Supporting Information

Thermoresponsive luminescent properties of polyfluorinated bistolane-type light-emitting liquid crystals

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1. Synthetic procedure and NMR spectra

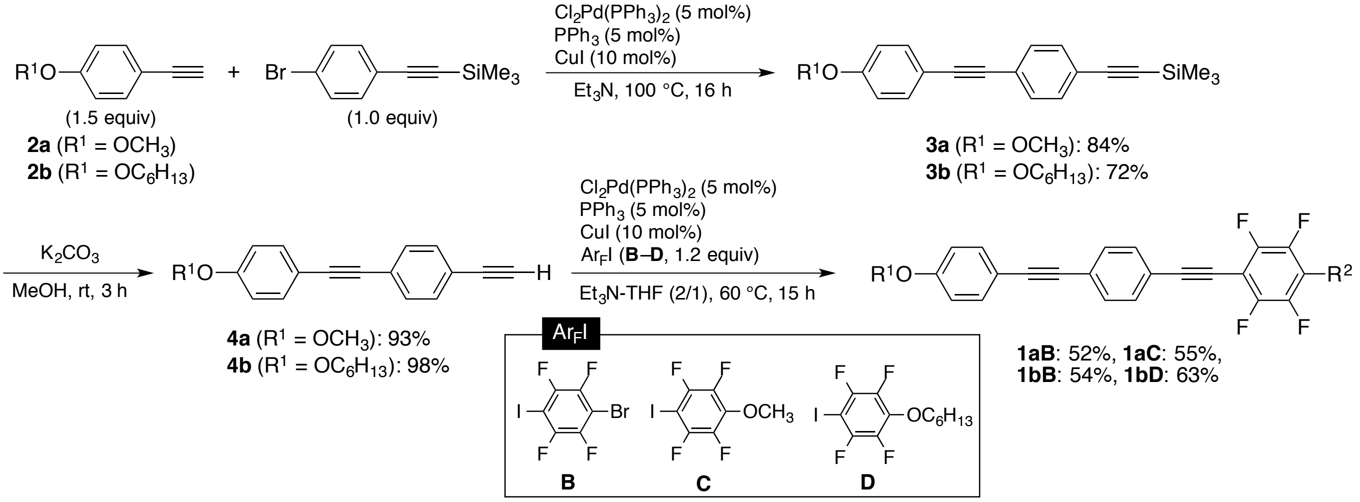
1-1. General method

^{1}H and ^{13}C NMR spectra were obtained with a Bruker AVANCE III 400 NMR spectrometer (^{1}H: 400 Mz and ^{13}C: 100 MHz) in chloroform-*d* ($CDCl_3$) solution and the chemical shifts are reported in parts per million (ppm) using the residual proton in the NMR solvent. ^{19}F NMR (376 MHz) spectra were obtained with a Bruker AVANCE III 400 NMR spectrometer in $CDCl_3$ solution with $CFCl_3$ (δ_F = 0 ppm) as an internal standard. Infrared spectra (IR) were recorded in a KBr method with a JASCO FT/IR-4100 type A spectrometer; all spectra were reported in wavenumber (cm^{-1}). High resolution mass spectra (HRMS) were recorded on a JEOL JMS-700MS spectrometer using fast atom bombardment (FAB) methods.

All chemicals including solvent were of reagent grade and where necessary were purified in the usual manner prior to use. Column chromatography was carried out on silica gel (Wakogel® 60N, 38–100 μm) and thin-layer chromatography (TLC) analysis was performed on silica gel TLC plates (Merck, Silica gel $60F_{254}$)

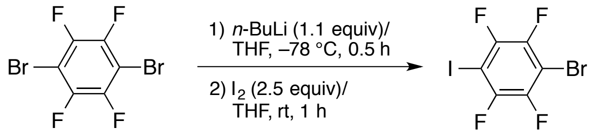
1-2. Preparation of bistolane derivatives **1**

According to our reported procedure, bistolane derivatives **1** reported here were synthesized from (4-alkoxyphenyl)acetylene (**2**) with easy three-step manipulations based on (i) the Pd(0)-catalyzed Sonogashira cross-coupling reaction with 1-bromo-4-[2-(trimethylsilyl)ethynyl]benzene, (ii) the deprotection of the TMS group, and (iii) the Sonogashira cross-coupling reaction with the corresponding polyfluorinated aromatic halides (Scheme S1).



Scheme S1. Synthetic procedure of polyfluorinated bistolane derivatives.

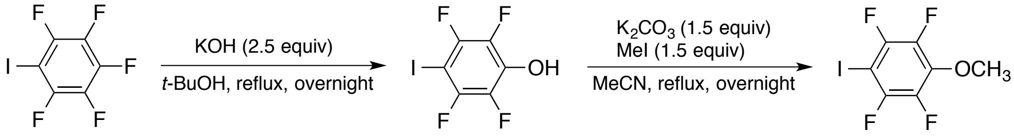
1-2-1. Preparation of 1-bromo-2,3,5,6-tetrafluoro-4-iodobenzene (**B**)



B

Polyfluoroaromatic iodide, **B**, was prepared according to the literature procedure with a slight modification:[1] In 50 mL two-necked round-bottomed flask were charged commercially available 1,4-dibromo-2,3,5,6-tetrafluorobenzene (0.31 g, 1.0 mmol) and THF (20 mL). To the solution was slowly added n-BuLi (1.6 M in hexane, 0.66 mL, 1.1 mmol) at –78 °C and the whole was stirred at that temperature for 0.5 h. To the resultant solution was added dropwise a solution of I_2 (0.64 g, 2.5 mmol) in THF (5 mL), followed by slowly raising up to room temperature, and the resulting solution was stirred at room temperature for additional 1 h. After completion of the reaction, reaction mixture was poured into aqueous $Na_2S_2O_3$ solution, followed by extraction with Et_2O (three times). The organic layers combined were dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by silica-gel column chromatography (eluent: hexane) to obtain the title compound (**B**, 0.31 g, 0.87 mmol) in 87% yield. The spectral data of **B** was completely consistent with reported data. ^{19}F NMR ($CDCl_3$): δ –119.39 (dd, J = 23.4, 8.8 Hz, 2F), –131.86 (dd, J = 23.4, 9.1 Hz, 2F).

1-2-2. Preparation of 2,3,5,6-tetrafluoro-4-iodoanisole (**C**)



C

Polyfluoroaromatic iodide, **C**, was prepared according to the literature procedure with a slight modification:[2] In 50 mL two-necked round-bottomed flask were charged KOH (1.4 g, 25 mmol) and *t*-butyl alcohol (20 mL). The solution was stirred at 65 °C for 1 h, in which was added commercially available 2,3,4,5,6-pentafluoroiodobenzene (1.3 mL, 10 mmol). The reaction mixture was stirred at reflux temperature overnight. After adding H_2O, *t*-butyl alcohol was removed under reduced pressure using a rotary evaporator. Product was extracted in the CH_2Cl_2 three times, followed by additional extraction with CH_2Cl_2 (three times) after aqueous solution being acidified by 10% HCl aq. The organic layers combined were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by recrystallization from Et_2O to give 2,3,5,6-tetrafluoro-4-iodophenol (1.6 g, 5.4 mmol) in 54% yield.

The tetrafluorinated phenol (3.0 mmol) was treated with iodomethane (0.28 mL, 4.5 mmol) in the presence of K_2CO_3 (0.63 g, 4.5 mmol) in MeCN (5.0 mL) and the whole was refluxed overnight. The reaction mixture was poured into aqueous NH_4Cl solution, followed by AcOEt (three times). The organic layers combined were dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by silica-gel column chromatography (eluent: hexane) to obtain the title compound (**C**, 0.80 g, 2.6 mmol) in 87% yield. The spectral data of **C** was consistent with reported data.[2b] ^{1}H NMR ($CDCl_3$): δ 4.09 (t, J = 1.4 Hz, 3H); ^{19}F NMR ($CDCl_3$): δ –121.90 (dd, J = 25.0, 9.8 Hz, 2F), –155.64 (dd, J = 25.0, 9.6 Hz, 2F).

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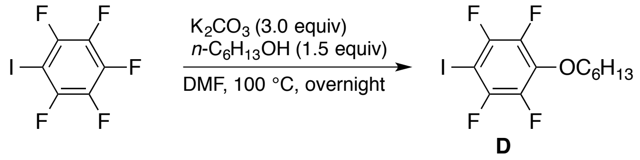
[1] C. B. Aakeröy, P. D. Chopade, J. Desper, *Cryst. Growth Des.* **2013**, *13*, 4145–4150.

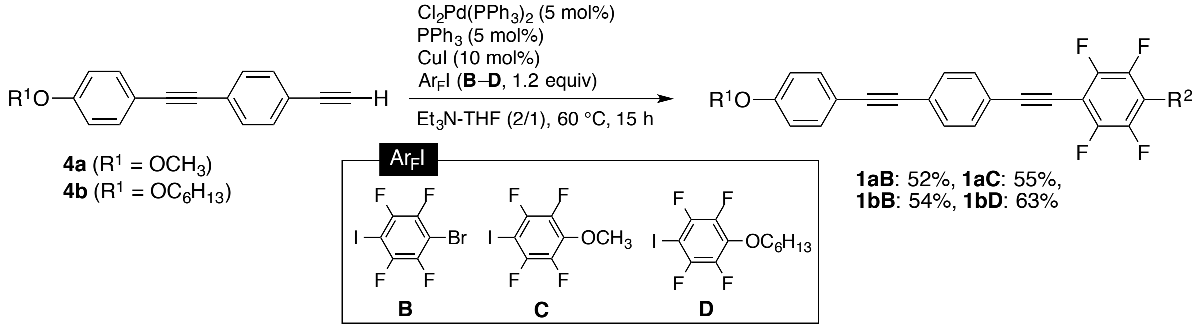
[2] (a) J. Wen, H. Yu, Q. Chen, *J. Mater. Chem.* **1994**, *4*, 1715–1717. (b) H. Q. Do, O. Daugulis, *Org. Lett.* **2009**, *11*, 421–423.

1-2-3. Preparation of 2,3,5,6-tetrafluoro4-iodo-1-hexyloxybenzene (**D**)

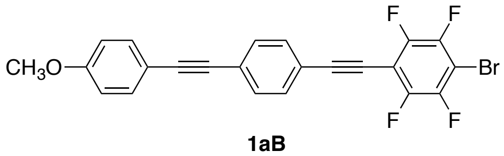


Polyfluoroaromatic iodide, **D**, was prepared as follows: In 50 mL two-necked round-bottomed flask were placed iodopentafluorobenzene (0.68 mL, 5.0 mmol), 1-hexanol (0.94 mL, 7.5 mmol), and K_2CO_3 (2.1 g, 15 mmol) in DMF (3.0 mL). The whole was stirred at 100 °C overnight. The resultant was poured into saturated aqueous NH_4Cl solution and the product was extracted with Et_2O three times. The organic layers combined were dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by silica-gel column chromatography (eluent: hexane) to obtain the title compound (**D**, 1.2 g, 3.3 mmol) in 65% yield. The spectral data of **D** was consistent with reported data.[3] ^{1}H NMR ($CDCl_3$): δ 0.90 (t, J = 7.0 Hz, 3H), 1.30–1.39 (m, 4H), 1.41–1.52 (m, 2H), 1.77 (quin, J = 6.5 Hz, 2H), 4.22 (t, J = 6.5 Hz, 2H); ^{19}F NMR ($CDCl_3$): δ –122.12 (m, 2H), –154.92 (m, 2H).

1-2-4. General procedure for Sonogashira cross-coupling reaction to obtain polyfluorinated bistolane **1**



To a mixture of $Cl_2Pd(PPh_3)_2$ (5 mol%), PPh_3 (5 mol%), [(4-methoxyphenyl)ethynyl]phenyl acetylene (**4a**, 1.0 equiv), 1-bromo-2,3,5,6-tetrafluoro-4-iodobenzene (1.2 equiv), and CuI (10 mol%) was added Et_3N and THF as a solvent, and the whole was stirred at 60 °C (bath temp) for 15 h. After removal of the solvent using a rotary evaporator, the crude product was extracted with AcOEt and washed with saturated aqueous NH_4Cl solution (three times). The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The resultant was purified by silica-gel column chromatography, providing the desired product **1**, which was recrystallized by slow evaporation from CH_2Cl_2/MeOH (1/1) to obtain the polyfluorinated bistolane in crystal.



1aB

Synthesis of 1-bromo-2,3,5,6-tetrafluoro-4-[4-[(4-methoxyphenyl)ethynyl]phenylethynyl]benzene (**1aB**)

Pd(0)-catalyzed Sonogashira cross-coupling reaction was carried out using $Cl_2Pd(PPh_3)_2$ (53 mg, 0.042 mmol), PPh_3 (11 mg, 0.042 mmol), **4a** (0.20 g, 0.85 mmol), CuI (16 mg, 0.084 mmol) in Et_3N (15 mL) and THF (8 mL) at 60 °C for 15 h. Pure **1aB** was obtained in 52% (0.20 g, 0.44 mmol) by performing column chromatography using hexane and CH_2Cl_2 (3:1 ratio) as an eluent. Yield: 52% (white solid); Mp: 192 °C (determined by DSC); ^{1}H NMR ($CDCl_3$): δ 3.84 (s, 3H), 6.89 (d, J = 8.8 Hz, 2H),

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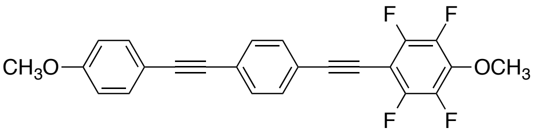
[3] D. W. Bruce, P. Metrangolo, F. Meyer, T. Pilati, C. Präsang, G. Resnati, G. Terraneo, S. G. Wainwright, A. C. Whitewood, *Chem. Eur. J.* **2010**, *16*, 9511–9524.

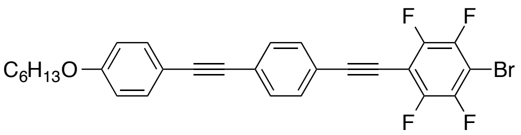
7.48 (d, *J* = 8.8 Hz, 2H), 7.52 (ABq, *J* = 8.4 Hz, 2H), 7.56 (ABq, *J* = 8.4 Hz, 2H); ^{19}F NMR ($CDCl_3$): δ –133.64 (dd, *J* = 21.8, 9.4 Hz, 2F), –133.67 (dd, *J* = 21.8, 9.8 Hz, 2F); ^{13}C NMR ($CDCl_3$): δ 55.3, 75.5 (t, *J* = 3.7 Hz), 87.6, 92.3, 100.6 (t, *J* = 22.7 Hz), 102.2 (t, *J* = 3.7 Hz), 104.2 (t, *J* = 16.2 Hz), 114.1, 114.9, 120.7, 125.2, 131.4, 131.8, 133.2, 144.9 (ddt, *J* = 247.2, 14.7, 3.6 Hz), 146.7 (ddt, *J* = 254.5, 14.0, 4.3 Hz), 159.9; IR (KBr): ν 3075, 2976, 2846, 2212, 1518, 1484, 1246, 1027, 967, 837 cm^{-1}; HRMS: (FAB+) *m/z* [M]$^+$ calcd for $C_{23}H_{11}O^{79}BrF_4$: 457.9929; found: 457.9926.



1aC

Synthesis of 2,3,5,6-tetrafluoro-4-[4-[(4-methoxyphenyl)ethynyl]phenylethynyl]anisole (**1aC**)

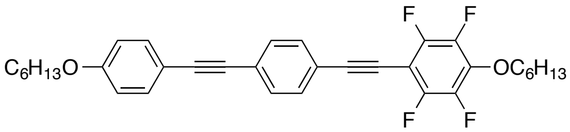
Pd(0)-catalyzed Sonogashira cross-coupling reaction was carried out using $Cl_2Pd(PPh_3)_2$ (53 mg, 0.075 mmol), PPh_3 (20 mg, 0.076 mmol), **4a** (0.35 g, 1.5 mmol), CuI (30 mg, 0.16 mmol) in Et_3N (15 mL) and THF (8 mL) at 60 °C for 15 h. Pure **1aC** was obtained in 55% (0.34 g, 0.82 mmol) by performing column chromatography using hexane and AcOEt (20:1 ratio) as an eluent. Yield: 55% (white solid); Mp: 120 °C (determined by DSC); ^{1}H NMR ($CDCl_3$): δ 3.84 (s, 3H), 4.13 (t, *J* = 1.6 Hz, 3H), 6.89 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.50 (ABq, *J* = 8.8 Hz, 2H), 7.54 (ABq, *J* = 8.9 Hz, 2H); ^{19}F NMR ($CDCl_3$): –137.75 (dd, *J* = 20.3, 7.9 Hz, 2F), –158.06 (dd, *J* = 20.7, 6.8 Hz, 2F); ^{13}C NMR ($CDCl_3$): δ 55.3, 62.2 (t, *J* = 4.4 Hz), 75.7 (t, *J* = 4.4 Hz), 87.7, 92.0, 97.9 (t, *J* = 19.1 Hz), 99.9, 114.1, 115.0, 121.2, 124.6, 131.4, 131.7, 133.2, 138.9 (tt, *J* = 11.8, 2.9 Hz), 140.7 (ddt, *J* = 247.0, 14.5, 4.4 Hz), 147.2 (ddt, *J* = 240.5, 13.2, 4.3 Hz), 159.9; IR (KBr): ν 3014, 2964, 2836, 2210, 1605, 1428, 1285, 1122, 1027, 980, 833 cm^{-1}; HRMS: (FAB+) *m/z* [M]$^+$ calcd for $C_{24}H_{14}O_2F_4$: 410.0930; found: 410.0934..



1bB

Synthesis of 1-bromo-2,3,5,6-tetrafluoro-4-[4-[(4-hexyloxyphenyl)ethynyl]phenylethynyl]benzene (**1bB**)

Pd(0)-catalyzed Sonogashira cross-coupling reaction was carried out using $Cl_2Pd(PPh_3)_2$ (53 mg, 0.042 mmol), PPh_3 (11 mg, 0.042 mmol), **4b** (0.20 g, 0.85 mmol), CuI (16 mg, 0.084 mmol) in Et_3N (15 mL) and THF (8 mL) at 60 °C for 15 h. Pure **1bB** was obtained in 54% (0.20 g, 0.44 mmol) by performing column chromatography using hexane and AcOEt (20:1 ratio) as an eluent. Yield: 54% (white solid); Mp: 130 °C (determined by DSC); ^{1}H NMR ($CDCl_3$): δ 0.91 (t, *J* = 6.8 Hz, 3H), 1.32–1.37 (m, 4H), 1.42–1.51 (m, 2H), 1.79 (tt, *J* = 7.2, 6.8 Hz, 2H), 3.98 (t, *J* = 6.8 Hz, 2H), 6.88 (ABq, *J* = 8.4 Hz, 2H), 7.46 (ABq, *J* = 8.4 Hz, 2H), 7.51 (ABq, *J* = 8.8 Hz, 2H), 7.56 (ABq, *J* = 8.8 Hz, 2H); ^{19}F NMR ($CDCl_3$): δ –133.66 (dd, *J* = 21.8, 9.4 Hz, 2F), –135.69 (dd, *J* = 21.8, 10.9 Hz, 2F); ^{13}C NMR ($CDCl_3$): δ 14.0, 22.6, 25.7, 29.2, 31.6, 68.1, 75.5 (t, *J* = 4.4 Hz), 87.5, 92.5, 100.6 (t, *J* = 22.7 Hz), 102.2 (t, *J* = 3.7 Hz), 104.2 (t, *J* = 18.3 Hz), 114.57, 114.61, 120.6, 125.2, 131.4, 131.8, 133.2, 144.9 (ddt, *J* = 262.6, 14.6, 4.4 Hz), 146.7 (ddt, *J* = 255.2, 14.7, 4.3 Hz), 159.6; IR (KBr): ν 3032, 2919, 2847, 2205, 1596, 1518, 1486, 1242, 1174, 967, 837 cm^{-1}; HRMS: (FAB+) *m/z* [M]$^+$ calcd for $C_{28}H_{21}O^{79}BrF_4$: 528.0712; found: 528.0706.



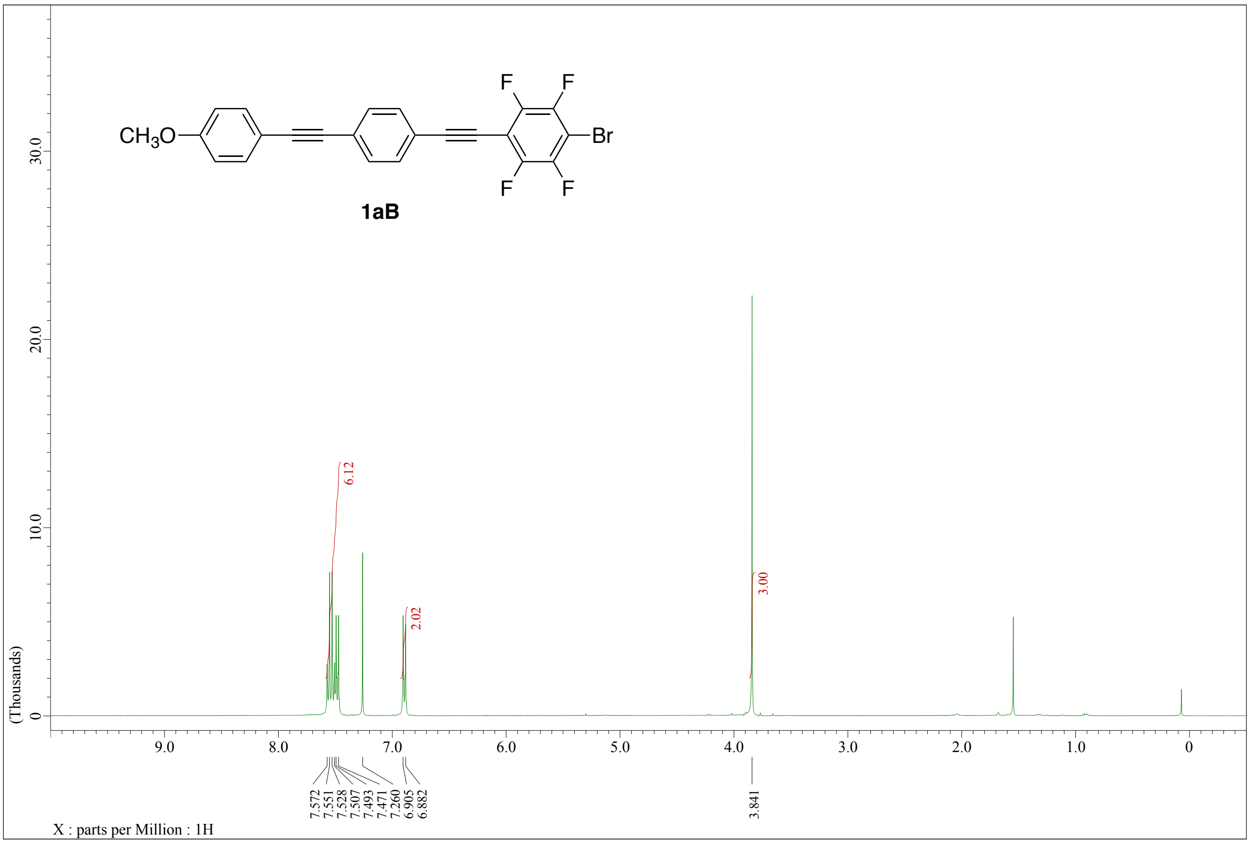
1bD

Synthesis of 2,3,5,6-tetrafluoro-4-[4-[(4-hexyloxyphenyl)ethynyl]phenylethynyl]-1-hexyloxybenzene (**1bD**)

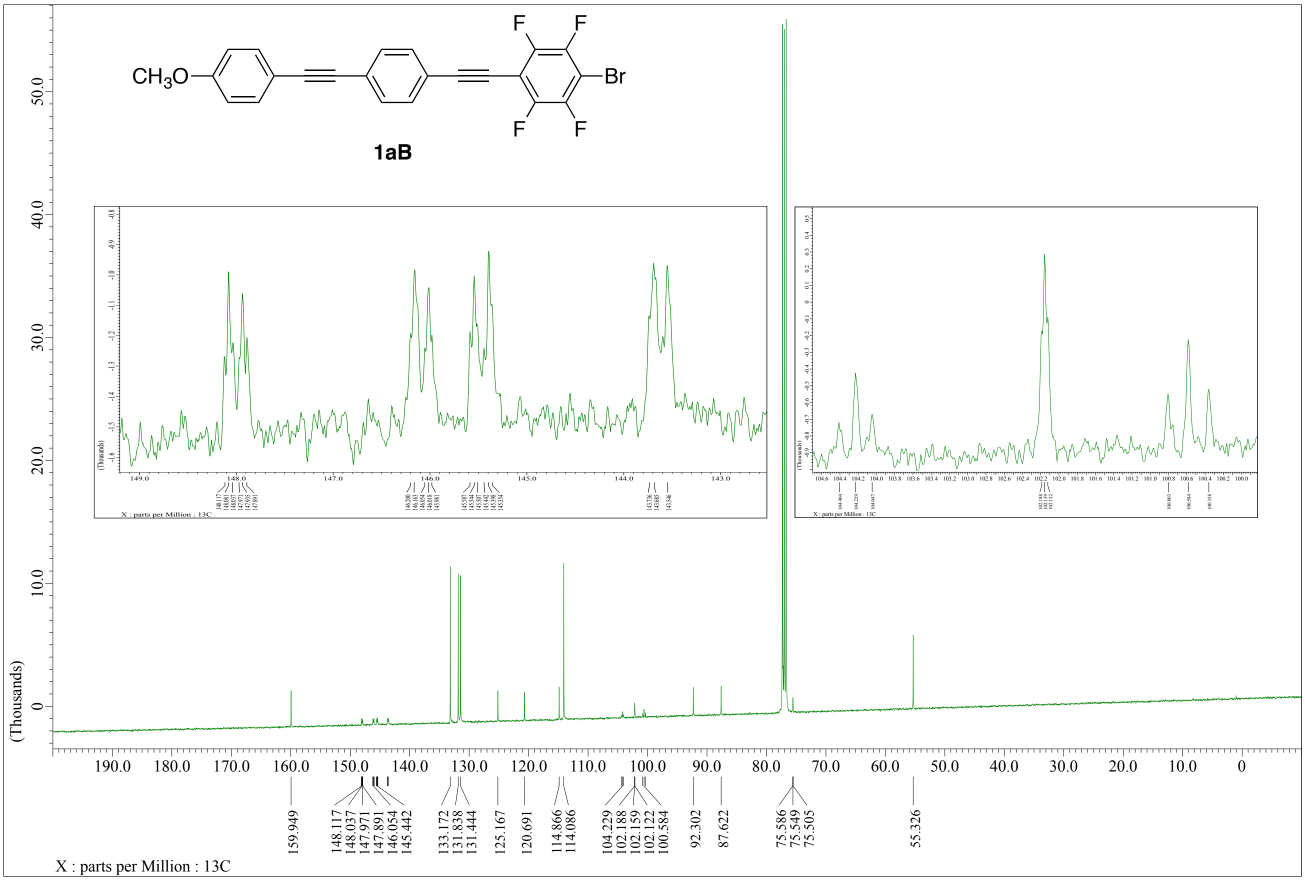
Pd(0)-catalyzed Sonogashira cross-coupling reaction was carried out using $Cl_2Pd(PPh_3)_2$ (53 mg, 0.042 mmol), PPh_3 (11 mg, 0.042 mmol), **4b** (0.20 g, 0.85 mmol), CuI (16 mg, 0.084 mmol) in Et_3N (15 mL) and THF (8 mL) at 60 °C for 15 h. Pure **1bD** was obtained in 52% (0.20 g, 0.44 mmol) by performing column chromatography using hexane and CH_2Cl_2 (3:1 ratio) as an eluent. Yield: 63% (yellow solid); Mp:

76 °C (determined by DSC); ^{1}H NMR (CDCl$_3$): δ 0.91(t, *J* = 7.2 Hz, 6H), 1.29–1.41 (m, 4H), 1.41–1.52 (m, 4H), 1.75–1.85 (m, 4H), 3.98 (t, *J* = 6.4 Hz, 2H), 4.27 (t, *J* = 6.4 Hz, 2H), 6.88 (ABq, *J* = 8.8 Hz, 2H), 7.46 (ABq, *J* = 8.8 Hz, 2H), 7.50 (ABq, *J* = 8.4 Hz, 2H), 7.53 (ABq, *J* = 8.4 Hz, 2H); ^{19}F NMR (CDCl$_3$): δ –138.48 (dd, *J* = 20.3, 7.9 Hz, 2F), –157.84 (dd, *J* = 20.3, 7.9 Hz, 2F); ^{13}C NMR (CDCl$_3$): δ 13.96, 14.02, 22.5, 22.6, 25.2, 25.7, 29.2, 29.9, 31.4, 31.6, 68.1, 75.5 (t, *J* = 2.9 Hz), 75.8 (t, *J* = 3.7 Hz), 87.6, 92.1, 97.8 (t, *J* = 17.6 Hz), 99.8 (t, *J* = 2.9 Hz), 114.6, 114.7, 121.2, 124.7, 131.4, 131.7, 133.1, 138.4 (tt, *J* = 12.3, 3.0 Hz), 141.1 (ddt, *J* = 249.4, 13.9, 4.4 Hz), 147.2 (ddt, *J* = 252.5, 13.2, 3.7 Hz), 159.5; IR (KBr): ν 3039, 2954, 2857, 2210, 1597, 1520, 1492, 1250, 1122, 1019, 984, 837 cm^{-1}; HRMS: (FAB+) *m/z* [M]$^+$ calcd for C$_{34}$H$_{34}$O$_2$F$_4$: 550.2495; found: 550.2492.

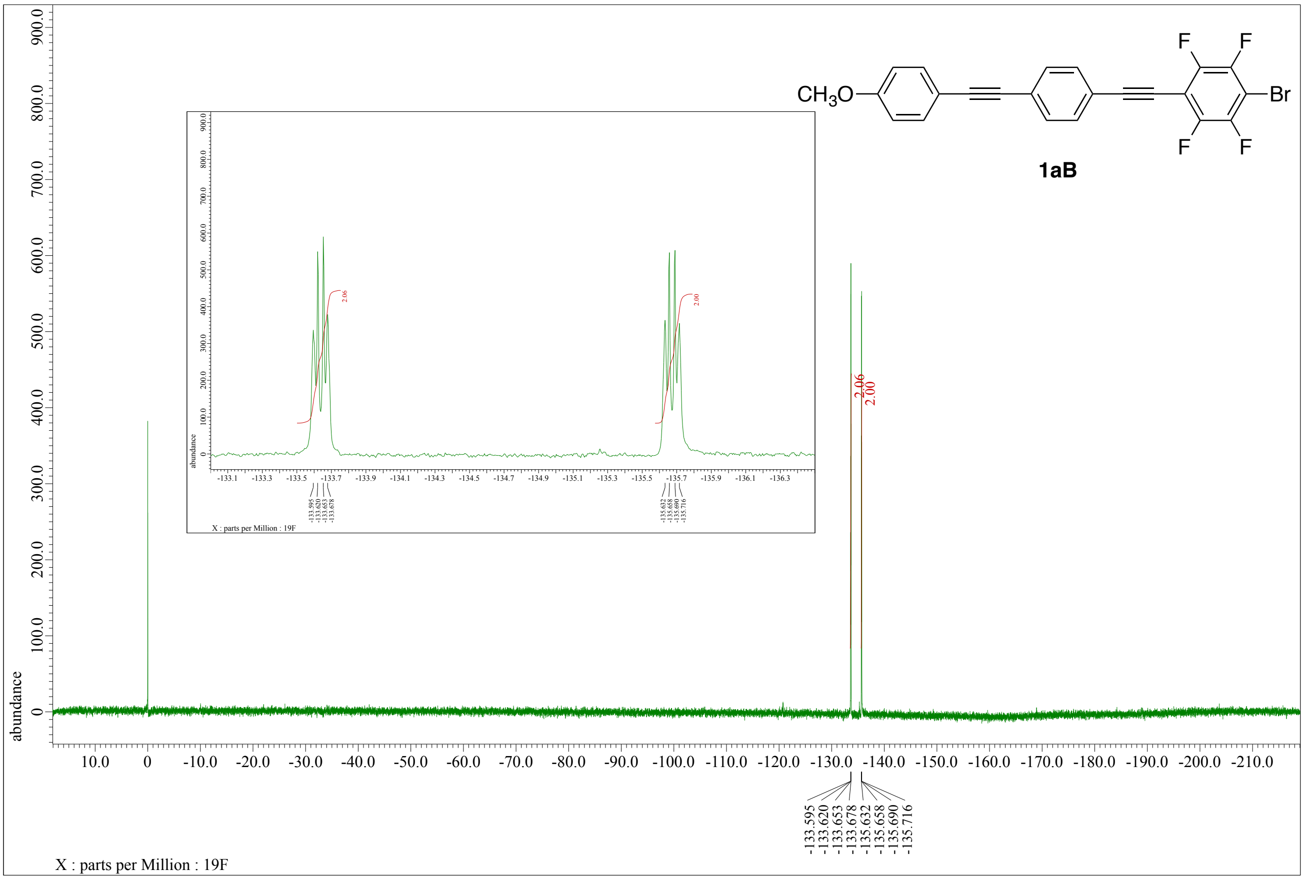
^{1}H NMR spectrum of **1aB** (Solvent: $CDCl_3$)



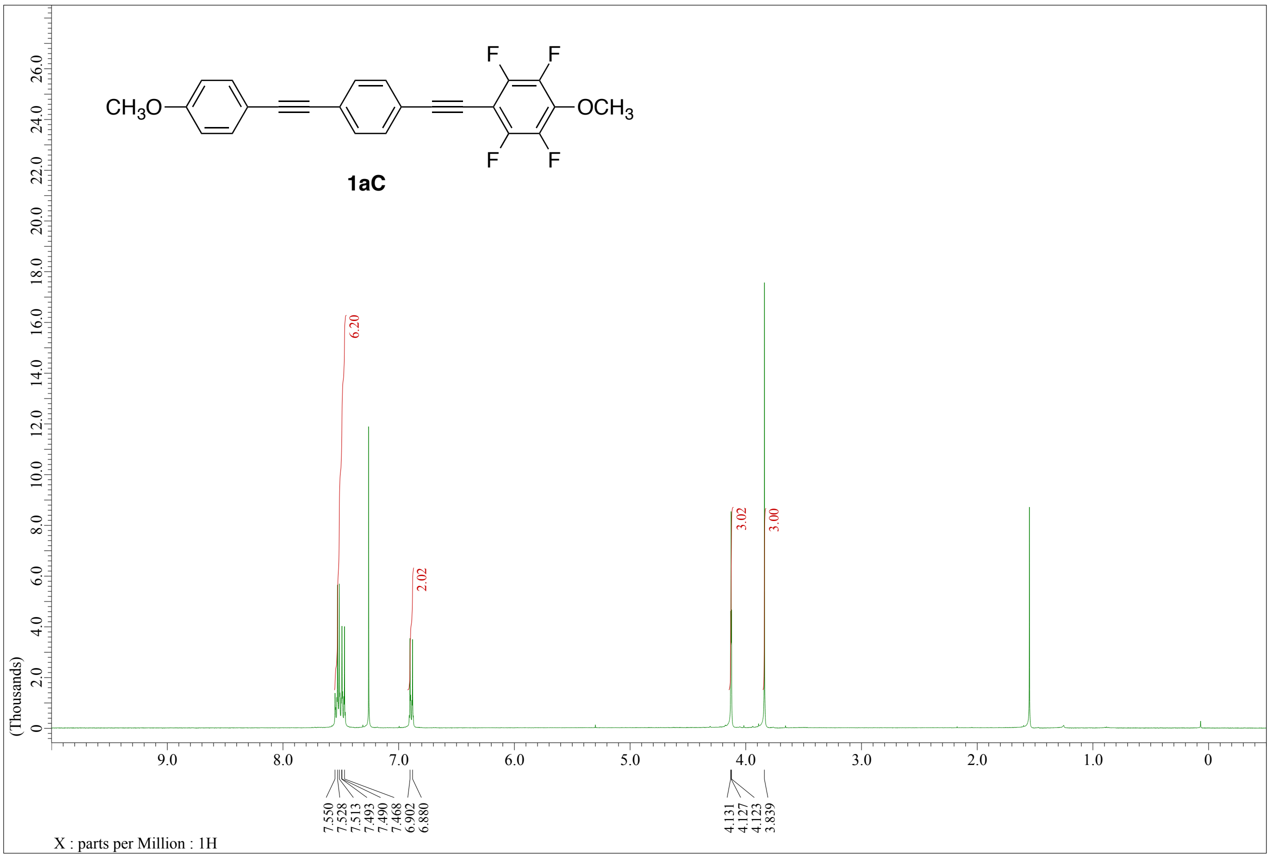
^{13}C NMR spectrum of **1aB** (Solvent: $CDCl_3$)



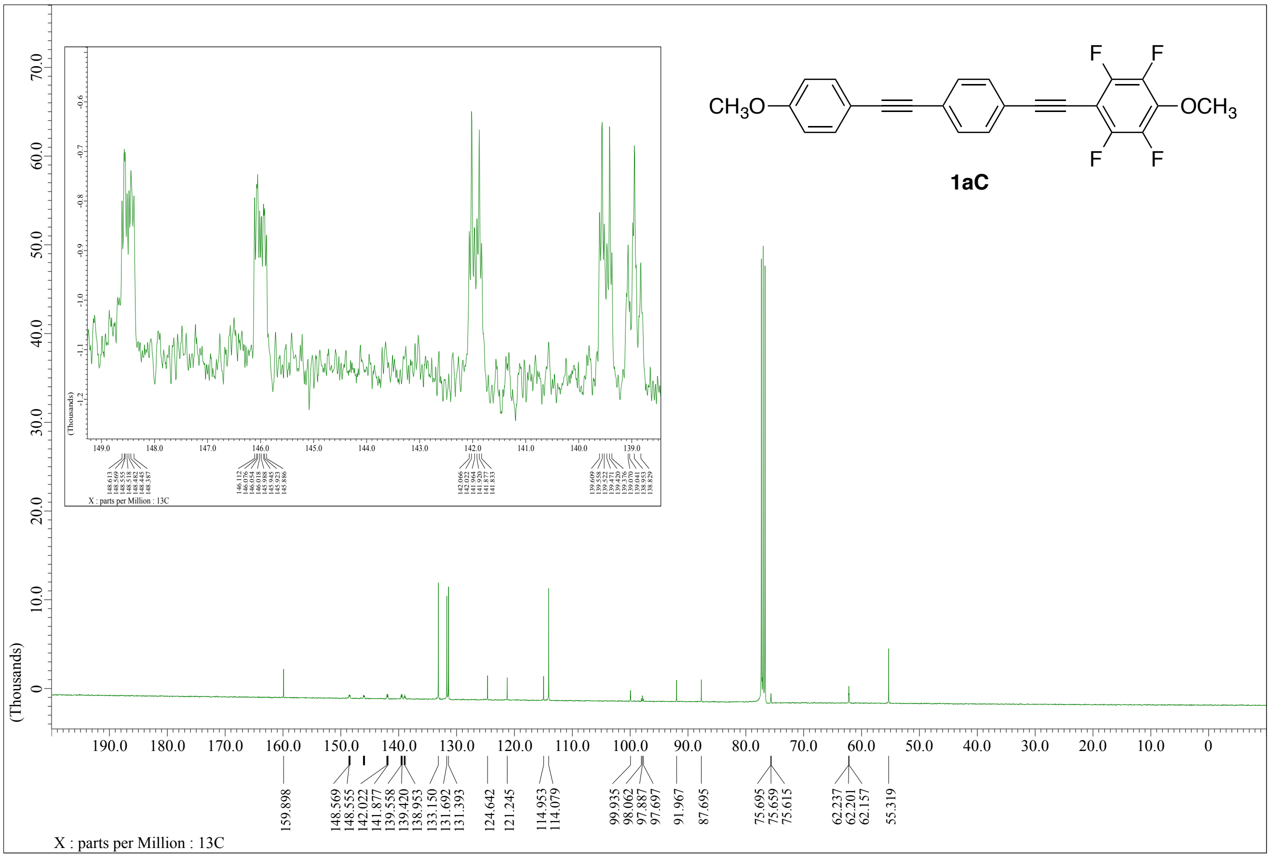
^{19}F NMR spectrum of **1aB** (Solvent: $CDCl_3$)



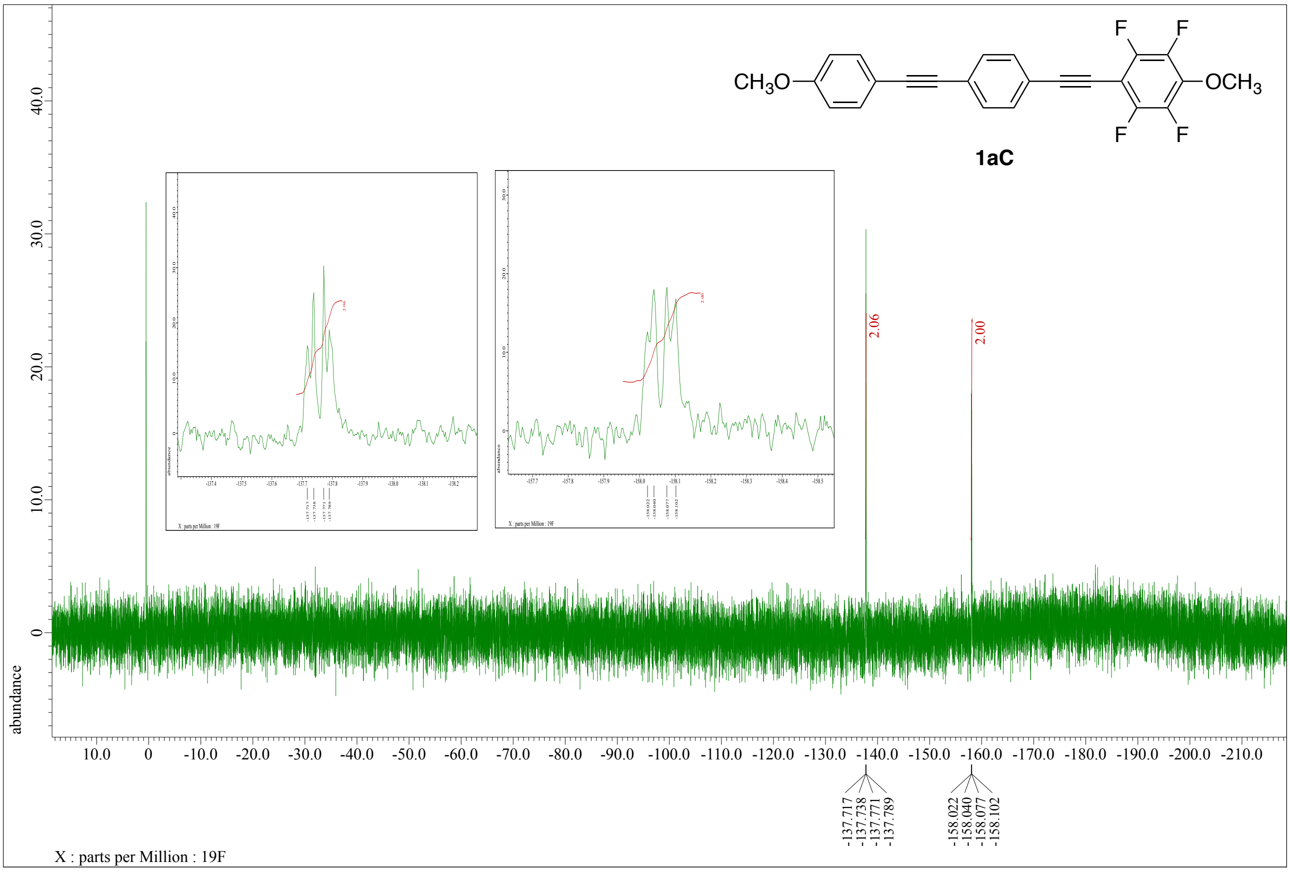
^{1}H NMR spectrum of **1aC** (Solvent: $CDCl_3$)



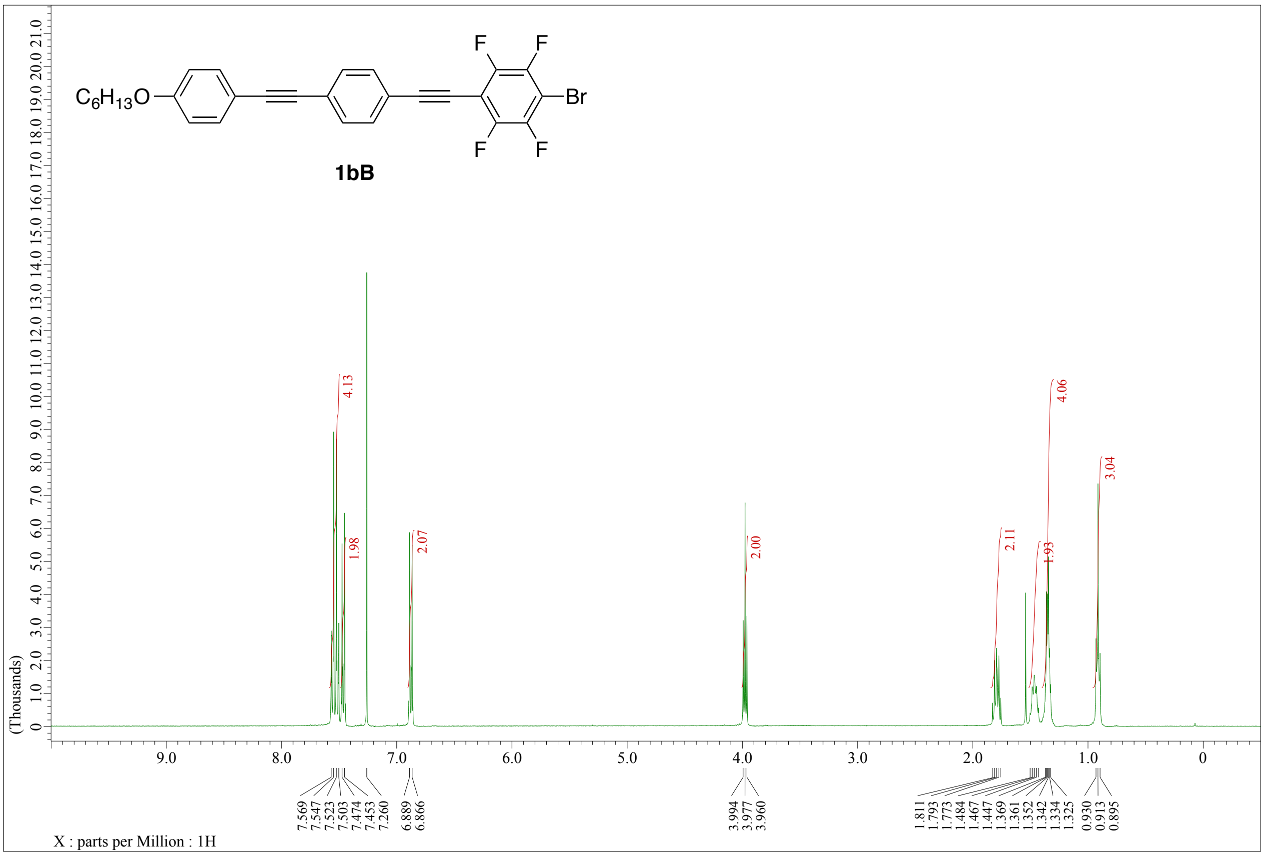
^{13}C NMR spectrum of **1aC** (Solvent: $CDCl_3$)



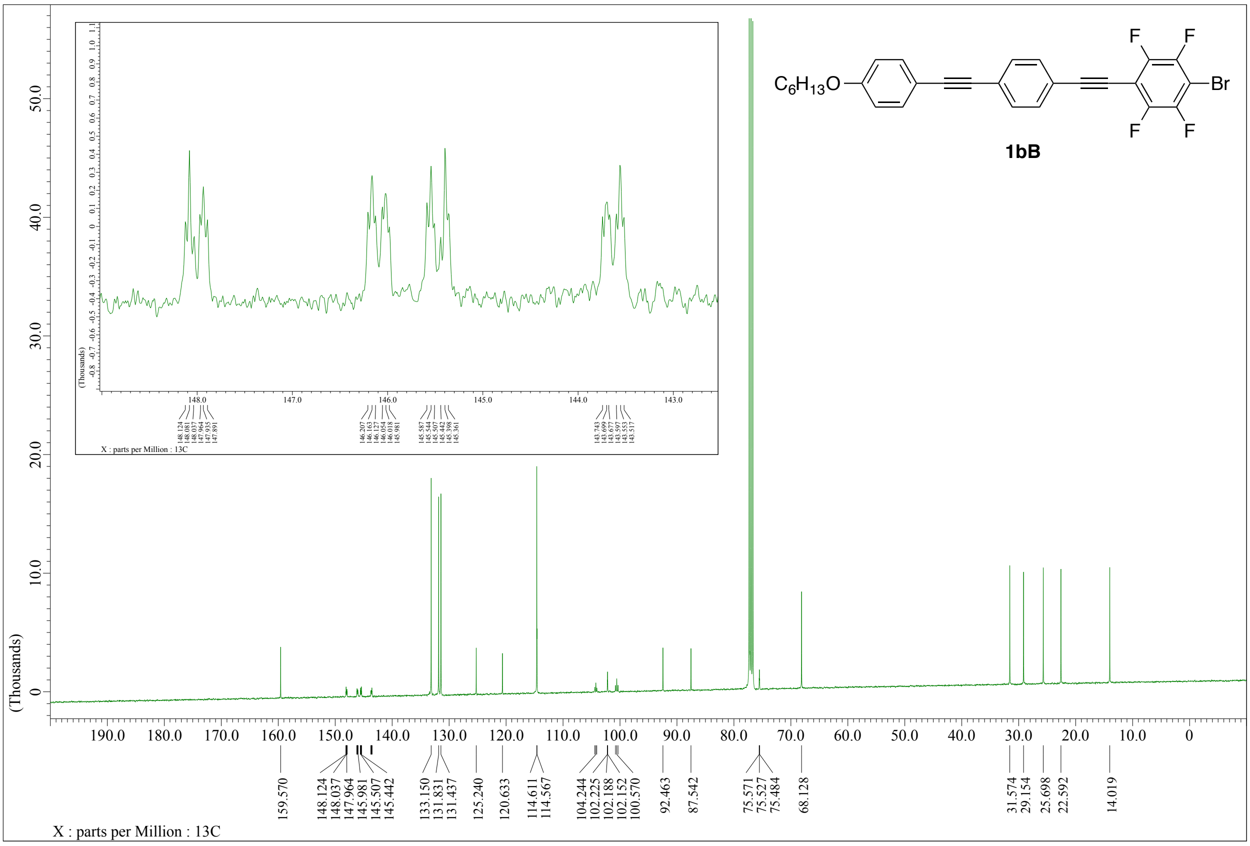
^{19}F NMR spectrum of **1aC** (Solvent: $CDCl_3$)



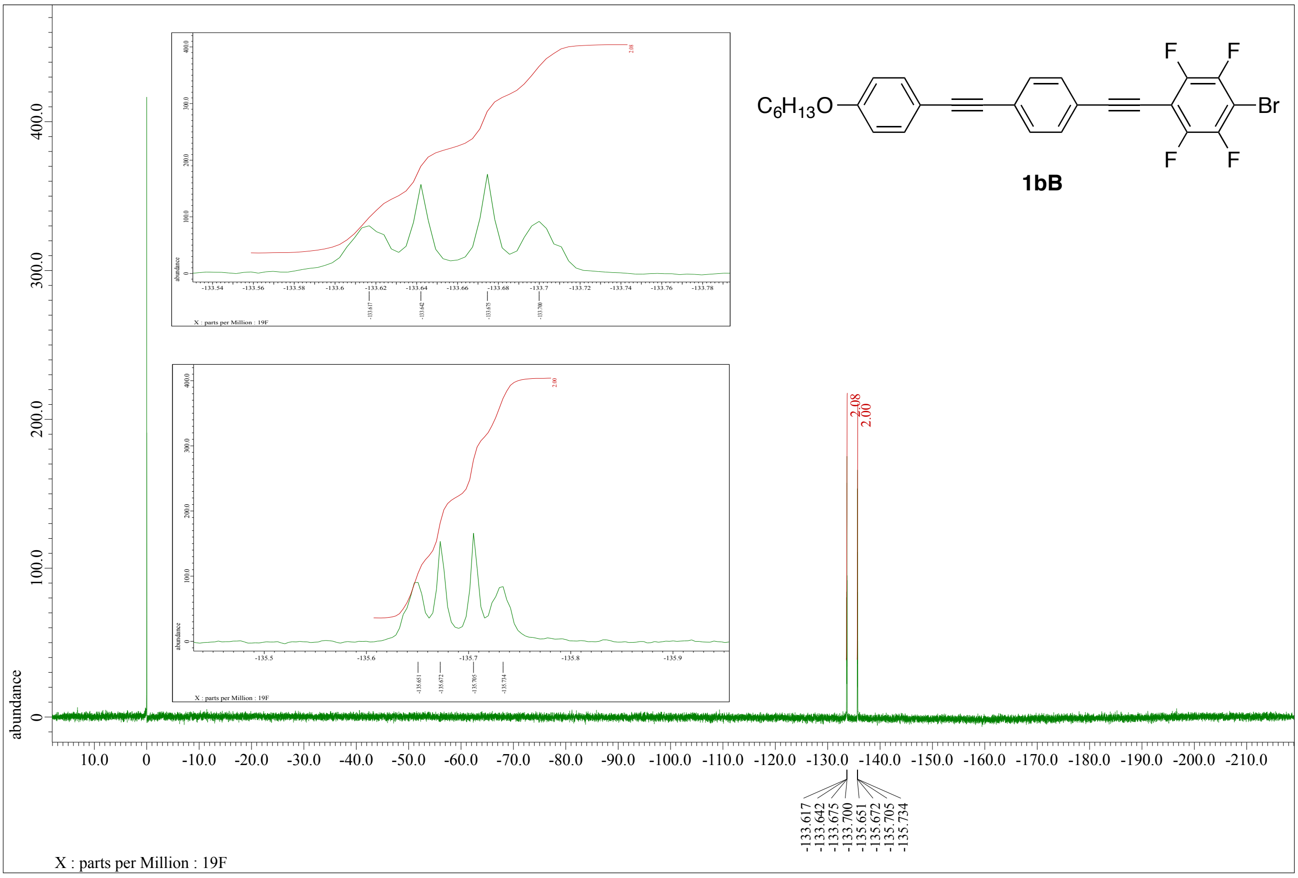
^{1}H NMR spectrum of **1bB** (Solvent: $CDCl_3$)



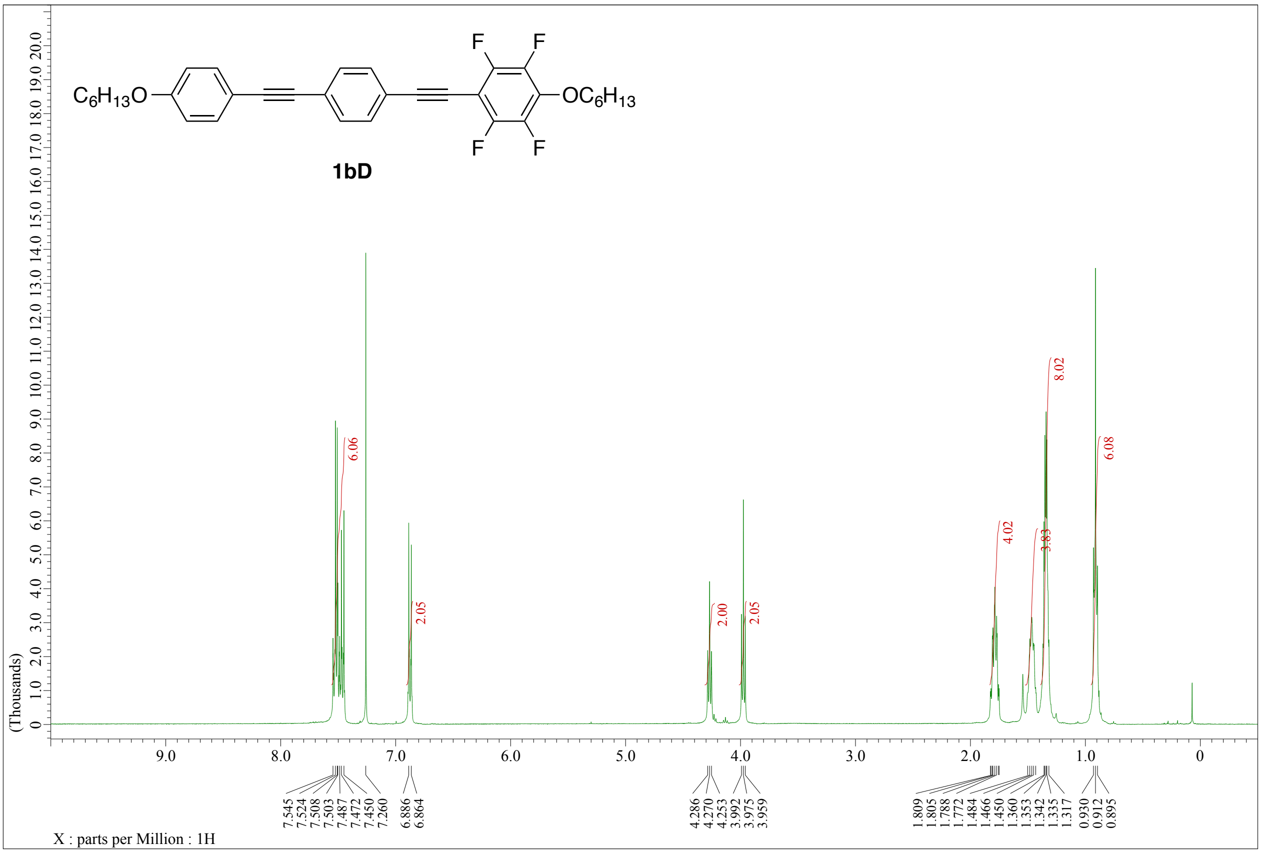
^{13}C NMR spectrum of **1bB** (Solvent: $CDCl_3$)



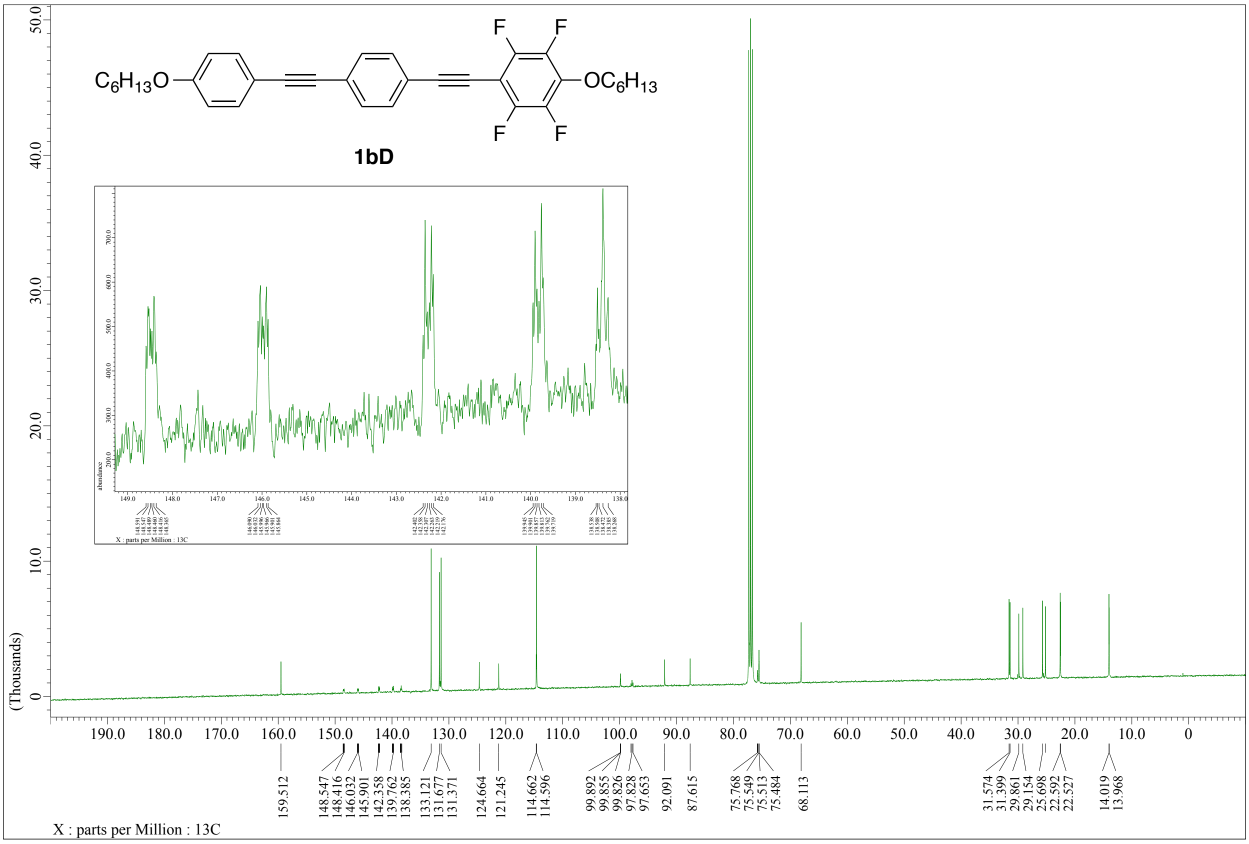
^{19}F NMR spectrum of **1bB** (Solvent: $CDCl_3$)



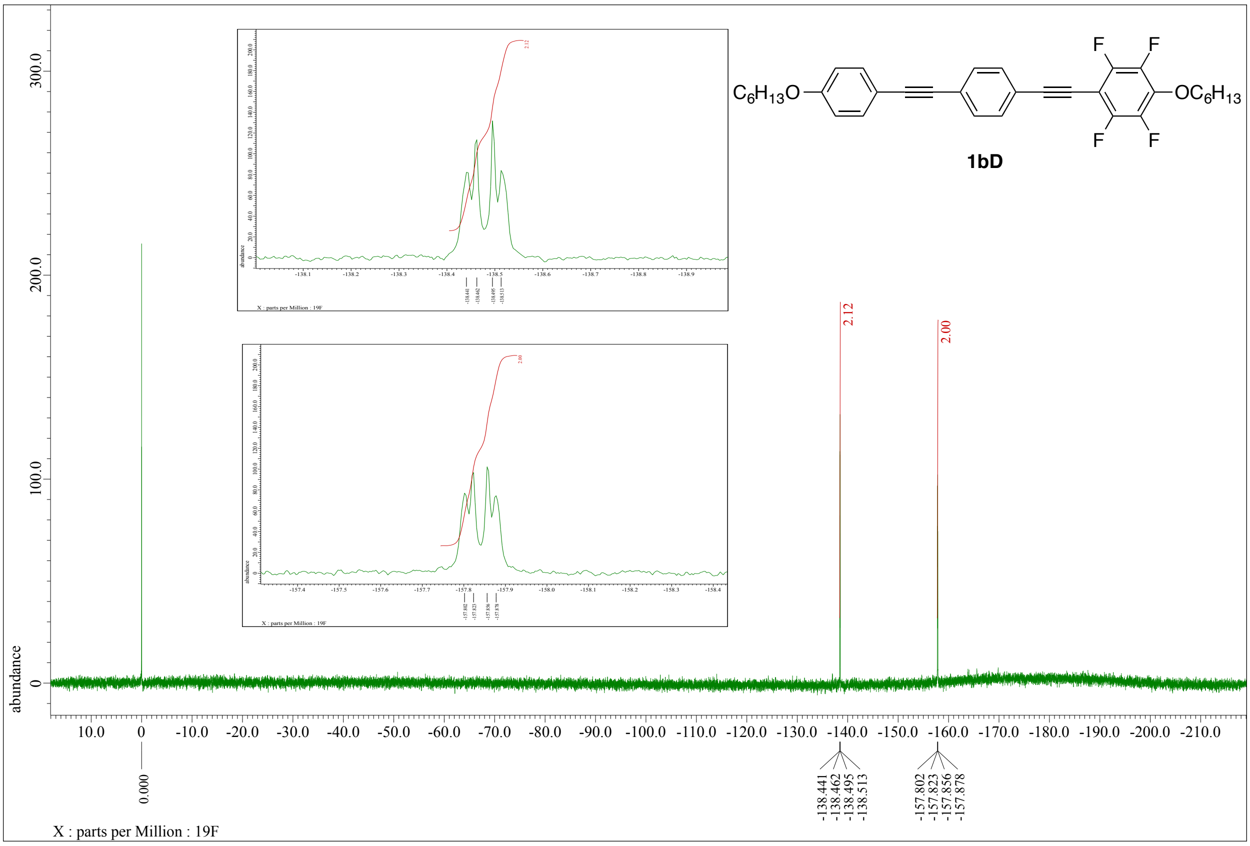
^{1}H NMR spectrum of **1bD** (Solvent: $CDCl_3$)



^{13}C NMR spectrum of **1bD** (Solvent: $CDCl_3$)



^{19}F NMR spectrum of **1bD** (Solvent: $CDCl_3$)



2. X-ray crystallography

Single crystals were obtained by purification of column chromatography, followed by recrystallization (CH_2Cl_2/MeOH = 1/1). The X-ray diffraction measurement was carried out at 298 or 173 K. Crystal data of **1aC** and **1bA** obtained were listed in Table S1 have been indexed, and are included in the Cambridge Crystallographic Center (CCDC) database with the following numbers: CCDC 1838805 for **1aC** and 1838806 for **1bA**. In Table S1 are also included crystallographic data for the reported **1aA**. The indexed database contains additional supplementary crystallographic data for this paper and may be accessed without charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html. 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 e-mail at deposit@ccdc.cam.ac.uk.

Table S1. Crystallographic data for bistolanes **1aC** and **1bA** as well as the reported **1aA**

Bistolane	**1aA** (reported)[4]	**1aC**	**1bA**
CCDC #	1552781	1838805	1838806
Empirical Formula	$C_{23}H_{11}F_5O$	$C_{24}H_{14}F_4O_2$	$C_{28}H_{21}F_5O$
Formula Weight	398.32	410.35	468.45
Temperature [K]	298	173(2)	173(2)
Crystal Color / Habit	Colorless / Block	Colorless / Platelet	Colorless / Platelet
Crystal Size [mm]	0.22 x 0.21 x 0.18	0.66 x 0.21 x 0.28	0.21 x 0.18 x 0.10
Crystal System	$P\,2_1/n$	$P\,2_1/n$	$Pna\,2_1$
Space Group	monoclinic	monoclinic	orthorhombic
a [Å]	5.9797(2)	15.9200(13)	11.4515(6)
b [Å]	7.5043(3)	5.8083(4)	4.9051(3)
c [Å]	40.9251(14)	20.4496(14)	39.555(2)
α [°]	90	90	90
β [°]	92.350(3)	100.147(7)	90
γ [°]	90	90	90
V [Å^3]	1834.91(11)	1861.4(2)	2221.8(2)
Z	4	4	4
$R\,[F^2 > 2\sigma(F^2)]$ [a]	0.0409	0.0578	0.0404
$wR\,(F^2)$ [b]	0.1064	0.1519	0.0909

[a] $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. [b] $wR = \{[\Sigma w(|F_o| - |F_c|)]/\Sigma w|F_o|\}^{1/2}$.

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[4] S. Yamada, K. Miyano, T. Konno, T. Agou, T. Kubota, T. Hosokai, *Org. Biomol. Chem.* **2017**, *15*, 5949–5958.

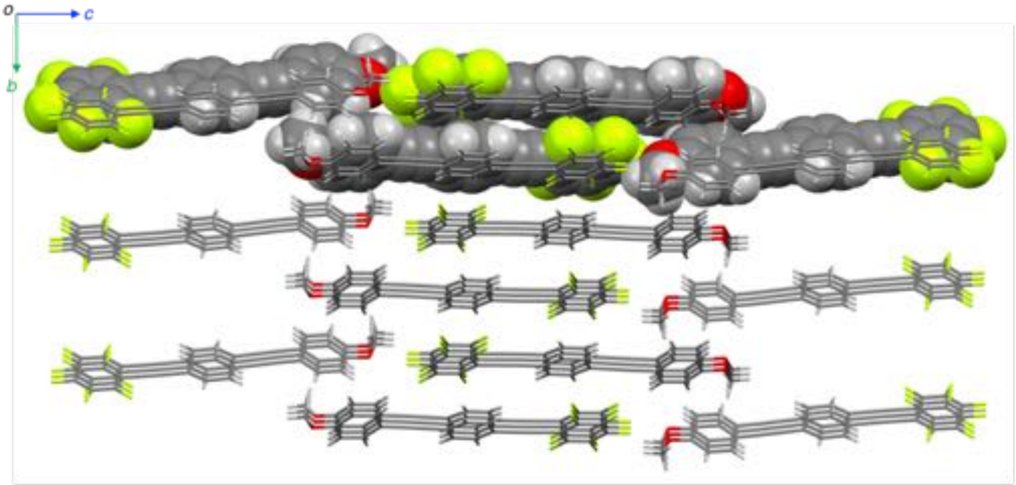


Figure S1. Packing structures of **1aA**.

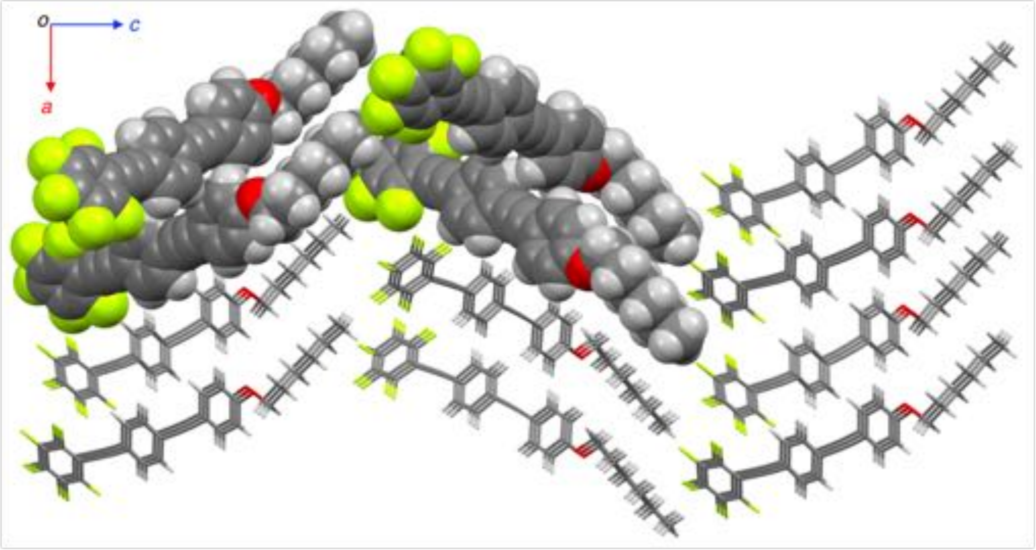


Figure S2. Packing structures of **1bA**.

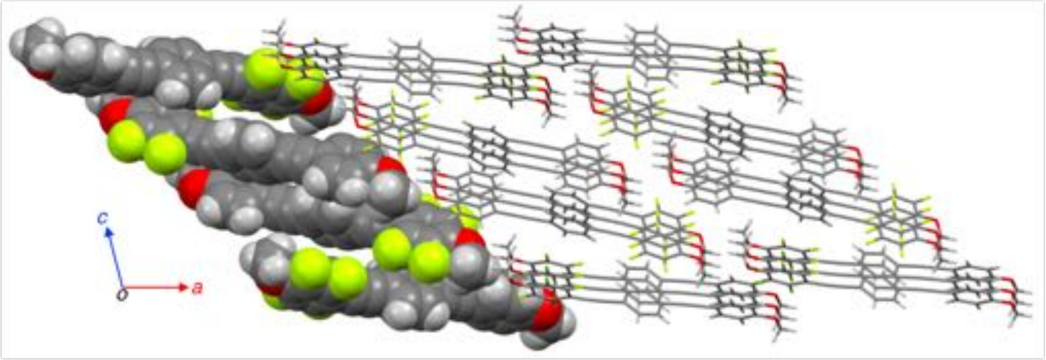


Figure S3. Packing structures of **1aC**.

3. Quantum chemical calculation

All computations were carried out with density functional theory (DFT) using the Gaussian 09 (Rev. C.01) package. Geometry optimizations were executed with the CAM-B3LYP hybrid functional and 6-31G+(d) basis set. The stationary points were characterized by frequency calculations to confirm that the minimum energy structures had no imaginary frequencies.

3-1. Cartesian coordinates of **1aB** at S_0 state after optimization calculation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	12.191481	–0.869263	0.000036
2	1	0	12.007000	–1.473845	0.895946
3	1	0	13.226854	–0.528518	0.000009
4	1	0	12.006993	–1.473968	–0.895790
5	8	0	11.398132	0.302297	–0.000042
6	6	0	10.046909	0.172984	–0.000023
7	6	0	9.320434	1.368983	–0.000115
8	1	0	9.865917	2.306898	–0.000192
9	6	0	7.939585	1.343276	–0.000105
10	1	0	7.381322	2.273962	–0.000176
11	6	0	7.241642	0.122489	–0.000005
12	6	0	7.980339	–1.063982	0.000087
13	1	0	7.457387	–2.015056	0.000164
14	6	0	9.371570	–1.047836	0.000078
15	1	0	9.911571	–1.986888	0.000149
16	6	0	5.813851	0.097872	0.000000
17	6	0	4.603464	0.081521	0.000001
18	6	0	2.448360	1.264219	–0.000263
19	1	0	2.982289	2.208711	–0.000468
20	6	0	1.064014	1.249354	–0.000263
21	1	0	0.508077	2.181282	–0.000468
22	6	0	0.367093	0.032364	0.000001
23	6	0	1.091602	–1.168362	0.000264
24	1	0	0.557069	–2.112734	0.000468
25	6	0	2.475986	–1.151673	0.000264
26	1	0	3.031283	–2.083777	0.000469
27	6	0	3.176484	0.064414	0.000001
28	6	0	–1.059135	0.016681	0.000002
29	6	0	–2.267483	0.005099	0.000004
30	6	0	–3.685737	–0.006670	0.000005
31	6	0	–4.427256	1.178187	0.000125
32	6	0	–5.810402	1.169531	0.000124
33	6	0	–6.512862	–0.028934	0.000003
34	6	0	–5.791509	–1.216112	–0.000117
35	6	0	–4.408376	–1.203084	–0.000116
36	9	0	–3.793651	2.353859	0.000243
37	9	0	–6.463840	2.333484	0.000242
38	9	0	–6.426561	–2.390238	–0.000236
39	9	0	–3.756269	–2.368630	–0.000233
40	35	0	–8.376521	–0.043916	0.000004

SCF Done: E(RCAM-B3LYP) = –3928.77712033 hartree
Dipole moment (Debye): X = 4.3761 Y = –1.2762 Z = 0.0001 Tot = 4.5584
Imaginary frequency: 0

3-2. Cartesian coordinates of **1aB** at S_1 state after optimization calculation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	12.160587	–0.873854	0.000075
2	1	0	11.978623	–1.476476	0.896896
3	1	0	13.191832	–0.522538	0.000047
4	1	0	11.978628	–1.476636	–0.896640
5	8	0	11.355829	0.294138	–0.000032
6	6	0	10.013152	0.167962	–0.000025
7	6	0	9.287915	1.372756	–0.000135
8	1	0	9.840374	2.306431	–0.000217
9	6	0	7.914336	1.355299	–0.000138
10	1	0	7.357000	2.286143	–0.000223
11	6	0	7.200992	0.125589	–0.000031
12	6	0	7.950242	–1.075039	0.000079
13	1	0	7.422778	–2.023227	0.000162
14	6	0	9.332937	–1.058122	0.000082
15	1	0	9.875258	–1.995748	0.000168
16	6	0	5.805468	0.103807	–0.000033
17	6	0	4.573439	0.087184	–0.000033
18	6	0	2.437569	1.290211	–0.000157
19	1	0	2.976149	2.232252	–0.000260
20	6	0	1.072489	1.275166	–0.000149
21	1	0	0.510342	2.203034	–0.000247
22	6	0	0.351649	0.035964	–0.000011
23	6	0	1.102001	–1.185557	0.000118
24	1	0	0.562277	–2.126648	0.000222
25	6	0	2.467077	–1.167854	0.000111
26	1	0	3.028053	–2.096754	0.000209
27	6	0	3.187609	0.069991	–0.000027
28	6	0	–1.031146	0.019875	–0.000003
29	6	0	–2.261825	0.007123	0.000003
30	6	0	–3.650722	–0.005624	0.000008
31	6	0	–4.413703	1.186527	0.000042
32	6	0	–5.788905	1.171958	0.000046
33	6	0	–6.498001	–0.030587	0.000018
34	6	0	–5.767822	–1.220436	–0.000015
35	6	0	–4.392558	–1.210995	–0.000021
36	9	0	–3.775622	2.363245	0.000070
37	9	0	–6.449873	2.335023	0.000077
38	9	0	–6.408326	–2.394933	–0.000042
39	9	0	–3.733885	–2.376355	–0.000053
40	35	0	–8.359293	–0.047252	0.000024

SCF Done: E(RCAM-B3LYP) = –3928.76800516 hartree

Dipole moment (Debye):   X = 5.4280   Y = –1.2864   Z = 0.0001   Tot = 5.5783

3-3. Cartesian coordinates of **1aC** at S_0 state after optimization calculation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	–11.483320	0.810019	0.053671
2	1	0	–11.298595	1.399193	0.959654
3	1	0	–12.516253	0.462160	0.052308
4	1	0	–11.307334	1.432218	–0.831730
5	6	0	–9.331283	–0.216324	0.023940
6	6	0	–8.596035	–1.406443	–0.001887
7	1	0	–9.134195	–2.348375	–0.016733
8	6	0	–7.215296	–1.370227	–0.008294
9	1	0	–6.650189	–2.296454	–0.028528
10	6	0	–6.526330	–0.144619	0.010889
11	6	0	–7.273999	1.035855	0.036604
12	1	0	–6.758264	1.990641	0.051688
13	6	0	–8.665157	1.009229	0.043258
14	1	0	–9.211962	1.944030	0.063381
15	6	0	–5.098447	–0.108928	0.004029
16	6	0	–3.888138	–0.082112	–0.002002
17	6	0	–2.460825	–0.051511	–0.009469
18	6	0	–1.720898	–1.243654	–0.029419
19	1	0	–2.245307	–2.193396	–0.039070
20	6	0	–0.336519	–1.215273	–0.037116
21	1	0	0.227967	–2.141824	–0.052936
22	6	0	0.349634	0.007702	–0.025156
23	6	0	–0.387187	1.200689	–0.005045
24	1	0	0.137951	2.150175	0.004228
25	6	0	–1.771588	1.170714	0.002689
26	1	0	–2.335333	2.097581	0.018113
27	6	0	1.776579	0.037306	–0.033924
28	6	0	2.984958	0.061539	–0.042399
29	6	0	4.404326	0.088667	–0.052781
30	6	0	5.164316	–1.081647	–0.062784
31	6	0	6.548884	–1.062758	–0.079426
32	6	0	7.257771	0.140166	–0.064647
33	6	0	6.502409	1.318296	–0.058170
34	6	0	5.122017	1.290172	–0.055747
35	6	0	9.424304	–0.692273	0.554162
36	1	0	9.013567	–0.943540	1.536514
37	1	0	10.389699	–0.200837	0.673010
38	1	0	9.535971	–1.596682	–0.046005
39	8	0	–10.681995	–0.355544	0.028217
40	8	0	8.595208	0.268106	–0.108090
41	9	0	4.551052	-2.269774	–0.074478
42	9	0	7.204708	-2.236412	–0.132520
43	9	0	4.461088	2.451770	–0.042546
44	9	0	7.134876	2.496317	–0.047208

SCF Done: E(RCAM-B3LYP) = –1472.02670537 hartree

Dipole moment (Debye): X = –1.7195 Y = 0.0284 Z = 0.9402 Tot = 1.9600

Imaginary frequency: 0

3-4. Cartesian coordinates of **1aC** at S_1 state after optimization calculation

Center	Atomicq	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	–11.451671	0.821419	0.057526
2	1	0	–11.266059	1.419686	0.956789
3	1	0	–12.481839	0.466523	0.062576
4	1	0	–11.278978	1.431724	–0.836197
5	6	0	–9.298733	–0.207508	0.034827
6	6	0	–8.565679	–1.406934	0.021239
7	1	0	–9.111765	–2.344458	0.018887
8	6	0	–7.191893	–1.381030	0.011140
9	1	0	–6.629238	–2.308680	0.000563
10	6	0	–6.484829	–0.147128	0.014275
11	6	0	–7.243074	1.048365	0.028100
12	1	0	–6.722257	2.000264	0.030681
13	6	0	–8.626050	1.022121	0.038197
14	1	0	–9.173918	1.956585	0.048581
15	6	0	–5.089847	–0.116413	0.004030
16	6	0	–3.856923	–0.090122	–0.005154
17	6	0	–2.472643	–0.060651	–0.015463
18	6	0	–1.709113	–1.274277	–0.030305
19	1	0	–2.238606	–2.221511	–0.033516
20	6	0	–0.344527	–1.246079	–0.040454
21	1	0	0.225779	–2.169031	–0.051946
22	6	0	0.365994	–0.000303	–0.036590
23	6	0	–0.396591	1.214168	–0.021858
24	1	0	0.134146	2.160483	–0.019078
25	6	0	–1.761146	1.184317	–0.011699
26	1	0	–2.330244	2.108257	–0.000647
27	6	0	1.749072	0.028807	–0.046826
28	6	0	2.979526	0.054121	–0.055832
29	6	0	4.370267	0.082235	–0.066747
30	6	0	5.148799	–1.096413	–0.083274
31	6	0	6.526128	–1.069557	–0.097076
32	6	0	7.237114	0.137772	–0.071508
33	6	0	6.478271	1.318310	–0.060907
34	6	0	5.103123	1.292753	–0.062037
35	6	0	9.384546	–0.630668	0.660141
36	1	0	8.957886	–0.749010	1.661333
37	1	0	10.358845	–0.146463	0.729418
38	1	0	9.484650	–1.605943	0.180357
39	8	0	–10.642745	–0.342339	0.043847
40	8	0	8.578115	0.252234	–0.125727
41	9	0	4.530881	–2.283885	–0.102661
42	9	0	7.195748	–2.236030	–0.153929
43	9	0	4.435698	2.452608	–0.042801
44	9	0	7.114107	2.496040	–0.042300

SCF Done: E(RCAM-B3LYP) = –1472.01729160 hartree

Dipole moment (Debye): X = –2.6271 Y = 0.1412 Z = 1.0951 Tot = 2.8497

3-5. Cartesian coordinates of **1bB** at S_0 state after optimization calculation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	9	0	–6.120498	–2.283716	0.439563
2	6	0	13.795033	1.162193	1.506930
3	1	0	13.643710	0.637718	2.459928
4	1	0	13.187473	2.075246	1.561303
5	9	0	–8.787642	–2.230150	0.559608
6	6	0	13.283124	0.286246	0.364165
7	1	0	13.440441	0.808933	–0.590013
8	1	0	13.888115	–0.630539	0.312724
9	6	0	11.806940	–0.083557	0.498718
10	1	0	11.201323	0.829431	0.537020
11	1	0	11.647363	–0.602078	1.455074
12	9	0	–6.061287	2.372048	–0.349418
13	6	0	11.308866	–0.969610	–0.642005
14	1	0	11.891586	–1.899793	–0.671994
15	1	0	11.466347	–0.467753	–1.604789
16	8	0	9.068355	–0.161287	–0.643521
17	6	0	9.844556	–1.348872	–0.528395
18	1	0	9.560695	–2.047808	–1.325829
19	1	0	9.641142	–1.826191	0.440210
20	9	0	–8.728678	2.426557	–0.229858
21	6	0	7.717152	–0.243433	–0.568197
22	6	0	7.006993	–1.429386	–0.374060
23	1	0	7.519391	–2.377735	–0.269890
24	6	0	5.617608	–1.397471	–0.312830
25	1	0	5.068835	–2.321546	–0.161674
26	6	0	4.913107	–0.197275	–0.442642
27	6	0	5.644442	0.987581	–0.638141
28	1	0	5.113400	1.928359	–0.741371
29	6	0	7.023913	0.965504	–0.699997
30	1	0	7.594167	1.876022	–0.851313
31	6	0	3.486708	–0.172672	–0.379156
32	6	0	2.277488	–0.146616	–0.325973
33	6	0	0.852131	–0.113760	–0.263302
34	6	0	0.118924	–1.289897	–0.042699
35	1	0	0.647463	–2.229304	0.080258
36	6	0	–1.263782	–1.258051	0.018703
37	1	0	–1.823769	–2.171577	0.189712
38	6	0	–1.953596	–0.047308	–0.139092
39	6	0	–1.224067	1.129822	–0.359853
40	1	0	–1.753162	2.069140	–0.482745
41	6	0	0.158610	1.096173	–0.420791
42	1	0	0.718038	2.009825	–0.591742
43	6	0	–3.378201	–0.014156	–0.075995
44	6	0	–4.585253	0.012741	–0.022404
45	6	0	–6.001809	0.042255	0.040928
46	6	0	–6.718038	1.230994	–0.125093
47	6	0	–8.099466	1.261078	–0.063409
48	6	0	–8.825780	0.099687	0.167944
49	6	0	–8.129485	–1.090652	0.335191
50	6	0	–6.748025	–1.116651	0.272658
51	6	0	15.268037	1.536807	1.359231
52	1	0	15.608656	2.161243	2.191782
53	1	0	15.902406	0.643171	1.331969
54	1	0	15.442603	2.094316	0.431724
55	35	0	–10.687055	0.137666	0.252176

SCF Done: E(RCAM-B3LYP) = –4125.23092216 hartree

Dipole moment (Debye): X = 4.7150 Y = –1.1776 Z = 0.0346 Tot = 4.8600

Imaginary frequency: 0

3-6. Cartesian coordinates of **1bB** at S$_1$ state after optimization calculation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	9	0	–6.094813	–2.291792	0.425470
2	6	0	13.755873	1.199473	1.482420
3	1	0	13.607160	0.693094	2.445521
4	1	0	13.144473	2.110857	1.518973
5	9	0	–8.766220	–2.232837	0.543903
6	6	0	13.247856	0.299038	0.357068
7	1	0	13.402115	0.803673	–0.607195
8	1	0	13.856684	–0.615883	0.323240
9	6	0	11.773423	–0.074846	0.500192
10	1	0	11.164431	0.836628	0.522044
11	1	0	11.617153	–0.575958	1.466256
12	9	0	–6.033662	2.385586	–0.337829
13	6	0	11.279524	–0.984854	–0.623473
14	1	0	11.867021	–1.912244	–0.636744
15	1	0	11.432727	–0.501539	–1.596258
16	8	0	9.031627	–0.189895	–0.639088
17	6	0	9.819109	–1.373415	–0.500363
18	1	0	9.535290	–2.086594	–1.284216
19	1	0	9.616620	–1.828280	0.478410
20	9	0	–8.705425	2.435005	–0.217922
21	6	0	7.689830	–0.265985	–0.562238
22	6	0	6.972802	–1.451918	–0.341242
23	1	0	7.486600	–2.397129	–0.217282
24	6	0	5.592334	–1.417961	–0.280443
25	1	0	5.037789	–2.334822	–0.109605
26	6	0	4.878626	–0.205299	–0.437529
27	6	0	5.627394	0.982754	–0.660727
28	1	0	5.098205	1.921865	–0.783929
29	6	0	6.998990	0.949654	–0.721086
30	1	0	7.577490	1.851466	–0.891679
31	6	0	3.485289	–0.176294	–0.375995
32	6	0	2.254349	–0.147994	–0.322274
33	6	0	0.870335	–0.114664	–0.261820
34	6	0	0.114535	–1.309827	–0.033947
35	1	0	0.647372	–2.246872	0.090955
36	6	0	–1.248974	–1.277416	0.026217
37	1	0	–1.815421	–2.186366	0.199188
38	6	0	–1.962417	–0.044991	–0.137424
39	6	0	–1.206594	1.151314	–0.365657
40	1	0	–1.740682	2.087340	–0.490441
41	6	0	0.156907	1.116626	–0.425176
42	1	0	0.722121	2.026655	–0.598172
43	6	0	–3.343984	–0.011922	–0.076782
44	6	0	–4.572932	0.015705	–0.022507
45	6	0	–5.960541	0.044705	0.039093
46	6	0	–6.696422	1.242958	–0.120358
47	6	0	–8.070165	1.268394	–0.058682
48	6	0	–8.804406	0.102586	0.166067
49	6	0	–8.101150	–1.092498	0.326523
50	6	0	–6.727486	–1.122879	0.265572
51	6	0	15.227161	1.577336	1.326620
52	1	0	15.564809	2.219780	2.146435
53	1	0	15.865460	0.686218	1.317413
54	1	0	15.399197	2.117015	0.388215
55	35	0	–10.663833	0.140569	0.249619

SCF Done: E(RCAM-B3LYP) = –4125.22180538 hartree

Dipole moment (Debye): X = 5.8623 Y = –1.2256 Z = 0.0209 Tot = 5.9890

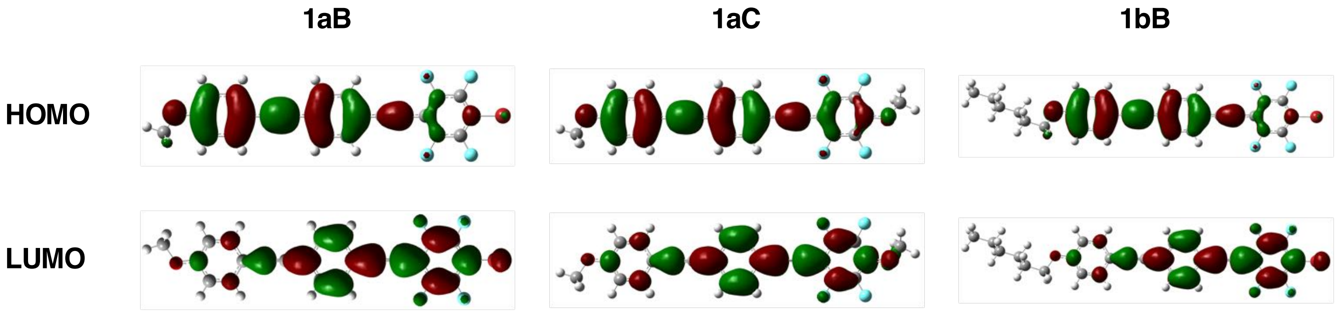


Figure S4. Frontier molecular orbitals at HOMO and LUMO for **1aB**, **1aC**, and **1bB**, calculated by DFT/CAM-B3LYP/6-31+G(d) level of theory.

Table S2. Orbital energies at the HOMO and LUMO and molecular dipole moment along long molecular axis calculated by DFT/CAM-B3LYP/6-31+G(d) level of theory

		1aB	**1aC**	**1bB**
S_0	HOMO [eV]	−7.06	−6.92	−7.04
	LUMO [eV]	−1.35	−1.06	−1.34
	$\mu_{\parallel}$ [D]	4.38	1.72	4.72
S1	HOMO [eV]	−6.77	−6.62	−6.73
	LUMO [eV]	-1.64	−1.39	−1.63
	$\mu_{\parallel}$ [D]	5.43	2.62	5.86

4. Powder X-ray diffraction

Powder X-ray diffraction measurement was performed using a Rigaku Smart-Lab with Cu$K\alpha$ radition (λ = 1.5418 Å) at 20 °C-intervals from 200 °C to 80 °C on the 2nd cooling process. The diffraction patterns for **1bA** and **1bB** obtained are shown in Figure S5.

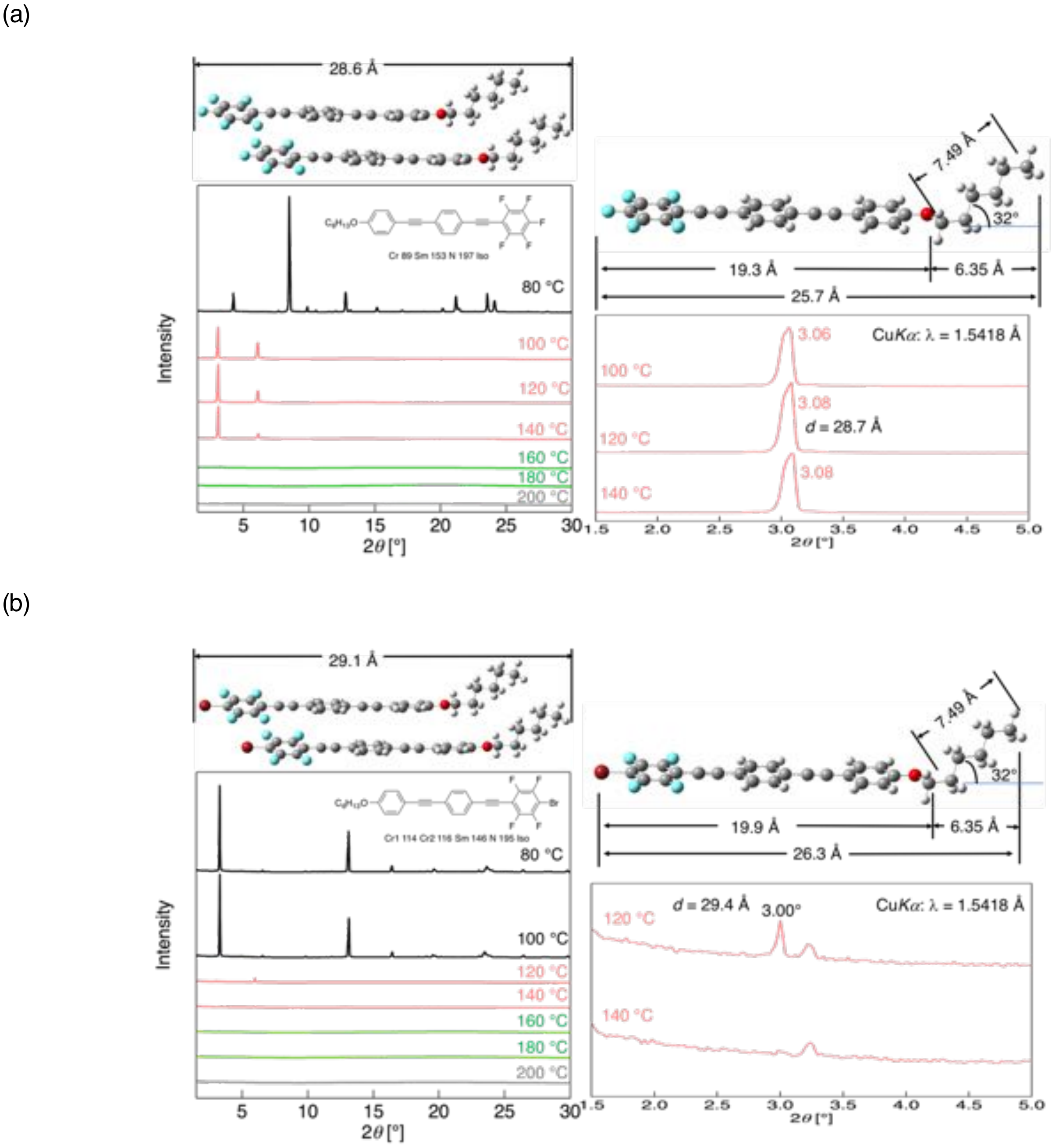
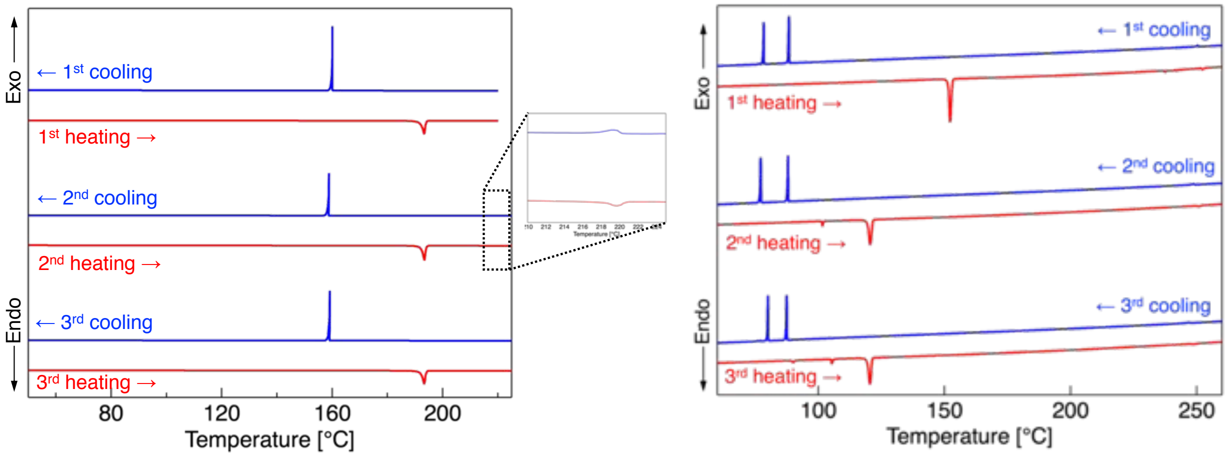


Figure S5. XRD pattern and calculated molecular and packing structures for (a) **1bA** and for (b) **1bB**

5. Phase transition behavior

Phase transition temperatures of polyfluoroinated bistolane derivatives were determined with a differential scanning calorimeter (DSC, SII, X-DSC7000 or SHIMDZU DSC-60-PLUS) at heating and cooling rate of 5.0 °C min^{-1}. The obtained thermograms were shown in Figure S6. At least three scans were carried out to obtain the reproducibility. In Table S3–S6 are summarized the phase transition sequence and thermodynamic parameters.

(a) **1aB** (b) **1aC**



(c) **1bB** (d) **1bD**

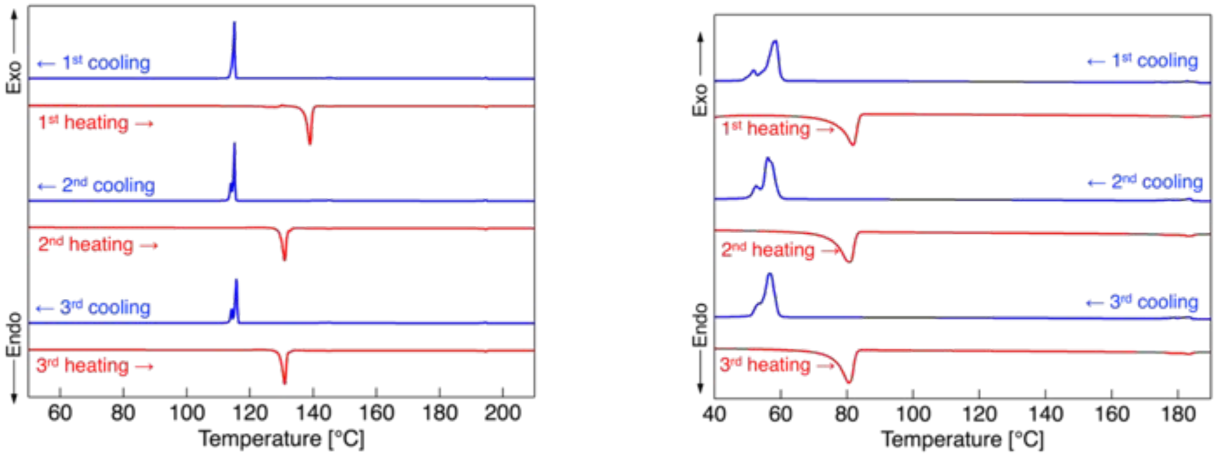


Figure S6. DSC thermograms of polyfluorinated bistolane derivatives, **1aB**, **1aC**, **1bB**, and **1bD**, under nitrogen atmosphere. Scan rate: 5.0 °C min^{-1}.

Table S3. Phase transition behaviors and thermodynamic parameters for **1aB**

Phase transition sequence and temperature [°C][a]			ΔH [kJ mol^{-1}]	ΔS [J mol^{-1} K^{-1}]
1st Heating	Cr – N	192	46.4	99.7
	N – Iso	220	0.54	1.09
1st Cooling	Cr – N	160	–45.9	–106.1
	N – Iso	220	–0.34	–0.69
2nd Heating	Cr – N	192	45.9	98.7
	N – Iso	218	0.39	0.80
2nd Cooling	Cr – N	159	–49.1	–113.8
	N – Iso	220	–0.38	–0.77
3rd Heating	Cr – N	192	44.6	95.9
	N – Iso	217	0.56	1.16
3rd Cooling	Cr – N	159	–42.3	–98.0
	N – Iso	220	–0.35	–0.72

[a] Abbreviations: Cr: crystalline, N: nematic, Iso: isotropic phases.

Table S4. Phase transition behaviors and thermodynamic parameters for **1aC**

Phase transition sequence and temperature [°C][a]			ΔH [kJ mol^{-1}]	ΔS [J mol^{-1} K^{-1}]
1st Heating	Cr – N	151	48.5	114.4
	N – Iso	252	1.18	2.25
1st Cooling	Cr^1 – Cr^2	78	–15.8	–45.0
	Cr^2 – N	88	–18.6	–51.5
	N – Iso	250	–1.15	–2.20
2nd Heating	Cr^1 – Cr^2	101	2.42	6.46
	Cr^2 – N	120	37.7	95.9
	N – Iso	250	1.28	2.45
2nd Cooling	Cr^1 – Cr^2	77	–17.9	–51.2
	Cr^2 – N	88	–18.1	–50.0
	N – Iso	249	–0.95	–1.83
3rd Heating	Cr^1 – Cr^2	89	2.06	5.69
	Cr^2 – Cr^3	105	2.67	7.05
	Cr^3 – N	119	36.6	93.2
	N – Iso	247	1.17	2.25
3rd Cooling	Cr^1 – Cr^2	80	–16.9	–47.9
	Cr^2 – N	88	–17.6	–48.8
	N – Iso	247	–0.48	–0.92

[a] Abbreviations: Cr: crystalline, N: nematic, Iso: isotropic phases.

Table S5. Phase transition behaviors and thermodynamic parameters for **1bB**

Phase transition sequence and temperature [°C][a]			ΔH [kJ mol^{-1}]	ΔS [J mol^{-1} K^{-1}]
1st Heating	Cr – SmA	137	52.9	129.0
	SmA – N	145	0.37	0.89
	N – Iso	194	0.85	1.82
1st Cooling	Cr – SmA	115	–36.0	–92.8
	SmA – N	147	–0.95	–2.27
	N – Iso	195	–0.87	–1.86
2nd Heating	Cr – SmA	130	41.0	101.8
	SmA – N	144	0.70	1.69
	N – Iso	194	0.75	1.61
2nd Cooling	Cr^1 – Cr^2	114	–[b]	–[b]
	Cr^2 – SmA	116	–36.0	–92.7
	SmA – N	143	–0.76	–1.81
	N – Iso	195	–0.82	–1.75
3rd Heating	Cr – SmA	130	41.0	101.9
	SmA – N	143	0.70	1.69
	N – Iso	194	0.91	1.96
3rd Cooling	Cr^1 – Cr^2	115	–[b]	–[b]
	Cr^2 – SmA	116	–36.0	–92.5
	SmA – N	146	–0.67	–1.60
	N – Iso	195	–0.74	–1.57

[a] Abbreviations: Cr: crystalline, SmA: smectic A, N: nematic, Iso: isotropic phases. [b] Not determined due to short period of Cr^2 phase.

Table S6. Phase transition behaviors and thermodynamic parameters for **1bD**

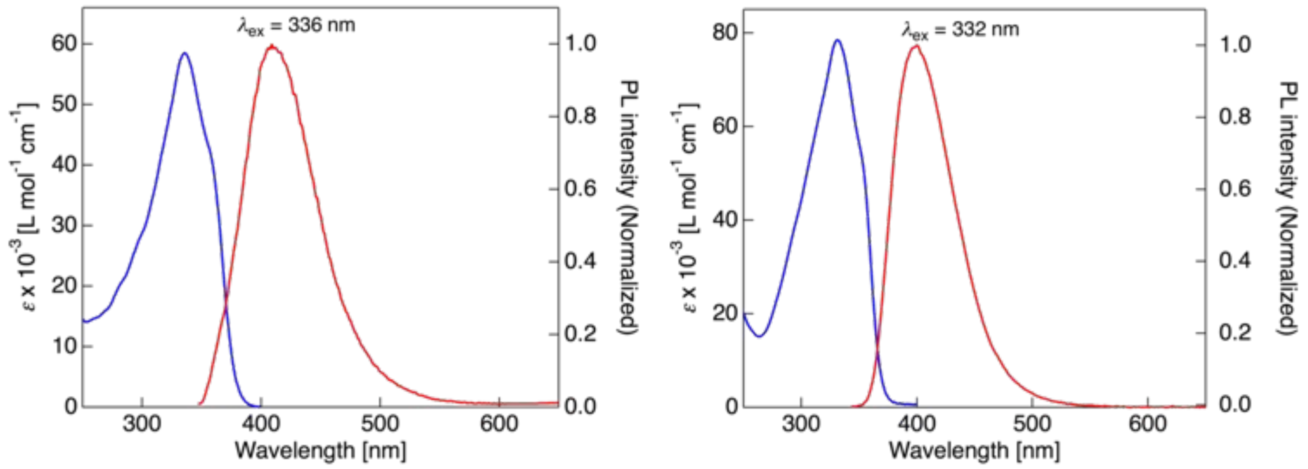
Phase transition sequence and temperature [°C][a]			ΔH [kJ mol^{-1}]	ΔS [J mol^{-1} K^{-1}]
1st Heating	Cr – N	77	27.6	79.0
	N – Iso	185	1.75	3.82
1st Cooling	Cr^1 – Cr^2	52	–[b]	–[b]
	Cr^2 – N	60	−25.3	−76.1
	N – Iso	188	−0.64	−1.41
2nd Heating	Cr – N	76	27.2	78.0
	N – Iso	182	2.03	4.46
2nd Cooling	Cr^1 – Cr^2	57	–[b]	–[b]
	Cr^2 – N	59	−24.8	−74.6
	N – Iso	185	−0.54	−1.19
3rd Heating	Cr – N	76	27.1	77.6
	N – Iso	181	1.92	4.23
3rd Cooling	Cr^1 – Cr^2	57	–[b]	–[b]
	Cr^2 – N	59	−25.0	−75.5
	N – Iso	184	−1.36	−2.97

[a] Abbreviations: Cr: crystalline, SmA: smectic A, N: nematic, Iso: isotropic phases. [b] Not determined due to short period of Cr^2 phase.

6. Absorption and photoluminescence spectra in CH_2Cl_2 solution

UV-Vis absorption spectra were recorded using a JASCO V-500 absorption spectrometer. Steady-state photoluminescence (PL) spectra were obtained using a Hitachi F-7000 or JASCO FP-8500 fluorescence spectrometer. PL quantum yields were estimated using a calibrated integrating sphere system (JASCO). Absorption and PL spectra obtained are shown in Figure S7.

(a) **1aB** (b) **1aC**



(c) **1bB** (d) **1bD**

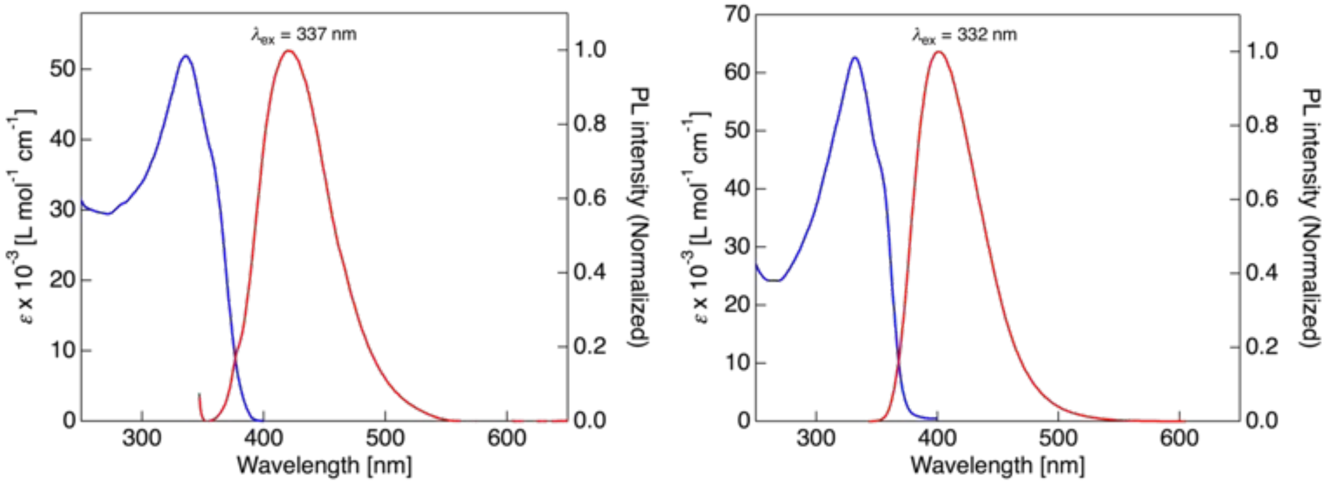
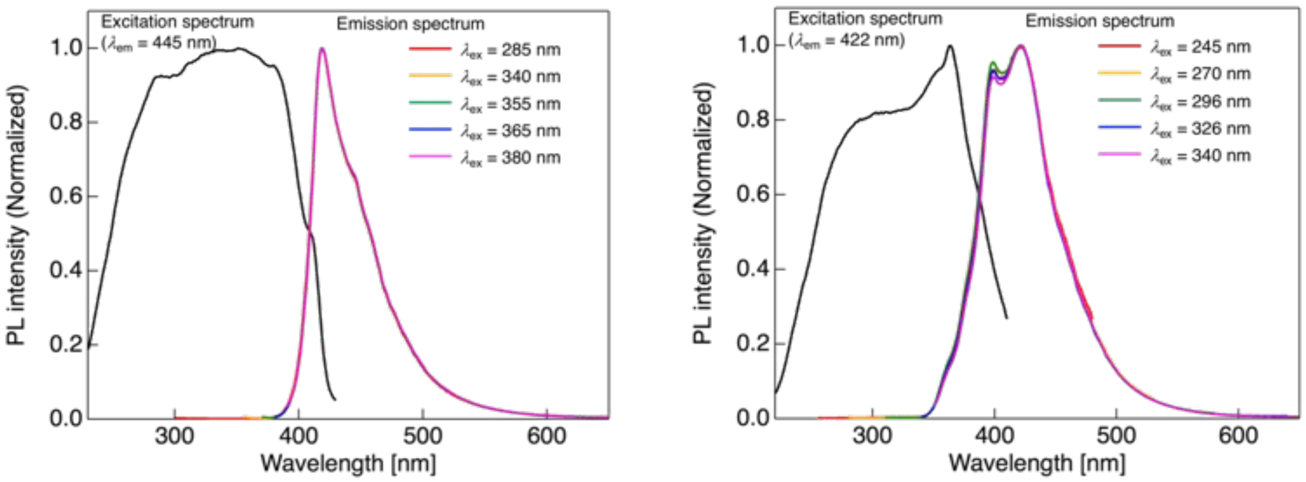


Figure S7. Absorption (blue line) and PL spectra (red line) of polyfluorinated bistolane derivatives, **1aB**, **1aC**, **1bB**, and **1bD**, measured in dilute CH_2Cl_2 solution (concentration: 10^{-5} mol L^{-1} for absorption and 10^{-6} mol L^{-1} for PL).

7. Excitation and PL spectra in crystal

Steady-state photoluminescence spectra were obtained using a Hitachi F-7000 or JASCO FP-8500 fluorescence spectrometer. PL quantum yields were estimated using a calibrated integrating sphere system (JASCO). Excitation and PL spectra in crystal are shown in Figure S8.


(a) **1aB** (b) **1aC**

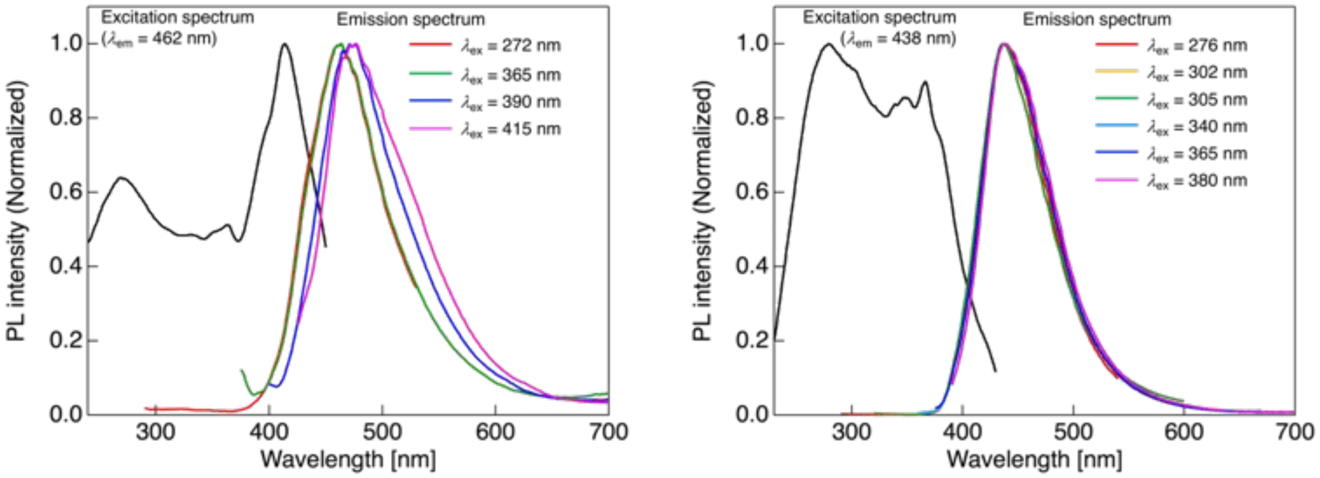
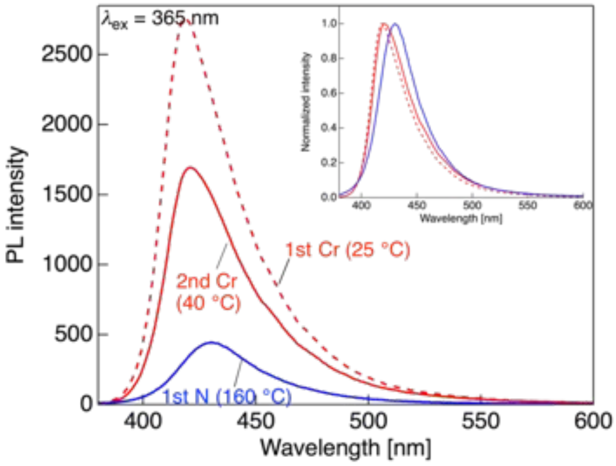

(c) **1bB** (d) **1bD**

Figure S8. Excitation (black line) and emission spectra of **1aB**, **1aC**, **1bB** and **1bD** in crystals excited by various excitation light.

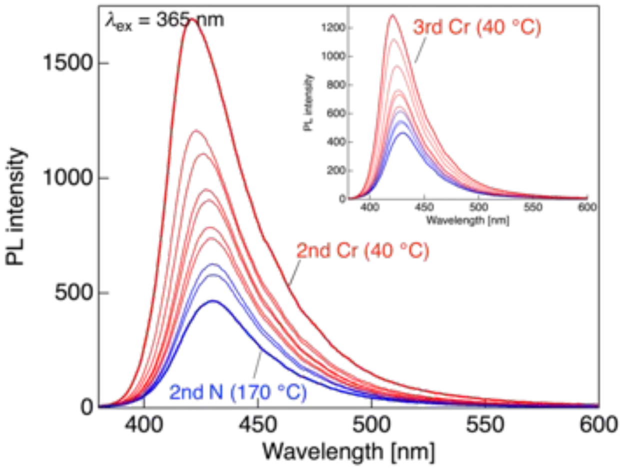
8. Temperature-dependent photoluminescence spectra

Temperature-dependent PL spectra were measured using a Hitachi F-7000 fluorescence spectrometer equipped with a home-made temperature control unit. The samples were prepared by holding as-prepared crystalline bistolanes by recrystallization between two quartz glass plates. Temperature-dependent PL behaviors obtained are shown in Figure S9..

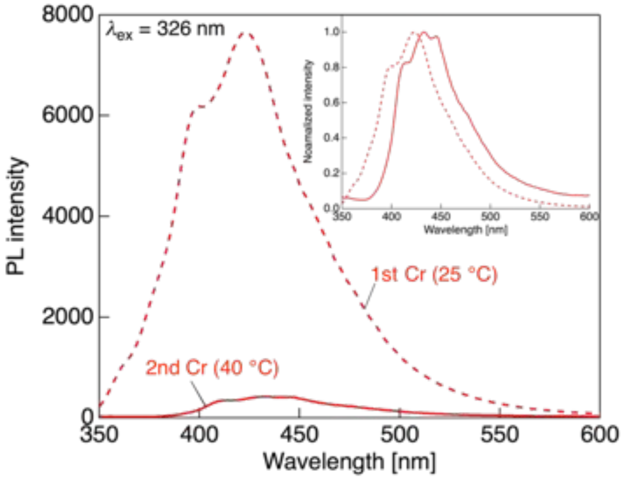
(a) **1aA** (1st cycle)



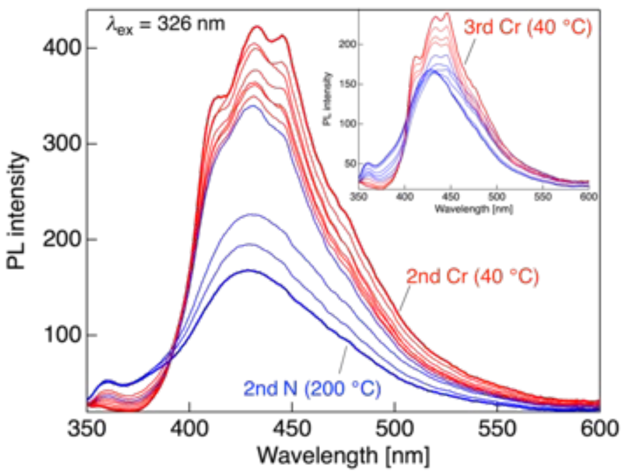
(b) **1aA** (2nd cycle)



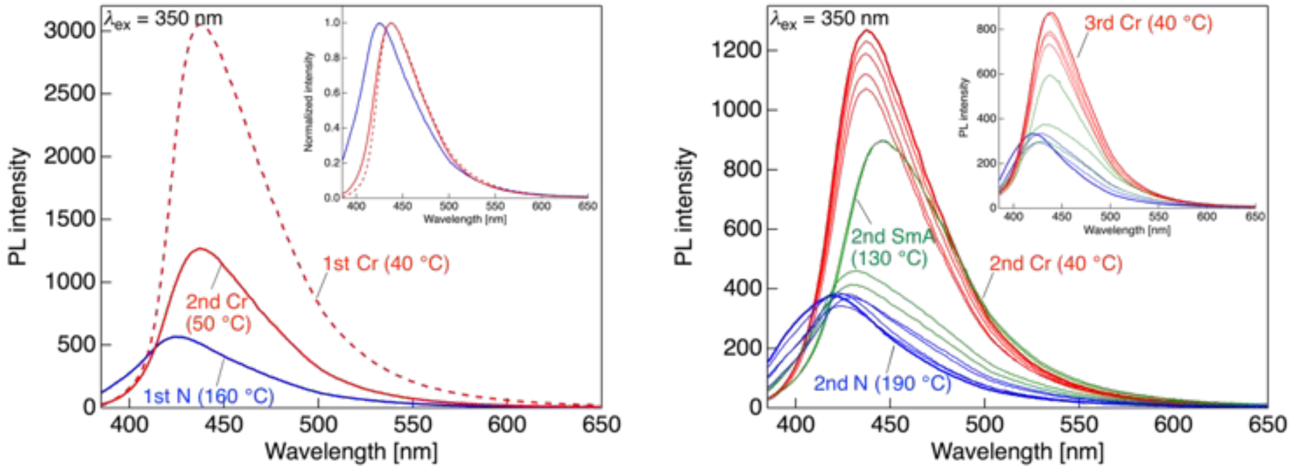
(c) **1aC** (1st cycle)



(d) **1aC** (2nd cycle)



(e) **1bA** (1st cycle) (f) **1bA** (2nd cycle)



(g) **1bD** (1st cycle) (h) **1bD** (2nd cycle)

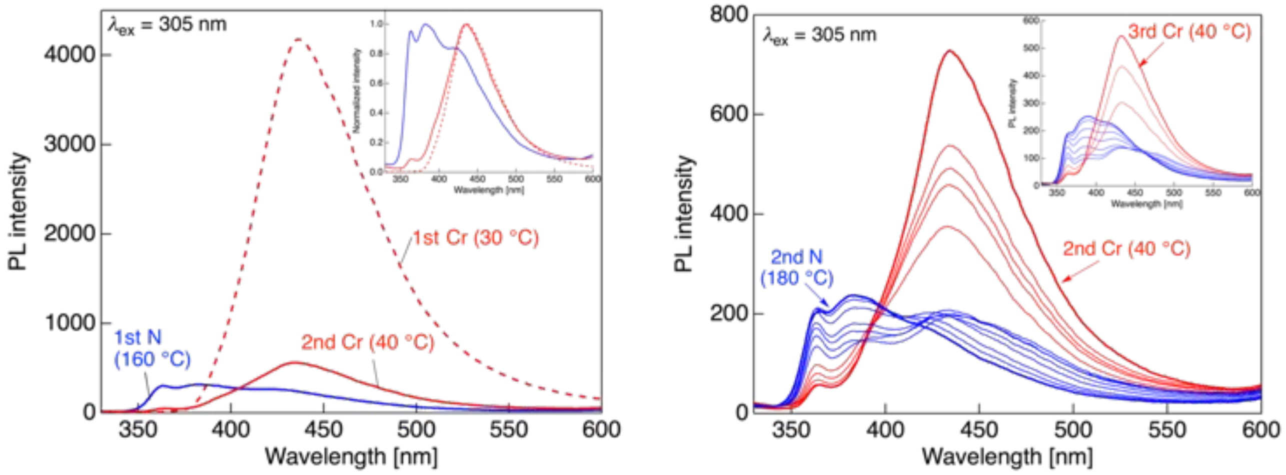
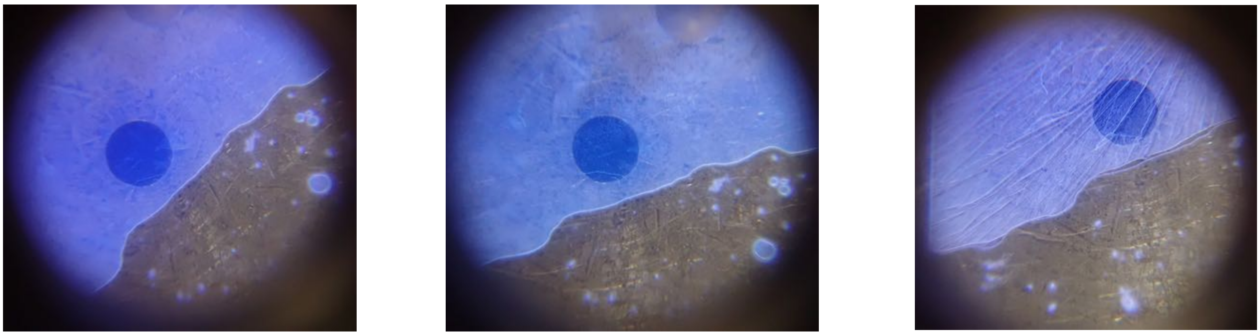


Figure S9. Temperature-dependent photoluminescence spectra of **1aA**, **1aC**, **1bA**, and **1bD**. (a),(c),(e) PL spectra in the 1st and 2nd Cr after heating-cooling process. Inset: normalized spectra. (b),(d),(f) PL spectra in the 2nd heating process. Inset: spectra in the 2nd cooling process. The line color of red, green, and blue indicates the spectra in Cr, SmA, and N phases, respectively.

Photographs of PL in LC states under UV light

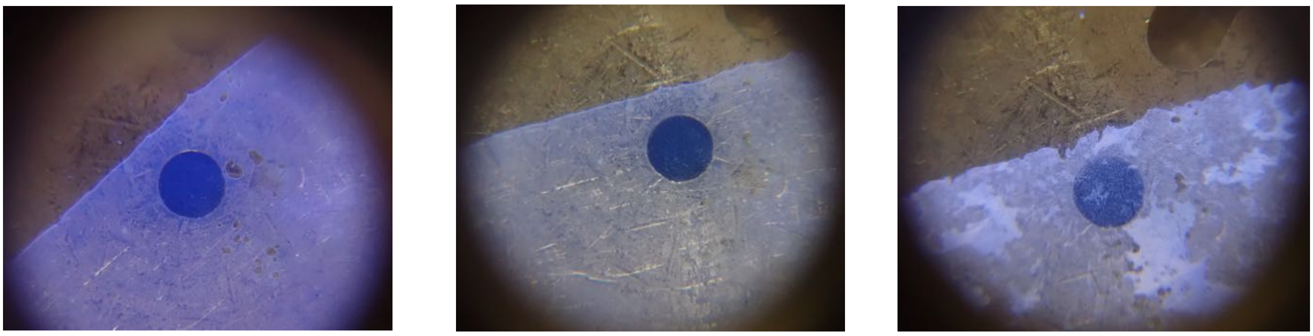
The photos were taken under UV irradiation (λ_{ex} = 365 nm) with a heating and a cooling process using a Yanaco micro melting point apparatus (MP-J3). Figure S10 (a)~(c) shows the photos of nematic (N) and crystalline (Cr) states of bistolane **1aC** and (d)~(f) shows those of bistolane **1bD** on the 1st cooling process.

For bistolane **1aC**:



(a) at 200 °C (N phase)
(b) at 100 °C (N phase)
(c) at 60 °C (Cr phase)

For bistolane **1bD**:



(d) at 200 °C (N phase)
(e) at 100 °C (N phase)
(f) at 50 °C (Cr phase)

Figure S10. PL color with varying measurement temperature under UV irradiation for bistolane **1aC** and **1bD** as selected examples.