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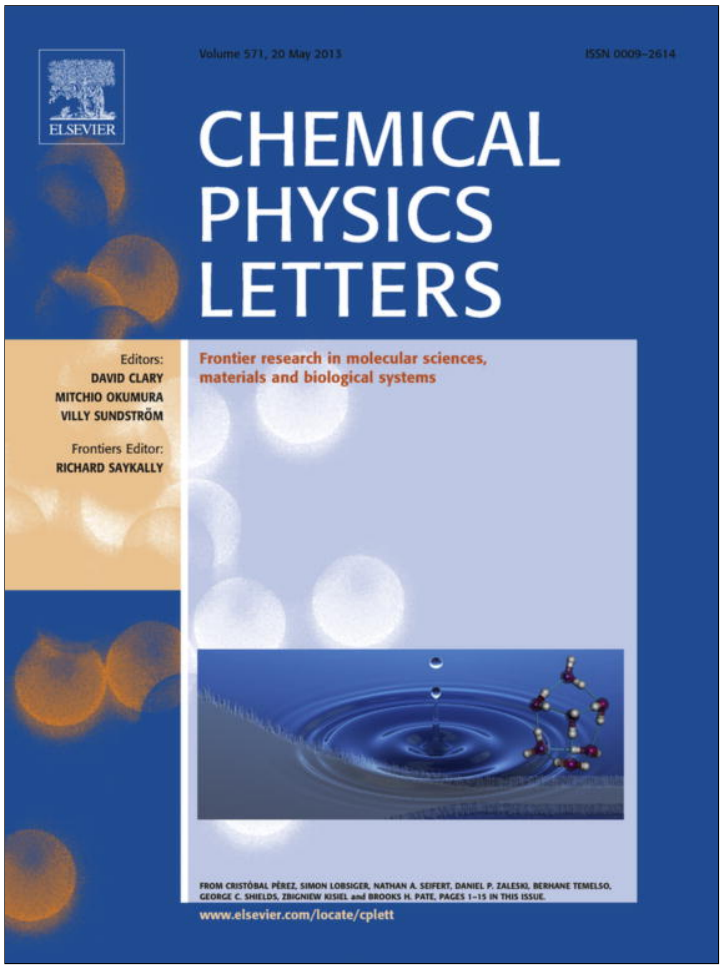

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Fluorescence lifetime study of intermolecular coupling between biphenyl–ester moieties of a thermotropic liquid crystal

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ABSTRACT

Using steady-state and time-resolved fluorescence spectroscopy, we investigated the intermolecular coupling between mesogenic biphenyl–ester moieties of a thermotropic liquid crystal under phase transition. In the crystalline-to-smectic C transition, a broad excitation band centered at 280 nm and a fluorescence redshift by 25 nm, followed by a drastic change in the fluorescence time-decay constant (from ~90 to ~230 ps), are consistently observed. These changes result from the intermolecular configurational change from biphenyl–biphenyl to biphenyl–ester. Emissions from intermolecular complexes such as J-aggregated biphenyls in crystalline and biphenyl–ester exciplexes in smectic C, smectic A, and isotropic phases are characterized.

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1. Introduction

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

In the early 1980s, Tamai et al. [9] reported the fluorescence behavior of a luminescent LC, 4-cyano-4n'-octyloxybiphenyl (8OCB), which has a phase that transitions from crystalline (k) to smectic A (s_A), nematic, and isotropic (i) forms. Various phases of 8OCB have been demonstrated to emit two kinds of fluorescence, i.e., emissions from singlet monomer and excimer. In the 1990s, Horie et al. [10,11] reported the fluorescence behavior of thermotropic LC polyesters such as BB-n (mesogenic 4,4′-biphenyldicarboxylate containing various methylene units) and PB-n (mesogenic 4,4′-dihydroxybiphenyl moieties containing various methylene units). However, because of the limited time resolution of nanosecond spectroscopy, kinetic information on intermolecular coupling between the mesogens could not be obtained [12,13].

In the present work, we focus on time-decay constants found by picosecond time-resolved fluorescence measurement on an LC material consisting of biphenyl–ester rods and poly(propylene oxide) coils under phase transition. The time-decay constants of the LCs are systematically influenced by mesophase transitions from k to smectic C (s_C), s_A, and i, thereby enabling us to demonstrate dipole resonance or electron transfer interactions between the mesogens.

The chemical structure of the LC rod-coil molecule is shown in Figure 1A. The rod-coil molecule has the systematic name ethyl 4-[4-[oxypoly(propyleneoxy)propyloxy]-4′-biphenylcarboxyloxy]-4′-biphenylcarboxylate with poly(propylene oxide) coils of $n = 8$. When heated, the material exhibits various LC mesophases, as shown by DSC, POM, and XRD studies [14]. A DSC trace shown in Figure 1B summarizes the heating temperature corresponding to each mesophase. It has been demonstrated that the rods in the k phase are fully interdigitated, whereas those in the s_C phase are tilted relative to the layer normal, as depicted in Figure 1B. In the s_A and i phases, the rods are randomly oriented. Based on this structural information, we performed the steady-state and time-resolved fluorescence study.

2. Experimental

Synthesis of the rod-coil molecules has been reported earlier [14]. The steady-state spectra are recorded using a Hitachi F-4500 fluorescence spectrophotometer equipped with a temperature-control unit (VTRC-640, JEIO TECH), while the time-resolved fluorescence decays are 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) [15]. The fluorescence-decay time constants are obtained by first deconvoluting the measured signal from the pump time profile (characterized by a full

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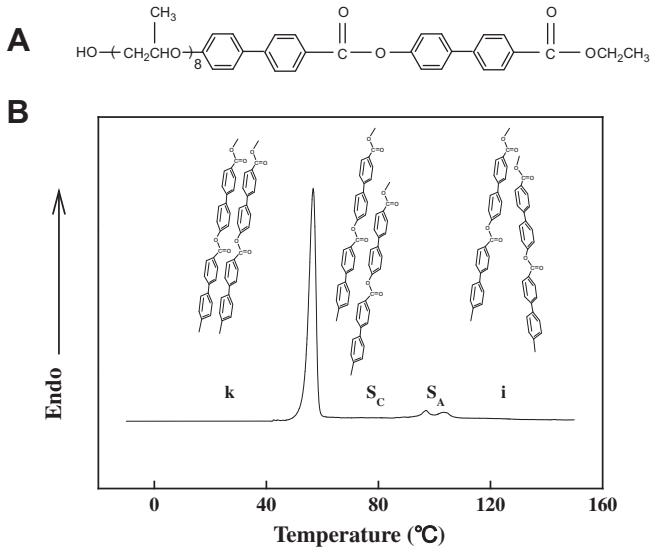

Figure 1. (A) Chemical structure of the LC rod-coil molecule. (B) DSC trace of the first heating scan of the material; mesophases (k, s_C, s_A, and i) and corresponding molecular orientations are indicated.

width at half maximum of ~50 ps) and then fitting to a sum of exponential terms [16]. The chi-square (χ^2) values for the fitting are 1.0–1.3.

3. Results and discussion

The steady-state excitation and fluorescence spectra of the rod-coil molecule as a function of temperature (20–110 °C) are shown in Figure 2. Following phase transition, the material shows systematic changes in the steady-state spectra. In the k (40 °C)-to-s_C (60 °C) transition, the fluorescence spectrum redshifts by 25 nm, while the narrow excitation spectrum peak at 350 nm broadens; these changes are particularly observed to result from an excitation that produced a new band centered at 280 nm. In transitions from s_C to s_A and i, the fluorescence spectra are further redshifted, similar to redshifts previously found for PB-n. In the k (40 °C)-to-s_C (60 °C) transition, the excitation and fluorescence spectra cooperatively change, consistent with the ground-state intermolecular configurational change from biphenyl–biphenyl to biphenyl–ester (inset of Figure 1B).

In an attempt to obtain kinetic information on coupling between the mesogens, we perform a picosecond time-resolved fluorescence study on the spectra shown in Figure 2B. The fluorescence time-decay profiles measured at shorter wavelengths (at 360 or 370 nm) are depicted in Figure 3. We measure multiple fluorescence-decay profiles 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 multiexponential terms for each decay (Table 1).

Figure 3 shows that the decay profiles are slower at higher temperatures, which is inconsistent with the fast deactivation of an excited-state monomer at high temperatures via accelerated vibronic relaxation. Thus, the slower decays indicate intermolecular defolding between the mesogens, as depicted in Figure 1B. The fluorescence time decays following the photoexcitation of the k phase are fitted to a sum of three exponential terms: an initial decay with a time constant τ_1 of 90 ± 4 ps and two subsequent decays characterized by τ_2 = 430 ± 46 ps and τ_3 = 1237 ± 123 ps (Table 1). The decays following the photoexcitation of s_C are fitted to a sum of two exponential terms: an initial decay with a time constant of 234 ± 11 ps and a subsequent decay characterized by a time constant of 1213 ± 75 ps.

The initial time-decay constant of τ_1 90 ± 4 ps found for k is interesting, because of the abrupt association between the fully

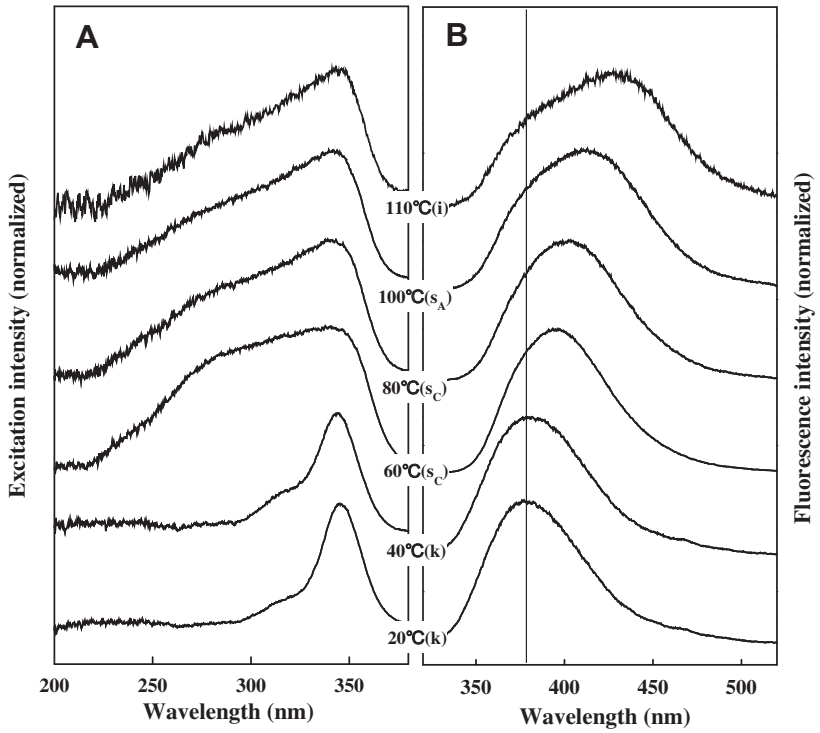

Figure 2. Steady-state excitation (A) and fluorescence (B) spectra of the rod-coil molecule as a function of temperature (20–110 °C); temperatures and corresponding mesophases are indicated. The excitation and emission wavelengths for the fluorescence and excitation spectra are 300 and 450 nm, respectively.

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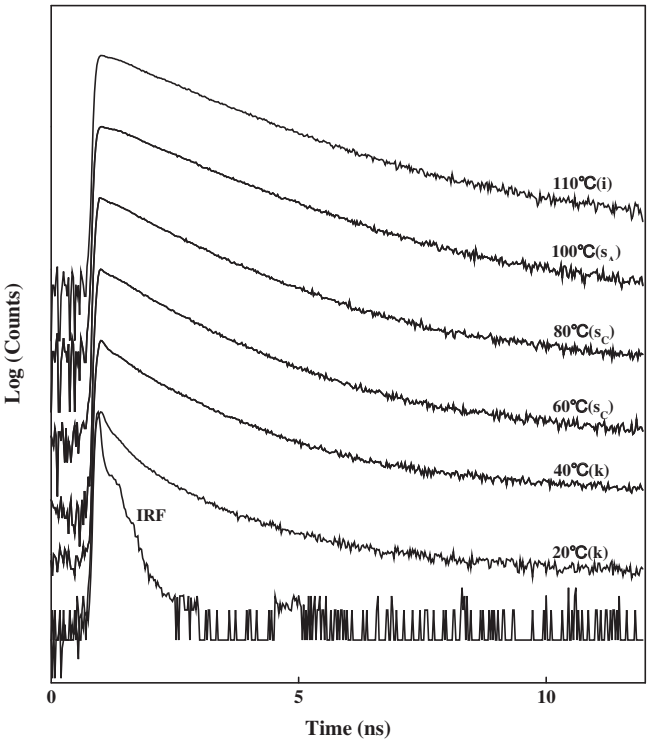

Figure 3. Time-dependent fluorescence decay profiles of the rod-coil molecule as a function of temperature (20–110 °C); temperatures and corresponding mesophases are indicated. The decays are measured at 360 nm for the 20–60 °C data and at 370 nm for the 80–110 °C data. The excitation wavelength is 293 nm. IRF indicates the instrument response function of the TCSPC system.

overlapped biphenyls, as depicted in the inset of Figure 1B. Coupling of two biphenyls results in H-type (cofacial rings) or J-type (stacked side by side) aggregates. The fluorescence lifetime of an H-aggregate is generally known to increase with respect to that of the monomer because of a disallowed transition to the ground state, while the J-aggregate has a reduced lifetime because of an allowed transition [17,18]. Another signature of the J-aggregate is a sharp and redshifted excitation band due to dipole resonance coupling between the chromophores, which follows Kasha's rule [19,20]. Two findings, i.e., the redshifted and narrow excitation band at 350 nm and the fast decay (time-decay constant of 90 ± 4 ps), suggest J-aggregation between the biphenyls in the k phase, which was not demonstrated by the earlier XRD study.

As seen in Table 1, the relative amplitude corresponding to the time-decay constant of 90 ± 4 ps is lower at increased heating temperatures (20–40 °C), indicating gradual defolding between the biphenyls in the k phase. Further heating at 60 °C greatly changes the time-decay characteristics because of the intermolecular configurational change from biphenyl–biphenyl to biphenyl–ester. Instead of time-decay constants of 90 ± 4 ps and 430 ± 46 ps in the k phase, a time-decay constant of 234 ± 11 ps is observed in the s_C phase, consistent with the notable spectral changes shown in Figure 2. We attribute the time-decay constant of 234 ± 11 ps to the rate of deactivation from the excited-state intermolecular charge-transfer (CT) complex, i.e., exciplex, between the biphenyl and ester groups. This deactivation will be further demonstrated.

The larger time-decay constants of $\tau_2 = 430 \pm 46$ ps and $\tau_3 = 1237 \pm 123$ ps found for k are consistent with the emission time-decay constants obtained from an earlier study on the solution phase [21]. The rod-coil molecule has been demonstrated to exhibit CT emission in methanol, characterized by a time constant of 379–510 ps. This emission is followed by a local excited-state (LE) emission characterized by a time constant of ~2 ns. By increasing the material concentration in methanol (from 1×10^{-6} M to 1×10^{-4} M), the CT emission lifetime was reduced from 510 to 379 ps because of intermolecular CT complex formation between the mesogens [21].

The time-decay constant (430 ± 46 ps) decreases (234 ± 11 ps) after the k-to-s_C phase transition primarily resulting from the decreased intermolecular distance between the biphenyl and ester moieties (insets of Figure 1B). This transition is succeeded by stronger intermolecular CT coupling, which similarly leads to a shorter decay time, as observed in its concentrated methanol solution in earlier studies. The time-decay constant of 234 ± 11 ps

Table 1
Decay parameters of the rod-coil molecule as a function of temperature[a].

Temperature (°C)	Phase	Emission wavelength (nm)	Fitted decay times[b] (ps)		
			τ1	τ2	τ3
20	k	360	87 (83%)	498 (10%)	1140 (7%)
		380	91 (80%)	455 (12%)	1138 (8%)
		420	94 (69%)	455 (16%)	1265 (15%)
40	k	360	85 (52%)	378 (18%)	1168 (30%)
		380	95 (46%)	406 (21%)	1250 (33%)
		420	91 (42%)	390 (29%)	1463 (29%)
60	S_C	360	240 (29%)	1102 (71%)	
		380	253 (33%)	1158 (67%)	
		420	232 (46%)	1244 (54%)	
80	S_C	370	220 (26%)	1201 (74%)	
		400	235 (33%)	1267 (67%)	
		430	225 (46%)	1307 (54%)	
100	S_A	370	260 (13%)	1262 (87%)	
		420	260 (18%)	1404 (82%)	
		460	277 (36%)	1549 (64%)	
110	i	370	395 (12%)	1283 (88%)	
		420	370 (22%)	1488 (78%)	
		460	350 (39%)	1607 (61%)	

[a] The excitation wavelength is consistently 293 nm.
[b] The following fitting function is used: $I(t) = A1 \exp(-t/\tau 1) + A2 \exp(-t/\tau 2) + A3 \exp(-t/\tau 3)$, where $I(t)$ is the time-dependent fluorescence intensity, A is the amplitude (noted in parentheses as the normalized percentage, i.e., $[Ai/(A1 + A2 + A3)] \times 100$), and τ is the fitted decay time. The χ^2 values for the fitting are 1.0–1.3.

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increases to 266 ± 11 and 372 ± 23 ps from s_C to s_A and i, possibly indicating a weakly bound intermolecular CT complex in the mobile phases.

In gas-phase jet spectroscopy, the formation of an intracluster exciplex between benzaldehyde and 1,4-dimethoxybenzene results in a broad excitation band located at higher energy, redshifted fluorescence, and a faster fluorescence time-decay profile [22], as in the case of the biphenyl–ester exciplex.

Finally, the time-decay constant 1294 ± 149 ps is consistently observed with all mesophases, while its relative amplitude is markedly increased by heating the material at higher temperatures, i.e., by accelerating the defolding process. Following these characteristics, we attribute the time-decay constant of 1294 ± 149 ps to the rate of deactivation from the excited-state monomeric mesogen, i.e., from the intramolecular CT or LE state.

4. Conclusion

From the analysis of the steady-state and time-resolved fluorescence spectroscopic data on a thermotropic LC composed of biphenyl–ester rod and poly(propylene oxide) coils, we demonstrate that the J-aggregated biphenyls in k are characterized by a lower energy excitation band at 350 nm and a faster fluorescence time decay (time-decay constant of ~90 ps). In s_C, an intermolecular CT complex between the biphenyl and ester moieties is characterized by a fluorescence redshift by ~25 nm, followed by deactivation from the excited-state biphenyl–ester exciplex, whose rate is characterized by a time-decay constant of ~230 ps. Transitions from s_C to s_A and i lead to further redshifts in the fluorescence spectra and subsequent increased fluorescence time-decay constants of 260–370 ps, indicating a weakly bound intermolecular CT complex in the mobile phases.

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