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### Supporting Information

## Rylene annulated phthalocyanine: a fully conjugated block for the construction of a supramolecular two-dimensional framework

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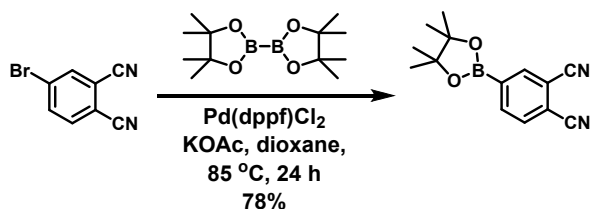
## 1. Materials and Methods

All chemicals and solvents were purchased from commercial suppliers and used without further purification unless otherwise specified.

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained in deuterated solvents on a Bruker ADVANCE 400 NMR or a Bruker ADVANCE 500 NMR Spectrometer. Chemical shifts are expressed in ppm using the residual protonated solvent as an internal standard. The signals have been named as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet doublet) and m (multiplets). High resolution mass spectra (HRMS) were determined on IonSpec 4.7 Tesla Fourier Transform Mass Spectrometer. UV-vis-NIR absorption spectra were measured with Hitachi (Model U-3010) UV-vis spectrophotometer in a 1 cm quartz cell unless otherwise specified. Cyclic voltammograms (CVs) were recorded on a Zahner IM6e electrochemical workstation, with glassy carbon discs as the working electrode, Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode at a scanning rate of 100 mV/s. 0.1 M tetrabutylammoniumhexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ) dissolved in *o*-dichlorobenzene (HPLC grade) was used as the supporting electrolyte, which was calibrated by the redox couple of ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ).

## 2. Synthesis and Characterization

The starting materials monobromo-PDI **1** was synthesized according to the literature procedure.<sup>[1]</sup>



**Scheme S1.** Synthetic route to dicyanobenzoboronate (**5**).

### Compound 5:

4-Bromophthalonitrile (1 g, 4.8 mmol), bis(pinacolato)diboron (1.35 g, 5.3 mmol), Pd(dppf)Cl<sub>2</sub> (351 mg, 0.48 mmol), and potassium acetate (2.35 g, 24 mmol) were added into a two-necked flask under an argon atmosphere. Then anhydrous dioxane (20 mL) was added by injection. The mixture was heated to 85 °C with vigorous stirring for 24 h. After cooling down and removal of the solvent under vacuum, the mixture was purified by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 1:1 v/v) to afford compound **5** as a white solid (962 mg, 78%).

$^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 8.20 (s, 1H), 8.12-8.09 (dd,  $J_1$  = 0.8 Hz,  $J_2$  = 7.7 Hz, 1H), 7.80-7.78 (d,  $J$  = 7.7 Hz, 1H), 1.35 (s, 12H),  $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 139.36, 138.76, 132.52, 117.49, 115.41, 115.37, 115.17, 85.22, 24.82.

### Compound 2:

A Schlenk flash was charged with compound **1** (1 g, 1.28 mmol), compound **5** (393 mg, 1.54 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (148 mg, 0.128 mmol) under argon. Then tetrahydrofuran (30 mL) and 2 M anhydrous potassium carbonate solution (15 mL) was added by injection, and the reaction mixture was heated to 90 °C for 12 h. After cooling down, the mixture was poured into water (600 mL), and the precipitate was collected by vacuum filtration, washed with methanol, dried, and purified by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 1:1 v/v) to afford compound **2** as a red solid (1 g, 95%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K): δ = 8.73-8.67 (m, 4H), 8.45 (s, 1H), 8.21 (s, 1H), 8.00-7.98 (m, 2H), 7.94-7.92 (m, 1H), 7.62-7.60 (d, *J* = 8.2 Hz, 1H), 5.18-5.15 (m, 2H), 2.24-2.20 (m, 4H), 1.86-1.81 (m, 4H), 1.29-1.26 (m, 24H), 0.84-0.81 (m, 12H), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K): δ = 164.25, 163.38, 162.98, 148.38, 136.39, 135.26, 134.91, 134.42, 133.99, 133.89, 133.78, 133.11, 133.01, 132.42, 131.69, 131.30, 130.37, 129.58, 129.28, 129.09, 128.09, 127.36, 124.11, 123.48, 118.02, 115.61, 114.89, 114.71, 54.99, 54.87, 32.26, 31.70, 31.69, 26.58, 26.56, 22.54, 22.53, 14.01. HRMS (MALDI, 100%): calcd (%) for C<sub>54</sub>H<sub>56</sub>N<sub>4</sub>O<sub>4</sub>: 824.4307; found, 824.4307.

### Compound 3:

In standard photocyclization glassware, compound **2** (10 × 100 mg) was dissolved in toluene (10 × 40 mL) and I<sub>2</sub> (10 × 5 mg) was added. The mixture was illuminated by blue light lamp (460-465 nm) under 95 °C for 48 h. Then the reaction mixture was extracted with saturated sodium solution (2 × 500 mL) and concentrated under reduced pressure. The pure compound **3** was obtained by recrystallization twice from the mixture of compound **3** (60%) and **3'** (38%) as an orange solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K): δ = 10.10 (s, 2H), 9.77 (s, 2H), 9.36-9.34 (d, *J* = 8.2 Hz, 2H), 9.15 (s, 2H), 5.33 (s, 2H), 2.39-2.32 (m, 4H), 2.00-1.93 (m, 4H), 1.44-1.25 (m, 24H), 0.86-0.84 (m, 12H), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K): δ = 164.53, 163.41, 133.82, 131.51, 131.13, 130.44, 128.02, 127.69, 127.03, 126.72, 126.37, 124.25, 124.17, 115.35, 113.40, 55.40, 32.39, 31.76, 26.71, 22.59, 14.04. HRMS (MALDI, 100%): calcd (%) for C<sub>54</sub>H<sub>54</sub>N<sub>4</sub>O<sub>4</sub>: 822.4150; found, 822.4149.

### ZnPcPDI4 4:

A microwave vial was charged with compound **3** (100 mg, 0.12 mmol), anhydrous zinc acetate (22 mg, 0.12 mmol), DBU (18 mg, 0.12 mmol), n-hexanol (5 mL) and degassed with argon. Then the reaction mixture was subjected to microwave heating under the condition of 160 °C and 150 W with vigorous stirring for 1 h. After cooling down, the mixture was poured into methanol, and the precipitate was collected by vacuum filtration, washed with methanol, dried, and purified by column chromatography on silica gel (CHCl<sub>3</sub>/ethyl acetate, 500:1 v/v) to afford the crude **ZnPcPDI4**. The pure **ZnPcPDI4** was obtained by recrystallization in CHCl<sub>3</sub> and methanol as a metallic dark-green thin slices (25 mg, 25%).

<sup>1</sup>H NMR (500 MHz, *o*-dichlorobenzene-d<sub>4</sub>/pyridine-d<sub>5</sub>, 373 K): δ = 11.80 (s, 8H), 11.25 (s, 8H), 9.31 (s, 16H), 6.12 (s, 8H), 3.22 (s, 16H), 2.40-2.38 (m, 16H), 2.02-1.94 (m, 32H), 1.80-1.69 (m, 32H), 1.58-1.54 (m,

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32H), 1.04-1.01 (m, 48H),  $^{13}\text{C}$  NMR (125 MHz, *o*-dichlorobenzene- $d_4$ /pyridine- $d_5$ , 373 K):  $\delta$  = 164.84, 155.33, 138.05, 134.41, 133.53, 133.18, 131.26, 130.95, 129.52, 128.25, 127.95, 126.22, 125.45, 124.44, 123.68, 119.89, 55.43, 33.67, 32.47, 27.31, 23.05, 14.04. HRMS (MALDI, 100%): calcd (%) for  $\text{C}_{216}\text{H}_{216}\text{N}_{16}\text{O}_{16}\text{Zn}$ : 3353.5877; found, 3353.5857.

### 3. Single-crystal X-ray Diffraction Analysis

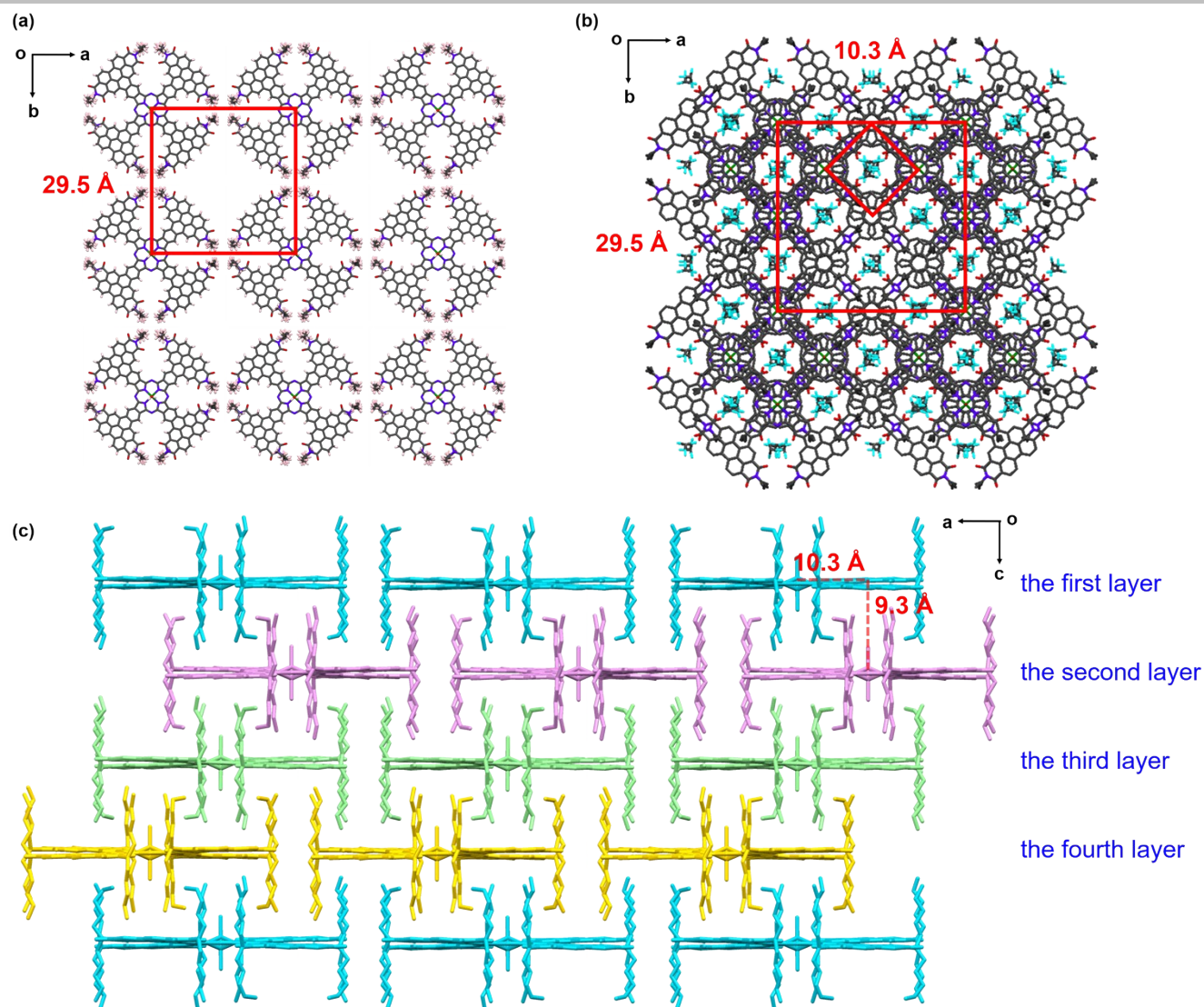
The single-crystal X-ray diffraction data for **ZnPcPDI4** was collected at 173 K on a Bruker SMART CCD area detector with graphite monochromated MoK $\alpha$  radiation ( $\lambda$  = 0.71073). All calculations were performed using the SHELXL and the CrystalStructure crystallographic software package.

#### *Crystal data for ZnPcPDI4:*

Empirical formula:  $\text{C}_{216}\text{H}_{216}\text{N}_{16}\text{O}_{16}\text{Zn} \cdot \text{H}_2\text{O} \cdot 16 \text{CHCl}_3$ ; Formula weight: 5285.32; Wavelength: 0.71073 Å; Crystal system: Tetragonal; Space group: P4(1)22; a = 29.4605(2) Å; b = 29.4605(2) Å; c = 37.2375(4) Å;  $\alpha$  =  $\beta$  =  $\gamma$  = 90°; Volume: 32319.2(5) Å<sup>3</sup>; Density: 1.086 mg/m<sup>3</sup>; Absorption coefficient: 0.521 mm<sup>-1</sup>; F(000): 10880; Crystal size: 0.30 × 0.28 × 0.25 mm<sup>3</sup>; No. of formula units per unit cell: 4; Reflections collected: 390794; Independent reflections: 28549 [R(int) = 0.1806]; GOF on F<sup>2</sup>: 1.141; R indices (all data): R<sub>1</sub> = 0.1767, wR<sub>2</sub> = 0.3753; Final R indices [I > 2 $\sigma$ (I)]: R<sub>1</sub> = 0.1301, wR<sub>2</sub> = 0.3435.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication on no. CCDC 1810666 (**ZnPcPDI4**).

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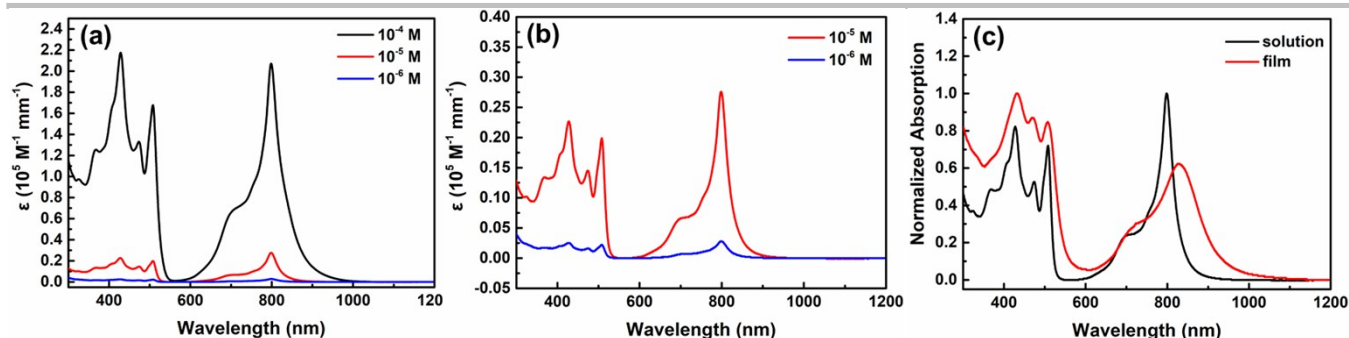


**Fig. S1.** Packing arrangement of **ZnPcPDI4·H<sub>2</sub>O**: (a) monolayer viewed from *a-b* plane; (b) cage-like arrangements are formed and the voids of these cages are filled with solvent CHCl<sub>3</sub> molecules by the intensive hydrogen-bonding interactions between CHCl<sub>3</sub> and perylene core; (c) four layers viewed from *a-c* plane to show a longitudinal displacement of 9.3 Å and a transversal displacement of 10.3 Å. In (a) and (c), the solvent molecules (CHCl<sub>3</sub>) are omitted for clarify.

### 4. Absorption Spectra

Absorption spectra with different concentrations and in film were measured with Hitachi (Model U-3010) UV-vis spectrophotometer in a 1 mm quartz cell or a quartz plate.

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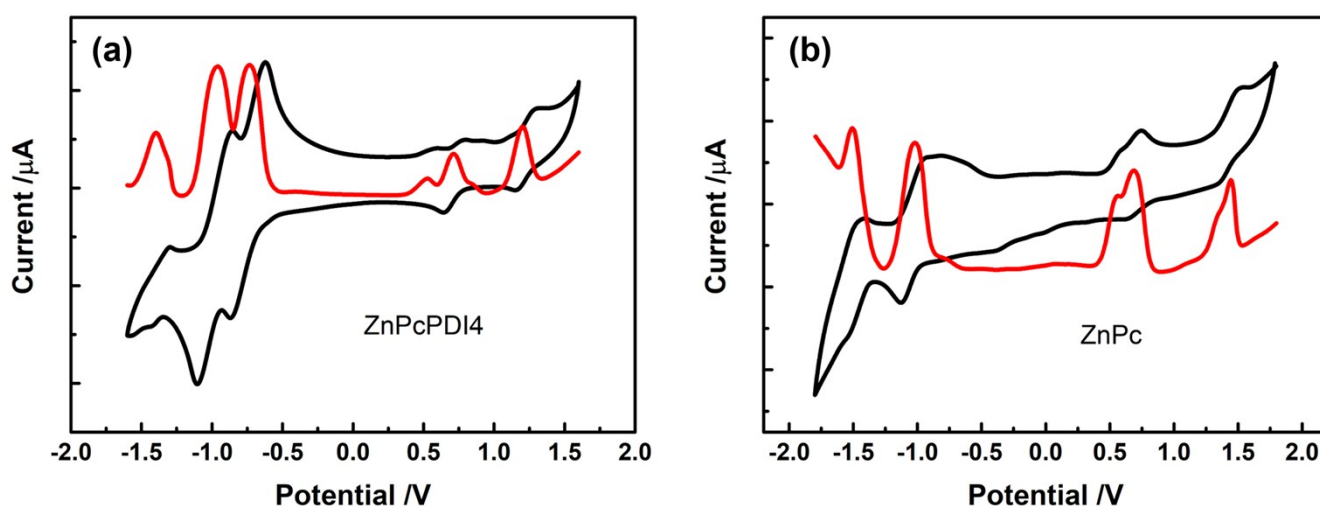
**Fig. S2.** Absorption spectra of **ZnPcPDI4**: (a) and (b) in  $\text{CHCl}_3$  solution with different concentrations; (c) in  $\text{CHCl}_3$  solution ( $1 \times 10^{-5} \text{ mol L}^{-1}$ ) and in film.

### 5. Electrochemical Properties

**Table S1.** Electrochemical properties of **ZnPcPDI4**, **ZnPc**, and **PDI**.

|                 | $E_{1r}$ [V] <sup>[a]</sup> | $E_{2r}$ [V] <sup>[a]</sup> | $E_{3r}$ [V] <sup>[a]</sup> | $E_{1o}$ [V] <sup>[a]</sup> | $E_{2o}$ [V] <sup>[a]</sup> | $E_{3o}$ [V] <sup>[a]</sup> |
|-----------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| <b>ZnPcPDI4</b> | -0.75                       | -0.98                       | -1.36                       | 0.53                        | 0.72                        | 1.23                        |
| <b>ZnPc</b>     | -1.03                       | -1.49                       | —                           | 0.56                        | 0.69                        | 1.45                        |
| <b>PDI</b>      | -0.62                       | -0.88                       | —                           | —                           | —                           | —                           |

[a] In deaerated *o*-dichlorobenzene solution containing  $\text{Bu}_4\text{NPF}_6$  (0.1 M) vs.  $\text{Ag}/\text{AgCl}$ .



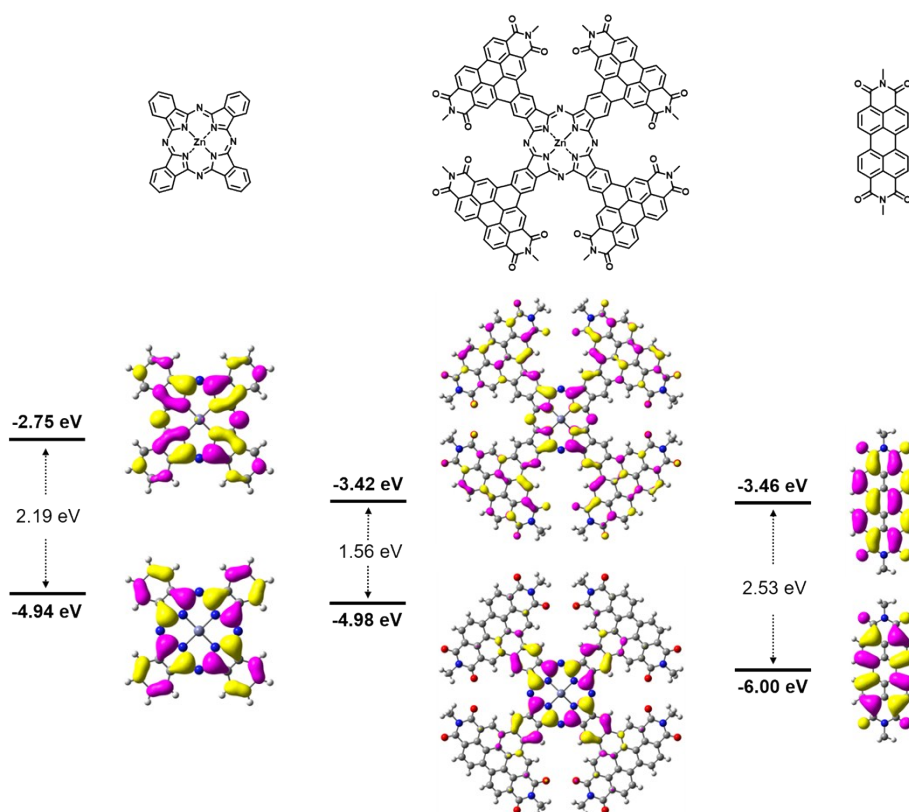
**Fig. S3.** The cyclic voltammetry (CV, black) and differential pulse voltammetry (DPV, red) profiles of **ZnPcPDI4** and **ZnPc**.

### 6. Computational Details

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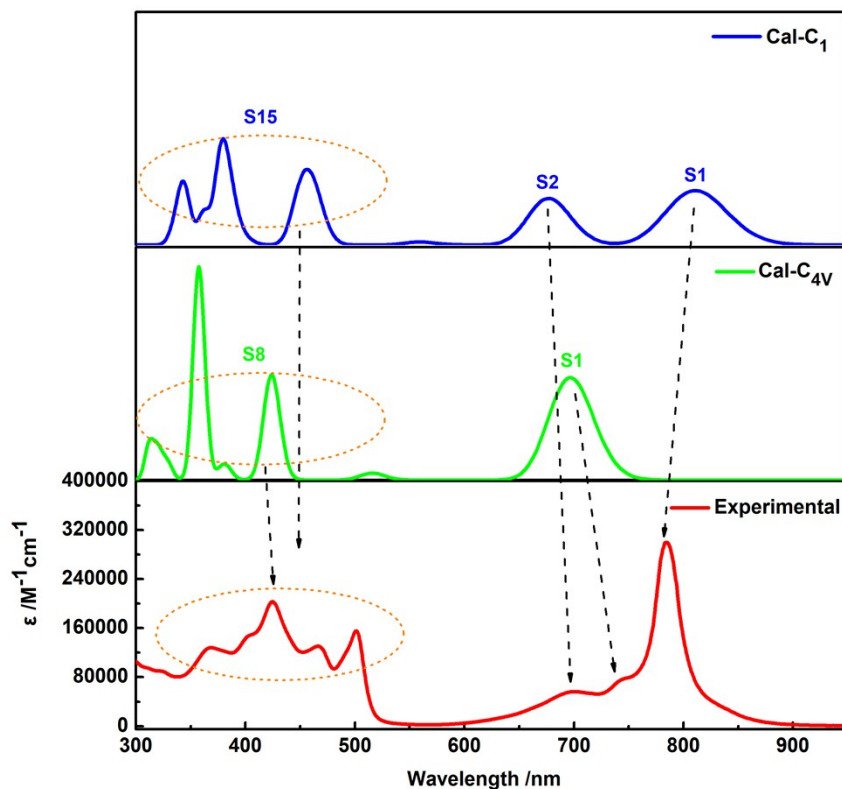
All calculations were carried out with Gaussian 09.<sup>[3]</sup> In the solvent, the symmetry of structure **ZnPcPDI4** may be broken. So based on optimized ground structures with two different spatial point groups ( $C_1$  and  $C_{4v}$ ), absorption spectra, displayed in Fig. S4, was obtained using time-dependent density functional theory (TD-DFT) at Cam-B3LYP/genecp level, where metal atom use LANL2DZ basis and other atoms use 6-31G basis. The effect of the solvent (THF) within polarizable continuum model (PCM) in a linear response has been considered. Due to the little effect of the alkyl-branched chain on electronic structures and optical properties, the all alkyl chain was replaced by the methyl groups.

In all structures of **ZnPcPDI4**, asymmetric structure is the main configuration due to the effect of solvent. Therefore, the main contribution of absorption mainly originates from the asymmetric structure. Combination with natural transition orbital (NTO) analysis, it clearly found that the hole and electron of  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_2$  for symmetric structure are mainly concentrated on the ZnPc. And there is the same maximum absorption wavelength ( $\lambda_{max}$ ) and weight for both transition, indicating that the absorption in long absorption wavelength come from two degenerate excited state. When the symmetry structure is broken, absorption split into two different peaks, which originates the excitation from ground state to the first state ( $S_1$ ) (~800 nm) and to the second state ( $S_2$ ) (~700 nm). NTO analysis indicates the holes and electrons of  $S_1$  and  $S_2$  distribute on the ZnPc for asymmetric structure. Eventually, **ZnPcPDI4** presents a wide absorption in the range of 650-900 nm in the solvent as seen Fig. S5. Additionally, the absorption in the range of 300-500 nm is the combination of local excitation (LE) and intramolecular charge transfer (ICT) displayed in Fig. S6, so the absorption intensity decrease.

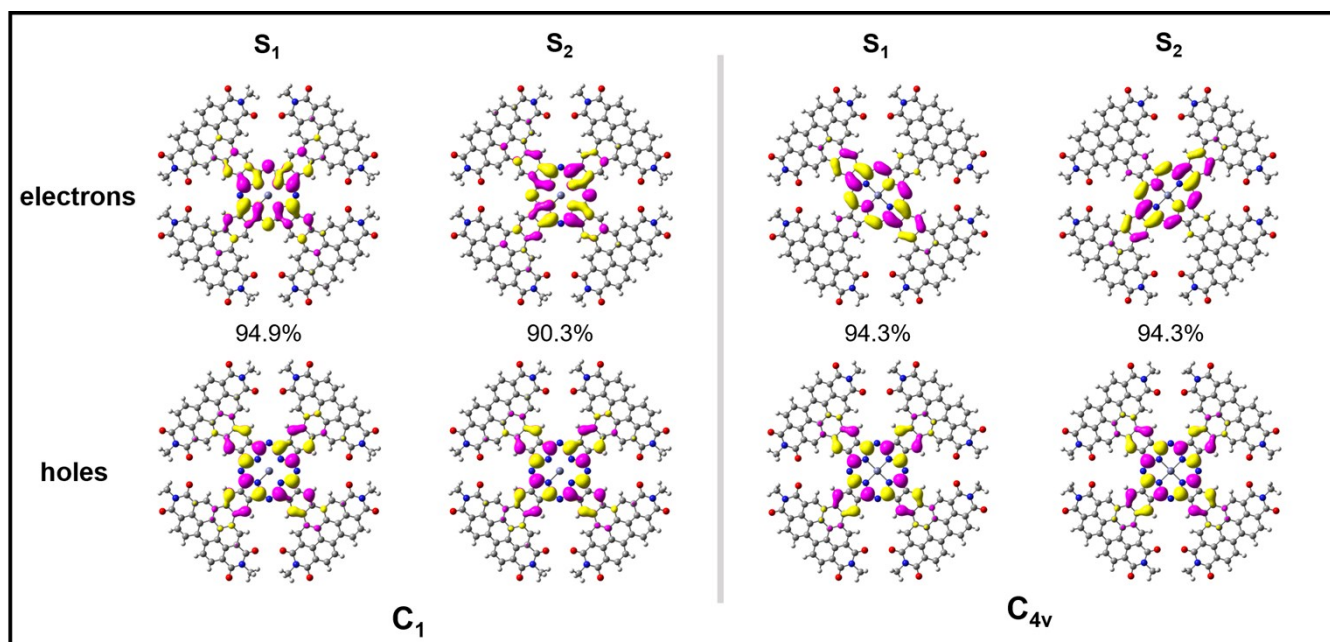


**Fig. S4.** Frontier molecular orbitals for ZnPc, model **ZnPcPDI4** and PDI at B3LYP/6-31G(d) level.

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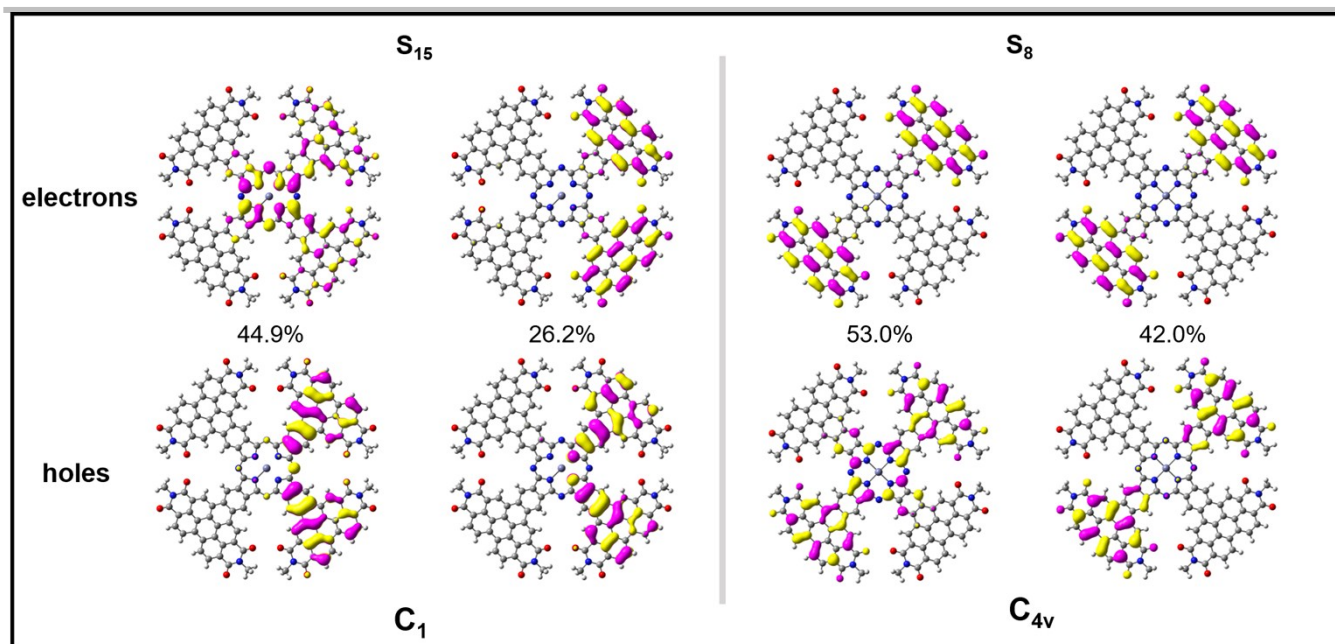
**Fig. S5.** UV/vis absorption spectra of **ZnPcPDI4** in THF solution (bottom), and simulated spectra at TDDFT/genecp (where metal atom use LANL2DZ basis, other atom use 6-31G) not including vibronic structures (top).



**Fig. S6.** The dominant natural transition orbital (NTO) pairs of  $S_1$  and  $S_2$  for  $C_1$  structure (left) and  $C_{4v}$  structure (right). The weight (%) of the hole-electron contribution to the excitation is also included.



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**Fig. S7.** The natural transition orbitals (NTOs) pairs of  $S_{15}$  for  $C_1$  structure (left) and  $S_8$  for  $C_{4v}$  structure (right). The weight (%) of the hole-electron contribution to the excitation is also included.

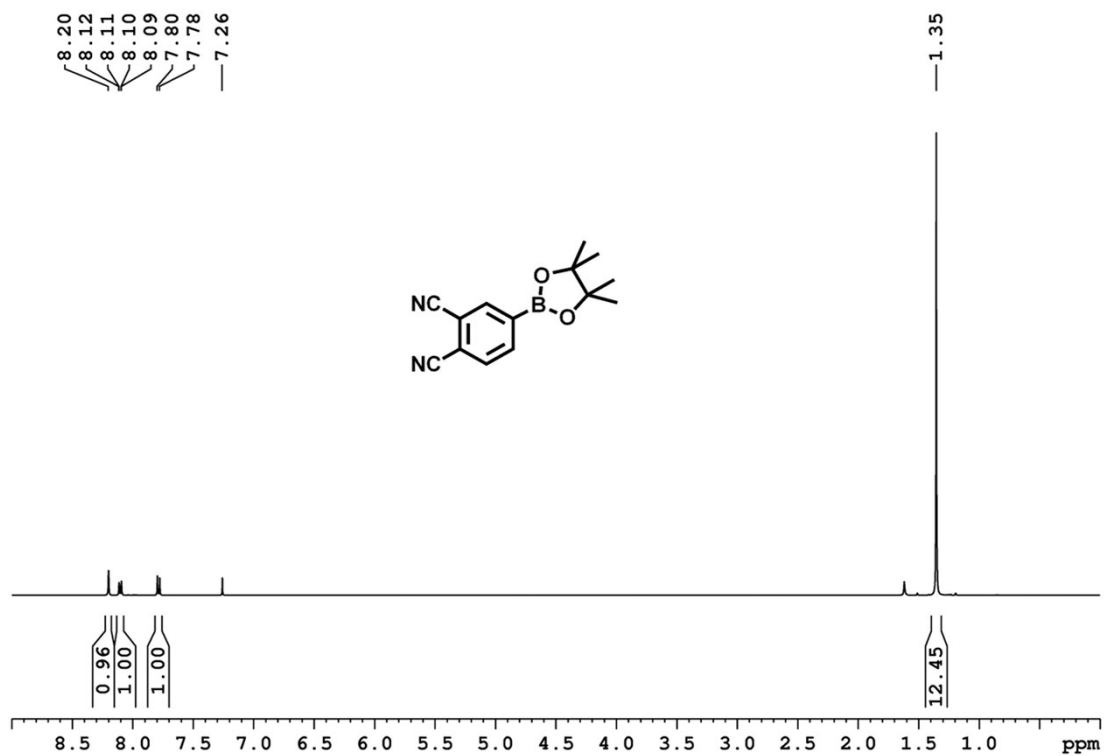
## 7. References

- [1] W. Jiang, L. Ye, X. Li, C. Xiao, F. Tan, W. Zhao, J. Hou, Z. Wang, *Chem. Commun.* **2014**, 50, 1024-1026.
- [2] J. Clavilier, *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, 107, 211-216.
- [3] Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, 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, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, 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, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

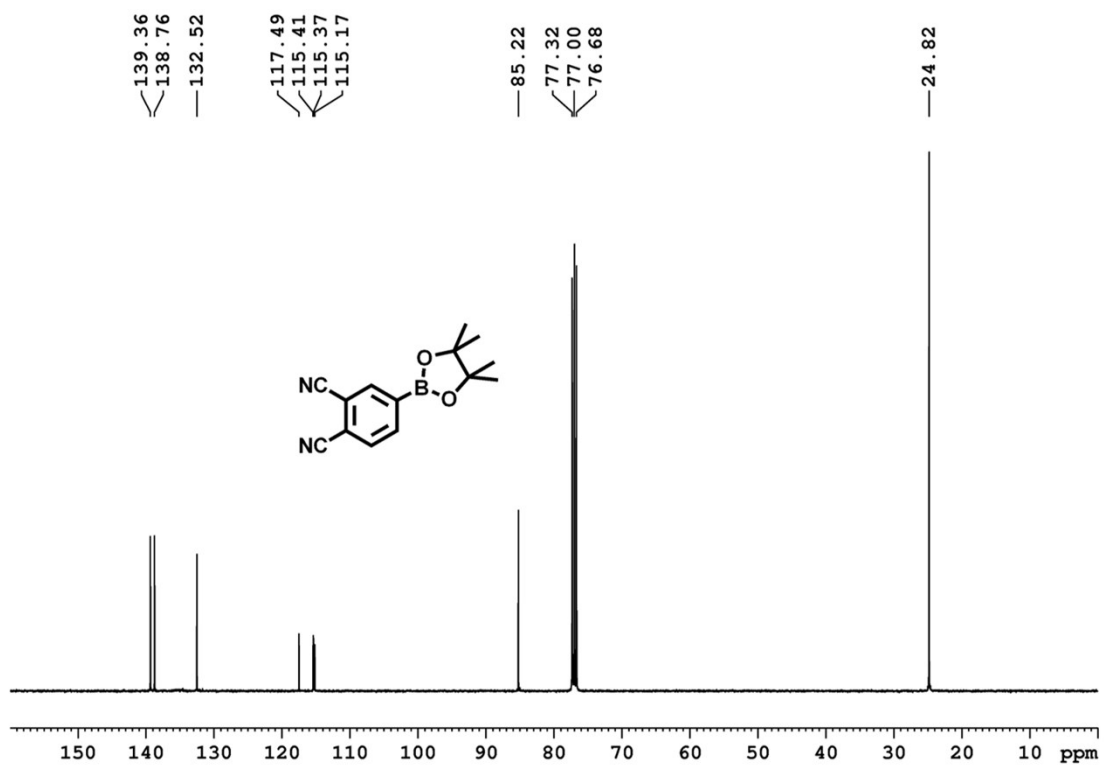
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## 8. NMR Spectra

$^1\text{H}$  NMR spectrum of **5** (400 MHz,  $\text{CDCl}_3$ , 298 K)

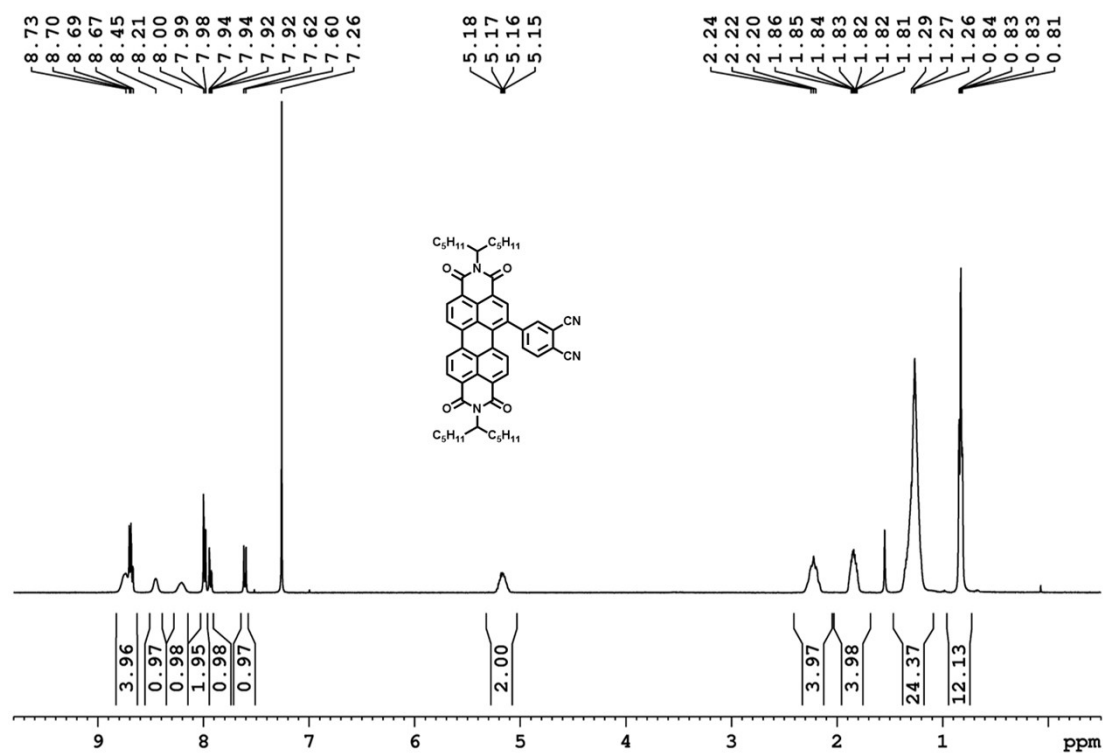


$^{13}\text{C}$  NMR spectrum of compound **5** (100 MHz,  $\text{CDCl}_3$ , 298 K)

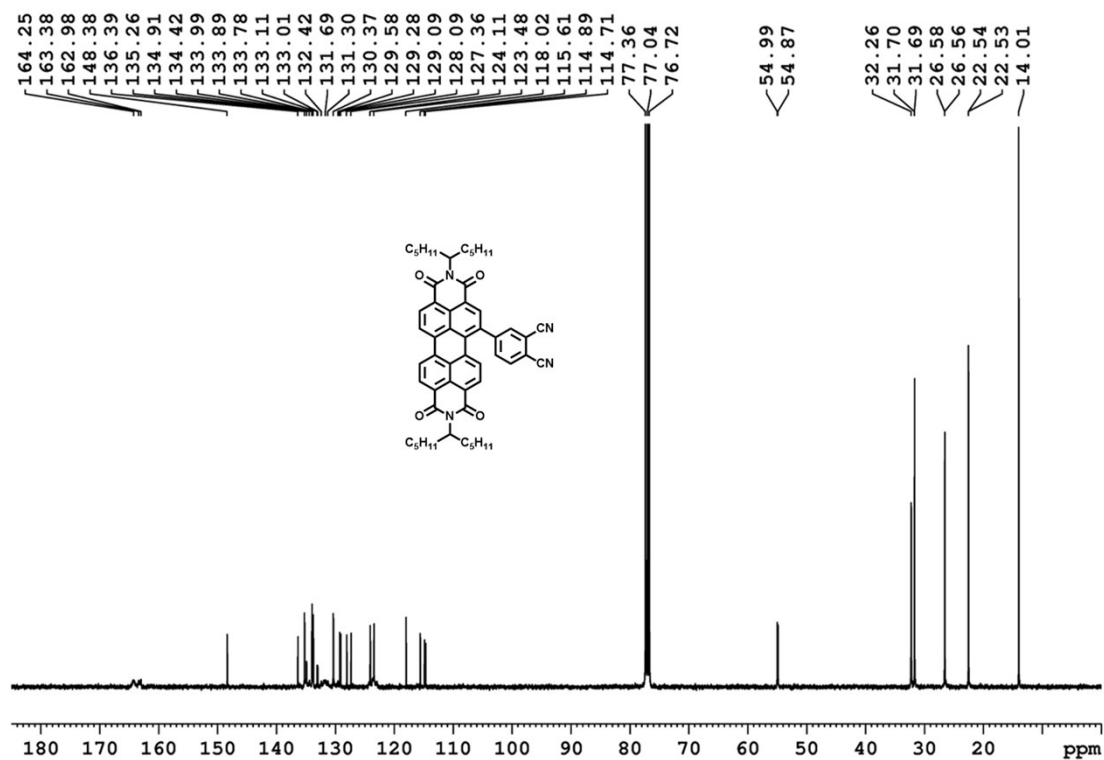


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$^1\text{H}$  NMR spectrum of compound **2** (400 MHz,  $\text{CDCl}_3$ , 298 K)

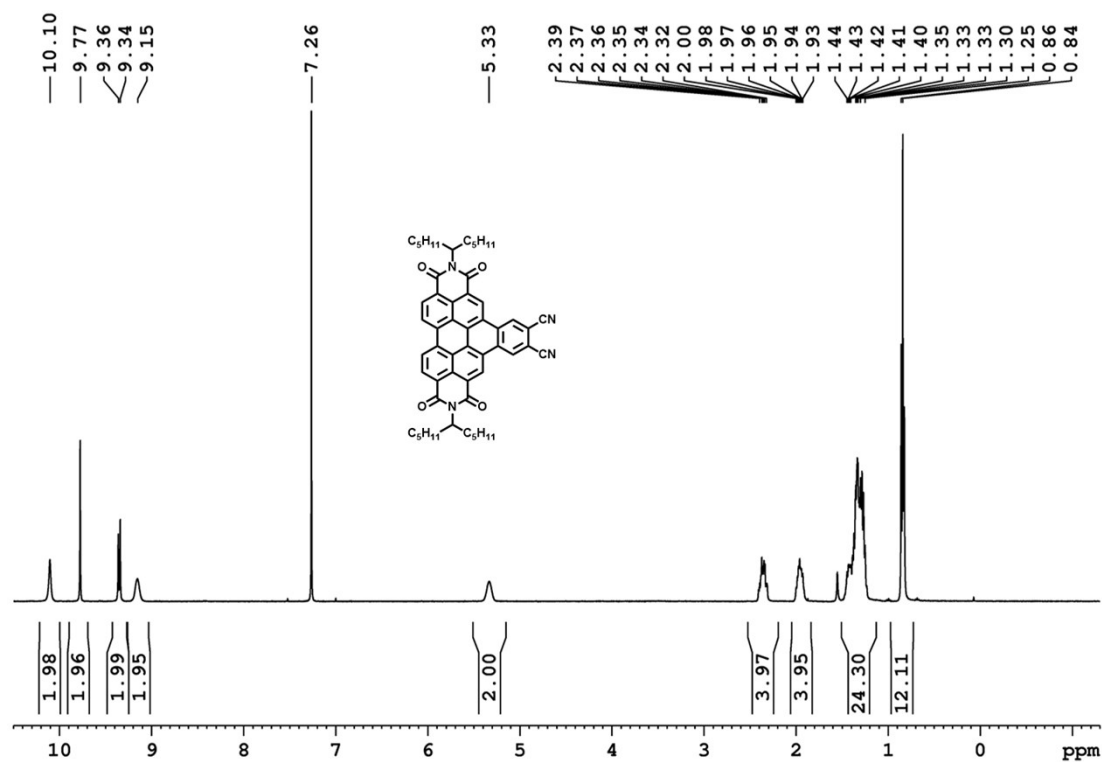


$^{13}\text{C}$  NMR spectrum of compound **2** (100 MHz,  $\text{CDCl}_3$ , 298 K)

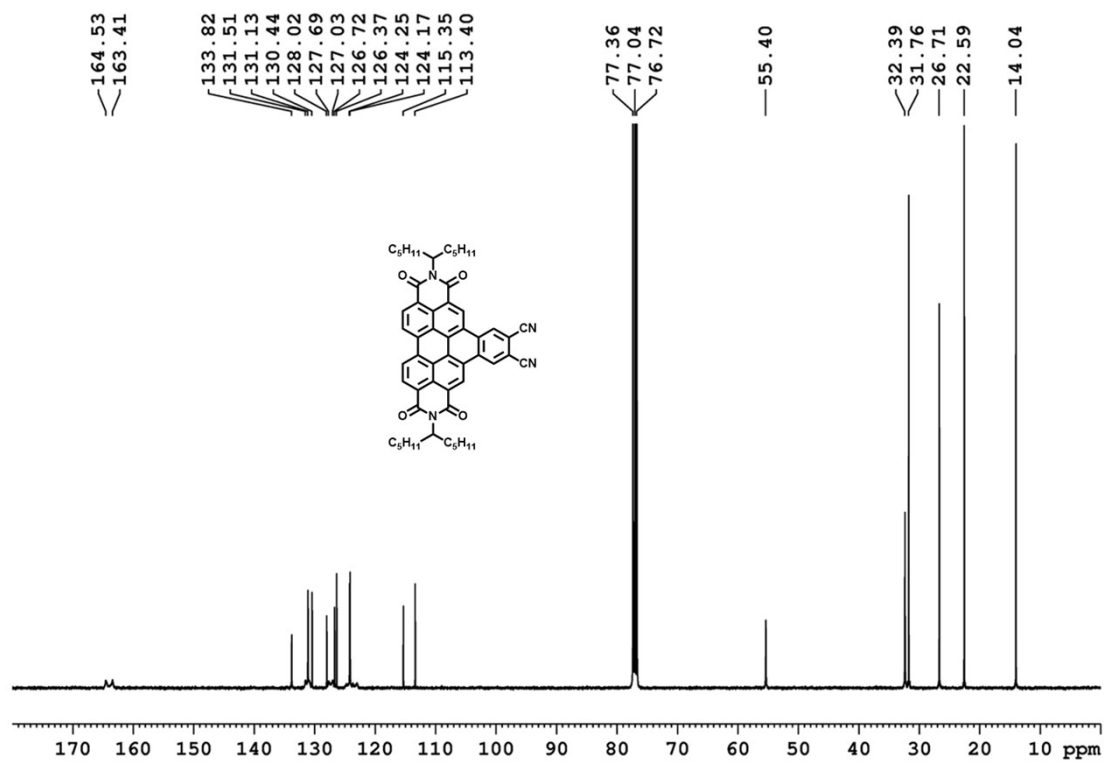


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$^1\text{H}$  NMR spectrum of compound **3** (400 MHz,  $\text{CDCl}_3$ , 298 K)

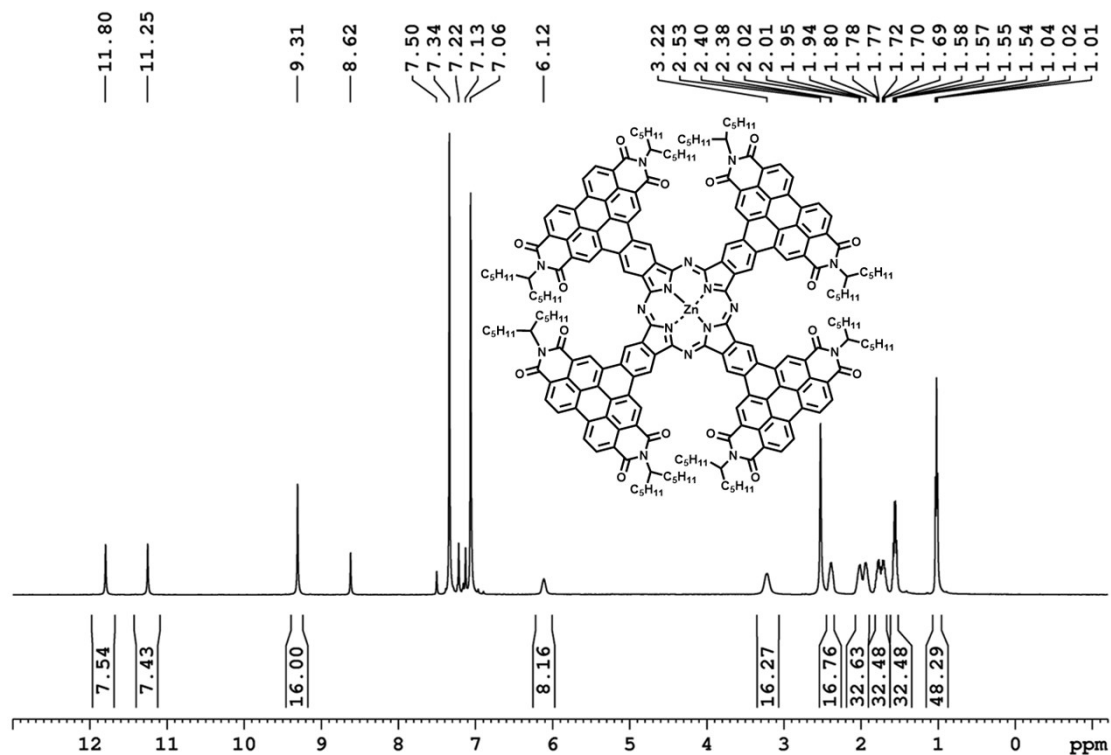


$^{13}\text{C}$  NMR spectrum of compound **3** (100 MHz,  $\text{CDCl}_3$ , 298 K)



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$^1\text{H}$  NMR spectrum of **ZnPcPDI4** (500 MHz, *o*-dichlorobenzene- $d_4$ :pyridine- $d_5$  (V/V = 5:1), 373 K)



$^{13}\text{C}$  NMR spectrum of **ZnPcPDI4** (125 MHz, *o*-dichlorobenzene- $d_4$ :pyridine- $d_5$  (V/V = 5:1), 373 K)

