Photoluminescent Liquid Crystals Based on Trithienylphosphine Oxides

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Trithienylphosphine oxides tethering three π-conjugated oligothiophene arms self-assemble into columnar liquid-crystalline structures that show high photoluminescent properties at ambient temperature.

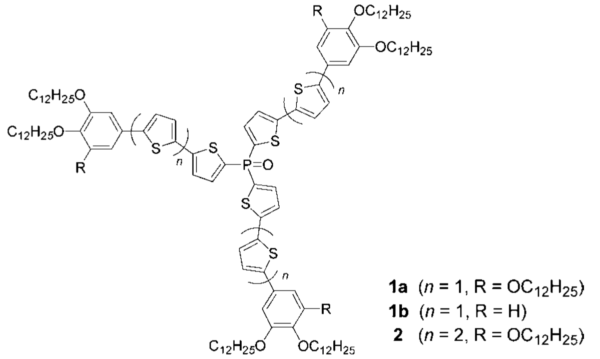
Self-organization of liquid-crystalline (LC) molecules leads to the preparation of functional materials with a variety of ordered nanostructures.[1,2] Columnar liquid crystals exhibit photo-,[2,3] electro-,[2,4] and ion-active[2,5] functions due to their designed molecular organization.

Photoluminescent (PL) molecular assemblies such as liquid crystals[3] and fibrous aggregates[6] composed of π-conjugated systems can be used for optical and sensing applications. For the enhancement of PL efficiency in the self-assembled states, modulation of the supramolecular structures through specific interactions is a key factor. The introduction of π-conjugated moieties into sterically bulky molecular architectures could enhance the PL efficiency of the materials in the ordered bulk states because of the suppression of intermolecular π–π interactions.

Our intention here is to prepare new photofunctional columnar LC oligothiophenes exhibiting high PL efficiency by introducing a triarylphosphine oxide moiety, which can act as a sterically bulky building block. We previously prepared a columnar liquid crystal containing a triarylphosphine oxide moiety to obtain an ion-active material.[7] An interesting aspect of the triarylphosphine oxide molecules is that the stacking distance[8] is quite large compared to the π–π stacking distance of conventional π-conjugated compounds.[9] Herein, we report C_3-symmetrical molecules **1a**, **1b**, and **2** composed of a polar phosphine oxide moiety, π-conjugated oligothiophene arms and lipophilic alkyl chains (Figure 1).

Until now, a number of examples of the LC oligothiophenes have been reported.[10] The preparation of oligothiophene-based columnar liquid crystals exhibiting high PL efficiency may lead to the development of new photofunctional materials. Compounds **1a** and **1b** were synthesized by palladium-catalyzed coupling reactions of tris(5′-bromo-2,2′-bithiophene-5-yl)phosphine oxide with three equivalents of phenylboronic acid derivatives.[11] Compound **2** was synthesized through phosphination of 5-bromo-5″-(3,4,5-trimethoxyphenyl)-2,2′:5′,2″-terthiophene with phosphorus tribromide, followed by an oxidation with hydrogen peroxide.

As summarized in Table 1, compounds **1a** and **2** exhibit enantiotropic columnar (Col) LC phases in wide temperature ranges, whereas **1b** shows a Col phase only on cooling from the isotropic melt. A key driving force in the formation of the Col phases should be nanosegregation of the central aromatic moieties from the surrounding alkyl chains as well as dipolar interactions of polar phosphine oxide moieties.



1a ($n = 1$, $R = OC_{12}H_{25}$)
1b ($n = 1$, R = H)
2 ($n = 2$, $R = OC_{12}H_{25}$)

Figure 1. Structures of liquid-crystalline compounds **1a**, **1b**, and **2**.

Table 1. Liquid-crystalline behavior of **1a**, **1b**, and **2**

Compound	Phase transition behavior[a]
1a	Cr −14 (31.1) Col_1 25 (5.2) Col_2 79 (2.6) Iso
1b	Cr [−13 (8.3) Col_1 25 (2.9) Col_2 78 (2.3)][b] 100 (50.2) Iso
2	Cr −14 (45.9) Col_1 23 (6.9) Col_2 109 (2.8) Iso

[a]Transition temperatures (°C) and enthalpies (kJ mol^{-1}, in parentheses) determined by DSC on the second heating at 5 °C min^{-1}. Cr: crystalline; Col: columnar; Iso: isotropic. [b]Monotropic phase transition.

The X-ray diffraction pattern of **1a** in the Col phase gives two peaks with *d*-spacing of 35.6 and 17.8 Å, which correspond to the (10) and (20) reflections, respectively. For compound **2**, the reflections of 40.3 (10) and 20.1 Å (20) are observed.[11] This increase in the intercolumnar distance can be attributed to the elongation of the oligothiophene arms. A molecular modeling study for **1a** has revealed that the molecule adopts a conical-shaped conformation and thereby possesses a large intrinsic dipole of approximately 6 debye along the longitudinal C_3 axis. In the Col phase, it is reasonable to assume that the molecules stack to form the 1D columnar structure (Figure 2). It was reported that triphenylphosphine oxide formed a similar 1D array with a stacking distance of 6.2 Å due to the steric effects of the phosphine oxide moiety, in single crystals.[8]

It is noteworthy that compound **1a** exhibits a high PL efficiency in the Col phase. As shown in Figure 3, compounds **1a** and **2** in the thin films exhibit intense green and yellow-green PL emissions with the peaks at 484 and 525 nm, respectively, upon photoexcitation. From the PL spectroscopy with an integrating sphere technique, the PL quantum yields of **1a** and **2** in the thin films have been determined to be 10.3 and 3.2%, re-

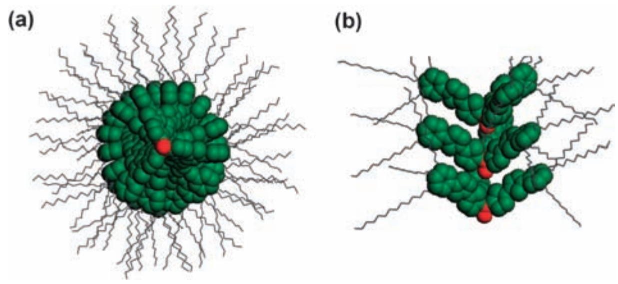


Figure 2. Representation of a possible assembled structure of **1a**: (a) top view and (b) side view. Hydrogen atoms are omitted for clarity. Green: π-conjugated moieties, red: phosphine oxide moieties.

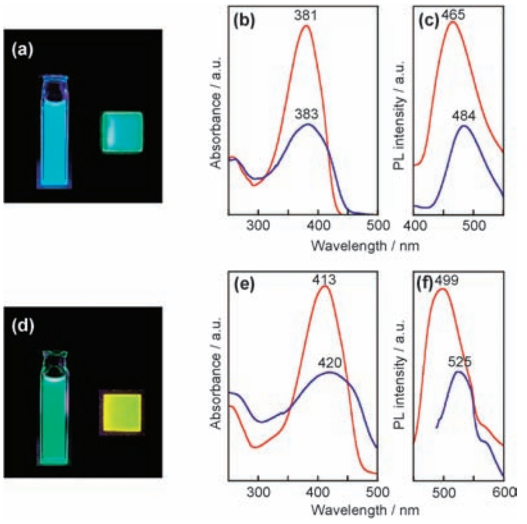


Figure 3. (a) Photograph of PL emission from a THF solution and thin film of **1a** under irradiation with UV light at 365 nm. (b) UV–vis and (c) PL spectra of **1a** in THF solution (red) and the Col phase (blue). (d) Photograph of PL emission from a THF solution and thin film of **2** under irradiation with UV light at 365 nm. (e) UV–vis and (f) PL spectra of **2** in THF solution (red) and the Col phase (blue).

spectively.[12] The value of **1a** is higher than those of conventional oligothiophenes in the solid states.[13] The relatively high PL properties observed for the thin film of **1a** should originate from the aforementioned unique stacked structure (Figure 2) that can prevent π–π electronic interactions of the oligothiophene arms between the neighboring stacked molecules.

The UV–vis spectra of **1a** both in the solution (the molecularly dissolved state) and in the thin film (the self-assembled condensed state) show that the peaks appear at almost the same position (Figure 3b). For **2**, a red shift of the absorption peak from the solution to the thin film together with a broadening of the peak is observed (Figure 3e). This observation suggests the presence of intermolecular electronic interactions in the thin film of **2**, which may result in the lower PL quantum yield.

In summary, we have developed π-conjugated oligothiophene-based columnar LC molecules having the phosphine oxide moiety. We expect that thin films of these liquid crystals with high luminescent functionalities are a promising candidate as polarized light-emitting materials.

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