



Article Effects of Tetrafluorocyclohexa-1,3-Diene Ring Position on Photoluminescence and Liquid-Crystalline Properties of Tricyclic π -Conjugated Molecules

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Abstract: Tetrafluorocyclohexa-1,3-diene ring-containing tricyclic π -conjugated molecules are promising negative-dielectric-anisotropy guest species for vertical-alignment-type liquid-crystalline (LC) displays. Building on our previous work reporting the excellent photoluminescence (PL) properties of tricyclic π -conjugated molecules with central tetrafluorocyclohexa-1,3-diene rings, we herein synthesized four analogous molecules with terminal tetrafluorocyclohexa-1,3-diene rings from commercially available precursors and investigated the effects of substituent type and diene ring position on PL and LC properties using microscopic and spectroscopic methods. One of the prepared molecules exhibited a relatively planar molecular structure and formed herringbone-type aggregates via π/F and CH/ π interactions instead of forming stacked aggregates via π/π stacking interactions, thus exhibiting relatively strong PL in solution and crystalline states. Moreover, the PL color of this compound depended on the electronic character of its terminal substituents along the long molecular axis. Of the four prepared species, two featured terminal ethyl groups and formed one or more LC phases. The PL properties of these phases indicated that the related phase transition induced changes in the aggregate structure, PL wavelength, and PL color. Our results expand the applicability of CF_2CF_2 moiety-containing tricyclic compounds as functional molecules for the fabrication of next-generation PL, LC, and PL-LC materials.

Keywords: fluorine; tetrafluorocyclohexa-1,3-diene; photoluminescence; liquid crystal; tricyclic molecule; aggregation

1. Introduction

Fluorinated organic molecules have drawn much attention as the structural components of pharmaceuticals [1,2] and agrichemicals [3,4], as well as major constituents of liquid crystals [5–7] and optoelectronic materials [8,9]. This popularity is due to the unique properties of fluorine [10], namely, its highest electronegativity among all elements (4.0 on the Pauling scale), second smallest atomic radius (147 pm according to Bondi [11]), and the high dissociation energy of C–F bonds (105.4 kcal·mol⁻¹). In view of these properties, the introduction of fluorine into molecular structures enhances latent functions or promotes the emergence of new ones and is, therefore, a powerful approach for the development of novel organic functional materials.

Our group has developed efficient and selective synthetic routes to various fluorinated organic molecules [12,13] including those exhibiting photoluminescence (PL) and liquidcrystalline (LC) properties [14]. The results obtained so far indicate that the introduction of fluorine atoms substantially increases PL intensity in the solid state and induces the emergence of mesophases between crystalline (Cry) and isotropic (Iso) phases.

Previously, we prepared a tricyclic molecule with a central tetrafluorocyclohexa-1,3diene ring (**1a**) as a guest molecule with negative dielectric anisotropy to develop vertical alignment-type LC materials [15–18] and showed that **1a** exhibits blue PL in the crystalline



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Copyright: © 2023 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/). and solution states. On this basis, we synthesized analogous tricyclic molecules with controlled electron density along the long molecular axis (**1b** and **1c**) and revealed that their PL behavior is greatly affected by the electron density distribution, which, in turn, is influenced by the electronic properties of terminal substituents (Figure 1) [19].



Figure 1. Previously synthesized tricyclic molecules 1a-c with central tetrafluorocyclohexa-1,3-diene rings.

Building on the abovementioned results, we herein synthesized and characterized molecules **2a–d** to examine how PL and LC properties are affected by the position of the tetrafluorocyclohexa-1,3-diene ring in the tricyclic structure and the electronic properties of terminal substituents (Figure 2) [15,18].



Figure 2. Structures of tricyclic molecules 2a-d with terminal tetrafluorocyclohexa-1,3-diene rings.

2. Materials and Methods

2.1. General Characterization

Melting points ($T_{\rm m}$) were measured on a Shimadzu DSC-60 Plus instrument using at least three heating/cooling cycles at a scan rate of 5.0 °C·min⁻¹. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE III 400 spectrometer (¹H: 400.13 MHz, ¹³C: 100.61 MHz) in chloroform-*d* (CDCl₃). Chemical shifts were reported on the basis of the residual proton or carbon signal of CHCl₃ ($\delta_{\rm H}$ = 7.26 ppm, $\delta_{\rm C}$ = 77 ppm) in parts per million (ppm). ¹⁹F-NMR (376.46 MHz) spectra were recorded on the Bruker AVANCE III 400 spectrometer in CDCl₃ using trichlorofluoromethane (CFCl₃, $\delta_{\rm F}$ = 0.00 ppm) as an internal standard. Infrared (IR) spectra were acquired using the KBr method on a JASCO FT/IR-4100 type A spectrometer. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-700MS spectrometer using fast atom bombardment (FAB+) methods. Column chromatography was performed using Wakogel[®] 60N (38–100 µm), and thin-layer chromatography was performed using the corresponding silica gel plates (silica gel 60F₂₅₄, Merck, Darmstadt, Germany).

2.2. Materials

The target molecules were synthesized according to a previously reported method from readily available precursors, namely, dimethyl 2,2,3,3-tetrafluorosuccinate (**2a** and **2d**; Scheme 1a) [18] and 4-bromo-3,3,4,4-tetrafluorobut-1-ene (**2b** and **2c**, Scheme 1b) [15].



Scheme 1. Syntheses of (a) 2a and 2d, and (b) 2b and 2c.

Detailed synthetic procedures are provided in Schemes S1 and S2, and Figures S1–S42 shown in the Supplementary Materials. Characterization data are presented below (for **2a–d**) and in the Supplementary Materials (for other molecules).

2.2.1. 4-Ethyl-5,5,6,6-tetrafluoro-1-[4-(4-n-propylphenyl)phenyl]cyclohexa-1,3-diene (2a)

Yield: 90% (0.25 g, 0.67 mmol); yellow solid; $T_{\rm m}$: 92 °C; ¹H-NMR (CDCl₃): δ 0.98 (t, J = 7.2 Hz, 3H), 1.20 (t, J = 7.6 Hz, 3H), 1.69 (sext, J = 7.6 Hz, 2H), 2.40 (q, J = 7.2 Hz, 2H), 2.64 (t, J = 7.2 Hz, 2H), 6.09 (d, J = 6.0 Hz, 1H), 6.39 (d, J = 6.0 Hz, 1H), 7.27 (d, J = 7.8 Hz, 2H), 7.53 (d, J = 8.4 Hz, 4H), 7.62 (d, J = 7.6 Hz, 2H); ¹³C-NMR (CDCl₃): δ 11.4, 13.8, 21.6, 24.5, 37.7, 114.0 (tt, J = 251.87, 26.82 Hz), 114.1 (tt, J = 251.9, 26.8 Hz), 123.1 (t, J = 9.2 Hz), 125.8 (t, J = 8.79 Hz), 126.8, 126.9, 127.4, 129.0, 131.7, 133.6 (t, J = 22.0 Hz), 137.6, 137.8 (t, J = 21.9 Hz), 141.5, 142.3; ¹⁹F-NMR (CDCl₃): δ -126.57 (d, J = 4.76 Hz, 2F), -122.23 (d, J = 4.86 Hz, 2F). The above characterization data were consistent with those reported previously [15,18].

2.2.2. 5,5,6,6-Tetrafluoro-1-(4-methoxyphenyl)phenylcyclohexa-1,3-diene (2b)

Yield: 80% (0.53 g, 1.6 mmol); white solid; *T*_m: 130 °C; ¹H-NMR (CDCl₃): δ 3.86 (s, 3H), 6.03–6.12 (m, 1H), 6.37–6.46 (m, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 7.51–7.63 (m, 6H); ¹³C-NMR (CDCl₃): δ 55.3, 110.0–116.0 (m, 2C of CF₂CF₂), 114.3, 122.9 (t, *J* = 25.8 Hz), 124.7 (t, *J* = 8.0 Hz), 126.7, 127.7, 128.1, 129.9 (t, *J* = 11.8 Hz), 130.9, 132.6, 136.4 (t, *J* = 22.0 Hz), 141.6, 159.5; ¹⁹F-NMR (CDCl₃): δ –121.29 (s, 2F), –121.67 (s, 2F); IR (KBr): *ν* 3026, 2968, 2844, 1649, 1604, 1576, 1530, 1445, 1399, 1312, 1289, 1202, 1183, 1021, 1011, 879, 787 cm⁻¹; HRMS (FAB) calculated for C₁₉H₁₄F₄O [M]⁺: 334.0980, found: 334.0980. Crystal data for C₁₉H₁₄F₄O (*M* = 334.30 g/mol): orthorhombic, space group *P* 2₁ 2₁ 2₁, *a* = 5.5586(7) Å, *b* = 9.2038(15) Å, *c* = 29.282(4) Å, *α* = 90°, *β* = 90°, *γ* = 90°, *V* = 1498.1(4) Å³, *Z* = 4, *T* = 173 K, μ(MoKα) = 0.710 mm⁻¹, *D*_{calc} = 1.482 g/cm³, 98,894 reflections measured (3.042° ≤ 2θ ≤ 27.480°), 7212 unique (*R*_{int} = 0.0476, *R*_{sigma} = 0.0950), which were used in all calculations. The final *R*₁ was 0.0631 (*I* > 2*σ*(*I*)) and *wR*₂ was 0.1269 (all data).

2.2.3. 5,5,6,6-Tetrafluoro-1-{4-(trifluoromethyl)phenyl}phenylcyclohexa-1,3-diene (2c)

Yield: 70% (0.15 g, 1.4 mmol); white solid; T_m : 138 °C; ¹H-NMR (CDCl₃): δ 6.06–6.18 (m, 1H), 6.40–6.54 (m, 2H), 7.60 (d, J = 8.8 Hz, 2H), 7.64 (d, J = 8.8 Hz, 2H), 7.72 (s, 4H); ¹³C-NMR (CDCl₃): δ 112.7 (tt, J = 249.4, 27.2 Hz), 113.4 (tt, J = 253.0, 26.5 Hz), 124.2 (q, J = 272.1 Hz), 123.4 (t, J = 25.6 Hz), 125.5 (t, J = 8.0 Hz), 125.8 (q, J = 3.6 Hz), 127.3, 127.4, 127.9, 129.7 (q, J = 32.3 Hz), 129.8 (t, J = 11.8 Hz), 132.6, 136.1 (t, J = 22.7 Hz), 140.4, 143.6; ¹⁹F-NMR (CDCl₃): δ –62.43 (s, 3F), –121.31 (s, 2F), –121.72 (s, 2F); IR (KBr): ν 3088, 2362, 1919, 1690, 1616, 1502, 1425, 1274, 1210, 968, 875, 794, 739, 729 cm⁻¹; HRMS (FAB) calculated for C₁₉H₁₁F₇ [M]⁺: 372.0749, found: 372.0759.

2.2.4. 4-Ethyl-5,5,6,6-tetrafluoro-1-[4-{4-(n-octyloxy)phenyl}phenyl]cyclohexa-1,3-diene(2d)

Yield: 83% (0.32 g, 0.69 mmol); pale-yellow solid; T_m : 71 °C; ¹H-NMR (CDCl₃): δ 0.90 (t, J = 6.8 Hz, 3H), 1.19 (t, J = 7.2 Hz, 3H), 1.26–1.42 (m, 8H), 1.48 (quin, J = 8.0 Hz, 2H), 1.81 (quin, J = 7.2 Hz, 2H), 2.40 (q, J = 7.2 Hz, 2H), 4.00 (t, J = 6.8 Hz, 2H), 6.09 (d, J = 6.0 Hz, 1H), 6.38 (d, J = 6.0 Hz, 1H), 6.98 (d, J = 8.8 Hz, 2H), 7.48–7.62 (m, 6H); ¹³C-NMR (CDCl₃):δ 11.5, 14.1, 21.7, 22.7, 26.1, 29.26, 29.31, 29.4, 31.8, 68.1, 110–125 (m, 2C of CF₂CF₂), 114.9, 123.1 (t, J = 8.8 Hz), 125.6 (t, J = 8.8 Hz), 126.7, 127.5, 128.0, 131.3, 132.6, 133.7 (t, J = 23.1 Hz), 137.8 (t, J = 21.2 Hz), 141.3, 159.1; ¹⁹F-NMR (CDCl₃): δ –123.55 (s, 2F), –127.90 (s, 2F); IR (KBr): ν 3038, 2926, 2852, 1885, 1654, 1606, 1579, 1529, 1500, 1253, 1132, 907, 864 cm⁻¹; HRMS (FAB) calculated for C₂₈H₃₂F₄O [M]⁺: 460.2389, found: 460.2382.

2.3. Single-Crystal X-ray Diffraction (XRD)

Single-crystal XRD patterns were recorded on an XtaLAB AFC11 diffractometer (Rigaku, Tokyo, Japan). The reflection data were integrated, scaled, and averaged using CrysAlisPro software (v. 1.171.39.43a; Rigaku Corporation, Akishima, Japan), and empirical absorption corrections were applied using the SCALE 3 ABSPACK scaling algorithm (CrysAlisPro). Structures were identified using a direct method (SHELXT-2018/2 [20]), refined using a full-matrix least-squares method (SHELXL-2018/3 [21]), and visualized using OLEX2 [22]. The crystallographic data were deposited in the Cambridge Crystallographic Data Center (CCDC) database (CCDC 2269760 for **2b**) and can be obtained free of charge

from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk.

2.4. Photophysical Properties

JASCO V-750 absorption (JASCO, Tokyo, Japan) and FP-6600 fluorescence (JASCO, Tokyo, Japan) spectrometers were used to acquire solution-phase ultraviolet/visible (UV/vis) absorption and PL spectra. A Quantaurus-QY C11347-01 instrument (Hamamatsu Photonics, Hamamatsu, Japan) was used for PL quantum yield measurements, and a Quantaurus-Tau fluorescence lifetime spectrometer (C11367-34; Hamamatsu Photonics, Japan) was employed for PL lifetime determination.

2.5. LC Properties

Polarizing optical microscopy (POM) measurements were carried out using an Olympus BX53 microscope (Tokyo, Japan) equipped with cooling and heating stages (10,002 L, Linkam Scientific Instruments, Surrey, UK) to assess LC properties. Thermodynamic properties were assessed using differential scanning calorimetry (DSC; DSC-60 Plus, Shimadzu, Kyoto, Japan) at heating and cooling rates of $5.0 \,^\circ \text{C} \cdot \text{min}^{-1}$ under N₂. Variable-temperature powder X-ray diffraction (VT-PXRD) analyses were carried out using an X-ray diffractometer (Rigaku, MiniFlex600, Tokyo, Japan) equipped with an X-ray tube (Cu K_{α} , $\lambda = 1.54 \,\text{\AA}$) and semiconductor detector (D/teX Ultra2). The sample powder was mounted on a nonreflecting silicon plate set on a benchtop stage (Anton Paar, BTS-500). The temperature, heating/cooling rate, and X-ray exposure time were controlled.

2.6. Theoretical Calculations

All computations were performed using the Gaussian 16 program set [23] with density functional theory (DFT) at the level of the M06-2X hybrid functional [24] and the 6-31+G(d) (for all atoms) basis set with a conductor-like polarizable continuum model (CPCM) [25] for CHCl₃. Theoretical vertical transitions were calculated using the time-dependent DFT (TD-DFT) method at the same theoretical level using the same solvation model.

3. Results and Discussion

3.1. Synthesis

Compounds **2a** and **2d**, featuring an ethyl group attached to the longitudinal molecular terminal, were synthesized from the readily available dimethyl 2,2,3,3-tetrafluorosuccinate according to a reported procedure (Scheme 1a) [18]. The reaction of dimethyl tetrafluorosuccinate with 4-(4-*n*-propylphenyl)phenylmagnesium bromide in THF at -78 °C overnight followed by hydrolysis under acidic conditions afforded ketoester **3a** in 64% yield. Compound **3a** was treated with 3.6 equivalents of vinylmagnesium chloride in Et₂O, and the reaction mixture was stirred overnight at reflux to afford 4,4,5,5-tetrafluoroocta-1,7-diene (**4a**) in 37% yield. In the presence of a second-generation Grubbs catalyst, the ring-closing metathesis of **4a** in CH₂Cl₂ (40 °C, 24 h) furnished 1-aryl-4-ethyl-5,5,6,6-tetrafluorocyclohex-2-ene-1,4-diol (**5a**) in 49% yield. The 24 h exposure of **5a** in methanol to H₂ at room temperature resulted in catalytic hydrogenation and furnished 1-aryl-4-ethyl 2,2,3,3-tetrafluorocyclohexan-1,4-diol (**6a**) in 70% yield. Subsequent dehydration with phosphoryl chloride in pyridine at 90 °C for 24 h produced **2a** in 90% yield. The octyloxy chain-bearing structural analog **2d** was prepared by a similar procedure starting with the addition of 4-(4-octyloxyphenyl)phenylmagnesium bromide.

Compound **2b**, featuring an electron-donating methoxy group, and **2c**, featuring an electron-withdrawing trifluoromethyl (CF₃) group at the longitudinal molecular end, were synthesized according to a previously reported procedure (Scheme 1b) [15]. The Barbier-type nucleophilic addition of 1,1,2,2-tetrafluorobut-3-envllithium (prepared in situ from 4-bromo-3,3,4-4-tetrafluorobut-1-ene and LiBr-free MeLi) to *p*-anisaldehyde in tetrahydrofuran (THF) at -78 °C for 2 h gave tetrafluorohomoallyl alcohol **7b** in 70% yield. The oxidation of **7b** with Oxone[®] in the presence of sodium 2-iodobenzenesulfonate

(*pre*-IBS; 5 mol%) in acetonitrile at 90 °C for 16 h afforded 1-aryl-2,2,3,3-tetrafluoropent-4en-1-one (**8b**) in 77% yield. Compound **8b** was treated with allylmagnesium bromide in THF at -78 °C for 2 h to produce 4-aryl-5,5,6,6-tetrafluoroocta-1,7-diene-4-ol (**9b**) in 58% yield. Compound **9b** underwent ring-closing metathesis upon treatment with a secondgeneration Grubbs catalyst (3 mol.%) to furnish 4-aryl-5,5,6,6-cyclohex-1-en-4-ol (**10b**) in 73% yield. The dehydration of **10b** with phosphoryl chloride in pyridine at 90 °C for 24 h produced the target methoxy-substituted species (**2b**) in 80% yield. The CF₃-substituted **2c** was synthesized using the same reaction sequence.

Compounds **2a–d** were purified by column chromatography (eluent: hexane/EtOAc = 3/1 for **2a** or 10/1 for **2b–d**) and recrystallization from a 1:1 (v/v) mixture of CH₂Cl₂ and hexane. The molecular structures of the target molecules were confirmed by NMR spectroscopy, IR spectroscopy, and HRMS, and the related purities were sufficient for photophysical and LC property analyses.

Among **2a**–**d**, only the methoxy-substituted **2b** furnished single crystals appropriate for X-ray crystallographic analysis upon recrystallization, whereas **2a**, **2c**, and **2d** did not furnish single crystals even after multiple recrystallizations. Figure 3 shows the crystal structure of **2b** obtained by X-ray structure analysis.



Figure 3. (a) Molecular structure and (b,c) packing of 2b in the crystalline lattice. Display notation: space-filling model for rearmost molecules, ball-and-stick model for middle molecules, and wire-frame model for frontmost molecules.

Compound **2b** crystallized in an orthorhombic system ($P \ 2_1 \ 2_1 \ 2_1 \ space group$) and featured a unit cell with four molecules. The dihedral angle between the two aromatic rings of the biphenyl moiety was approximately 4°, and that between the tetrafluorocyclohexa-1,3-diene ring and the biphenyl moiety was approximately 19° (Figure 3a). In **1b**, which has a central tetrafluorocyclohexa-1,3-diene ring, the dihedral angle between the cyclohexa-1,3-diene ring and the adjacent aromatic ring was at least 31° [19]. On the basis of the molecular structures of **1b** and **2b**, we concluded that the change in the position of the tetrafluorocyclohexa-1,3-diene ring from central to terminal favored a more planar structure. The space-filling model representation in Figure 3b suggests that the π /F interactions [26,27] between the π -electrons and F atoms of tetrafluorocyclohexa-1,3-diene resulted in the formation of a stacked structure along the *a*-axis. The C(sp²)…F interatomic distance corresponding to the π /F interaction (304.4 pm) was shorter than the sum of van der Waals radii (317 pm) of carbon (170 pm) and fluorine (147 pm) atoms [10]. The molecule

represented by the space-filling model formed molecular packings featuring two pairs of CH/ π interactions [28] with the molecule represented by the ball-and-stick model along the *b*-axis direction. The C(sp²)…H interatomic distance corresponding to the CH/ π interaction worked (284.5 pm) was also shorter than the sum of the van der Waals radii (290 pm) of carbon (170 pm) and hydrogen (120 pm). In addition to the short distance between the C(sp²) and H atoms, the carbon atom of the methoxy group was in close contact with the fluorine atom at a distance (302.3 pm) shorter than the sum of carbon (170 pm) and fluorine (147 pm) van der Waals radii. The molecule represented by the ball-and-stick model also formed a stacked structure with the molecule represented by the wire-frame model along the *a*-axis via CH/ π interactions (short contact: 286.7 pm) and O/H hydrogen bonds (short contact: 270.5 pm) (Figure 3c). Accordingly, herringbone-type packing structures were formed through multiple intermolecular interactions. However, unlike the packing structure of **1b** [19], which features a central cyclohexa-1,3-diene ring, the packing structure of **2b** did not feature intermolecular π/π stacking.

3.2. Photophysical Properties

Figure 4 shows the UV/vis absorption spectra, PL spectra, and PL color chromaticity diagrams (as defined by the Commission Internationale de l'Eclailage (CIE)) of **2a–d**, and Table 1 lists the related photophysical data.



Figure 4. (a) Ultraviolet/visible absorption spectra (concentration: $1.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$) and (b) photoluminescence (PL) spectra (concentration: $1.0 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$) of **2a–d** measured in chloroform (CHCl₃). Inset: photographs of PL in CHCl₃ solution under UV irradiation ($\lambda_{ex} = 365 \text{ nm}$). (c) Commission Internationale de l'Eclailage (CIE) chromaticity diagram for PL colors of **2a–d**.

Molecule	$\lambda_{ m abs} [m nm]^{1}$ ($arepsilon [10^3, m L\cdot mol^{-1} \cdot cm^{-1}]$)	$\lambda_{\mathrm{PL}} [\mathrm{nm}]^{2}$ $(\Phi_{\mathrm{PL}})^{3}$	τ [ns]	$k_{ m r}$ [10 ⁸ , s ⁻¹] ⁴	$k_{ m nr}$ [10 ⁸ , s ⁻¹] ⁵	CIE (<i>x, y</i>)
2a	330 (18.5)	437 (0.94)	2.08	4.52	0.28	(0.155, 0.102)
2b	337 (27.6)	463 (0.60)	1.84	3.29	2.15	(0.153, 0.193)
2c	320 (37.4)	416 (0.24)	0.73	3.30	10.44	(0.157, 0.036)
2d	337 (28.9)	463 (0.89)	2.11	4.21	0.53	(0.150, 0.145)

Table 1. Photophysical data of 2a–d in CHCl₃ solution.

¹ Concentration: 1.0×10^{-5} mol·L⁻¹. ² Concentration: 1.0×10^{-6} mol·L⁻¹. ³ Measured using an integrating sphere. ⁴ Radiative deactivation rate constant (k_r) = Φ_{PL}/τ . ⁵ Nonradiative deactivation rate constant (k_{nr}) = $(1 - \Phi_{PL})/\tau$.

Compound **2a**, possessing ethyl and *n*-propyl substituents at longitudinal molecular terminals, exhibited a single absorption band with a maximum absorption wavelength (λ_{abs}) of ~330 nm in CHCl₃. Compound **2b**, featuring a strongly electron-donating methoxy group, exhibited a red-shifted λ_{abs} of 337 nm, whereas **2c**, featuring a strongly electron-withdrawing CF₃ group, exhibited a blue-shifted λ_{abs} of 320 nm. In CHCl₃, the λ_{abs} of **2d** with ethyl and *n*-octyloxy groups as longitudinal terminal substituents was 337 nm, i.e., equal to that of **2b**.

The theoretical vertical transition was modeled using Gaussian software [23] with time-dependent density functional theory (TD-DFT). Figure 5 shows the distributions of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) for **2a–d**, with the related theoretical data summarized in Table 2. The detailed orbital distributions are shown in Figures S44–47 in Supplementary Materials.



Figure 5. Highest occupied molecular orbital (HOMO, left) and lowest unoccupied molecular orbital (LUMO, right) distributions of (a) 2a, (b) 2b, (c) 2c, and (d) 2d.

Molecule	HOMO Energy [eV]	LUMO Energy [eV]	Theoretical λ_{calcd} [nm]	Oscillator Strength (f)	Theoretical Transition (Probability)
2a	-7.33	-1.50	331	1.00	HOMO→LUMO (85%) HOMO–1→LUMO (12%)
2b	-7.22	-1.66	338	0.90	HOMO→LUMO (77%) HOMO–1→LUMO (20%)
2c	-7.75	-1.76	325	0.87	HOMO→LUMO (91%) HOMO–2→LUMO (6%)
2d	-7.14	-1.48	335	1.04	HOMO→LUMO (78%) HOMO–1→LUMO (19%)

Table 2. Theoretical data of **2a**–**d** obtained using Gaussian software with time-dependent density functional theory ¹.

 1 Calculated at the M06-2X/6-31+G(d) level of theory using a conductor-like polarizable continuum model for CHCl_3.

According to Figure 5, the HOMOs of **2a–d** were spread throughout the π -conjugated structure, whereas the LUMOs were localized on the tetrafluorocyclohexa-1,3-diene ring of the tricyclic π -conjugated framework. Substituents at longitudinal molecular ends affected the HOMO and LUMO energies, e.g., electron-donating substituents such as alkoxy groups increased the HOMO energy, whereas electron-withdrawing substituents had the opposite effect. The alkoxy group at the opposite end did not affect the energy of the LUMO, as this orbital was localized on the tetrafluorocyclohexa-1,3-diene ring, whereas the electron-donating ethyl group introduced into the tetrafluorocyclohexa-1,3-diene skeleton increased the LUMO energies of **2a** and **2d**. The absorption wavelengths (λ_{calcd}) of **2a–d** determined by TD-DFT calculations (331 nm for **2a**, 338 nm for **2b**, 325 nm for **2c**, and 335 nm for **2d**) were close to the measured λ_{abs} values listed in Table 1. The transitions from the ground to the first excited states were calculated to be of π - π^* HOMO \rightarrow LUMO and HOMO–1/HOMO–2 \rightarrow LUMO types.

When a solution of **2a** in CHCl₃ was excited by irradiation with UV light at λ_{abs} (330 nm), a single PL band with a maximum PL wavelength (λ_{PL}) of approximately 437 nm was observed (Figure 4b). Compared to that of **2a**, the PL band of **2b** with an electron-donating methoxy group ($\lambda_{PL} = 463$ nm in CHCl₃) was red-shifted by 26 nm, whereas the PL band of **2c** with an electron-withdrawing CF₃ group ($\lambda_{PL} = 416$ nm) was substantially blue-shifted. Similar to the methoxy-substituted **2b**, the *n*-octyloxy-substituted **2d** exhibited PL ($\lambda_{PL} = 463$ nm). In the case of **2c** with a large HOMO–LUMO overlap, radiative deactivation probably occurred from the locally excited state, whereas **2b** or **2d** with a locally existing LUMO luminesced through the radiative deactivation of the intramolecular charge transfer (ICT) excited state, which can be reasonably explained by the Lippert-Mataga plot [29,30] shown in Figure S49.

The high-energy PL of **2c** corresponded to dark-blue color represented by CIE chromaticity coordinates of (x, y) = (0.157, 0.036) (Figure 4c). In contrast, the low-energy PL of **2b** and **2d** emitted from ICT states corresponded to light-blue color with CIE coordinates of (x, y) = (0.153, 0.189). The quantum yields (Φ_{PL}) and PL lifetimes (τ) of **2a–d** were determined as 0.24–0.94 and ~2.11 ns, respectively. This value of τ indicates that the light emitted by **2a–d** was fluorescent. Among the four compounds, **2c** exhibited the lowest Φ_{PL} (0.24) and a very short τ (<1.0 ns). The radiative (k_r) and nonradiative (k_{nr}) deactivation rate constants of **2c** were calculated from Φ_{PL} and τ as $3.30 \times 10^8 \text{ s}^{-1}$ and $10.44 \times 10^8 \text{ s}^{-1}$, respectively. Notably, k_r was not significantly different between **2a** and **d**, whereas the k_{nr} of **2c** was 5–37 times higher than those of other derivatives. These results suggested the occurrence of fluorescence reabsorption (self-absorption) in **2c**, which resulted in decreased Φ_{PL} and increased k_{nr} .

Most molecules exhibiting luminescence in solution generally experience luminescence quenching through intermolecular energy transfer at high concentrations or in the solid state. However, **2a–d** exhibited strong luminescence even in the crystalline state. Figure 6 shows the PL spectra of crystalline **2a–d**, the related CIE chromaticity diagram, and photographs of crystals under 365 nm UV light. The corresponding photophysical data are summarized in Table 3.



Figure 6. (a) PL spectra of crystalline **2a**–**d**. (b) CIE chromaticity diagram and photographs of **2a**–**d** crystals under 365 nm ultraviolet light.

Table 3.	Photo	physical	data c	of crys	talline	2a-d

Molecule	$\lambda_{ m PL}$ [nm] ($arPhi_{ m PL}$) 1	$ au_{ave} [ns]$	$ au_1$ [ns]	$ au_2$ [ns]	$k_{ m r} [10^8, { m s}^{-1}]^{2}$	$k_{ m nr} \ [10^8,{ m s}^{-1}]^{3}$	CIE (<i>x, y</i>)
2a	509 (0.99)	1.84	_	_	5.38	0.054	(0.265, 0.570)
2b	463 (0.63)	2.43	2.06	4.47	2.56	1.55	(0.162, 0.200)
2c	413 (0.31)	3.04	-	_	1.03	2.26	(0.155, 0.175)
2d	458 (0.93)	3.19	-	_	2.92	0.21	(0.182, 0.423)

¹ Measured using an integrating sphere. ² Radiative deactivation rate constant (k_r) = Φ_{PL}/τ . ³ Nonradiative deactivation rate constant (k_{nr}) = $(1 - \Phi_{PL})/\tau$.

Crystalline **2a** with two alkyl groups at longitudinal molecular ends exhibited green PL with a single PL band at λ_{PL} around 509 nm, which was red-shifted relative to the value in CHCl₃ solution by 72 nm. However, the PL behavior of **2b–d** did not substantially change upon the transition from the CHCl₃ solution to the crystalline state. In the crystalline state, **2b** crystallized mainly via CH/ π , π /F, and hydrogen bonds; π / π stacking between the intermolecular aromatic rings was not observed. The similarity between the λ_{PL} and Φ_{PL} values observed in the crystalline state and CHCl₃ solution was ascribed to the absence of π/π stacking interactions in crystalline **2b**, which suppressed the nonradiative deactivation induced by the formation of molecular aggregates. Given that crystalline 2c and 2d also exhibited PL behavior similar to that in the CHCl₃ solution state, we concluded that their conjugated structures were also not involved in intermolecular interactions, although their crystal structures have not yet been elucidated. On the other hand, we inferred that crystalline **2a**, which featured a PL wavelength and PL color different from those observed in the solution state, interacted with the π -conjugated site through the formation of molecular aggregates, unlike in the dilute solution, although the crystal structure of **2a** also remained veiled. PL lifetime measurements showed that the τ of crystalline **2a–d** was 1.84–3.19 ns and, therefore, also indicative of fluorescence. The PL decays of 2a, 2c, and 2d were well modeled by a mono-exponential function, and the related PL originated from a single excited state. In contrast, the PL decay of **2b** was fitted by a biexponential function assuming a radiative deactivation pathway from any two excited states, although the related excited-state details remain unknown.

Compared with the previously reported **1b** and **1c** with a central tetrafluorocyclohexa-1,3-diene ring [19], **2b** and **2c** featured a shorter (by 20–25 nm) λ_{abs} in CHCl₃, which was ascribed to the significantly increased LUMO level of the latter molecules. However, λ_{PL} was found to be almost the same, except for **2c**, which had a CF₃ group at the molecular terminal. In the crystalline state, the λ_{PL} of **2c** was blue-shifted relative to that of **1c**, although almost identical λ_{PL} values were observed for **2b** and **1b**. The CHCl₃ solution-phase Φ_{PL} values of **2b** and **2c** exceeded those of **1b** and **1c**. In contrast, the opposite trend was observed in the crystalline state, i.e., the Φ_{PL} values of **2b** and **2c** were lower than those of **1b** and **1c**. In **2b** and **2c**, which greatly differ from **1b** and **1c** [19], the biphenyl moiety was planar and formed a herringbone structure because of CH/ π interactions. We concluded that weak intermolecular interactions did not lead to molecular motion suppression, resulting in decreased Φ_{PL} . Accordingly, the positional change of the tetrafluorocyclohexa-1,3-diene ring in the tricyclic scaffold had a relatively large effect on the crystalline-state behavior, and the position of this ring affected intermolecular interactions and, hence, the extent of molecular motion inhibition and Φ_{PL} .

3.3. LC Properties

The previously reported **1a–c** exhibited transitions only between their Cry and Iso phases upon heating and cooling, i.e., no LC phases were observed [15]. To understand how the position of the tetrafluorocyclohexa-1,3-diene ring in tricyclic molecules affects their LC properties, we used POM and DSC to examine the LC behavior of **2a–d**, which showed PL in both dilute solution and crystalline states (Figures S53–S56 in Supplementary Materials). Compounds **2b** and **2c** exhibited only a Cry→Iso phase transition but did not form any mesophase upon heating and cooling. In contrast, for **2a** and **2d**, a fluid bright-field POM image was observed between the Cry and Iso phases, indicating the formation of an LC phase upon cooling (**2a**) or heating/cooling (**2d**). Figure 7 shows the DSC curves of **2a** and **2d** and the POM images of the corresponding mesophases. Table 4 lists the phase transition behaviors of **2a–d**, namely, their phase sequences, as well as phase transition temperatures and enthalpies in the second heating and cooling processes.



Figure 7. Differential scanning calorimetry (DSC) curves of (**a**) **2a** and (**b**) **2d** recorded during the second heating and cooling processes at a scan rate of 5 $^{\circ}$ C·min⁻¹ under N₂. Polarizing optical microscopy textures in the mesophases of (**c**) **2a** and (**d**) **2d**.

Molecule	Process	Phase Transition Temperatures [°C] and Enthalpies [kJ·mol $^{-1}$] 1
2a	Heating	Cry 92 (14.0) Iso
	Cooling	Cry 81 (-4.9) N 90 (-6.2) Iso
2b	Heating	Cry 130 (16.4) Iso
	Cooling	Cry 93 (-12.1) Iso
2c	Heating	Cry 138 (11.8) Iso
	Cooling	Cry 98 (-8.2) Iso
2d	Heating	Cry 71 (12.6) SmA 110 (0.88) N 133 (0.72) Iso
	Cooling	Cry 40 (-8.1) SmC 68 (-1.1) SmA 114 (-1.0) N 136 (-0.85) Iso

Table 4. Phase transition data of 2a-d during the second heating and cooling processes.

¹ Determined by DSC (scan rate: 5 $^{\circ}$ C·min⁻¹, atmosphere: N₂). Abbreviations: Cry, crystal; Iso, isotropic; N, nematic; SmA, smectic A; SmC, smectic C phase.

In the case of the **2a** mesophase, POM revealed that a fluid four-brush Schlieren texture formed at 90 °C after the slow cooling from the dark-field-image Iso phase. Given that POM indicated the formation of a nematic (N) phase with only orientational order, the mesophase appearing during the cooling of **2a** was classified as the N phase. Further cooling from the N-phase state of 2a resulted in fluidity loss at 81 °C and a phase transition to the hard Cry phase. In the case of the **2d** mesophase, the nonfluidic bright-field POM image corresponding to the Cry phase changed to a fluidic fan-shaped POM image at 71 °C upon heating. Further heating induced an optical texture change to a Schlieren-patterned N phase at 110 °C followed by a phase transition to the Iso phase in the dark-field POM image at 133 °C. Upon cooling, the N-phase Schlieren texture appeared at 136 °C, and a transition to a phase with a fan-shaped texture occurred at 114 °C. Upon further cooling, a broken fan-shaped texture was observed at 68 °C, followed by a phase transition to the nonfluidic Cry phase at 40 °C. The fan-shaped optical texture observed in the mesophase of 2d is characteristic of the smectic (Sm) phase, which has an orientational and positional order. Notably, in the case of **2d**, the Sm phase appeared at a lower temperature than the N phase.

Further insights into the LC phases exhibited by **2a** and **2d** were provided by VT-PXRD measurements. The pattern of **2a** recorded after cooling from the Iso phase and holding at 70 °C featured no Cry phase peaks but contained a halo peak centered around $2\theta = 18^{\circ}$ (Figure S57). This result strongly suggests that the mesophase appearing in **2a** is the N phase without positional order. PXRD measurements were also performed for **2d** at 124, 89, and 49 °C after cooling from the Iso phase. A halo peak centered around 18° was also observed in the pattern recorded at 124 °C, and the mesophase appearing at this temperature was determined to be the N phase (Figure S57). The PXRD pattern recorded at 89 °C featured a sharp peak at 3.75° and a weak peak at 7.45° (Figure 8a).



Figure 8. Powder X-ray diffraction patterns of 2d recorded at (a) 89 and (b) 49 °C.

These diffraction peaks corresponded to the plane indices of (hkl) = (001) and (002). The peak at 3.75° in the low-angle region corresponded to a *d*-spacing of 2.35 nm, according to Bragg's equation, which was consistent with the longitudinal molecular length of **2d** (Figure 8a) This consistency of the interlayer distance with the molecular length agreed with the formation of a smectic A (SmA) phase with a layered periodic structure wherein the long molecular axis was oriented in the direction of the layer normal. In the pattern recorded at 49 °C, the peak of the (001) plane appeared at 3.95° and corresponded to a *d*-spacing of 2.23 nm, which was shorter than the molecular length along the long molecular axis (2.35 nm) (Figure 8b). This result indicated the presence of a smectic C (SmC) phase featuring a tilt angle with respect to the layer normal (Figure 8b).

3.4. PL Properties of 2d in Various Molecular Aggregation States

Compound **2d**, which forms various mesophases, was selected to investigate PL behavior changes associated with the phase transition-induced alterations in molecular aggregate structure. PL behavior was examined using a fluorescence spectrometer equipped with a self-made temperature control unit. The samples were cooled from the Iso phase and held for 5 min at each temperature during cooling. Figure 9 shows the thus obtained PL spectra and CIE chromaticity diagrams, and Table 5 summarizes the related photophysical data.



Figure 9. (a) PL spectra of 2d recorded at different temperatures upon cooling. (b) CIE chromaticity diagram for PL color of 2d at different temperatures.

Table 5. Photo	physica	l data o	f 2d in	various phases	
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Temp. [°C]/Phase	λ_{PL} [nm]	I/I _N ¹	CIE (<i>x</i> , <i>y</i>)
130/N	466	7.8	(0.156, 0.171)
100/SmA	470	1.6	(0.152, 0.217)
50/SmC	468	2.0	(0.158, 0.199)
25/Cry	454	1.0	(0.164, 0.121)

¹ PL intensity *I* of each phase with respect to the PL intensity (I_N) of the N phase.

In the case of **2d**, a PL band with $\lambda_{PL} \approx 466$ nm appeared in the N phase; however, the related PL intensity (I_N) decreased because of the accelerated nonradiative deactivation by micro-Brownian motion upon heating. The N \rightarrow SmA phase transition observed upon cooling induced a 2.0-fold PL intensity increase ($I/I_N = 2.0$) along with a slight red shift in λ_{PL} . No significant change was observed in λ_{PL} or PL intensity upon the transition to the SmC phase, whereas the transition to the Cry phase induced a blue shift of λ_{PL} by 12 nm and a 7.8-fold increase in PL intensity relative to the N phase ($I/I_N = 7.8$). The CIE chromaticity diagram shown in Figure 9b demonstrates that the PL color of **2d** changed from dark blue to light blue owing to the phase transition-induced alteration of the molecular aggregate structure.

4. Conclusions

Tricyclic π -conjugated molecules with terminal tetrafluorocyclohexa-1,3-diene rings and different substituents introduced at the longitudinal molecular ends (2a-d) were synthesized in five steps from dimethyl 2,2,3,3-tetrafluorosuccinate or 4-bromo-3,3,4,4tetrafluorobut-1-ene and evaluated in terms of their photophysical and LC behaviors. All four molecules exhibited PL in both dilute solutions and crystalline states. In dilute solutions, the PL wavelength varied in the range of 416–463 nm, which reflected the effect of substituent electron-donating/withdrawing nature on molecular orbital energy. $\Phi_{\rm PL}$ was maximal (0.94) for **2a** and minimal (0.24) for **2c**, which had the shortest λ_{PL} . The low Φ_{PL} observed in the latter case was ascribed to self-absorption caused by the overlap of absorption and PL spectra. In the crystalline state, the PL behaviors of **2b–d** were similar to those in dilute solution, whereas 2a, which had two alkyl groups at both ends, exhibited green PL with substantially red-shifted λ_{PL} . Regarding phase transition behavior, a mesophase was observed for **2a** and **2d** with an ethyl group at one molecular end. Only the N phase with an orientational order appeared in the case of **2a**, whereas the Sm phase with both orientational and positional orders, as well as the N phase, appeared in the case of 2d. The N phase observed for 2d exhibited weak blue PL during cooling. The PL intensity increased upon the N \rightarrow SmA phase transition during cooling, did not substantially change upon the SmA \rightarrow SmC phase transition, and strongly increased upon the SmC \rightarrow Cry phase transition on further cooling. Concomitantly, the PL color changed from dark blue to light blue, i.e., temperature-responsive PL behavior was observed. The results described herein expand the applicability of CF_2CF_2 -containing tricyclic molecules as next-generation PL, LC, and PL-LC materials.

Supplementary Materials: The following supporting information can be downloaded from https://www.mdpi.com/article/10.3390/cryst13081208/s1: Scheme S1. Synthetic procedure of **2a** and **2d** starting from commercially available dimethyl 2,2,3,3-tetrafluorosuccinate. Scheme S2. Synthetic procedure of **2b** and **2c** starting from commercially available 4-bromo-3,3,4,4-tetrafluorobut-1-ene. Figures S1–S42. ¹H-, ¹³C-, and ¹⁹F-NMR spectra; Figure S43. ORTEP-type crystal structure of **2b**; Figures S44–S47. HOMO-1/HOMO-2, HOMO, and LUMO distributions and differential density between HOMO and LUMO; Figure S48. UV/vis absorption and PL spectra of **2a–d** in CHCl₃ solution; Figure S49. PL spectra of **2a–c** in different solvents and related Lippert–Mataga plots; Figure S50. PL decay profiles of **2a–d** in CHCl₃ solution; Figure S51. Excitation and PL spectra of **2a–d** in crystalline states; Figure S52. PL decay profiles of **2a–d** in crystalline states; Figure S52. PL decay profiles of **2a–d**; Figure S57. VT-PXRD patterns of **2a** and **2d** recorded at different temperatures; Table S1. Crystallographic data for **2b**; Tables S2–S5. Cartesian coordinates for **2a–d**; Tables S6–S9. Phase transition behaviors of **2a–d** observed by DSC.

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