



# Article Unsymmetrical and C<sub>3</sub>-Symmetrical Partially Fluorinated Hexaarylbenzenes: Effect of Terminal Alkoxy Chain Length on Photophysical and Thermophysical Behavior

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Abstract: Solution-state photoluminescence (PL) is affected by the electronic state; however, solidstate PL varies widely depending on the aggregated state. Although the synthesis and photophysical properties of unsymmetrical and C<sub>3</sub>-symmetrical hexaarylbenzenes (HABs) have been reported, the influence of their terminal alkoxy chains on their physical properties remains unclear. Therefore, we synthesized a series of unsymmetrical and  $C_3$ -symmetrical partially fluorinated HABs with different alkoxy chains and investigated the effects of alkoxy chain length on the thermophysical and photophysical properties. While investigating phase transition behavior, the ethoxy-substituted unsymmetrical derivative revealed a columnar liquid-crystalline phase, whereas the other derivatives only exhibited a phase transition between crystalline and isotropic phases. While evaluating PL behavior, both the unsymmetrical and C<sub>3</sub>-symmetrical analogs exhibited relatively strong blue PL, independent of the alkoxy chain length. Through-space  $\pi$ -conjugation caused the PL spectra of  $C_3$ -symmetrical derivatives to redshift compared to those of unsymmetrical derivatives. Partially fluorinated HABs exhibited relatively strong fluorescence, even in the crystalline state, depending on the alkoxy chain length, owing to the formation of various aggregated structures. Crystalline fluorinated HABs exhibited photochromism, resulting in the appearance of long-wavelength PL bands when exposed to ultraviolet (UV) irradiation, making them promising candidates for PL sensing materials for UV detection.

**Keywords:** fluorine; hexaarylbenzenes; phase transition behavior; photoluminescence; dual-state photoluminescence; photochromism

#### 1. Introduction

Dual-state-emitting (DSE) molecules, emitting luminescence not only in solution but also in solid state, have been used in various applications [1,2]. Therefore, the development of new DSE molecules has been extensively investigated [3,4]. Although extended  $\pi$ conjugation within the molecular structure is necessary for the development of solutionstate luminophores, their luminescence disappears in the solid state owing to the  $\pi/\pi$ stacking formation [5,6]. In contrast, typical solid-state luminescent materials that utilize the aggregation-induced emission (AIE) phenomenon do not emit luminescence in the solution state because they rely on the restriction of molecular motion in the aggregated states [7–9]. Solution-state luminescent materials and solid-state luminescent materials require distinct molecular designs. Therefore, an efficient molecular design for DSE molecules is highly desired.

Hexaarylbenzenes (HABs) have six aromatic structures on the benzene ring, with the introduced aromatic rings twisted away from the central benzene core owing to steric repulsion between the adjacent aromatic rings. Therefore, the HAB scaffold is a well-known AIE luminophore [10,11]. HABs exhibit distinct photophysical properties owing to strong interactions between peripherally adjacent aromatic rings via space  $\pi$  conjugation.



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**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Our group recently synthesized and evaluated photophysical behavior for three each of unsymmetrical 1,2,4-substituted HABs and  $C_3$ -symmetrical 1,3,5-substituted HABs [12]. The first is HAB molecules that do not have any fluorine atoms on the lateral sides of the peripheral aromatic rings (Figure 1a); the second is a partially fluorinated HAB molecule in which fluorine atoms are introduced only on the lateral sides of the aromatic rings with a CF<sub>3</sub> terminal group among the peripheral aromatic rings (Figure 1b); and the third is polyfluorinated HAB molecules in which the lateral sides of the peripheral aromatic rings are perfluorinated (Figure 1c). The photophysical property evaluation of the above three unsymmetrical and  $C_3$ -symmetrical HABs revealed that partially fluorinated HABs exhibited distinct photophysical properties, such as different photoluminescence (PL) wavelengths due to differences in molecular symmetry and higher fluorescence quantum yields ( $\Phi_{PL}$ ) when compared to less-fluorinated and polyfluorinated analogs.



**Figure 1.** Research concept and chemical structures of (**a**–**c**) various hexaarylbenzenes reported in our previous studies [12] and (**d**) partially fluorinated hexaarylbenzenes, e.g., **1b**–**f** and **2b**–**f**, with a various length of alkoxy chain used in this study.

The flexible chains introduced at the end of the peripheral ring of HAB have a significant effect on the molecular aggregated structures, contributing to dramatic alterations in solid-state luminescence properties and the emergence of liquid-crystalline states [13,14], in which luminescent liquid crystals with both properties are well recognized as one of the promising functional materials [15]. As part of our research project on partially fluorinated HAB-based fluorescent molecules, we synthesized unsymmetrical partially fluorinated HABs 1 with alkoxy chain terminals of various lengths and  $C_3$ -symmetrical analogs 2 and investigated their thermophysical and photophysical properties (Figure 1d).

#### 2. Materials and Methods

# 2.1. General

Melting temperature  $(T_m)$  was measured using a DSC-60 differential scanning calorimeter (SHIMADZU, Kyoto, Japan) under a nitrogen atmosphere at a scan rate of  $5 \,^{\circ}$ C min<sup>-1</sup> or 10 °C min<sup>-1</sup>. <sup>1</sup>H nuclear magnetic resonance (NMR) (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were acquired using an AVANCE III 400 NMR spectrometer (Bruker, Rheinstetten, Germany) in a chloroform-d (CDCl<sub>3</sub>) solution, and chemical shifts were reported in parts per million (ppm) based on the residual protons or carbon in the NMR solvent. <sup>19</sup>F NMR (376 MHz) spectra were acquired using an AVANCE III 400 NMR spectrometer (Bruker, Rheinstetten, Germany) in CDCl<sub>3</sub> solution with CFCl<sub>3</sub> ( $\delta_F = 0$  ppm) or C<sub>6</sub>F<sub>6</sub> ( $\delta_F = -163$  ppm) as an internal standard. Infrared (IR) spectra were recorded using the KBr method on an FTIR-4100 type A spectrometer (JASCO, Tokyo, Japan). All IR spectra are reported in wavenumber (cm<sup>-1</sup>) units. High-resolution mass spectra (HRMS) were recorded on a JMS700MS spectrometer (JEOL, Tokyo, Japan) using the fast atom bombardment (FAB) method. Before use, all chemicals were reagent-grade and purified using standard methods. The progress of the reaction was monitored by thin-layer chromatography (TLC) on silica gel TLC plates (Merck, Silica Gel, 60F254; Kenilworth, NJ, USA). Column chromatography was performed using silica gel (FUJIFILM Wako Pure Chemical Corporation, Wako-gel<sup>®</sup> 60 N, 38 μm to 100 μm; Osaka, Japan).

#### 2.2. Materials

Unsymmetrical partially fluorinated HABs 1a-f and symmetrical analogs 2a-f were synthesized using cobalt-catalyzed [2 + 2 + 2] cyclotrimerization of donor- $\pi$ -acceptortype fluorinated tolanes 3a-f, according to the reaction sequence shown in Scheme 1 [12]. Although the synthetic procedures and compound characterization data for 1a and 2a with a methoxy substituent on the electron-rich aromatic ring have been reported previously [12], the synthetic methods and characterization data for 1b-f and 2b-f are described below. The <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F-NMR spectra of 1b-f and 2b-f are demonstrated in Figures S2–S30, and their spectra proved that the compounds were of sufficient purity to enable evaluation of their photophysical behavior.



**Scheme 1.** Synthesis of unsymmetrical fluorinated HABs **1b**–**f** and the  $C_3$ -symmetrical analogs **2b**–**f** using unsymmetrical partially fluorinated tolanes **3b**–**f** via a cobalt-catalyzed [2 + 2 + 2] cyclotrimerization.

#### 2.3. Typical Synthetic Procedures for 1,2,4-Adduct 1b and 1,3,5-Adduct 2b

In a two-necked round-bottomed flask with a Teflon<sup>®</sup>-coated stirring bar and reflux condenser, placed **3b** (1.45 g, 4.00 mmol) and  $Co_2(CO)_8$  (0.28 g, 0.80 mmol) in 50 mL of 1,4-dioxane. The whole was heated to 120 °C and stirred for 16 h. Following the specified reaction time, the solvent was removed using a rotary evaporator under reduced pressure, and the metal catalyst residues were removed from the crude product by flash column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as eluent. The solvent was removed using a rotary evaporator under reduced pressure, and the residue was purified via silica-gel chromatography using elution with hexane/ethyl acetate (20/1, v/v), followed by recrystallization from CH<sub>2</sub>Cl<sub>2</sub> and methanol (1/1, v/v) to afford **1b** (0.56 g, 0.52 mol, 39% yield) and **2b** (0.46 g, 0.42 mol, 32% yield) as white solids.

# 2.3.1. 1,2,4-Tris(4-ethoxyphenyl)-3,5,6-tris{4-(trifluoromethyl)-2,3,5,6-tetrafluorophenyl}benzene (**1b**)

Yield: 39% (white solid);  $T_{\rm m}$ : 257 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.32 (t, J = 6.8 Hz, 6H), 1.33 (t, J = 6.8 Hz, 3H), 3.88 (q, J = 6.8 Hz, 4H), 3.91 (q, J = 6.8 Hz, 2H), 6.54–6.58 (m, 4H), 6.63 (d, J = 8.8 Hz, 2H), 6.82–6.88 (m, 4H), 6.94 (d, J = 8.8 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  14.5, 14.6, 63.2, 63.4, 108.0–111.0 (m), 113.7, 114.1, 120.3 (q, J = 276.5 Hz), 121.0–123.2 (m), 125.2 (q, J = 262.6 Hz), 128.4, 128.7, 128.9, 129.1, 129.3, 129.5, 130.1, 130.4, 141.8–142.6 (m), 142.7, 143.1, 144.3–145.1 (m), 144.9, 158.07, 158.09, 158.8; <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  –56.78 (t, J = 20.1 Hz, 3F), -56.86 (t, J = 21.7 Hz, 6F), -135.72 to –135.91 (m, 2F), -136.07 to –136.23 (m, 4F), -140.29 to –140.54 (m, 4F), -141.58 to –141.92 (m, 2F); IR (KBr):  $\nu$  2987, 2933, 1482, 1394, 1250, 1154, 1047, 876 cm<sup>-1</sup>; HRMS (FAB+) m/z [M]<sup>+</sup> calcd for C<sub>51</sub>H<sub>27</sub>F<sub>21</sub>O: 1086.1625; found: 1086.1624.

2.3.2. 1,3,5-Tris(4-ethoxyphenyl)-2,4,6-tris{4-(trifluoromethyl)-2,3,5,6-tetrafluorophenyl}benzene (**2b**)

Yield: 32% (white solid);  $T_{\rm m}$ : 240 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.34 (t, J = 7.2 Hz, 9H), 3.91 (q, J = 7.2 Hz, 6H), 6.62 (d, J = 8.8 Hz, 6H), 6.95 (d, J = 8.8 Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  14.5, 63.4, 108.0–110.0 (m), 114.1, 120.5 (q, J = 274.3 Hz), 123.4 (t, J = 19.1 Hz), 127.3, 128.6, 128.7, 141.8–142.2 (m), 144.5, 144.6, 158.8; <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  –56.80 (t, J = 21.8 Hz, 9F), –135.67 to –135.86 (m, 6F), –141.48 to –141.74 (m, 6F); IR (KBr):  $\nu$  3045, 2990, 2934, 1416, 1393, 1289, 1146, 1051, 988, 877 cm<sup>-1</sup>; HRMS (FAB+) m/z [M]<sup>+</sup> calcd for C<sub>51</sub>H<sub>27</sub>F<sub>21</sub>O: 1086.1625; found: 1086.1627.

2.3.3. 1,2,4-Tris{4-(trifluoromethyl)-2,3,5,6-tetrafluorophenyl}-3,5,6-tris(4-propoxyphenyl)-benzene (**1c**)

Yield: 28% (white solid);  $T_{\rm m}$ : 237 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.97 (t, J = 7.2 Hz, 6H), 0.98 (t, J = 7.2 Hz, 4H), 1.73 (quin, J = 7.2 Hz, 6H), 3.78 (t, J = 7.2 Hz, 4H), 3.80 (t, J = 7.2 Hz, 2H), 6.52–6.58 (m, 4H), 6.62 (d, J = 8.8 Hz, 2H), 6.77–6.85 (m, 4H), 6.89 (d, J = 8.8 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  10.29, 10.34, 22.38, 22.43, 69.3, 69.4, 108.0–111.0 (m), 113.8, 114.2, 120.4 (q, J = 263.3 Hz), 121.0–123.2 (m), 125.2 (q, J = 261.1 Hz), 128.4, 128.7, 128.9, 129.3, 129.5, 130.0, 130.4, 141.8–142.6 (m), 142.7, 143.1, 144.2–145.3 (m), 158.2, 159.0; <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  –56.72 to –56.97 (m, 9F), –135.68 to –135.88 (m, 2F), –135.99 to –136.20 (m, 4F), –140.28 to –140.64 (m, 4F), –141.60 to –141.92 (m, 2F); IR (KBr):  $\nu$  3042, 2974, 2882, 1496, 1247, 1153, 1071, 933, 876 cm<sup>-1</sup>; HRMS (FAB+) m/z [M]+ calcd for C<sub>54</sub>H<sub>33</sub>F<sub>21</sub>O<sub>3</sub>: 1128.2094; found: 1128.2104.

2.3.4. 1,3,5-Tris{4-(trifluoromethyl)-2,3,5,6-tetrafluorophenyl}-2,4,6-tris(4-propoxyphenyl)-benzene (**2c**)

Yield: 30% (white solid); *T*<sub>m</sub>: 209 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.98 (t, *J* = 7.2 Hz, 9H), 1.68–1.78 (m, 6H), 3.80 (t, *J* = 6.4 Hz, 6H), 6.63 (d, *J* = 8.8 Hz, 6H), 6.94 (d, *J* = 8.8 Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 10.3, 22.4, 108.0–110.0 (m), 114.2, 120.5 (q, *J* = 272.8 Hz), 123.4 (t, *J* = 19.7 Hz), 127.2, 128.5, 128.7, 141.7–142.3 (m), 144.5, 144.6, 159.0; <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ –56.84 (t, *J* = 21.8 Hz, 9F), 135.70 to –135.86 (m, 6F), –141.49 to –141.76 (m, 6F); IR (KBr):  $\nu$  2971, 2881, 1479, 1416, 1252, 1140, 1049, 991, 877 cm<sup>-1</sup>; HRMS (FAB+) m/z [M]+ calcd for C<sub>54</sub>H<sub>33</sub>F<sub>21</sub>O<sub>3</sub>: 1128.2094; found: 1128.2105.

2.3.5. 1,2,4-Tris(4-butoxyphenyl)-3,5,6-tris{4-(trifluoromethyl)-2,3,5,6-tetrafluorophenyl}benzene (1d)

Yield: 29% (white solid);  $T_{\rm m}$ : 158 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.929 (t, J = 7.2 Hz, 3H), 0.934 (t, J = 7.6 Hz, 6H), 1.35–1.48 (m, 6H), 1.68 (quin, J = 7.2 Hz, 6H), 3.81 (t, J = 6.4 Hz, 4H), 3.84 (t, J = 6.4 Hz, 2H), 6.52–6.58 (m, 4H), 6.62 (d, J = 8.8 Hz, 2H), 6.77–6.85 (m, 4H), 6.89 (d, J = 8.8 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  13.7, 13.8, 19.12, 19.15, 31.1, 31.2, 67.6, 67.7, 108.0–111.0 (m), 113.8, 114.2, 120.4 (q, J = 275.8 Hz), 121.0–123.2 (m), 125.2 (q, J = 259.0 Hz), 128.4, 128.7, 129.0, 129.3, 129.5, 130.1, 130.4, 141.5–142.6 (m), 142.7, 143.1, 144.1–145.2 (m), 144.9, 158.27, 158.29, 159.0; <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  –56.70 to –56.98 (m, 9F), –135.71 to –135.88 (m, 2F), –135.98 to –136.26 (m, 4F); IR (KBr):  $\nu$  3040, 2968, 2878, 1428, 1384, 1250, 1158, 1070, 988, 877 cm<sup>-1</sup>; HRMS (FAB+) m/z [M]+ calcd for C<sub>57</sub>H<sub>39</sub>F<sub>21</sub>O<sub>3</sub>: 1170.2564; found: 1170.2571.

2.3.6. 1,3,5-Tris (4-butoxyphenyl)-2,4,6-tris {4-(trifluoromethyl)-2,3,5,6-tetrafluorophenyl} benzene (2d)

Yield: 26% (white solid);  $T_{\rm m}$ : 172 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.93 (t, J = 7.6 Hz, 9H), 1.37–1.48 (m, 6H), 1.69 (quin, J = 7.6 Hz, 6H), 3.84 (t, J = 6.8 Hz, 6H), 6.63 (d, J = 8.4 Hz, 6H), 6.94 (d, J = 8.4 Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  13.7, 19.1, 31.1, 67.7, 108.0–110.0 (m), 114.2, 120.5 (q, J = 266.9 Hz), 123.5 (t, J = 19.8 Hz), 127.3, 128.6, 128.7, 141.7–142.4 (m), 144.5, 144.6, 159.0; <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  –56.82 (t, J = 21.8 Hz, 9F), –135.68 to –135.86 (m, 6F), –141.50 to –141.71 (m, 6F); IR (KBr):  $\nu$  3042, 2964, 2875, 1610, 1481, 1162, 1070, 992, 879 cm<sup>-1</sup>; HRMS (FAB+) m/z [M]+ calcd for C<sub>57</sub>H<sub>39</sub>F<sub>21</sub>O<sub>3</sub>: 1170.2564; found: 1170.2565.

2.3.7. 1,2,4-Tris{4-(trifluoromethyl)-2,3,5,6-tetrafluorophenyl}-3,5,6-tris(4-pentyloxyphenyl)benzene (**1e**)

Yield: 5% (white solid);  $T_{\rm m}$ : 119 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.87–0.93 (m, 9H), 1.28–1.44 (m, 12H), 1.69 (quin, *J* = 7.6 Hz, 6H), 3.81 (t, *J* = 6.8 Hz, 4H), 3.83 (t, *J* = 6.8 Hz, 2H), 6.52–6.58 (m, 4H), 6.62 (d, *J* = 8.8 Hz, 2H), 6.77–6.84 (m, 4H), 6.89 (d, *J* = 8.8 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  13.91, 13.94, 22.39, 22.41, 28.0, 28.1, 28.7, 28.8, 67.9, 68.0, 108.0–111.0 (m), 113.7, 114.1, 120.4 (q, *J* = 289.8 Hz), 121.0–123.2 (m), 128.4, 128.7, 129.0, 129.2, 129.5, 130.0, 130.4, 141.8–142.5 (m), 142.7, 143.1, 144.4 to 145.2 (m), 144.9, 158.2, 158.3, 159.0, one CF<sub>3</sub> carbon signal was not detected due to complex splitting induced by spin-spin coupling between carbon and fluorine atoms; <sup>19</sup>F NMR (CDCl<sub>3</sub>, C<sub>6</sub>F<sub>6</sub>):  $\delta$  –57.48 to –57.73 (m, 9F), –136.46 to –136.64 (m, 2F), –136.76 to –136.98 (m, 4F), –141.02 to –141.43 (m, 4F), –142.30 to –142.62 (m, 2F); IR (KBr):  $\nu$  2963, 2874, 1660, 1496, 1251, 1154, 1107, 1025, 990, 853 cm<sup>-1</sup>; HRMS (FAB+) *m*/*z* [M]+ calcd for C<sub>60</sub>H<sub>45</sub>F<sub>21</sub>O<sub>3</sub>: 1212.3033; found: 1212.3039.

2.3.8. 1,3,5-Tris {4-(trifluoromethyl)-2,3,5,6-tetrafluorophenyl}-2,4,6-tris (4-pentyloxyphenyl)<br/>benzene (2e)

Yield: 15% (white solid);  $T_{\rm m}$ : 126 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.89 (t, J = 7.2 Hz, 9H), 1.29–1.43 (m, 12H), 1.69 (quin, J = 6.8 Hz, 6H), 3.82 (t, J = 6.8 Hz, 6H), 6.63 (d, J = 8.8 Hz, 6H), 6.89 (d, J = 8.8 Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  13.9, 22.4, 28.0, 28.7, 68.0, 107.8–109.6 (m), 114.2, 120.5 (q, J = 272.8 Hz), 123.4 (t, J = 17.6 Hz), 127.2, 128.5, 128.7, 141.4–142.5 (m), 144.5, 144.6, 159.0; <sup>19</sup>F NMR (CDCl<sub>3</sub>, C<sub>6</sub>F<sub>6</sub>):  $\delta$  –57.40 (t, J = 20.3 Hz, 9F), –136.18 to –136.36 (m, 6F), –142.15 to –142.40 (m, 6F); IR (KBr):  $\nu$  3048, 2926, 1660, 1469, 1053, 980, 877 cm<sup>-1</sup>; HRMS (FAB+) m/z [M]+ calcd for C<sub>60</sub>H<sub>45</sub>F<sub>21</sub>O<sub>3</sub>: 1212.3033; found: 1212.3038.

2.3.9. 1,2,4-Tris {4-(trifluoromethyl)-2,3,5,6-tetrafluorophenyl}-3,5,6-tris (4-hexyloxyphenyl)benzene  $({\bf 1f})$ 

Yield: 14% (white solid);  $T_{\rm m}$ : 112 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.88 (t, J = 7.2 Hz, 9H), 1.25–1.46 (m, 18H), 1.6 (quin, J = 8.0 Hz, 6H), 3.81 (t, J = 7.2 Hz, 4H), 3.82 (t, J = 7.2 Hz, 2H), 6.52–6.58 (m, 4H), 6.62 (d, J = 8.8 Hz, 2H), 6.78–6.84 (m, 4H), 6.89 (d, J = 8.8 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  13.96, 13.97, 22.5, 25.6, 29.0, 29.1, 31.6, 67.9, 68.0, 107.0–112.0 (m), 113.7, 114.1, 120.8 (q, *J* = 291.2 Hz), 121.0–123.2 (m), 128.4, 128.9, 129.2, 130.0, 130.4, 141.4–143.0 (m), 142.7, 143.1, 144.4–145.3 (m), 144.9, 158.2, 158.3, 159.0, one CF<sub>3</sub> carbon signal was not detected due to complex splitting induced by spin-spin coupling between carbon and fluorine atoms; <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  –56.12 to –56.42 (m, 9F), –135.12 to –135.30 (m, 2F), –135.42 to –135.64 (m, 4F), –139.64 to –140.02 (m, 4F), –141.01 to –141.26 (m, 2F); IR (KBr):  $\nu$  2960, 1661, 1482, 1251, 1146, 989, 877 cm<sup>-1</sup>; HRMS (FAB+) *m*/*z* [M]<sup>+</sup> calcd for C<sub>63</sub>H<sub>51</sub>F<sub>21</sub>O<sub>3</sub>: 1254.3503; found: 1254.3511.

# 2.3.10. 1,3,5-Tris{4-(trifluoromethyl)-2,3,5,6-tetrafluorophenyl}-2,4,6-tris(4-hexyloxyphenyl)benzene (**2f**)

Yield: 19% (white solid);  $T_{\rm m}$ : 104 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.88 (t, J = 6.8 Hz, 9H), 1.25–1.46 (m, 18H), 1.70 (quin, J = 6.8 Hz, 6H), 3.83 (t, J = 6.8 Hz, 6H), 6.62 (d, J = 8.8 Hz, 6H), 6.94 (d, J = 8.8 Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  13.9, 22.5, 25.6, 29.0, 31.5, 68.0, 107.4–110.6 (m), 114.2, 120.5 (q, J = 274.4 Hz), 123.4 (t, J = 18.3 Hz), 127.2, 128.5, 128.7, 141.7–142.5 (m), 144.5, 144.6, 159.0; <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  –56.81 (t, J = 20.3 Hz, 9F), –135.69 to –135.87 (m, 6F), –141.45 to –141.80 (m, 6F); IR (KBr):  $\nu$  3044, 2956, 2874, 1658, 1483, 1143, 1027, 984, 877 cm<sup>-1</sup>; HRMS (FAB+) m/z [M]<sup>+</sup> calcd for C<sub>63</sub>H<sub>51</sub>F<sub>21</sub>O<sub>3</sub>: 1254.3503; found: 1254.3503.

#### 2.4. Photophysical Properties

Ultraviolet-visible light absorption spectroscopy was performed using a V-750 absorption spectrometer (JASCO, Tokyo, Japan), and the PL spectra of the solution and crystalline samples were obtained using an RF-6000 spectrofluorophotometer (Shimadzu, Kyoto, Japan). The absolute  $\Phi_{PL}$  of the solutions and crystalline samples were determined using a Quantaurus-QY absolute PL quantum yield spectrometer (C11347-01; Hamamatsu Photonics, Hamamatsu, Japan). The absolute PLQY measurement system was tested using sodium salicylate ( $\Phi = 0.44$  for 350 nm excitation light) as a standard and proved satisfactory [16]. The PL lifetimes were measured using a Quantaurus-Tau fluorescence lifetime spectrometer (C11367-34, Hamamatsu Photonics, Japan).

#### 2.5. Phase Transition Properties

The phase transition behavior was observed using polarizing optical microscopy (POM) using a BX53 microscope (Olympus, Tokyo, Japan) equipped with a heating and cooling stage (10.002 L, Linkam Scientific Instruments, Redhill, UK). The phase sequences and transition enthalpies were determined using DSC-60 Plus (Shimadzu Corporation, Kyoto, Japan) with heating and cooling rates of 5 or 10 °C min<sup>-1</sup> in a N<sub>2</sub> atmosphere.

### 2.6. Theoretical Assessment

Density functional theory (DFT) calculations were performed using the Gaussian 16 (Rev. B.01) suite of programs (Gaussian, Wallingford, CT, USA) [17], and geometry optimizations were performed at the M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p) level of theory [18] with an implicit solvation model, the conductor-like polarizable continuum model (CPCM) [19], for CH<sub>2</sub>Cl<sub>2</sub>. Vertical electronic transitions were calculated using time-dependent DFT at the same level of theory.

#### 3. Results and Discussion

#### 3.1. Thermophysical Behavior

Methoxy-substituted partially fluorinated HABs **1a** and **2a**, previously reported, showed only a phase transition from a crystalline (Cr) to an isotropic (Iso) phase, with  $T_{\rm m}$  values of approximately 271 and 313 °C, respectively [12].  $T_{\rm m}$  is defined here as the temperature at which a Cr phase transitions to another. To clarify the effect of the alkoxy chain length on thermophysical behavior, such as phase transition behavior and phase transition temperature, we evaluated the thermophysical properties of unsymmetrical HABs **1b–f** and  $C_3$ -symmetrical HABs **2b–f**. The phase transition behavior was evaluated using

POM and differential scanning calorimetry (DSC). Figure 2 depicts the DSC thermogram of the second heating–cooling cycle of unsymmetrical **1b**, the POM texture observed at the mesophase, and the thermograms of the second heating process for unsymmetrical **1b–f** and  $C_3$ -symmetrical **2b–f**. Table 1 summarizes the observed thermophysical data.



**Figure 2.** (a) DSC thermogram of unsymmetrical **1b** in the second heating and cooling processes, and (b) POM texture image at 170 °C during the cooling process. (c,d) DSC thermograms of **1b**–**f** and **2b**–**f** during the second heating process and melting temperature.

Unsymmetrical HAB **1b** with ethoxy chains showed only a phase transition from the Cr phase to the Iso phase during heating, indicating that it did not exhibit an LC phase. During cooling, however, a bright and fluidic POM texture was observed between the Cr and Iso phases (Figure 2a), implying that **1b** exhibited monotropic LC characteristics. The POM texture image is dendritic, as shown in Figure 2b, which is typical for the columnar phase. This indicates that the columnar phase is the mesophase that forms during the cooling process in unsymmetrical **1b**. However, unlike unsymmetrical **1b**, *C*<sub>3</sub>-symmetrical **2b** did not exhibit any mesophase. Furthermore, other derivatives, namely unsymmetrical **1c**-**f** and *C*<sub>3</sub>-symmetrical **2c**-**f**, underwent a phase transition from Cr to iso phases during the heating and cooling processes, indicating that there were no LC phases.

Compound	Phase Transition Temperature [°C] (Enthalpy [kJ mol <sup>-1</sup> ]) <sup>1</sup>		Compound	Phase Transition Temperature [°C] (Enthalpy [kJ mol <sup>-1</sup> ]) <sup>1</sup>		
1b	[H]	Cr 257 (28.6) Iso	2b	[H]	Cr 240 (23.4) Iso	
	[C]	Cr 141 (-9.9) Col 176 (-2.8) Iso		[C]	Cr 224 (-9.1) Iso	
1c	[H]	Cr 237 (52.1) Iso	2c	[H]	Cr 209 (43.4) Iso	
	[C]	Cr 132 (-31.3) Iso		[C]	Cr 154 (-29.3) Iso	
1d	[H]	Cr 158 (45.4) Iso	2d	[H]	Cr 172 (25.7) Iso	
	[C]	Cr 96 (-32.7) Iso		[C]	Cr 129 (-20.2) Iso	
1e	[H]	Cr 119 (56.0) Iso	2e	[H]	G 62 (-15.0) Cr 126 (20.3) Iso	
	[C]	Cr 104 (-44.2) Iso		[C]	$G - {}^2$ Iso	
1f	[H]	Cr 112 (60.7) Iso	2f	[H]	G 44 (-1.2) Cr <sup>1</sup> 58 (-8.1) Cr <sup>2</sup> 104 (24.6) Iso	
	[C]	Cr 105 (-69.6) Iso		[C]	$G - {}^2$ Iso	

Table 1. Phase transition behavior of un	symmetrical $1b-f$ and $C_3$ -symmetrical $2b-f$ .
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<sup>1</sup> Determined by DSC under N<sub>2</sub> atmosphere (scan rate: 5 or 10 °C min<sup>-1</sup>) in the second heating [H] and cooling [C] processes. Abbreviations: Cr, crystalline; Col, columnar; G, glassy; Iso, isotropic. <sup>2</sup> There are no clear glass transitions.

Furthermore, the alkoxy chains introduced at the ends of the peripheral aromatic rings exhibited a significant effect on the molecular arrangement, influencing the  $T_{\rm m}$  of each derivative. The  $T_{\rm m}$  of the unsymmetrical and  $C_3$ -symmetrical HABs decreased as the alkoxy chain lengthened from the ethoxy to the hexyloxy chains (Figure 2c,d). This is because, as the chain length increased, the ordered molecular arrangements in the Cr phase were rapidly disrupted by the molecular motion caused via thermal stimulation.

#### 3.2. Photophysical Behavior

#### 3.2.1. Solution State

We investigated the photophysical behavior of unsymmetrical **1b**–**f** and  $C_3$ -symmetrical **2b**–**f** compounds in solution. A solution sample was prepared by dissolving each compound in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) and adjusting the concentration to  $1.0 \times 10^{-5}$  mol L<sup>-1</sup>. Figure 3 depicts the absorption spectra of unsymmetrical **1b**–**f** and  $C_3$ -symmetrical **2b**–**f** in CH<sub>2</sub>Cl<sub>2</sub> solution, theoretical electronic transitions in absorption behavior calculated from quantum chemical calculations [17–19], PL spectra, and a color diagram defined by the Commission Internationale de l'Eclailage (CIE) to visually represent the emitted PL color. The obtained photophysical data are summarized in Table 2.

Table 2. Photophysical data of unsymmetrical 1b-f and  $C_3$ -symmetrical 2b-f in  $CH_2Cl_2$  solution.

Compound	$\lambda_{ m abs}~[ m nm]$ ( $arepsilon~[ m 10^3,$ L mol $^{-1}~ m cm^{-1}$ ]) $^1$	$\lambda_{\mathrm{PL}}  [\mathrm{nm}]^1 \ (\Phi_{\mathrm{PL}})^2$	CIE $(x, y)$	τ [ns]	$k_{ m r}$ [10 <sup>7</sup> , s <sup>-1</sup> ] <sup>3</sup>	$k_{ m nr}[10^7,{ m s}^{-1}]^{4}$	k <sub>r</sub> /k <sub>nr</sub>
1b	276 (27.4)	428 (0.45)	(0.156, 0.071)	5.01	9.04	11.2	0.81
1c	276 (37.1)	427 (0.49)	(0.157, 0.079)	5.06	9.70	10.4	0.93
1d	273 (26.4)	425 (0.61)	(0.155, 0.067)	5.05	12.0	8.00	1.51
1e	272 (34.3)	427 (0.54)	(0.153, 0.051)	4.99	10.8	9.47	1.14
1f	274 (31.1)	426 (0.48)	(0.153, 0.051)	5.06	9.49	10.6	0.89
2b	274 (35.0)	392 (0.40)	(0.158, 0.036)	3.61	11.0	12.4	0.89
2c	274 (37.2)	392 (0.39)	(0.158, 0.036)	3.69	10.6	12.4	0.85
2d	275 (21.4)	391 (0.40)	(0.158, 0.037)	3.68	10.7	12.4	0.87
2e	274 (35.8)	394 (0.40)	(0.158, 0.037)	3.64	10.9	12.3	0.89
2f	275 (30.5)	393 (0.42)	(0.158, 0.034)	3.66	11.4	11.9	0.96

<sup>1</sup> Concentration:  $1.0 \times 10^{-5}$  mol L<sup>-1</sup>. <sup>2</sup> Determined using an absolute quantum yield measurement system equipped with an integrated sphere. <sup>3</sup> Radiative deactivation rate constant  $k_r = \Phi/\tau$ . <sup>4</sup> Non-radiative deactivation rate constant  $k_{nr} = (1 - \Phi)/\tau$ .



**Figure 3.** (a) Ultraviolet (UV)-visible light absorption spectra of **1b**–**f** and **2b**–**f** in CH<sub>2</sub>Cl<sub>2</sub> solution (concentration:  $1.0 \times 10^{-5}$  mol L<sup>-1</sup>). (b) Theoretical transitions of **1f** and **2f** from ground S<sub>0</sub> to excited S<sub>n</sub> states obtained by TD-DFT calculation. (c) Photoluminescence spectra of **1b**–**f** and **2b**–**f** in CH<sub>2</sub>Cl<sub>2</sub> solution (inset: picture for photoluminescence under UV irradiation using a handy UV light ( $\lambda_{ex} = 254$  nm)) and (d) CIE color diagram of the PL color.

Unsymmetrical **1b**–**f** and *C*<sub>3</sub>-symmetrical **2b**–**f** absorbed ultraviolet (UV) light with maximum absorption wavelengths ( $\lambda_{abs}$ ) of 272–276 nm and 274–275 nm, respectively, and showed single absorption bands in their absorption spectra (Figure 3a). Because changes in alkoxy chain length do not affect the electron density distribution of the entire molecule, the absorption behavior was the same for unsymmetrical **1** and *C*<sub>3</sub>-symmetrical **2**. To understand the electronic transitions involved in the absorption behavior of unsymmetrical HABs and *C*<sub>3</sub>-symmetrical analogs, we performed excited-state calculations using time-dependent (TD)-DFT for **1f** and **2f** as representatives. The optimized geometries of **1f** and **2f** were obtained via structural optimization calculations with the M06-2X hybrid meta-GGA functional [18] and the 6-31+G(d,p) basis set. Excited-state calculations were performed using the 6-311++G(d,p) basis set. Under similar experimental conditions, a CPCM [19] with CH<sub>2</sub>Cl<sub>2</sub> as the solvent. Table 3 summarizes theoretical transitions and absorption wavelengths ( $\lambda_{cacld}$ ) for large oscillator strengths (*f*) derived from TD-DFT calculations.

Compound	Main Electronic Transition (Contribution, %)	$\lambda_{calcd} [nm]$	Oscillator Strength (f)
1f	HOMO $\rightarrow$ LUMO+1 (48.1%)	275.1	0.4475
2f	HOMO-1 $\rightarrow$ LUMO+1 (24.2%) HOMO-2 $\rightarrow$ LUMO (23.9%)	269.4	0.7058

Table 3. Theoretical transition and absorption wavelengths of 1f and 2f were calculated with TD-DFT<sup>1</sup>.

<sup>1</sup> Calculated using Gaussian 16 W (Rev. B.01) with the TD-SCF method using an M06-2X functional and the 6-311++G(d,p) basis set.

The theoretical absorption wavelength ( $\lambda_{cacld}$ ) of unsymmetrical **1f** is approximately 275.1 nm, which is roughly the same as the experimentally measured  $\lambda_{abs}$ . The primary electronic transition involved in this absorption behavior was calculated to be from the highest occupied molecular orbital (HOMO) to the next lowest unoccupied molecular orbital (LUMO+1), with a contribution rate of 48.1%. The HOMO of 1f had electron lobes localized on two adjacent hexyloxy-substituted benzene rings, whereas those of LUMO+1 were located on three fluorinated aromatic rings (Figure 3b). Based on the orbital distributions of **1f**, the absorption behavior is likely a  $\pi\pi^*$  transition with intramolecular charge transfer (ICT). For **2f** with a  $C_3$ -symmetrical skeleton, on the other hand,  $\lambda_{cacld}$ was 269.4 nm, similar to the measured  $\lambda_{abs}$  but slightly blue-shifted. According to DFT calculations, the absorption behavior of **2f** primarily involves two transitions: HOMO-1  $\rightarrow$ LUMO+1 (24.2%) and HOMO-2  $\rightarrow$  LUMO (23.9%). HOMO-1 and HOMO-2 have electron lobes localized on two of the three hexyloxy-substituted aromatic rings, whereas LUMO and LUMO+1 have electron lobes localized on three or two fluorinated aromatic rings (Figure 3b). That is, the electronic transition of **2f** can be attributed to a  $\pi\pi^*$  transition with ICT character.

To investigate the solution-state PL behavior, we irradiated the CH<sub>2</sub>Cl<sub>2</sub> solutions of **1b**–**f** and **2b**–**f** with light in the  $\lambda_{abs}$ . Unsymmetrical **1b**–**f** exhibited a single PL band with a maximum PL wavelength ( $\lambda_{PL}$ ) of 425–428 nm and emitted a deep blue color with CIE color coordinates (x, y) of (0.155, 0.064) on average (Figure 3c,d). The hexaphenylbenzene derivatives have been reported to have AIE properties [10,11], whereas 1b-f were revealed to emit relatively strong PL even in a dilute solution state; the PL  $\Phi_{PL}$  was discovered to be between 0.45 and 0.61. Similar to the absorption behavior, alterations in the alkoxy chain length had little effect on PL behavior. Because the PL of methoxy-substituted **1a** is radiatively deactivated from the ICT excited state [12], the PL emitted by the current unsymmetrical **1b–f** is also radiatively deactivated from the ICT excited state. In contrast, PL behavior of  $C_3$  symmetrical **2b**-**f** was independent of the alkoxy chain length and exhibited a dark blue PL, CIE coordinates (*x*, *y*) on average (0.158, 0.036), with  $\lambda_{PL}$  at approximately 391–394 nm, which was more blue-shifted than that of the unsymmetrical analog (Figure 3c,d). C<sub>3</sub>-symmetrical **2b**-f exhibited relatively strong PL ( $\Phi_{PL} = 0.39 - 0.42$ ) even in dilute solutions, but the  $\Phi_{PL}$  was slightly lower compared to the unsymmetrical analogs.

To understand the difference in  $\Phi_{PL}$  between the unsymmetrical **1** and the  $C_3$ -symmetrical **2**, we measured the PL lifetime ( $\tau$ ) and calculated the radiative deactivation rate constant ( $k_r$ ) and the non-radiative deactivation rate constant ( $k_{nr}$ ); the  $\tau$  of the unsymmetrical **1** was 4.99–5.06 ns, and that of the  $C_3$ -symmetrical **2** was 3.61–3.69 ns (Table 2). The PL emitted by each compound was fluorescent due to the nanosecond duration of  $\tau$  **1** and **2**. Calculating  $k_r$  and  $k_{nr}$  from  $\Phi_{PL} \tau$ ,  $k_r$  of unsymmetrical **1** was  $10.2 \times 10^7 \text{ s}^{-1}$  on average,  $k_{nr}$  was  $9.93 \times 10^7 \text{ s}^{-1}$  on average, while  $k_r$  of  $C_3$ -symmetrical **2** was  $10.9 \times 10^7 \text{ s}^{-1}$  on average, and  $k_{nr}$  was  $12.3 \times 10^7 \text{ s}^{-1}$  on average. Focusing on  $k_r$  and  $k_{nr}$  for **1** and **2**, it was discovered that the  $k_r$  values were comparable, but the  $k_{nr}$  values of  $C_3$ -symmetrical **2** were 1.24 times higher than those of unsymmetrical **1**. The molecular structure of  $C_3$ -symmetrical **2** allows for easy energy transfer between an electron-rich aromatic ring and an electron-poor fluorinated aromatic ring via through-space conjugation, resulting in increased  $k_{nr}$  and decreased  $\Phi_{PL}$ .

## 3.2.2. Crystalline State

Our next interest was directed toward the PL behavior of unsymmetrical **1b**–**f** and  $C_3$ -symmetrical **2b**–**f** in the Cr states. The Cr samples were purified using column chromatography and recrystallization. Figure 4 depicts the PL spectra and a CIE diagram that visualizes the PL color. The observed photophysical data are summarized in Table 4.



**Figure 4.** (a) PL spectra of unsymmetrical **1b**–**f** and (b) the CIE color diagram expressed PL color. (c) Photoluminescence spectra of C3-symmetrical **2b**–**f** and (d) the CIE color diagram expressed PL color. Excitation wavelength: 339 nm for **1b**, 345 nm for **1c**, 331 nm for **1d**, 323 nm for **1e**, 307 nm for **1f**, 328 nm for **2b**, 316 nm for **2c**, 325 nm for **2d**, 310 nm for **2e**, and 316 nm for **2f**.

Table 4. Photophysical data of unsymmetrical 1b–f and C<sub>3</sub>-symmetrical 2b–f in crystalline state.

Compound	$\lambda_{ m PL}$ [nm] ( $\Phi_{ m PL}$ ) $^1$	CIE (x, y)	τ [ns]	$k_{ m r}~[10^7,{ m s}^{-1}]^{2}$	$k_{ m nr}$ [10 <sup>7</sup> , s <sup>-1</sup> ] <sup>3</sup>	$k_{\rm r}/k_{\rm nr}$
1b	390 (0.37)	(0.201, 0.202)	3.28	11.4	12.8	0.89
1c	382 (0.50)	(0.203, 0.144)	3.48	14.3	10.3	1.39
1d	379 (0.45)	(0.225, 0.132)	3.21	13.9	11.3	1.23
1e	397 (0.15)	(0.206, 0.223)	3.10	4.87	17.4	0.28
1f	387, 476 (0.37)	(0.192, 0.271)	3.44	10.8	12.9	0.84
2b	360 (0.34)	(0.173, 0.070)	2.30	14.7	13.5	1.09
2c	354 (0.38)	(0.190, 0.118)	1.57	23.9	12.8	1.88
2d	363 (0.34)	(0.210, 0.145)	2.19	15.3	13.6	1.13
2e	367, 487 (0.38)	(0.193, 0.297)	1.83	20.6	12.7	1.62
2f	370 (0.25)	(0.179, 0.156)	2.03	12.4	15.3	0.81

<sup>1</sup> Determined using an absolute quantum yield measurement system with an integrated sphere. <sup>2</sup> Radiative deactivation rate constant  $k_{\rm r} = \Phi/\tau$ . <sup>3</sup> Non-radiative deactivation rate constant  $k_{\rm nr} = (1 - \Phi)/\tau$ .

Unsymmetrical **1b**–**f** and *C*<sub>3</sub>-symmetrical **2b**–**f** emitted PL, even in the Cr state (Figure 4a,c). Compounds **1b**–**f** exhibited a PL band with a  $\lambda_{PL}$  of approximately 379–397 nm, whereas **2b**–**f** exhibited a slight blue shift with a  $\lambda_{PL}$  of approximately 354–370 nm (Table 4). In the Cr state, alterations in the alkoxy chain length at the peripheral aromatic ring terminal significantly impacted PL behavior. For example,  $\lambda_{PL}$  for **1b**–**f** and **2b**–**f** shifted from 379 to 476 nm and 354 to 487 nm, respectively. The CIE diagram shows that the color of the PL changed from dark blue to light blue depending on the alkoxy chain length (Figure 4b,d), which was significantly different from a dilute solution in which the molecules were in a dispersed state. Furthermore, these partially fluorinated HABs had a relatively high  $\Phi_{PL}$  even in the Cr state, with the  $\Phi_{PL}$  of unsymmetrical **1** and *C*<sub>3</sub>-symmetrical **2** at 0.15 to 0.50 and 0.25 to 0.38, respectively. PL lifetime measurements revealed that the PLs of **1** and **2** were also fluorescent, even in the Cr state. *C*<sub>3</sub>-symmetrical **2** 

According to the PL spectral shapes shown in Figure 4a,c, in addition to the PL bands on the short-wavelength side, PL bands or broad shoulder peaks were observed in the long-wavelength region. This phenomenon was also observed visually, and when a white crystal sample of **1e** was irradiated with 323 nm excitation light, it turned yellow (Figure 5).



**Figure 5.** Photograph of a crystalline **1e** sample under and after UV irradiation ( $\lambda_{ex}$  = 323 nm).

The observed phenomenon is photochromism in the crystalline state, which causes a color change when irradiated with light [20–22], however, to our knowledge, there are only limited reports on fluorinated photochromism materials [23,24]. Partially fluorinated HABs are considered novel crystalline photochromic molecules. To learn about the crystalline photochromism of partially fluorinated HABs, we investigated the PL behavior of the sample and the changes in the PL behavior depending on the UV irradiation time using crystals of unsymmetrical **1d** and  $C_3$ -symmetrical **2d** with a butoxy chain and **1f** and **2f** with a hexyloxy chain as representative examples. Figure 6 depicts the PL spectra and color changes before and after UV irradiation.

Crystalline samples of unsymmetrical **1d** and  $C_3$ -symmetrical **2d** exhibited PL bands around  $\lambda_{PL}$  at 379 and 363 nm, respectively, with a small shoulder peak on the longerwavelength side before UV irradiation. UV irradiation reduces the intensity of the PL band on the short wavelength side while increasing its intensity on the long wavelength side. Following 30 min of UV irradiation, clear PL bands were observed at 517 and 511 nm for **1d** and **2d**, respectively (Figure 6a,b). Visually observing the changes in PL under UV irradiation, it was discovered that the PL color changed from dark purple with CIE coordinates (0.367, 0.190) to yellow with coordinates (0.373, 0.403) after **1d**, or from dark blue with coordinates (0.225, 0.178) to yellow-green with coordinates (0.278, 0.446) after **2d**. In the powder X-ray diffraction patterns before and after UV irradiation in **1d** and **2d**, obvious changes in the diffraction peaks were observed in both cases (Figure S44). This fact indicates that the aggregated structure changes due to UV irradiation, and it is inferred that the alteration in the aggregated structures switches the PL behavior. Similarly, for **1f** and **2f**  with hexyloxy chains, the PL band intensity on the short-wavelength side decreased after UV irradiation, whereas following 30 min of UV irradiation, the PL intensity on the long-wavelength side increased. Before UV irradiation, the PL color of **1f** was pale blue with coordinates (0.192 and 0.270), but following UV irradiation, it changed to yellow-green with coordinates (0.238 and 0.461). Before UV irradiation, the  $C_3$ -symmetrical **2f** also changed from deep blue with coordinates (0.181, 0.142), but following UV irradiation, it changed to yellow-green with coordinates (0.247, 0.396). Unfortunately, no reverse color change was observed when we irradiated the sample with visible light or heated it following UV irradiation. The photochromism induced by these compounds is expected to be based on a  $6\pi$ -electrocyclization between adjacent aromatic rings upon UV irradiation, and the reason why the reverse reaction is unlikely to occur has not yet been elucidated.



**Figure 6.** PL behavior of a recrystallized sample (t = 0 min) and after UV irradiation time (t min) for (a) 1d ( $\lambda_{ex}$  = 335 nm) and (b) 2d ( $\lambda_{ex}$  = 319 nm). (c) PL color change of 1d and 2d before and after UV irradiation. PL behavior of a recrystallized sample (t = 0 min) and after UV irradiation time (t min) for (d) 1f ( $\lambda_{ex}$  = 307 nm) and (e) 2f ( $\lambda_{ex}$  = 316 nm). (f) PL color change of 1f and 2f before and after UV irradiation.

## 4. Conclusions

The thermophysical and photophysical properties of unsymmetrical and  $C_3$ -symmetrical partially fluorinated HABs with various alkoxy chains and chain lengths were investigated. Unsymmetrical HAB containing ethoxy groups exhibited a monotropic liquid crystalline phase, with a columnar mesophase. The other derivatives lacked an intermediate phase and only exhibited a crystalline-to-isotropic phase transition. Unsymmetrical and  $C_3$ -symmetrical HABs demonstrated relatively strong PL even in a dilute solution state, unlike many AIE-active HAB molecules. The maximum PL wavelength and  $\Phi_{PL}$  varied based on molecular symmetry.  $C_3$ -symmetrical compounds exhibited bluer PL bands and lower  $\Phi_{PL}$  compared to their unsymmetrical analogs. Furthermore, the partially fluorinated HABs exhibited fluorescence even in their crystalline state, indicating that they are dual-state emitting molecules, and demonstrated photochromism in the crystalline

state, with the color of the crystalline sample changing before and after UV irradiation. Unfortunately, no reverse reactions were observed with visible light or heat, implying that the partially fluorinated HABs became irreversible owing to rapid HF desorption following photochromism caused via UV irradiation. The partially fluorinated HABs developed in this study represent a new crystalline photochromic molecule with potential applications as UV-sensing materials.

**Supplementary Materials:** The following supporting information can be downloaded at: https:// www.mdpi.com/article/10.3390/sym16030314/s1, Figures S1–S30: NMR spectrum of **1b–f** and **2b–f**; Figures S31–S40: DSC thermograms of **1b–f** and **2b–f**; Figure S41: absorption and PL spectra of **1b–f** and **2b–f** in CH<sub>2</sub>Cl<sub>2</sub> solution; Figure S42: PL decay profile and the residual of **1b–f** and **2b–f** in CH<sub>2</sub>Cl<sub>2</sub> solution; Figure S43: excitation and PL spectra of **1b–f** and **2b–f** in crystal; Figure S44: Powder X-ray diffraction pattern; Figure S45: PL decay profile and the residual of **1b–f** and **2b–f** in crystal; Figure S46: Molecular orbital distributions of **1f** and **2f**; Tables S1–S10: Phase transition data; Table S11: theoretical electronic transition; Tables S12 and S13: cartesian coordinates of **1f** and **2f**.

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#### References

- Belmonte-Vézquez, J.L.; Amador-Sánchez, Y.A.; Rodríguez-Cortés, L.A.; Rodríguez-Molina, B. Dual-state emission (DSE) in organic fluorophores: Design and applications. *Chem. Mater.* 2021, *33*, 7160–7184. [CrossRef]
- Xia, G.; Si, L.; Wang, H. Dual-state emission: The compatible art of substantial rigidity and twisting conformation within a single molecule. *Mater. Today Chem.* 2023, 30, 101596. [CrossRef]
- Yin, Y.; Ding, A.; He, F.; Wang, C.; Kong, L.; Yang, J. Alkyl-engineered dual-state luminogens with pronounced odd-even effects: Quantum yields with up to 48% difference and crystallochromy with up to 22 nm difference. J. Phys. Chem. B 2022, 126, 2921–2929. [CrossRef] [PubMed]
- 4. Zhao, F.; Du, J.; Li, Z.; Sun, T. Achieving dual-state emission and high-contrast mechanochromic luminescence based on donor-acceptor type phenothiazine methanone derivatives. *J. Lumin.* **2023**, 254, 119529. [CrossRef]
- 5. Förster, T.; Kasper, K. Ein Konzentrationsumschlag der Fluoreszenz. Z. Phys. Chem. 1954, 1, 275–277. [CrossRef]
- 6. Birks, J.B. Photophysics of Aromatic Molecules; Wiley: London, UK, 1970.
- Wang, D.; Tang, B.Z. Aggregation-induced emission luminogens for activity-based sensing. Acc. Chem. Res. 2019, 52, 2559–2570. [CrossRef] [PubMed]
- 8. Zhao, Z.; Zhang, H.; Lam, J.W.Y.; Tang, B.Z. Aggregation-induced emission: New vistas at the aggregate level. *Angew. Chem. Int. Ed.* **2020**, *59*, 9888–9907. [CrossRef]
- Cai, X.; Liu, B. Aggregation-induced emission: Recent advances in materials and biomedical applications. *Angew. Chem. Int. Ed.* 2020, 59, 9868–9886. [CrossRef] [PubMed]
- 10. Vij, V.; Bhalla, V.; Kumar, M. Hexaarylbenzene: Evolution of properties and applications of multitalented scaffold. *Chem. Rev.* **2016**, *116*, 9565–9627. [CrossRef] [PubMed]
- 11. Bhalla, V.; Vij, V.; Dhir, A.; Kumar, M. Hetero-oligophenylene-based AIEE material as a multiple probe for biomolecules and metal ions to construct logic circuits: Application in bioelectronics and chemionics. *Chem. Eur. J.* 2012, *18*, 3765–3772. [CrossRef]
- 12. Wang, Y.; Yamada, S.; Konno, T. Effects of peripheral ring fluorination on the photophysical properties of hexaarylbenzenes. *J. Fluor. Chem.* **2023**, *266*, 110086. [CrossRef]

- 13. Geng, Y.; Fechtenkötter, A.; Müllen, K. Star-like substituted hexaarylbenzenes: Synthesis and mesomorphic properties. *J. Mater. Chem.* **2001**, *11*, 1634–1641. [CrossRef]
- Tomović, Ž.; van Dongen, J.; George, S.J.; Xu, H.; Pisula, W.; Leclère, P.; Smulders, M.M.J.; De Feyter, S.; Meijer, E.W.; Schenning, A.P.H.J. Star-shaped oligo(p-phenylenevinylene) substituted hexaarylbenzene: Purity, stability, and chiral self-assembly. J. Am. Chem. Soc. 2007, 129, 16190–16196. [CrossRef] [PubMed]
- 15. Luo, S.; Yang, G.; Zhang, M.; Lu, L.; Mo, X.; Irfan, M.; Zeng, Z. Difluoromethoxy bridged substituted 2-cyano-pyrrole based pure organic luminescent liquid crystals towards white light emitting single-molecule. *Liq. Cryst.* **2023**, *50*, 1699–1708. [CrossRef]
- 16. Horigome, J.; Wakui, T.; Shirasaki, T. A simple correction method for determination of absolute fluorescence quantum yields of solid samples with a conventional fluorescence spectrophotometer. *Bunseki Kagaku* **2009**, *58*, 553–559. [CrossRef]
- 17. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Petersson, G.A.; Nakatsuji, H.; et al. *Gaussian 16, Revision B.01*; Gaussian, Inc.: Wallingford, CT, USA, 2016.
- Hohenstein, E.G.; Chill, S.T.; Sherrill, C.D. Assessment of the performance of the M05-2X and M06-2X exchange-correlation functionals for noncovalent interactions in biomolecules. *J. Chem. Theory Comput.* 2008, *4*, 1996–2000. [CrossRef] [PubMed]
- 19. Li, H.; Jensen, J.H. Improving the efficiency and convergence of geometry optimization with the polarizable continuum model: New energy gradients and molecular surface tesselation. *J. Comput. Chem.* **2004**, *25*, 1449–1462. [CrossRef]
- 20. Kawano, M.; Sano, T.; Abe, J.; Ohashi, Y. The first in situ direct observation of the light-induced radical pair from a hexaarylbiimidazolyl derivative by X-ray crystallography. J. Am. Chem. Soc. **1999**, 121, 8106–8107. [CrossRef]
- 21. Abe, J.; Sano, T.; Kawano, M.; Ohashi, Y.; Matsushita, M.M.; Iyoda, T. EPR and density functional studies of light-induced radical pairs in a single crystal of a hexa-arylbiimidazolyl derivative. *Angew. Chem. Int. Ed.* **2001**, *40*, 580–582. [CrossRef]
- Yamada, T.; Kobatake, S.; Muto, K.; Irie, M. X-ray crystallographic study on single-crystalline photochromism of bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene. J. Am. Chem. Soc. 2000, 122, 1589–1592. [CrossRef]
- 23. Li, Z.; Twieg, R.J. Photocyclodehydrofluorination. Chem. Eur. J. 2015, 21, 15534–15539. [CrossRef] [PubMed]
- 24. Zhang, M.; Lu, L.; Guo, J.; Zhao, Z.; Majeed, I.; Zeng, Z. Toward high contrast photochromism materials via fluorinated TPE-based medium ring. *Dye. Pigment.* **2023**, *219*, 111637. [CrossRef]

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