Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Supplementary information

Optical properties and solvatofluorochromism of fluorene derivatives bearing *S,S*-dioxidized thiophene

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Contents

1. Synthesis of materials

*2,7-Bis(5-phenylthiophen-2-yl)-9,9-dioctylfluorene (**FPT**)*

2,7-Diiodo-9,9-dioctylfluorene[S1] (780 mg, 1.4 mmol) was dissolved in anhydrous THF (8.0 mL) under argon atmosphere. 1.6 M *n*-BuLi hexane solution (2.0 mL, 3.2 mmol) was slowly added dropwise to the solution at −78 °C, and the mixture was stirred for 1.5 h. Tri-*n*-butyl borate (0.91 mL, 3.4 mmol) was slowly added to the solution at the temperature, and the mixture was stirred for 1.5 h. Adequate amount of distilled water was added to the mixture to quench the reaction. 2-Iodo-5-phenylthiophene[S2] (810 mg, 2.8 mmol), tetrakis(triphenylphosphine)palladium(0) (23 mg, 0.020 mmol) and 20 wt% Na_2CO_3 aqueous solution (2.2 mL) were added to the solution, and the mixture was refluxed for 8 h. The reaction mixture was neutralized by HCl aqueous solution, extracted with dichloromethane, washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by column chromatography and HPLC on silica gel using *n*-hexane/ethyl acetate (80:20) as the eluent to give 460 mg of **FPT** in 46% yield. **FPT**: ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 0.71 (br, 4H, CH_2), 0.79 (t, *J* = 7 Hz, 6H, CH_3), 1.0-1.2 (m, 20H, CH_2), 2.0-2.1 (m, 4H, CH_2), 7.2-7.5 (m, 10H, Aromatic H), 7.5-7.8 (m, 10H, Aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 14.2, 22.7, 23.9, 29.3, 29.4, 30.1, 31.9, 40.5, 55.4, 119.9, 120.3, 124.0, 124.2, 124.8, 125.7, 127.6, 129.0, 133.3, 134.5, 140.4, 143.4, 144.4, 151.9. HR-MS (FAB): *m/z* = 706.3668 (M^+, 100%). Calcd. for $C_{49}H_{54}S_2$ = 706.3667.

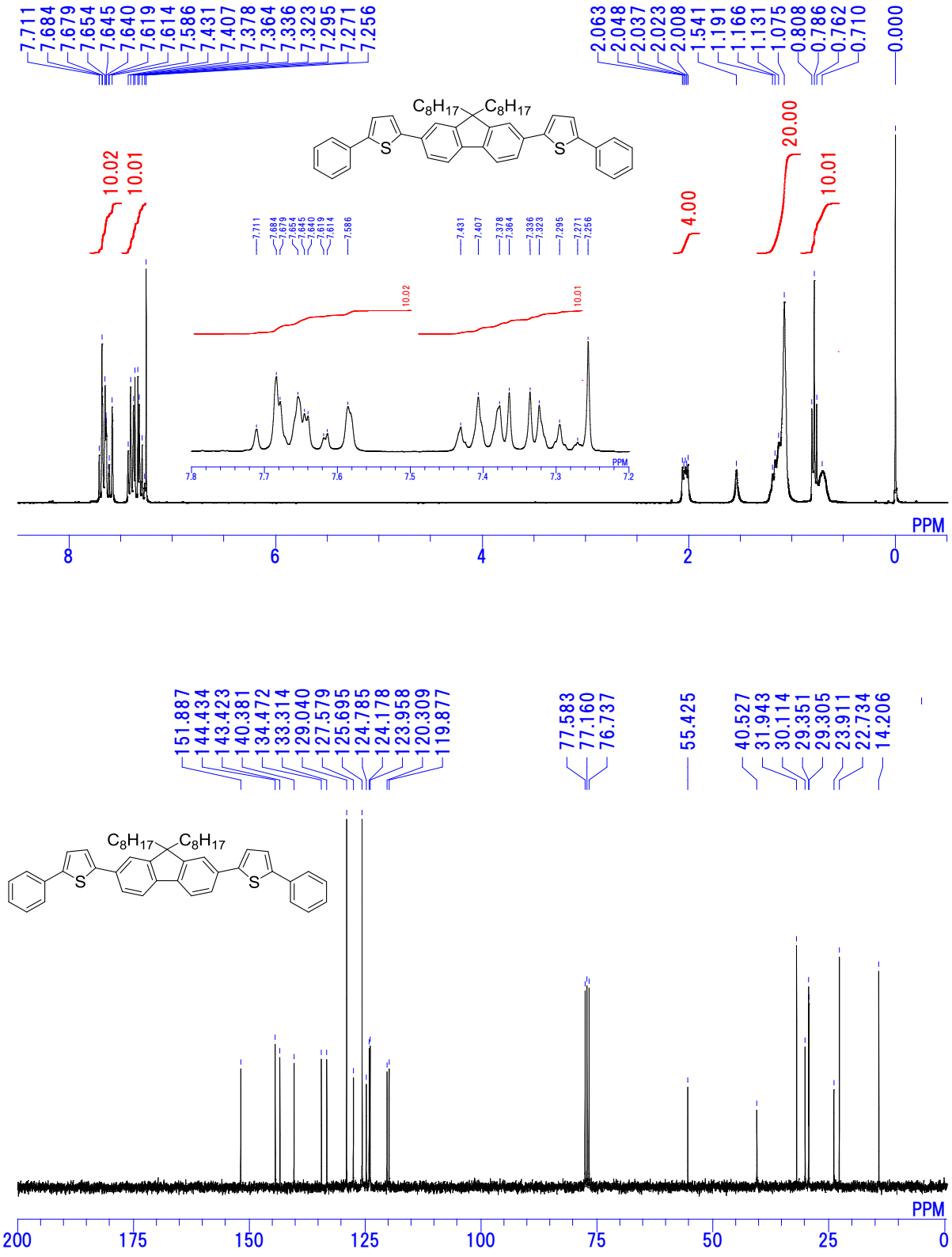

Figure S1. ^{1}H and ^{13}C NMR spectra of **FPT** in $CDCl_3$.

*2-(5-Phenyl-S,S-dioxidized thiophen-2-yl)-7-(5-phenylthiophen-2-yl)-9,9-dioctylfluorene (**FPTO$_2$**)*

FPT (50 mg, 0.071 mmol) and *m*-CPBA (25 mg, 0.14 mmol) were dissolved in dichloromethane (10 mL), and the mixture was stirred at room temperature for 24 h. The reaction mixture was neutralized by $NaHCO_3$ aqueous solution, extracted with dichloromethane, washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by column chromatography on silica gel using *n*-hexane/ethyl acetate (85:15) as the eluent and by HPLC using *n*-hexane/ethyl acetate (60:40) as the eluent to give 11 mg of **FPTO$_2$** in 23% yield. **FPTO$_2$**: ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 0.69 (br, 4H CH_2), 0.79 (t, *J* = 7 Hz, 6H, CH_3), 1.0-1.2 (m, 20H, CH_2), 2.0-2.1 (m, 4H, CH_2), 7.05 (d, *J* = 5 Hz, 1H, Aromatic H), 7.06 (d, *J* = 5 Hz, 1H, Aromatic H), 7.2-7.5 (m, 8H, Aromatic H), 7.6-7.9 (m, 10H, Aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 14.2, 22.7, 23.9, 29.3, 29.4, 30.1, 31.9, 40.4, 55.6, 119.5, 120.0, 120.5, 120.6, 121.0, 124.2, 124.3, 124.3, 124.9, 125.8, 125.8, 125.9, 126.5, 127.5, 127.7, 129.1, 129.4, 130.3, 134.3, 134.4, 139.7, 141.4, 142.4, 143.1, 143.8, 144.2, 152.0, 152.4. HR-MS (FAB): *m/z* = 738.3550 (M^+, 100%). Calcd. for $C_{49}H_{54}O_2S_2$ = 738.3565.

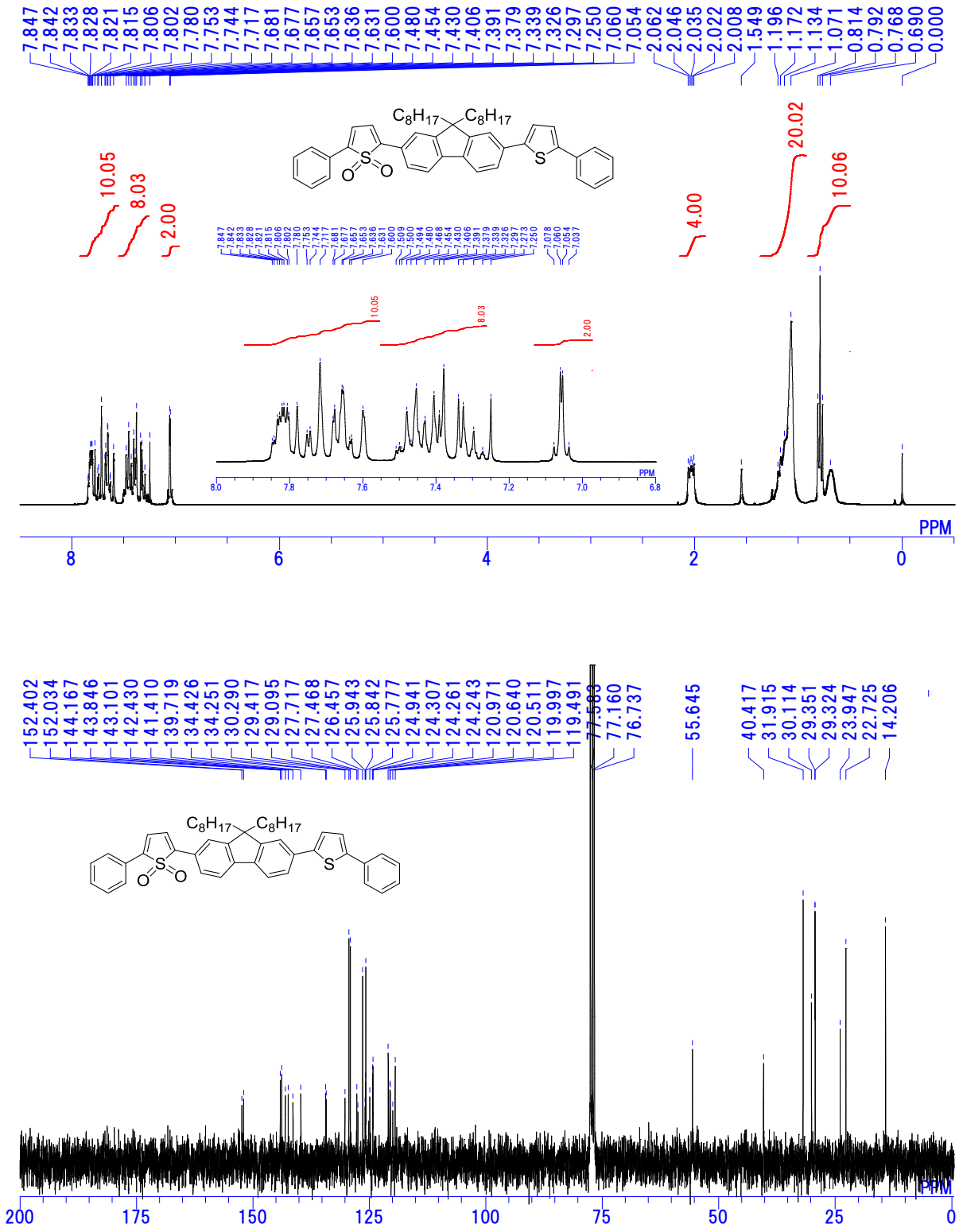

Figure S2. ^{1}H and ^{13}C NMR spectra of **FPTO$_2$** in $CDCl_3$.

*2,7-Bis(5-phenyl-S,S-dioxidized thiophen-2-yl)-9,9-dioctylfluorene (**FPTO$_4$**)*

FPT (100 mg, 0.14 mmol) and *m*-CPBA (250 mg, 1.4 mmol) were dissolved in dichloromethane (50 mL), and the mixture was stirred at room temperature for 24 h. The reaction mixture was neutralized by $NaHCO_3$ aqueous solution, extracted with dichloromethane, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography and HPLC on silica gel using *n*-hexane/ethyl acetate (70:30) as the eluent and recycling preparative HPLC using chloroform as the eluent to give 14 mg of **FPTO$_4$** in 12% yield. **FPTO$_4$**: ^{1}H-NMR (300 MHz, $CDCl_3$, TMS): δ = 0.67 (br, 4H, CH_2), 0.80 (t, *J* = 7 Hz, 6H, CH_3), 1.0-1.3 (m, 20H, CH_2), 2.0-2.1 (m, 4H, CH_2), 7.07 (d, *J* = 5 Hz, 2H, Aromatic H), 7.11 (d, *J* = 5 Hz, 2H, Aromatic H), 7.4-7.6 (m, 6H, Aromatic H), 7.73 (s, 2H, Aromatic H), 7.8-7.9 (m, 8H, Aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 14.2, 22.7, 24.0, 29.3, 29.4, 30.1, 31.9, 40.3, 55.9, 120.1, 120.6, 120.8, 121.3, 125.9, 126.5, 126.8, 127.4, 129.4, 130.4, 141.7, 142.2, 142.3, 152.5. HR-MS (FAB): *m/z* = 770.3463 (M^+, 100%). Calcd. for $C_{49}H_{54}O_4S_2$ = 770.3464.

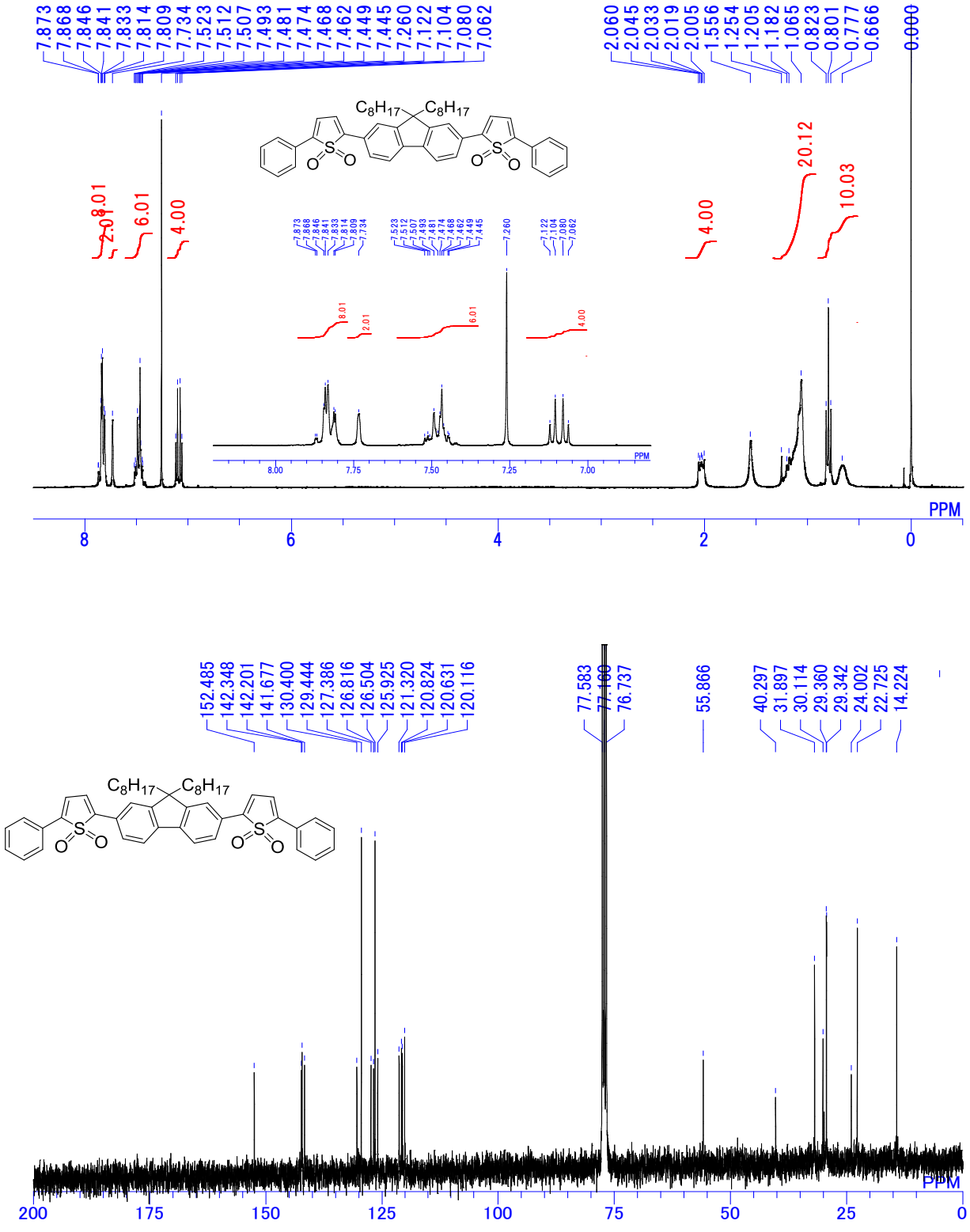

Figure S3. ^{1}H and ^{13}C NMR spectra of **FPTO4** in $CDCl_3$.

*2,7-Bis(1-benzothiophen-2-yl)-9,9-dioctylfluorene (**FBT**)*

2-Bromo-1-benzothiophene[S3] (1.2 g, 5.6 mmol) was dissolved in anhydrous THF (20 mL) under argon atmosphere at −78 °C. 1.6 M *n*-BuLi hexane solution (5.5 mL, 8.4 mmol) was slowly added dropwise to the solution, and the mixture was stirred for 1.5 h. Tri-*n*-butyl borate (2.5 mL, 8.4 mmol) was slowly added to the solution at −78 °C, and the mixture was stirred for 1.5 h. Adequate amount of distilled water was added to the mixture to quench the reaction. 2,7-Dibromo-9,9-dioctylfluorene[S4] (1.7 g, 2.8 mmol), tetrakis(triphenylphosphine)palladium(0) (320 mg, 0.28 mmol) and 20 wt% Na_2CO_3 aqueous solution (6.0 mL) were added to the solution, and the mixture were refluxed at 80 °C for 12 h. The reaction mixture was neutralized by HCl aqueous solution, extracted with dichloromethane, washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by column chromatography on silica gel using hexane 100% as the eluent to give 1.1 g of **FBT** in 60% yield. **FBT**: ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.73 (br, 4H CH_2), 0.77 (t, *J* = 7 Hz, 6H, CH_3), 1.0-1.2 (m, 20H, CH_2), 2.0-2.1 (m, 4H, CH_2), 7.2-7.4 (m, 4H, Aromatic H), 7.63 (s, 2H, Aromatic H), 7.6-7.9 (m, 10H, Aromatic H). HR-MS (FAB). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 14.2, 22.7, 23.9, 29.3, 29.3, 30.1, 31.9, 40.5, 55.5, 119.4, 120.5, 120.8, 122.4, 123.6, 124.4, 124.7, 125.8, 133.5, 139.6, 141.0, 141.0, 145.0, 152.0. HR-MS (FAB): *m*/*z* = 654.3357 (M^+, 100%). Calcd. for $C_{45}H_{50}S_2$ = 654.3354.

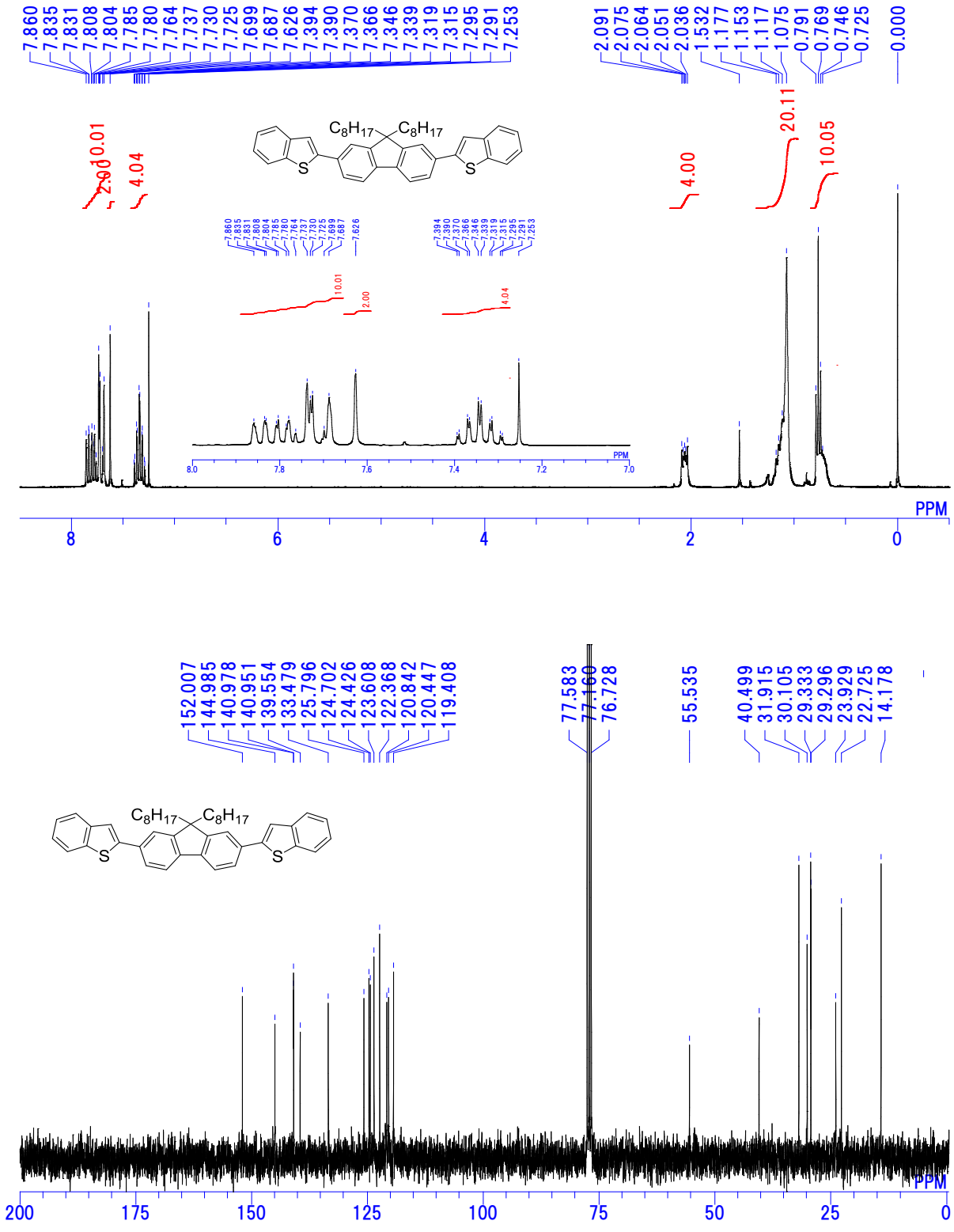

Figure S4. ^{1}H and ^{13}C NMR spectra of **FBT** in $CDCl_3$.

*2-(S,S-Dioxidized 1-benzothiophen-2-yl)-7-(benzothiophen-2-yl)-9,9-dioctylfluorene (**FBTO$_2$**) and 2,7-(S,S-dioxidized 1-benzothiophen-2-yl)-9,9-dioctylfluorene (**FBTO$_4$**)*

FBT (50 mg, 0.076 mmol) and *m*-CPBA (27 mg, 0.15 mmol) were dissolved in dichloromethane (5.0 mL), and the mixture was stirred at room temperature for 48 h. The reaction mixture was neutralized by $NaHCO_3$ aqueous solution, extracted with dichloromethane, washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by column chromatography on silica gel using ethyl acetate 100% as the eluent and HPLC using hexane/ethyl acetate (75:25) as the eluent to give 10 mg of **FBTO$_2$** in 18% yield and 28 mg of **FBTO$_4$** in 51%. **FBTO$_2$**: ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.70 (br, 4H CH_2), 0.77 (t, *J* = 7 Hz, 6H, CH_3), 1.0-1.2 (m, 20H, CH_2), 2.0-2.1 (m, 4H, CH_2), 7.3-7.9 (m, 16H, Aromatic H). ^{13}C NMR (75 Hz, $CDCl_3$) δ = 14.2, 22.7, 24.0, 29.3, 29.3, 30.1, 31.9, 40.4, 55.7, 119.7, 120.7, 120.8, 120.9, 121.0, 121.6, 122.4, 122.9, 123.7, 124.5, 124.7, 125.0, 125.9, 125.9, 126.1, 129.8, 131.6, 133.9, 134.2, 137.3, 139.6, 140.5, 140.9, 143.0, 143.3, 144.7, 152.1, 152.3. HR-MS (FAB): *m/z* = 686.3234 (M^+, 100%). Calcd. for $C_{45}H_{50}O_2S_2$ = 686.3252. **FBTO$_4$**: ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.68 (br, 4H CH_2), 0.76 (t, *J* = 7 Hz, 6H, CH_3), 1.0-2.0 (m, 20H, CH_2), 2.0-2.1 (m, 4H, CH_2), 7.38 (s, 2H, Aromatic H), 7.4-7.6 (m, 6H, Aromatic H), 7.7-7.9 (m, 6H, Aromatic H), 7.9-8.0 (m, 6H, Aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 14.2, 22.7, 24.0, 29.3, 29.3, 30.1, 31.8, 40.2, 55.9, 120.8, 121.2, 121.6, 123.3, 125.1, 126.0, 126.8, 129.9, 131.4, 133.9, 137.2, 142.3, 143.0, 152.4. HR-MS (FAB): *m/z* = 718.3144 (M^+, 100%). Calcd. for $C_{45}H_{50}O_4S_2$ = 718.3151.

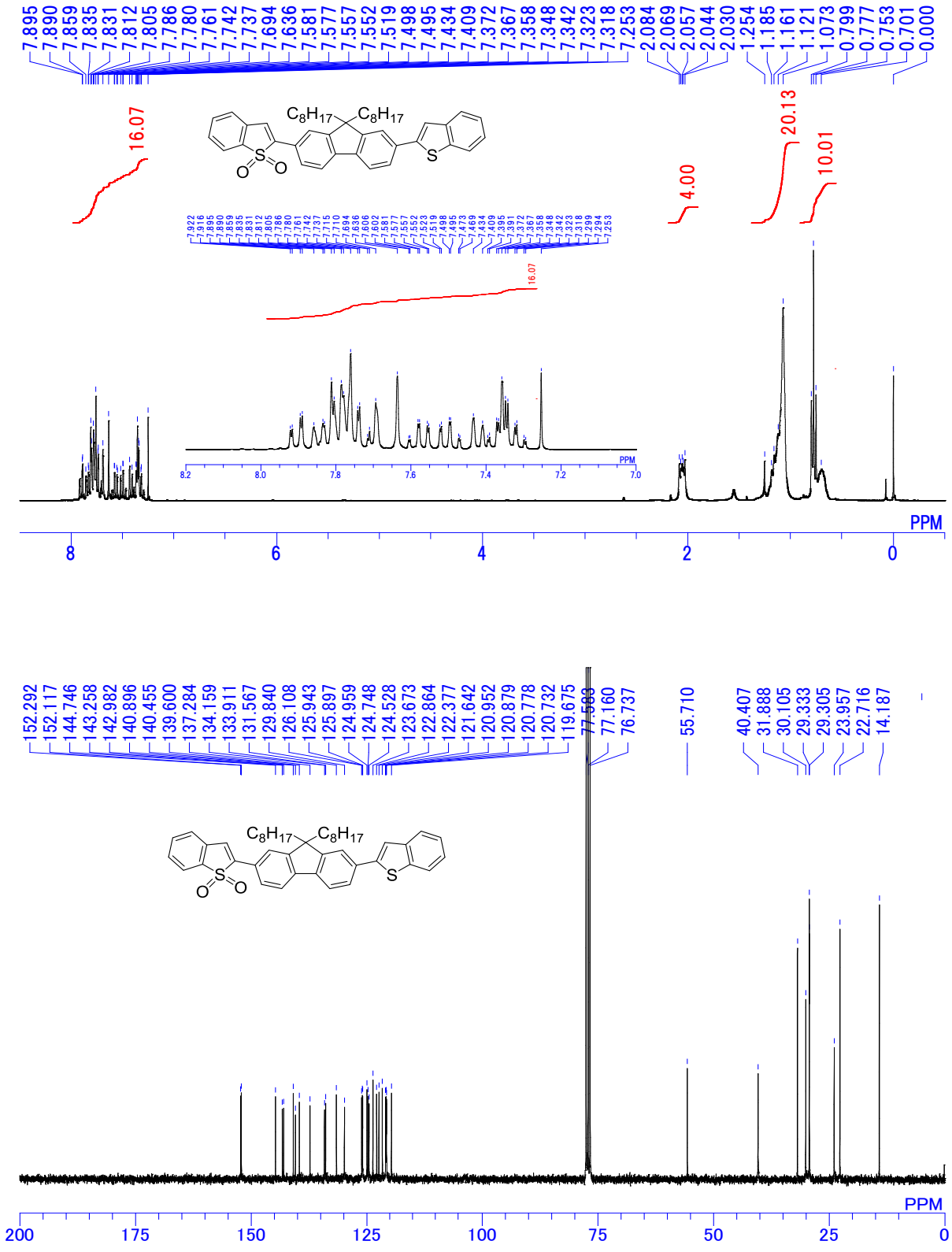

Figure S5. ^{1}H and ^{13}C NMR spectra of **FBTO₂** in $CDCl_3$.

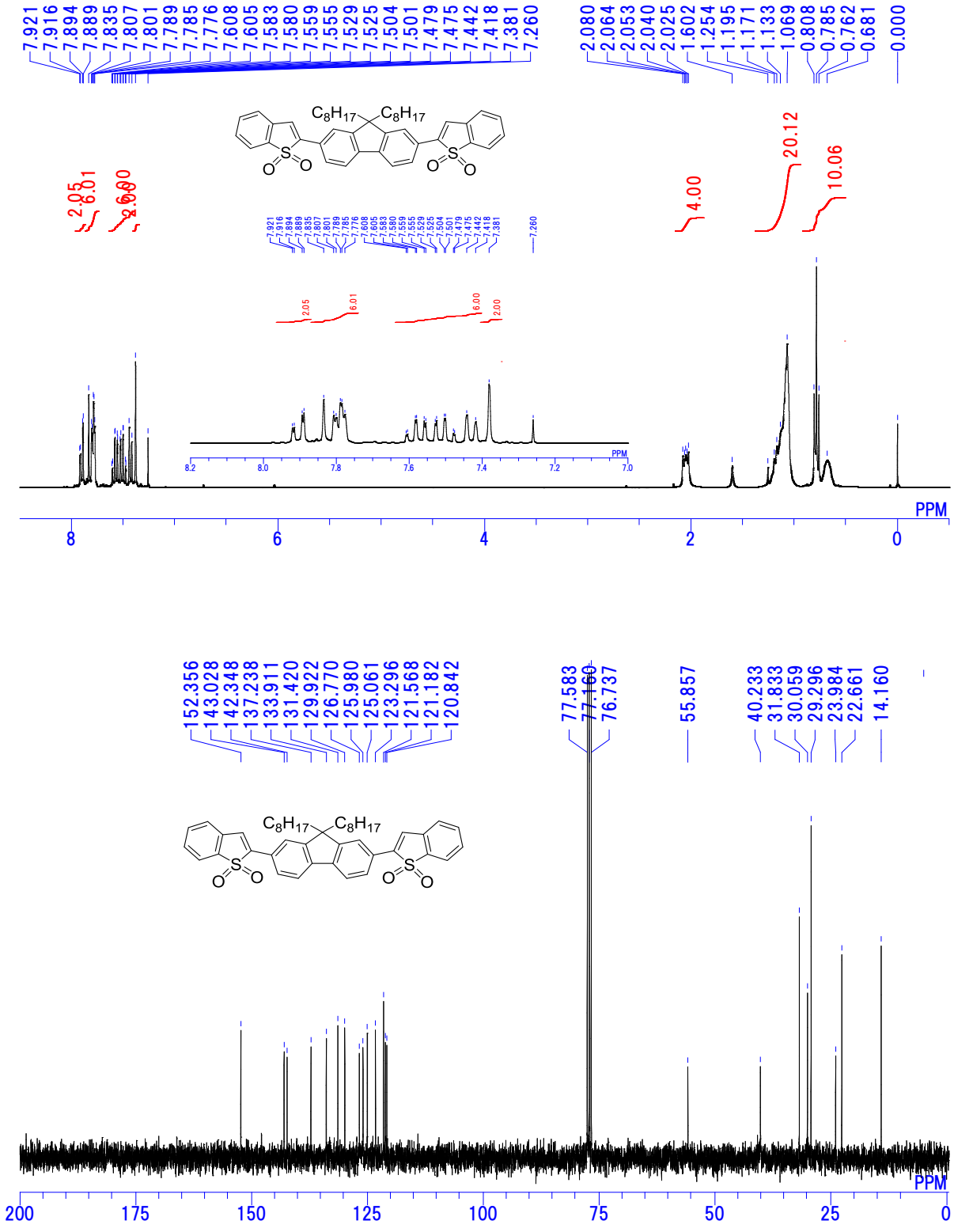

Figure S6. ^{1}H and ^{13}C NMR spectra of **FBTO$_4$** in $CDCl_3$.

2. Top and side views of FPT molecule at geometry-optimized ground and excited state

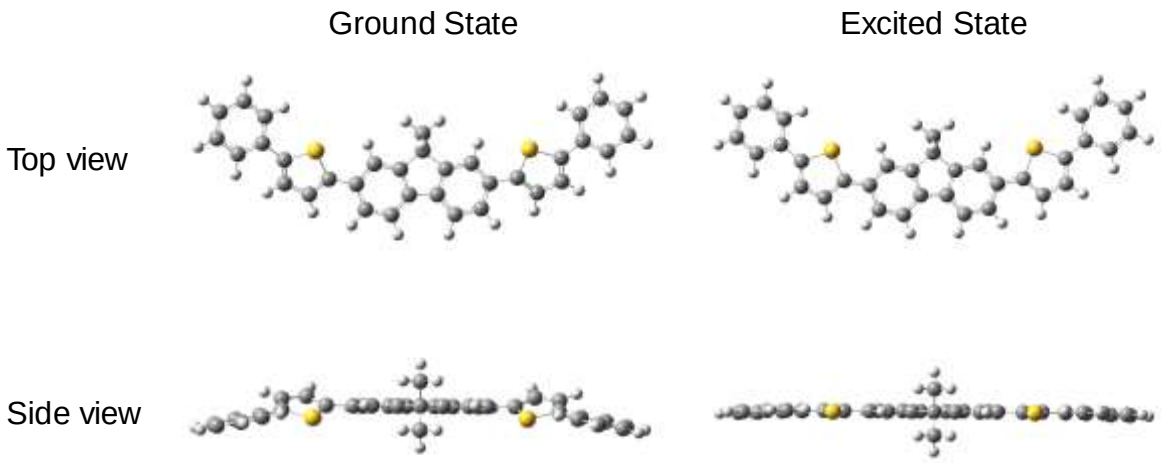

Figure S7. Top and side views of **FPT** molecule at the geometry-optimized ground and excited states.

3. Fluorescence decay curves in *n*-hexane

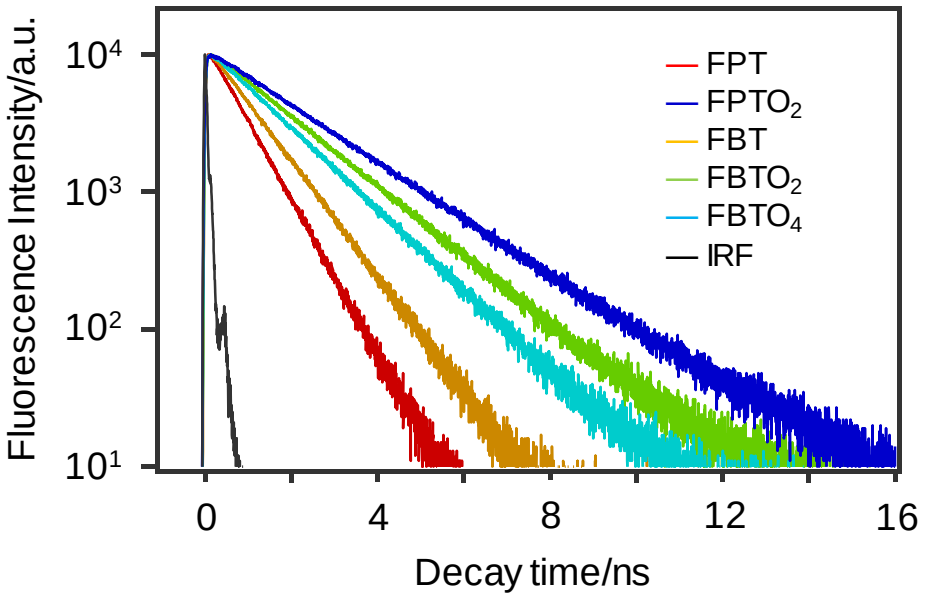

Figure S8. Fluorescence decay curves of fluorene derivatives in *n*-hexane.

4. Solvent effect

Table S1. Solvent dependence of optical properties of fluorene derivatives.

Solvent	λ_{abs}/nm						λ_{flu}/nm					
	FPT	**FPTO$_2$**	**FPTO$_4$**	**FBT**	**FBTO$_2$**	**FBTO$_4$**	**FPT**	**FPTO$_2$**	**FPTO$_4$**	**FBT**	**FBTO$_2$**	**FBTO$_4$**
n-Hexane	383	432	441	366	390	392	423	502	–	393	429	426
Toluene	388	440	448	370	392	397	430	533	–	399	464	436
THF	389	436	446	369	390	396	428	570	–	397	478	464
Ethyl acetate	389	432	443	367	387	394	425	564	–	395	477	461
Chloroform	388	442	450	368	396	400	429	593	–	398	500	470
DMF	391	437	448	368	392	396	430	611	–	399	517	466
DMSO	394	441	450	371	393	399	434	618	–	402	526	471
Acetonitrile	385	429	440	363	385	390	425	617	–	394	521	464
Ethanol	385	428	444	367	388	394	424	603	–	397	525	468
Methanol	384	441	442	364	387	395	423	610	–	393	530	482

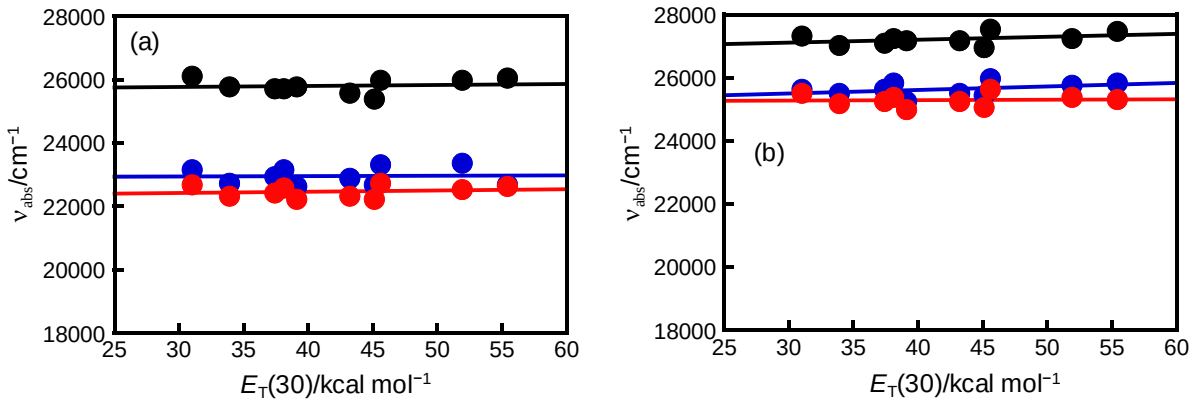

Figure S9. Absorption peak energy (ν_{abs}/cm^{-1}) of **FPT** (a: black), **FPTO$_2$** (a: blue), **FPTO$_4$** (a: red), **FBT** (b: black), **FBTO2** (b: blue) and **FBTO$_4$** (b: red) versus the solvent polarity parameter, E_T(30). The slopes of the linear relationship are −3.19 for **FPT**, 1.24 for **FPTO$_2$**, 3.85 for **FPTO$_4$**, 9.35 for **FBT**, 10.91 for **FBTO$_2$** and −1.53 for **FBTO$_4$**.

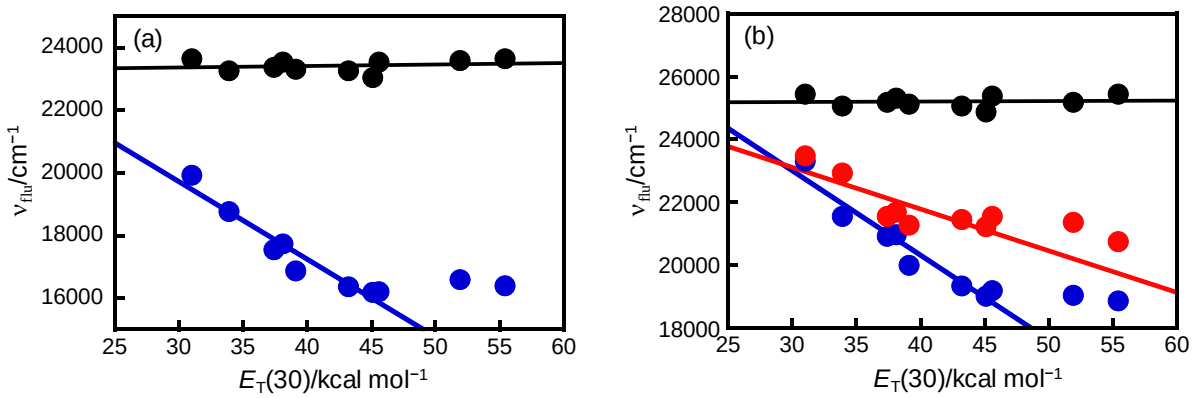

Figure S10. Fluorescence peak energy (ν_{flu}/cm^{-1}) of **FPT** (a: black), **FPTO$_2$** (a: blue), **FBT** (b: black), **FBTO2** (b: blue) and **FBTO$_4$** (b: red) versus the solvent polarity parameter, E_T(30). The slopes of the linear relationship are 5.0 for **FPT**, −247 for **FPTO$_2$**, 1.65 for **FBT**, −269 for **FBTO$_2$** and −133 for **FBTO$_4$**. In the case of **FPTO$_2$**, **FBTO$_2$** and **FBTO$_4$**, the slope of the linear relationship was calculated except in methanol and ethanol.

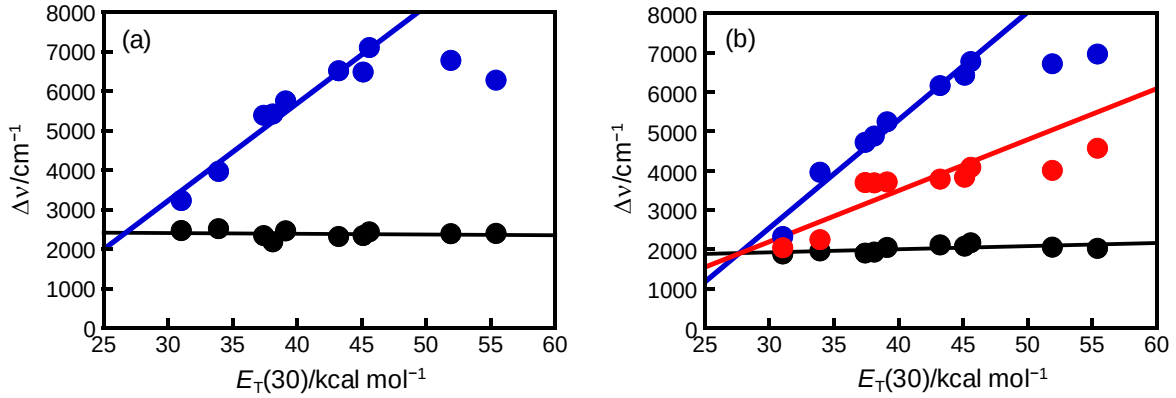

Figure S11. Stokes shift ($\Delta\nu$/cm^{-1}) of **FPT** (a: black), **FPTO$_2$** (a: blue), **FBT** (b: black), **FBTO$_2$** (b: blue) and **FBTO$_4$** (b: red) versus the solvent polarity, E_T(30). The slopes of the linear relationship are −1.89 for **FPT**, 246 for **FPTO$_2$**, 7.72 for **FBT**, 274 for **FBTO$_2$** and 130 for **FBTO$_4$**. In the case of **FPTO$_2$**, **FBTO$_2$** and **FBTO$_4$**, the slope of the linear relationship was calculated except in methanol and ethanol.

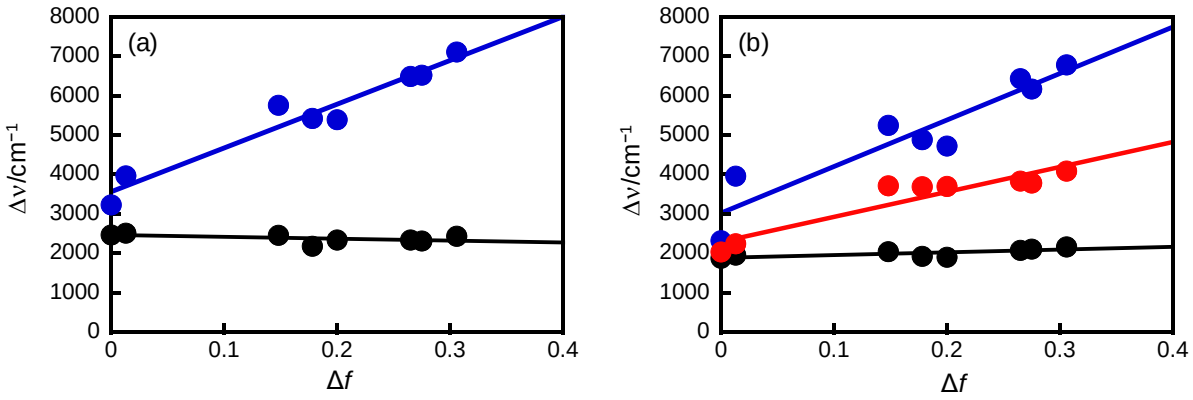

Figure. S12. Stokes shift ($\Delta\nu$/cm^{-1}) of **FPT** (a: black), **FPTO$_2$** (a: blue), **FBT** (b: black), **FBTO$_2$** (b: blue) and **FBTO$_4$** (b: red) versus orientation polarizability function (Δf). Only aprotic solvent was used. The slopes of the linear relationship are −470 ± 337 for **FPT** (r = 0.495), 11102 ± 1102 for **FPTO$_2$** (r = 0.972), 684 ± 243 for **FBT** (r = 0.754), 11794 ± 1855 for **FBTO$_2$** (r = 0.933) and 6342 ± 956 for **FBTO$_4$** (r = 0.938).

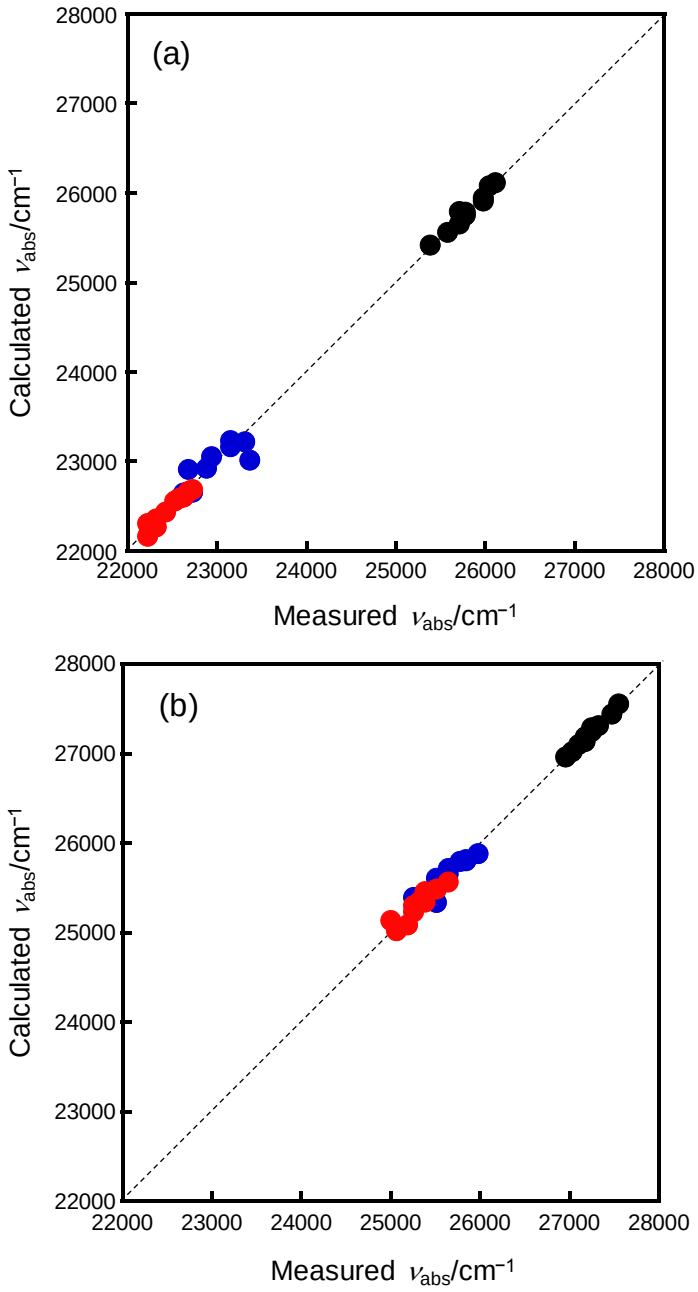

Figure S13. Relationship between the measured and calculated ν_{abs} values according to the Catalán equation for **FPT** (a: black), **FPTO$_2$** (a: blue), **FPTO$_4$** (a: red), **FBT** (b: black), **FBTO$_2$** (b: blue) and **FBTO$_4$** (b: red).

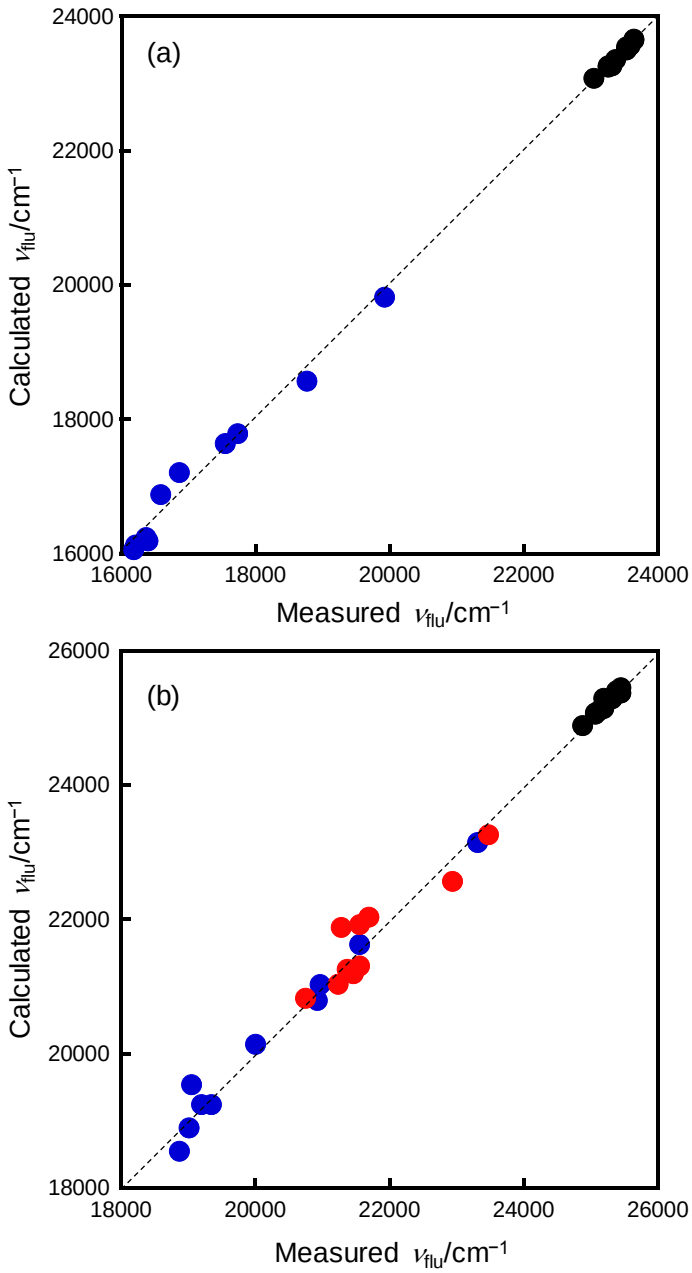

Figure S14. Relationship between the measured and calculated ν_{flu} values according to the Catalán equation for **FPT** (a: black), **FPTO$_2$** (a: blue), **FBT** (b: black), **FBTO$_2$** (b: blue) and **FBTO$_4$** (b: red).

5. Fluorescence decay curves in THF and acetonitrile

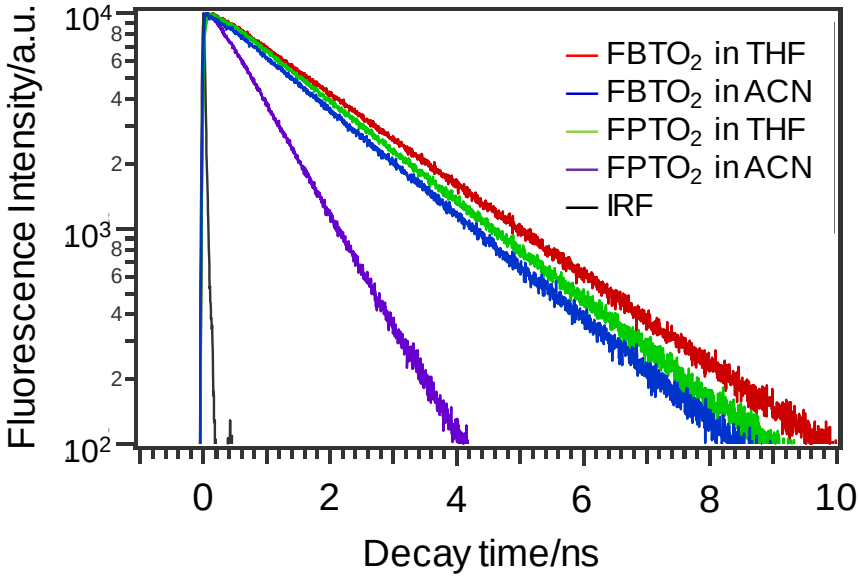

Figure S15. Fluorescence decay curves of **$FPTO_2$** and **$FBTO_2$** in THF and acetonitrile.

6. Atomic coordinates

Table S2. Cartesian coordinates of **FPT** optimized at the B3LYP/6-31G* level. The octyl groups are replaced to the methyl groups.

Atom	X/Å	Y/Å	Z/Å
C	1.332876	0.014854	3.482744
C	1.896648	-0.11042	0.731458
C	0.309883	0.237543	2.536227
C	2.632923	-0.27474	3.016455
C	2.920925	-0.33165	1.656201
C	0.59034	0.171387	1.180705
H	-0.69245	0.482014	2.879613
H	3.419099	-0.47935	3.736925
H	3.931312	-0.55979	1.326498
C	-0.35759	0.384133	0
C	0.59034	0.171387	-1.18071
C	1.896648	-0.11042	-0.73146
C	0.309883	0.237543	-2.53623
H	-0.69245	0.482014	-2.87961
C	1.332876	0.014854	-3.48274
C	2.632923	-0.27474	-3.01646
H	3.419099	-0.47935	-3.73693
C	2.920925	-0.33165	-1.6562
H	3.931312	-0.55979	-1.3265
C	-1.50192	-0.65437	0
H	-2.1352	-0.5314	0.886117
H	-1.10874	-1.67596	0
H	-2.1352	-0.5314	-0.88612
C	-0.94327	1.814306	0
H	-0.14794	2.566388	0
H	-1.56778	1.976222	0.886076
H	-1.56778	1.976222	-0.88608
C	1.069922	0.082325	4.922306
C	1.9459	0.375968	5.945379

C	1.352863	0.355881	7.233739
C	0.010055	0.047402	7.225978
S	-0.52366	-0.24196	5.580683
H	2.983348	0.640485	5.771708
H	1.893437	0.602585	8.141209
C	-0.91126	-0.05978	8.362142
C	-2.65367	-0.25636	10.57226
C	-0.42169	-0.37493	9.644153
C	-2.29476	0.148827	8.213743
C	-3.15467	0.046731	9.305009
C	-1.282	-0.46436	10.73523
H	0.638046	-0.57177	9.776943
H	-2.69563	0.412268	7.238638
H	-4.21934	0.214146	9.165202
H	-0.88073	-0.71058	11.71483
H	-3.32464	-0.33294	11.42333
C	1.069922	0.082325	-4.92231
S	-0.52366	-0.24196	-5.58068
C	0.010055	0.047402	-7.22598
C	1.352863	0.355881	-7.23374
C	1.9459	0.375968	-5.94538
H	1.893437	0.602585	-8.14121
H	2.983348	0.640485	-5.77171
C	-0.91126	-0.05978	-8.36214
C	-2.65367	-0.25636	-10.5723
C	-0.42169	-0.37493	-9.64415
C	-2.29476	0.148827	-8.21374
C	-3.15467	0.046731	-9.30501
C	-1.282	-0.46436	-10.7352
H	0.638046	-0.57177	-9.77694
H	-2.69563	0.412268	-7.23864
H	-4.21934	0.214146	-9.1652
H	-0.88073	-0.71058	-11.7148
H	-3.32464	-0.33294	-11.4233

Table S3. Cartesian coordinates of **FPTO$_2$** optimized at the B3LYP/6-31G* level. The octyl groups are replaced to the methyl groups.

Atom	X/Å	Y/Å	Z/Å
H	0.604145	3.560237	-0.546968
C	1.085082	2.609707	-0.331814
C	2.351243	0.145307	0.200207
C	0.330663	1.44222	-0.170055
C	2.469009	2.539659	-0.231577
C	3.123671	1.317587	0.040163
C	0.972083	0.214242	0.092704
H	3.061135	3.436419	-0.388088
H	2.842679	-0.795283	0.429054
C	-1.111543	1.212362	-0.227431
C	-3.739988	0.219665	-0.225026
C	-2.177901	2.087038	-0.450308
C	-1.356431	-0.158291	0.000231
C	-2.651498	-0.649463	0.009012
C	-3.476575	1.586996	-0.451777
H	-2.005255	3.14485	-0.63107
H	-2.842293	-1.698615	0.216954
H	-4.304358	2.261296	-0.652586
C	-0.048146	-0.915669	0.228737
C	0.000136	-1.550808	1.63692
H	0.969637	-2.030998	1.810461
H	-0.7779	-2.315624	1.741867
H	-0.15385	-0.797513	2.416137
C	0.170468	-2.00192	-0.848781
H	0.140384	-1.57203	-1.854945
H	-0.606566	-2.772109	-0.781202
H	1.142214	-2.489717	-0.714224
C	4.573756	1.280926	0.15905
C	5.477309	2.252537	0.416488
C	6.88077	1.844472	0.40071
C	7.120497	0.544008	0.127926

S	5.507189	-0.259425	-0.127562
C	-5.106947	-0.306011	-0.234178
C	-5.531482	-1.591736	-0.494285
C	-6.93778	-1.75868	-0.421464
C	-7.62112	-0.60492	-0.104404
S	-6.488711	0.713525	0.125546
C	8.366371	-0.213988	0.07646
C	10.791114	-1.632338	-0.0388
C	8.473028	-1.388784	-0.692077
C	9.494907	0.23133	0.792725
C	10.695164	-0.468541	0.729637
C	9.676617	-2.088299	-0.744409
H	7.619472	-1.73734	-1.264182
H	9.418342	1.116786	1.417201
H	11.554591	-0.113372	1.291728
H	9.743246	-2.991672	-1.344188
H	11.727376	-2.181939	-0.081093
C	-9.066882	-0.412346	0.051342
C	-11.853573	-0.08357	0.336961
C	-9.888462	-1.493281	0.424052
C	-9.673887	0.837676	-0.168476
C	-11.049867	0.999724	-0.022662
C	-11.264832	-1.330926	0.557625
H	-9.437808	-2.459615	0.630289
H	-9.06432	1.683067	-0.476086
H	-11.496024	1.974608	-0.200358
H	-11.878648	-2.179601	0.847805
H	-12.926967	0.042978	0.447346
H	7.67161	2.563088	0.591007
H	5.198832	3.278835	0.632395
H	-4.851679	-2.389955	-0.771983
H	-7.437805	-2.696601	-0.637622
O	5.350821	-0.691351	-1.528204
O	5.25222	-1.233786	0.948711

Table S4. Cartesian coordinates of **FPTO$_4$** optimized at the B3LYP/6-31G* level. The octyl groups are replaced to the methyl groups.

Atom	X/Å	Y/Å	Z/Å
H	0.923194	3.480123	-0.55008
C	1.417885	2.536102	-0.33821
C	2.718879	0.087584	0.18708
C	0.681476	1.355621	-0.18788
C	2.801868	2.486561	-0.23001
C	3.473128	1.272476	0.038351
C	1.339133	0.136159	0.072158
H	3.381321	3.392979	-0.37739
H	3.22371	-0.84641	0.413434
C	-0.75664	1.105315	-0.25616
C	-3.36457	0.083421	-0.2693
C	-1.83161	1.968755	-0.47991
C	-0.98142	-0.27172	-0.03543
C	-2.26821	-0.77865	-0.03633
C	-3.12586	1.457811	-0.48648
H	-1.6704	3.029428	-0.65216
H	-2.44775	-1.83152	0.163903
H	-3.96145	2.120481	-0.6843
C	0.336581	-1.01024	0.197487
C	0.386469	-1.65009	1.603615
H	1.363284	-2.11341	1.781441
H	-0.37796	-2.42965	1.700033
H	0.213415	-0.90334	2.384988
C	0.578812	-2.08851	-0.88319
H	0.546487	-1.65581	-1.88806
H	-0.18472	-2.87262	-0.82185
H	1.558031	-2.55996	-0.74535
C	4.923388	1.256079	0.165247
C	5.809908	2.238015	0.440422
C	7.219783	1.851495	0.430172
C	7.480633	0.558146	0.143525
S	5.881156	-0.26647	-0.13327
C	-4.7169	-0.45539	-0.29144
C	-5.17249	-1.71011	-0.50122
C	-6.62059	-1.89039	-0.41931

C	-7.34348	-0.78408	-0.14281
S	-6.16796	0.592529	0.059008
C	8.737662	-0.18097	0.091272
C	11.18308	-1.56252	-0.02432
C	8.866561	-1.34416	-0.69141
C	9.854381	0.271596	0.821398
C	11.06493	-0.41025	0.758309
C	10.08051	-2.02544	-0.74401
H	8.022319	-1.69766	-1.27418
H	9.760573	1.147757	1.456507
H	11.91508	-0.05018	1.331203
H	10.16463	-2.91985	-1.35486
H	12.12747	-2.09797	-0.06677
C	-8.77952	-0.59463	0.032736
C	-11.555	-0.2714	0.342423
C	-9.59192	-1.68052	0.415132
C	-9.3828	0.659172	-0.18269
C	-10.7585	0.813494	-0.02688
C	-10.9654	-1.51968	0.562573
H	-9.13674	-2.64554	0.618516
H	-8.77521	1.50289	-0.49243
H	-11.2091	1.786855	-0.19945
H	-11.5765	-2.36656	0.862494
H	-12.6272	-0.14581	0.464971
H	7.998115	2.57967	0.634769
H	5.514304	3.257286	0.66679
H	-4.52146	-2.54245	-0.74816
H	-7.07189	-2.85976	-0.60489
O	5.740352	-0.68355	-1.5399
O	5.632876	-1.2569	0.929708
O	-6.35497	1.594414	-1.00935
O	-6.14375	1.042227	1.459487

Table S5. Cartesian coordinates of **FBT** optimized at the B3LYP/6-31G* level. The octyl groups are replaced to the methyl groups.

Atom	X/Å	Y/Å	Z/Å
H	1.325151	3.276404	-0.01858
C	1.655558	2.240888	-0.00944
C	2.53635	-0.43153	-0.01087
C	0.731663	1.192293	-0.00313
C	3.015835	1.947487	-0.02124
C	3.481285	0.615901	-0.01395
C	1.180315	-0.14386	-0.00762
H	3.736062	2.758938	-0.05971
H	2.880283	-1.4628	0.01044
C	-0.73165	1.192295	0.003221
C	-3.48129	0.615903	0.014005
C	-1.65555	2.240887	0.009486
C	-1.18031	-0.14386	0.007757
C	-2.53635	-0.43152	0.01099
C	-3.01583	1.947489	0.021254
H	-1.32515	3.276406	0.018621
H	-2.88027	-1.46279	-0.01027
C	-1E-06	-1.11593	0.000063
C	-4.92242	0.34256	0.005398
C	-5.93119	1.134228	-0.47051
C	-7.24191	0.566873	-0.3272
C	-7.20341	-0.71184	0.283622
S	-5.55542	-1.1732	0.674928
H	-5.75296	2.092566	-0.94662
C	4.922419	0.342556	-0.00537
C	5.9312	1.134206	0.470539
C	7.241924	0.566862	0.327154
C	7.2034	-0.71185	-0.28367
S	5.555398	-1.17319	-0.67496
H	5.752945	2.092514	0.9467
H	-8.53844	2.073973	-1.18329

C	-8.48905	1.096567	-0.71015
H	-10.6089	0.773358	-0.77234
C	-9.64574	0.365347	-0.47874
H	-10.5026	-1.45818	0.305804
C	-9.58649	-0.90045	0.132453
H	-8.32264	-2.42775	0.98715
C	-8.36718	-1.44938	0.517338
C	8.489075	1.096567	0.710045
H	8.538475	2.073969	1.183198
C	9.645754	0.36535	0.478584
H	10.60896	0.773368	0.772135
C	9.586491	-0.90045	-0.1326
H	10.50257	-1.45818	-0.30597
C	8.367162	-1.44939	-0.51743
H	8.322597	-2.42776	-0.98723
H	-3.73604	2.758957	0.059674
C	-0.00688	-2.002	-1.26587
H	-0.01237	-1.39195	-2.17468
H	-0.89251	-2.64752	-1.28093
H	0.87937	-2.64634	-1.29099
C	0.006884	-2.00204	1.265952
H	-0.87937	-2.64639	1.291058
H	0.012378	-1.39204	2.174789
H	0.892511	-2.64757	1.28098

Table S6. Cartesian coordinates of **FBTO$_2$** optimized at the B3LYP/6-31G* level. The octyl groups are replaced to the methyl groups.

Atom	X/Å	Y/Å	Z/Å
H	-0.92034	3.413412	0.082133
C	-1.27197	2.387254	0.014955
C	-2.20328	-0.27224	-0.12899
C	-0.37014	1.319182	-0.03304
C	-2.63644	2.120934	-0.00505
C	-3.12275	0.798264	-0.08359
C	-0.84371	-0.00693	-0.1018
H	-3.34254	2.94298	0.06649
H	-2.56938	-1.29152	-0.20503
C	1.092176	1.290669	-0.01748
C	3.828826	0.662631	-0.01399
C	2.034822	2.32097	0.043719
C	1.514628	-0.05255	-0.082
C	2.865295	-0.36537	-0.07844
C	3.388951	2.002417	0.038581
H	1.723635	3.361753	0.082221
H	3.189582	-1.4028	-0.10332
C	0.316974	-1.00035	-0.14004
C	5.264319	0.361713	0.003271
C	6.279373	1.111879	0.530565
C	7.581571	0.527034	0.381515
C	7.529514	-0.72142	-0.28807
S	5.880137	-1.13357	-0.72506
H	6.110852	2.050509	1.047663
C	-4.5612	0.552776	-0.12345
C	-5.57364	1.341376	-0.54281
C	-6.92374	0.787786	-0.40017
C	-6.94167	-0.49686	0.160275
S	-5.25783	-1.00845	0.523871
H	-5.41606	2.321367	-0.9836
H	8.891398	1.968758	1.32572

C	8.831837	1.015268	0.807169
H	10.94415	0.649448	0.88612
C	9.978432	0.273688	0.559657
H	10.81432	-1.52814	-0.29445
C	9.90585	-0.96171	-0.10973
H	8.628322	-2.42433	-1.0528
C	8.683229	-1.46947	-0.53795
C	-8.13718	1.377263	-0.76056
H	-8.15564	2.371756	-1.19844
C	-9.32701	0.67194	-0.55022
H	-10.2731	1.127861	-0.82783
C	-9.31691	-0.60832	0.009582
H	-10.2508	-1.14024	0.16461
C	-8.10519	-1.21315	0.372854
H	-8.08148	-2.20827	0.806355
H	4.12492	2.80036	0.052998
O	-4.87018	-2.14776	-0.32727
O	-5.0394	-1.0988	1.975606
C	0.284351	-1.94725	1.081215
H	0.290532	-1.38297	2.019057
H	1.15468	-2.61341	1.075558
H	-0.61713	-2.56954	1.0627
C	0.31164	-1.82378	-1.44786
H	1.184443	-2.48531	-1.48939
H	0.334764	-1.17127	-2.32657
H	-0.92034	3.413412	0.082133

Table S7. Cartesian coordinates of **FBTO$_4$** optimized at the B3LYP/6-31G* level. The octyl groups are replaced to the methyl groups.

Atom	X/Å	Y/Å	Z/Å
H	-1.318893	3.496747	-0.01877
C	-1.651508	2.462256	-0.038497
C	-2.533	-0.218504	-0.061309
C	-0.731041	1.409307	-0.018957
C	-3.010337	2.170269	-0.065686
C	-3.470932	0.836034	-0.084778
C	-1.178319	0.072413	-0.027403
H	-3.73231	2.981256	-0.046911
H	-2.880141	-1.246739	-0.091126
C	0.731024	1.409327	0.018459
C	3.470917	0.836081	0.084497
C	1.651477	2.462284	0.038068
C	1.178329	0.072437	0.026903
C	2.533007	-0.218473	0.060906
C	3.01031	2.170306	0.065369
H	1.318862	3.496774	0.018309
H	2.880152	-1.246707	0.090712
C	0.000014	-0.899593	-0.000285
C	4.904463	0.562696	0.136989
C	5.919899	1.307601	0.623001
C	7.263577	0.738756	0.477867
C	7.272173	-0.511734	-0.155243
S	5.588693	-0.970439	-0.585571
H	5.768683	2.262789	1.117289
C	-4.904474	0.562643	-0.137096
C	-5.920019	1.30759	-0.622812
C	-7.263661	0.738737	-0.477451
C	-7.272163	-0.511838	0.155492
S	-5.588594	-0.970567	0.585501
H	-5.768957	2.262851	-1.117008
H	8.503221	2.251236	1.394094

C	8.477997	1.28419	0.898847
H	10.607182	0.99146	0.999759
C	9.660087	0.570052	0.674993
H	10.568681	-1.215454	-0.121598
C	9.640801	-0.675774	0.042412
H	8.397226	-2.204144	-0.873345
C	8.42782	-1.236145	-0.382689
C	-8.478153	1.284312	-0.898049
H	-8.503414	2.251434	-1.393148
C	-9.660231	0.570218	-0.674008
H	-10.607386	0.991725	-0.998469
C	-9.640851	-0.675702	-0.041612
H	-10.56872	-1.215356	0.122547
C	-8.427801	-1.236206	0.383112
H	-8.397162	-2.204294	0.87359
O	5.161631	-2.149447	0.188715
O	5.402731	-0.971147	-2.04452
H	3.732282	2.981297	0.04664
O	-5.161627	-2.149575	-0.188825
O	-5.402458	-0.971253	2.044436
C	-0.03066	-1.786257	1.265669
H	-0.052953	-1.177445	2.175123
H	0.854735	-2.430514	1.30426
H	-0.917457	-2.429464	1.263002
C	0.030707	-1.786123	-1.266339
H	0.917506	-2.429333	-1.263735
H	0.053014	-1.177218	-2.175731
H	-0.854683	-2.430383	-1.305019

Table S8. Cartesian coordinates of **FPT** optimized at the B3LYP/6-31G* level in the excited state. The octyl groups are replaced to the methyl groups.

Atom	X/Å	Y/Å	Z/Å
C	1.366547	0.010114	3.488981
C	1.944384	0.013823	0.714065
C	0.310846	0.008343	2.523745
C	2.712504	0.014312	3.001632
C	3.002129	0.01629	1.654669
C	0.59446	0.010025	1.180809
H	-0.72178	0.005626	2.863683
H	3.530714	0.015368	3.714184
H	4.036799	0.019269	1.322163
C	-0.37808	0.007671	0
C	0.59446	0.010025	-1.18081
C	1.944384	0.013823	-0.71407
C	0.310846	0.008343	-2.52375
H	-0.72178	0.005626	-2.86368
C	1.366547	0.010114	-3.48898
C	2.712504	0.014312	-3.00163
H	3.530714	0.015368	-3.71418
C	3.002129	0.01629	-1.65467
H	4.036799	0.019269	-1.32216
C	-1.25997	-1.26069	0
H	-1.90406	-1.28329	0.886667
H	-0.64664	-2.16727	0
H	-1.90406	-1.28329	-0.88667
C	-1.26634	1.27159	0
H	-0.65758	2.181253	0
H	-1.91056	1.290937	0.886653
H	-1.91056	1.290937	-0.88665
C	1.101103	0.006912	4.894602
C	2.005371	0.011434	5.968611
C	1.401647	0.005977	7.227572
C	0.00442	-0.00259	7.201845

S	-0.55078	-0.00646	5.529523
H	3.080443	0.021795	5.832408
H	1.971189	0.016019	8.149852
C	-0.92336	-0.00834	8.313185
C	-2.72197	-0.02009	10.50272
C	-0.45628	-0.08445	9.649069
C	-2.32378	0.060319	8.116151
C	-3.20314	0.054016	9.192086
C	-1.3409	-0.08911	10.71924
H	0.609577	-0.14674	9.844028
H	-2.7226	0.124922	7.107454
H	-4.27285	0.109041	9.007468
H	-0.95194	-0.14951	11.73246
H	-3.41108	-0.02478	11.34242
C	1.101103	0.006912	-4.8946
S	-0.55078	-0.00646	-5.52952
C	0.00442	-0.00259	-7.20185
C	1.401647	0.005977	-7.22757
C	2.005371	0.011434	-5.96861
H	1.971189	0.016019	-8.14985
H	3.080443	0.021795	-5.83241
C	-0.92336	-0.00834	-8.31319
C	-2.72197	-0.02009	-10.5027
C	-0.45628	-0.08445	-9.64907
H	-0.95194	-0.14951	-11.7325
H	-3.41108	-0.02478	-11.3424

8. Calculated ground state energy

Table S9. Calculated ground and excited state energies of the fluorene derivatives including zero-point correction. The octyl groups are replaced to the methyl groups.

Molecule	*E*/hartree
FPT (in ground state)	−2145.296391
FPT (in excited state)	−2145.199482
FPTO$_2$	−2295.638368
FPTO$_4$	−2445.979712
FBT	−1990.547641
FBTO$_2$	−2140.896861
FBTO$_4$	−2291.245715

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