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Synthesis and characterization of ionic liquids: viologen bis{tetrakis[3,5-bis(trifluoromethyl)phenyl]borate} salts[§]

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Several viologen bis{tetrakis[3,5-bis(trifluoromethyl)phenyl]borate} salts were prepared by metathesis reaction of the corresponding viologen dibromides (diiodide) with sodium bis{tetrakis[3,5-bis(trifluoromethyl)phenyl]borate} salt in a polar organic solvent. They were characterized for their physical and thermal properties by experimental techniques including variable temperature X-ray diffraction. All exhibited low T_g and T_m, and their T_g/T_m (K) ratios were in the range 0.66–0.79. Several exhibited polymorphism and formed isotropic ionic melts at <150°C. They were soluble in many common organic solvents such as ethers, alcohols, acetonitrile and methylene chloride. They exhibited photoluminescence in both 1,2-dimethoxyethane and methanol, as well as in the solid state. In the solid state, the emission spectra exhibited hypsochromic shift when compared with those in solutions of 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 that 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 ranges of thermotropic LC phase for a series of these compounds with variation of alkyl chain lengths (n=5–10 and 18) and anions (X^-=Cl^-, Br^-, I^-, $^-BF_4$, $^-OOCCF_3$, $^-O_3SCH_3$, and ^-OTs) are sensitive to both the alkyl chain length and the anion. For a fixed alkyl chain length of n=10, considerable variability in thermal transitions is observed even when the anions are restricted to the halide ions. Among these compounds containing halide anions, the reversibility of various thermal transitions is poor; all three compounds decompose before exhibiting a stable isotropic liquid phase [2]. Other anions show thermal properties ranging from the absence of an LC phase formation with $^-BF_4$ to reversible polymesomorphism (more than one LC phase) with $^-O_3SCH_3$. Generally, all of them form very viscous melts when compared with conventional, non-ionic thermotropic LC compounds [2].

1,1′-Di(3,6,9-trioxatridecyl)-4,4′-bipyridinium dibromide and 1,1′-di(3,6,9,12-tetraoxatetradecyl)-4,4′-bipyridinium diiodide have LC properties from room temperature up to about 200 and 154°C, respectively. The third compound, 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 dialkylbenzene sulphonates that contain alkyl chain lengths of 10, 13, and 15 carbon atoms have T_m values (205, 190 and 168°C, respectively) above which each of them exhibits a Smectic A (SmA) phase; the SmA phase for each persists up to the decomposition temperature (280–290°C) [6]. Thus, it is evident that viologen compounds having suitably designed chemical architecture (dicationic salts), such as 1-alkyl-3-methylimidazolium, N-alkylpyridinium, quaternary ammonium and quaternary phosphonium salts, each of which is a monocationic salt [7–12], have great potential for the preparation of both RT ionic liquids (green solvents) and RTLC ionic liquids (ordered reaction media). There

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[§] This article is dedicated to Professor Robert W. Lenz with best wishes on the occasion of his 80th birthday.

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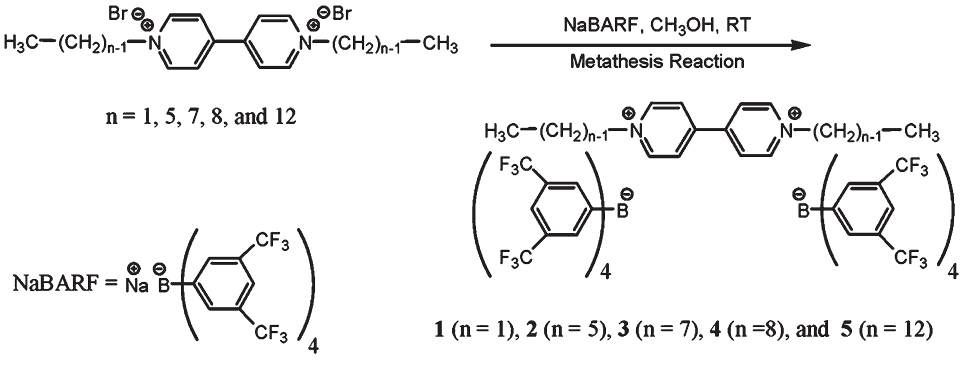
has also been recent development in the structural features of RTLC ionic salts, for example, as ordered solvents that can impart selectivity in reactions by ordering reactants [13], as templates for the synthesis of mesoporous and zeolitic materials [14], and in the formation of ordered thin films [15].

In this article, we describe the facile preparation of a new series of viologen bis{tetrakis[3,5-bis(trifluoromethyl)phenyl]borate} salts (**1**–**5**) by the metathesis reaction of either the corresponding 1,1′-dialkyl-4,4′-bipyridinium dibromides or 1,1′-dibenzyl-4,4′-bipyridinium dibromide with sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBARF) in a polar organic solvent (scheme 1), and the characterization of their thermal properties by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and thermogravimetric analysis (TGA). To our knowledge, they are novel examples of viologen bis{tetrakis[3,5-bis(trifluoromethyl)phenyl]borate} salts that exhibit low glass transition temperatures (T_g) and polymorphism as determined by a number of experimental techniques. The study of their photoluminescence properties in both non-polar and polar organic solvents as well as in the solid state was also included in this work. Their emission spectra in the solid state displayed hypsochromic shift when compared with those in solutions of nonpolar solvent such as 1,2-dimethyoxyethane (DME) or the polar solvent methanol.

The BARF organic counterion was selected to explore further the chemical architectures of ionic salts, since the 1-ethyl-3-methylimidazolium BARF salt medium effectively activates the Wilke's catalyst precursor—a (η_3-allyl)Ni(II)Cl_2 complex that contains a unique chiral 1,2-substituted 1-azaphospholene ligand—for the hydrovinylation of styrene with alkene in an ionic salt/compressed CO_2 system. The high activity of this catalyst precursor in this ionic salt leads to significant consecutive isomerization and oligomerization, even at room temperature [16]. It is well known that the presence of electron-withdrawing –CF_3 groups renders this counterion virtually inert to strongly acidic solution such as H_2SO_4. This result may possibly be attributed to low electron density in the vicinity of boron–carbon bonds that reduces the susceptibility toward electrophilic attack. Indeed, this counterion has been used to stabilize highly reactive base-free cationic group four metallocene complexes. It is also found to be resistant to a variety of oxidants and to be extremely lipophilic [17–21]. Thus, it is of significant interest to prepare and characterize several viologen salts containing this BARF counterion for the repertoire of ionic liquids.

2. Experimental

The 1,1′-dialkyl-4,4′-bipyridinium dibromides (diiodide) were prepared by adding the corresponding slight excess of two equivalents of alkyl bromides (diiodide) to a solution of one equivalent of 4,4′-bipyridyl in acetonitrile. After heating at reflux for 24 h the yellow crystalline dialkylated product was filtered from the reaction mixture (0°C), washed with acetone, and recrystallized twice from H_2O/acetone (15/85) [2]. Their purity was checked by ^1H NMR spectroscopy (the absence of peaks at δ=7.83, 8.32, 8.64 and 8.83 ppm of monoalkylated product in D_2O) and elemental analysis. The viologens **1**–**5** were prepared by the metathesis reaction of the corresponding 1,1′-dialkyl-4,4′-bipyridinium dibromides (diiodide) with sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBARF) in a common organic solvent. A typical procedure was as follows. 1.0 g (2.3 mmol) of 1,1′-dimethyl-4,4′-bipyridinium diiodide was dissolved in 30 ml methanol. To this solution, 20 ml of NaBARF (4.5 g, 5.1 mmol, 10% excess) in methanol was slowly added with stirring. The resulting solution was stirred overnight. After removing methanol by evaporation, deionized water was added to the solid products to



Scheme 1

dissolve NaI, leaving the desired crude viologen **1** mixed with excess NaBARF. It was further purified by recrystallization several times from methanol and water, and dried in a vacuum at 65°C for 24 h. The yield of the metathesis reaction for the preparation of this viologen **1** was essentially quantitative. Its purity was checked by both ^{1}H and ^{13}C NMR spectroscopy, and elemental analysis. No part of the synthesis of these salts was carried out in inert atmosphere glove boxes, which are often required for the synthesis of ionic salts that are sensitive to atmospheric moisture.

Selected characterization data. **1**: IR (KBr)/$\nu_{\max}$ cm^{-1}: 3448, 3073, 1631, 1358, 1280, 1129, 892, 834, 678; δ_H (CD$_3$OD, 400 MHz, ppm): 9.25–9.35 (4H, bd), 8.65–8.75 (4H, bd), 7.60 (24H, bs), 4.53 (6H, s); δ_C (CD$_3$OD, 100 MHz, ppm): 163.70, 163.19, 162.71, 162.21 (q, $^1J_{BC}$=50.3 Hz, C$_{ipso}$), 151.45, 148.19, 135.87 (C$_o$), 131.01, 130.66, 130.35, 130.04 (C$_m$), 127.83, 127.18, 124.48, 121.78 (CF$_3$), 118.51 (C$_p$), 49.05; Anal: calcd for $C_{76}H_{38}B_2N_2F_{48}$ (1912.71) C 47.73, H 2.00, N 1.46; found C 47.46, H 2.01, N 1.55%. **2**: IR (KBr)/$\nu_{\max}$ cm^{-1}: 3439, 3130, 3067, 2968, 2880, 1788, 1638, 1611, 1560, 1505, 1469, 1447, 1356, 1278, 1130, 1000, 935, 889, 870, 838, 804, 745, 713, 682, 670, 580, 450; δ_H (CD$_3$OD, 400 MHz, ppm): 9.25–9.35 (4H, bd), 8.65–8.75 (4H, bd), 7.61 (24H, bs), 4.75–4.85 (4H, t), 2.25–2.35 (4H, bm), 1.25–1.50 (8H, m), 0.82–0.95 (6H, t); δ_C (CD$_3$OD, 100 MHz, ppm): 163.71, 163.21, 162.72, 162.23 (q, $^1J_{BC}$=50.3 Hz, C$_{ipso}$), 151.47, 147.19, 135.89 (C$_o$), 131.00, 130.68, 130.37, 130.04, 129.89 (C$_m$), 128.27, 127.20, 124.50, 121.80 (CF$_3$), 118.53 (C$_p$), 63.44, 32.34, 29.34, 23.20, 14.11; Anal: calcd for $C_{84}H_{54}B_2N_2F_{48}$ (2024.90) C 49.82, H 2.69, N 1.38; found C 49.90, H 2.64, N 1.44%. **3**: IR (KBr)/$\nu_{\max}$ cm^{-1}: 3444, 3073, 2943, 2871, 1629, 1453, 1358, 1281, 1131, 892, 835, 708, 677; δ_H (CD$_3$OD, 400 MHz, ppm): 9.25–9.35 (4H, bd), 8.65–8.75 (4H, bd), 7.65 (16H, s), 7.59 (8H, s), (24H, m), 4.75–4.85 (4H, m), 2.25–2.35 (4H, bm), 1.25–1.50 (16H, m), 0.82–0.95 (6H, m); δ_C (CD$_3$OD, 100 MHz, ppm): 163.70, 163.20, 162.71, 162.21 (q, $^1J_{BC}$=50.3 Hz, C$_{ipso}$), 151.41, 147.17, 135.88 (C$_o$), 130.91, 130.80, 130.61, 130.30, 130.14, 129.98, 129.85 (C$_m$), 128.22, 127.15, 124.45, 121.75 (CF$_3$), 118.43 (C$_p$), 63.41, 32.69, 32.63, 29.79, 27.19, 23.53, 14.30; Anal: calcd for $C_{88}H_{62}B_2N_2F_{48}$ (2081.04) C 50.79, H 3.00, N 1.35; found C 50.46, H 3.27, N 1.20%. **4**: IR (KBr)/$\nu_{\max}$ cm^{-1}: 3073, 2939, 1629, 1453, 1358, 1280, 1131, 892, 835, 678; δ_H (CD$_3$OD, 400 MHz, ppm): 9.25–9.35 (4H, bd), 8.65–8.75 (4H, bd), 7.63 (16H, s), 7.59 (8H, s), 4.75–4.85 (4H, m), 2.25–2.35 (4H, bm), 1.25–1.50 (20H, m), 0.82–0.95 (6H, t); δ_C (CD$_3$OD, 100 MHz, ppm): 163.72, 163.21, 162.72, 162.23 (q, $^1J_{BC}$=50.3 Hz, C$_{ipso}$), 151.44, 147.17, 135.90 (C$_o$), 130.96, 130.64, 130.33, 130.02, 129.89 (C$_m$), 128.25, 127.19, 124.49, 121.79 (CF$_3$), 118.49 (C$_p$), 63.46, 32.84, 32.66, 30.17, 30.11, 27.26, 23.63, 14.34; Anal: calcd for $C_{90}H_{66}B_2N_2F_{48}$ (2109.09) C 51.26, H 3.15, N 1.33; found C 51.49, H 2.91, N 1.43%. **5**: IR (KBr)/$\nu_{\max}$ cm^{-1}: 3073, 2931, 2859, 1638, 1609, 1469, 1446, 1356, 1280, 1221, 1129, 896, 889, 839, 712, 683, 671; δ_H (CD$_3$OD, 400 MHz, ppm): 9.25–9.35 (4H, bd), 8.65–8.75 (4H, bd), 7.65 (16H, s), 7.58 (8H, s), 4.75–4.85 (4H, t), 2.25–2.35 (4H, bm), 1.25–1.50 (36H, m), 0.82–0.95 (6H, t); δ_C (CD$_3$OD, 100 MHz, ppm): 163.72, 163.21, 162.72, 162.23 (q, $^1J_{BC}$=50.3 Hz, C$_{ipso}$), 151.44, 147.17, 135.90 (C$_o$), 130.96, 130.64, 130.33, 130.02, 129.89 (C$_m$), 128.25, 127.19, 124.49, 121.79 (CF$_3$), 118.49 (C$_p$), 63.46, 33.04, 32.67, 30.71, 30.62, 30.52, 30.43, 30.16, 27.28, 23.71, 14.40; Anal: calcd for $C_{98}H_{82}B_2N_2F_{48}$ (2221.28) C 52.99, H 3.72, N 1.26; found C 52.85, H 4.07, N 1.12%. The NaBARF was prepared by a minor modification of the procedure described in the literature [22–24].

The FTIR spectra of viologens **1**–**5** were recorded with a Nicolet FTIR analyzer with neat films on KBr pellets. Their ^{1}H and ^{13}C NMR spectra were recorded with two RF channels operating at 400 and 100 MHz, respectively, in CD$_3$OD using TMS as an internal standard. The phase transition temperatures were measured by differential scanning calorimetry (TA 2100 DSC) in nitrogen at heating and cooling rates of 10°C min^{-1}, unless specified otherwise. The binary mixtures of viologens **3** and **4** in various compositions (by wt%) were prepared directly in aluminum DSC pans by weighing appropriate amounts of these compounds and then sealing the pans hermetically. The mixtures were then heated in the DSC cell compartment at a 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 viologens **3** and **4**, since the subsequent heating and cooling cycles for each of these mixtures resulted in reproducible DSC thermograms. The TGA measurements were performed with a TA 2100 instrument at a heating rate of 20°C min^{-1} in nitrogen, unless specified otherwise. The morphology of thermal behaviour of viologens **1**–**5** and the mixtures of **3** and **4** having variable compositions were observed using a Nikon polarizing optical microscope equipped with a Mettler FP80 hot stage.

Structural studies of polymer **4** were carried out at the Advanced Photon Source of Argonne National Laboratory using the Midwestern Universities Collaborative Access Team's beamline 6IDB on Sector 6. The sample was sealed in 1 mm diameter and 10 μm thick Lindeman capillary and powder (or, unaligned sample) X-ray diffraction (XRD) patterns recorded at different temperatures and at different conditions using high resolution image plate detector MAR345. Sample temperature was controllable with a precision of ±0.1°C using a homemade oven and temperature controller. A wavelength of 0.7653 Å was used. The diffraction patterns were collected with the area detector placed at a distance of 586.62 mm from the sample.

UV-vis absorption spectra of viologens **1**–**5** in spectrograde DME and methanol were recorded with a Varian Cary 3 Bio UV-Vis spectrophotometer at room temperature. Their photoluminescence spectra in solutions of both DME and methanol were recorded with a Perkin-Elmer LS 55 luminescence spectrometer with a xenon lamp source. The photoluminescence spectra of viologen **1** in thin films cast from both DME and methanol were also recorded with this instrument by using a front surface accessory. The photoluminescence quantum yields of viologen **1** in both DME and methanol were determined at an excitation wavelength of 350 nm using external standard 9,10-diphenylanthracene in cyclohexene (ϕ_f=0.90) by following a previously reported procedure [25].

3. Results and discussion

All of the viologens **1**–**5** are soluble in diethyl ether, tetrahydrofuran and DME, in contrast to many room temperature ionic liquids, such as [C$_8$mim]BF$_4$ and [C$_8$mim]PF$_6$ [26]. They are also soluble in ethyl acetate, acetone, alcohols and acetonitrile. These results suggest that this class of ionic salts have solubility in a wide range of organic solvents having low-to-high dielectric constants. However, they are slightly soluble in methylene chloride and toluene, but in-soluble in chloroform and hexane.

The 1,1′-dimethyl-4,4′-bipyridinium diiodide had a weak crystal-to-crystal transition at 264°C (ΔH=1.1 kJ mol^{-1}), and a crystal-to-liquid transition (T_m)at 365°C (m.p. 325°C [27]), accompanied by immediate decomposition as determined by DSC at a heating rate of 10°C min^{-1} in nitrogen. In contrast, viologen **1** recrystallized from methanol/water showed a low temperature endotherm at 108°C (ΔH=26.4 kJ mol^{-1}) and a high temperature endotherm at T_{max}=231°C (ΔH=91.5 kJ mol^{-1}) in the first heating cycle. In the subsequent cooling and heating cycles, there was a single T_g at 62°C (ΔC_p=0.3 kJ mol^{-1}), but no exotherm and endotherm, respectively. In conjunction with POM studies, it was found that the low temperature endotherm corresponded to the crystal-to-crystal transition, while the high temperature endotherm corresponded to crystal-to-liquid transition (T_m), which was far below its decomposition temperature (T_d) at 273°C determined at a heating rate of 20°C min^{-1} in nitrogen. These results suggested that, once this salt melted into the liquid state, it did not crystallize under the experimental conditions used. Thus, like other neutral organic compounds having low T_g and T_m values [28], viologen **1** was an ionic compound having low T_g and T_m. It had a much lower T_m than 1,1′-dimethyl-4,4′-bipyridinium diiodide, which was related to the presence of the larger BARF counterion in this salt in comparison with the iodide ion.

1,1′-Dipentyl-4,4′-bipyridinium dibromide exhibited a crystal-to-crystal transition at 192°C (ΔH=29.3 kJ mol^{-1}) in the first heating cycle of a DSC thermogram, but it showed three endotherms (164, 187 and 208°C) in the second heating cycle, none of which was related to crystal-to-liquid transition. Its melting transition was also very close to its decomposition temperature at 261°C as determined by DSC at a heating rate of 10°C min^{-1}. The TGA measurement also confirmed its T_d at 272°C [27] at a heating rate of 20°C min^{-1} in nitrogen. In contrast, viologen **2** recrystallized from methanol/water exhibited an endotherm with a T_{max}=180°C (ΔH=85.1 kJ mol^{-1}) in the first heating cycle. In the second heating cycle, it also exhibited a distinct T_g at 44°C (ΔC_p=0.5 kJ mol^{-1}), a cold-crystallization exotherm (T_c) at 106°C along with two additional shoulder peaks, and an endotherm at identical peak temperature and enthalpy change to that in the first heating cycle. However, in each of the cooling cycles, there was a single T_g, but no exotherm. The POM studies indicated that this endotherm was related to the crystal-to-isotropic transition (T_m). Furthermore, on cooling from the isotropic liquid phase at a rate of 10°C min^{-1}, it did not crystallize, since there was no crystallization exotherm in the cooling cycle. Unlike viologen **1**, the appearance of T_c as it traversed through the T_g region accounted for the melting endotherm in the second heating cycle. These thermal properties are consistent with those of neutral organic compounds employed for electronic and optoelectronic devices [29]. As expected, its T_m was much lower than 1,1′-dipentyl-4,4′-bipyridinium dibromide because of the presence of the larger BARF counterion in this salt in comparison with the bromide ion. Its T_m was well below its T_d=281°C as determined at a heating rate of 20°C min^{-1} in nitrogen.

1,1′-Diheptyl-4,4′-bipyridinium dibromide had a reversible crystal-to-crystal transition at 107°C (ΔH=15.6 kJ mol^{-1}), but no melting transition up to 277°C at which a weight loss of 5% occurred at a

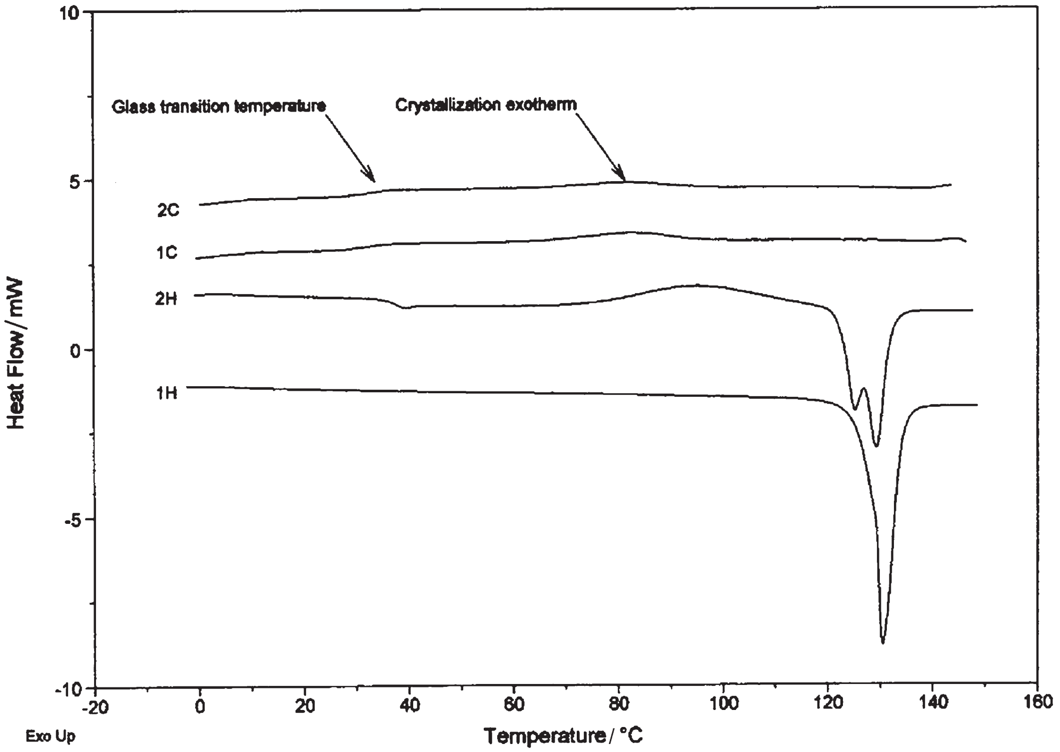


Figure 1. DSC thermograms of viologen **3** obtained at heating and cooling rates of 10°C min^{-1}.

heating rate of 20°C min^{-1} in nitrogen. In contrast, viologen **3** recrystallized from methanol/water showed a skewed endotherm (ΔH=61.6 kJ mol^{-1}) with a T_{max}=130°C in the first heating cycle (figure 1). Correspondingly, there was a broad exotherm at 83°C and a T_{g} in the first cooling cycle. In the second heating cycle, there were a T_{g} at 37°C (ΔC_p=0.2 kJ mol^{-1}), a broad T_{c} at 95°C ($-\Delta H$=25.8 kJ mol^{-1}), and two but partially overlapped endotherms at 127 and 129°C. The sum of enthalpy changes for these two transitions was qualitatively much lower than that for the endotherm in the first heating cycle (figure 1). As in the first cooling cycle, there was an exceedingly broad exotherm and a T_{g} in the second cooling cycle. All of these DSC data and POM studies confirmed that this salt transformed into a birefringent fluid at 127°C and became isotropic at 129°C, most likely due to the coexistence of crystal and liquid phases. In other words, this salt exhibited the phenomenon of polymorphism, like other organic compounds [29, 30]. Its T_{m} was far below its T_{d} at 261°C, determined at a heating rate of 20°C min^{-1} in nitrogen.

Similarly 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 (ΔH=20.5 kJ mol^{-1}), but no melting transition up to 275°C. TGA indicated that a weight loss of 5% occurred at 291°C in nitrogen at a heating rate of 20°C min^{-1}, but it decomposed at 280°C as determined by DSC in nitrogen at a heating rate of 10°C min^{-1}, presumably via Hofmann elimination that is associated with quaternary ammonium salts [11]. In contrast, viologen **4** recrystallized from methanol/water exhibited a T_{g} (ΔC_p=0.4 kJ mol^{-1}) at 33°C, a broad cold-crystallization exotherm (T_{c} at 78°C with $-\Delta H$=34.3 kJ mol^{-1}), and two endotherms at 103°C (ΔH=10.5 kJ mol^{-1}) and 116°C (ΔH=27.9 kJ mol^{-1}) in the DSC thermogram obtained at a heating rate of 10°C min^{-1} (figure 2). The high temperature endotherm also had a shoulder peak at 110°C (ΔH=0.5 kJ mol^{-1}) in the first heating cycle of its DSC thermogram. In the subsequent cooling cycle, there was a T_{g} but no exotherms. The second heating cycle exhibited a T_{g} at 33°C, a T_{c} at 85°C and two endotherms at 110 and 116°C, similar to the first heating cycle. It was also found that the shoulder peak in the high temperature endotherm in the first heating cycle overlapped with the low temperature endotherm in the second heating cycle. The DSC thermogram in the second cooling cycle was essentially identical to that in the first cooling cycle (not shown). Figure 2 displays several additional thermograms obtained at slow heating rates of 1 and 5°C min^{-1}. It is clear that the peak shapes of its DSC thermograms were heating rate-dependent. Furthermore, at the lowest heating rate of

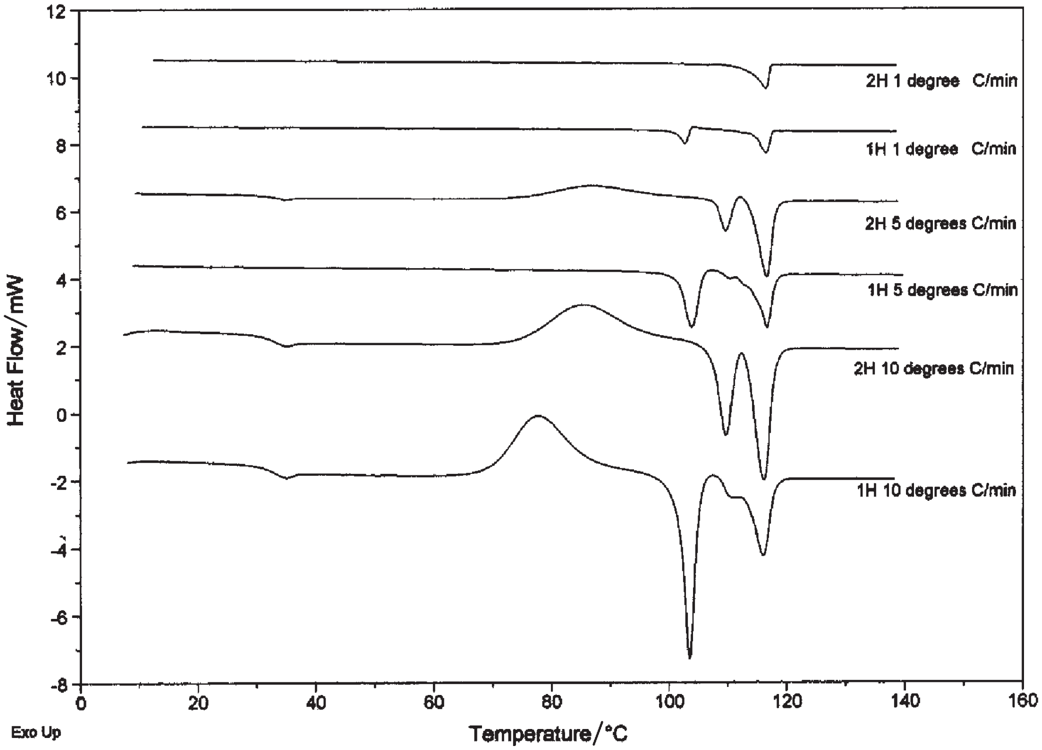


Figure 2. DSC thermograms of viologen **4** obtained at various heating rates.

1°C min^{-1}, only one endotherm was seen (excluding an indistinct shoulder peak) with ΔH=50.9 kJ mol^{-1} in the second heating cycle. It is, therefore, speculated that more than one transition process was involved in these thermograms. This result was further corroborated when the heating rate was increased to 10°C min^{-1}; two endotherms (excluding a shoulder peak) with high ΔH were clearly observed.

At a heating rate faster than 5°C min^{-1}, an exothermic process was clearly observed at low temperature, indicating that further development of the ordered structure took place when the pre cooling rate was correspondingly fast. In corroboration with the POM studies, it was established that viologen **4** was a crystalline ionic compound see figure 3 (*a*); it transformed at 112°C to a birefringent fluid, figure 3 (*b*), that continued up to 114°C and finally formed an isotropic liquid phase at 116°C, figure 3 (*c*). Viologen **4** thus exhibited polymorphism phenomenon similar viologen **3** [29, 30]. Variable temperature XRD patterns are shown in figure 4. Figure 4 (*a*) shows the crystalline phase at room temperature or below the melting endotherm; figures 4 (*b*) and 4(*c*) show the isotropic liquid phases at 112 and 132°C, respectively, when heated at a rate of 10°C min^{-1}, indicating the melting of two crystalline forms. The XRD pattern of the isotropic phase was preserved on cooling at a rate of 10°C min^{-1}, even after standing at room temperature for 12 h.

Although 1,1′-didodecyl-4,4′-bipyridinium dibromide showed two reversible endotherms at 119°C with ΔH=43.6 kJ mol^{-1} and at 170°C with ΔH=3.6 kJ mol^{-1} in each of the heating cycles of the DSC thermograms, it exhibited no melting endotherm up to its decomposition at T_d=283°C, as determined by TGA measurement at a heating rate of 10°C min^{-1} in nitrogen. In contrast, viologen **5** recrystallized from methanol/water showed only an endotherm at T_{max}=139°C with high ΔH=61.0 kJ mol^{-1} in the first heating cycle (not shown). In the first cooling cycle it exhibited a T_g, but no cooling exotherm. In the subsequent heating and cooling cycles, there were no endotherm and exotherm, respectively, but there was a T_g at 26°C in each of these cycles. The POM studies suggested that it transformed into isotropic liquid at 139°C. It did not crystallize at a cooling rate of 10°C min^{-1}, which accounted for the absence of exotherms in the cooling cycles. Furthermore, it did not exhibit a T_c as it traversed through the T_g, accounting for the absence of the melting endotherm in the second heating cycle. Like viologen **1**, it was an ionic compound that had low meting and glass transition temperatures because

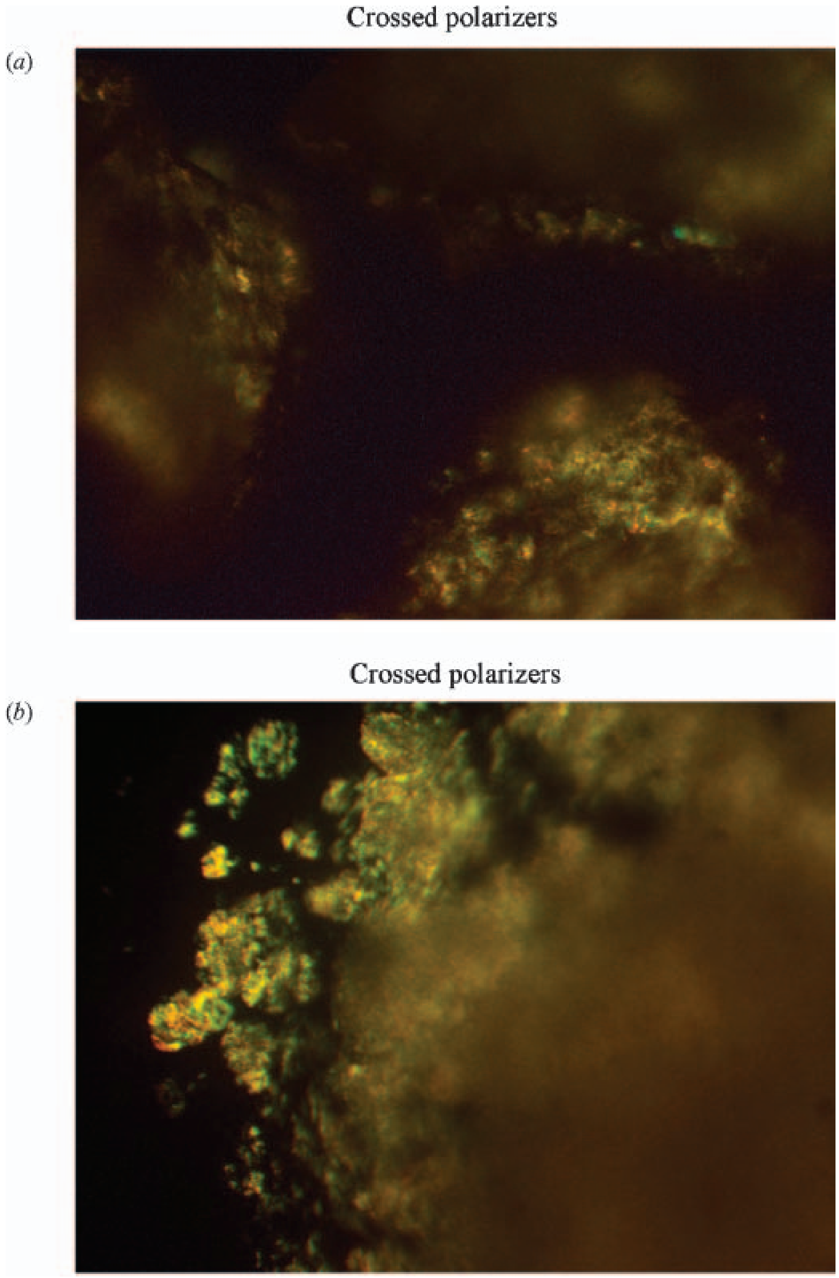


Figure 3. Photomicrographs of viologen **4** obtained (*a*) at room temperature, (*b*) at 112, (*c*) 114, (*d*) at 116°C (magnification 400 ×).

of the presence of the bulky BARF counterion [28]. Its T_m was well below its T_d=254°C as determined at a heating rate of $10^\circ\mathrm{C\,min^{-1}}$ in nitrogen.

Note here that the ratios $T_\mathrm{g}/T_\mathrm{m}$ (K) for all of the viologen compounds **1**–**5** were in the range 0.66–0.79, which is in excellent agreement with what is know as the 2/3 rule of the interrelationship between the T_g and T_m for other neutral organic compounds [31]. The thermal stability for each of the viologens **1**–**5** was determined in nitrogen at a heating rate of 10 or $20^\circ\mathrm{C\,min^{-1}}$ by TGA. The thermal stability limit was the temperature at which a 5% weight loss for each of the salts occurred. It was in the temperature range 254–281°C, which was generally higher than that of the corresponding dibromide salts (*vide supra*). Figure 5 shows the illustrative TGA plots of viologen **2** and its corresponding dibromide salt, revealing their relative thermal stabilities. It was also found that viologen **5**, containing the longest methylene units, had the lowest thermal stability among all of the viologens studied.

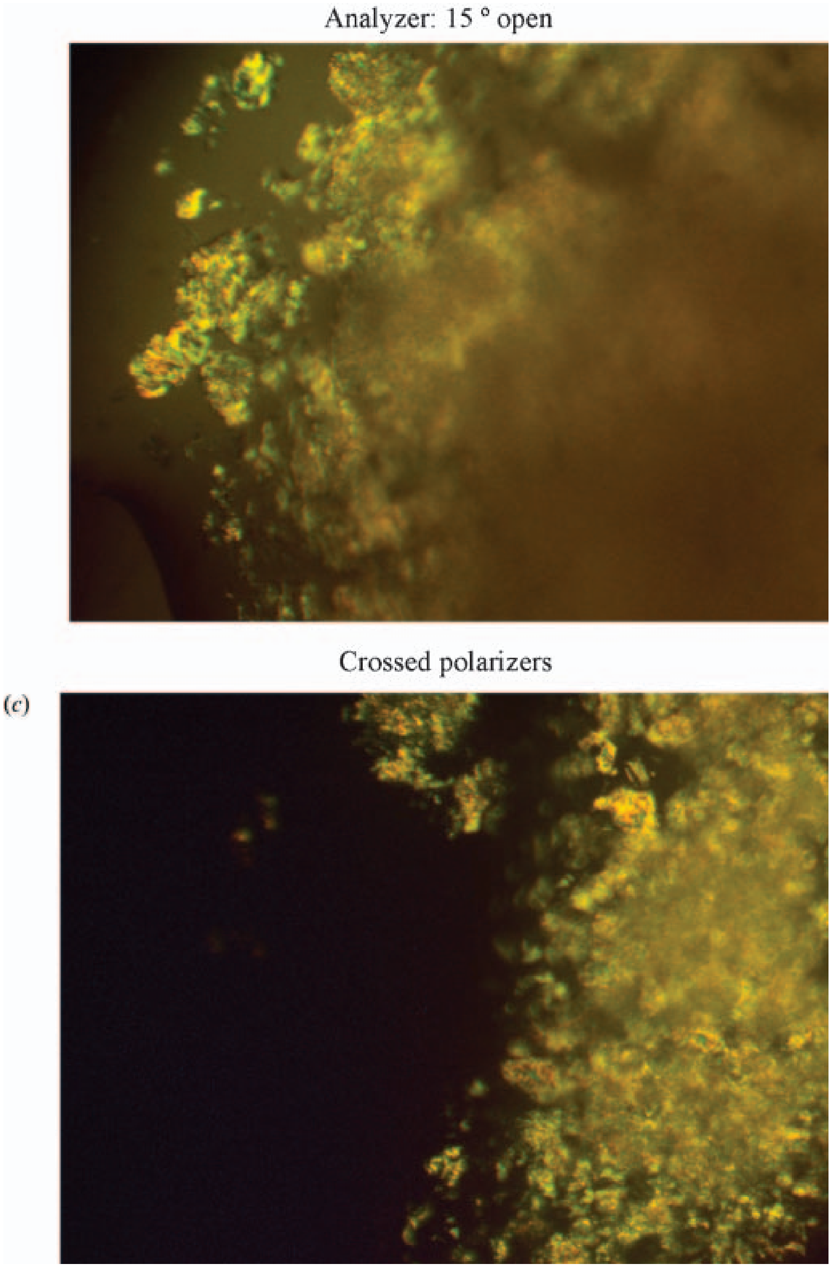


Figure 3. Continued.

In an attempt to produce ionic salts with decreased melting transitions, a study of the effect of mixing **3** and **4** in various proportions 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 [32]. Figure 6 shows DSC thermograms of mixtures of **3** and **4** in various proportions in their first heating cycles after homogenization. As expected, T_m transitions for each of these mixtures appeared broadened when compared with the individual components (**3** and **4**), since one component acts as an impurity for the other in these mixtures. Thus, all of these transitions were rather broad and occurred over a relatively wide range of temperature. However, T_m values for all of the mixtures increased slightly over the compositions studied, thus resulting in essentially similar melting transitions to those observed for the individual components. Furthermore, the thermal behaviour of a mixture was usually reminiscent

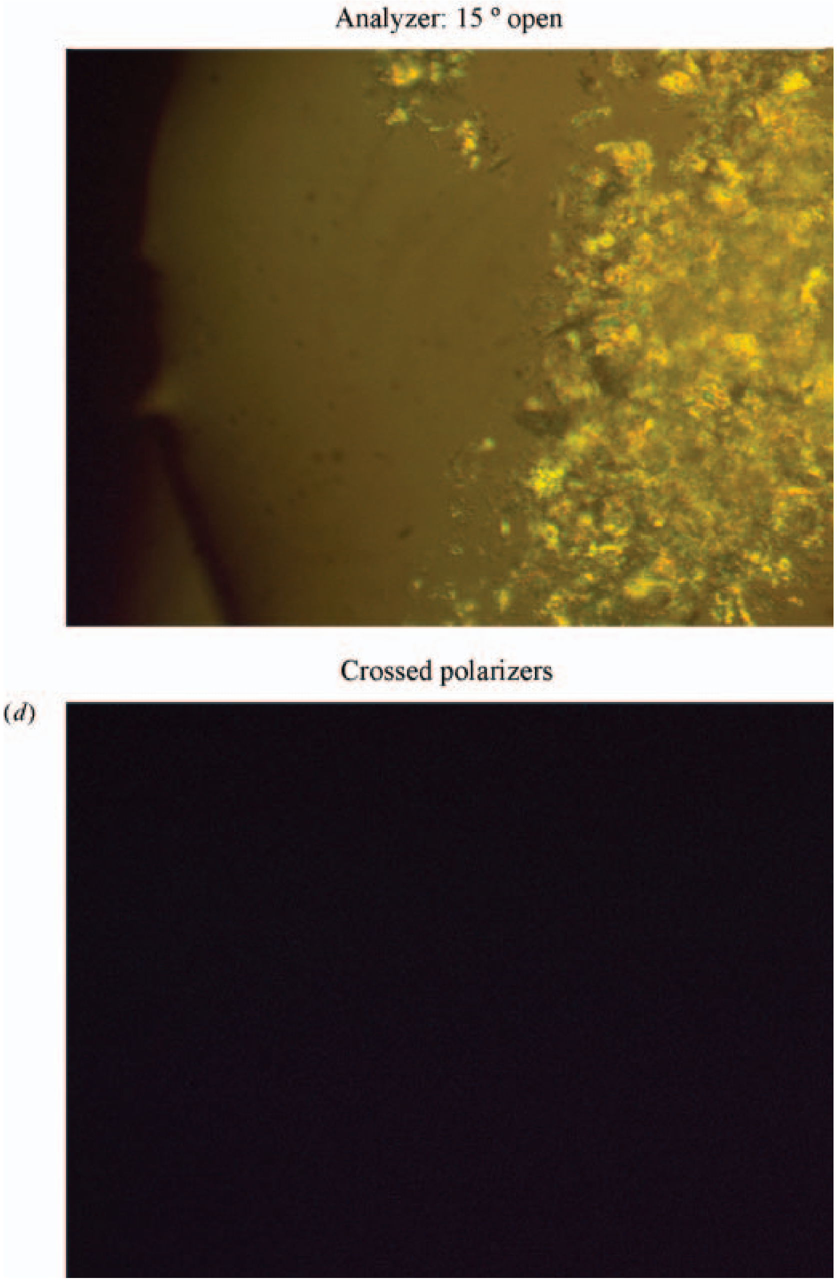


Figure 3. Continued.

to that of the major amount (wt %) of the component in the mixture. For example, the DSC thermograms (a, b and c) of three mixtures showed essentially similar thermal behaviour to that of component **4**, and those (d and e) of two other mixtures exhibited essentially similar thermal behaviour to that of the component **3**. Thus, it was found that a depression in T_m values did not occur for all of the mixtures of **3** with **4**. These results may be a reflection of the similarity in the structures of viologens **3** and **4**, since they differ by only two methylene units in the alkyl tails. Like viologens **3** and **4**, their mixtures also exhibited polymorphism as determined by POM studies. Figure 7 shows a photomicrograph of such a mixture displaying the coexistence of isotropic and crystalline phases.

All of the results for viologens **1**–**5** suggested that viologens **3**–**5** and mixtures of **3** and **4** of various compositions had the unique property to form ionic

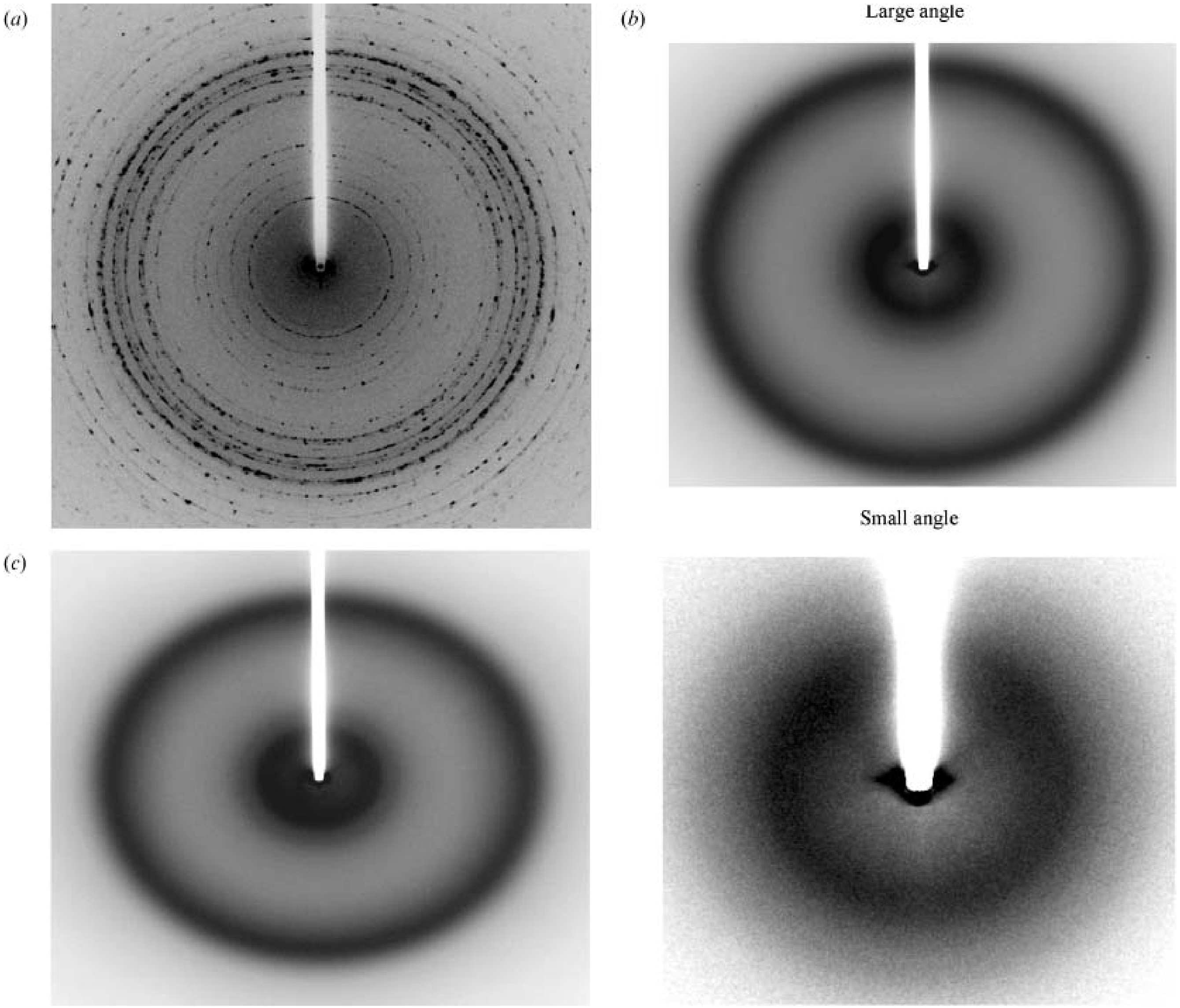


Figure 4. Small and wide angle X-ray diffraction patterns of viologen **4** obtained at (*a*) room temperature, (*b*) 112, (*c*) 132°C.

liquids at <150°C. A useful guideline for the upper limit of melting points for salts described as ionic liquids is 150°C, the temperature around which the lowest melting purely 'inorganic' or 'classical' salt eutectics melt [33]. Higher melting ionic solvents are basically an extension of structural variants to the popular room temperature ionic solvents. They offer advantages over room temperature ionic liquids: they are non-corrosive and, being solid at room temperature, they are more easily manipulated and reaction product separation is simple, being accomplished by decantation rather than the usual biphasic extraction with organic solvents. Furthermore, they are stable to much higher temperatures, thereby enabling more harsh reaction conditions to be applied. For example, the catalytic hydroformylation reaction is carried out successfully in high melting phosphonium tosylates as ionic solvents [8]. Additionally, the hydrovinylation of styrene with various alkenes could be carried out in this class of high-melting ionic solvents [16].

All of the viologens **1**–**5** in DME (relatively non-polar solvent) and in CH_3OH (polar solvent) showed essentially identical absorption spectra at room temperature: λ_{max} values are collected in table 1. It has been reported in the literature [34, 35] that viologen **1** forms a charge-transfer complex with a discrete absorption maximum at 475 nm in DME and at 420 nm in methanol at 20°C. These charge-transfer bands were not detected in any of

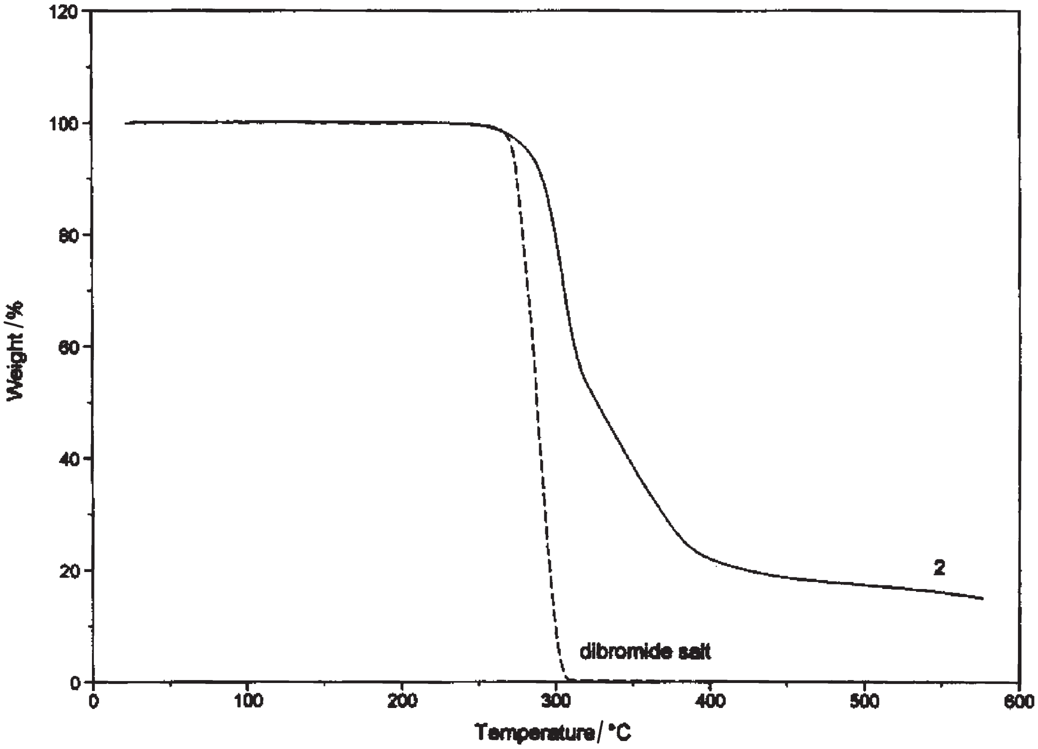


Figure 5. TGA plots of **2** and its corresponding dibromide salt in nitrogen at a heating rate of 20°C min^{-1}.

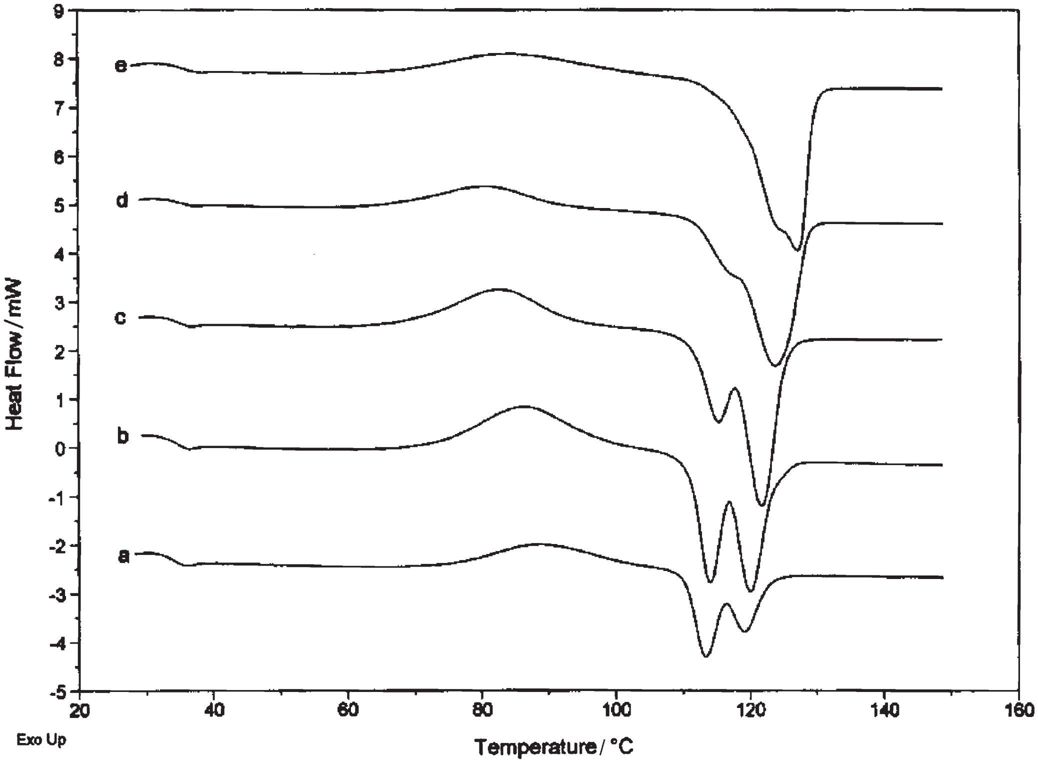


Figure 6. DSC thermograms of viologens **3** and **4** in various compositions by wt in their first heating cycles, obtained at a heating rate of 10°C min^{-1}, after homogenization: **3**/**4**=(*a*) 17/83, (*b*) 33/67, (*c*) 50/50, (*d*) 67/33, (*e*) 83/17.

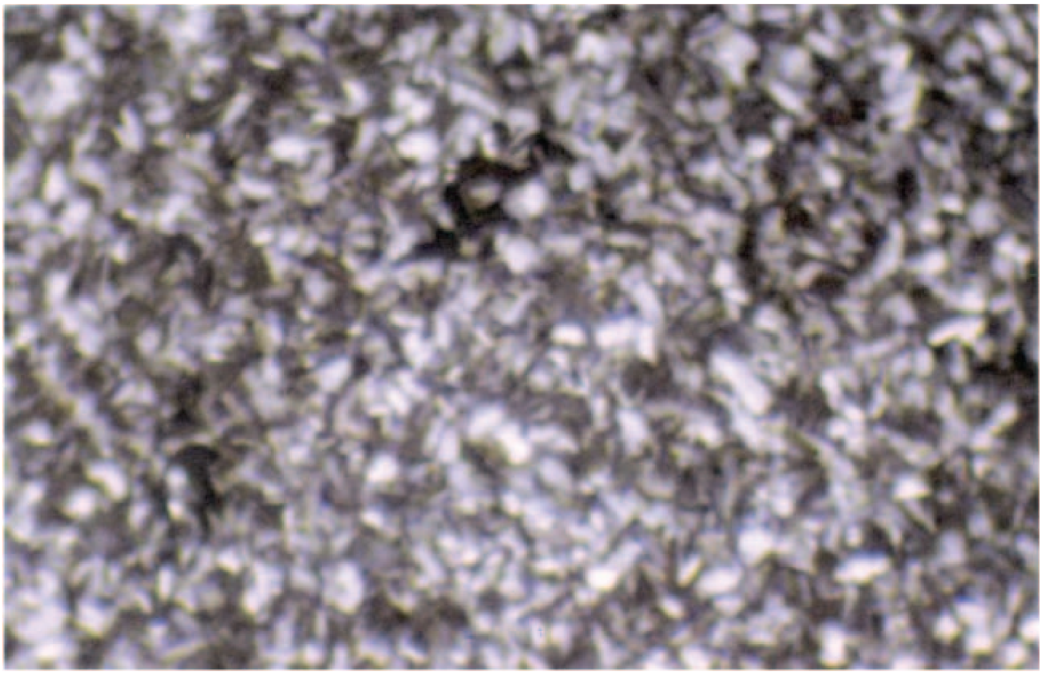


Figure 7. Photomicrograph of a mixture of viologen **3** with **4** (83/17 by wt) exhibiting isotropic liquid and crystalline phases (magnification 400 ×).

these viologens at high concentrations having the absorbances typically 1–2 at room temperature in either DME or methanol.

Figure 8 shows the emission spectra of viologen **1** in DME and methanol recorded at room temperature at various excitation wavelengths. In DME, the spectra showed λ_{em}=530 nm at various excitation wavelengths, hypsochromically shifted by 23 nm when compared with those at 20°C [34]. The λ_{em} value was independent of the excitation wavelength used, but the intensity of emission spectrum was dependent on the excitation wavelength. The excitation spectrum consisted of a major peak at λ_{ex}=474 nm along with two additional peaks at 252 and 290 nm during monitoring at 530 nm. In methanol, the emission spectra of viologen **1** were rather broad, consisting of a number of vibrational fine structures when compared with those in DME. The λ_{em} value was found to be hypsochromically shifted to 429 nm at various excitation wavelengths. As in DME, the λ_{em} value was independent of the excitation wavelength, but

Table 1. Absorption peak wavelengths (λ_{max}), excitation peak wavelengths (λ_{ex}), and emission peak wavelengths (λ_{em}) of viologens **1**–**5** in organic solvents at room temperature.

Viologen	Solvent	λ_{max}/nm	λ_{ex}/nm	λ_{em}/nm
1	DME	221, 266	252, 290, 474 (530)[a]	530 (280, 310, 320, 330, 480)[b]
2	DME	217, 267	253, 288, 479 (530)	530 (255, 470, 480)
3	DME	218, 262	251, 289, 476 (530)	531 (250, 290, 480, 490)
4	DME	218, 265	303, 468 (530)	531 (400, 430, 460, 480)
5	DME	218, 265	240, 301, 467 (530)	530 (400, 420, 440, 460)
1	CH_3OH	268	307 (430)	429 (285, 315, 350)
2	CH_3OH	269	336, 345, 396, 425 (530)	305 (220, 235), 530 (430, 440)
3	CH_3OH	268	243, 310, 430 (530)	530 (390, 410, 430, 450)
4	CH_3OH	268	308, 413 (530)	531 (360, 380, 410, 430)
5	CH_3OH	268	306, 339, 415, 439 (530)	531 (380, 400, 420, 440)

[a] The number in parentheses is the monitored wavelength in nanometers for the measurement of excitation spectrum. [b] The numbers in parentheses are the excitation wavelengths in nanometers for the measurements of emission spectra.

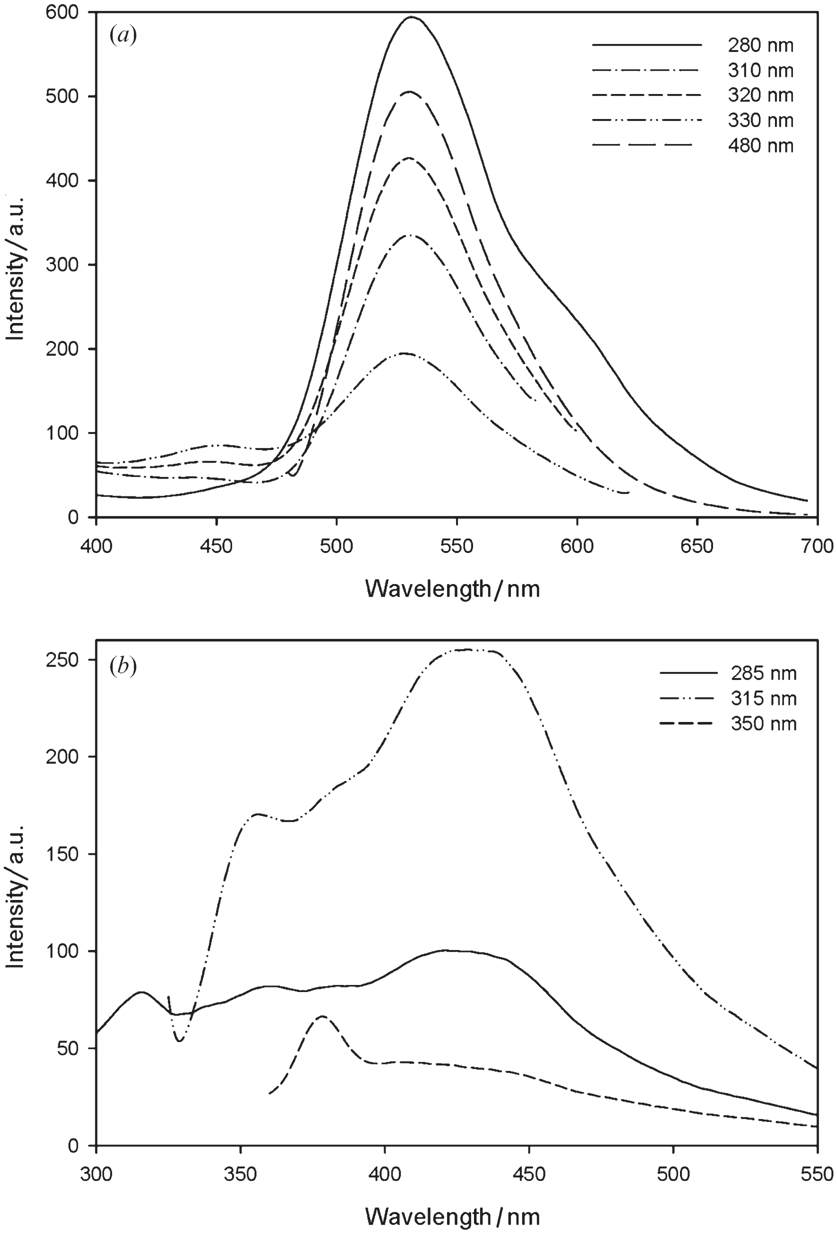


Figure 8. Emission spectra of viologen **1** at room temperature at various excitation wavelengths: (*a*) in DME and (*b*) in methanol.

the intensity of emission spectrum was dependent on the excitation wavelength. The excitation spectrum in methanol during monitoring at 430 nm consisted of a single peak at 307 nm, in contrast to that in DME. The observed emission spectra of viologen **1** in methanol at various excitation wavelengths at room temperature were at variance with the fact that viologen **1** in methanol at 20°C does not exhibit light emission during monitoring at 420 nm [34]. The measured photoluminescence quantum yields of viologen **1** in both DME and methanol were essentially identical, being measured as 0.014 and 0.015, respectively.

Figure 9 shows the emission spectra of viologen **2** in both DME and methanol at room temperature at various excitation wavelengths. In DME, both the excitation and emission spectra were essentially identical to those of viologen **1**. Similarly, the other viologens **3**–**5** had essentially identical excitation and emission spectra to those of viologen **1** (table 1). However, viologen **2** in methanol on one hand exhibited λ_{em}=530 nm at excitation wavelengths of 430 and 440 nm; on the other hand, it exhibited λ_{em}=305 nm at excitation wavelengths of 220 and 235 nm. The emission spectra at low excitation

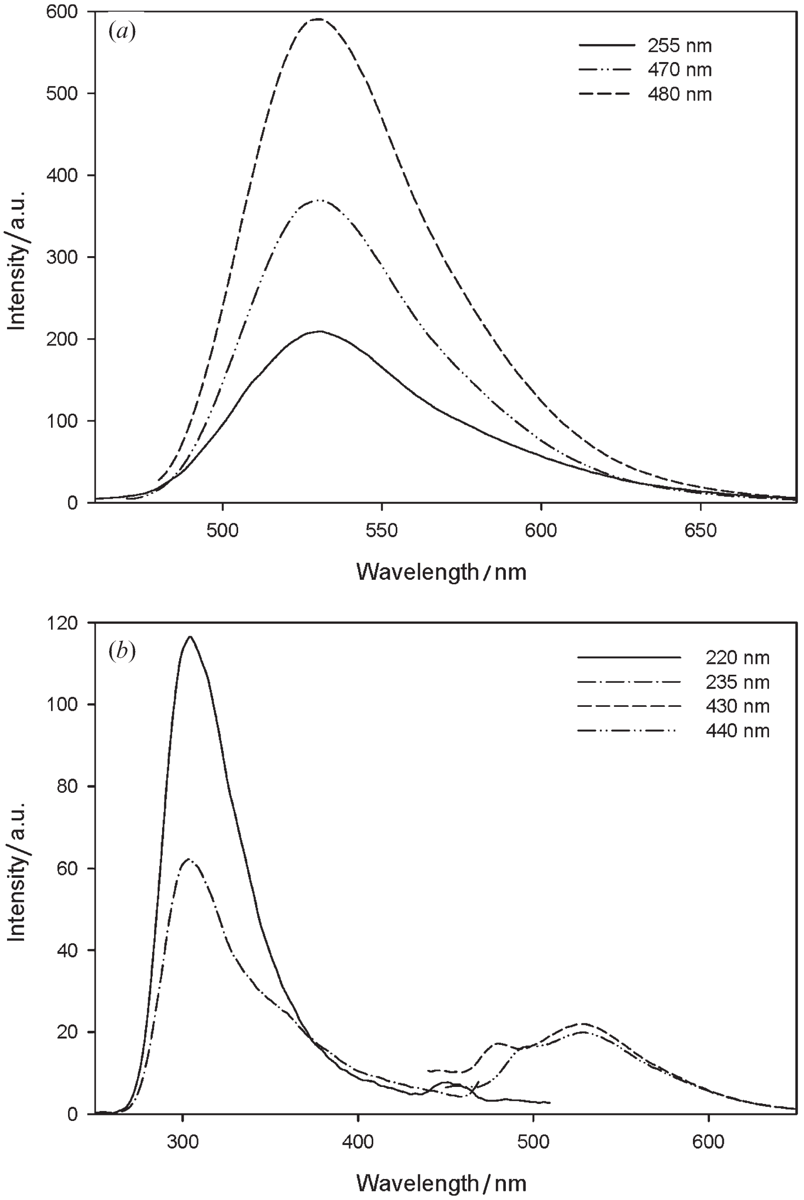


Figure 9. Emission spectra of viologen **2** at room temperature at various excitation wavelengths: (*a*) in DME and (*b*) in methanol, respectively.

wavelengths were much more intense than those at high excitation wavelengths. Viologens **3**–**5** in methanol at room temperature showed $\lambda_{em}=531$ nm at various excitation wavelengths (table 1), which was essentially identical to that in DME. However, their excitation spectra in methanol at room temperature exhibited different λ_{ex} values (table 1) when compared with those in DME.

Figure 10 shows the emission spectra of viologen **1** in thin films cast from both DME and methanol at various excitation wavelengths. Its excitation spectrum exhibited $\lambda_{ex}=242$ nm when monitored at 380 nm, irrespective of the nature of the solvent used for casting the films. Its emission spectra exhibited $\lambda_{em}=377$ (380) nm at various excitation wavelengths, which was also independent of the nature of the solvent used for casting the films. Thus, it was found that the emission spectra of viologen **1** in the solid state exhibited λ_{em} hypsochromically shifted when compared with spectra in either DME or methanol.

Although the photoluminescence quenching processes of numerous π–conjugated viologen-based polymers in aqueous solution open an opportunity for the development of biological and chemical sensors for use

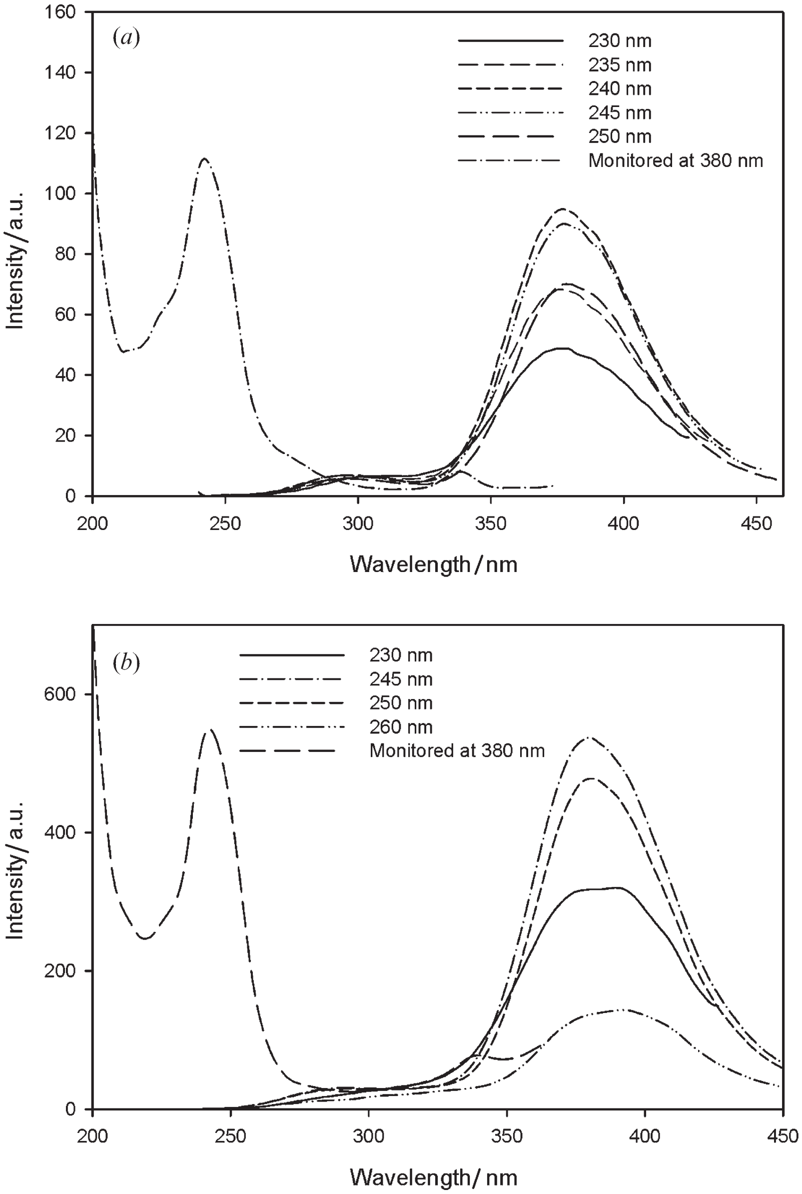


Figure 10. Emission spectra of viologen **1** in thin films cast from (*a*) DME and (*b*) methanol at various excitation wavelengths.

in medical diagnostics and toxicology [36–39], the fluorescence of viologens **1**–**5** in both non-polar and polar organic solvents, as well as in the solid state, is undoubtedly an additional attribute to this class of ionic salts. This new property of these ionic salts can be exploited further for the development of chemical sensors.

4. Conclusions

The viologen bis{tetrakis[3,5-bis(trifluoromethyl)phenyl]borate} salts **1**–**5** were prepared by metathesis reaction in a common organic solvent from the corresponding viologen dihalides and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate and their thermal and optical properties characterized by various experimental techniques. In general, they exhibited low T_g and T_m transitions and their T_g/T_m (K) ratios were in the range 0.66–0.79. Given their low T_g and T_m values, they are attractive candidates for future studies of molecular dynamics of glassy ionic compounds. Viologens **3** and **4** exhibited polymorphism, as did their mixtures at various compositions. However, viologens **3**–**5** and all of the binary mixtures of **3** and **4** formed isotropic ionic melts at <150°C, which is the upper limit of melting transitions for salts described as ionic liquids.

All of these viologens had high thermal stability in nitrogen in the temperature range 254–281°C. These high-melting ionic salts could be potentially useful for hydrovinylation and hydroformylation reactions. All of these viologens were soluble in many common organic solvents, such as diethyl ether, THF, methanol and acetonitrile. They exhibited photoluminescence in both DME and methanol as well as in the solid state. For example, their emission spectra in DME showed $\lambda_{em}=530$ nm at various excitation wavelengths irrespective of the chemical structure. The fluorescence property of these ionic salts could be further exploited for the development of chemical sensors.

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