# Supporting Information

## *for*

# AIE-Active 9,10-Azaboraphenanthrene-Containing Viologens for Reversible Electrochromic and Electrofluorochromic Applications

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**Contents**

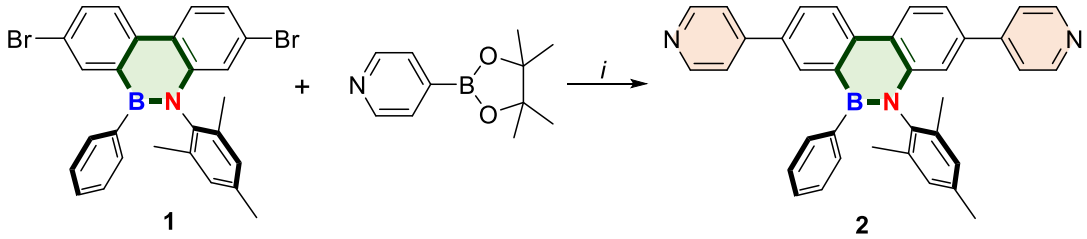
## 1. Materials and instrumentation

**General.** All reactions were performed using standard Schlenk and glovebox (Vigor) techniques under argon atmosphere. $Et_2O$, THF, hexanes and toluene were distilled from sodium/benzophenone prior to use. Trimethyltin chloride (99%), tetrakis(triphenylphosphine) palladium ($Pd(Ph_3P)_4$) (99%), potassium carbonate (99%), and were purchased from Energy Chemical Inc. Dimethyltin dichloride ($Me_2SnCl_2$) (99%) purchased from TCI. Phenylborondichloride ($PhBCl_2$) were obtained from Sigma-Aldrich. 4-Pyridineboronic acid pinacol ester (98%) were purchased from Energy Chemical. Unless otherwise indicated, all other reagents and solvents were used as commercially available without further purification. Compound **5** prepared according to literature procedures.[1] EC and EFC Device fabrication prepared according to literature procedures.[2] Column chromatographic purification of products was accomplished using 200-300 mesh silica gel.

NMR spectra were measured on a Bruker Avance-400 spectrometer in the solvents indicated; chemical shifts are reported in units (ppm) by assigning $CHCl_3$ resonance in the $^1H$ spectrum as 7.26 ppm, $CDCl_3$ resonance in the $^{13}C$ spectrum as 77.0 ppm. Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). UV-vis measurements were performed using DH-2000-BAL Scan spectrophotometer. Fluorescence measurements were conducted on an FLS920 system. Single crystal X-ray diffraction analysis was carried out on a Bruker Apex Duo instrument. The cyclic voltammetry (CV) were measured using a CHI660E B157216 set up. EPR was measured using a Bruker EMX PLUS6/1 instrument at room temperature in dry degassed DMF.

## 2. Experimental procedures and data

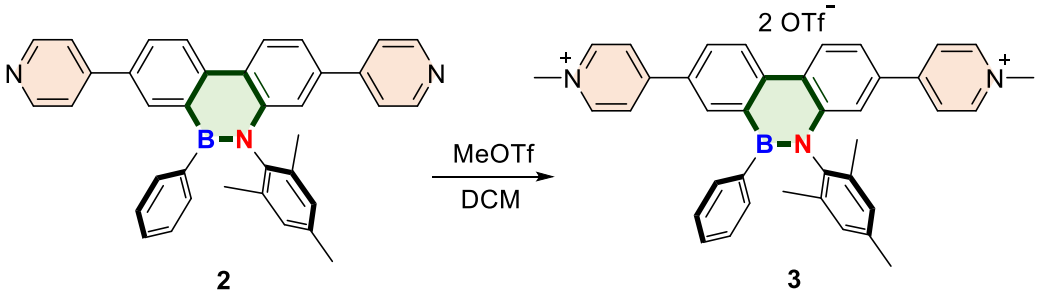
### 2.1 Synthesis of 5-mesityl-6-phenyl-3,8-di(pyridin-4-yl)-5,6-dihydrodibenzo[c,e][1,2]azaborinine (2):




*i*) Suzuki cross-coupling: $Pd(PPh_3)_4$, 5 mol%, $Aliquant_{336}$, 10 mol%, $K_2CO_3$ (2M),Toluene;

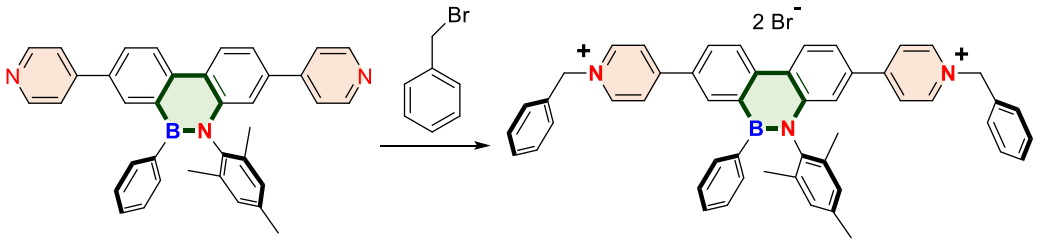
Compound **1** (0.212g, 0.4 mmol), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) pyridine (0.246 g, 1.2 mmol), $Pd(PPh_3)_4$ (24 mg, 5 mmol%), Aliquant336 (16 mg, 10 mmol%) and $Ar_2$-sparged aqueous potassium carbonate (2.0 M, 3.6 mL, 2.0 mmol) were dissolved in 8 mL of toluene in a Schlenk flask. The reaction mixture was stirred for 48 h at 110 °C. The reaction mixture was then cooled to room temperature, the solvent was removed in vacuo, the product was purified via column chromatography (silica gel, Petroleum ether/ ethyl acetate = 1 : 1) afforded the white title compound, recrystallized from hexanes and $CH_2Cl_2$ at -30 °C to give **2** as white crystals (0.108g, 51%). $^1$H NMR (400 MHz, $CDCl_3$): δ 8.70 (dd, *J* = 8.8 Hz, 2.0 Hz, 2H, Ar*H*), 8.64 (dd, *J* = 4.4 Hz, 1.6 Hz, 2H, Ar*H*), 8.61 (dd, *J* = 4.4 Hz, 1.6 Hz, 2H, Ar*H*), 8.22 (d, *J* = 2.0 Hz, 1H, Ar*H*), 8.10 (dd, *J* = 4.8 Hz, 2.0 Hz, 1H, Ar*H*), 7.63 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H, Ar*H*), 7.53 (dd, *J* = 4.4 Hz, 1.6 Hz, 2H, Ar*H*), 7.36-7.24 (m, 5H, Ar*H*), 7.10 (d, *J* = 1.6 Hz, 1H, Ar*H*), 6.90 (s, 1H, Ar*H*), 2.30 (s, 3H, C*H*$_3$), 1.93 (s, 6H, C*H*$_3$). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 150.3, 150.3, 147.9, 147.8, 140.8, 139.1, 138.5, 138.3, 136.9, 136.0, 135.8, 134.6, 132.5, 129.7, 129.4, 127.7, 127.0, 125.2, 124.6, 123.1, 121.6, 120.7, 115.4 (Ar-C), 21.1, 18.0 ($CH_3$-C). $^{11}$B NMR (128 MHz, $CDCl_3$) δ 37.7 (bs). HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{37}H_{30}BN_3$, 528.2606, found, 528.2608. UV/vis (in DMF): $\lambda_{max}$ (ε) = 352 nm ($2.27 \times 10^4\ M^{-1}\ cm^{-1}$). Fluorescence emission (in DMF) ($\lambda_{ex}$ = 350 nm): $\lambda_{emis}$ = 515 nm. Lifetime (in DMF): τ = 8.22 ns. Mp (°C): 243.1-244.4.

### 2.2 Synthesis of 4,4'-(9-mesityl-10-phenylphenanthrene-2,7-diyl)bis(1-methylpyridin-1-ium)·OTf (3) :



To a suspension of **2** (105 mg, 0.2 mmol) in dichloromethane at 0 °C was added methyl triflate (328 mg, 2.0 mmol). The mixture was brought to room temperature and left to stir overnight. The precipitate was collected via vacuum filtration and washed with DCM to afford the title product **3** as a white powder (152 mg, 86%). $^{1}$H NMR (400 MHz, DMSO): δ 9.15 (dd, *J* = 8.8 Hz, 2.8 Hz, 2H, Ar*H*), 8.98-8.94 (m, 4H, Ar*H*), δ 8.52 (dd, *J* = 8.8 Hz, 2.0 Hz, 1H, Ar*H*), 8.37 (d, *J* = 6.4 Hz, 2H, Ar*H*), 8.22 (s, 1H, Ar*H*), 8.15 (d, *J* = 6.8 Hz, 2H, Ar*H*), 8.02 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.33-7.27 (m, 5H, Ar*H*), 7.08 (s, 1H, Ar*H*), 7.00 (s, 2H, Ar*H*), 4.32 (s, 3H, C*H*$_3$), 4.30 (s, 3H, C*H*$_3$), 2.27 (s, 3H, C*H*$_3$), 1.90 (s, 6H, C*H*$_3$). $^{19}$F NMR (376 MHz, DMSO), δ -77.75 ppm; $^{13}$C NMR (100 MHz, DMSO) δ 154.6, 154.4, 146.3, 146.3, 141.1, 140.7, 138.3, 137.1, 135.7, 134.7, 133.2, 132.6, 131.5, 129.9, 128.6, 127.7, 126.2, 125.4, 125.0, 124.9, 122.6, 119.5, 116.1 (Ar-C), 47.7, 21.1, 18.0 ($CH_3$-C). $^{11}$B NMR (128 MHz, DMSO) δ 31.3 (bs). HRMS (ESI) *m*/*z*: $[M]^+$ calcd for $C_{39}H_{36}BN_3^{2+}$, 278.6496, found, 278.6483. UV/vis (in DMF): $\lambda_{max}$ (ε) = 381 nm ($3.22 \times 10^4$ $M^{-1}$ $cm^{-1}$). Lifetime (solid): τ = 15.0 ns. Mp (°C): 256.2-258.0.

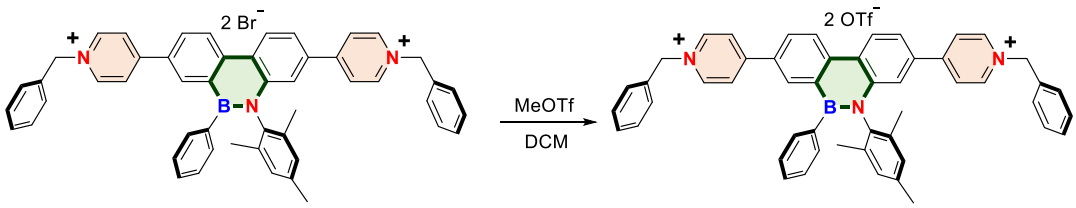
### 2.3 Synthesis of 4,4'-(5-mesityl-6-phenyl-5,6-dihydrodibenzo[c,e][1,2]azaborinine-3,8-diyl)bis(1-benzylpyridin-1-ium)·Br (4a) :




**2** **4a**

To a suspension of **2** (105 mg, 0.2 mmol) at room temperature was added benzyl bromide (2 mL), the temperature was allowed to rise to 60 °C and left to stir overnight. The precipitate was collected via vacuum filtration and washed with DCM to afford the title product **4a** as a yellow powder (128 mg, 90%). $^{1}$H NMR (400 MHz, DMSO): δ 9.23-9.18 (m, 4H, Ar*H*), 9.14 (dd, *J* = 8.8 Hz, 2.4 Hz, 2H, Ar*H*), 8.53 (d, *J* = 8.8 Hz, 1H, Ar*H*), 8.41 (d, *J* = 6.4 Hz, 2H, Ar*H*), 8.22-8.20 (m, 3H, Ar*H*), 8.04 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.59-7.57 (m, 4H, Ar*H*), 7.46-7.43 (m, 6H, Ar*H*), 7.31-7.27 (m, 5H, Ar*H*), 7.12 (d, *J* = 1.6 Hz, 1H, Ar*H*), 6.98 (s, 2H, Ar*H*), 5.86 (s, 2H, C*H*$_2$), 5.85 (s, 2H, C*H*$_2$), 2.26 (s, 3H, C*H*$_3$), 1.89 (s, 6H, C*H*$_3$). $^{13}$C NMR (100 MHz, DMSO) δ 154.9, 154.5, 145.0, 144.9, 140.7, 140.4, 137.8, 136.8, 136.6, 135.0, 134.4, 134.3, 134.2, 132.6, 132.1, 131.3, 129.4, 129.4, 129.3, 129.0, 128.9, 128.1, 127.2, 125.9, 125.2, 125.0, 122.3, 115.7, 62.5, 39.5, 20.7, 17.6. $^{11}$B NMR (128 MHz, DMSO) δ 37.0 (bs). HRMS (ESI) *m*/*z*: $[M]^+$ calcd for $C_{51}H_{44}BN_3^{2+}$, 354.6809, found, 354.6797. UV/vis (in DMF): $\lambda_{max}$ (ε) = 383 nm ($2.65 \times 10^4$ $M^{-1}$ $cm^{-1}$). Lifetime (solid): τ = 3.6 ns. Mp (°C): 266.2-268.1.

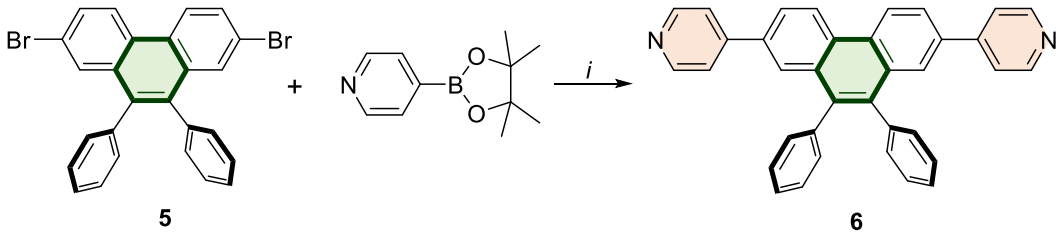
## 2.4 Synthesis of 4,4'-(5-mesityl-6-phenyl-5,6-dihydrodibenzo[c,e][1,2]azaborinine-3,8-diyl)bis(1-benzylpyridin-1-ium)·OTf (4b):




**4a** **4b**

To a suspension of **4a** (100 mg, 0.14 mmol) in dichloromethane at 0 °C was added methyl triflate (328 mg, 2.0 mmol). The mixture was brought to room temperature and left to stir overnight. The precipitate was collected via vacuum filtration and washed with hexane to afford the title product **4b** as a yellow powder (114 mg, 81%). $^{1}$H NMR (400 MHz, DMSO): δ 9.18-9.13 (m, 6H, Ar*H*), 8.51 (dd, *J* = 6.8 Hz, 1.6 Hz, 1H, Ar*H*), 8.40 (d, *J* = 6.4 Hz, 2H, Ar*H*), 8.22 (d, *J* = 1.6 Hz, 1H, Ar*H*), 8.19 (d, *J* = 6.8 Hz, 2H, Ar*H*), 8.04 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.56-7.54 (m, 4H, Ar*H*), 7.48-7.43 (m, 6H, Ar*H*), 7.31-7.23 (m, 5H, Ar*H*), 7.12 (d, *J* = 1.6 Hz, 1H, Ar*H*), 6.98 (s, 2H, Ar*H*), 5.82 (s, 2H, C$H_2$), 5.80 (s, 2H, C$H_2$), 2.25 (s, 3H, C$H_3$), 1.88 (s, 6H, C$H_3$). $^{19}$F NMR (376 MHz, DMSO), δ -77.75 ppm; $^{13}$C NMR (100 MHz, DMSO) δ 155.4, 155.1, 145.5, 145.4, 141.2, 140.8, 138.2, 137.1, 135.4, 134.7, 134.7, 134.6, 133.1, 132.5, 129.9, 129.8, 129.7, 129.4, 129.3, 128.5, 128.5, 127.6, 126.9, 126.4, 125.7, 125.4, 122.8, 119.6, 116.2, 63.2, 63.1, 21.1, 18.0. $^{11}$B NMR (128 MHz, DMSO) δ 29.0 (bs). HRMS (ESI) *m/z*: $[M]^+$ calcd for $C_{51}H_{44}BN_3^{2+}$, 354.6809, found, 354.6797. UV/vis (in DMF): $\lambda_{max}$ (ε) = 385 nm ($2.39 \times 10^4$ $M^{-1}$ $cm^{-1}$). Lifetime (solid): τ = 4.0 ns. Mp (°C): 178.2-180.1.

## 2.5 Synthesis of 4,4'-(9,10-diphenylphenanthrene-2,7-diyl)dipyridine (6):



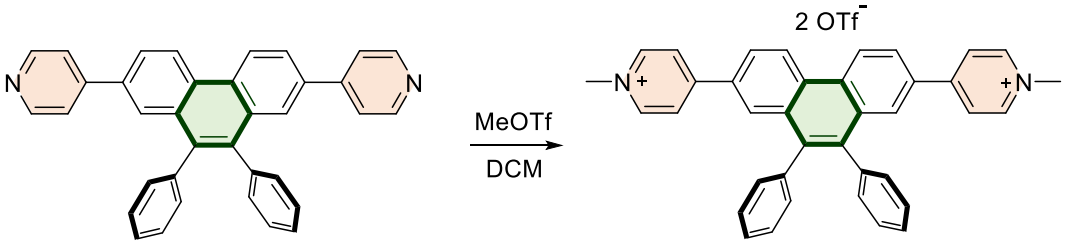

**5** **6**

*i*) Suzuki cross-coupling: $Pd(PPh_3)_4$, 5 mol%, $Aliquant_{336}$, 10 mol%, $K_2CO_3$ (2M),Toluene;

Monomer **5** (0.256g, 0.57 mmol), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) pyridine (0.35g, 1.71 mmol), $Pd(PPh_3)_4$ (35 mg, 5 mmol%), $Cs_2CO_3$ (0.69 g, 2.12 mmol), and a 1:1 mixture of dry PhMe/DMF (16 mL) was heated to 130 ºC under microwave for 1 h before the hot reaction mixture was rendered acidic (pH 2–3) by adding dropwise concentrated HCl, which caused the crude product to precipitate from solution. Then, the reaction mixture was cooled to room temperature, filtered, and washed with $CH_2Cl_2$. The solid was dispersed in $H_2O$ at 80 ºC and the insoluble material was filtered off before an aqueous NaOH solution (10 M) was added dropwise to the filtrate until the pH was 8~9, resulting in precipitation of the desired product. The

solid was filtered and washed with $H_2O$, dissolved in $CHCl_3$, and filtered through Celite. The filtrate was concentrated in vacuo, yielding pure **6** (80 mg, 30%) as a white solid. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.94 (d, *J* = 8.8 Hz, 2H, Ar*H*), 8.63 (d, *J* = 5.2 Hz, 4H, Ar*H*), 7.99 (dd, *J* = 8.4 Hz, 2.0 Hz, 2H, Ar*H*), 7.87 (d, *J* = 2.0 Hz, 2H, Ar*H*), 7.47 (d, *J* = 6.0 Hz, 4H, Ar*H*), 7.31-7.19 (m, 10H, Ar*H*); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 150.0, 148.1, 138.7, 138.2, 136.4, 132.6, 130.9, 130.0, 127.9, 127.0, 126.4, 125.1, 123.8, 121.7. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{36}H_{25}N_2$, 485.2012, found, 485.2013. UV/vis (in DMF): $\lambda_{max}$ (ε) = 286 nm ($4.21 \times 10^4$ $M^{-1}$ $cm^{-1}$). Fluorescence emission (in DMF) ($\lambda_{ex}$ = 330 nm): $\lambda_{emis}$ = 397 nm. Lifetime (in DMF): τ = 15.6 ns. Mp (°C): > 300.

**2.6 Synthesis of 4,4'-(9,10-diphenylphenanthrene-2,7-diyl)bis (1-methylpyridin-1-ium)·OTf (7) :**




**6** **7**

To a suspension of **6** (59 mg, 0.12 mmol) in dichloromethane at 0 °C was added methyl triflate (164 mg, 1 mmol). The mixture was brought to room temperature and left to stir overnight. The precipitate was collected via vacuum filtration and washed with DCM to afford the title product **7** as a white powder (93 mg, 92%). $^1$H NMR (400 MHz, DMSO): δ 9.39 (d, *J* = 4.4 Hz, 2H, Ar*H*), 8.98 (d, *J* = 6.4 Hz, 4H, Ar*H*), 8.38 (d, *J* = 8.4 Hz, 2H, Ar*H*), 8.29 (d, *J* = 6.4 Hz, 4H, Ar*H*), 7.90 (s, 2H, Ar*H*), 7.36-7.28 (m, 10H, Ar*H*), 4.32 (s, 6H, C*H*$_3$). $^{19}$F NMR (376 MHz, DMSO), δ -77.75 ppm; $^{13}$C NMR (100 MHz, DMSO) δ 154.6, 146.3, 143.2, 138.7, 138.2, 133.9, 132.8, 131.3, 131.2, 128.4, 127.8, 127.6, 127.4, 126.6, 126.1, 125.1, 122.8, 119.6 (Ar-C), 47.7 ($CH_3$-C). HRMS (ESI) *m*/*z*: $[M]^+$ calcd for $C_{38}H_{30}N_2^{2+}$, 257.1199, found, 257.1190. UV/vis (in DMF): $\lambda_{max}$ (ε) = 347 nm ($3.72 \times 10^4$ $M^{-1}$ $cm^{-1}$). Fluorescence emission (in DMF) ($\lambda_{ex}$ = 365 nm): $\lambda_{emis}$ = 506 nm. Lifetime (in DMF): τ = 18.0 ns. Mp (°C): > 300.

## 3. DFT computations

All calculations were carried out with the GAUSSIAN 09 program package.[3] The geometries for the ground state of compounds **2**, **3**, **4a**, **4b**, **6** and **7** were optimized at the B3LYP level with the 6-31G* basis set.[4-6]

The simulated UV–Vis spectra for optimized molecules were performed at the time dependent density functional theory (TD-DFT)[7, 8] at the ground-state equilibrium geometries were determined using the B3LYP,[4-6] in association with the 6-31G* basis set.

It should be pointed out that the structures of all stationary points were fully optimized, and frequency calculations were performed at the same level. The frequency calculations confirmed the nature of all revealed equilibrium geometries: there were no imaginary frequencies.

## 4. Single-crystal X-ray structure determination

**X-ray Crystallography.** Crystals of appropriate quality for X-ray diffraction studies were removed from a vial (in a glove box) and immediately covered with a thin layer of hydrocarbon oil (Paratone-N). A suitable crystal was then selected, attached to a glass fiber, and quickly placed in a glass vial. All data were collected using a Bruker APEX II CCD detector/D8 diffractometer using Mo/Cu Kα radiation. The data were corrected for absorption through Gaussian integration from indexing of the crystal faces. Structures were solved using the direct methods programs SHELXS-97, and refinements were completed using the program SHELXL-97.

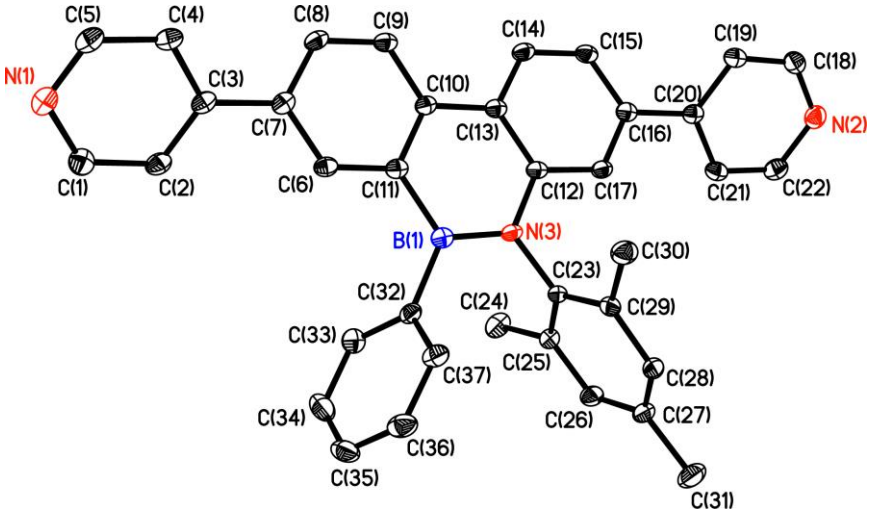



**Figure S1.** Molecular Structure of **2** (CCDC 1878987) with thermal ellipsoids presented at a 50% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): N(1)—C(12), 1.412(4); N(1)—B(1), 1.414(5); N(1)—C(19), 1.452(5); B(1)—C(1), 1.551(6); B(1)—C(14), 1.576(5). Bond angles (deg): C(12)—N(1)—B(1), 123.2(3); C(12)—N(1)—C(19), 116.1(3); B(1)—N(1)—C(19), 120.7(3); N(1)—B(1)—C(1), 116.0(3); N(1)—B(1)—C(14), 121.8(3); C(1)—B(1)—C(14), 122.2(3).

**Table S1.** Crystallographic experimental details for compound **2** (CCDC 1878987).

| | | |
|---|---|---|
| Empirical formula | $C_{27}H_{22}BBr_2N$ | |
| Formula weight | 531.08 | |
| Temperature | 153(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system, space group | Monoclinic, P2(1) | |
| Unit cell dimensions | a = 11.2690(4) Å | $\alpha$ = 90 deg. |
| | b = 7.3358(3) Å | $\beta$ = 101.4180(10) deg. |
| | c = 14.2605(5) Å | $\gamma$ = 90 deg. |
| Volume | 1155.54(7) Å^3 | |
| Z, Calculated density | 2, 1.526 Mg/m^3 | |
| Absorption coefficient | 3.522 mm^-1 | |
| F(000) | 532 | |
| Crystal size | 0.410 x 0.225 x 0.231 mm | |
| Theta range for data collection | 2.111 to 26.415 deg. | |
| Limiting indices | -14<=h<=14, -9<=k<=9, -17<=l<=17 | |
| Reflections collected / unique | 28928 / 4728 [R(int) = 0.0361] | |
| Completeness to theta = 25.242 | 99.7 % | |
| Refinement method | Full-matrix least-squares on F^2 | |
| Data / restraints / parameters | 4728 / 1 / 283 | |
| Goodness-of-fit on F^2 | 1.051 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0271, wR2 = 0.0646 | |
| R indices (all data) | R1 = 0.0304, wR2 = 0.0664 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.608 and -0.865 e. Å^-3 | |

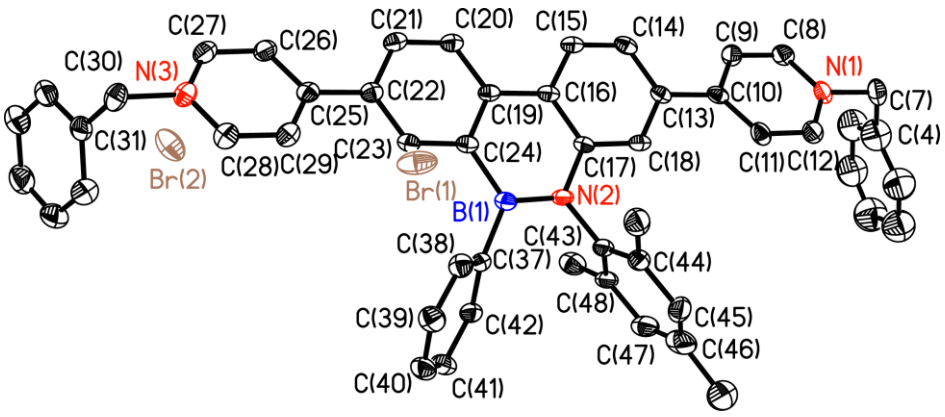



**Figure S2.** Molecular Structure of **4a** (CCDC 1878986) with thermal ellipsoids presented at a 50% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): N(2)—B(1), 1.416(7); N(2)—C(17), 1.417(6); N(2)—C(43), 1.463(7); N(3)—C(27), 1.337(7); N(3)—C(28), 1.343(7); N(3)—C(30), 1.500(7); N(1)—C(8), 1.338(7); N(1)—C(12), 1.356(7); N(1)—C(7), 1.489(8); C(37)—B(1), 1.576(8); C(24)—B(1), 1.538(8). Bond angles (deg): B(1)—N(2)—C(17), 122.5(4); B(1)—N(2)—C(43), 121.6(4); C(17)—N(2)—C(43), 115.8(4); C(27)—N(3)—C(28), 120.3(5); C(27)—N(3)—C(30), 119.6(5); C(28)—N(3)—C(30), 120.0(5); C(8)—N(1)—C(12), 119.6(5); C(8)—N(1)—C(7), 120.5(5) ; C(12)—N(1)—C(7), 119.9(5); C(18)—C(17)—N(2), 120.2(4); N(2)—C(17)—C(16), 120.3(4); C(44)—C(43)—N(2), 118.4(5); C(48)—C(43)—N(2), 118.7(5); C(23)—C(24)—B(1), 121.6(5); C(19)—C(24)—B(1), 119.6(5); N(3)—C(27)—C(26), 121.4(5); N(3)—C(28)—C(29), 120.2(5); N(1)—C(8)—C(9), 121.4(5); N(1)—C(7)—C(4), 110.9(6); N(1)—C(12)—C(11), 120.8(5); N(2)—B(1)—C(24), 117.1(5); N(2)—B(1)—C(37), 122.0(5); C(24)—B(1)—C(37), 121.0(5).

**Table S2.** Crystallographic experimental details for compound **4a** (CCDC 1878986).

| | | |
|---|---|---|
| Empirical formula | $C_{54}H_{52}BBr_2N_4O_2$ | |
| Formula weight | 959.62 | |
| Temperature | 296(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system, space group | Monoclinic, P2(1) | |
| Unit cell dimensions | a = 12.306(4) Å | $\alpha$ = 90 deg. |
| | b = 14.658(5) Å | $\beta$ = 99.846(5) deg. |
| | c = 27.238(10) Å | $\gamma$ = 90 deg. |
| Volume | 4841(3) Å^3 | |
| Z, Calculated density | 4, 1.317 Mg/m^3 | |
| Absorption coefficient | 1.719 mm^-1 | |
| F(000) | 1980 | |
| Crystal size | 0.286 x 0.244 x 0.220 mm | |
| Theta range for data collection | 1.518 to 24.962 deg. | |
| Limiting indices | -14<=h<=12, -16<=k<=17, -32<=l<=32 | |
| Reflections collected / unique | 47181 / 8362 [R(int) = 0.0476] | |
| Completeness to theta = 25.242 | 95.5 % | |
| Refinement method | Full-matrix least-squares on F^2 | |
| Data / restraints / parameters | 8362 / 108 / 577 | |
| Goodness-of-fit on F^2 | 1.017 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0726, wR2 = 0.1896 | |
| R indices (all data) | R1 = 0.1028, wR2 = 0.2121 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 1.354 and -1.065 e. Å^-3 | |

## 5. The UV-vis and emission spectra

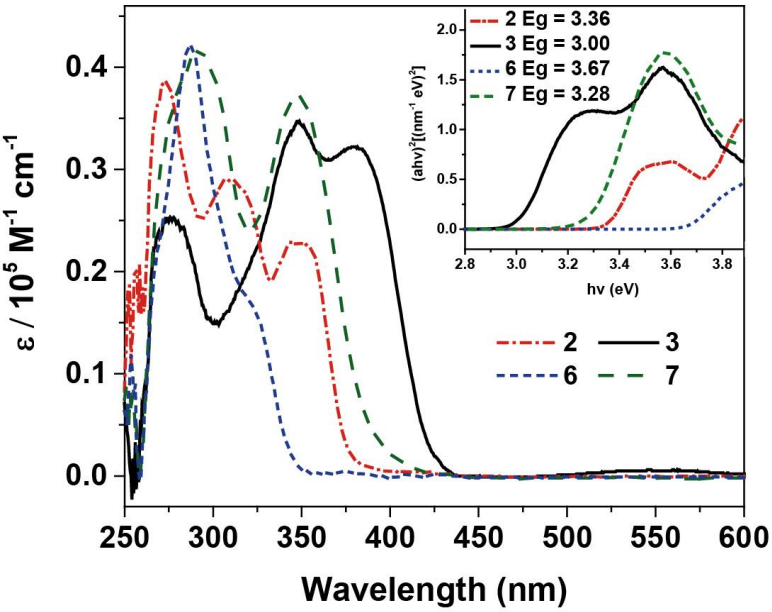



**Figure S3.** UV-vis absorption and extrapolated optical band gaps (Eg) of **2** (dotted line), **3** (solid line), **6** (dashed line) and **7** (dashed line), [M] = 0.01 mM.

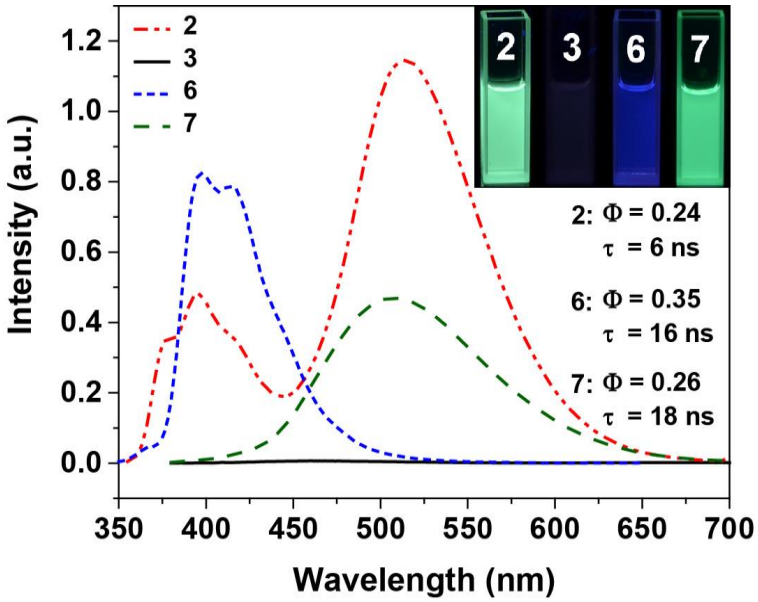



**Figure S4.** PL spectra of **2** (dotted line), $\lambda_{exc}$ = 350 nm; **3** (solid line), $\lambda_{exc}$ = 365 nm in DMF; **6** (dashed line), $\lambda_{exc}$ = 330 nm, **7** (dashed line), $\lambda_{exc}$ = 365 nm (Inset: photographs of the DMF solutions of **2**, **3**, **6** and **7**), [M] = 0.01 mM.

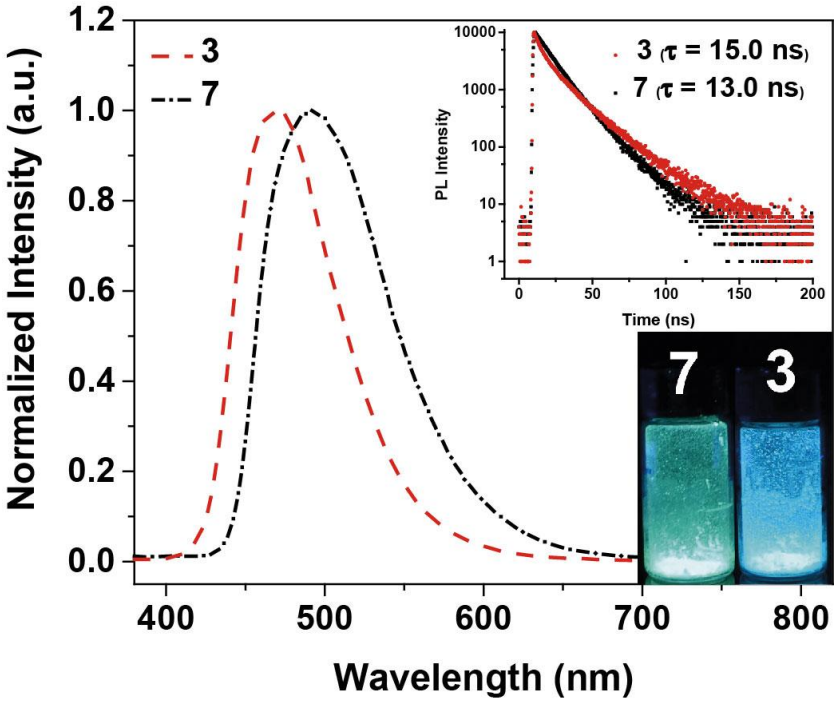



**Figure S5.** Emission spectra of **3** and **7** in solid state (inset: fluorescence lifetime decay of **3** and **7**).

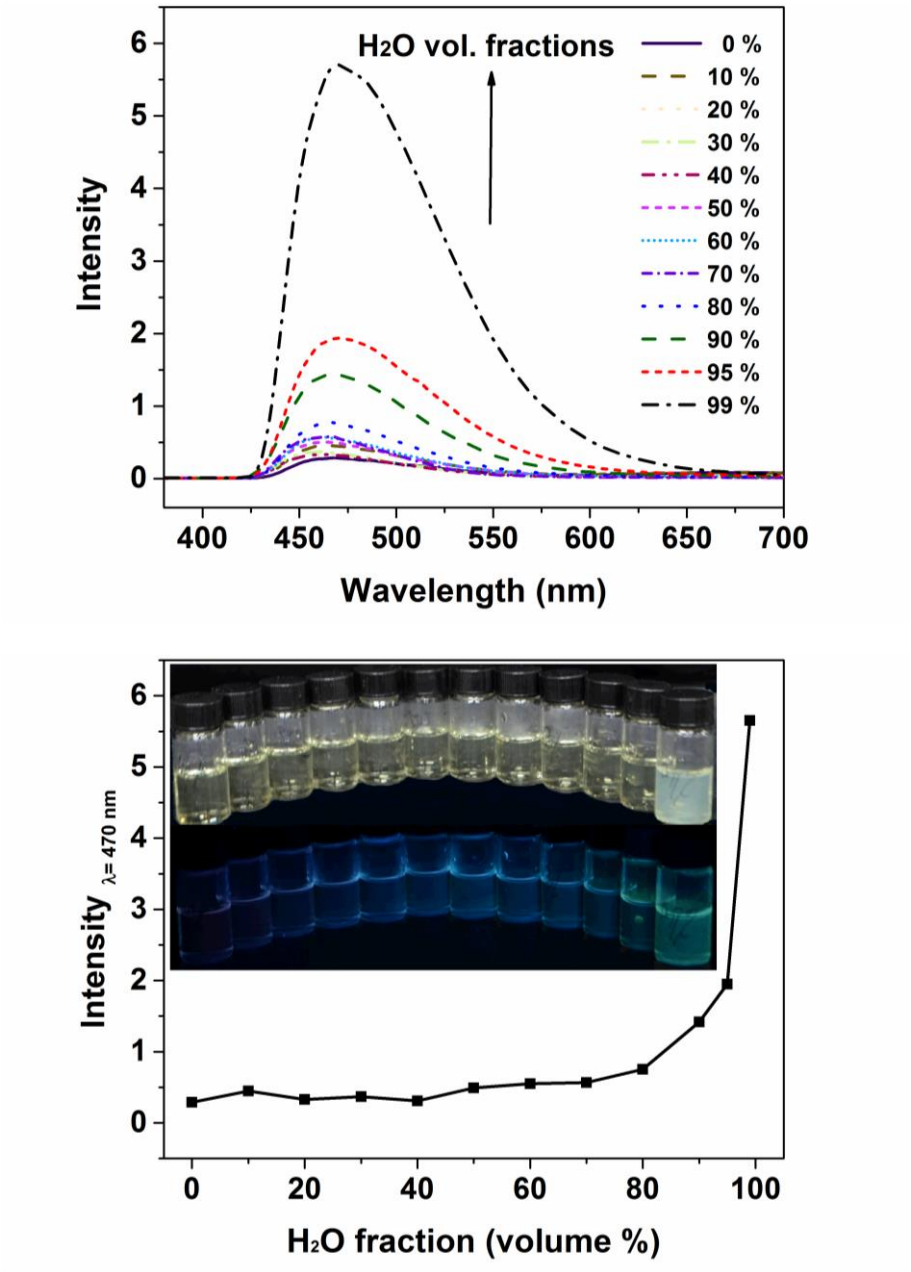



**Figure S6.** (Top) Photoluminescence (PL) spectra of **3** in different DMF/water ratios; (bottom) emission intensity of **3** as the DMF/water ratio is altered. Inset: aggregates under UV light ($\lambda_{exc}$ = 365 nm).

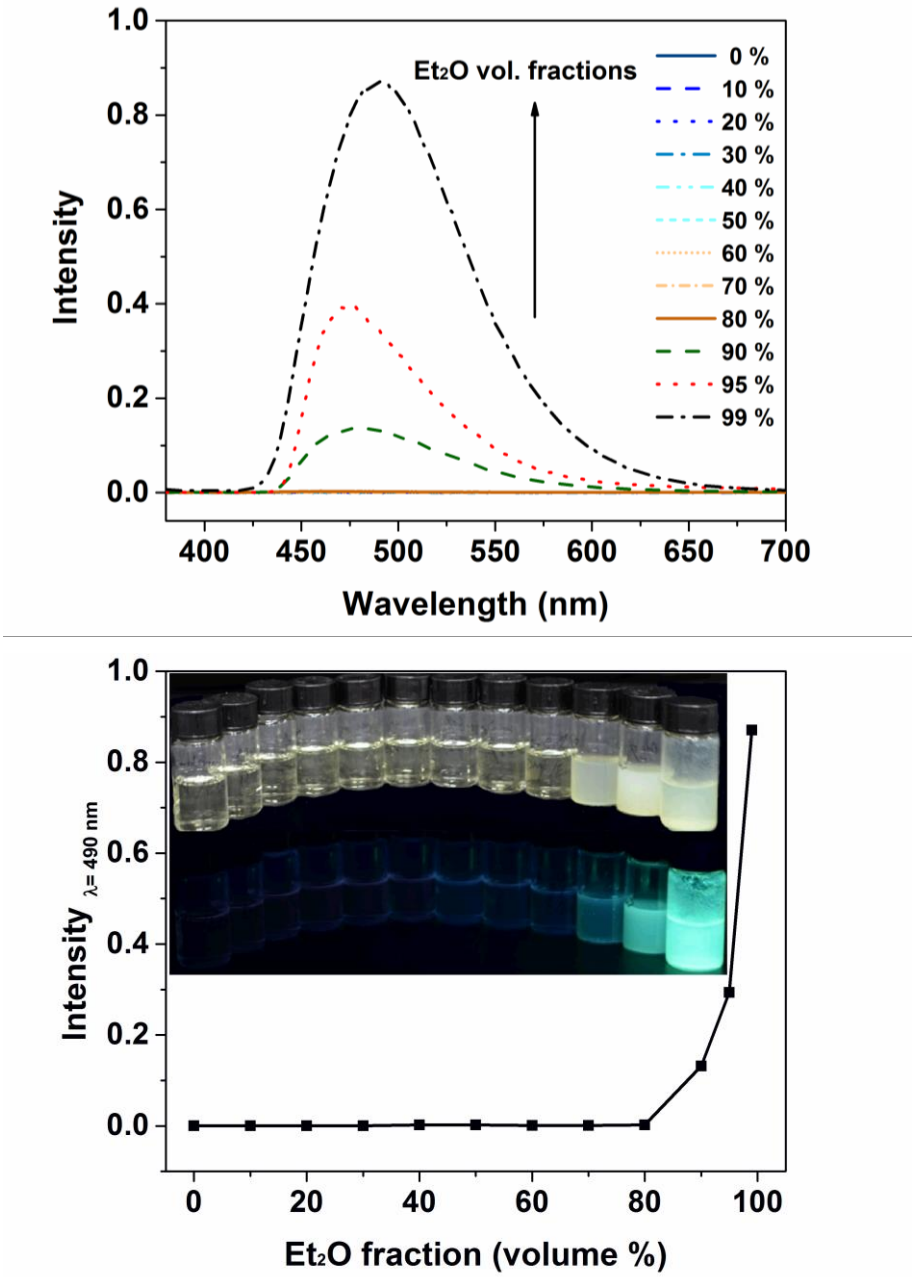



**Figure S7.** (Top) Photoluminescence (PL) spectra of **3** in different DMF/$Et_2O$ ratios; (bottom) emission intensity of **3** as the DMF/$Et_2O$ ratio is altered. Inset: aggregates under UV light ($\lambda_{exc}$ = 365 nm).

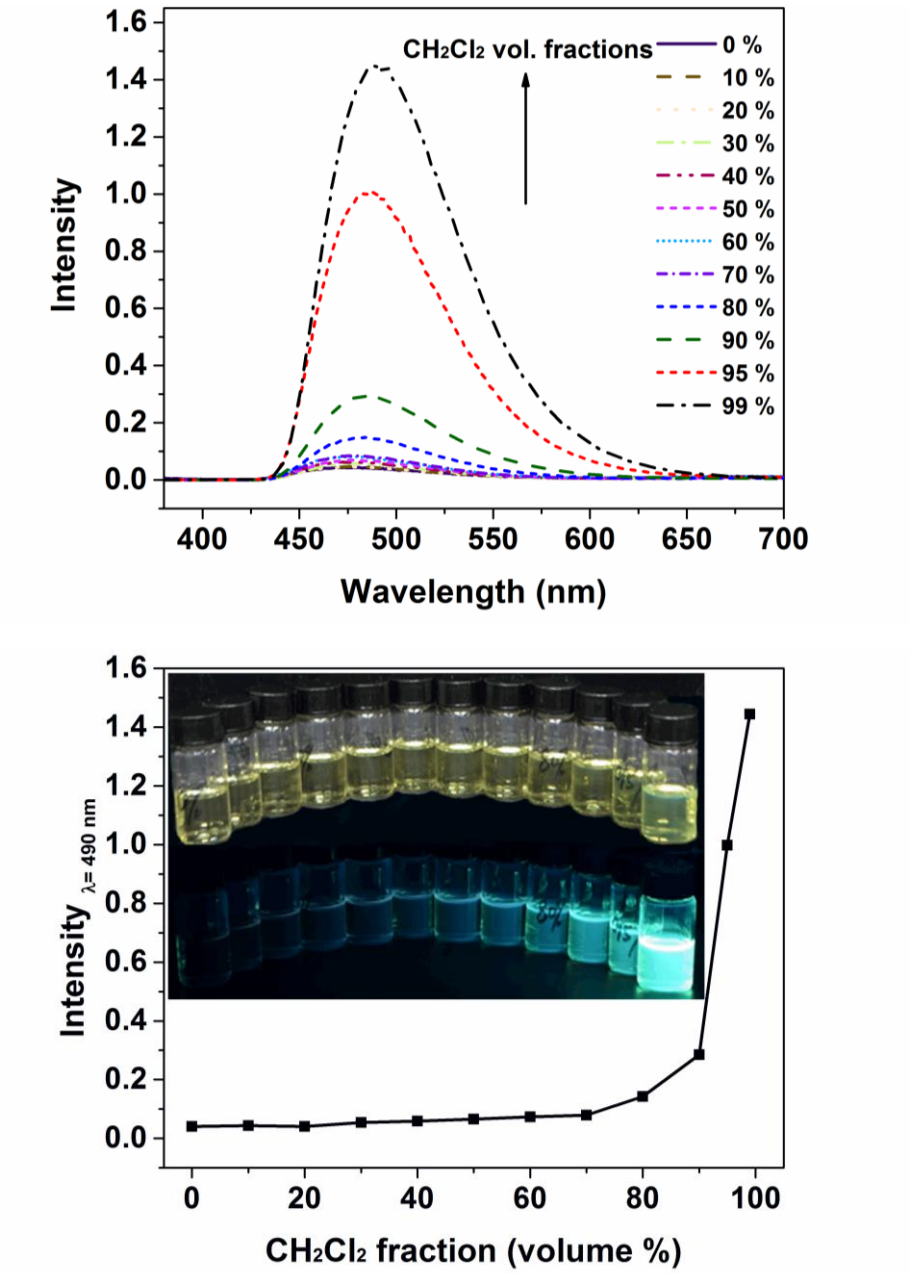



**Figure S8.** (Top) Photoluminescence (PL) spectra of **4b** in different DMF/DCM ratios; (bottom) emission intensity of **4b** as the DMF/DCM ratio is altered. Inset: aggregates under UV light ($\lambda_{exc}$ = 365 nm).

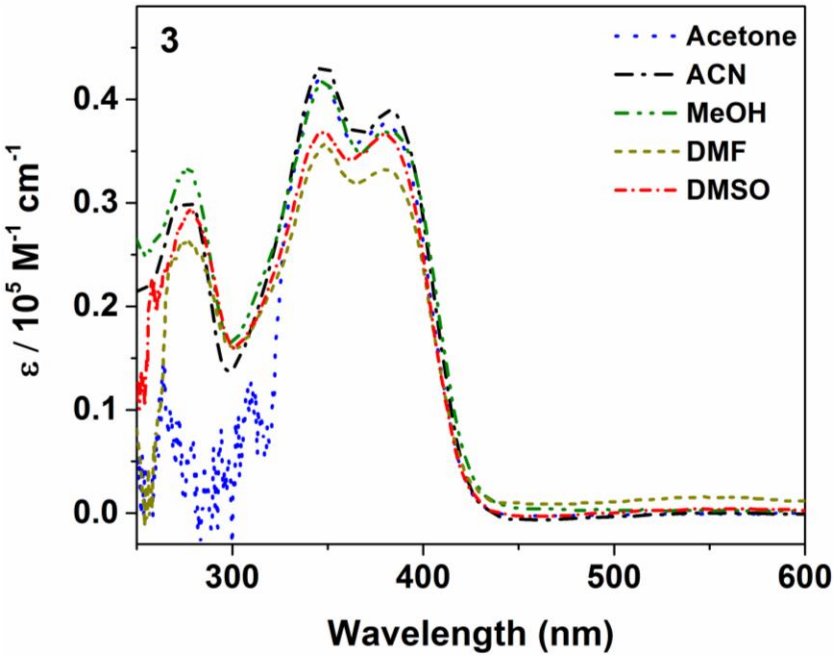



**Figure S9.** UV-vis absorption spectra of **3** in different polarities solutions, c = 0.01 M.

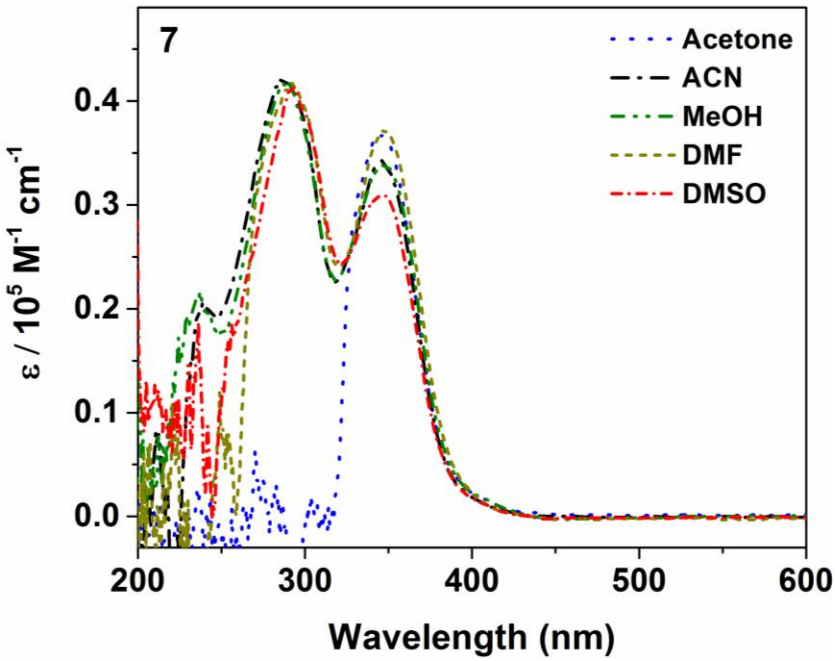



**Figure S10.** UV-vis absorption spectra of **7** in different polarities solutions, c = 0.01 M.

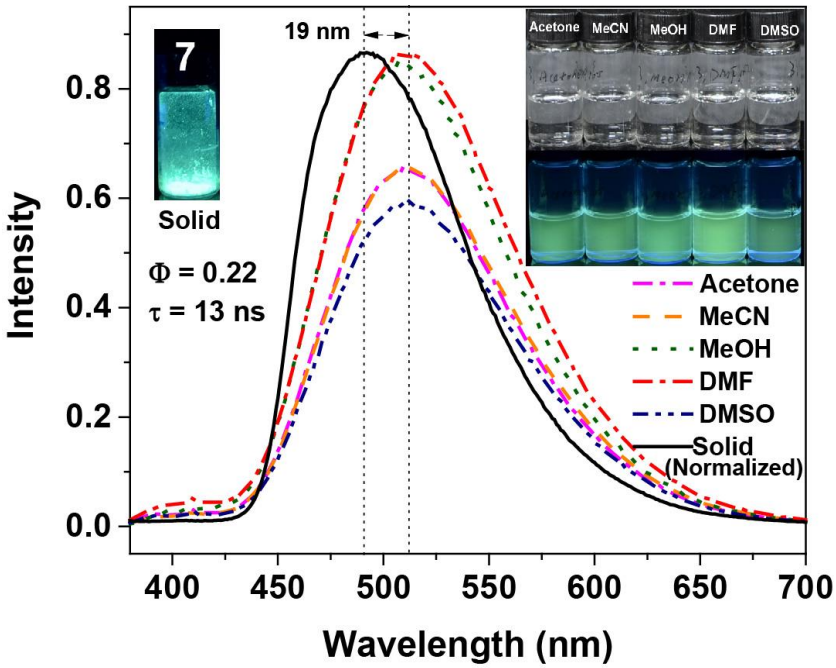



**Figure S11.** Emission spectra of **7** in different polarities solutions and solid (Inset: photographs under UV light, $\lambda_{exc}$ = 365 nm), c = 0.01 M.

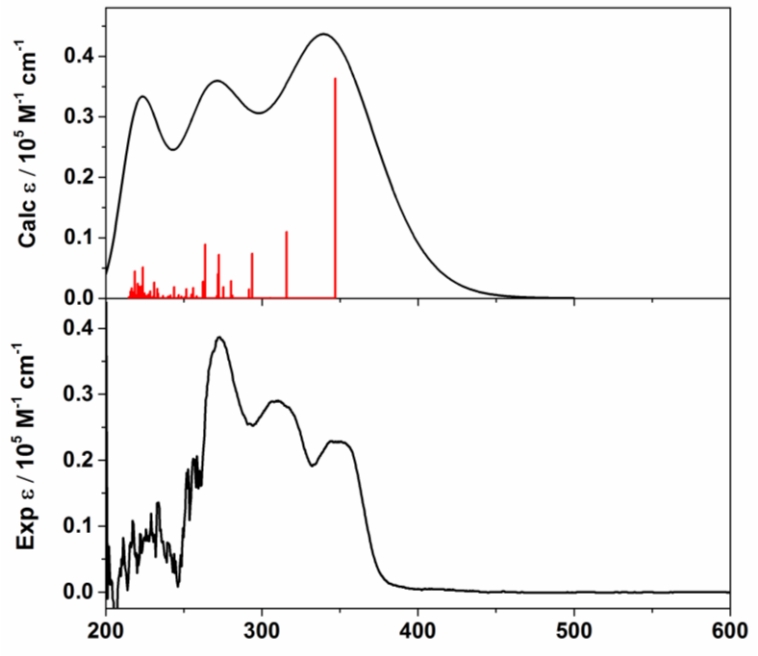



**Figure S12.** Computed, at the B3LYP level with the 6-31G* basis set in DMF, and experimental UV-vis spectra of **2**. [**2**] = 0.01 mM.

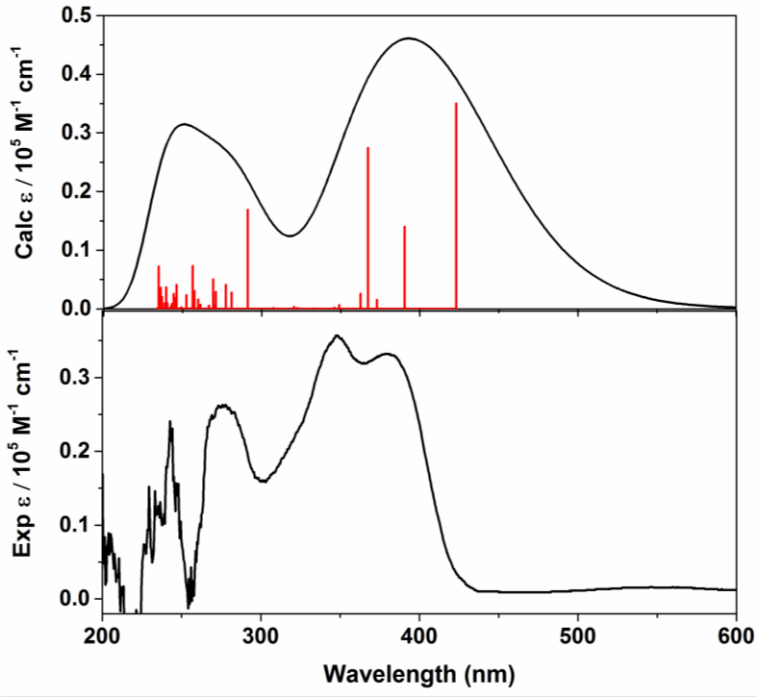



**Figure S13.** Computed, at the B3LYP level with the 6-31G* basis set in DMF, and experimental UV-vis spectra of **3**. [**3**] = 0.01 mM.

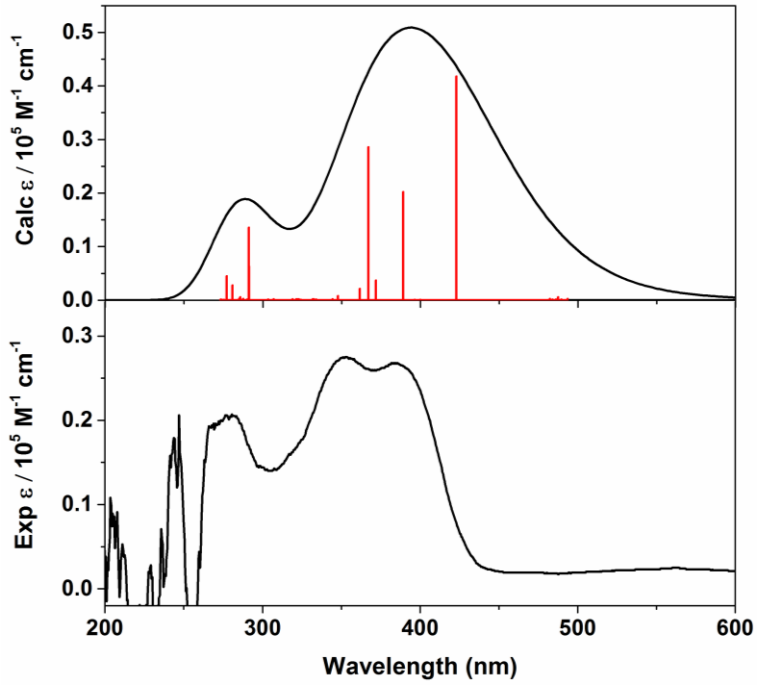



**Figure S14.** Computed, at the B3LYP level with the 6-31G* basis set in DMF, and experimental UV-vis spectra of **4a**. [**4a**] = 0.01 mM.

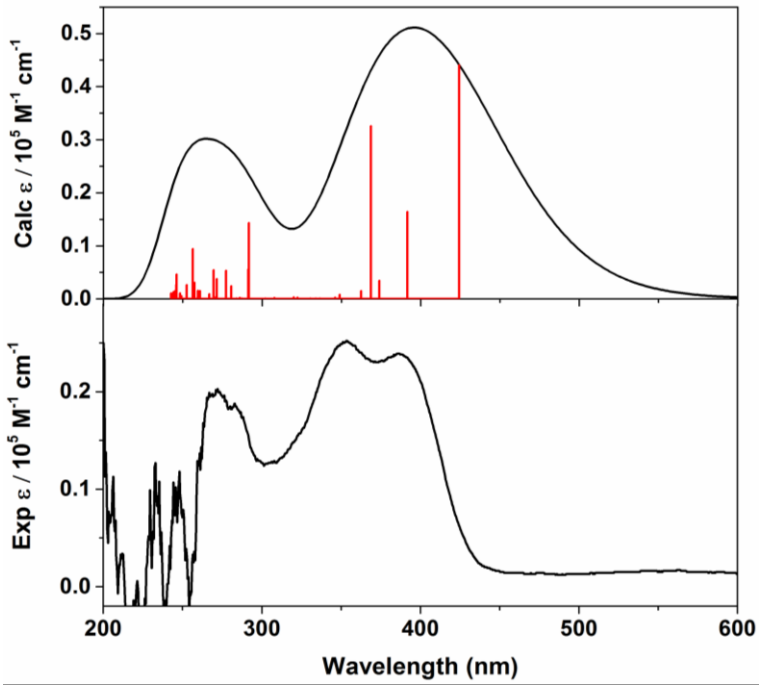



**Figure S15.** Computed, at the B3LYP level with the 6-31G* basis set in DMF, and experimental UV-vis spectra of **4b**. [**4b**] = 0.01 mM.

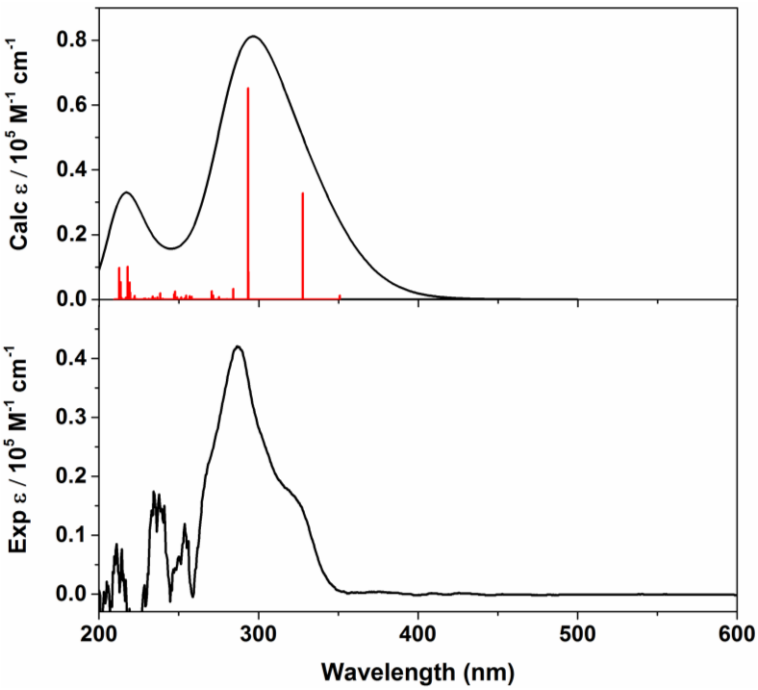



**Figure S16.** Computed, at the B3LYP level with the 6-31G* basis set in DMF, and experimental UV-vis spectra of **6**. [**6**] = 0.01 mM.

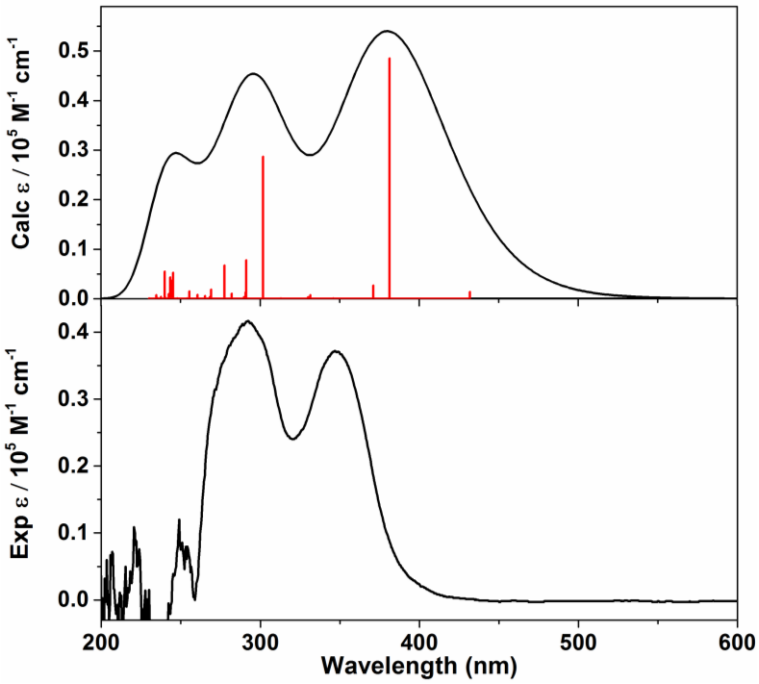



**Figure S17.** Computed, at the B3LYP level with the 6-31G* basis set in DMF, and experimental UV-vis spectra of **7**. [**7**] = 0.01 mM.

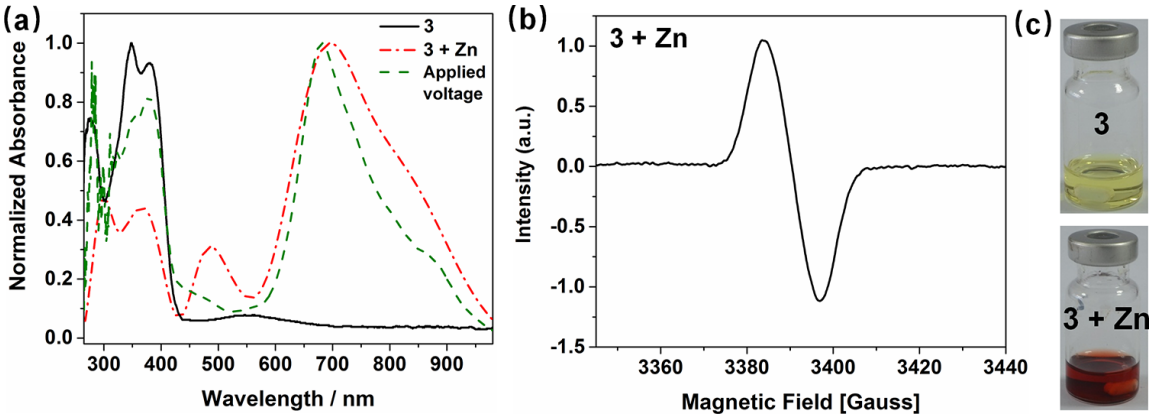



**Figure S18.** (a) UV−vis spectrum of DMF solution (solid line), isolated redox states after added Zn (dashed dotted line) and applied voltage (dashed line) of **3**; (b) EPR spectrum of isolated redox states of **3**; (c) Chemical reduction of **3** and Zn.

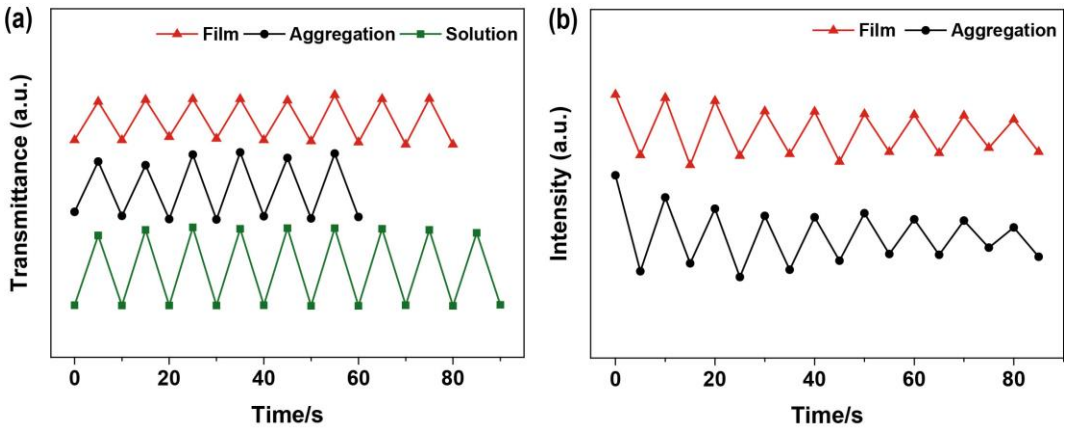



**Figure S19.** The optical stability test for electrochromic switching of **3**. (a) Repetitive UV-vis switching in film, aggregation and solution at 681 nm upon potential step between -0.6 V and 0.6 V with a residence time of 5 s; (b) Repetitive fluorescence switching in film (490 nm) and aggregation (480 nm) upon potential step between -0.6 V and 0.6 V with a residence time of 5 s.

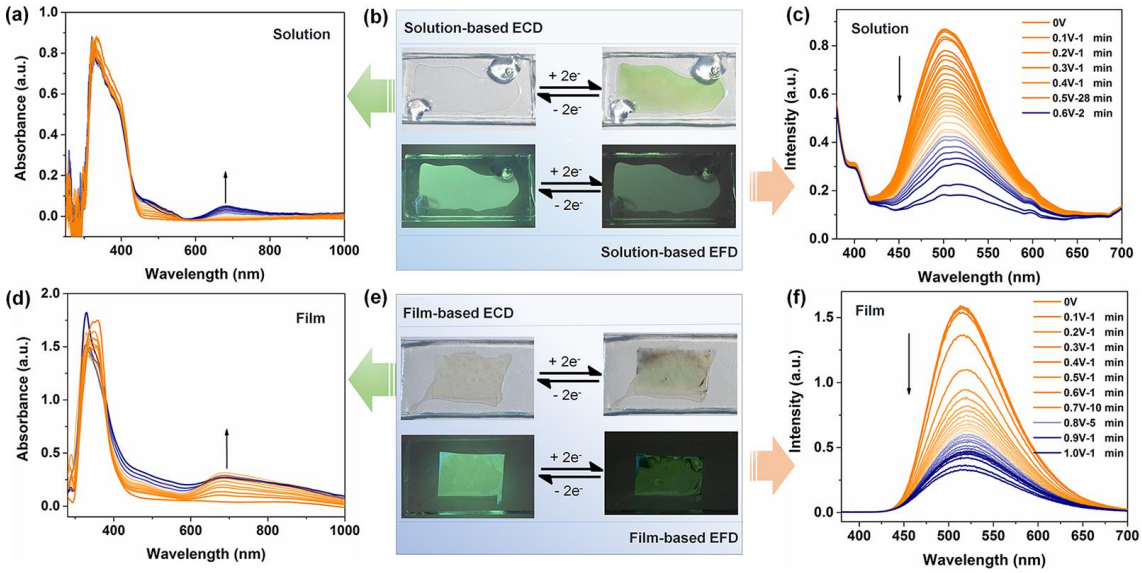



**Figure S20.** (a) Spectroelectrochemistry of **7** in solution of DMF; (b) Solution-based ECD and EFD of **7** under a glass FTO electrode window in daylight lamp (above) and UV illumination (below); (c) Fluorescence spectral changes in solution of DMF upon different applied potentials; (d) Spectroelectrochemistry of **7** in film; (e) film-based ECD and EFD of **7** under a glass FTO electrode window in daylight lamp (above) and UV illumination (below); (f) Fluorescence spectral changes in film upon different applied potentials.

## 6. Electrochemical properties

Cyclic voltammograms were recorded with a CHI660E/B15721b electrochemical analyzer using degassed and dried DMF under an argon atmosphere in the glovebox. The CV cell consisted of a gold electrode, a Pt wire counter electrode, and an Ag/AgCl reference electrode. All measurements were performed using DMF solutions of samples with a concentration of 1 mM and 0.1 M $Bu_4N^+PF_6^-$ as a supporting electrolyte. Potentials are determined against a ferrocene/ferrocenyl ion couple ($Fc/Fc_+$).

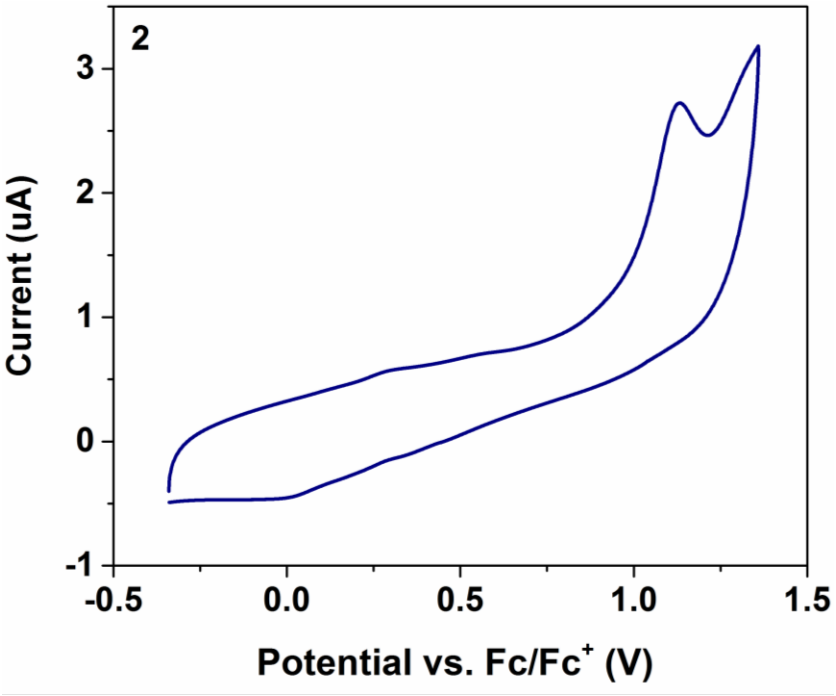



**Figure S21.** Cyclic voltammograms of **2** in DMF with $Bu_4N^+PF_6^-$ (0.1 M) as a supporting electrolyte, Fc = ferrocene.

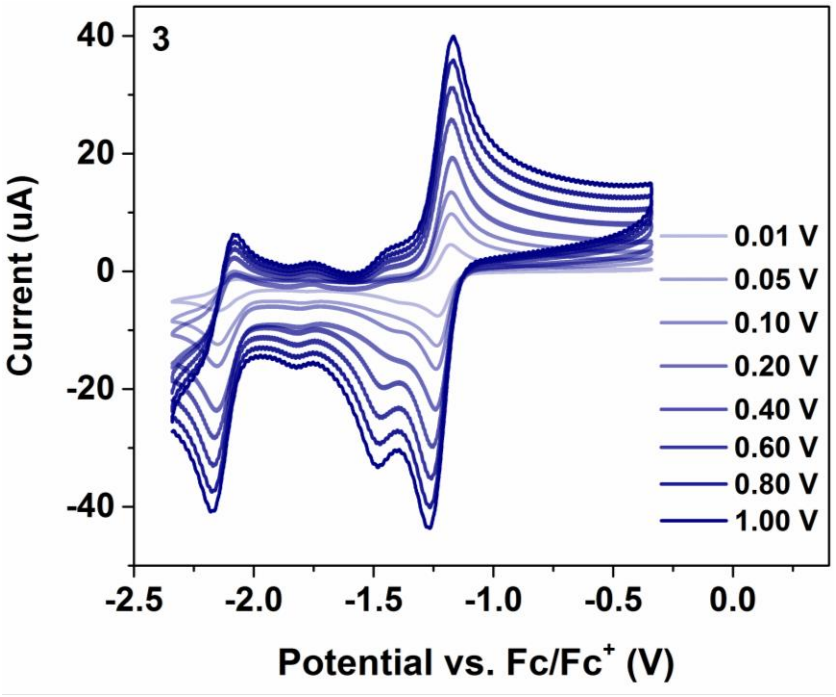



**Figure S22.** Cyclic voltammograms of **3** in DMF with $Bu_4N^+PF_6^-$ (0.1 M) as a supporting electrolyte, Fc = ferrocene.

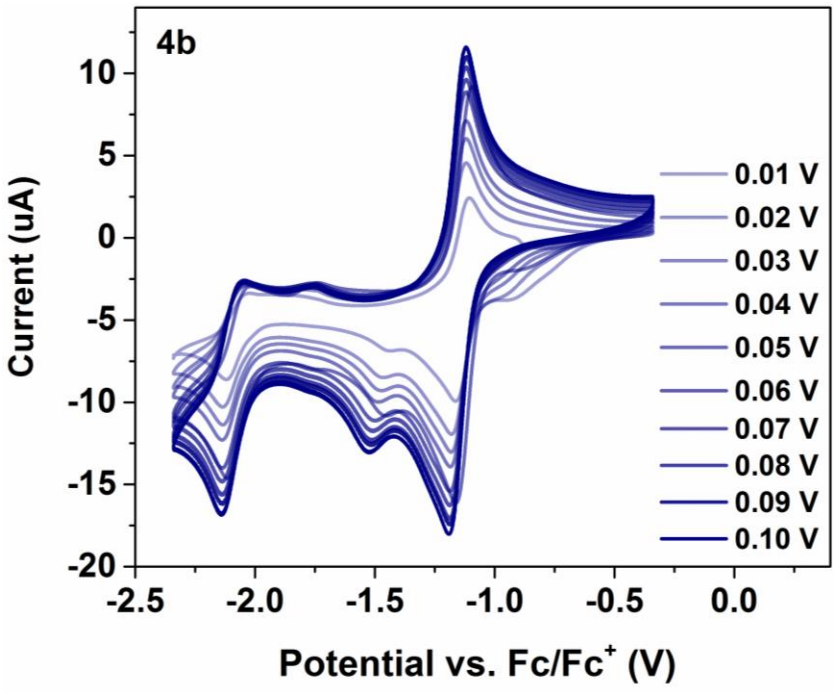



**Figure S23.** Cyclic voltammograms of **4b** in DMF with $Bu_4N^+PF_6^-$ (0.1 M) as a supporting electrolyte, Fc = ferrocene.

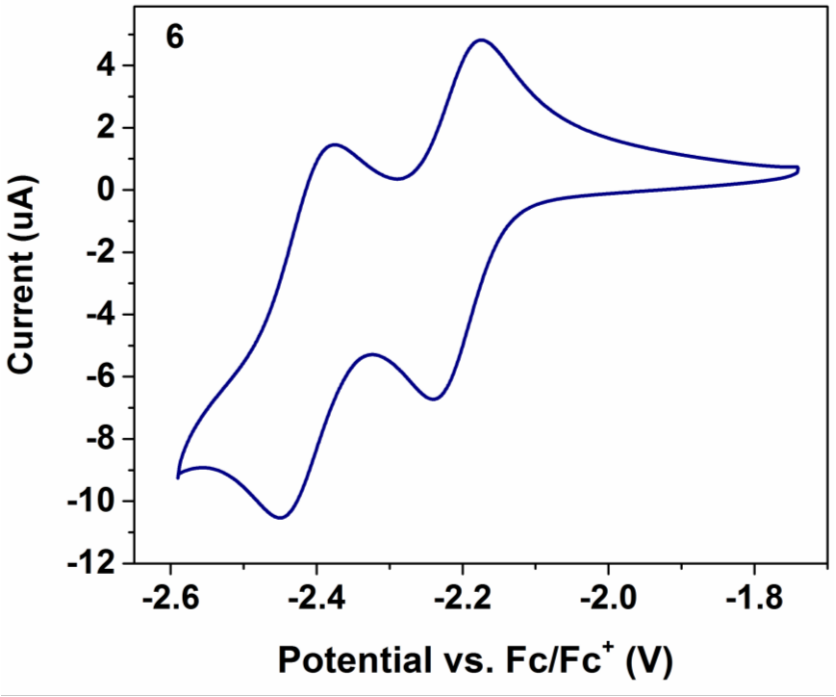



**Figure S24.** Cyclic voltammograms of **6** in DMF with $Bu_4N^+PF_6^-$ (0.1 M) as a supporting electrolyte, Fc = ferrocene.

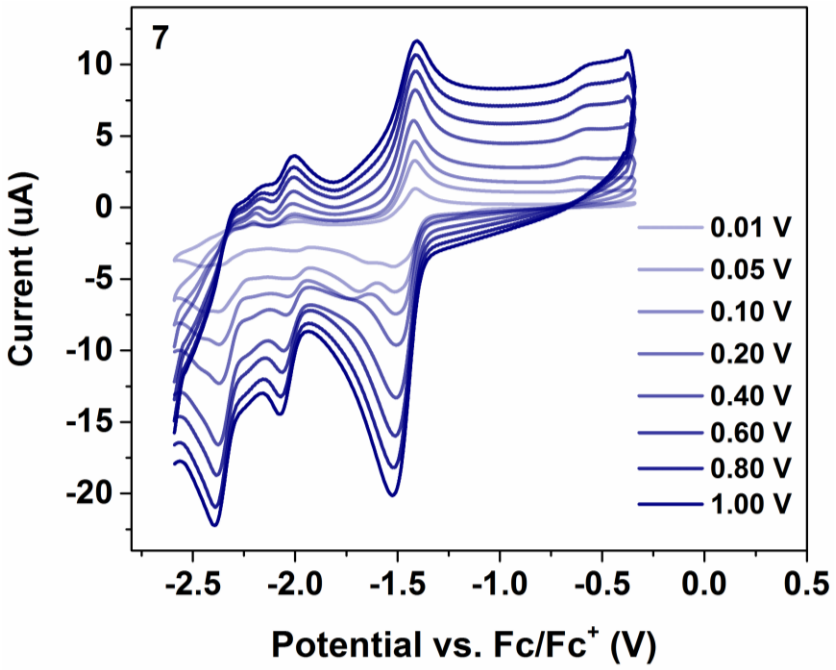
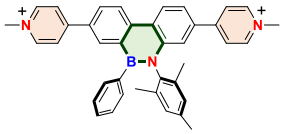
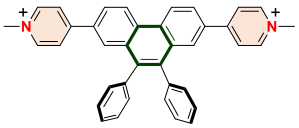



**Figure S25.** Cyclic voltammograms of **7** in DMF with $Bu_4N^+PF_6^-$ (0.1 M) as a supporting electrolyte, Fc = ferrocene.

## 7. DFT calculations

**Table S3** Calculated and measured dipole moments (D) in gas and DMF solution[a].

| |  |  | Δμ |
|---|---|---|---|
| Gas [μ/D] | 12.74 | 10.50 | 2.24 |
| DMF [μ/D] | 16.36 | 13.73 | 2.63 |

[a]Theoretical calculations have been carried out by using the GAUSSIAN09.

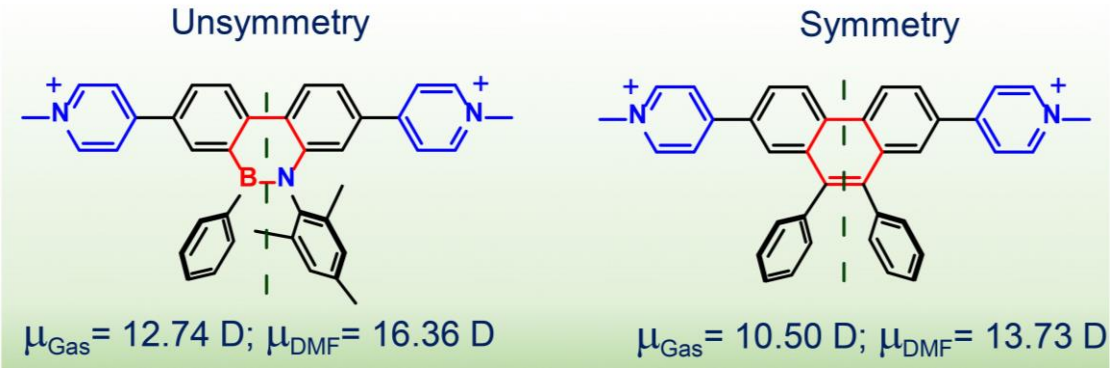



**Figure S26**. Calculated and measured dipole moments (D) in gas and DMF solution by using the GAUSSIAN09 suite.

**Table S4** Electronic properties of **2**, **3**, **5**, **6** and **7b**.

| | LUMO (Exp)[a] | HOMO (Exp)[a] | Eg (Exp)[a] | LUMO (Calc)[b] | HOMO (Calc)[b] | Eg (Calc)[b] |
|---|---|---|---|---|---|---|
| **2** | -2.40 | -5.76 | 3.36 | -1.84 | -5.89 | 4.05 |
| **3** | -3.66 | -6.66 | 3.00 | -2.88 | -6.25 | 3.37 |
| **4b** | -3.74 | -6.71 | 2.97 | -2.88 | -6.25 | 3.37 |
| **6** | -2.66 | -6.33 | 3.67 | -1.82 | -5.99 | 4.17 |
| **7** | -3.42 | -6.70 | 3.28 | -2.86 | -6.23 | 3.37 |

[a]Energy levels vs vacuum level were calculated from CV data and from the optically determined energy gap. [b]Theoretical calculations have been carried out by using the GAUSSIAN09 suite of programs in gas-phase.

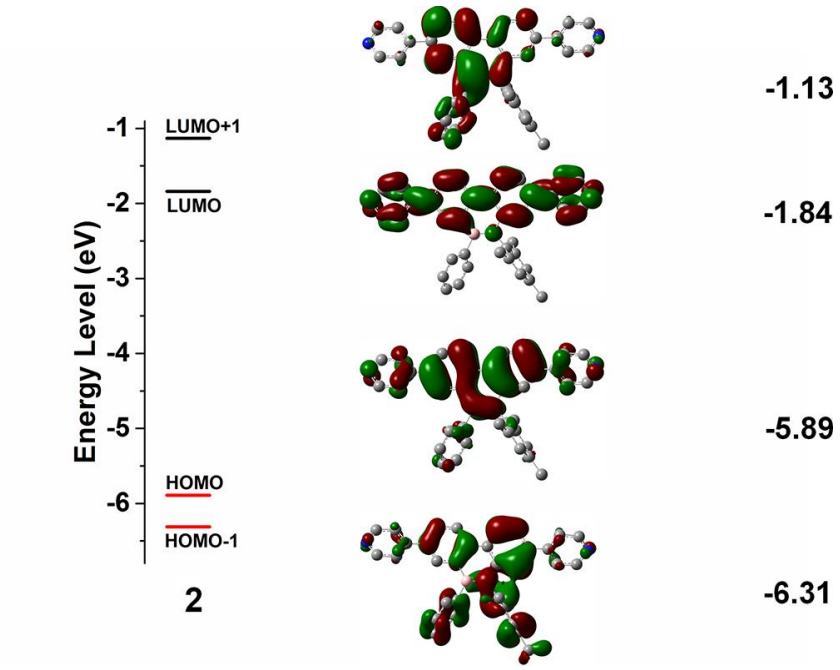



**Figure S27**. Computed molecular orbital plots for **2**.

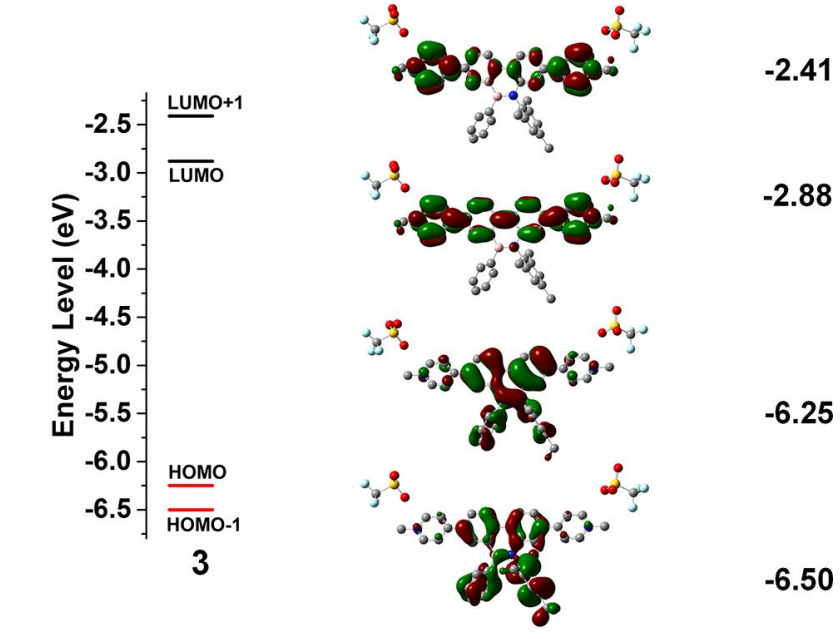



**Figure S28**. Computed molecular orbital plots for **3**.

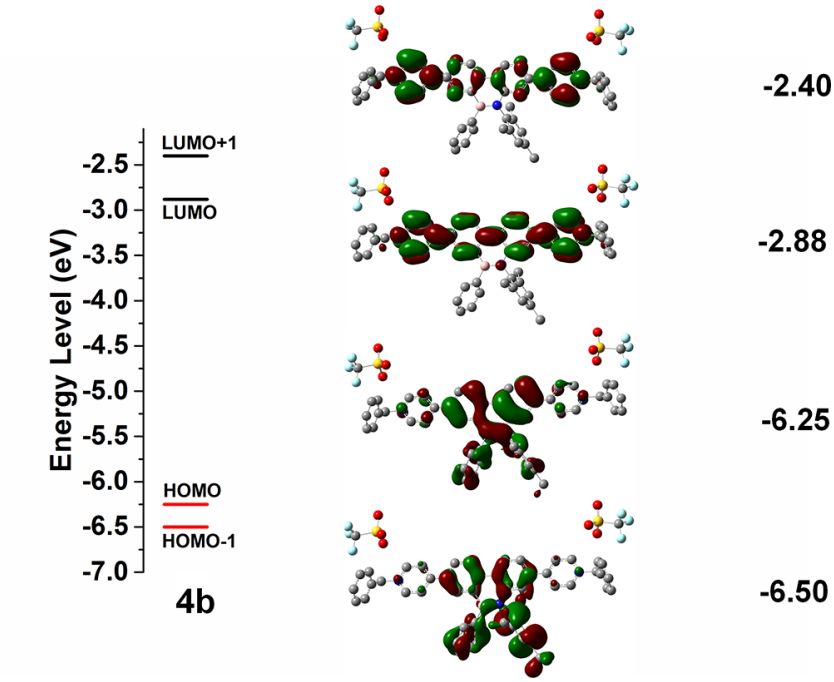



**Figure S29**. Computed molecular orbital plots for **4b**.

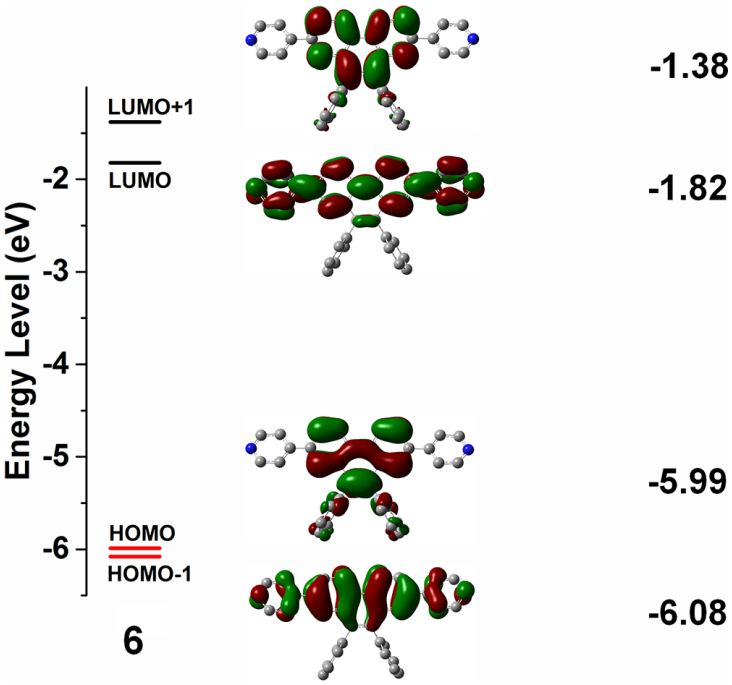



**Figure S30**. Computed molecular orbital plots for **6**.

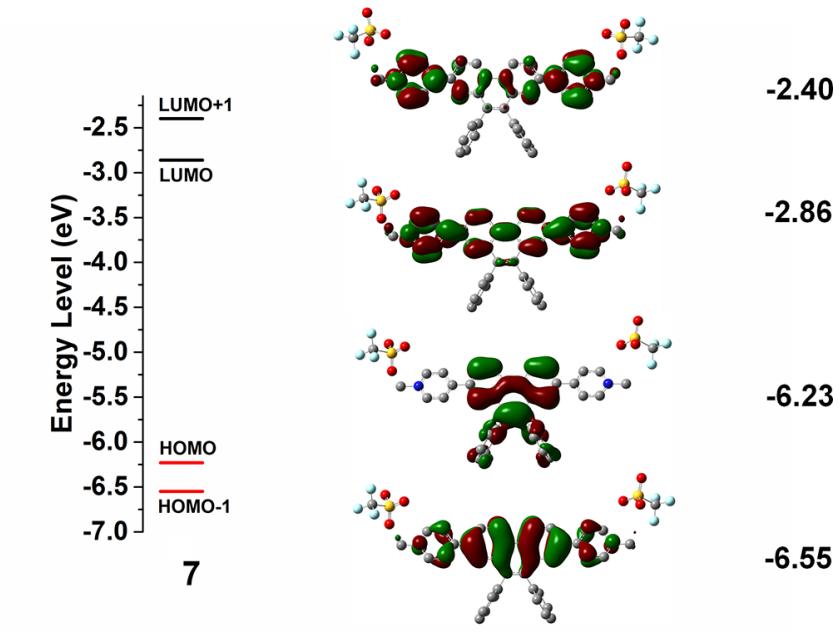
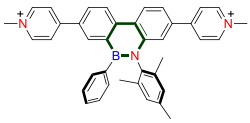
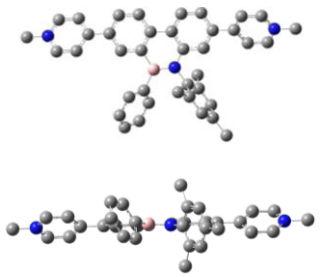
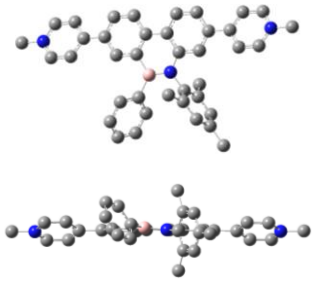
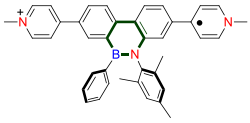
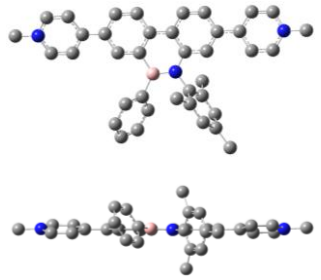
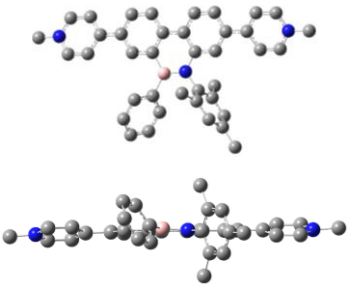
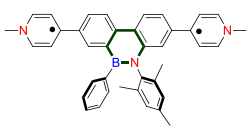
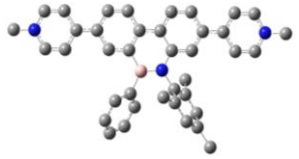
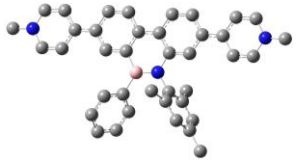
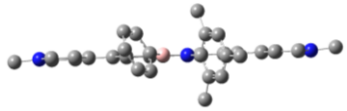



**Figure S31**. Computed molecular orbital plots for **7**.

**Table S5** Calculated conformations in gas and DMF solution by using the GAUSSIAN09

| | DMF | gas |
|---|---|---|
|  |  |  |
|  |  |  |
|  |  |  |



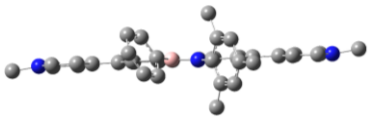


**Table S6.** Calculated ($\lambda_{TD\text{-}DFT}$) wavelengths of **2**. Molecular orbitals (MOs) involved in the main electronic transition，f corresponds to the oscillator strength. (TD-DFT, B3LYP/6-31g*)

| $\lambda_{TD\text{-}DFT}$ | Oscillator Strength, f | MOs | |
|---|---|---|---|
| 327.4 | 0.7299 | HOMO-1 ->LUMO | 88.69% |
| | | HOMO ->LUMO+1 | 10.65% |
| 293.4 | 0.1903 | HOMO-2 ->LUMO | 22.40% |
| | | HOMO-1 ->LUMO+1 | 57.05% |
| | | HOMO ->LUMO | 12.63% |
| | | HOMO ->LUMO+1 | 3.74% |
| 293.16 | 1.4489 | HOMO-1 ->LUMO | 9.69% |
| | | HOMO-1 ->LUMO+1 | 2.68% |
| | | HOMO ->LUMO+1 | 80.01% |
| 218.88 | 0.1182 | HOMO-12 ->LUMO | 23.27% |
| | | HOMO-11 ->LUMO | 2.61% |
| | | HOMO-9 ->LUMO+2 | 2.98% |
| | | HOMO-1 ->LUMO+8 | 2.65% |
| | | HOMO-1 ->LUMO+9 | 11.64% |
| | | HOMO-1 ->LUMO+10 | 47.03% |

**Table S7.** Calculated ($\lambda_{TD\text{-}DFT}$) wavelengths of **3**. Molecular orbitals (MOs) involved in the main electronic transition，f corresponds to the oscillator strength. (TD-DFT, B3LYP/6-31g*)

| $\lambda_{TD\text{-}DFT}$ | Oscillator Strength, f | MOs | |
|---|---|---|---|
| 381.18 | 1.2336 | HOMO-1 ->LUMO | 93.58% |
| | | HOMO ->LUMO+1 | 4.88% |
| 301.72 | 0.7306 | HOMO-8 ->LUMO | 5.05% |
| | | HOMO-1 ->LUMO+5 | 2.29% |
| | | HOMO ->LUMO+2 | 85.55% |
| 291.16 | 0.1985 | HOMO-8 ->LUMO | 78.86% |
| | | HOMO-7 ->LUMO+1 | 9.04% |
| | | HOMO ->LUMO+2 | 4.55% |

| | | | |
|---|---|---|---|
| 277.41 | 0.1714 | HOMO-2 ->LUMO+2 | 83.77% |
| | | HOMO-2 ->LUMO+4 | 2.89% |
| | | HOMO ->LUMO+4 | 7.07% |
| 245.28 | 0.1343 | HOMO-9 ->LUMO+1 | 52.28% |
| | | HOMO-1 ->LUMO+5 | 9.39% |
| | | HOMO ->LUMO+6 | 14.11% |
| | | HOMO ->LUMO+7 | 16.57% |
| 243.32 | 0.1108 | HOMO-17 ->LUMO | 13.82% |
| | | HOMO-17 ->LUMO+1 | 3.53% |
| | | HOMO-16 ->LUMO | 51.28% |
| | | HOMO-5 ->LUMO+2 | 2.23% |
| | | HOMO-3 ->LUMO+3 | 3.97% |
| | | HOMO-3 ->LUMO+4 | 5.31% |
| | | HOMO-1 ->LUMO+4 | 6.02% |
| | | HOMO ->LUMO+6 | 2.53% |
| 239.96 | 0.1406 | HOMO-19 ->LUMO | 2.87% |
| | | HOMO-17 ->LUMO | 5.08% |
| | | HOMO-9 ->LUMO+1 | 13.63% |
| | | HOMO-1 ->LUMO+5 | 56.10% |
| | | HOMO ->LUMO+2 | 2.31% |
| | | HOMO ->LUMO+7 | 3.69% |

**Table S8.** Calculated ($\lambda_{TD\text{-}DFT}$) wavelengths of **5**. Molecular orbitals (MOs) involved in the main electronic transition，f corresponds to the oscillator strength. (TD-DFT, B3LYP/6-31g*) DMF

| $\lambda_{TD\text{-}DFT}$ | Oscillator Strength, f | MOs | |
|---|---|---|---|
| 346.75 | 0.9083 | HOMO ->LUMO | 94.54% |
| 315.49 | 0.2743 | HOMO-2 ->LUMO | 3.66% |
| | | HOMO-1 -> LUMO | 74.84% |
| | | HOMO -> LUMO | 2.50% |
| | | HOMO -> LUMO+1 | 15.95% |
| 293.55 | 0.1856 | HOMO-11 -> LUMO | 5.70% |
| | | HOMO-4 -> LUMO | 21.82% |
| | | HOMO-3 -> LUMO | 41.35% |
| | | HOMO-2 -> LUMO | 22.13% |
| | | HOMO-1 -> LUMO | 5.18% |

| | | | |
|---|---|---|---|
| | | HOMO -> LUMO+1 | 44.19% |
| 280.05 | 0.0719 | HOMO-4 -> LUMO | 82.48% |
| | | HOMO-1 -> LUMO+1 | 7.29% |
| | | HOMO -> LUMO+1 | 5.51% |
| 272.16 | 0.1804 | HOMO-7 -> LUMO | 28.94% |
| | | HOMO-7 -> LUMO+2 | 5.79% |
| | | HOMO-6 -> LUMO | 7.26% |
| | | HOMO-5 -> LUMO | 5.96% |
| | | HOMO-4 -> LUMO | 2.54% |
| | | HOMO-1 -> LUMO+1 | 40.78% |
| 271.66 | 0.1008 | HOMO-11 -> LUMO | 4.57% |
| | | HOMO-7 -> LUMO | 40.96% |
| | | HOMO-7 -> LUMO+2 | 8.00% |
| | | HOMO-4 -> LUMO | 2.70% |
| | | HOMO-1 -> LUMO+1 | 30.88% |
| 263.5 | 0.2223 | HOMO-2 -> LUMO+1 | 92.62% |

**Table S9.** Calculated ($\lambda_{TD\text{-}DFT}$) wavelengths of **6**. Molecular orbitals (MOs) involved in the main electronic transition，f corresponds to the oscillator strength. (TD-DFT, B3LYP/6-31g*)

| $\lambda_{TD\text{-}DFT}$ | Oscillator Strength, f | MOs | |
|---|---|---|---|
| 422.78 | 0.631 | HOMO -> LUMO | 98.24% |
| 390.22 | 0.2523 | HOMO-1 -> LUMO | 97.98% |
| 367.01 | 0.4948 | HOMO-3 -> LUMO | 87.29% |
| | | HOMO -> LUMO+1 | 6.26% |
| 291 | 0.3046 | HOMO-8 -> LUMO | 13.76% |
| | | HOMO -> LUMO+2 | 73.61% |
| | | HOMO -> LUMO+3 | 2.31% |
| | | HOMO -> LUMO+4 | 2.22% |
| 277.26 | 0.0742 | HOMO-9 -> LUMO | 2.75% |
| | | HOMO-8 -> LUMO | 2.98% |
| | | HOMO-1 -> LUMO+2 | 48.50% |
| | | HOMO-1 -> LUMO+4 | 16.78% |
| | | HOMO -> LUMO+4 | 20.96% |
| 269.15 | 0.0914 | HOMO-3 -> LUMO+2 | 46.23% |
| | | HOMO-3 -> LUMO+4 | 5.88% |

| | | | |
|---|---|---|---|
| | | HOMO-2 -> LUMO+2 | 11.05% |
| | | HOMO-2 -> LUMO+4 | 2.19% |
| | | HOMO -> LUMO+5 | 26.60% |
| 256.31 | 0.1325 | HOMO-9 -> LUMO+1 | 2.83% |
| | | HOMO-5 -> LUMO+2 | 5.70% |
| | | HOMO-5 -> LUMO+4 | 3.68% |
| | | HOMO-4 -> LUMO+2 | 4.03% |
| | | HOMO-3 -> LUMO+2 | 18.52% |
| | | HOMO-3 -> LUMO+3 | 2.95% |
| | | HOMO-1 -> LUMO+4 | 3.30% |
| | | HOMO -> LUMO+5 | 41.67% |

**Table S10.** Calculated ($\lambda_{TD\text{-}DFT}$) wavelengths of **7a**. Molecular orbitals (MOs) involved in the main electronic transition，f corresponds to the oscillator strength. (TD-DFT, B3LYP/6-31g*)

| $\lambda_{TD\text{-}DFT}$ | Oscillator Strength, f | MOs | |
|---|---|---|---|
| 422.46 | 0.6838 | HOMO-6 -> LUMO | 98.19% |
| 388.76 | 0.3305 | HOMO-7 -> LUMO | 97.92% |
| 371.48 | 0.0608 | HOMO-8 -> LUMO | 95.94% |
| 366.69 | 0.4676 | HOMO-9 -> LUMO | 87.19% |
| | | HOMO-8 -> LUMO | 2.09% |
| | | HOMO-6 -> LUMO+1 | 5.29% |
| 291.17 | 0.1022 | HOMO-16 -> LUMO | 3.86% |
| | | HOMO-6 -> LUMO+2 | 24.49% |
| | | HOMO-2 -> LUMO+3 | 37.99% |
| | | HOMO-2 -> LUMO+4 | 26.31% |
| 290.96 | 0.2217 | HOMO-16 -> LUMO | 9.35% |
| | | HOMO-6 -> LUMO+2 | 48.06% |
| | | HOMO-2 -> LUMO+3 | 19.73% |
| | | HOMO-2 -> LUMO+4 | 11.92% |
| 276.88 | 0.0738 | HOMO -17 -> LUMO | 3.31% |
| | | HOMO-16 -> LUMO | 3.46% |
| | | HOMO-17 -> LUMO+2 | 51.07% |
| | | HOMO-17 -> LUMO+4 | 15.55% |
| | | HOMO-6 -> LUMO+4 | 19.06% |

**Table S11.** Calculated ($\lambda_{TD\text{-}DFT}$) wavelengths of **7b**. Molecular orbitals (MOs) involved in the

main electronic transition，f corresponds to the oscillator strength. (TD-DFT, B3LYP/6-31g*)

| $\lambda_{TD-DFT}$ | Oscillator Strength, f | MOs | |
|---|---|---|---|
| 424.1 | 0.7209 | HOMO -> LUMO | 98.27% |
| 391.34 | 0.2689 | HOMO-1 -> LUMO | 98.11% |
| 373.66 | 0.0569 | HOMO-2 -> LUMO | 96.59% |
| 368.39 | 0.5332 | HOMO-3 -> LUMO | 89.98% |
| | | HOMO -> LUMO+1 | 3.39% |
| 291.5 | 0.235 | HOMO-12 -> LUMO | 8.53% |
| | | HOMO-7 -> LUMO+1 | 3.01% |
| | | HOMO-6 -> LUMO | 2.87% |
| | | HOMO-6 -> LUMO+1 | 27.70% |
| | | HOMO -> LUMO+2 | 48.91% |
| 256.1 | 0.1542 | HOMO -13-> LUMO+1 | 3.20% |
| | | HOMO-12 -> LUMO+1 | 2.25% |
| | | HOMO-5 -> LUMO+2 | 3.81% |
| | | HOMO-5 -> LUMO+4 | 2.63% |
| | | HOMO-4 -> LUMO+2 | 3.29% |
| | | HOMO-3 -> LUMO+2 | 15.93% |
| | | HOMO-2 -> LUMO+3 | 5.46% |
| | | HOMO-1 -> LUMO+4 | 4.75% |
| | | HOMO -> LUMO+5 | 44.57% |

## 9. 1H NMR and 13C NMR spectra

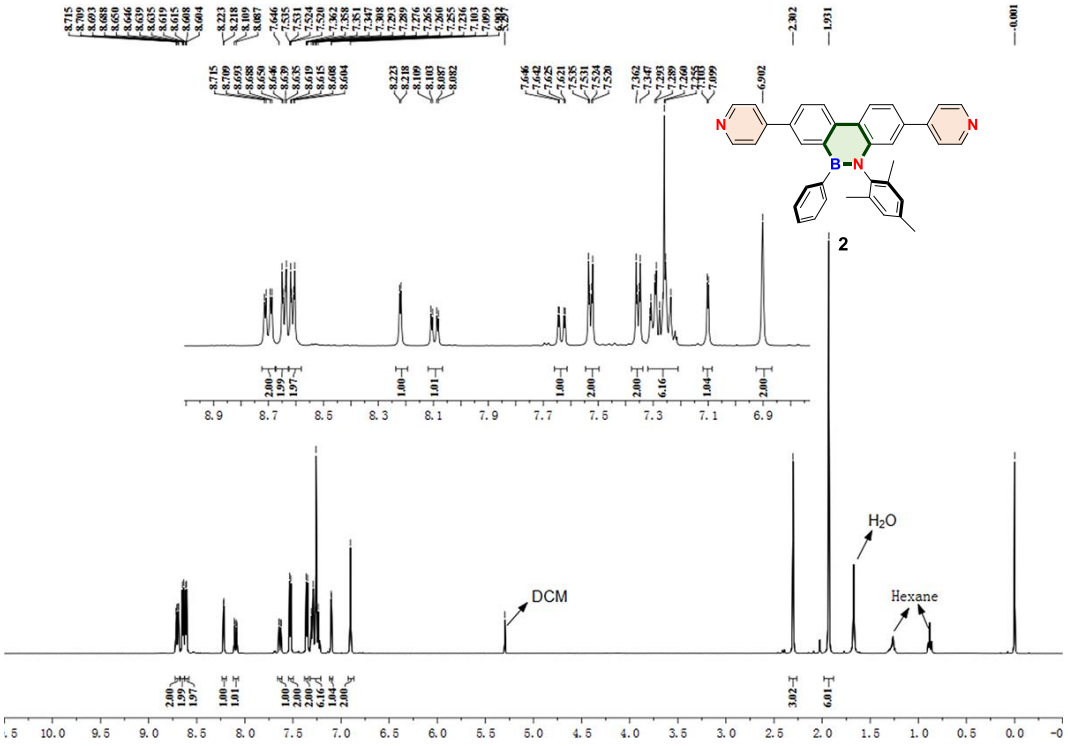



**Figure S32.** $^{1}$H NMR spectrum of **2** in $CDCl_3$

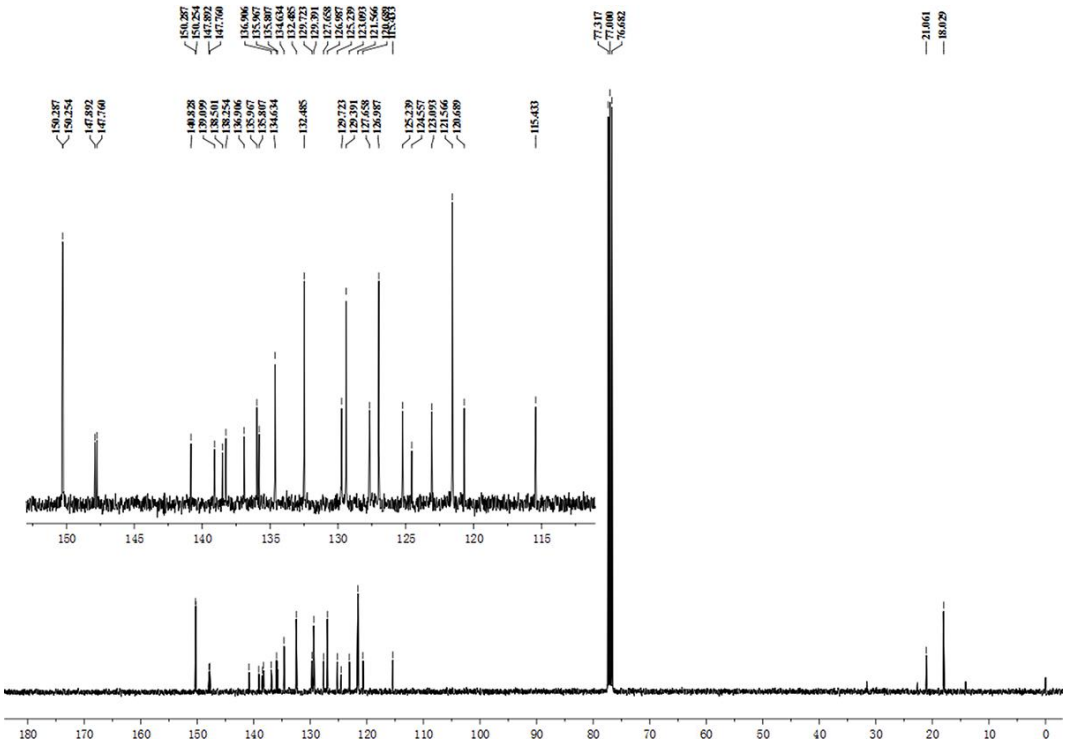


**Figure S33.** $^{13}$C NMR spectrum of **2** in $CDCl_3$

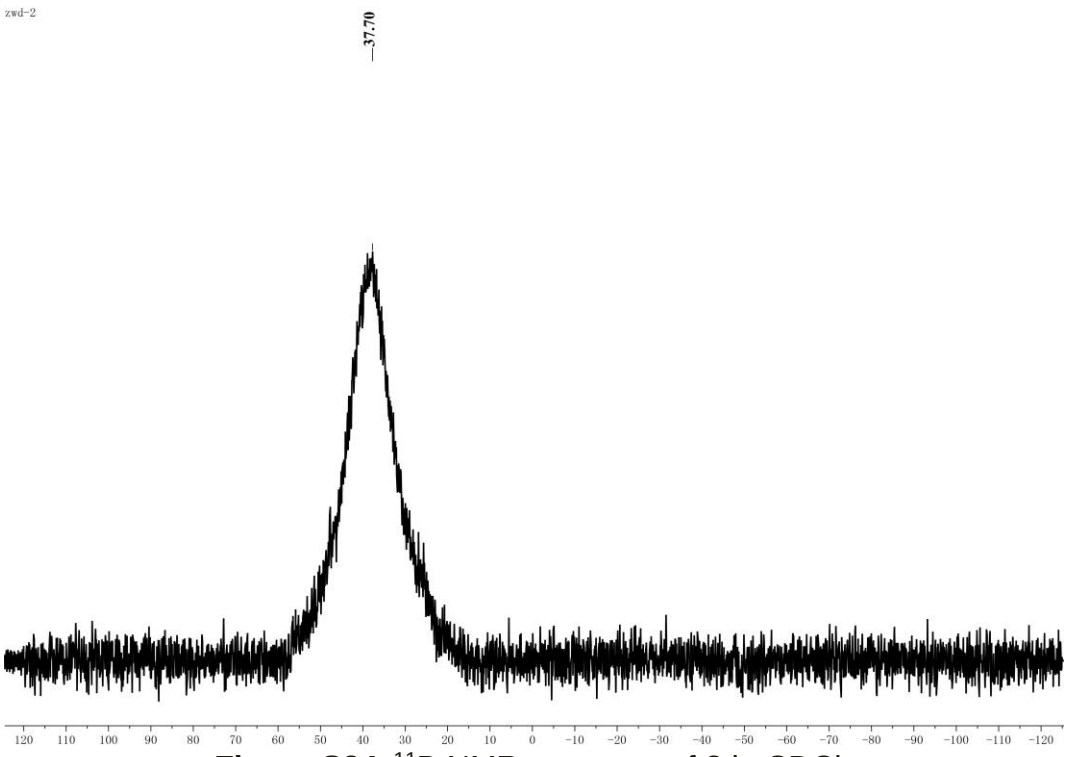



**Figure S34.** $^{11}B$ NMR spectrum of **2** in $CDCl_3$

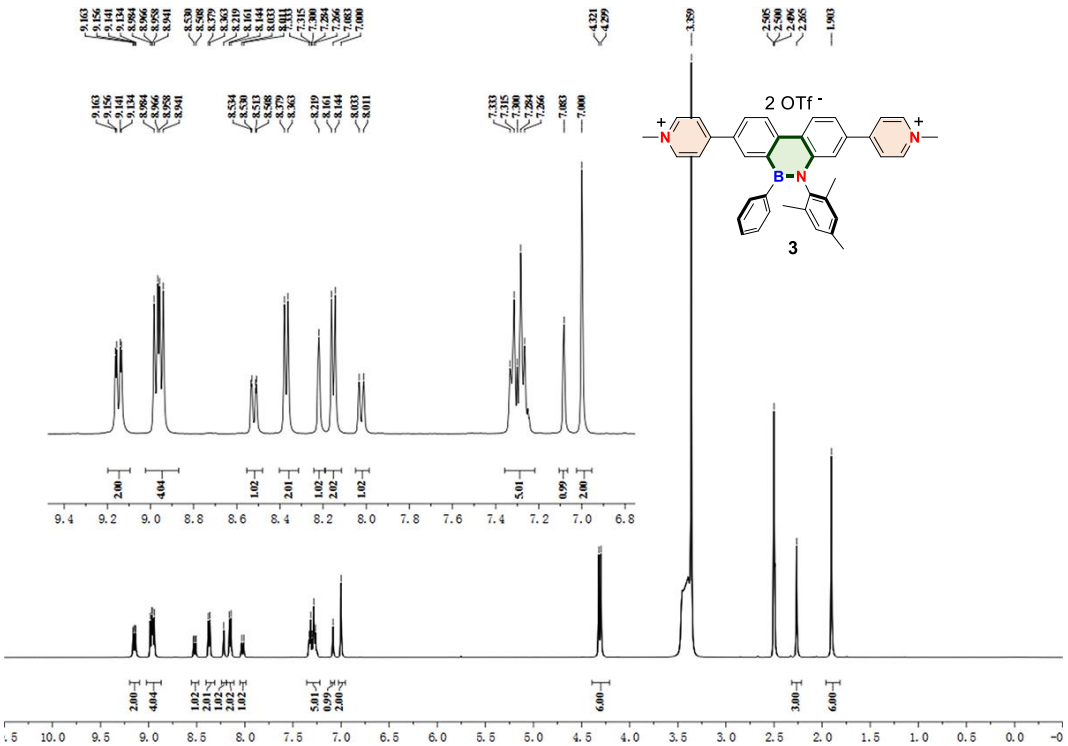



**Figure S35.** $^{1}H$ NMR spectrum of **3** in DMSO

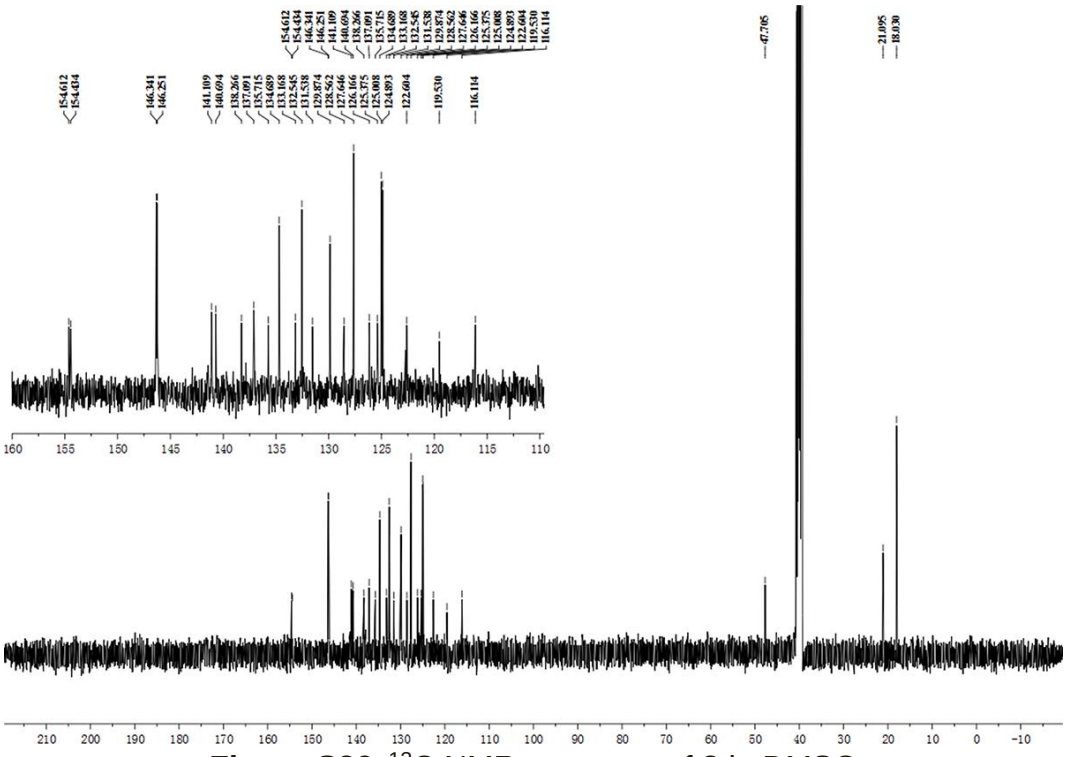


**Figure S36.** $^{13}$C NMR spectrum of **3** in DMSO

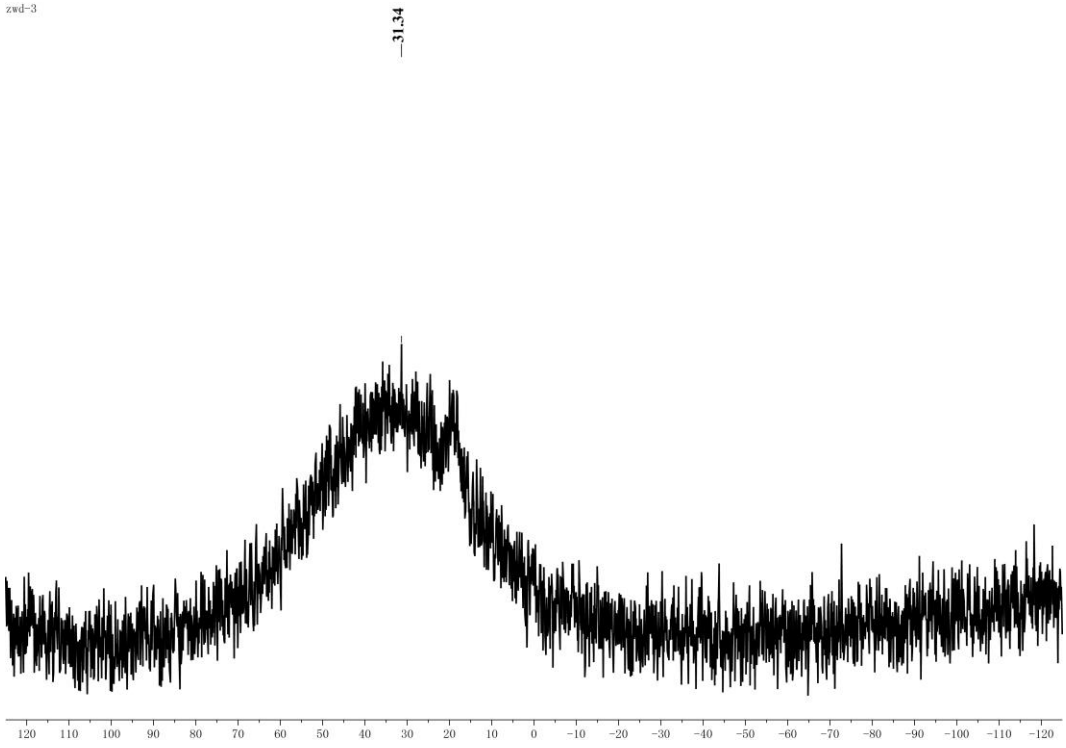


**Figure S37.** $^{11}$B NMR spectrum of **3** in DMSO

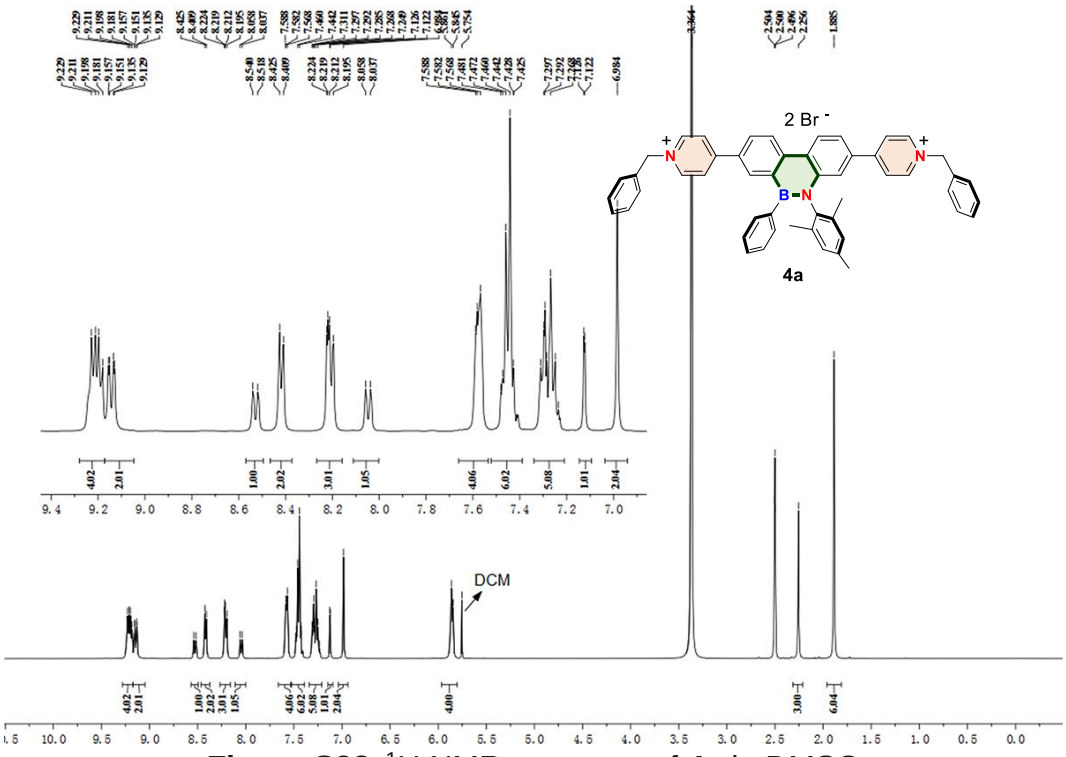



**Figure S38.** $^{1}$H NMR spectrum of **4a** in DMSO

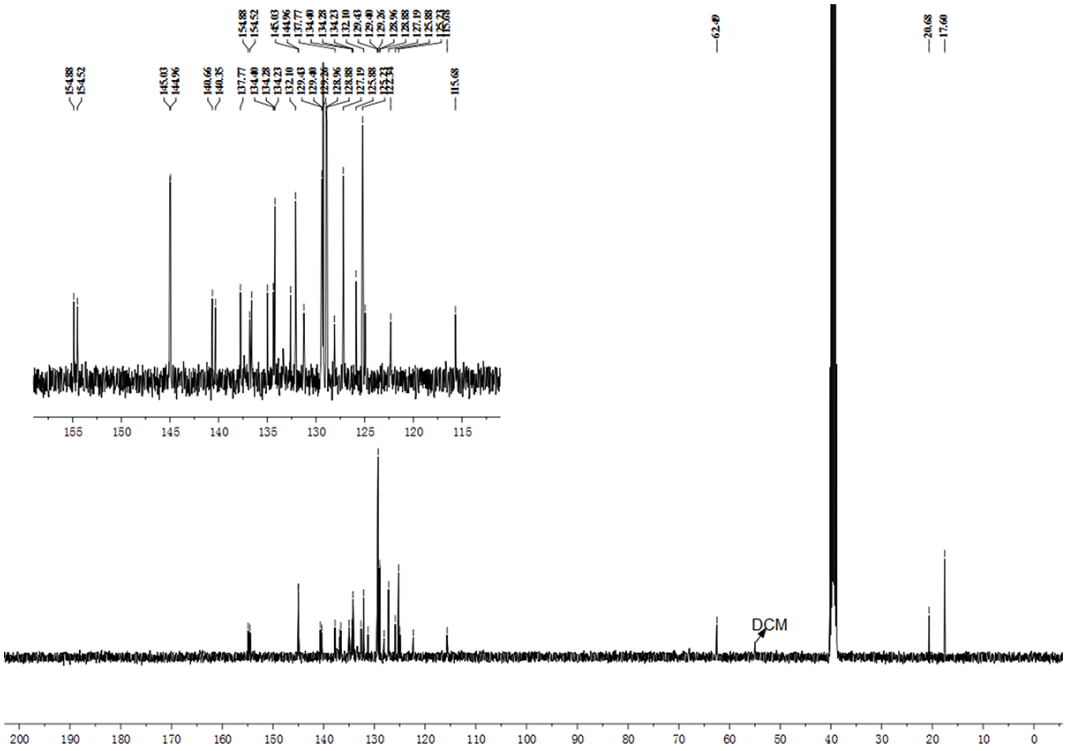



**Figure S39.** $^{13}$C NMR spectrum of **4a** in DMSO

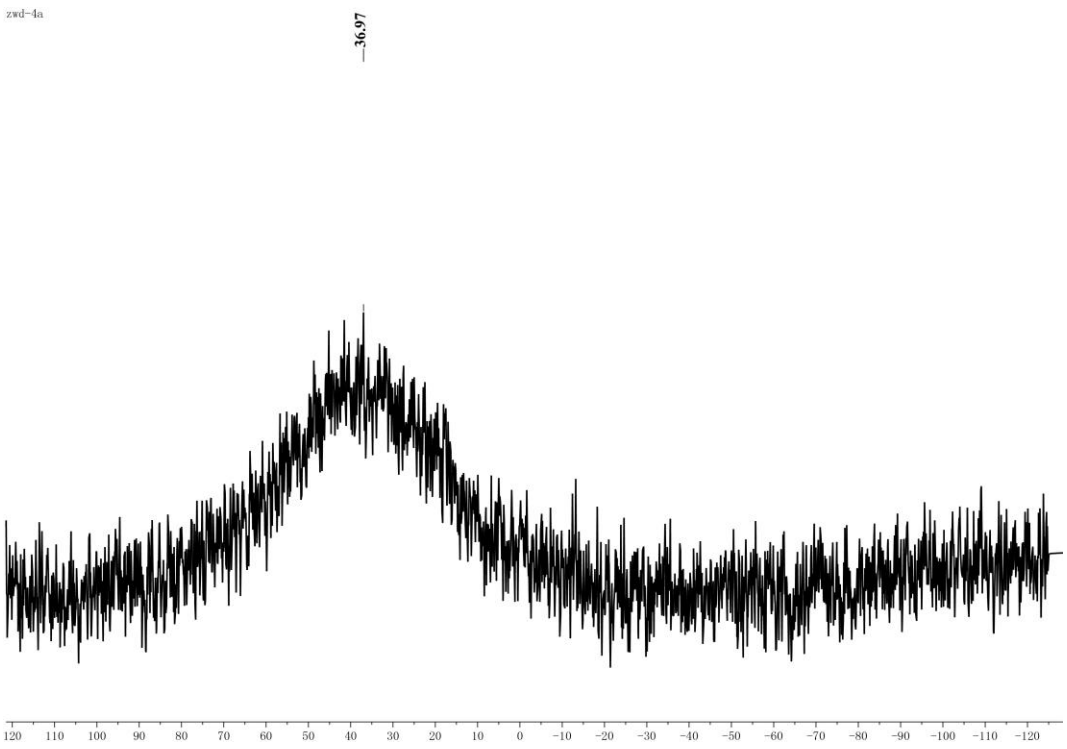



**Figure S40.** $^{11}$B NMR spectrum of **4a** in DMSO

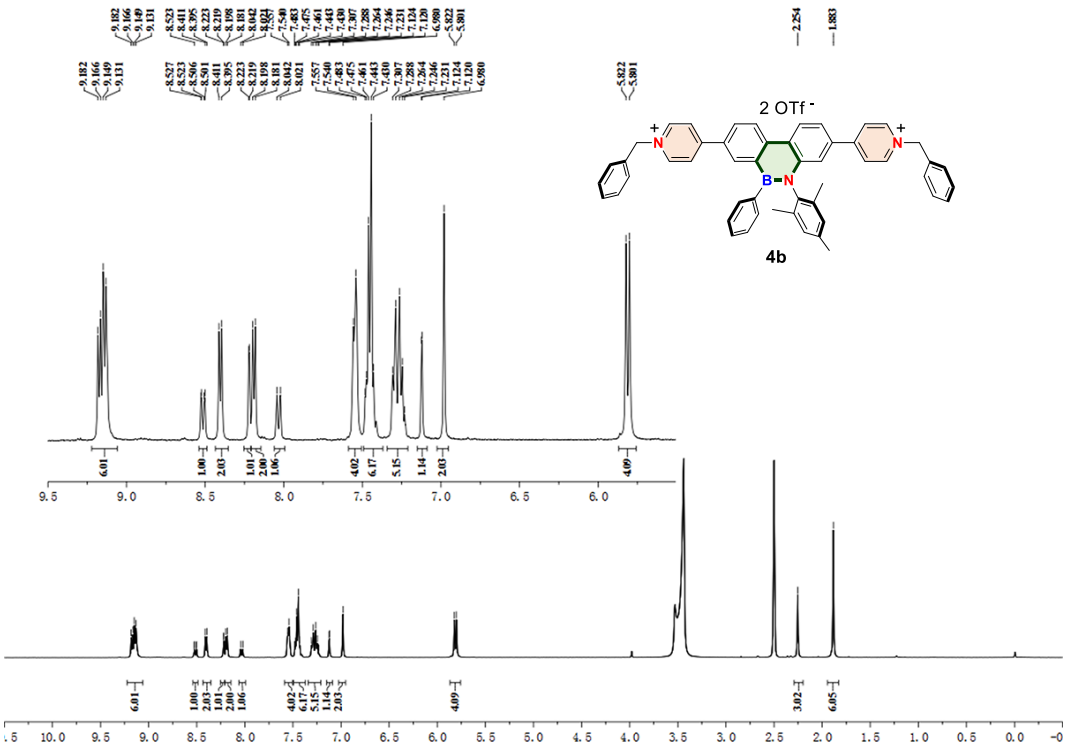



**Figure S41.** $^{1}$H NMR spectrum of **4b** in DMSO

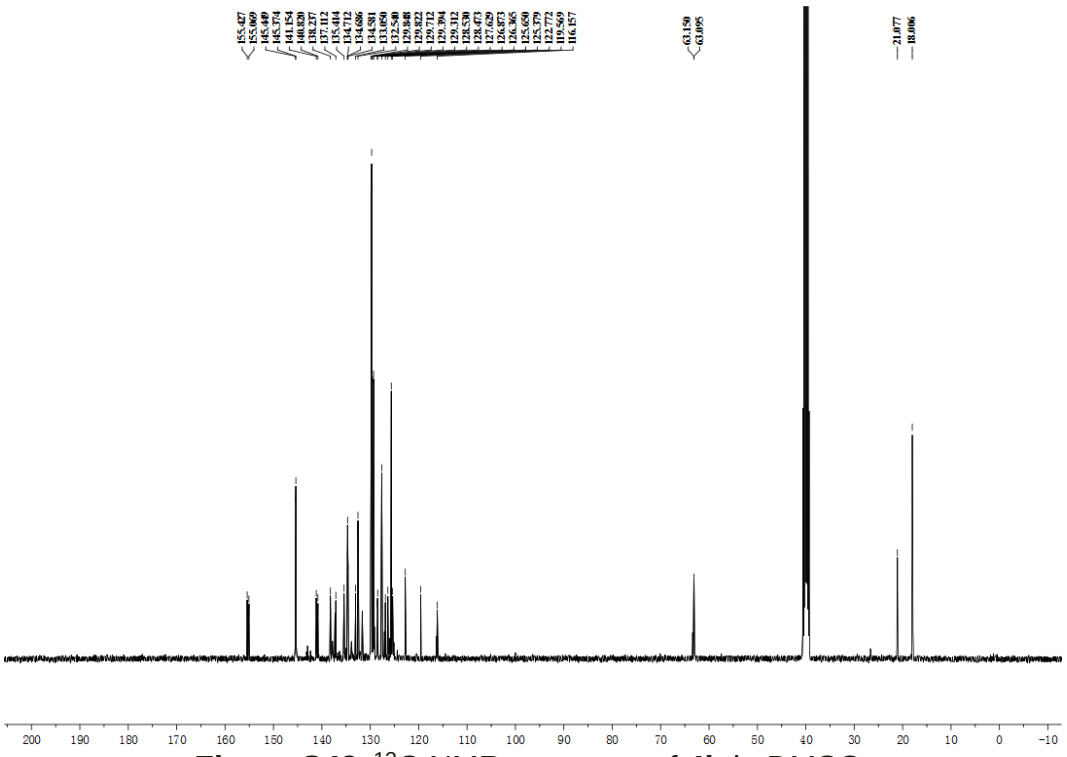



**Figure S42.** $^{13}$C NMR spectrum of **4b** in DMSO.

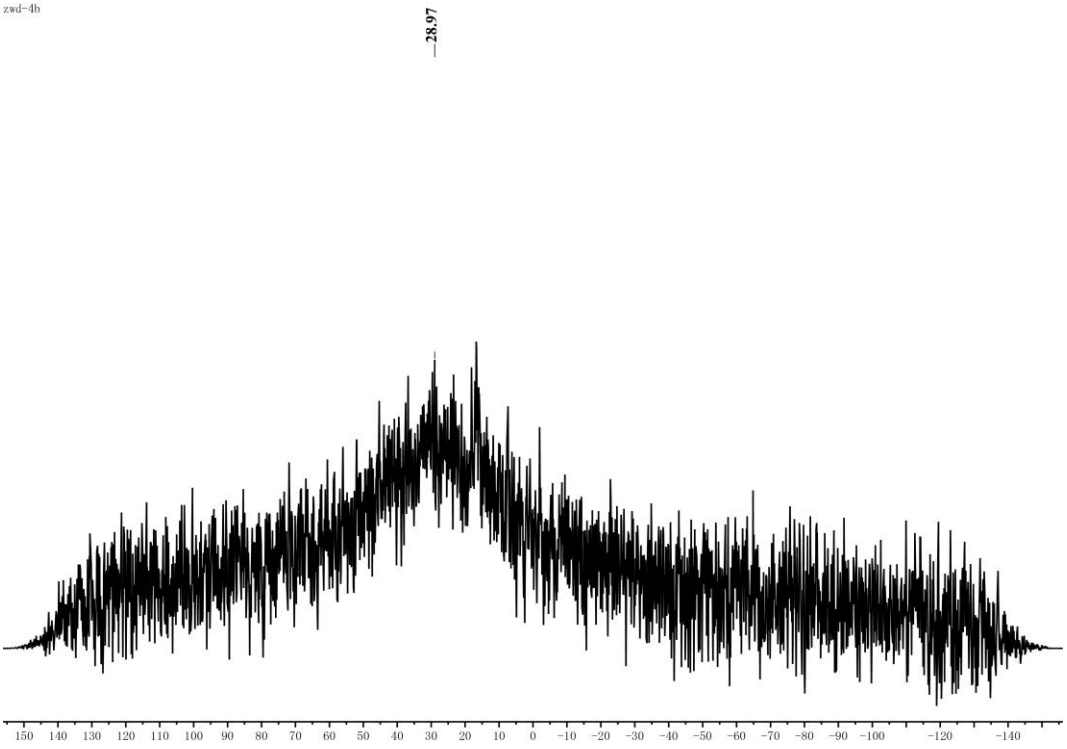



**Figure S43.** $^{11}$B NMR spectrum of **4b** in DMSO

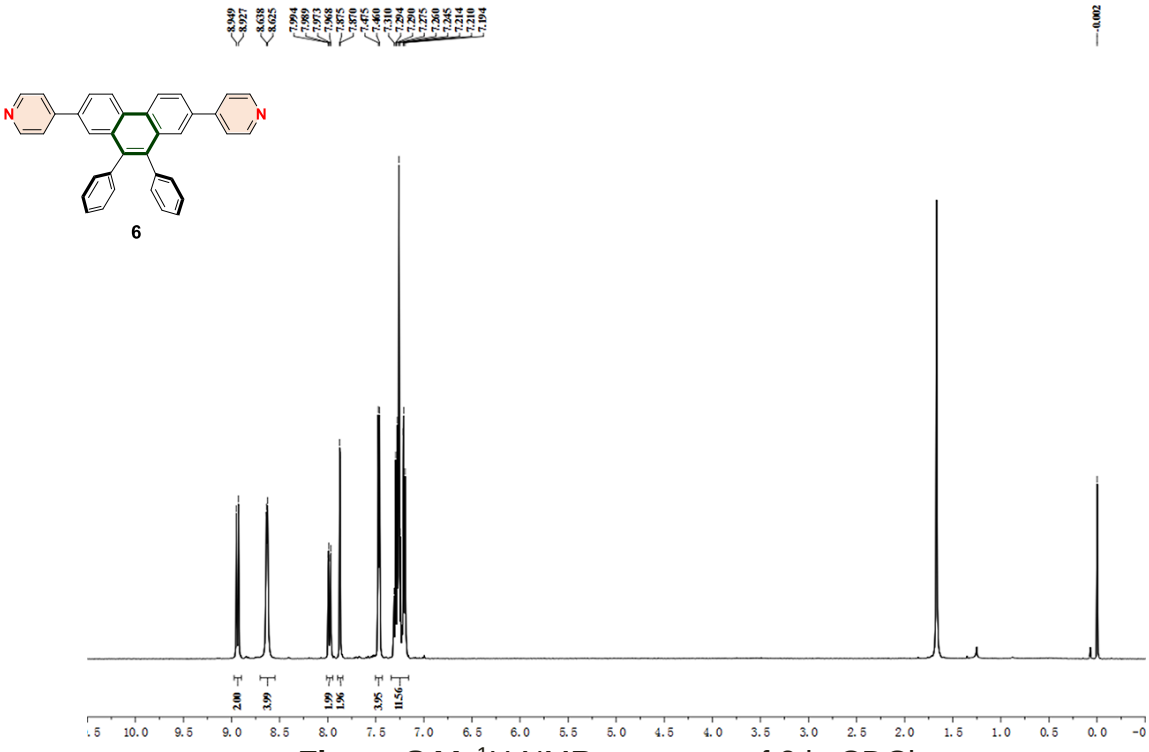



**Figure S44.** $^{1}$H NMR spectrum of **6** in $CDCl_3$.

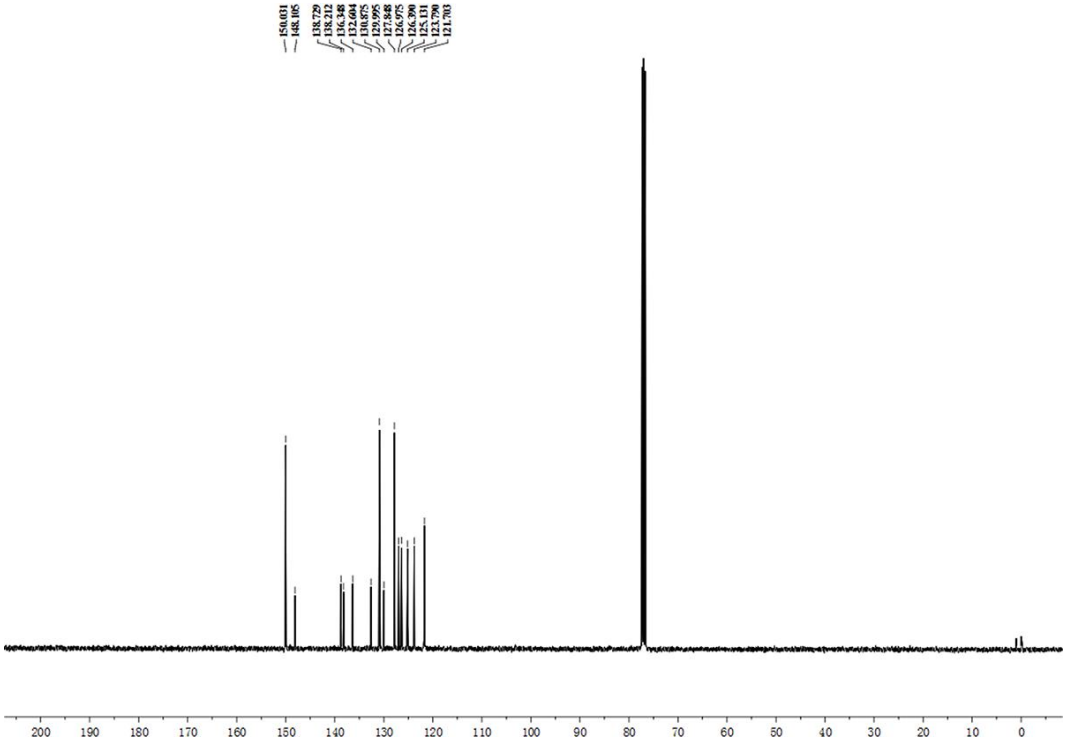


**Figure S45.** $^{13}$C NMR spectrum of **6** in $CDCl_3$.

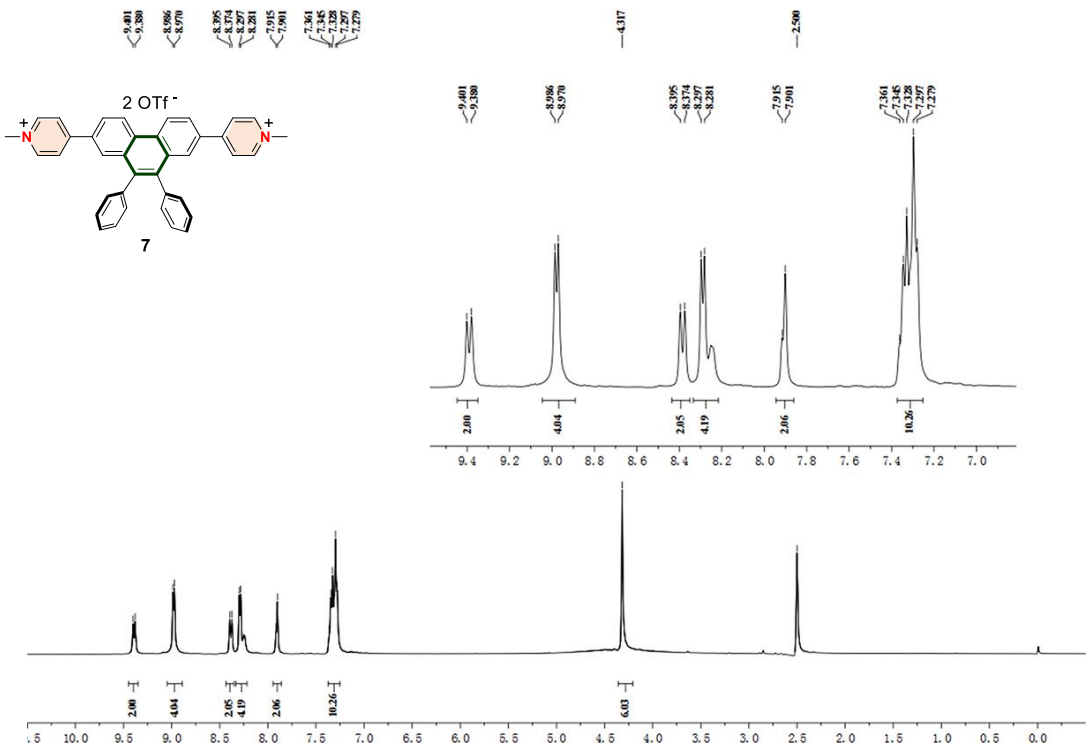



**Figure S46.** $^{1}$H NMR spectrum of **7** in DMSO

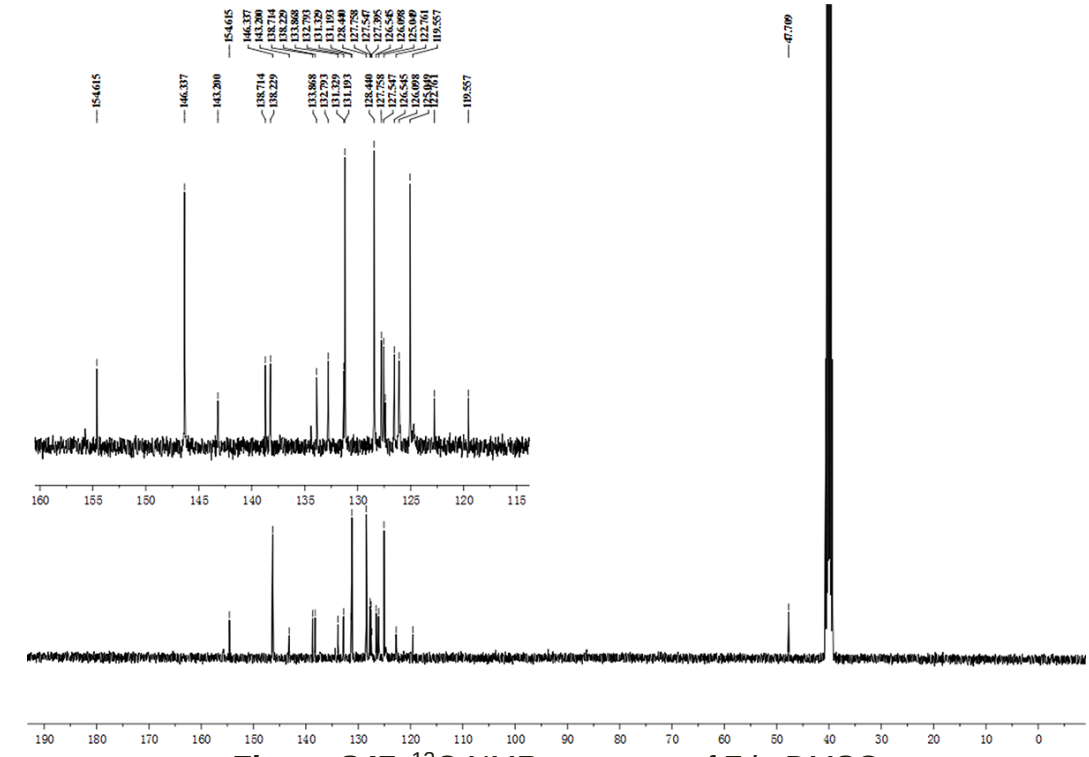


**Figure S47.** $^{13}$C NMR spectrum of **7** in DMSO

## 10. Coordinates of molecular structure

**Table S12** Cartesian coordinates of optimized geometry of **2** (DFT, B3LYP/6-31g*)
Standard orientation: (Ground State)

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 3.150823 | 0.570165 | 0.016391 |
| 2 | 6 | 0 | 1.745332 | 0.657784 | 0.008265 |
| 3 | 6 | 0 | 1.13879 | 1.941409 | 0.023298 |
| 4 | 6 | 0 | 1.973355 | 3.080491 | 0.076378 |
| 5 | 6 | 0 | 3.352007 | 2.960434 | 0.094917 |
| 6 | 6 | 0 | 3.975705 | 1.695505 | 0.063447 |
| 7 | 6 | 0 | 1.138465 | 0.876321 | 0.015591 |
| 8 | 6 | 0 | 2.538481 | 1.012824 | 0.017282 |
| 9 | 6 | 0 | 3.164415 | 2.25926 | 0.061789 |
| 10 | 6 | 0 | 2.357084 | 3.411631 | 0.074298 |
| 11 | 6 | 0 | 0.979819 | 3.292135 | 0.042629 |
| 12 | 6 | 0 | 0.32315 | 2.043616 | 0.000714 |
| 13 | 5 | 0 | 0.8599 | 0.61373 | 0.019603 |
| 14 | 7 | 0 | 0.556265 | 0.411859 | 0.037871 |
| 15 | 6 | 0 | 1.491642 | 2.060469 | 0.116506 |
| 16 | 6 | 0 | 1.458435 | 1.548144 | 0.09776 |
| 17 | 6 | 0 | 2.251847 | 2.406361 | 1.253081 |
| 18 | 6 | 0 | 2.847824 | 3.66326 | 1.384592 |
| 19 | 6 | 0 | 2.717839 | 4.607216 | 0.36403 |
| 20 | 6 | 0 | 1.984838 | 4.284477 | 0.780592 |
| 21 | 6 | 0 | 1.377569 | 3.03228 | 0.895753 |
| 22 | 6 | 0 | 1.943356 | 1.975537 | 1.348631 |
| 23 | 6 | 0 | 2.792346 | 3.086176 | 1.386834 |
| 24 | 6 | 0 | 3.177319 | 3.766277 | 0.225689 |
| 25 | 6 | 0 | 2.689977 | 3.303259 | 0.999599 |
| 26 | 6 | 0 | 1.836071 | 2.196885 | 1.090132 |
| 27 | 6 | 0 | 1.344823 | 1.726313 | 2.438658 |
| 28 | 6 | 0 | 1.580322 | 1.254888 | 2.626581 |
| 29 | 6 | 0 | 4.117538 | 4.94736 | 0.295994 |
| 30 | 1 | 0 | 3.604223 | 0.415727 | 0.02545 |
| 31 | 1 | 0 | 1.551412 | 4.078473 | 0.102308 |
| 32 | 1 | 0 | 3.958696 | 3.861192 | 0.114036 |
| 33 | 1 | 0 | 3.14676 | 0.118125 | 0.039921 |

| | | | | | |
|---|---|---|---|---|---|
| 34 | 1 | 0 | 2.80858 | 4.398415 | 0.085167 |
| 35 | 1 | 0 | 0.392363 | 4.202384 | 0.053206 |
| 36 | 1 | 0 | 2.379451 | 1.680087 | 2.053243 |
| 37 | 1 | 0 | 3.417538 | 3.901063 | 2.279366 |
| 38 | 1 | 0 | 3.185787 | 5.583732 | 0.457733 |
| 39 | 1 | 0 | 1.882914 | 5.009623 | 1.584128 |
| 40 | 1 | 0 | 0.809321 | 2.811193 | 1.7947 |
| 41 | 1 | 0 | 3.162211 | 3.4278 | 2.351398 |
| 42 | 1 | 0 | 2.981934 | 3.812916 | 1.915343 |
| 43 | 1 | 0 | 1.488021 | 0.647899 | 2.56846 |
| 44 | 1 | 0 | 0.274655 | 1.927394 | 2.567826 |
| 45 | 1 | 0 | 1.879953 | 2.239306 | 3.243035 |
| 46 | 1 | 0 | 0.496004 | 1.167487 | 2.758403 |
| 47 | 1 | 0 | 1.981216 | 0.234097 | 2.637508 |
| 48 | 1 | 0 | 1.984764 | 1.782868 | 3.494688 |
| 49 | 1 | 0 | 5.162168 | 4.61797 | 0.373444 |
| 50 | 1 | 0 | 4.038069 | 5.575455 | 0.596902 |
| 51 | 1 | 0 | 3.911186 | 5.5709 | 1.172661 |
| 52 | 6 | 0 | 4.643505 | 2.3605 | 0.101654 |
| 53 | 6 | 0 | 5.290006 | 3.394239 | 0.798388 |
| 54 | 6 | 0 | 5.469665 | 1.432733 | 0.553129 |
| 55 | 6 | 0 | 6.681871 | 3.44938 | 0.807864 |
| 56 | 1 | 0 | 4.720572 | 4.136748 | 1.347958 |
| 57 | 6 | 0 | 6.853383 | 1.57612 | 0.480882 |
| 58 | 1 | 0 | 5.044928 | 0.618927 | 1.132138 |
| 59 | 7 | 0 | 7.473005 | 2.563271 | 0.184153 |
| 60 | 1 | 0 | 7.187474 | 4.24605 | 1.351027 |
| 61 | 1 | 0 | 7.497934 | 0.861984 | 0.990668 |
| 62 | 6 | 0 | 5.452226 | 1.567798 | 0.087979 |
| 63 | 6 | 0 | 6.113425 | 0.52677 | 0.584476 |
| 64 | 6 | 0 | 6.263515 | 2.478817 | 0.783954 |
| 65 | 6 | 0 | 7.502737 | 0.44687 | 0.528527 |
| 66 | 1 | 0 | 5.557134 | 0.202599 | 1.164381 |
| 67 | 6 | 0 | 7.646511 | 2.311527 | 0.775742 |
| 68 | 1 | 0 | 5.82715 | 3.297884 | 1.346794 |
| 69 | 7 | 0 | 8.279527 | 1.316523 | 0.135692 |
| 70 | 1 | 0 | 8.019403 | 0.356168 | 1.051625 |
| 71 | 1 | 0 | 8.27874 | 3.012665 | 1.31809 |
| 71 | 1 | 0 | 8.27874 | 3.012665 | 1.31809 |

**Table S13** Cartesian coordinates of optimized geometry of **3** (DFT, B3LYP/6-31g*)
Standard orientation: (Ground State)

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -2.92324 | 1.253145 | -0.338034 |
| 2 | 6 | 0 | -1.51729 | 1.234452 | -0.346741 |
| 3 | 6 | 0 | -0.85195 | -0.004064 | -0.544748 |
| 4 | 6 | 0 | -1.62834 | -1.171624 | -0.726936 |
| 5 | 6 | 0 | -3.00929 | -1.12305 | -0.713099 |
| 6 | 6 | 0 | -3.69019 | 0.098619 | -0.518952 |
| 7 | 6 | 0 | 1.367033 | 1.146356 | -0.28699 |
| 8 | 6 | 0 | 2.771425 | 1.078002 | -0.302194 |
| 9 | 6 | 0 | 3.452258 | -0.11537 | -0.5507 |
| 10 | 6 | 0 | 2.705987 | -1.282207 | -0.802234 |
| 11 | 6 | 0 | 1.325843 | -1.224313 | -0.805806 |
| 12 | 6 | 0 | 0.611989 | -0.034291 | -0.547197 |
| 13 | 5 | 0 | -0.69646 | 2.526671 | -0.09413 |
| 14 | 7 | 0 | 0.726104 | 2.377272 | -0.031551 |
| 15 | 6 | 0 | -1.39898 | 3.932917 | 0.057373 |
| 16 | 6 | 0 | 1.571609 | 3.52122 | 0.265833 |
| 17 | 6 | 0 | -2.16792 | 4.436173 | -1.012953 |
| 18 | 6 | 0 | -2.82322 | 5.667351 | -0.930685 |
| 19 | 6 | 0 | -2.74582 | 6.421954 | 0.241456 |
| 20 | 6 | 0 | -2.00579 | 5.937977 | 1.323012 |
| 21 | 6 | 0 | -1.33899 | 4.715122 | 1.226496 |
| 22 | 6 | 0 | 2.007193 | 3.728316 | 1.587369 |
| 23 | 6 | 0 | 2.802993 | 4.848392 | 1.854023 |
| 24 | 6 | 0 | 3.177125 | 5.748273 | 0.851076 |
| 25 | 6 | 0 | 2.746485 | 5.494915 | -0.455326 |
| 26 | 6 | 0 | 1.946928 | 4.391403 | -0.773082 |
| 27 | 6 | 0 | 1.511064 | 4.155738 | -2.199978 |
| 28 | 6 | 0 | 1.659883 | 2.764479 | 2.698625 |
| 29 | 6 | 0 | 4.009504 | 6.968101 | 1.170576 |
| 30 | 1 | 0 | -3.4202 | 2.198199 | -0.147669 |
| 31 | 1 | 0 | -1.15858 | -2.135393 | -0.880537 |
| 32 | 1 | 0 | -3.5671 | -2.039138 | -0.879932 |
| 33 | 1 | 0 | 3.334728 | 1.975731 | -0.084757 |
| 34 | 1 | 0 | 3.201469 | -2.219227 | -1.032192 |

| | | | | | |
|---|---|---|---|---|---|
| 35 | 1 | 0 | 0.783231 | -2.134439 | -1.028767 |
| 36 | 1 | 0 | -2.25341 | 3.857715 | -1.930598 |
| 37 | 1 | 0 | -3.39733 | 6.032296 | -1.77848 |
| 38 | 1 | 0 | -3.26003 | 7.376741 | 0.313195 |
| 39 | 1 | 0 | -1.94498 | 6.514359 | 2.242634 |
| 40 | 1 | 0 | -0.76723 | 4.366176 | 2.081381 |
| 41 | 1 | 0 | 3.140088 | 5.017955 | 2.874272 |
| 42 | 1 | 0 | 3.041932 | 6.17218 | -1.253863 |
| 43 | 1 | 0 | 1.701173 | 3.125206 | -2.519423 |
| 44 | 1 | 0 | 0.437361 | 4.339844 | -2.325558 |
| 45 | 1 | 0 | 2.045006 | 4.825709 | -2.87994 |
| 46 | 1 | 0 | 0.583669 | 2.567852 | 2.755413 |
| 47 | 1 | 0 | 2.149611 | 1.793537 | 2.553705 |
| 48 | 1 | 0 | 1.983469 | 3.159429 | 3.665592 |
| 49 | 1 | 0 | 4.685643 | 7.218241 | 0.346139 |
| 50 | 1 | 0 | 3.372631 | 7.845613 | 1.34404 |
| 51 | 1 | 0 | 4.609982 | 6.817875 | 2.07344 |
| 52 | 6 | 0 | 4.927617 | -0.146058 | -0.551659 |
| 53 | 6 | 0 | 5.63883 | -1.294932 | -0.15722 |
| 54 | 6 | 0 | 5.692555 | 0.967084 | -0.948336 |
| 55 | 6 | 0 | 7.018954 | -1.310988 | -0.164517 |
| 56 | 1 | 0 | 5.121305 | -2.183894 | 0.181949 |
| 57 | 6 | 0 | 7.070551 | 0.906699 | -0.940354 |
| 58 | 1 | 0 | 5.221695 | 1.879573 | -1.292507 |
| 59 | 7 | 0 | 7.718241 | -0.216996 | -0.554211 |
| 60 | 1 | 0 | 7.601746 | -2.177036 | 0.143625 |
| 61 | 1 | 0 | 7.689315 | 1.740002 | -1.247161 |
| 62 | 6 | 0 | -5.16273 | 0.151216 | -0.494613 |
| 63 | 6 | 0 | -5.86806 | 1.306738 | -0.891794 |
| 64 | 6 | 0 | -5.93667 | -0.946658 | -0.076399 |
| 65 | 6 | 0 | -7.24442 | 1.330702 | -0.860934 |
| 66 | 1 | 0 | -5.3486 | 2.185986 | -1.251909 |
| 67 | 6 | 0 | -7.3164 | -0.878701 | -0.063321 |
| 68 | 1 | 0 | -5.47165 | -1.862366 | 0.267247 |
| 69 | 7 | 0 | -7.95407 | 0.250115 | -0.452622 |
| 70 | 1 | 0 | -7.82021 | 2.195785 | -1.16574 |
| 71 | 1 | 0 | -7.94808 | -1.701169 | 0.259248 |
| 72 | 8 | 0 | 9.924908 | -3.429131 | -1.424805 |
| 73 | 8 | 0 | -10.2846 | -4.465911 | -0.888966 |

| | | | | | |
|---|---|---|---|---|---|
| 74 | 16 | 0 | 9.864473 | -4.210932 | -0.163668 |
| 75 | 16 | 0 | -10.5054 | -3.949257 | 0.479982 |
| 76 | 8 | 0 | -9.56442 | -2.872973 | 0.899624 |
| 77 | 8 | 0 | -10.7626 | -4.974427 | 1.515183 |
| 78 | 8 | 0 | 8.752499 | -3.820912 | 0.744001 |
| 79 | 8 | 0 | 10.06651 | -5.667656 | -0.314115 |
| 80 | 6 | 0 | 11.37709 | -3.648472 | 0.759627 |
| 81 | 6 | 0 | -12.1222 | -3.041651 | 0.350113 |
| 82 | 9 | 0 | 11.46403 | -4.257145 | 1.953085 |
| 83 | 9 | 0 | 12.49076 | -3.927581 | 0.063731 |
| 84 | 9 | 0 | 11.34005 | -2.31945 | 0.97125 |
| 85 | 9 | 0 | -12.0298 | -2.031827 | -0.537089 |
| 86 | 9 | 0 | -13.1022 | -3.863582 | -0.057866 |
| 87 | 9 | 0 | -12.478 | -2.520242 | 1.535125 |
| 88 | 6 | 0 | -9.43275 | 0.318698 | -0.431801 |
| 89 | 1 | 0 | -9.82564 | -0.654497 | -0.14406 |
| 90 | 1 | 0 | -9.74238 | 1.07631 | 0.290523 |
| 91 | 6 | 0 | 9.198214 | -0.261903 | -0.529262 |
| 92 | 1 | 0 | 9.537997 | -0.195736 | 0.506174 |
| 93 | 1 | 0 | 9.583068 | 0.581835 | -1.100008 |
| 94 | 1 | 0 | 9.52967 | -1.204053 | -0.969081 |
| 95 | 1 | 0 | -9.7877 | 0.587693 | -1.42788 |

**Table S14** Cartesian coordinates of optimized geometry of **4a** (DFT, B3LYP/6-31g*) Standard orientation: (Ground State)

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 2.980989 | 0.291464 | -0.53715 |
| 2 | 6 | 0 | 1.584939 | 0.354883 | -0.38125 |
| 3 | 6 | 0 | 0.8273 | -0.83833 | -0.51848 |
| 4 | 6 | 0 | 1.506649 | -2.04656 | -0.79746 |
| 5 | 6 | 0 | 2.882248 | -2.08197 | -0.92629 |
| 6 | 6 | 0 | 3.652697 | -0.90556 | -0.80061 |
| 7 | 6 | 0 | -1.2905 | 0.463858 | -0.15407 |
| 8 | 6 | 0 | -2.68899 | 0.479256 | -0.00853 |
| 9 | 6 | 0 | -3.45253 | -0.68858 | -0.06077 |
| 10 | 6 | 0 | -2.79736 | -1.9169 | -0.2706 |
| 11 | 6 | 0 | -1.42474 | -1.9439 | -0.42372 |

| | | | | | |
|---|---|---|---|---|---|
| 12 | 6 | 0 | -0.62832 | -0.77965 | -0.36898 |
| 13 | 5 | 0 | 0.868537 | 1.703997 | -0.10892 |
| 14 | 7 | 0 | -0.56177 | 1.668555 | -0.0611 |
| 15 | 6 | 0 | 1.679947 | 3.039295 | 0.122856 |
| 16 | 6 | 0 | -1.32055 | 2.894652 | 0.119986 |
| 17 | 6 | 0 | 2.57123 | 3.12347 | 1.212892 |
| 18 | 6 | 0 | 3.322421 | 4.275455 | 1.459371 |
| 19 | 6 | 0 | 3.218859 | 5.372326 | 0.601931 |
| 20 | 6 | 0 | 2.356899 | 5.308346 | -0.49573 |
| 21 | 6 | 0 | 1.596507 | 4.160156 | -0.72525 |
| 22 | 6 | 0 | -1.84987 | 3.547321 | -1.00927 |
| 23 | 6 | 0 | -2.56072 | 4.736002 | -0.81366 |
| 24 | 6 | 0 | -2.76048 | 5.280202 | 0.459981 |
| 25 | 6 | 0 | -2.24047 | 4.590881 | 1.559388 |
| 26 | 6 | 0 | -1.52089 | 3.39845 | 1.416734 |
| 27 | 6 | 0 | -0.98771 | 2.683517 | 2.635702 |
| 28 | 6 | 0 | -1.68792 | 2.981821 | -2.40162 |
| 29 | 6 | 0 | -3.50256 | 6.584189 | 0.638176 |
| 30 | 1 | 0 | 3.550662 | 1.206886 | -0.41846 |
| 31 | 1 | 0 | 0.963474 | -2.97438 | -0.92881 |
| 32 | 1 | 0 | 3.362134 | -3.02641 | -1.16308 |
| 33 | 1 | 0 | -3.17552 | 1.424847 | 0.190362 |
| 34 | 1 | 0 | -3.36057 | -2.84085 | -0.34455 |
| 35 | 1 | 0 | -0.95441 | -2.90518 | -0.58853 |
| 36 | 1 | 0 | 2.677922 | 2.274815 | 1.885395 |
| 37 | 1 | 0 | 3.99112 | 4.312318 | 2.315504 |
| 38 | 1 | 0 | 3.806598 | 6.268027 | 0.784956 |
| 39 | 1 | 0 | 2.274388 | 6.154496 | -1.17313 |
| 40 | 1 | 0 | 0.931005 | 4.139962 | -1.58332 |
| 41 | 1 | 0 | -2.96924 | 5.248742 | -1.68185 |
| 42 | 1 | 0 | -2.40017 | 4.98674 | 2.559963 |
| 43 | 1 | 0 | -1.24898 | 1.619564 | 2.63045 |
| 44 | 1 | 0 | 0.105585 | 2.74716 | 2.690498 |
| 45 | 1 | 0 | -1.39316 | 3.128069 | 3.549078 |
| 46 | 1 | 0 | -0.64494 | 2.736419 | -2.62976 |
| 47 | 1 | 0 | -2.26314 | 2.056085 | -2.52727 |
| 48 | 1 | 0 | -2.04007 | 3.696409 | -3.15072 |
| 49 | 1 | 0 | -4.30975 | 6.689328 | -0.09455 |
| 50 | 1 | 0 | -3.93615 | 6.664009 | 1.640133 |

| | | | | | |
|---|---|---|---|---|---|
| 51 | 1 | 0 | -2.83032 | 7.441953 | 0.503797 |
| 52 | 6 | 0 | -4.91721 | -0.63159 | 0.110303 |
| 53 | 6 | 0 | -5.63285 | -1.69814 | 0.682531 |
| 54 | 6 | 0 | -5.66776 | 0.492918 | -0.28819 |
| 55 | 6 | 0 | -7.00433 | -1.62979 | 0.839024 |
| 56 | 1 | 0 | -5.1242 | -2.58509 | 1.040131 |
| 57 | 6 | 0 | -7.03407 | 0.517224 | -0.11264 |
| 58 | 1 | 0 | -5.19527 | 1.347688 | -0.75608 |
| 59 | 7 | 0 | -7.68804 | -0.53075 | 0.44296 |
| 60 | 1 | 0 | -7.59209 | -2.42763 | 1.294656 |
| 61 | 1 | 0 | -7.64096 | 1.361579 | -0.41301 |
| 62 | 6 | 0 | 5.120311 | -0.93943 | -0.93346 |
| 63 | 6 | 0 | 5.845619 | 0.171734 | -1.41108 |
| 64 | 6 | 0 | 5.86935 | -2.07894 | -0.58802 |
| 65 | 6 | 0 | 7.218458 | 0.119934 | -1.50854 |
| 66 | 1 | 0 | 5.342308 | 1.074657 | -1.73361 |
| 67 | 6 | 0 | 7.246142 | -2.08701 | -0.70573 |
| 68 | 1 | 0 | 5.388979 | -2.96859 | -0.19918 |
| 69 | 7 | 0 | 7.905271 | -0.99386 | -1.15676 |
| 70 | 1 | 0 | 7.803885 | 0.953151 | -1.87513 |
| 71 | 1 | 0 | 7.859923 | -2.9516 | -0.45069 |
| 72 | 6 | 0 | -9.1836 | -0.48072 | 0.591772 |
| 73 | 1 | 0 | -9.43728 | -1.23165 | 1.344926 |
| 74 | 1 | 0 | -9.41931 | 0.513108 | 0.977467 |
| 75 | 6 | 0 | 9.40678 | -0.99736 | -1.23107 |
| 76 | 1 | 0 | 9.707473 | -2.04857 | -1.23772 |
| 77 | 1 | 0 | 9.668405 | -0.54056 | -2.18758 |
| 78 | 6 | 0 | 10.03277 | -0.26054 | -0.06617 |
| 79 | 6 | 0 | 10.32772 | -0.95215 | 1.117629 |
| 80 | 6 | 0 | 10.31796 | 1.108745 | -0.15259 |
| 81 | 6 | 0 | 10.88442 | -0.27505 | 2.20375 |
| 82 | 1 | 0 | 10.14716 | -2.02416 | 1.165767 |
| 83 | 6 | 0 | 10.87356 | 1.784056 | 0.935734 |
| 84 | 1 | 0 | 10.11976 | 1.650037 | -1.07485 |
| 85 | 6 | 0 | 11.15256 | 1.093715 | 2.1175 |
| 86 | 1 | 0 | 11.1154 | -0.81846 | 3.115885 |
| 87 | 1 | 0 | 11.09391 | 2.844924 | 0.857383 |
| 88 | 1 | 0 | 11.58713 | 1.618244 | 2.96401 |
| 89 | 6 | 0 | -9.89584 | -0.7592 | -0.71426 |

| | | | | | |
|---|---|---|---|---|---|
| 90 | 6 | 0 | -10.2027 | -2.07982 | -1.07265 |
| 91 | 6 | 0 | -10.2549 | 0.288481 | -1.57272 |
| 92 | 6 | 0 | -10.8443 | -2.34508 | -2.28337 |
| 93 | 1 | 0 | -9.96576 | -2.8864 | -0.38158 |
| 94 | 6 | 0 | -10.8959 | 0.0204 | -2.78372 |
| 95 | 1 | 0 | -10.0485 | 1.318495 | -1.29129 |
| 96 | 6 | 0 | -11.1866 | -1.29769 | -3.14296 |
| 97 | 1 | 0 | -11.0842 | -3.37017 | -2.55221 |
| 98 | 1 | 0 | -11.1733 | 0.839935 | -3.4406 |
| 99 | 1 | 0 | -11.6877 | -1.50685 | -4.08409 |
| 100 | 35 | 0 | 9.826839 | -4.59408 | -0.16082 |
| 101 | 35 | 0 | -9.47798 | -3.84682 | 2.304598 |

**Table S15** Cartesian coordinates of optimized geometry of **4b** (DFT, B3LYP/6-31g*)
Standard orientation: (Ground State)

| Center | Atomic | Atomic | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| Number | Number | Type | X | Y | Z |
| 1 | 6 | 0 | 2.958784 | 1.228465 | -0.28195 |
| 2 | 6 | 0 | 1.552787 | 1.233238 | -0.26922 |
| 3 | 6 | 0 | 0.866692 | -0.00419 | -0.15116 |
| 4 | 6 | 0 | 1.623346 | -1.19371 | -0.04412 |
| 5 | 6 | 0 | 3.004865 | -1.16759 | -0.05821 |
| 6 | 6 | 0 | 3.706584 | 0.051914 | -0.17855 |
| 7 | 6 | 0 | -1.33227 | 1.1957 | -0.3444 |
| 8 | 6 | 0 | -2.73757 | 1.148222 | -0.34615 |
| 9 | 6 | 0 | -3.43917 | -0.04692 | -0.17457 |
| 10 | 6 | 0 | -2.71224 | -1.23782 | 0.014 |
| 11 | 6 | 0 | -1.33154 | -1.20243 | 0.028501 |
| 12 | 6 | 0 | -0.59744 | -0.01057 | -0.15392 |
| 13 | 5 | 0 | 0.753592 | 2.553093 | -0.43365 |
| 14 | 7 | 0 | -0.67054 | 2.430635 | -0.51354 |
| 15 | 6 | 0 | 1.478763 | 3.955575 | -0.47724 |
| 16 | 6 | 0 | -1.49733 | 3.604155 | -0.73859 |
| 17 | 6 | 0 | 2.250269 | 4.362297 | 0.631654 |
| 18 | 6 | 0 | 2.925487 | 5.585241 | 0.647392 |
| 19 | 6 | 0 | 2.865643 | 6.429083 | -0.46334 |
| 20 | 6 | 0 | 2.122733 | 6.042414 | -1.58155 |
| 21 | 6 | 0 | 1.435909 | 4.826837 | -1.58231 |

| | | | | | |
|---|---|---|---|---|---|
| 22 | 6 | 0 | -1.91864 | 3.905755 | -2.04675 |
| 23 | 6 | 0 | -2.70084 | 5.049375 | -2.24279 |
| 24 | 6 | 0 | -3.07416 | 5.883269 | -1.18371 |
| 25 | 6 | 0 | -2.65662 | 5.537729 | 0.105561 |
| 26 | 6 | 0 | -1.87163 | 4.4061 | 0.353967 |
| 27 | 6 | 0 | -1.44998 | 4.068809 | 1.76462 |
| 28 | 6 | 0 | -1.56805 | 3.017876 | -3.2187 |
| 29 | 6 | 0 | -3.89119 | 7.13078 | -1.42687 |
| 30 | 1 | 0 | 3.470952 | 2.175327 | -0.41374 |
| 31 | 1 | 0 | 1.137464 | -2.15723 | 0.049064 |
| 32 | 1 | 0 | 3.546778 | -2.10181 | 0.049647 |
| 33 | 1 | 0 | -3.28423 | 2.06629 | -0.51533 |
| 34 | 1 | 0 | -3.22301 | -2.17901 | 0.185805 |
| 35 | 1 | 0 | -0.80478 | -2.13293 | 0.199221 |
| 36 | 1 | 0 | 2.32157 | 3.713664 | 1.502343 |
| 37 | 1 | 0 | 3.501138 | 5.87427 | 1.522949 |
| 38 | 1 | 0 | 3.395373 | 7.378064 | -0.45949 |
| 39 | 1 | 0 | 2.075308 | 6.68937 | -2.4538 |
| 40 | 1 | 0 | 0.861533 | 4.554418 | -2.46281 |
| 41 | 1 | 0 | -3.02766 | 5.291258 | -3.25172 |
| 42 | 1 | 0 | -2.95139 | 6.16278 | 0.945802 |
| 43 | 1 | 0 | -1.64762 | 3.019375 | 2.008877 |
| 44 | 1 | 0 | -0.37647 | 4.237506 | 1.912071 |
| 45 | 1 | 0 | -1.98662 | 4.692379 | 2.485394 |
| 46 | 1 | 0 | -0.49107 | 2.828373 | -3.28668 |
| 47 | 1 | 0 | -2.05502 | 2.038059 | -3.13986 |
| 48 | 1 | 0 | -1.89067 | 3.475537 | -4.15798 |
| 49 | 1 | 0 | -4.54079 | 7.35601 | -0.57456 |
| 50 | 1 | 0 | -3.24242 | 8.00348 | -1.57943 |
| 51 | 1 | 0 | -4.51752 | 7.031783 | -2.31933 |
| 52 | 6 | 0 | -4.91463 | -0.05538 | -0.18857 |
| 53 | 6 | 0 | -5.63899 | -1.17706 | -0.62852 |
| 54 | 6 | 0 | -5.66816 | 1.056917 | 0.239809 |
| 55 | 6 | 0 | -7.02111 | -1.17072 | -0.63594 |
| 56 | 1 | 0 | -5.13321 | -2.06207 | -0.99445 |
| 57 | 6 | 0 | -7.04461 | 1.017963 | 0.21797 |
| 58 | 1 | 0 | -5.18655 | 1.950427 | 0.617312 |
| 59 | 7 | 0 | -7.7064 | -0.08221 | -0.21548 |
| 60 | 1 | 0 | -7.61559 | -2.01424 | -0.97691 |

| | | | | | |
|---|---|---|---|---|---|
| 61 | 1 | 0 | -7.6548 | 1.845973 | 0.555433 |
| 62 | 6 | 0 | 5.179795 | 0.0804 | -0.20866 |
| 63 | 6 | 0 | 5.907982 | 1.201939 | 0.241935 |
| 64 | 6 | 0 | 5.93264 | -1.00727 | -0.68696 |
| 65 | 6 | 0 | 7.284246 | 1.203136 | 0.204751 |
| 66 | 1 | 0 | 5.406167 | 2.071425 | 0.648057 |
| 67 | 6 | 0 | 7.31355 | -0.96179 | -0.70669 |
| 68 | 1 | 0 | 5.450726 | -1.89683 | -1.07343 |
| 69 | 7 | 0 | 7.973004 | 0.13383 | -0.26369 |
| 70 | 1 | 0 | 7.874207 | 2.039173 | 0.558041 |
| 71 | 1 | 0 | 7.927336 | -1.7798 | -1.0745 |
| 72 | 8 | 0 | -8.82194 | -4.04684 | 0.74133 |
| 73 | 8 | 0 | 9.179127 | -3.8025 | 0.61293 |
| 74 | 16 | 0 | -9.43271 | -4.33576 | -0.57881 |
| 75 | 16 | 0 | 9.791175 | -4.06848 | -0.71152 |
| 76 | 8 | 0 | 9.461207 | -3.05371 | -1.7519 |
| 77 | 8 | 0 | 9.724599 | -5.47243 | -1.17068 |
| 78 | 8 | 0 | -9.13059 | -3.32017 | -1.62702 |
| 79 | 8 | 0 | -9.33455 | -5.74058 | -1.02957 |
| 80 | 6 | 0 | -11.2515 | -4.08689 | -0.28504 |
| 81 | 6 | 0 | 11.60467 | -3.77875 | -0.42279 |
| 82 | 9 | 0 | -11.9539 | -4.32885 | -1.40322 |
| 83 | 9 | 0 | -11.6973 | -4.90873 | 0.678142 |
| 84 | 9 | 0 | -11.5 | -2.82056 | 0.097813 |
| 85 | 9 | 0 | 11.82543 | -2.50795 | -0.03732 |
| 86 | 9 | 0 | 12.07242 | -4.59254 | 0.536855 |
| 87 | 9 | 0 | 12.30883 | -4.00169 | -1.54382 |
| 88 | 6 | 0 | 9.474812 | 0.175989 | -0.30277 |
| 89 | 1 | 0 | 9.78977 | -0.77507 | -0.73409 |
| 90 | 1 | 0 | 9.747186 | 0.976244 | -0.99489 |
| 91 | 6 | 0 | -9.20957 | -0.08314 | -0.23929 |
| 92 | 1 | 0 | -9.50184 | -1.05002 | -0.65108 |
| 93 | 1 | 0 | -9.51092 | 0.697301 | -0.94188 |
| 94 | 6 | 0 | -9.80785 | 0.15054 | 1.12899 |
| 95 | 6 | 0 | -9.79366 | -0.87139 | 2.090316 |
| 96 | 6 | 0 | -10.3883 | 1.385311 | 1.444701 |
| 97 | 6 | 0 | -10.3427 | -0.64964 | 3.352844 |
| 98 | 1 | 0 | -9.36677 | -1.8402 | 1.843285 |
| 99 | 6 | 0 | -10.9415 | 1.603487 | 2.708976 |

| | | | | | |
|---|---|---|---|---|---|
| 100 | 1 | 0 | -10.4187 | 2.175133 | 0.697936 |
| 101 | 6 | 0 | -10.9155 | 0.587422 | 3.665286 |
| 102 | 1 | 0 | -10.3307 | -1.44532 | 4.09252 |
| 103 | 1 | 0 | -11.3923 | 2.563781 | 2.942455 |
| 104 | 1 | 0 | -11.3452 | 0.754725 | 4.649025 |
| 105 | 6 | 0 | 10.08169 | 0.402873 | 1.062958 |
| 106 | 6 | 0 | 10.10155 | -0.63383 | 2.008202 |
| 107 | 6 | 0 | 10.63628 | 1.645943 | 1.39225 |
| 108 | 6 | 0 | 10.65816 | -0.41881 | 3.268545 |
| 109 | 1 | 0 | 9.695046 | -1.60846 | 1.750113 |
| 110 | 6 | 0 | 11.19729 | 1.857493 | 2.654276 |
| 111 | 1 | 0 | 10.64031 | 2.447934 | 0.657904 |
| 112 | 6 | 0 | 11.20489 | 0.826472 | 3.594755 |
| 113 | 1 | 0 | 10.67244 | -1.22594 | 3.99568 |
| 114 | 1 | 0 | 11.62777 | 2.824472 | 2.898335 |
| 115 | 1 | 0 | 11.64059 | 0.988687 | 4.576714 |

**Table S16** Cartesian coordinates of optimized geometry of **6** (DFT, B3LYP/6-31g*) Standard orientation: (Ground State)

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -2.83709 | -0.53914 | -0.01466 |
| 2 | 6 | 0 | -1.42307 | -0.52869 | -0.02384 |
| 3 | 6 | 0 | -0.72402 | -1.77079 | -0.05487 |
| 4 | 6 | 0 | -1.48639 | -2.96284 | -0.08659 |
| 5 | 6 | 0 | -2.86579 | -2.94405 | -0.08153 |
| 6 | 6 | 0 | -3.57208 | -1.71887 | -0.04471 |
| 7 | 6 | 0 | 1.42547 | -0.52746 | -0.00787 |
| 8 | 6 | 0 | 2.839515 | -0.53556 | -0.0217 |
| 9 | 6 | 0 | 3.575394 | -1.71437 | -0.06411 |
| 10 | 6 | 0 | 2.870583 | -2.94054 | -0.09515 |
| 11 | 6 | 0 | 1.491221 | -2.96103 | -0.09311 |
| 12 | 6 | 0 | 0.727748 | -1.77005 | -0.05143 |
| 13 | 6 | 0 | -1.45503 | 2.010618 | 0.051113 |
| 14 | 6 | 0 | 1.453448 | 2.012146 | 0.080073 |
| 15 | 6 | 0 | -2.00663 | 2.543473 | -1.12437 |
| 16 | 6 | 0 | -2.72549 | 3.740148 | -1.09569 |
| 17 | 6 | 0 | -2.9097 | 4.418988 | 0.111278 |
| 18 | 6 | 0 | -2.37167 | 3.893462 | 1.28811 |

| | | | | | |
|---|---|---|---|---|---|
| 19 | 6 | 0 | -1.65088 | 2.697735 | 1.258089 |
| 20 | 6 | 0 | 1.988961 | 2.486144 | 1.287515 |
| 21 | 6 | 0 | 2.702765 | 3.685589 | 1.328255 |
| 22 | 6 | 0 | 2.897845 | 4.425932 | 0.159868 |
| 23 | 6 | 0 | 2.376081 | 3.959074 | -1.04868 |
| 24 | 6 | 0 | 1.660629 | 2.760427 | -1.0881 |
| 25 | 1 | 0 | -3.35905 | 0.408279 | 0.044343 |
| 26 | 1 | 0 | -0.98837 | -3.92481 | -0.1215 |
| 27 | 1 | 0 | -3.41027 | -3.88204 | -0.12994 |
| 28 | 1 | 0 | 3.361074 | 0.412856 | 0.025572 |
| 29 | 1 | 0 | 3.416149 | -3.8775 | -0.15081 |
| 30 | 1 | 0 | 0.9941 | -3.92321 | -0.1344 |
| 31 | 1 | 0 | -1.8663 | 2.018885 | -2.06587 |
| 32 | 1 | 0 | -3.14025 | 4.141358 | -2.01653 |
| 33 | 1 | 0 | -3.46965 | 5.349868 | 0.134586 |
| 34 | 1 | 0 | -2.51258 | 4.413263 | 2.232002 |
| 35 | 1 | 0 | -1.23585 | 2.292465 | 2.176731 |
| 36 | 1 | 0 | 3.105389 | 4.040687 | 2.273107 |
| 37 | 1 | 0 | 2.525272 | 4.527195 | -1.963 |
| 38 | 6 | 0 | 5.058308 | -1.6887 | -0.07594 |
| 39 | 6 | 0 | 5.817945 | -2.69053 | 0.549272 |
| 40 | 6 | 0 | 5.77512 | -0.66276 | -0.7129 |
| 41 | 6 | 0 | 7.208879 | -2.6206 | 0.511371 |
| 42 | 1 | 0 | 5.33726 | -3.50584 | 1.080349 |
| 43 | 6 | 0 | 7.167634 | -0.68391 | -0.6916 |
| 44 | 1 | 0 | 5.258417 | 0.132649 | -1.24024 |
| 45 | 7 | 0 | 7.895577 | -1.64005 | -0.09436 |
| 46 | 1 | 0 | 7.802162 | -3.39232 | 0.999053 |
| 47 | 1 | 0 | 7.727895 | 0.106988 | -1.18752 |
| 48 | 6 | 0 | -5.05496 | -1.69416 | -0.03368 |
| 49 | 6 | 0 | -5.7817 | -0.66418 | -0.65281 |
| 50 | 6 | 0 | -5.80496 | -2.70024 | 0.596398 |
| 51 | 6 | 0 | -7.17369 | -0.68578 | -0.61038 |
| 52 | 1 | 0 | -5.27338 | 0.1354 | -1.18201 |
| 53 | 6 | 0 | -7.19631 | -2.63051 | 0.579982 |
| 54 | 1 | 0 | -5.31636 | -3.51882 | 1.115016 |
| 55 | 7 | 0 | -7.89236 | -1.64616 | -0.00866 |
| 56 | 1 | 0 | -7.74153 | 0.108393 | -1.09223 |
| 57 | 1 | 0 | -7.78197 | -3.40562 | 1.071472 |

| | | | | | |
|---|---|---|---|---|---|
| 58 | 6 | 0 | -0.68706 | 0.723013 | 0.018432 |
| 59 | 6 | 0 | 0.688002 | 0.723216 | 0.036231 |
| 60 | 1 | 0 | 1.256735 | 2.401478 | -2.03073 |
| 61 | 1 | 0 | 1.840606 | 1.913373 | 2.199205 |
| 62 | 1 | 0 | 3.45373 | 5.359027 | 0.190881 |

**Table S17** Cartesian coordinates of optimized geometry of **7** (DFT, B3LYP/6-31g*) Standard orientation: (Ground State)

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -2.84203 | 1.33212 | -0.45388 |
| 2 | 6 | 0 | -1.43017 | 1.353239 | -0.42236 |
| 3 | 6 | 0 | -0.71757 | 0.15385 | -0.71762 |
| 4 | 6 | 0 | -1.46166 | -1.00512 | -1.04617 |
| 5 | 6 | 0 | -2.83946 | -1.00087 | -1.06947 |
| 6 | 6 | 0 | -3.5578 | 0.181239 | -0.76916 |
| 7 | 6 | 0 | 1.410052 | 1.368726 | -0.32553 |
| 8 | 6 | 0 | 2.822273 | 1.374022 | -0.30335 |
| 9 | 6 | 0 | 3.570132 | 0.234254 | -0.58234 |
| 10 | 6 | 0 | 2.886049 | -0.96262 | -0.90295 |
| 11 | 6 | 0 | 1.509108 | -0.98755 | -0.95092 |
| 12 | 6 | 0 | 0.732081 | 0.161931 | -0.66894 |
| 13 | 6 | 0 | -1.50156 | 3.808315 | 0.227223 |
| 14 | 6 | 0 | 1.409279 | 3.822893 | 0.334046 |
| 15 | 6 | 0 | -2.05218 | 4.575703 | -0.81106 |
| 16 | 6 | 0 | -2.79046 | 5.726993 | -0.52998 |
| 17 | 6 | 0 | -2.99448 | 6.123677 | 0.793841 |
| 18 | 6 | 0 | -2.45682 | 5.362587 | 1.834158 |
| 19 | 6 | 0 | -1.7164 | 4.21253 | 1.552915 |
| 20 | 6 | 0 | 1.932621 | 4.000616 | 1.624064 |
| 21 | 6 | 0 | 2.635105 | 5.161764 | 1.952506 |
| 22 | 6 | 0 | 2.82983 | 6.158844 | 0.993757 |
| 23 | 6 | 0 | 2.31912 | 5.987951 | -0.29495 |
| 24 | 6 | 0 | 1.614578 | 4.827778 | -0.62274 |
| 25 | 1 | 0 | -3.3737 | 2.237275 | -0.18831 |
| 26 | 1 | 0 | -0.9508 | -1.92787 | -1.29298 |
| 27 | 1 | 0 | -3.36712 | -1.9065 | -1.34983 |

| | | | | | |
|---|---|---|---|---|---|
| 28 | 1 | 0 | 3.327141 | 2.291677 | -0.0281 |
| 29 | 1 | 0 | 3.441311 | -1.86175 | -1.1488 |
| 30 | 1 | 0 | 1.025311 | -1.91897 | -1.21855 |
| 31 | 1 | 0 | -1.8957 | 4.271291 | -1.84261 |
| 32 | 1 | 0 | -3.20432 | 6.313531 | -1.34571 |
| 33 | 1 | 0 | -3.56946 | 7.019128 | 1.013001 |
| 34 | 1 | 0 | -2.61321 | 5.662436 | 2.866804 |
| 35 | 1 | 0 | -1.30102 | 3.623111 | 2.365419 |
| 36 | 1 | 0 | 3.02861 | 5.286566 | 2.957626 |
| 37 | 1 | 0 | 2.468236 | 6.757543 | -1.04745 |
| 38 | 6 | 0 | 5.044483 | 0.27266 | -0.53659 |
| 39 | 6 | 0 | 5.801002 | -0.85949 | -0.17982 |
| 40 | 6 | 0 | 5.764473 | 1.441772 | -0.84832 |
| 41 | 6 | 0 | 7.179794 | -0.80661 | -0.13906 |
| 42 | 1 | 0 | 5.320484 | -1.7912 | 0.092394 |
| 43 | 6 | 0 | 7.142386 | 1.450181 | -0.79262 |
| 44 | 1 | 0 | 5.259374 | 2.346669 | -1.16259 |
| 45 | 7 | 0 | 7.834263 | 0.340713 | -0.44301 |
| 46 | 1 | 0 | 7.79491 | -1.65963 | 0.140965 |
| 47 | 1 | 0 | 7.727019 | 2.328889 | -1.03261 |
| 48 | 6 | 0 | -5.03322 | 0.193084 | -0.77995 |
| 49 | 6 | 0 | -5.76163 | 1.355131 | -1.09869 |
| 50 | 6 | 0 | -5.78281 | -0.95753 | -0.47023 |
| 51 | 6 | 0 | -7.1406 | 1.339482 | -1.09389 |
| 52 | 1 | 0 | -5.26132 | 2.275289 | -1.37392 |
| 53 | 6 | 0 | -7.16283 | -0.92784 | -0.47758 |
| 54 | 1 | 0 | -5.29694 | -1.88458 | -0.19169 |
| 55 | 7 | 0 | -7.82555 | 0.213369 | -0.7867 |
| 56 | 1 | 0 | -7.73147 | 2.212085 | -1.34043 |
| 57 | 1 | 0 | -7.77246 | -1.79602 | -0.23451 |
| 58 | 8 | 0 | 10.17961 | -2.71792 | -1.36642 |
| 59 | 8 | 0 | -8.91556 | -3.51267 | 0.198337 |
| 60 | 16 | 0 | 10.12187 | -3.58208 | -0.16001 |
| 61 | 16 | 0 | -10.035 | -3.26097 | 1.144812 |
| 62 | 8 | 0 | -10.0586 | -1.88735 | 1.70876 |
| 63 | 8 | 0 | -10.2884 | -4.3455 | 2.116974 |
| 64 | 8 | 0 | 8.961727 | -3.31002 | 0.730134 |
| 65 | 8 | 0 | 10.4078 | -5.01328 | -0.39552 |
| 66 | 6 | 0 | 11.57107 | -3.00141 | 0.849651 |

| | | | | | |
|---|---|---|---|---|---|
| 67 | 6 | 0 | -11.5325 | -3.29506 | 0.043428 |
| 68 | 9 | 0 | 11.6574 | -3.686 | 2.001354 |
| 69 | 9 | 0 | 12.71998 | -3.16763 | 0.175101 |
| 70 | 9 | 0 | 11.44919 | -1.69456 | 1.149261 |
| 71 | 9 | 0 | -11.4453 | -2.34682 | -0.90827 |
| 72 | 9 | 0 | -11.6524 | -4.4856 | -0.56553 |
| 73 | 9 | 0 | -12.6507 | -3.07115 | 0.751946 |
| 74 | 6 | 0 | -9.30607 | 0.203764 | -0.80799 |
| 75 | 1 | 0 | -9.6663 | -0.32431 | 0.076444 |
| 76 | 1 | 0 | -9.66273 | 1.232649 | -0.81003 |
| 77 | 6 | 0 | 9.312432 | 0.370671 | -0.36178 |
| 78 | 1 | 0 | 9.608945 | 0.425035 | 0.687733 |
| 79 | 1 | 0 | 9.673949 | 1.248789 | -0.89471 |
| 80 | 1 | 0 | 9.708067 | -0.54049 | -0.8134 |
| 81 | 1 | 0 | -9.64479 | -0.30893 | -1.71054 |
| 82 | 6 | 0 | -0.71451 | 2.569023 | -0.07595 |
| 83 | 6 | 0 | 0.659041 | 2.574182 | -0.0203 |
| 84 | 1 | 0 | 1.21911 | 4.699035 | -1.62637 |
| 85 | 1 | 0 | 1.783565 | 3.227649 | 2.373376 |
| 86 | 1 | 0 | 3.37676 | 7.062248 | 1.249096 |

## 11. Reference


1. B. He, H. Tian, Y. Geng, F. Wang and K. Müllen, *Org Lett*, 2008, **10**, 773-776.
2. H. Oh, D. G. Seo, T. Y. Yun, C. Y. Kim and H. C. Moon, *ACS Appl Mater Interfaces*, 2017, **9**, 7658-7665.
3. G. W. T. M. J. Frisch, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, Jr., J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision B.01; Gaussian, Inc., Wallingford, CT, **2010**.
4. A. D. Becke, *J Chem Phys*, 1993, **98**, 5648-5652.
5. P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J Phys Chem*, 1994, **98**, 11623-11627.
6. C. T. Lee, W. T. Yang and R. G. Parr, *Phys Rev B*, 1988, **37**, 785-789.
7. R. Bauernschmitt and R. Ahlrichs, *Chem Phys Lett*, 1996, **256**, 454-464.
8. M. E. Casida, C. Jamorski, K. C. Casida and D. R. Salahub, *J Chem Phys*, 1998, **108**, 4439-4449.