

Fluorescence study of two- and three-dimensional organization of a thermotropic liquid crystal containing biphenyl–ester moieties

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ABSTRACT

Fluorescence dynamics of biphenyl–ester moieties of two- or three-dimensional phases of a thermotropic liquid crystal were explored. In the 2D crystalline-to-3D cubic phase transition, a broad excitation band centered at 280 nm and a 10 nm fluorescence redshift were observed. A drastic change in the fluorescence time-decay constant from ~90 to ~130 ps was seen. These changes resulted from cooperative contribution of intermolecular configurational change from biphenyl–biphenyl to biphenyl–ester and polarity alterations surrounding the charge transfer emissive chromophores. The material exhibited higher charge transfer emissions in the cubic and columnar 3D phases than in the 2D crystalline phase.

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1. Introduction

The physical properties of liquid crystalline materials are primarily determined by molecular orientation and intermolecular coupling [1–4]. Mesophase transitions and the molecular orientation of liquid crystals (LCs) can be studied using differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffraction (XRD), while dipole or electronic interactions between mesogen molecules can be examined using fluorescence spectroscopy [5–8].

In the late 1990s, Lee et al. [9] reported the interesting self-assembly behavior of a luminescent LC, 4-[4-[oxypropyleneoxy]propyloxy]-4'-biphenylcarboxyloxy]-4'-biphenylcarboxylate with poly(propylene oxide) (PPO) ($n = 15$, where n represents the number of repeating units) (Figure 1A). It was shown that this can undergo a transition from the lamellar 2D sheet-like crystalline (k) phase to the 3D bicontinuous cubic (cub), hexagonal columnar (col), and isotropic (i) phases (Figure 1B). Estimations based on the lattice parameters and densities were given, although no details on intermolecular coupling were reported.

We recently performed a fluorescence spectroscopic study of intermolecular coupling between the biphenyl–ester moieties of a thermotropic LC over the 2D phases of crystalline, smectic C, and smectic A [10]. The material used for this study, designated LC-8, consisted of a biphenyl–ester rod and a shorter PPO coil ($n = 8$). In the present work, we focus on the transition from the 2D k to 3D cub and col phases. The LC material utilized in the study

was designated LC-15, and comprised a biphenyl–ester rod and a long PPO coil ($n = 15$) (Figure 1A). The fluorescence obtained from the 3D phases exhibited remarkably different characteristics from those of the 2D phases, likely due to the smaller size of the aggregates of the material. The excitation and fluorescence spectra, and the fluorescence time-decay profiles, are systematically altered by mesophase transitions, thereby enabling dipole resonance or electron transfer interactions between the mesogens to be identified.

When heated, LC-15 exhibits 3D mesophases, as shown by DSC, POM, and XRD studies [9]. It has been demonstrated that the rods in the k phase are tilted relative to the layer normal, whereas those in the cub and col phases are randomly oriented, as depicted in Figure 1B. The DSC trace shown in Figure 1C demonstrates the temperature at which each mesophase is present. Based on this structural information, we performed a steady state and time-resolved fluorescence study.

2. Experimental

The LC-15 material was synthesized according to a previously reported method [9]. The steady state spectra were recorded using a Hitachi F-4500 fluorescence spectrophotometer equipped with a temperature control unit (VTRC-640, JEIO TECH). The time-resolved fluorescence decays were measured using a time-correlated single photon counting (TCSPC) system comprising a cavity-dumped dual-jet dye laser (700 series, Coherent) pumped with a picosecond Nd-YAG laser (Antares 76-YAG, Coherent) [11]. The fluorescence-decay time constants were obtained by first deconvoluting the measured signal from the pump time profile (characterized by a full width at half maximum of ~50 ps) and

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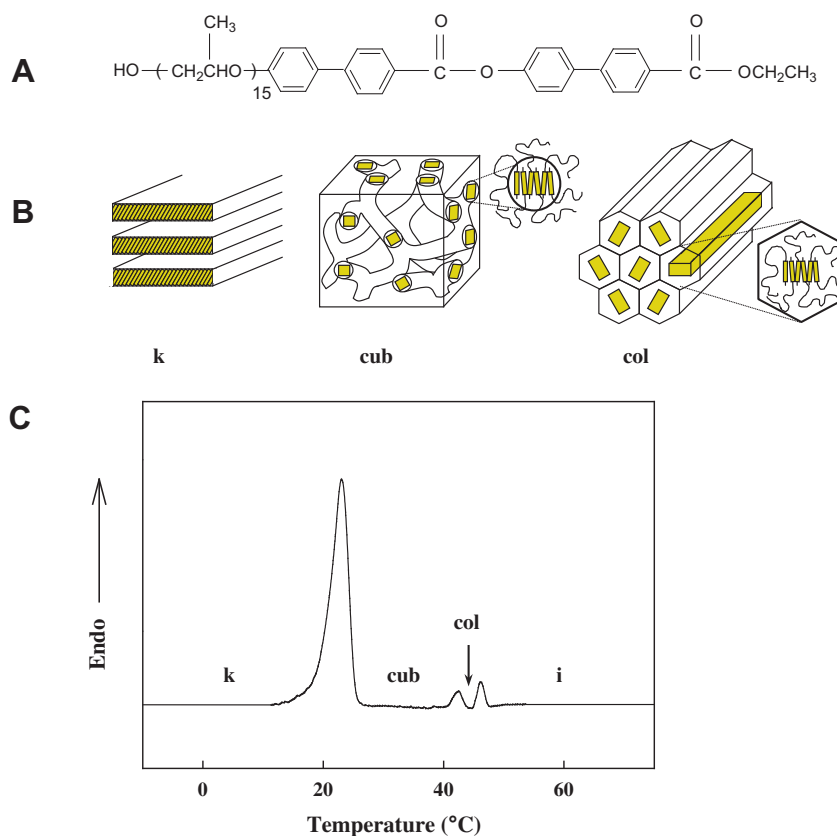


Figure 1. (A) Chemical structure of LC-15. (B) Molecular orientations of respective mesophases, adapted from [9]. (C) DSC trace of the first heating scan of the material; mesophases (k, cub, col, and i) are indicated.

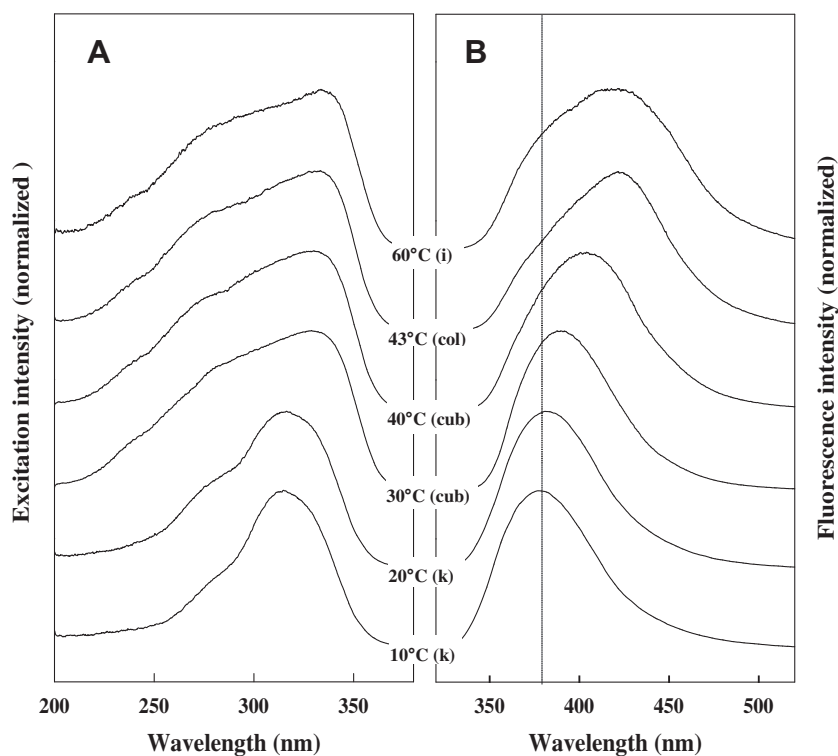


Figure 2. Steady state excitation (A) and fluorescence (B) spectra of LC-15 as a function of temperature (10–60 °C); temperatures and corresponding mesophases are indicated. The excitation and emission wavelengths for the fluorescence and excitation spectra were 300 and 400 nm, respectively.

then fitting to a sum of exponential terms [12]. The chi-square (χ^2) values for the fitting were 1.0–1.3.

3. Results and discussion

The steady state excitation and fluorescence spectra of the LC-15 as a function of temperature (10–60 °C) are shown in Figure 2. On undergoing a transition, the material shows systematic changes in the steady state spectra. In the k (20 °C)-to-cub (30 °C) transition, the fluorescence spectrum can be seen to be red-shifted by 10 nm, while the peak at 320 nm in the excitation spectrum is broader. These changes result from the formation of a new band centered at 280 nm owing to an excitation; these results are similar to those previously found for LC-8. In transitions from the cub to col and i, the fluorescence spectra are further redshifted. In the 2D k (20 °C)-to-3D cub (30 °C) transition, the excitation and fluorescence spectra cooperatively change, which is consistent with the ground state intermolecular configurational change shown in Figure 1B. Further details on the origin of the red-shifted fluorescence spectra including an intermolecular charge transfer emission will be demonstrated.

In an attempt to obtain kinetic information on coupling between the mesogens, a picosecond time-resolved fluorescence study was performed. The fluorescence time-decay profiles measured at a short wavelength (360 nm) are depicted in Figure 3. Multiple fluorescence-decay profiles were measured, corresponding to the entire spectral range for the spectra shown in Figure 2B. These profiles are summarized by time-decay constants and relative amplitudes obtained from the fitting procedure with multi-exponential terms for each decay (Table 1).

Figure 3 demonstrates that the decay profiles were faster at higher temperatures, which is inconsistent with those previously found for 2D LC-8. Thus, the faster decays appear to be inherent characteristic of the 3D phase of LC-15. The fluorescence time-decays following the photoexcitation of the k phase can be fitted to a sum of three exponential terms: an initial decay with a time constant 93 ± 2 ps, and two subsequent decays characterized by 258 ± 14 and 863 ± 44 ps (Table 1). The decays following the photoexcitation of the cub phase can be fitted to a sum of two exponential terms: an initial decay with a time constant of 130 ± 15 ps, and a subsequent decay characterized by a time constant of 626 ± 22 ps.

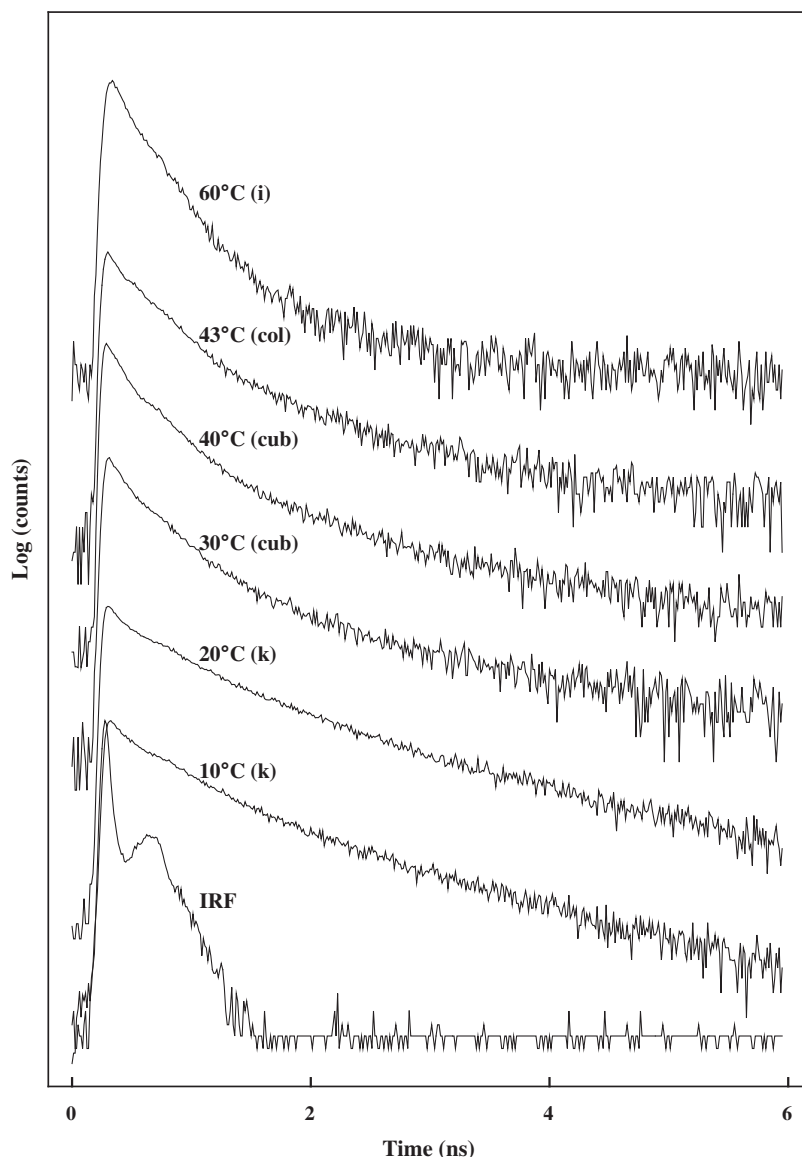


Figure 3. Time-dependent fluorescence decay profiles of LC-15 as a function of temperature (10–60 °C); temperatures and corresponding mesophases are indicated. The decays were probed at 360 nm. The excitation wavelength was 293 nm. IRF indicates the instrument response function of the TCSPC system.

Table 1
Decay parameters of LC-15 as a function of temperature^a.

Temperature (°C)	Phase	Emission wavelength (nm)	Fitted decay times ^b (ps)		
			τ_1	τ_2	τ_3
10	k	360	89 (49%)	252 (40%)	825 (11%)
		380	92 (31%)	280 (52%)	936 (17%)
		420	95 (17%)	270 (37%)	837 (36%)
20	k	360	95 (42%)	250 (46%)	860 (12%)
		380	95 (32%)	246 (47%)	886 (21%)
		420	94 (19%)	250 (35%)	810 (46%)
30	cub	360	126 (95%)	619 (5%)	
		380	149 (93%)	665 (7%)	
		440	139 (84%)	617 (16%)	
40	cub	360	105 (98%)	634 (2%)	
		380	129 (94%)	601 (6%)	
		440	130 (81%)	620 (19%)	
43	col	360	147 (98%)	599 (2%)	
		380	160 (95%)	615 (5%)	
		440	150 (88%)	600 (12%)	
60	i	360	126 (99%)	616 (1%)	
		380	139 (96%)	605 (4%)	
		450	148 (88%)	584 (12%)	

^a The excitation wavelength is consistently 293 nm.

^b The following fitting function is used: $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3)$, where $I(t)$ is the time-dependent fluorescence intensity, A is the amplitude (noted in parentheses as the normalized percentage, i.e., $[A_i/(A_1 + A_2 + A_3)] \times 100$), and τ is the fitted decay time. The χ^2 values for the fitting are 1.0–1.3.

The initial time-decay constant of 93 ± 2 ps and the redshifted excitation band at 320 nm with respect to the 300 nm excitation band of LC-15 monomer [13] is consistent with those previously found for the k phase of LC-8. These characteristics were attributed to J-aggregated biphenyls, which led to faster deactivation because of an allowed transition to the ground state, and a redshifted excitation band because of dipole resonance coupling [14–17]. As shown in Figure 2A, the k phase of LC-15 gave a blueshifted, broader excitation band at 320 nm compared to the spectrum for the k phase of LC-8, which had a sharp excitation band at 350 nm. In addition, the relative amplitude ($\sim 30\%$) of 93 ± 2 ps probed at 380 nm (wavelength of the highest intensity fluorescence) is seen to be smaller than that of the k phase of LC-8 ($\sim 80\%$ at 380 nm) (Table 1 of this report and Table 1 of Reference [10]). These findings consistently demonstrate that the coupling between the biphenyl moieties of LC-15 is closer to the biphenyl–ester coupling. In the previous XRD studies [9], the LC-15 rods were characterized as tilted relative to the layer normal in the k phase, while the LC-8 rods were fully interdigitated in the k phase. Our results are consistent with these descriptions.

As seen in Figure 3 and Table 1, further heating at 30 °C greatly changed the time-decay characteristics because of the 2D k-to-3D cub transition followed by the intermolecular configurational change indicated in Figure 2B. The time-decay constant dominantly observed for the cubic phase was found to be 130 ± 15 ps, as opposed to the 93 ± 2 and 258 ± 14 ps values for the k phase. This is consistent with the notable spectral changes shown in Figure 2.

The time-decay constant of 258 ± 14 ps found for k is comparable to the 234 ± 11 ps that was previously observed for the smectic C phase of LC-8 and attributed to the rate of deactivation from the excited state biphenyl–ester exciplexes. After the 2D k-to-3D cub phase transition, the time-decay constant decreased from 258 ± 14 to 130 ± 15 ps (Table 1). As shown in Figure 1B, the hydrophilic PPO coil segments completely surround the coupled rod units in the 3D phases of cub and col, which is in contrast to the 2D k phase. The polar environment of PPO aggregates may result in a stronger charge transfer (CT) complex between the biphenyl and ester moieties, leading to a faster decay time. This is similar to the shorter decay time previously observed in studies involving concentrated methanol solutions [13]. Note that in Table 1, the time-decay constant of 130 ± 15 ps is dominant for the 3D phases

of cub, col, and i (>90% relative amplitude when probed at 380 nm), while it changed from 130 ± 15 ps (cub) to 152 ± 7 ps (col) and 138 ± 11 ps (i). The time-decay constant of 130–150 ps can be attributed to the rate of deactivation from the excited state intermolecular CT complexes of LC-15, i.e., an exciplex between the biphenyl and ester groups.

The existence of intermolecular biphenyl–ester exciplexes in the 3D phases of the material is further evident from the broad excitation bands centered at 280 nm (see the top left of Figure 2). In gas-phase jet spectroscopy, the formation of an intracuster exciplex between benzaldehyde and 1,4-dimethoxybenzene has been shown to result in a broad excitation band located at higher energy [18], which is in agreement with the biphenyl–ester exciplexes of LC-8 and LC-15.

Finally, the time-decay constant of 600–850 ps was consistently observed for all mesophases. Following this characteristic, we attribute this time-decay constant to the rate of deactivation from the excited state monomeric mesogen, i.e., from the intramolecular CT or local excited state.

4. Conclusion

From the analysis of the steady state and time-resolved fluorescence spectroscopic data obtained for thermotropic LC-15 on phase transition from 2D to 3D organization, we have demonstrated that the J-aggregated biphenyls in the 2D k phase are characterized by a lower energy excitation band centered at 320 nm and a fast fluorescence time decay (time-decay constant of ~ 90 ps). In the cub, col, and i 3D phases, an intermolecular CT complex between the biphenyl and ester moieties is observed, characterized by fluorescence redshifts of 10–45 nm. This is followed by deactivation from the excited state biphenyl–ester exciplexes, the rates of which are characterized by time-decay constants of 130–150 ps. The strong CT complex formation in the 3D phases may be facilitated by the polar environment of hydrophilic aggregates of the long PPO coils.

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References

- [1] G.P. Bryan-Brown, C.V. Brown, I.C. Sage, V.C. Hui, *Nature* 392 (1998) 365.
- [2] S.A. Jenekhe, X.L. Chen, *Science* 279 (1998) 1903.
- [3] S.A. Jenekhe, X.L. Chen, *Science* 283 (1999) 372.
- [4] N.I. Zahid, O.K. Abou-Zied, R. Hashim, T. Heidelberg, *Langmuir* 28 (2012) 4989.
- [5] S. Aldmoto, H. Nishizawa, T. Yamazaki, I. Yamazaki, Y. Hayashi, M. Fujimaki, K. Ichimura, *Chem. Phys. Lett.* 276 (1997) 405.
- [6] S. Kato, F.-Q. Chen, T. Shimada, T. Yatsuhashi, H. Inoue, C. Pac, *J. Phys. Chem. B* 104 (2000) 2642.
- [7] J.A. Osaheni, S.A. Jenekhe, *J. Am. Chem. Soc.* 117 (1995) 7389.
- [8] D. Oelkrug, A. Tompert, J. Gierschner, H.-J. Egelhaaf, M. Hanack, M. Hohloch, E. Steinhuber, *J. Phys. Chem. B* 102 (1998) 1902.
- [9] M. Lee, B.-K. Cho, H. Kim, J.-Y. Yoon, W.-C. Zin, *J. Am. Chem. Soc.* 120 (1998) 9168.
- [10] I.-W. Hwang, Y.-R. Kim, *Chem. Phys. Lett.* 571 (2013) 34.
- [11] I.-W. Hwang, N.W. Song, D. Kim, Y.T. Park, Y.-R. Kim, *J. Polym. Sci. Part B: Polym. Phys.* 37 (1999) 2901.
- [12] D.V. O'Connor, D. Philips, *Time-Correlated Single Photon Counting*, Academic Press, New York, 1984.
- [13] I.-W. Hwang, H.-H. Choi, B.-K. Cho, M. Lee, Y.-R. Kim, *Chem. Phys. Lett.* 325 (2000) 219.
- [14] N.C. Maiti, S. Mazumdar, N. Periasamy, *J. Phys. Chem. B* 102 (1998) 1528.
- [15] N.C. Maiti, M. Ravikanth, S. Mazumdar, N. Periasamy, *J. Phys. Chem.* 99 (1995) 17192.
- [16] M. Kasha, M.A. El-Bayoumi, W.J. Rhodes, *J. Chim. Phys.* 58 (1961) 916.
- [17] R.M. Hochstrasser, M. Kasha, *Photochem. Photobiol.* 3 (1964) 317.
- [18] A. Kawai, R. Kohno, N. Oki, K. Obi, *Chem. Phys. Lett.* 318 (2000) 85.