Supporting Information

Fluorescence Behavior of 2,6,10-Trisubstituted 4,8,12-Triazatriangulene Cations in Solution and in the Solid State

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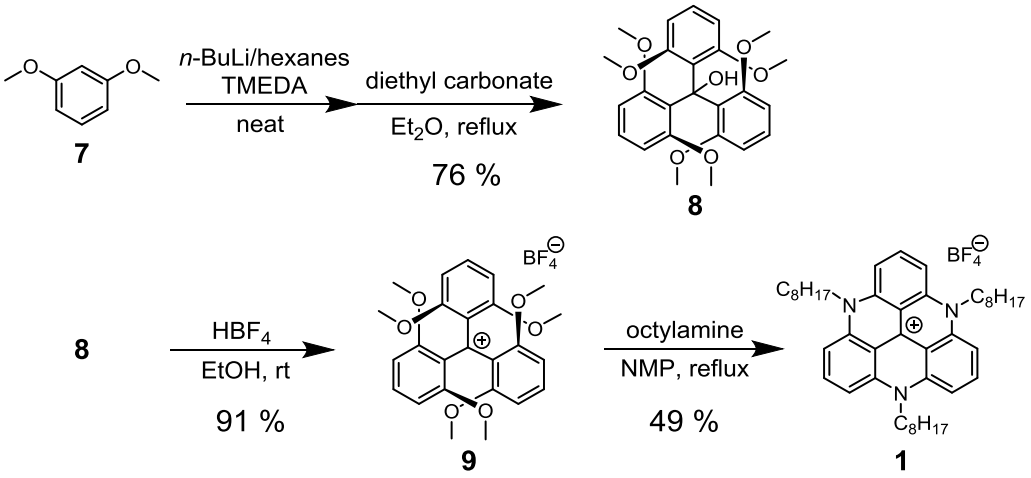
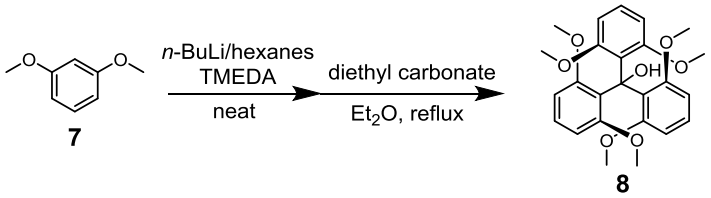
Experimental details

A. Syntheses of Materials



Scheme S1. Synthesis of 4,8,12-trioctyl-4,8,12-triazatriangulene cation tetrafluoroborate salt ($TATA^+BF_4^-$) (**1**)

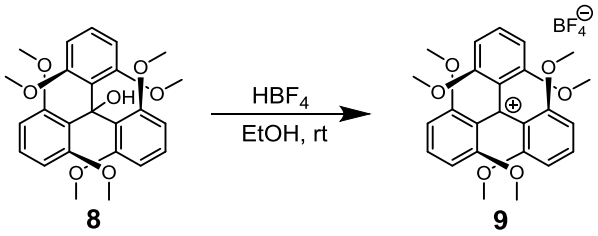
*Synthesis of tris(2,6-dimethoxyphenyl)carbinol (**8**)*[S1]



To a solution of 1,3-dimethoxybenzene (**7**) (22.5 g, 163 mmol) in *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (1.0 mL) was added *n*-BuLi (1.6 M in hexanes, 100 mL, 160 mmol) dropwise with keeping the temperature below 10 °C. The mixture was stirred for 1 h under ice bath. Then, a solution of diethylcarbonate (3.0 mL, 24.8 mmol) in dry Et_2O (100 mL) was added to the resulting mixture with keeping under 10 °C. The reaction mixture was stirred for 1 h at room temperature, and then refluxed for 2 days. The reaction mixture was quenched by water under ice bath. An excess amount of hexane was added to the solution and the mixture was cooled at 0 °C for 2 h. The resulting precipitate was collected by filtration. The collected solid was washed with water and hexane to give compound **8** (8.27 g, 18.8 mmol, 76 %) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 3.44 (s, 18H), 6.49 (d, *J* = 7.9 Hz, 6H), 6.84 (s, 1H), 7.04 (t, *J* = 8.2 Hz, 3H).

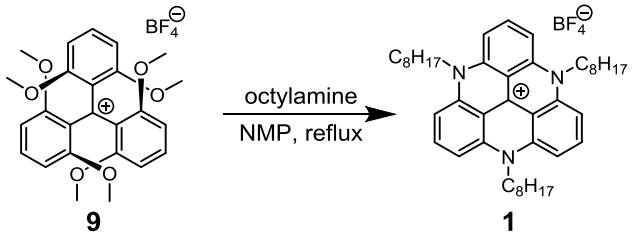
*Synthesis of tris(2,6-dimethoxyphenyl)carbenium tetrafluoroborate (**9**)*[S2]



To a solution of compound **8** (8.26 g, 18.7 mmol) in absolute EtOH (100 mL) was added aqueous HBF_4 solution (42%, 4.5 mL, 26 mmol). Then Et_2O (150 mL) was added to the solution, followed by hexane (150 mL). The resulting black precipitate was collected by filtration and washed with Et_2O to give compound **9** (8.74 g, 17.1 mmol, 91%) as a dark-green solid.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 3.60 (s, 18H), 6.54 (d, *J* = 8.5 Hz, 6H), 7.60 (t, *J* = 8.3 Hz, 3H).

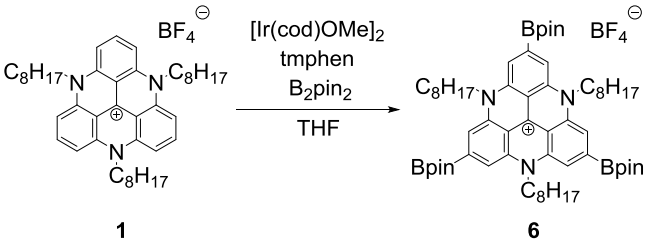
*Synthesis of 4,8,12-tri-n-octyl-4,8,12-triazatriangulenium tetrafluoroborate (**1**)*[S2]



To a solution of compound **9** (3.10 g 6.07 mmol) in NMP (5 mL) was added *n*-octylamine (15 mL, 90 mmol). The reaction mixture was heated to 180 °C under argon atmosphere. After cooling to room temperature, the resulting solution was poured into Et_2O (300 mL). The generated precipitation was collected with filtration and washed with ether to give compound **1** (2.11 g, 2.99 mmol, 49%) as a red crystal.

^{1}H NMR (500 MHz, $(CH_3)_2SO$, δ): 0.87 (t, *J* = 6.7 Hz, 9H), 1.24–1.45 (m, 24H), 1.55 (quint, *J* = 7.6 Hz, 6H), 1.71–1.82 (m, 6H), 4.35 (t, *J* = 7.6 Hz, 6H), 7.36 (d, *J* = 8.5 Hz, 6H), 8.05 (t, *J* = 8.5 Hz, 3H).

*Synthesis of 2,6,10-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4,8,12-tri-n-octyl-4,8,12-triazatriangulenium tetrafluoroborate (**6**)*



Compound **1** (0.17 g, 0.27 mmol), $[Ir(cod)OMe]_2$ (37 mg, 0.056 mmol), 3,4,7,8-tetramethyl-1,10-phenanthroline (21 mg, 0.089 mmol), and bis(pinacolato)diboron (0.40 g, 1.6 mmol) were placed in a Schlenk tube. The tube was evacuated and then refilled with N_2 three times. Under a positive flow of N_2, dry THF (5 mL) was added to the tube. The tube was covered with aluminum foil to avoid light and the reaction mixture was stirred for 4

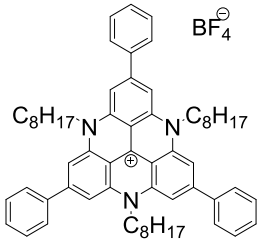
h at 60 °C. The resulting solution was cooled in an ice bath and hexane (20 mL) was then added. The purple precipitate was collected by filtration and was washed with hexane and water to give compound **6** (0.25 g, 0.23 mmol, 85 %) as a purple solid.

^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 7.22 (s, 6H), 3.93–4.17 (m, 6H), 1.57–1.70 (m, 6H), 1.38–1.56 (m, 42H), 1.25–1.38 (m, 24H), 0.85–0.94 (m, 9H); HRMS–MALDI–Orbitrap (*m*/*z*): $[M]^+$ calcd for $C_{61}H_{93}B_3N_3O_6^+$, 996.7338; found, 996.7388.

General procedure for synthesis of compounds **2**–**5**

Compound **6** (50 mg, 0.046 mmol) and $Pd(PPh_3)_4$ (14 mg, 12 μmol) were placed in a flask. The flask was evacuated and then refilled with N_2 three times. To the reaction vessel, aryl halide (0.84 mmol), aq. K_3PO_4 (2 M, 1 mL), and 1,4-dioxane (3 mL) were added under N_2 atmosphere. The reaction mixture was refluxed for 4 h. The reaction product was extracted with CH_2Cl_2, dried over $MgSO_4$, filtered, and evaporated. The crude product was purified by silica gel column chromatography (CH_2Cl_2/MeOH = 98/2). Further purification was carried out by recrystallization from CH_2Cl_2/toluene or CH_3CN/toluene and GPC (eluent, chloroform).

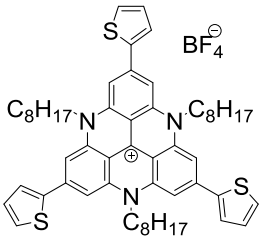
*2,6,10-triphenyl-4,8,12-tri-n-octyl-4,8,12-triazatriangulenium tetrafluoroborate (**2**)*



2

Compound **2**: starting from **6** (23 mg, 0.021 mmol) and iodobenzene (90 mg, 0.44 mmol), a red solid (11 mg, 0.013 mmol, 57%); ^{1}H NMR (500 MHz, $CDCl_3$, δ) 7.80 (d, *J* = 7.3 Hz, 6H), 7.62 (t, *J* = 7.3 Hz, 6H), 7.56 (t, *J* = 7.3 Hz, 3H), 7.31 (s, 6H), 4.48–4.56 (m, 6H), 2.00–2.06(m, 6H), 1.56–1.68 (m, 6H), 1.46–4.52 (m, 6H), 1.25–1.40 (m, 18H), 0.85–0.90 (m, 9H); ^{13}C NMR (151 MHz, $CDCl_3$, δ): 14.1, 22.6, 25.1, 26.8, 29.16, 29.23, 31.7, 48.3, 104.4, 109.8, 128.0, 129.45, 129.52, 139.0, 140.2, 140.9, 150.8; HRMS–MALDI–Orbitrap (*m*/*z*) $[M]^+$ calcd for $C_{61}H_{72}N_3^+$, 846.5721; found, 846.5716.

*2,6,10-tri(2-thienyl)-4,8,12-tri-n-octyl-4,8,12-triazatriangulenium tetrafluoroborate (**3**)*

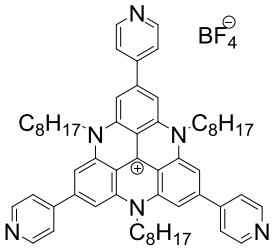


3

Compound **3**: starting from **6** (50 mg, 0.046 mmol) and 2-bromothiophene (0.14 g, 0.86 mmol), a red solid (12 mg, 0.013 mmol, 28%); ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.02–8.10 (m, 3H), 7.95 (d, *J* = 5.0 Hz, 3H), 7.38 (t, *J* = 5.0 Hz,

3H), 7.17 (s, 6H), 3.96–4.22 (m, 6H), 1.56–1.74 (m, 6H), 1.38–1.54 (m, 6H), 1.20–1.36 (m, 24H), 0.84–0.92 (m, 9H); ^{13}C NMR (151 MHz, $CDCl_3$, δ): 14.1, 22.6, 25.0, 26.3, 29.2, 29.3, 31.8, 47.1, 102.1, 108.5, 128.2, 128.3, 129.9, 136.6, 140.3, 141.8, 143.0; HRMS–MALDI–Orbitrap (*m*/*z*): $[M]^+$ calcd for $C_{55}H_{66}N_3S_3^+$, 864.4413; found, 864.4446.

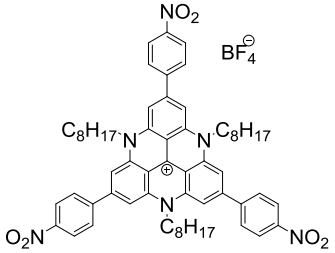
*2,6,10-tri(4-pyridyl)-4,8,12-tri-n-octyl-4,8,12-triazatriangulenium tetrafluoroborate (**4**)*



4

Compound **4**: starting from **6** (0.10 g, 0.092 mmol) and 4-bromopyridine (0.29 g, 1.5 mmol), a red solid (8.8 mg, 0.0094 mmol, 10 %); ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.87 (d, *J* = 5.5 Hz, 6H), 7.77 (d, *J* = 5.5 Hz, 6H), 7.40 (s, 6H), 4.66–4.72 (m, 6H), 1.96–2.08 (m, 6H), 1.64–1.72 (m, 6H), 1.47–1.53 (m, 6H), 1.46–1.54 (m, 18H), 0.86–0.90 (m, 9H). ^{13}C NMR (151 MHz, $CDCl_3$, δ): 14.1, 22.6, 25.2, 26.8, 29.2, 29.4, 31.8, 48.5, 104.6, 110.7, 122.4, 139.2, 141.1, 147.2, 148.1, 150.9; HRMS–MALDI–Orbitrap (*m*/*z*): $[M]^+$ calcd for $C_{58}H_{69}N_6^+$, 849.5578; found, 849.5540.

*2,6,10-tri(4-nitrophenyl)-4,8,12-tri-n-octyl-4,8,12-triazatriangulenium tetrafluoroborate (**5**)*



5

Compound **5**: starting from **6** (0.10 g, 0.092 mmol) and 4-iodonitrobenzene (0.36 g, 1.4 mmol), a red solid (39 mg, 0.036 mmol, 39 %); ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.42 (d, *J* = 8.5 Hz, 6H), 8.05 (d, *J* = 8.5 Hz, 6H), 7.38 (s, 6H), 4.71 (t, *J* = 7.5 Hz, 6H), 1.98–2.07 (m, 6H), 1.63–1.71 (m, 6H), 1.44–1.51 (m, 6H), 1.25–1.39 (m, 18H), 0.86 (t, *J* = 7.0 Hz, 9H); ^{13}C NMR (151 MHz, $CDCl_3$, δ): 13.9, 22.1, 24.8, 26.1, 28.7, 28.8, 31.3, 46.1, 104.4, 109.4, 123.4, 129.5, 140.0, 145.0, 146.7, 147.4; HRMS–MALDI–Orbitrap (*m*/*z*) $[M]^+$ calcd for $C_{61}H_{69}N_6O_6^+$, 981.5273; found, 981.5305.

Supporting Data

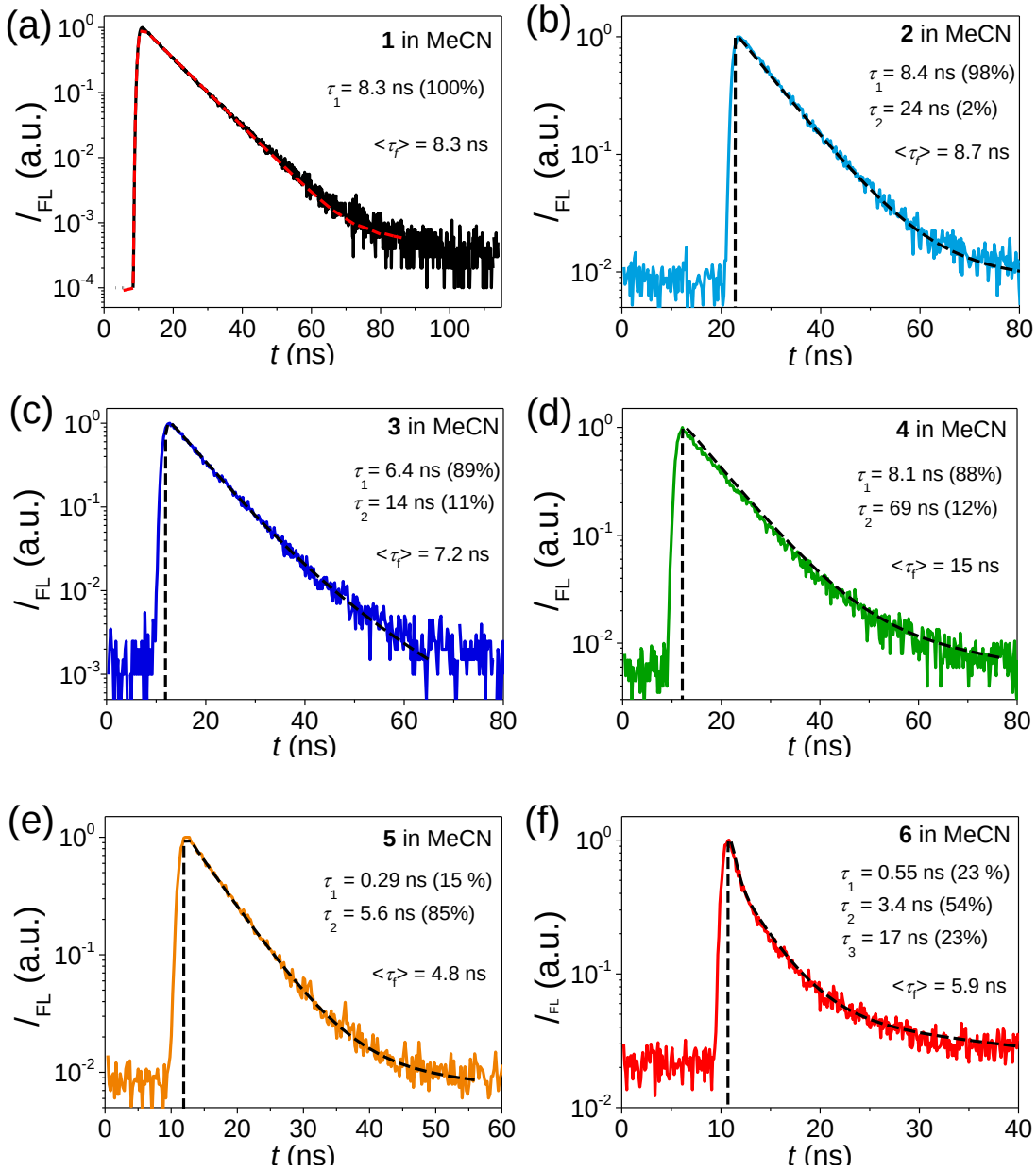


Figure S1. Fluorescence decay curves of (a) **1** (black), (b) **2** (sky blue), (c) **3** (blue), (d) **4** (green), (e) **5** (orange), and (f) **6** (red) in MeCN at room temperature. Red dashed line for **1** and black dashed line for compounds **2**–**6** denote the best fitting curves.

Table S1. Fluorescence lifetime of compounds **1**–**6** in MeCN at room temperature.

compound	τ_1 (ns)[a]	τ_2 (ns)[a]	τ_3 (ns)[a]	$<\tau_f>$ (ns)[b]	χ^2
1[c]	8.3 (100%)	–	–	8.3	1.52
2	8.4 (98%)	24 (2%)	–	8.7	1.38
3	6.4 (89%)	14 (11%)	–	7.2	1.23
4	8.1 (88%)	69 (12%)	–	15	1.42
5	0.29 (15%)	5.6 (85%)	–	4.8	1.36
6	0.55 (23%)	3.4 (54%)	17 (23%)	5.9	1.22

[a] The area-weighted ratio ($A_n\tau_n$) are shown in parentheses. [b] The area-weighted mean fluorescence lifetime $<\tau_f>$ was calculated as follows: $<\tau_f> = \Sigma(A_n\tau_n^2)/\Sigma(A_n\tau_n)$ where A_n is the coefficient of exponential function of the *n*-th component. [c] Fluorescence decay was measured by time-correlated single photon counting (TCSPC) method, excited at λ_{ex} = 495 nm and monitored at λ_{em} = 570 nm.

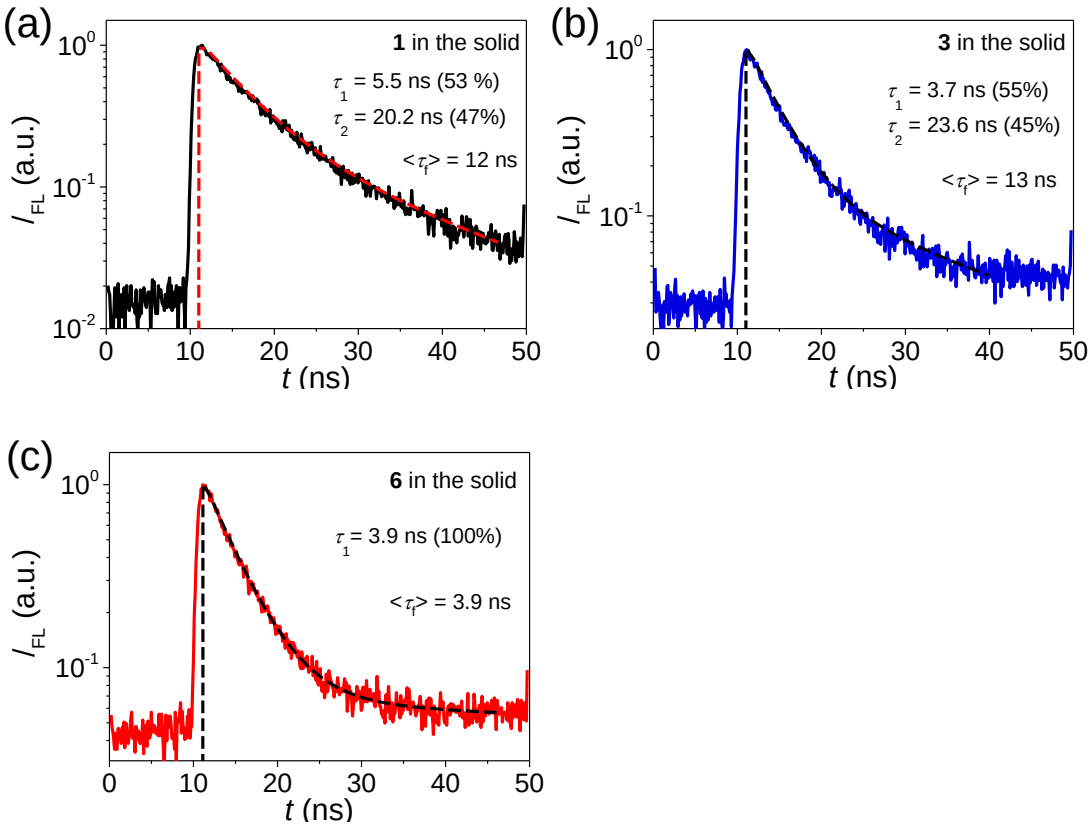


Figure S2. Fluorescence decay curves of (a) **1** (black), (b) **3** (blue), and (c) **6** (red) in the solid state at room temperature. Red dashed line for **1** and black dashed line for compounds **3** and **6** denote the best fitting curves.

Table S2. Fluorescence lifetime of compounds **1**, **3**, and **6** in the solid state at room temperature.

compound	τ_1 (ns)[a]	τ_2 (ns)[a]	$<\tau_f>$ (ns)[b]	χ^2
1	5.5 (53%)	20.2 (47%)	12	1.14
3	3.7 (55%)	23.6 (45%)	13	1.45
6	3.9 (100%)	-	3.9	1.20

[a] The area-weighted ratio ($A_n\tau_n$) are shown in parentheses. [b] The area-weighted mean fluorescence lifetime $<\tau>$ was calculated as follows: $<\tau> = \Sigma(A_n\tau_n^2)/\Sigma(A_n\tau_n)$ where A_n is the coefficient of exponential function of the *n*-th component.

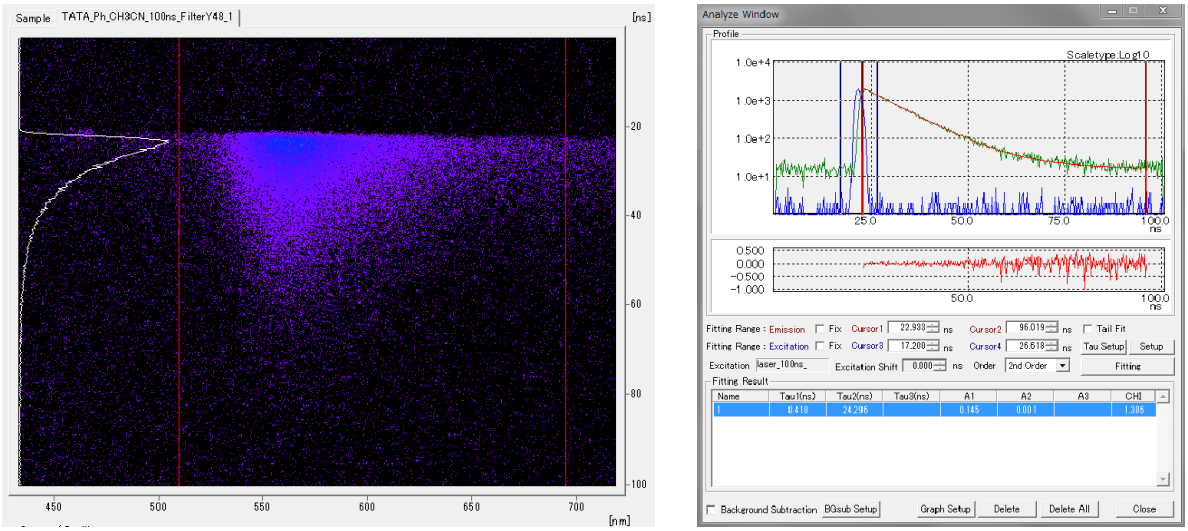


Figure S3. Streak image (left) and fluorescence decay analysis (right) of **2** in MeCN at room temperature.

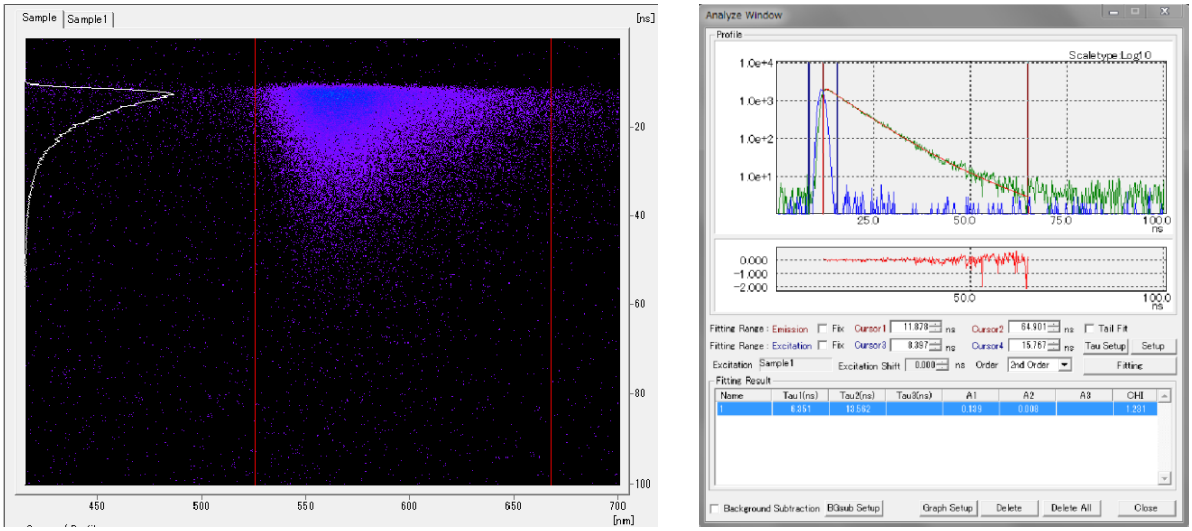


Figure S4. Streak image (left) and fluorescence decay analysis (right) of **3** in MeCN at room temperature.

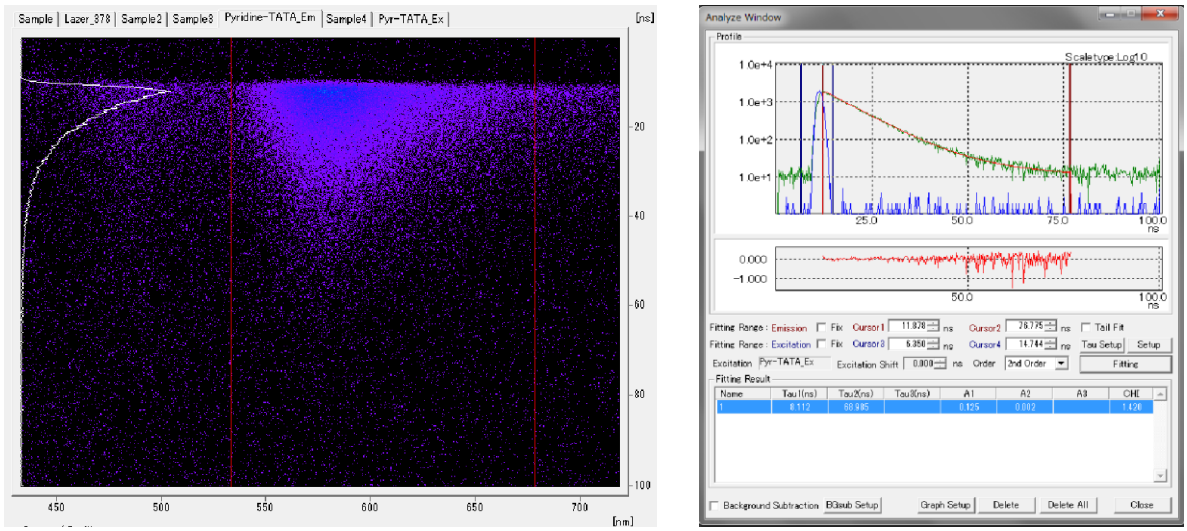


Figure S5. Streak image (left) and fluorescence decay analysis (right) of **4** in MeCN at room temperature.

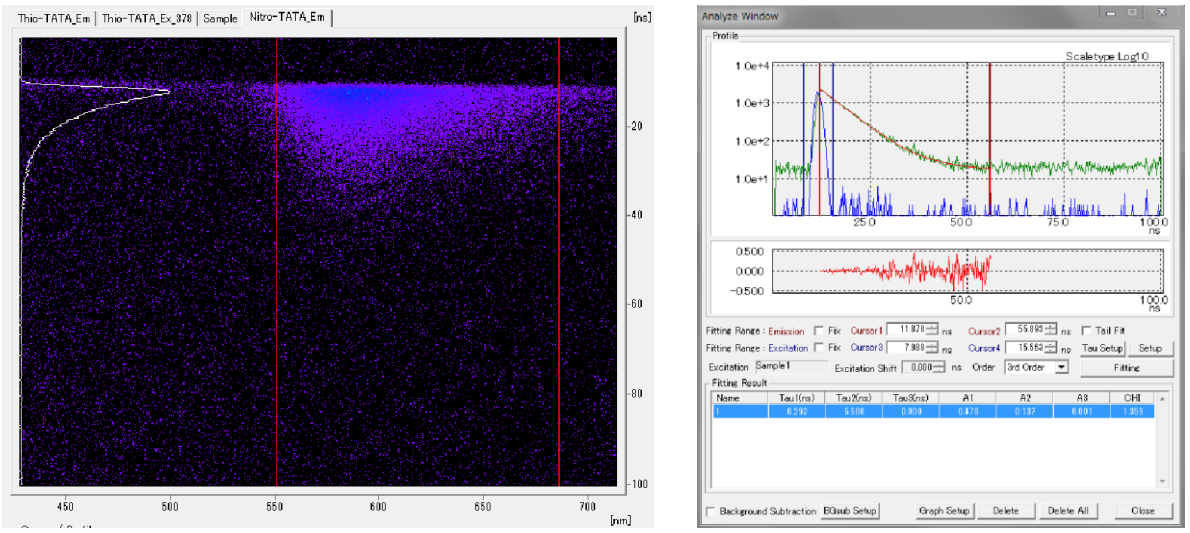


Figure S6. Streak image (left) and fluorescence decay analysis (right) of **5** in MeCN at room temperature.

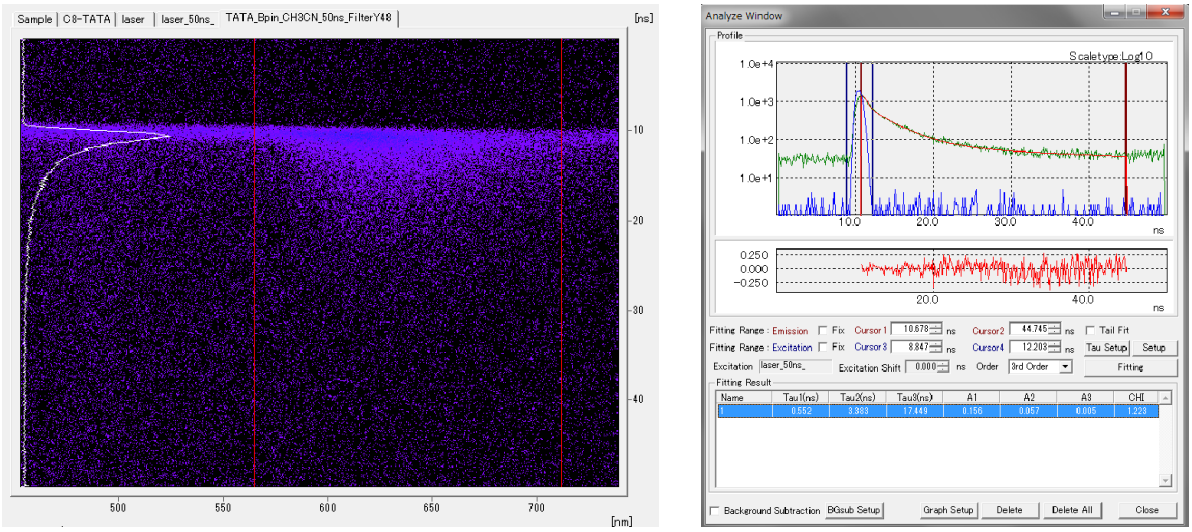


Figure S7. Streak image (left) and fluorescence decay analysis (right) of **6** in MeCN at room temperature.

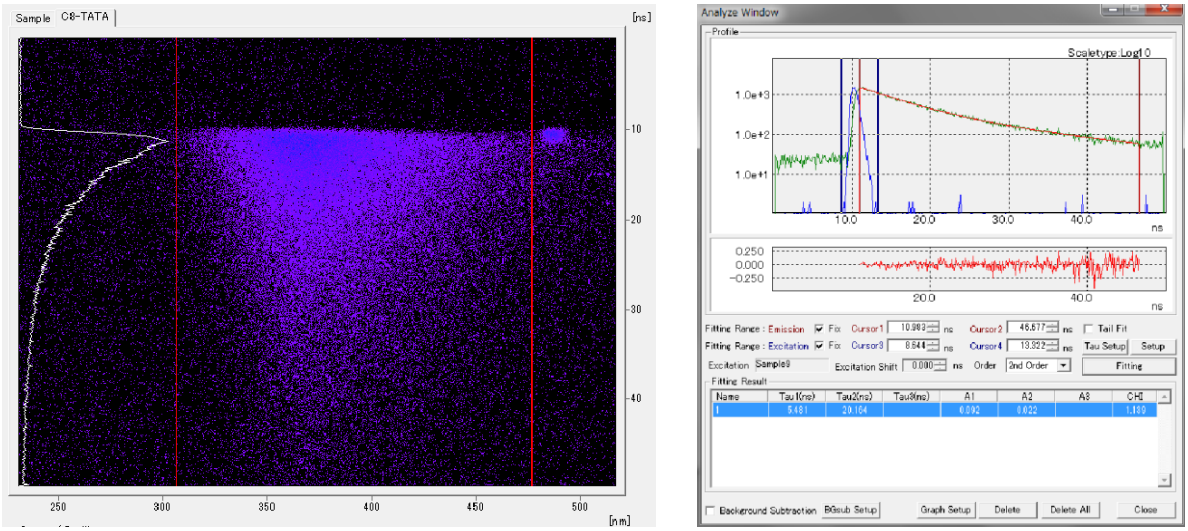


Figure S8. Streak image (left) and fluorescence decay analysis (right) of **1** in the solid state at room temperature.

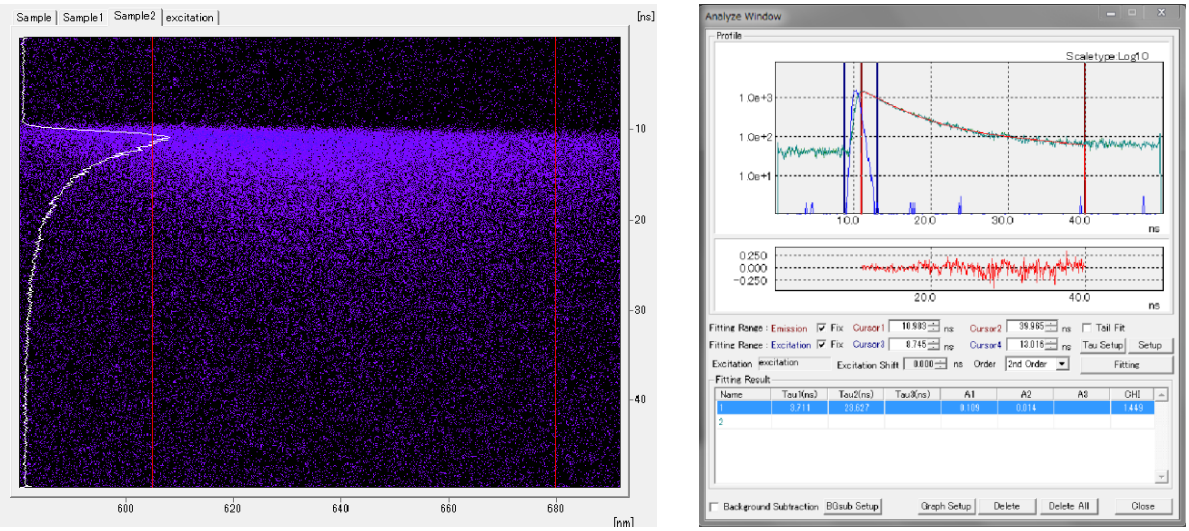


Figure S9. Streak image (left) and fluorescence decay analysis (right) of **3** in the solid state at room temperature.

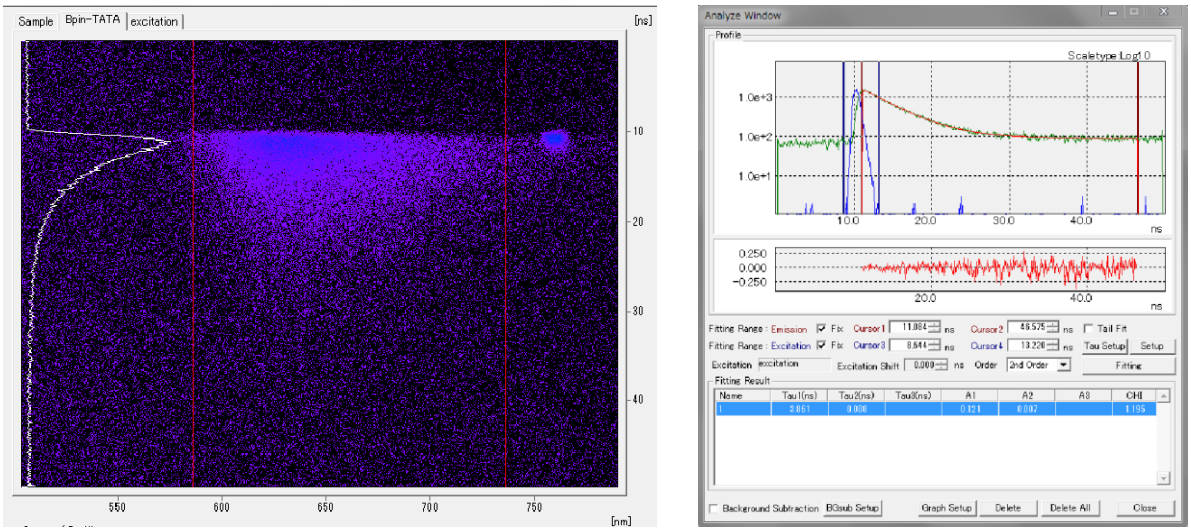


Figure S10. Streak image (left) and fluorescence decay analysis (right) of **6** in the solid state at room temperature.

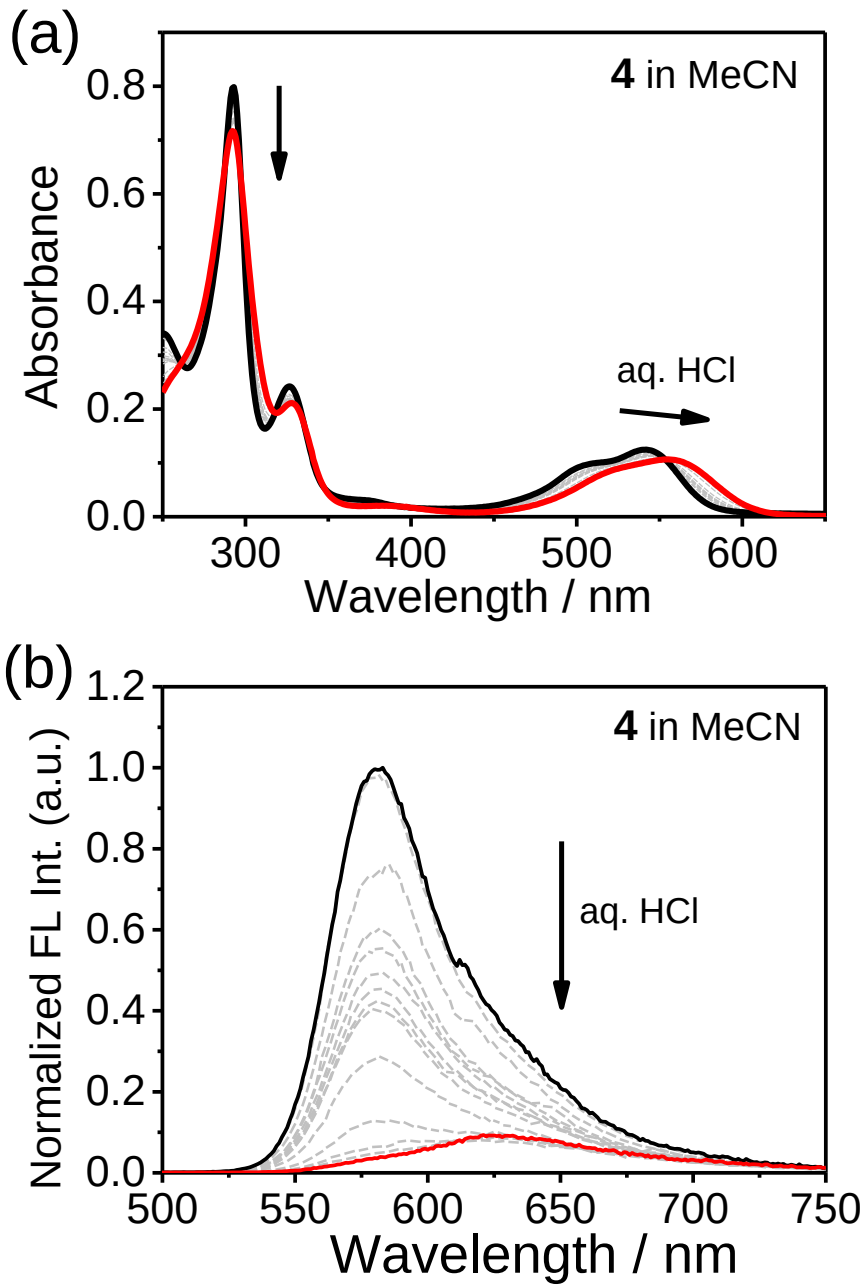


Figure S11. (a) Absorption and (b) fluorescence spectral change of compound **4** in MeCN upon addition of aq. HCl.

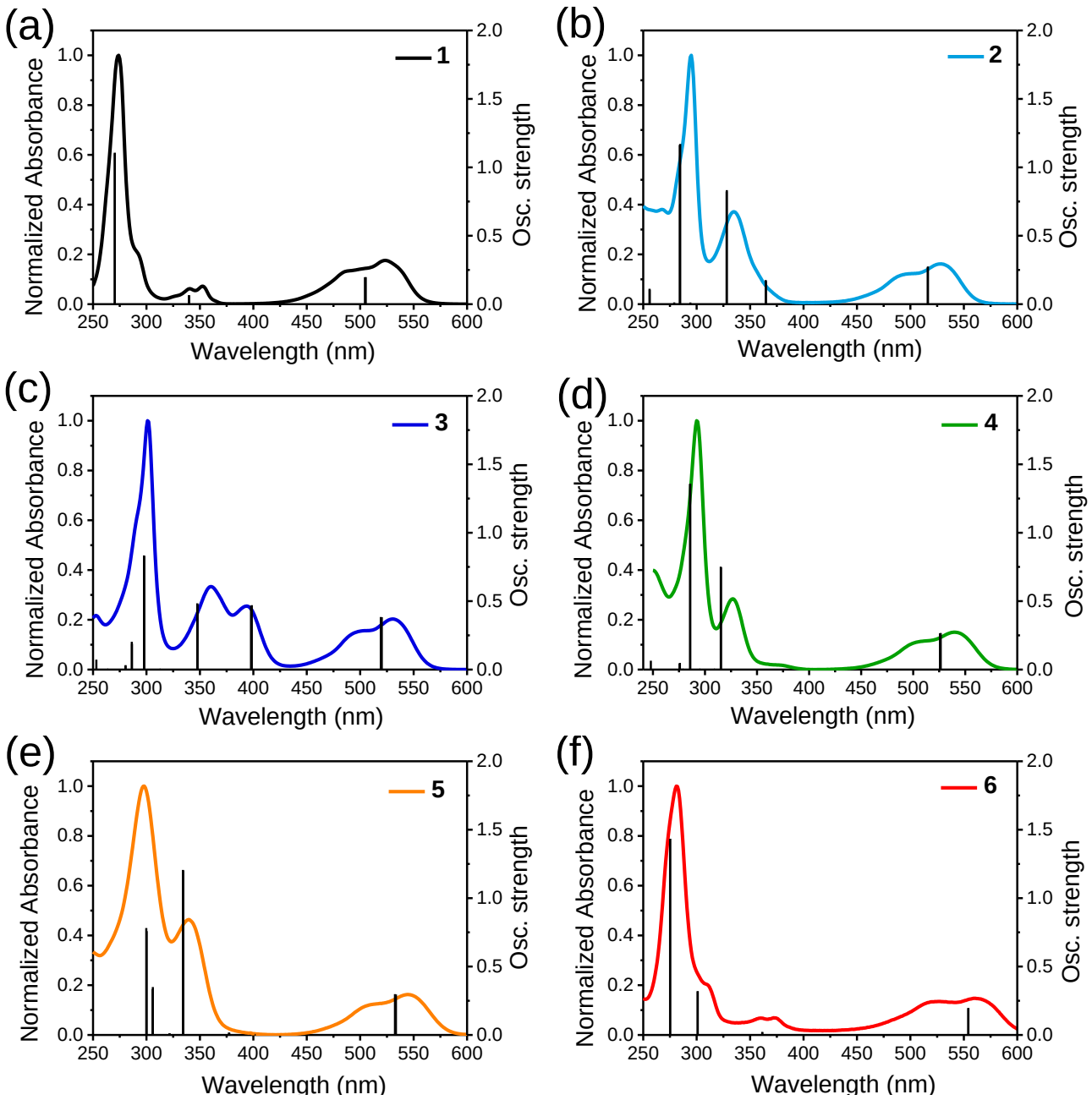


Figure S12. Comparison between experimentally observed absorption spectra in MeCN (solid line) and calculated ones (bars) for compounds (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5**, and (f) **6**.

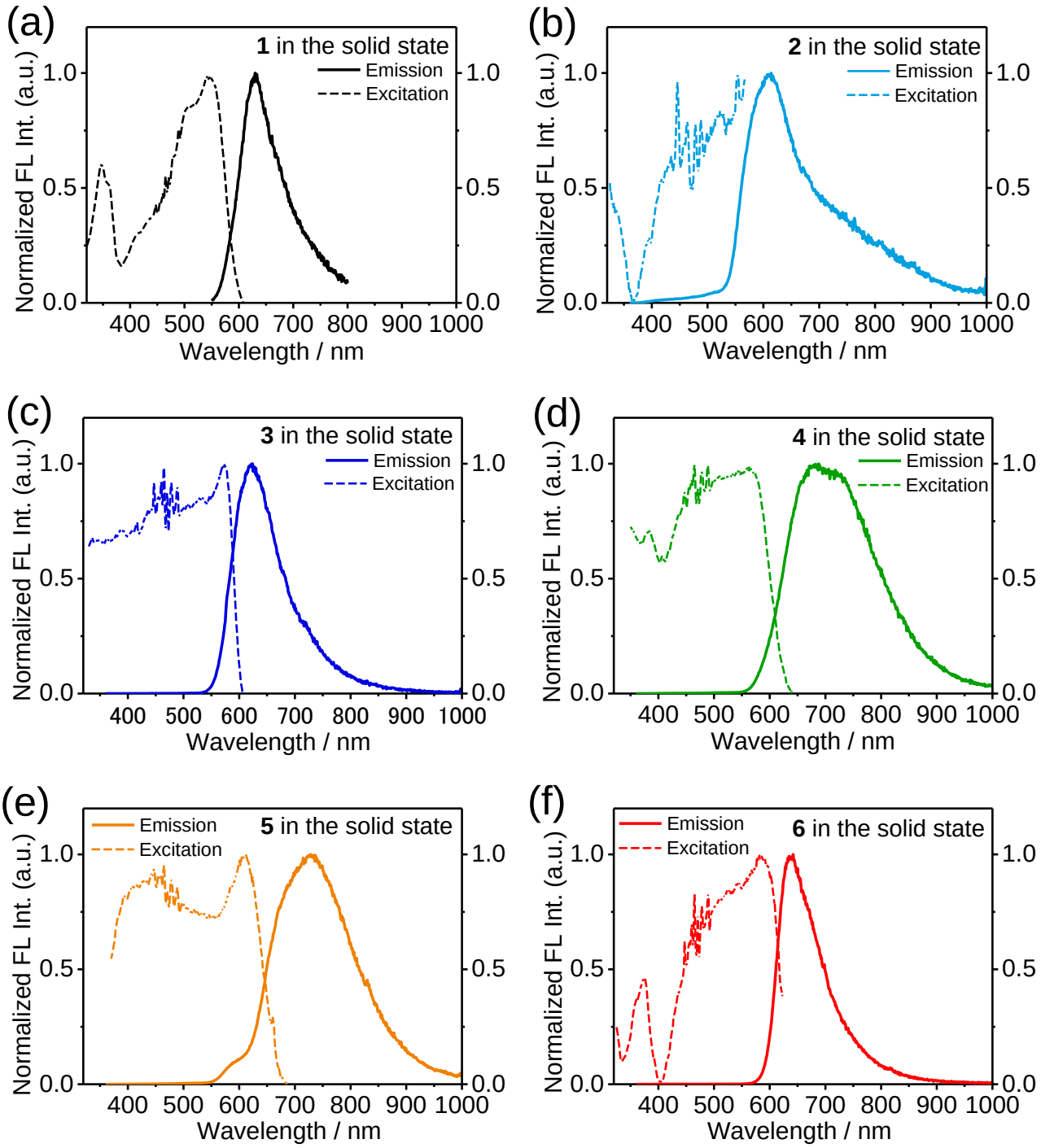


Figure S13. Fluorescence and excitation spectra of compounds (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5**, and (f) **6** in the solid state.

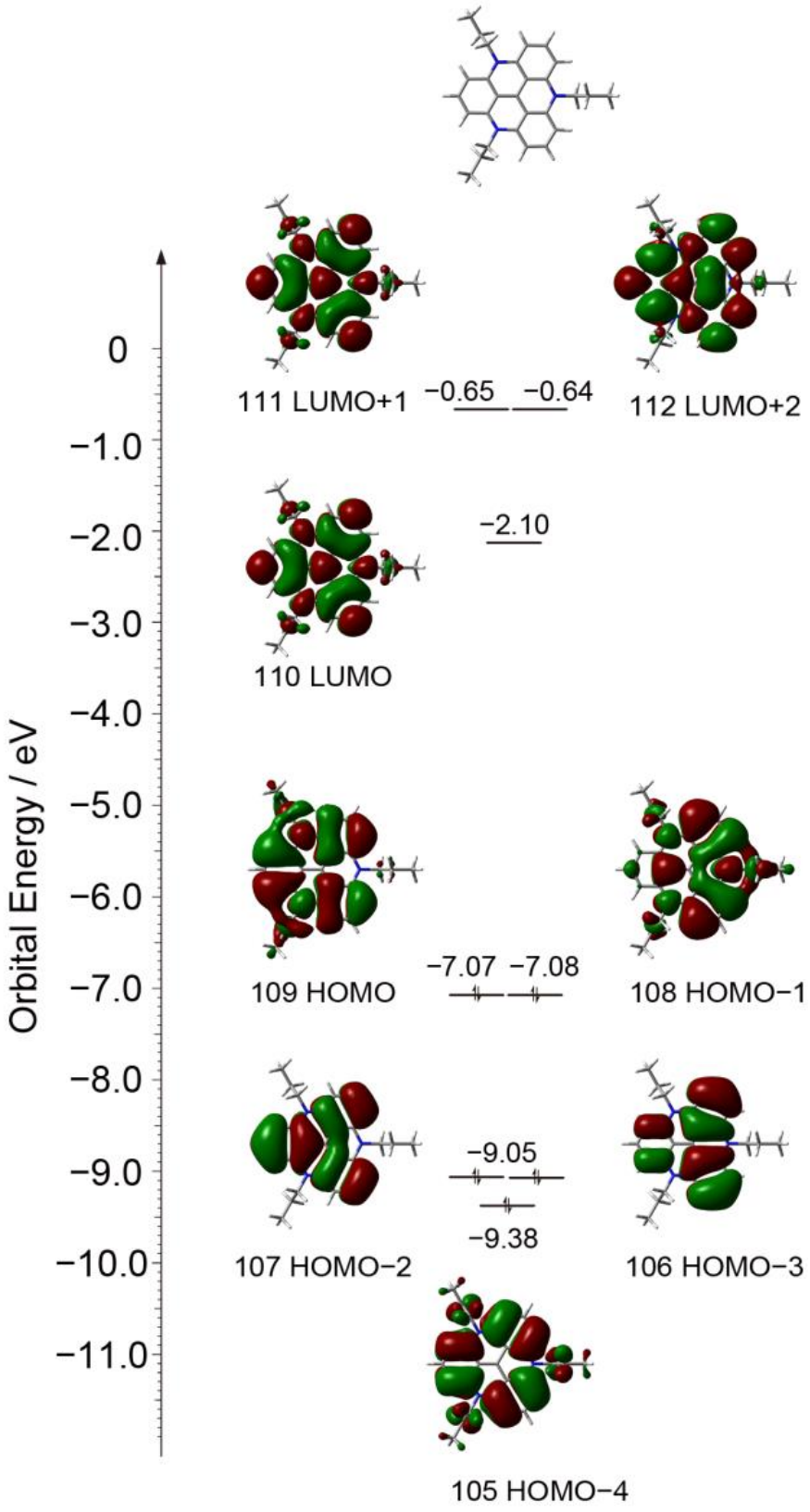


Figure S14. Orbital correlation diagram of **1** in the ground state calculated with M062X/6-311g(2d,p)-SCRF(PCM)//B3LYP/6-31g(d) level of theory. Acetonitrile (ε = 35.688) was specified as a solvent in the calculations with PCM method.

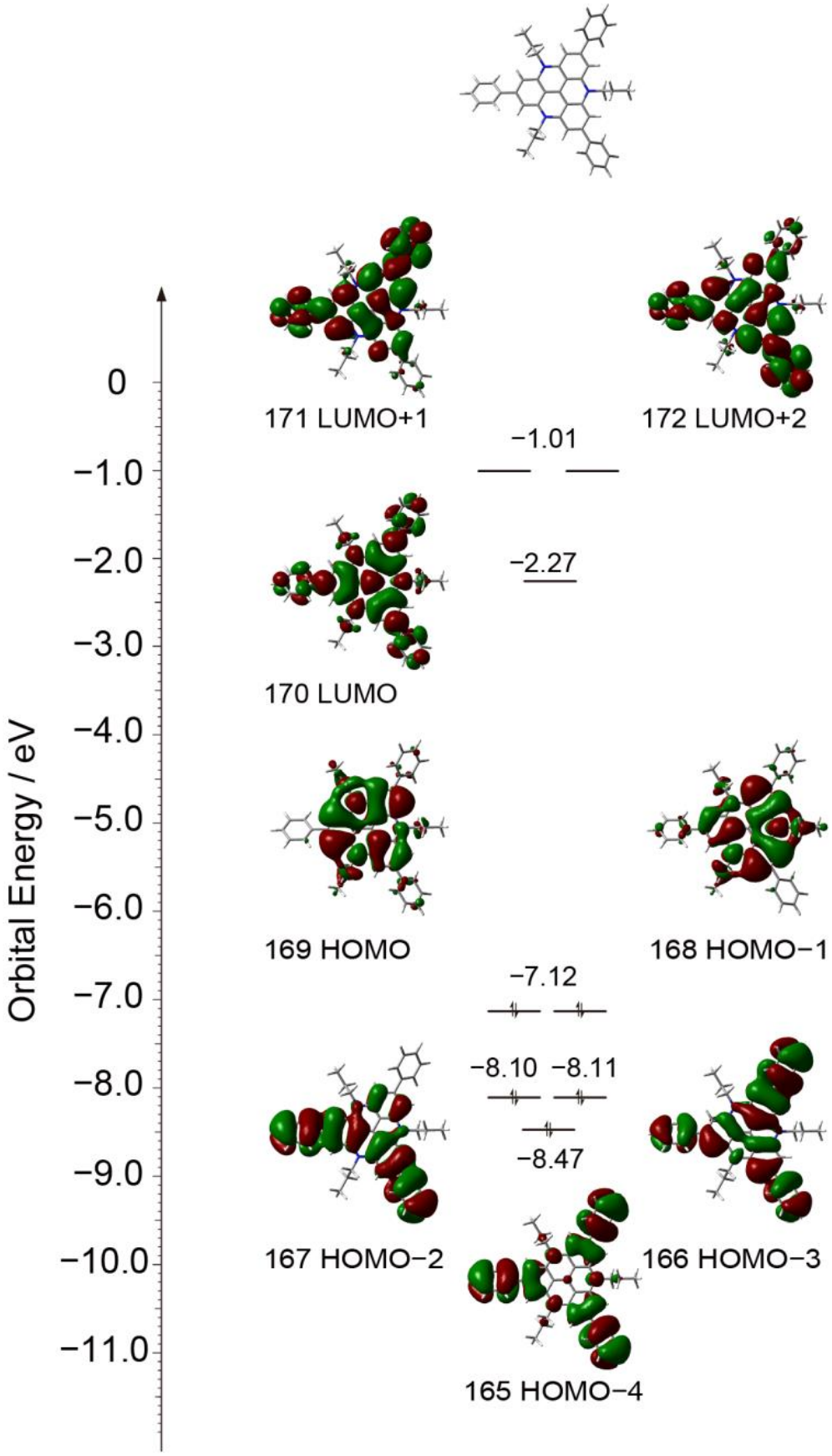


Figure S15. Orbital correlation diagram of **2** in the ground state calculated with M062X/6-311g(2d,p)-SCRF(PCM)//B3LYP/6-31g(d) level of theory. Acetonitrile (ε = 35.688) was specified as a solvent in the calculations with PCM method.

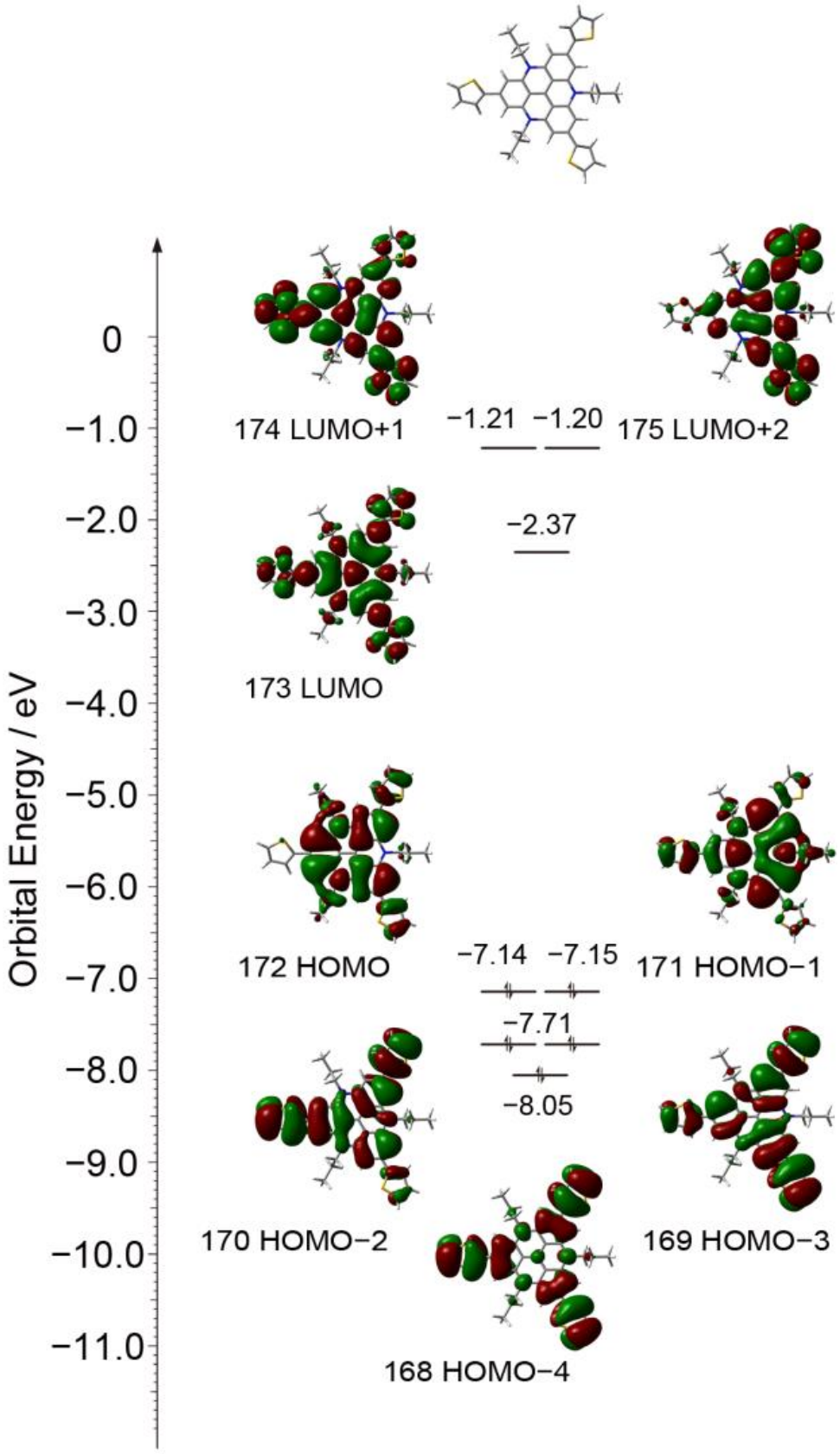


Figure S16. Orbital correlation diagram of **3** in the ground state calculated with M062X/6-311g(2d,p)-SCRF(PCM)//B3LYP/6-31g(d) level of theory. Acetonitrile (ε = 35.688) was specified as a solvent in the calculations with PCM method.

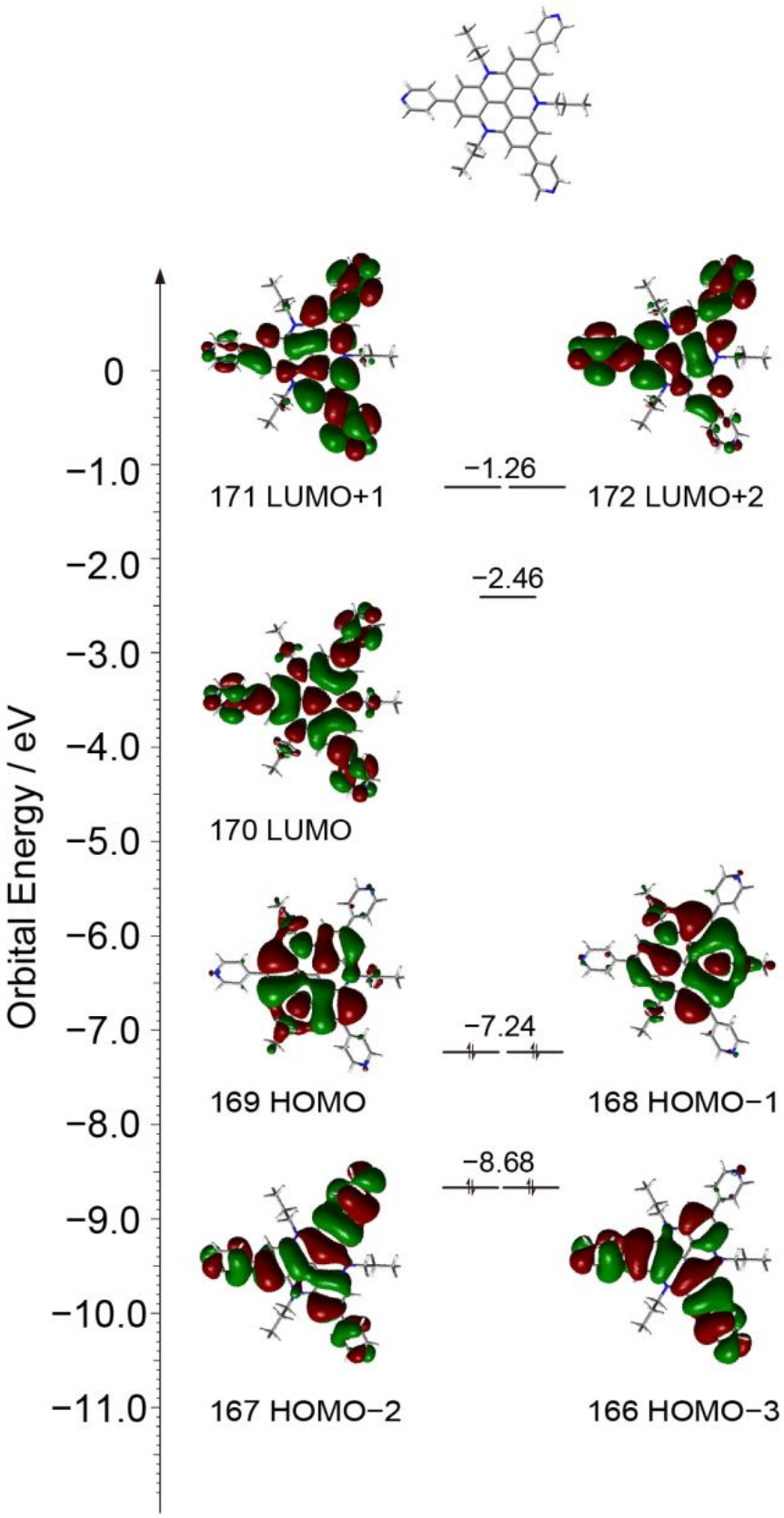


Figure S17. Orbital correlation diagram of **4** in the ground state calculated with M062X/6-311g(2d,p)-SCRF(PCM)//B3LYP/6-31g(d) level of theory. Acetonitrile (ε = 35.688) was specified as a solvent in the calculations with PCM method.

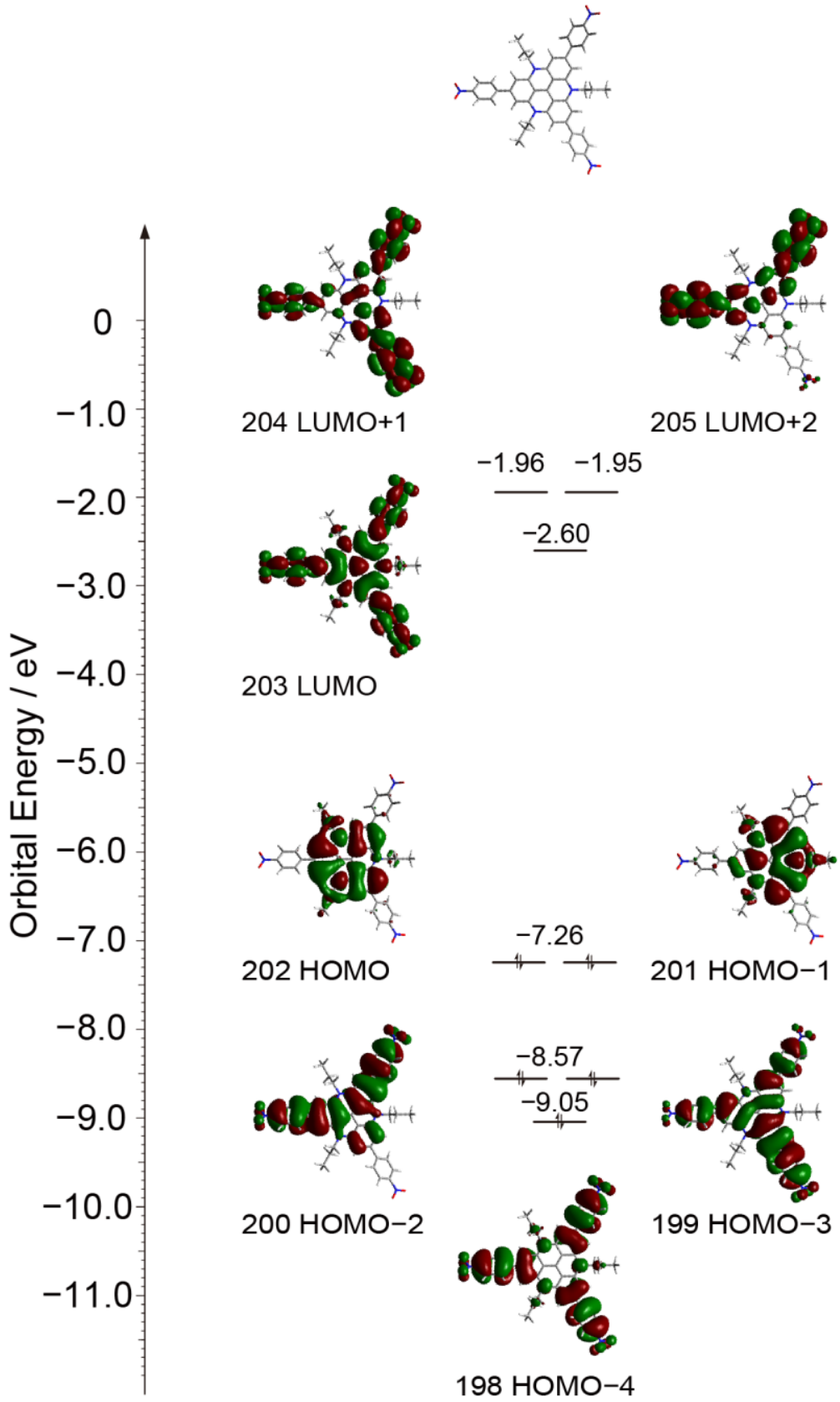


Figure S18. Orbital correlation diagram of **5** in the ground state calculated with M062X/6-311g(2d,p)-SCRF(PCM)//B3LYP/6-31g(d) level of theory. Acetonitrile (ε = 35.688) was specified as a solvent in the calculations with PCM method.

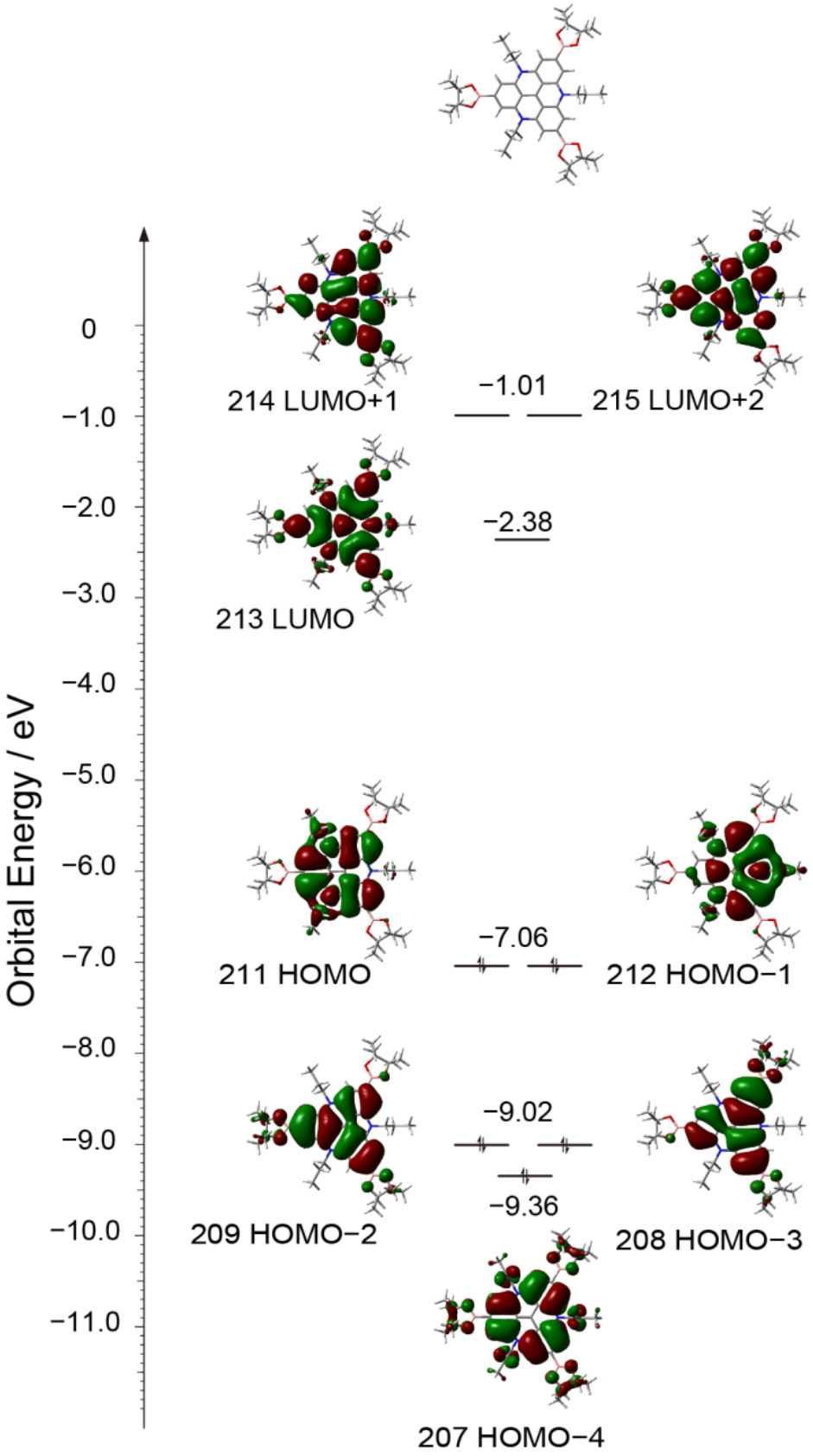


Figure S19. Orbital correlation diagram of **6** in the ground state calculated with M062X/6-311g(2d,p)-SCRF(PCM)//B3LYP/6-31g(d) level of theory. Acetonitrile (ε = 35.688) was specified as a solvent in the calculations with PCM method.

Excited States Calculated by TD-DFT

Compound **1** calculated at M062X/6-311g(2d,p)-SCRF(PCM, solvent=acetonitrile)

```
Excited State   1:      Singlet-A      2.9540 eV  419.72 nm  f=0.1975  <S**2>=0.000
    109 ->110        0.70146
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) =  -1248.94210281

Excited State   2:      Singlet-A      2.9579 eV  419.17 nm  f=0.1967  <S**2>=0.000
    108 ->110        0.70145

Excited State   3:      Singlet-A      3.9135 eV  316.81 nm  f=0.0000  <S**2>=0.000
    108 ->111        0.48548
    109 ->112        0.48801

Excited State   4:      Singlet-A      4.1482 eV  298.89 nm  f=0.0653  <S**2>=0.000
    106 ->110        0.26240
    108 ->111        0.44721
    109 ->112       -0.44400

Excited State   5:      Singlet-A      4.1483 eV  298.88 nm  f=0.0656  <S**2>=0.000
    107 ->110        0.26332
    108 ->112        0.44383
    109 ->111        0.44684

Excited State   6:      Singlet-A      4.7796 eV  259.41 nm  f=0.0000  <S**2>=0.000
    108 ->112       -0.48710
    109 ->111        0.50196

Excited State   7:      Singlet-A      4.8018 eV  258.20 nm  f=0.0000  <S**2>=0.000
    107 ->110       -0.43483
    108 ->112        0.19734
    109 ->111        0.14636
    109 ->113        0.47830

Excited State   8:      Singlet-A      4.8038 eV  258.10 nm  f=0.0000  <S**2>=0.000
    106 ->110        0.43624
    108 ->111       -0.17101
    108 ->113        0.47864
    109 ->112        0.17198

Excited State   9:      Singlet-A      5.0416 eV  245.92 nm  f=0.0008  <S**2>=0.000
    105 ->110        0.67103

Excited State  10:      Singlet-A      5.0850 eV  243.83 nm  f=1.1069  <S**2>=0.000
    107 ->110        0.47408
    109 ->113        0.48250
```

Compound **2** calculated at M062X/6-311g(2d,p)-SCRF(PCM, solvent=acetonitrile)

```
Excited State   1:      Singlet-A     2.9035 eV  427.01 nm  f=0.2974  <S**2>=0.000
    169 -> 170       0.69490
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) =  -1942.01912823

Excited State   2:      Singlet-A     2.9070 eV  426.50 nm  f=0.2951  <S**2>=0.000
    168 -> 170       0.69496

Excited State   3:      Singlet-A     3.7914 eV  327.02 nm  f=0.0000  <S**2>=0.000
    168 -> 171      -0.21956
    168 -> 172       0.41621
    169 -> 171       0.42698
    169 -> 172       0.22074

Excited State   4:      Singlet-A     3.9106 eV  317.05 nm  f=0.0951  <S**2>=0.000
    159 -> 170       0.14321
    166 -> 170      -0.20390
    167 -> 170       0.40525
    168 -> 171      -0.19496
    168 -> 172      -0.28235
    169 -> 171       0.27469
    169 -> 172      -0.20014

Excited State   5:      Singlet-A     3.9130 eV  316.85 nm  f=0.0941  <S**2>=0.000
    160 -> 170      -0.14388
    166 -> 170       0.40282
    167 -> 170       0.20448
    168 -> 171      -0.28114
    168 -> 172       0.20306
    169 -> 171      -0.19491
    169 -> 172      -0.27596

Excited State   6:      Singlet-A     4.2781 eV  289.81 nm  f=0.8924  <S**2>=0.000
    166 -> 170      -0.19651
    167 -> 170       0.44562
    168 -> 171       0.20082
    168 -> 172       0.25298
    169 -> 171      -0.25103
    169 -> 172       0.20087

Excited State   7:      Singlet-A     4.2817 eV  289.57 nm  f=0.9039  <S**2>=0.000
    166 -> 170       0.44780
    167 -> 170       0.19613
    168 -> 171       0.25218
    168 -> 172      -0.19918
    169 -> 171       0.19916
    169 -> 172       0.25030

Excited State   8:      Singlet-A     4.5945 eV  269.85 nm  f=0.0001  <S**2>=0.000
    165 -> 170      -0.22941
    168 -> 171      -0.40612
    168 -> 172      -0.21211
    169 -> 171      -0.21264
    169 -> 172       0.40855

Excited State   9:      Singlet-A     4.7271 eV  262.29 nm  f=0.0004  <S**2>=0.000
    165 -> 170       0.59168
    166 -> 171       0.17305
    167 -> 172      -0.17183
    168 -> 171      -0.15356
    169 -> 172       0.15074

Excited State  10:      Singlet-A     4.8155 eV  257.47 nm  f=1.1159  <S**2>=0.000
    168 -> 173       0.58182
    169 -> 173       0.29961
```

Compound **3** calculated at M062X/6-311g(2d,p)-SCRF(PCM, solvent=acetonitrile)

```
Excited State   1:      Singlet-A     2.8834 eV  429.99 nm  f=0.3829  <S**2>=0.000
    172 -> 173       0.69417
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) =  -2904.33320903

Excited State   2:      Singlet-A     2.8874 eV  429.40 nm  f=0.3839  <S**2>=0.000
    171 -> 173       0.69428

Excited State   3:      Singlet-A     3.6104 eV  343.41 nm  f=0.4705  <S**2>=0.000
    162 -> 173      -0.11014
    169 -> 173      -0.10607
    170 -> 173       0.59678
    171 -> 174      -0.20416
    172 -> 175       0.20411

Excited State   4:      Singlet-A     3.6168 eV  342.80 nm  f=0.4658  <S**2>=0.000
    163 -> 173       0.11118
    169 -> 173       0.59433
    170 -> 173       0.10574
    171 -> 175      -0.19756
    172 -> 174      -0.21629

Excited State   5:      Singlet-A     3.7179 eV  333.48 nm  f=0.0003  <S**2>=0.000
    169 -> 174       0.12043
    170 -> 175       0.11638
    171 -> 175       0.45609
    172 -> 174      -0.45518

Excited State   6:      Singlet-A     4.0646 eV  305.04 nm  f=0.4784  <S**2>=0.000
    168 -> 174      -0.11282
    169 -> 173       0.12137
    169 -> 175      -0.11040
    170 -> 173      -0.23765
    170 -> 174      -0.12229
    171 -> 174      -0.37996
    171 -> 175       0.15484
    172 -> 174       0.15115
    172 -> 175       0.38059

Excited State   7:      Singlet-A     4.0674 eV  304.82 nm  f=0.4843  <S**2>=0.000
    168 -> 175      -0.11613
    169 -> 173       0.24199
    169 -> 174      -0.11538
    170 -> 173       0.12112
    170 -> 175       0.11458
    171 -> 174       0.15443
    171 -> 175       0.38217
    172 -> 174       0.37553
    172 -> 175      -0.15219

Excited State   8:      Singlet-A     4.1804 eV  296.59 nm  f=0.0007  <S**2>=0.000
    168 -> 173       0.61365
    169 -> 174      -0.10453
    169 -> 175      -0.19904
    170 -> 174       0.19228
    170 -> 175      -0.10557

Excited State   9:      Singlet-A     4.4698 eV  277.38 nm  f=0.0001  <S**2>=0.000
    171 -> 174       0.47705
    172 -> 175       0.47793

Excited State  10:      Singlet-A     4.6617 eV  265.97 nm  f=0.8301  <S**2>=0.000
    162 -> 173      -0.13558
    168 -> 174      -0.23150
    169 -> 175      -0.23944
    170 -> 173       0.12544
    170 -> 174      -0.25477
    170 -> 177       0.14344
    172 -> 176       0.42234
```

Compound **4** calculated at M062X/6-311g(2d,p)-SCRF(PCM, solvent=acetonitrile)

```
Excited State   1:      Singlet-A     2.8549 eV  434.29 nm  f=0.2673  <S**2>=0.000
    169 -> 170       0.69058
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) =  -1990.13886376

Excited State   2:      Singlet-A     2.8580 eV  433.81 nm  f=0.2656  <S**2>=0.000
    168 -> 170       0.69068

Excited State   3:      Singlet-A     3.7086 eV  334.32 nm  f=0.0000  <S**2>=0.000
    168 -> 171      -0.22870
    168 -> 172       0.41234
    169 -> 171       0.41989
    169 -> 172       0.22847

Excited State   4:      Singlet-A     3.9177 eV  316.48 nm  f=0.0000  <S**2>=0.000
    166 -> 170       0.10096
    167 -> 170      -0.28257
    168 -> 172       0.41208
    169 -> 171      -0.40559

Excited State   5:      Singlet-A     3.9201 eV  316.28 nm  f=0.0000  <S**2>=0.000
    166 -> 170      -0.28216
    167 -> 170      -0.10130
    168 -> 171       0.40946
    169 -> 172       0.40741

Excited State   6:      Singlet-A     4.4309 eV  279.81 nm  f=0.7467  <S**2>=0.000
    167 -> 170       0.58875
    168 -> 172       0.19445
    169 -> 171      -0.19395
    169 -> 173      -0.11208

Excited State   7:      Singlet-A     4.4343 eV  279.60 nm  f=0.7520  <S**2>=0.000
    166 -> 170       0.58906
    168 -> 171       0.19678
    168 -> 173      -0.11075
    169 -> 172       0.19126

Excited State   8:      Singlet-A     4.5161 eV  274.54 nm  f=0.0001  <S**2>=0.000
    168 -> 171      -0.42549
    168 -> 172      -0.23583
    169 -> 171      -0.23329
    169 -> 172       0.42848

Excited State   9:      Singlet-A     4.7086 eV  263.31 nm  f=0.0001  <S**2>=0.000
    160 -> 171      -0.16695
    160 -> 172       0.27182
    160 -> 176      -0.15867
    160 -> 178      -0.11565
    160 -> 179      -0.11182
    161 -> 170       0.11171
    161 -> 171       0.19432
    162 -> 170       0.33112
    162 -> 172       0.13205
    162 -> 174      -0.24629

Excited State  10:      Singlet-A     4.7121 eV  263.12 nm  f=0.0017  <S**2>=0.000
    160 -> 170       0.28836
    160 -> 172       0.16491
    160 -> 174      -0.23027
    161 -> 170      -0.19537
    161 -> 171      -0.19081
    161 -> 174       0.15424
    161 -> 178      -0.10176
    162 -> 171      -0.22330
    162 -> 172       0.18818
    162 -> 176      -0.12714
    162 -> 178      -0.13310
```

Compound **5** calculated at M062X/6-311g(2d,p)-SCRF(PCM, solvent=acetonitrile)

```
Excited State   1:      Singlet-A     2.8243 eV  438.99 nm  f=0.2963  <S**2>=0.000
    201 -> 203       -0.10735
    202 -> 203        0.66943
    202 -> 206        0.17337
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) =  -2555.49937402

Excited State   2:      Singlet-A     2.8282 eV  438.38 nm  f=0.2986  <S**2>=0.000
    201 -> 203        0.66924
    201 -> 206        0.17373
    202 -> 203        0.10687

Excited State   3:      Singlet-A     3.5888 eV  345.47 nm  f=0.0001  <S**2>=0.000
    201 -> 204        0.34253
    201 -> 205        0.21340
    201 -> 207        0.24645
    201 -> 208       -0.11962
    202 -> 204       -0.21788
    202 -> 205        0.34011
    202 -> 207        0.11886
    202 -> 208        0.24745

Excited State   4:      Singlet-A     3.7843 eV  327.63 nm  f=0.0159  <S**2>=0.000
    200 -> 203        0.25665
    201 -> 204       -0.30562
    201 -> 205        0.21328
    201 -> 208        0.23078
    202 -> 204        0.21387
    202 -> 205        0.30956
    202 -> 207        0.23472

Excited State   5:      Singlet-A     3.7871 eV  327.38 nm  f=0.0176  <S**2>=0.000
    199 -> 203        0.25813
    201 -> 204        0.21585
    201 -> 205        0.30700
    201 -> 207        0.23429
    202 -> 204        0.30844
    202 -> 205       -0.21190
    202 -> 208       -0.23197

Excited State   6:      Singlet-A     3.9698 eV  312.32 nm  f=0.0028  <S**2>=0.000
    185 -> 203        0.17792
    185 -> 204       -0.41832
    185 -> 206       -0.28665
    185 -> 208       -0.18828
    185 -> 213        0.14013
    187 -> 204       -0.21787
    187 -> 206       -0.14506

Excited State   7:      Singlet-A     3.9708 eV  312.24 nm  f=0.0026  <S**2>=0.000
    185 -> 205       -0.18189
    185 -> 206       -0.13295
    186 -> 203        0.14135
    186 -> 204        0.14319
    186 -> 205       -0.31768
    186 -> 206       -0.23262
    186 -> 208        0.14277
    187 -> 203       -0.11192
    187 -> 204       -0.11187
    187 -> 205        0.24034
    187 -> 206        0.18427
    187 -> 208       -0.10935

Excited State   8:      Singlet-A     3.9717 eV  312.17 nm  f=0.0026  <S**2>=0.000
    186 -> 203        0.13068
    186 -> 204        0.19350
    186 -> 205        0.26478
    186 -> 206       -0.22223
    186 -> 207       -0.16155
```

```
    186 -> 215      -0.11467
    187 -> 203       0.13175
    187 -> 204       0.19513
    187 -> 205       0.27575
    187 -> 206      -0.22411
    187 -> 207      -0.16640
    187 -> 215      -0.11589

Excited State   9:      Singlet-A     4.2074 eV  294.68 nm  f=1.2026  <S**2>=0.000
    198 -> 205      -0.15673
    199 -> 203       0.10521
    199 -> 205      -0.13541
    200 -> 203       0.55605
    200 -> 204       0.13802
    201 -> 205      -0.12214
    201 -> 206       0.13886
    202 -> 204      -0.15285
    202 -> 205      -0.11082

Excited State  10:      Singlet-A     4.2102 eV  294.49 nm  f=1.2064  <S**2>=0.000
    198 -> 204       0.15906
    199 -> 203       0.55635
    199 -> 204      -0.13223
    200 -> 203      -0.10376
    200 -> 205      -0.13414
    201 -> 204      -0.13000
    201 -> 205      -0.11249
    202 -> 205       0.14418
    202 -> 206       0.14054
```

Compound **6** calculated at M062X/6-311g(2d,p)-SCRF(PCM, solvent=acetonitrile)

```
Excited State   1:      Singlet-A     2.7344 eV  453.43 nm  f=0.2206  <S**2>=0.000
    211 -> 212        0.70112
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) =  -2480.89814252

Excited State   2:      Singlet-A     2.7376 eV  452.89 nm  f=0.2202  <S**2>=0.000
    210 -> 212        0.70113

Excited State   3:      Singlet-A     3.6409 eV  340.53 nm  f=0.0000  <S**2>=0.000
    210 -> 213        0.46259
    210 -> 214        0.15051
    211 -> 213       -0.15218
    211 -> 214        0.46449

Excited State   4:      Singlet-A     3.9065 eV  317.38 nm  f=0.0342  <S**2>=0.000
    209 -> 212        0.22335
    210 -> 213       -0.11152
    210 -> 214        0.44006
    211 -> 213        0.44224
    211 -> 214        0.11346

Excited State   5:      Singlet-A     3.9068 eV  317.35 nm  f=0.0337  <S**2>=0.000
    208 -> 212        0.22292
    210 -> 213        0.44251
    210 -> 214        0.11265
    211 -> 213        0.11229
    211 -> 214       -0.43982

Excited State   6:      Singlet-A     4.4843 eV  276.49 nm  f=0.0000  <S**2>=0.000
    210 -> 213       -0.15376
    210 -> 214        0.47184
    211 -> 213       -0.47013
    211 -> 214       -0.15378

Excited State   7:      Singlet-A     4.6348 eV  267.51 nm  f=0.2405  <S**2>=0.000
    209 -> 212        0.58222
    210 -> 214       -0.16555
    211 -> 213       -0.16331
    211 -> 215        0.28934

Excited State   8:      Singlet-A     4.6362 eV  267.42 nm  f=0.2397  <S**2>=0.000
    208 -> 212        0.58245
    210 -> 213       -0.16415
    210 -> 215       -0.28902
    211 -> 214        0.16454

Excited State   9:      Singlet-A     4.8338 eV  256.50 nm  f=0.0000  <S**2>=0.000
    204 -> 212        0.15369
    207 -> 212        0.65731

Excited State  10:      Singlet-A     4.9681 eV  249.56 nm  f=1.4440  <S**2>=0.000
    208 -> 212        0.12465
    209 -> 212       -0.26402
    210 -> 215        0.14333
    211 -> 215        0.59833
```

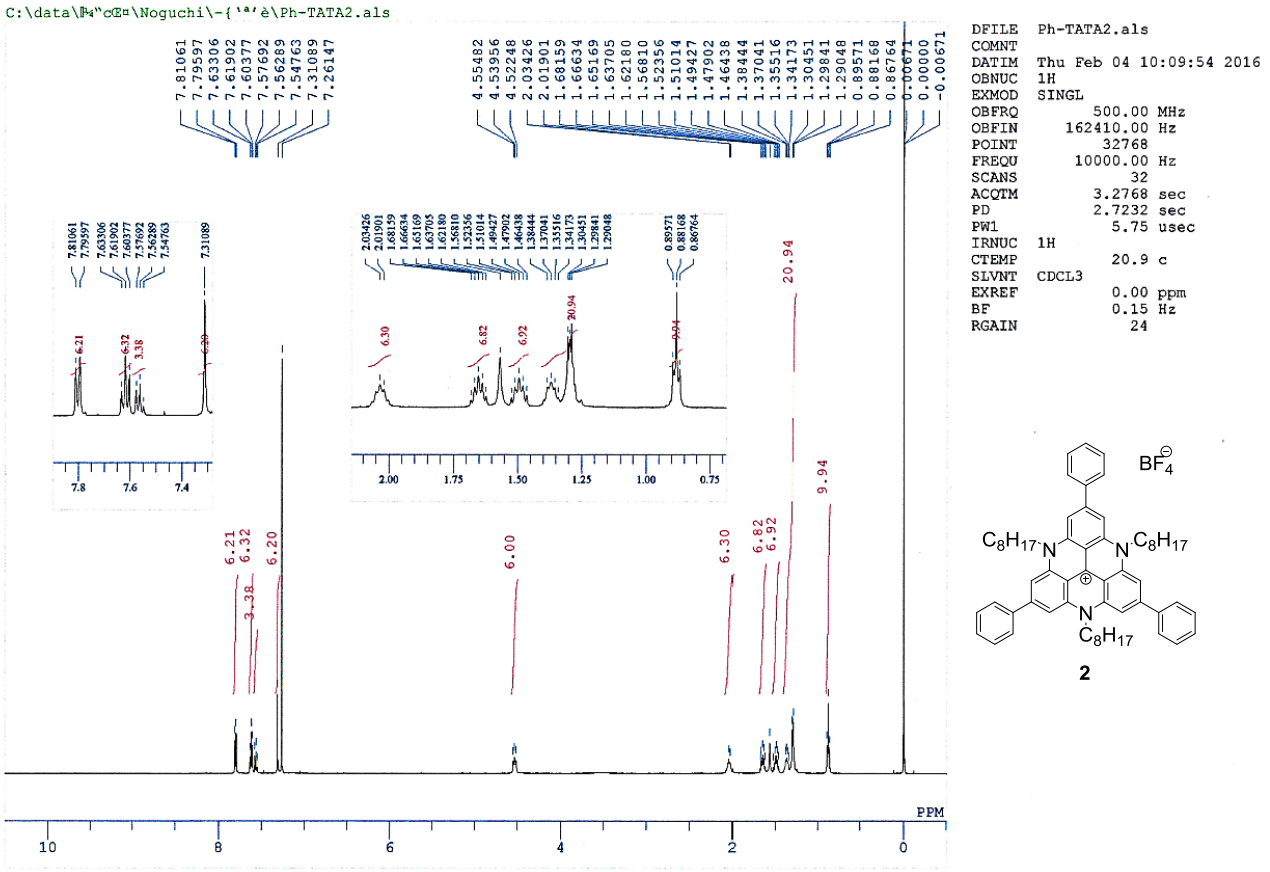


Figure S20. ^{1}H NMR spectrum of compound **2** at room temperature (500 MHz, $CDCl_3$).

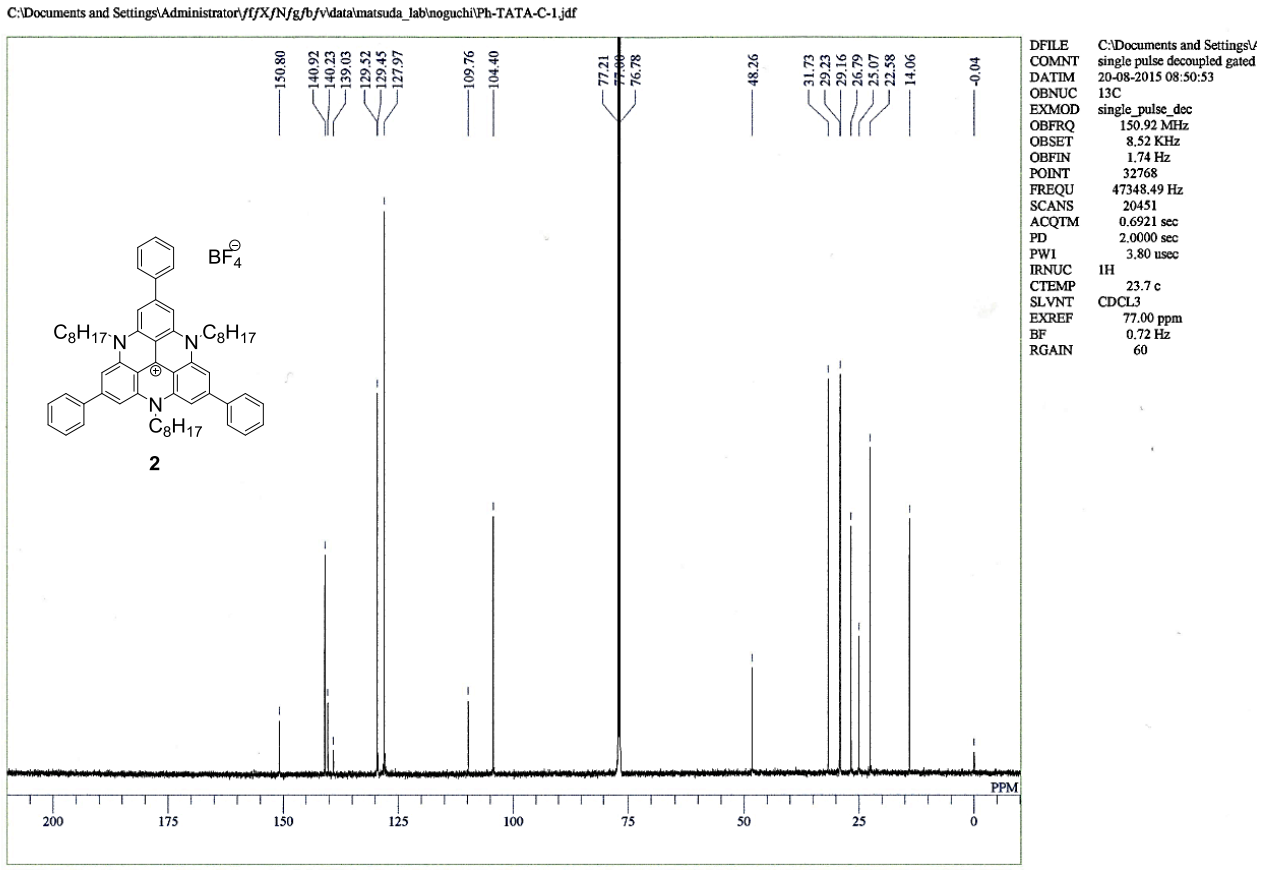


Figure S21. ^{13}C NMR spectrum of compound **2** at room temperature (151 MHz, $CDCl_3$).

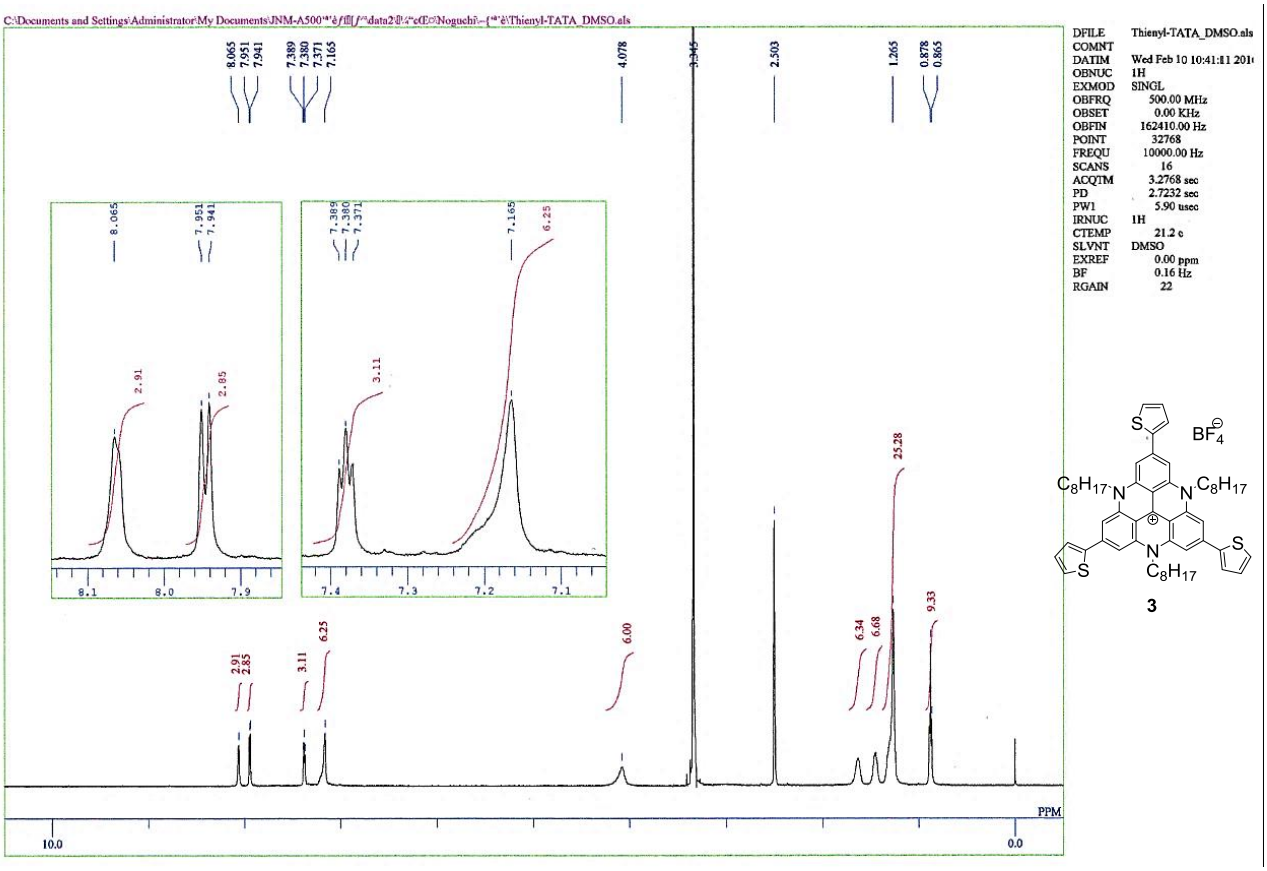


Figure S22. ^{1}H NMR spectrum of compound **3** at room temperature (500 MHz, $(CD_3)_2SO$).

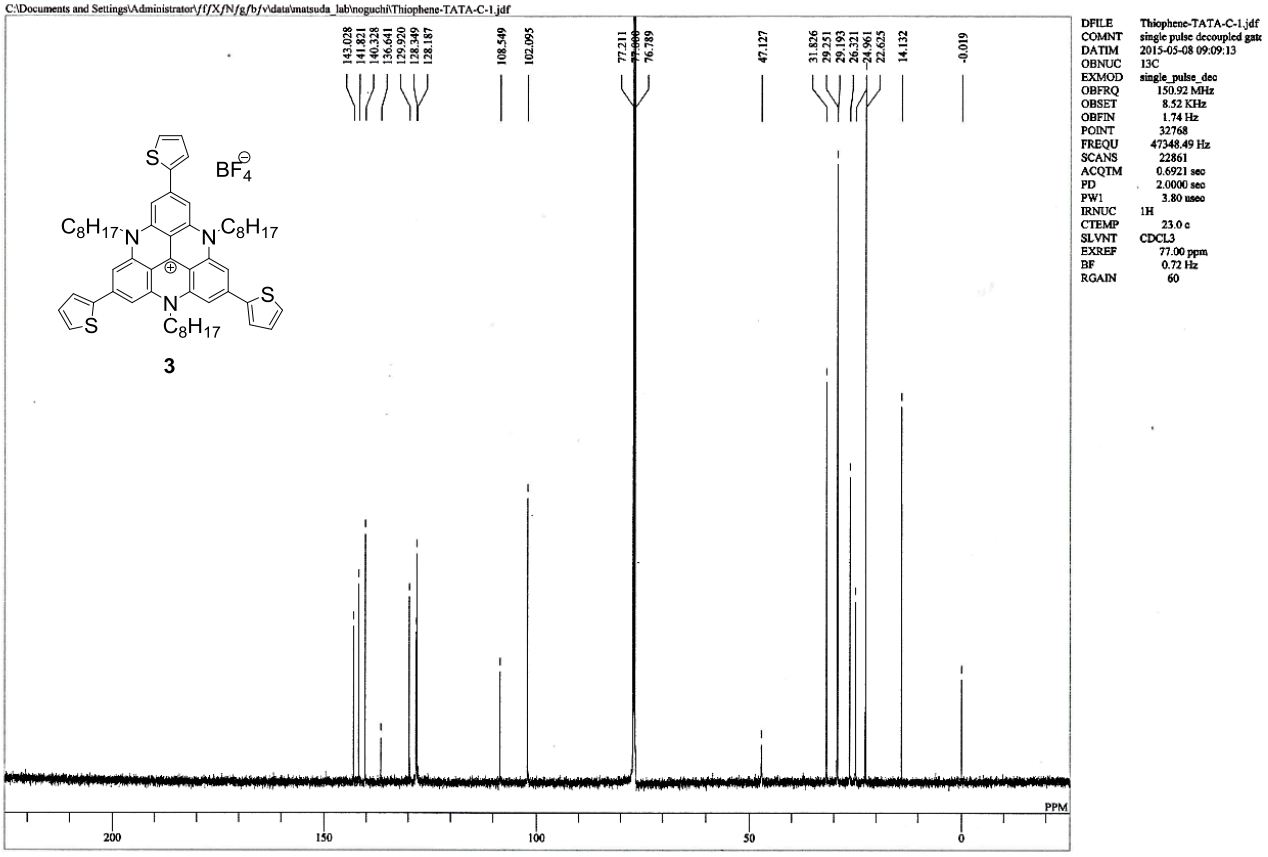


Figure S23. ^{13}C NMR spectrum of compound **3** at room temperature (151 MHz, $CDCl_3$).

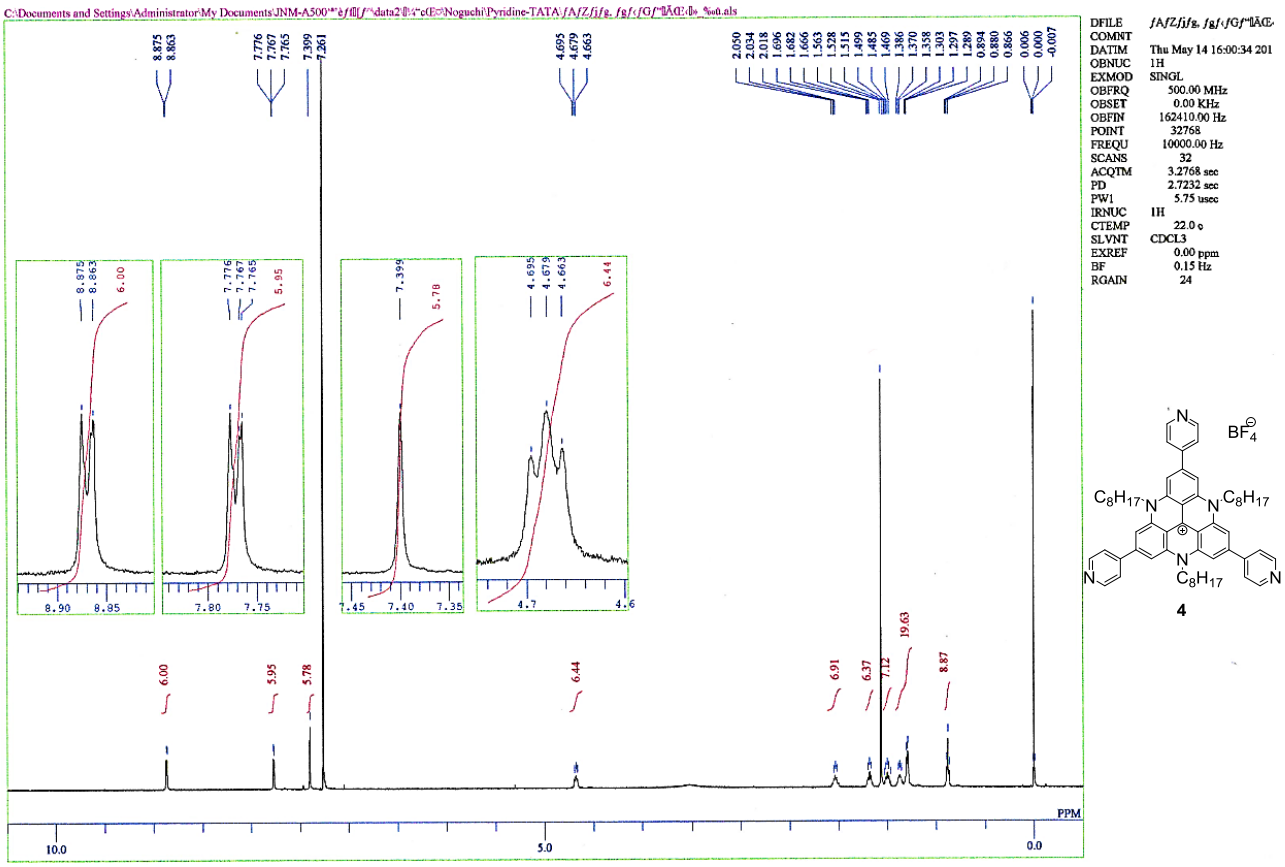


Figure S24. ^{1}H NMR spectrum of compound **4** at room temperature (500 MHz, $CDCl_3$).

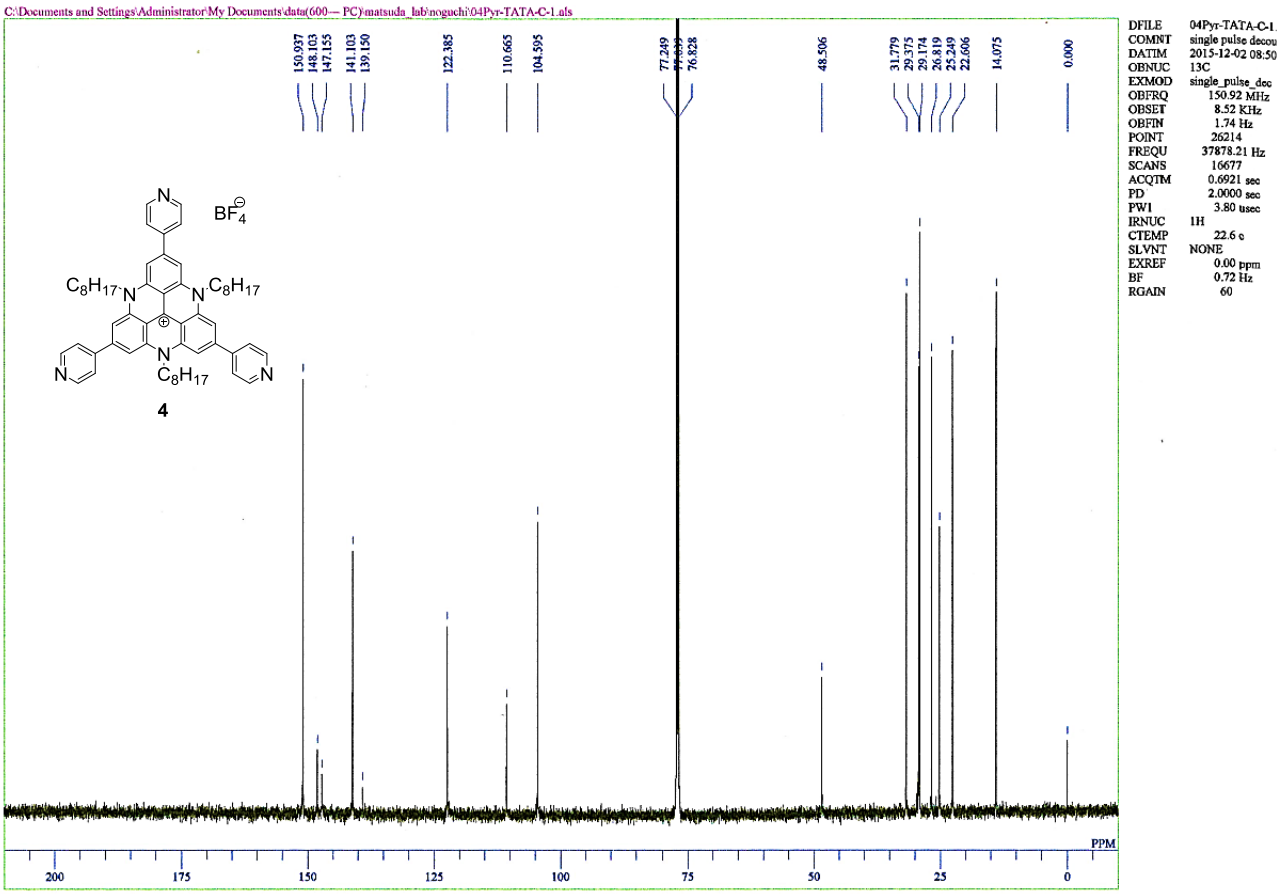


Figure S25. ^{13}C NMR spectrum of compound **4** at room temperature (151 MHz, $CDCl_3$).

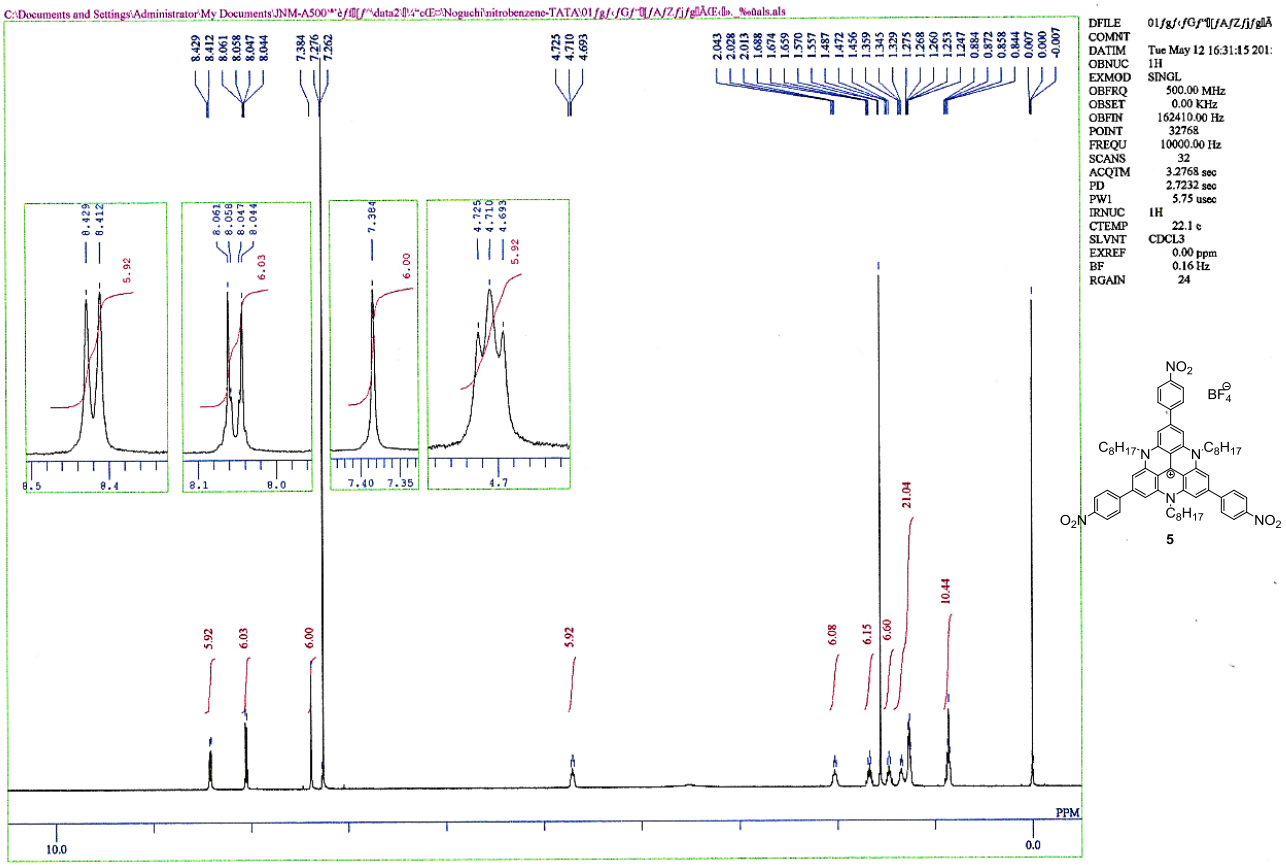


Figure S26. ^{1}H NMR spectrum of compound **5** at room temperature (500 MHz, $CDCl_3$).

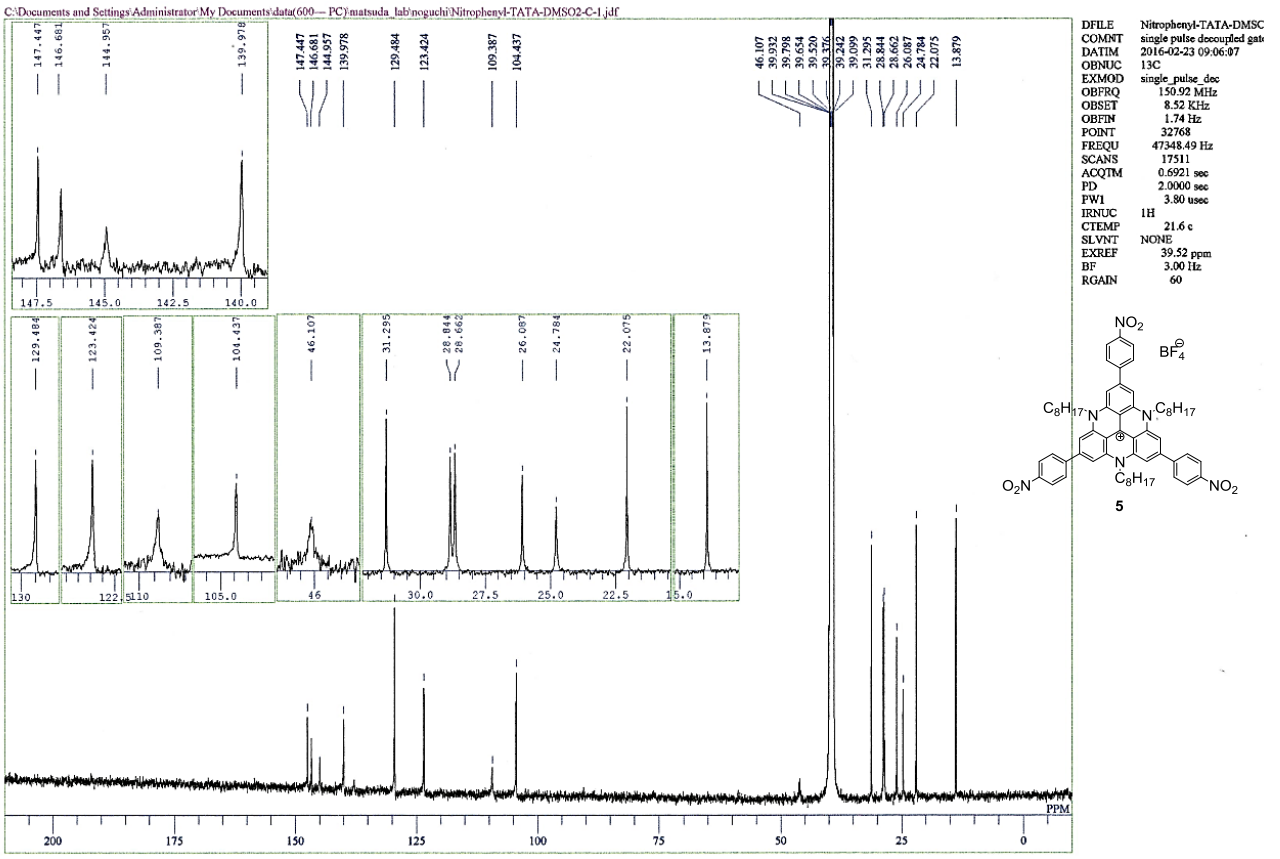


Figure S27. ^{13}C NMR spectrum of compound **5** at room temperature (151 MHz, $(CD_3)_2SO$).

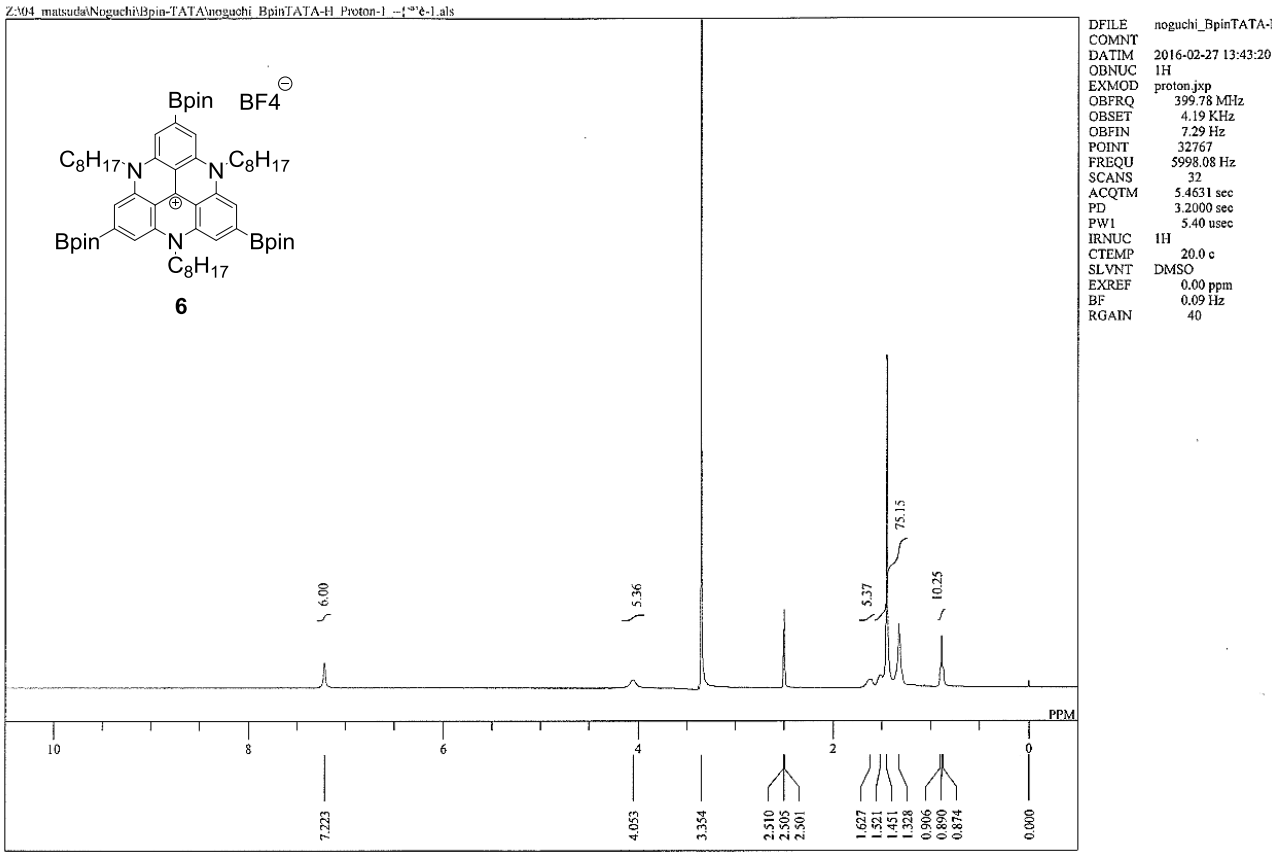
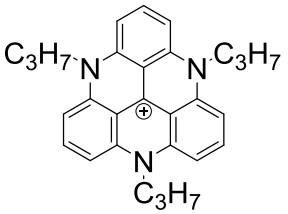


Figure S28. ^{1}H NMR spectrum of compound **6** at room temperature (400 MHz, $(CD_3)_2SO$).

Table S3. Cartesian Coordinates (Å) of optimized structure of compound **1** at the ground state (S_0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.706649	3.662196	0.043382
2	6	0	-0.008602	2.458982	0.119825
3	6	0	0.706340	1.224618	0.021638
4	6	0	2.126195	1.217273	-0.145116
5	6	0	2.809925	2.440706	-0.173403
6	6	0	2.090657	3.627774	-0.087567
7	7	0	-1.388735	2.429506	0.291090
8	6	0	-2.112136	1.241549	0.262621
9	6	0	-1.405991	0.000142	0.207207
10	6	0	0.002905	0.000000	0.089360
11	6	0	0.706093	-1.224760	0.021634
12	6	0	2.125949	-1.217702	-0.145124
13	7	0	2.784383	-0.000281	-0.285006
14	6	0	-2.112386	-1.241122	0.262621
15	7	0	-1.389225	-2.429225	0.291090
16	6	0	-0.009099	-2.458981	0.119818
17	6	0	-3.513419	1.221376	0.296657
18	6	0	-4.179270	0.000421	0.303831
19	6	0	-3.513664	-1.220669	0.296658
20	6	0	0.705908	-3.662339	0.043366
21	6	0	2.089923	-3.628196	-0.087592
22	6	0	2.809431	-2.441273	-0.173423
23	6	0	-2.110238	3.700392	0.520283
24	6	0	4.227684	-0.000427	-0.609471
25	6	0	5.144083	-0.000521	0.621266
26	6	0	6.623606	-0.000673	0.222326
27	6	0	-2.579729	4.392972	-0.766045
28	6	0	-3.317940	5.701452	-0.464316
29	6	0	-2.110985	-3.699964	0.520290
30	6	0	-2.580627	-4.392450	-0.766033
31	6	0	-3.319103	-5.700779	-0.464297
32	1	0	0.210351	4.621157	0.070937
33	1	0	3.886396	2.488504	-0.248827
34	1	0	2.632580	4.567953	-0.127020
35	1	0	-4.094740	2.131785	0.286767
36	1	0	-5.265133	0.000530	0.309937
37	1	0	-4.095167	-2.130962	0.286770
38	1	0	0.209417	-4.621200	0.070920
39	1	0	2.631656	-4.568484	-0.127054
40	1	0	3.885891	-2.489288	-0.248855
41	1	0	-1.452117	4.352620	1.097385
42	1	0	-2.953959	3.484786	1.178311
43	1	0	4.422402	-0.868628	-1.241683
44	1	0	4.422579	0.867737	-1.241681
45	1	0	4.920269	0.876510	1.240635
46	1	0	4.920088	-0.877505	1.240636
47	1	0	7.262883	-0.000737	1.110125
48	1	0	6.879812	-0.885923	-0.371601
49	1	0	6.879992	0.884523	-0.371603
50	1	0	-3.231582	3.712685	-1.327490
51	1	0	-1.713848	4.588035	-1.410235
52	1	0	-3.646178	6.182074	-1.390669
53	1	0	-2.675296	6.411901	0.068896
54	1	0	-4.207125	5.528266	0.153261
55	1	0	-2.954658	-3.484184	1.178323
56	1	0	-1.452992	-4.352325	1.097388
57	1	0	-1.714791	-4.587690	-1.410230
58	1	0	-3.232346	-3.712031	-1.327474
59	1	0	-3.647449	-6.181333	-1.390647
60	1	0	-4.208246	-5.527410	0.153288
61	1	0	-2.676599	-6.411360	0.068908



1

B3LYP/6-31g(d)
Int = Ultrafine

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    E = -1249.20165325 hartree
    # of imaginary frequencies = 0

     Zero-point correction=                          0.527096 (Hartree/Particle)
     Thermal correction to Energy=                   0.553403
     Thermal correction to Enthalpy=                 0.554347
     Thermal correction to Gibbs Free Energy=        0.471121
     Sum of electronic and zero-point Energies=          -1248.674557
     Sum of electronic and thermal Energies=             -1248.648250
     Sum of electronic and thermal Enthalpies=           -1248.647306
     Sum of electronic and thermal Free Energies=        -1248.730533
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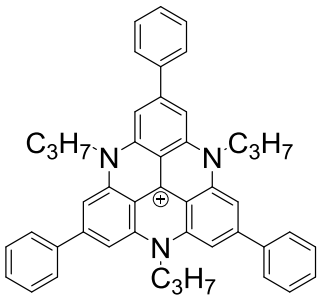
Table S4. Cartesian Coordinates (Å) of optimized structure of compound **2** at the ground state (S_0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.497928	-1.281066	0.104315
2	6	0	-2.099951	-1.275823	0.145337
3	6	0	-1.410793	-0.028242	0.062337
4	6	0	-2.142890	1.191593	-0.053994
5	6	0	-3.540672	1.146367	-0.046484
6	6	0	-4.216024	-0.079918	0.023220
7	7	0	-1.357723	-2.450166	0.255654
8	6	0	0.034655	-2.455742	0.185843
9	6	0	0.727755	-1.208228	0.160590
10	6	0	-0.000040	-0.000528	0.097450
11	6	0	0.683681	1.233443	0.051159
12	6	0	-0.053150	2.450293	-0.066720
13	7	0	-1.441461	2.390023	-0.172297
14	6	0	2.154103	-1.178034	0.187535
15	7	0	2.800838	0.055530	0.237104
16	6	0	2.109329	1.259898	0.121758
17	6	0	0.774481	-3.642004	0.162827
18	6	0	2.175861	-3.610662	0.142737
19	6	0	2.858064	-2.386388	0.164489
20	6	0	2.767555	2.492578	0.065887
21	6	0	2.041002	3.688552	-0.016587
22	6	0	0.640615	3.664631	-0.073063
23	6	0	2.942281	-4.880473	0.092039
24	6	0	-5.699377	-0.107284	0.007942
25	6	0	2.758736	4.986724	-0.046926
26	6	0	2.312625	6.035877	-0.869015
27	6	0	2.989384	7.253520	-0.899339
28	6	0	4.120068	7.448002	-0.103523
29	6	0	4.572098	6.415392	0.720477
30	6	0	3.900333	5.194880	0.746188
31	6	0	-6.409180	-1.013981	0.813963
32	6	0	-7.802358	-1.036877	0.802596
33	6	0	-8.511957	-0.159466	-0.019731
34	6	0	-7.819332	0.743914	-0.828306
35	6	0	-6.426312	0.772673	-0.812295
36	6	0	4.128169	-5.032987	0.830711
37	6	0	4.845992	-6.226520	0.786091
38	6	0	4.396410	-7.286756	-0.003338
39	6	0	3.221825	-7.147177	-0.745274
40	6	0	2.499050	-5.956886	-0.695435
41	6	0	-3.182091	-5.768088	-0.552419
42	6	0	-2.452341	-4.450429	-0.833413
43	6	0	-2.068014	-3.728302	0.465047
44	6	0	-3.406683	5.661972	0.478380
45	6	0	-2.635938	4.383080	0.822059
46	6	0	-2.192081	3.633444	-0.441504
47	6	0	6.579811	0.115525	-0.603758
48	6	0	5.071672	0.082245	-0.872332
49	6	0	4.264508	0.086495	0.433103
50	1	0	-4.054235	-2.206338	0.086186
51	1	0	-4.130012	2.051178	-0.047910
52	1	0	0.288076	-4.606057	0.165516
53	1	0	3.935722	-2.404301	0.097333
54	1	0	3.845395	2.551077	0.038006
55	1	0	0.116410	4.608683	-0.075277
56	1	0	1.451516	5.884742	-1.513960
57	1	0	2.638295	8.048382	-1.551084
58	1	0	4.645605	8.398209	-0.125362
59	1	0	5.444494	6.563006	1.350536
60	1	0	4.242714	4.408056	1.412513
61	1	0	-5.867071	-1.680514	1.478924
62	1	0	-8.334456	-1.734895	1.442502
63	1	0	-9.597795	-0.179546	-0.030365
64	1	0	-8.364278	1.422010	-1.478740
65	1	0	-5.896465	1.459141	-1.466775



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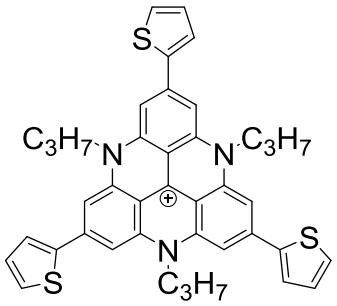
66	1	0	4.470966	-4.224602	1.470519
67	1	0	5.752946	-6.331391	1.374545
68	1	0	4.957679	-8.215828	-0.040063
69	1	0	2.871653	-7.963635	-1.370273
70	1	0	1.602404	-5.848624	-1.299354
71	1	0	-3.448517	-6.270294	-1.487286
72	1	0	-2.558346	-6.456999	0.029483
73	1	0	-4.108336	-5.601757	0.010242
74	1	0	-3.083628	-3.791824	-1.441991
75	1	0	-1.547494	-4.638377	-1.424167
76	1	0	-1.433037	-4.360337	1.088896
77	1	0	-2.952610	-3.517934	1.069410
78	1	0	-3.715765	6.183911	1.388929
79	1	0	-2.793390	6.355080	-0.109638
80	1	0	-4.310930	5.442640	-0.101730
81	1	0	-3.258246	3.721450	1.436652
82	1	0	-1.754770	4.625237	1.428377
83	1	0	-1.563327	4.267885	-1.069393
84	1	0	-3.052373	3.370903	-1.060425
85	1	0	7.140306	0.111691	-1.543378
86	1	0	6.869294	1.015433	-0.048199
87	1	0	6.903508	-0.754748	-0.020542
88	1	0	4.812137	-0.809105	-1.456186
89	1	0	4.778280	0.944567	-1.483012
90	1	0	4.497843	0.969274	1.031875
91	1	0	4.530546	-0.768584	1.057682

B3LYP/6-31g(d)
Int = Ultrafine
E = -1942.37953215 hartree
# of imaginary frequencies = 0

Zero-point correction=	0.769461 (Hartree/Particle)
Thermal correction to Energy=	0.810410
Thermal correction to Enthalpy=	0.811354
Thermal correction to Gibbs Free Energy=	0.693640
Sum of electronic and zero-point Energies=	-1941.610071
Sum of electronic and thermal Energies=	-1941.569122
Sum of electronic and thermal Enthalpies=	-1941.568178
Sum of electronic and thermal Free Energies=	-1941.685892

Table S5. Cartesian Coordinates (Å) of optimized structure of compound **3** at the ground state (S_0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.803470	3.256794	0.095334
2	6	0	-1.581237	1.878277	0.134352
3	6	0	-0.242363	1.388365	0.055819
4	6	0	0.850796	2.299970	-0.046254
5	6	0	0.593900	3.673069	-0.021014
6	6	0	-0.723866	4.153744	0.038855
7	7	0	-2.627849	0.962996	0.236409
8	6	0	-2.418215	-0.413066	0.162941
9	6	0	-1.080111	-0.906249	0.127210
10	6	0	0.001321	-0.001328	0.077052
11	6	0	1.325293	-0.486905	0.029155
12	6	0	2.415994	0.428545	-0.073447
13	7	0	2.143281	1.792629	-0.166887
14	6	0	-0.832948	-2.312330	0.135991
15	7	0	0.486212	-2.761725	0.194938
16	6	0	1.569788	-1.891878	0.086530
17	6	0	-3.478058	-1.322577	0.123626
18	6	0	-3.234297	-2.704849	0.091351
19	6	0	-1.916898	-3.192473	0.113621
20	6	0	2.886786	-2.353984	0.022501
21	6	0	3.960356	-1.451424	-0.041779
22	6	0	3.721782	-0.067565	-0.073580
23	6	0	-4.347747	-3.652260	0.026760
24	6	0	-0.988869	5.592534	0.042214
25	6	0	5.338574	-1.940684	-0.081379
26	6	0	-2.074818	6.259953	0.570358
27	6	0	-2.011363	7.670273	0.407450
28	6	0	-0.878829	8.075131	-0.247924
29	16	0	0.128765	6.737081	-0.677926
30	6	0	-4.352756	-4.932790	-0.486820
31	6	0	-5.616085	-5.577643	-0.398312
32	6	0	-6.571091	-4.789112	0.186516
33	16	0	-5.940226	-3.243995	0.639324
34	6	0	6.448955	-1.325260	-0.621750
35	6	0	7.641556	-2.087520	-0.494417
36	6	0	7.438802	-3.281123	0.146117
37	16	0	5.785034	-3.491984	0.605490
38	6	0	-6.187315	2.264019	-0.558990
39	6	0	-4.773680	1.747585	-0.846783
40	6	0	-4.000447	1.465529	0.448842
41	6	0	5.072579	4.235189	0.501694
42	6	0	3.929284	3.272441	0.839068
43	6	0	3.256360	2.727751	-0.428432
44	6	0	1.118545	-6.491075	-0.633074
45	6	0	0.855575	-5.006648	-0.907346
46	6	0	0.742999	-4.202529	0.395062
47	1	0	-2.803579	3.661299	0.061847
48	1	0	1.401465	4.390101	-0.005039
49	1	0	-4.500543	-0.980965	0.057296
50	1	0	-1.769457	-4.261629	0.116218
51	1	0	3.104320	-3.410890	-0.022600
52	1	0	4.572258	0.596824	-0.053371
53	1	0	-2.879898	5.757064	1.094854
54	1	0	-2.770457	8.355516	0.767164
55	1	0	-0.580177	9.080871	-0.511971
56	1	0	-3.484244	-5.388674	-0.949476
57	1	0	-5.809185	-6.581623	-0.758744
58	1	0	-7.607011	-5.027667	0.387432
59	1	0	6.405858	-0.368240	-1.130083
60	1	0	8.607308	-1.766702	-0.868017
61	1	0	8.165552	-4.046467	0.383841
62	1	0	-6.724817	2.460384	-1.491513
63	1	0	-6.772098	1.535190	0.014517
64	1	0	-6.165045	3.198416	0.014476
65	1	0	-4.220107	2.478121	-1.448958



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    66         1          0       -4.822607    0.831270   -1.447381
    67         1          0       -4.527178    0.733507    1.064487
    68         1          0       -3.929005    2.365712    1.063030
    69         1          0        5.542250    4.613207    1.414696
    70         1          0        5.851176    3.742221   -0.092644
    71         1          0        4.714337    5.099384   -0.070051
    72         1          0        3.180095    3.779930    1.458636
    73         1          0        4.305358    2.435149    1.439375
    74         1          0        3.979832    2.208146   -1.060165
    75         1          0        2.865205    3.542121   -1.041745
    76         1          0        1.194721   -7.050628   -1.570242
    77         1          0        2.055081   -6.637320   -0.082176
    78         1          0        0.311493   -6.940026   -0.041827
    79         1          0       -0.067163   -4.886870   -1.488186
    80         1          0        1.660517   -4.589140   -1.524114
    81         1          0        1.654464   -4.294874    0.989042
    82         1          0       -0.056088   -4.595033    1.027242

   B3LYP/6-31g(d)
   Int = Ultrafine
   E = -2904.64584028 hartree
   # of imaginary frequencies = 0

    Zero-point correction=                          0.668027 (Hartree/Particle)
    Thermal correction to Energy=                    0.708196
    Thermal correction to Enthalpy=                  0.709140
    Thermal correction to Gibbs Free Energy=         0.592222
    Sum of electronic and zero-point Energies=          -2903.977813
    Sum of electronic and thermal Energies=             -2903.937645
    Sum of electronic and thermal Enthalpies=           -2903.936701
    Sum of electronic and thermal Free Energies=        -2904.053618
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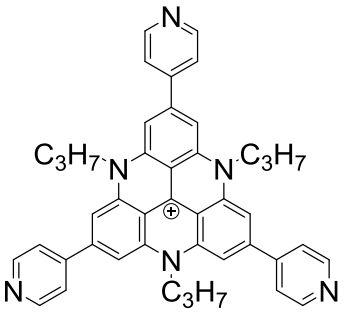
Table S6. Cartesian Coordinates (Å) of optimized structure of compound **4** at the ground state (S_0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.553958	-1.116765	0.107077
2	6	0	-2.156506	-1.177133	0.144863
3	6	0	-1.410690	0.037759	0.060608
4	6	0	-2.083784	1.291328	-0.057683
5	6	0	-3.482896	1.311436	-0.053359
6	6	0	-4.209931	0.117245	0.021361
7	7	0	-1.471102	-2.384249	0.256119
8	6	0	-0.081483	-2.454218	0.187330
9	6	0	0.670606	-1.241032	0.161943
10	6	0	0.000034	-0.000492	0.097060
11	6	0	0.740921	1.200306	0.050653
12	6	0	0.060533	2.449749	-0.069723
13	7	0	-1.327955	2.454957	-0.176964
14	6	0	2.097129	-1.276276	0.190781
15	7	0	2.800804	-0.075454	0.240912
16	6	0	2.166451	1.158687	0.123757
17	6	0	0.602100	-3.674536	0.161727
18	6	0	2.001957	-3.703959	0.145455
19	6	0	2.744064	-2.516966	0.171093
20	6	0	2.881953	2.360012	0.071073
21	6	0	2.208828	3.584588	-0.017049
22	6	0	0.810869	3.630792	-0.079329
23	6	0	2.708762	-5.009400	0.093971
24	6	0	-5.694416	0.159296	0.006407
25	6	0	2.987173	4.849087	-0.047375
26	6	0	4.122452	5.027260	0.756096
27	6	0	4.815720	6.235823	0.692387
28	7	0	4.467173	7.252929	-0.103967
29	6	0	3.385648	7.079441	-0.872326
30	6	0	2.617941	5.915025	-0.880212
31	6	0	-6.392310	1.048255	-0.823552
32	6	0	-7.786868	1.044362	-0.801055
33	7	0	-8.516622	0.238638	-0.021014
34	6	0	-7.848591	-0.606320	0.772681
35	6	0	-6.457155	-0.688561	0.822221
36	6	0	2.241740	-6.062583	-0.705169
37	6	0	2.945883	-7.266446	-0.719879
38	7	0	4.053705	-7.489922	-0.003661
39	6	0	4.495358	-6.484714	0.760893
40	6	0	3.871718	-5.239794	0.842543
41	6	0	-3.449789	-5.614123	-0.551884
42	6	0	-2.660958	-4.330986	-0.833665
43	6	0	-2.241077	-3.629471	0.465035
44	6	0	-3.138839	5.816091	0.473554
45	6	0	-2.427740	4.503055	0.817523
46	6	0	-2.020261	3.733695	-0.446365
47	6	0	6.580003	-0.192916	-0.598281
48	6	0	5.072029	-0.155642	-0.867936
49	6	0	4.265986	-0.113101	0.437407
50	1	0	-4.154717	-2.013945	0.097413
51	1	0	-4.030952	2.241833	-0.062648
52	1	0	0.072172	-4.615427	0.156446
53	1	0	3.820042	-2.587250	0.111390
54	1	0	3.961545	2.370228	0.052055
55	1	0	0.333168	4.599166	-0.090262
56	1	0	4.445750	4.253105	1.445477
57	1	0	5.692503	6.395379	1.316972
58	1	0	3.119962	7.912435	-1.520283
59	1	0	1.766979	5.832038	-1.549585
60	1	0	-5.863497	1.711294	-1.501662
61	1	0	-8.344781	1.719918	-1.446557
62	1	0	-8.455992	-1.249054	1.406927
63	1	0	-5.979615	-1.379740	1.510194
64	1	0	1.363789	-5.941382	-1.332624
65	1	0	2.604074	-8.090670	-1.342893



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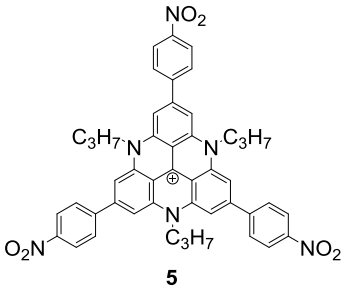
66	1	0	5.392525	-6.684615	1.343521
67	1	0	4.270326	-4.476817	1.504444
68	1	0	-3.740822	-6.101848	-1.486906
69	1	0	-2.857119	-6.331872	0.027455
70	1	0	-4.366263	-5.406362	0.012798
71	1	0	-3.262736	-3.643650	-1.440424
72	1	0	-1.767272	-4.559606	-1.427158
73	1	0	-1.635126	-4.290370	1.087599
74	1	0	-3.112901	-3.378555	1.072267
75	1	0	-3.422207	6.351536	1.384445
76	1	0	-2.494878	6.480118	-0.115051
77	1	0	-4.052990	5.638798	-0.105204
78	1	0	-3.079383	3.871193	1.433097
79	1	0	-1.535994	4.704475	1.423345
80	1	0	-1.362903	4.336909	-1.075455
81	1	0	-2.891233	3.511439	-1.065819
82	1	0	7.139361	-0.223319	-1.537920
83	1	0	6.911356	0.692668	-0.043292
84	1	0	6.862661	-1.077192	-0.014985
85	1	0	4.771349	-1.033969	-1.451861
86	1	0	4.819772	0.719133	-1.479366
87	1	0	4.539587	0.757340	1.036882
88	1	0	4.490804	-0.978785	1.063287

B3LYP/6-31g(d)
Int = Ultrafine
E = -1990.47542776 hartree
# of imaginary frequencies = 0

Zero-point correction=	0.733766 (Hartree/Particle)
Thermal correction to Energy=	0.774414
Thermal correction to Enthalpy=	0.775358
Thermal correction to Gibbs Free Energy=	0.657779
Sum of electronic and zero-point Energies=	-1989.741662
Sum of electronic and thermal Energies=	-1989.701014
Sum of electronic and thermal Enthalpies=	-1989.700070
Sum of electronic and thermal Free Energies=	-1989.817648

Table S7. Cartesian Coordinates (Å) of optimized structure of compound **5** at the ground state (S_0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.198417	-1.911752	0.106297
2	6	0	-1.825232	-1.646277	0.148285
3	6	0	-1.382011	-0.290817	0.074020
4	6	0	-2.327993	0.773338	-0.033010
5	6	0	-3.693369	0.468440	-0.022106
6	6	0	-4.123772	-0.862927	0.037117
7	7	0	-0.878847	-2.660858	0.271069
8	6	0	0.489218	-2.406111	0.207153
9	6	0	0.939215	-1.051589	0.177309
10	6	0	-0.000863	-0.000686	0.109633
11	6	0	0.441179	1.339037	0.059727
12	6	0	-0.510332	2.396272	-0.064610
13	7	0	-1.862683	2.079664	-0.164956
14	6	0	2.334922	-0.754640	0.208275
15	7	0	2.740836	0.576749	0.252742
16	6	0	1.837553	1.629363	0.130031
17	6	0	1.437750	-3.434431	0.190131
18	6	0	2.806871	-3.138896	0.175814
19	6	0	3.252432	-1.811227	0.195390
20	6	0	2.255530	2.963331	0.068550
21	6	0	1.317274	3.999144	-0.024223
22	6	0	-0.053807	3.719003	-0.082171
23	6	0	3.797556	-4.245052	0.132887
24	6	0	-5.578415	-1.165807	0.023229
25	6	0	1.781662	5.409383	-0.063777
26	6	0	4.970782	-4.184880	0.905521
27	6	0	5.901941	-5.217867	0.872869
28	6	0	5.653495	-6.315658	0.053572
29	6	0	4.504663	-6.408841	-0.727316
30	6	0	3.579668	-5.370951	-0.680712
31	6	0	-6.079260	-2.239107	-0.734327
32	6	0	-7.440263	-2.526295	-0.753789
33	6	0	-8.301680	-1.732034	-0.001932
34	6	0	-7.841705	-0.663052	0.762170
35	6	0	-6.478905	-0.383864	0.767842
36	6	0	2.841072	5.837313	0.755928
37	6	0	3.279958	7.156973	0.726222
38	6	0	2.652147	8.050519	-0.137296
39	6	0	1.602110	7.662871	-0.965182
40	6	0	1.170469	6.341198	-0.921406
41	6	0	-2.056087	-6.265053	-0.520874
42	6	0	-1.582474	-4.836375	-0.808710
43	6	0	-1.339105	-4.050209	0.486343
44	6	0	-4.403373	4.932747	0.473683
45	6	0	-3.406277	3.822473	0.822009
46	6	0	-2.832811	3.162322	-0.439038
47	6	0	6.447355	1.334226	-0.579997
48	6	0	4.972630	1.019462	-0.852744
49	6	0	4.174685	0.881132	0.450983
50	7	0	-9.747005	-2.032520	-0.015407
51	8	0	-10.480405	-1.304749	0.649265
52	8	0	-10.117584	-2.989793	-0.690430
53	7	0	3.114199	9.452263	-0.176325
54	8	0	2.530780	10.217094	-0.940467
55	8	0	4.050472	9.757863	0.558027
56	7	0	6.638392	-7.414686	0.011371
57	8	0	6.382688	-8.373329	-0.713171
58	8	0	7.646301	-7.295396	0.703575
59	1	0	-3.575832	-2.922435	0.148947
60	1	0	-4.441768	1.244363	-0.082643
61	1	0	1.139667	-4.472277	0.192049
62	1	0	4.314996	-1.628541	0.134249
63	1	0	3.303748	3.221223	0.043600
64	1	0	-0.743906	4.549446	-0.093152
65	1	0	5.141985	-3.337941	1.562781



5

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   66         1          0        6.803951   -5.191165    1.471811
   67         1          0        4.356449   -7.276457   -1.358449
   68         1          0        2.694873   -5.421758   -1.307794
   69         1          0       -5.403606   -2.835600   -1.339661
   70         1          0       -7.842224   -3.341913   -1.342227
   71         1          0       -8.545762   -0.077399    1.340429
   72         1          0       -6.107740    0.430235    1.382824
   73         1          0        3.305134    5.140059    1.446624
   74         1          0        4.086439    7.503850    1.360513
   75         1          0        1.149275    8.388655   -1.629441
   76         1          0        0.371768    6.022619   -1.584096
   77         1          0       -2.224547   -6.811775   -1.453372
   78         1          0       -1.315604   -6.824174    0.063042
   79         1          0       -2.996628   -6.270991    0.042379
   80         1          0       -2.324094   -4.308253   -1.420427
   81         1          0       -0.658932   -4.856155   -1.400238
   82         1          0       -0.597183   -4.549128    1.112391
   83         1          0       -2.245423   -4.006634    1.093198
   84         1          0       -4.802633    5.392291    1.382603
   85         1          0       -3.931442    5.725424   -0.118661
   86         1          0       -5.251309    4.545843   -0.103635
   87         1          0       -3.892170    3.059070    1.441949
   88         1          0       -2.585393    4.228019    1.425756
   89         1          0       -2.333006    3.898196   -1.071645
   90         1          0       -3.628722    2.742957   -1.057274
   91         1          0        7.001419    1.429228   -1.518404
   92         1          0        6.562848    2.275413   -0.029695
   93         1          0        6.925573    0.542832    0.009082
   94         1          0        4.885616    0.092368   -1.432221
   95         1          0        4.526464    1.808429   -1.470173
   96         1          0        4.237237    1.794482    1.045758
   97         1          0        4.592307    0.094900    1.082740

   B3LYP/6-31g(d)
   Int = Ultrafine
   E = -2555.86221637 hartree
   # of imaginary frequencies = 0

    Zero-point correction=                          0.776536 (Hartree/Particle)
    Thermal correction to Energy=                    0.825333
    Thermal correction to Enthalpy=                  0.826277
    Thermal correction to Gibbs Free Energy=         0.688023
    Sum of electronic and zero-point Energies=          -2555.085680
    Sum of electronic and thermal Energies=             -2555.036884
    Sum of electronic and thermal Enthalpies=           -2555.035939
    Sum of electronic and thermal Free Energies=        -2555.174193
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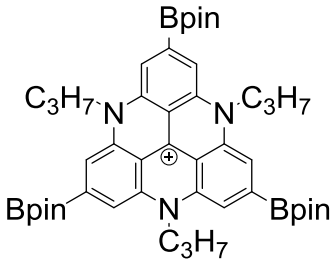
Table S8. Cartesian Coordinates (Å) of optimized structure of compound **6** at the ground state (S_0)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.888020	-2.355998	-0.088930
2	6	0	1.566537	-1.895462	-0.138663
3	6	0	1.325622	-0.488095	-0.066848
4	6	0	2.416081	0.428996	0.047961
5	6	0	3.722529	-0.074957	0.053351
6	6	0	3.953053	-1.453181	-0.006344
7	7	0	0.482403	-2.760746	-0.259217
8	6	0	-0.834290	-2.310978	-0.205385
9	6	0	-1.084474	-0.904319	-0.175489
10	6	0	-0.000320	0.000232	-0.108604
11	6	0	-0.243341	1.392119	-0.066100
12	6	0	0.854309	2.300729	0.047062
13	7	0	2.144483	1.789900	0.161970
14	6	0	-2.423662	-0.406335	-0.204866
15	7	0	-2.630407	0.969705	-0.256868
16	6	0	-1.584895	1.881176	-0.136000
17	6	0	-1.924383	-3.189771	-0.186930
18	6	0	-3.233651	-2.697761	-0.171287
19	6	0	-3.483365	-1.321592	-0.190111
20	6	0	-1.801468	3.263604	-0.081987
21	6	0	-0.722135	4.149892	-0.006135
22	6	0	0.592831	3.676380	0.047529
23	5	0	5.424525	-1.993357	0.023692
24	8	0	5.724083	-3.325811	0.027731
25	6	0	7.173553	-3.442481	-0.160408
26	6	0	7.687403	-2.016613	0.291441
27	8	0	6.514544	-1.170897	0.048575
28	6	0	7.674118	-4.610985	0.684297
29	6	0	7.393693	-3.730708	-1.650115
30	6	0	8.855467	-1.460459	-0.518368
31	6	0	7.986662	-1.918910	1.792030
32	5	0	-4.436755	-3.701758	-0.124510
33	8	0	-5.738400	-3.294539	-0.053153
34	6	0	-6.573641	-4.483982	-0.246618
35	6	0	-5.580229	-5.656979	0.125679
36	8	0	-4.271341	-5.057179	-0.151568
37	6	0	-7.799449	-4.360542	0.654297
38	6	0	-6.994920	-4.480437	-1.720862
39	6	0	-5.718554	-6.918660	-0.721922
40	6	0	-5.583928	-6.015030	1.616522
41	5	0	-0.989694	5.694278	0.022314
42	8	0	0.011907	6.617249	0.123471
43	6	0	-0.591779	7.934577	-0.100425
44	6	0	-2.116380	7.664881	0.221561
45	8	0	-2.243779	6.230008	-0.052141
46	6	0	0.098124	8.940043	0.817532
47	6	0	-0.327249	8.286869	-1.569008
48	6	0	-3.109477	8.411860	-0.664585
49	6	0	-2.474820	7.856023	1.699999
50	6	0	1.119452	-6.485120	0.579008
51	6	0	0.856014	-4.999933	0.847909
52	6	0	0.736102	-4.202853	-0.457705
53	6	0	5.074552	4.230213	-0.499999
54	6	0	3.926841	3.273294	-0.838434
55	6	0	3.260315	2.721293	0.428567
56	6	0	-6.181424	2.259565	0.583423
57	6	0	-4.767575	1.733671	0.851616
58	6	0	-4.003736	1.478060	-0.454371
59	1	0	3.120516	-3.411348	-0.102740
60	1	0	4.581471	0.579728	0.094262
61	1	0	-1.786337	-4.261286	-0.155190
62	1	0	-4.513031	-0.994044	-0.164015
63	1	0	-2.798358	3.680976	-0.087562
64	1	0	1.391215	4.404143	0.079715
65	1	0	7.238106	-5.544479	0.315101



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66	1	0	8.764032	-4.699081	0.616915
67	1	0	7.398043	-4.501263	1.735248
68	1	0	8.452554	-3.892800	-1.874684
69	1	0	6.843878	-4.636538	-1.922983
70	1	0	7.028634	-2.910997	-2.277066
71	1	0	9.112754	-0.461275	-0.153335
72	1	0	9.740615	-2.096696	-0.409156
73	1	0	8.613114	-1.380476	-1.580253
74	1	0	8.889959	-2.476872	2.057754
75	1	0	8.143433	-0.868802	2.056586
76	1	0	7.155349	-2.299493	2.393973
77	1	0	-8.402544	-3.503548	0.338616
78	1	0	-8.425195	-5.256918	0.582429
79	1	0	-7.522547	-4.212240	1.700278
80	1	0	-7.675389	-5.307764	-1.945301
81	1	0	-7.513270	-3.542302	-1.941094
82	1	0	-6.129510	-4.553827	-2.387152
83	1	0	-4.968837	-7.653370	-0.412158
84	1	0	-6.707636	-7.369941	-0.586763
85	1	0	-5.571878	-6.713287	-1.784475
86	1	0	-6.508159	-6.526133	1.903659
87	1	0	-4.744136	-6.685043	1.824187
88	1	0	-5.471038	-5.125531	2.244467
89	1	0	1.152135	9.030478	0.536996
90	1	0	-0.361218	9.930137	0.722979
91	1	0	0.052010	8.633505	1.864748
92	1	0	-0.694440	9.288560	-1.813273
93	1	0	0.751255	8.264053	-1.752265
94	1	0	-0.801298	7.569833	-2.246799
95	1	0	-4.130937	8.133394	-0.387287
96	1	0	-3.008472	9.494724	-0.532580
97	1	0	-2.969710	8.175489	-1.721625
98	1	0	-2.463933	8.913635	1.981427
99	1	0	-3.481830	7.465830	1.875946
100	1	0	-1.783187	7.316626	2.354948
101	1	0	1.201798	-7.040006	1.518565
102	1	0	0.308349	-6.937062	-0.004176
103	1	0	2.053103	-6.632376	0.023282
104	1	0	1.664640	-4.577929	1.456661
105	1	0	-0.065158	-4.879932	1.430827
106	1	0	-0.069612	-4.595924	-1.080317
107	1	0	1.644145	-4.298443	-1.055958
108	1	0	5.539356	4.615383	-1.412708
109	1	0	4.721471	5.089944	0.081761
110	1	0	5.855236	3.728939	0.084366
111	1	0	4.298502	2.438541	-1.444818
112	1	0	3.174359	3.787759	-1.448219
113	1	0	2.871980	3.531798	1.047938
114	1	0	3.986194	2.195989	1.051901
115	1	0	-6.713325	2.436756	1.523171
116	1	0	-6.158926	3.206082	0.030390
117	1	0	-6.770844	1.544091	-0.002153
118	1	0	-4.814946	0.803813	1.431095
119	1	0	-4.208092	2.451484	1.463454
120	1	0	-3.934746	2.390766	-1.049166
121	1	0	-4.534295	0.758069	-1.080064

B3LYP/6-31g(d)
Int = Ultrafine
E = -2481.29190910 hartree
# of imaginary frequencies = 0

Zero-point correction= 1.044650 (Hartree/Particle)
Thermal correction to Energy= 1.102176
Thermal correction to Enthalpy= 1.103120
Thermal correction to Gibbs Free Energy= 0.949954
Sum of electronic and zero-point Energies= -2480.247259
Sum of electronic and thermal Energies= -2480.189733
Sum of electronic and thermal Enthalpies= -2480.188789
Sum of electronic and thermal Free Energies= -2480.341955

References

(S1) J. C. Martin, R. G. Smith, *J. Am. Chem. Soc.*, 1964, **86**, 2252.

(S2) B. W. Laursen, F. C. Krebs, *Chem. Eur. J.*, 2001, **7**, 1773.