

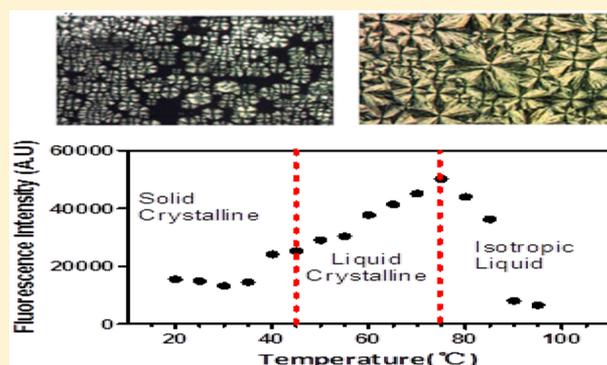
Spectral and Physicochemical Characterization of Dysprosium-Based Multifunctional Ionic Liquid Crystals

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S Supporting Information

ABSTRACT: We report on the synthesis and characterization of multifunctional ionic liquid crystals (melting points below 100 °C) which possess chirality and fluorescent behavior as well as mesomorphic and magnetic properties. In this regard, (1*R*,2*S*)-(-)-*N*-methylephedrine ((-)-MeEph), containing a chiral center, is linked with variable alkyl chain lengths (e.g., 14, 16, and 18 carbons) to yield liquid crystalline properties in the cations of these compounds. A complex counteranion consisting of trivalent dysprosium (Dy³⁺) and thiocyanate ligand (SCN⁻) is employed, where Dy³⁺ provides fluorescent and magnetic properties. Examination of differential scanning calorimetry (DSC) and hot-stage polarizing optical microscopy (POM) data confirmed liquid crystalline characteristics in these materials. We further report on phase transitions from solid to liquid crystal states, followed by isotropic liquid states with increasing temperature. These compounds exhibited two characteristic emission peaks in acetonitrile solution and the solid state when excited at $\lambda_{\text{ex}} = 366$ nm, which are attributed to transitions from ⁴F_{9/2} to ⁶H_{15/2} and ⁴F_{9/2} to ⁶H_{13/2}. The emission intensities of these compounds were found to be very sensitive to the phase.



INTRODUCTION

Ionic liquid crystals (ILCs) are a class of liquid-crystalline compounds that contain ions (anions and cations) and possess the collective characteristics of ionic liquids (ILs) as well as liquid crystals.¹ Thus, these compounds have the properties of ionic liquids, such as low volatility, nonflammability, high ionic conductivity, and large electrochemical windows, which differentiates them from conventional organic liquid crystals. Similarly, the basic properties of liquid crystals, e.g. as ordered molecular arrangement, make these ILCs highly structured solvents and birefringence. Because of their unique properties, ILCs have been investigated for multiple applications, including as electrolytes for solar cells,² anisotropic ion conductors,^{3–5} templating agents for the synthesis of inorganic nanostructures,⁶ and as organized reaction media.^{7–10}

Over the past few decades, intense research has been conducted to incorporate functional groups either into the anion or the cation of ILs in order to develop multifunctional materials.^{11–16} Multifunctional ILCs which integrate chiral, magnetic, and luminescence functionalities as well as inherent properties of ILCs into single ion pairs provide advantages that reach beyond the sum of the individual properties. Chirality is an important feature for functionalization of ILCs.¹⁷ Much effort has been concentrated into developing asymmetric synthesis and catalysis using chiral ionic liquids as solvents, and preliminary results suggest that chiral ionic liquids are promising reaction media for chiral discrimination.^{7–10} In addition, if chiral ionic liquids, which are used as solvents, show

thermotropic mesophases, they have the potential to offer increased selectivity for asymmetric synthesis and stereoselective polymerization due to their abilities to order reactants.^{18–21}

Several advantages of metal-containing ILCs have been widely explored as multifunctional materials due to a combination of the mesomorphic behavior and unique properties of metal ions redox activity, magnetism, and luminescence.^{22–26} Functional materials with optoelectronic characteristics can be developed by introducing lanthanide ions into ILCs.^{13,27} These metal containing ILCs provide distinct advantages of simple design and synthesis for π -conjugated molecular crystals. One application of these lanthanide ion containing ILCs is that polarized light can be produced to merge the luminescence characteristic of metal ions and the anisotropic feature of these compounds. By exploiting the high magnetic anisotropy of the lanthanide ion in ILCs, alignment of the mesophase in an external magnetic field can be achieved. Such compounds provide potential applications as electric and magnetic switchable device.¹³

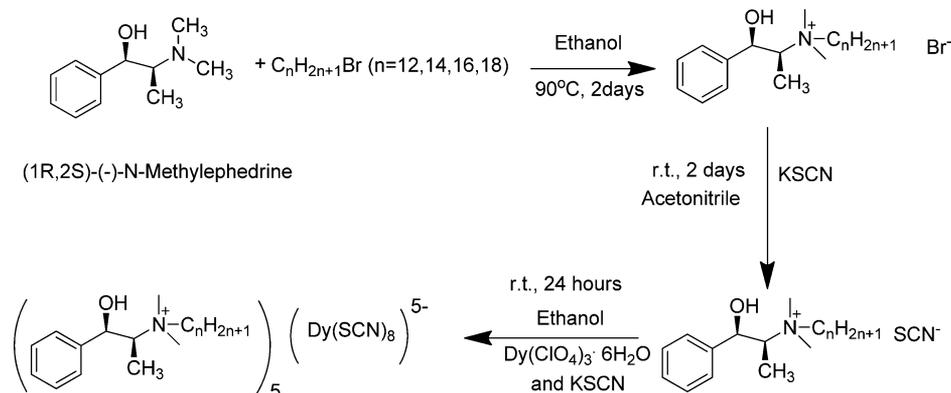
To the best of our knowledge, multifunctional ILCs that possess chirality, luminescence, paramagnetism, and mesophases in a single compound have not yet to be reported in the literature. The compound (1*R*,2*S*)-(-)-*N*-methylephedrine

Received: February 4, 2015

Revised: April 20, 2015

Published: April 22, 2015

Scheme 1. Synthesis of Multifunctional Ionic Liquid Crystals



[(-)-MeEph] is a natural chiral resource which is used as the starting material for syntheses of the multifunctional metal containing ILCs described herein. In this study, (-)-MeEph-dysprosium-based multifunctional ionic liquid crystals (MFILCs) consisting of chiral cations and metal-containing anions were synthesized and characterized. The thermal and photophysical properties of these compounds were also investigated in detail. Evaluation of the properties measured in this study suggests potential applications of these materials as organized reaction media and temperature sensors.

EXPERIMENTAL SECTION

Materials. The compounds (1R,2S)-(-)-N-methylephedrine, (1S,2R)-(+)-N-methylephedrine, 1-bromotetradecane, 1-bromohexadecane, 1-bromooctadecane, potassium thiocyanate, dysprosium(III) oxide, and perchloric acid (70%) were obtained from Sigma-Aldrich (Milwaukee, WI) and used without further purification. Ethanol, methanol, acetonitrile, chloroform, and dichloromethane were of anhydrous grade (Sigma-Aldrich, Milwaukee, WI), and all other solvents such as acetone, hexane, and water were of HPLC grade (J.T. Baker, Phillipsburg, NJ).

Material Synthesis. A facile three-step synthesis procedure was used to prepare (1R,2S)-(-)-N-methylephedrine-dysprosium-based MFILCs. In the first step, (1R,2S)-(-)-N-methylephedrine ((-)-MeEph) (1500 mg, 8.37 mmol) was dissolved in dry ethanol. A 1.1 mol equiv of 1-bromotetradecane or 1-bromohexadecane or 1-bromooctadecane as needed was dissolved separately in dry ethanol. The two solutions were mixed and the reaction mixture was refluxed for 2 days at 90 °C under an argon atmosphere. After cooling to room temperature, the majority of the solvent was removed by use of a rotary evaporator. Upon addition of the concentrated ethanol solution to cold diethyl ether, the product [(-)-MeEphC_nH_{2n+1}][Br] (*n* = 14, 16, 18) precipitated as a white powder. The product was then filtered, washed two times using diethyl ether, and then dried under vacuum. In the second step, three methylephedrin-dysprosium compounds were synthesized according to a previously described procedure. The compounds [(-)-MeEphC_nH_{2n+1}][Br] (*n* = 14, 16, 18) and 2 mol equiv of potassium thiocyanate (KSCN) were dissolved separately in dry acetonitrile. The two solutions were then mixed, and the reaction mixture was stirred for 2 days. The compound KBr, the reaction byproduct, formed as a white precipitate and was removed by filtration. Acetonitrile was removed by use of a rotary evaporator. To further purify the compounds produced, the resulting solid was redissolved in 30

mL of cold dichloromethane (DCM), and the solution was kept in a refrigerator for 24 h in order to precipitate the excess KSCN. After filtration of the excess KSCN, the solvent was evaporated and the product, [(-)-MeEphC_nH_{2n+1}][SCN] (*n* = 14, 16, 18), was dried under vacuum for 48 h. In the third step, Dy(ClO₄)₃·6H₂O was prepared by dissolving Dy₂O₃ in a 70% HClO₄ aqueous solution, with subsequent removal of water by use of lyophilization. A mixture of [(-)-MeEphC_nH_{2n+1}][SCN] (*n* = 14, 16, 18) (5 equiv), KSCN (3 equiv), and Dy(ClO₄)₃·6H₂O (1 equiv) was stirred in anhydrous ethanol at room temperature for 24 h. The byproduct (KClO₄) was removed by filtration, and the final products, [(-)-MeEphC_nH_{2n+1}]₅[Dy(SCN)₈] (*n* = 14, 16, 18), were purified and collected employing the method described above.

Instruments and Methods. The ¹H NMR (400 MHz) spectra were acquired by use of a Bruker Avance 400 NMR spectrometer. The ¹H chemical shifts are given in parts per million (δ) with TMS as an internal standard. Mass spectra were collected using an Agilent 6210 electrospray time-of-flight mass spectrometer using both positive and negative ion mode. FT-IR spectra were obtained by use of a Bruker Alpha FT-IR spectrometer. Samples were analyzed in pure form using a Platinum ATR apparatus. Elemental analyses were contracted to Atlantic Microlab (Atlanta, GA). Luminescence spectra were recorded at temperatures ranging from 25 to 100 °C using a Spex Fluorolog-3 spectrofluorometer (model FL3-22TAU3; Jobin Yvon, Edison, NJ) equipped with a 450 W xenon lamp and R928P photomultiplier tube (PMT) emission detector. All CD measurements were obtained by analyzing 1 mM methanolic solutions at room temperature in 4 mm quartz cuvettes on a Jasco-815 CD spectrometer. Magnetic properties were measured using approximately 80–100 mg of sample in a Quantum Design Superconducting Quantum Interference Device (SQUID) magnetometer (San Diego, CA) at temperatures between 2 and 300 K and magnetic fields between -70 000 and 70 000 Oe. Thermal properties of MFILCs were investigated using a DSC Q 100 differential calorimeter (TA Instruments, USA) by cooling 5–10 mg of MFILCs to -20 °C and subsequently heating at a rate of 5 °C/min to 150 °C. Polarized optical microscopy (POM) was performed using an Olympus BH polarizing optical microscope with a hot stage and MD 1900 camera. Samples for POM were prepared by redissolving the MFILCs in DCM and ethanol and coating the solution on the surface of glass slides using spin-coating. Images were acquired at temperatures ranging from 25 to 100 °C. The samples were incubated for 30 min to allow the mesophase to equilibrate before acquiring images.

RESULTS AND DISCUSSION

Synthesis of Multifunctional Ionic Liquid Crystals.

(1*R*,2*S*)-(-)-Methylephedrine ((-)-MeEph) were alkylated

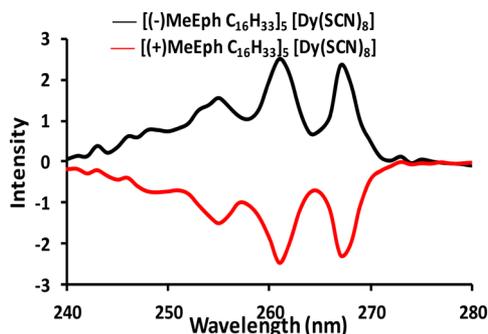


Figure 1. Circular dichroism spectra of [(-)-MeEph C₁₆H₃₃]₅ [Dy(SCN)₈] (black) and [(+)-MeEph C₁₆H₃₃]₅ [Dy(SCN)₈] (red) in ethanol.

using *n*-alkyl bromides containing 14, 16, and 18 carbons to obtain cations with chiral centers. The metal containing MFILCs were obtained via an anion exchange reaction, followed by an addition reaction with the above (-)-MeEph-based salts. In the first anion exchange, the reaction was performed to replace the Br⁻ ion with the SCN⁻ ion. A second step involved addition of the metal and formation of a SCN⁻ anion complex, resulting in a dysprosium–thiocyanate complex anion. Synthesis of the MFILCs is outlined in Scheme 1.

Chiroptical Activity of Multifunctional Ionic Liquid Crystals. Ephedrine possesses two chiral centers which give rise to four stereoisomers.^{9,28} The enantiomers with opposite stereochemistry around the chiral centers (1*R*,2*S*-(-) and 1*S*,2*R*-(+)) are named ephedrine, while the enantiomers with the same stereochemistry around the chiral carbons (1*R*,2*R* and 1*S*,2*S*) are designated pseudoephedrine. In this study, only (1*R*,2*S*)-(-)-methylephedrine was used for structural modification and production of MFILCs used in this study. To investigate the chiral properties of MFILCs, the enantiomer of [(-)-MeEph C₁₆H₃₃]₅ [Dy(SCN)₈] and [(+)-MeEph C₁₆H₃₃]₅ [Dy(SCN)₈] were synthesized to perform circular dichroism studies using (1*R*,2*S*)-(-)-methylephedrine and (1*S*,2*R*)-(+)-methylephedrine as starting materials. The same protocol as described earlier for [(-)-MeEph C₁₆H₃₃]₅ [Dy(SCN)₈] was used for synthesis of [(+)-MeEph C₁₆H₃₃]₅ [Dy(SCN)₈]. The

CD spectra of [(-)-MeEph C₁₆H₃₃]₅ [Dy(SCN)₈], and [(+)-MeEph C₁₆H₃₃]₅ [Dy(SCN)₈] are presented in Figure 1. Three bands were observed at 255, 261, and 267 nm for both compounds, while positive and negative signals were represented by [(-)-MeEph C₁₆H₃₃]₅ [Dy(SCN)₈] and [(+)-MeEph C₁₆H₃₃]₅ [Dy(SCN)₈], respectively. Evaluation of these results demonstrates that the MFILCs isomers retain chiroptical properties and exhibit an extremely precise mirror image relationship after structural modification.

Luminescence Spectroscopy of Multifunctional Ionic Liquid Crystals. The emission spectra of these MFILCs were recorded at an excitation wavelength of 366 nm both in the solid state and in acetonitrile solution. Solid samples were prepared by spin-coating (3000 rpm) an ethanolic solution of MFILCs onto glass slides and then allowed to dry under vacuum overnight. Trivalent dysprosium, Dy³⁺, with a 4*f*⁹ electron configuration, has been found to be fluorescent in the blue and yellow-orange regions of the electromagnetic spectrum due to respective 4*F*_{9/2} to 6*H*_{15/2} and 4*F*_{9/2} to 6*H*_{13/2} transitions.¹³ As depicted in Figure 2, two characteristic emission peaks were observed in both solution and solid states for all three MFILCs of variable alkyl chain length. The intensity and relative intensities of these two emission peaks, however, are quite different in solution and in solid states. This suggests that transitions are hypersensitive to the environment. The relative orders of emission intensity for these MFILCs in acetonitrile solution were [(-)-MeEph C₁₄H₂₉]₅ [Dy(SCN)₈] > [(-)-MeEph C₁₆H₃₃]₅ [Dy(SCN)₈] > [(-)-MeEph C₁₈H₃₇]₅ [Dy(SCN)₈]. In contrast, the emission intensity of the MFILCs films showed a reverse order. The transition 4*F*_{9/2} to 6*H*_{13/2} at 573 nm is the most intense peak for all compounds in acetonitrile, which is in agreement with previous studies.¹⁵ It is well established that the 4*f*–4*f* transitions are parity forbidden. The excitation of Dy (III) at 366 nm is due to the existence of (-)-MeEph-based cation which serves as an antenna for energy transfer to Dy³⁺.¹⁵ The forbidden 4*f*–4*f* transitions also result in long-lived excited states and consequently a reduction in photobleaching.

Magnetic Properties of Multifunctional Ionic Liquid Crystals. In addition to luminescence arising from the 4*f*⁹ electron configuration, the Dy³⁺ ion is also magnetically active. As a result, the MFILCs exhibited paramagnetic behavior at room temperature. These magnetic susceptibilities were measured by use of a superconducting quantum interference device (SQUID) magnetometer. The magnetic property of

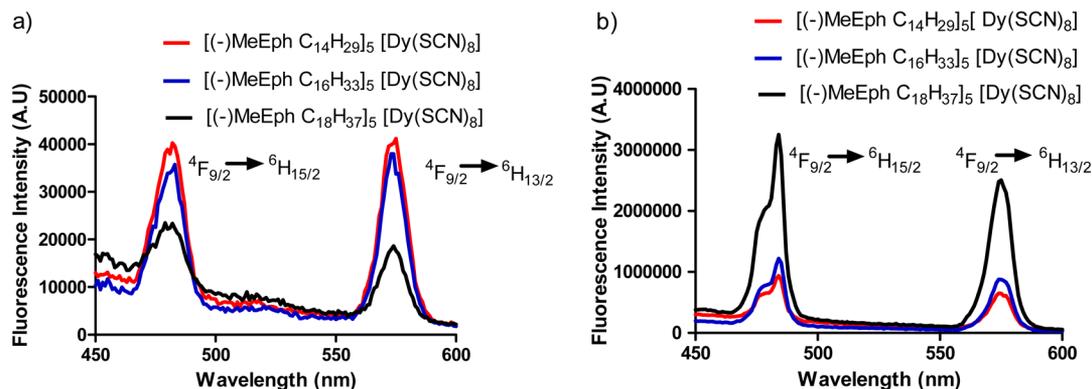


Figure 2. Emission spectra with transition assignments of [(-)-MeEph C₁₄H₂₉]₅ [Dy(SCN)₈] (red), [(-)-MeEph C₁₆H₃₃]₅ [Dy(SCN)₈] (blue), and [(-)-MeEph C₁₈H₃₇]₅ [Dy(SCN)₈] (black) in acetonitrile solution (a) and at solid state (b) under excitation at $\lambda_{\text{ex}} = 366$ nm.

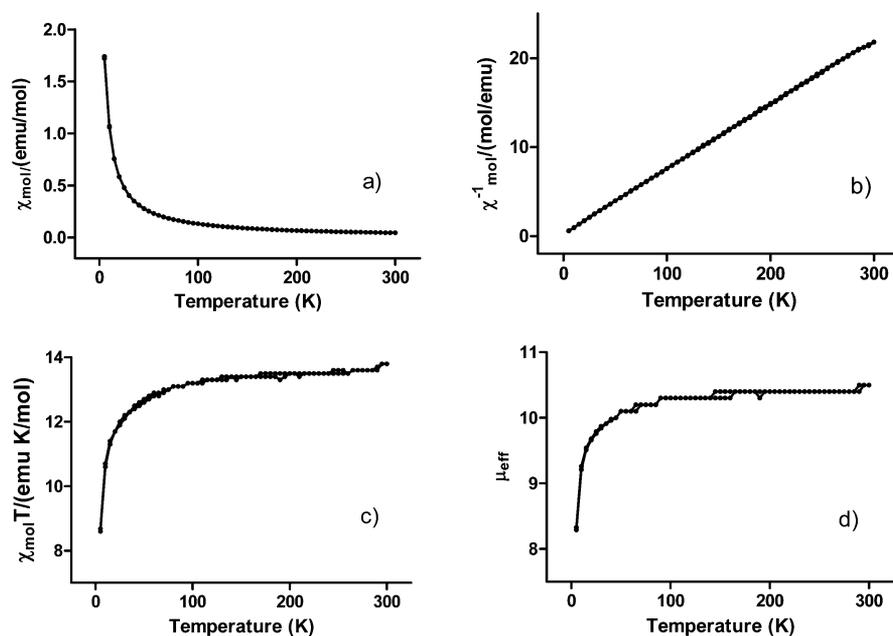


Figure 3. Magnetic property of $[(-)\text{MeEphC}_{16}\text{H}_{33}]_5[\text{Dy}(\text{SCN})_8]$. Temperature dependence of the static molar susceptibility (a) and reciprocal molar susceptibility (b) at a field of 10 000 Oe. Temperature dependence of the product of the temperature and the static molar susceptibility (c) and the effective magnetic moment (d) at a field of 10 000 Oe.

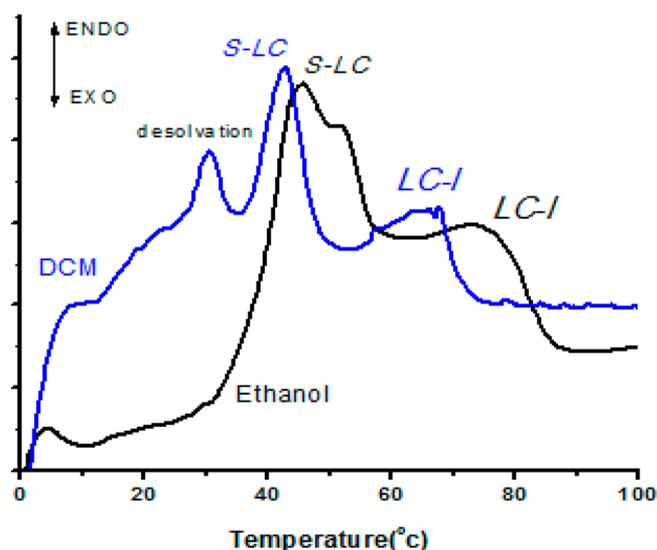


Figure 4. DSC traces observed on heating of $[(-)\text{MeEphC}_{16}\text{H}_{33}]_5[\text{Dy}(\text{SCN})_8]$ prepared with DCM (in blue) and ethanol (in black) (closed aluminum pan, heating rate $5\text{ }^\circ\text{C}/\text{min}$; S-LC: solid to liquid crystalline transition; LC-I: liquid crystalline to isotropic liquid transition).

$[(-)\text{MeEphC}_{16}\text{H}_{33}]_5[\text{Dy}(\text{SCN})_8]$ is summarized in Figure 3. Examination of Figure 3 clearly shows a decrease in static molar magnetic susceptibility with increasing temperature in a plot of χ_{mol} against temperature (K). This observation suggests that $[(-)\text{MeEphC}_{16}\text{H}_{33}]_5[\text{Dy}(\text{SCN})_8]$ is paramagnetic (Figure 3a). The respective molar magnetic susceptibilities of $[(-)\text{MeEphC}_{16}\text{H}_{33}]_5[\text{Dy}(\text{SCN})_8]$ and $[(-)\text{MeEphC}_{18}\text{H}_{37}]_5[\text{Dy}(\text{SCN})_8]$ at 300 K were obtained as $\chi_{\text{mol}} = 0.046$ and $0.044\text{ emu mol}^{-1}$, all of which fit well with the expected value for Dy^{3+} .²⁹ The effective magnetic moment (μ_{eff}) for Dy^{3+} has been calculated as $10.48\ \mu_{\text{B}}$. The measured respective μ_{eff} values of $[(-)\text{MeEphC}_{16}\text{H}_{33}]_5[\text{Dy}(\text{SCN})_8]$ and $[(-)\text{MeEphC}_{18}\text{H}_{37}]_5[\text{Dy}(\text{SCN})_8]$

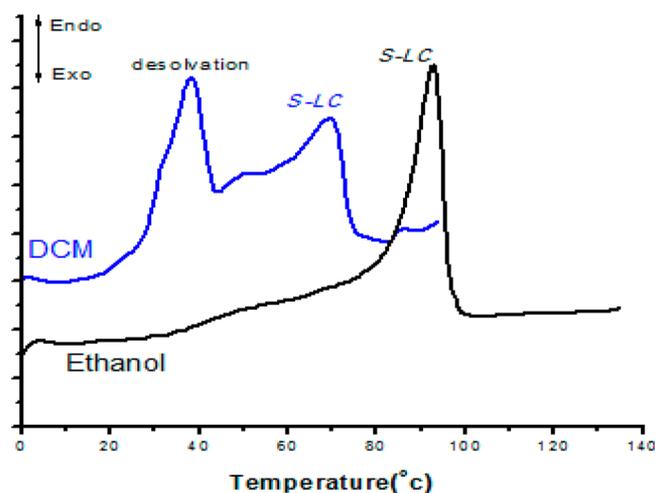


Figure 5. DSC traces observed on heating of $[(-)\text{MeEphC}_{18}\text{H}_{37}]_5[\text{Dy}(\text{SCN})_8]$ prepared with DCM (in blue) and ethanol (in black) (closed aluminum pan, heating rate $5\text{ }^\circ\text{C}/\text{min}$; S-LC: solid to liquid crystalline transition; LC-I: liquid crystalline to isotropic liquid transition).

were 10.5 and $10.3\ \mu_{\text{B}}$, which are very close to the calculated value.²⁹ Because of the large anisotropic magnetic moment of Dy^{3+} in ionic liquid crystals, these MFILCs can be manipulated in an external magnetic field. Therefore, these MFILCs are expected to align in the direction of an applied external magnetic field. Paramagnetic properties of $[(-)\text{MeEphC}_{18}\text{H}_{37}]_5[\text{Dy}(\text{SCN})_8]$ are listed in the Supporting Information.

Thermal Properties of Multifunctional Ionic Liquid Crystals. Thermal properties of all compounds were examined using differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). Two different solvents, i.e. dichloromethane (DCM) and ethanol, were independently used to recrystallize MFILCs. The MFILCs were dissolved in a solvent, followed by drying in a vacuum desiccator prior to

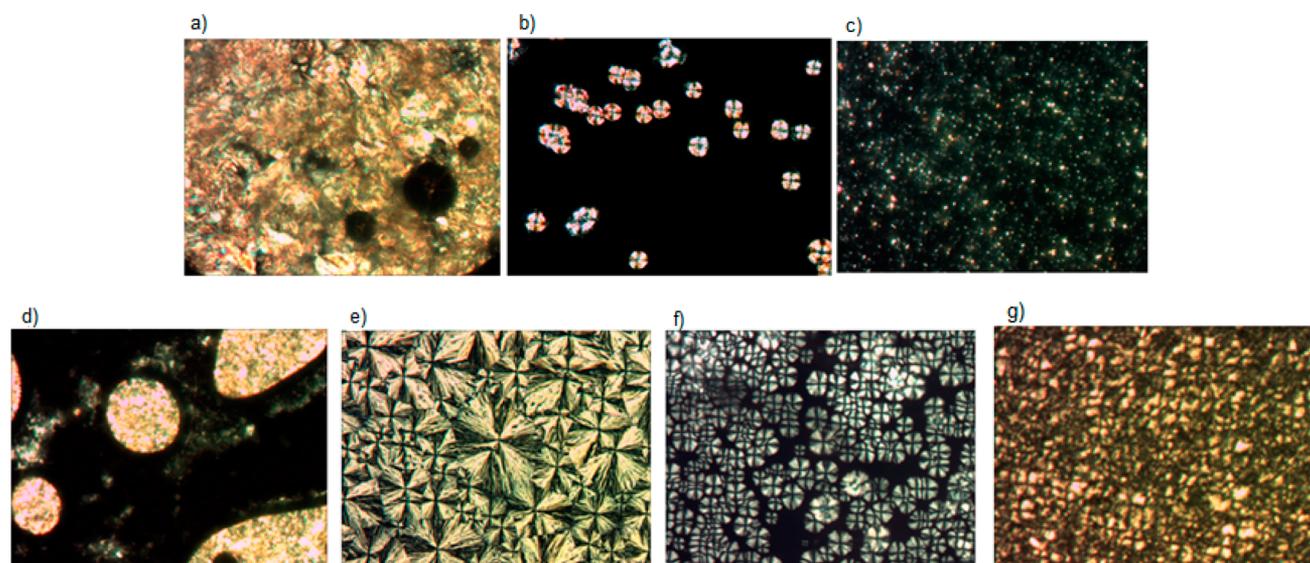


Figure 6. Micrographs of the textures observed by POM (200 \times magnification). Textures of $[(-)\text{MeEphC}_{16}\text{H}_{33}]_5 [\text{Dy}(\text{SCN})_8]$ ethanol sample at 70 $^{\circ}\text{C}$ (a) and DCM sample at 60 $^{\circ}\text{C}$ (b), second heating at 75 $^{\circ}\text{C}$ (c); $[(-)\text{MeEphC}_{18}\text{H}_{37}]_5 [\text{Dy}(\text{SCN})_8]$ ethanol sample at 95 $^{\circ}\text{C}$ (d) and DCM sample at 85 $^{\circ}\text{C}$ (e), second heating at 70 $^{\circ}\text{C}$ (f), and second heating at 90 $^{\circ}\text{C}$ (g).

analyses (for convenience, we called these samples DCM sample or ethanol sample). Interestingly, we observed that the thermal properties of these compounds are impacted by the solvent used for recrystallization. The thermal properties of $[(-)\text{MeEphC}_{14}\text{H}_{29}]_5 [\text{Dy}(\text{SCN})_8]$ will not be discussed since it did not exhibit a mesophase upon heating, likely due its short alkyl chain. The DSC thermograms of $[(-)\text{MeEphC}_{18}\text{H}_{37}]_5 [\text{Dy}(\text{SCN})_8]$ and $[(-)\text{MeEphC}_{16}\text{H}_{33}]_5 [\text{Dy}(\text{SCN})_8]$ are respectively shown in Figures 4 and 5. Only the first DSC heating traces are displayed since the phase transition could not be detected by use of DSC in the cooling trace and second scan. In the DCM samples for both $[(-)\text{MeEphC}_{18}\text{H}_{37}]_5 [\text{Dy}(\text{SCN})_8]$ and $[(-)\text{MeEphC}_{16}\text{H}_{33}]_5 [\text{Dy}(\text{SCN})_8]$, an additional peak was observed prior to the solid-to-mesophase transition peak. This additional peak is likely due to desolvation of trace DCM that remains in the compounds. The $[(-)\text{MeEphC}_{16}\text{H}_{33}]_5 [\text{Dy}(\text{SCN})_8]$ DCM sample displayed a mesophase range from 41.9 to 66.9 $^{\circ}\text{C}$, while the ethanol sample displayed a mesophase range from 44.1 to 74.9 $^{\circ}\text{C}$. The $[(-)\text{MeEphC}_{18}\text{H}_{37}]_5 [\text{Dy}(\text{SCN})_8]$ DCM sample showed a much lower crystalline solid to liquid crystalline transition temperature than that of the ethanol sample. The transition of liquid crystalline to isotropic liquid for the DCM sample was observed at 85.6 $^{\circ}\text{C}$. However, the phase transition of the ethanol sample could not be detected by use of DSC.

A POM investigation was performed in order to examine alterations of anisotropic behavior upon heating of $[(-)\text{MeEphC}_{18}\text{H}_{37}]_5 [\text{Dy}(\text{SCN})_8]$ and $[(-)\text{MeEphC}_{16}\text{H}_{33}]_5 [\text{Dy}(\text{SCN})_8]$. Microscopy images of the textures of these compounds are shown in Figure 6. For both compounds, the ethanol samples exhibited a nematic phase, while the DCM samples displayed a typical fan-shaped texture of an SmA phase. Examination of POM data for $[(-)\text{MeEphC}_{16}\text{H}_{33}]_5 [\text{Dy}(\text{SCN})_8]$ confirmed that the optical data agreed well with DSC data. In addition to confirming the DSC studies, POM examination also provided further information which could not be detected by use of DSC. A POM investigation of $[(-)\text{MeEphC}_{18}\text{H}_{37}]_5 [\text{Dy}(\text{SCN})_8]$ indicated that the liquid crystalline to isotropic liquid transition occurs at 98 $^{\circ}\text{C}$, regardless of the recrystalline

method. Furthermore, although no thermal events were observed during the cooling and second heating process by use of DSC, the POM investigations revealed mesophases during the second heating for these MFILCs (Figure 6).

Phase-Dependent Luminescence Intensity of Multifunctional Ionic Liquid Crystals. In order to investigate the influence of phase transitions on luminescence, two emission transitions (${}^4\text{F}_{9/2}$ to ${}^6\text{H}_{15/2}$ and from ${}^4\text{F}_{9/2}$ to ${}^6\text{H}_{13/2}$) were recorded over a wide range of temperatures (20–100 $^{\circ}\text{C}$). Figure 7 shows changes in ${}^4\text{F}_{9/2}$ to ${}^6\text{H}_{15/2}$ emission intensities of $[(-)\text{MeEphC}_{16}\text{H}_{33}]_5 [\text{Dy}(\text{SCN})_8]$ and $[(-)\text{MeEphC}_{18}\text{H}_{37}]_5 [\text{Dy}(\text{SCN})_8]$ as a function of temperature. Based on DSC studies and optical data, the temperature-dependent luminescence intensity changes were divided into three regions: (i) solid crystalline state, (ii) liquid crystalline state, and (iii) isotropic liquid state. All samples exhibited enhanced luminescence intensity upon second heating in the liquid crystalline state except $[(-)\text{MeEphC}_{16}\text{H}_{33}]_5 [\text{Dy}(\text{SCN})_8]$. It was observed that $[(-)\text{MeEphC}_{16}\text{H}_{33}]_5 [\text{Dy}(\text{SCN})_8]$ and $[(-)\text{MeEphC}_{18}\text{H}_{37}]_5 [\text{Dy}(\text{SCN})_8]$ DCM samples showed a sharp decrease in luminescence intensity in the solid state with increasing temperature due to the presence of trace DCM remaining in samples, as previously noted. In the liquid crystalline state, the luminescence intensity displayed a linear increase with increasing temperature until a full liquid crystal state was achieved. Interestingly, $[(-)\text{MeEphC}_{18}\text{H}_{37}]_5 [\text{Dy}(\text{SCN})_8]$ exhibited two luminescence intensity increases in the liquid crystalline state during the second heating. This was because the sample first formed fan-shaped SmA phase and then formed a nematic phase with increasing temperature. As the temperature increased, a dramatic decrease in luminescence intensity was observed at the liquid crystalline to isotropic liquid transition. Typically, these MFILCs in isotropic liquid state are nonfluorescent; this may be due to a hindrance of energy transfer as a result of increased distance between the cations and the anions in the liquid state. Because of a specific linear response range with temperature and dramatically enhanced luminescence intensity in the liquid crystalline state, we believe that these MFILCs are potential candidates

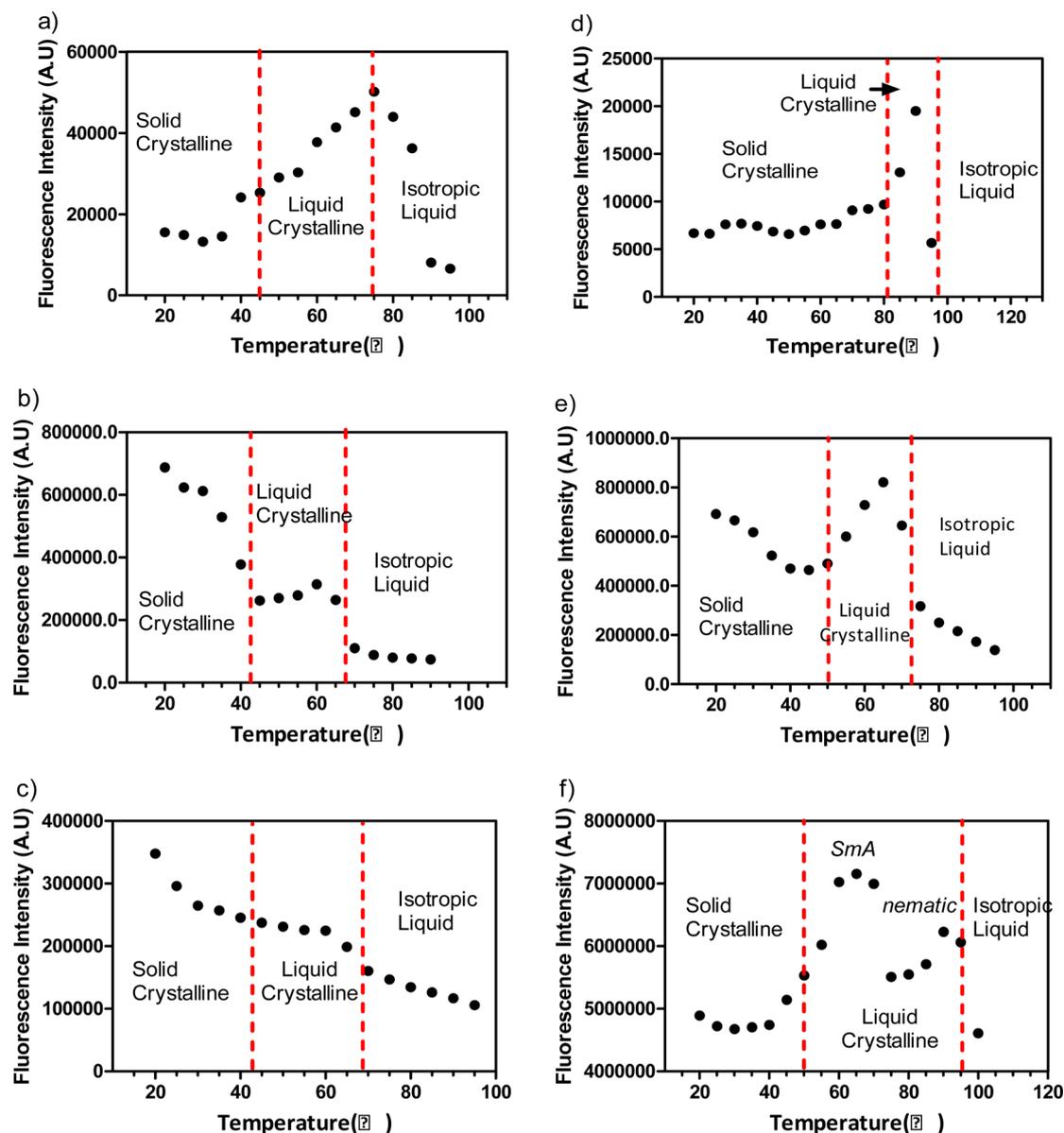


Figure 7. Temperature-dependent luminescence intensity from ${}^4\text{F}_{9/2}$ to ${}^6\text{H}_{15/2}$ transition (blue light emission, excitation at 366 nm) of $[(-)\text{EphC}_{16}\text{H}_{33}]_5 [\text{Dy}(\text{SCN})_8]$ ethanol sample (a); DCM sample (b); second heating (c); as well as of $[(-)\text{EphC}_{18}\text{H}_{37}]_5 [\text{Dy}(\text{SCN})_8]$ ethanol sample (d); DCM sample (e) and second heating (f).

for use in construction of sensitive chemosensors or optoelectronic devices.

CONCLUSIONS

We have synthesized and characterized a group of novel MFILCs which incorporate luminescence, chirality, paramagnetism, and mesophase into a single ion pair. These MFILCs retain the chirality of the starting material and may be used as reaction media for synthesis of chiroptically active compounds in combination with liquid crystalline and magnetic properties. These compounds show structure and solvent dependent liquid crystalline mesophases below 100 °C and in turn show phase-dependent luminescence intensities. Appending longer alkyl chains lead to easier formation of mesophase textures but reduce the mesophase window. Use of DCM for recrystallization of these compounds results in SmA mesophase, while the use of ethanol induces nematic mesophases. Both compounds exhibit enhanced luminescence intensity in the

liquid crystalline state and dramatically decreased luminescence in the isotropic liquid state. Based on these unique properties, these compounds or similar compounds can be potentially useful for preparation of optical devices.

ASSOCIATED CONTENT

Supporting Information

Characterization results; more optical and magnetic properties of multifunctional ionic liquid crystals. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.5b01180.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation under Grant CHE-1307611.

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