Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Color-Tuning and Boosting Circularly Polarized Luminescence Performance of Axially Chiral Tetra-BF_2 Complexes by Post-Modifications

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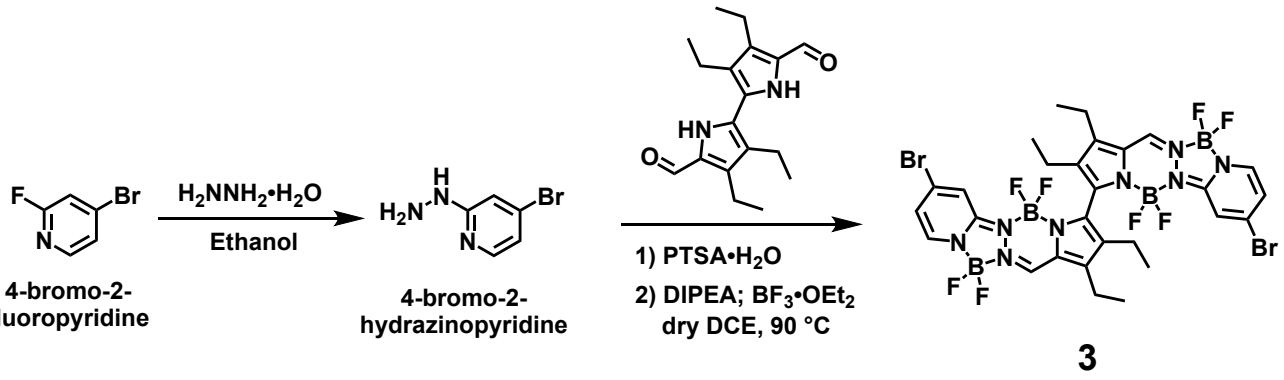
Materials and measurements

All chemical reagents and solvents used in this study were obtained from commercial sources and used as received unless otherwise stated. The NMR spectra (^{1}H, ^{13}C, ^{19}F, and ^{11}B NMR) were recorded by using a Bruker Avance 400 NMR spectrometer. The chemical shifts (in ppm) of ^{1}H NMR were referenced relative to tetramethylsilane $(CH_3)_4Si$, with the residual solvent peak of dimethyl sulfoxide-d_6 (DMSO-d_6) at 2.50 ppm, as an internal standard, respectively. The chemical shifts (in ppm) of ^{13}C NMR were referenced relative to the residual solvent peak of DMSO-d_6 at 39.5 ppm. The chemical shifts (in ppm) of ^{19}F and ^{11}B NMR were referenced relative to hexafluorobenzene (C_6F_6) at –162.90 ppm and boron trifluoride-ethyl ether complex (BF_3•OEt_2) at 0.0 ppm in DMSO-d_6, respectively. The coupling constants, J are reported in Hertz (Hz). Multiplicity is abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, and dd = double doublet. The high-resolution mass spectra (HRMS, FAB-MS) were performed with a JEOL JMS-700 instrument. Melting points (m.p.) were measured with a DTM-01 melting point meter (AS ONE Corporation). UV–vis absorption spectra were recorded using a Hitachi U-3900H spectrophotometer. Fluorescence excitation and emission spectra were collected at room temperature on a Hitachi F-7000 fluorescence spectrophotometer. Emission spectra were collected in the range between 300-800 nm, with a scan speed of 240 nm/min, and the slits were set at 5.0 nm (excitation slit) and 5.0 nm (emission slit). Temperature-dependent photoluminescence spectra were recorded with a JASCO FP-8500 fluorescence spectrometer with Optistat DN (OXFORD instruments). The absolute photoluminescence quantum yields (Φ_{PL}) were determined using absolute PL quantum yields measurement system C9920-02 (Hamamatsu photonics) after excitation at maximum absorption wavelength (λ_{abs}^{max}). Time-resolved photoluminescence lifetimes were carried out by using time-correlated single photon counting lifetime spectroscopy system, Quantaurus-Tau C11367-05 (Hamamatsu photonics). The decay constants and fitting parameters (τ_1, τ_2, A_1, A_2) for transient decays were determined using the embedded software of Quantaurus-Tau. All the products were isolated by silica-gel column chromatography (Kanto Chemicals, 60N); and then isolated products were identified by HRMS (FAB-MS), ^{1}H, ^{13}C, ^{19}F, and ^{11}B NMR.

Note: Compounds **1** and **2** were synthesized according to the established method.[1] Tetra-ethyl modified 5,5'-diformyl-2,2'-bipyrrole was synthesized by the established method as the intermediate in our porphycene synthesis.[2-5]

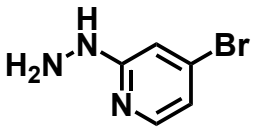
(1) Synthesis of compound **3**



Scheme S1. Synthesis of compound **3**.

(1-1) Synthesis of compound **4-bromo-2-hydrazinopyridine**

4-Bromo-2-fluoropyridine (512 μL, 5.0 mmol) was added dropwise in ethanol (25 mL) with hydrazine monohydrate (1.22 mL, 25.0 mmol) under a nitrogen atmosphere. The reaction mixture was then refluxed until complete consumption of 4-bromo-2-fluoropyridine by TLC monitoring. After refluxing for 4 hours, the solvent was removed under reduced pressure and the dichloromethane (DCM) was added. Subsequently, the mixture was poured into water and extracted with DCM. The extracted organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to yield **4-bromo-2-hydrazinopyridine** as a white solid (580 mg, 62%).



4-bromo-2-hydrazinopyridine

m.p.: 88～95℃.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.84 (dd, J = 5.1, 1.1 Hz, 1H), 7.70 (s, 1H), 6.91 (s, 1H), 6.70-6.69 (m, 1H), 4.19 (s, 2H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 163.1, 148.9, 132.2, 114.9, 107.9.

HRMS (FAB, positive): *m/z* calcd. for $C_5H_6BrN_3$ $[M]^+$ 186.9745; found: 186.9733.

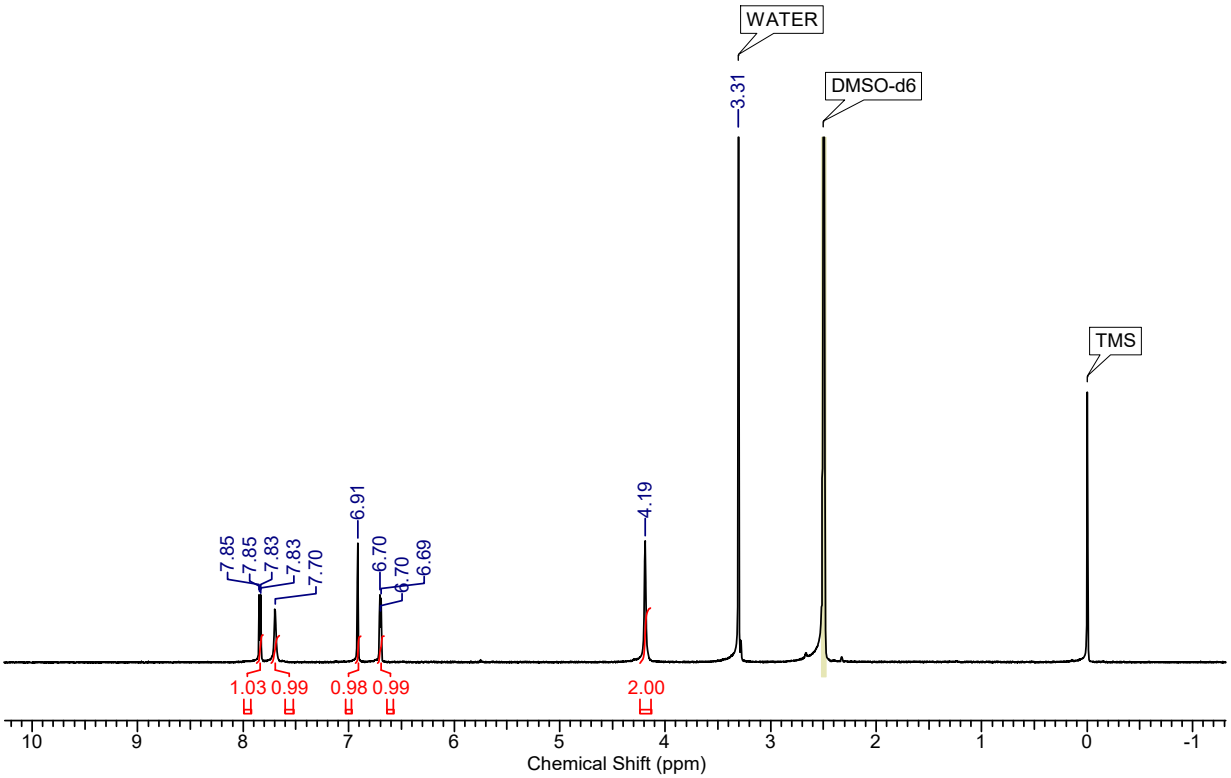


Figure S1-1. [1]H NMR spectrum of compound **4-bromo-2-hydrazinopyridine** in DMSO-d_6 at room temperature.

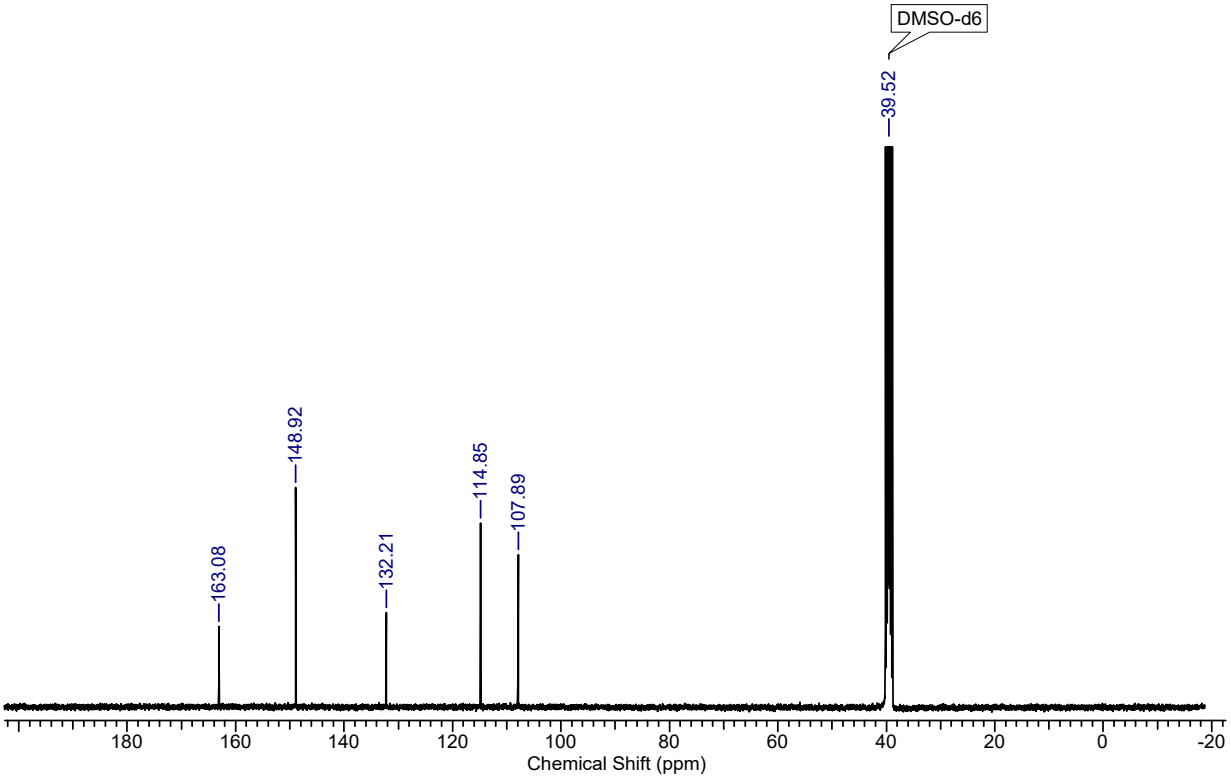
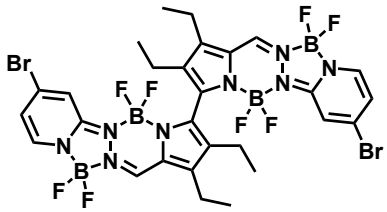


Figure S1-2. [13]C NMR spectrum of compound **4-bromo-2-hydrazinopyridine** in DMSO-d_6 at room temperature.

(1-2) Synthesis of compound **3**



3

The reaction was performed following the established method[1] for 6 h refluxing starting with tetra-ethyl modified 5,5'-diformyl-2,2'-bipyrrole (150 mg, 0.50 mmol) and 4-bromo-2-hydrazinopyridine (197 mg, 1.05 mmol). Compound **3** was obtained as a yellow solid (75 mg, 18 %).

m.p. > 280~284℃.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.85 (s, 2H), 8.37 (d, J = 6.6 Hz, 2H), 7.41 (d, J = 1.6 Hz, 1H), 7.39 (d, J = 1.8 Hz, 1H), 7.37 (s, 2H), 2.85 (m, 4H), 2.29 (m, 4H), 1.21 (t, J = 7.6 Hz, 6H), 0.98 (t, J = 7.6 Hz, 6H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 151.1, 140.8, 139.8, 138.5, 136.2, 132.8, 132.0, 123.0, 119.6, 112.4, 17.4, 17.0, 16.9, 14.2.

^{19}F NMR (377 MHz, DMSO-d_6): δ = (–133.72)-(–134.13) (m, 2F), (–142.56)-(–142.92) (m, 2F), (–143.45)-(–143.70) (m, 4F).

^{11}B NMR (128 MHz, DMSO-d_6): δ = 3.40 (brs, 2B), 1.27 (brs, 2B).

HRMS (FAB, positive): *m/z* calcd. for $C_{28}H_{28}B_4Br_2F_8N_8$ $[M]^+$ 830.1048; found: 830.1050.

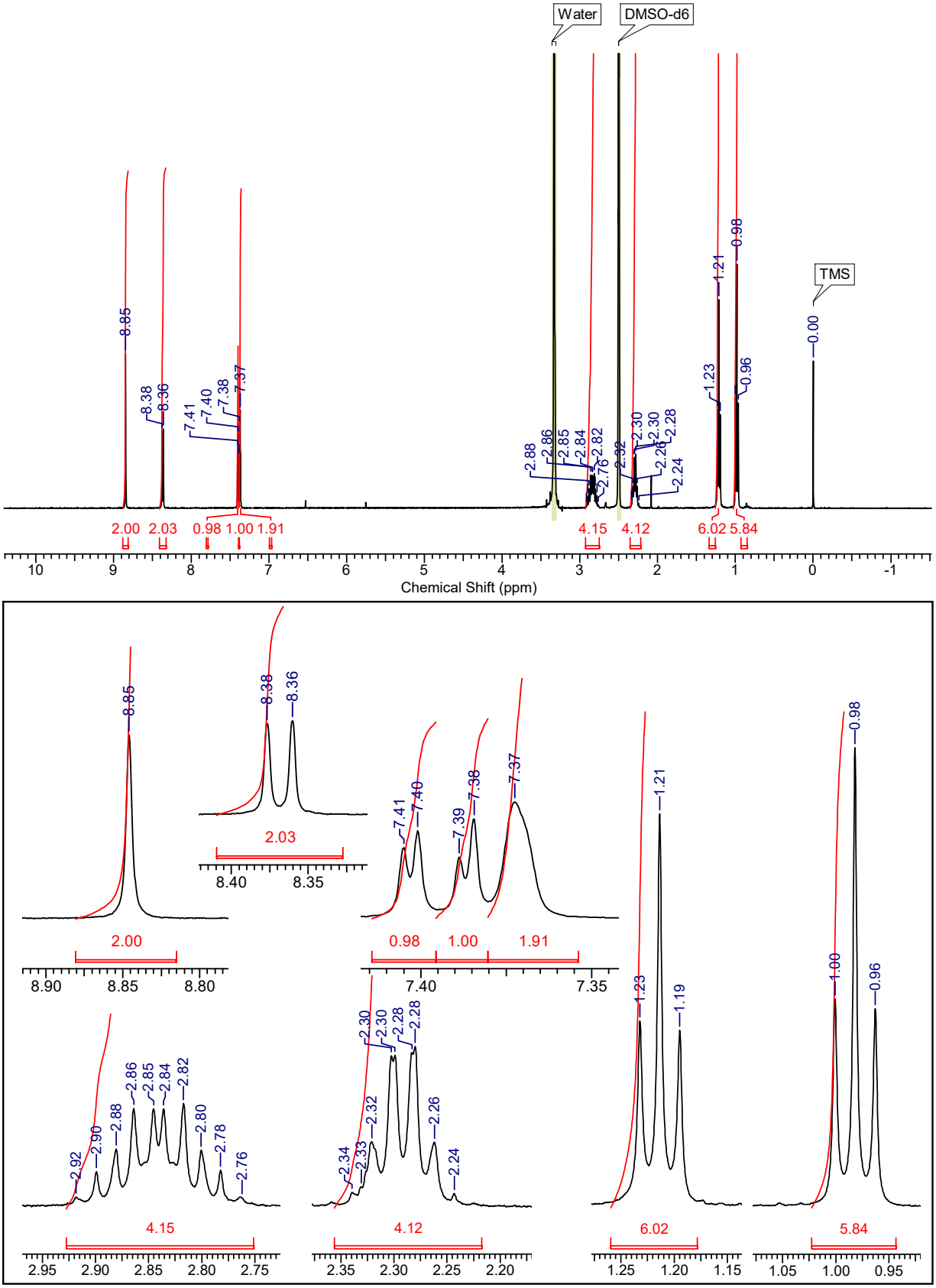


Figure S2-1. ^{1}H NMR spectrum of compound **3** in DMSO-d_6 at room temperature.

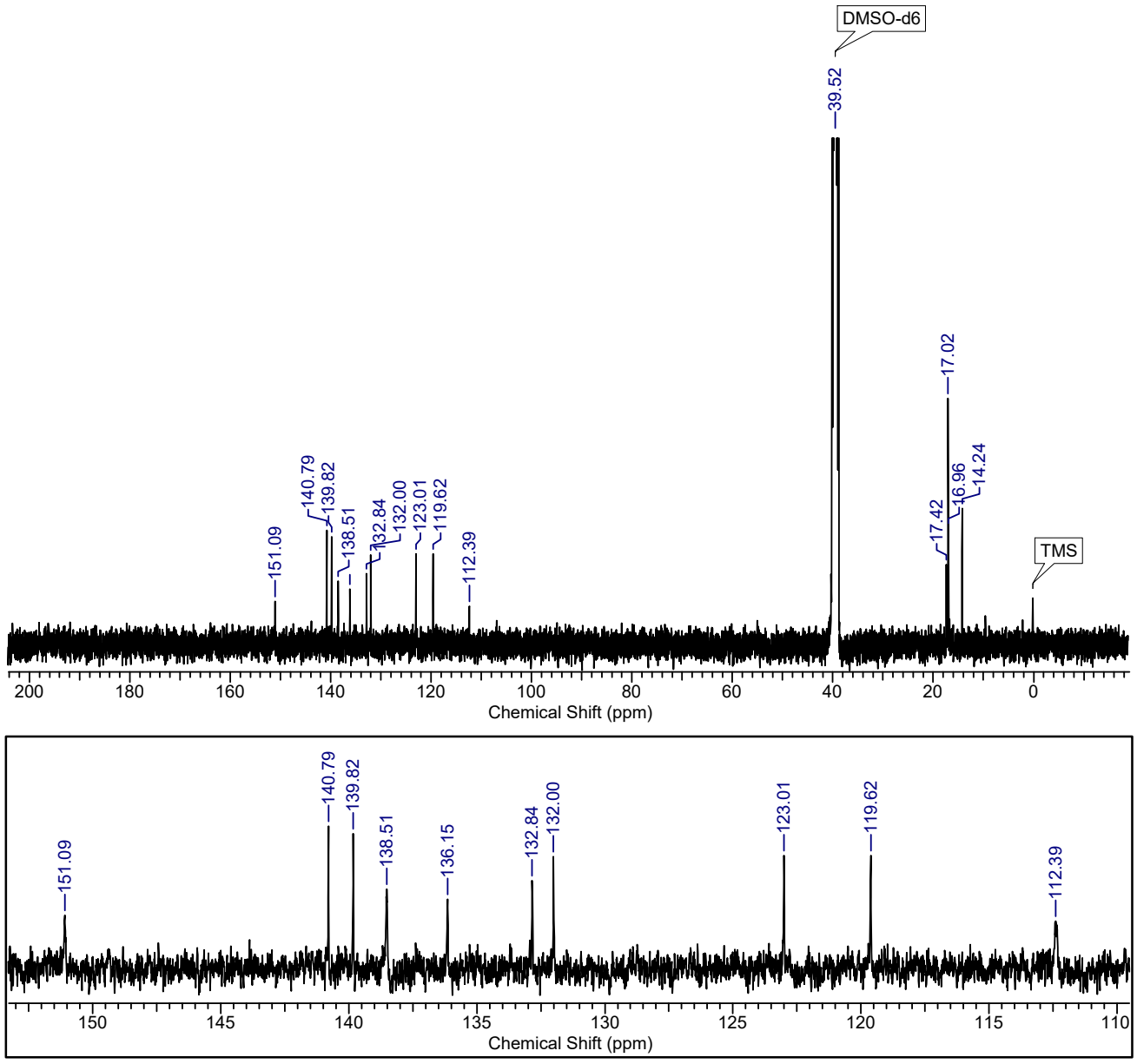


Figure S2-2. ^{13}C NMR spectrum of compound **3** in DMSO-d_6 at room temperature.

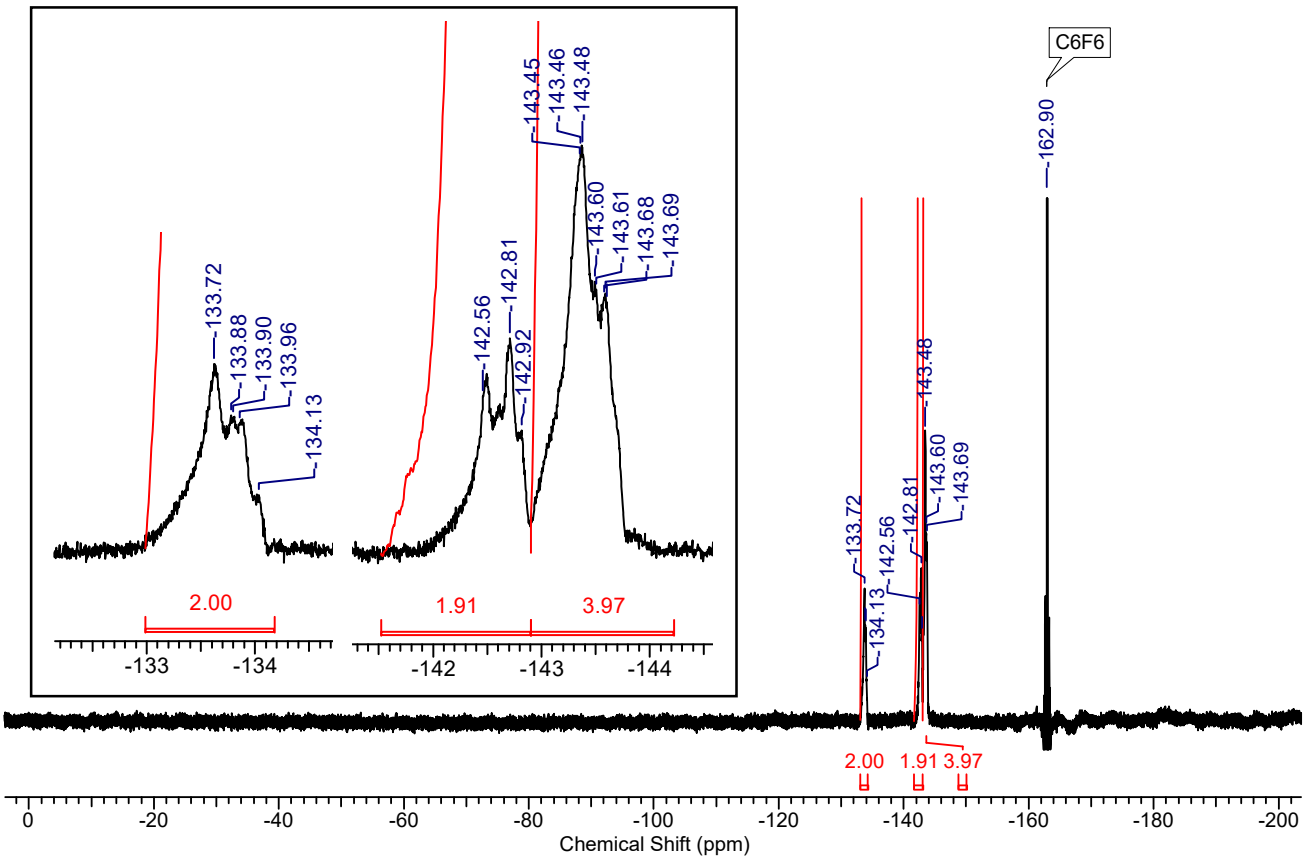


Figure S2-3. ^{19}F NMR spectrum of compound **3** in DMSO-d_6 at room temperature.

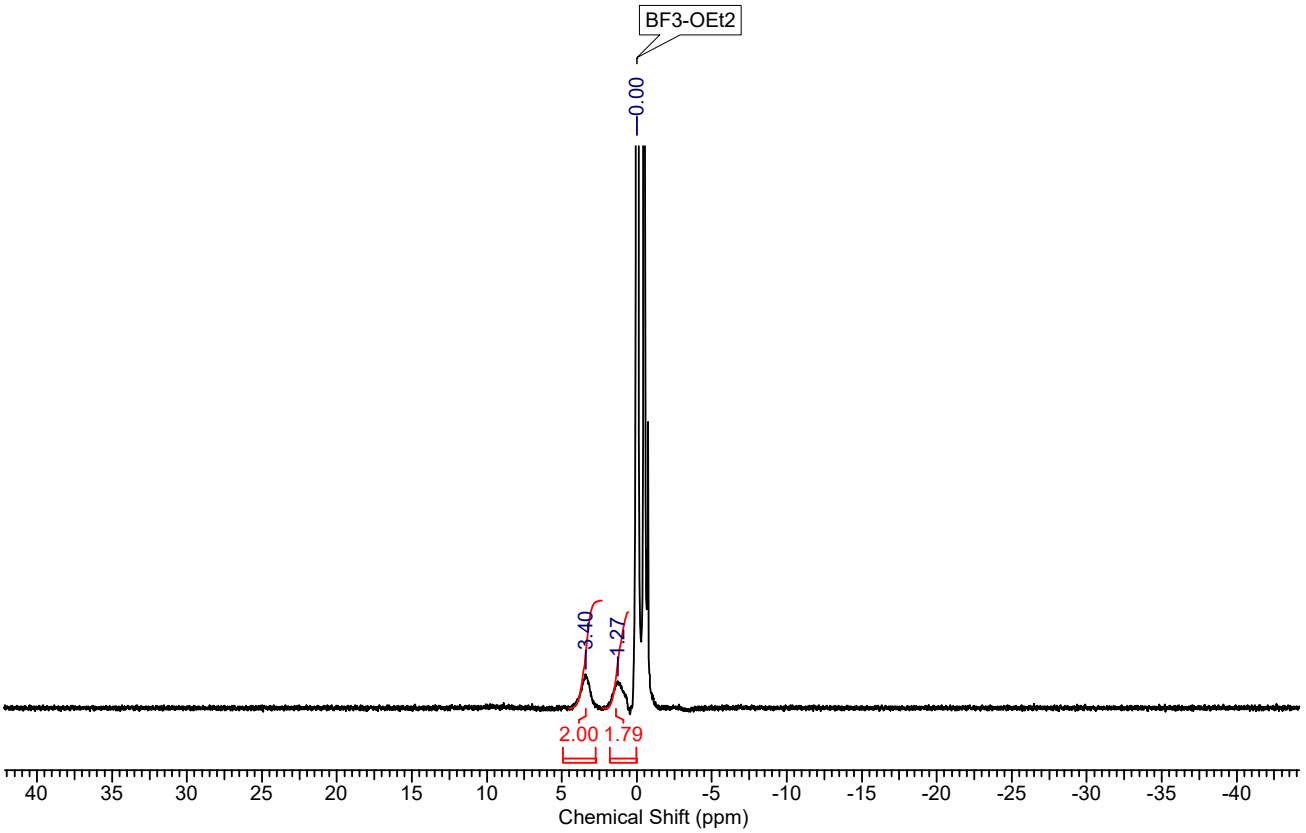


Figure S2-4. ^{11}B NMR spectrum of compound **3** in DMSO-d_6 at room temperature.

(2) Synthesis of compound **4**

To a Schlenk tube loaded with **2** (14.1 mg, 17 μmol), 2,2′:5′,2″-terthiophene-5-boronic acid pinacol ester (31.8 mg, 85 μmol), potassium carbonate (K_2CO_3) (16.5 mg, 119 μmol), tris(dibenzylideneacetone)dipalladium(0) [$Pd_2(dba)_3$] (3.1 mg, 3.4 μmol), and 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (X-Phos) (6.5 mg, 13.6 μmol) were added with 1,4-dioxane (4.0 mL) and H_2O (0.4 mL). After carrying out freeze-pump-thaw cycles for 3 times, the reaction mixture was then heated to 90 °C, stirred for 12 hours, filtered through a thin pad of Celite, and eluted with dichloromethane (DCM) or tetrahydrofuran (THF). The obtained organic solution was washed with water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to obtain the crude product. The crude product was then purified by silica-gel column chromatography using dichloromethane and hexane as eluent. Finally, the desired product **4** was obtained as an orange-red solid (10.3 mg, 49.8 %).

m.p. > 300℃.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.81 (m, 4H), 8.33 (dd, J = 9.4, 2.1 Hz, 2H), 7.70 (d, J = 3.8 Hz, 2H), 7.54 (dd, J = 5.1, 1.1 Hz, 2H), 7.40 (d, J = 3.9 Hz, 2H), 7.35-7.32 (m, 6H), 7.30 (d, J = 3.9 Hz, 2H), 7.11-7.09 (m, 2H), 2.85 (m, 4H), 2.32 (m, 4H), 1.23 (t, J = 7.6 Hz, 6H), 0.99 (t, J = 7.6 Hz, 6H).

^{13}C NMR: No analyzable ^{13}C NMR spectrum could be recorded due to the low solubility.

^{19}F NMR (377 MHz, DMSO-d_6): δ = (–133.52)-(–133.92) (m, 2F), (–142.35)-(–142.70) (m, 2F), (–143.05)-(–143.51) (m, 4F).

^{11}B NMR (128 MHz, DMSO-d_6): δ = 3.63 (brs, 2B), 1.45 (brs, 2B).

HRMS (FAB, positive): *m/z* calcd. for $C_{52}H_{42}B_4F_8N_8S_6$ $[M]^+$ 1166.2101; found: 1166.2099.

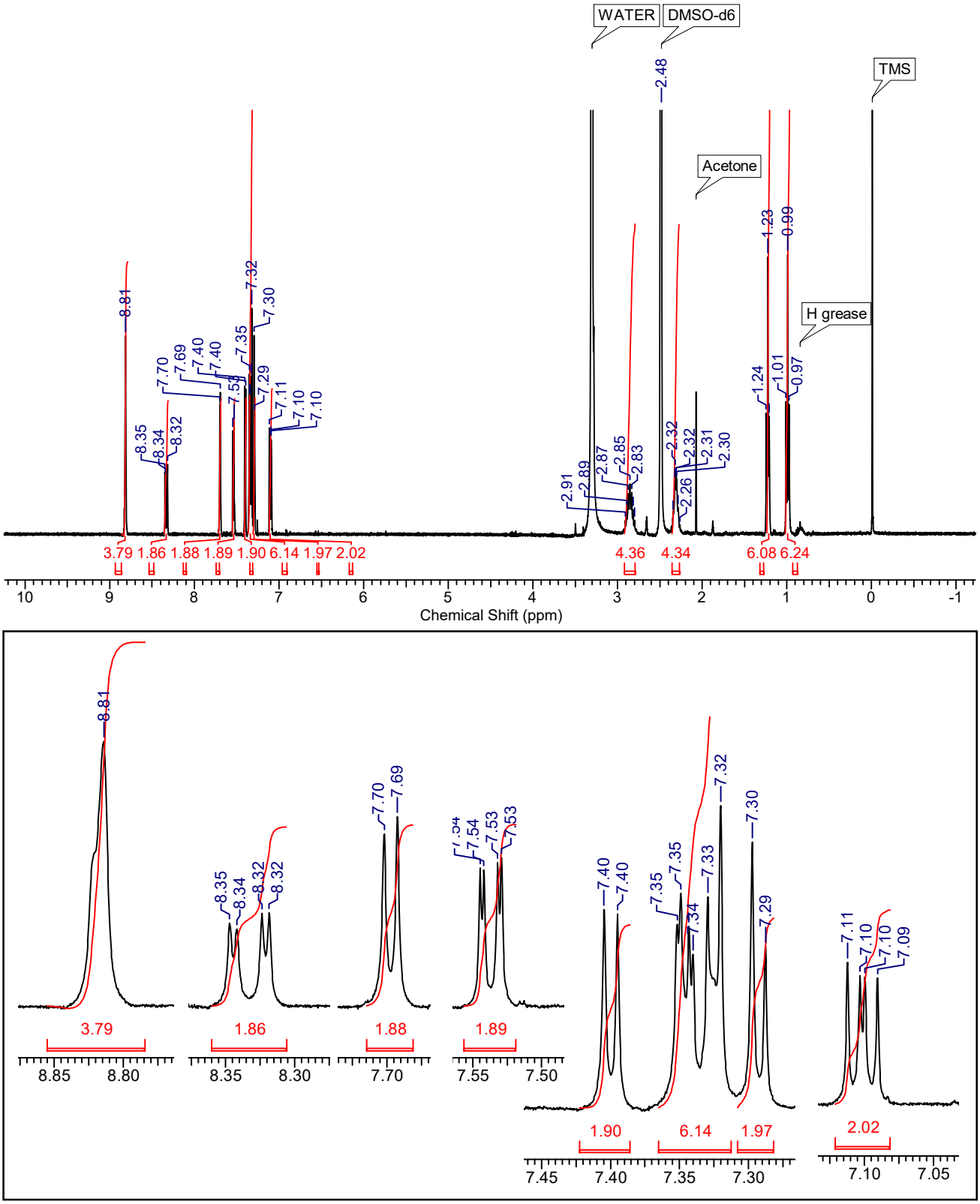


Figure S3-1. ^{1}H NMR spectrum of compound **4** in DMSO-d_6 at room temperature.

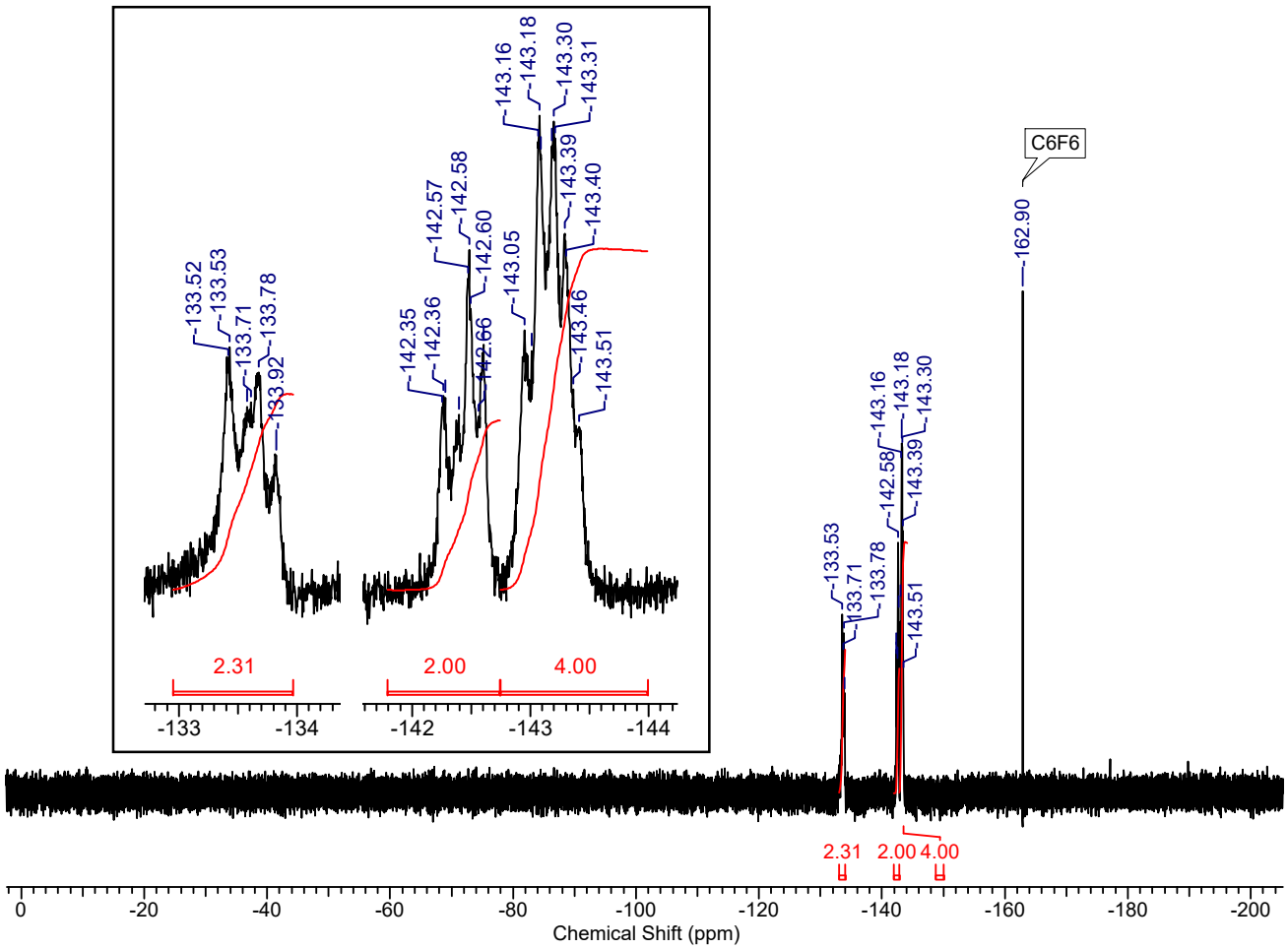


Figure S3-2. ^{19}F NMR spectrum of compound **4** in DMSO-d_6 at room temperature.

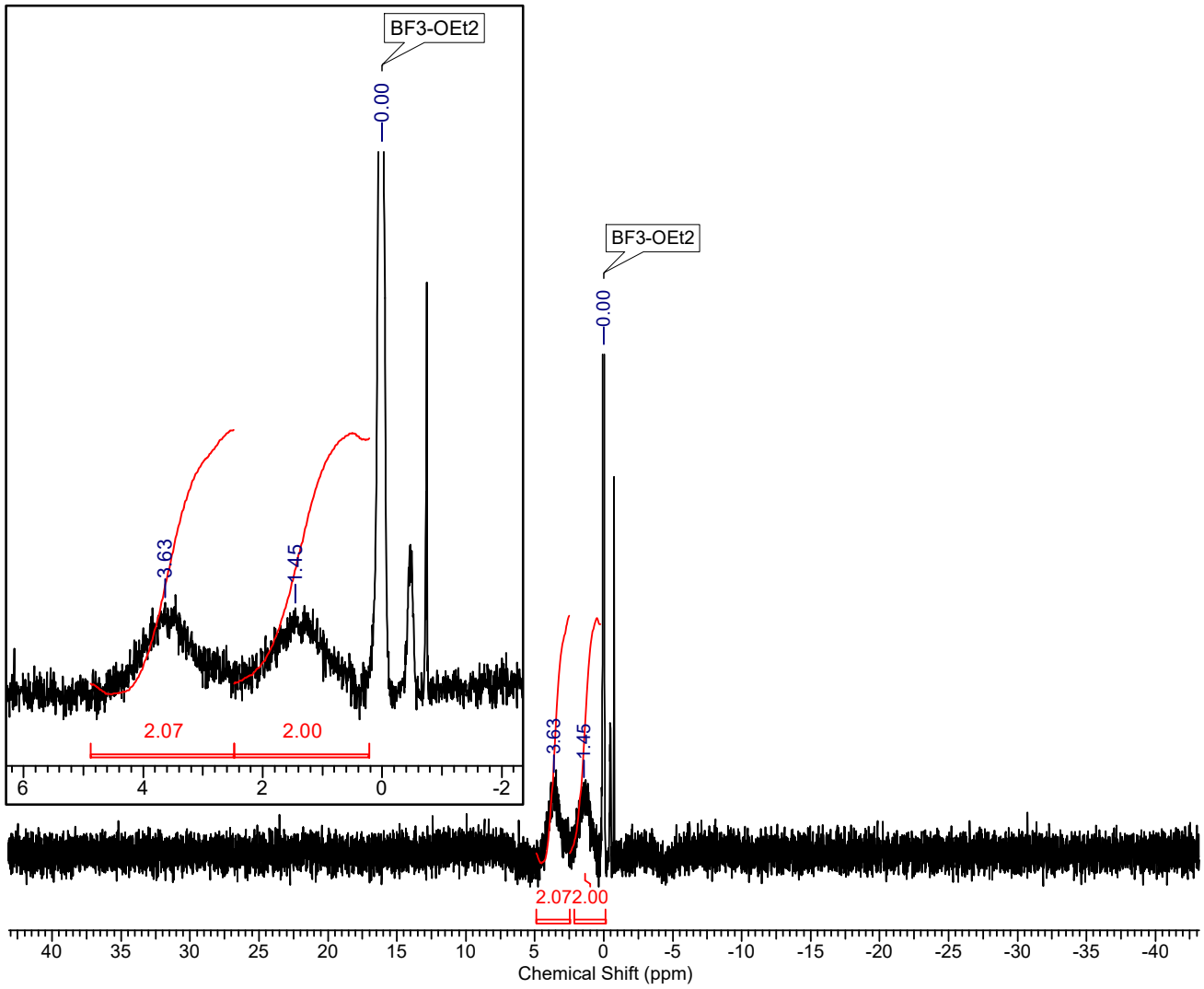


Figure S3-3. ^{11}B NMR spectrum of compound **4** in DMSO-d_6 at room temperature.

(3) Synthesis of compound **5**

To a Schlenk tube loaded with **3** (14.1 mg, 17 μmol), 2,2′:5′,2″-terthiophene-5-boronic acid pinacol ester (31.8 mg, 85 μmol), potassium carbonate (K_2CO_3) (16.5 mg, 119 μmol), tris(dibenzylideneacetone)dipalladium(0) [$Pd_2(dba)_3$] (3.1 mg, 3.4 μmol), and 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (X-Phos) (6.5 mg, 13.6 μmol) were added with 1,4-dioxane (4.0 mL) and H_2O (0.4 mL). After carrying out freeze-pump-thaw cycles for 3 times, the reaction mixture was then heated to 90 °C, stirred for 12 hours, filtered through a thin pad of Celite, and eluted with DCM or THF. After the removal of solvents under reduced pressure, the desired product **5** was obtained by reprecipitation from THF and methanol as a red solid (10 mg, 50 %).

m.p. > 219~223℃.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.83 (s, 2H), 8.42 (d, J = 6.8 Hz, 2H), 8.04 (d, J = 4.00 Hz, 2H), 7.58-7.56 (m, 6H), 7.49 (d, J = 4.0 Hz, 2H), 7.40 (dd, J = 3.6, 1.1 Hz, 2H), 7.31 (d, J = 3.8 Hz, 2H), 7.17 (s, 2H), 7.12 (m, 2H), 2.93 (m, 2H), 2.83 (m, 2H), 2.30 (m, 4H), 1.25 (t, J = 7.5 Hz, 6H), 0.99 (t, J = 7.6 Hz, 6H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 151.4, 147.5, 141.5, 139.0, 137.5, 136.2, 135.6, 133.7, 132.2, 132.0, 128.6, 127.5, 126.4, 125.2, 124.9, 112.2, 105.9, 17.5, 17.1, 17.0, 14.2.

^{19}F NMR (377 MHz, DMSO-d_6): δ = (–133.27)-(–133.70) (m, 2F), (–142.38)-(–142.74) (m, 2F), (–143.21)-(–143.55) (m, 2F), (–144.01)-(–144.36) (m, 2F).

HRMS (FAB, positive): *m/z* calcd. for $C_{52}H_{42}B_4F_8N_8S_6$ $[M]^+$ 1166.2101; found: 1166.2091.

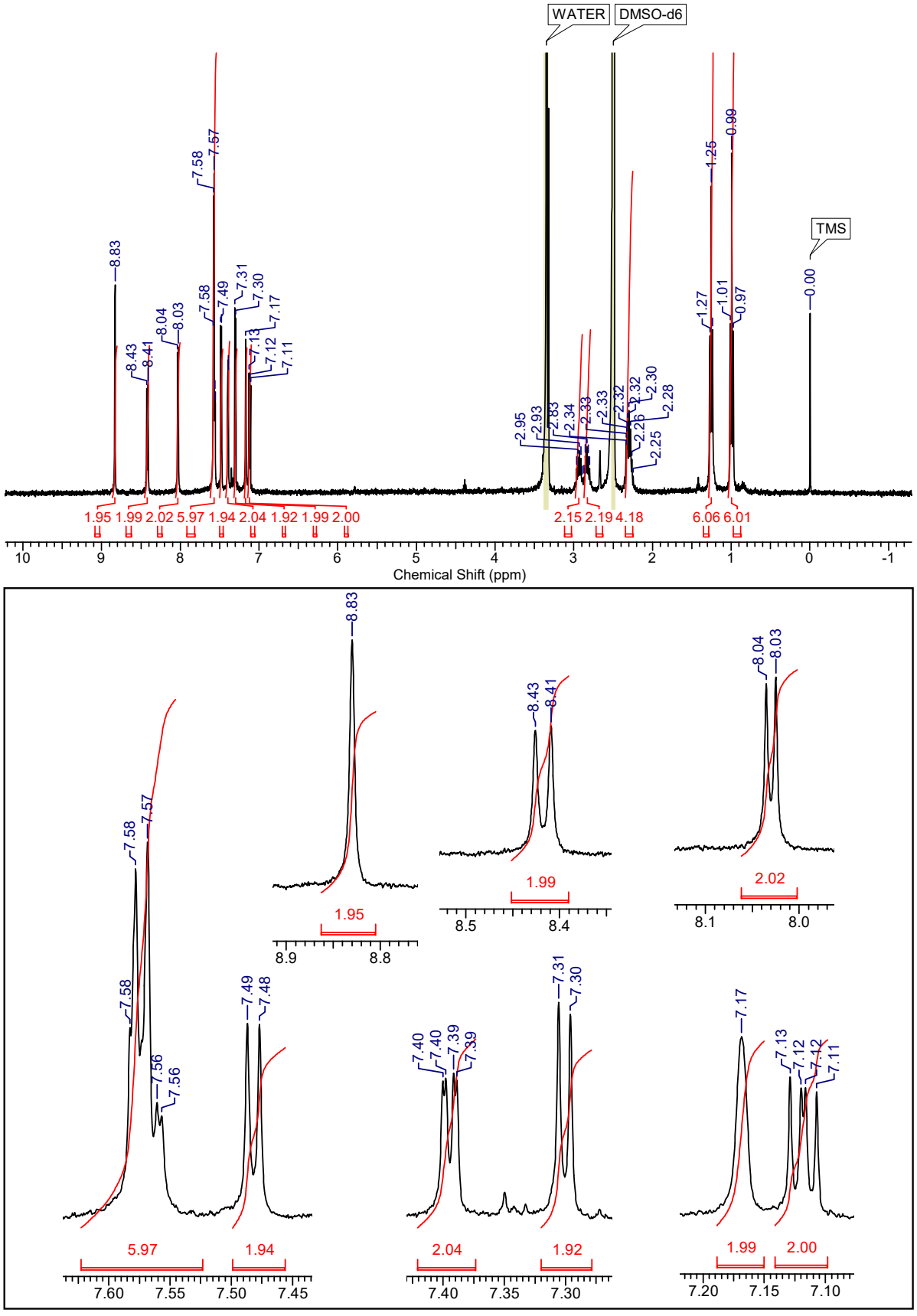


Figure S4-1. ^{1}H NMR spectrum of compound **5** in DMSO-d_6 at room temperature.

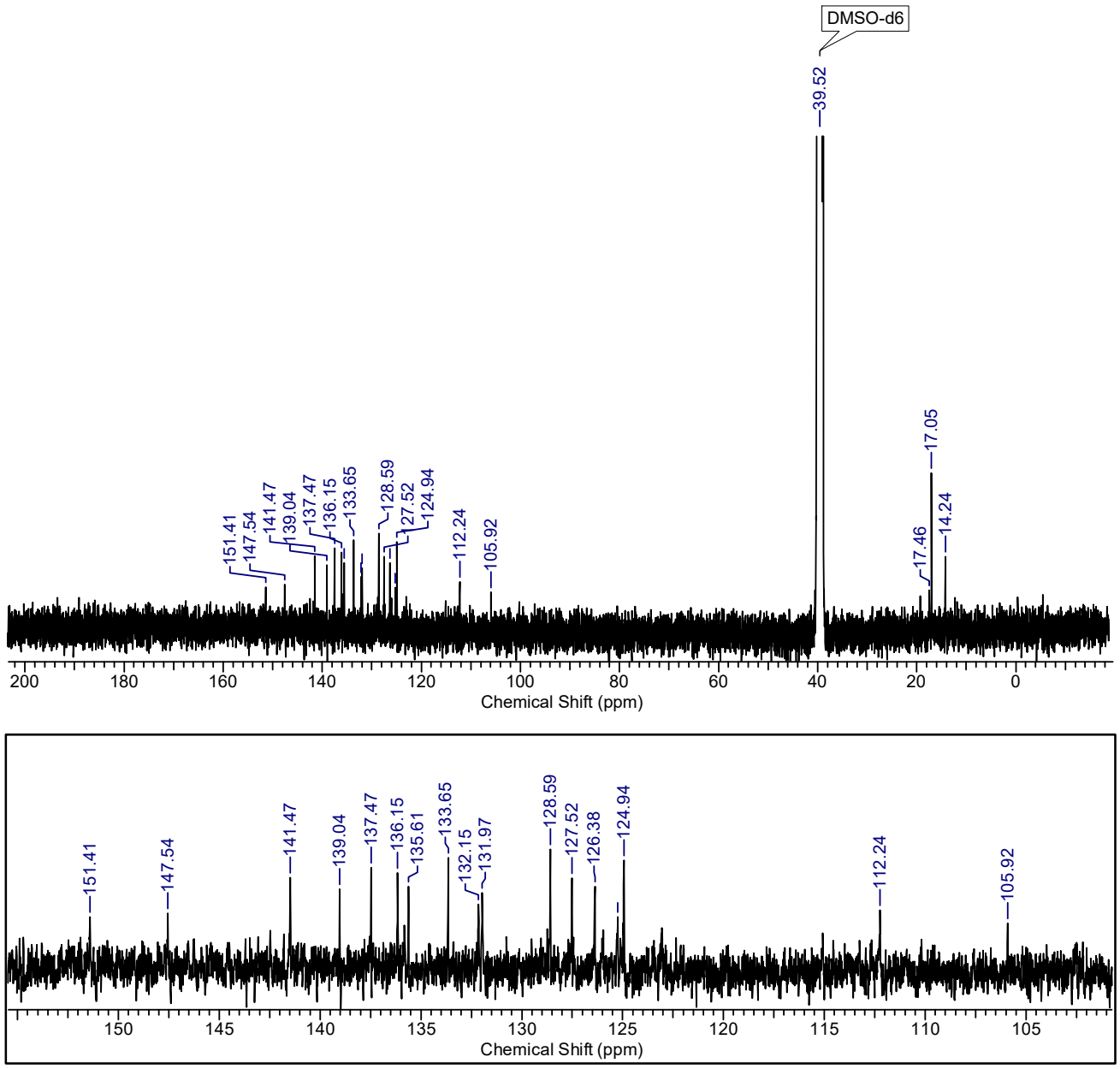


Figure S4-2. ^{13}C NMR spectrum of compound **5** in DMSO-d_6 at room temperature.

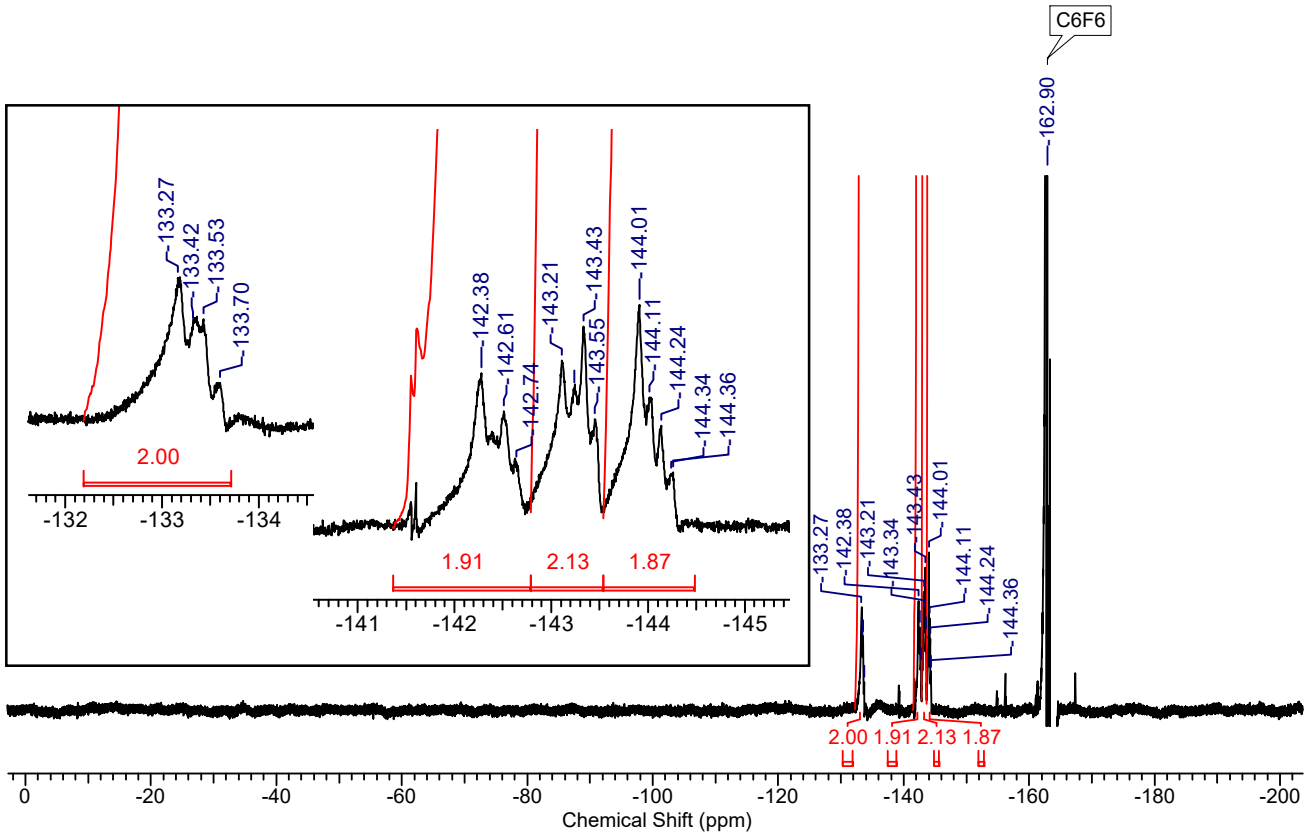


Figure S4-3. ^{19}F NMR spectrum of compound **5** in DMSO-d_6 at room temperature.

Optical properties in various solvents

Optical properties of compounds **1** and **2** in various solvents were reported in the previous work.[1] The optical properties of compounds **3**–**5** in various solvents are shown as follows.

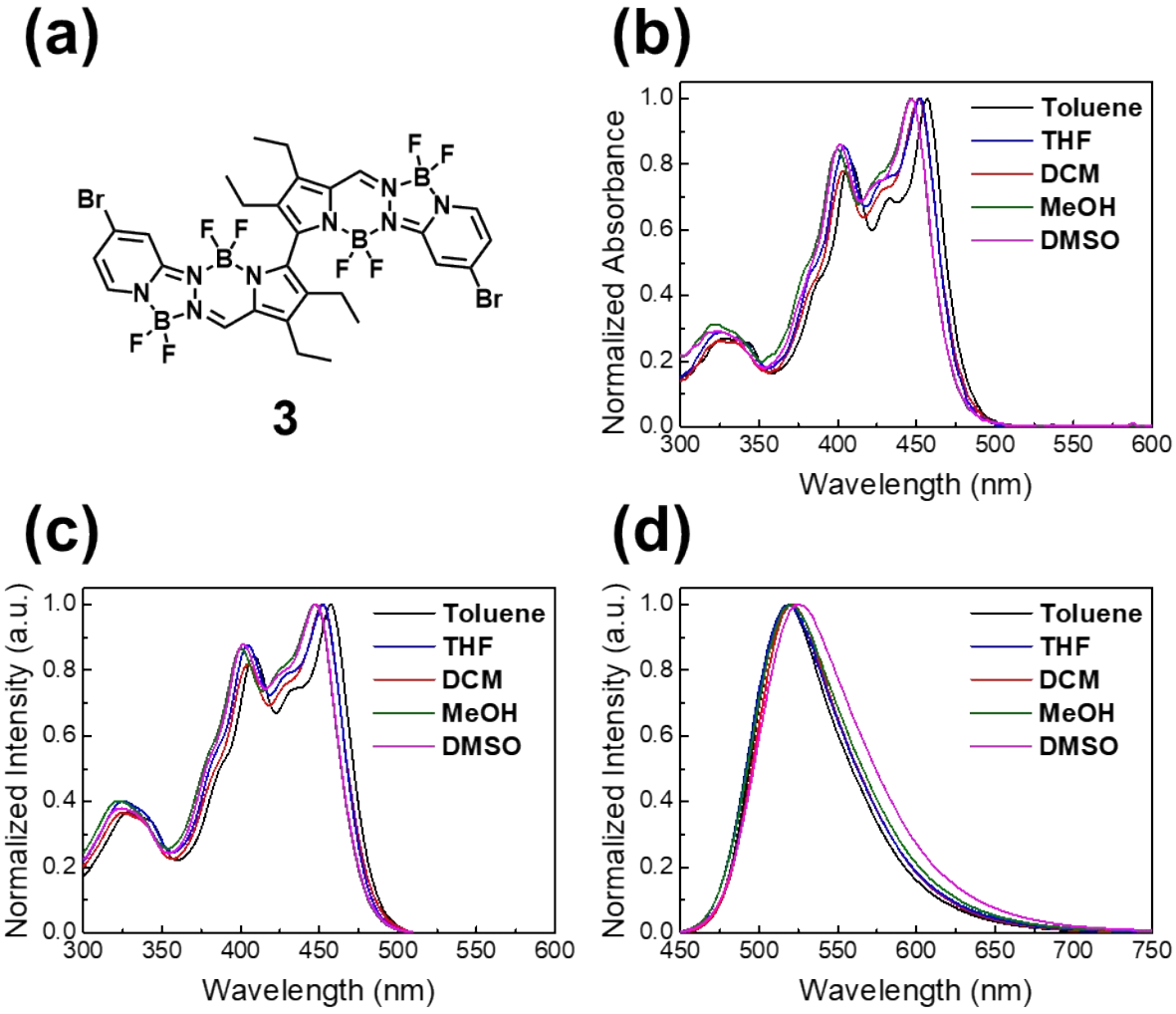


Figure S5. (a) Chemical structure of **3**. Normalized (b) UV–vis absorption spectra, (c) excitation spectra (emission wavelength at λ_{em}^{max}), and (d) emission spectra (excited at λ_{abs}^{max}) of **3** in various solvents ($c = 10^{-6}$ M).

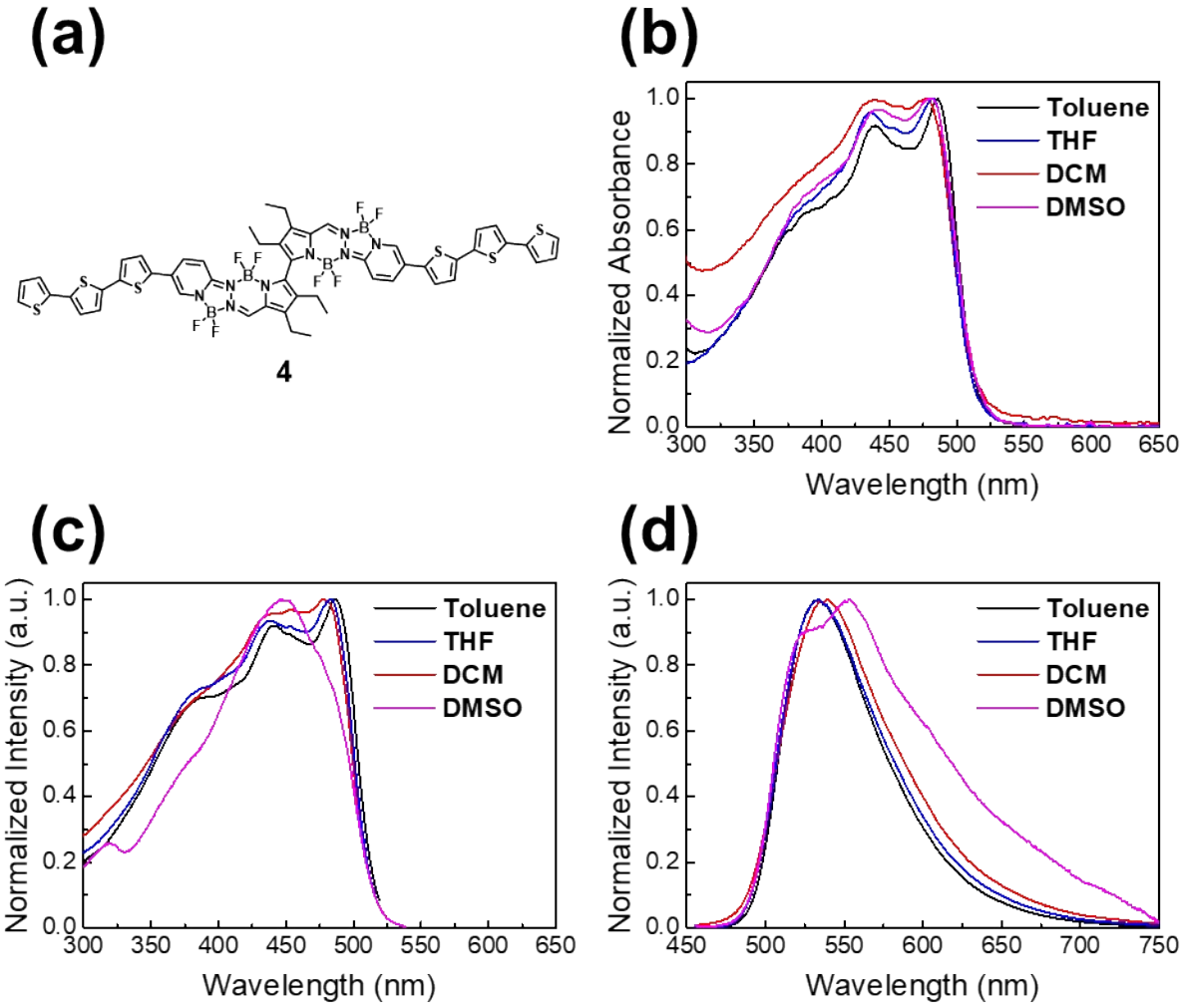


Figure S6. (a) Chemical structure of **4**. Normalized (b) UV–vis absorption spectra, (c) excitation spectra (emission wavelength at λ_{em}^{max}), and (d) emission spectra (excited at λ_{abs}^{max}) of **4** in various solvents ($c = 10^{-6}$ M).

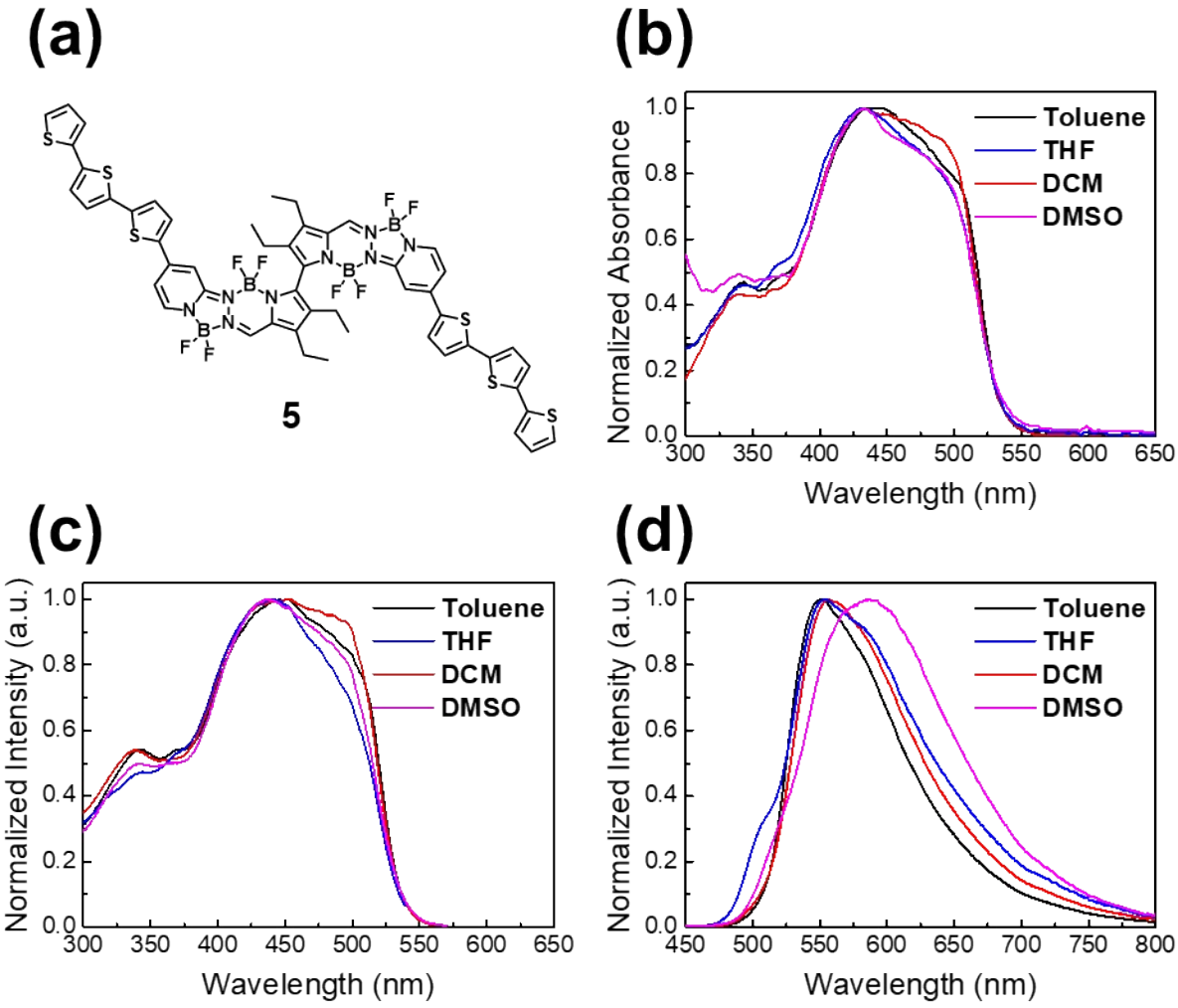


Figure S7. (a) Chemical structure of **5**. Normalized (b) UV–vis absorption spectra, (c) excitation spectra (emission wavelength at λ_{em}^{max}), and (d) emission spectra (excited at λ_{abs}^{max}) of **5** in various solvents ($c = 10^{-6}$ M).

Table S1. Photophysical properties of **1**–**5** in various solvents.

Compd.[a]	Solvent	λ_{abs}^{max} / nm[b]	λ_{em}^{max} / nm[c]	Φ_{PL}[d]	τ_{av} / ns	Stokes shift / cm^{-1}
1	Toluene	404, 452	514	0.58	2.06	2700
	THF	400, 448	514	0.60	2.13	2900
	DCM	400, 446	515	0.57	2.11	3000
	MeOH	396, 442	514	0.53	2.22	3200
	DMSO	397, 443	519	0.57	2.04	3300
2	Toluene	414, 464	522	0.58	2.15	2400
	THF	411, 460	523	0.44	1.90	2600
	DCM	412, 460	526	0.59	2.11	2700
	MeOH	406, 454	524	0.41	1.74	2900
	DMSO	409, 454	530	0.41	1.42	3200
3	Toluene	408, 457	519	0.54	1.76	2600
	THF	404, 452	519	0.42	1.68	2900
	DCM	404, 452	521	0.48	1.75	2900
	MeOH	400, 446	520	0.42	1.52	3200
	DMSO	401, 447	524	0.55	1.58	3300
4	Toluene	440, 486	534	0.54	1.57	1900
	THF	437, 481	534	0.45	1.59	2100
	DCM	440, 478	535	0.27	1.39	2200
	DMSO	440, 481	553	0.021	0.68	2700
5	Toluene	436	550	0.36	1.70	4800
	THF	430	554	0.14	0.68	5200
	DCM	433	557	0.18	1.01	5100
	DMSO	432	585	0.13	0.57	6100

[a] $c = 10^{-6}$ M in solutions. [b] Absorption maxima. [c] Emission maxima, excited at λ_{abs}^{max}. [d] Absolute photoluminescence quantum yields, excited at λ_{abs}^{max}.

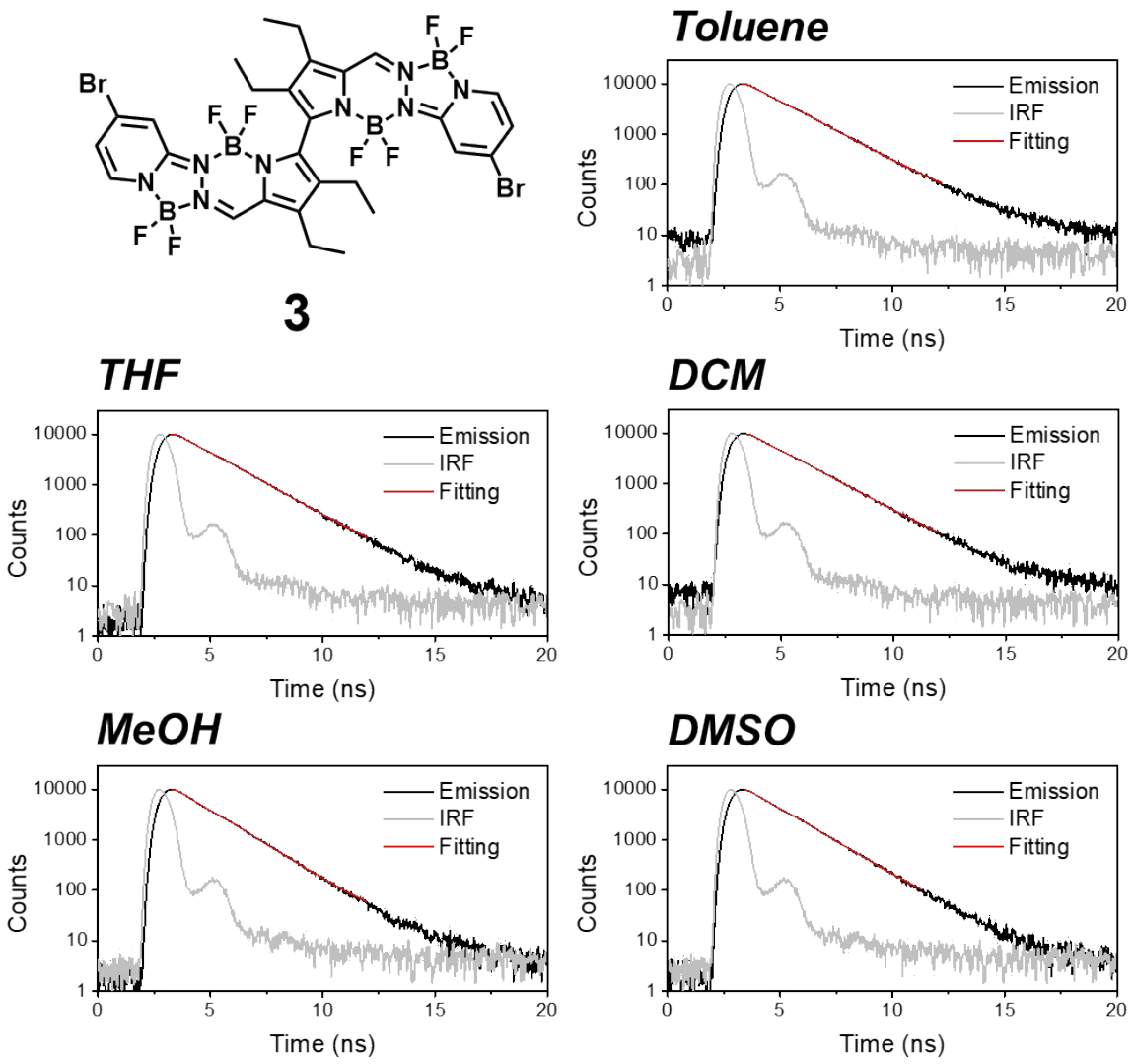


Figure S8. Emission decay curves (black line), fits (red line), and instrument response function (IRF) (gray line) of **3** in various solvents. Excited at 405 nm and emission wavelength at λ_{em}^{max}.

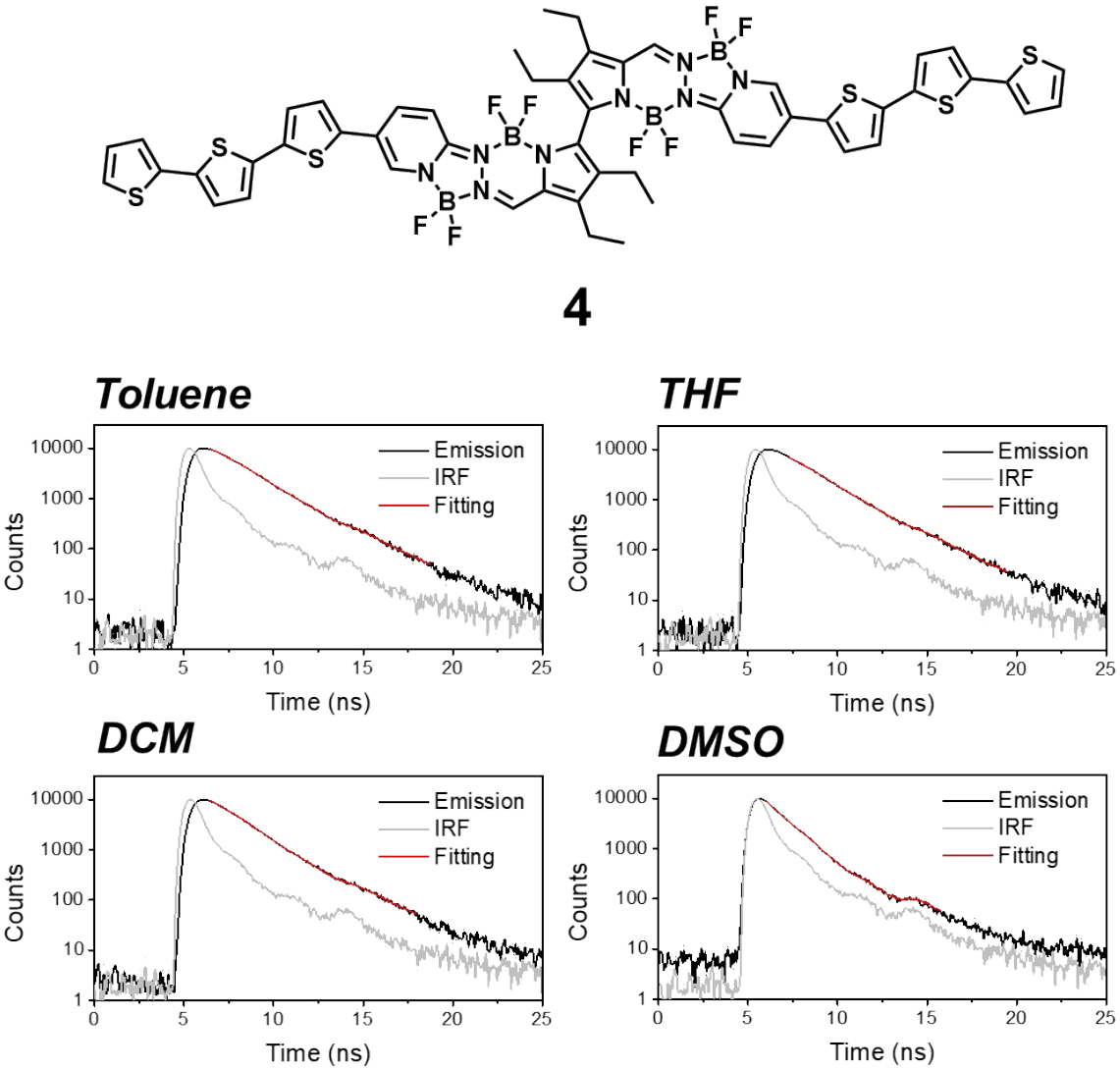


Figure S9. Emission decay curves (black line), fits (red line), and instrument response function (IRF) (gray line) of **4** in various solvents. Excited at 470 nm and emission wavelength at λ_{em}^{max}.

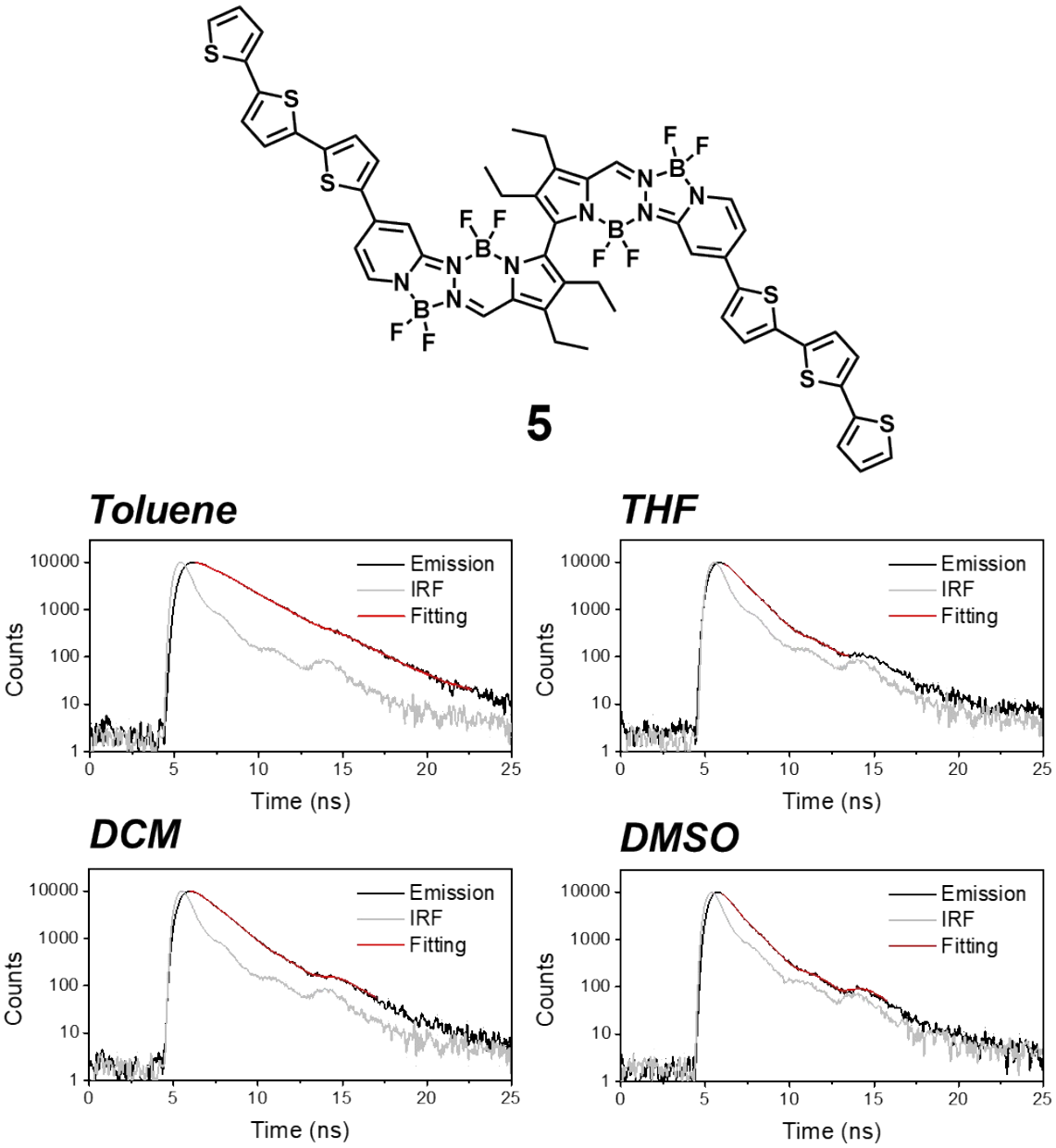


Figure S10. Emission decay curves (black line), fits (red line), and instrument response function (IRF) (gray line) of **5** in various solvents. Excited at 470 nm and emission wavelength at λ_{em}^{max}.

Table S2. Summary of lifetime analyses for **3**–**5** in various solvents. Emission lifetimes (τ), pre-exponential factor (A) and intensity average lifetime (τ_{av}).

Compd.	Solvent	λ_{ex} / nm[a]	λ_{em} / nm[b]	CHI	τ_{av} / ns	τ_1 / ns	τ_2 / ns	A_1	A_2
3	Toluene	405	519	1.09	1.76	1.76	–	385.02	–
	THF	405	519	1.04	1.68	1.68	–	390.44	–
	DCM	405	521	1.08	1.75	1.75	–	372.52	–
	MeOH	405	520	1.06	1.52	1.52	–	403.25	–
	DMSO	405	524	1.13	1.58	1.58	–	396.31	–
4	Toluene	470	534	1.11	1.57	1.57	–	868.20	–
	THF	470	534	1.17	1.59	1.59	–	813.02	–
	DCM	470	535	1.06	1.39	1.39	–	882.72	–
	DMSO	470	553	1.04	0.68	0.088	0.95	2685.12	561.21
5	Toluene	470	550	1.01	1.70	1.70	–	804.53	–
	THF	470	554	1.16	0.68	0.68	–	1123.68	–
	DCM	470	557	1.10	1.01	1.01	–	964.26	–
	DMSO	470	585	1.14	0.57	0.57	–	1315.59	–

[a] Excitation wavelength. [b] Emission wavelength.

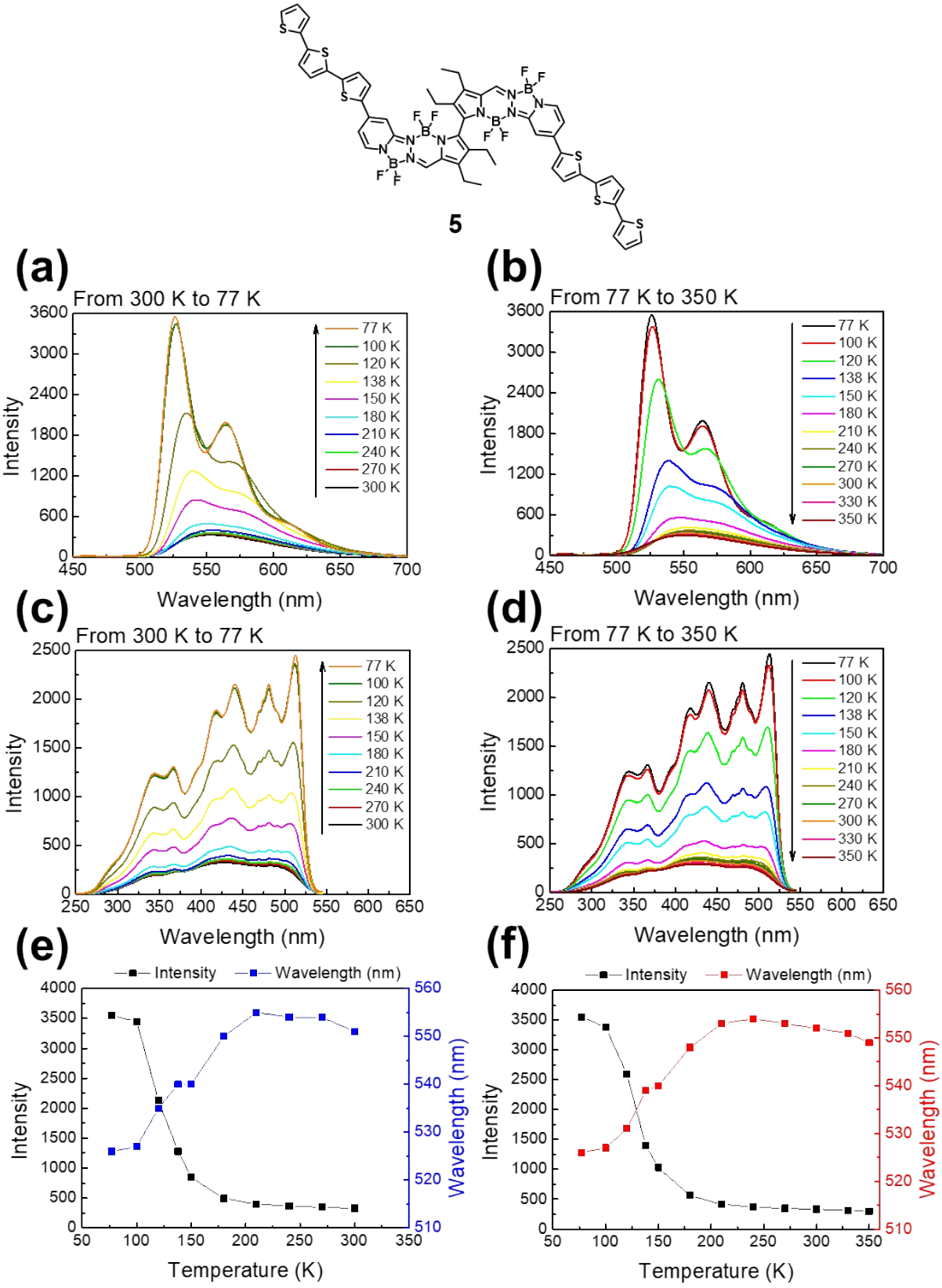


Figure S11. Optical properties of **5** in 2-MeTHF (c = 10^{-6} M) cooling from 300 K to 77 K (a, c, e), and heating from 77 K to 350 K (b, d, f). (a, b) Emission spectra (excited at 430 nm), (c, d) excitation spectra (emission wavelength at 560 nm), and (e, f) relationships of emission intensity and wavelength at different temperatures.

Optical resolution by Recycling Preparative Chiral HPLC

For compounds **1** and **5**, optical resolution was performed using LaboACE LC-5060 instrument with UV detector (UV-4ch 400 LA) by Japan Analytical Industry Co., Ltd. equipped with a CHIRALPAK® ID (Particle Size: 5μm; Dimensions: 20mm Ø × 250mm L).

For compound **4**, optical resolution was performed using LC-9201 apparatus with a UV-3702 attachment by Japan Analytical Industry Co., Ltd. equipped with a CHIRALPAK® IB N-5 (Particle Size: 5μm; Dimensions: 10mm Ø × 250mm L).

Table S3. Chiral HPLC conditions for the separation of enantiomers of **1**, **4** and **5**.

Compd.	Chiral column[a]	Eluent (*v* / *v*)	Flow rate / mL min^{-1}	λ / nm of UV detection
1	CHIRALPAK® ID	hexane / CH_2Cl_2 (1 / 1)	10	400
4	CHIRALPAK® IB N-5	hexane / ethyl acetate (2 / 3)	3	390
5	CHIRALPAK® ID	hexane / ethyl acetate (1 / 1)	10	400

[a] For CHIRALPAK® ID: Particle Size: 5μm; Dimensions: 20mm Ø × 250mm L; For CHIRALPAK® IB N-5: Particle Size: 5μm; Dimensions: 10mm Ø × 250mm L.

Preparation of [5]-doped polymer films

The [**5**]-doped polymer films were prepared using poly (methyl methacrylate) (PMMA, SigmaAldrich, Mw ~120,000) or polystyrene (PS, SigmaAldrich, Mw ~35, 000) as the inert matrix. 300 μL of toluene solution of **(*R*)-5** or **(*S*)-5** adjusted to a maximum absorbance of 1.2 (c = 1.73 × 10^{-5} mol/L) was mixed with 300 μL of toluene solution of PMMA or PS (0.1 g/mL). A 100 μL of the mixture was cast onto a quartz substrate (1 cm × 1 cm), air-dried, and vacuumed for 3 hours to obtain the hybrid PMMA or PS films.

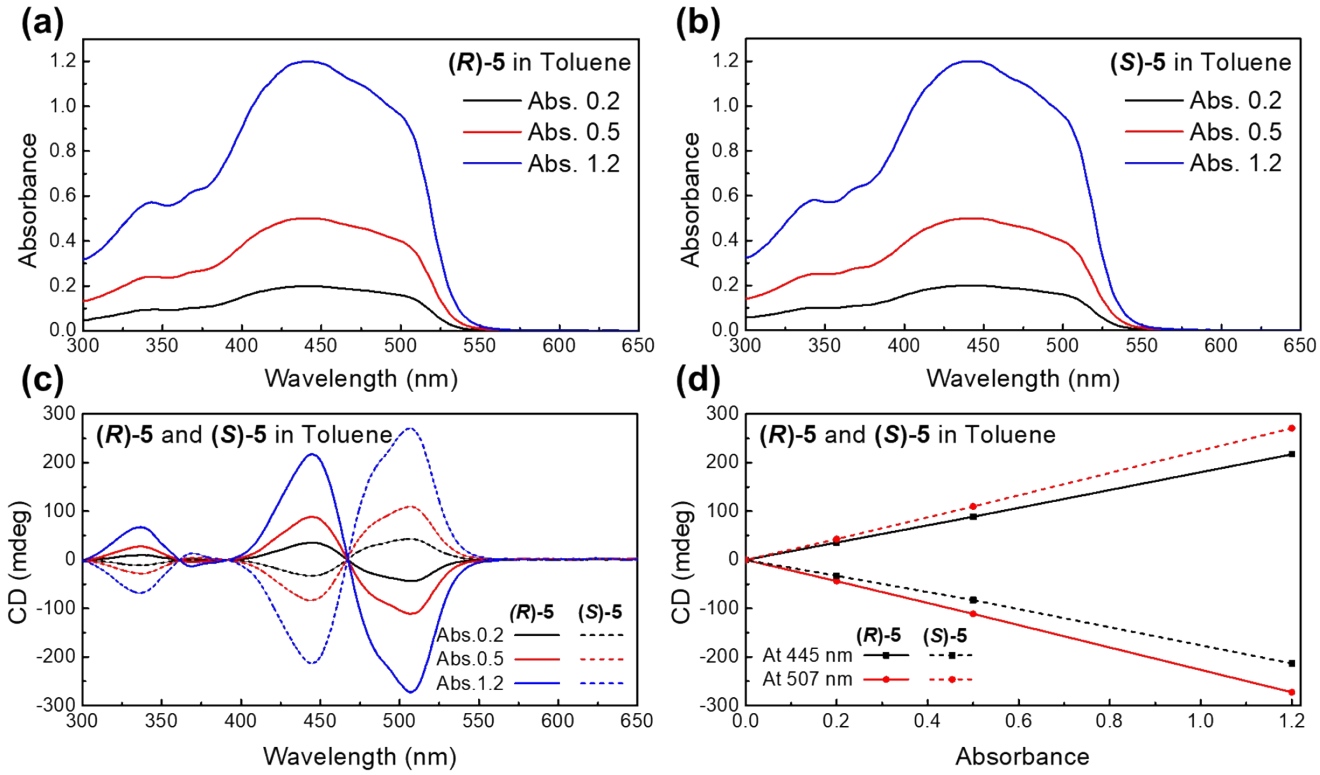


Figure S12. Concentration-dependent UV–vis absorption and CD spectra of **(*R*)-5** and **(*S*)-5** in toluene measured at 298 K. (a, b) UV–vis absorption spectra at maximum absorbance of 0.2, 0.5, 1.2, and their (c) CD spectra. (d) A linear correlation between absorbance and ellipticity at 445 nm (black line) and 507 nm (red line) in toluene.

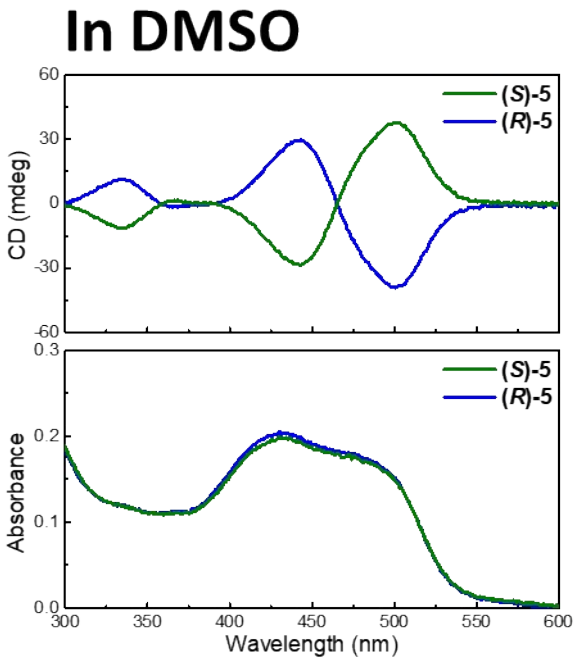


Figure S13-1. CD and absorption spectra of **(*S*)-5** (green) and **(*R*)-5** (blue) in DMSO ($c = 10^{-6}$ M).

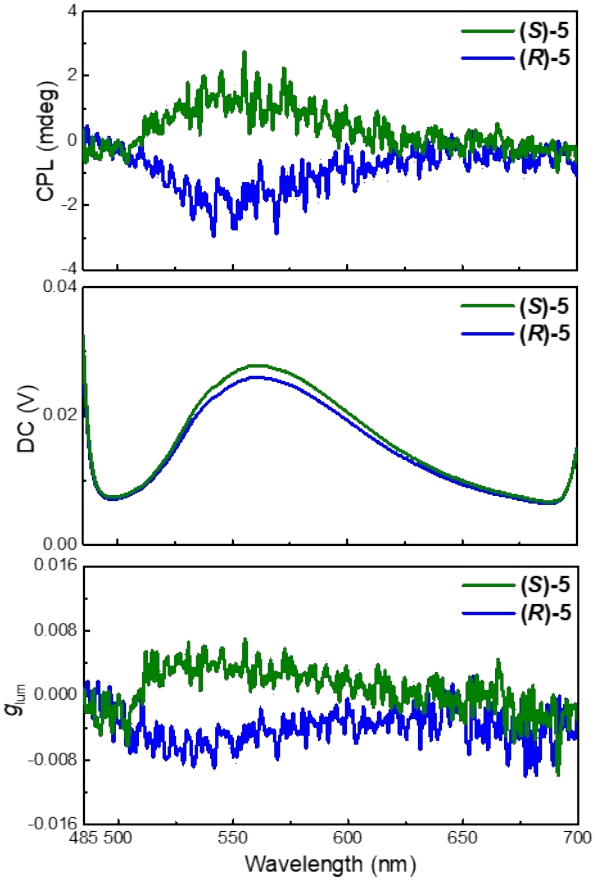


Figure S13-2. CPL, DC (nonpolarized fluorescence) and g_{lum} spectra of **(*S*)-5** (green) and **(*R*)-5** (blue) in DMSO ($c = 10^{-6}$ M). Excited at 420 nm.

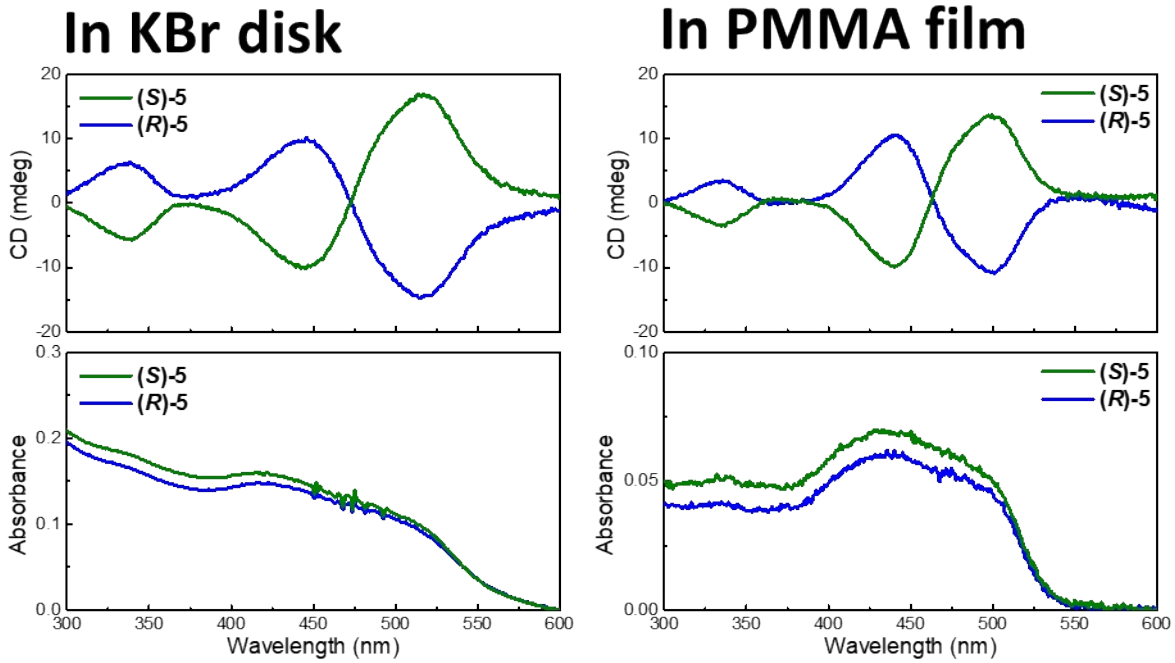


Figure S14-1. CD and absorption spectra of **(*S*)-5** (green) and **(*R*)-5** (blue) in KBr disk (left) and PMMA film (right).

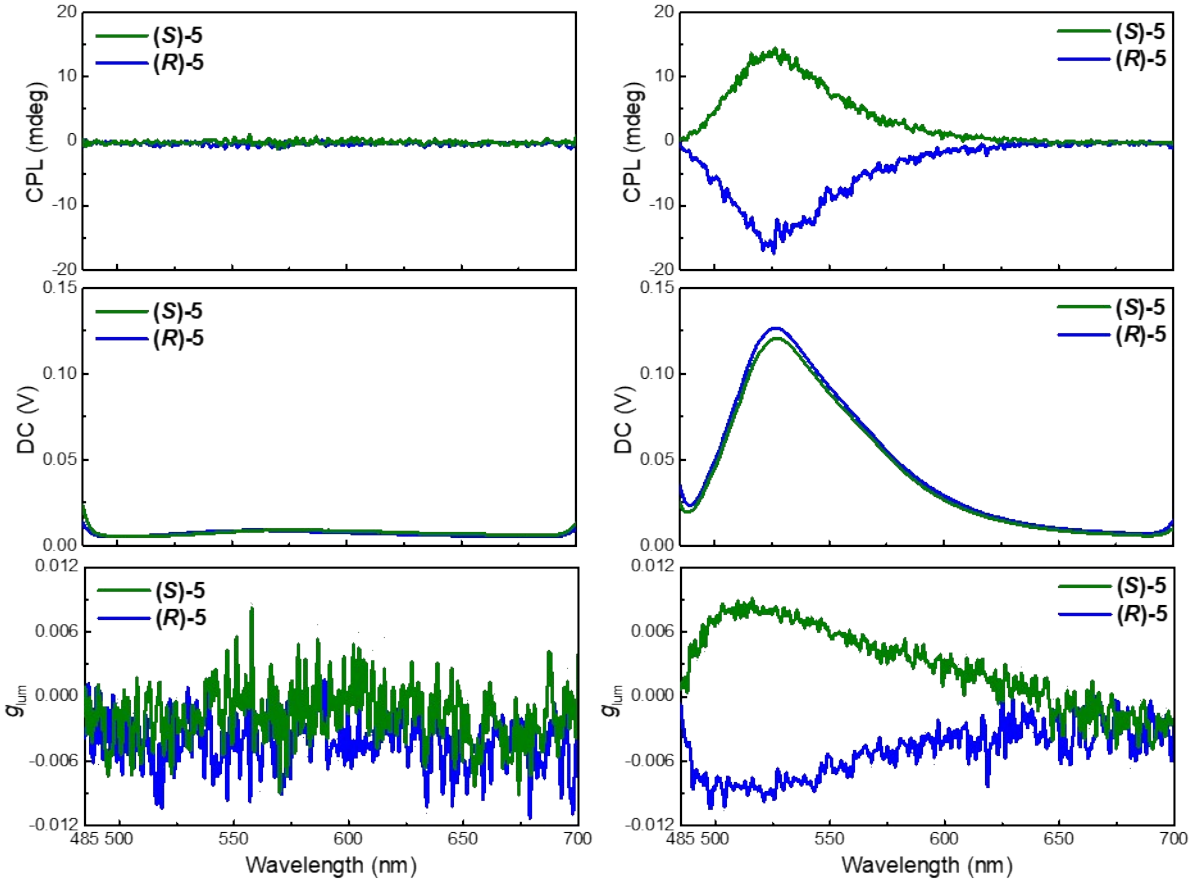


Figure S14-2. CPL, DC (nonpolarized fluorescence) and g_{lum} spectra of **(*S*)-5** (green) and **(*R*)-5** (blue) in KBr disk (left) and PMMA film (right). Excited at 420 nm.

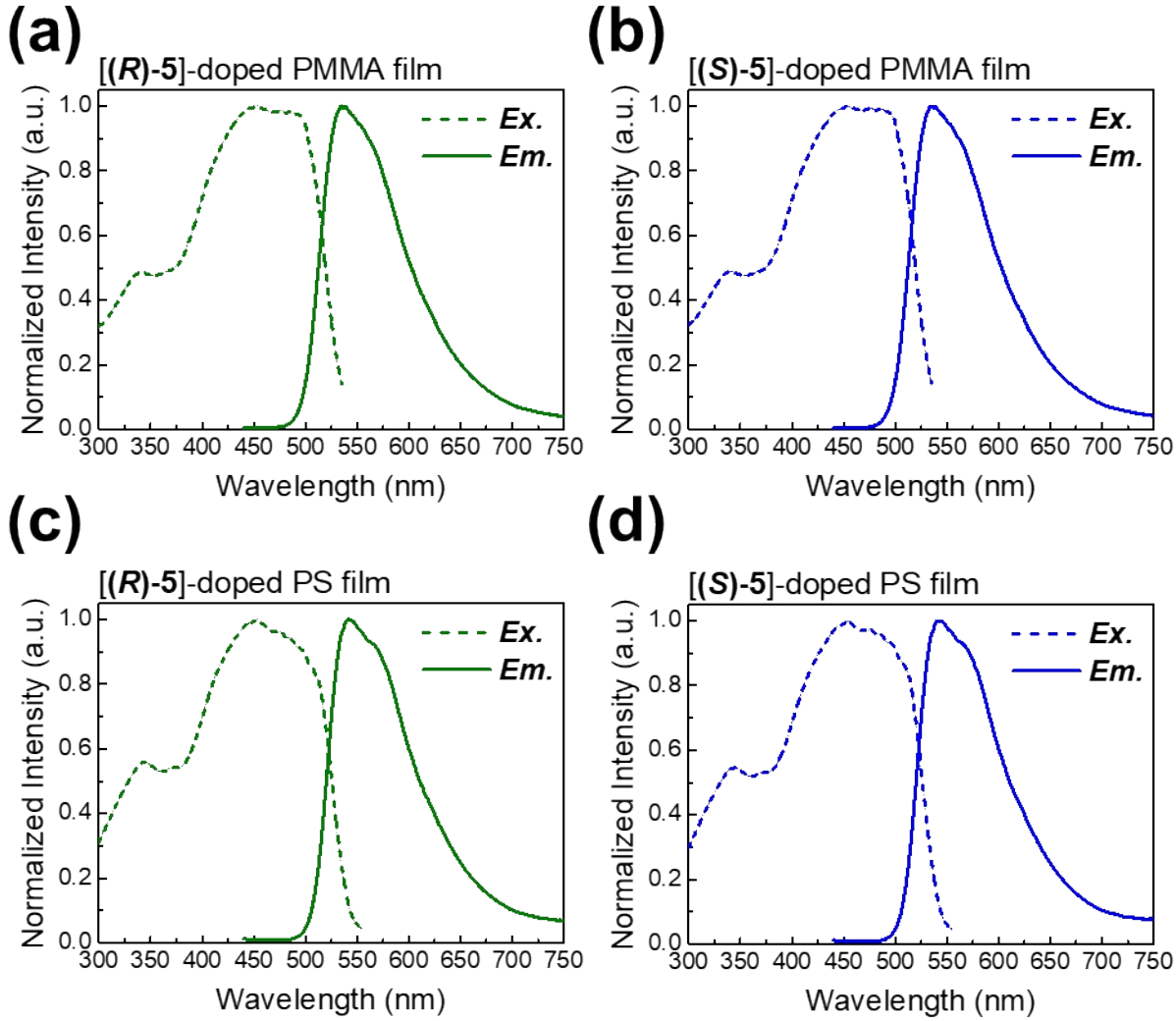


Figure S15. Normalized excitation and emission spectra of [**5**]-doped polymer films.

Table S4. Photophysical properties of [**5**]-doped polymer films.

Compd.	λ_{em}^{max} / nm[a]	λ_{ex}^{max} / nm[b]	Φ_{PL}[c]	τ_{av} / ns	Stokes shift / cm^{-1}
[(***R***)-**5**]-doped PMMA film	534	454	0.36	2.03	3300
[(***S***)-**5**]-doped PMMA film	534	454	0.36	2.00	3300
[(***R***)-**5**]-doped PS film	542	454	0.43	2.08	3576
[(***S***)-**5**]-doped PS film	542	454	0.43	2.07	3576

[a] Emission maxima, excited at 420 nm. [b] Excitation maxima, emission wavelengths at 550 nm for PMMA films and 570 nm for PS films. [c] Absolute photoluminescence quantum yields. Excited at 450 nm.

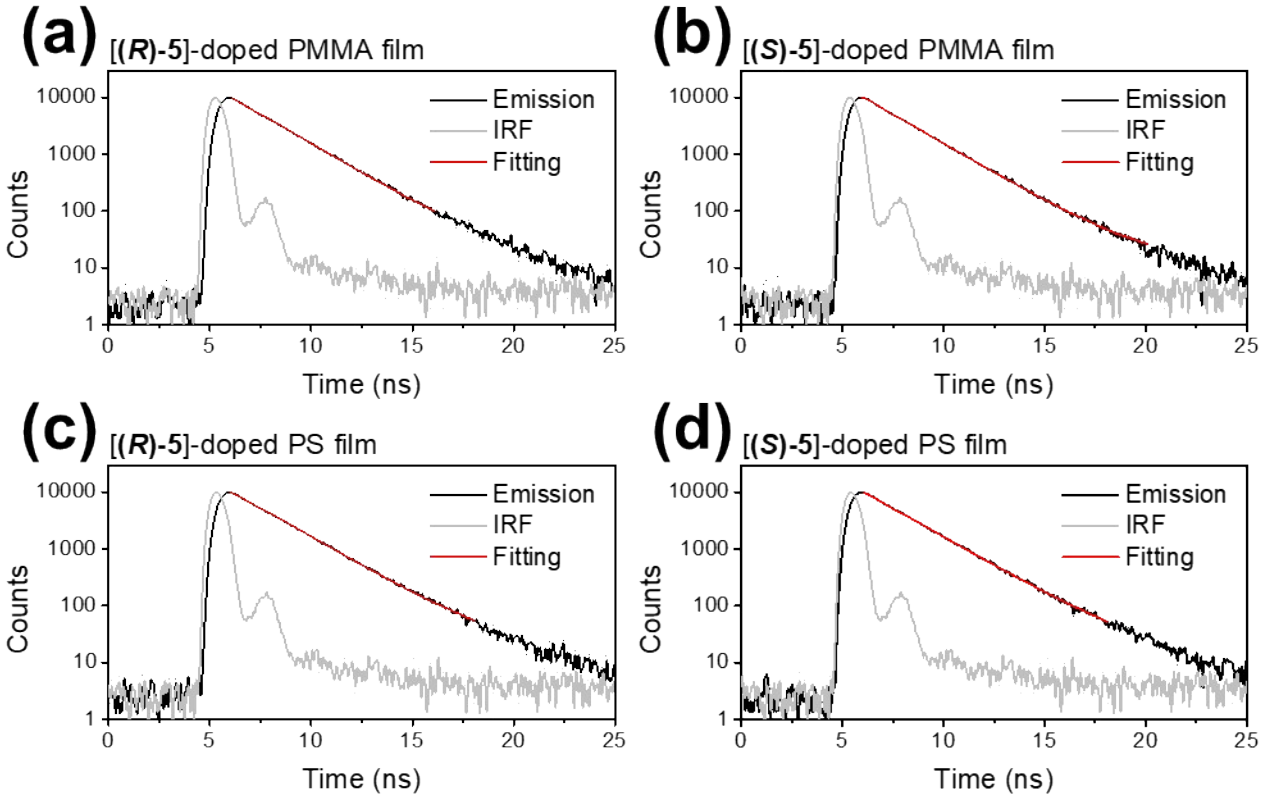


Figure S16. Emission decay curves (black line), fits (red line), and instrument response function (IRF) (gray line) of [**5**]-doped polymer films. Excited at 405 nm and emission wavelength at λ_{em}^{max}.

Table S5. Summary of lifetime analyses for [**5**]-doped polymer films. Emission lifetimes (τ), pre-exponential factor (A) and intensity average lifetime (τ_{av}).

Compd.	λ_{ex} / nm[a]	λ_{em} / nm[b]	CHI	τ_{av} / ns	τ_1 / ns	τ_2 / ns	A_1	A_2
[(***R***)-**5**]-doped PMMA film	405	534	1.14	2.03	2.03	—	883.76	—
[(***S***)-**5**]-doped PMMA film	405	534	1.03	2.00	0.72	2.07	123.17	798.69
[(***R***)-**5**]-doped PS film	405	542	1.09	2.08	2.08	—	868.87	—
[(***S***)-**5**]-doped PS film	405	542	1.12	2.07	0.89	2.13	90.98	781.63

[a] Excitation wavelength. [b] Emission wavelength.

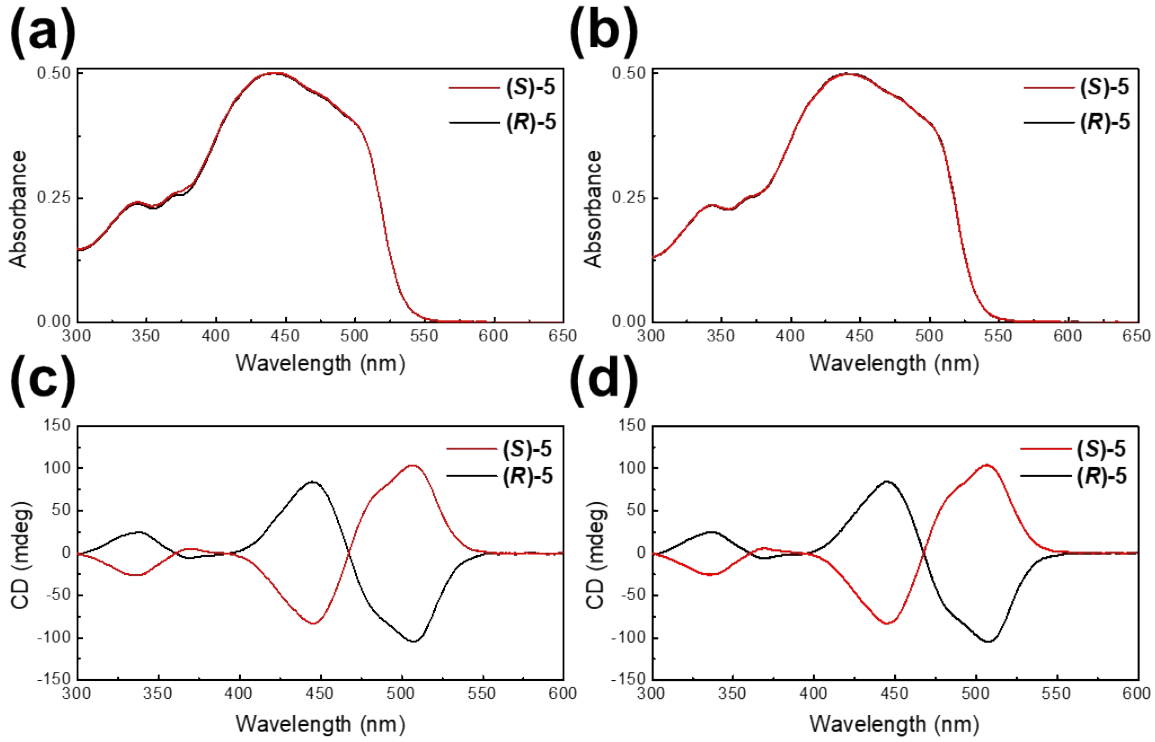


Figure S17. (a, b) UV–vis absorption spectra of **(*R*)-5** and **(*S*)-5** in toluene measured at 298 K (a) before and (b) after 24 h incubation at 358 K. (c, d) CD spectra of **(*R*)-5** and **(*S*)-5** in toluene measured at 298 K (c) before and (d) after 24 h incubation at 358 K.

Density-Functional Theory Calculations

Theoretical calculations were performed using Gaussian 16, revision A.03. Ground state (S_0) geometries were optimized by density-functional theory (DFT) level with the B3LYP/6-31G(d,p) level. Equilibrium geometries were verified via frequency calculation, where no imaginary frequency was found. TD-DFT calculations were performed using TD-cam-B3LYP/6-31G(d,p) level for the first 30 singlet–singlet transitions with an additional keyword of IOP(9/40=2). First singlet excited state (S_1) geometries were optimized using cam-B3LYP/6-31G(d,p) level. DFT data were visualized and analyzed with Chemcraft or GaussView 6.0.

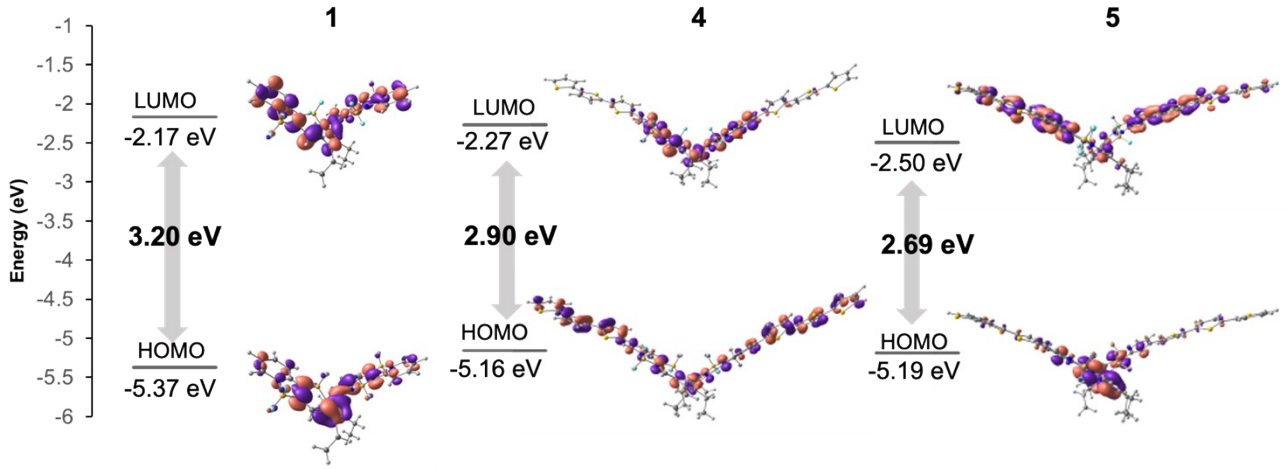


Figure S18. Frontier molecular orbitals of **(*S*)-1**, **(*S*)-4**, and **(*S*)-5**.

Table S6. Calculated photophysical property data of the ground state for **1**, **4**, and **5** at the cam-B3LYP/6-31G(d,p) level.

	Electronic Transition	TD//cam-B3LYP/6-31G(d,p)			
		Energy/eV[a]		f[b]	Major contributions
1	$S_0 \rightarrow S_1$	3.2415 eV	382.49 nm	1.0638	H-1->L+1 (19%), HOMO->LUMO (76%)
	$S_0 \rightarrow S_2$	3.5889 eV	345.47 nm	0.4394	H-1->LUMO (41%), HOMO->L+1 (54%)
	$S_0 \rightarrow S_3$	4.1747 eV	296.99 nm	0.0510	H-2->LUMO (22%), H-1->L+1 (29%), HOMO->L+2 (25%)
4	$S_0 \rightarrow S_1$	2.9838 eV	415.53 nm	3.1741	H-2->LUMO (10%), H-1->L+1 (21%), HOMO->LUMO (46%)
	$S_0 \rightarrow S_2$	3.2284 eV	384.04 nm	0.9174	H-1->LUMO (27%), H-1->L+2 (11%), HOMO->L+1 (39%)
	$S_0 \rightarrow S_3$	3.4413 eV	360.29 nm	0.4678	H-2->LUMO (18%), H-1->L+1 (14%), H-1->L+3 (19%), HOMO->L+2 (35%)
5	$S_0 \rightarrow S_1$	2.8886 eV	429.22 nm	2.3517	H-1->L+1 (25%), HOMO->LUMO (47%)
	$S_0 \rightarrow S_2$	3.0902 eV	401.22 nm	0.5853	H-2->L+1 (15%), H-1->LUMO (38%), HOMO->LUMO+1 (33%)
	$S_0 \rightarrow S_3$	3.3567 eV	369.37 nm	1.1534	H-3->L+1 (15%), H-2->LUMO (39%), H-1->L+1 (16%), HOMO->L+2 (13%)

[a]Only the selected low-lying excited states are presented. [b]Oscillator strength.

Table S7. Calculated photophysical property data of the S_1 excited state for **1**, **4**, and **5** at the cam-B3LYP/6-31G(d,p) level.

	Electronic Transition	TD//cam-B3LYP/6-31G(d,p)			
		Energy/eV[a]		f[b]	Major contributions
1	$S_1 \rightarrow S_0$	2.7554 eV	449.97 nm	1.1313	HOMO->LUMO(91%)
4	$S_1 \rightarrow S_0$	2.6543 eV	467.11nm	2.4764	HOMO->LUMO(78%)
5	$S_1 \rightarrow S_0$	2.6012 eV	476.64 nm	1.775	H-1->L+1 (12%), HOMO->LUMO (61%) HOMO->L+1(15%)

[a]Only the selected low-lying excited states are presented. [b]Oscillator strength.

Table S8. Coordinates of electric transition dipole moments (μ) and magnetic transition dipole moments (m) of the ground state of **1**, **4**, and **5** at the cam-B3LYP/6-31G(d,p) level.

	Electronic Transition	μ [a.u.]			m [a.u.]		
		x	y	z	x	y	z
1	$S_0 \rightarrow S_1$	3.5269	0.9780	0.0038	-0.7343	-1.8044	-0.0067
	$S_0 \rightarrow S_2$	-0.0001	-0.0084	2.2354	-0.0001	-0.0057	1.5092
	$S_0 \rightarrow S_3$	0.0492	0.7045	0.0026	1.0636	0.5255	0.0019
4	$S_0 \rightarrow S_1$	4.2169	-5.0635	0.0000	-4.2013	-1.8997	-0.0000
	$S_0 \rightarrow S_2$	0.0000	-0.0000	3.4051	0.0000	-0.0000	1.4056
	$S_0 \rightarrow S_3$	-1.8354	1.4778	0.0000	-0.1390	0.7875	0.0000
5	$S_0 \rightarrow S_1$	2.5830	-5.1535	-0.0000	-3.1326	1.7876	-0.0000
	$S_0 \rightarrow S_2$	-0.0000	0.0000	-2.7805	0.0000	-0.0000	-5.6468
	$S_0 \rightarrow S_3$	-3.6921	0.6274	-0.0000	-0.1271	0.2891	-0.0000

Table S9. Calculated transition dipole moments (μ, m, and θ) and g_{abs} values of **1**, **4**, and **5**.

	Electronic Transition	Energy [nm]	$\lvert\mu\rvert$ [10^{-20} esu cm]	$\lvert m\rvert$ [10^{-20} erg G^{-1}]	θ [º]	cos θ	$\lvert g_{abs}\rvert^{cal}$
1	$S_0 \rightarrow S_1$	382	930.28	1.81	127.6	-0.61	4.74×10^{-3}
	$S_0 \rightarrow S_2$	345	568.19	1.40	0	1.00	9.85×10^{-3}
	$S_0 \rightarrow S_3$	297	179.50	1.10	59.7	0.50	1.24×10^{-2}
4	$S_0 \rightarrow S_1$	415	1674.88	4.28	105.5	-0.27	2.72×10^{-3}
	$S_0 \rightarrow S_2$	384	865.49	1.30	0	1.00	6.02×10^{-3}
	$S_0 \rightarrow S_3$	360	598.94	0.74	41.2	0.75	3.73×10^{-3}
5	$S_0 \rightarrow S_1$	429	1465.21	3.34	146.3	-0.83	7.60×10^{-3}
	$S_0 \rightarrow S_2$	401	706.73	5.24	0	1.00	2.96×10^{-2}
	$S_0 \rightarrow S_3$	369	951.89	0.29	56.6	0.55	6.77×10^{-4}

Table S10. Coordinates of electric transition dipole moments (μ) and magnetic transition dipole moments (m) of the excited state of **1**, **4**, and **5** at the cam-B3LYP/6-31G(d,p) level.

	Electronic Transition	μ [a.u.]			m [a.u.]		
		x	y	z	x	y	z
1	$S_1 \rightarrow S_0$	-4.0599	-0.5246	0	0.6452	1.2750	0
4	$S_1 \rightarrow S_0$	0.9452	-6.0983	0	-3.2144	0.5232	0
5	$S_1 \rightarrow S_0$	-2.9739	4.3598	0	3.4821	-0.391	0

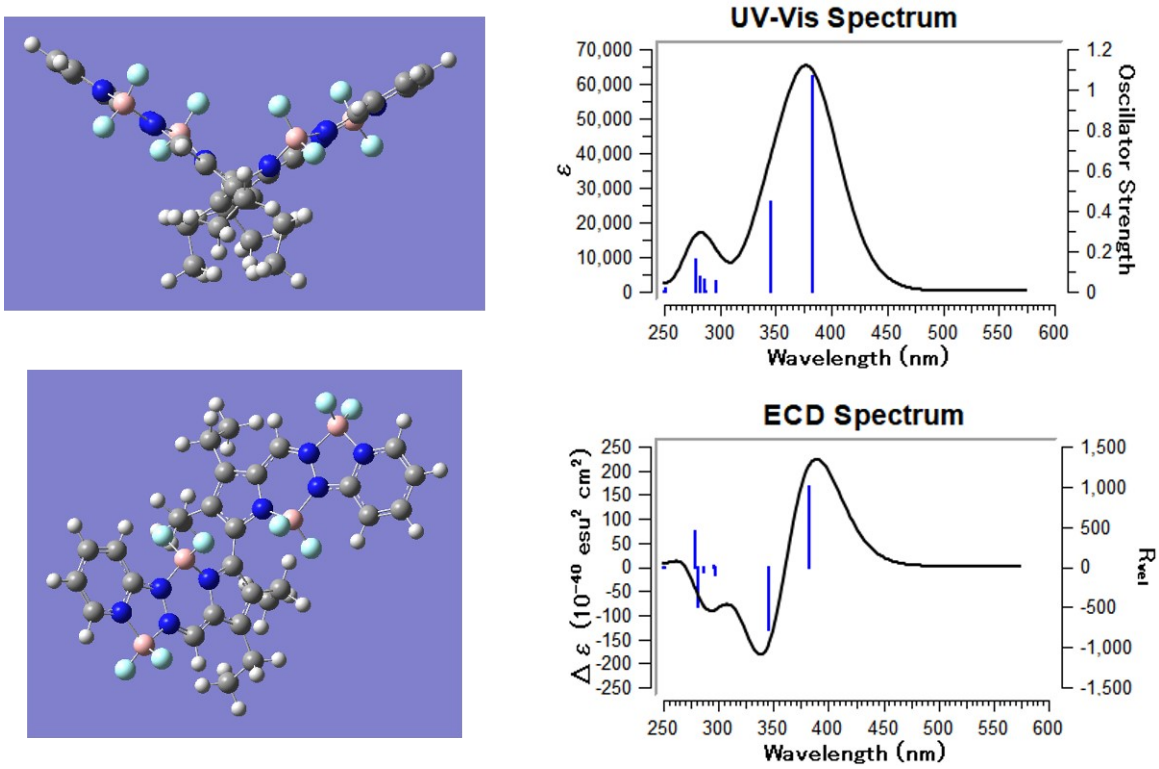


Figure S19. Calculated UV–vis and ECD spectra of **(*S*)-1** by TD-DFT method [cam-B3LYP/6-31G(d,p)].

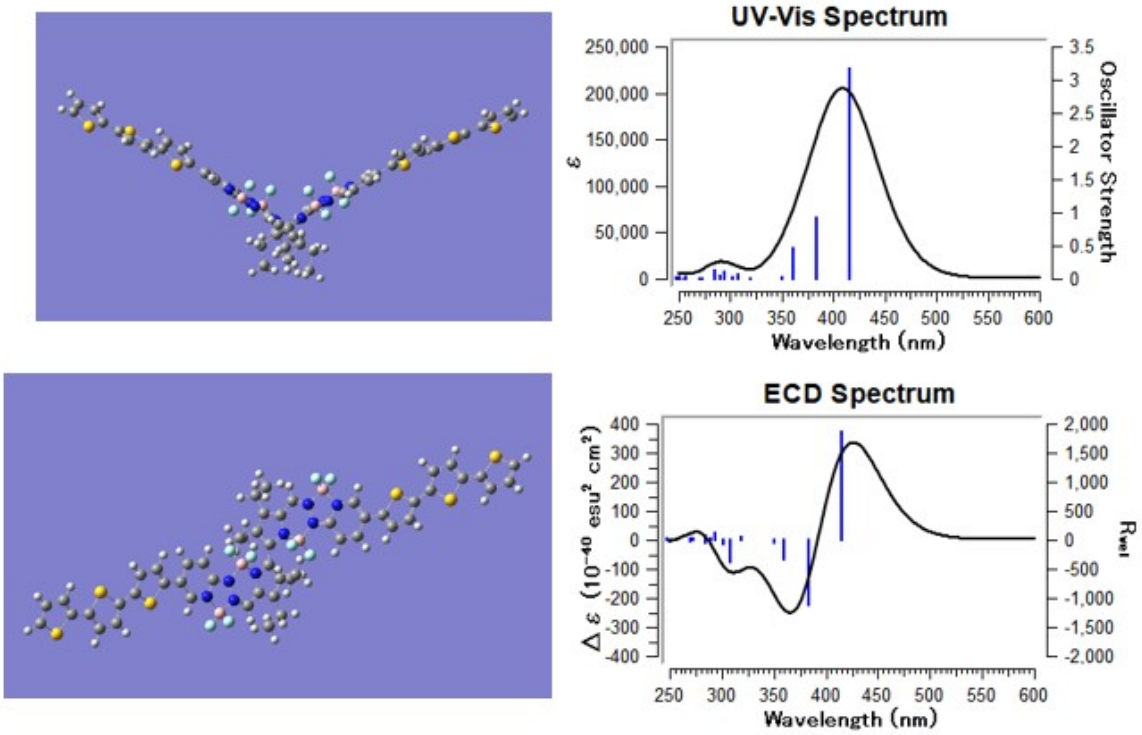


Figure S20. Calculated UV–vis and ECD spectra of **(*S*)-4** by TD-DFT method [cam-B3LYP/6-31G(d,p)].

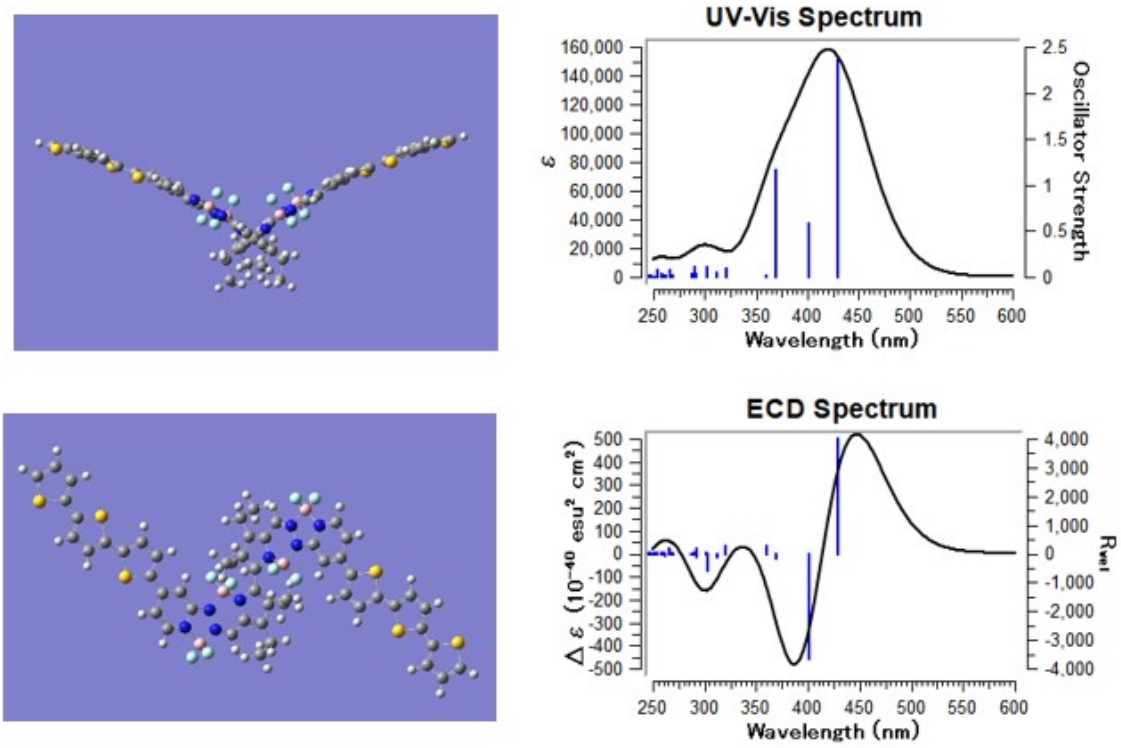


Figure S21. Calculated UV–vis and ECD spectra of **(*S*)-5** by TD-DFT method [cam-B3LYP/6-31G(d,p)].

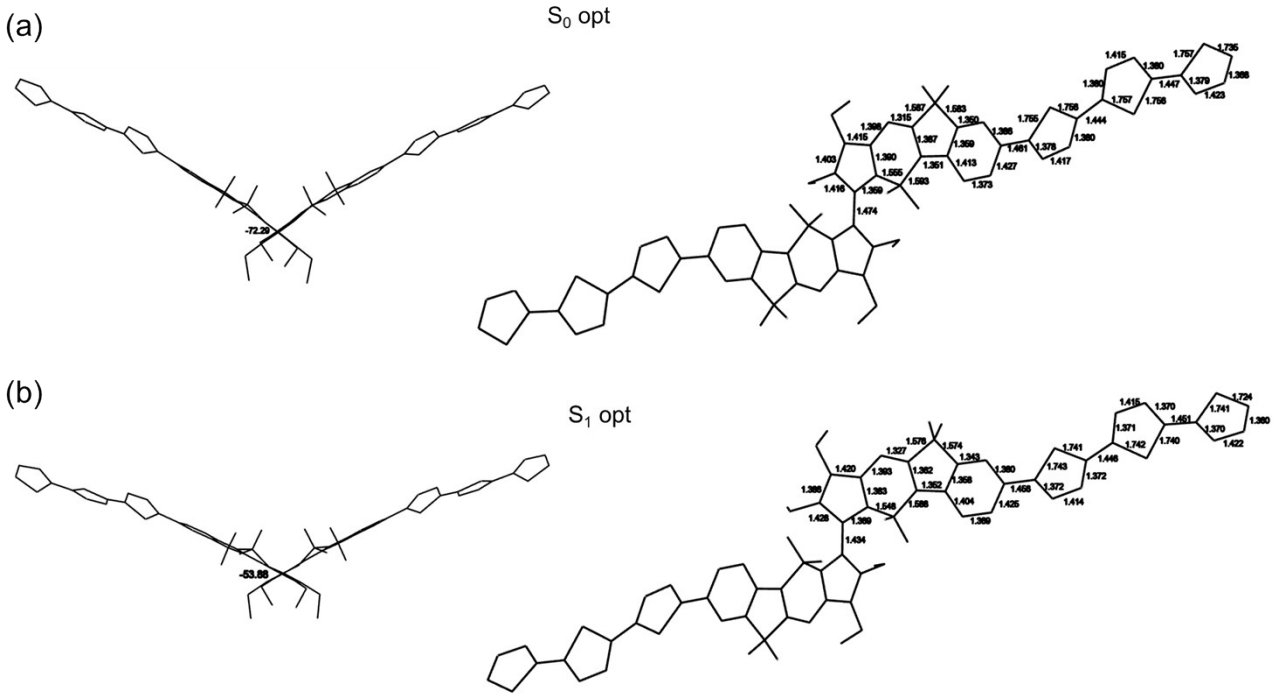


Figure S22. Optimized geometries of **4** in (a) S_0 and (b) S_1 showing representative bond length (Å). The bond length between the carbon atoms of bipyrrole is 1.474Å in S_0, but it is shortened to 1.434Å in S_1. The torsion angle is -72.29 degrees for S_0, while it is -53.88 degrees in the S_1 state, suggesting that the compound is more planar conformation in the S_1 state than in the S_0 state.

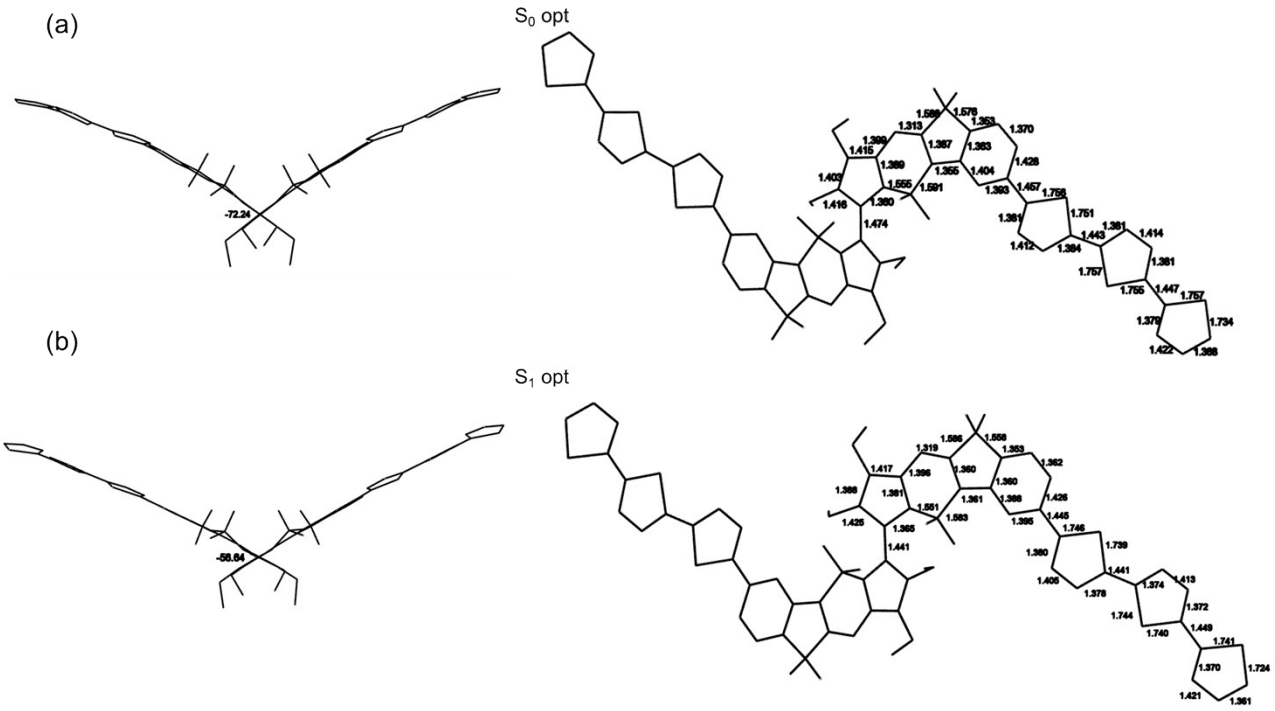


Figure S23. Optimized geometries of **5** in (a) S_0 and (b) S_1 showing representative bond length (Å). The bond length between the carbon atoms of bipyrrole is 1.474Å in S_0, but it is shortened to 1.441Å in S_1. The torsion angle is -72.24 degrees for S_0, while it is -56.64 degrees in the S_1 state, suggesting that the compound is more planar conformation in the S_1 state than in the S_0 state.

The ground states of 1 optimized at B3LYP/6-31G(d,p) level.

B	2.104292699	0.707113771	-0.409785415
B	5.633819011	-0.937296291	-1.310624659
C	0.511938151	-0.534719878	1.273925651
C	0.470410875	-1.789488312	1.929157032
C	1.659802436	-2.458425765	1.603987313
C	2.392450417	-1.584474044	0.766189521
C	3.625439419	-1.774243795	0.134731976
H	4.161843568	-2.711573345	0.226328753
C	4.458804340	1.182632712	-1.458999335
C	4.233571972	2.530175353	-1.817027046
H	3.318779372	3.012296669	-1.502096022
C	5.212121805	3.172652779	-2.543610819
H	5.063799063	4.208503581	-2.832673257
C	6.406312277	2.509449623	-2.912396799
H	7.178014263	3.012419792	-3.481319673
C	6.572465413	1.201439840	-2.526862767

H	7.454464555	0.616376531	-2.760418178
C	-0.644332701	-2.284681925	2.811247526
H	-0.891912537	-3.315803549	2.531337632
H	-1.545204706	-1.703256244	2.604032293
C	-0.329097868	-2.227361340	4.315784923
H	-0.098873225	-1.204863183	4.631743842
H	-1.184279125	-2.576938429	4.903859256
H	0.530915993	-2.853209927	4.573575562
C	2.104432893	-3.823649166	2.052301642
H	1.230131206	-4.385601860	2.397452153
H	2.498720142	-4.382734497	1.193836839
C	3.168274780	-3.804413472	3.167287652
H	4.078493499	-3.292127503	2.840059772
H	2.800495427	-3.282026927	4.055268550
H	3.440877857	-4.823574616	3.459740946
F	1.350238572	0.673505163	-1.559721255
F	2.079663297	1.970920569	0.173000526
F	6.637506536	-1.163777190	-0.403354065
F	5.646498839	-1.828157061	-2.351540063
N	1.679235688	-0.405243699	0.590245468
N	4.216962966	-0.860992562	-0.601886817
N	3.626035103	0.385135807	-0.753104164
N	5.615161227	0.559832503	-1.817186513
B	-2.104270288	-0.703925737	-0.415077661
B	-5.633726987	0.947234171	-1.303792891
C	-0.511974813	0.525273953	1.277924416
C	-0.470515684	1.775040175	1.942643453
C	-1.659977292	2.446327154	1.622634461
C	-2.392538509	1.578750664	0.778144286
C	-3.625505540	1.773252609	0.148077748
H	-4.161980275	2.709813370	0.246823560
C	-4.458745538	-1.171548808	-1.467924734
C	-4.233555070	-2.516409331	-1.835926040
H	-3.318761121	-3.000882479	-1.524636724
C	-5.212171436	-3.153494288	-2.567154915
H	-5.063890759	-4.187188798	-2.863857608
C	-6.406381175	-2.487573891	-2.930940265
H	-7.178138673	-2.986322903	-3.503492522
C	-6.572477055	-1.182437249	-2.535764634
H	-7.454487415	-0.595657882	-2.764932848
C	0.644280085	2.263638843	2.828321927
H	0.891282742	3.297097917	2.556636840
H	1.545351812	1.684321510	2.616139250
C	0.329537561	2.194081621	4.332443502

H	0.099884465	1.168963836	4.640230913
H	1.184734318	2.539317387	4.923054658
H	-0.530696353	2.817436413	4.595492538
C	-2.104726545	3.808037400	2.081418948
H	-1.230456502	4.367451990	2.430765697
H	-2.499180753	4.373614736	1.227295621
C	-3.168449329	3.780174318	3.196340018
H	-4.078612474	3.270222354	2.865328800
H	-2.800498454	3.251165337	4.080320060
H	-3.441197734	4.797050115	3.496512177
F	-1.350127709	-0.661807102	-1.564679042
F	-2.079745029	-1.972042954	0.158270674
F	-6.637528179	1.167041112	-0.395008318
F	-5.646197049	1.845800413	-2.338066739
N	-1.679264851	0.400922627	0.593272547
N	-4.216959479	0.865586080	-0.595468521
N	-3.625965601	-0.379327567	-0.756121707
N	-5.615110320	-0.546098925	-1.821443014

The ground states of 4 optimized at B3LYP/6-31G(d,p) level.

F	-0.958567957	6.680098319	2.013327801
F	-0.027761841	5.965750944	0.052810995
F	-2.510549904	1.349499925	2.501702712
F	-1.023527920	1.109479524	0.783615545
N	-0.492465406	4.288430936	1.788512520
N	-2.285369909	5.186491724	0.589414278
N	-1.491774404	3.340137130	1.628992822
N	-0.136913038	1.724059964	2.958000077
C	0.346220626	0.650420541	3.636811697
C	1.551221853	0.995770874	4.296247366
C	1.819599858	2.335569906	3.979361974
C	0.763157589	2.766626993	3.142028255
C	0.560524540	4.003002036	2.521796673
H	1.284457839	4.803492144	2.620794803
C	-3.187173239	5.905021769	-0.113361482
H	-2.890108896	6.919827202	-0.352385644
C	-4.398084336	5.361741205	-0.511176313
C	-4.641249183	4.005197423	-0.139750962
C	-3.723991961	3.266404546	0.566824839
H	-3.905085544	2.245795875	0.873848865
C	-2.510549904	3.890516474	0.932211014
C	2.365684108	0.084265756	5.174833467
H	2.093235085	-0.951372692	4.960819149
H	3.423360254	0.170940626	4.898023394

C	2.209864893	0.356393844	6.680830595
H	2.806624459	-0.351671802	7.265488850
H	2.536958723	1.366559218	6.945936596
H	1.165795027	0.255217529	6.993863703
C	2.978732882	3.178744546	4.435274707
H	3.783803193	2.519483284	4.776599446
H	3.388769154	3.733111183	3.581170287
C	2.629132546	4.176151901	5.557066878
H	2.245668994	3.658233925	6.441000904
H	3.513255816	4.749146651	5.854508308
H	1.860303352	4.885106241	5.234139923
B	-0.863738997	5.666398337	1.095214228
B	-1.313859573	1.788328557	1.943880834
F	0.958567957	-6.680098319	2.013327801
F	0.027761841	-5.965750944	0.052810995
F	2.510549904	-1.349499925	2.501702712
F	1.023527920	-1.109479524	0.783615545
N	0.492465406	-4.288430936	1.788512520
N	2.285369909	-5.186491724	0.589414278
N	1.491774404	-3.340137130	1.628992822
N	0.136913038	-1.724059964	2.958000077
C	-0.346220626	-0.650420541	3.636811697
C	-1.551221853	-0.995770874	4.296247366
C	-1.819599858	-2.335569906	3.979361974
C	-0.763157589	-2.766626993	3.142028255
C	-0.560524540	-4.003002036	2.521796673
H	-1.284457839	-4.803492144	2.620794803
C	3.187173239	-5.905021769	-0.113361482
H	2.890108896	-6.919827202	-0.352385644
C	4.398084336	-5.361741205	-0.511176313
C	4.641249183	-4.005197423	-0.139750962
C	3.723991961	-3.266404546	0.566824839
H	3.905085544	-2.245795875	0.873848865
C	2.510549904	-3.890516474	0.932211014
C	-2.365684108	-0.084265756	5.174833467
H	-2.093235085	0.951372692	4.960819149
H	-3.423360254	-0.170940626	4.898023394
C	-2.209864893	-0.356393844	6.680830595
H	-2.806624459	0.351671802	7.265488850
H	-2.536958723	-1.366559218	6.945936596
H	-1.165795027	-0.255217529	6.993863703
C	-2.978732882	-3.178744546	4.435274707
H	-3.783803193	-2.519483284	4.776599446
H	-3.388769154	-3.733111183	3.581170287

C	-2.629132546	-4.176151901	5.557066878
H	-2.245668994	-3.658233925	6.441000904
H	-3.513255816	-4.749146651	5.854508308
H	-1.860303352	-4.885106241	5.234139923
B	0.863738997	-5.666398337	1.095214228
B	1.313859573	-1.788328557	1.943880834
C	-5.384365120	6.124792626	-1.272565861
C	-6.354671933	5.648921042	-2.127305167
S	-5.466687267	7.874919269	-1.178663279
C	-7.141042184	6.665468315	-2.723503985
H	-6.475314820	4.596096938	-2.355262433
C	-6.787668782	7.941464631	-2.333959646
H	-7.926823355	6.468517644	-3.443796947
C	-7.353454619	9.208320257	-2.735349713
C	-6.832544918	10.478416352	-2.592674393
S	-8.924228910	9.282396181	-3.518435498
C	-7.661267341	11.497359634	-3.120334729
H	-5.863468231	10.668819248	-2.145341205
C	-8.833400874	11.028704228	-3.677348183
H	-7.392285487	12.547486061	-3.117838811
C	-9.901809211	11.768268910	-4.314369818
C	-10.899054109	11.308347416	-5.148840810
S	-10.070358991	13.499488103	-4.068091378
C	-11.783598963	12.329842761	-5.594419066
H	-10.980199471	10.269829286	-5.449362533
C	-11.461277948	13.564724703	-5.102522116
H	-12.620118019	12.153204030	-6.260417527
H	-11.953897992	14.510084989	-5.281239227
C	5.384365120	-6.124792626	-1.272565861
C	6.354671933	-5.648921042	-2.127305167
S	5.466687267	-7.874919269	-1.178663279
C	7.141042184	-6.665468315	-2.723503985
H	6.475314820	-4.596096938	-2.355262433
C	6.787668782	-7.941464631	-2.333959646
H	7.926823355	-6.468517644	-3.443796947
C	7.353454619	-9.208320257	-2.735349713
C	6.832544918	-10.478416352	-2.592674393
S	8.924228910	-9.282396181	-3.518435498
C	7.661267341	-11.497359634	-3.120334729
H	5.863468231	-10.668819248	-2.145341205
C	8.833400874	-11.028704228	-3.677348183
H	7.392285487	-12.547486061	-3.117838811
C	9.901809211	-11.768268910	-4.314369818
C	10.899054109	-11.308347416	-5.148840810

S	10.070358991	-13.499488103	-4.068091378
C	11.783598963	-12.329842761	-5.594419066
H	10.980199471	-10.269829286	-5.449362533
C	11.461277948	-13.564724703	-5.102522116
H	12.620118019	-12.153204030	-6.260417527
H	11.953897992	-14.510084989	-5.281239227
H	-5.590381020	3.551735495	-0.405365117
H	5.590381020	-3.551735495	-0.405365117

The ground states of 5 optimized at B3LYP/6-31G(d,p) level.

F	-4.371775501	-5.155092309	1.572524301
F	-4.480872238	-3.974666822	-0.379639929
F	0.652661422	-2.764423425	2.016686045
F	-0.178703314	-1.505671583	0.300953271
N	-2.892508471	-3.218384886	1.336410636
N	-2.392603519	-5.147219390	0.125138008
N	-1.521278126	-3.337645044	1.168654913
N	-1.205084845	-1.245228861	2.485696889
C	-0.716852543	-0.170390163	3.160215294
C	-1.770809615	0.504176832	3.822947927
C	-2.953871780	-0.184013568	3.513912001
C	-2.580804757	-1.262148219	2.677585555
C	-3.374784651	-2.238312028	2.065795985
H	-4.453497068	-2.228154196	2.170051333
C	-2.314620377	-6.300471482	-0.578592979
H	-3.260511851	-6.778504544	-0.805376149
C	-1.108720652	-6.809934974	-0.980882107
C	0.095710284	-6.120756909	-0.642721240
C	0.005586270	-4.944622367	0.098737147
H	0.875226493	-4.399600244	0.435642530
C	-1.262537614	-4.463709872	0.460234182
C	-1.624165397	1.720927240	4.697104175
H	-0.668281617	2.201456844	4.478266130
H	-2.390126530	2.455616797	4.420367969
C	-1.720252947	1.429815606	6.204527149
H	-1.583278956	2.348091245	6.785462060
H	-2.692813943	1.006604625	6.474340182
H	-0.951898471	0.715832554	6.517797223
C	-4.350947248	0.125319544	3.977829921
H	-4.389579616	1.165871361	4.317319124
H	-5.043532749	0.062446368	3.128411090
C	-4.858521699	-0.795353273	5.104789641
H	-4.210414916	-0.737271053	5.984126783
H	-5.871794147	-0.513274785	5.408778078

H	-4.881143830	-1.841545770	4.783931303
B	-3.683962438	-4.410031941	0.647587702
B	-0.481254667	-2.170999698	1.467218801
F	4.371775501	5.155092309	1.572524301
F	4.480872238	3.974666822	-0.379639929
F	-0.652661422	2.764423425	2.016686045
F	0.178703314	1.505671583	0.300953271
N	2.892508471	3.218384886	1.336410636
N	2.392603519	5.147219390	0.125138008
N	1.521278126	3.337645044	1.168654913
N	1.205084845	1.245228861	2.485696889
C	0.716852543	0.170390163	3.160215294
C	1.770809615	-0.504176832	3.822947927
C	2.953871780	0.184013568	3.513912001
C	2.580804757	1.262148219	2.677585555
C	3.374784651	2.238312028	2.065795985
H	4.453497068	2.228154196	2.170051333
C	2.314620377	6.300471482	-0.578592979
H	3.260511851	6.778504544	-0.805376149
C	1.108720652	6.809934974	-0.980882107
C	-0.095710284	6.120756909	-0.642721240
C	-0.005586270	4.944622367	0.098737147
H	-0.875226493	4.399600244	0.435642530
C	1.262537614	4.463709872	0.460234182
C	1.624165397	-1.720927240	4.697104175
H	0.668281617	-2.201456844	4.478266130
H	2.390126530	-2.455616797	4.420367969
C	1.720252947	-1.429815606	6.204527149
H	1.583278956	-2.348091245	6.785462060
H	2.692813943	-1.006604625	6.474340182
H	0.951898471	-0.715832554	6.517797223
C	4.350947248	-0.125319544	3.977829921
H	4.389579616	-1.165871361	4.317319124
H	5.043532749	-0.062446368	3.128411090
C	4.858521699	0.795353273	5.104789641
H	4.210414916	0.737271053	5.984126783
H	5.871794147	0.513274785	5.408778078
H	4.881143830	1.841545770	4.783931303
B	3.683962438	4.410031941	0.647587702
B	0.481254667	2.170999698	1.467218801
H	-1.085120580	-7.720260338	-1.566712586
H	1.085120580	7.720260338	-1.566712586
C	-1.397325944	6.628985512	-1.055411733
C	-2.600777446	5.953616380	-1.109926504

S	-1.614500646	8.290866133	-1.579974440
C	-3.677121451	6.740040131	-1.574599618
H	-2.698702214	4.905342127	-0.853829031
C	-3.320782462	8.040466921	-1.885971083
H	-4.683639032	6.359674563	-1.704766066
C	1.397325944	-6.628985512	-1.055411733
C	2.600777446	-5.953616380	-1.109926504
S	1.614500646	-8.290866133	-1.579974440
C	3.677121451	-6.740040131	-1.574599618
H	2.698702214	-4.905342127	-0.853829031
C	3.320782462	-8.040466921	-1.885971083
H	4.683639032	-6.359674563	-1.704766066
C	-4.148987619	9.113115978	-2.382232375
C	-3.770291859	10.314691875	-2.947680036
S	-5.900764961	9.003201630	-2.310285849
C	-4.858521699	11.128850070	-3.338711643
H	-2.733110452	10.590032376	-3.102376797
C	-6.093517404	10.567800528	-3.080723790
H	-4.741443413	12.091367763	-3.823267010
C	-7.411363967	11.099803425	-3.351941937
C	-8.621807235	10.439677508	-3.396252170
S	-7.642453502	12.809837641	-3.680728403
C	-9.721666692	11.289708523	-3.698063662
H	-8.714253918	9.371273776	-3.236844054
C	-9.350874522	12.593224755	-3.884486298
H	-10.745165555	10.943330951	-3.780791190
H	-9.974458686	13.441968123	-4.127651695
C	4.148987619	-9.113115978	-2.382232375
C	3.770291859	-10.314691875	-2.947680036
S	5.900764961	-9.003201630	-2.310285849
C	4.858521699	-11.128850070	-3.338711643
H	2.733110452	-10.590032376	-3.102376797
C	6.093517404	-10.567800528	-3.080723790
H	4.741443413	-12.091367763	-3.823267010
C	7.411363967	-11.099803425	-3.351941937
C	8.621807235	-10.439677508	-3.396252170
S	7.642453502	-12.809837641	-3.680728403
C	9.721666692	-11.289708523	-3.698063662
H	8.714253918	-9.371273776	-3.236844054
C	9.350874522	-12.593224755	-3.884486298
H	10.745165555	-10.943330951	-3.780791190
H	9.974458686	-13.441968123	-4.127651695

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