

## SUPPORTING INFORMATION

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## 1. General Techniques

All chemicals and solvents were used without further purification unless otherwise specified. THF and Hexane were purified according to literature and saved under argon atmosphere. **5a** and **5b** were synthesized according to earlier literature.

The reactions were monitored using analytical thin Layer Chromatography (TLC) with Merck silica gel plate purchased from Kangbinuo commercial company. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded on Bruker Avance spectrometers, quoted chemical shifts are in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard. The signals have been designated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), and m (multiplets). ESI-MS were recorded on a micro TOF-Q II 10280 spectrometer. UV-vis spectra were measured with Hitachi (Model U-3010) UV-vis spectrophotometer in a 1-cm quartz cell. Fluorescence excitation and emission spectra were recorded with a Hitachi FP-6600 FL fluorimeter at room temperature. Cyclic voltammograms (CVs) were recorded on a Chenhua electrochemical workstation at a scan rate of 100 mV/s, with using glassy carbon discs as the working electrode, Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode. 0.1 M tetrabutylammonium hexafluorophosphate (*n*Bu<sub>4</sub>NPF<sub>6</sub>) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (freshly distilled from sodium) was employed as the supporting electrolyte.

## 2. Experiment section

**Anti-6b:** 2,3,6,7,9,10-hexamethoxy-1,5,9-triamino-triphenylene (453 mg, 1 mmol), 1,2-dichlorobenzene (15 mL), triethylamine (0.4 mL, 0.36 g, 2.88 mmol) were added into a Schlenk tube under an atmosphere of argon. Dichlorophenylphosphine (0.4 mL, 0.536 g, 3 mmol) was added dropwise. The mixture was heated under 180 °C for 2 hours. After sulfur (0.32 g, 10 mmol) was added, the reaction mixture was cooling to room temperature and stirred overnight, all the solvent was then removed and the residue purified by flash chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub> / Petro ether (1:1, v/v) to afford pure product as a white solid. Yield: 35%. Mp: 241-242 °C. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ= 8.62 (d, *J*=1.2, 1H), 8.74 (d, *J*=2.0, 1H), 8.82 (d, *J*=2.4, 1H), 8.09-8.15 (m, 6H), 7.57-7.61 (m, 9H), , 3.72 (s, 1H), 3.68 (s, 1H), 3.67 (s, 1H), 3.55 (s, 1H), 3.45 (s, 1H), 3.37 (s, 1H). <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>), CH: 153.5 (*J*=3.0), 153.1 (*J*=10.1); C: 132.3 (*J*=4.0), 132.2 (*J*=5.0), 128.1 (*J*=3.0), 128.0 (*J*=3.0), 110.0, 109.6(*J*=28.2), CH<sub>3</sub>: 60.9, 60.7, 60.6, 59.8, 59.7, 59.6. <sup>31</sup>P NMR (162 MHz, DMSO-d<sub>6</sub>): δ= 38.37, 39.90, 40.94. HRMS: *m/z* called for C<sub>42</sub>H<sub>36</sub>N<sub>3</sub>O<sub>6</sub>P<sub>3</sub>S<sub>3</sub>[M+H<sup>+</sup>] 868.1057, Found: 868.1119. Elemental analysis: calcd, C, 58.13; H, 4.18; O, 11.06; N, 4.84; P, 10.71; S, 11.08; found C, 58.13; H, 4.14; O, 11.09; N, 4.86; P, 10.65; S, 11.01.

**Anti-6a** was synthesized with the same procedure. Yield: 30%. Mp: 274-275 °C. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ=9.83-9.85 (m, 3H),

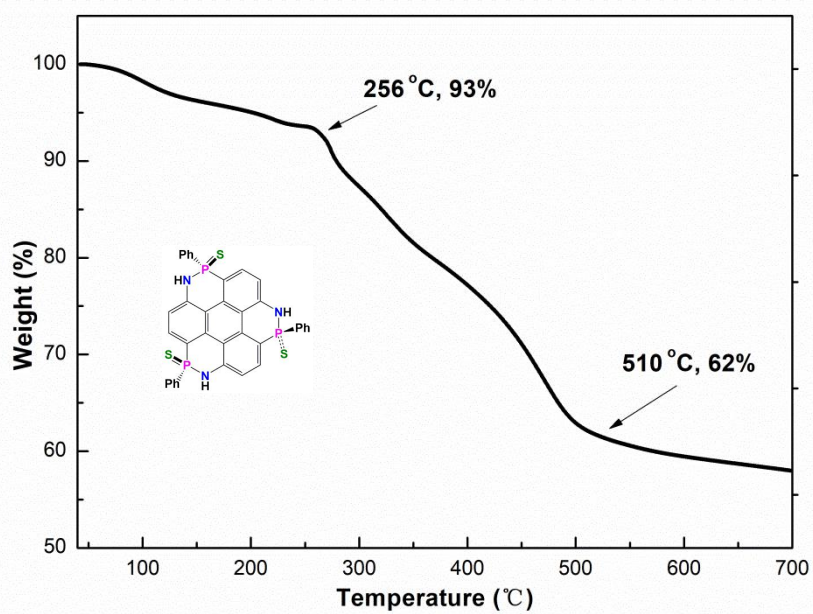
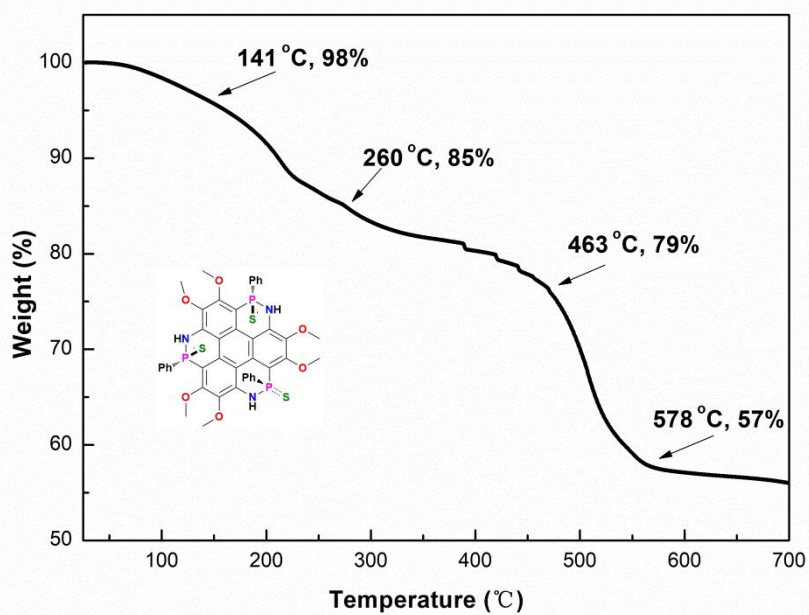
7.81-7.97 (m, 3H), 7.77 (m, 6H), 7.57 (m, 3H), 7.45-7.54 (m, 9H). <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>), CH: 142.5 (*J*=9.0), CH: 137.5 (*J*=7.0), 137.2, 136.9, 136.8, 136.5, C:132.7, 132.6, 132.5, 132.5, 131.7, 130.6, 129.0, 128.9, 128.6, 128.6, 128.5 (*J*=3.0), 128.4, 117.5 (*J*=5.0), 115.8, (*J*=6.0), 112.2. <sup>31</sup>P NMR (162 MHz, DMSO-d<sub>6</sub>): δ= 41.91, 41.98, 42.02. HRMS: *m/z* called for C<sub>36</sub>H<sub>24</sub>N<sub>3</sub>P<sub>3</sub>S<sub>3</sub>[M+H<sup>+</sup>] 688.0423, Found: 688.0426. Elemental analysis: calcd, C, 61.54; H, 4.43; N, 5.13; O, 17.57; P, 11.34; found, C, 61.57; H, 4.42; N, 5.23; O, 17.53; P, 11.39.

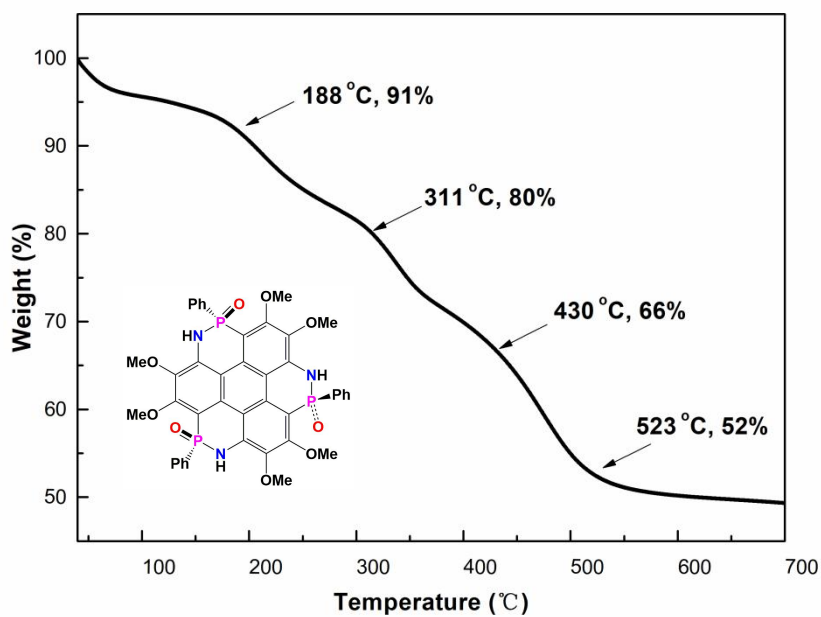
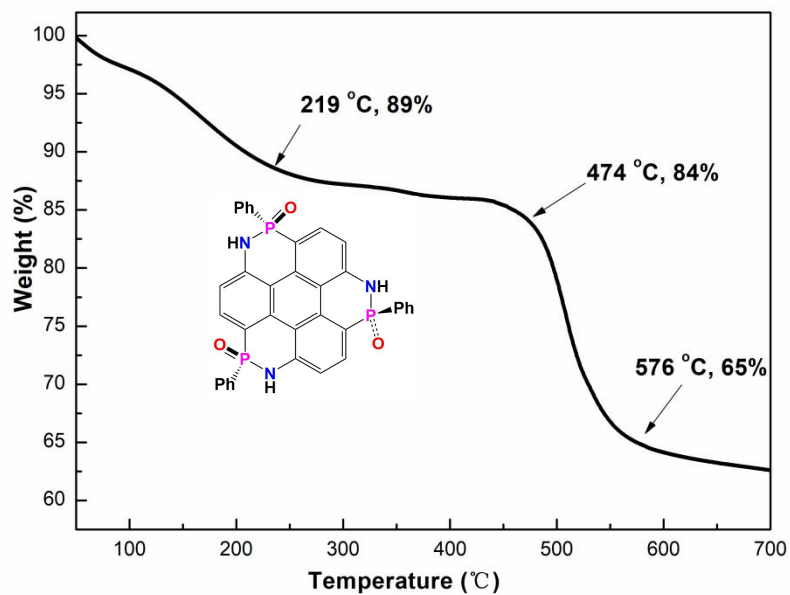
***Anti-7b***: Yield: 85%. Mp >320 °C. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ =9.185-9.203 (m, 3H), 7.779-7.829 (m, 6H), 7.512-7.580 (m, 9H), 3.755-3.777 (t, *J*=4.0, 9H), 3.572 (s, 3H), 3.548 (s, 3H), 3.501 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>), CH: 153.9 (*J*=11.1), C:137.7 (*J*=17.1), 135.3, 132.(*J*=10.1), 131.1 (*J*=14.1), 109.2 (*J*=15.1), CH<sub>3</sub>: 60.4, 59.7, 59.7, 59.6. <sup>31</sup>P NMR (162 MHz, DMSO-d<sub>6</sub>): δ = 3.70, 3.63, 3.45. HRMS: *m/z* called for C<sub>42</sub>H<sub>36</sub>N<sub>3</sub>O<sub>9</sub>P<sub>3</sub>[M+H<sup>+</sup>] 820.1698 , Found: 820.1772. Elemental analysis: calcd, C, 67.61; H, 3.78; N, 6.57; O, 7.51; P, 14.53; found, C, 67.59; H, 3.67; N, 6.71; O, 7.62; P, 14.34.

***Anti-7a***: Yield: 82%. Mp: 252-253 °C. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ =10.01-10.025 (m, 3H), 7.841-7.895 (m, 3H), 7.765-7.798 (m, 6H), 7.512-7.748 (m, 12H). <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>), CH: 143.4, CH<sub>2</sub>: 135.7, 135.5, 134.2, 132.8, 132.4, 132.3, 130.9, 129.1, 129.0, 117.2, 116.1, 114.5, 112.5. <sup>31</sup>P NMR (162 MHz, DMSO-d<sub>6</sub>): δ = 7.88, 7.84,

7.69. HRMS:  $m/z$  called for  $C_{36}H_{24}N_3P_3O_3[M+H^+]$  640.1064, Found: 640.1097. Elemental analysis: calcd, C, 61.54; H, 4.43; N, 5.13; O, 17.57; P, 11.34; found, C, 61.36; H, 4.48; N, 5.19; O, 17.55; P, 11.30.

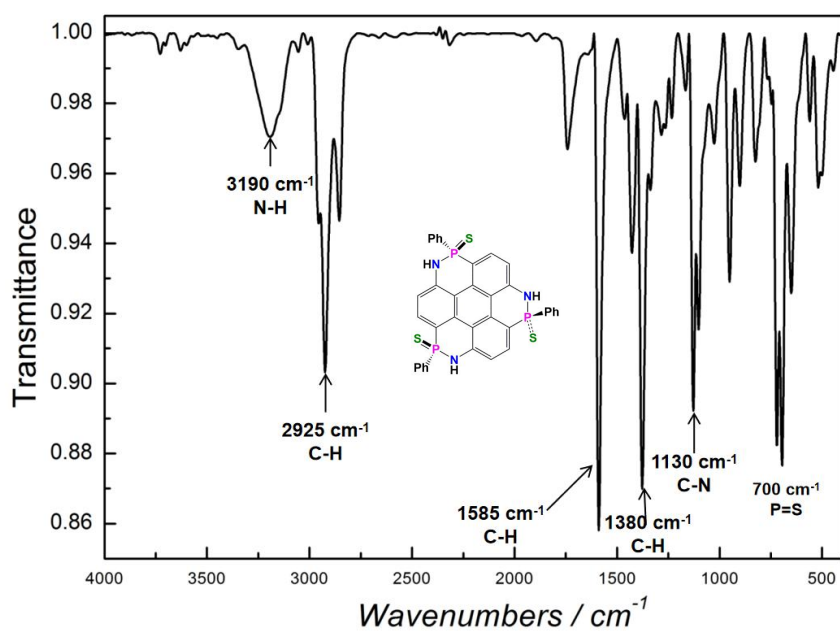
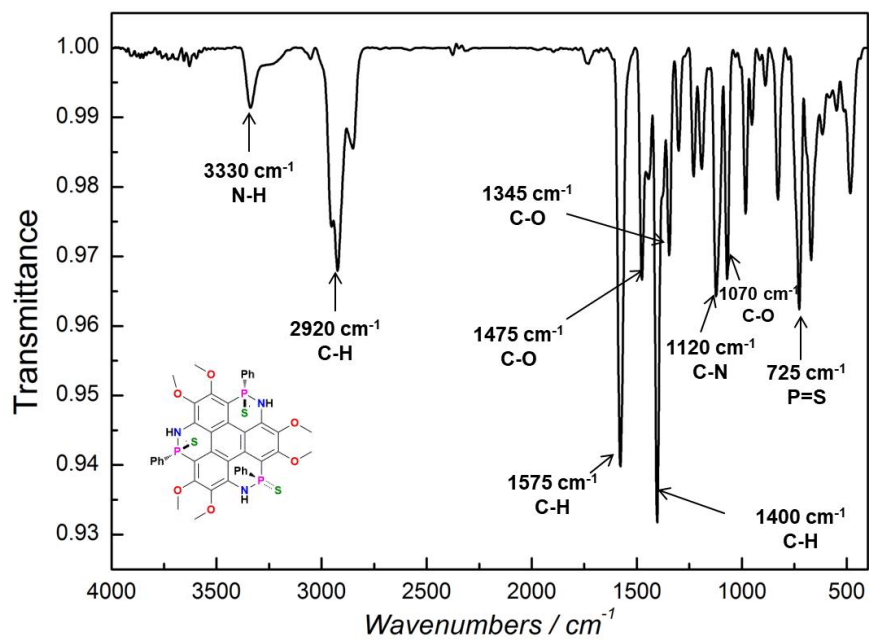
### 3. Thermogravimetric Analysis (TGA)



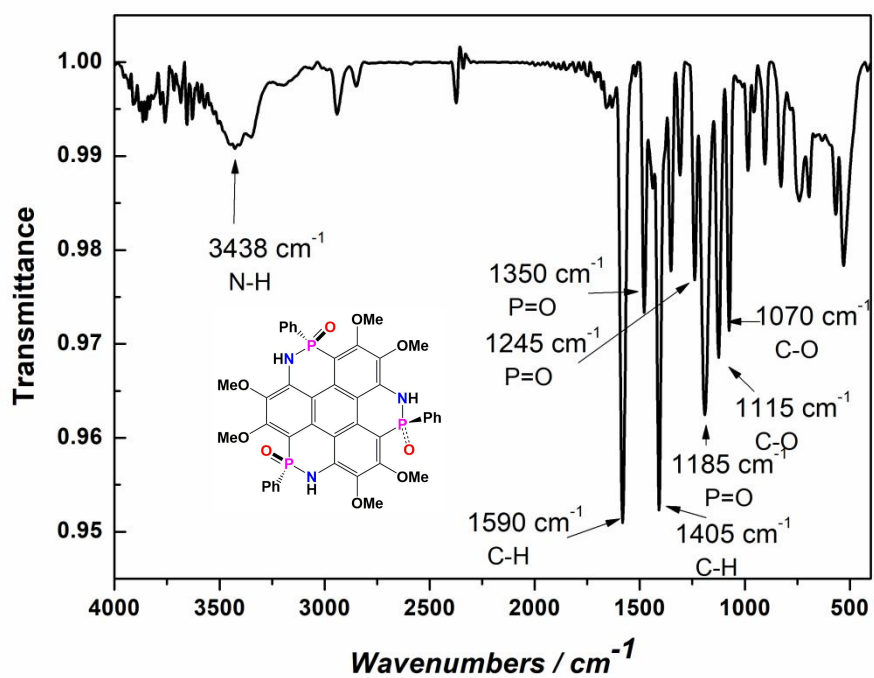
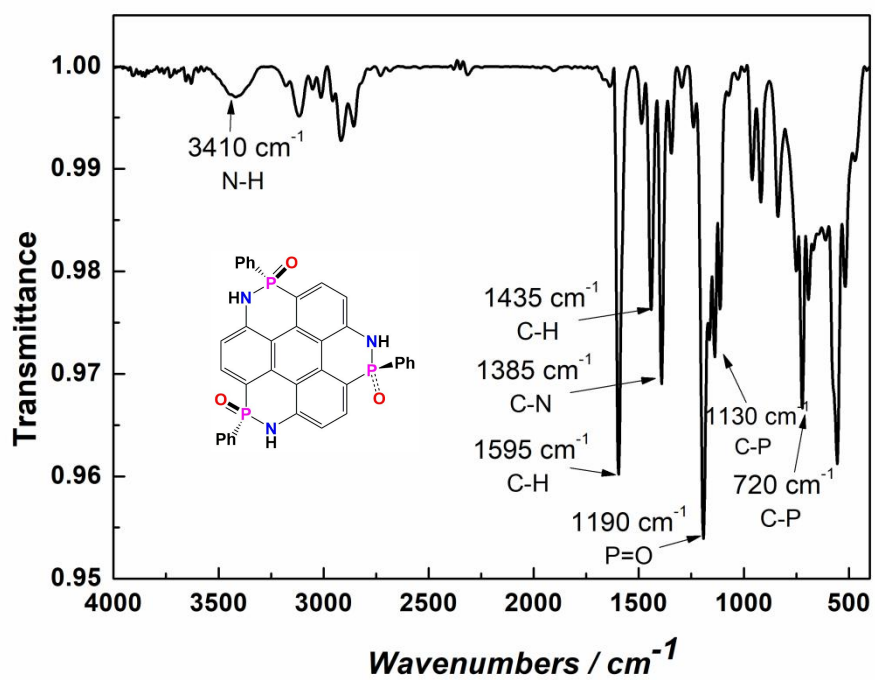


**Figure S1.** TGA curve of compounds *anti-6a*, *anti-6b*, *anti-7a* and *anti-7b*. (Heating rate: 10 °C/min under nitrogen flow). The first slope is loss of volatiles (solvent residue or moisture).

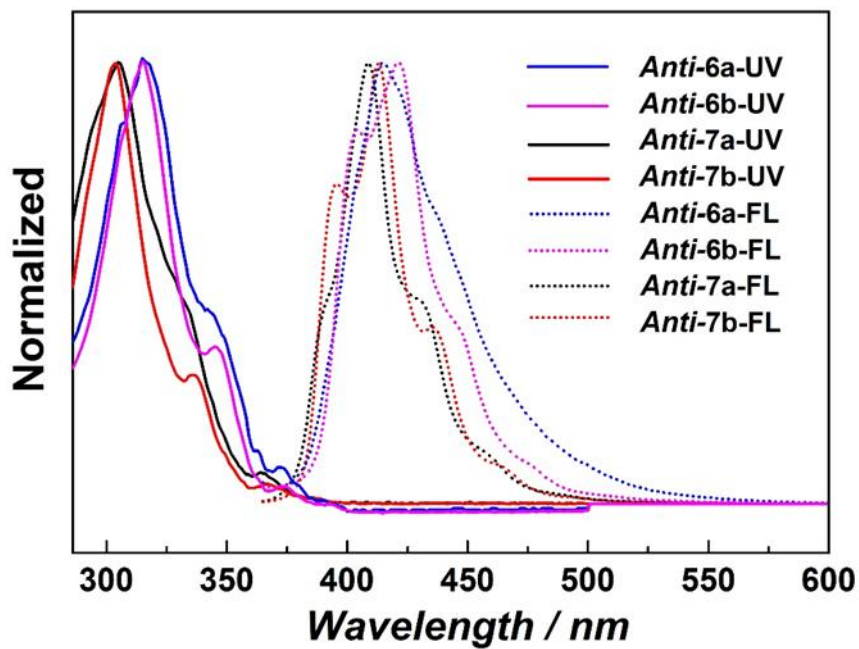
## 4. Infrared Spectrometer (IR)





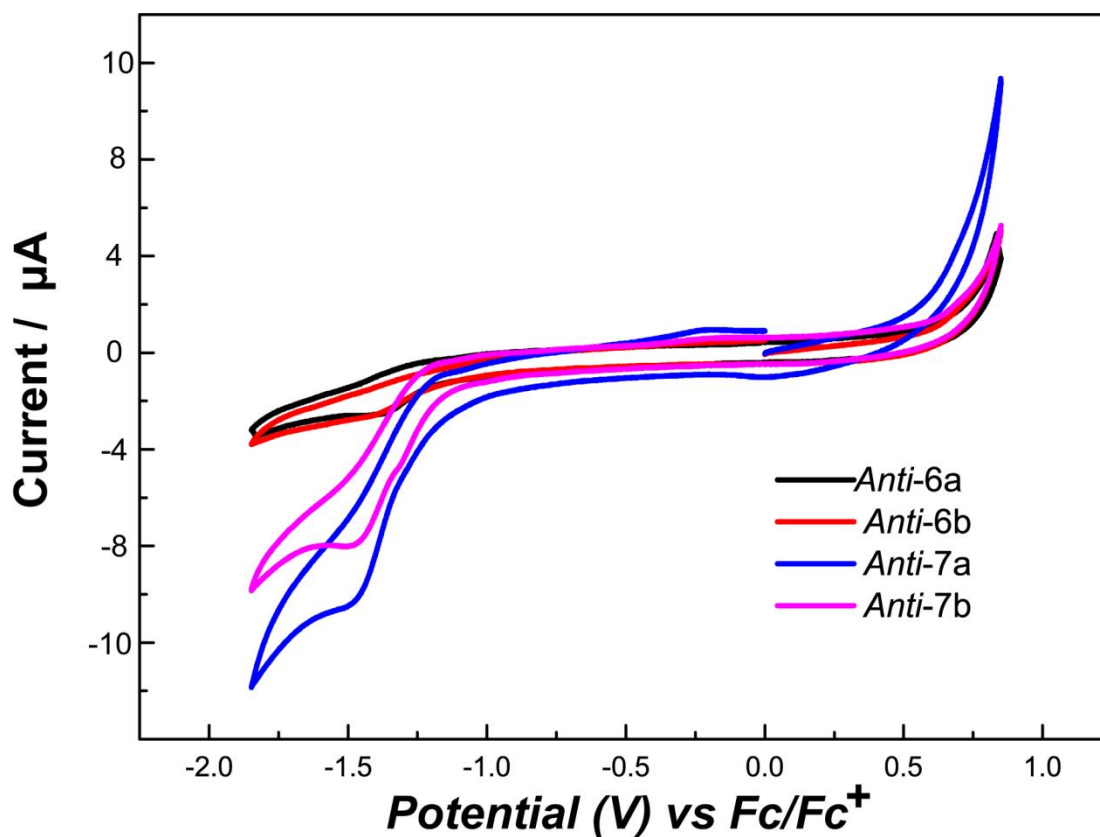


## 5. UV-vis Absorption and Fluorescence Emission Spectra



**Figure S2.** Comparison of the absorption and fluorescence spectra of compounds *anti-6a*, *anti-6b*, *anti-7a* and *anti-7b* in CH<sub>2</sub>Cl<sub>2</sub>.

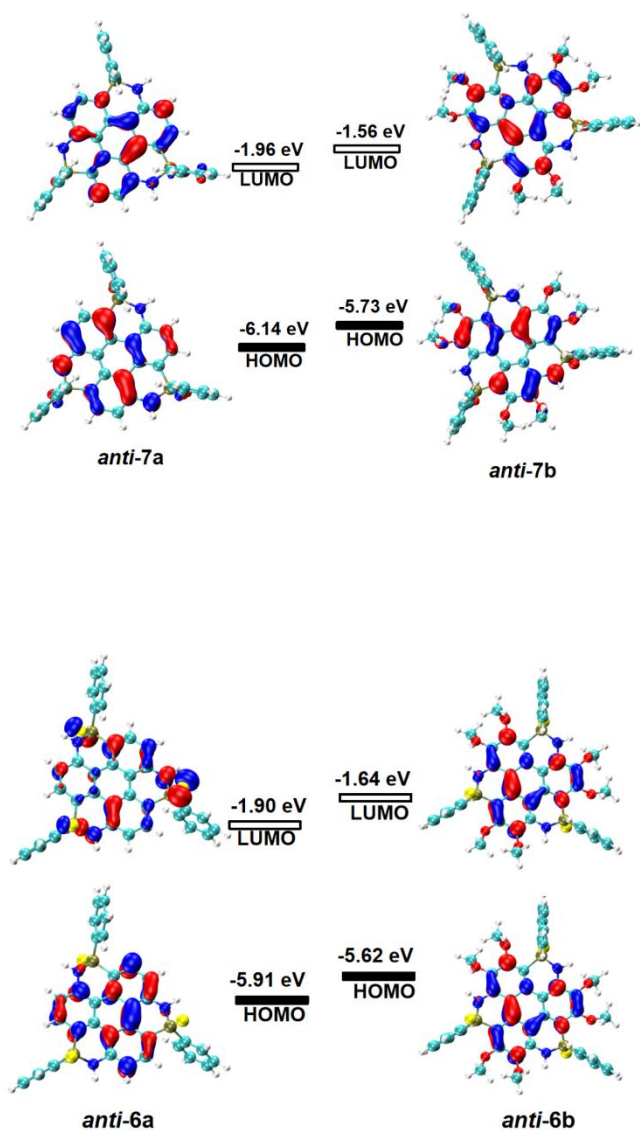
## 6. Cyclic Voltammograms



**Figure S3.** Cyclic voltammograms of compounds *anti-6a*, *anti-6b*, *anti-7a* and *anti-7b* in THF ( $1 \times 10^{-5}$  M) with 0.1 M  $n\text{Bu}_4\text{NPF}_6$  as supporting electrolyte and ferrocene as an external standard. The HOMO energy level is estimated from the equation  $\text{HOMO} = -[4.65 - E_{\text{ox}(\text{onset})}]$  based on the oxidation onset.

## 7. Theoretical methodology

Calculations were performed using the Gaussian 09 software package. The geometries were optimized at the B3LYP/6-31G(d,p) level, and energies were calculated at the same level.

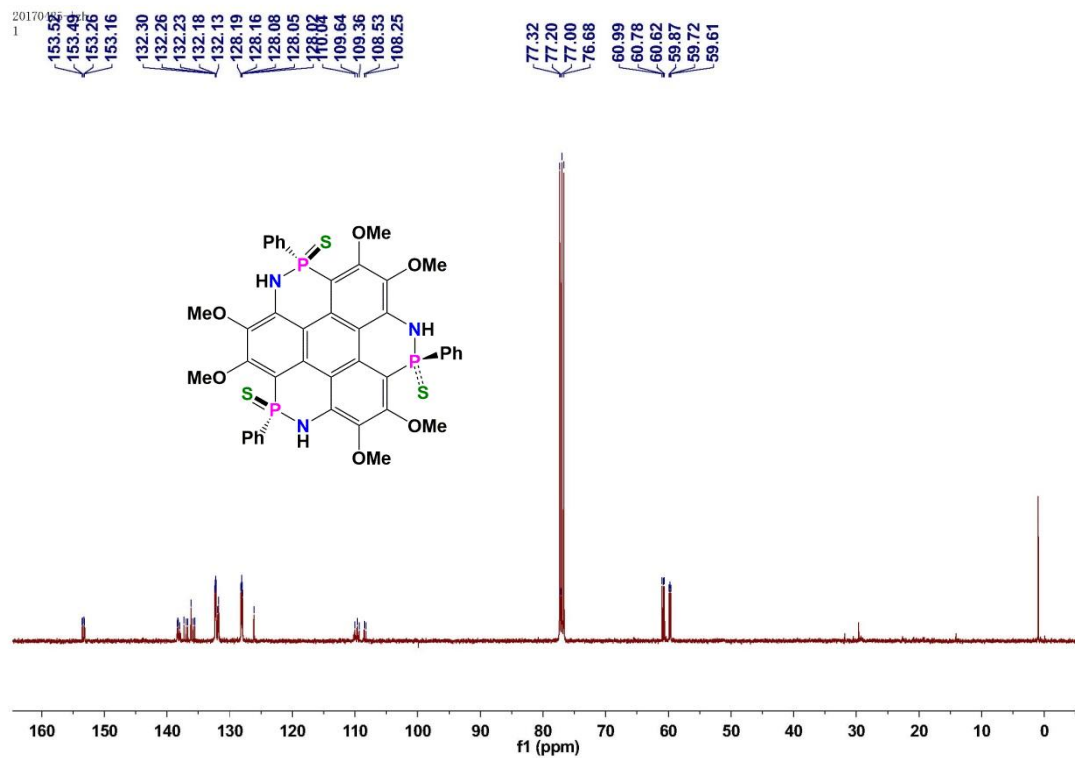
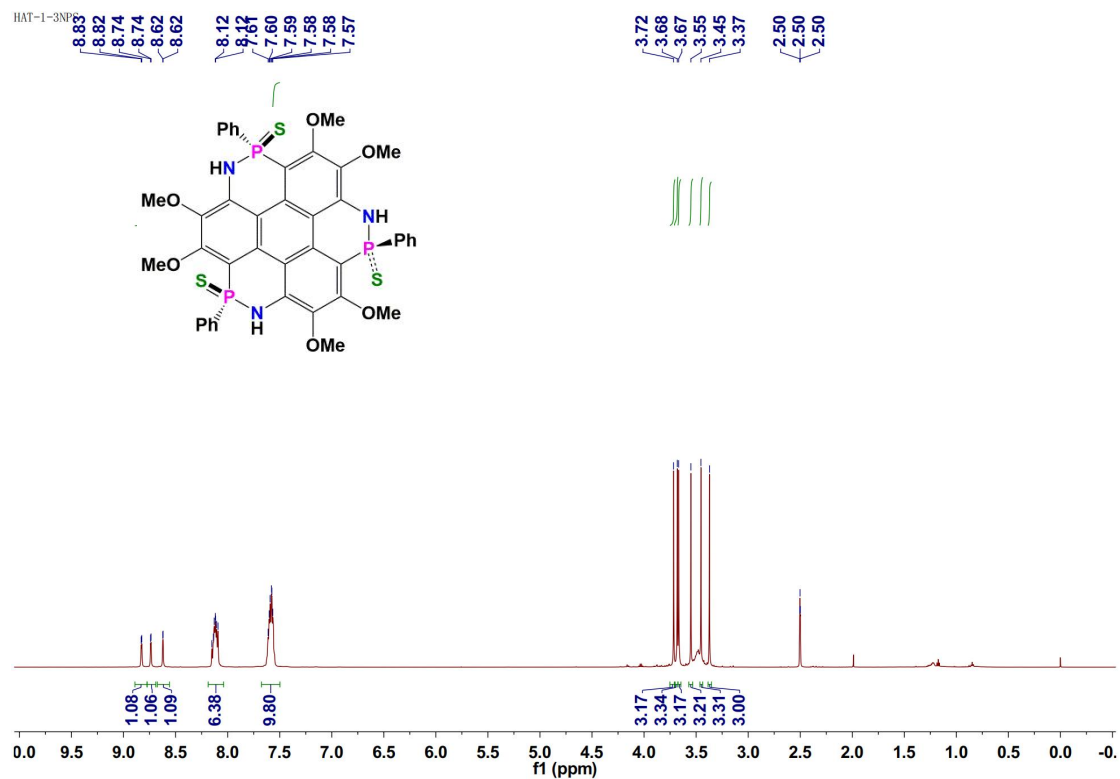


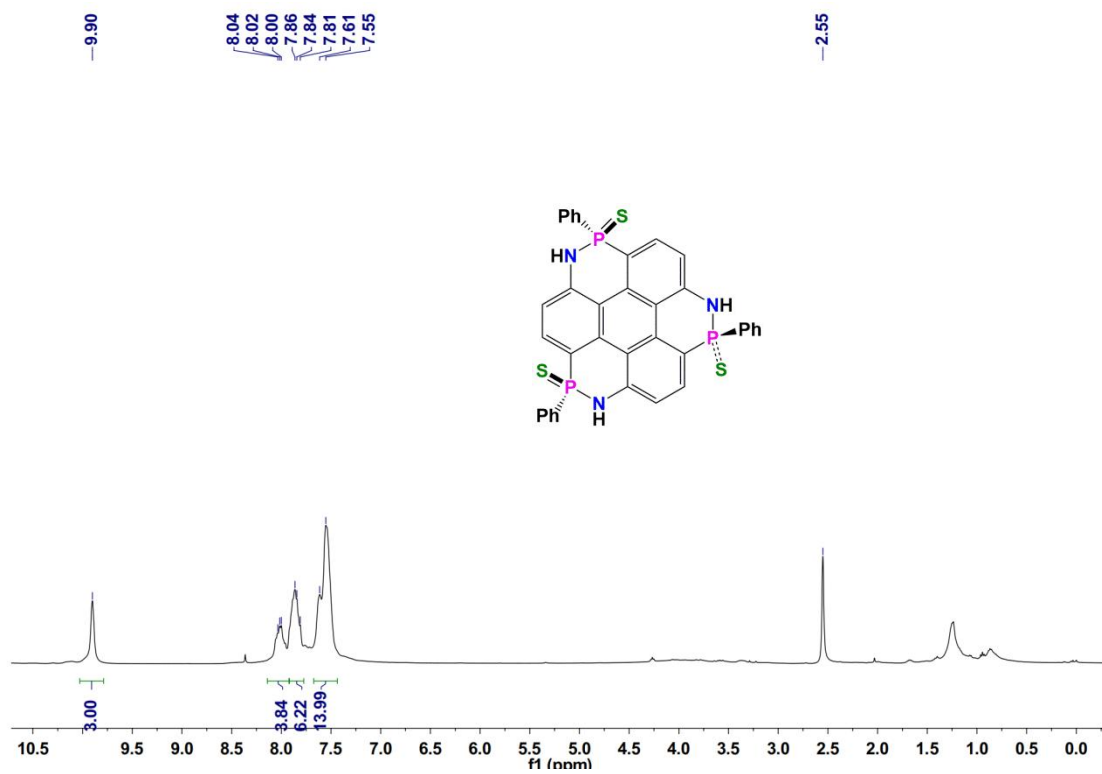
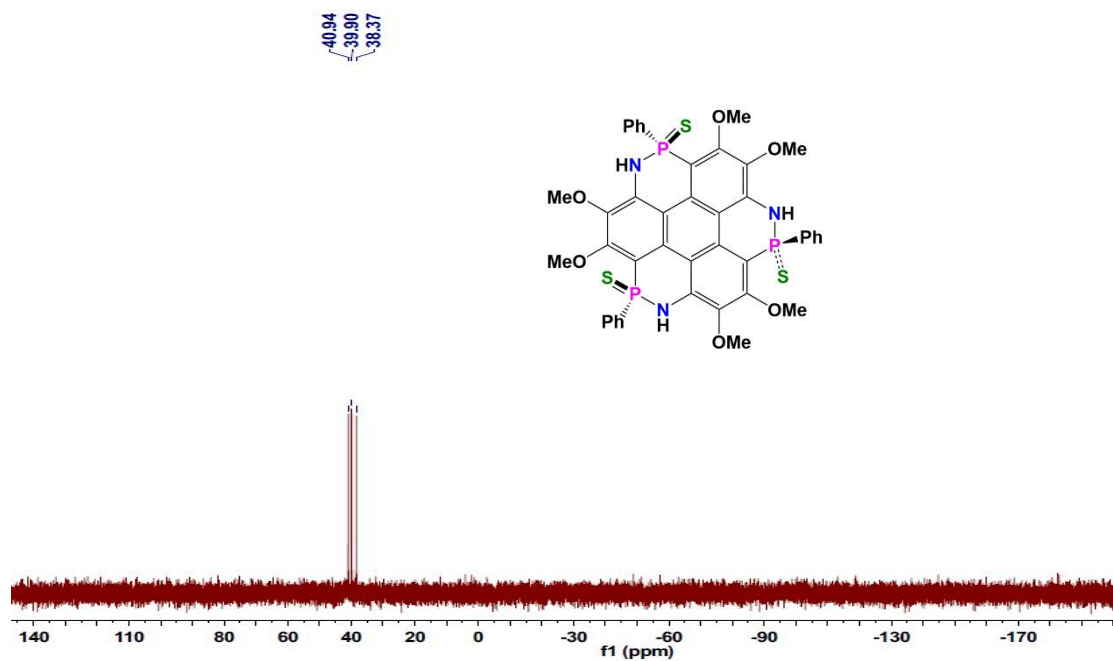
**Figure S4.** Degenerate HOMO and LUMO levels and their molecular orbitals of compounds *anti-6a*, *anti-6b*, *anti-7a* and *anti-7b*.

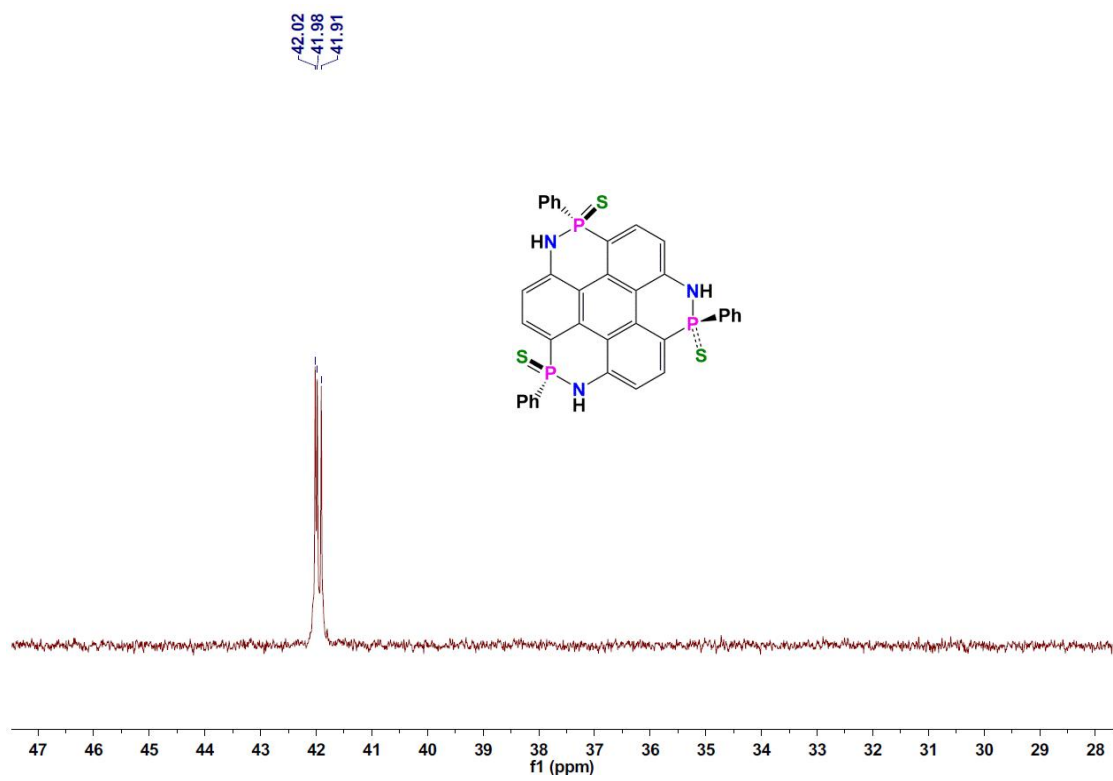
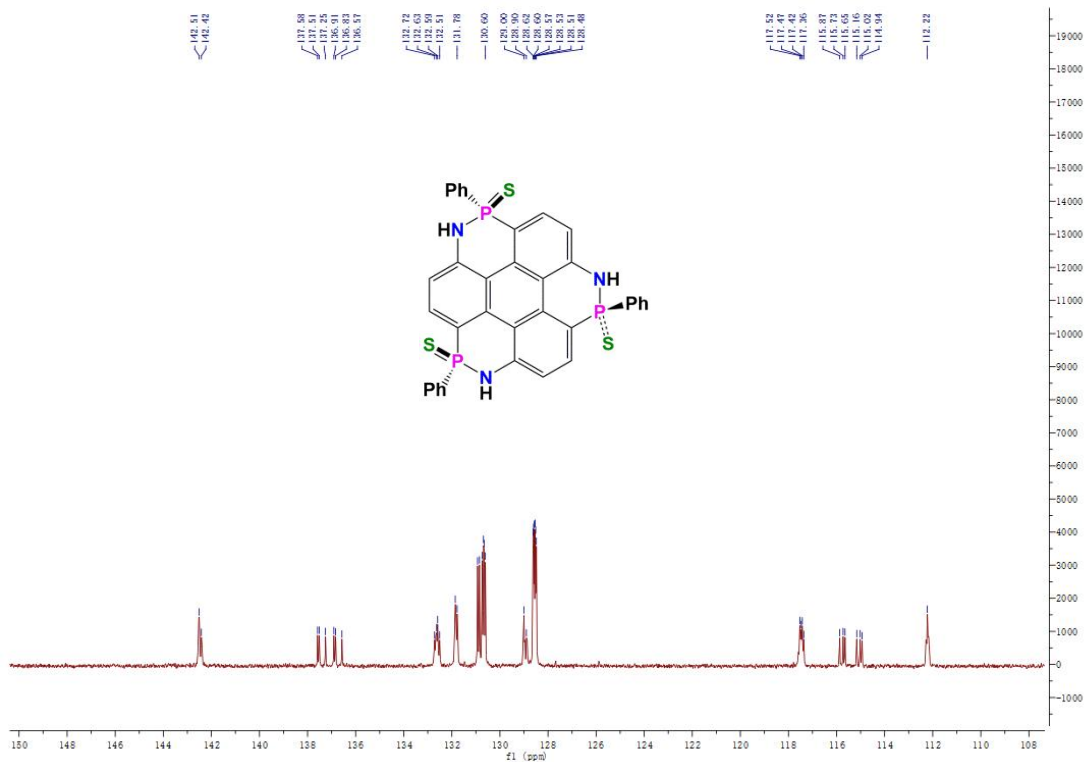
## References:

- [1] Gaussian 09, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2010.
- [2] (a) Q. Tan, H. Chen, H. Xia, B. Liu and B. Xu, *Chem. Commun.*, 2016, **52**, 537–540. (b) G. Li, W. W. Xiong, P. Y. Gu, J. Cao, J. Zhu, R. Ganguly, Y. Li, A. C. Grimdale and Q. Zhang, *Org. Lett.*, 2015, **17**, 560–563. (c) X.-Y. Wang, F.-D. Zhuang, X.-C. Wang, X.-Y. Cao, J.-Y. Wang and J. Pei, *Chem. Commun.*, 2015, **51**, 4368–4371.

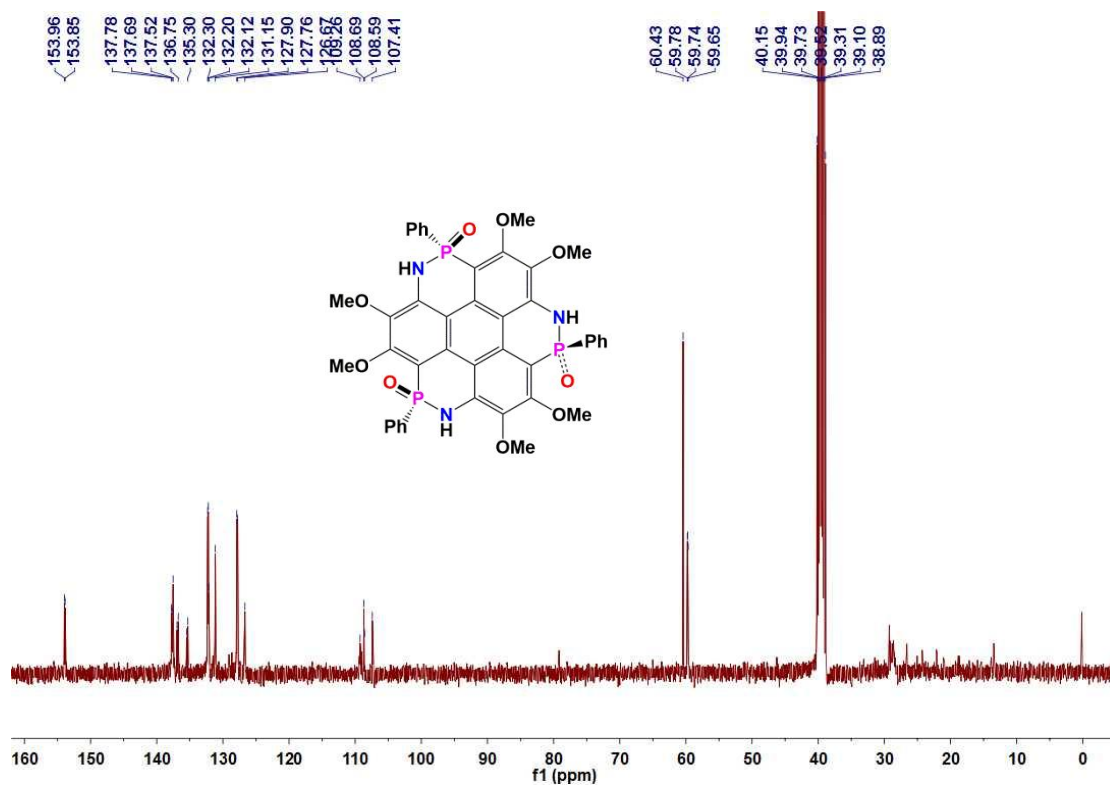
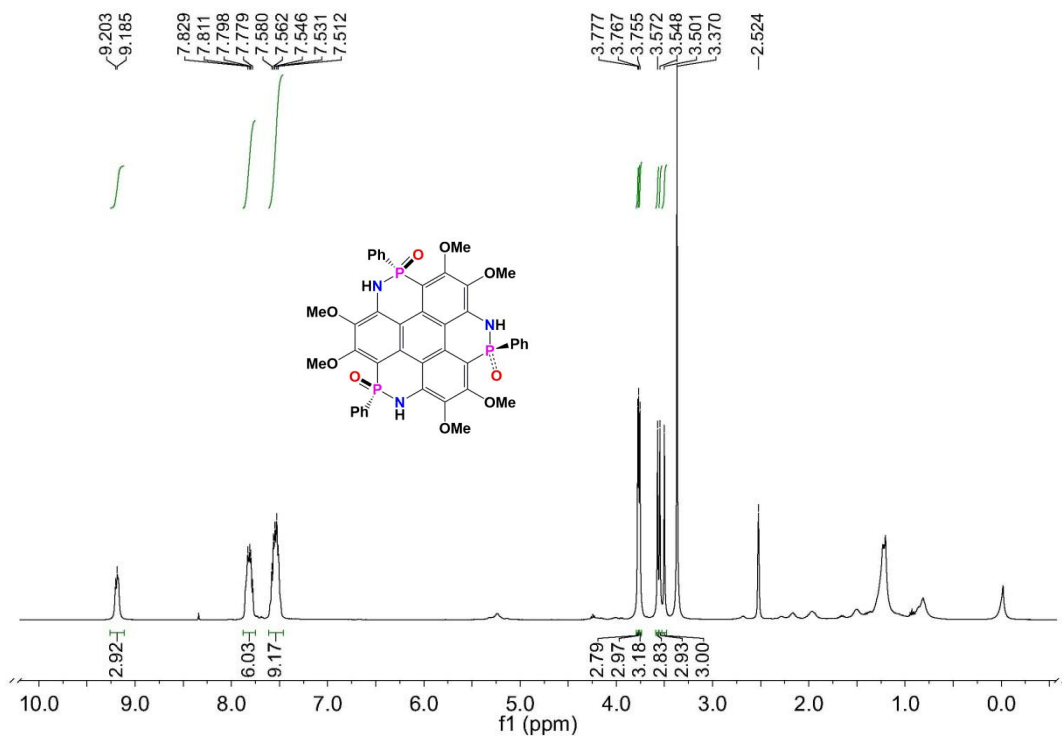
## 8. $^1\text{H}$ NMR, $^{13}\text{C}$ NMR and $^{31}\text{P}$ NMR Spectra

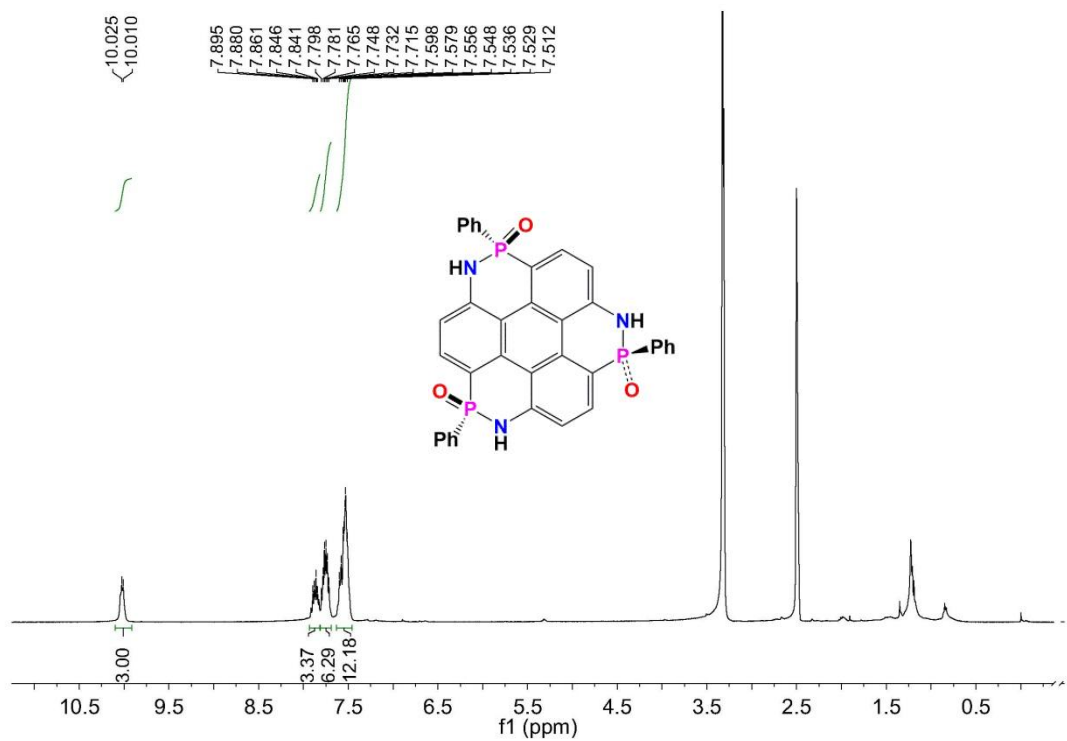
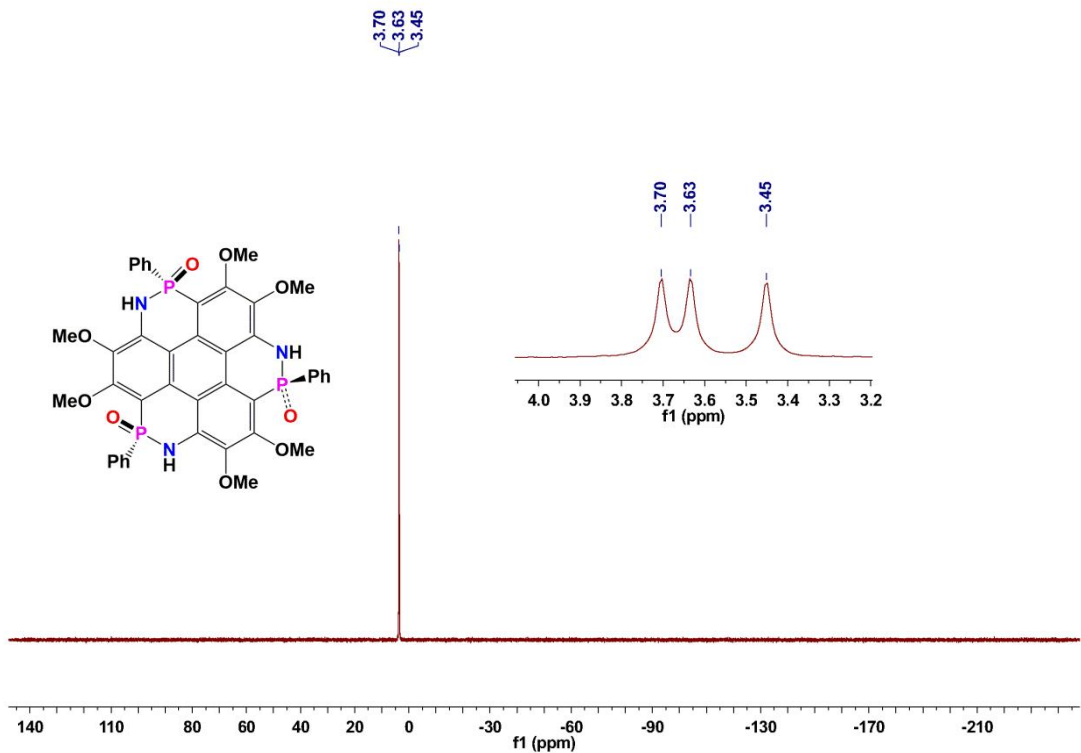


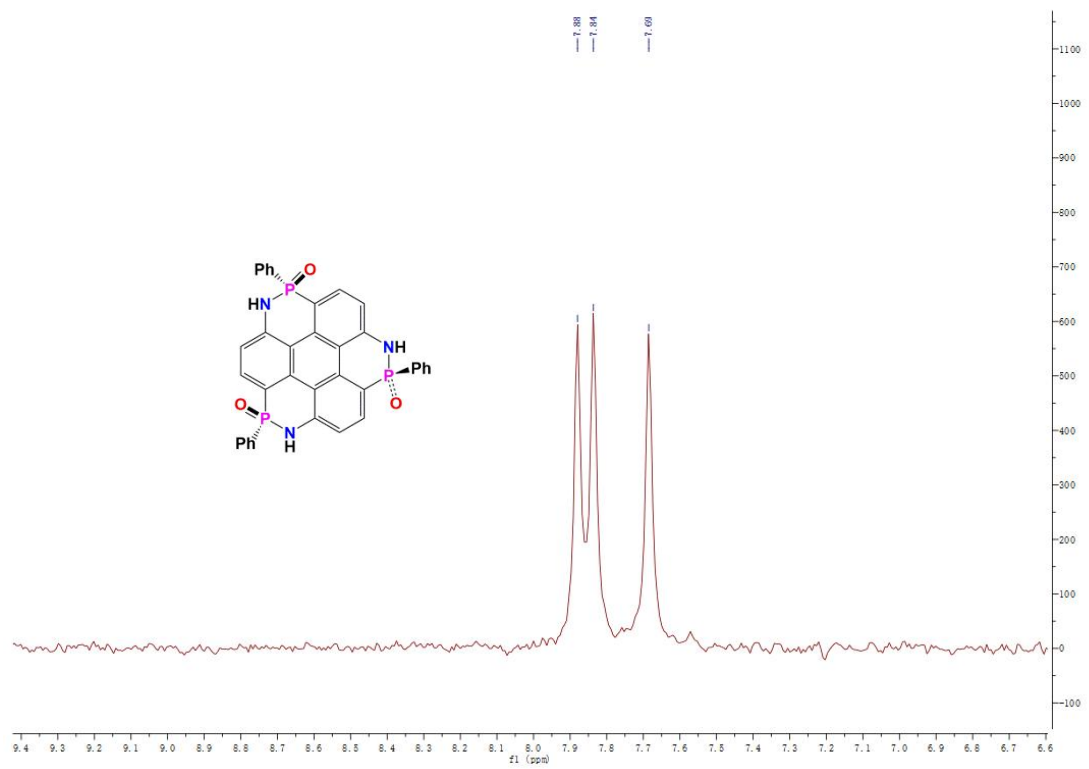
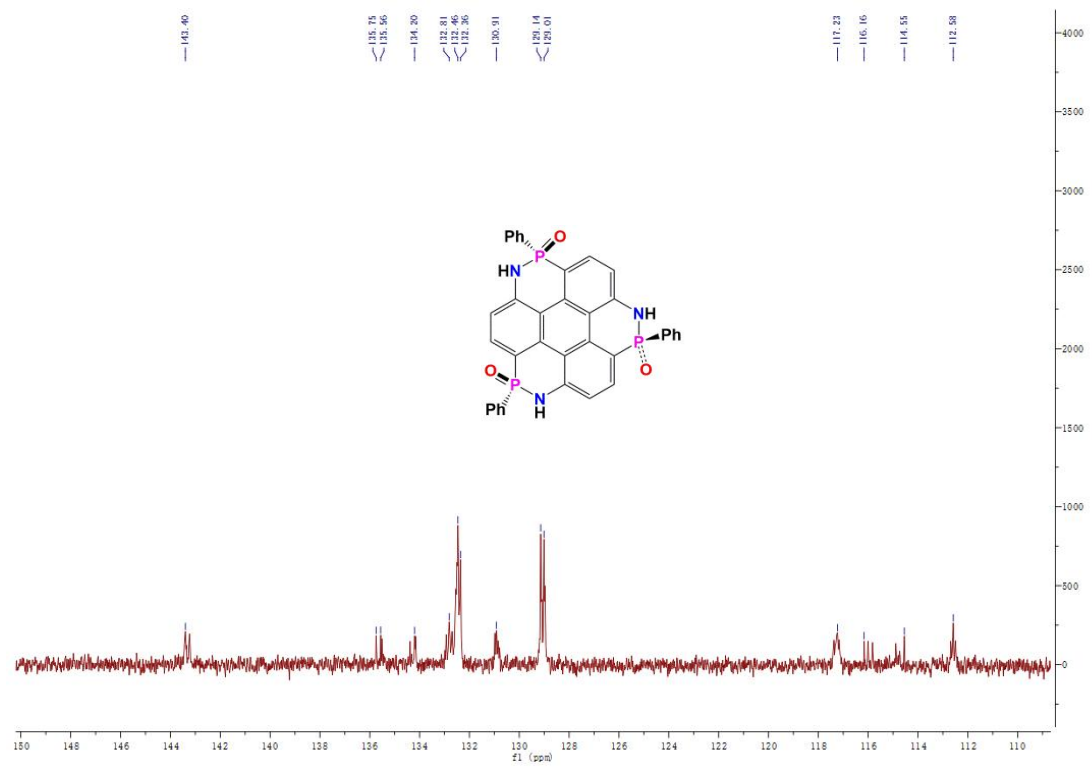












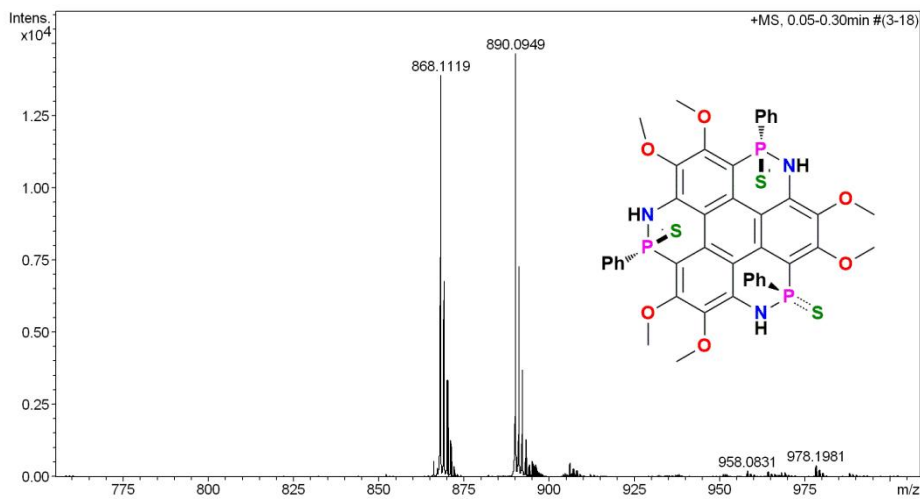
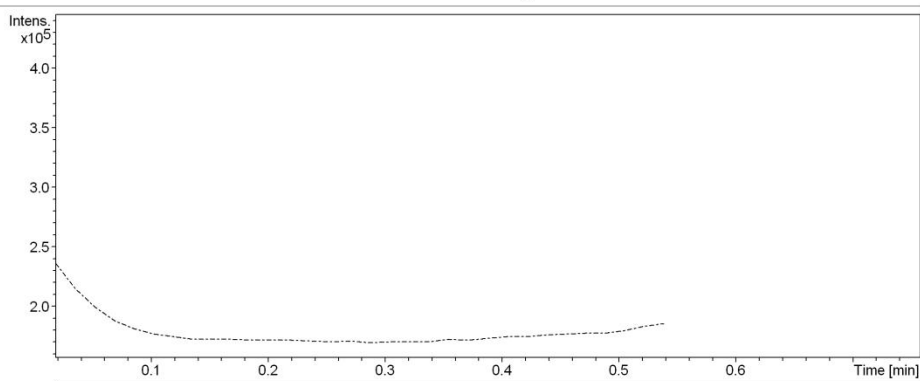
# 9. High Resolution Mass Spectrometry

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Instrument: micrOTOF-Q II 10280

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## Display Report

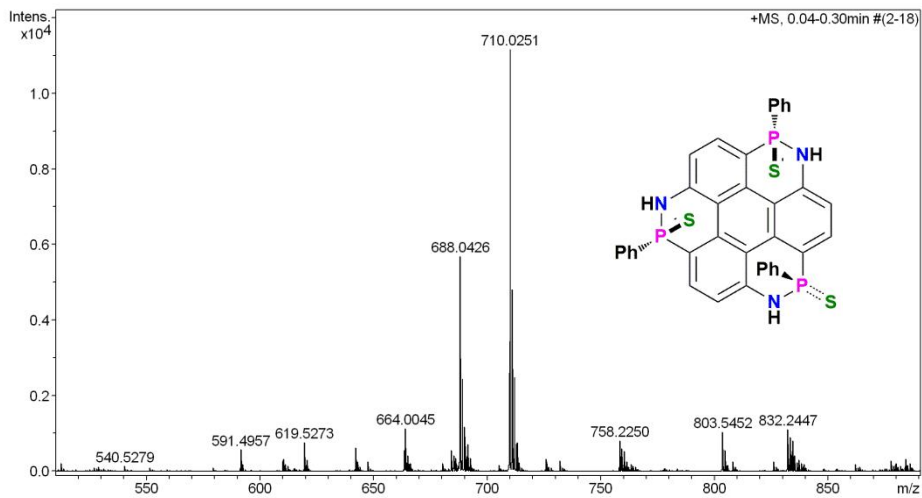
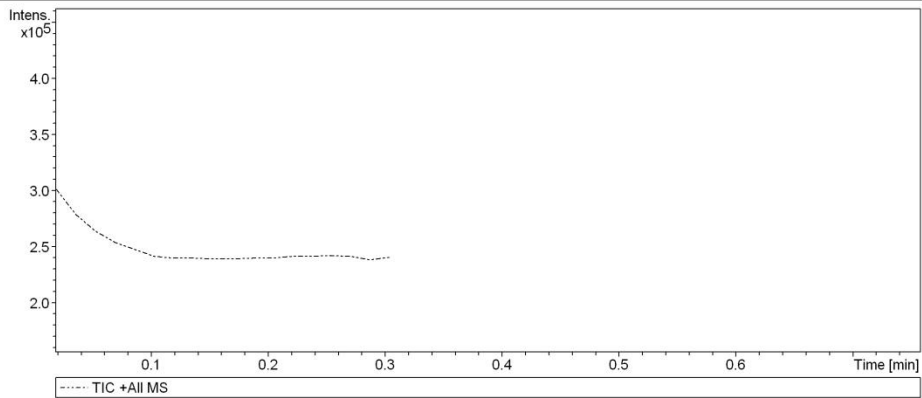
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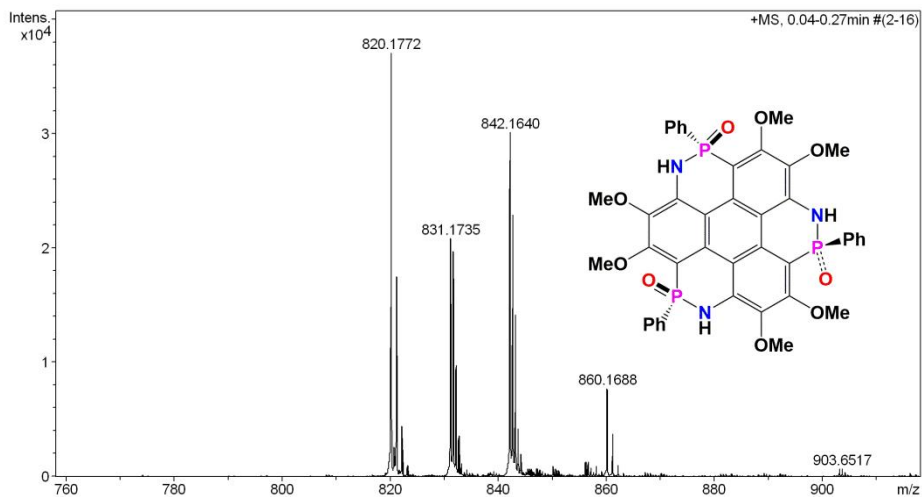
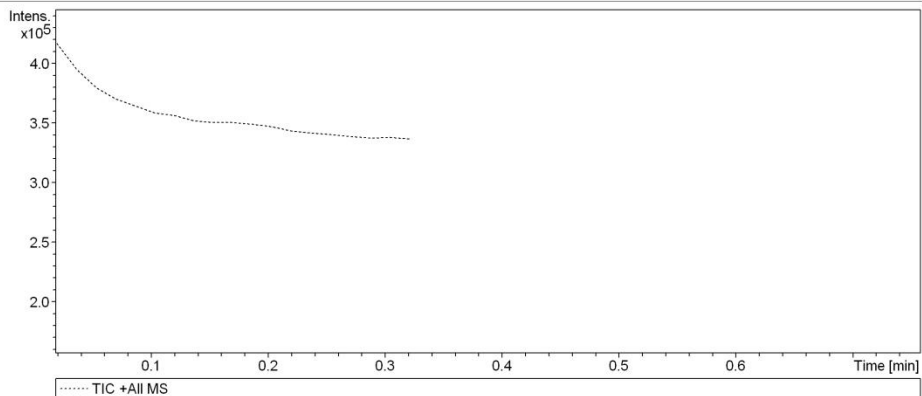
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## Display Report

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