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Ambient temperature thermotropic liquid crystalline viologen bis(triflimide) salts

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Two dicationic salts with bis(triflimide) as counterions exhibited crystal-to-smectic liquid crystalline phase transitions ($T_m=41$ and 37°C) and smectic-to-isotropic liquid phase transitions ($T_i=112$, 136°C). They had a broad liquid crystalline phase range (71 – 99°C) and an excellent range of thermal stability (360 – 364°C). Their mixtures of various compositions also displayed liquid crystalline properties from r.t. to an extended range of temperatures. They exhibited fluorescence in 1, 2-dimethoxyethane and methanol.

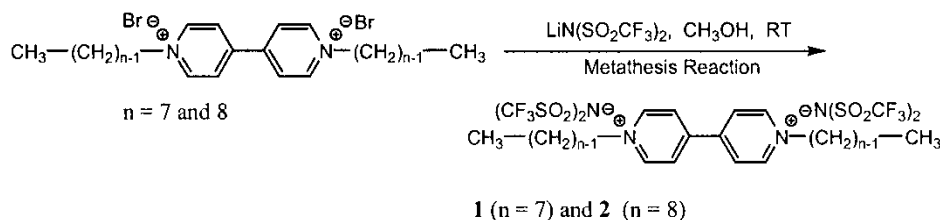
1. Introduction

The 1,1'-dialkyl-4,4'-bipyridinium salts are usually known as viologens. They are an important class of compounds, which exhibit a number of interesting properties including electrical conductivity, photochromism, electrochromism, and thermochromism [1]. With suitably modified chemical architectures, they also exhibit thermotropic liquid crystalline (LC) properties [2–6]. For example, the thermotropic LC phase range for a series of these compounds with variation of alkyl chain lengths ($n=5$ – 10 and 18) and anions ($X^- = \text{Cl}^-$, Br^- , I^- , BF_4^- , OOCF_3^- , O_3SCH_3^- , and OTs^-) are sensitive to both the alkyl chain length and the anion. For a fixed alkyl chain length, considerable variability in thermal transitions is observed even when the anions are restricted to the halide ions. Among these compounds, the reversibility of various thermal transitions is poor; all three halide compounds decompose before exhibiting the isotropic liquid phase. Compounds with other anions show thermal properties ranging from the absence of an LC phase with BF_4^- , to reversible polymesomorphism with O_3SCH_3^- . In general, they all form very viscous melts when compared with conventional, non-ionic thermotropic LC compounds [2].

The compounds 1,1'-di(3,6,9-trioxatridecyl)-4,4'-bipyridinium dibromide and 1,1'-di(3,6,9,12-tetraoxatradecyl)-4,4'-bipyridinium diiodide have LC properties from room temperature up to about 200 and 154°C , respectively. 1,1'-Di(3,6,9-trioxatridecyl)-4,4'-bipyridinium diiodide, has a crystal-to-LC phase transition (T_m) at 63°C and an LC-to-isotropic transition (T_i) at 216°C [3, 4]. In contrast, 1,1'-di(3,6,9-trioxadecyl)-4,4'-bipyridinium bis(tetrafluoroborate) and 1,1'-di(3,6,9-trioxadecyl)-4,4'-bipyridinium ditosylate are room-temperature (RT) ionic liquids [5]. The 1,1'-diphenyl-4,4'-bipyridinium dialkylbenzenesulfonates that contain alkyl chains of length 10, 13, and 15 carbon atoms have T_m values (205 , 190 and 168°C , respectively) above which each exhibits a SmA phase; the SmA phase for each then persists up to their decomposition temperatures (280 – 290°C) [6]. Thus, it is evident that viologen compounds having suitably designed chemical architectures (dicationic salts), such as 1-alkyl-3-methylimidazolium, *N*-alkylpyridinium, and quaternary ammonium salts each of which is a monocationic salt [7–9], have great potential for the preparation of both RT ionic liquids (green solvents) and room temperature liquid crystalline (RTL) ionic liquids (ordered reaction media).

With this objective in mind, we describe in this article the ready preparation of two new viologen compounds; 1,1'-diheptyl-4,4'-bipyridinium bis(triflimide) (**1**) and 1,1'-dioctyl-4,4'-bipyridinium bis(triflimide) (**2**). We

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have used the metathesis reaction of the corresponding 1,1'-dialkyl-4,4'-bipyridinium dibromides with lithium triflimide in a common organic solvent (see the scheme 1). Their thermotropic LC properties have been characterized by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), thermogravimetric analysis (TGA), and X-ray diffraction (XRD). The triflimide organic counterion was selected because of its unique ability to depress the melting points of ionic salts [10, 11]. It also has great thermal stability when compared with other organic counterions. For example, the thermal stability of 1-ethyl-3-methylimidazolium triflimide—a RT ionic liquid—in both air and nitrogen persists up to 400°C [10]. Note here that the triflimide is an interesting organic counterion, since it plays a pivotal role for the generation two major classes of RT ionic liquids [10, 11].

2. Experimental

The 1,1'-dialkyl-4,4'-bipyridinium dibromides were prepared by adding the appropriate slight excess of two equivalents of alkyl bromides to a solution of one equivalent of 4,4'-bipyridine in acetonitrile. After heating at reflux for 24 h the yellow crystalline dialkylated products were filtered from the reaction mixture (0°C), washed with acetone, and recrystallized twice from H₂O/acetone (15/85) [2]. Their purity was checked by ¹H and ¹³C NMR spectroscopy (the absence of peaks at $\delta = 7.83, 8.32, 8.64,$ and 8.83 ppm of the monoalkylated product in D₂O) and elemental analysis. The viologens **1** and **2** were prepared by metathesis of the corresponding 1,1'-dialkyl-4,4'-bipyridinium dibromides with lithium triflimide in a common organic solvent. In a typical procedure, 1.0 g (1.9 mmol) of 1,1'-diheptyl-4,4'-bipyridinium dibromide was dissolved in 20 ml methanol. To this solution, 30 ml of lithium triflimide (1.2 g, 4.2 mmol, 10% excess) in methanol was slowly added with stirring; the resulting solution was stirred overnight. After removing methanol in a rotary evaporator, water was added to the solid products to dissolve LiBr and excess lithium triflimide, thus giving the desired compound **1**. It was further purified by simply washing with water several times, and dried in vacuum at RT for several days. The yield was essentially quantitative.

Typical data for **1**: IR (KBr)/ ν_{max} cm⁻¹: 3073, 2932, 2862, 1642, 1563, 1507, 1450, 1351, 1195, 1137, 1058, 835, 788, 740, 654, 620, 600, 571, 514. δ_{H} (CD₃OD, 400 MHz, ppm): 9.22–9.23 (4H, d, $J = 6.61$ Hz), 8.61–8.62 (4H, d, $J = 6.24$ Hz), 4.70–4.74 (4H, t, $J = 7.56$ Hz), 2.08 (4H, m), 1.33–1.43 (16H, m), 0.89–0.92 (6H, t, $J = 6.76$ Hz); δ_{C} (CD₃OD, 100 MHz, ppm): 151.49, 147.04, 128.37, 125.97, 122.79, 119.60, 116.41, 63.44, 32.68, 32.54, 29.79, 27.16, 23.57, 14.34. Anal: calcd for C₂₈H₃₈N₄O₈F₁₂S₄ C 36.76, H 4.19, N 6.12, S 14.02; found C 36.42, H 4.30, N 6.13, S 14.12%.

Data for **2**: IR (KBr)/ ν_{max} cm⁻¹: 3135, 3074, 2930, 2861, 1644, 1563, 1514, 1474, 1454, 1347, 1236, 1201, 1133, 1057, 838, 790, 742, 648, 621, 600, 571, 516. δ_{H} (CD₃OD, 400 MHz, ppm): 9.31–9.33 (4H, d, $J = 6.89$ Hz), 8.70–8.73 (4H, d, $J = 6.66$ Hz), 4.75–4.79 (4H, t, $J = 7.59$ Hz), 2.08 (4H, m), 1.33–1.43 (20H, m), 0.89–0.92 (6H, t, $J = 6.76$ Hz); δ_{C} (CD₃OD, 100 MHz, ppm): 151.47, 147.04, 128.36, 125.96, 122.78, 119.59, 116.41, 63.42, 32.87, 32.54, 30.13, 30.08, 27.21, 23.64, 14.38. Anal: calcd for C₃₀H₄₂N₄O₈F₁₂S₄ C 38.22, H 4.49, N 5.94, S 13.60; found C 38.04, H 4.44, N 5.92, S 13.87%.

The FTIR spectra of compounds **1** and **2** were recorded with a Nicolet FTIR analyser with their neat films on KBr pellets. The ¹H and ¹³C NMR spectra were recorded with three RF channels operating at 400 and 100 MHz, respectively, in CD₃OD using TMS as an internal standard. The phase transition temperatures were measured by DSC (TA 2100 DSC) in nitrogen at both heating and cooling rates of 10°C min⁻¹. Binary mixtures of **1** and **2** in various compositions (by wt%) were prepared directly in aluminum DSC pans by weighing appropriate amounts of the compounds and sealing the pans hermetically. The mixtures were then heated in the DSC cell compartment at a heating rate of 10°C min⁻¹ in nitrogen well above each of their T_i values for complete homogenization, and cooled at a rate of 10°C min⁻¹ to -10°C. This procedure gave homogeneous mixtures of **1** and **2**, since the subsequent heating and cooling cycles for each of these mixtures resulted in reproducible DSC thermograms.

TGA measurements were performed with a TA 2100 instrument at a heating rate of 20°C min⁻¹ in nitrogen. The optical textures of LC phases of compounds **1**, **2**

and their variable composition mixtures were observed with a Nikon polarizing optical microscope equipped with a Mettler FP80 hot-stage. X-ray diffraction patterns were recorded from a Siemens X-1000 system with an area detector using a graphite monochromator to select CuK_α radiation. An *in situ* magnetic field of ~ 3 kG was applied to orient the LC director. Absorption spectra of these viologen compounds **1** and **2** in spectrograde 1,2-dimethoxyethane (DME) and methanol were recorded with a Varian Cary 3 Bio UV-Vis spectrophotometer at room temperature. Their photoluminescence spectra in solutions of DME and methanol were recorded with a Perkin-Elmer LS 55 luminescence spectrometer with a xenon lamp source.

3. Results and discussion

1,1'-Diheptyl-4,4'-bipyridinium dibromide had a reversible crystal-to-crystal transition at 107°C ($\Delta H = 15.6 \text{ kJ mol}^{-1}$), but no melting transition up to 277°C , where a weight loss of 5% occurred at a heating rate of $20^\circ\text{C min}^{-1}$ in nitrogen. In contrast, the viologen **1** showed two endotherms in the first and second heating cycles of its DSC thermograms. In each of the corresponding cooling cycles, there were three exotherms, as shown in figure 1. In conjunction with the POM studies, it was determined that the low temperature endotherm corresponded to the crystal-to-smectic LC phase transition ($T_m = 41^\circ\text{C}$ with $\Delta H_m = 14.4 \text{ kJ mol}^{-1}$); the high temperature endotherm corresponded to the smectic LC-to-isotropic transition ($T_i = 112^\circ\text{C}$ with $\Delta H_i = 8.7 \text{ kJ mol}^{-1}$). Thus, **1** had a large LC phase range (71°C). The highest temperature exotherm that underwent a low hysteresis (that is, a few degrees of supercooling) corresponded to the transition from the isotropic phase to the LC phase. The two low

temperature exotherms (24 and 29°C), which underwent a degree of supercooling of 17 and 12°C , respectively, were related to the transitions from the LC to crystalline phases. Their corresponding transition enthalpies were 12.6 and 0.6 kJ mol^{-1} , respectively. Thus, it was found that viologen **1** exhibited an enantiotropic LC phase at a lower temperature than many 1-alkyl-3-methylimidazolium tetrafluoroborates or hexafluorophosphates and *N*-alkylpyridinium hexafluorophosphates, all of which contain a long alkyl chain typically containing 12, 14, 16 or 18 carbon atoms [12, 13]. On the other hand, the enantiotropic LC phase of **1** was in contrast to 1-alkyl-3-methylimidazolium (alkyl chain lengths of 12, 14, 16 and 18 carbon atoms) triflimide salts, all of which undergo crystal-isotropic transitions at relatively low temperatures (16.6 – 44.8°C) [14].

Similar to 1,1'-diheptyl-4,4'-bipyridinium dibromide, the 1,1'-dioctyl-4,4'-bipyridinium dibromide had a reversible crystal-to-crystal transition at 129°C ($\Delta H = 20.5 \text{ kJ mol}^{-1}$), but no melting transition up to 275°C . Its TGA study indicated that a weight loss of 5% occurred at 291°C in nitrogen at a heating rate of $20^\circ\text{C min}^{-1}$; but it decomposed at 280°C , as determined by DSC in nitrogen at a heating rate of $10^\circ\text{C min}^{-1}$, presumably via Hofmann elimination associated with quaternary ammonium salts [9]. In comparison, the viologen **2**, like **1**, showed two endotherms at 37 and 136°C in the first heating cycle of its DSC thermogram. Correspondingly, in the first cooling cycle it showed two exotherms at 11 and 133°C . In contrast the second heating cycle showed two low temperature endotherms at 17 and 28°C and a high temperature endotherm at 137°C , but it showed two exotherms at 9 and 133°C in the second cooling cycle, similar to the first cooling cycle (not shown). The low temperature endotherm at 37°C in the first heating cycle was its T_m , with $\Delta H_m = 33.4 \text{ kJ mol}^{-1}$, which had a high degree of supercooling of 26°C . The high temperature endotherm at 136°C was its T_i with $\Delta H_i = 9.3 \text{ kJ mol}^{-1}$, which had a low degree supercooling of 3°C .

Thus, compound **2** had a larger LC phase range (99°C) than **1**, by 28°C , because of the even number of methylene units in its alkyl tails, commonly known as odd-even effect. This effect usually reflects the more efficient packing (or ordering) of even-numbered methylene units, both in the crystalline state and in the LC phase, than that of odd-numbered methylene units [15]. In the second heating cycle, its T_m appeared at 28°C along with a crystal-to-crystal transition at 17°C , presumably because of polymorphism, but its T_i remained essentially identical to that in the first heating cycle, which also had a low degree of supercooling.

It is relevant to note here that the LC-to-crystalline

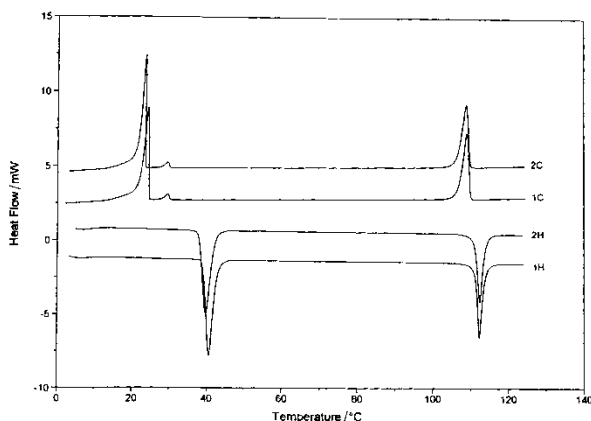


Figure 1. DSC thermograms of viologen **1** obtained at heating and cooling rates of $10^\circ\text{C min}^{-1}$.

phase transitions for many ionic compounds usually show a large hysteresis, which is simply related to the induction periods of their crystallization processes. Additionally, the crystalline state at low temperature, especially when cooling from the melt, shows a complex polymorphism, with a variety of coexisting metastable states. Consequently, the melting transition into the LC phase is quite difficult to detect unambiguously [16]. Thus, it was found that viologen **2**, similar to viologen **1**, also exhibited an enantiotropic LC phase at a lower temperature than those of many 1-alkyl-3-methylimidazolium tetrafluoroborates or hexafluorophosphates and *N*-alkylpyridinium hexafluorophosphates. The alkyl chain length in each of these salts is typically 12, 14, 16 or 18 carbon atoms [12, 13]. The observation of an enantiotropic LC phase of **2** was also in contrast to 1-alkyl-3-methylimidazolium triflimide salts that contain 12, 14, 16, or 18 carbon atoms in their alkyl chains [14].

In an attempt to produce RTLC ionic liquids, preferably without decreasing the LC temperature ranges, a study of the effect of mixing **1** and **2** in various compositions was conducted. Such a procedure is routinely used to lower the melting transitions of both ionic salts (solid-to-liquid) and ionic/neutral LC compounds (solid-to-LC phase) by the formation of eutectic mixtures. Figure 2 shows the DSC thermograms of mixtures of **1** and **2** in various compositions in their first heating cycles after homogenization. As expected, the T_m and T_i transitions for each of these mixtures were not as sharp as the transitions observed for the individual components, since one component acts as an impurity for the other in these mixtures. All of these transitions were rather broad and occurred

over a relatively wide range of temperature. However, the T_m values for all of the mixtures decreased gradually over the compositions studied and T_i values remained essentially between 112 and 137°C, which were the T_i values of **1** and **2**, respectively. Thus, the mixture of **1** and **2** (20:80 by wt%) had not only the lowest T_m value at 22°C but also the highest T_i value at 132°C among the mixtures studied. It also exhibited a wider LC phase range (112°C) than those of the individual components (71 and 99°C).

For viologens **1** and **2** the thermal stability limit (the temperature at which a 5% weight loss occurred) was determined in nitrogen at a heating rate of 20°C min⁻¹ by TGA. The limit was 364 and 360°C, respectively for **1** and **2**, much higher than those of the corresponding precursor dibromide compounds (*vide supra*).

The compounds **1**, **2** and their mixtures of various compositions formed turbid melts above their T_m values (22–41°C) that exhibited strong stir opalescence. This property was taken as a preliminary indication of their LC nature. Further characterization of their melt morphology was evaluated by visual observations by POM. Their optical textures were essentially identical. Typically, they formed schlieren textures after immediate melting transitions, mixed with small mosaic textures, which grew into large mosaic textures before the T_i transitions. On cooling from the isotropic phase, each compound/mixture exhibited various types of mosaic textures and spherical birefringent particles having a more or less regular cloverleaf shape (figure 3). All of them were indicative of smectic LC phases [17–20]. The viologen **2** and all of its mixtures with **1**, but not the viologen **1** itself, retained these LC phases down to RT, since their crystallization exotherms were below RT.

The XRD studies at different temperatures suggested that the LC phases exhibited by the two viologens **1** and **2** were essentially identical. Upon cooling from the isotropic liquid to the LC phase in the presence of a magnetic field, the two-dimensional XRD pattern of each showed two sharp quasi-Bragg peaks at small angle and two diffuse crescents at wide angle (figure 4). The diffuse crescents and the quasi-Bragg peaks are oriented normal to each other indicating that the LC phase is smectic A (SmA) [20]. From the observed peaks at small angles, the experimental lamellar thicknesses for the viologens **1** and **2** were found to be 21.01 and 22.06 Å, which were in quite good agreement with the calculated values of 24.22 and 26.74 Å, respectively, from molecular mechanics (figure 5). The diffuse crescents at the large angle for both the viologens were observed at $2\theta = 17^\circ$, which corresponds to an intermolecular distance of 5.2 Å.

The UV-Vis absorption spectra of **1** and **2** in DME

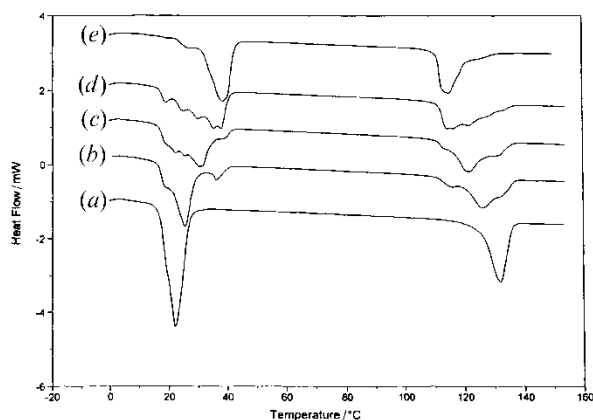


Figure 2. DSC thermograms of mixtures of **1** and **2** in various compositions by wt% in their first heating cycles, obtained at a heating rate of 10°C min⁻¹, after homogenization. **1:2** (a) 20:80, (b) 40:60, (c) 50:50, (d) 60:40, and (e) 80:20.

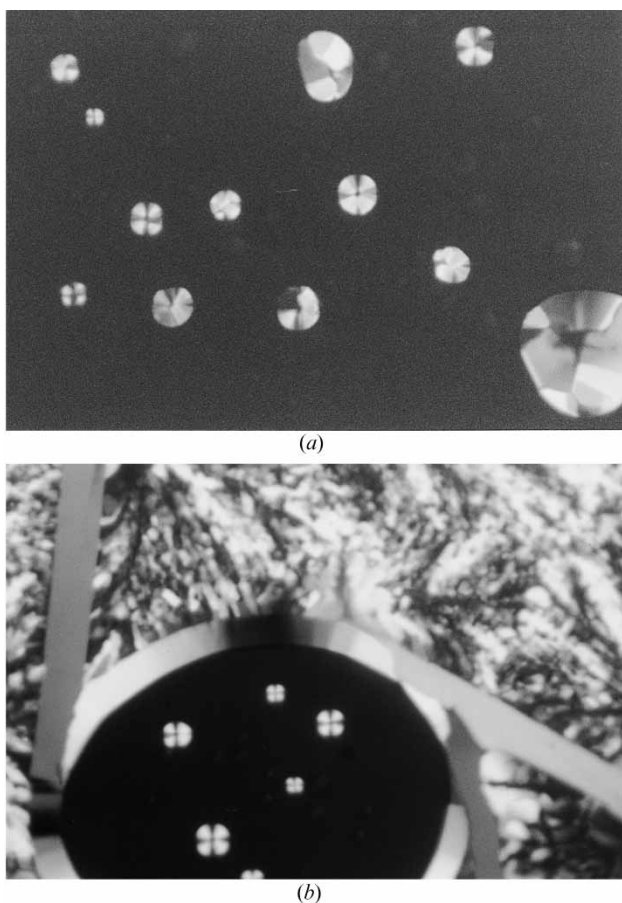


Figure 3. Photomicrographs of (a) **1** and (b) **2** obtained on cooling at a rate of $10^{\circ}\text{C min}^{-1}$ from the isotropic phase under crossed polarizers, each exhibiting a smectic LC phase (magnification $400\times$).

showed two λ_{max} values at 209 and 264 nm. In contrast, their absorption spectra in methanol contained a single peak at $\lambda_{\text{max}}=265$ nm. The excitation spectrum of **1** in DME during monitoring at 530 nm contained three major peaks at $\lambda_{\text{ex}}=225$, 319 and 476 nm, along with a shoulder peak at 487 nm. In contrast, its excitation spectrum in methanol during monitoring at 530 nm contained two major peaks at $\lambda_{\text{ex}}=337$, and 430 nm, along with a shoulder peak at 404 nm. The excitation spectra of **2**, in both DME and methanol, consisted of two major peaks with several shoulders during monitoring at 530 nm. These λ_{ex} values were at 251 and 476 nm (271, 286 and 489 nm as shoulder peaks) and at 227 and 429 nm (316 and 351 nm as shoulder peaks), respectively.

The emission spectra of **1** in both DME and methanol contained several λ_{em} values depending on the excitation wavelengths used. For example, in DME at excitation wavelengths of 215, 220 and 225 nm it exhibited λ_{em} values at 307 (strong) and 532 nm (weak).

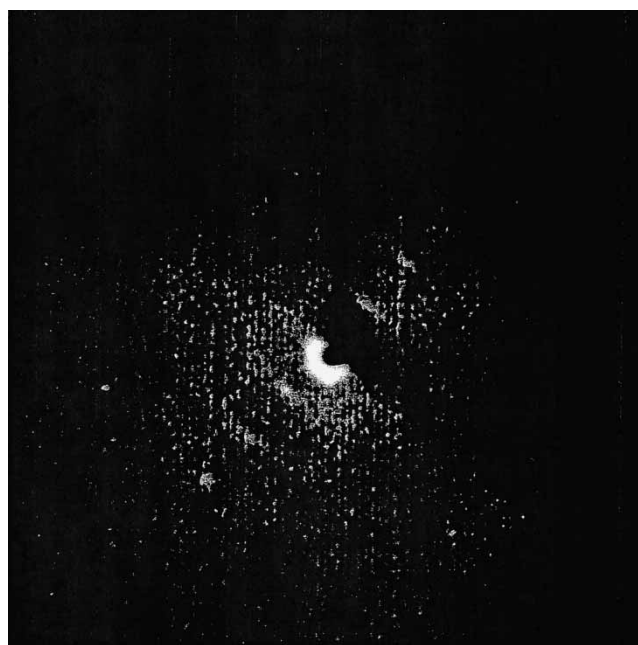
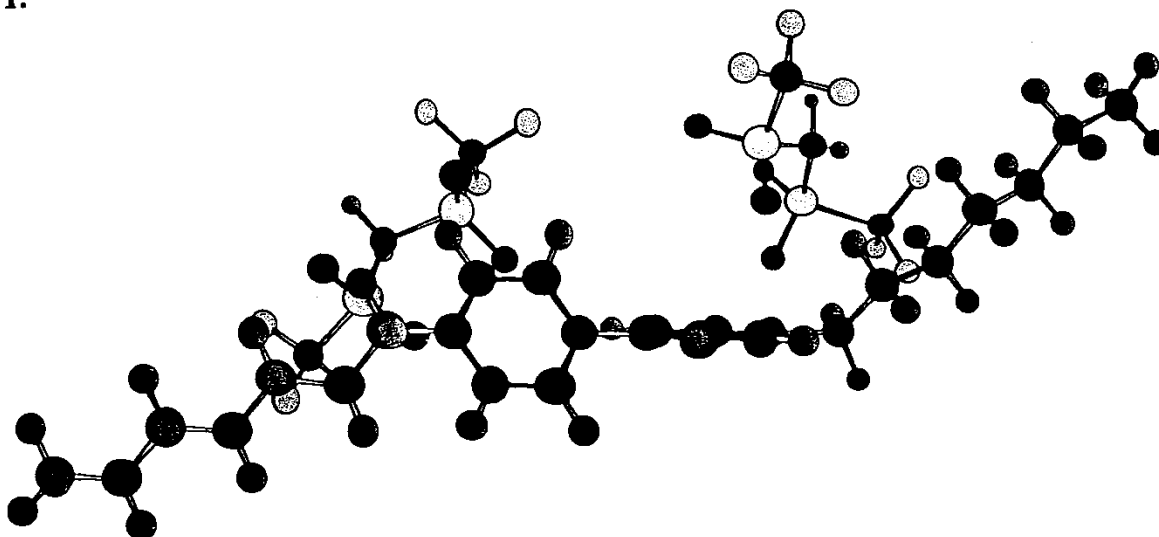


Figure 4. X-ray diffraction pattern of viologen **1** in the LC phase taken at 90°C exhibiting a SmA phase.

At excitation wavelengths of 310, 320 and 330 nm, each of the emission spectra consisted of two peaks at $\lambda_{\text{em}}=358$ and 442 nm of almost equal intensity. At excitation wavelengths of 360, 470 and 500 nm, the λ_{em} value was located at 532 nm, which was the highest intensity among all the emission spectra. In methanol, at excitation wavelengths of 220, 225 and 230 nm, each of the emission spectra showed at $\lambda_{\text{em}}=307$ nm; at excitation wavelengths 310 and 330 nm, each of emission spectra exhibited λ_{em} values at 360 and 443 nm; at further higher excitation wavelengths of 390, 410 and 430 nm, each of the emission spectra exhibited λ_{em} values at 443, and 531 nm. At an excitation wavelength of 330 nm, the emission spectrum had the highest intensity among all the emission spectra.

Figure 6 gives the emission spectra of **2** in both DME and methanol at various excitation wavelengths, showing that λ_{em} values were dependent both on the excitation wavelength and on the nature of the solvent (non-polar or polar) used. Although the photoluminescence quenching process of a π -conjugated polymer by numerous viologens in aqueous solution opens an opportunity for the development of biological and chemical sensors for use in medical diagnostics and toxicology [21–24], the fluorescence property of viologens **1** and **2** in both non-polar and polar organic solvents, to our knowledge, is the first report of such a study. This property of the ionic salt can be exploited further for the development of chemical sensors.

1.



2.

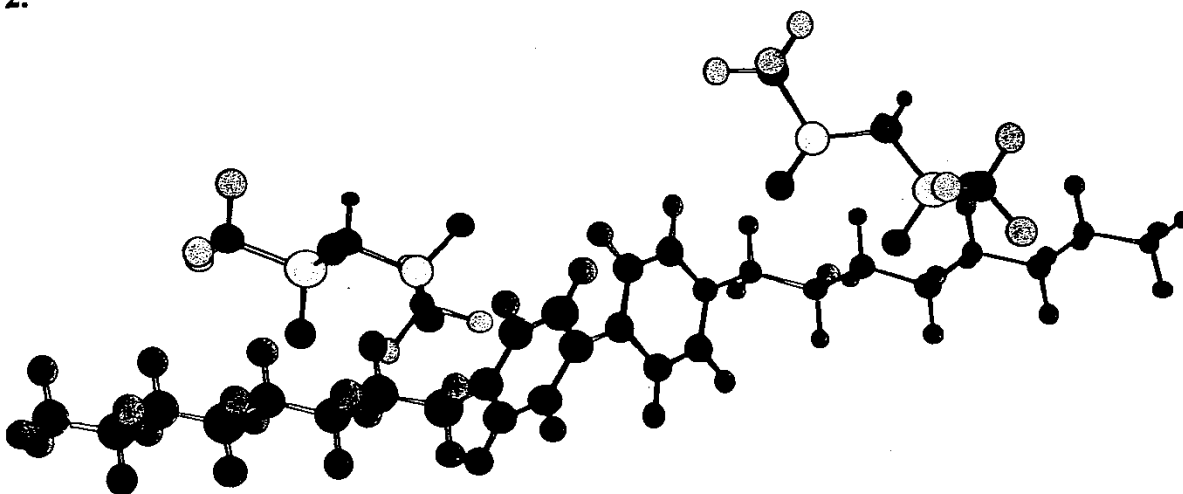


Figure 5. Molecular models of 1 and 2 on the basis of molecular mechanics calculation.

4. Conclusions

The two new dicationic bis(triflimide) salts, otherwise known as viologens, and their mixtures of various composition displayed LC properties from RT to extended temperature ranges as determined with a number of experimental techniques. Thus, the triflimide anion is a useful organic counterion for the generation of not only RT ionic liquids but also RT liquid crystalline ionic liquids. In fact, they are the first examples of ambient temperature liquid crystalline ionic salts containing bis(triflimide) as counterions. They have high potential as unique solvents, since their LC properties are maintained over a wide temperature range. The rigidity of molecular ordering and mobility

make these ionic liquids suitable for many stereochemically controlled organic reactions [25]. The interesting fluorescent properties of these ionic salts can be exploited further for the development of chemical sensors. Studies are now underway to facilitate synthetic variation in the length of alkyl chains in these dicationic salts and, therefore, to design a class of RTLC ionic liquids with predictable LC properties.

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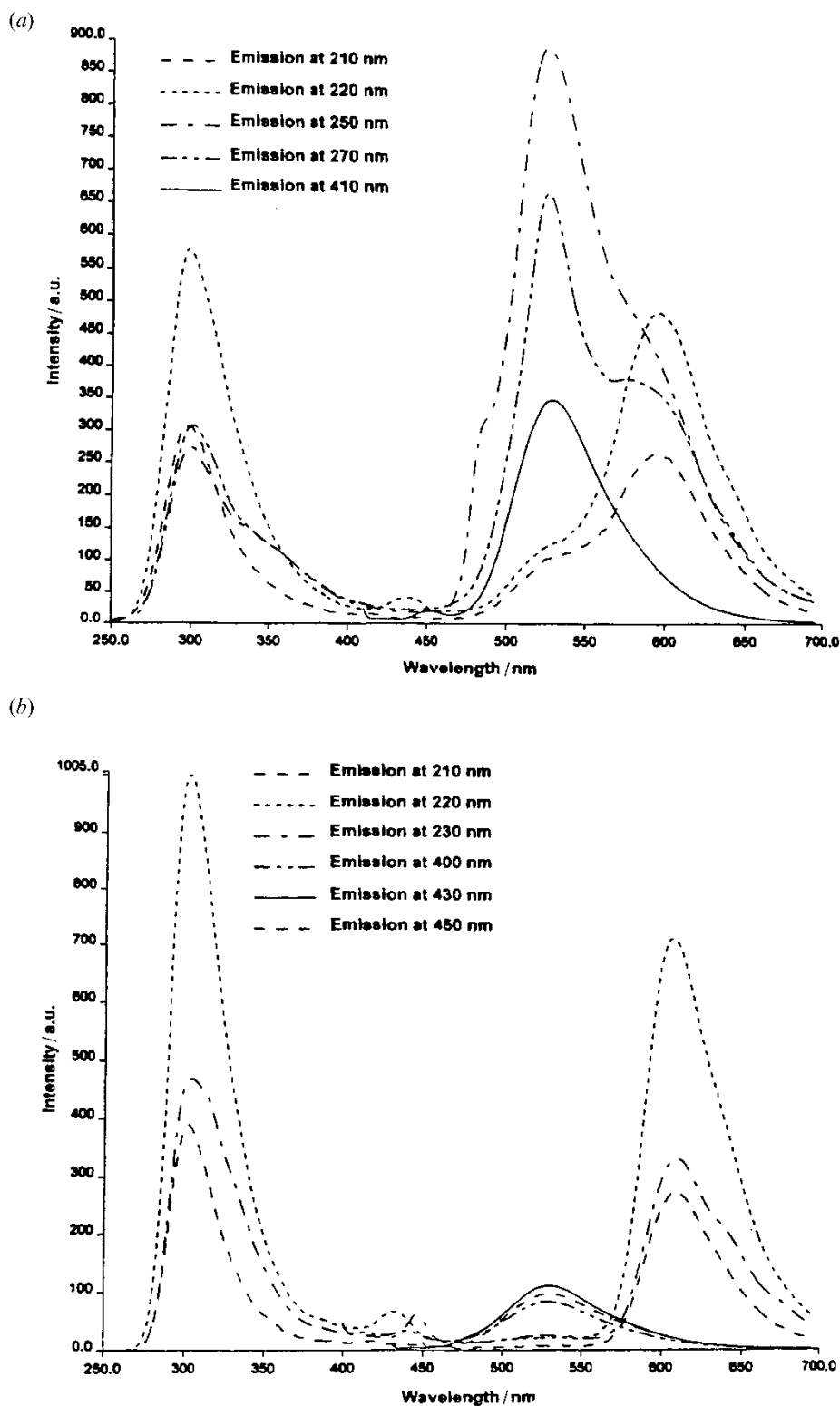


Figure 6. Emission spectra of **2** at various excitation wavelengths: (a) in DME, (b) in methanol.

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References

- [1] MONK, P. M. S., 1998, *The Viologens Physicochemical Properties, Synthesis and Applications of the Salts of 4,4'-Bipyridine* (New York: Wiley), pp. 1–311.
- [2] YU, L.-P., and SAMULSKI, E. T., 1984, *Oriented Fluids and Liquid Crystals*, Vol. 4, edited by A. C. Griffin, and J. F. Johnson (New York: Plenum) p. 697.
- [3] TABUSHI, I., YAMAMURA, K., and KOMINAMI, K., 1986, *J. Am. chem. Soc.*, **108**, 6409.
- [4] YAMAMURA, K., OKADA, Y., ONO, S., KOMINAMI, K., and TABUSHI, I., 1987, *Tetrahedron Lett.*, **28**, 6475.
- [5] HARAZAWA, T., TERRILL, R. H., and MURRAY, R. W., 1996, *Anal. Chem.*, **68**, 597.
- [6] HARAMOTO, Y., YIN, M., MATUKAWA, Y., UJIIE, S., and NANASAWA, M., 1995, *Liq. Cryst.*, **19**, 319.
- [7] SEDDON, K. R., 1997, *J. chem. Technol. Biotechnol.*, **68**, 351.
- [8] WELTON, T., 1999, *Chem. Rev.*, **99**, 2071.
- [9] WASSERSCHIED, P., and KEIM, W., 2000, *Angew. Chem. int. Ed. Engl.*, **39**, 3772.
- [10] BONHÔTE, P., DIAS, A.-P., PAPAGEORGIOU, N., KALYANASUNDARAM, K., and GRÄTZEL, M., 1996, *Inorg. Chem.*, **35**, 1168.
- [11] SUN, J., FORSYTH, M., and MACFARLANE, D. R., 1998, *J. phys. Chem. B*, **102**, 8858.
- [12] HOLBREY, J. D., and SEDDON, K. R., 1999, *J. chem. Soc. Dalton Trans.*, 2133.
- [13] GORDON, C. M., HOLBREY, J. D., KENNEDY, A. R., and SEDDON, K. R., 1998, *J. mater. Chem.*, **8**, 2627.
- [14] BRADLEY, A. E., HARDACRE, C., HOLBREY, J. D., JOHNSTON, S., MCMATH, S. E. J., and NIEUWENHUYZEN, M., 2002, *Chem. Mater.*, **14**, 629.
- [15] OBER, C., JIN, J.-I., and LENZ, R. W., 1982, *Polym. J.*, **14**, 9.
- [16] ALAMI, E., LEVY, H., ZANA, R., WEBER, P., and SKOULIOS, A., 1993, *Liq. Cryst.*, **13**, 201.
- [17] DEMUS, D., and RICHTER, L., 1978, *Textures of Liquid Crystals* (Weinheim: Verlag Chemie), pp. 1–219.
- [18] CANDAU, F., BALLEST, F., DEBEAUVAIS, F., and WHITTMANN, J.-C., 1982, *J. colloid interface Sci.*, **87**, 356.
- [19] GRAY, G. W., and GOODBY, J. W. G., 1984, *Smectic Liquid Crystals, Textures and Structures* (Leonard Hill: Glasgow), pp. 1–162.
- [20] 2001, *Liquid Crystals, Experimental Study of Physical Properties and Phase Transitions*, edited by S. Kumar, (Cambridge: Cambridge University Press).
- [21] WANG, D., WANG, J., MOSES, D., BAZAN, G. C., and HEEGER, A. J., 2001, *Langmuir*, **17**, 1262.
- [22] GAYLORD, B. S., WANG, S., HEEGER, A. J., and BAZAN, G. C., 2001, *J. Am. chem. Soc.*, **123**, 6417.
- [23] WANG, J., WANG, D., MILLER, E. K., MOSES, D., BAZAN, G. C., and HEEGER, A. J., 2000, *Macromolecules*, **33**, 5153.
- [24] CHEN, L., MCBRANCH, D. W., WANG, H.-L., HELGESON, R., WUDL, F., and WHITTEN, D. G., 1999, *Proc. natl. Acad. Sci. USA*, **96**, 12287.
- [25] KANSUI, H., HIRAOKA, S., and KUNIEDA, T., 1996, *J. Am. chem. Soc.*, **118**, 5346.