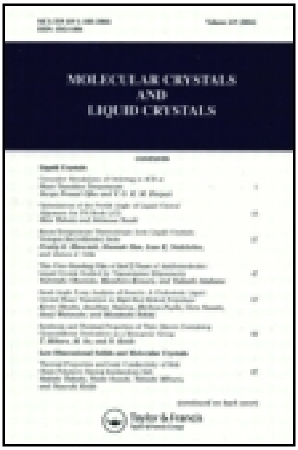

Molecular Crystals and Liquid Crystals

Room-Temperature Thermotropic Ionic Liquid Crystals: Viologen Bis(Triflimide) Salts

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ROOM-TEMPERATURE THERMOTROPIC IONIC LIQUID CRYSTALS: VIOLOGEN BIS(TRIFLIMIDE) SALTS

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Several dicationic salts with bis(triflimide) as counterions—otherwise known as viologens—were prepared by metathesis reaction of the corresponding viologen dibromides (diiodides) with lithium triflimide in a polar solvent. They were characterized for their thermotropic liquid-crystalline properties with various experimental techniques. Two of them had low crystal-to-smectic phase transitions (T_m) at –4 and 28°C; the other two also had low T_m values, at 51 and 58°C. Each had a wide range of LC phase. Two had relatively low crystal-to-isotropic (T_m) transitions at 117 and 131°C. Each had excellent thermal stability in the temperature range of 327–396°C. They exhibited photoluminescence property in both nonpolar and polar solvents as well as in the solid state. Their emission spectra in the solid state exhibited hypsochromic shift when compared with those in solution of dimethoxyethane.

Keywords: hypsochromic; ionic liquid; photoluminescence; smectic phase; thermotropic; viologen bis(triflimide salt)s

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

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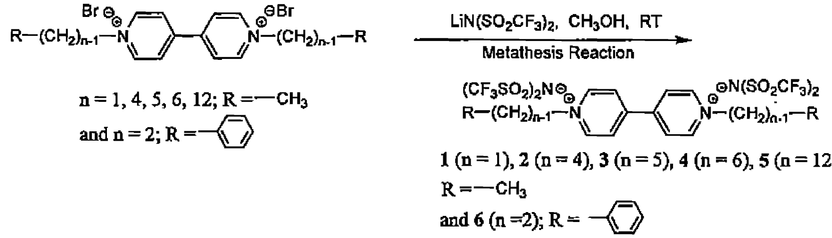
*Corresponding author. E-mail: bhowmikp@unlv.nevada.edu properties, including electrical conductivity, photochromism, electrochromism, and thermochromism [1]. With the suitably modified chemical architectures, they also exhibit thermotropic liquid crystalline (LC) properties [2–6]. For example, the ranges 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 lengths and the anions. 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 compounds decompose prior to exhibiting a stable isotropic liquid phase. 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, nonionic thermotropic LC compounds [2]. The 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 other 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, the 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 sulfonates 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 exhibits a S_A phase, and the S_A phase for each persists up to their decomposition temperatures (280–290°C) [6]. Thus, it is evident that the viologen compounds, having suitably designed chemical architectures (dicationic salts), like 1-alkyl-3-methylimidazolium, N-alkylpyridinium, quaternary ammonium, and quaternary phosphonium salts, each of which is a monocationic salt [7–10], have great potential for the preparation of both RT ionic liquids (green solvents) and RTLC ionic liquids (ordered reaction media). Additionally, there has 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 [11], as templates for the synthesis of mesoporous and zeolitic materials [12], and in the formation of ordered thin films [13].

In this article, we describe the facile preparation of a new series of viologen bis(triflimide) salts (**1–6**) by the metathesis reaction of either the corresponding 1,1′-dialkyl-4,4′-bipyridinium dibromides or 1,1′-dibenzyl -4,4′-bipyridinium dibromide with lithium triflimide in a polar organic solvent (Scheme 1) and the characterization of their thermotropic LC properties by differential scanning calorimetry (DSC), polarizing light



SCHEME 1

microscopy (PLM), and thermogravimetric analysis (TGA). To our knowledge, they are the first examples of viologen bis(triflimide) salts that exhibit thermotropic LC properties at as low as room temperature, as well as at relatively low temperatures (51 and 58°C). Their photoluminescent property in both nonpolar and polar organic solvents as well as in the solid state is also included in this study. Their emission spectra in the solid state displayed hypsochromic shift when compared with those in solution of nonpolar solvent such as dimethyoxyethane. The triflimide organic counterion is selected because of its unique ability to depress the melting points of ionic salts [14–16]. It also has great thermal stability when compared with other inorganic or organic counterions. For example, the thermal stability of 1-ethyl-3-methylimidazolium triflimide—a RT ionic liquid—in both air and nitrogen is up to 400°C [14]. Triflimide is undoubtedly an interesting organic counterion, because it plays a pivotal role for the synthesis of several major classes of RT ionic liquids [14,15].

EXPERIMENTAL

The 1,1′-dialkyl-4,4′-bipyridinium dibromides (diiodides) were prepared by adding the corresponding slight excess of two equivalents of alkyl bromides (diiodides) to a solution of one equivalent of 4,4′-bipyridyl in acetonitrile. After heating to 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 $\delta = 7.83$, 8.32, 8.64, and 8.83 ppm of monoalkylated product in D_2O) and elemental analysis. The viologens **1–6** were prepared by the metathesis reaction of either the corresponding 1,1′-dialkyl -4,4′-bipyridinium dibromides (diiodides for **1** and **2**) or 1,1′-dibenzyl -4,4′-bipyridinium dibromide with lithium triflimide in a common organic solvent. A typical procedure was as follows: 2.0 g (4.5 mmol) of 1,1′-dimethyl-4,4′-dipyridinium diiodide was dissolved in 30 ml methanol. To the methanol solution of diiodide salt, 30 ml of lithium triflimide (2.9 g, 10.1 mmol, 11% excess) in methanol was slowly added on stirring. The resulting solution was stirred overnight. After removing methanol by a rotary evaporator, deionized water was added to the solid products to dissolve LiI and excess lithium triflimide, thus resulting the desired compound **1**. It was further purified by simply washing with deionized water several times and dried in vacuum at RT for several days. The yield of metathesis reaction for the preparation of this compound **1** was essentially quantitative. Its purity was checked by both ^{1}H and ^{13}C NMR spectroscopy, as well as elemental analysis. No special equipments, such as a glove box, and precautions were adopted for the synthesis of these viologen salts.

Selected data for **1**: IR (KBr)/ν_{max} cm^{-1}: 3136, 3069, 1644, 1572, 1507, 1439, 1354, 1193, 1136, 1048, 833, 795, 741, 706, 618, 570, 515; δ_H (CD$_3$OD, 400 MHz, ppm): 9.12–9.14 (4H, d, J = 6.56 Hz), 8.58–8.59 (4H, d, J = 6.23 Hz), 4.51–4.53 (6H, d, J = 7.29 Hz); δ_C (CD$_3$OD, 100 MHz, ppm): 151.21, 148.02, 127.94, 125.96, 122.77, 119.59, 116.40, 49.06; Anal. Calcd for $C_{16}H_{14}N_4O_8F_{12}S_4$: C, 25.74; H, 1.89; N, 7.50; S, 17.18. Found: C, 25.83; H, 2.12; N, 7.57; S, 17.01.

Selected data for **2**: IR (KBr)/ν_{max} cm^{-1}: 3068, 2974, 2882, 1639, 1558, 1509, 1453, 1352, 1231, 1194, 1137, 1049, 841, 788, 739, 620, 570, 515; δ_H (CD$_3$OD, 400 MHz, ppm): 9.20–9.21 (4H, d, J = 6.79 Hz), 8.59–8.61 (4H, d, J = 6.32 Hz), 4.71–4.75 (4H, t, J = 7.70 Hz), 2.05–2.20 (4H, m), 1.44–1.55 (4H, m), 1.01–1.05 (6H, t, J = 7.35 Hz); δ_C (CD$_3$OD, 100 MHz, ppm): 151.46, 147.97, 147.02, 146.11, 128.36, 125.93, 122.74, 119.56, 116.37, 63.22, 34.40, 20.42, 13.72; Anal. Calcd for $C_{22}H_{26}N_4O_8F_{12}S_4$: C, 31.81; H, 3.15; N, 6.74; S, 15.44. Found: C, 31.84; H, 3.44; N, 6.85; S, 15.63.

Selected data for **3**: IR (KBr)/ν_{max} cm^{-1}: 3135, 3074, 2965, 2877, 1640, 1564, 1509, 1449, 1352, 1192, 1136, 1056, 838, 787, 739, 652, 620, 598, 570, 512; δ_H (CD$_3$OD, 400 MHz, ppm): 9.20–9.21 (4H, d, J = 6.79 Hz), 8.59–8.61 (4H, d, J = 6.32 Hz), 4.71–4.75 (4H, t, J = 7.70 Hz), 2.05–2.20 (4H, m), 1.44–1.55 (4H, m), 1.01–1.05 (6H, t, J = 7.35 Hz); δ_C (CD$_3$OD, 100 MHz, ppm): 151.39, 146.95, 128.29, 125.86, 122.67, 119.49, 116.30, 63.30, 32.13, 29.19, 23.07, 14.04; Anal. Calcd for $C_{24}H_{30}N_4O_8F_{12}S_4$: C, 33.57; H, 3.52; N, 6.52; S, 14.93. Found: C, 33.60; H, 3.41; N, 6.78; S, 14.74.

Selected data for **4**: IR (KBr)/ν_{max} cm^{-1}: 3130, 3072, 2941, 2869, 1640, 1564, 1509, 1449, 1350, 1329, 1193, 1133, 1060, 842, 787, 738, 648, 597, 572, 511; δ_H (CD$_3$OD, 400 MHz, ppm): 9.21–9.22 (4H, d, J = 5.30 Hz), 8.60–8.61 (4H, d, J = 5.56 Hz), 4.71–4.74 (4H, t, J = 8.47 Hz), 2.07–2.20 (4H, m), 1.38–1.45 (12H, m), 0.91–0.94 (6H, m); δ_C (CD$_3$OD, 100 MHz, ppm): 151.47, 147.02, 128.36, 125.96, 122.77, 119.58, 116.40, 63.42, 32.49, 32.27, 26.86, 23.43, 14.25; Anal. Calcd for $C_{26}H_{34}N_4O_8F_{12}S_4$: C, 35.21; H, 3.86; N, 6.32; S, 14.47. Found: C, 35.11; H, 3.78; N, 6.11; S, 14.54.

Selected data for **5**: IR (KBr)/ν_{max} cm^{-1}: 2922, 2853, 1684, 1643, 1560, 1509, 1470, 1351, 1195, 1136, 1060, 835, 789, 740, 654, 621, 600, 514; δ_H (CD_3OD, 400 MHz, ppm): 9.21–9.22 (4H, d, J = 6.89 Hz), 8.60–8.62 (4H, d, J = 6.63 Hz), 4.70–4.74 (4H, t, J = 5.97 Hz), 2.07–2.20 (4H, m), 1.29–1.43 (36H, m), 0.87–0.91 (6H, t, J = 6.68 Hz); δ_C (CD_3OD, 100 MHz, ppm): 151.44, 147.03, 128.35, 125.94, 122.76, 119.57, 116.38, 63.42, 33.04, 32.53, 30.69, 30.61, 30.44, 30.11, 27.20, 23.70, 14.42; Anal. Calcd for $C_{38}H_{58}N_4O_8F_{12}S_4$: C, 43.26; H, 5.54; N, 5.31; S, 12.15. Found: C, 43.30; H, 5.62; N, 5.48; S, 12.31.

Selected data for **6**: IR (KBr)/ν_{max} cm^{-1}: 3067, 1684, 1634, 1558, 1508, 1497, 1450, 1364, 1331, 1201, 1139, 1052, 853, 813, 793, 748, 725, 701, 616, 570, 552, 515; δ_H (CD_3OD, 400 MHz, ppm): 9.23–9.25 (4H, d, J = 6.52 Hz), 8.58–8.60 (4H, d, J = 6.44 Hz), 7.47–7.54 (10H, m), 5.93 4H, s); δ_C (CD_3OD, 100 MHz, ppm): 151.80, 146.99, 134.06, 131.29, 130.86. 130.40, 128.63, 125.94, 122.75, 119.57, 116.38, 66.04; Anal. Calcd for $C_{28}H_{22}N_4O_8F_{12}S_4$: C, 37.42; H, 2.47; N, 6.23; S, 14.27. Found: C, 37.56; H, 2.43; N, 6.26; S, 14.53;

The FTIR spectra of compounds **1–6** were recorded with a Nicolet FTIR analyzer with their neat films on KBr pellets. Their ^1H and ^{13}C NMR spectra were recorded with three RF channels operating at 400 and 100 MHz, respectively, in CD_3OD using TMS as an internal standard. The phase transition temperatures were measured by the differential scanning calorimetry (TA 2100 DSC) in nitrogen at both heating and cooling rates of 10°C/min. The TGA measurements were performed with a TA 2100 instrument at a heating rate of 20°C/min in nitrogen. The optical textures of LC phases were observed by using a Nikon polarizing light microscope equipped with a Mettler FP80 hot-state. UV-vis absorption spectra of compounds **1–6** in spectrograde dimethoxyethane (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 **3** and **5** in thin films cast from DME were also recorded with this instrument by using a front surface accessory.

RESULTS AND DISCUSSION

The 1,1′-dimethyl-4, 4′-bipyridinium diiodide had a weak crystal-to-crystal transition at 264°C ($\Delta H = 1.1$ kJ/mol), and a crystal-to-liquid transition at 365°C (mp 325°C [17]), accompanied by immediate decomposition as determined by DSC at a heating rate of 10°C/min in nitrogen. In contrast, the viologen **1** showed a single endotherm in the first and second heating cycles of its DSC thermograms under identical conditions. In each of the corresponding cooling cycles, there were several exotherms. Among them, two exotherms at 103 and 108°C were more prominent than others. These multiple exotherms were presumably related to the polymorphism of an ionic compound on cooling from the isotropic liquid phase [18]. In conjunction with the PLM studies, it was determined that the endotherm corresponded to the crystal-to-liquid transition ($T_m = 132°C$ with $\Delta H_m = 39.0$ kJ/mol), which was far below its decomposition temperature at 396°C (Table 1). Thus, **1** had no thermotropic LC property, but its much lower melting transition was related to the presence of bis(triflimide) counterions in this salt when compared with the 1,1′-dimethyl-4,4′-bipyridinium diiodide.

The 1,1′-dibutyl-4,4′-bipyridinium diiodide exhibited no crystal-to-crystal transition but did exhibit a melting endotherm at 270°C [17] with the concomitant decomposition as determined by DSC at a heating rate of 10°C/min in nitrogen. The TGA measurement also indicated its decomposition temperature at 269°C at a heating rate of 10°C/min in nitrogen. Figure 1 shows the DSC thermograms of **2** obtained at both heating and cooling rates of 10°C/min. In each of the heating cycles there were distinctly two endotherms. Correspondingly, there were two major exotherms

TABLE 1 Transition Temperatures and Enthapies from DSC Thermograms and Decomposition Temperatures from TGA Measurements for Viologen Salts

		First heading		Second heading		
Compound	Transition	T(°C)	ΔH (kJ/mol)	T(°C)	ΔH (kJ/mol)	T_d [a](°C)
1	cryst-iso	132.3	39.0	132.3	39.0	395.5
2	cryst-S_A	51.1	14.7	50.4	5.7	366.2
	S_A-iso	87.8	27.6	87.8	27.2	
3	cryst-S_A	– 4.3	3.9	–[b]		364.4
	S_A-iso	42.2	19.0	42.2	19.3	
4	cryst-S_A	58.4	31.0	58.1	30.3	361.7
	S_A-iso	78.2	5.0	78.3	5.0	
5	cryst-S_X	28.3[c]	27.2	18.3	18.5	355.5
	S_X-$S_{X'}$	120.3	8.0	119.3	1.4	
	$S_{X'}$-$S_{X''}$	198.8	9.9	201.9	3.6	
6	glass transition	68.0		68.0		327.3
	cryst-iso	117.5	34.9	117.7	34.9	

[a] Thermal stability (T_d) was determined in nitrogen at a heating rate of 20°C/min at which 5 wt% loss of the compound occurred, with the exceptions of **2** and **5**, which were determined at a heating rate of 10°C/min.

[b] This transition was not detected in the second heating cycle for this salt.

[c] There was a shoulder peak at 24.3°C with ΔH = 0.8 kJ/mol in the first heating cycle.

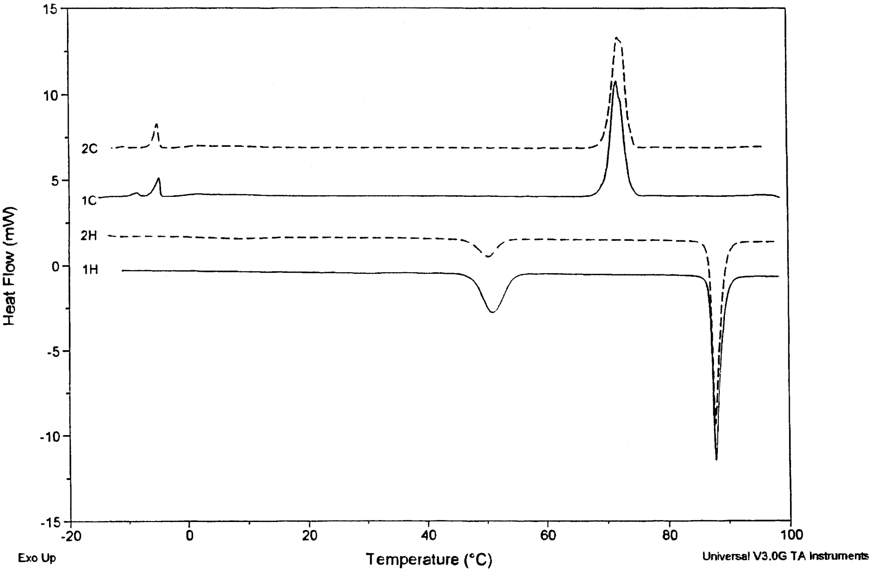


FIGURE 1 DSC thermograms of viologen **2** obtained at both heating and cooling rates of 10°C/min.

in each of the cooling cycles. In conjunction with PLM studies, it was determined that the low-temperature endotherm was related to the crystal-to-smectic LC phase transition ($T_m = 51°C$) and the high-temperature endotherm was related to the smectic-to-isotropic transition ($T_i = 88°C$). Both of these transitions were conveniently well below its decomposition temperature at 366°C (Table 1). The high-temperature exotherm ($-\Delta H = 26.3$ kJ/mol) in the second cooling cycle, which underwent a low degree of hysteresis (i.e., a supercooling of 16°C), corresponded to the transition from the isotropic liquid phase to the smectic LC phase.

The low-temperature exotherm ($-\Delta H = 2.7$ kJ/mol), which underwent a high degree of supercooling of 56°C, was related to the transition from the smectic LC phase to crystalline phase. Additionally, the enthalpy change for the T_i remained essentially identical in both the heating cycles, but the enthalpy change for the T_m in the second heating cycle was much lower than that in the first heating cycle (Table 1). This result was presumably related to the imperfect crystallization under the experimental conditions used. Thus **2**, unlike the 1,1′-dibutyl-4-4′-bipyridinium diiodide, exhibited an enantiotropic LC phase and had a wide range of LC phase of 37°C. These results suggested that a simple exchange of diiodide counterion of viologen salt by bis(triflimide) as counterions was conducive to the formation of LC ionic salt.

The 1,1′-dipentyl-4,4′-bipyridinium dibromide exhibited a crystal-to-crystal transition at 192°C ($\Delta H = 29.3$ kJ/mol) in the first heating cycle of 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. The TGA measurement also confirmed its decomposition temperature at 272°C [17] at a heating rate of 20°C/min in nitrogen. Figure 2 displays the DSC thermograms of **3** obtained at both heating and cooling rates of 10°C/min. In the first heating cycle, this salt showed distinctly two endotherms. The low-temperature endotherm was its T_m (− 4°C), and the high-temperature one was its T_i (42°C), as verified with PLM studies. In the first cooling cycle, there was a rather broad exotherm that corresponded to the transition from isotropic liquid phase to the smectic LC phase. The absence of exotherm for smectic LC phase-to-crystalline phase in the first cooling cycle and the absence of T_m in the second heating cycle suggested that this salt retained the smectic LC phase without the interference of crystallization even at low temperature (−30°C) on cooling at a rate of 10°C/min. Thus, it was found that **3** is a RT ionic salt that has a

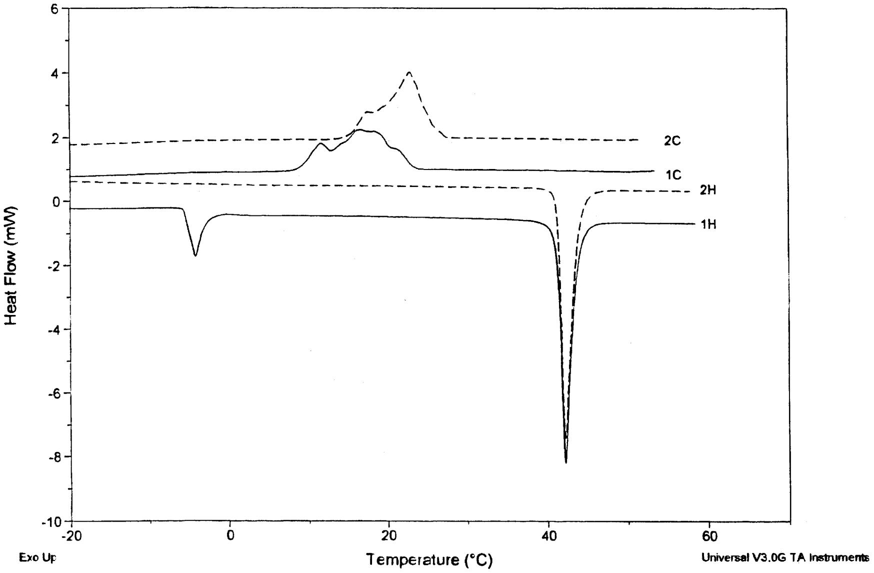


FIGURE 2 DSC thermograms of viologen **3** obtained at both heating and cooling rates of 10°C/min.

range of LC phase of 46°C. It also has excellent thermal stability as high as 364°C (Table 1).

The 1,1′-dihexyl-4,4′-bipyridinium dibromide showed clearly an endotherm in each of the heating cycles. Correspondingly, there was an exotherm in each of the cooing cycles of its DSC thermograms. In conjunction with PLM studies it was found that the endotherm was the crystal-to-LC phase transition ($T_m = 144°C$, and $\Delta H = 14.2$ kJ/mol), which persisted up to its decomposition temperature at 286°C by DSC. The TGA measurement showed its $T_d = 269°C$ obtained at a heating rate of 10°C/min in nitrogen. The exotherm in the cooling cycle at 124°C ($\Delta H = 12.0$ kJ/mol) mol) corresponded to the LC-to-crystal phase transition that underwent a relatively low degree of supercooling of 20°C. Figure 3 displays the DSC thermograms of **4** obtained at both heating and cooling rate of 10°C/min. In the first heating cycle, there were two endotherms. In the first cooling cycle, there were two exotherms at low-temperature region and an exotherm at high-temperature region. The DSC thermograms in the second heating and cooling cycles were essentially identical to those in the first heating and cooling cycles. Again in corroboration with PLM studies, it was found that the low-temperature endotherm corresponded to the crystal-to-smectic LC phase transition ($T_m = 58°C$) and the high-temperature one corresponded to the smectic LC phase-to-isotropic

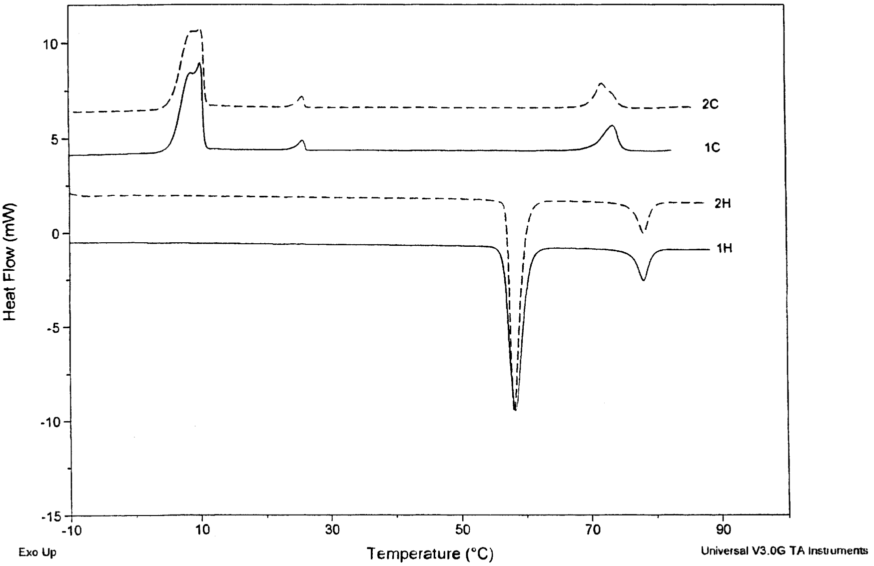


FIGURE 3 DSC thermograms of viologen **4** obtained at both heating and cooling rates of 10°C/min.

transition ($T_i = 78°C$), thus resulting in a range of LC phase of 20°C for **4**. As expected, the high-temperature exotherm exhibited the lowest degree of supercooling among the exotherms observed for **4.** Additionally, the enthalpy changes for the T_m and T_i were essentially identical in both the heating cycles. Thus, similar to **2** and **3, 4** also exhibited an enantiotropic LC phase. It also had excellent thermal stability up to 362°C (Table 1), which was exceedingly higher than its T_m and $T_{i.}$

Although the 1,1′-didodecyl-4,4′-bipyridinium dibromide showed two reversible endotherms (at 119°C with $\Delta H = 43.6$ and at 170°C with $\Delta H = 3.6$ kJ/mol) in each of the heating cycles of DSC thermograms, it exhibited no melting endotherm up to its decomposition temperature ($T_d = 283°C$), which was determined by TGA measurement at a heating rate of 10°C/min in nitrogen. In contrast, the viologen salt **5** exhibited three endotherms in each of the heating cycles of its DSC thermograms. Correspondingly, there were three exotherms in each of the cooling cycles (Figure 4). The enthalpy changes for all of these transitions in the first heating cycle were much higher than those in the second heating cycle (Table 1). The lowest temperature was related to its crystal-to-smectic LC phase transition ($T_m = 28°C$). The other two endotherms at 120 and 199°C were related to the high-order-smectic-phase–to–low-order-

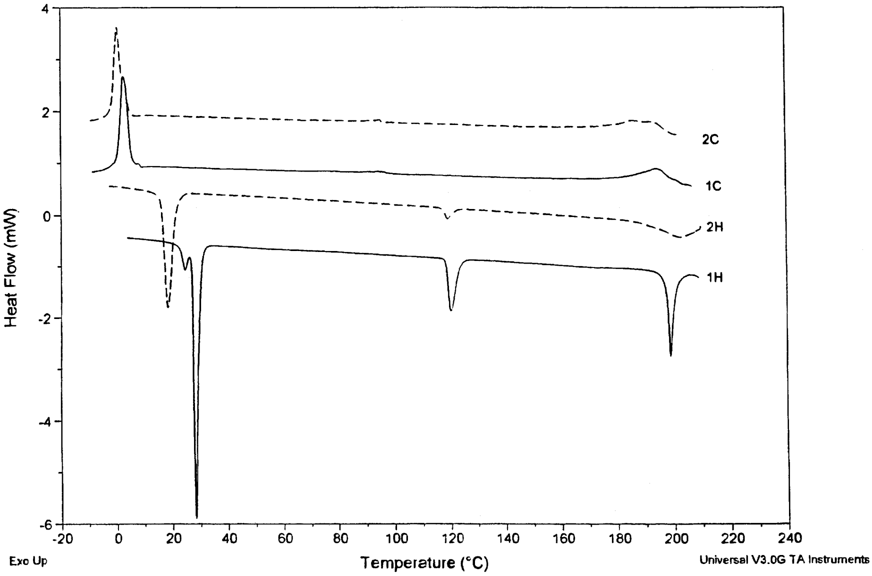


FIGURE 4 DSC thermograms of viologen **5** obtained at both heating and cooling rates of 10°C/min.

smectic-phase transitions, i.e., to the polymesomorphic phases. These results are in excellent agreement with those of analogous viologen salts than contain $^{-}O_3SCH_3$ as counterions in which the polymesomorphic nature also increases with the length of alkyl chains [2]. The smectic phase of **5** persisted up to its decomposition temperature at 356°C (Table 1). Thus, it exhibited the widest range of LC phase among all of the viologen salts (**2–5**).

The 1,1′-dibenzyl-4,4′-bipyridinium dibromide exhibited neither crystal-to-crystal transition nor melting transition up to the decomposition temperature (248°C) at which a loss of 5 wt% of this compound occurred at a heating rate of 20°C/min in nitrogen. In contrast, the viologen salt **6** exhibited a T_g at 68°C and a sharp endotherm in each of the heating cycles of its DSC thermograms. Correspondingly, there were a T_g and a sharp exotherm ineach of the cooling cycles of DSC thermograms. The sharp endotherm corresponded to the crystal-to-liquid transition ($T_m = 117°C$) and the sharp exotherm to liquid-to-crystal transition with a relatively low degree of supercooling of 30°C. Its T_m was also far below its $T_d = 327°C$ (Table 1). Thus, similar to **1, 6** exhibited no thermotropic LC property, but its much lower melting transition was again related to the presence of triflimide counterion in this salt when compared with the 1,1′-dibenzyl-4,4′-bipyridinium dibromide.

All of these results (*vide supra*), on the one hand, suggested that the viologens **2–5** exhibited an enantiotropic LC phase at lower temperatures when compared with those of several 1-alkyl-3-methylimidazolium (alkyl chain lengths of 14, 16, and 18) hexafluorophosphate and N-alkylpyridinium (alkyl chain lengths 16 and 18) hexafluorophosphate. On the other hand, the salts **3** and **5** exhibited an enantiotropic LC phase at much lower temperatures when compared with those of several 1-alkyl-3-methylimidazolium (alkyl chain lengths of 13–18) tetrafluoroborates; the salts **2** and **4** formed an enantiotropic LC phase at temperatures that are comparable with those of several 1-alkyl-3-methylimidazolium (alkyl chain lengths of 13–18) tetrafluoroborates. The ranges of LC phase for these salts were much higher in some cases and in other cases were much lower than those of 1-alkyl-3-methylimidazolium and N-alkylpyridinium salts [19,20]. Furthermore, the observation of enentiotropic LC phase for each of the viologen salts **2–5** is in contrast to several 1-alkyl-3-methylimidazolium (alkyl chain lengths of 12, 14, 16, and 18) triflimide salts, all of which undergo crystal-to-isotropic transitions at relatively low temperatures in the range of 16.6–44.8°C [16]. Thus, it appeared that triflimide is an interesting counterion that has a unique capacity not only to decrease the crystal-to-isotropic (T_m) in the cases of **1** and **6** but also to decrease crystal-to-LC phase (T_m) and LC-to-isotropic (T_i) transitions in the cases of **2–5,** thus depending on the chemical structures of the ionic salts employed.

The thermal stability of each of the viologen salts **1–6** was determined in nitrogen at a heating rate of either 10 or 20°C/min by TGA measurement. The thermal stability limit was the temperature at which a 5% weight loss of **1–6** occurred. They were in the range of 327–396°C, which was much higher than those of the corresponding dibromide compounds (*vide supra*). Figure 5 shows the illustrative thermogravimetric analysis plots of dibromide salt and bis(triflimide) salt **5**, revealing the much greater thermal stability of **5** when compared with the corresponding dibromide salt. These results are in excellent agreement with those of other ionic salts containing triflimide anion [14].

The viologen salts **2–5** formed turbid melts above their T_m values as low as −4°C to as high as 58°C, which exhibited strong stir opalescence. This property was taken as a preliminary indication of their LC property. For further characterization of their melt morphology, they were evaluated by visual observations with a PLM. Their optical textures were essentially identical in the cases **2–4**. They typically formed, after immediate melting transitions, Schlieren textures mixed with small mosaic textures that grew into large mosaic textures before their T_i transitions. On cooling from the isotropic phase, each of them exhibited various types of mosaic textures along with spherical birefringent particles that have the appearance of

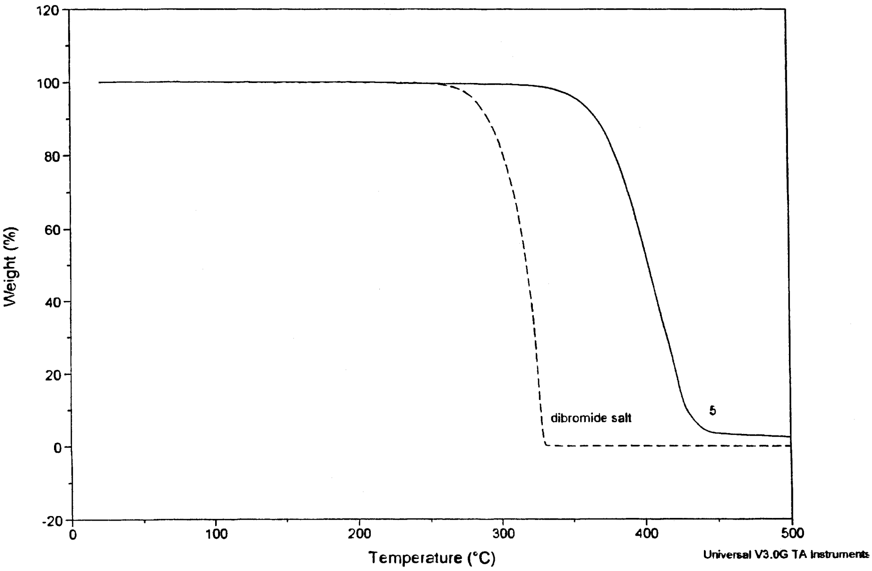


FIGURE 5 TGA plots of **5** and its corresponding dibromide salt in nitrogen at a heating rate of 10°C/min.

more or less regular cloverleaf in shape (Figure 6). All of them were indicative of smectic LC phases, specifically S_A, on the basis of PLM studies [21–23]. Figure 7 shows the photomicrographs of **5** taken at various temperatures, revealing its polymesomorphic phases.

All of the viologens **1–6** in DME (relatively nonpolar solvent) showed essentially identical absorption, excitation and emission spectra. Figure 8(a) shows the illustrative emission spectra of **3** in DME at various excitation wavelengths. One the one hand, at low excitation wavelengths (210–240 nm), it exhibited two major λ_{em} values at 298 and 598 nm along with a shoulder peak at 622 nm. On the other hand, it showed a single λ_{em} at 531 nm at high excitation wavelengths of 410–475 nm. The peak and intensity of emission spectra were dependent on the excitation wavelengths used. The excitation spectra of **3** in DME showed several λ_{ex} values at 251, 272, 286, and 476 nm, which were not equivalent to its absorption spectrum ($\lambda_{abs} = 218$ and 265 nm). In contrast, viologens **1–6** in CH_3OH (polar solvent) showed essentially identical absorption spectra, but their excitation and emission spectra were quite different depending on the length of alkyl chain groups or benzyl group. For example, **1** in CH_3OH showed emission spectra at $\lambda_{em} = 305$ nm at excitation wavelengths of 220–230 nm, but it showed different emission spectra at $\lambda_{em} = 356$ nm at excitation wavelengths of 310 and 320 nm. **2** exhibited λ_{em} values at 310 and 622 nm at excitation wavelengths of 220–230 nm, but showed a single $\lambda_{em} = 529$ nm at excitation wavelengths of 390, 410, 430, 450, and 470 nm. Figure 8(b) shows the emission spectra of **3** in CH_3OH at various excitation wavelengths. Its emission spectra contained several λ_{em} values depending on the excitation wavelengths used. **4** exhibited only a single $\lambda_{em} = 530$ nm irrespective of the excitation wavelengths of 380, 400, 420, 440, 460, and 480 nm used. The emission spectrum of **5** in CH_3OH obtained at excitation wavelength of 220 nm contained two λ_{em} values at 390 and 622 nm, but its emission spectra obtained at excitation wavelengths of 360, 400, 440, and 480 nm contained a major $\lambda_{em} = 529$ nm. However, at excitation wavelengths of 360 and 400 nm, there were also additional shoulder peaks in the emission spectra. **6** exhibited a single $\lambda_{em} = 533$ nm nm at various excitation wavelengths of 370, 390, 410, 430, 450, and 470 nm. The intensity of emission spectrum was sensitive to the excitation wavelength used.

Figure 9 shows the emission spectra of **3** and **5** in thin films cast from DME, that is, in their RT LC phase. The viologen salt **3** had two λ_{em} values at 293 and 375 nm at various excitation wavelengths; the viologen salt **5** had a single $\lambda_{em} = 346$ nm at excitation wavelengths 265, 275, and 285 nm. Additionally, it exhibited a single $\lambda_{em} = 360$ nm at low excitation wavelength of 240 nm. Their excitation spectra contained a major $\lambda_{ex} = 241$ nm along with a minor peak(s) during monitoring at 376 nm.

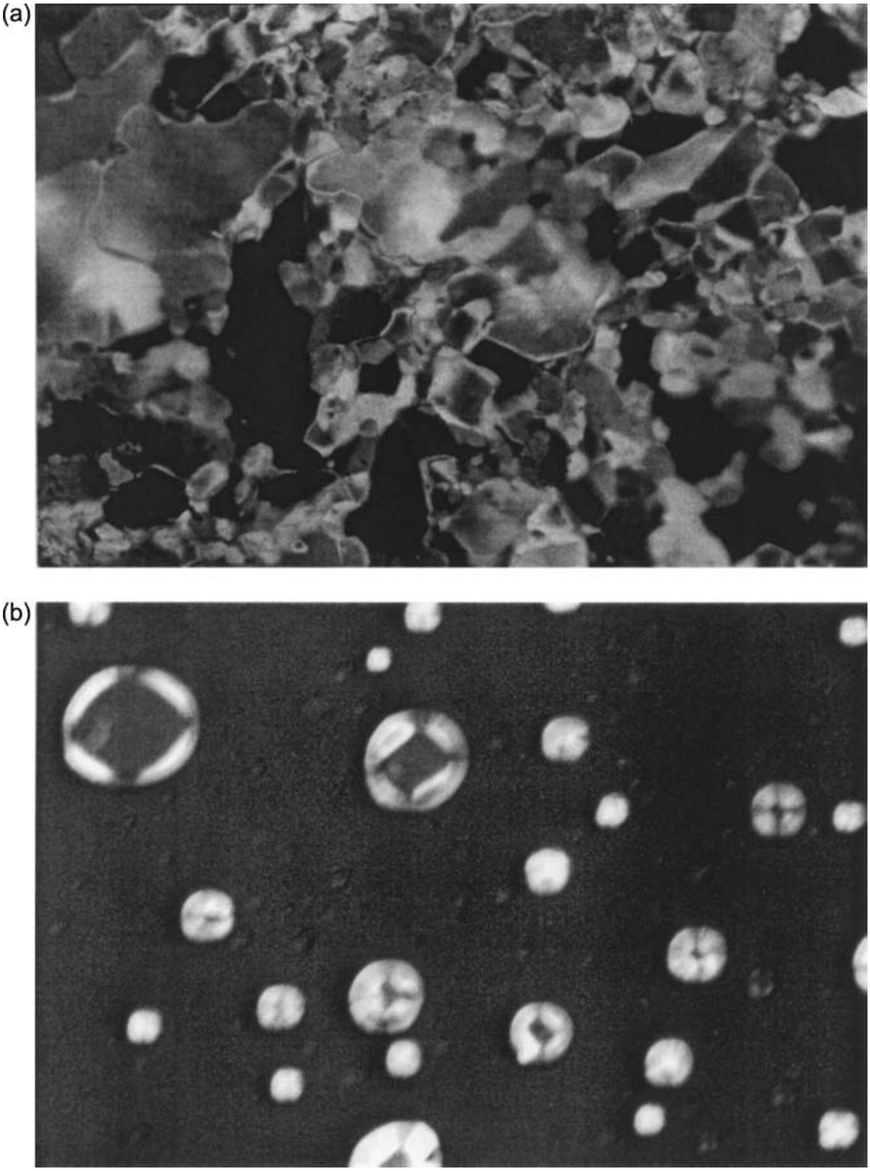


FIGURE 6 Photomicrographs of **3** and **4**: (a) taken at room temperature, and (b) obtained on immediate cooling at a rate of 10°C/min from the isotropic phase under crossed polarizers, respectively, both of which exhibited a smectic LC phase (magnification 400×).

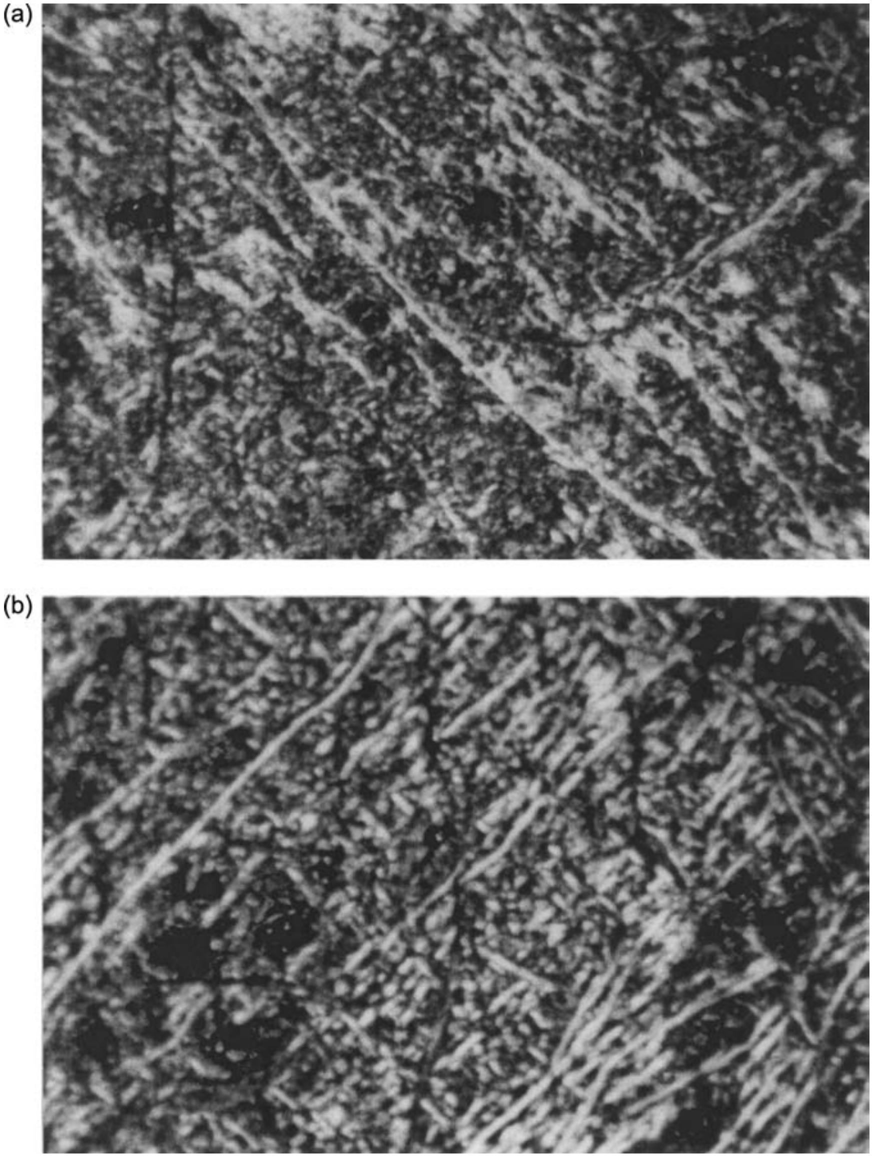


FIGURE 7 Photomicrogaphs of **5** taken at (a) 35, (b) 80, (c) 230, and (d) 270°C under crossed polarizers displaying its various LC phases (magnification 400×).

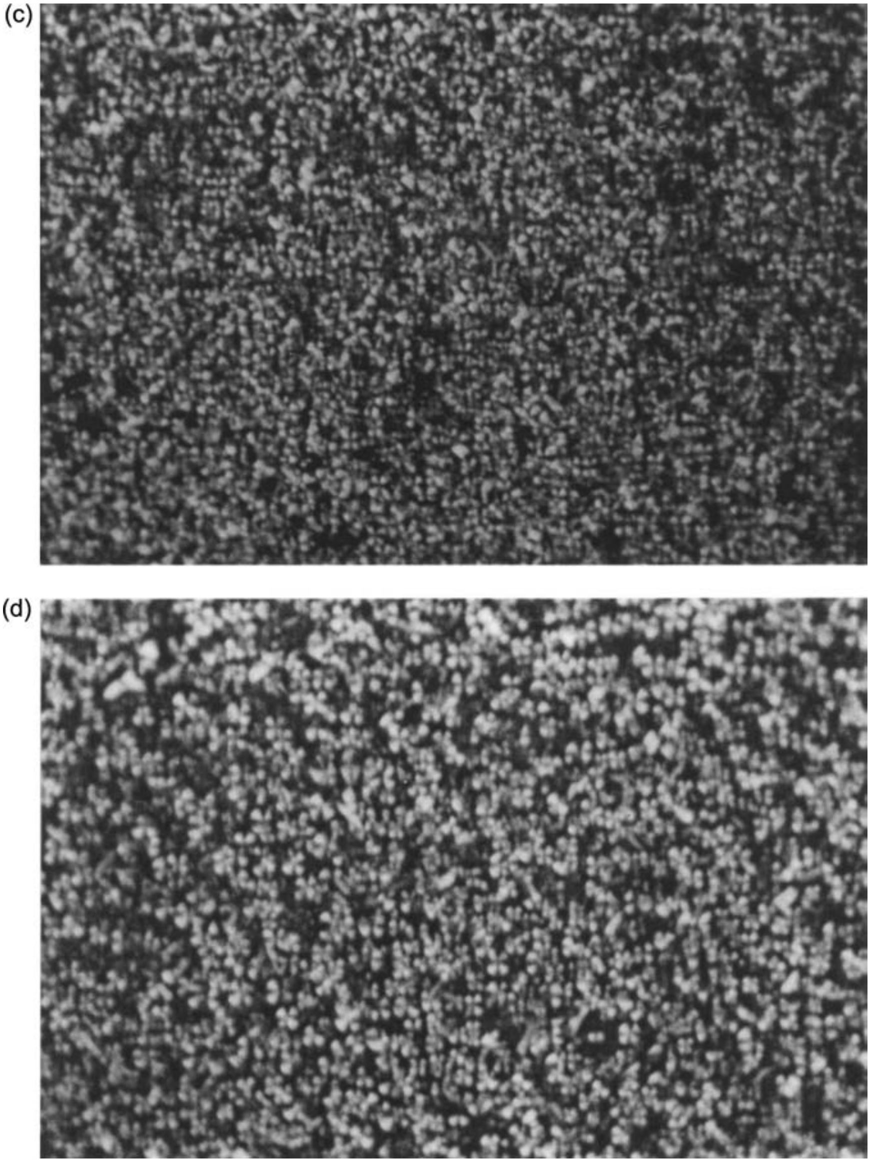


FIGURE 7 Continued.

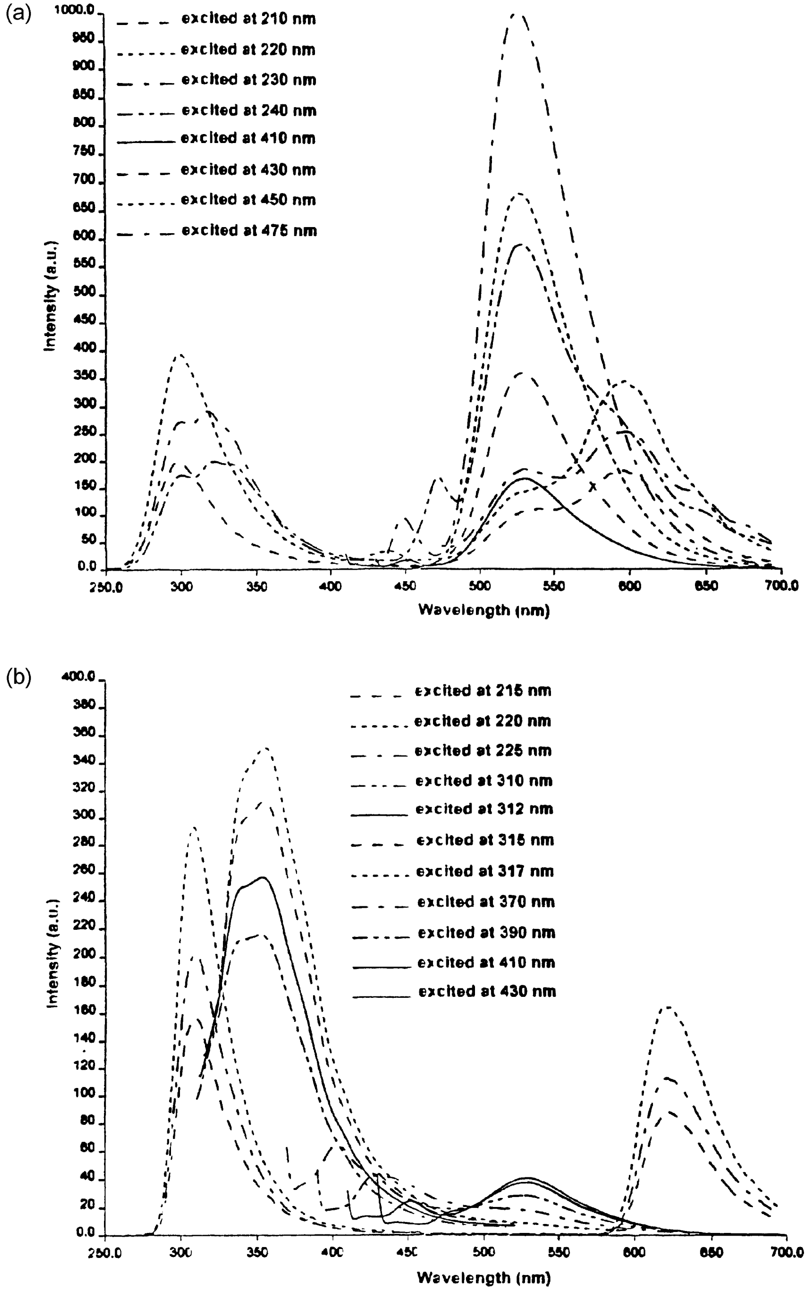


FIGURE 8 Emission spectra of **3** at various excitation wavelengths, (a) in DME and (b) in methanol, respectively.

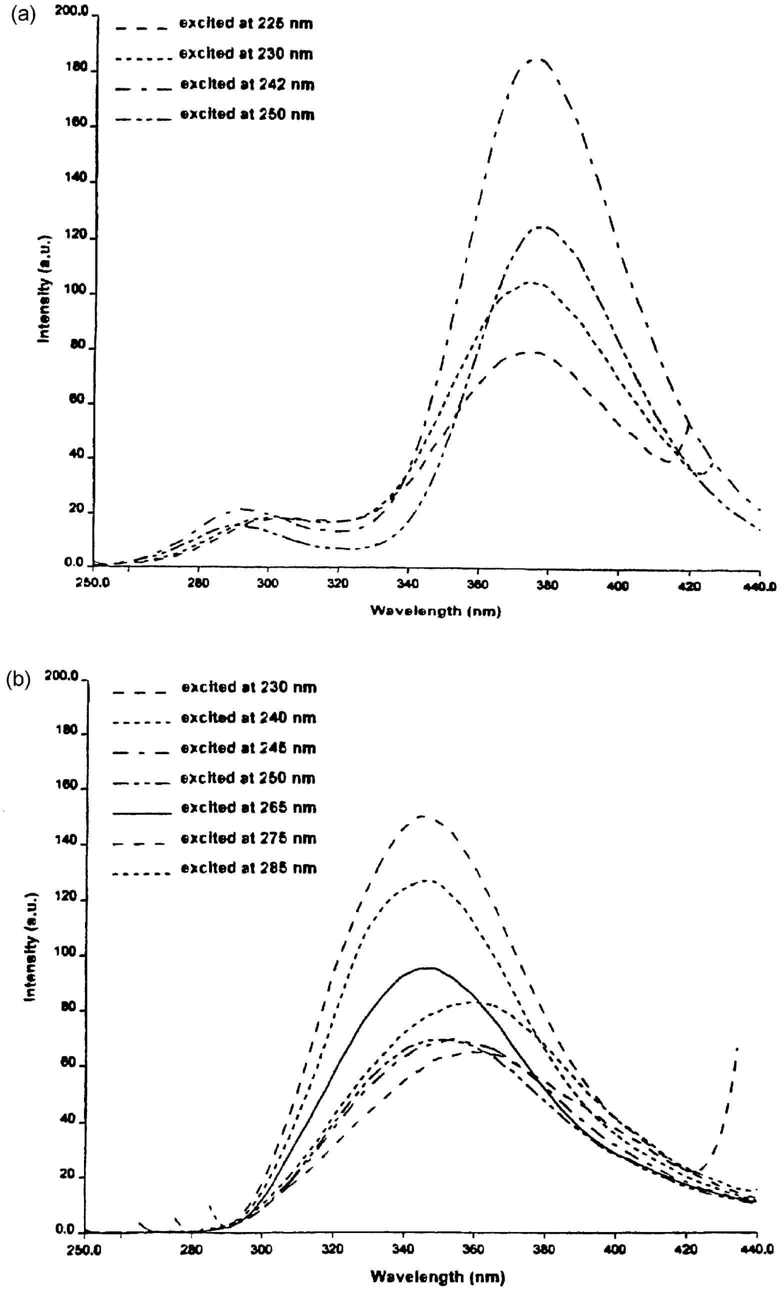


FIGURE 9 (a) and (b) Emission spectra of **3** and **5** in thin films cast from DME at various excitation wavelengths.

Their λ_{em} values were hypsochromically shifted in the LC phase when compared with those of solution spectra in DME.

Although the photoluminescence quenching processes of a π-conjugated polymer by numerous viologens in aqueous solution open an opportunity for the development of biological and chemical sensors for use in medical diagnostics and toxicology [24–27], the fluorescence property of viologens **1–6** in both nonpolar and polar organic solvents as well as in the solid state is undoubtedly an additional attribute to this class of ionic salts. This property of these ionic salts can be exploited further for development of chemical sensors.

CONCLUSIONS

Several dicationic bis(triflimide) salts, that is, viologens, displayed LC properties either at RT (-4 and 28°C) or at relatively low temperatures (51 and 58°C), and their LC phases persisted over a broad range of temperatures as determined with a number of experimental techniques on one hand. On the other hand, two viologens had relatively low crystal-to-isotropic transitions (117 and 131°C). All of them had much better thermal stability in the temperature range of 327–396°C when compared with that of the corresponding viologen dihalides. Thus, triflimide anion is a useful organic counterion for the generation of not only RT ionic liquids but also RT LC ionic liquids. They have high potential as unique solvents, since their LC properties were maintained over a wide range of temperatures. Rigidity of molecular ordering and mobility make these ionic liquids suitable for many stereochemically controlled organic reactions [11,28]. Their fluorescence property both in solution and in the solid state also imparted an additional attribute to this class of ionic salts that could be further exploited for the development of chemical sensors.

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