Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

(*o*-Phenyleno)naphthalene Diimides: A Pink Fluorescent Chromophore

Yingjie Ma, [+]†¶ Xiaojie Zhang, [+]†± Sebastian Stappert,† Zhongyi Yuan, †§ Chen Li,*†δ and Klaus Müllen*†‡

College of Chemistry/Institute of Polymers
Nanchang University
999 Xuefu Avenue, Nanchang 330031, China

[+]These authors contributed equally to this work.

†Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

δSchool of Environment and Civil Engineering, Dongguan University of Technology, No.1, Daxue Rd., Songshan Lake, Dongguan, Guangdong Province, P. R. China

‡Institute of Physical Chemistry, Johannes Gutenberg University Mainz, Duesbergweg 10-14, 55128 Mainz, Germany

¶Current address: National Center for Nanoscience and Technology, Beijing 100190, P.R.China

±Current address: Changchun Institute Of Applied Chemistry, No.5625, Ren Min Street, Changchun, P.R.China

§Current address: Institute of Polymers/Jiangxi Provincial Key Laboratory of New Energy Chemistry, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, P.R.China

Corresponding author: *lichen@mpip-mainz.mpig.de*

muellen@mpip-mainz.mpg.de

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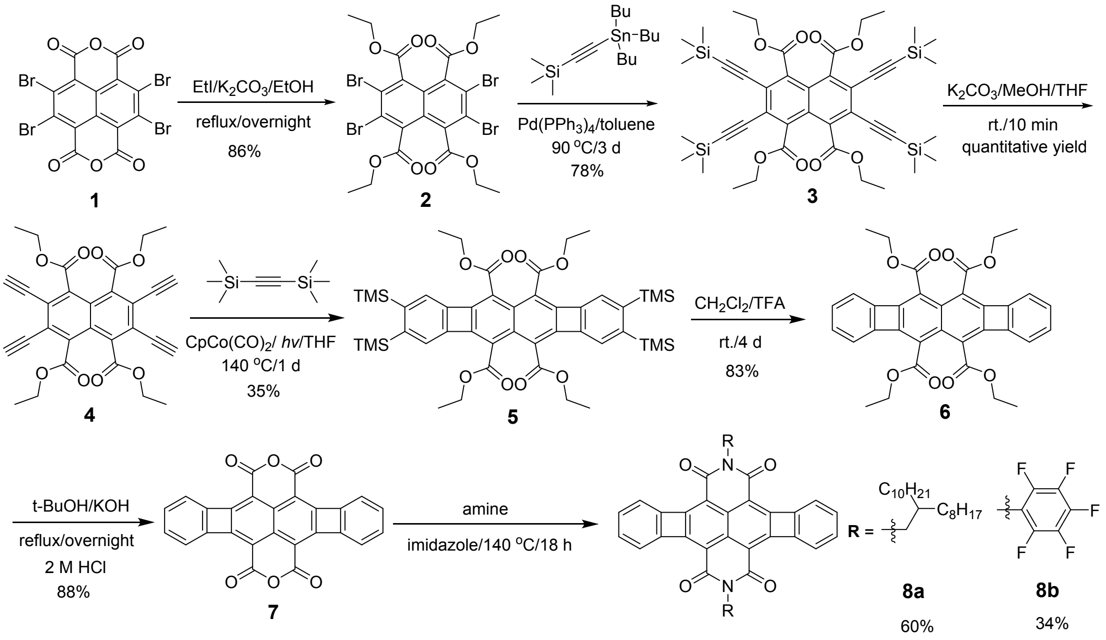
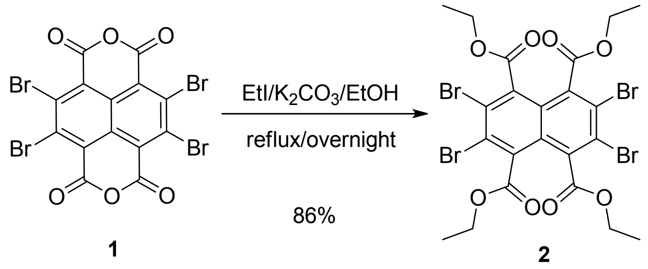
1. General

All reactions were carried out under an inert argon atmosphere. Photo irradiation reaction was carried out in a normal reactor with irradiation of an 80 or 250 W halogen display/optic lamp (OSRAM GmbH). Column chromatography was performed on silica gel. ^{1}H NMR,^{13}C NMR and ^{19}F NMR spectra were recorded in deuterated solvents using a Bruker DPX 250 spectrometer and Bruker DPX 700 spectrometer, with the solvent proton or carbon signal as an internal standard. MALDI-TOF mass spectra were measured using a Bruker Reflex II. UV–vis absorption spectra were recorded at room temperature using a Perkin-Elmer Lambda 9 spectrophotometer. Fluorescence spectra were recorded on a SPEX-Fluorolog II (212) spectrometer. CV measurements were carried out on a computer-controlled GSTAT12 in a three-electrode cell in a DCM solution of Bu_4NPF_6 (0.1 M) with a scan rate of 100 mV/s at room temperature. A Pt wire, a silver wire, and a glassy carbon electrode were used as the counter electrode, the reference electrode, and the working electrode, respectively.

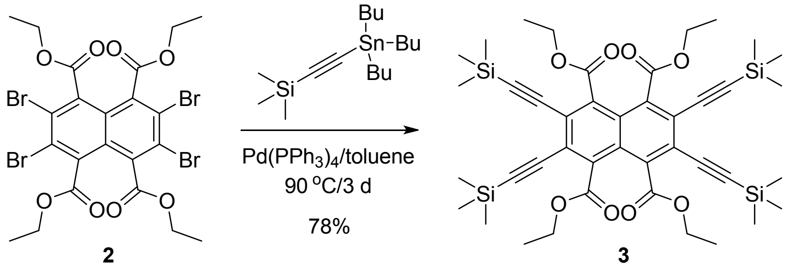
2. Synthetic routes of 8a and 8b



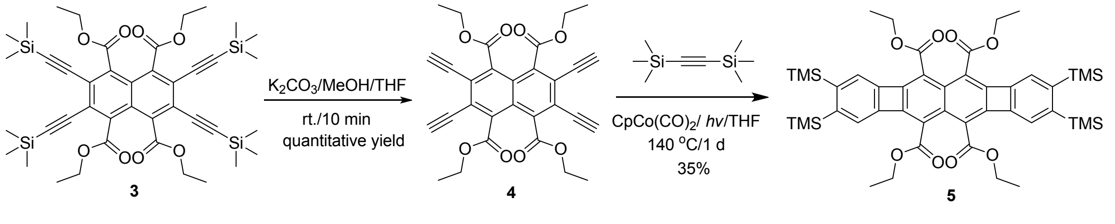
Scheme S1. Reagents and conditions: (a) EtI, K_2CO_3, EtOH, reflux, overnight; (b) 1-tributylstannyl-2-trimethylsilylacetylene, $Pd(PPh_3)_4$, toluene, 90 °C, 3 days; (c) K_2CO_3, MeOH/THF, 10 min, room temperature; (d) bis(trimethylsilyl)acetylene, $CpCo(CO)_2$, *hv*, THF, 140 °C, overnight; (e) CH_2Cl_2, trifluoroacetic acid, room temperature, 4 days; (f) *t*-BuOH, KOH, reflux, overnight; (g) amine, imidazole, 140 °C, overnight.



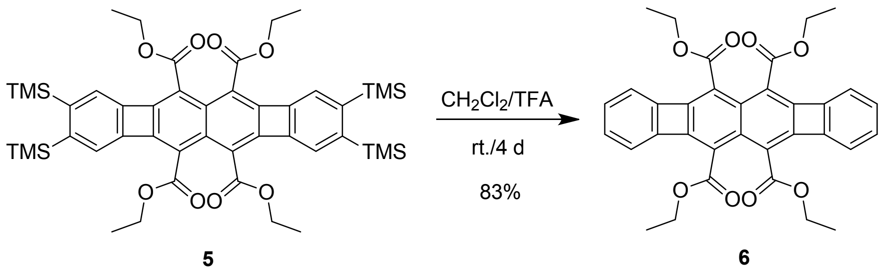
A mixture of 4 g of tetrabromonaphthalene dianhydride **1** (prepared according to a literature procedure, *J. Org. Chem.*, **2009**, *74*, 8616-8625), K_2CO_3 (5.68 g, 41.1 mmol), 10 ml of ethyl iodide and 40 ml of ethanol were heated to reflux under argon atmosphere. After stirring overnight, the reaction mixture was quenched by water and extracted with dichloromethane. The organic layer was washed with brine and dried over anhydrous $MgSO_4$. After removal of solvent, the residue was further purified by washing with methanol to afford **2** (4.3 g, 86%) as a white solid. ^{1}H NMR (250 MHz, CD_2Cl_2, 300 K): δ [ppm] = 4.41 (q, *J* = 7.2 Hz, 8H), 1.42 (t, *J* = 7.2 Hz, 12H). ^{13}C NMR (63 MHz, CD_2Cl_2, 300 K): δ [ppm] = 165.85, 135.50, 126.05, 125.32, 63.51, 13.76. MS (FD): calcd. for $C_{22}H_{20}Br_4O_8$: 732.0; found: 731.3.



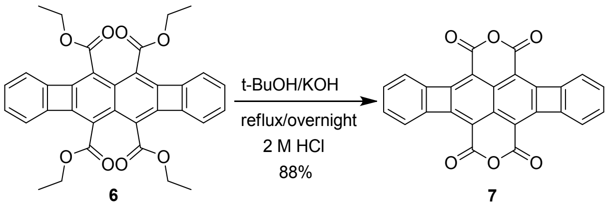
A mixture of compound **2** (3.0 g, 4.1 mmol), 1-tributylstannyl-2-trimethylsilylacetylene (12.7 g, 32.8 mmol), $Pd(PPh_3)_4$ (950 mg, 0.82 mmol) and 100 ml of dry toluene were stirred at 90 °C under argon atmosphere. After stirring for 3 days, the reaction mixture was quenched and extracted with dichloromethane. The organic layer was washed with brine and dried over anhydrous $MgSO_4$. After removal of solvent, the residue was further purified by column chromatography on silica gel (DCM/*n*-hexane = 4:1, $_{Rf}$ = 0.5) to afford **3** (2.56 g, 78%) as a light yellow solid. ^{1}H NMR (250 MHz, CD_2Cl_2, 300 K): δ [ppm] = 4.32 (q, *J* = 7.2 Hz, 8H), 1.40 (t, *J* = 7.2 Hz, 12H), 0.29 (s, 36H). ^{13}C NMR (63 MHz, CD_2Cl_2, 300 K): δ [ppm] = 167.04, 136.57, 124.10, 107.05, 99.93, 62.92, 13.99, 0.00. MS (FD): calcd. for $C_{42}H_{56}O_8Si_4$: 800.3; found: 799.4.



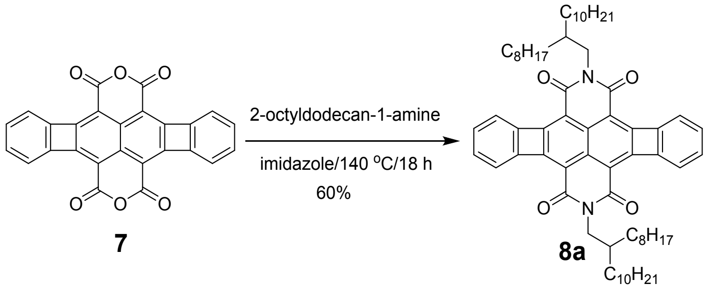
A mixture of **3** (1.0 g, 1.25 mmol), K_2CO_3 (50 mg, 0.36 mmol), 10 ml of methanol and 10 ml of THF were stirred under argon atmosphere for 10 min at room temperature. Afterwards the reaction mixture was quenched by water and extracted with dichloromethane. The organic layer was washed with brine and dried over anhydrous $MgSO_4$. After removal of solvent, the crude product **4** was obtained as a light yellow solid. The crude product was used for the next step as soon as possible. A solution of compound **4** (100 mg, 0.20 mmol) and $CpCo(CO)_2$ (10 µL, 0.008 mmol) in 5 ml of bis(trimethylsilyl)acetylene and 15 mL of THF was added via syringe to boiling bis(trimethylsilyl)acetylene (25 mL) (bath temperature 145 ^{o}C) over a period of 14 h with magnetic stirring. During the reaction, the flask was irradiated with a slide projector lamp (OSRAM, 250 W) at a distance of ca. 4 cm from the center of the flask. The power source for the lamp was regulated with a variable transformer to 24 V. Heating to reflux and irradiation was continued overnight after the addition was complete. The reaction mixture was then cooled and filtered through a silica column to give **5** (60 mg, 35%) as a yellow solid. ^1H NMR (250 MHz, CD_2Cl_2, 300 K): δ [ppm] = 7.43 (s, 4H), 4.34-4.42 (m, 8H), 1.46-1.52 (m, 12H), 0.42 (s, 36H). ^{13}C NMR (63 MHz, CD_2Cl_2, 300 K): δ [ppm] = 164.00, 150.24, 150.17, 145.79, 130.67, 124.29, 120.29, 59.63, 12.58, 0.00. MS (FD): calcd. for $C_{46}H_{60}O_8Si_4$: 852.3; found: 851.1.



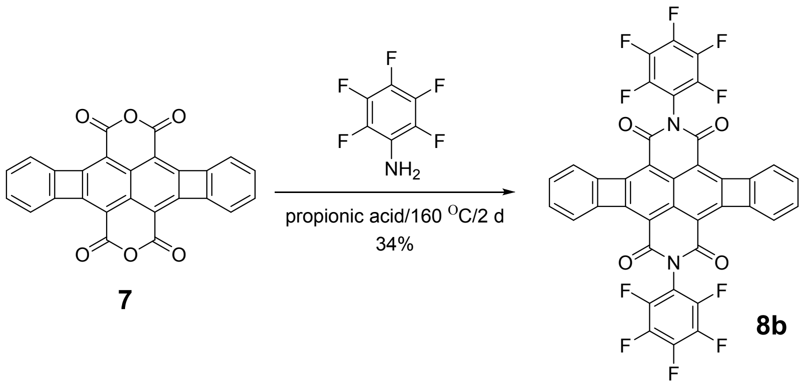
A mixture of **5** (200 mg, 0.24 mmol), 5 mL of DCM and 10 ml of trifluoroacetic acid were stirred under argon atmosphere for 4 days. Afterwards the reaction mixture was quenched by water and extracted with dichloromethane. The organic layer was washed with brine and dried over anhydrous $MgSO_4$. After removal of solvent and recrystallization with *n*-hexane, 110 mg of product **6** was obtained as a light yellow solid in a yield of 83%. ^1H NMR (250 MHz, CD_2Cl_2, 300 K): δ [ppm] = 7.15 (m, 8H), 4.37 (q, *J* = 7.2 Hz, 8H), 1.46 (t, *J* = 7.2 Hz, 12H). ^{13}C NMR (63 MHz, CD_2Cl_2, 300 K): δ [ppm] = 166.05, 151.65, 149.13, 131.78, 122.38, 121.33, 61.83, 14.64. MS (FD): calcd. for $C_{34}H_{28}O_8$: 564.2; found: 563.2.



A mixture of **6** (100 mg, 0.18 mmol), KOH (500 mg, 8.9 mmol), 5 mL of *tert*-butyl alcohol and 1 ml of water were refluxed under argon atmosphere for 12 h. After cooling to room temperature, 200 ml of 2 M HCl solution was added to quench the reaction. The red precipitate was collected by filtration, washed with water and *n*-hexane, and dried in vacuum to afford 65 mg of crude product **7** as a red solid, yield 88%. The compound was used directly without further purification because of the bad solubility.



A mixture of **7** (40 mg, 0.096 mmol), 2-octyldodecan-1-amine (500 mg, 1.69 mmol) and 2 grams of imidazole were heated at 140 °C under argon atmosphere for 18 h. After cooling to room temperature, 40 ml of 2 M HCl solution was added to quench the reaction. The red precipitate was collected by filtration, washed with water and *n*-hexane, and dried in vacuum. Compound **8a** (56 mg, 60%) was isolated by column chromatography (DCM/*n*-hexane = 1:1). ^{1}H NMR (250 MHz, CD_2Cl_2, 300 K): δ [ppm] = 7.26-7.11 (m, 8H), 3.88-3.85 (q, *J* = 7.5 Hz, 4H), 1.91 (s, 2H), 1.28 (m, 64H), 0.86-0.81 (t, *J* = 2.5 Hz, 12H). ^{13}C NMR (63 MHz, CD_2Cl_2, 300 K): δ [ppm] = 162.25, 154.43, 150.33, 132.84, 128.42, 122.82, 115.33, 32.33, 31.82, 30.47, 30.28–29.62 (m), 26.74, 23.09, 14.28. MALDI-TOF-MS: calcd. for $C_{66}H_{90}N_2O_4$: 975.4; found: 975.8.



A mixture of **7** (80 mg, 0.19 mmol), pentafluoroaniline (1.5 mg, 8.2 mmol), 20 mL of propionic acid were heated at 160 °C under argon atmosphere for two days. After cooling to room temperature, 200 ml of water was added to quench the reaction. The red-purple precipitate was collected by filtration, washed with water, 2 M HCl solution, 2 M NaOH solution, water and methanol, and dried in vacuum. Compound **8b** (48 mg, 34%) was isolated by column chromatography (DCM). ^{1}H NMR (700 MHz, 1,2-dichlorobenzene-d_4, 373 K): δ [ppm] = 7.47 (m, 4H), 7.24 (m, 4H). ^{19}F NMR (659 MHz, 1,2-dichlorobenzene-d_4, 373 K) δ [ppm] = -142.58 (d, *J* = 18.0 Hz, 4F), -151.68 (m, 2F), -161.44 (t, *J* = 19.0 Hz, 4F). MALDI-TOF-MS: calcd. for $C_{38}H_8F_{10}N_2O_4$: 746.03; found: 746.15.

3. Charaterization of 2, 3, 5, 6, 8a and 8b

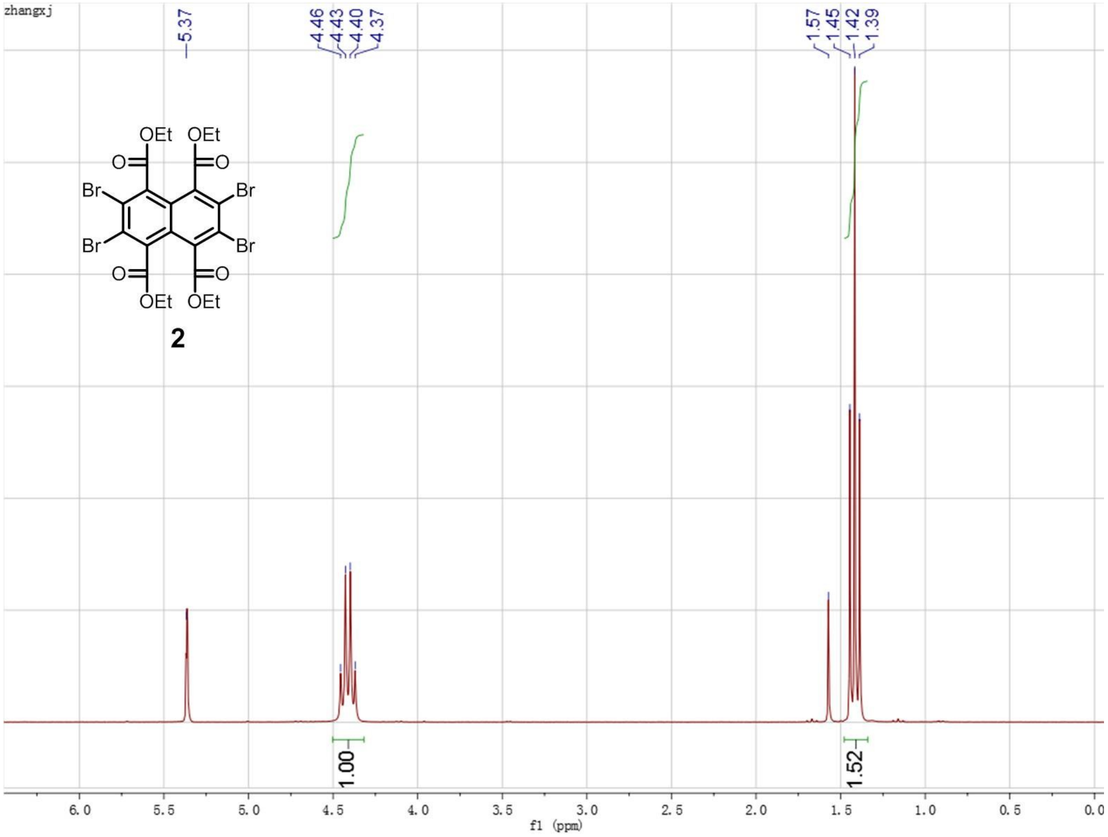


Figure S1. ^{1}H NMR spectrum (250 MHz, CD_2Cl_2, 300K) of **2**.

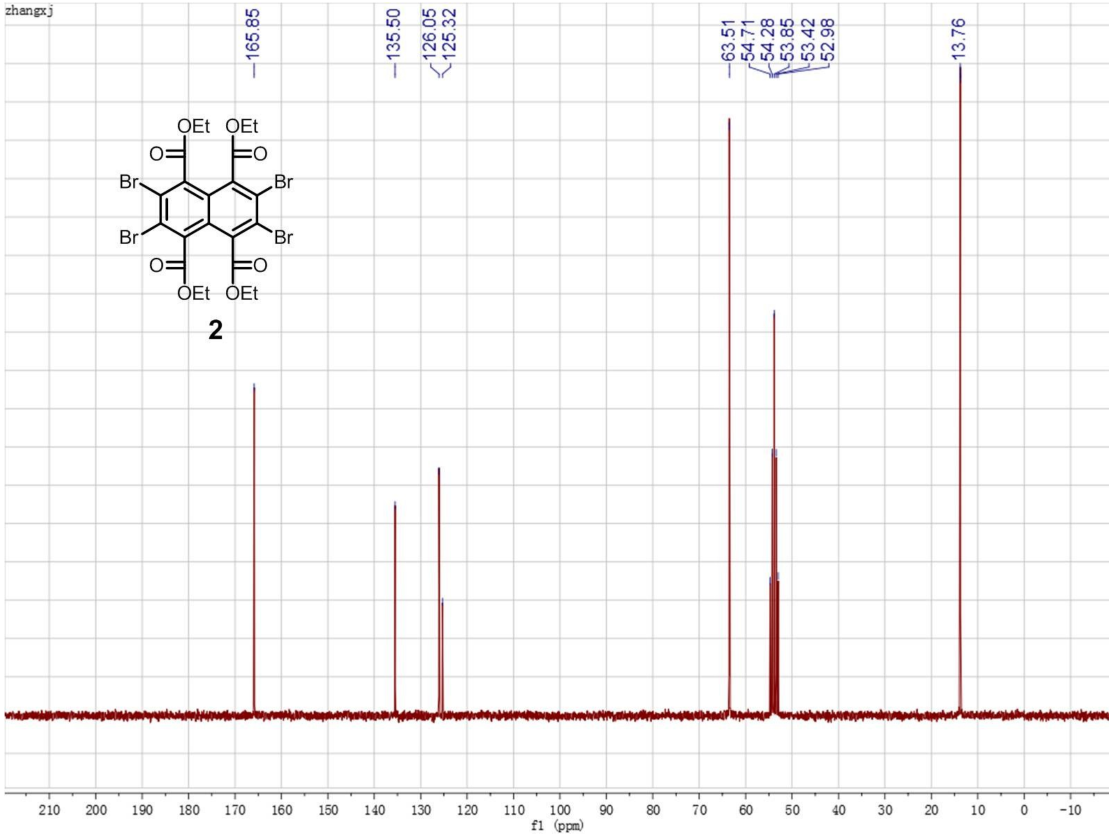


Figure S2. ^{13}C NMR spectrum (63 MHz, CD_2Cl_2, 300K) of **2**.

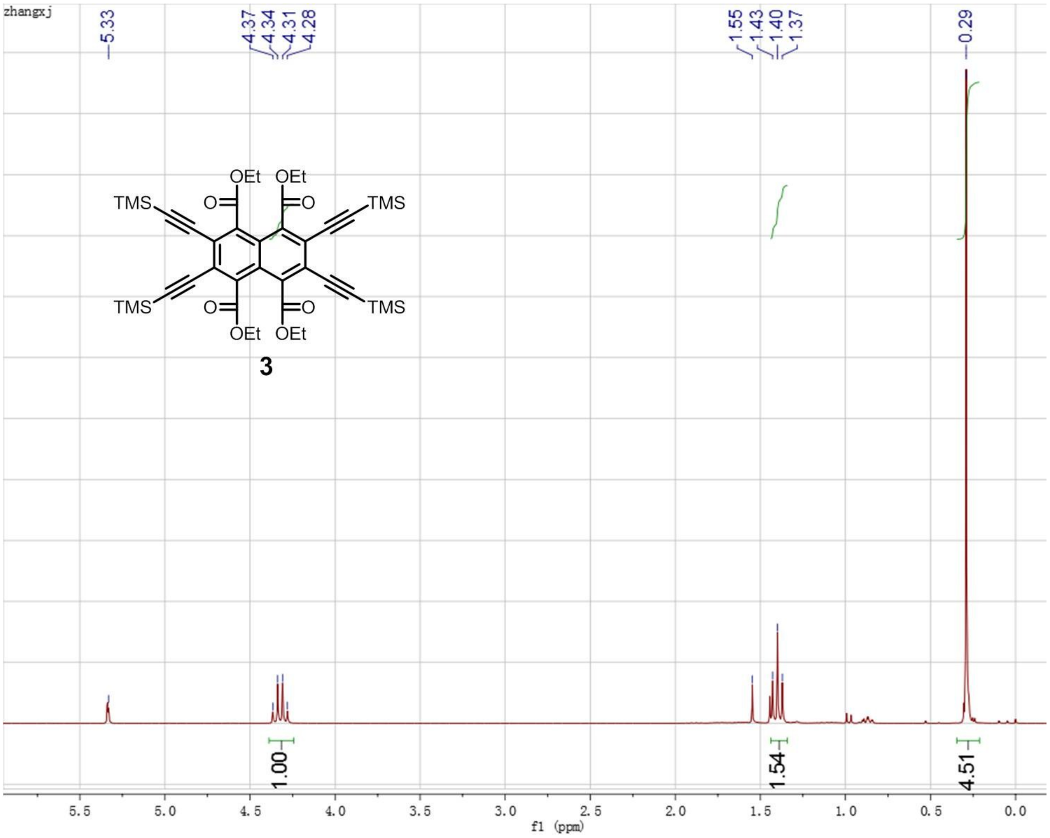


Figure S3. ^{1}H NMR spectrum (250 MHz, CD_2Cl_2, 300K) of **3**.

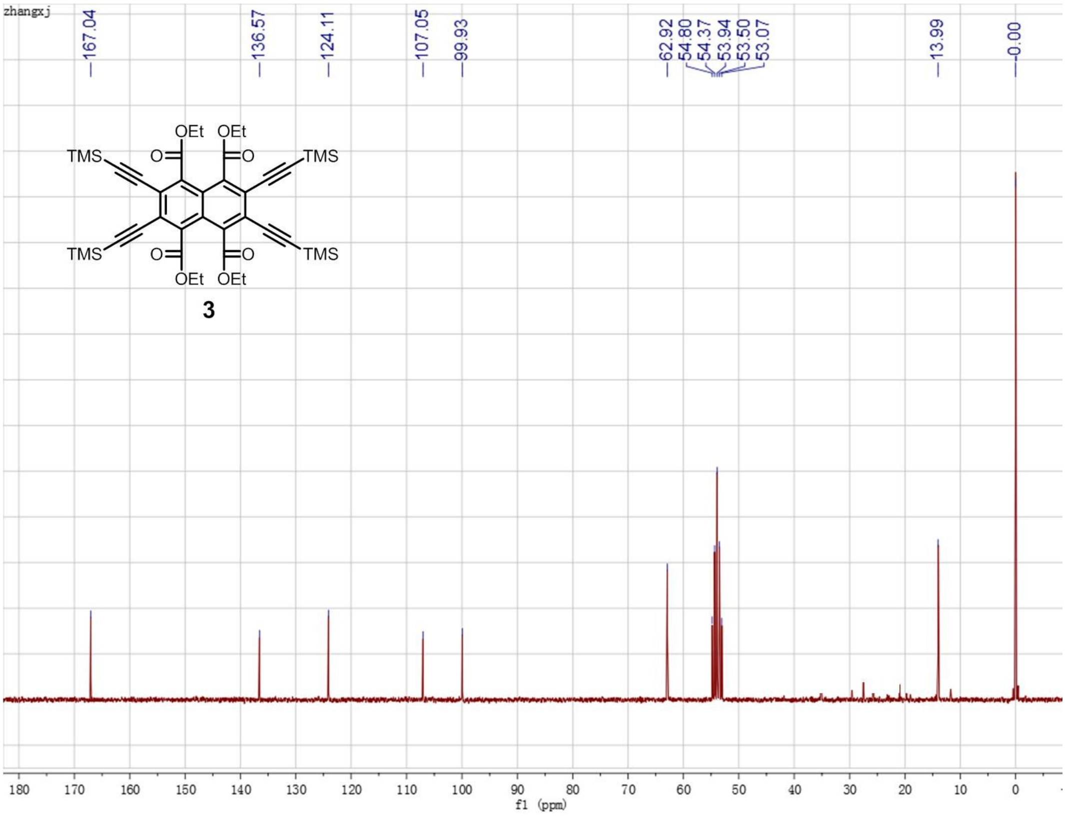


Figure S4. ^{13}C NMR spectrum (63 MHz, CD_2Cl_2, 300K) of **3**.

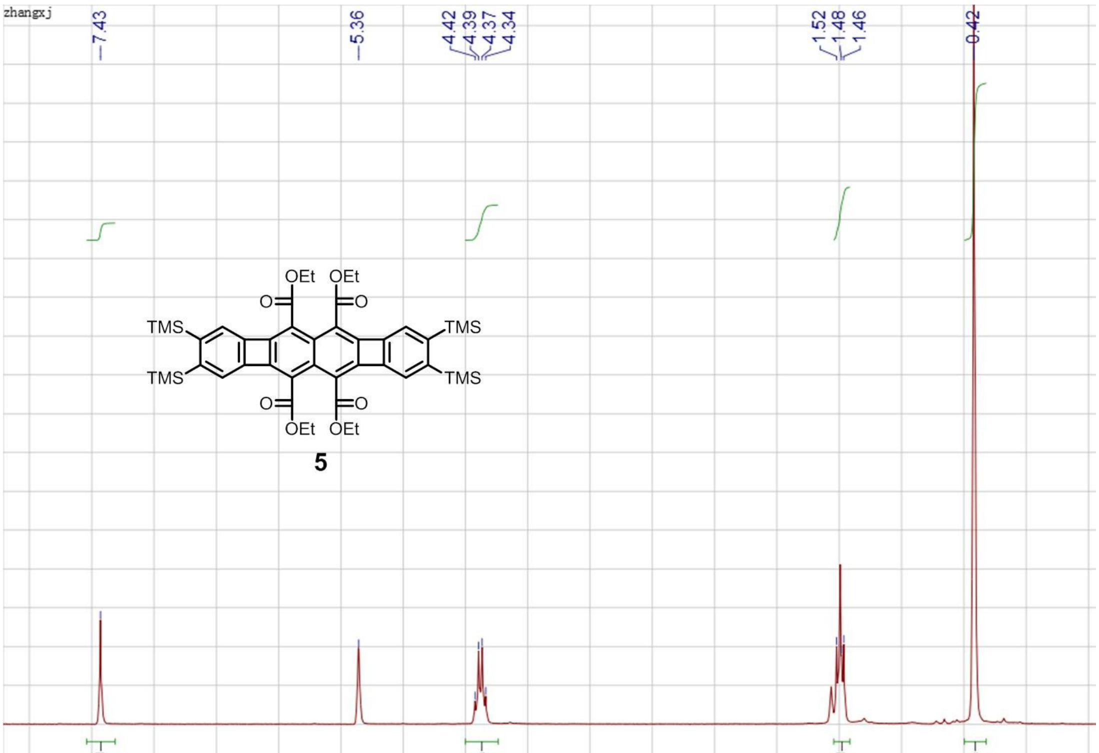


Figure S5. ^{1}H NMR spectrum (250 MHz, CD_2Cl_2, 300K) of **5**.

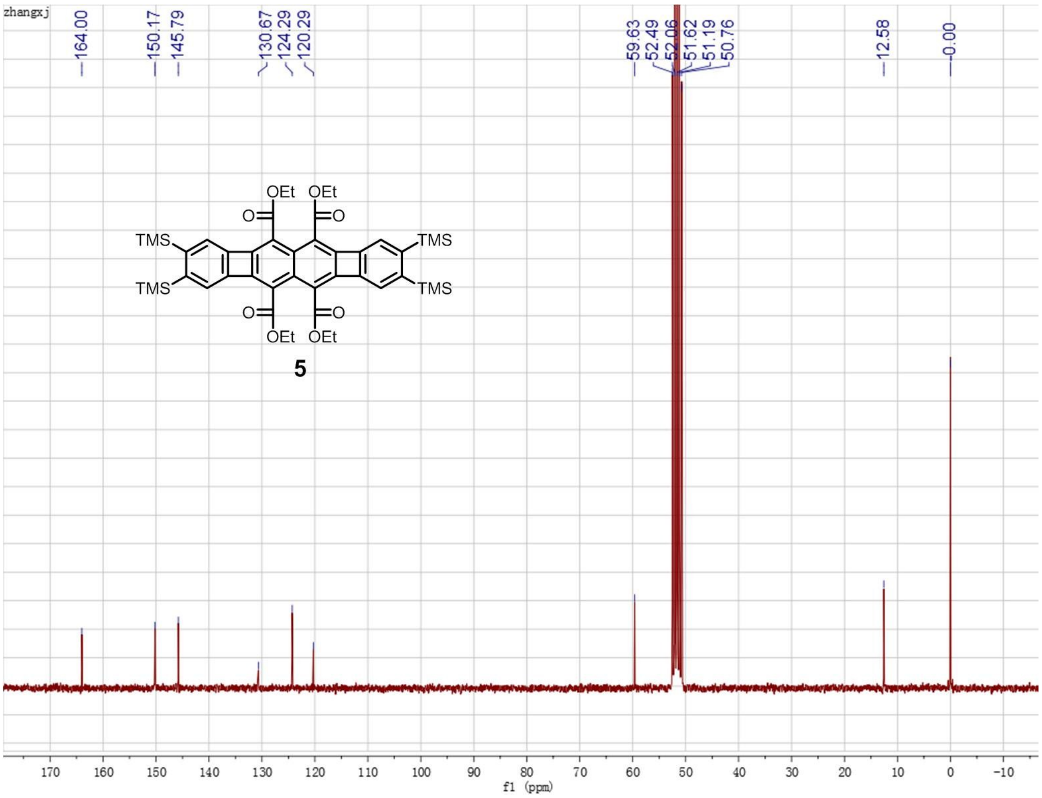


Figure S6. ^{13}C NMR spectrum (63 MHz, CD_2Cl_2, 300K) of **5**.

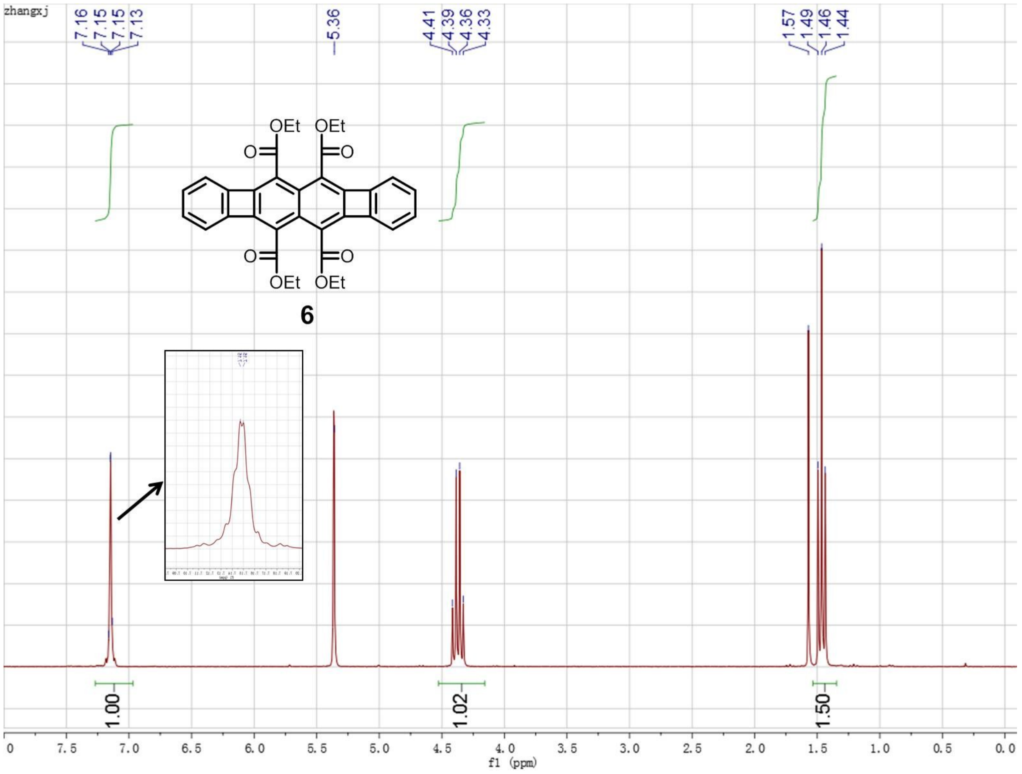


Figure S7. ^{1}H NMR spectrum (250 MHz, CD_2Cl_2, 300K) of **6**.

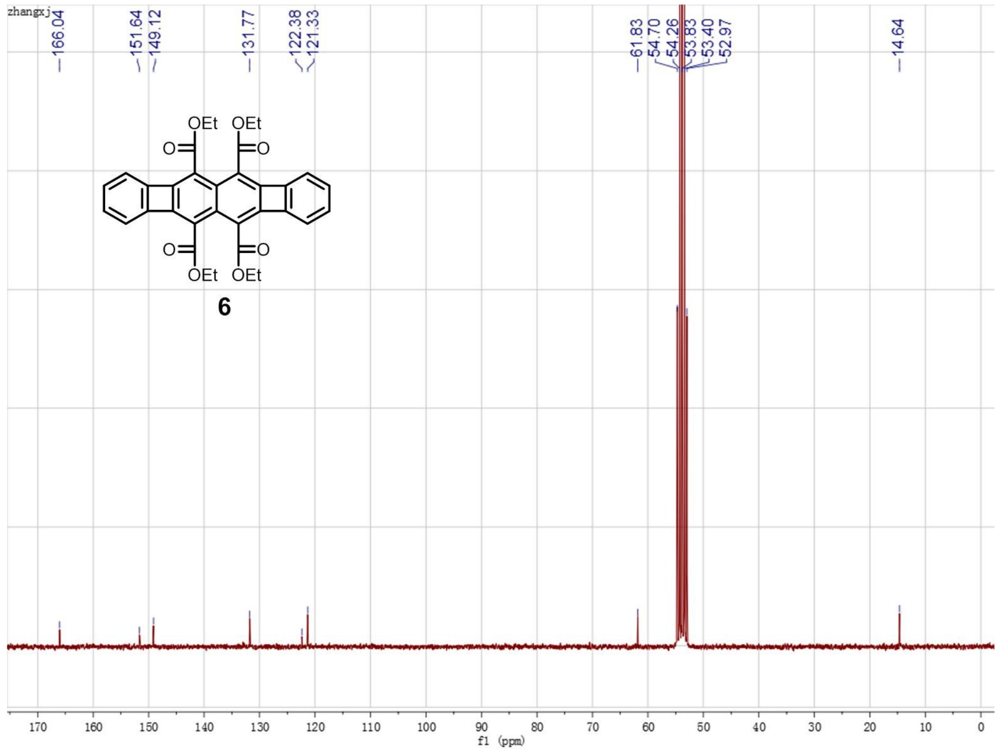


Figure S8. ^{13}C NMR spectrum (63 MHz, CD_2Cl_2, 300K) of **6**.

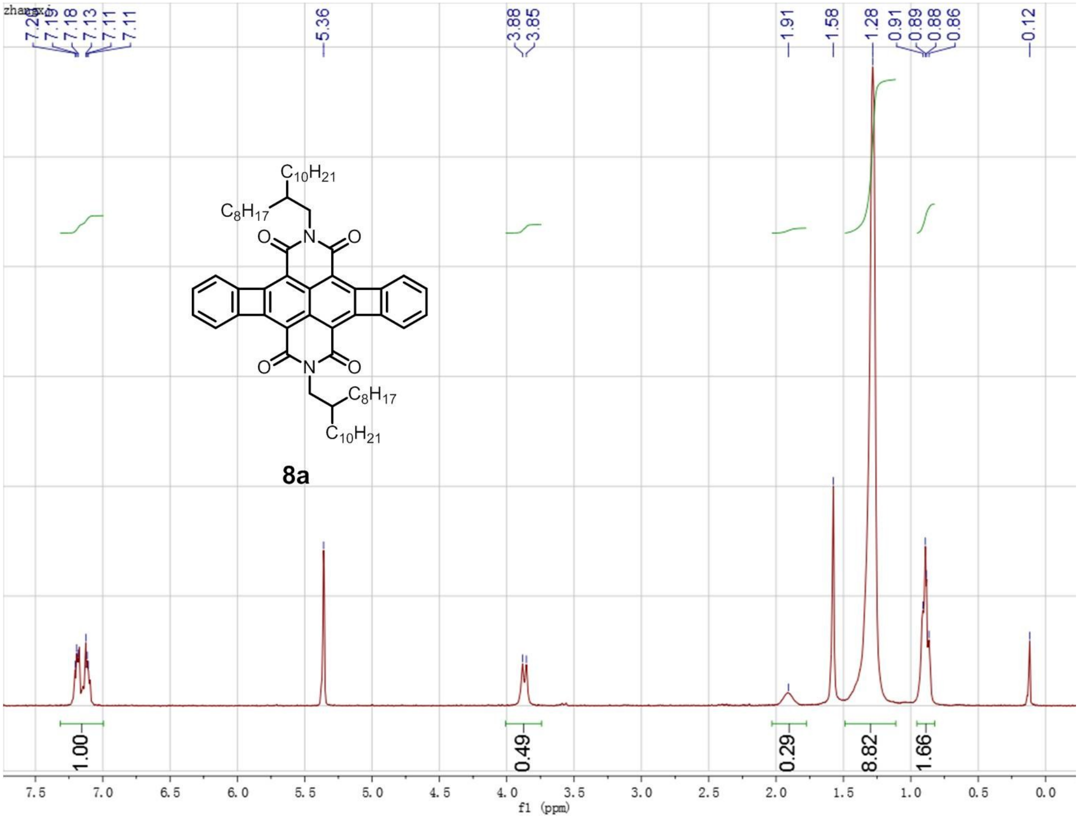


Figure S9. ^{1}H NMR spectrum (250 MHz, CD_2Cl_2, 300K) of **8a**.

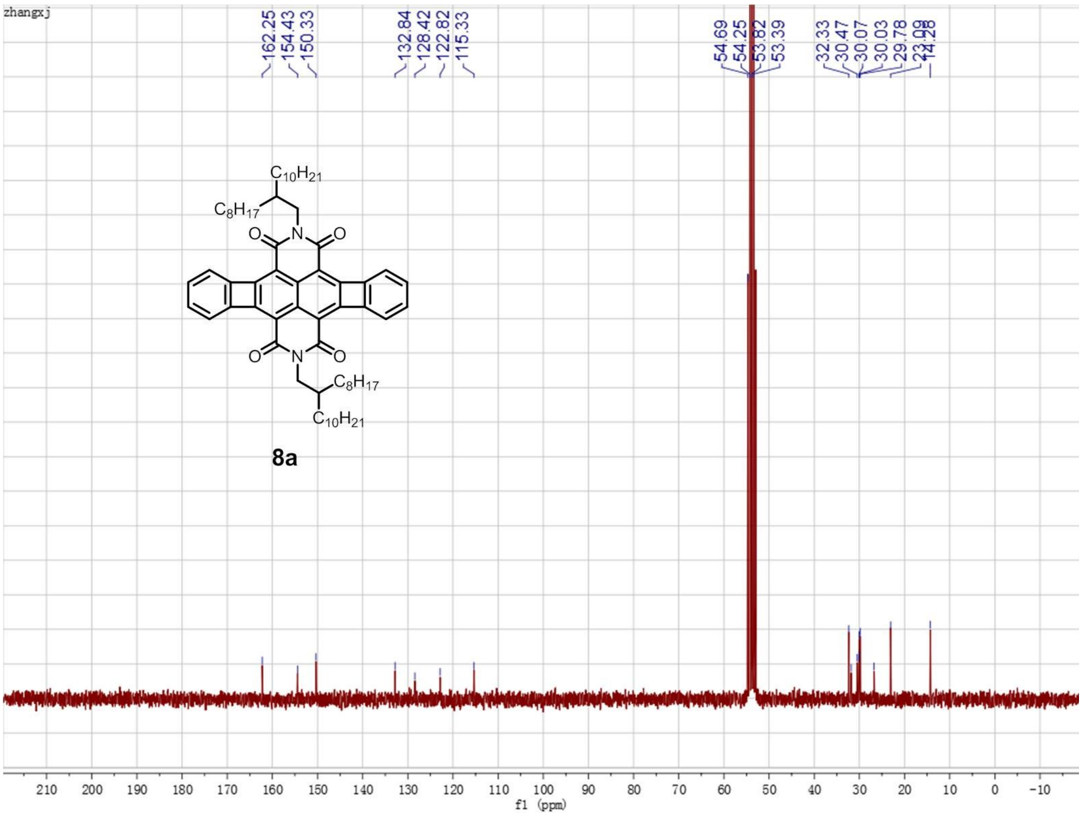


Figure S9. ^{13}C NMR spectrum (63 MHz, CD_2Cl_2, 300K) of **8a**.

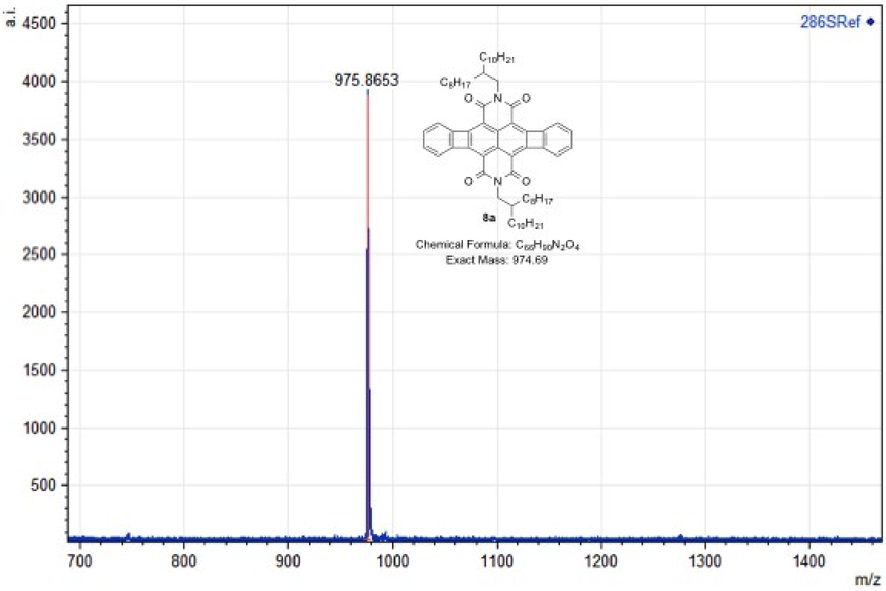


Figure S10. MALDI-TOF spectrum of [**8a**].

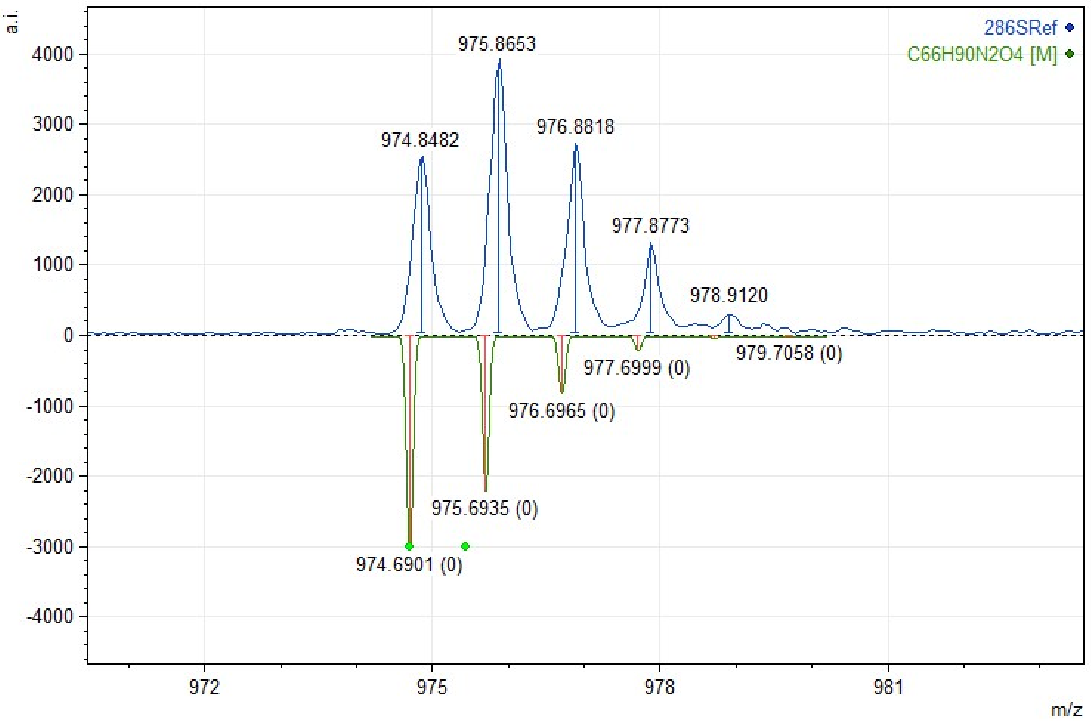


Figure S11. Experimental (top) and Theoretical (bottom) MALDI-TOF spectrum of [**8a**].

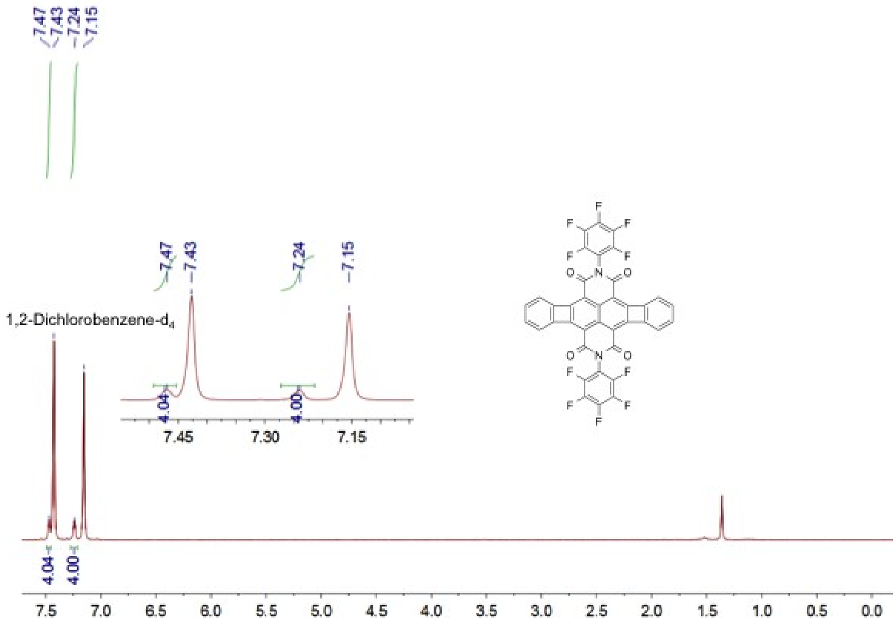


Figure S12. ^{1}H NMR spectrum (700 MHz, 1,2-dichlorobenzene-d_4, 373K) of **8b**.

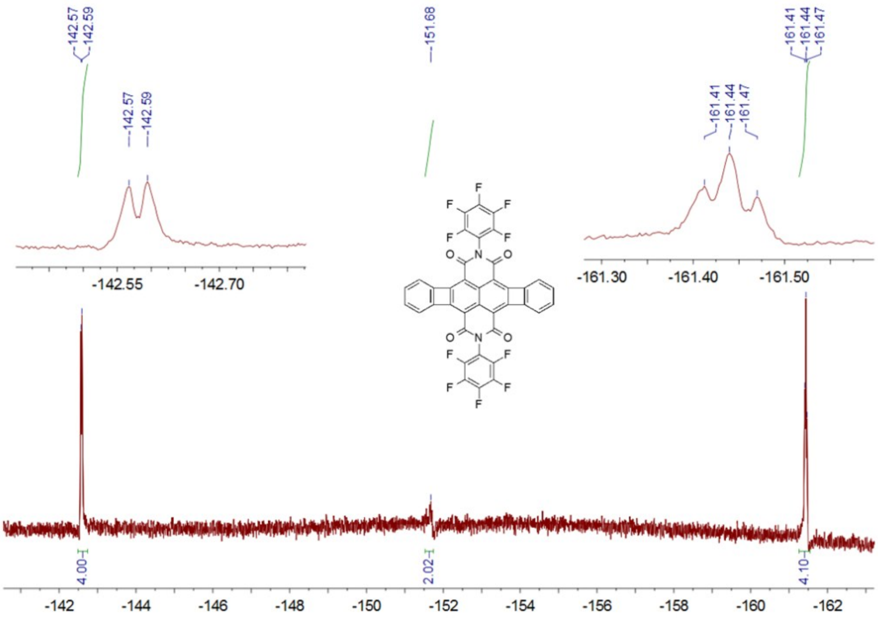


Figure S13. ^{19}F NMR (659 MHz, 1,2-dichlorobenzene-d_4,, 373 K) of **8b**.

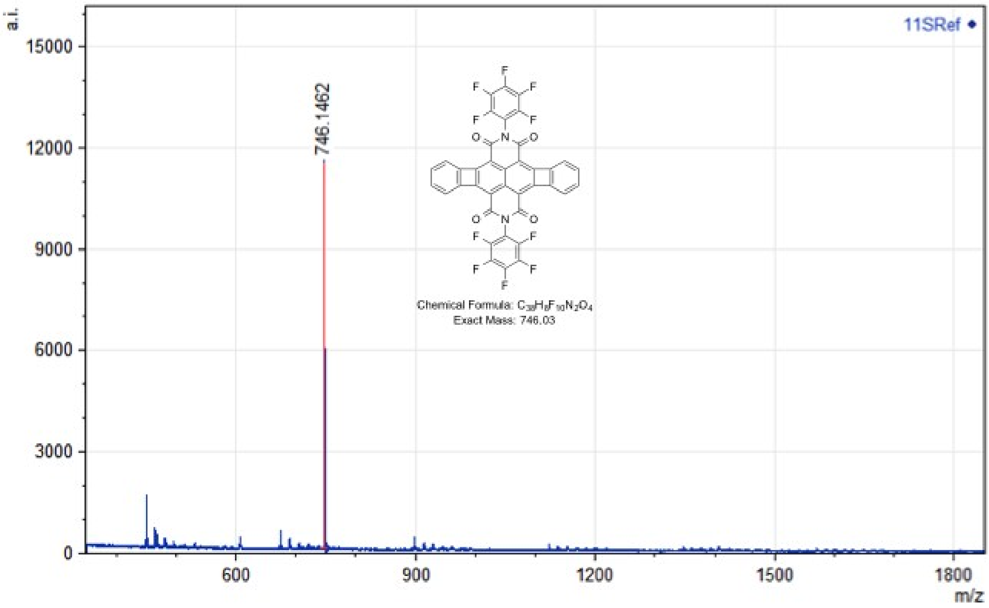


Figure S14. MALDI-TOF spectrum of [**8b**].

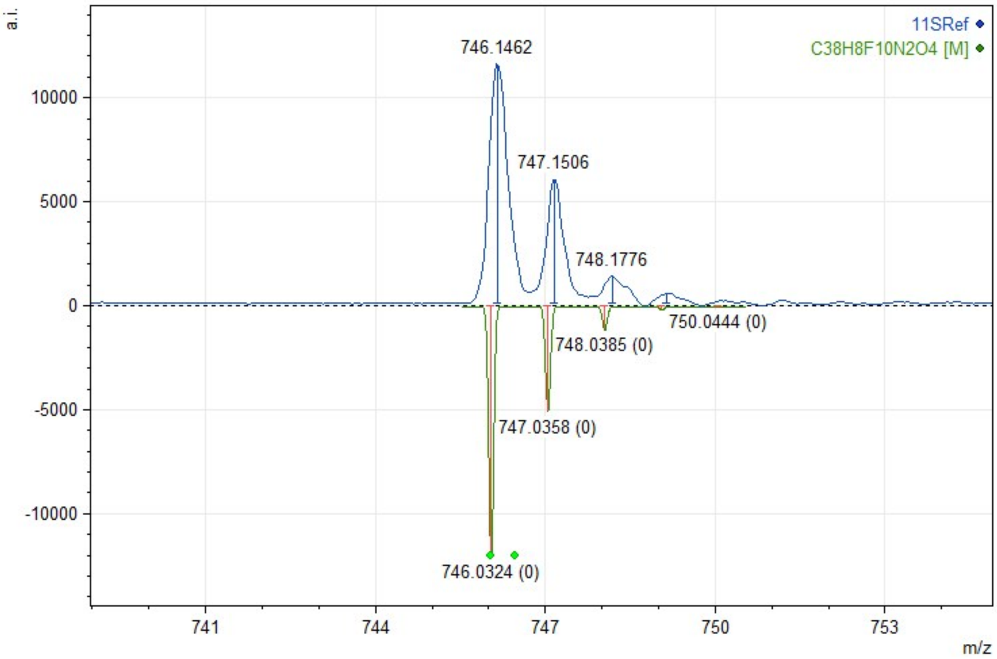


Figure S15. Experimental (top) and Theoretical (bottom) MALDI-TOF spectrum of [**8b**].

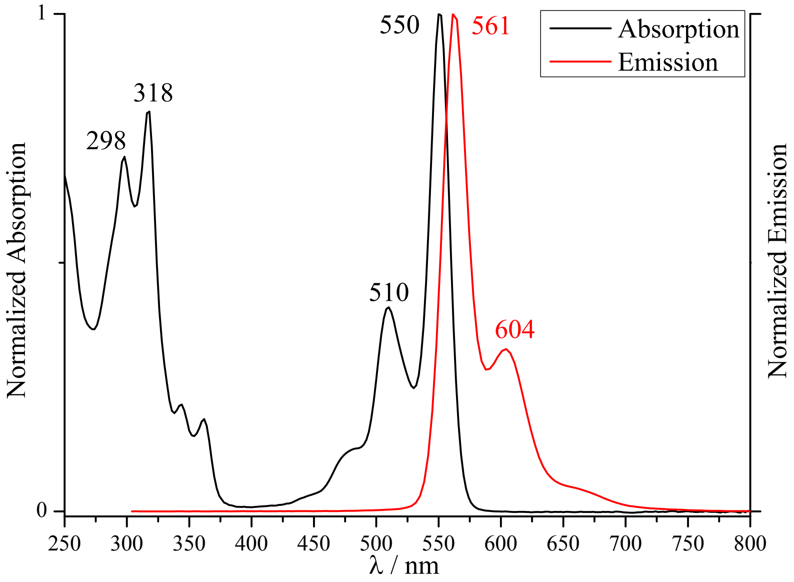


Figure S16. Normalized absorption (black) and emission (red, $\lambda_{exc.}$ = 550 nm) of [**8b**] in CH_2Cl_2.

4. Calculating procedure of fluorescence quantum yields of 5, 6 and

8a

The fluorescence quantum yields were calculated via the single-point method according to the following equation:

$$\Phi_{fl,sample} = \Phi_{fl,reference} \times \left(\frac{OD_{reference}}{OD_{sample}}\right) \times \left(\frac{I_{sample}}{I_{reference}}\right) \times \left(\frac{n_{sample}^{2}}{n_{reference}^{2}}\right)$$

Here: $\Phi_{fl,sample}$ is the fluorescence quantum yield of the target compound.

$\Phi_{fl,reference}$ is the fluorescence quantum yield of reference compound, i.e. *N*,*N*'-(2,6-di*iso*propylphenyl)-perylene-3,4,9,10-tetracarboxylic acid diimide. According to the literature, the $\emptyset_{f,reference}$ is 1.

OD is the optical density of the solution of sample or reference at the excitation wavelength. We have prepare the solutions for both sample and reference with optical densities at 0.7.

I is the integrated fluorescence intensity.

n is the refractive index of the solvents. Here we prepared the solution of the sample and reference in dichloromethane.

Since for both, sample and reference, the OD and *n* are the same, therefore the above equation can be simplified to:

$$\Phi_{fl,sample} = \Phi_{fl,reference} \times \left(\frac{I_{sample}}{I_{reference}}\right)$$