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Highly Fluorescent Free-Standing Films Assembled from Perylenediimide Microcrystals for Boosting Aniline Sensing

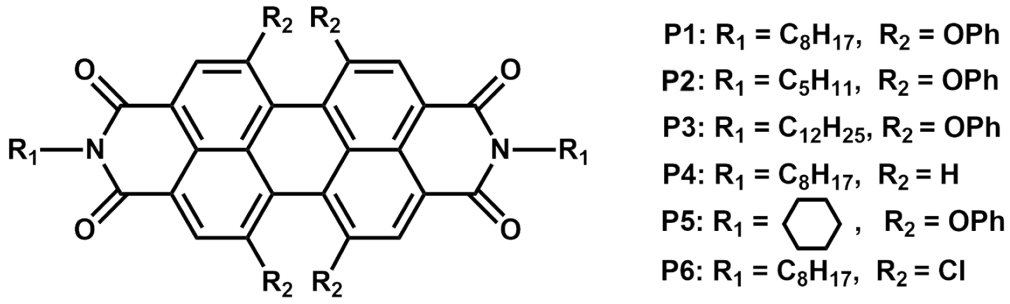
Baozhong Lü,[a] *Pengyu Li,*[a] *Pengfei Li,*[a] *Yantu Zhang**[,b], *Klaus Müllen*[c] *and Meizhen Yin**[,a]

[a]State Key Laboratory of Chemical Resource Engineering, Beijing Laboratory of Biomedical Materials, Beijing University of Chemical Technology, Beijing 100029, P. R. China

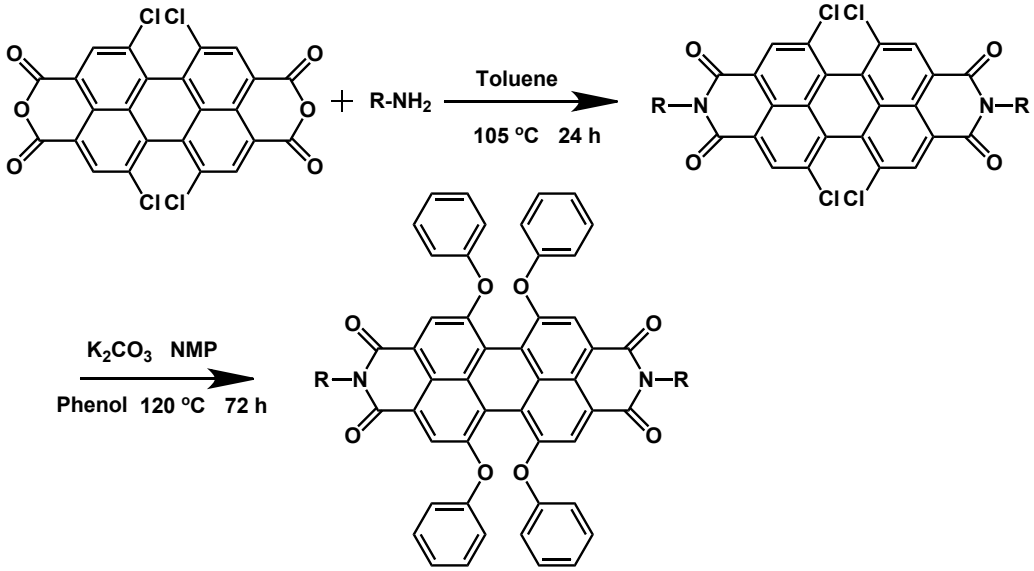
[b]College of Chemistry and Chemical Engineering, Yan'an University, Yan'an, Shaanxi Province 716000, P. R. China

[c]Max Planck Institute for Polymer Research, Institute of Physical Chemistry, Johannes Gutenberg University Mainz, Duesbergweg 10-14, 55128 Mainz, Germany.

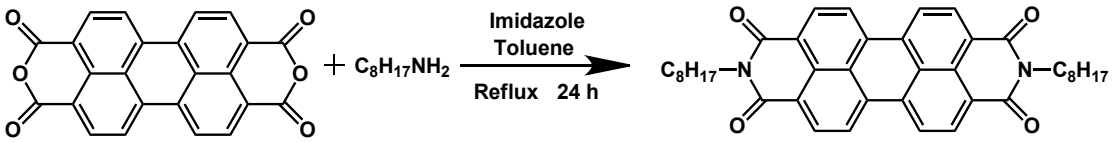
*Corresponding author, E-mail: yinmz@mail.buct.edu.cn, zhyt1969@163.com



Scheme S1 Chemical structures of **P1-P6**.



Scheme S2 Synthetic routes for **P1-P3** and **P5-P6**.



Scheme S3 Synthetic route for **P4**.

Synthesis of precursors 4Cl-PDIs and P6

4Cl-PDA (2 mmol) was stirred under nitrogen with a variety of amines (amylamine, octylamine, dodecylamine, cyclohexane respectively) (6 mmol) in toluene (60 mL) in a 250 mL round flask. The temperature was maintained at 105 ^{o}C for 24 h under N_2. After cooling to room temperature, the resulting solution was added dropwise into methanol to generate an orange precipitate. The precipitate was collected by filtration. Then the obtained solid was dried under vacuum. The crude product was purified by column chromatography on silica gel with a mixture solvent of dichloromethane/hexane (1:1) to give the product as orange red solid. Yields of precursors of **P1**, **P2**, **P3**, **P5** are 90%, 92%, 86%, and 80% respectively.

Synthesis of P1, P2, P3 and P5

4Cl-PDI (2 mmol) was stirred under N_2 with phenol (16 mmol) in N-methyl-pyrrolidone (60 mL) in a 250 mL round flask in the presence of powdered anhydrous K_2CO_3 (8 mmol). The temperature was maintained at 120 ^{o}C for 72 h under N_2. After cooling to room temperature, the resulting solution was added dropwise into a solvent mixture of methanol and 5 wt% aqueous citric acid (v/v=1/1) to generate a red precipitate. The precipitate was collected by filtration. Then the obtained solid was washed with saturated aqueous NaCl to neutral pH, and dried under vacuum. The crude product was purified by column chromatography on silica gel with a mixture solvent of dichloromethane/hexane (16:9) to give the product as a red solid. Yields of **P1**, **P2**, **P3**, **P5** are 85%, 88%, 78% and 72% respectively.

Synthesis of P4

Perylene-3,4,9,10-tetracarboxylic dianhydride (0.1 mmol), octylamine (0.3 mmol) and imidazole (1 g) in toluene (20 ml) were heated to reflux under a nitrogen atmosphere and kept at reflux for 24 h. The solvent was removed under reduced pressure and the residue was washed with dilute hydrochloric acid (10%, 100 mL) and then water. The product was purified by column chromatography with chloroform as the eluent, and

collected as a dark red solid with a yield of 80 %. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.69 (m, 8H), 4.24 (t, 4H), 1.81 (m, 4H), 1.31 (m, 20H), 0.91 (t, 6H).

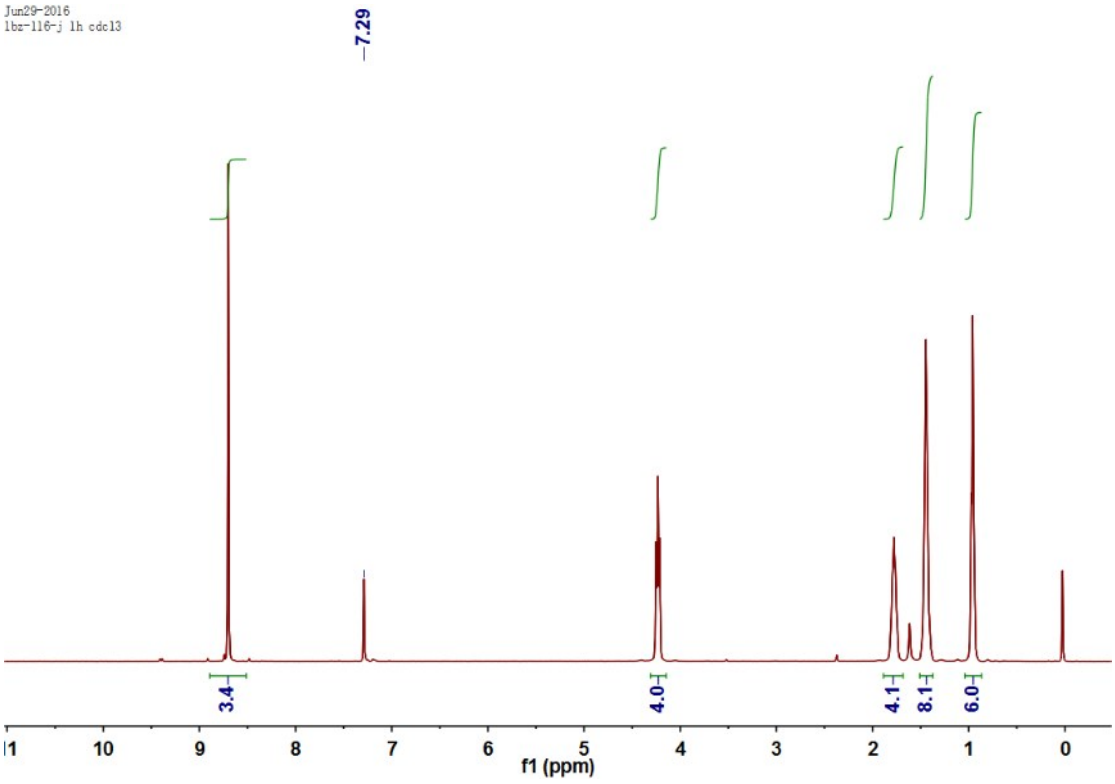


Fig. S1 ^{1}H NMR spectrum of **P2** precursor.

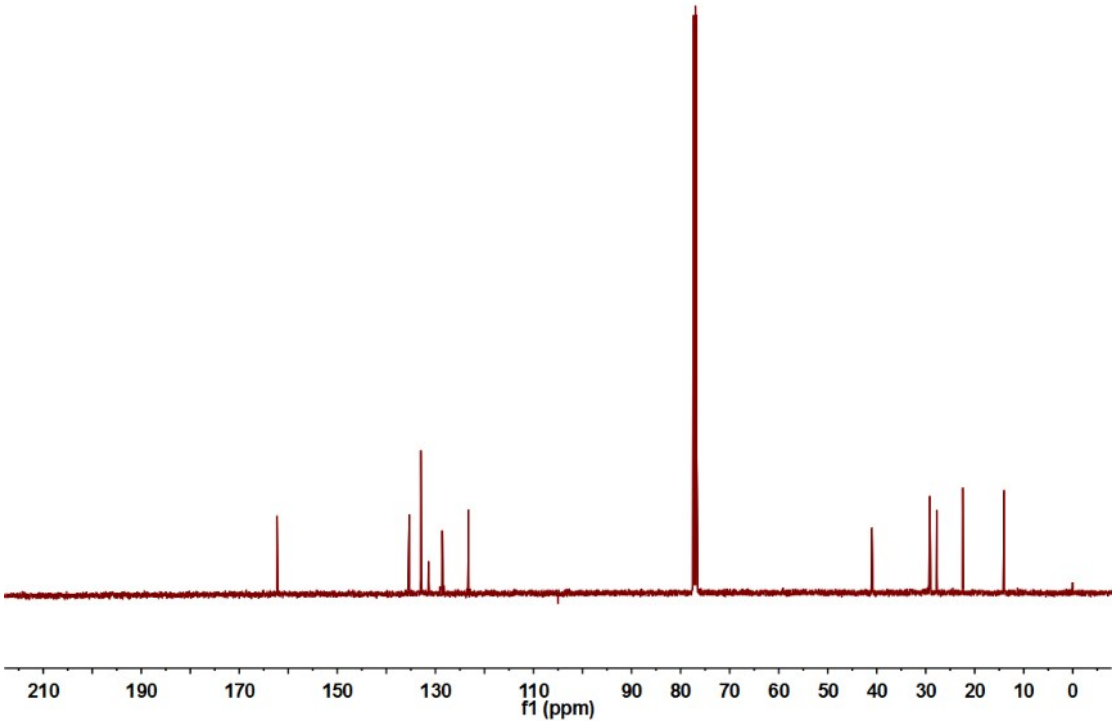


Fig. S2 ^{13}C NMR spectrum of **P2** precursor.

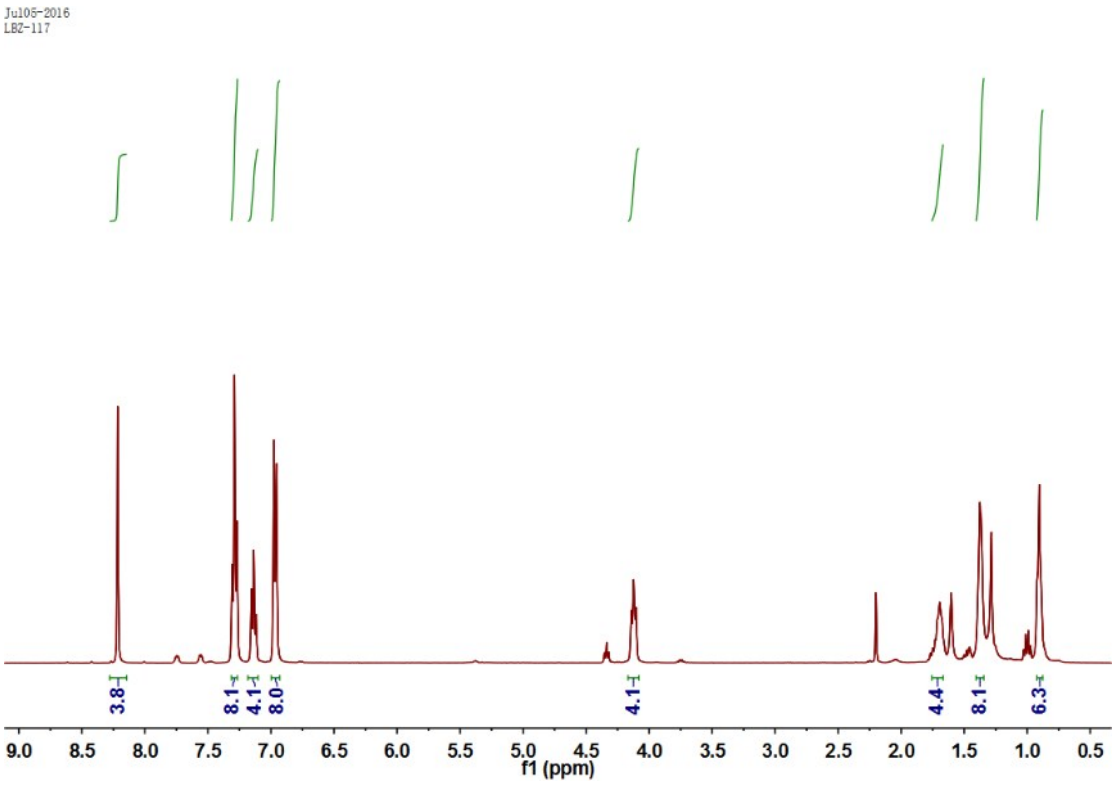


Fig. S3 ^{1}H NMR spectrum of **P2**.

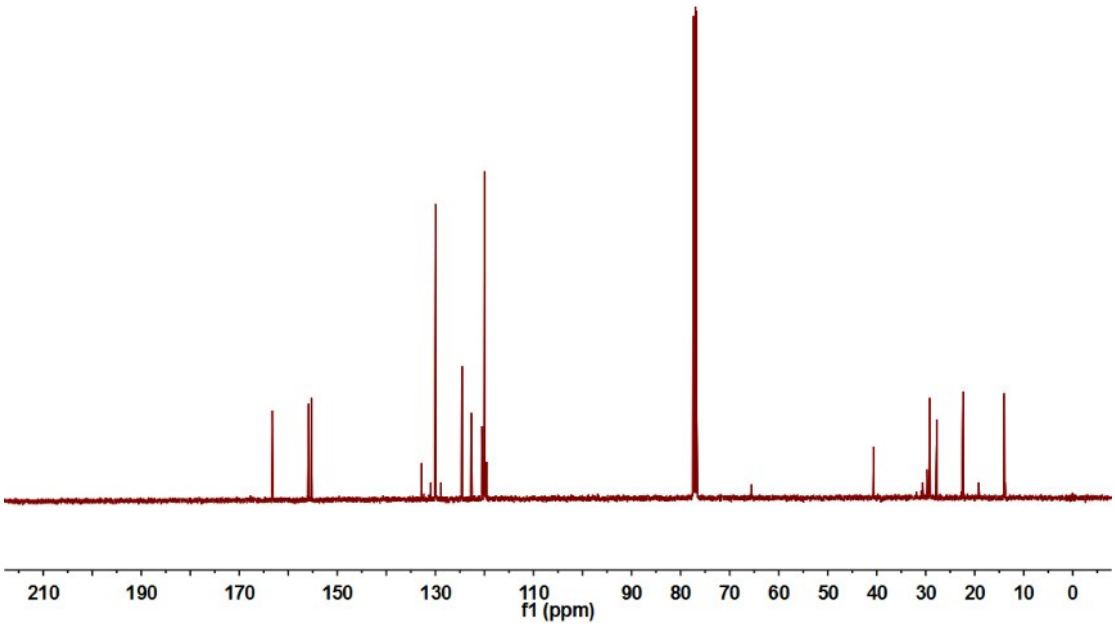


Fig. S4 ^{13}C NMR spectrum of **P2**.

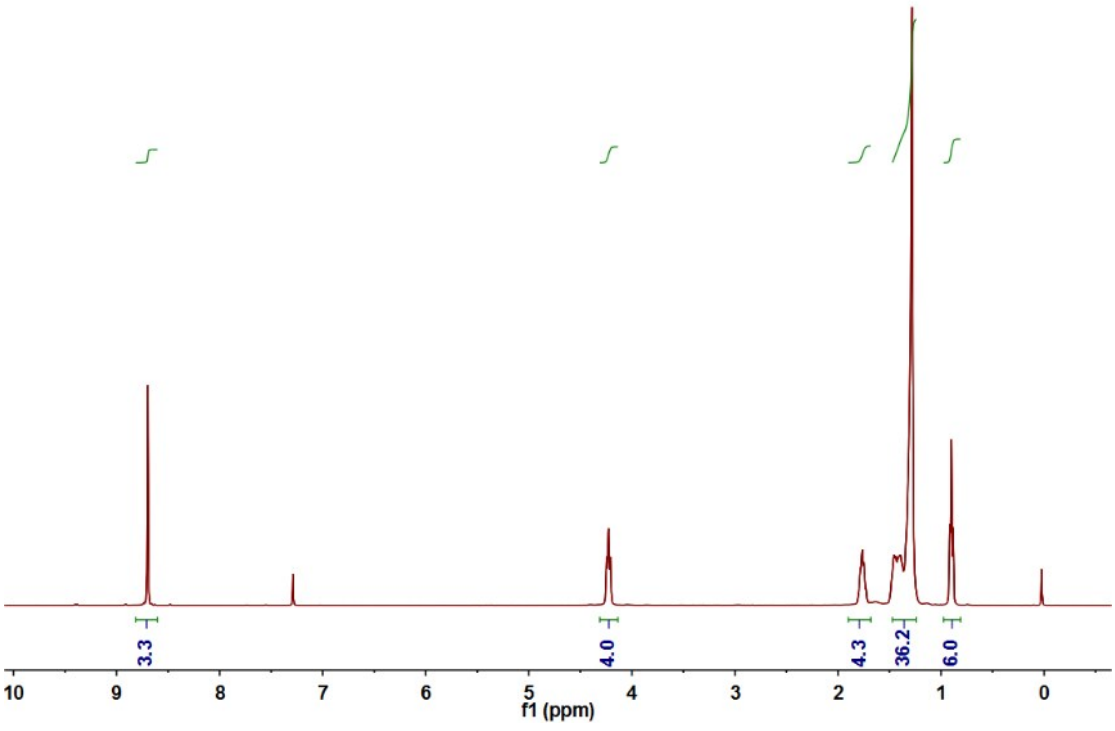


Fig. S5 ^{1}H NMR spectrum of precursor **P3** precursor.

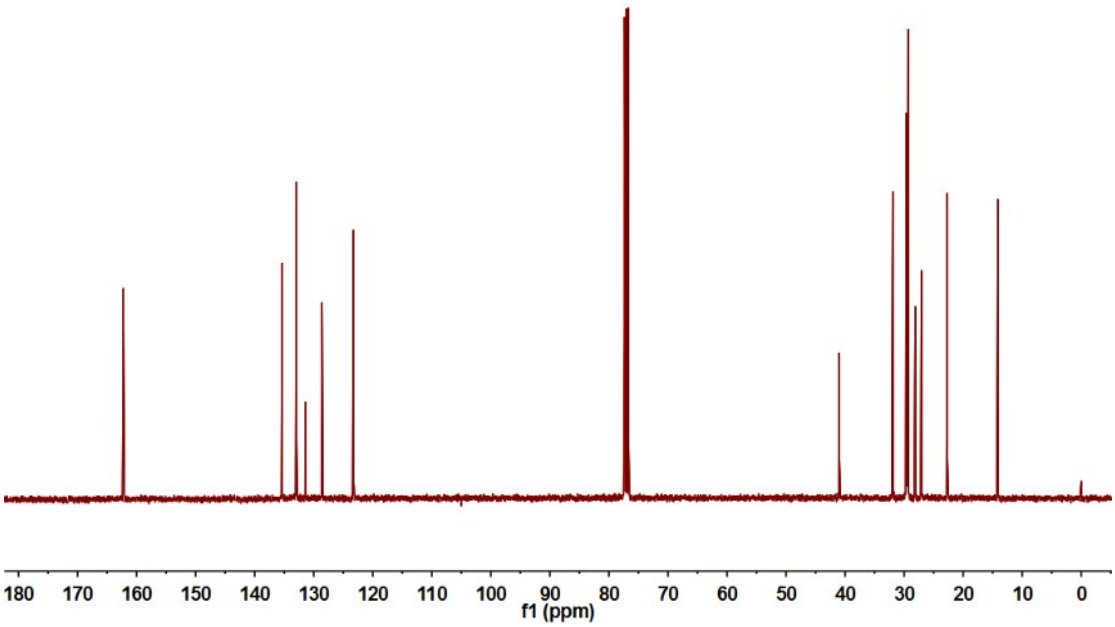


Fig. S6 ^{13}C NMR spectrum of **P3** precursor.

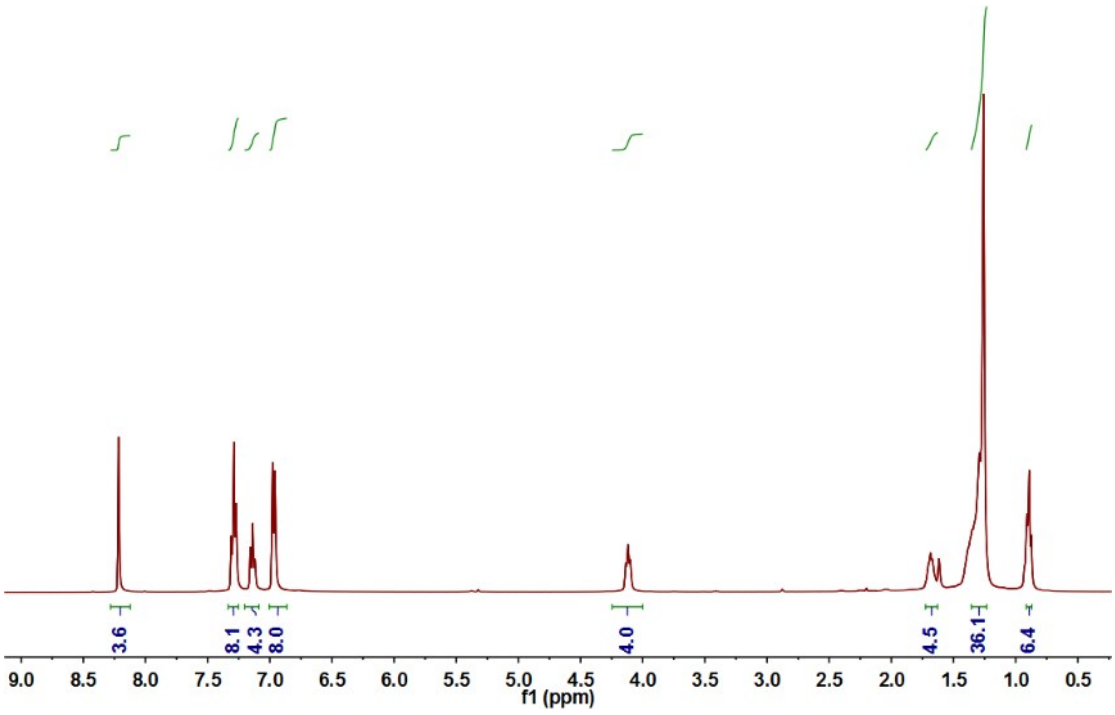


Fig. S7 ^{1}H NMR spectrum of **P3**.

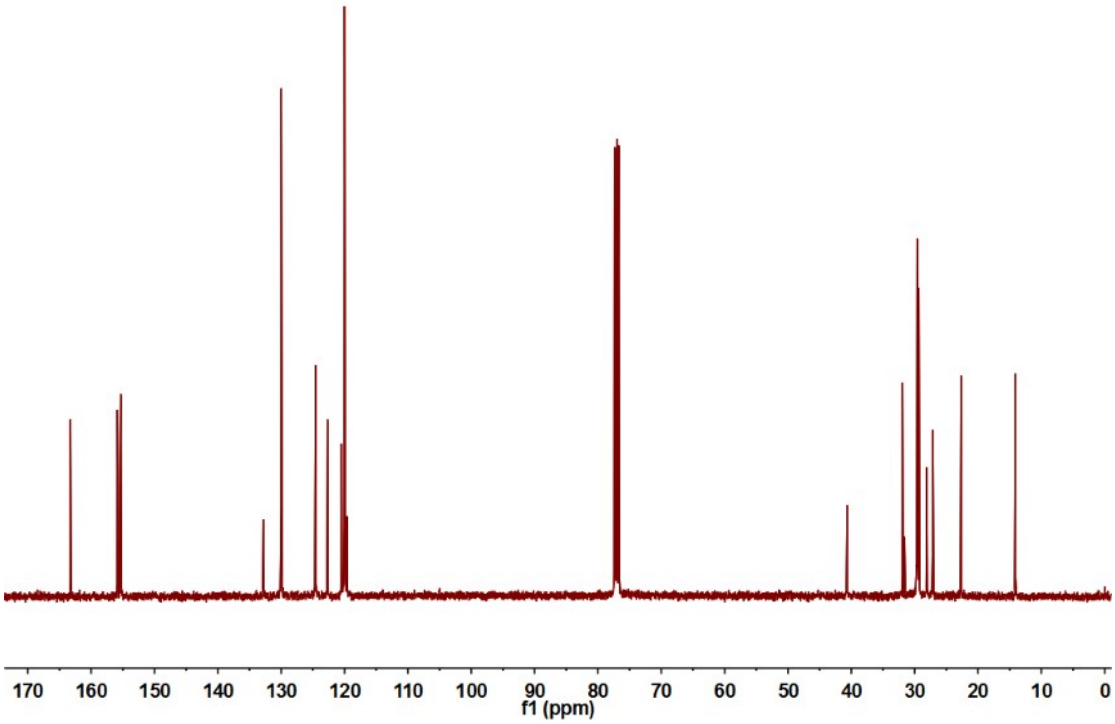


Fig. S8 ^{13}C NMR spectrum of **P3**.

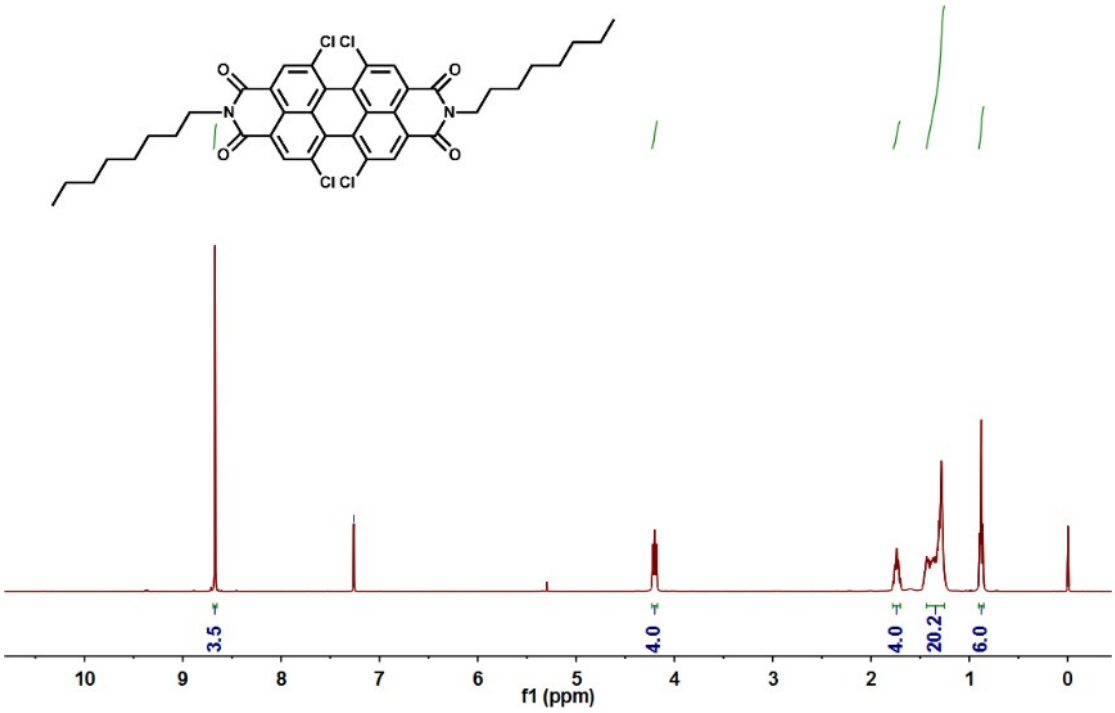


Fig. S9 ^{1}H NMR spectrum of **P1** precursor (**P6**).

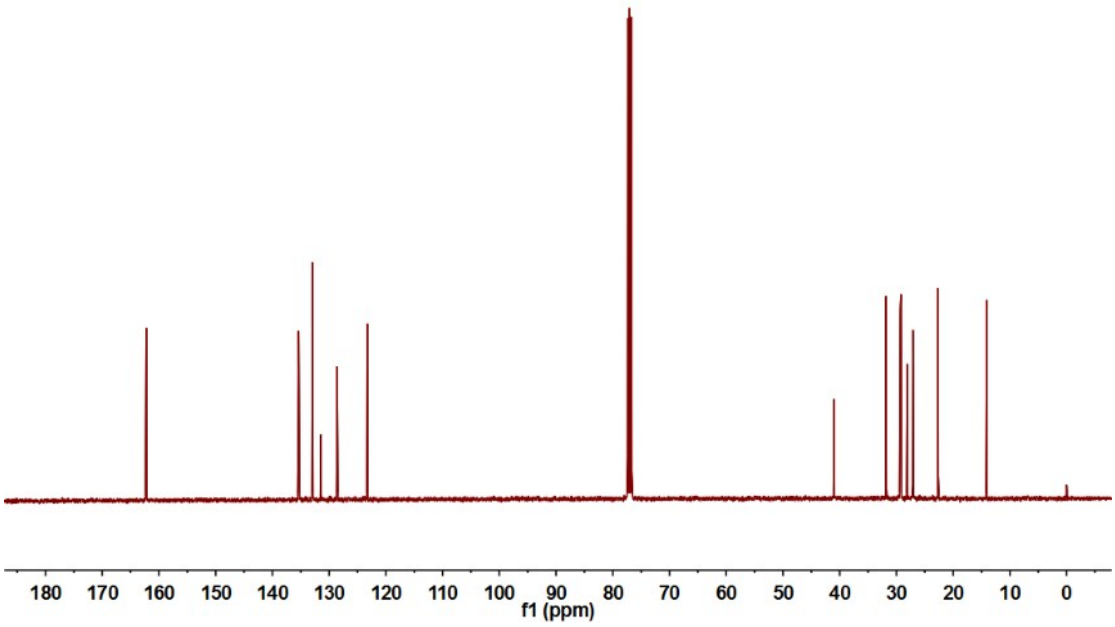


Fig. S10 ^{13}C NMR spectrum of **P1** precursor (**P6**).

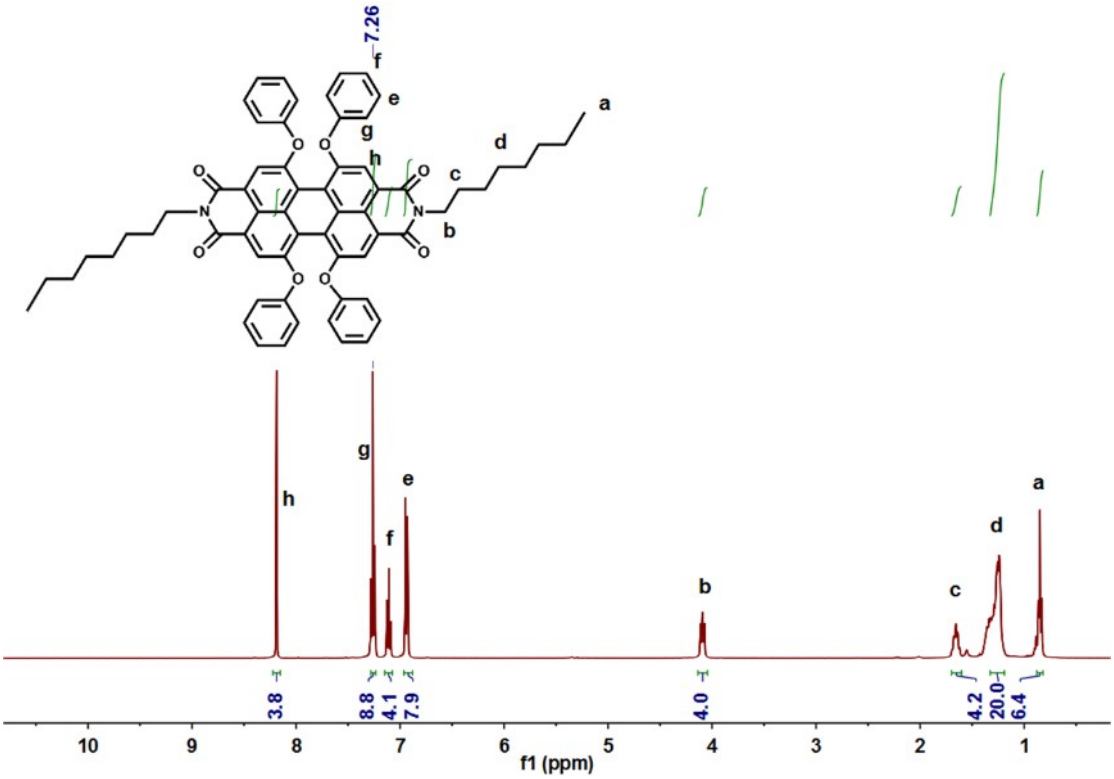


Fig. S11 ^{1}H NMR spectrum of **P1**.

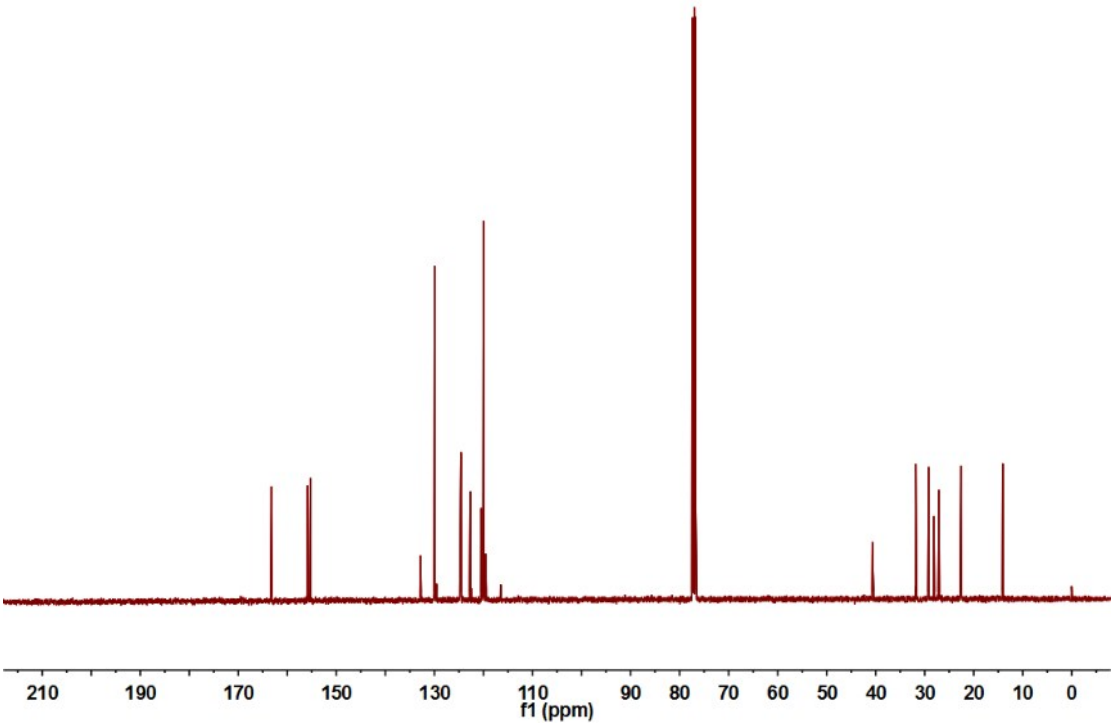


Fig. S12 ^{13}C NMR spectrum of **P1**.

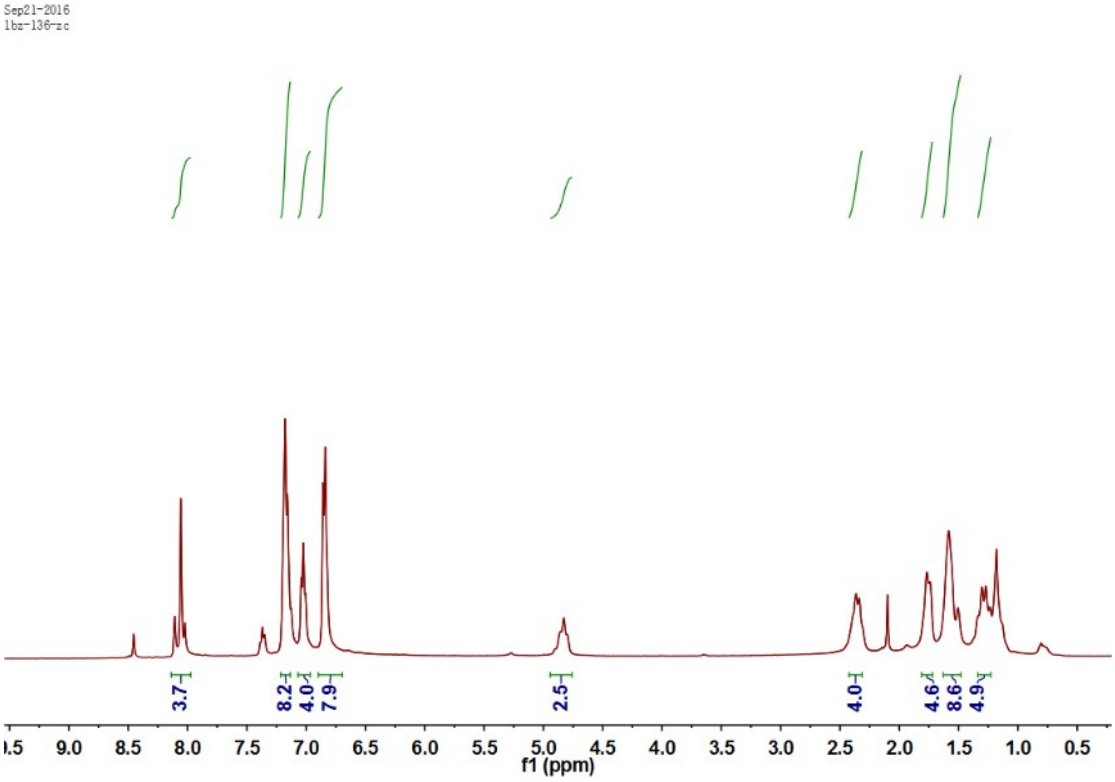


Fig. S13 ^{1}H NMR spectrum of **P5**.

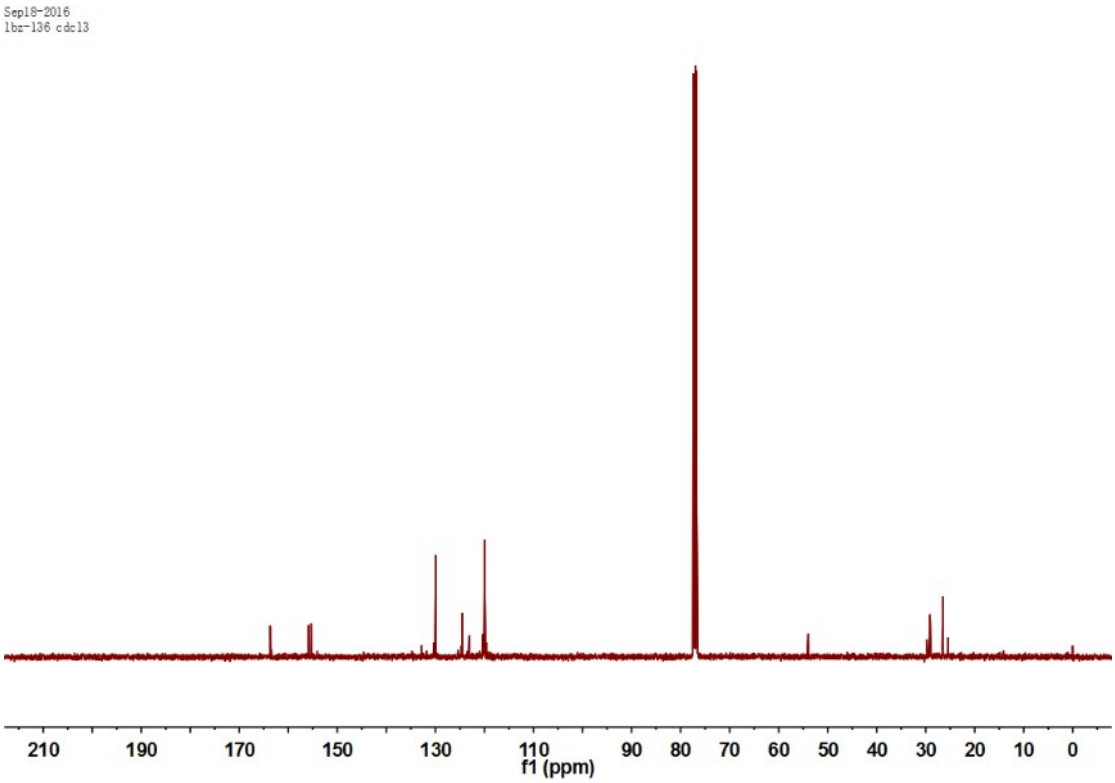


Fig. S14 ^{13}C NMR spectrum of **P5**.

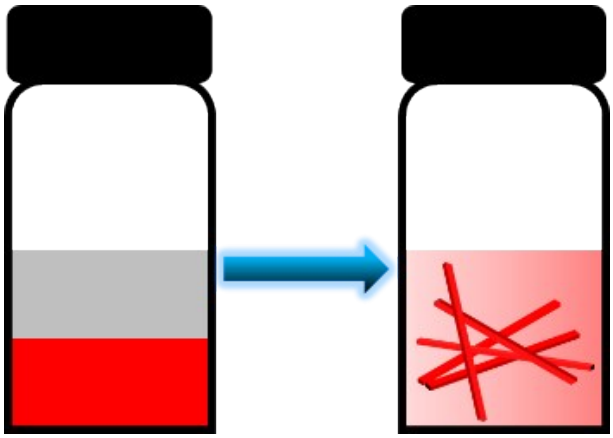


Fig. S15 Schematic diagram of self-assembly toward micocrystals.

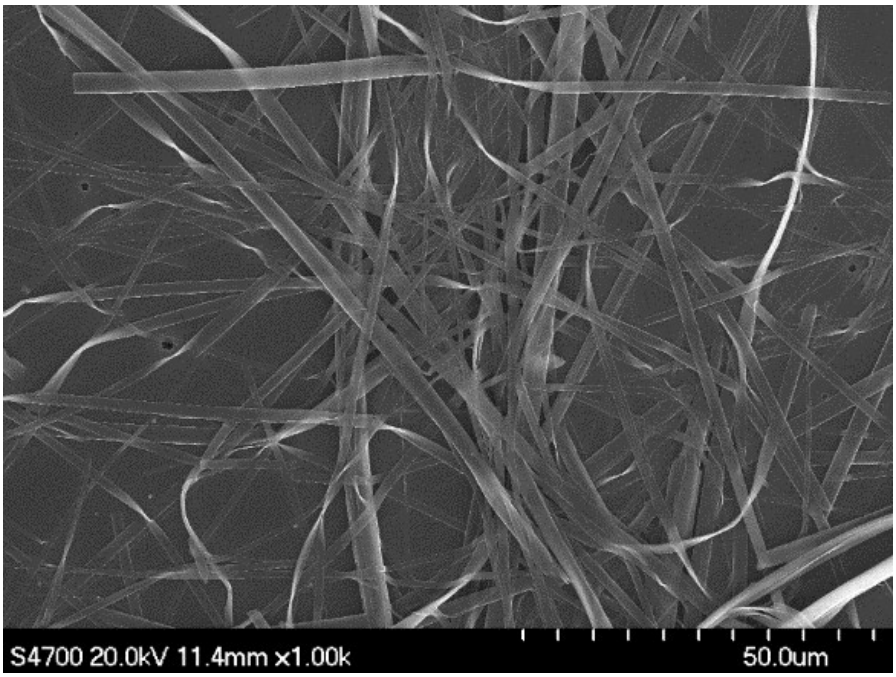


Fig. S16 SEM image of **P2** microcrystals.

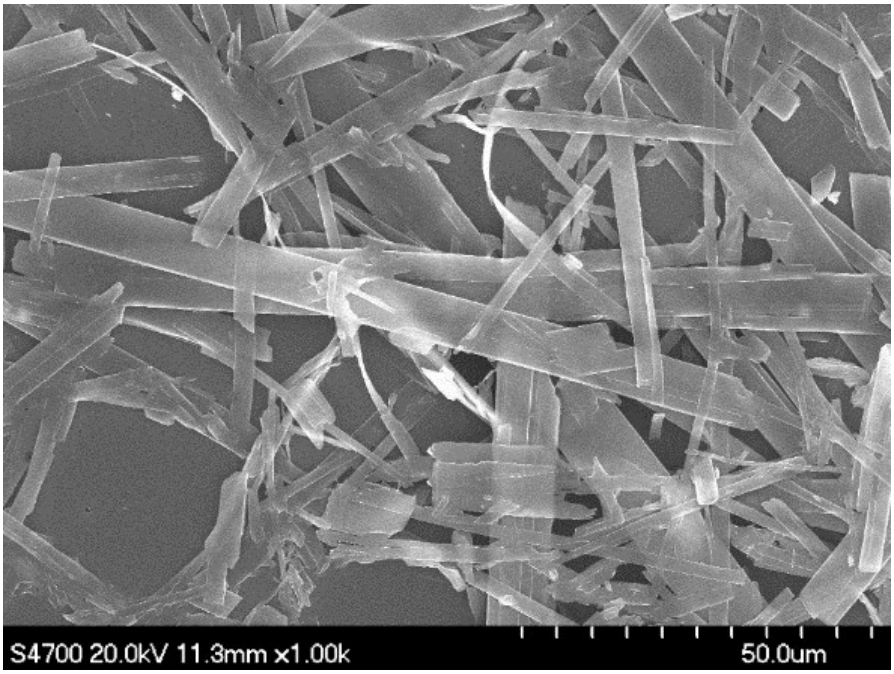


Fig. S17 SEM image of **P3** microcrystals.

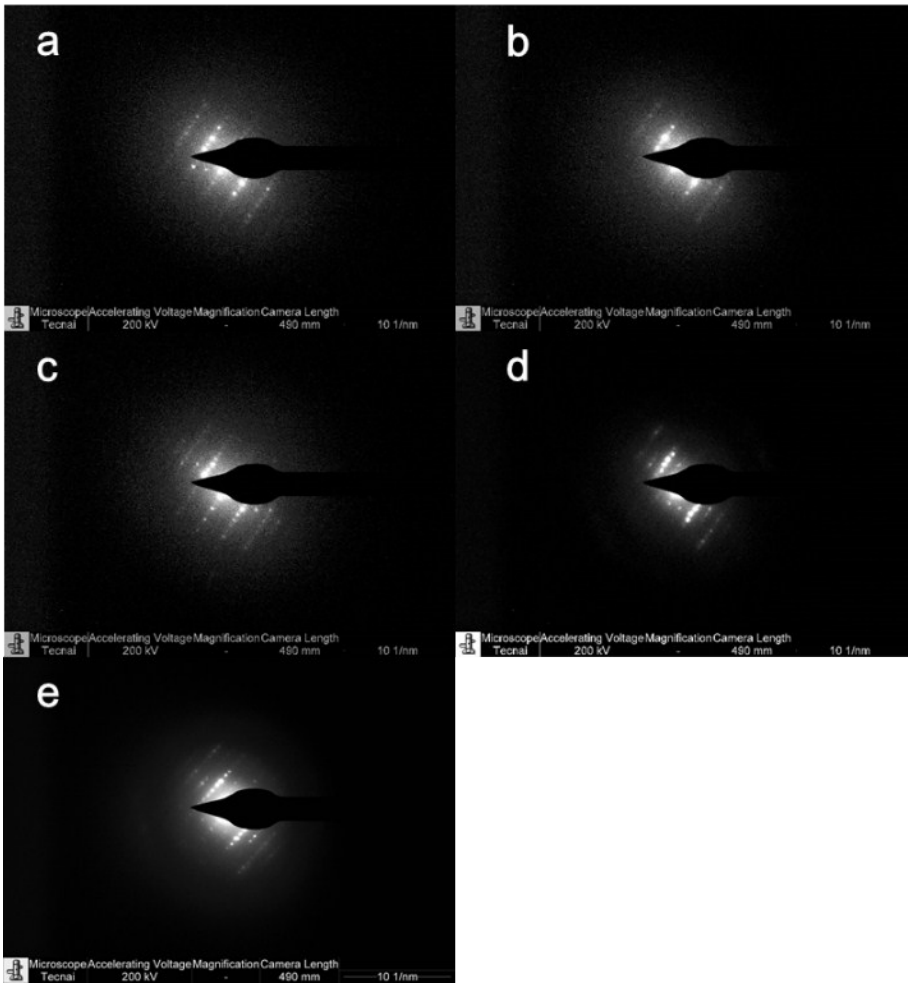


Fig. S18 Five continuous electron diffraction images recorded at different positions along the long axis of the same microcrystal of **P1**. The same diffraction pattern indicates the single crystalline phase of the whole microcrystal.

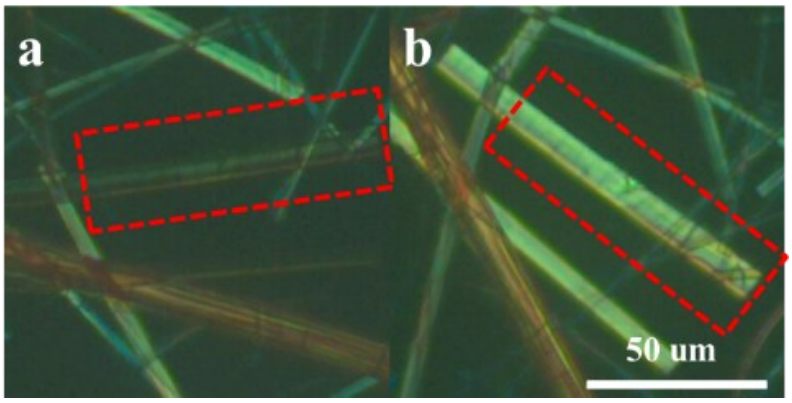


Fig. S19 Polarizing optical microscopy (POM) images of **P1** micropcrystals, b is the corresponding visions of a deflection of 45°.

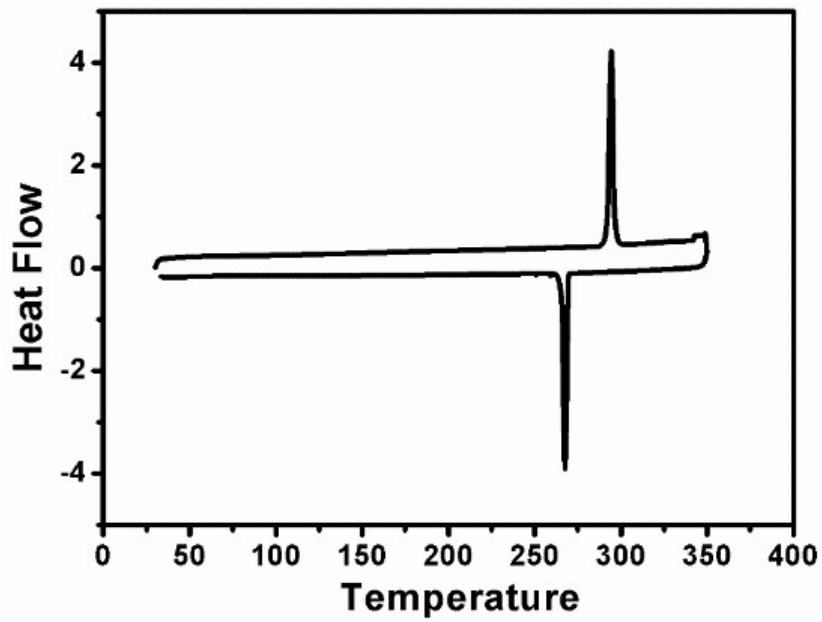


Fig. S20 DSC heat-cool thermogram of the dry **P1** films at a heating rate of 10 °C/min and cooling rate of 5 °C/min under N_2 flow.

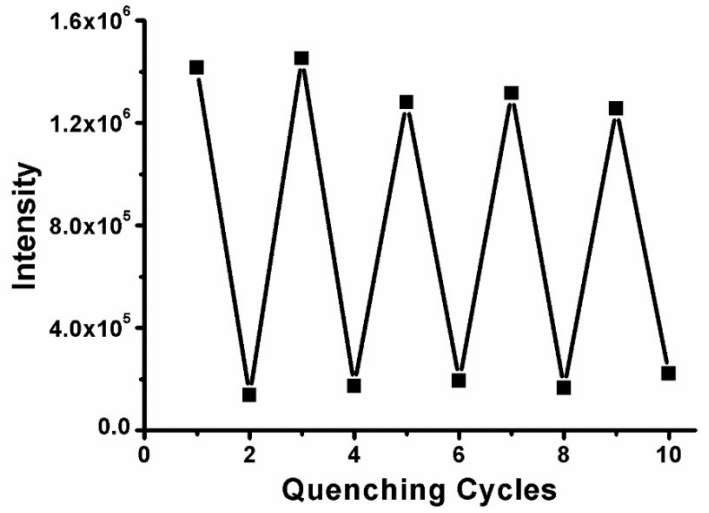


Fig. S21 Cycles of fluorescence quenching and recovery.

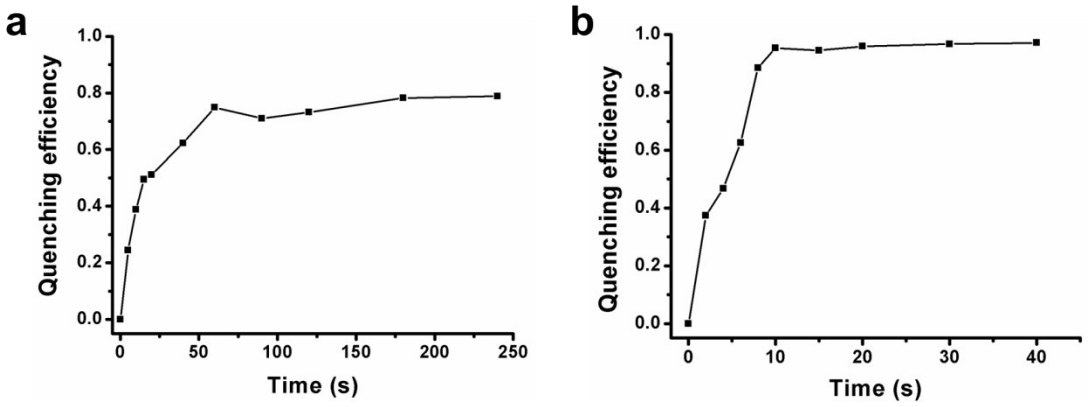


Fig. S22 Fluorescence response of (a) **P1** powders and (b) **P1** FFSF to the presence of aniline. **P1** powders showed an inferior response to aniline with a quenching efficiency of 79% in 240 s, while **P1** FFSF showed a quick response to aniline with a quenching efficiency of 97% in 40 s.

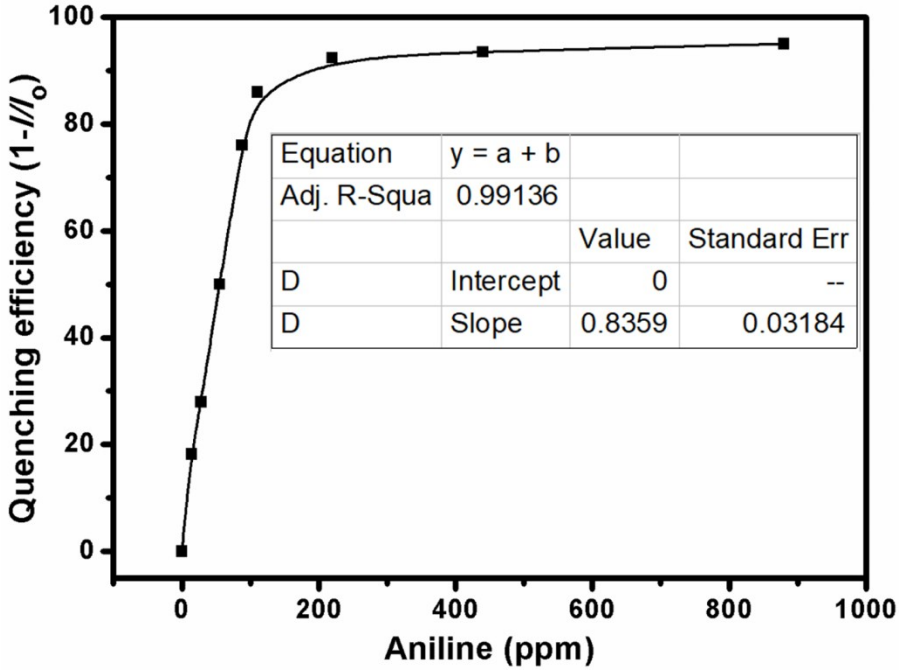


Fig. S23 Fluorescence quenching efficiency as a function of the concentration of aniline vapor.

The calibration curve was obtained from the plot of fluorescence quenching efficiency against the concentration of aniline vapor (Fig. S24).

LOD= 3×S.D/k

Where k is the slope of curve equation, and S.D. represents the standard deviation for fluorescence quenching efficiency of **P1** FFSF in the absence of aniline vapor.

$y=0.836x$ ($R^2=0.991$)

LOD=3×0.03/0.836= 0.1 ppm

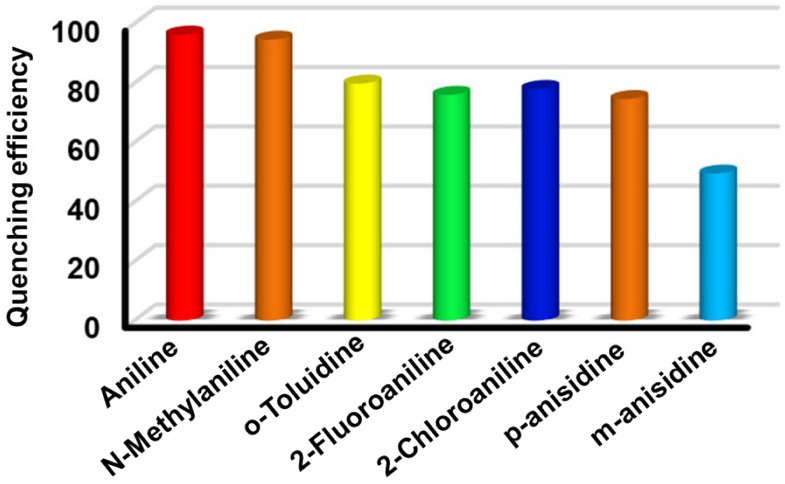


Fig. S24 Fluorescence response of a **P1** film to the presence of aniline and its analogue vapors at the same temperature.

Table S1 Comparison with previously reported aniline sensing materials.

Contrast Sample	Detection limit	Quenching efficiency	Reference
PDI-Cyclodextrin	33 ppm	80% (irreversible)	[1]
PTCDI	200 ppt	95% (irreversible)	[2]
C12PhBPVB	1.16 ppm	95% (6 cycles)	[3]
C12PhBPCP	769 ppt	80% (4 cycles)	[4]
P1 FFSF	0.1 ppm	97% (5 cycles)	This work

Supplementary References

[1] Liu, Y.; Wang, K. R.; Guo, D. S.; Jiang, B. P. Supramolecular Assembly of Perylene Bisimide with β-Cyclodextrin Grafts as a Solid-State Fluorescence Sensor for Vapor Detection. *Adv. Funct. Mater.* **2009,** *19*, 2230-2235.

[2] Che, Y.; Yang, X.; Loser, S.; Zang, L. Expedient Vapor Probing of Organic Amines Using Fluorescent Nanofibers Fabricated From an n-Type Organic Semiconductor. *Nano Lett.* **2008,** *8*, 2219-2223.

[3] Xue P.; Xu Q.; Gong P.; Qian C.; Ren A.; Zhang Y.; Lu R. Fibrous Film of A Two-Component Organogel as A Sensor to Detect and Discriminate Organic Amines. *Chem. Commun.* **2013**, *49*, 5838-5840.

[4] Xue P.; Yao B.; Wang P.; Gong P.; Zhang Z.; Lu R. Strong fluorescent smart organogel as a dual sensing material for volatile acid and organic amine vapors. *Chem. Eur. J* **2015**, *21*, 17508-17515.