 0.21 mole) for 2 h. Brown solid, which precipitated from solution, was collected, washed with ether, and recrystallized twice from warm methanol and ether. IR: 3420 cm^{-1}, 3120 cm^{-1}, mult (C–H); 1631 cm^{-1}, s, 1603 cm^{-1}, s, (C=C, C=N, conj); 831 cm^{-1}, s, (*o*-phenylene H). ^{1}H-NMR: (D_2O, SSD) peaks at 5.99 ppm, s, (2H), benzyl; 7.61 ppm, s, (5H), phenyl; 8.58 ppm, d, (4H), 9.22 ppm, d, (4H), pyridyl.

(viii) *Benzyl-8+ 4Cl⁻ 4Br⁻*

Tetrabromodurene with excess 1-benzyl-4-(4′-pyridine)-pyridinum chloride was refluxed strongly for 4 h. The solid which precipitated from cooled (scarlet) solution was collected by Buchner filtration, and ether washed then recrystallized twice from warm ethanol and ether. IR: 3210 cm^{-1}, mult, (C–H); 1633 cm^{-1}, s, (C=C, C=N conj); 1436 cm^{-1}, s, (arom C=C); 810 cm^{-1}, s, (*o*-phenylene H). ^{1}H-NMR: (D_2O, SSD) peaks at 6.08 ppm, s, (8H), benzylic; 6.42 ppm, s, (8H), benzylic; 7.68 ppm, s, (2H), phenyl; 8.71 and 8.77 ppm, d of d, (16H), 9.20 and 9.32 ppm, d of d, (16H), bipyridyl.