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Fluorinated Tolane-Based Photoluminescence Liquid Crystals with Both Photoluminescence and Room-Temperature Smectic Liquid-Crystalline Properties

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ABSTRACT

In this study, we observed different photoluminescence (PL) behaviors and the formation of enantiotropic smectic A (SmA) phases in the crystalline (Cr) phase for fluorinated tolane derivatives with imidazolium salts at the end of the decyleneoxy flexible chains. Notably, the derivatives with large counteranion formed the SmA phase in the room temperature region, and the PL behaviors were found to significantly change via phase transition between Cr and SmA phases.

1 Introduction

The smectic A (SmA) phase, in which molecules are arranged in layers perpendicular to the layer normal, combines both fluidity and molecular order. Its layered structure undergoes significant changes during phase transitions, making it an attractive smart material for temperature-responsive sensors, field-effect transistors [1], actuators [2], and other advanced devices. However, the practical use of an organic material exhibiting SmA phase is limited if the phase only appears at high temperature region. In contrast, numerous materials are known to exhibit a nematic phase at room temperature. One typical example is 4-cyano-4'-pentylbiphenyl (5CB) [3], a fundamental molecular material widely used in liquid-crystalline (LC) displays. On the other hand, 4-cyano-4'-octylbiphenyl (8CB), which has a longer alkyl chain, is known to form a SmA phase at room temperature. However, the number of known LC materials that exhibit SmA phase at room temperature is still relatively limited compared to room-temperature nematic LCs [4].

Our group has been actively developing solid-state photoluminescent molecules and has demonstrated that partial fluorination of linearly extended π-conjugated bistolane [5,6] and tolane derivatives [7,8] yields excellent solid-state luminescence at room temperature. Since bistolane and tolane frameworks also serve as effective mesogenic cores for LC materials, we have developed photoluminescent liquid crystals (PLLCs) using these structures as fluorescent mesogens. Although we introduced flexible chains of varying lengths, the fluorinated bistolane derivatives were not suitable for practical applications due to their high crystallinity and elevated melting temperatures [7,8]. In contrast, the fluorinated tolanes exhibited reduced mesogenic rigidity, leading to a significant lowering of the melting temperature [9]. Recent investigations into the flexible chain structures revealed that incorporating imidazolium salt units at the end of the chains further decreased the melting temperature [10]. Depending on the type of conteranion, some of these materials also exhibited LC behavior at room temperature. Here presents the synthesis and evaluation of their PL and LC properties. Some of the results presented in this paper have been reorganized and revised from content previously published in the *Journal of Molecular Liquids* (Elsevier) [10].

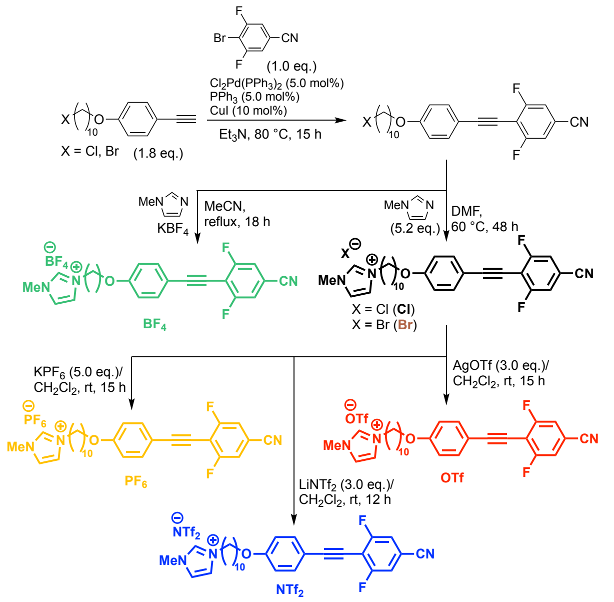
2 Experimental

Melting temperature was measured by polarized optical microscropy using a BX-53 microscope (Olympus) or by differential scanning calorimetry (DSC) using a DSC-60 Plus instrument (Shimadzu). ^{1}H, ^{13}C, and ^{19}F nuclear magnetic resonance (NMR) spectroscopy experiments were performed using an AVANCE III 400 NMR spectrometer with $CDCl_3$ (^{1}H: 400 MHz; ^{13}C: 100 MHz; ^{19}F: 376 MHz). Infrared (IR) spectroscopy was performed using the KBr method and an FT/IR-4100 type A spectrometer (JASCO), with wavenumber-based spectra being acquired. High-resolution mass spectrometry (HRMS) was conducted using a JMS-700MS spectrometer (JEOL) and the fast atom bombardment (FAB) method. Elemental analysis was performed using a CHN Corder MT-5 device (Yanaco).

All reaction were conducted using dried glassware with magnetic stirrer bars in an argon atmosphere. Column chromatography was performed using silica gel (Wakogel® 60N, 38–100 μm), and thin-layer chromatography (TLC) was conducted using slica gel TLC plates (silica gel 60F_{254}).

3 Results and discussion

The target compounds, fluorinated tolane derivatives with different counteranions (**Cl**, **Br**, **BF_4**, **PF_6**, **OTf**, and **NTf_2**), were synthesized according to Scheme 1.



Scheme 1. Synthetic procedures for target compounds.

Treatment of the readily prepared 4-(10-chlorodecyloxy)phenylacetylene or its bromide analog with 4-bromo-3,5-difluorobenzonitrile in the presence of a palladium catalyst smoothly afforded the corresponding Sonogashira coupling product. Subsequent treatment with *N*-methylimidazole successfully afforded the target compounds, **Cl** and **Br**. When *N*-methylimidazole was applied in the presence of KBF_4, both the S_N2 substitution and anion exchange occurred in a single step, yielding the corresponding target compound **BF_4**. Furthermore, when the Cl or Br precursors were treated with KPF_6, AgOTf, or $LiNTf_2$, smooth anion exchange reactions occurred to afford the corresponding **PF_6**, **OTf**, and **NTf_2**, respectively.

The photoluminescence (PL) behavior of six compounds, viz., **Cl**, **Br**, **BF_4**, **PF_6**, **OTf**, and **NTf_2**, with various conteranions synthesized as described above was investigated. In dilute dichloromethane solution (1.0×10^{-6} mol L^{-1}), the PL spectra showed little change across the different conteranions. The PL wavelengths (λ_{PL}) ranged from 410 to 415 nm, and all compounds exhibited dark blue fluorescence with chromaticity coordinates around (0.156, 0.054) (Fig. 1a).

The PL quantum yields (Φ_{PL}) of the six compounds in solution ranged from 0.21 to 0.24. It is known that non-substituted tolane does not fluoresce at room temperature due to internal conversion from the linear ππ* excited states to the forbidden πσ* excited state, which adopts a *trans*-bend geometry after photoexcitation [11]. The Φ_{PL} values observed for the six compounds are comparable to previously reported enhancements achieved by designing donor-acceptor structures, where electron-donating (EDG) and electron-withdrawing (EWG) groups are introduced along the longitudinal molecular axis [12].

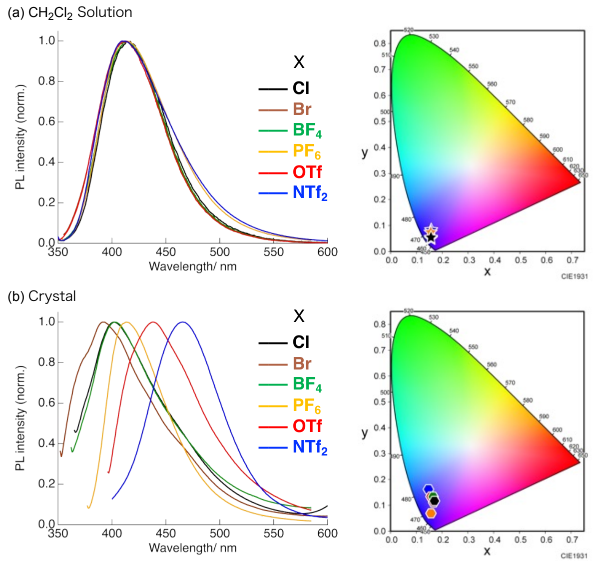


Fig. 1 PL spectra and chromaticity diagram for six target compounds (a) in dichloromethane solution and (b) in crystalline states.

Subsequently, unlike in solution, the PL properties of the six compounds in the crystalline state exhibited varied PL spectra depending on the counteranions. The PL color ranged from dark blue (CIE coordinate: 0.157, 0.069) to blue (CIE coordinate: 0.147, 0.162) (Fig. 1b). This result suggests that the counteranions significantly influence the crystal packing structure and that the nature of the intermolecular interactions changes with the size of the counteranion. In a previous study, we found that partial fluorination of the tolane skeleton suppressed non-radiative deactivation and enhanced Φ_{PL} due to the formation of intermolecular H/F hydrogen bonds [7]. Among the ionic compounds synthesized in this study, the **PF_6** exhibited the highest Φ_{PL} (0.42), representing a substantial increase compared to the solution state. In contrast, the other derivatives showed a significant decrease in Φ_{PL}, to around 0.05. Although we have not yet identified a clear reason for the dramatic changes in Φ_{PL} with different counteranions, one possible explanation is that variation in the size of the counteranions affect the strength of intermolecular interactions. We also speculate that the pronounced decrease in Φ_{PL} observed for salts with smaller counteranions may be due to dominant ion-ion electrostatic interactions during crystallization, which suppress the formation of intermolecular hydrogen bonds between mesogenic units [13].

Next, the phase transition behavior of six target compounds was investigated using polarized optical microscopy (POM) and differential scanning calorimetry (DSC) to determine the phase transition temperatures and the types of phases present, as shown in Fig. 2.

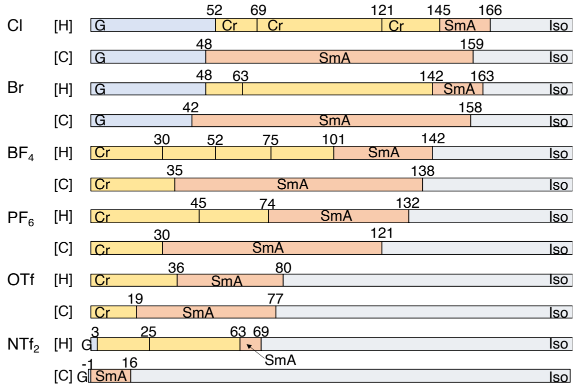


Fig. 2 Phase sequence and transition temperature of six compounds, obtained by DSC (scan rate: 5 °C min^{-1}, N_2 atmosphere).

All derivatives exhibited enantiotropic LC behavior, forming mesophases on both heating and cooling processes. During heating, the melting and clearing temperatures decreased progressively in the order **Cl** > **Br** > **BF_4** > **PF_6** > **OTf**, whereas for **NTf_2** only the clearing temperature followed this trend. These trends correlate strongly with the counteranion size; we attribute them to increasing destabilization of both the crystal lattice and the mesophase as the anion becomes larger [14].

As shown in Fig. 3, the optical microstructures of the mesophases exhibited clearly defined fan-shaped textures, indicating the presence of smectic (Sm) phases with a layered aggregated structure.

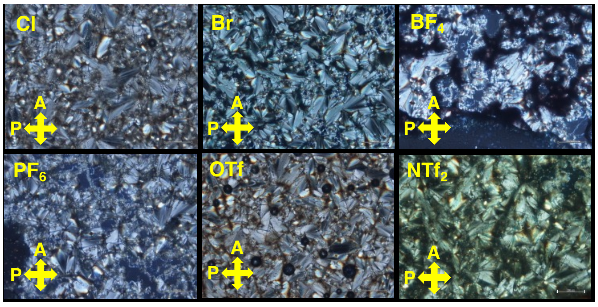


Fig. 3 Optical microstructures of the mesophases for six target compounds observed by POM.

Furthermore, PXRD measurements of the mesophases revealed that the *d*-spacing of the (001) diffraction peak was smaller than twice the molecular length, suggesting that the SmA phase adopts an interdigitated structure composed of flexible chains and mesogenic moieties. The phase transition behavior of **PF_6**, **OTf**, and **NTf_2**, which have relatively large counteranions, was investigated during the cooling process at temperatures below 30 °C. As a result, a new room-temperature smectic LCs was successfully developed.

Finally, PL properties in the SmA phase were investigated using compound **PF_6**, which exhibited high Φ_{PL} in the Cr state, as a representative example (Fig. 4).

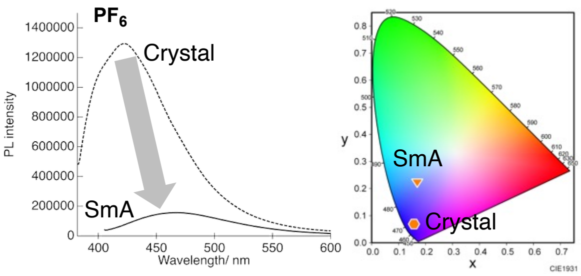


Fig. 4 PL spectral and color changes of **PF6** via a phase transition from crystal to SmA phases.

PL spectra were measured at 100 °C, where a clear SmA phase was observed. Compared to the PL spectrum in the crystalline state, a significant redshift in λ_{PL} was observed, although the PL intensity was greatly reduced due to thermal deactivation. Notably, the PL color changed from dark blue (CIE coordinate: 0.157, 0.069) to light blue (CIE coordinate: 0.169, 0.225), indicating the potential for PL switching between the crystal and SmA LC phases.

4 Conclusions

In this study, we synthesized six fluorinated tolane derivatives bearing imidazolium salts at the end of decyleneoxy flexible chains, each with a different counteranion, and investigated their photophysical properties and phase transition behavior in relation to the counteranion species. In dilute solution, all compounds exhibited dark blue PL, regardless of the counteranion. However, in the crystalline state, their PL behavior varied significantly depending on the counteranion. Phase transition behavior analysis revealed that all compounds formed the SmA phase upon both heating and cooling processes. Notably, derivatives with relatively large counteranions exhibited SmA phase formation at room temperature. Furthermore, PL measurements across the crystalline and SmA phases showed that the phase transition from the crystalline to the SmA phase induced a change in the molecular aggregated structures, resulting in red-shifted PL, although the PL intensity decreased due to thermal deactivation. We believe these findings provide a new molecular design strategy for room-temperature smectic LCs, and anticipate that the diversity of such LC molecules will expand in the future. Additionally, the room-temperature PL switching associated with the phase transition holds promise for application in PL thermosensors.

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