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Ionic perylene-3,4-dicarboximide as chromonic mesogens and the use of a fluorescence technique in determining phase-transition temperatures

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We report a study of the chromonic liquid-crystalline properties of 2-(*N,N*-diethyl-*N*-methylammonium)ethylperylene-3,4-dicarboximide formate (**1**) in aqueous solution by polarised optical microscopy (POM), ^2H nuclear magnetic resonance (NMR) spectroscopy and fluorescence spectroscopy. Compound **1** shows chromonic liquid-crystalline properties at concentrations higher than 4 wt% at room temperature. We showed that fluorescence spectroscopy could be used to determine the concentration-dependent, phase-transition temperatures of this chromonic liquid crystal. The values determined by fluorescence spectroscopy are consistent with the values determined by ^2H NMR spectroscopy and POM.

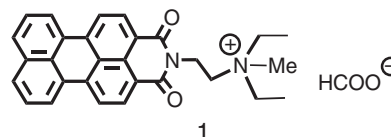
Keywords: chromonic liquid crystals; supramolecular chemistry; aggregation; fluorescence

1. Introduction

The use of chromonic liquid crystals for preparing functional materials has gained increasing attention in recent years [1]. Mesogens (liquid crystal-forming molecules) of the chromonic type are generally aromatic compounds with peripheral hydrophilic, hydrogen-bonding or ionic groups [1–3]. In aqueous solution, these compounds aggregate and stack into columns in liquid-crystalline phases in which the molecules are mobile as in liquid, but there is a more-or-less parallel, long-range alignment of the director. There is no critical concentration for the formation of aggregates or optimum size of aggregates [4, 5]. Chromonic liquid crystals have potential applications as colour filters, linear polarisers [6–12], optical compensators [13, 14], retarders, micropatterns of anisotropic aromatic materials [15–19] and biosensors [20–23]. The synthesis and study of new chromonic mesogens with useful properties are important for providing the building blocks of new functional materials and for furthering our knowledge of the structural factors that govern chromonic liquid-crystalline properties. This knowledge is essential for the future design of chromonic mesogens and the molecular level control of material properties.

To this end, we synthesised ionic perylene-3,4-dicarboximides (also called perylenemonoimides) and explored their potential use as chromonic mesogens. Perylene-3,4-dicarboximides have been reported in the literature and are potentially useful as fluorophores, photonic wires, light harvesting systems and in photovoltaic applications [24–29]. However,

previous studies of perylene-3,4-dicarboximides have focused on the properties of non-ionic derivatives in organic solvents, polymers and the solid state [24–36]. The properties of ionic perylene-3,4-dicarboximides in aqueous solution are largely unexplored. We revealed previously the anisotropic properties of 2-(*N,N*-diethyl-*N*-methylammonium)ethylperylene-3,4-dicarboximide tosylate in the solid state [18]. In this manuscript, we describe the study of the liquid-crystalline properties of 2-(*N,N*-diethyl-*N*-methylammonium)ethylperylene-3,4-dicarboximide formate (**1**) in aqueous solution. The change from tosylate to formate ion significantly increases the solubility of the ionic perylene-3,4-dicarboximide in water and allows the formation of the liquid-crystalline phase in aqueous solution at room temperature. The aggregation and chromonic liquid-crystalline properties of **1** were examined by polarised optical microscopy (POM), ^2H nuclear magnetic resonance (NMR) spectroscopy and fluorescence spectroscopy.



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2. Results and discussion

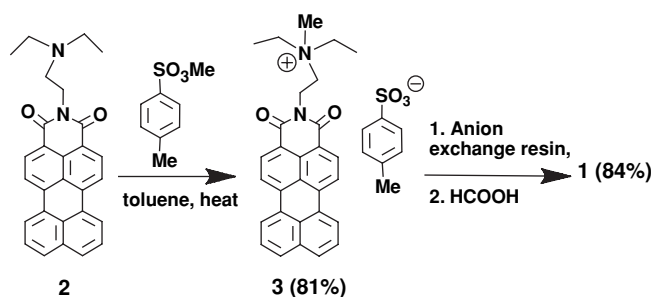
2.1 Synthesis

The synthesis of 2-(*N,N*-diethyl-*N*-methylammonium)ethyl-*perylene*-3,4-dicarboximide formate (**1**) is outlined in Scheme 1. Quaternisation of 2-(*N,N*-diethylamino)ethylperylene-3,4-dicarboximide (**2**) with methyl *p*-toluenesulphonate according to a procedure reported previously yielded the tosylate salt (**3**) [37]. The formate salt **1** was obtained readily from **3** by ion exchange.

2.2 Studies of chromonic liquid-crystalline properties by POM

The solubility of **1** in water allows solutions of high concentrations (e.g. a 20 wt% solution) to be prepared for examining its liquid-crystalline properties. A 4 wt% (about 0.1 M) aqueous solution of **1** was added to a glass slide and covered with a glass cover-slip. The sample was isotropic when viewed between

crossed polarisers under an optical microscope. Upon concentration of this solution by peripheral evaporation of water at room temperature, a schlieren optical texture emerged signalling the transition from an isotropic (I) phase to a liquid-crystalline phase (Figure 1(a) and (b)). The schlieren optical texture is indicative of the formation of a chromonic N phase in which molecules stack to form columns (not necessarily one molecule wide), which have orientational order but no positional order [1–3]. As shown in Figure 1(c), further evaporation of solvent resulted in the herringbone optical texture characteristics of the ordered arrangement of the columns in the chromonic M phase [1–3]. Examination of solutions of different concentrations showed that an aqueous solution of **1** is liquid-crystalline at a concentration of 5 wt% or higher. The N phase persists at concentrations as high as 20 wt%. For a 20 wt% solution, the M phase does not appear at room temperature and even when the solution was cooled to 6°C, no optical



Scheme 1. Synthetic scheme of compound **1**.

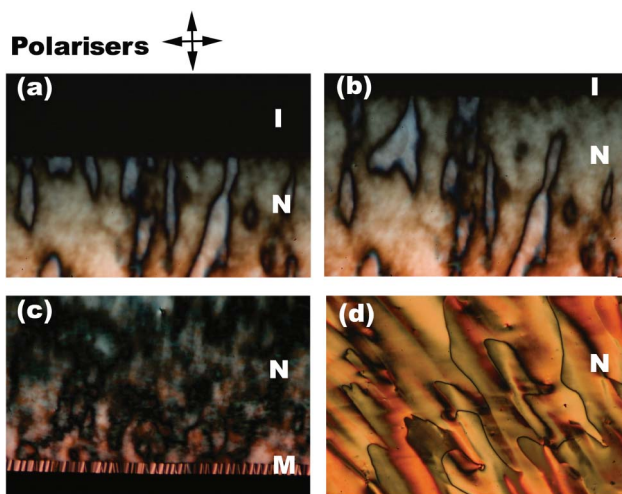


Figure 1. Optical micrographs of the liquid-crystalline phases of **1** in water showing: (a) the development of the chromonic N phase from the isotropic (I) phase of a 4 wt% solution of **1** upon peripheral evaporation of solvent (from the lower edge); (b) the growth of the N phase upon further evaporation of solvent; (c) the transition of the chromonic N phase to the M phase as the concentration of the solution was increased further; (d) an optical image showing the schlieren optical texture of the N phase of a 17 wt% solution of **1**. The samples were viewed between crossed polarisers at room temperature (colour version online).

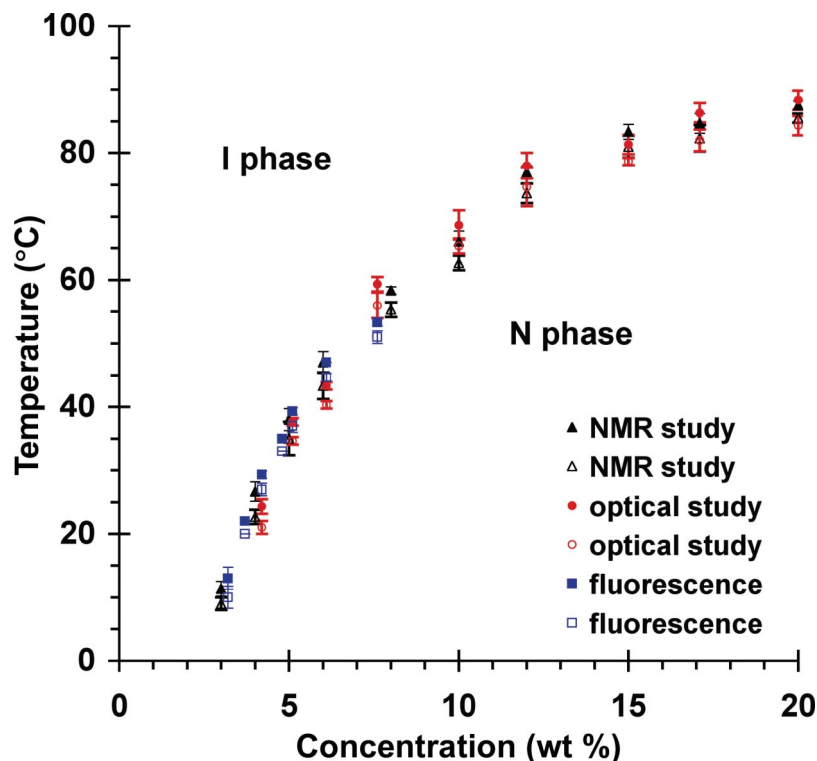


Figure 2. Phase diagrams showing the temperatures at which the I phase converts to the N+I two phase region and the N+I two phase region converts to the N phase at different concentrations of **1**. The transition temperatures, determined by ^2H nuclear magnetic resonance spectroscopy, for the I to N+I two phase region conversion and N+I two phase region to N phase conversion are shown in filled triangles and open triangles, respectively. The transition temperatures, determined by optical microscopy, for the I to N+I two phase region conversion and N+I two phase region to N phase conversion are shown by the filled circles and open circles, respectively. The transition temperatures, determined by fluorescence spectroscopy, for the I to N+I two phase region conversion and N+I two phase region to N phase conversion are shown by the filled squares and open squares, respectively (colour version online).

textures characteristic of an M phase were observed. This showed that, at room temperature, the M phase is not formed at a concentration of 20 wt% or less.

2.3 Determination of phase-transition temperature by POM, ^2H NMR and fluorescence spectroscopies

The effect of concentration on the phase-transition temperature of **1** was studied by POM. The temperatures for the N to N+I transition and N+I to I transition were recorded. The phase diagram is shown in Figure 2.

We further studied the effect of concentration on the phase-transition temperature of **1** by ^2H NMR spectroscopy. In an isotropic medium, the deuterium resonance appears as a single peak. In an anisotropic environment such as that in a liquid-crystalline phase, the quadrupole moment of ^2H interacts with the electric field gradients and causes the deuterium resonance to split into two peaks ($2I$ peaks, where the spin quantum number $I = 1$) as shown in Figure 3 [37]. By analysing the deuterium peaks of $^2\text{H}_2\text{O}$ using ^2H NMR spectroscopy, we determined the transition temperatures of the I to N+I and N+I to N transitions at different concentrations of **1** in $^2\text{H}_2\text{O}$.

As shown in Figure 2, the transition temperatures for the I to N+I two phase region conversion and the N+I to N phase conversion of a 4 wt% solution is close to room temperature. This result is consistent with that observed in the studies by POM. The phase-transition temperatures increase as the concentration of the sample increases. At a concentration of 15 wt%

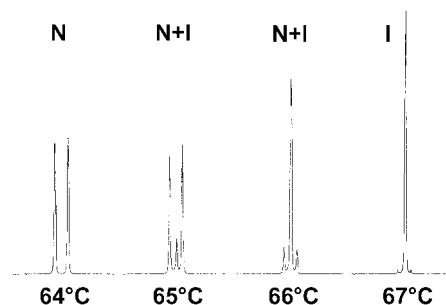


Figure 3. Offset ^2H nuclear magnetic resonance spectra of a solution of **1** (10.0 wt%) in $^2\text{H}_2\text{O}$. The spectra illustrate the presence of a doublet only in the N phase at 64°C, the presence of a singlet and a doublet in the N+I two phase region at 65 and 66°C, and the presence predominantly of a single peak in the isotropic phase at 67°C.

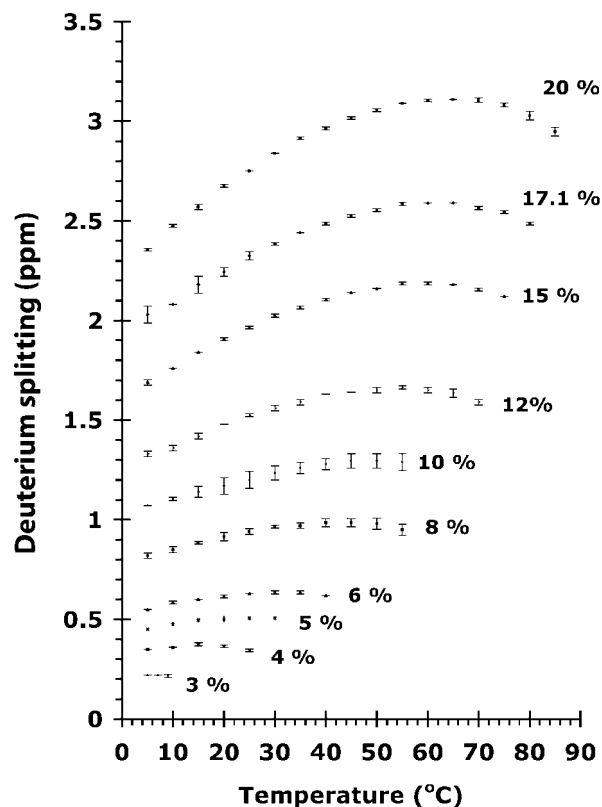


Figure 4. Temperature dependence of deuterium splitting for solutions at various concentrations of **1** in $^2\text{H}_2\text{O}$.

or higher, the sample can be heated to about 80°C before the liquid-crystalline order is disrupted to give an isotropic solution.

The effect of temperature and concentration on the magnitude of deuterium splitting of **1** in $^2\text{H}_2\text{O}$ is shown in Figure 4. The samples were heated to above the clearing temperature and then cooled to 5°C . At any given temperature, a larger splitting was observed when the concentration of **1** was increased. At a given concentration, and more notably at higher concentrations, the magnitude of deuterium splitting increased initially as the temperature was decreased from the clearing temperature and the N+I phase was gradually converted to the N phase. After reaching a maximum value, the magnitude of splitting decreased as the temperature of the N phase was lowered. There was no indication of transition from the N phase to M phase when the samples were cooled. This result is consistent with the studies by POM.

We found that fluorescence emission from samples in the liquid-crystalline phase can also be used for determining the temperature for transition from the N phase to isotropic solution. The λ_{max} of fluorescence emission of a 4.2 wt% solution (in the N phase) is about 700 nm, substantially red-shifted from the λ_{max}

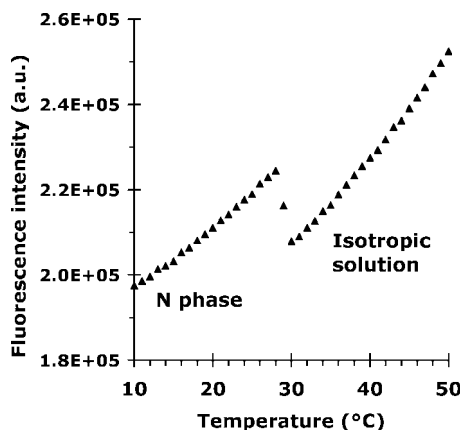


Figure 5. The effect of temperature and phase transition on fluorescence emission intensity (at 730 nm) of a 4.2 wt% solution of **1** in water. The sample was excited at 467 nm.

at 590 nm observed for dilute solutions. As shown in Figure 5, the emission intensity from a 4.2 wt% solution (in the N phase) at 10°C increases initially as the temperature increases. The increase in emission intensity can be attributed to a small decrease in the extent of interactions among the columns and aggregation of molecules within the columns at a higher temperature, consequently reducing the extent of self-quenching. The emission intensity drops substantially from 26 to 28°C , the same temperature range in which the sample transits from the N phase to an isotropic solution as determined by ^2H NMR spectroscopy. A plausible cause of the decrease in emission intensity is that a significant increase in collision quenching by water occurs as the order of the columns decreases dramatically during phase transition. During phase transition, the increase in collision quenching by water is more substantial than the decrease in the self-quenching of **1**, thereby, resulting in the net decrease in emission intensity. After the solution becomes isotropic at temperatures higher than 28°C , the emission intensity increases steadily with temperature again as the extent of aggregation of molecules within the columns decreases, and thus, there is less self-quenching.

In fact, the effect of temperature on the fluorescent properties of this compound is also observed in a very dilute isotropic solution of **1**. Unlike many fluorophores that show a decrease in emission at elevated temperature because of increased vibrational relaxation and collisional quenching, the emission of **1** (1.0×10^{-5} M) in water increases by about 13 times as the temperature increases from 10 to 80°C (Figure 6). At a low temperature, the aggregation of **1** in water results in significant self-quenching. The extent of aggregation decreases at a higher temperature, consequently reducing the extent of self-quenching.

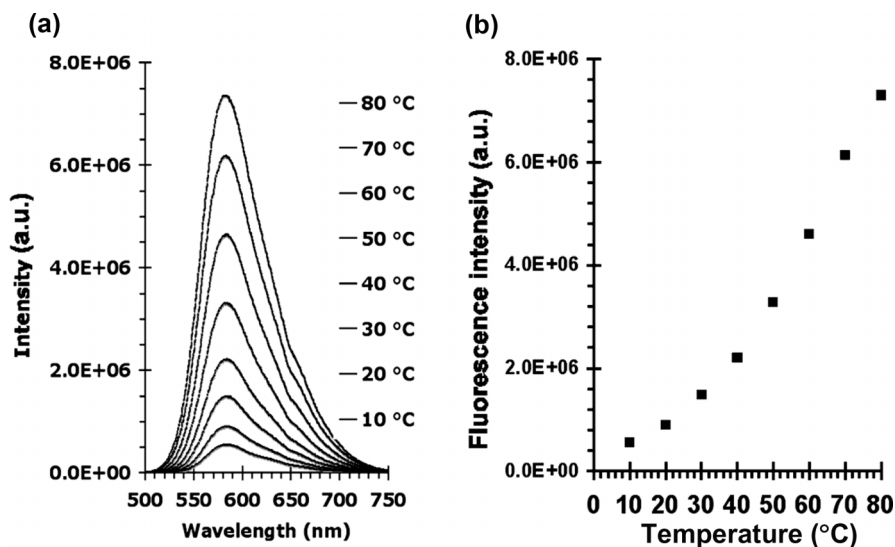


Figure 6. (a) Temperature-dependent fluorescence emission spectra of **1** (1.0×10^{-5} M) in water. Spectra were taken at increments of 10°C in temperature. Excitation spectra were acquired at an emission wavelength of 586 nm and the emission spectra were acquired at an excitation wavelength of 491 nm. (b) A plot showing the effect of temperature on fluorescent emission intensity at λ_{max} of emission.

Similar changes in emission intensity with temperature were observed for liquid-crystalline samples at other concentrations. As shown in Figure 2, the temperatures for the N to N+I phase transition and the N+I to I phase transition determined from the changes in fluorescence emission intensity are similar to the values determined by ^2H NMR spectroscopy. These results suggest that fluorescence spectroscopy is a useful technique for determining the N-I phase transition temperatures of **1**. An advantage of using the fluorescence technique is that only a small volume of sample is required for each study. In a typical experiment, $100 \mu\text{l}$ of solution is used for fluorescence studies compared with 1 ml of solution required for the standard probe of the NMR spectrometer. In addition, fluorescence experiments do not require the use of $^2\text{H}_2\text{O}$ as solvent. Limitations of this method are that it is only applicable to mesogens that fluoresce and it cannot be used for studying samples at very high concentrations because of significant reabsorption and self-quenching.

3. Experimental details

2-(*N,N*-Diethyl-*N*-methylammonium)ethylperylene-3,4-dicarboximide tosylate (**3**) was prepared and characterised as reported previously [37]. A total of 0.160 g (MW 606.73, 2.64 mmol) of **3** was dissolved in 60 ml of double distilled water at 60°C . A total of 30 g of anion exchange resin (Dowex 1X8, 100–200 mesh, a strongly basic, anion exchange resin) (J.T. Baker Chemical Co.,

Phillipsburg, NJ, USA) was packed into a 3-mm diameter glass column. Then the resin was washed with 5% KOH (aq) and double-distilled water. The red solution of **3** prepared above was poured into the anion exchange column and double-distilled water was used to elute the sample. A red solution was collected from the bottom of the column until the eluent was almost colourless. A total of 200 ml of red solution was collected and 4.6 ml of formic acid was added. After the solvent was removed by rotary evaporation, a total of 50 ml of a mixture of ether and acetone (v/v:70/30) was added to precipitate **1**. The solids were collected after filtration and air dried. A total of 0.107 g (MW 480.55, 2.23 mmol, 84% yield) of dark red solid of **1** was collected. ^1H NMR (500 MHz, deuterated dimethyl sulphoxide ($\text{DMSO-}D_6$)): δ = 8.48 (s, 1H, OOC-H), 8.44 (d, 2H, $^3J(\text{H,H}) = 7.5$ Hz, Ar-H), 8.40 (d, 2H, $^3J(\text{H,H}) = 8.0$ Hz, Ar-H), 8.21 (d, 2H, $^3J(\text{H,H}) = 8.0$ Hz, Ar-H), 7.93 (t, 2H, $^3J(\text{H,H}) = 8.5$ Hz, Ar-H), 7.57 (d, 2H, $^3J(\text{H,H}) = 8.5$ Hz, Ar-H), 4.30 (t, 2H, $^3J(\text{H,H}) = 8.0$ Hz, $\alpha\text{-CH}_2$), 3.46 (m, 4H, $-\text{N}(\text{CH}_2)_2-$), 3.36 (t, 2H, $^3J(\text{H,H}) = 8.0$ Hz, $-\text{CH}_2\text{-N}(\text{CH}_2)_2$), 3.04 (s, 3H, $-\text{N}(\text{CH}_3)$), 1.29 (t, 6H, $^3J(\text{H,H}) = 7.0$ Hz, $-\text{CH}_2\text{-CH}_3$) ppm; ^{13}C NMR (125 MHz, $\text{DMSO-}D_6$): δ = 164.9, 162.8, 136.7, 133.6, 131.2, 131.0, 130.9, 128.9, 128.0, 127.2, 126.7, 125.7, 124.6, 120.7, 119.6, 56.3, 55.0, 47.0, 33.0, 7.5 ppm; UV (MeOH, 1.0×10^{-5} M) $\lambda_{\text{max}} = 492$ nm ($\epsilon = 31560$); UV (water, 1.0×10^{-5} M) $\lambda_{\text{max}} = 490$ nm ($\epsilon = 19170$); IR (KBr): $\nu = 3576, 3033, 2981, 1687, 1644, 1592, 1572, 1497, 1366, 1293, 1245, 1171, 1056, 839 \text{ cm}^{-1}$.

DMSO-d₆ D-99.9% was purchased from Cambridge Isotopes Laboratories, Inc. (Andover, MA, USA). Solvents and reagents were used as purchased. ¹H and ¹³C NMR spectra were acquired on a Varian VT 500 MHz spectrometer. Infrared spectra were recorded on a Perkin-Elmer Spectrum 2000 FTIR spectrometer.

To study the liquid-crystalline properties, accurately weighed amounts of **1** were dissolved in double-distilled water to give solutions of the desired concentrations. The samples were mixed with a mixer (Eppendorf Thermomixer R, Brinkmann Instruments, Inc., Westbury, NY, USA) until all the solids were dissolved. About 2 μl of each sample was added to a glass slide and covered with a glass coverslip. The samples were viewed under a Nikon E600POL microscope equipped with crossed polarisers. Optical images of liquid crystals developed upon peripheral evaporation of solvent at room temperature were acquired using a Canon EOS 20D digital camera mounted on a trinocular head of the microscope with strain-free objectives. For the determination of phase-transition temperatures by POM, the samples were held between two glass coverslips and the edges were sealed to prevent evaporation of water. The sample temperature was controlled by a hot stage.

The NMR studies of the mesophases of **1** in ²H₂O were performed with a Varian Unity Plus 500 MHz NMR spectrometer. For all samples, the spinning axis of the sample tube was parallel to the direction of the magnetic field. The samples were shimmed on the lock deuterium channel, then the lock cable was removed and the observe cable was connected to the lock for observation of the ²H signal. The sweep width was 7500 Hz and only one transient was acquired per spectrum. The quadrupolar splitting was measured using the peak picking capabilities of the Varian software. For each sample, a spectrum of the liquid-crystalline sample was acquired at a temperature below the transition temperature to the isotropic phase. The temperature was then increased at an increment of 1°C and a spectrum was acquired at each temperature until the sample became an isotropic solution. The dwell time between temperature increments was 3 min.

Fluorescence spectra of a dilute solution of **1** (1.0 × 10⁻³ M) were acquired using a Jobin-Yvon Horiba Fluorolog 3-222 spectrophotometer and software FluorEssence. Fluorescence spectra were acquired in a 1-cm path-length cuvette. In temperature studies, the temperature of the cuvette holder was controlled using a temperature-controlled circulating water bath (Fisher Scientific model 9105, Pittsburgh, PA, USA).

The fluorescence emission spectra of mesophases of **1** were acquired using a 1-mm path length cuvette and an excitation wavelength of 467 nm. The

temperature of the cuvette holder was controlled using a peltier heating device with a temperature controller (LFI-3751, Wavelength Electronics, Inc., Bozeman, MT, USA). For each sample, the emission spectrum of the liquid-crystalline sample was acquired at a temperature below the transition temperature to the isotropic phase. The temperature was increased at an increment of 1°C and the dwell time between each temperature increment was 2 min.

4. Conclusions

This study showed that aqueous solutions of ionic perylene-3,4-dicarboximide **1** begin to form a chromonic N phase at concentrations of about 4 wt% at room temperature, and for samples of 15 wt% this mesophase is stable up to 80°C. We also demonstrated that fluorescence spectroscopy can be used to monitor phase transition of chromonic liquid crystals. To the best of our knowledge, this is the first report in the literature of the use of a fluorescence technique to yield phase-transition temperatures and the results are compatible with those from POM and ²H NMR spectroscopy.

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