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Negative Thermal Quenching of Photoluminescence from Liquid-Crystalline Molecules in Condensed Phases

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Abstract: The luminescence of materials in condensed phases is affected by not only their molecular structures but also their aggregated structures. In this study, we designed new liquid-crystalline luminescent materials based on biphenylacetylene with a bulky trimethylsilyl terminal group and a flexible alkoxy chain. The luminescence properties of the prepared materials were evaluated, with a particular focus on the effects of phase transitions, which cause changes in the aggregated structures. The length of the flexible chain had no effect on the luminescence in solution. However, in crystals, the luminescence spectral shape depended on the chain length because varying the chain length altered the crystal structure. Interestingly, negative thermal quenching of the luminescence from these materials was observed in condensed phases, with the isotropic phase obtained at high temperatures exhibiting a considerable increase in luminescence intensity. This thermal enhancement of the luminescence suggests that the less- or nonemissive aggregates formed in crystals are dissociated in the isotropic phase. These findings can contribute toward the development of new material design concepts for useful luminescent materials at high temperatures.

Keywords: photoluminescence; liquid crystal; negative thermal quenching; aggregated structure



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1. Introduction

Organic materials that luminesce strongly in the solid state are crucial elements of organic light-emitting diodes [1–3]. However, although most luminescent organic molecules exhibit efficient photoluminescence in dilute solution, their luminescence is usually partially or completely quenched by luminophore aggregation in condensed phases (e.g., crystals and solid films). This phenomenon, called aggregation-caused quenching (ACQ), is common in organic molecules with π -electron systems and prevents their practical use [4,5]. Recently, organic materials that exhibit enhanced luminescence through molecular aggregation (aggregation-induced emission (AIE)) were developed, paving the way for the design of efficient solid-state emitters [6–9]. AIE effects are mainly explained by the restriction of the internal motion of molecules by aggregation.

As molecular aggregation is an essential process for luminescent materials with AIE activity, the aggregate structure plays a crucial role in their luminescence behavior. In particular, the luminescence properties of AIE materials are expected to be sensitive to both their aggregated structures and their molecular structures [9–20]. Therefore, structural control over molecular aggregates is a key technology for developing organic light-emitting materials and for tuning their luminescence properties (e.g., luminescence intensity and color). Liquid crystals (LCs) have the potential to control the aggregate structures of luminescent materials. LCs are a unique class of soft materials that flow similar to liquids and possess long-range orientational order similar to crystals. Furthermore, the material

properties and aggregated structures of LC molecules can be controlled by external stimuli such as electric fields, magnetic fields, and light [21–23].

We developed various luminescent LC materials with rod-like or disk-like molecular shapes [24–28]. The photoluminescence behavior of these LC materials was found to switch upon phase transition [26]. Inspired by our previous work, in this study, we investigated the luminescence behavior of LC luminophores in crystalline (Cry), LC, and isotropic (Iso) phases. In LC materials, a rigid mesogenic core are a key structure for achieving both liquid crystallinity and luminescence behavior. Here, we employed a biphenyl unit with an ethynyl group, which functioned as both the rod-like (calamitic) core of the mesogens and an efficient luminophore [22,23,29–32]. Increasing the steric bulkiness of a luminophore to prevent the aggregate formation in the excited state is a general strategy for enhancing the luminescence intensity in condensed phases [9]. Accordingly, orthogonal aromatic rings, spiro-ring structures, and bulky substituents (e.g., *t*-butyl groups) are often introduced into luminophores. Therefore, in the present study, a trimethylsilyl group was attached to the terminal of the LC molecules as a bulky substituent (Figure 1). Varying the length of a flexible alkoxy chain on the biphenyl unit was found to affect not only the LC behaviors [31] but also the luminescence spectral shape in crystals. Moreover, investigations of the effects of phase transitions on the luminescence behavior in condensed phases revealed abnormal negative thermal quenching effects at high temperatures, which can provide a new approach for designing highly luminescent solid-state materials.

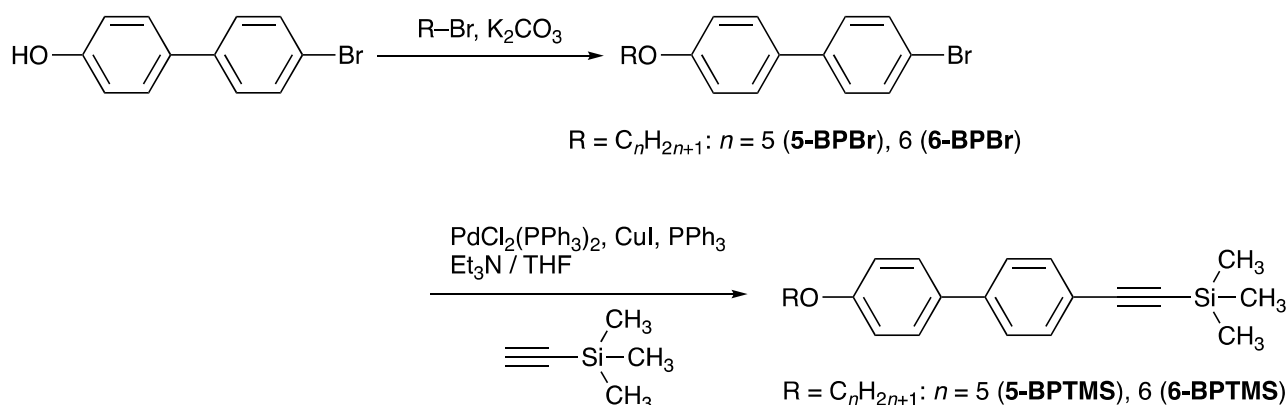


Figure 1. Molecular structures and synthetic routes for compounds **5-BPTMS** and **6-BPTMS**.

2. Materials and Methods

2.1. Materials

In this study, rod-like LC compounds **5-BPTMS** and **6-BPTMS** were prepared through a two-step synthetic route using 4-bromo-4'-hydroxybiphenyl as a starting material (Figure 1) [30–32]. The reagents and solvents used for the synthesis were obtained from commercial sources and used without further purification. A ^1H NMR analysis was performed using a JEOL ECS-400 spectrometer at 400 MHz, and the residual proton in the NMR solvent was used as an internal reference (Figure S1). Electrospray ionization mass spectrometry (ESI-MS) was carried out using a Bruker micrOTOF II instrument (Figure S2). An elemental analysis (C, H, and N) was performed using a Micro Corder JM10 analyzer (J-Science).

2.1.1. Compound 4-Bromo-4'-pentyloxybiphenyl (**5-BPBr**)

Compounds 4-Bromo-4'-hydroxybiphenyl (2.0 g, 8.0 mmol), 1-bromopentane (1.3 g, 8.8 mmol), and K_2CO_3 (1.7 g, 12 mmol) were added to dimethylformamide (25 mL), and the resultant mixture was stirred for 20 h at 90 °C. After filtering off the solids in the reaction mixture, the filtrate was dissolved in ethyl acetate and washed with deionized water followed by saturated aqueous NaCl. Anhydrous sodium sulfate was used to dry the organic layer, which was then concentrated under reduced pressure. Compound **5-BPBr**

was obtained as a white powder (2.0 g, 6.2 mmol, 78% yield). The ^1H NMR (400 MHz, CDCl_3 , δ): 7.54 (dd, $J = 11.2$ and 2.4 Hz, 2H; 3,5-H in biphenyl), 7.49 (dd, $J = 11.9$ and 2.0 Hz, 2H; 3',5'-H in biphenyl), 7.42 (dd, $J = 8.8$ and 1.6 Hz, 2H; 2,6-H in biphenyl), 6.99 (dd, $J = 8.4$ and 1.6 Hz, 2H; 2',6'-H in biphenyl), 4.00 (t, $J = 6.8$ Hz, 2H; OCH_2CH_2), 1.85–1.78 (quin, $J = 7.1$ Hz, 2H; OCH_2CH_2), 1.49–1.35 (m, 4H; $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), and 0.96 (t, $J = 7.4$ Hz, 3H; $(\text{CH}_2)_4\text{CH}_3$).

2.1.2. Compound 4-Bromo-4'-hexyloxybiphenyl (6-BPBr)

Compound **6-BPBr** (92% yield) was synthesized by the same procedure as **5-BPBr**, except that 1-bromohexane was used instead of 1-bromopentane. The ^1H NMR (400 MHz, CDCl_3 , δ): 7.53 (dd, $J = 11.0$ and 2.3 Hz, 2H; 3,5-H in biphenyl), 7.64 (dd, $J = 11.0$ and 2.0 Hz, 2H; 3',5'-H in biphenyl), 7.53 (dd, $J = 8.8$ and 3.0 Hz, 2H; 2,6-H in biphenyl), 6.99 (dd, $J = 8.8$ and 2.3 Hz, 2H; 2',6'-H in biphenyl), 4.01 (t, $J = 6.6$ Hz, 2H; OCH_2CH_2), 1.85–1.80 (m, 2H; OCH_2CH_2), 1.51–1.30 (m, 6H; $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), and 0.91 (t, $J = 7.2$ Hz, 3H; $(\text{CH}_2)_5\text{CH}_3$).

2.1.3. Compound 5-BPTMS

Then, **5-BPBr** (1.3 g, 4.0 mmol), trimethylsilylacetylene (0.63 g, 6.0 mmol), triphenylphosphine (50 mg, 0.20 mmol), CuI (40 mg, 0.20 mmol), and bis(triphenylphosphine)palladium dichloride (140 mg, 0.20 mmol) were added to a mixture of triethylamine (20 mL) and tetrahydrofuran (THF; 10 mL), and the resultant mixture was refluxed for 17 h with stirring. After filtering off the solids, the filtrate was evaporated under reduced pressure. The residue was dissolved in ethyl acetate and washed with saturated aqueous NH_4Cl , deionized water, and saturated aqueous NaCl . After the organic layer was dried with anhydrous sodium sulfate, the solution was concentrated under reduced pressure. Purification of the crude product by silica gel column chromatography (eluent: hexane) provided **5-BPTMS** as a white solid (1.2 g, 3.6 mmol, 90% yield), m.p. 116°C . The ^1H NMR (400 MHz, CDCl_3 , δ): 7.52–7.50 (m, 6H; 3,5,2',3',5',6'-H in biphenyl), 6.97 (dd, $J = 9.8$ and 1.5 Hz, 2H; 2,6-H in biphenyl), 4.00 (t, $J = 6.9$ Hz, 2H; CH_2O), 1.90–1.85 (m, 2H; $\text{CH}_2\text{CH}_2\text{O}$), 1.80 (quin, $J = 6.4$ Hz, 2H; $\text{CH}_2(\text{CH}_2)_2\text{O}$), 1.48–1.36 (m, 6H; $(\text{CH}_2)_2\text{CH}_3$), 0.94 (t, $J = 7.0$ Hz, 3H; $(\text{CH}_2)_3\text{CH}_3$), 0.26 (s; 9H; $\text{Si}(\text{CH}_3)_3$). FTIR (KBr, cm^{-1}): 2954, 2932, 2871, 2861, 2533, 2154, 1601, 1492, 1393, 1249, 984, 860, 837, and 820. ESI-MS m/z : $[\text{M}]^+$ calcd for $\text{C}_{22}\text{H}_{28}\text{OSi}$, 336.1909 found, 336.5246. Anal. calcd for $\text{C}_{22}\text{H}_{28}\text{OSi}$: C, 78.51; H, 8.39 found: C, 78.37; H, 8.67.

2.1.4. Compound 6-BPTMS

Compound **6-BPTMS** was synthesized by the same procedure as **5-BPTMS** and obtained 49% yield, m.p. 107°C . The ^1H NMR (400 MHz, CDCl_3 , δ): 7.52–7.50 (m, 6H; 3,5,2',3',5',6'-H in biphenyl), 6.96 (dd, $J = 9.6$ and 3.0 Hz, 2H; 2,6-H in biphenyl), 3.99 (t, $J = 6.6$ Hz, 2H; CH_2O), 1.81 (quin, $J = 7.2$ Hz, 2H; $\text{CH}_2\text{CH}_2\text{O}$), 1.48–1.36 (m, 6H; $(\text{CH}_2)_3\text{CH}_3$), 0.92 (t, $J = 6.3$ Hz, 3H; $(\text{CH}_2)_3\text{CH}_3$), 0.25 (s; 9H; $\text{Si}(\text{CH}_3)_3$). FTIR (KBr, cm^{-1}): 2954, 2938, 2869, 2157, 1605, 1493, 1473, 1394, 1248, 864, 841, 822. ESI-MS m/z : $[\text{M}-\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{29}\text{OSi}$, 349.1988 found, 349.2584. Anal. calcd for $\text{C}_{23}\text{H}_{29}\text{OSi}$: C, 78.80; H, 8.63 found: C, 78.84; H, 8.99.

2.2. X-ray Crystallography

Single crystals were prepared by slow evaporation of a mixed solvent system (CH_2Cl_2 / *n*-hexane). The obtained crystal was mounted on a glass fiber. The omega scanning technique was applied to collect the reflection data using a Bruker D8 goniometer with a monochromatized $\text{Mo K}\alpha$ radiation ($\lambda = 0.71075 \text{ \AA}$). To estimate the actual crystal structure of the synthesized materials, measurements were performed at an ambient temperature (296 K). The initial structure of the unit cell was determined through a direct method using APEX2. The structural model was refined by a full-matrix least-squares method using SHELXL-2014/6 [33,34]. All calculations were performed using the SHELXL software. The crystallographic data for the synthesized compounds are summarized in the Supplementary Material, and the indexed data were deposited in the Cambridge Crystallographic Data

Centre (CCDC) database (CCDC 2125441 for **5-BPTMS** and 2125479 for **6-BPTMS**). The indexed database contains additional supplementary crystallographic data for this study and may be accessed without charge at <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, accessed on 11 December 2021. The CCDC may be contacted by mail at 12 Union Road, Cambridge CB2 1EZ, U.K., by fax at (44) 1223-336-033, or by email at deposit@ccdc.cam.ac.uk.

2.3. Phase Transition Behavior

The LC behavior was observed by polarized optical microscopy (POM) using an Olympus BX51 microscope equipped with a hot stage (Instec HCS302 hot stage with an Mk1000 controller, Instec). To assess the thermochemical stability, a thermogravimetric–differential thermal analysis (TG–DTA) was carried out using a DTG-60AH instrument (Shimadzu) at a heating rate of $5.0\text{ }^{\circ}\text{C min}^{-1}$. The thermodynamic parameters were determined by differential scanning calorimetry (DSC; X-DSC7000, SII) at a scanning rate of $5.0\text{ }^{\circ}\text{C min}^{-1}$. At least three scans were performed to confirm reproducibility. The interlayer spacing of the smectic (Sme) LC phase was estimated using X-ray diffraction (XRD; Ultima IV XRD-DSC IIX, Rigaku). A D/tex-Ultra detector was employed for the small-angle region and a scintillation counter for the wide-angle region. Measurements were carried out at a scanning rate of $10\text{ }^{\circ}\text{C min}^{-1}$, and the temperature was controlled using a built-in unit (ThermoPlus2, DSC8230, Rigaku).

2.4. Photophysical Properties

UV-visible absorption and steady-state photoluminescence spectra were recorded on a JASCO V-550 absorption spectrometer and a Hitachi F-7000 fluorescence spectrometer with a R928 photomultiplier (Hamamatsu) as the detector, respectively. The crystals prepared for single-crystal X-ray structural analysis were also used for measurements in the Cry and LC phases. The crystals were placed between a pair of quartz plates and set on a homemade heating stage to record the spectra at controlled temperatures. The photoluminescence quantum yields were determined using a calibrated integrating sphere (Hitachi). The photoluminescence lifetimes were measured at an excitation wavelength of 280 nm using a Quantaaurus Tau photoluminescence lifetime measurement system (C1136-21, Hamamatsu).

2.5. Computations

All computations were performed using the density functional theory (DFT) with the B3LYP hybrid functional and the 6-311+G(d,p) basis set in the Gaussian 16 (revision C.01) program package [35]. The optimized geometries were determined by DFT calculations using the same basis set. The stationary points were characterized by frequency calculations to confirm that the minimum energy structures had no imaginary frequencies.

3. Results and Discussion

3.1. Synthesis and Characterization of Biphenylacetylene Compounds

In this study, **5-BPTMS** and **6-BPTMS**, biphenylacetylene compounds with a terminal trimethylsilyl group, were synthesized according to the synthetic route shown in Figure 1. Following purification by column chromatography and recrystallization from a mixed solvent system of CH_2Cl_2 and hexane, the compounds were fully characterized by a ^1H NMR spectroscopy, infrared spectroscopy, high-resolution mass spectrometry, and an elemental analysis. All analytical data (presented in the Material and Methods section) confirmed that the desired compounds were obtained.

To clarify the molecular structure of the synthesized compounds in the condensed phase, a single-crystal X-ray structural analysis was performed. Both **5-BPTMS** and **6-BPTMS** furnished single crystals suitable for X-ray crystallography. The key crystallographic data are summarized in Table S1, and the crystal structures are shown in Figure 2. Both compounds crystallized in the *P*-1 triclinic space group with four (**5-BPTMS**) or six (**6-BPTMS**) formula units per unit cell. The unit cells of **5-BPTMS** and **6-BPTMS** contain two and three types of conformational isomers, respectively, which can be characterized by the dihedral angle

of the biphenyl moiety (Table 1). It should be noted that the biphenyl dihedral angles of some conformational isomers were extremely small, with the two benzene rings of the biphenyl moiety forming an almost coplanar structure. In the molecular model obtained by the DFT structural optimization, the C2–C1–C1′–C2′ dihedral angle in the biphenyl moiety was approximately 38° (Figure S3 and Table 1). Therefore, the molecules in the crystal lattice are distorted, probably because of intermolecular interactions, which allows tight packing. Selected interatomic distances between neighboring molecules are listed in Figures S4 and S5, and the results indicate that intermolecular interactions exist in the Cry phase.

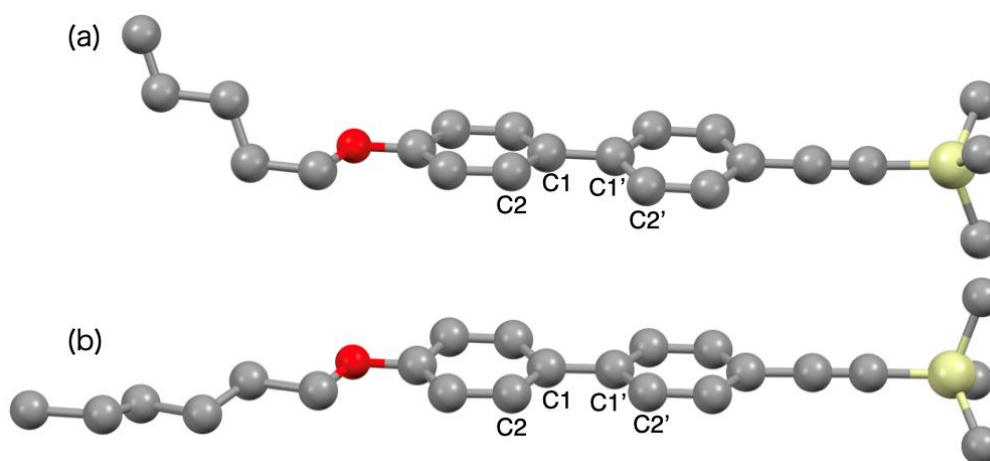


Figure 2. Molecular structures with the smallest C2–C1–C1′–C2′ dihedral angle, as determined by single-crystal X-ray structural analysis at room temperature: (a) **5-BPTMS** and (b) **6-BPTMS**. The hydrogen atoms are omitted for clarity. Atom color legend: gray—C; red—O; yellow—Si.

Table 1. Key structural parameters of biphenylacetylene compounds determined by single-crystal X-ray structural analysis and DFT calculations.

Compound	Biphenyl Dihedral Angle ¹ (°)	Molecular Length ² (Å)
5-BPTMS in crystals	9.17, 11.37	—
5-BPTMS optimized ³	37.99	20
6-BPTMS in crystals	5.96, 15.84, 30.48	—
6-BPTMS optimized ³	37.98	21

¹ Dihedral angle of C2–C1–C1′–C2′. ² Length between the carbon atoms in the terminal methyl groups of the trimethylsilyl moiety and alkoxy chain. ³ Structure optimized by DFT calculations using the B3LYP hybrid functional with the 6-311+G(d,p) basis set (Figure S3).

3.2. Thermal Behavior of Biphenylacetylene Compounds

The thermochemical stability of the compounds was evaluated by TG–DTA (Figure S6). The thermal decomposition temperature was defined as the temperature at which 5% weight loss occurs. The TG–DTA thermograms showed that **5-BPTMS** and **6-BPTMS** were thermally stable up to 204 and 208 °C, respectively.

The thermodynamic behavior of the compounds was observed using DSC and POM. As shown by the DSC thermogram in Figure 3a, **5-BPTMS** exhibited two endothermic peaks during the heating process and four or more exothermic peaks during the cooling process. In contrast, the DSC thermogram of **6-BPTMS** (Figure 3b) showed two distinct exothermic peaks during the cooling process, whereas two overlapping peaks were not clearly separated during the heating process. These two peaks could not be completely separated by changing the scan rate, suggesting that this compound exhibits an LC phase in a very narrow temperature range during the heating process. As the DSC results suggest that the synthesized compounds exhibited liquid crystallinity, we used POM to observe the phase transition behavior of **5-BPTMS** and **6-BPTMS** and determine their phase structures (Figure 4). POM observations during the cooling process revealed a fan-shaped texture

for both compounds, which suggests the formation of a Sme phase. For **5-BPTMS**, no significant change in the optical texture was observed at 103 °C, where an exothermic peak appeared in the DSC thermogram. During the heating process, **5-BPTMS** showed the same fan-shaped texture between 108 and 116 °C, but this characteristic optical texture was not observed for **6-BPTMS** because of the narrow temperature range of the LC phase.

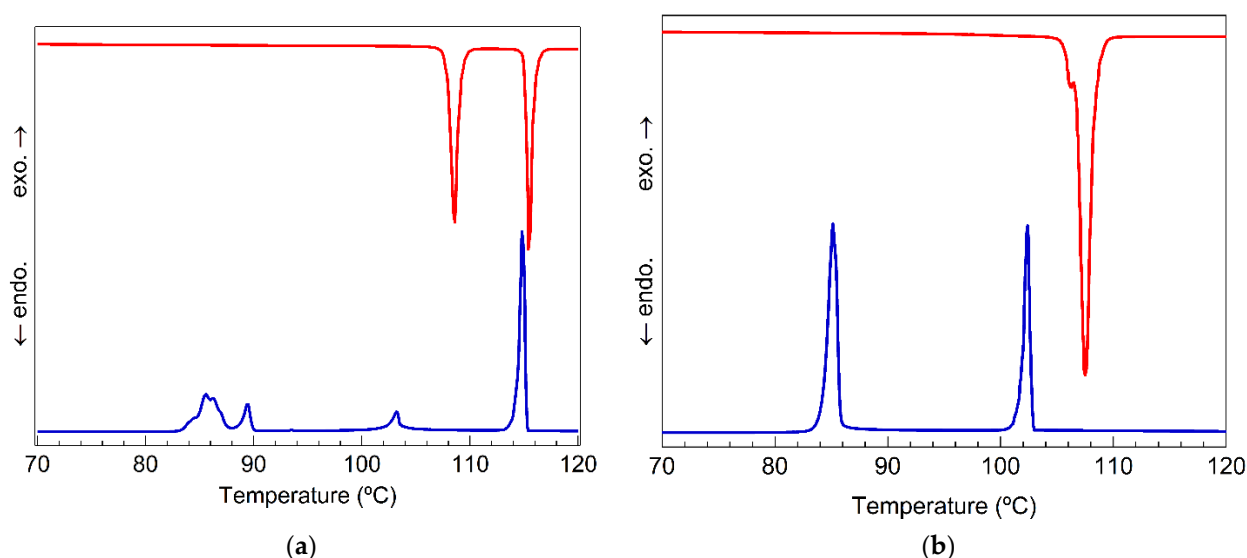


Figure 3. Differential scanning calorimetry (DSC) thermograms of (a) **5-BPTMS** and (b) **6-BPTMS** (red, 2nd heating scan; blue, 2nd cooling scan; scanning rate, 5 °C min^{−1}).

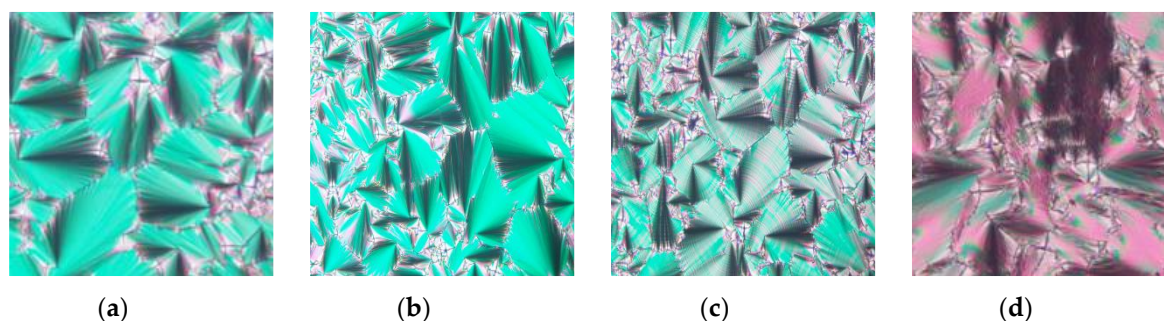


Figure 4. Optical textures observed by polarized optical microscopy (POM) during the cooling process: (a) **5-BPTMS** at 111 °C (smectic A; SmeA), (b) **5-BPTMS** at 96 °C (higher-order smectic; SmeX), (c) **5-BPTMS** at 87 °C (crystalline; Cry'), and (d) **6-BPTMS** at 103 °C (SmeA).

To confirm the LC phase structures in more detail, XRD measurements were performed at various temperatures during the cooling process (Figure 5). In the LC temperature range (115–103 °C for **5-BPTMS** and 104–86 °C for **6-BPTMS**), diffraction peaks appeared in the small-angle region ($\sim 3.5^\circ$) for both compounds (Figure 5a,b), which are attributable to the Sme layer spacing (d). In both materials, the d values were slightly larger than the molecular lengths estimated from the DFT-optimized structures (Table 1). Thus, we proposed a packing model for the LC phase of these compounds, as schematically shown in Figure 5. In this model, because of the bulkiness of the terminal trimethylsilyl group, the molecules cannot overlap to form Sme layers. Instead, the molecules are shifted in the layers to avoid steric hindrance. This model provides an explanation for the interlayer spacing of the Sme phase being longer than the molecular length of each compound. Based on the optical textures observed by POM and the XRD results, we conclude that the observed LC phase is the smectic A (SmeA) phase.

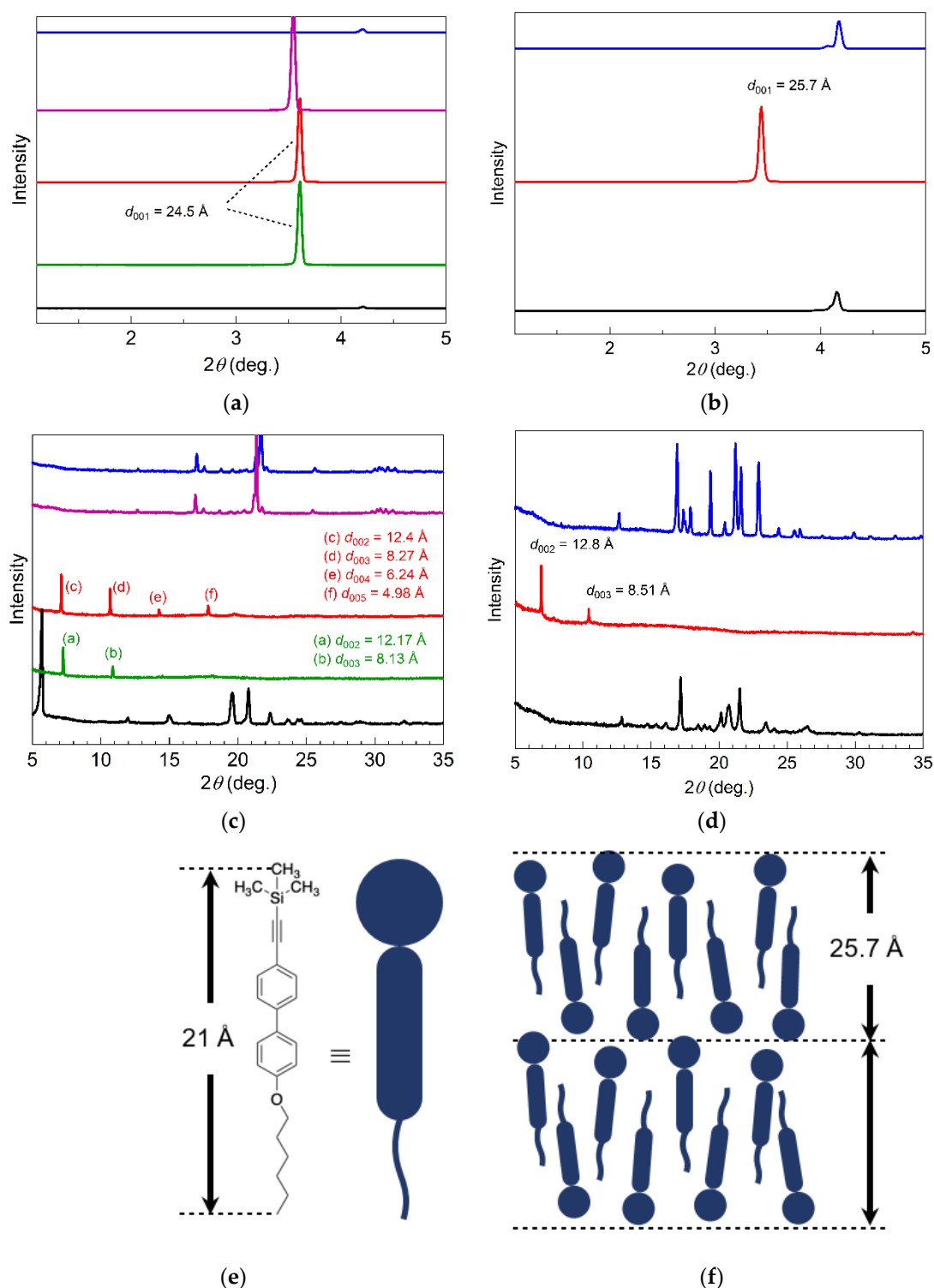


Figure 5. X-ray diffraction (XRD) patterns at various temperatures and plausible packing structure in the SmeA phase. Small-angle XRD patterns for (a) 5-BPTMS and (b) 6-BPTMS. Wide-angle XRD patterns for (c) 5-BPTMS and (d) 6-BPTMS. XRD measurements were performed in the temperature ranges of 30–38 °C (1st heating, Cry, black), 114–109 °C (1st cooling, SmeA, green), 96–92 °C (1st cooling, SmeX, red), 89–88 °C (1st cooling, Cry', violet), and 31–30 °C (1st cooling, Cry, blue) for 5-BPTMS, and 23–51 °C (1st heating, Cry, black), 109–95 °C (1st cooling, SmeA, red), and 39–30 °C (1st heating, Cry, blue) for 6-BPTMS. (e) Molecular model of 6-BPTMS and (f) schematic model of the packing structure in the SmeA phase.

The phase sequences and transition temperatures obtained from the DSC and POM observations are summarized in Table 2. Compound **5-BPTMS** showed another LC phase upon cooling below the temperature range of the SmeA phase ($<103^{\circ}\text{C}$). In the temperature range of $103\text{--}89^{\circ}\text{C}$, the optical texture was not significantly different from that observed for the SmeA phase, and the XRD results indicated that the layer spacing was the same as that in the SmeA phase. However, this phase showed higher-order diffraction peaks in the wide-angle XRD measurements (Figure 5c). At present, although the detailed phase structure is unclear, this phase can be considered a higher-order Sme (SmeX) phase. Additionally, in the temperature range of $89\text{--}85^{\circ}\text{C}$, the optical texture changed slightly, with striped patterns appearing in the fan shape. This texture was unchanged in the Cry phase at temperatures below 85°C . Thus, we conclude that the phase observed in the temperature range of $89\text{--}85^{\circ}\text{C}$ was another Cry phase (Cry') and that a Cry'-to-Cry phase transition occurred at 85°C .

Table 2. Thermal and photophysical properties of biphenylacetylene compounds.

Compound	Phase Sequences ¹ and Transition Temperatures ($^{\circ}\text{C}$) ²	τ (ns) ³	Φ (%) ⁴
5-BPTMS	Heating Cooling Cry 108 SmeA 116 Iso Cry 85 Cry' 89 SmeX 103 SmeA 115 Iso	1.6	22
6-BPTMS	Heating Cooling Cry 107 Iso Cry 86 SmeA 104 Iso	1.7	30

¹ Cry, crystalline; SmeX, unidentified smectic; SmeA, smectic A; Iso, isotropic. ² The phase transition temperatures were determined by DSC during the 2nd scanning process. ³ τ , luminescence lifetime in crystals at room temperature. ⁴ Φ , luminescence quantum yield in crystals at room temperature.

3.3. Photophysical Properties in Solution and Crystals at Room Temperature

The UV-visible absorption and photoluminescence spectra of **5-BPTMS** and **6-BPTMS** were measured in dilute CH_2Cl_2 solution. Compound **5-BPTMS** in CH_2Cl_2 solution ($2.0 \times 10^{-5} \text{ mol L}^{-1}$) exhibited a UV absorption band at 290 nm, and the molar extinction coefficient at the absorption maxima was $4 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ (Figure 6a). This absorption band was attributed to the $\pi\text{--}\pi^*$ transition of the biphenyl moiety. Compound **6-BPTMS** in the CH_2Cl_2 solution showed a similar absorption behavior (Figure 6c). Both compounds were completely transparent in the visible light region ($>340 \text{ nm}$), which is an important characteristic for light-emitting materials.

The photoluminescence spectra of **5-BPTMS** and **6-BPTMS** were also measured in dilute CH_2Cl_2 solution ($2.0 \times 10^{-6} \text{ mol L}^{-1}$). Both compounds exhibited a luminescence band with an emission peak maximum ($\lambda_{\text{max}}^{\text{em}}$) in the UV region at 355 nm (Figure 6a,c). Thus, the length of the terminal alkoxy chain in the biphenylacetylene compounds had no effect on the spectral shape and $\lambda_{\text{max}}^{\text{em}}$ of the luminescence in the solution.

These compounds also emitted photoluminescence in crystals at room temperature (Figure 6b,d). The deep-blue photoluminescence from the crystals was visible to the naked eye under UV irradiation at 365 nm. In sharp contrast to the photoluminescence behavior in the solution, the luminescence spectral shape in crystals showed a clear dependence on the terminal chain length, meaning that photoluminescence of the present materials dramatically depends on the intermolecular interactions (aggregated structure). For the **6-BPTMS** crystal, the luminescence band appeared at 377 nm with a shoulder at 355 nm. Although $\lambda_{\text{max}}^{\text{em}}$ was shifted 22 nm toward longer wavelengths due to a difference in polarity around the molecules, this luminescence band can be considered to be the same as that observed in the dilute solution. Therefore, we conclude that the luminescence of the **6-BPTMS** crystal exhibited a vibronic structure and was emitted by a monomer.

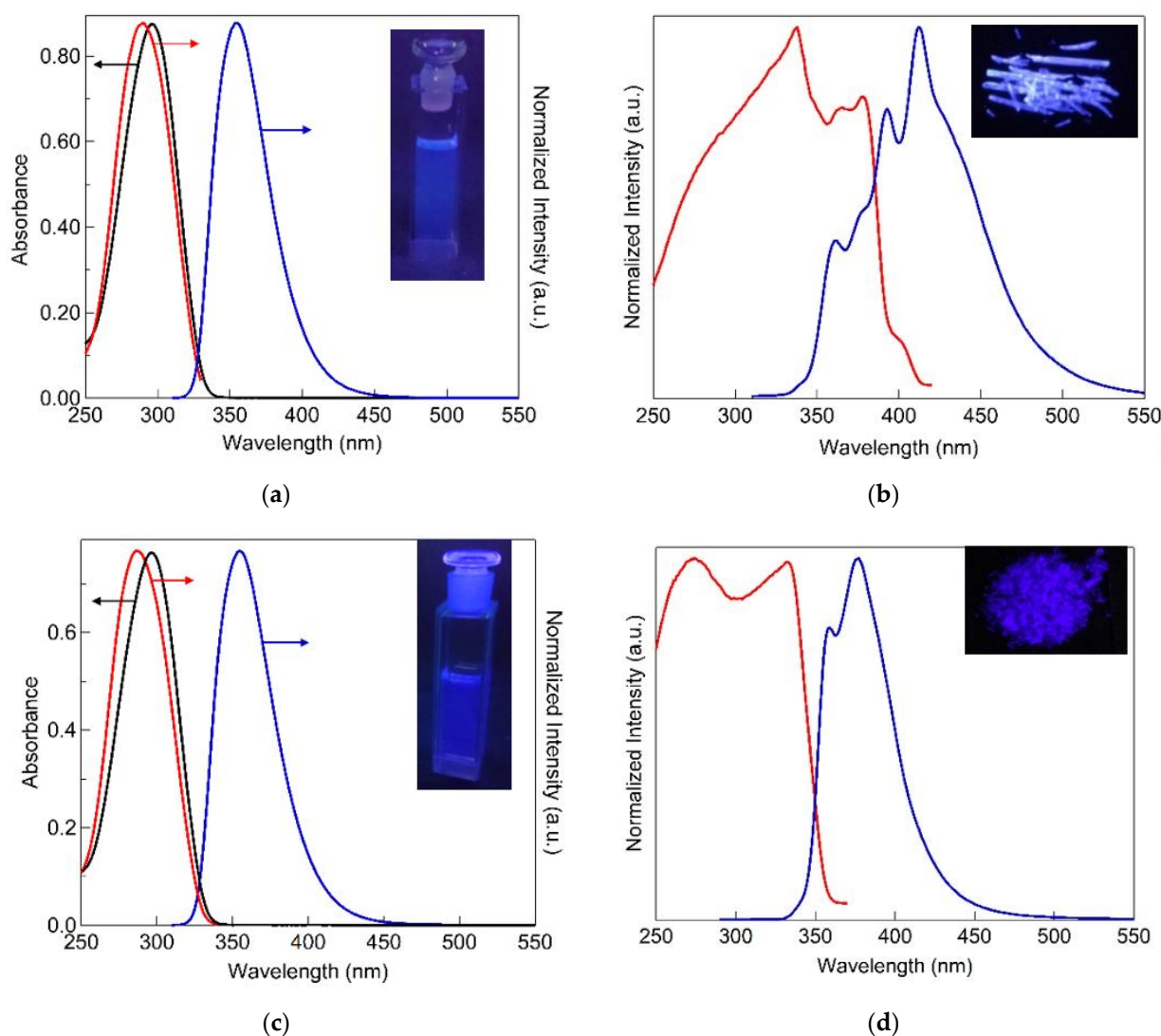


Figure 6. Photophysical properties of biphenylacetylene compounds. Absorption (black, $2.0 \times 10^{-5} \text{ mol L}^{-1}$), corrected photoluminescence (blue, $2.0 \times 10^{-6} \text{ mol L}^{-1}$, $\lambda_{\text{ex}} = 313 \text{ nm}$), and excitation (red, $\lambda_{\text{em}} = 355 \text{ nm}$, $2.0 \times 10^{-6} \text{ mol L}^{-1}$) spectra of (a) **5-BPTMS** and (c) **6-BPTMS** in CH_2Cl_2 solution. Excitation (red) and corrected photoluminescence (blue) spectra of (b) **5-BPTMS** and (d) **6-BPTMS** in crystals. Insets: corresponding photographs of the solutions and crystals under UV irradiation at 365 nm.

In contrast, for the **5-BPTMS** crystal, the luminescence band was broader than that in the solution, suggesting that the luminescence spectrum of the **5-BPTMS** crystal contained at least two luminescence bands at ~ 370 and 410 nm . Similar to **6-BPTMS**, the band at $\sim 370 \text{ nm}$ was a monomer emission with vibronic structures and corresponded to the band observed in a dilute solution. However, the luminescence at longer wavelengths was likely emitted by molecular aggregates. As aforementioned, the biphenyl moiety of **5-BPTMS** formed the coplanar structure in the Cry, and that allows it to form the ground state aggregates. The ground state aggregates can be considered as pre-excimer formation sites, and they become excited aggregates, such as excimer, by photoexcitation, resulting in luminescence at longer wavelength [36–44]. In the Cry, **5-BPTMS** molecules may form several types of the ground state aggregates. Different from the excimer in solutions, the structural relaxation of the excited aggregates cannot occur in the Cry phase owing to the restriction by the lattice. Therefore, the complicated spectral shape was observed in the luminescence in the **5-BPTMS** Cry (Figure 6b).

As shown in Table 1, some components in the **6-BPTMS** crystal have a large dihedral angle of 30.48° , which is similar to that of the optimized structure (37.98°). In contrast, small dihedral angles (9.17° and 11.37°) were observed for the **5-BPTMS** crystal. Thus, **5-BPTMS** molecules can pack more tightly than **6-BPTMS** molecules in crystals, facilitating the formation of aggregates. The densities of the crystals estimated from the crystallographic data (1.061 g cm^{-3} for **5-BPTMS** and 1.032 g cm^{-3} for **6-BPTMS**) are also consistent with this packing behavior. Therefore, the crystallographic data strongly support our hypothesis regarding the photoluminescence behavior of the compounds in crystals.

To further investigate the luminescence behavior of the materials, the luminescence lifetimes (τ) and quantum yields (Φ) were measured in the crystals at room temperature, and the results are summarized in Table 2. Although the spectral shapes differed, both compounds showed similar luminescence lifetimes ($\sim 1.6\text{ ns}$) in crystals; thus, the observed luminescence can be considered to be fluorescence (Figure S7). The Φ values for the crystals of these compounds were relatively high (22% for **5-BPTMS** and 30% for **6-BPTMS**).

3.4. Photoluminescence Behavior in LC Phases

To determine the effects of the aggregated structures (i.e., phase structures) on the luminescence behavior, the photoluminescence spectra were recorded at various temperatures. Figure 7 shows the luminescence spectra of **5-BPTMS** and **6-BPTMS** at various temperatures during the cooling process. The compounds exhibited strong emissions at high temperatures in the LC and Iso phases. Compared with the aforementioned emission spectra in the crystals, slight changes in the spectral shape were observed in the SmeA and Iso phases for **5-BPTMS**, with the relative intensity of the shorter wavelength band becoming larger than that of the longer wavelength band. However, no significant changes in spectral shape were observed for **6-BPTMS** in the LC and Iso phases. As mentioned above, the **5-BPTMS** crystal shows dual emissions from monomers and aggregates. Thus, the luminescence behavior suggests that a portion of the aggregates formed in the crystal dissociated in the LC and Iso phases. In contrast, **6-BPTMS** showed only monomer emission in the Cry phase, and the luminescence spectrum did not change in the LC and Iso phases.

In Figure 7c,d, the luminescence intensities at 391 nm are plotted as a function of temperature. In the Cry phase, the photoluminescence intensity of each compound decreased slightly as the temperature increased. This type of temperature dependence for the luminescence intensity is a common phenomenon, known as thermal quenching, which originates from an increase in the nonradiative relaxation of excited states with increasing temperature owing to thermally activated molecular motion. However, in the SmeA phase, the luminescence intensity increased with increasing temperature. Furthermore, in the Iso phase, the luminescence intensity was almost twice that in the Cry phase. This negative thermal quenching of the luminescence, where the intensity of photoluminescence increases with increasing temperature, is an abnormal phenomenon that has occasionally been observed in inorganic materials, such as semiconductor nanomaterials, and metal-organic frameworks [45–49]. Generally, the luminescence intensity of organic materials is reduced by aggregation because the excited states of molecular aggregates are less emissive than those of their monomeric forms [4,5]. Therefore, we assume that less emissive aggregates are formed in the **5-BPTMS** crystal and nonemissive aggregates are formed in the **6-BPTMS** crystal, and that these aggregates dissociate in the LC and Iso phases at high temperatures. As discussed above, this assumption is consistent with the temperature dependence observed for the luminescence spectral shape in these systems.

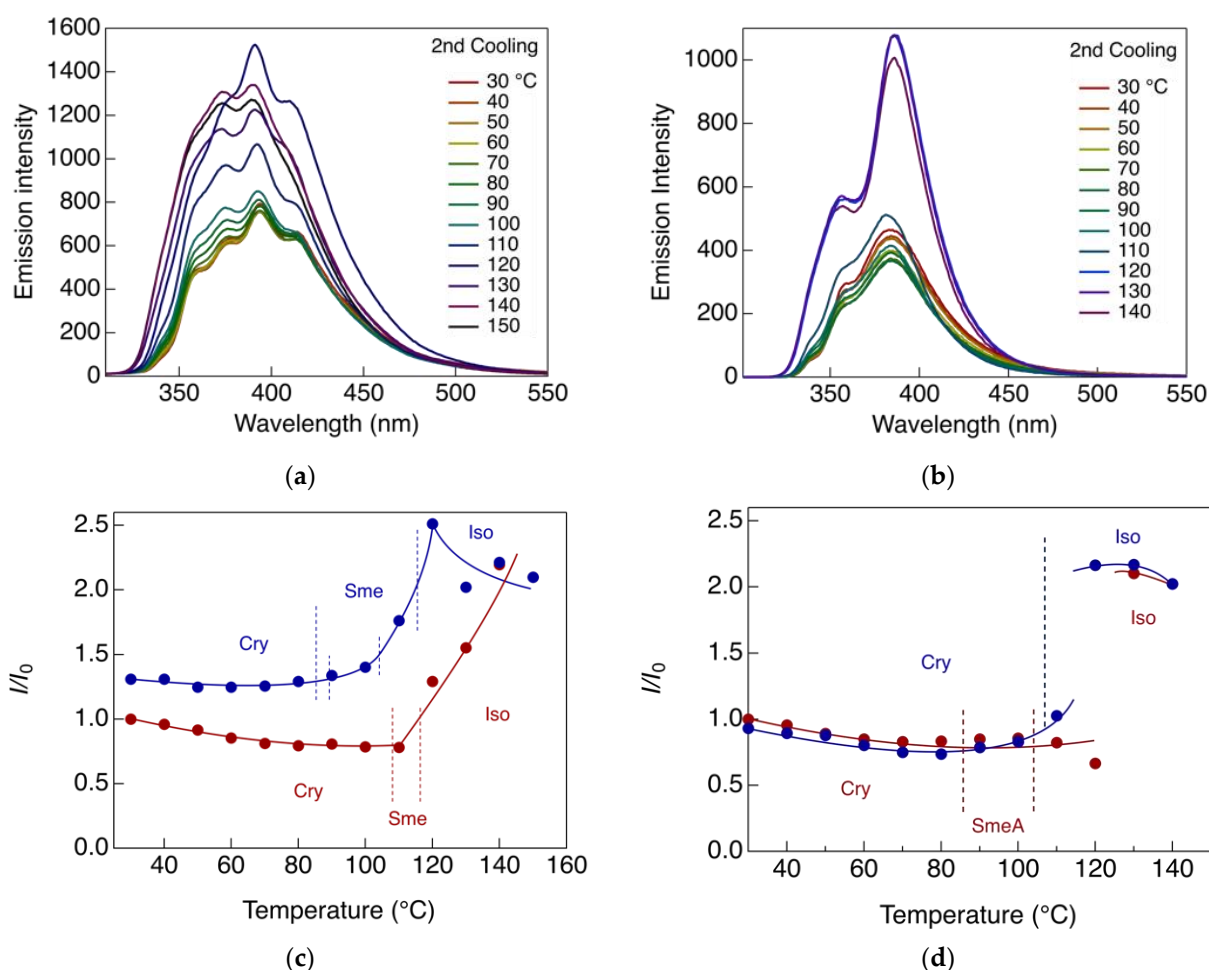


Figure 7. Photoluminescence behavior of biphenylacetylene compounds at various temperatures. Photoluminescence spectra of (a) **5-BPTMS** and (b) **6-BPTMS** at various temperatures during the 2nd cooling process ($\lambda_{\text{ex}} = 296$ nm). Relative emission intensity (I/I_0 , where I_0 is the intensity at 30 °C during the heating process) of (c) **5-BPTMS** and (d) **6-BPTMS** at 391 nm as a function of temperature (red, 2nd heating scan; blue, 2nd cooling scan).

To gain further insight into the origin of this abnormal phenomenon, the luminescence spectra were obtained in a mixed solvent system of good and poor solvents (Figure S8). Both compounds showed good solubility in THF but were insoluble in water; thus, increasing the water fraction in the mixed solvent caused the aggregation of the molecules. As shown in Figure S8b, the luminescence intensity gradually decreased with increasing water fraction owing to molecular aggregation. These results indicate that neither compound showed AIE activity; instead, both compounds showed ACQ. For **5-BPTMS**, a slight blue shift was observed at >80 vol% water, as aggregates were formed owing to the polarity effects of the solvent. In addition, at >80 vol% water, the $\lambda_{\text{max}}^{\text{em}}$ and spectral shape of **5-BPTMS** differed from that observed for the crystal (Figure 6) because the crystal packing structure depended on the crystallization conditions or crystal size [28]. Compound **6-BPTMS** exhibited a similar blue shift upon increasing the water fraction. However, in this case, the luminescence band observed at ~400 nm at 80 vol% water was the same as that observed for the crystal.

The observation of ACQ properties for these materials supported our proposed negative thermal quenching mechanism. In the crystal, owing to dense packing, the molecules form aggregates. Because both materials have ACQ properties, the aggregates are less- or nonemissive. In the Cry phase, the materials exhibit normal thermal quenching, and the luminescence intensity decreases with increasing temperature. However, the less- or nonemissive aggregates dissociate by Cry-to-LC and LC-to-Iso phase transitions, and the

resultant monomeric compounds show intense luminescence at high temperatures. As the molecules are packed more densely in the SmeA LC phase than in the Iso phase, the most intense luminescence is produced by the Iso phase.

Here, it is important to compare the emission behavior of the present materials with conventional LC compounds with the biphenyl core, e.g., 4'-*n*-pentyl-4-cyanobiphenyl (**5CB**) [50–53]. It was reported that **5CB** exhibited UV fluorescence at ~330 nm in dilute solutions (10^{-6} mol L $^{-1}$) [51]. Comparing the $\lambda_{\max}^{\text{em}}$ with **5-BPTMS** and **6-BPTMS** in solutions, the $\lambda_{\max}^{\text{em}}$ of **5CB** appeared at shorter wavelength due to the electron-withdrawing nature of the cyano group. In the concentrated solution (10^{-1} mol L $^{-1}$) and the nematic LC phase (at room temperature), **5CB** showed intense luminescence at ~400 nm, and this luminescence was attributed to the excimer emission. This red-shift of the $\lambda_{\max}^{\text{em}}$ in the condensed phases is similar luminescence behavior to **5-BPTMS**, and it supports that its luminescence in the condensed phases is emitted from the aggregates. However, in contrast to **5-BPTMS** and **6-BPTMS**, the luminescence intensity of **5CB** decreased in the Iso phase. Therefore, we conclude that the negative thermal quenching effect observed in the present materials is not common in the luminescent LC materials.

4. Conclusions

In this study, we discussed the effects of phase transitions, namely, changes in the aggregated structures, on the luminescence behavior of LC materials based on biphenylacetylene with a bulky trimethylsilyl terminal group and a flexible alkoxy chain. No effect of the terminal chain length on the photoluminescence was observed in the solution; however, the luminescence spectral shape in the crystals showed a clear dependence on the terminal chain length, meaning that photoluminescence of the present materials dramatically depends on the intermolecular interactions (aggregated structure). Notably, these materials showed the negative thermal quenching of the luminescence in condensed phases. In particular, in the Iso phase at high temperatures, the luminescence intensity increased considerably. In the crystals, the molecules formed less- or nonemissive aggregates. However, these aggregates dissociated by Cry-to-LC and LC-to-Iso phase transitions, and the resultant monomeric compounds showed intense luminescence at high temperatures. We believe that this phenomenon can pave the way for the development of new material design concepts for useful luminescent materials at high temperatures.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/cryst11121555/s1>, Table S1: Crystallographic data, Figure S1: ^1H NMR spectra; Figure S2: ESI-MS spectra; Figure S3: Calculated molecular structure; Figures S4 and S5: Molecular structure and selected interatomic distances between neighboring molecules; Figure S6: TG/DTA thermograms; Figure S7: Luminescence decay profile; Figure S8: Luminescence spectra in THF/water mixtures.

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