Effect of Fusion Manner of Concave Molecule on the Properties of Resulted Nanoboats

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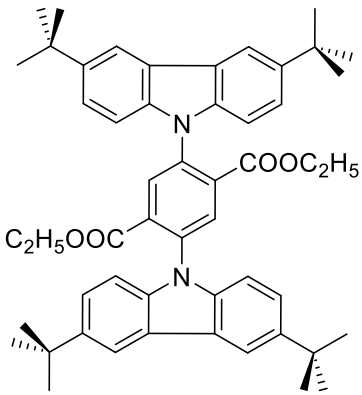
1. General Remarks

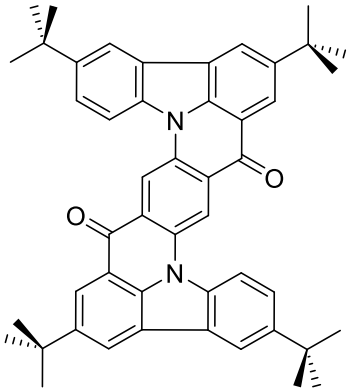
All reagents and solvents were commercially available and were used without further purification unless otherwise noted. For thin layer chromatography Silica gel 60 F254 plates from Merck were used and examined under UV-light irradiation (254 nm and 365 nm). Flash column chromatography was performed on silica gel (particle size: 200-300 mesh). Melting points were measured with a MPA100 OptiMelt. IR-Spectra were recorded as KBr-pellets on a Bruker VERTEX 80V spectrometer. NMR spectra were taken on a Bruker AVANCE NEO (400MHz). Chemical shifts (δ) are reported in parts per million (ppm) relative to traces of DMSO in the corresponding deuterated solvent. HRMS experiments were carried out on a ThermoFisher LTQ Orbitrap XL. Absorption spectra were recorded on a Shimadzu UV2600. Emission spectra, absolute quantum yields and fluorescence lifetimes were measured on FluoroMax-4 spectrometer equipped with an integral sphere and a time-correlated single photon counting system with a NanoLED laser. Electrochemical data were obtained in dichloromethane solution of tetrabutylammonium hexafluorophosphate (0.1 M) and ferrocene was used as an internal standard. Cyclic voltammetry was obtained using a glassy carbon working electrode, a platinum counter electrode and a silver wire reference electrode tested on CHI660E station. 3,6-di-*tert*-butylcarbazole **4** was synthesized according to the reported method.[S1]

2. Experimental section

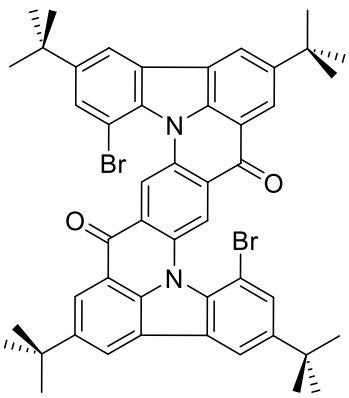


A 120 mL screw capped glass vial was charged with 3,6-di-*tert*-butylcarbazole **4** (5.29 g, 18.9 mmol), diethyl 2,5-dibromoterephthalate **5** (3.42 g, 9 mmol), K_2CO_3 (4.98 g, 36 mmol) and CuI (686 mg, 3.6 mmol). Under the protection of argon, dry 1,2-dichlorobenzene (19 mL) and 18-crown-6 ether (952 mg, 3.6 mmol) were added to the vial and the mixture was bubbled with argon for 3 minutes. The vial was quickly capped and heated in an oil bath at 180°C for 24 hours. After cooling down to room temperature, the reaction mixture was diluted with dichloromethane (200 mL) and washed with water (3×200 mL). The solvent was removed by rotatory evaporation and the crude product was purified by silica gel column chromatography (dichloromethane/light petroleum, 1:4) to give compound **6** as yellow solid. (4.50 g, 64%). m.p. 357 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.28 (s, 2H), 8.15 (s, 4H), 7.48 (dd, J = 8.6, 1.9 Hz, 4H), 7.21 (d, J = 8.6 Hz, 4H), 3.77 (q, J = 7.1 Hz, 4H), 1.48 (s, 36H), 0.52 (t, J = 7.1 Hz, 6H); ^{13}CNMR (100 MHz, $CDCl_3$) (All signals represent 2C except noted.) δ (ppm) = 165.0, 143.4 (4C), 140.0 (4C), 136.5, 134.6, 133.4, 124.0 (4C), 123.7 (4C), 116.5 (4C), 108.9 (4C), 61.9, 34.9 (4C), 32.2 (12CH_3), 13.1; IR (KBr) $\tilde{\nu}$ (cm^{-1}) = 2959, 2903, 2866, 1712, 1629, 1501, 1473, 1426, 1391, 1362, 1324,

1296, 1277, 1243, 1125, 1015, 897, 804, 612, 534; HRMS(ESI) (*m/z*): $[M+H]^+$ calcd. for $C_{52}H_{61}N_2O_4$, 777.4626; found, 777.4633.

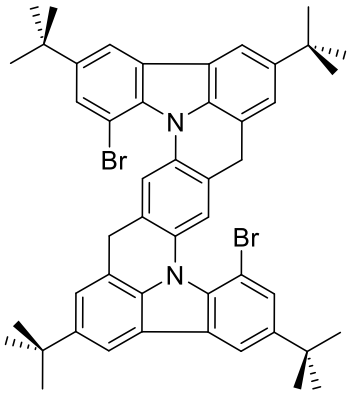


Compound **6** (3.91 g, 5.0 mmol) was suspended in the mixture of THF (100 mL), methanol (50 mL) and water (50 mL). NaOH (1.20 g, 30 mmol) was added to the suspension and the reaction was heated in an oil bath at 80 ℃ for 16 hours. After cooling down to room temperature, the solvent was removed by rotatory evaporation. The obtained solid was suspended in water (100 mL) and the pH value was adjusted to 1 by concentrated HCl aqueous solution. The suspension was filtered off and the solid was further washed with water (200 mL) to give the terephthalic acid as yellow solid, which was dried in the oven and used directly for the next step. A 250 mL two-necked flask was charged with the terephthalic acid, anhydrous CH_2Cl_2 (150 mL), oxalyl chloride (20 mL) and DMF (5 mL). The flask was heated in an oil bath at 45 ℃ for 3 hours. Then stannic chloride (11.7 mL, 100 mmol) was added and the reaction was further heated at the same temperature for another 21 hours. After cooling down to room temperature, the flask was cooled in an ice bath and reaction solution was neutralized by sodium hydroxide aqueous solution to pH = 10. The suspension was further diluted by CH_2Cl_2 (200 mL), washed with water (3×250 mL). The solvent was removed by rotatory evaporation and the crude product was purified by silica gel column chromatography (dichloromethane/light petroleum, 1:1) to give compound **7** (3.12 g, 91 %) as orange-red solid. m.p. > 400 ℃ (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 9.61 (s, 2H), 8.51 (d, J = 9.1 Hz, 2H), 8.49 (s, 2H), 8.47 (s, 2H), 8.20 (d, J = 2.0 Hz, 2H), 7.78 (d, J = 8.7 Hz, 2H), 1.58 (s, 18H), 1.54 (s, 18H); ^{13}CNMR (100 MHz, $CDCl_3$) (All signals represent 2C except noted.) δ (ppm) = 178.4, 146.9, 146.7, 137.8, 137.6, 134.4, 128.7, 126.3, 126.0, 125.5, 123.6, 120.9, 118.4, 118.0, 115.8, 114.0, 35.6, 35.1, 32.1 ($6CH_3$), 31.9 ($6CH_3$); IR (KBr) $\tilde{\nu}$ (cm^{-1}) = 2959, 2903, 2868, 1651, 1611, 1492, 1426, 1363, 1301, 1268, 1231, 1202, 1163, 1144, 1023, 878, 796, 621, 497; HRMS(ESI) (*m/z*): $[M+H]^+$ calcd. for $C_{48}H_{49}N_2O_2$, 685.3789; found, 685.3775.

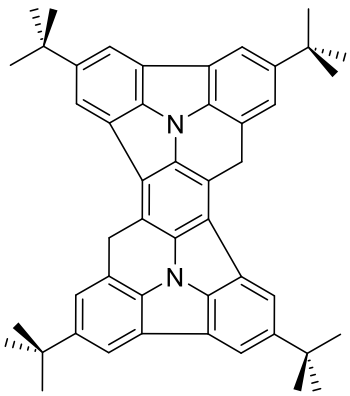


Br_2 (5.12 g, 32 mmol) was added to the dichloromethane (80 mL) solution of compound **7** (1.10 g, 1.60 mmol) in a 250 mL one-neck flask. The mixture was stirred at room temperature for 48 hours. Saturated sodium sulfite solution was added to remove the unreacted Br_2. The reaction suspension was diluted with dichloromethane (200 mL). The organic layer was washed with water (3×150 mL) and dried over Na_2SO_4. After removal of the solvent by rotatory evaporation, the crude product was purified by silica gel column chromatography (dichloromethane/light petroleum, 1:2) to give

compound **8** (887 mg, 66%) as orange solid. m.p. > 400 ℃ (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.34 (s, 2H), 8.49 (s, 2H), 8.45 (s, 2H), 8.19 (s, 2H), 7.92 (s, 2H), 1.54 (s, 18H), 1.53 (s, 18H); ^{13}CNMR (100 MHz, $CDCl_3$) (All signals represent 2C except noted.) δ (ppm) = 179.4, 148.7, 147.4, 139.2, 136.1, 133.0, 131.7, 130.0, 127.1, 124.7, 123.2, 121.8, 120.9, 119.1, 117.0, 106.9, 35.6, 35.1, 32.1 ($6CH_3$), 31.8 ($6CH_3$); IR (KBr) $\tilde{\nu}$ (cm^{-1}) = 2954, 2864, 1655, 1616, 1546, 1471, 1384, 1362, 1294, 1262, 1240, 1201, 1153, 1091, 1023, 917, 889, 873, 833, 791, 725, 633, 559, 512; HRMS(ESI) (*m/z*): $[M+Na]^+$ calcd. for $C_{48}H_{46}Br_2N_2O_2Na$, 865.1798; found, 865.1831.

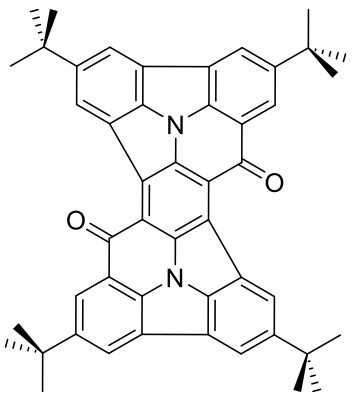


A 100 mL two-neck flask was charged with compound **8** (656 mg, 0.77 mmol) and dry THF (15 mL) under the protection of Argon. The mixture was stirred at room temperature until the solid completely dissolved. Then borane-tetrahydrofuran complex (3.5 mL, 1 M in THF, 3.5 mmol) solution was slowly added to the mixture. The mixture was refluxed for 16 hours. After cooling down to room temperature, the mixture was carefully quenched with methanol (2 mL). The reaction suspension was diluted with dichloromethane (50 mL). The organic layer was washed with water (3×150 mL) and dried over Na_2SO_4. After removal of the solvent by rotatory evaporation, the crude product was purified by silica gel column chromatography (dichloromethane/light petroleum, 1:15) to give compound **9** (497 mg, 79%) as colorless solid. m.p. > 400 ℃ (dec.); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.10 (s, 2H), 7.86 (s, 2H), 7.80 (s, 2H), 7.50 (s, 2H), 7.40 (s, 2H), 4.26 (s, 4H), 1.49 (s, 18H), 1.42 (s, 18H); ^{13}CNMR (100 MHz, CD_2Cl_2) (All signals represent 2C except noted.) δ (ppm) = 147.4, 147.2, 140.9, 137.0, 132.8, 131.3, 129.4, 124.2, 122.6, 122.2, 121.5, 120.5, 117.1, 114.3, 107.9, 35.4, 35.2, 32.8, 32.2 ($6CH_3$), 31.9 ($6CH_3$); IR (KBr) $\tilde{\nu}$ (cm^{-1}) = 2959, 2903, 2865, 1631, 1545, 1502, 1479, 1437, 1390, 1363, 1312, 1280, 1250, 1218, 1168, 1132, 1084, 992, 948, 905, 846, 780, 760, 733, 683, 642, 527, 469; HRMS(ESI) (*m/z*): $[M+Na]^+$ calcd. for $C_{48}H_{50}Br_2N_2Na$, 837.2213; found, 837.2212.



A 38 mL screw capped glass vial was charged with compound **9** (245 mg, 0.3 mmol), $Pd(OAc)_2$ (14 mg, 0.06mmol) and K_2CO_3 (332 mg, 2.4 mmol). Under the protection of argon, dry DMA (1 mL) and PCy_3HBF_4 (44 mg, 0.12 mmol) was added to the vial. The vial was quickly capped and the mixture was heated in an oil bath at 170 ℃ for 48 hours. After cooling down to room temperature, the mixture was diluted with dichloromethane (50 mL) and washed with water (3×100 mL) and dried over Na_2SO_4. After removal of the solvent by rotatory evaporation, the crude product was purified by silica gel

column chromatography (dichloromethane/light petroleum, 1:15) to give compound **10** (99 mg, 51%) as light yellow solid. m.p. > 400 ℃ (dec.); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.71 (s, 2H), 7.62 (s, 2H), 7.61 (s, 2H), 7.17 (s, 2H), 4.82 (br s, 2H), 4.49 (br s, 2H), 1.41 (s, 18H), 1.27 (s, 18H); ^{13}CNMR (100 MHz, CD_2Cl_2) (All signals represent 2C except noted.) δ (ppm) = 160.7, 150.4, 148.7, 145.7, 145.4, 132.4, 131.5, 130.9, 128.8, 122.0, 120.7, 119.0, 118.7, 118.3, 117.0, 36.0, 35.5, 32.6, 32.2 ($6CH_3$), 30.9 ($6CH_3$); IR (KBr) $\tilde{\nu}$ (cm^{-1}) = 2959, 2903, 2866, 1619, 1498, 1463, 1405, 1362, 1284, 1254, 1197, 1163, 1090, 996, 852, 652; HRMS(ESI) (*m/z*): $[M+H]^+$ calcd. for $C_{48}H_{49}N_2$, 653.3891; found, 653.3924.



A 100 mL two-neck flask was charged with compound **10** (99 mg, 0.15 mmol), DCM (8 mL), dioxane (4 mL) and water (1 mL). The mixture was cooled by an ice bath and DDQ (232 mg, 1 mmol) was added. The ice bath was removed and the reaction was stirred at room temperature overnight. The mixture was diluted with dichloromethane (50 mL), washed with saturated sodium bicarbonate solution (3×100 mL) and water (100 mL) for last time, and was dried over Na_2SO_4. After removal of the solvent by rotatory evaporation, the crude product was purified by silica gel column chromatography (light petroleum/ethyl acetate, 20:1) to give compound **11** (88 mg, 85%) as orange solid. m.p. > 400 ℃ (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 2H), 8.05 (s, 2H), 8.00 (s, 2H), 7.84 (s, 2H), 1.49 (s, 18H), 1.42 (s, 18H); ^{13}CNMR (100 MHz, $CDCl_3$) (All signals represent 2C except noted.) δ (ppm) = 182.3, 156.8, 150.8, 149.4, 147.0, 146.8, 133.2, 129.6, 129.4, 129.3, 125.3, 124.8, 122.1, 121.7, 120.8, 120.3, 36.3, 36.0, 32.7 ($6CH_3$), 32.2 ($6CH_3$); IR (KBr) $\tilde{\nu}$ (cm^{-1}) = 2960, 2866, 1653, 1576, 1480, 1415, 1364, 1331, 1270, 1186, 1155, 1086, 1041, 953, 886, 868, 852, 829, 796, 649, 615, 575; HRMS(ESI) (*m/z*): $[M+Na]^+$ calcd. for $C_{48}H_{44}N_2O_2Na$, 703.3295; found, 703.3329.

3. NMR Spectra

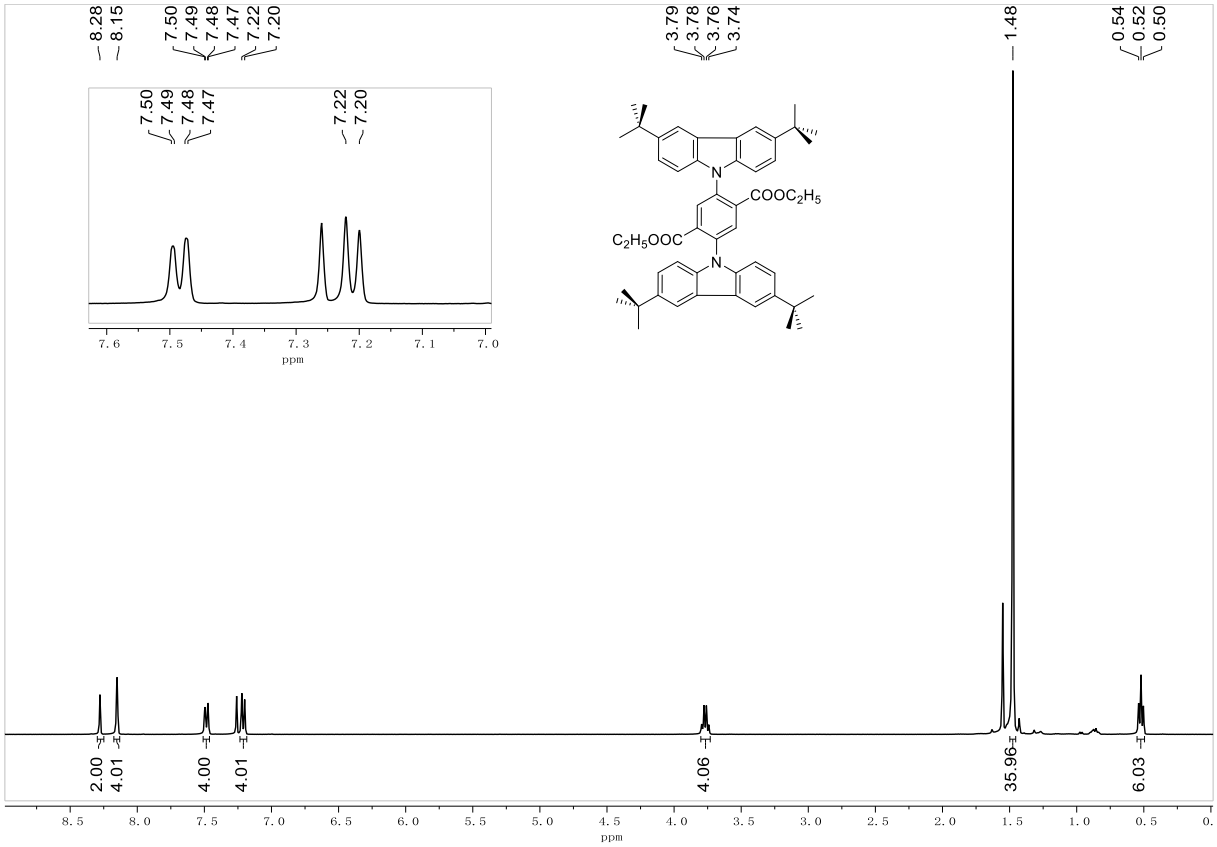


Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **6**

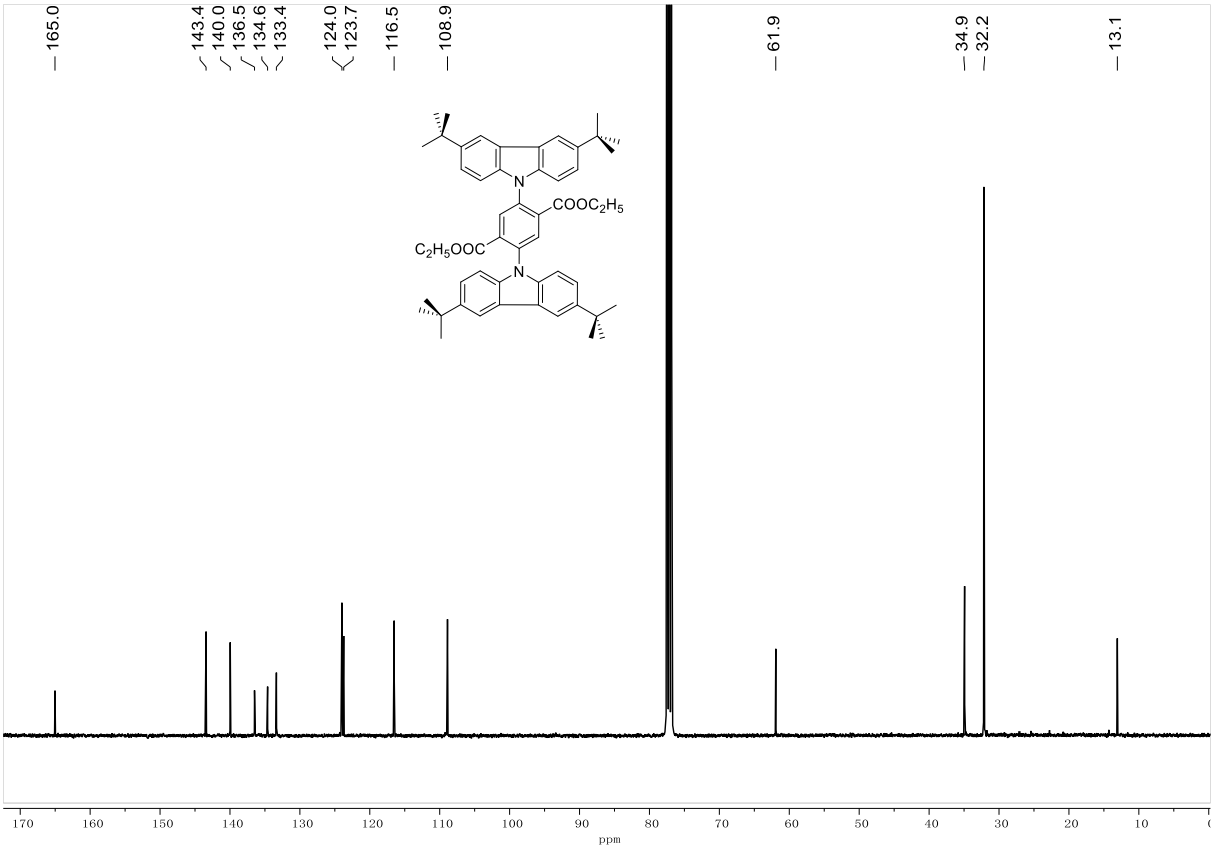


Figure S2. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of compound **6**

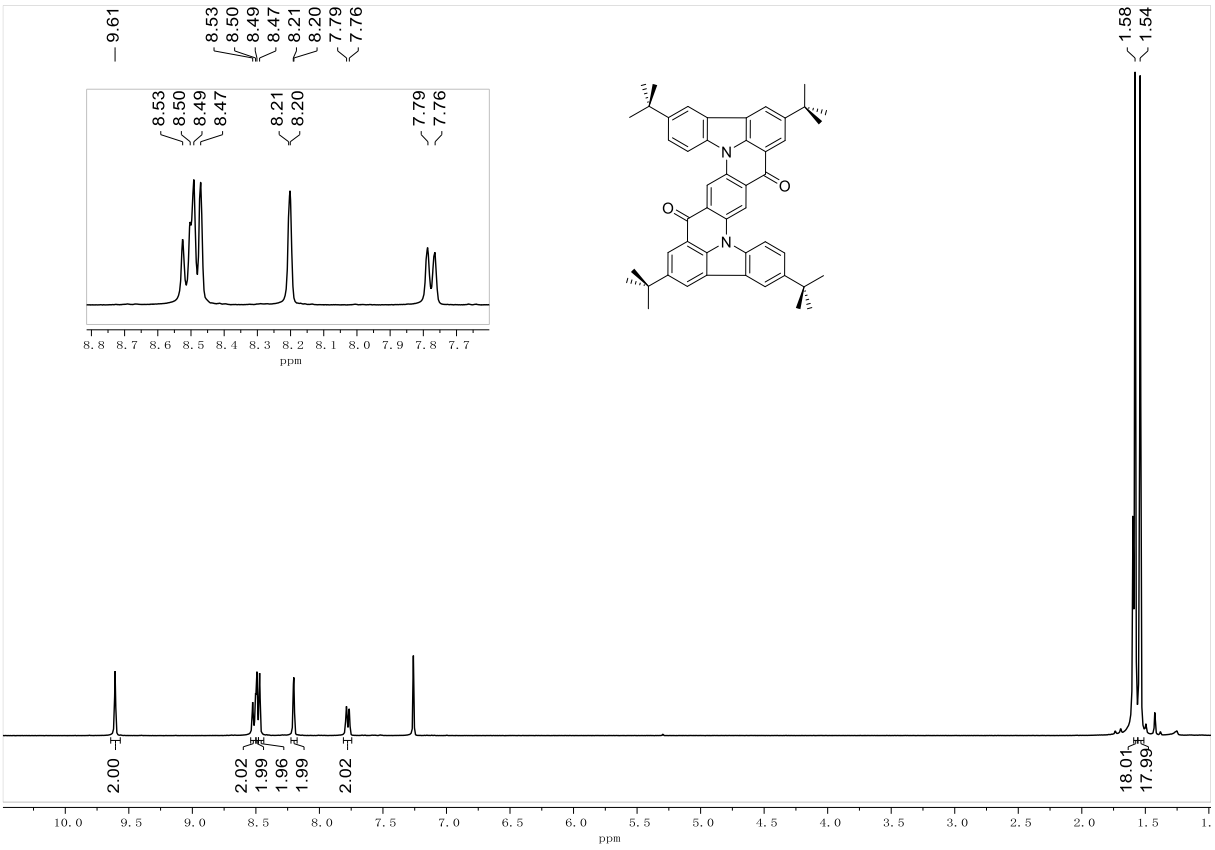


Figure S3. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **7**

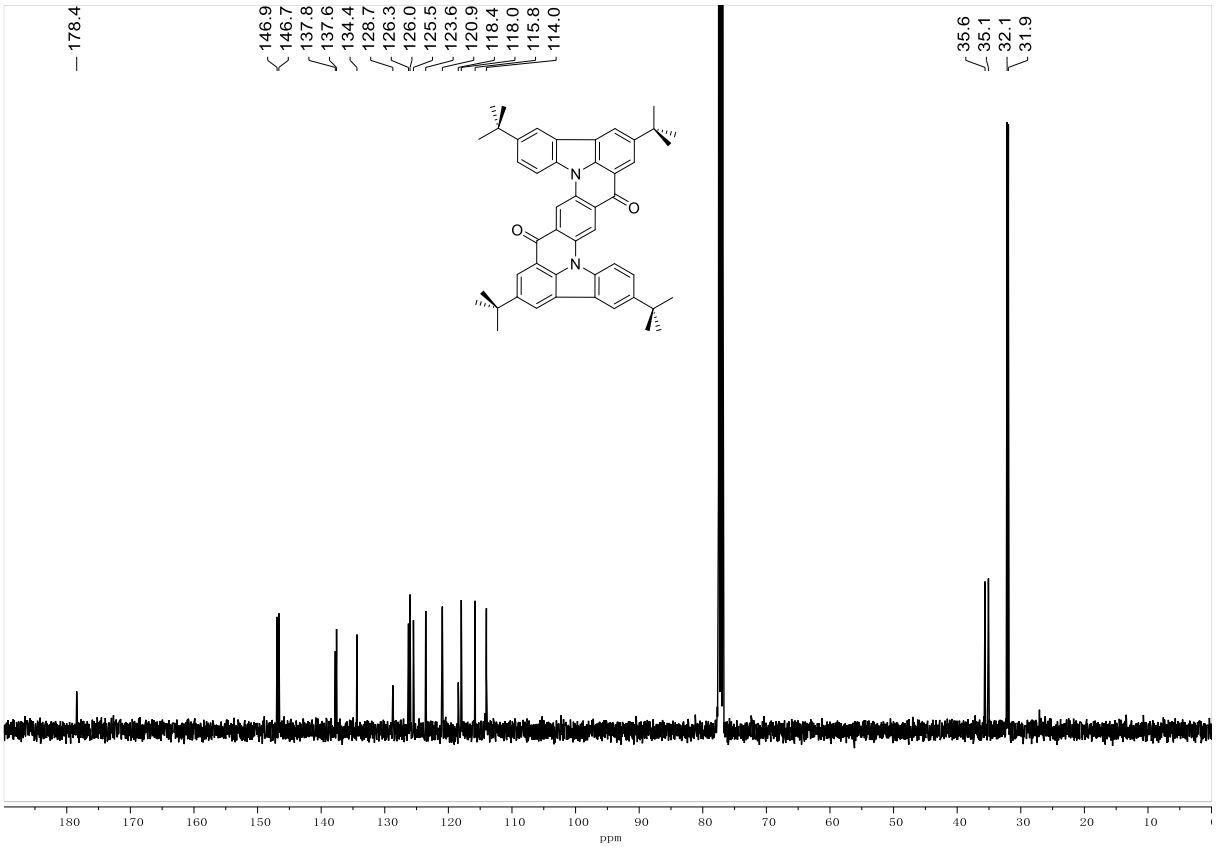


Figure S4. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of compound **7**

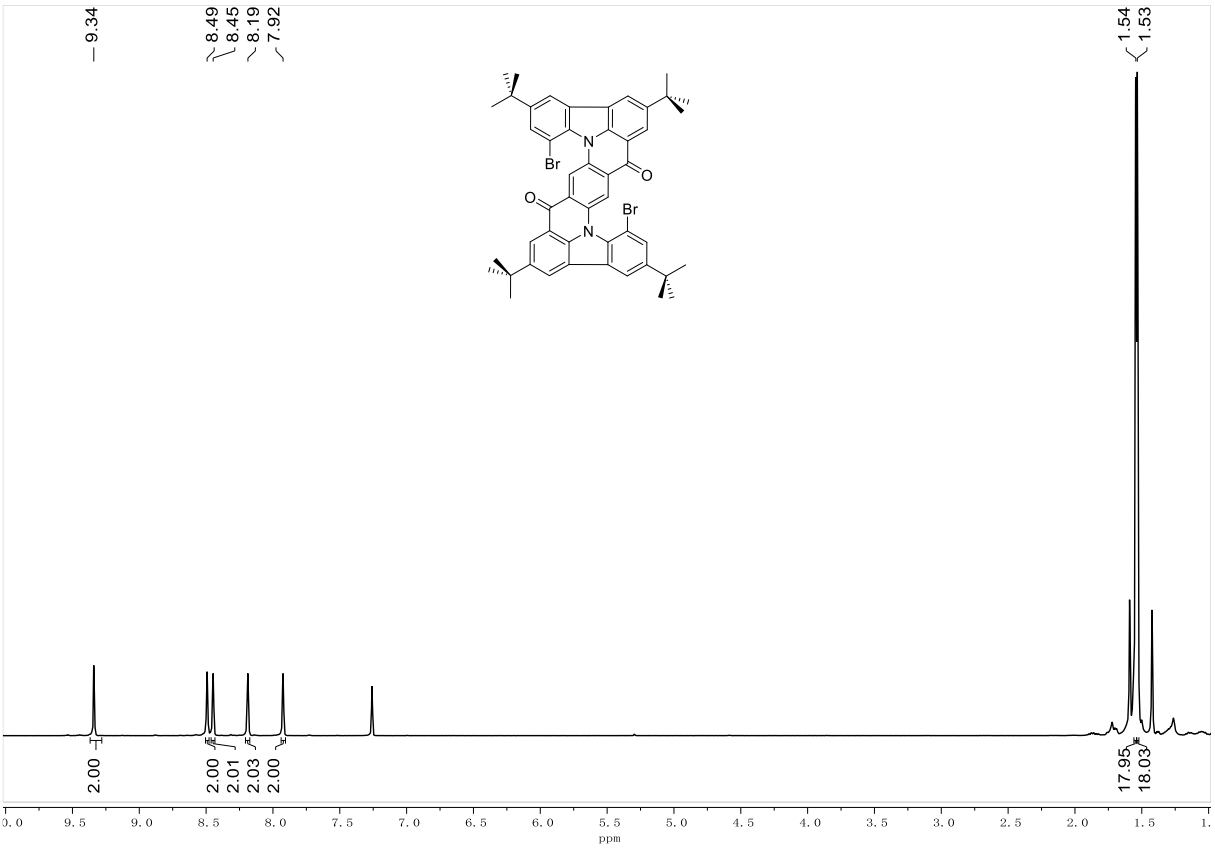


Figure S5. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **8**

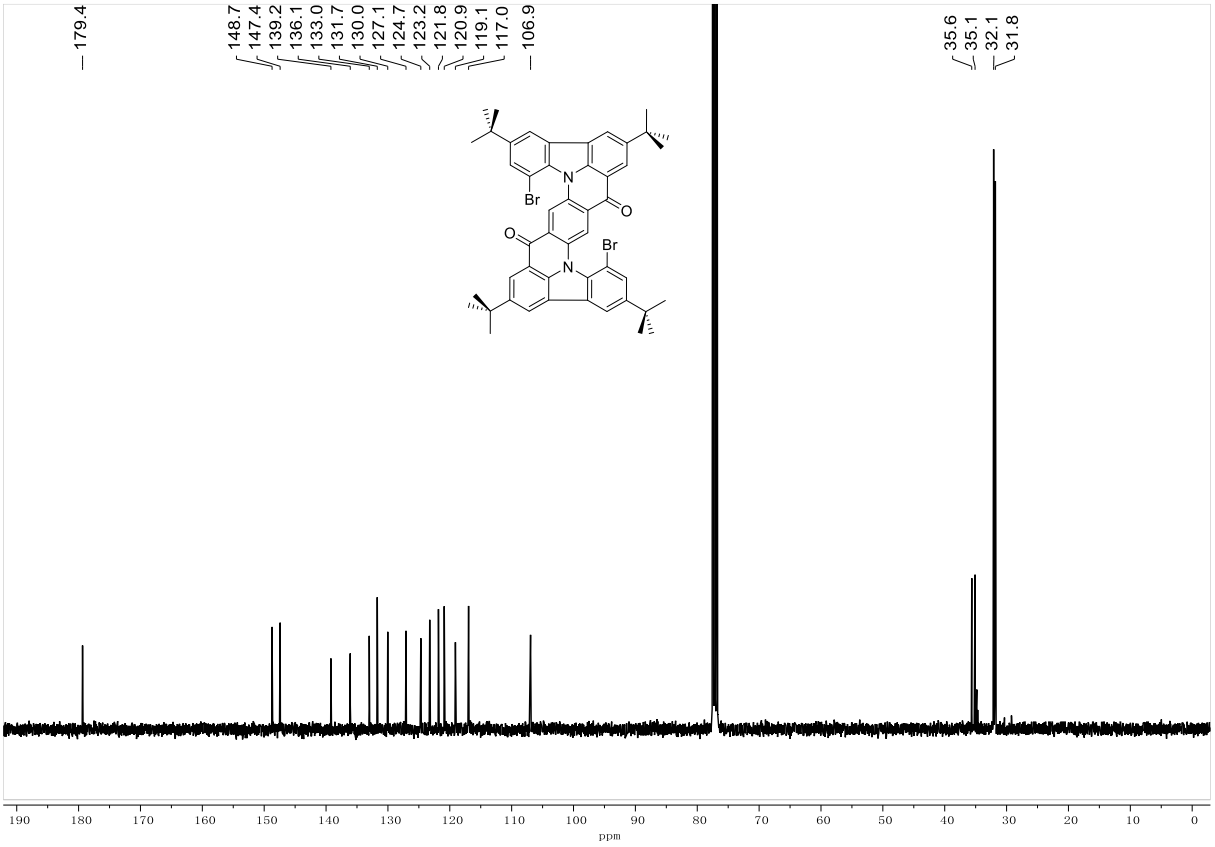


Figure S6. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of compound **8**

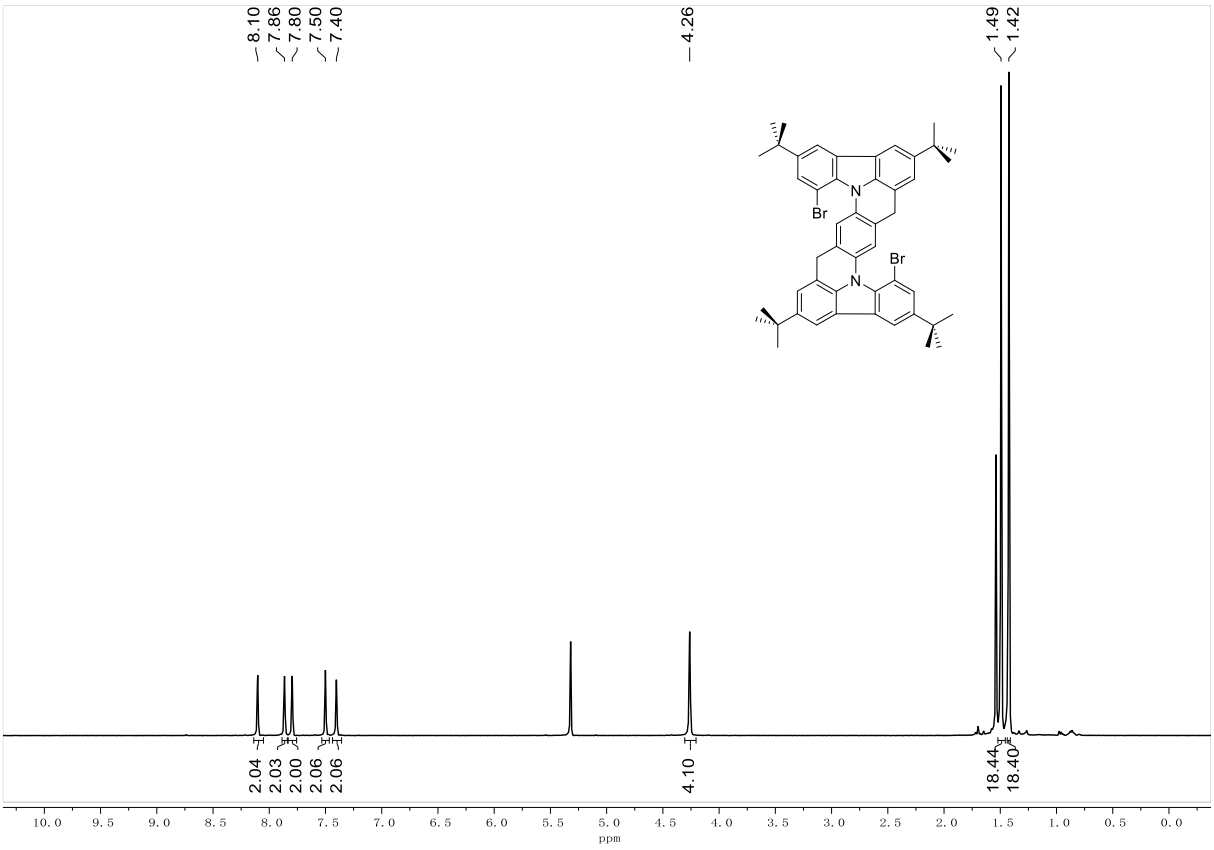


Figure S7. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz) of compound **9**

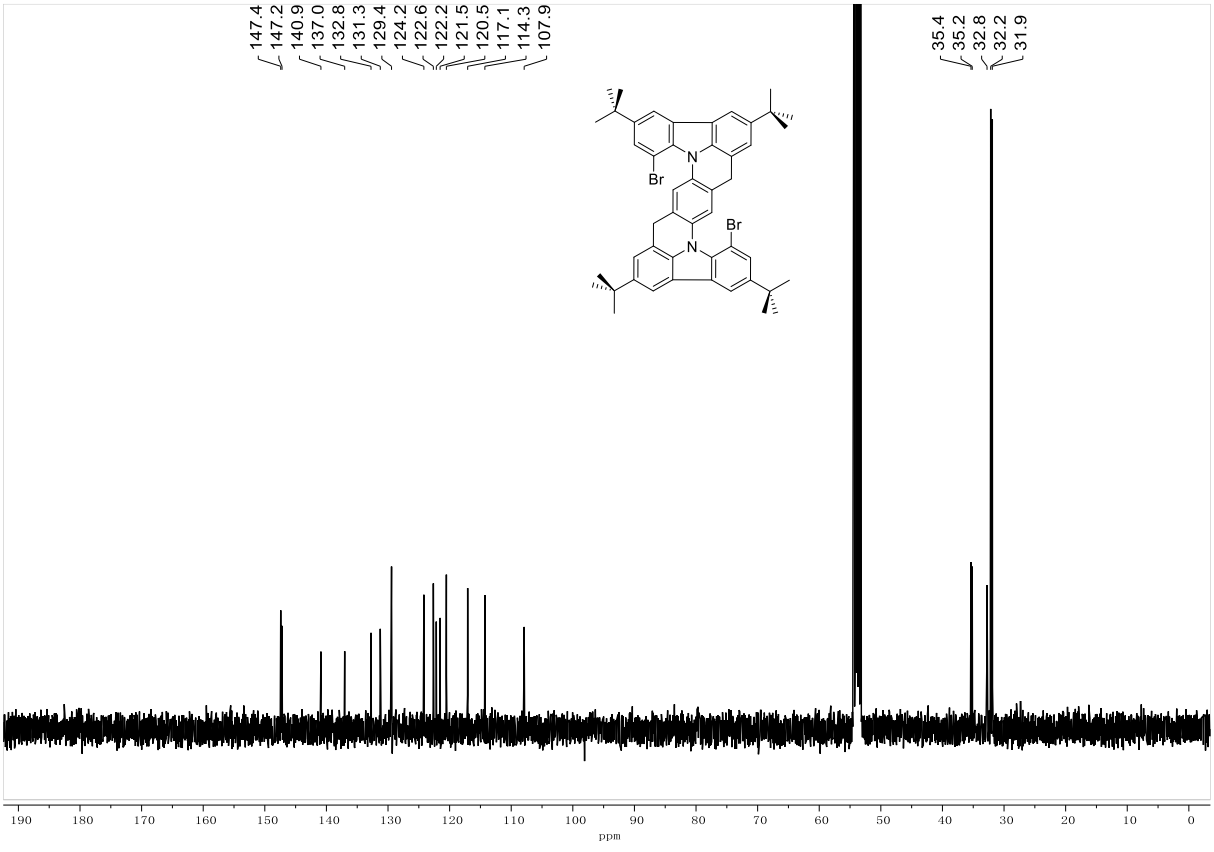


Figure S8. ^{13}C NMR spectrum (CD_2Cl_2, 100 MHz) of compound **9**

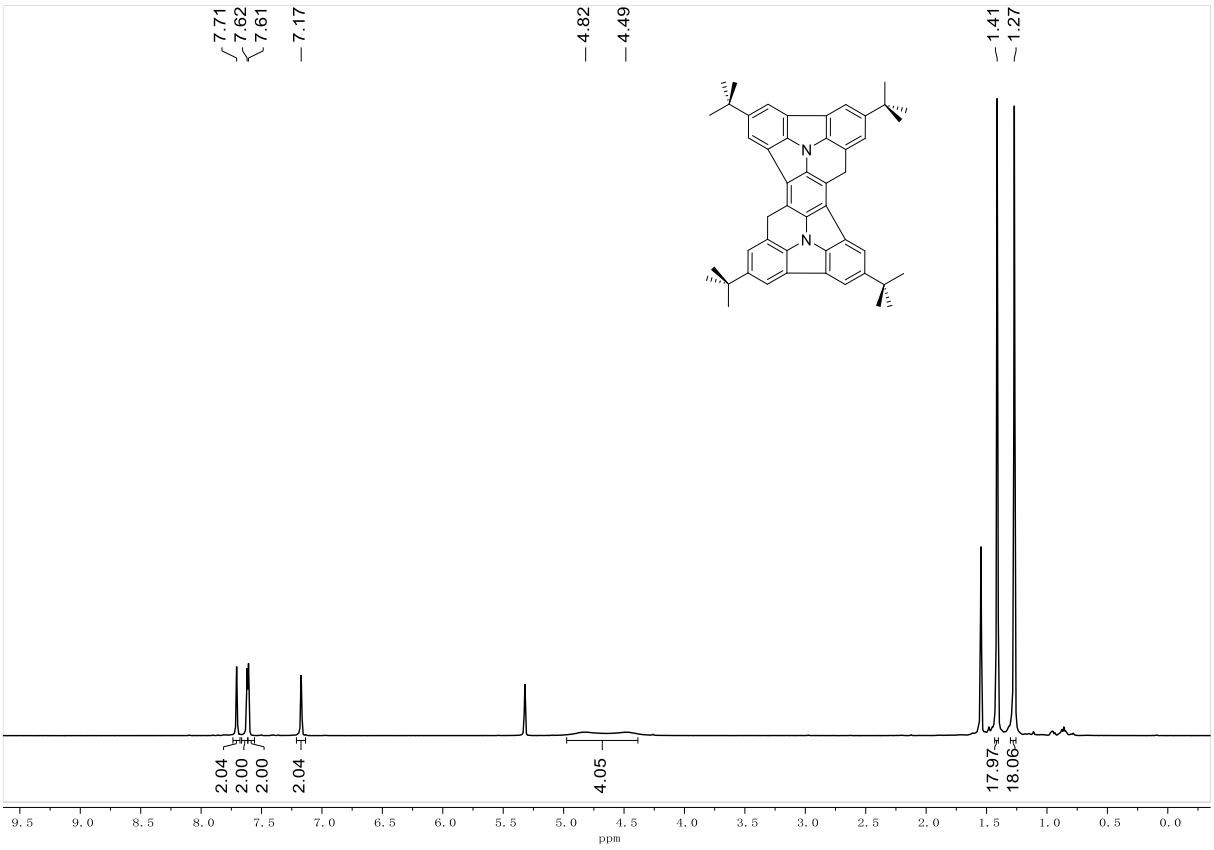


Figure S9. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz) of compound **10**

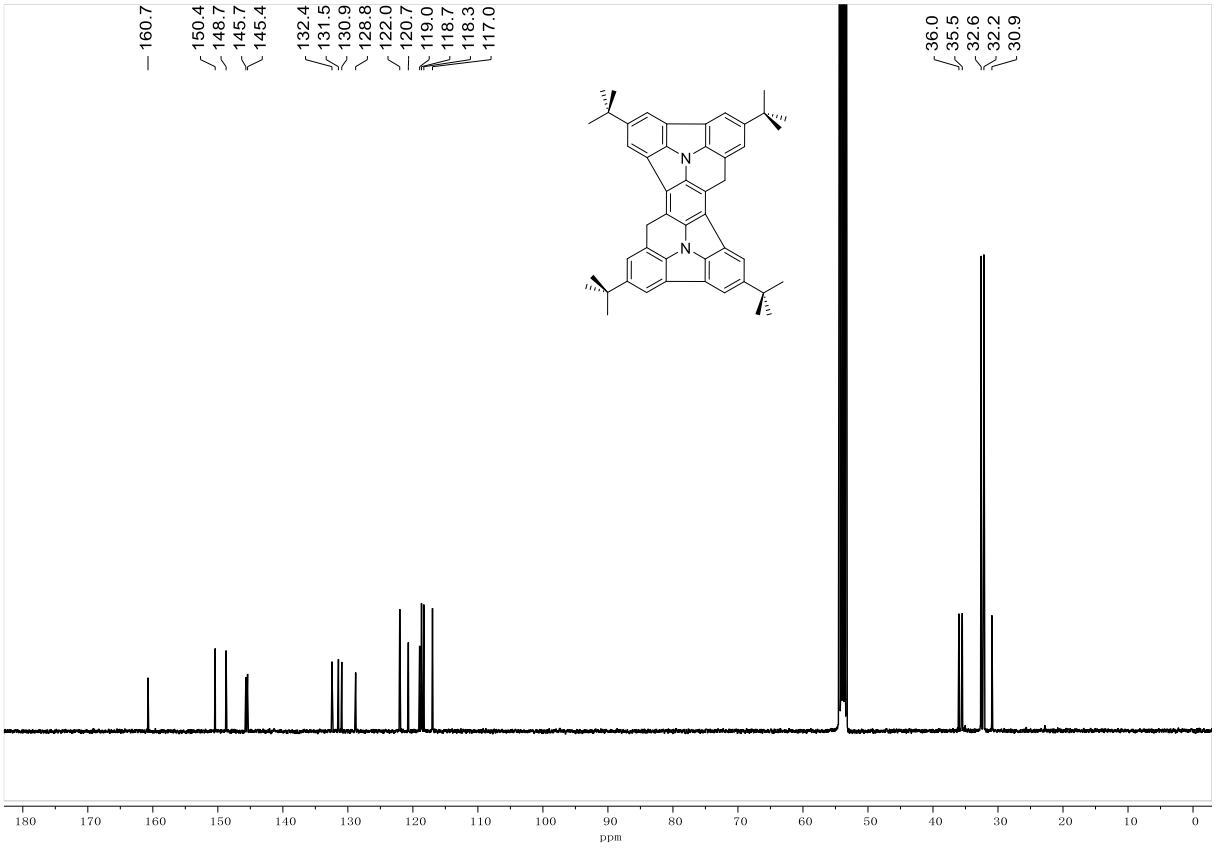


Figure S10. ^{13}C NMR spectrum (CD_2Cl_2, 100 MHz) of compound **10**

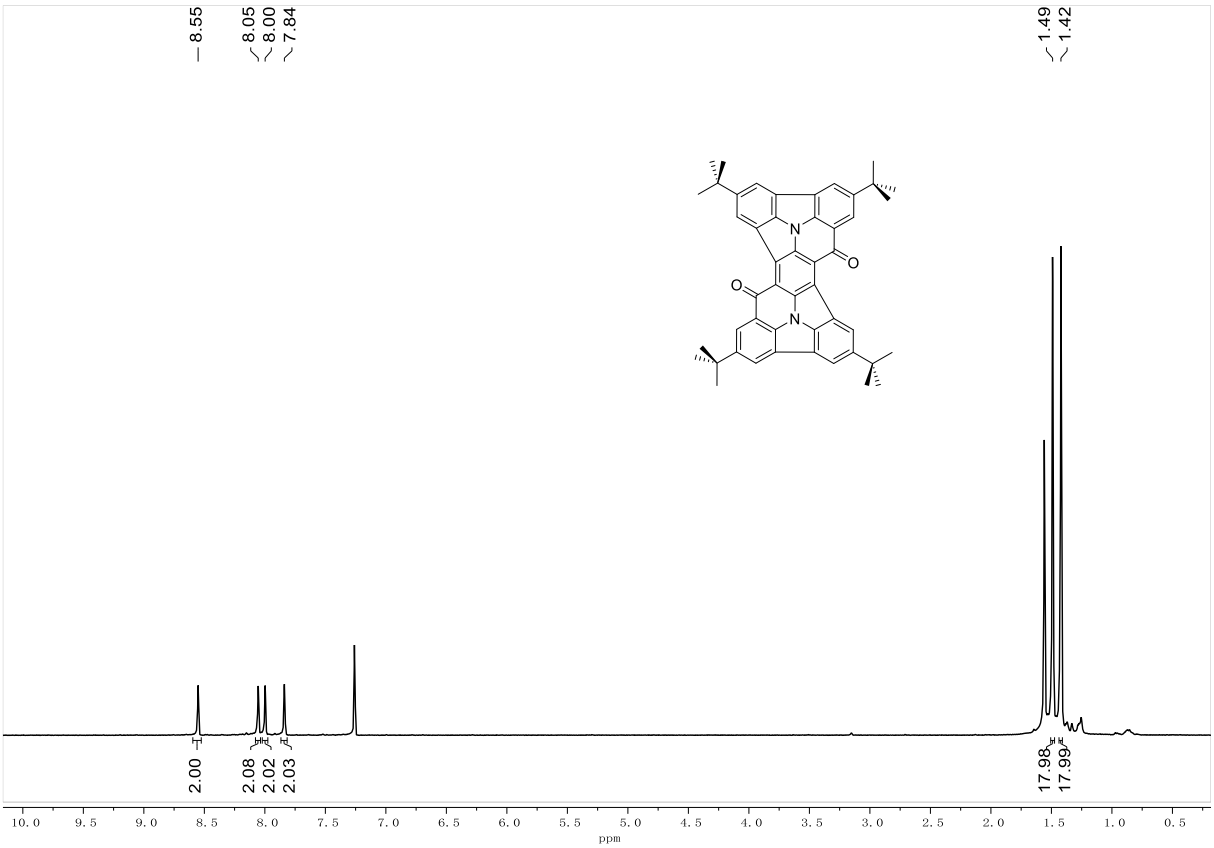


Figure S11. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **11**

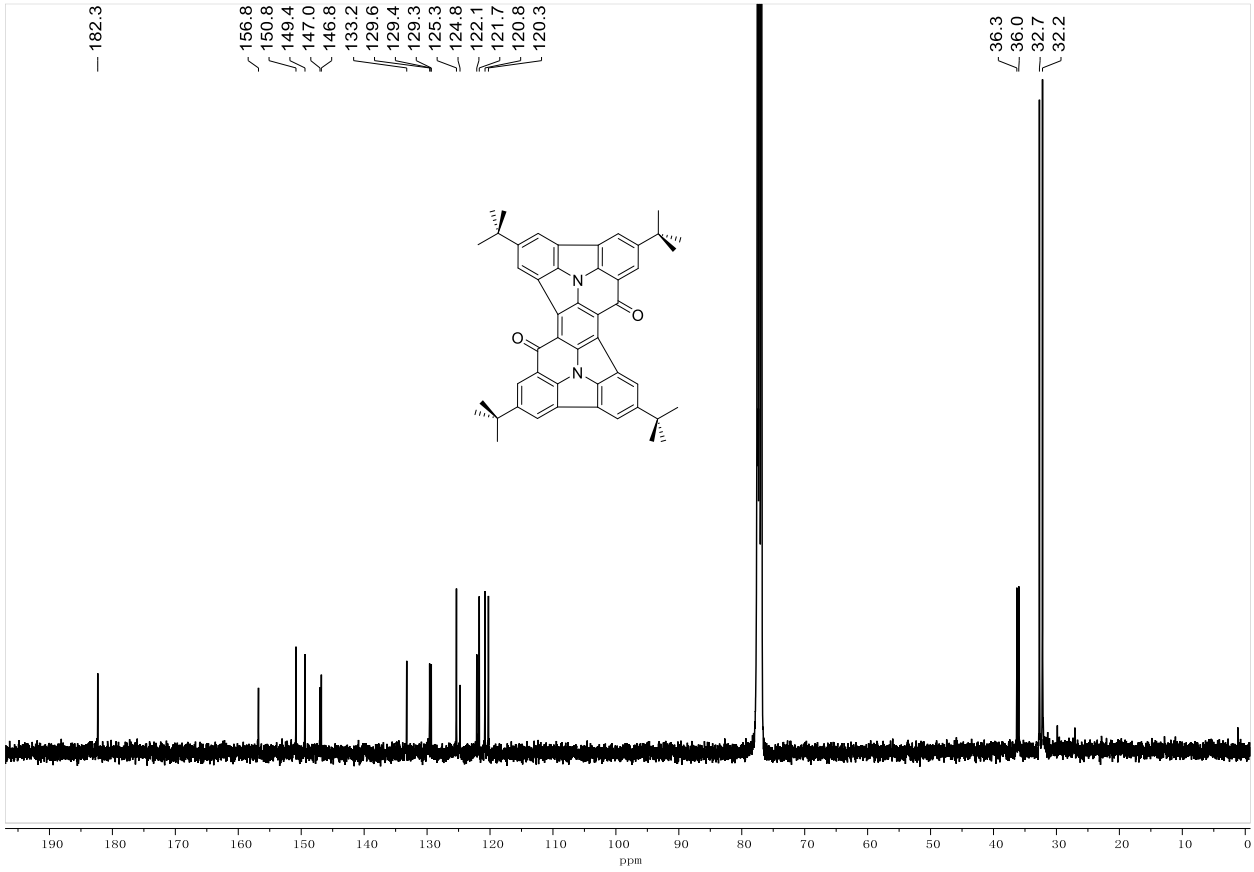


Figure S12. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of compound **11**

4. X-ray crystallographic structure determination

Single crystals of **7** and **11** suitable for X-ray diffraction analysis were obtained by slow evaporation of their dichloromethane/methanol solutions. A colorless crystal was mounted on a glass fiber at a random orientation. The data were collected by a diffractometer Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu Kα radiation (1.54178 Å) by using a w scan mode. The crystal was kept at 99.99(11) K during data collection. The structures were solved by direct methods using Olex2 software, [S2] and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXL-2018 using a full-matrix least squares procedure based on F2. [S3] The weighted R factor, wR and goodness-of-fit S values were obtained based on F2.The hydrogen atom positions were fixed geometrically at the calculated distances and allowed to ride on their parent atoms. Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Center and allocated with the deposition numbers: CCDC 2046269 and 2046270 for compounds **7** and **11**, respectively.

Table S1. Crystal data and structure refinement for 7

Empirical formula	$C_{49}H_{50}Cl_2N_2O_2$
Formula weight	769.81
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	11.4141(4)
b/Å	14.0206(7)
c/Å	15.4624(5)
α/°	66.346(4)
β/°	82.955(3)
γ/°	70.081(4)
Volume/Å^3	2130.71(17)
Z	2
ρ_{calc}g/cm^3	1.200
μ/mm^{-1}	1.678
F(000)	816.0
Crystal size/mm^3	0.12 × 0.1 × 0.08
Radiation	Cu Kα (λ = 1.54184)

2Θ range for data collection/°	6.242 to 147.914
Index ranges	$-14 \leq h \leq 13$, $-17 \leq k \leq 15$, $-19 \leq l \leq 17$
Reflections collected	15620
Independent reflections	8369 [R_{int} = 0.0815, R_{sigma} = 0.0848]
Data/restraints/parameters	8369/0/518
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0688, wR_2 = 0.1848
Final R indexes [all data]	R_1 = 0.0762, wR_2 = 0.1940
Largest diff. peak/hole / e $Å^{-3}$	0.59/-0.92

Table S2. Crystal data and structure refinement for 11

Empirical formula	$C_{48}H_{44}N_2O_2$
Formula weight	680.85
Temperature/K	99.99(11)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	18.9829(14)
b/Å	9.1829(5)
c/Å	21.9711(16)
α/°	90
β/°	104.095(8)
γ/°	90
Volume/$Å^3$	3714.6(5)
Z	4
$\rho_{calc}g/cm^3$	1.217
μ/mm^{-1}	0.571
F(000)	1448.0
Crystal size/mm^3	0.13 × 0.11 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.526 to 133.198
Index ranges	$-22 \leq h \leq 21$, $-6 \leq k \leq 10$, $-25 \leq l \leq 26$
Reflections collected	13596
Independent reflections	6522 [R_{int} = 0.0825, R_{sigma} = 0.0795]
Data/restraints/parameters	6522/0/489

Goodness-of-fit on F^2	1.285
Final R indexes [I>=2σ (I)]	R_1 = 0.1209, wR_2 = 0.3240
Final R indexes [all data]	R_1 = 0.1371, wR_2 = 0.3503
Largest diff. peak/hole / e $Å^{-3}$	0.62/-0.46

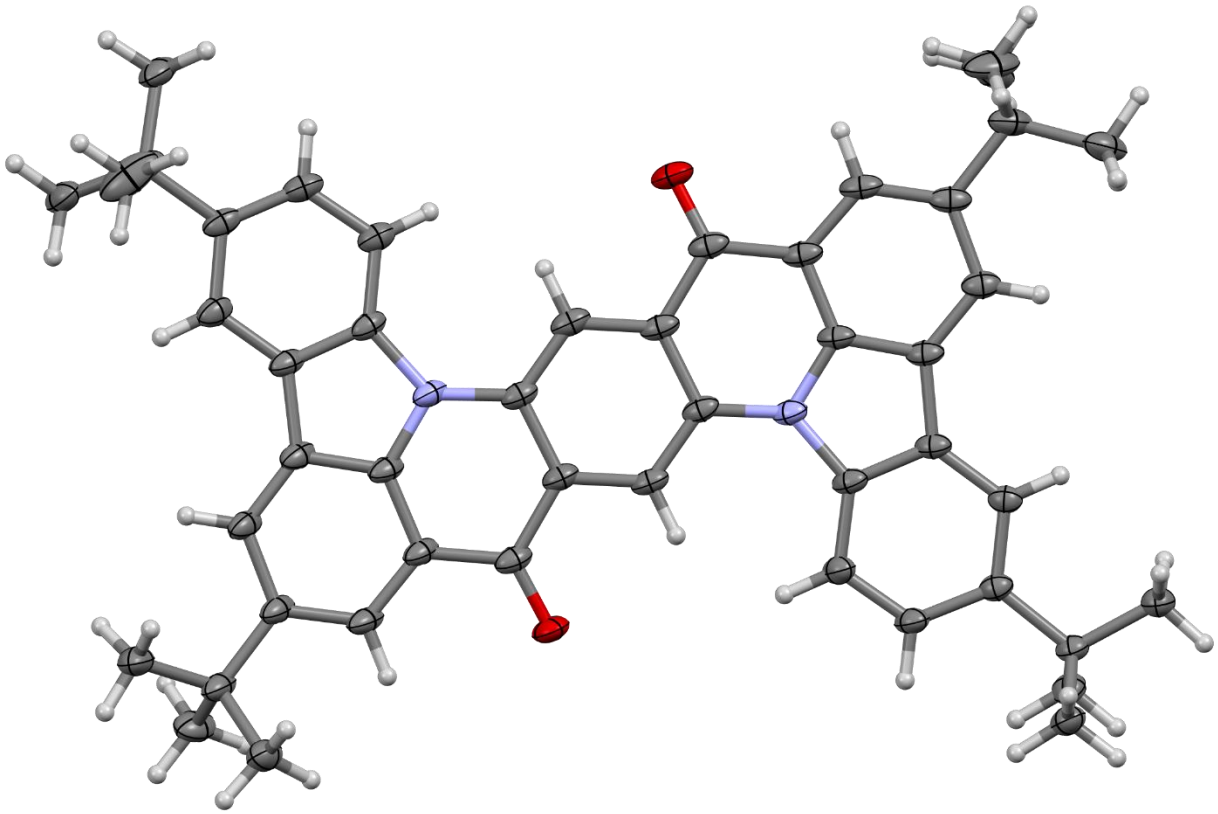


Figure S13. Crystal structure of **7** obtained at 100 K. Thermal ellipsoids are set at 50% probability level.

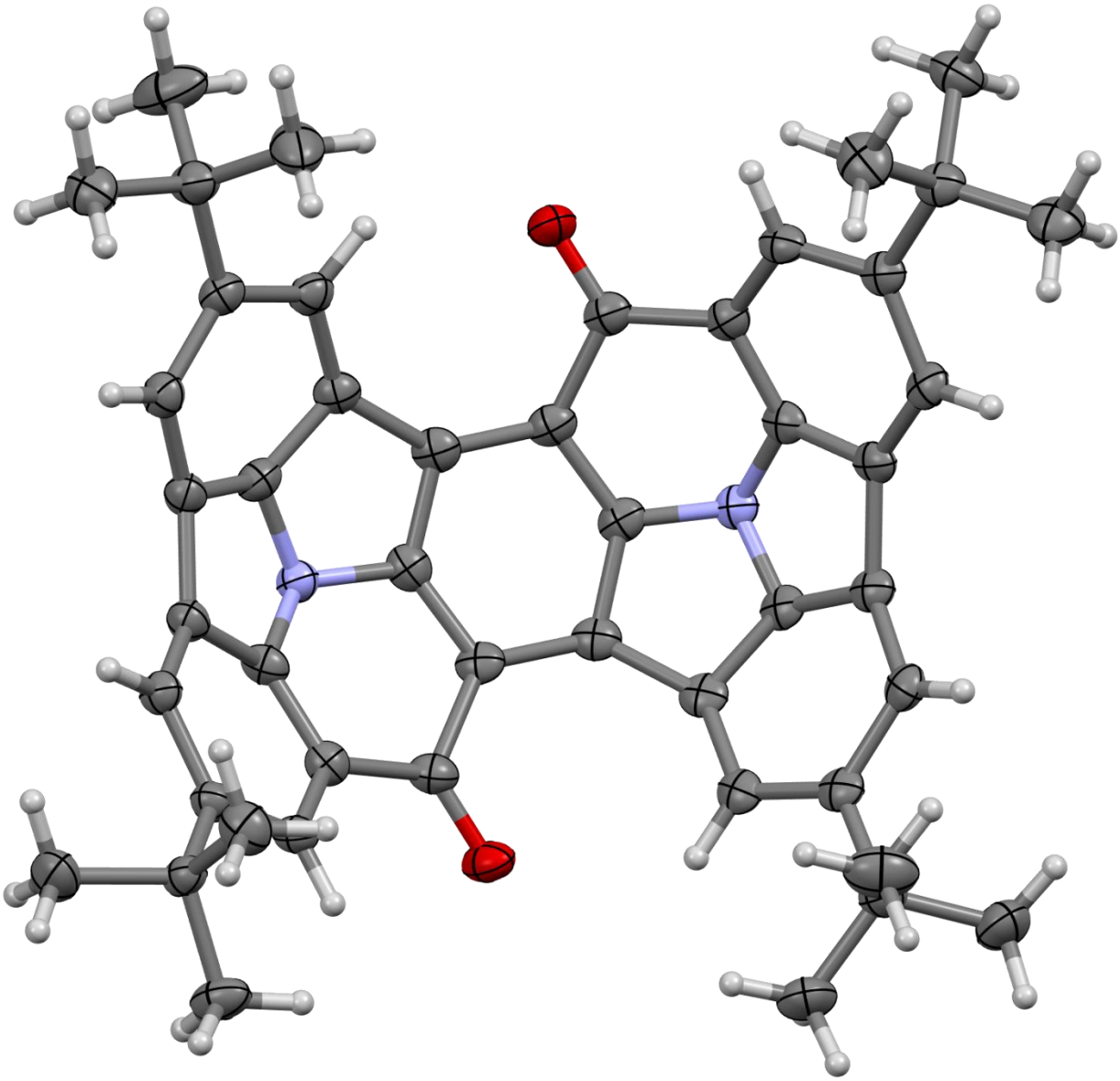


Figure S14. Crystal structure of **11** obtained at 100 K. Thermal ellipsoids are set at 50% probability level.

5. Optical spectra and fluorescence decay curve

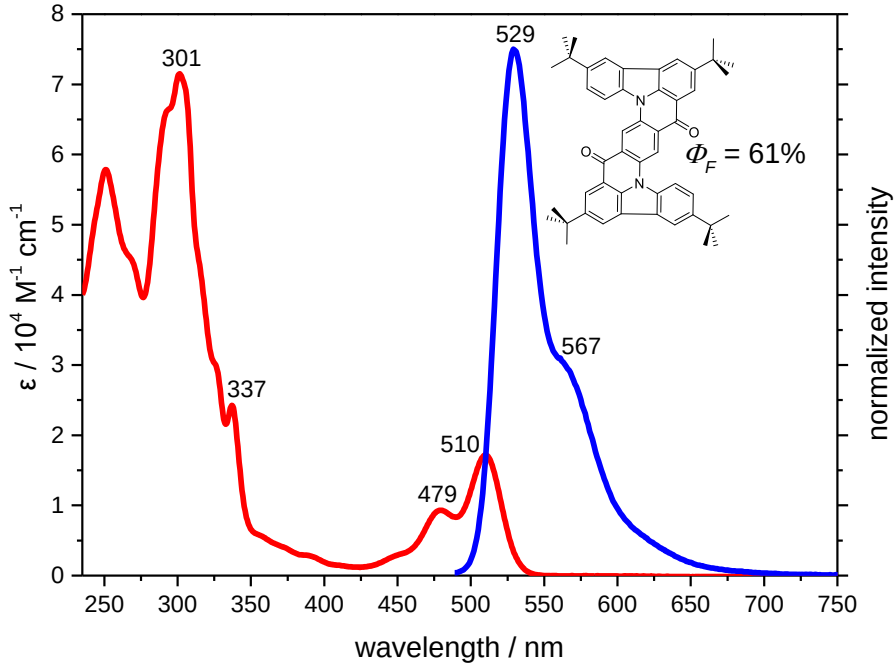


Figure S15. UV/Vis (red), emission (blue) spectra and quantum yield of **7** measured in dichloromethane at room temperature.

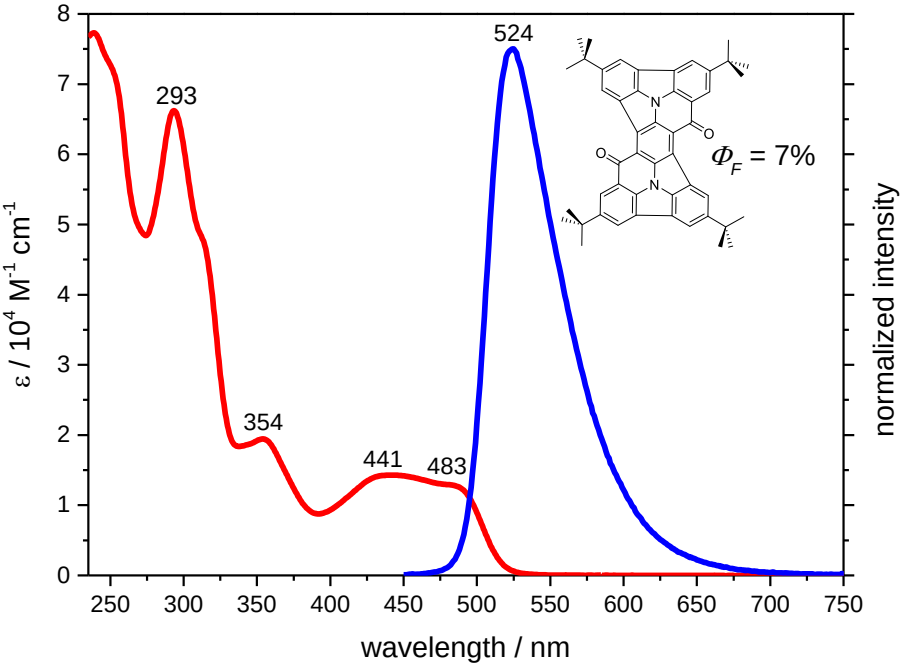


Figure S16. UV/Vis (red), emission (blue) spectra and quantum yield of **11** measured in dichloromethane at room temperature.

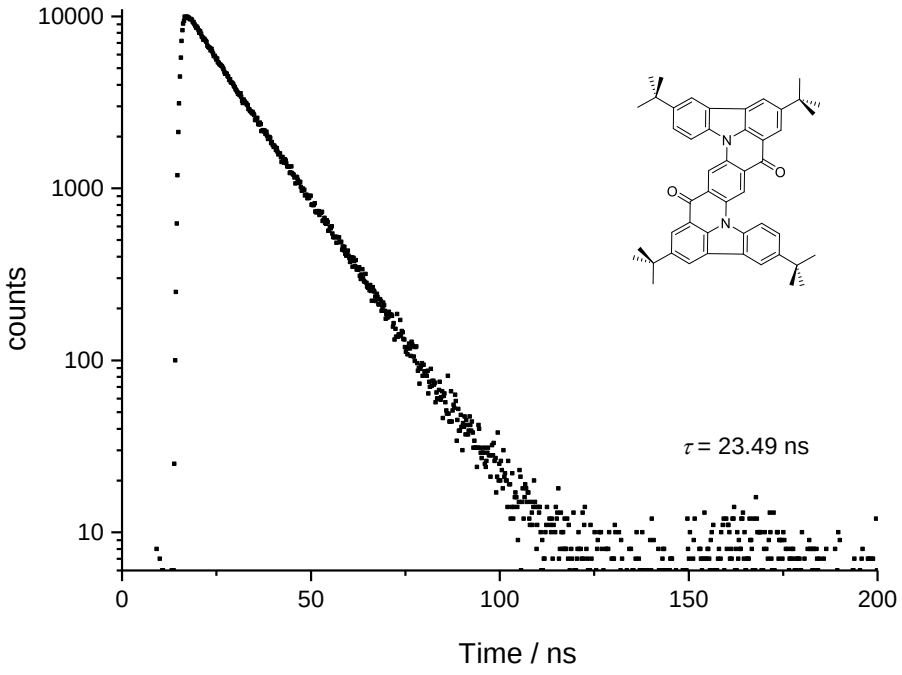


Figure S17. Fluorescence decay curve of **7** in dichloromethane at room temperature.

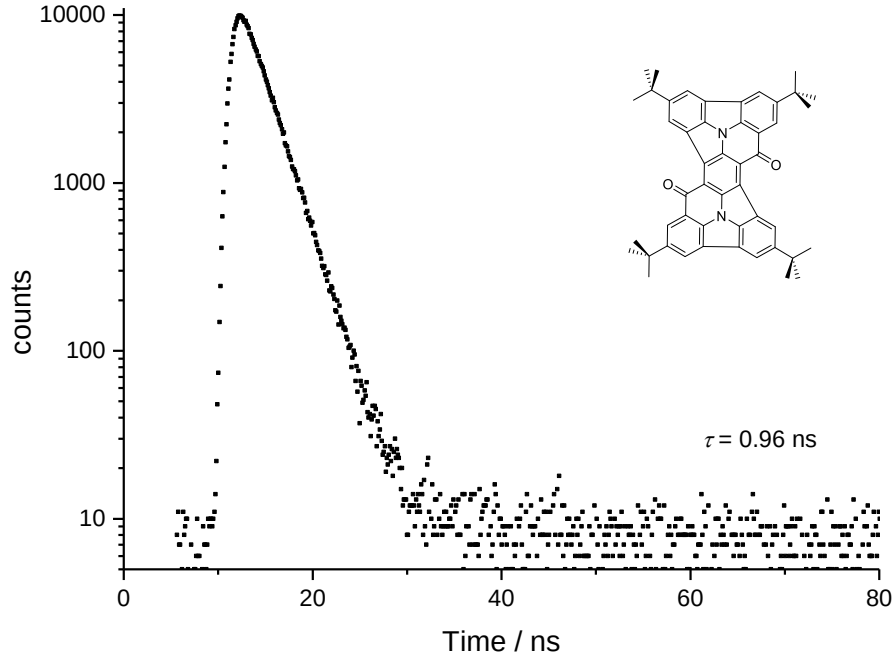


Figure S18. Fluorescence decay curve of **11** in dichloromethane at room temperature.

6. CV and DPV curves

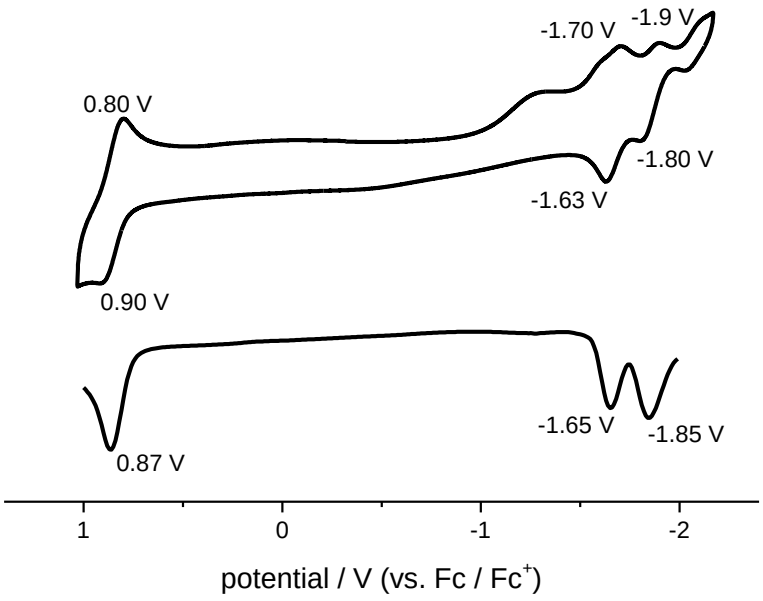


Figure S19. CV and DPV curves of **7** measured in dichloromethane using tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte and ferrocene as internal standard with a scan speed of 0.1 V/s

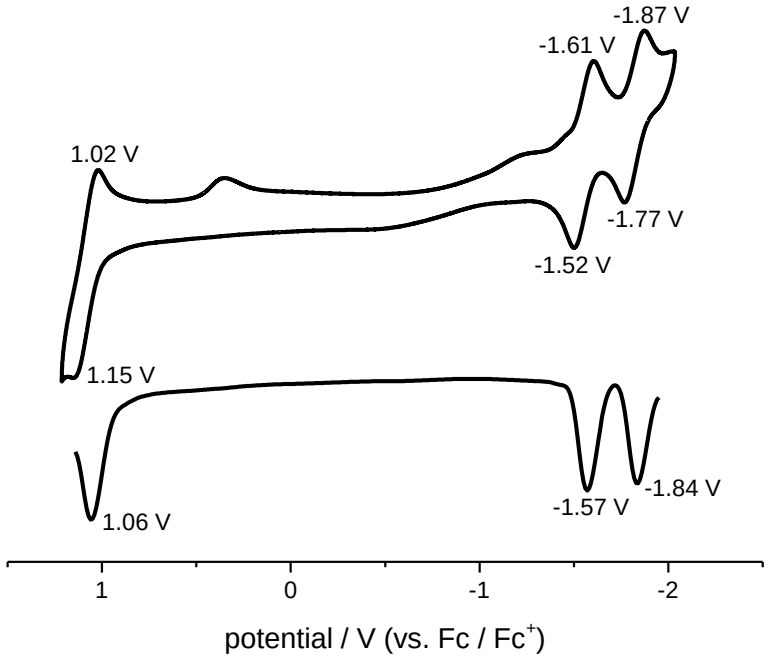


Figure S20. CV and DPV curves of **11** measured in dichloromethane using tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte and ferrocene as internal standard with a scan speed of 0.1 V/s

7. Theoretical calculations

All the theoretical calculations were carried out using a *Gaussian 16* software.[S4] All the calculations were based on the optimized geometries at B3LYP/6-31G(d,p) level of theory. The bowl-to-bowl inversion energy was calculated at B3LYP/6-311+G(2d,p) level of theory for the single-point energy, the planar transition state was checked by frequency calculations at B3LYP/6-31G(d,p) level of theory.[S5] The frontier molecular orbitals are calculated at the B3LYP/6-311+G(2d,p) level of theory. The nucleus-independent chemical shift (NICS) calculation was done at GIAO-B3LYP/6-311+G(d) level of theory. Bq atoms were inserted at the calculated positions and the Bq positions that are at the 1 Å away above and below the bowls were fixed with the assistant of Multiwfn software, as well as the calculated NICS values at the *zz* tensor.[S6] The calculations of excited state properties were performed using time-depended DFT methods at B3LYP/6-311G+(2d,p) level of theory in the solvent dichloromethane.

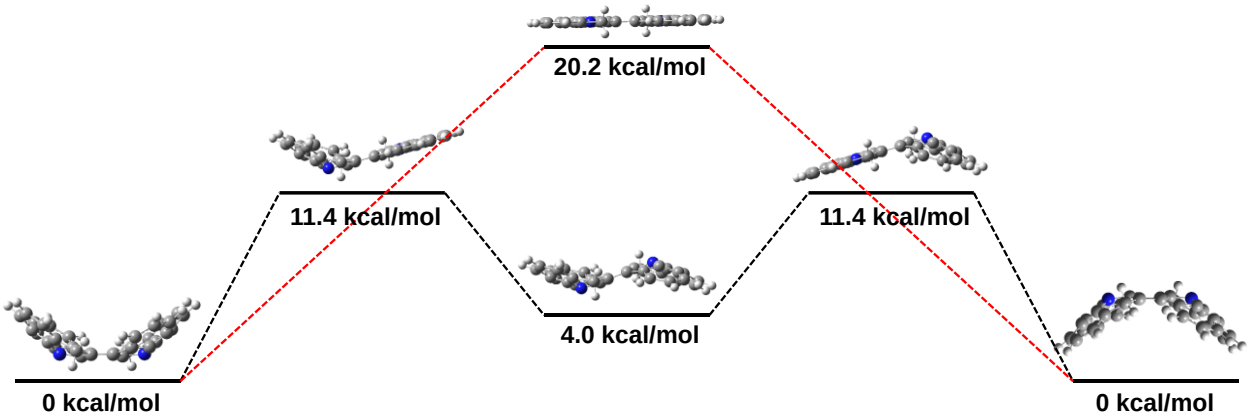


Figure S21. Energy diagram of the inversion process of the unsubstituted **10**.

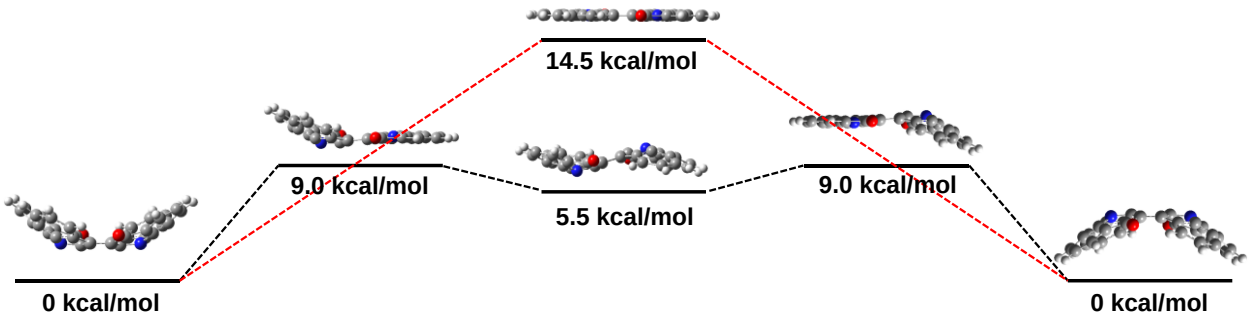


Figure S22. Energy diagram of the inversion process of the unsubstituted **11**.

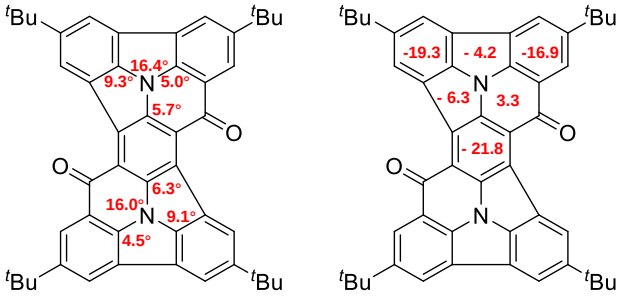


Figure S23. POAV angles and NICS(1)$_{zz}$ values of nanoboat **11**.

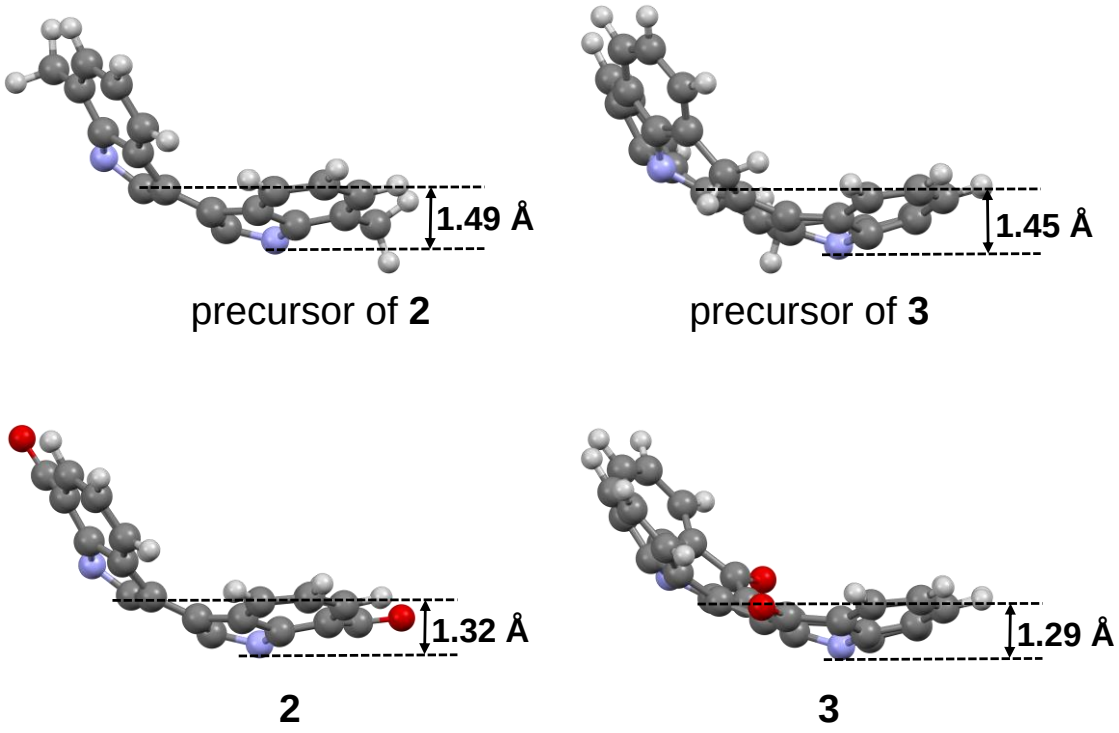


Figure S24. Optimized structures and related bowl depth of the concave parent moiety of **2**, **3** and their precursors at B3LYP/6-31G(d,p) level of theory in vacuo.

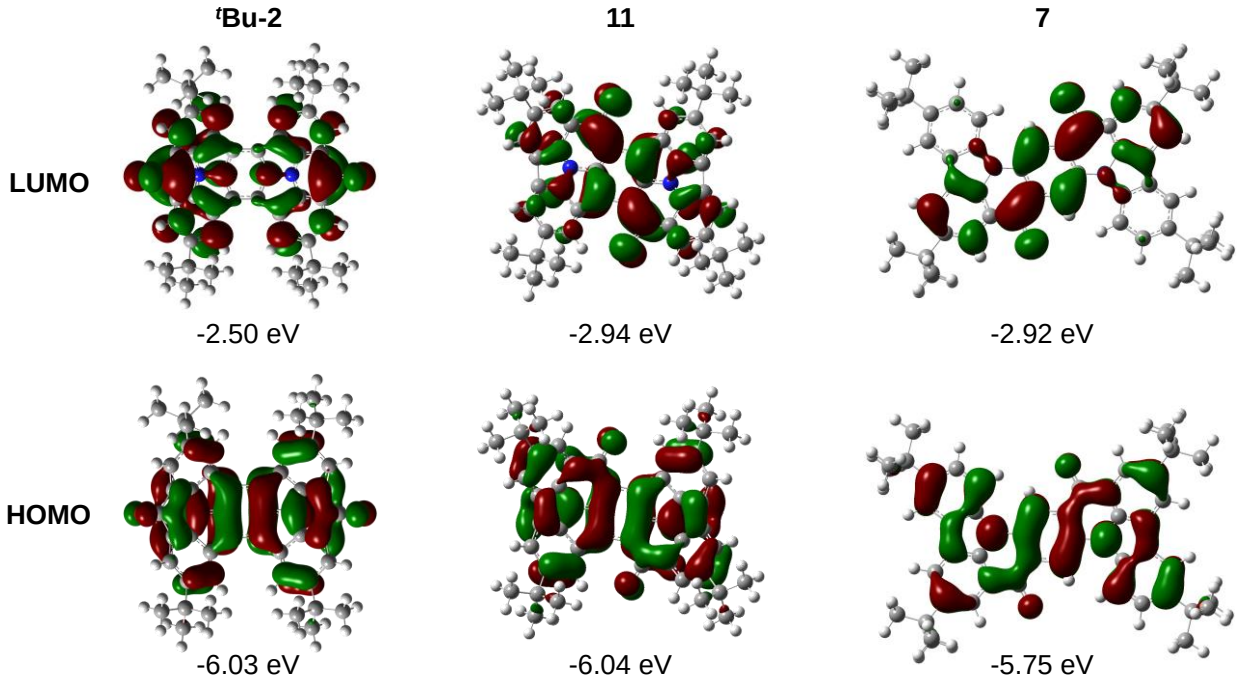


Figure S25. Frontier molecular orbitals and energy levels of *tert*-butylated **2**, **11** and **7** calculated by TD-DFT at B3LYP/6-311G+(d,p) level of theory in the solvent dichloromethane.

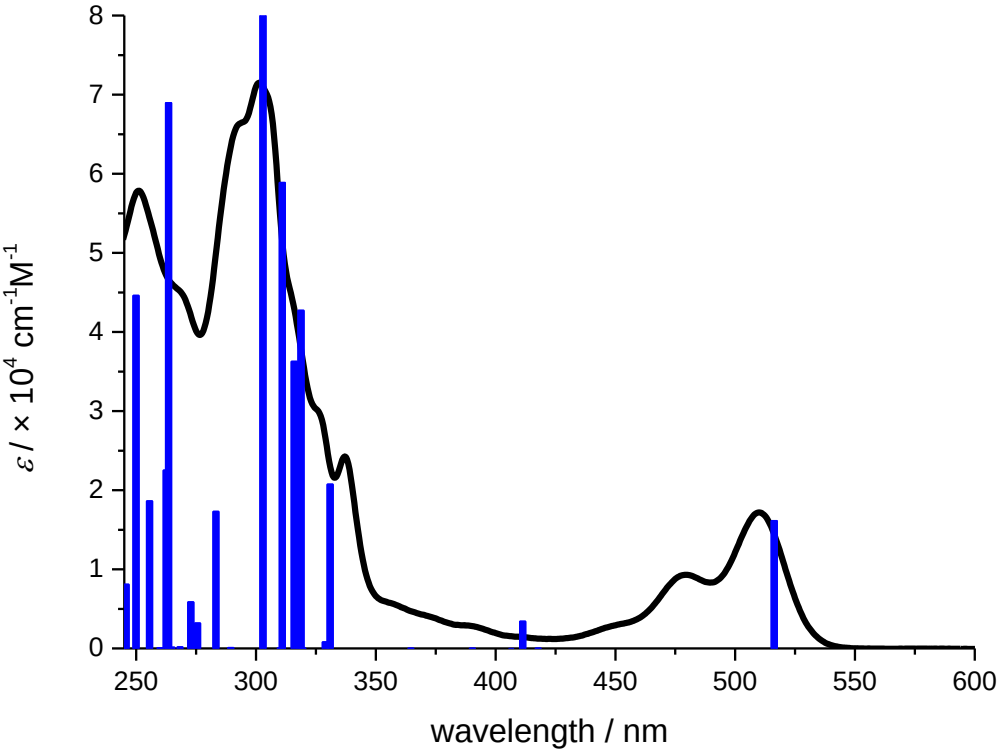


Figure S26. UV/Vis absorption spectrum of **7** and TD-DFT calculated oscillator strength (blue column) in dichloromethane at B3LYP/6-311G+(d,p) level.

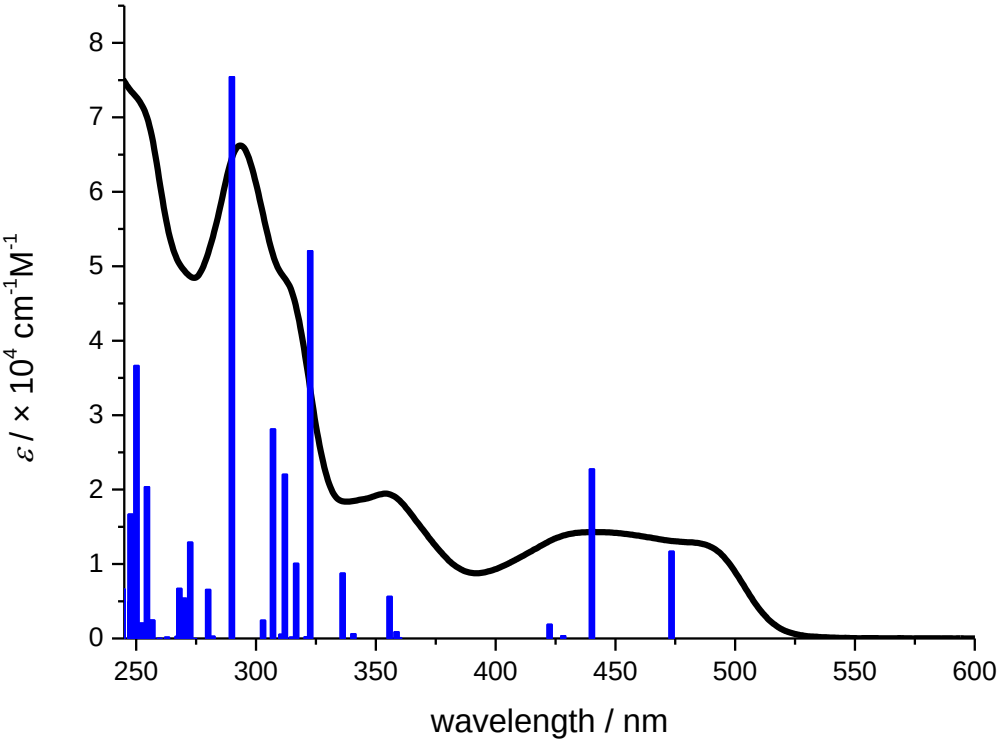


Figure S27. UV/Vis absorption spectrum of **11** and TD-DFT calculated oscillator strength (blue column) in dichloromethane at UB3LYP/6-311G+(d,p) level.

Table S3. TD-DFT calculated first-ten electron transitions of **7** in dichloromethane at B3LYP/6-311G+(d,p) level

Excited State 1:	Singlet-A	2.4012 eV	516.33 nm	f=0.1513	<S**2>=0.000
183 -> 184	0.70357				
Excited State 2:	Singlet-A	2.9677 eV	417.79 nm	f=0.0003	<S**2>=0.000
180 -> 184	0.11746				
182 -> 184	0.69245				
Excited State 3:	Singlet-A	3.0141 eV	411.34 nm	f=0.0323	<S**2>=0.000
181 -> 184	0.70254				
Excited State 4:	Singlet-A	3.0494 eV	406.59 nm	f=0.0001	<S**2>=0.000
180 -> 184	0.68731				
182 -> 184	-0.11080				
Excited State 5:	Singlet-A	3.1765 eV	390.32 nm	f=0.0002	<S**2>=0.000
183 -> 185	0.69345				
Excited State 6:	Singlet-A	3.3999 eV	364.67 nm	f=0.0003	<S**2>=0.000
176 -> 185	0.18891				
177 -> 184	0.67062				
Excited State 7:	Singlet-A	3.4736 eV	356.93 nm	f=0.0000	<S**2>=0.000
176 -> 184	0.66275				
177 -> 185	0.21524				
Excited State 8:	Singlet-A	3.7460 eV	330.97 nm	f=0.1946	<S**2>=0.000
180 -> 185	-0.13091				
182 -> 185	0.48366				
183 -> 186	-0.46993				
Excited State 9:	Singlet-A	3.7684 eV	329.01 nm	f=0.0078	<S**2>=0.000
175 -> 184	0.17365				
179 -> 184	0.47967				
180 -> 185	-0.13011				
182 -> 185	-0.10053				
183 -> 186	-0.17784				
183 -> 187	-0.40606				
Excited State 10:	Singlet-A	3.8798 eV	319.56 nm	f=0.0004	<S**2>=0.000
178 -> 184	0.43037				
181 -> 185	0.53683				

183: HOMO; 184: LUMO

Table S4. TD-DFT calculated first-ten electron transitions of **11** in dichloromethane at B3LYP/6-311G+(d,p) level

Excited State 1:	Singlet-A	2.6188 eV	473.44 nm	f=0.1033	<S**2>=0.000
Excited State 2:	Singlet-A	2.8165 eV	440.20 nm	f=0.2009	<S**2>=0.000
178 -> 182	0.11825				
180 -> 182	0.68897				
Excited State 3:	Singlet-A	2.8951 eV	428.25 nm	f=0.0033	<S**2>=0.000
179 -> 182	0.70055				
Excited State 4:	Singlet-A	2.9341 eV	422.56 nm	f=0.0168	<S**2>=0.000
178 -> 182	0.69174				
180 -> 182	-0.11792				
Excited State 5:	Singlet-A	2.9798 eV	416.08 nm	f=0.0000	<S**2>=0.000
177 -> 182	0.69754				
Excited State 6:	Singlet-A	3.3859 eV	366.17 nm	f=0.0000	<S**2>=0.000
173 -> 183	-0.15289				
174 -> 182	0.51460				
175 -> 182	0.39730				
181 -> 183	-0.16382				
Excited State 7:	Singlet-A	3.4464 eV	359.75 nm	f=0.0010	<S**2>=0.000
174 -> 182	0.15478				
181 -> 183	0.67299				
Excited State 8:	Singlet-A	3.4567 eV	358.68 nm	f=0.0080	<S**2>=0.000
173 -> 182	0.49023				
174 -> 183	-0.16002				
175 -> 183	-0.11336				
176 -> 182	0.41033				
181 -> 184	-0.18022				
Excited State 9:	Singlet-A	3.4846 eV	355.81 nm	f=0.0499	<S**2>=0.000
173 -> 182	0.15052				
177 -> 183	-0.11457				
181 -> 184	0.66214				
Excited State 10:	Singlet-A	3.6392 eV	340.69 nm	f=0.0056	<S**2>=0.000
178 -> 183	-0.13807				
179 -> 184	-0.17477				
180 -> 183	0.65212				

181: HOMO; 182: LUMO

Cartesian coordinates for theoretically optimized structures of 7, 10 and 11.

7 opt B3LYP/6-31G(d,p)

C	0.78491900	-1.16129600	-0.01236400
C	-0.60680400	-1.25011500	-0.01253800
C	-1.41735000	-0.11581200	0.01271600
C	-0.78490200	1.16125300	-0.01217500
C	0.60681600	1.25007400	-0.01254600
C	1.41736100	0.11576900	0.01252000
C	-3.53632500	1.01406900	-0.04402000
C	-3.75250800	-1.23075400	0.10401400
C	-3.00204100	2.30017600	-0.09954500
C	-4.91874500	0.76669600	-0.05130900
C	-3.58991700	-2.60746000	0.24115400
C	-5.06150800	-0.67721800	0.04092000
C	-3.90712800	3.36764600	-0.17211200
C	-5.79226400	1.85088800	-0.12726500
C	-4.73287100	-3.41065600	0.28769100
C	-6.18000500	-1.50593500	0.08897400
C	-5.29774900	3.17050600	-0.18996300
H	-3.48319300	4.36530200	-0.21252300
H	-6.86060900	1.66935400	-0.13557800
C	-6.03845400	-2.89547000	0.20791700
H	-4.58170600	-4.47800000	0.39293400
H	-7.16773700	-1.05779000	0.03687800
C	3.75249500	1.23074100	0.10366500
C	3.53634500	-1.01408800	-0.04443400
C	3.58986300	2.60745500	0.24063700
C	5.06150400	0.67721800	0.04067700
C	3.00207000	-2.30020000	-0.09994800
C	4.91876100	-0.76670000	-0.05160900
C	4.73280200	3.41066700	0.28724500
C	6.17998600	1.50595100	0.08878300
C	3.90717100	-3.36766200	-0.17246500
C	5.79229400	-1.85088500	-0.12751300
C	6.03840300	2.89548800	0.20767400
H	4.58160700	4.47802400	0.39231800
H	7.16772700	1.05781300	0.03677800

C	5.29779100	-3.17050600	-0.19023900
H	3.48324500	-4.36532100	-0.21288900
H	6.86063900	-1.66934500	-0.13574300
C	-1.54262500	2.45090000	-0.06656500
O	-0.97005300	3.54014800	-0.08780200
C	1.54265200	-2.45093600	-0.06692000
O	0.97009200	-3.54019700	-0.08819400
N	-2.81679900	-0.16591900	0.03306500
N	2.81680800	0.16589600	0.03259900
C	-6.23139000	4.39511600	-0.27315200
C	-5.98555600	5.31300600	0.94780300
C	-5.93425500	5.18054000	-1.57260600
C	-7.72003100	3.99935400	-0.28279400
H	-6.19631600	4.78519100	1.88365300
H	-4.95142200	5.66644000	0.98970800
H	-6.63670500	6.19298900	0.89982900
H	-6.10734500	4.55691200	-2.45575200
H	-6.58544600	6.05889500	-1.64378900
H	-4.89870000	5.53043100	-1.60900400
H	-8.33864300	4.90021200	-0.34338400
H	-7.97086300	3.37084300	-1.14379800
H	-8.00752400	3.46508500	0.62889400
C	-7.29128600	-3.79117500	0.25305700
C	-6.93991300	-5.28500900	0.38621100
C	-8.16692200	-3.39347200	1.46502400
C	-8.10462200	-3.60297300	-1.04955000
H	-6.34105400	-5.64037200	-0.45861600
H	-6.38940900	-5.49448800	1.30912100
H	-7.85957600	-5.87818800	0.41023200
H	-8.49133200	-2.35011400	1.40919200
H	-9.06573000	-4.01879800	1.50785100
H	-7.61821200	-3.52224600	2.40358300
H	-9.00409300	-4.22860200	-1.03180700
H	-8.42460000	-2.56541800	-1.18390800
H	-7.51163500	-3.88501400	-1.92554200
C	7.29121600	3.79120400	0.25305800
C	6.93976800	5.28510800	0.38522600

C	8.16604500	3.39401800	1.46579700
C	8.10540400	3.60241800	-1.04891400
H	6.34115300	5.63992000	-0.46000400
H	6.38898200	5.49515600	1.30783900
H	7.85941200	5.87831700	0.40919900
H	8.49040700	2.35061000	1.41059600
H	9.06485100	4.01932600	1.50897800
H	7.61669500	3.52320600	2.40392300
H	9.00486400	4.22805000	-1.03081500
H	8.42551400	2.56482500	-1.18265700
H	7.51302200	3.88410200	-1.92543000
C	6.23144900	-4.39510100	-0.27345300
C	5.98553800	-5.31312300	0.94738400
C	5.93441200	-5.18038700	-1.57301600
C	7.72008500	-3.99931800	-0.28293100
H	6.19623600	-4.78541300	1.88330800
H	4.95140800	-5.66657900	0.98919200
H	6.63669800	-6.19309400	0.89935200
H	6.10755700	-4.55665800	-2.45608000
H	6.58561200	-6.05873100	-1.64425400
H	4.89885700	-5.53027200	-1.60951600
H	8.33871300	-4.90015900	-0.34361800
H	7.97097300	-3.37067300	-1.14382200
H	8.00750500	-3.46518300	0.62885800
H	-2.62260400	-3.08026700	0.33102100
H	-1.00880500	-2.25021800	-0.05796700
H	1.00882400	2.25018300	-0.05793900
H	2.62252900	3.08026200	0.33030800

Unsubstituted 10 opt B3LYP/6-31G(d,p)

C	0.67872900	-1.32179300	-1.07689700
C	-0.72616700	-1.25199400	-1.05048800
C	-1.28237600	0.06808100	-1.18241100
C	-0.67872600	1.32178500	-1.07690900
C	0.72617000	1.25198600	-1.05049500
C	1.28237900	-0.06809000	-1.18240700

C	-3.37436500	0.87673700	-0.28920700
C	-2.97094800	-1.27665100	-0.61799400
C	-2.91286900	2.17211600	-0.11903700
C	-4.34628600	0.18374500	0.47613000
C	-1.86063100	-2.13173100	-0.64692700
C	-4.05702500	-1.26803000	0.27011500
C	-3.65259400	2.92147500	0.80225300
C	-5.08680000	0.98283200	1.35786000
C	-2.08622200	-3.35118200	0.01632100
C	-4.24778200	-2.49604300	0.92356600
C	-4.74322500	2.33786800	1.48077900
H	-3.37706100	3.94817600	1.02856300
H	-5.87120400	0.56625400	1.98248200
C	-3.29493600	-3.51974400	0.72544000
H	-1.33306600	-4.13169000	0.06644300
H	-5.05227700	-2.65242500	1.63593500
C	2.97095000	1.27664600	-0.61799500
C	3.37436500	-0.87673900	-0.28919100
C	1.86063300	2.13172600	-0.64693800
C	4.05702400	1.26803200	0.27011600
C	2.91286900	-2.17211700	-0.11901200
C	4.34628500	-0.18374200	0.47614400
C	2.08622200	3.35118300	0.01630100
C	4.24777900	2.49605000	0.92355900
C	3.65259200	-2.92146900	0.80228600
C	5.08679600	-0.98282200	1.35788100
C	3.29493400	3.51974900	0.72542200
H	1.33306600	4.13169000	0.06641600
H	5.05227300	2.65243800	1.63592900
C	4.74322000	-2.33785700	1.48081000
H	3.37705800	-3.94816800	1.02860300
H	5.87119900	-0.56623900	1.98250300
C	-1.60273500	2.54010800	-0.84965300
C	1.60273700	-2.54011500	-0.84962900
N	-2.65678200	-0.02240300	-1.04946700
N	2.65678500	0.02239500	-1.04946000
H	-3.45172700	-4.46352400	1.23987700

H	-5.30466300	2.95325900	2.17751100
H	3.45172400	4.46353300	1.23985300
H	5.30465700	-2.95324200	2.17754800
H	-1.06681700	3.30696600	-0.28100600
H	-1.84030600	2.99434500	-1.82299300
H	1.06681800	-3.30696800	-0.28097800
H	1.84031100	-2.99435900	-1.82296500

11 opt B3LYP/6-31G(d,p)

C	-0.79702000	1.25101800	-1.72840700
C	0.61174100	1.33253900	-1.73669700
C	1.28113900	0.06420100	-1.87100200
C	0.79702200	-1.25100200	-1.72841800
C	-0.61174000	-1.33252200	-1.73671700
C	-1.28114000	-0.06418400	-1.87101000
C	3.46057100	-0.54131600	-1.05476900
C	2.84622000	1.56461400	-1.34766300
C	3.13199200	-1.87206400	-0.84300700
C	4.40581000	0.23626300	-0.33950900
C	1.66507600	2.31074800	-1.34255200
C	3.95969600	1.66135700	-0.51223300
C	4.01392300	-2.55937400	0.00644900
C	5.26049700	-0.49834600	0.48733600
C	1.78987900	3.53991400	-0.67758700
C	4.04492400	2.90126100	0.14444100
C	5.09797800	-1.90150600	0.62788600
H	3.81228700	-3.60399400	0.21771900
H	6.01514900	0.01224900	1.07311000
C	2.99722300	3.85190400	0.00656200
H	0.93945900	4.20828600	-0.62134300
H	4.86660700	3.11161200	0.81760200
C	-2.84622200	-1.56460300	-1.34768800
C	-3.46057300	0.54132600	-1.05477300
C	-1.66507500	-2.31073200	-1.34257200
C	-3.95969100	-1.66135000	-0.51224800
C	-3.13198900	1.87206900	-0.84298900
C	-4.40580900	-0.23625900	-0.33951500

C	-1.78986600	-3.53989600	-0.67760100
C	-4.04491000	-2.90125200	0.14443200
C	-4.01390900	2.55936700	0.00649100
C	-5.26048400	0.49833500	0.48735400
C	-2.99720300	-3.85188900	0.00656100
H	-0.93944400	-4.20826500	-0.62136400
H	-4.86659200	-3.11160100	0.81759500
C	-5.09796300	1.90149100	0.62792300
H	-3.81227300	3.60398600	0.21776300
H	-6.01513100	-0.01226500	1.07313300
C	1.76608400	-2.33797100	-1.29184200
O	1.40646300	-3.50556900	-1.18089100
C	-1.76607900	2.33798400	-1.29181500
O	-1.40646300	3.50558600	-1.18087200
N	2.62555800	0.27965800	-1.75372900
N	-2.62556300	-0.27964300	-1.75374900
C	6.04519900	-2.73304600	1.52200900
C	5.24629400	-3.36600800	2.68617800
C	6.68917100	-3.85447700	0.67214400
C	7.18098900	-1.88712000	2.12890600
H	4.77932400	-2.59361600	3.30593900
H	4.45469800	-4.02979500	2.32729400
H	5.91070300	-3.95839000	3.32509600
H	7.27259300	-3.43437900	-0.15364700
H	7.36141200	-4.46140600	1.28885700
H	5.93713200	-4.52237100	0.24260200
H	7.84005900	-2.53078300	2.71982800
H	7.79272500	-1.40977900	1.35630700
H	6.80178900	-1.10797400	2.79844400
C	3.08755800	5.23399100	0.69554800
C	2.92356200	6.34150200	-0.37284200
C	1.96577700	5.37149000	1.75274600
C	4.43702000	5.45897400	1.40468300
H	3.71405000	6.27700600	-1.12784000
H	1.96248400	6.26827500	-0.88929200
H	2.97887800	7.33188500	0.09308400
H	2.05909500	4.59934300	2.52354700

H	2.02445600	6.34964000	2.24334200
H	0.97018400	5.28266000	1.30967400
H	4.46145800	6.46654100	1.83170600
H	4.59281800	4.75388800	2.22797700
H	5.28130700	5.37268600	0.71279800
C	-3.08752800	-5.23397700	0.69554600
C	-2.92342200	-6.34148500	-0.37282900
C	-1.96580600	-5.37142900	1.75281200
C	-4.43702500	-5.45901500	1.40459900
H	-3.71387000	-6.27702700	-1.12787300
H	-1.96231800	-6.26821900	-0.88922500
H	-2.97872200	-7.33186700	0.09309900
H	-2.05920200	-4.59928300	2.52360500
H	-2.02447400	-6.34958000	2.24340900
H	-0.97019100	-5.28256000	1.30980000
H	-4.46145300	-6.46658600	1.83161300
H	-4.59290000	-4.75394200	2.22788900
H	-5.28127300	-5.37275400	0.71266300
C	-6.04522400	2.73301700	1.52201100
C	-5.24639000	3.36618200	2.68611500
C	-6.68936300	3.85428100	0.67203400
C	-7.18087600	1.88700900	2.12902400
H	-4.77929700	2.59391000	3.30593400
H	-4.45490000	4.03006400	2.32718300
H	-5.91088200	3.95851400	3.32499200
H	-7.27274300	3.43402000	-0.15370200
H	-7.36167300	4.46120400	1.28868100
H	-5.93740000	4.52220400	0.24240600
H	-7.83994600	2.53063100	2.71999000
H	-7.79263900	1.40959900	1.35649000
H	-6.80153200	1.10790900	2.79854000

Unsubstituted 11 opt B3LYP/6-31G(d,p)

C	-0.72239200	-1.29687000	0.94515800
C	0.68847000	-1.29643100	0.95187600
C	1.27957800	0.01105400	1.08023900
C	0.72239300	1.29686900	0.94515900

C	-0.68847000	1.29643000	0.95187800
C	-1.27957700	-0.01105600	1.08023900
C	3.43267200	0.74732500	0.28830500
C	2.93386300	-1.39495100	0.56672400
C	3.02990100	2.06220900	0.09543100
C	4.44787000	0.02172400	-0.39600000
C	1.79922700	-2.21267700	0.57067500
C	4.08202100	-1.42647000	-0.23254800
C	3.89791000	2.81533800	-0.71757100
C	5.28383100	0.81397500	-1.18565100
C	2.01444600	-3.44843400	-0.06706000
C	4.25982600	-2.66941100	-0.86224900
C	5.01573300	2.19779200	-1.29605900
H	3.66859700	3.85396500	-0.93180400
H	6.09645000	0.38295600	-1.76278400
C	3.25390800	-3.65427700	-0.71054000
H	1.22774000	-4.19087800	-0.13422600
H	5.10087100	-2.87120500	-1.51861300
H	5.67140400	2.79610400	-1.92119400
H	3.40722900	-4.60614200	-1.21051100
C	-2.93386200	1.39495100	0.56672500
C	-3.43267100	-0.74732500	0.28830300
C	-1.79922600	2.21267600	0.57067700
C	-4.08202000	1.42647100	-0.23254700
C	-3.02990100	-2.06220900	0.09542800
C	-4.44786900	-0.02172300	-0.39600000
C	-2.01444500	3.44843400	-0.06705600
C	-4.25982500	2.66941300	-0.86224600
C	-3.89791000	-2.81533700	-0.71757400
C	-5.28383100	-0.81397300	-1.18565200
C	-3.25390700	3.65427800	-0.71053700
H	-1.22773800	4.19087800	-0.13422200
H	-5.10087000	2.87120700	-1.51861100
C	-5.01573300	-2.19779000	-1.29606100
H	-3.66859700	-3.85396400	-0.93180800
H	-6.09645000	-0.38295400	-1.76278400
H	-3.40722700	4.60614300	-1.21050700

H	-5.67140500	-2.79610100	-1.92119700
C	1.63187900	2.44147200	0.52832600
O	1.20562500	3.58648400	0.42501100
C	-1.63187800	-2.44147200	0.52832200
O	-1.20563000	-3.58648800	0.42502500
N	2.63217600	-0.12559300	0.96066300
N	-2.63217500	0.12559200	0.96066300

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