

Electronic Supplementary Information (ESI) for

Laminated nanotapes fabricated from conformation specific self-assembly of *N*-annulated perylene derivatives

Kai Sun, Yan Li,* and Wenxin Fu*

Beijing National Laboratory for Molecular Science (BNLMS), Institute of Chemistry,
Chinese Academy of Sciences, Beijing 100190, China

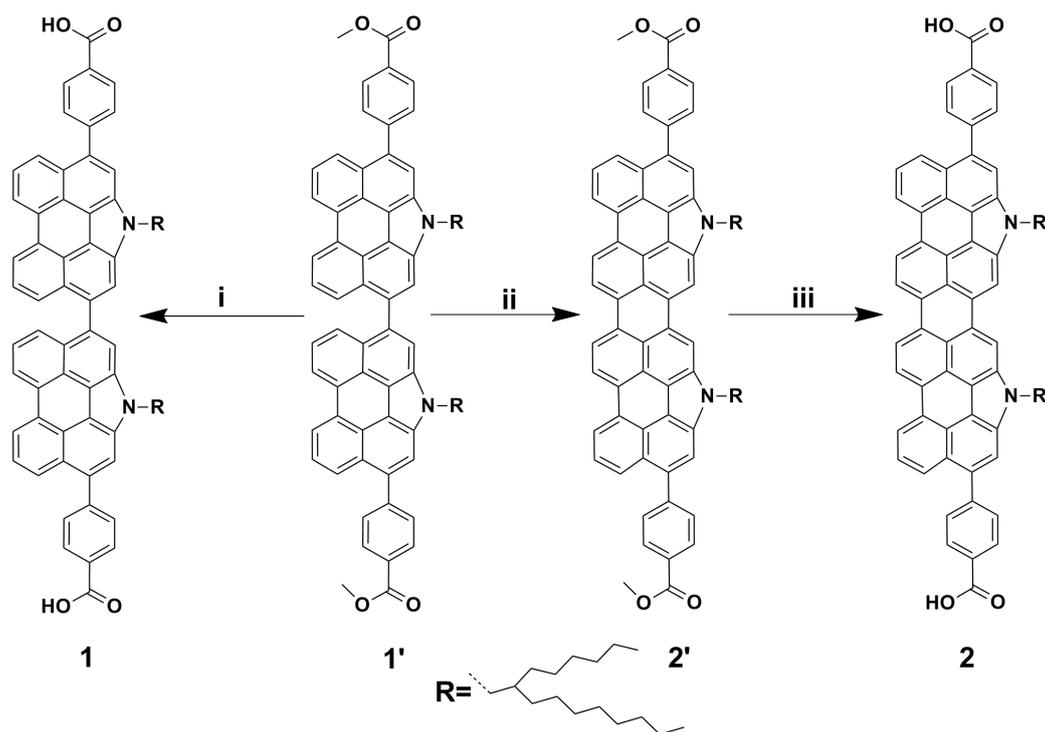
*Corresponding authors, email: fuwenxin@iccas.ac.cn, yanli@iccas.ac.cn

1. Materials and methods

¹H NMR and ¹³C NMR spectra were recorded in deuterated solvents on a Bruker ADVANCE 400NMR Spectrometer. ¹H NMR chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard. Mass spectra (MALDI-TOF-MS) were determined on a Bruker BIFLEX III Mass spectrometer. High resolution mass spectra (HRMS) were determined on Bruker Apex IV Fourier Transform Mass Spectrometer. Elemental analysis was determined on Flash EA 1112. UV/Vis absorption spectra were measured with a Jasco V-570 UV-Vis-NIR spectrophotometer in a 1-cm quartz cell. Fluorescence spectra were recorded on a Jasco FP-6600 spectrofluorometer and all fluorescence spectra were normalized. X-ray diffraction (XRD) analysis was performed on a Rigaku D/MAX 2500 diffractometer. SEM measurement was performed with JEOL-6700 field-emission scanning electron microscope. Cryo-TEM samples were prepared in a controlled environment vitrification system (CEVS) at 28 °C. The vitrified samples were then stored in liquid nitrogen until they were transferred to a cryogenic sample holder (Gatan 626) and examined using a JEM-2200FS TEM (200 KV) at about - 174 °C. SAED images were obtained from Hitachi H-800 instrument.

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

2. Synthesis of NPD 1 and 2



Scheme S1 Synthetic route of **1** and **2**: (i) KOH, THF, 66 °C, 24 h, 98%; (ii) Sc(OTf)₃, DDQ, toluene, 110 °C, 8 h, 60%; (iii) KOH, THF, 66 °C, 24 h, 98%.

Starting material **1'** was synthesized according to the method previously developed in our lab.¹

NPD 1:

A solution of 540 mg (30 equiv) KOH in 2 mL water and 8 mL methanol was added to a 400 mg (1 equiv) NPD **1'** dissolved in 50 mL THF under an inert atmosphere and refluxed for 24 h. When the mixture was cooled down to room temperature, 2 mL 25% hydrochloric acid was added dropwise and stirred for 30 min. The mixture was poured into water and the product was extracted with toluene and THF (1:3, v/v). The organic layer was separated, dried with sodium sulfate, and the solvent was removed under reduced pressure. The remaining precipitate was filtered, washed with hexane and dried under vacuum to yield the yellow solid product (383 mg, 98%).

¹H NMR (THF-*d*₈, 400 MHz, 298 K): δ = 8.83-8.78 (dd, 4H), 8.27 (d, 4H), 8.20-8.16 (m, 4H), 8.00 (s, 2H), 7.88 (d, 4H), 7.82-7.79 (m, 4H), 7.64 (t, 2H), 4.78 (m, 4H), 2.43 (m, 2H), 1.46-1.12 (m, 48H), 0.75-0.73 (m, 12H). ¹³C NMR (THF-*d*₈, 100 MHz, 298 K): δ = 167.8, 147.7, 137.9, 137.6, 133.7, 133.4, 132.0, 131.7, 131.2, 130.9, 130.8, 130.6, 129.8, 126.1, 125.9, 125.8, 125.6, 124.8, 122.2, 122.1, 118.4, 118.0, 116.9, 115.8, 115.8, 41.1, 33.0, 32.9, 32.9, 32.8, 31.2, 31.1, 30.9, 30.8, 30.6, 30.4,

27.5, 27.4, 23.6, 14.5, 14.5. MS (MALDI-TOF): m/z (M^+) = 1216.6 (calcd for $C_{86}H_{92}N_2O_4$: 1216.7). HRMS $[M]^+$: 1216.70585 (calcd for $C_{86}H_{92}N_2O_4^+$: 1216.70516).

NPD 2':

A mixture of NPD **1'** (300 mg, 1 equiv), $Sc(OTf)_3$ (592 mg, 5 equiv), DDQ (274 mg, 5 equiv) in 50 mL toluene was stirred at 110 °C for 8 h under nitrogen. After cooling down to room temperature, 0.5 mL $N_2H_4 \cdot H_2O$ was added and stirred for 30 min. The solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography on silica gel (THF/ CH_2Cl_2 , 1/10) to yield the deep black solid product (180 mg, 60%).

MS (MALDI-TOF): m/z (M^+) = 1242.6 (calcd for $C_{88}H_{94}N_2O_4$: 1242.7). Elemental analysis: calcd (%) for $C_{88}H_{94}N_2O_4$: C 84.98, H 7.62, N 2.25; found C 83.36, H 7.59, N 2.39. FT-IR (KBr) ν [cm^{-1}]: 1724 for C=O stretching frequency and 1282 for CO-O-C stretching frequency.

NPD 2:

A solution of 202 mg (30 equiv) KOH in 1 mL water and 4 mL methanol was added to a 150 mg (1 equiv) NPD **2'** dissolved in 30 mL THF under an inert atmosphere and refluxed for 24 h. When the mixture was cooled down to room temperature, 1 mL 25% hydrochloric acid was added dropwise and stirred for 30 min. The mixture was poured into water and the product was extracted with toluene and THF (1:3, v/v). The organic layer was separated, dried with sodium sulfate, and the solvent was removed under reduced pressure. The remaining precipitate was filtered, washed with hexane and dried under vacuum to yield the deep black solid product (143 mg, 98%).

MS (MALDI-TOF): m/z (M^+) = 1214.6 (calcd for $C_{86}H_{90}N_2O_4$: 1214.7). HRMS $[M]^+$: 1214.69015 (calcd for $C_{86}H_{90}N_2O_4^+$: 1214.68951). FT-IR (KBr) ν [cm^{-1}]: 1686 for C=O stretching frequency and 1259 for CO-O-C stretching frequency.

3. Additional Results

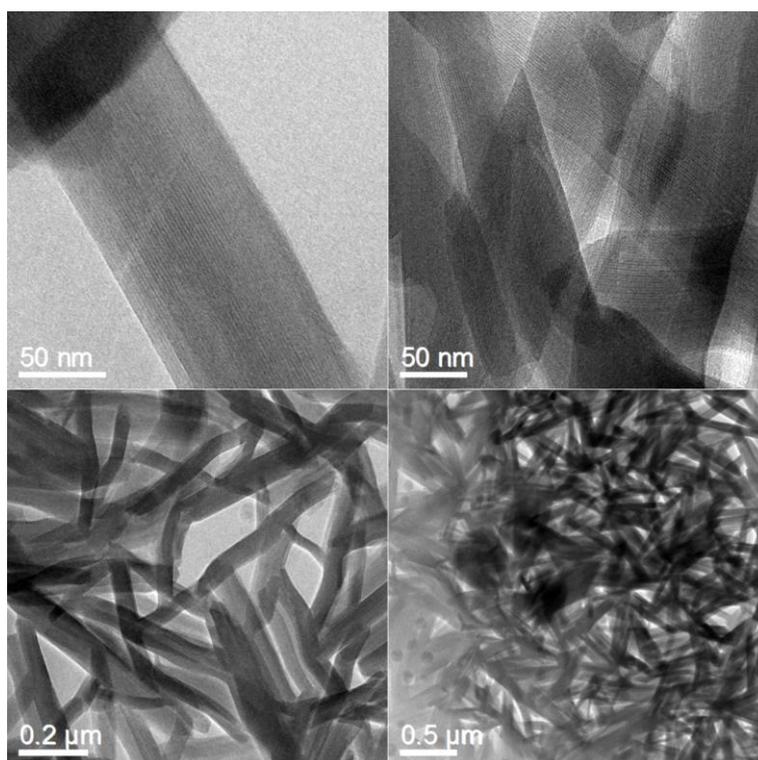


Fig. S1 Cryo-TEM images of assemblies formed from **1** in 1 mM THF.

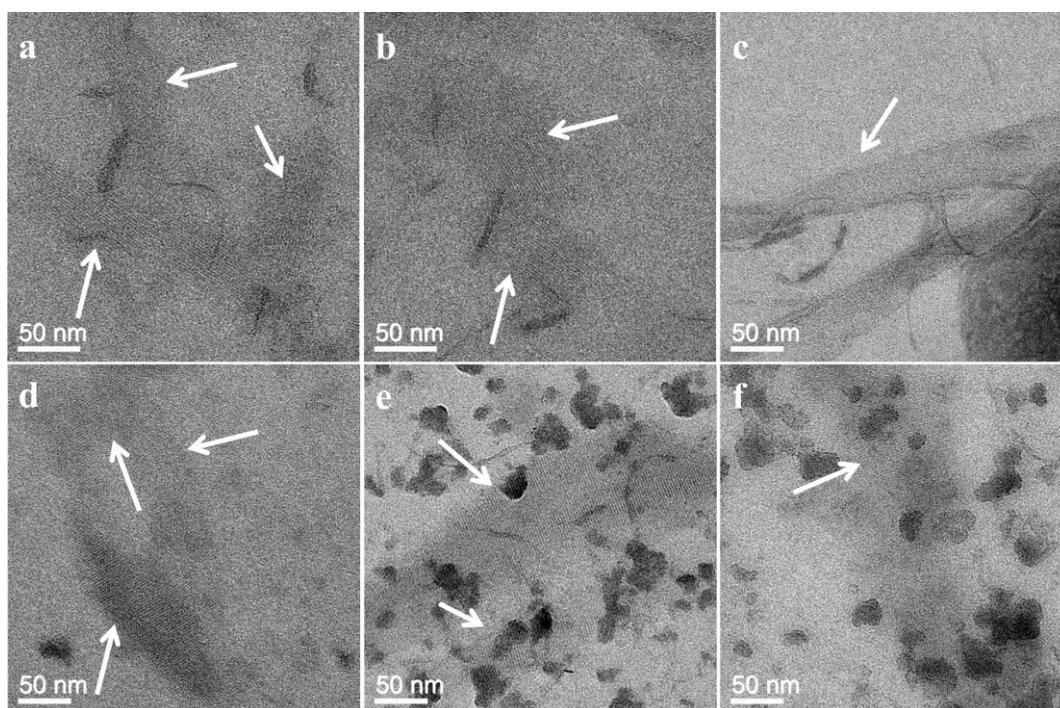


Fig. S2 Cryo-TEM images of assemblies formed from **1** (a, b, c) and **2** (d, e, f) in THF: (a, d) 10^{-4} M; (b, e) 10^{-5} M; (c, f) 10^{-6} M. The white arrows in images are directing to nanotapes. While the dark aggregates represent some aggregates formed from water vapor during sample preparation and transferring.

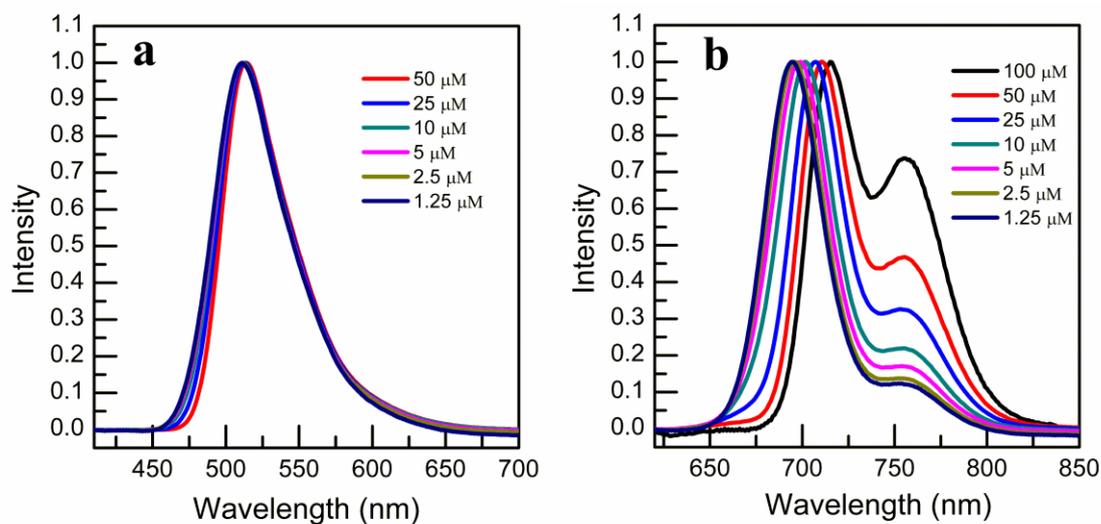
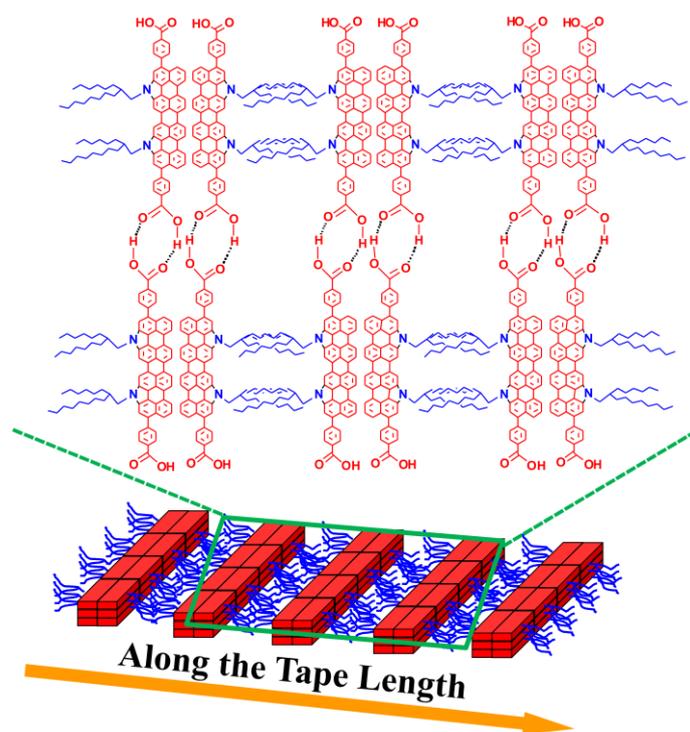


Fig. S3 Fluorescence spectra of **1** (a) and **2** (b) in THF at different concentrations. The spectra are both normalized ($\lambda_{\text{ex}} = 400$ nm for **1** and 610 nm for **2**, respectively).



Scheme S2 Schematic illustration of self-assembly mechanism for **2** with head-to-head and tail-to-tail model. The black dash line represents hydrogen bonds.

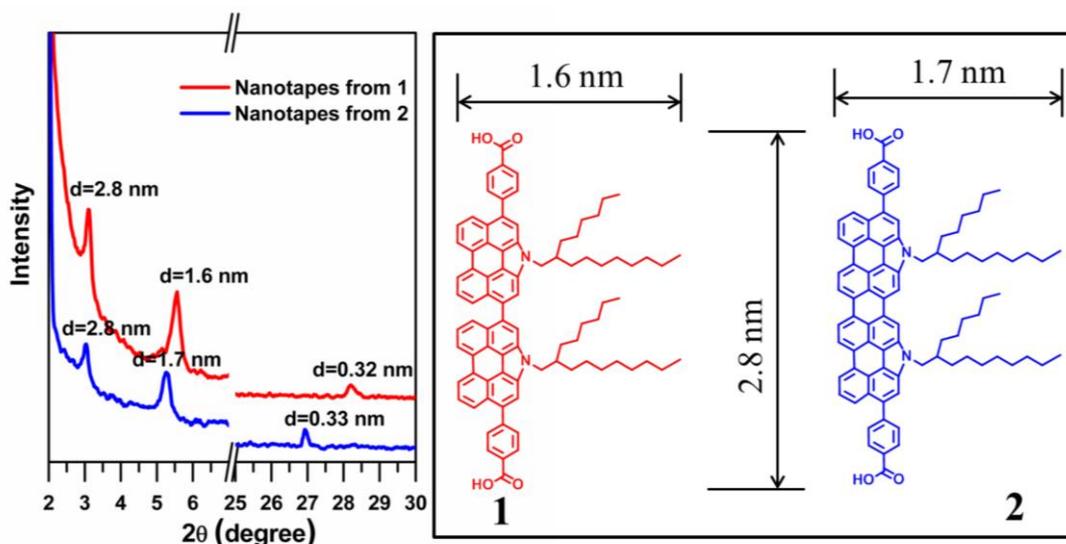


Fig. S4 XRD patterns of nanotapes from **1** and **2**, and corresponding molecular dimensions.

In order to further confirm the proposed mechanisms of nanotapes formed from the two N-annulated perylene derivatives, we conducted XRD measurements. There are three diffraction peaks in the XRD profiles in **Fig. S4**. As for nanotapes from **1**, the corresponding *d* values are 2.8 nm (the length of fully extended molecules), 1.6 nm (the width of molecules) and 0.32 nm (π - π stacking distance), respectively, while for **2**, which are 2.8 nm, 1.7 nm and 0.33 nm. Due to the different π -system and solvent-solute interaction, π - π interaction changes, which cause different π - π stacking distances.²

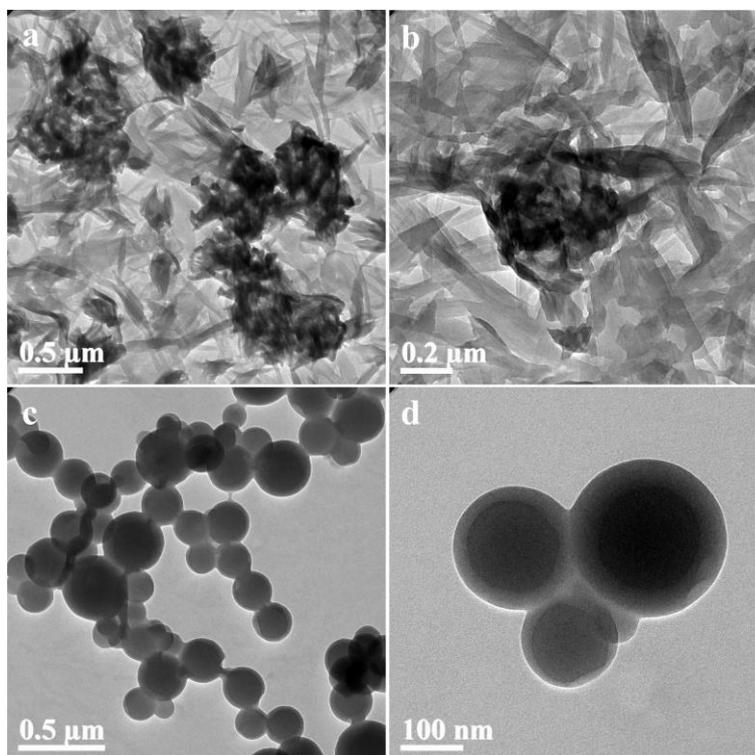


Fig. S5 TEM images of assemblies formed from **1'** (**a**, **b**) and **2'** (**c**, **d**) in 1 mM THF.

We conducted the self-assembly experiments of two esters, **1'** and **2'**, and compared the differences between esters and carboxylic acids using TEM. For esters, the corresponding aggregates of **1'** and **2'** in 1 mM THF are nanostrips and nanospheres, respectively (**Fig. S5**). The nanostrips tend to aggregate to form amorphous structures. These results revealed that hydrogen bonds play an important role in self-assembly process.

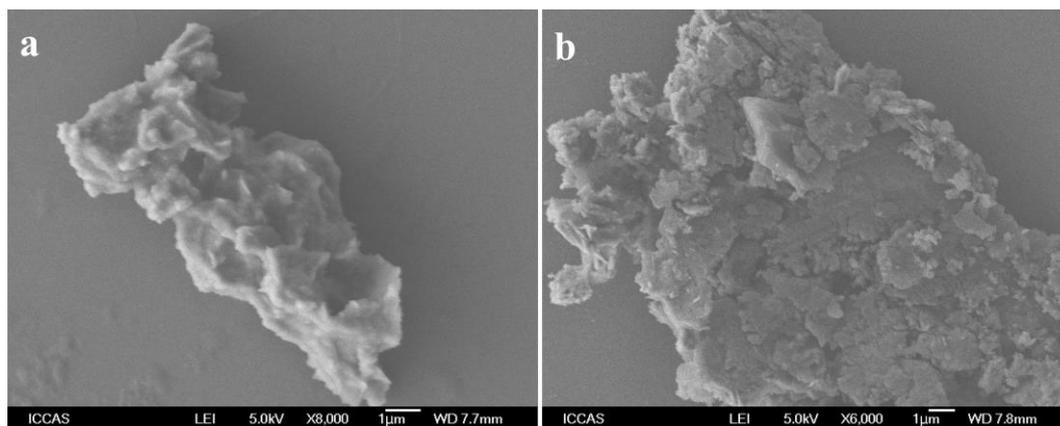


Fig. S6 SEM images of assemblies formed from **2** in THF/toluene mixed solvents: (a) in THF/toluene (1/3, v/v) mixed solvents ($C = 0.25$ mM); (b) in THF/toluene (1/9, v/v) mixed solvents ($C = 0.1$ mM), respectively.

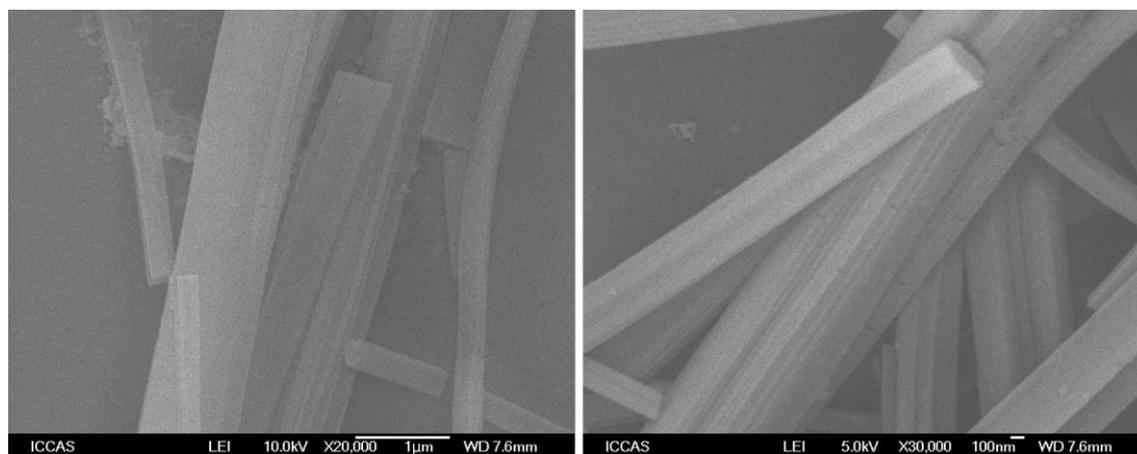


Fig. S7 SEM images of assemblies formed from **1** in THF/toluene (1/19, v/v) mixed solvents ($C = 0.05$ mM).

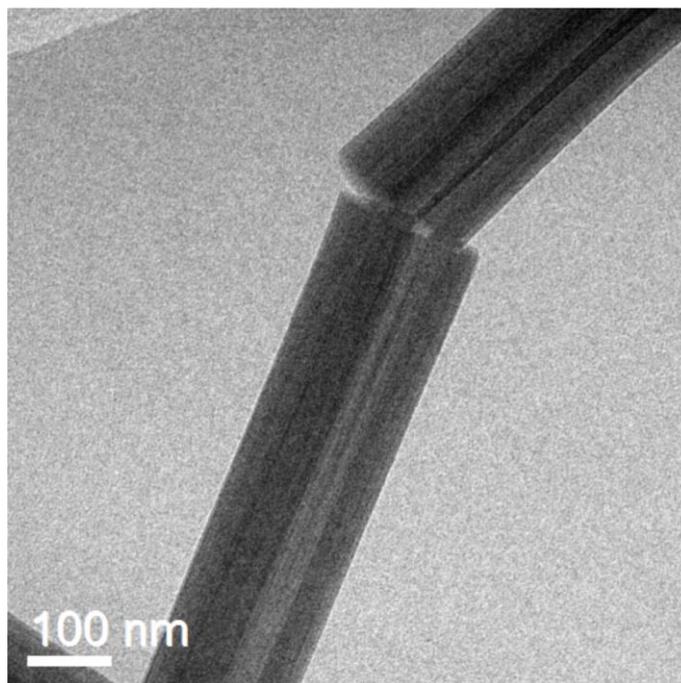


Fig. S8 Cryo-TEM image of assemblies formed from **1** in THF/toluene (1/19, v/v) mixed solvents ($C = 0.05$ mM).



Fig. S9 SAED image of assemblies formed from **1** in THF/toluene (1/19, v/v) mixed solvents ($C = 0.05$ mM).

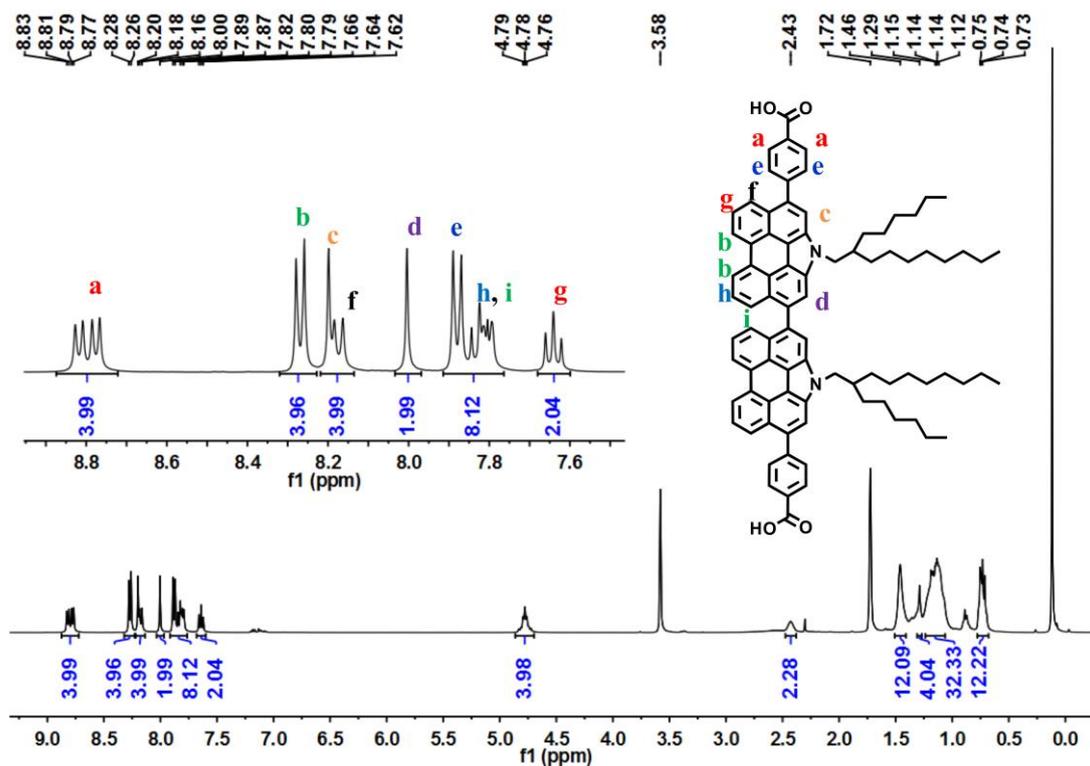


Fig. S10 ¹H NMR spectrum of **1** in THF-*d*₈.

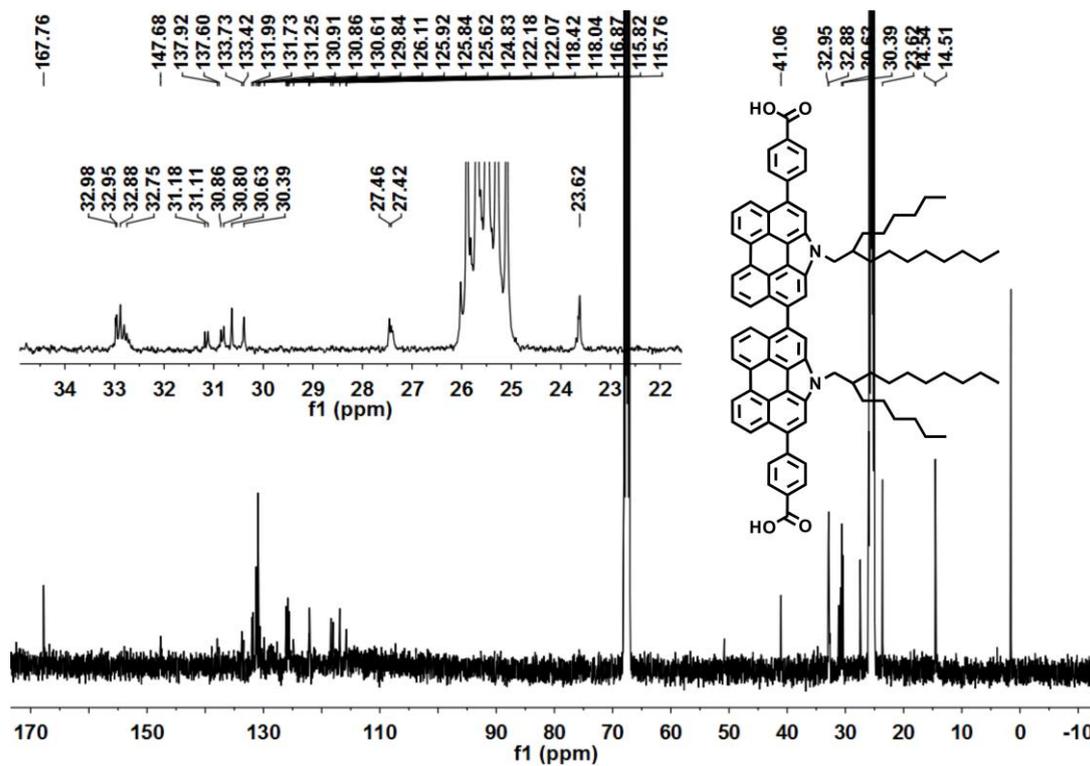


Fig. S11 ¹³C NMR spectrum of **1** in THF-*d*₈.

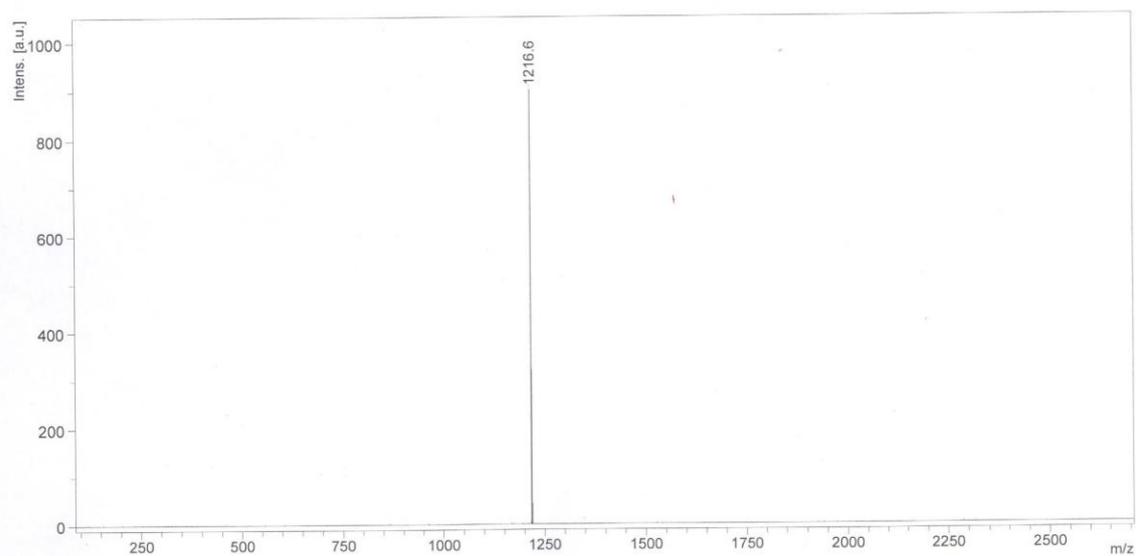


Fig. S12 MALDI-TOF Mass Spectra of **1**.

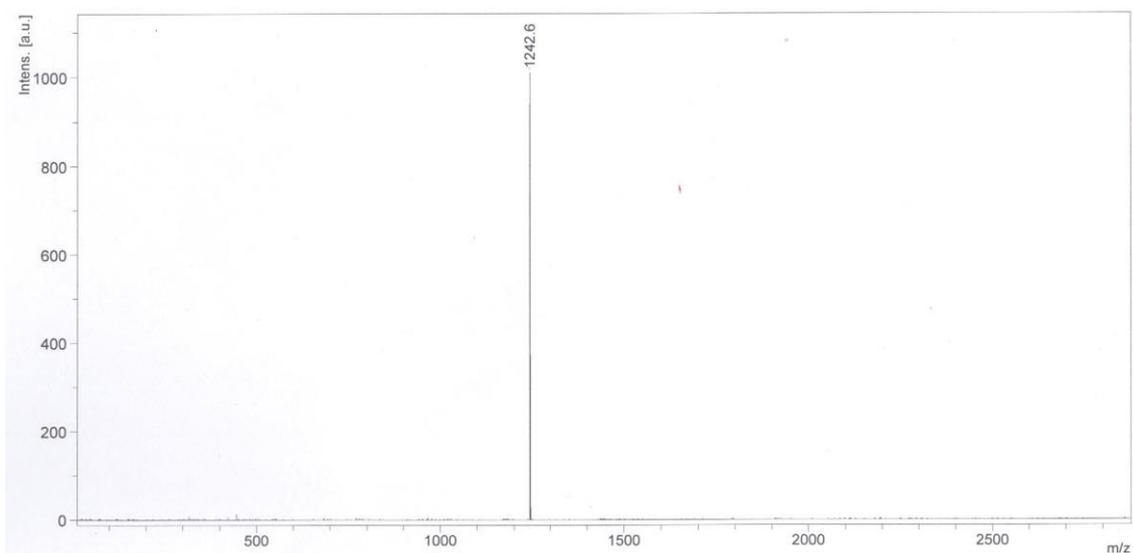


Fig. S13 MALDI-TOF Mass Spectra of **2'**.

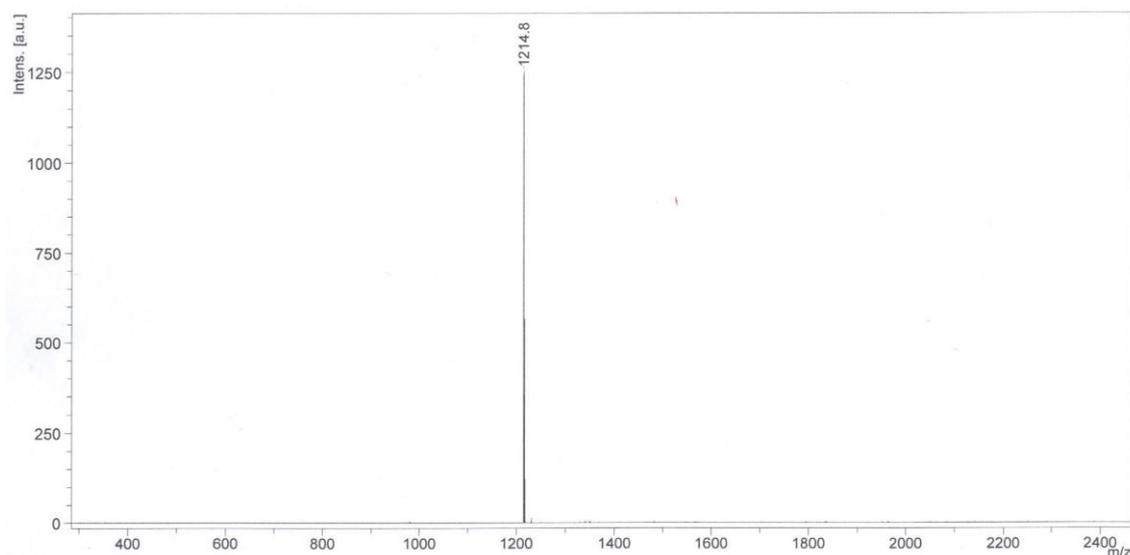


Fig. S14 MALDI-TOF Mass Spectra of **2**.

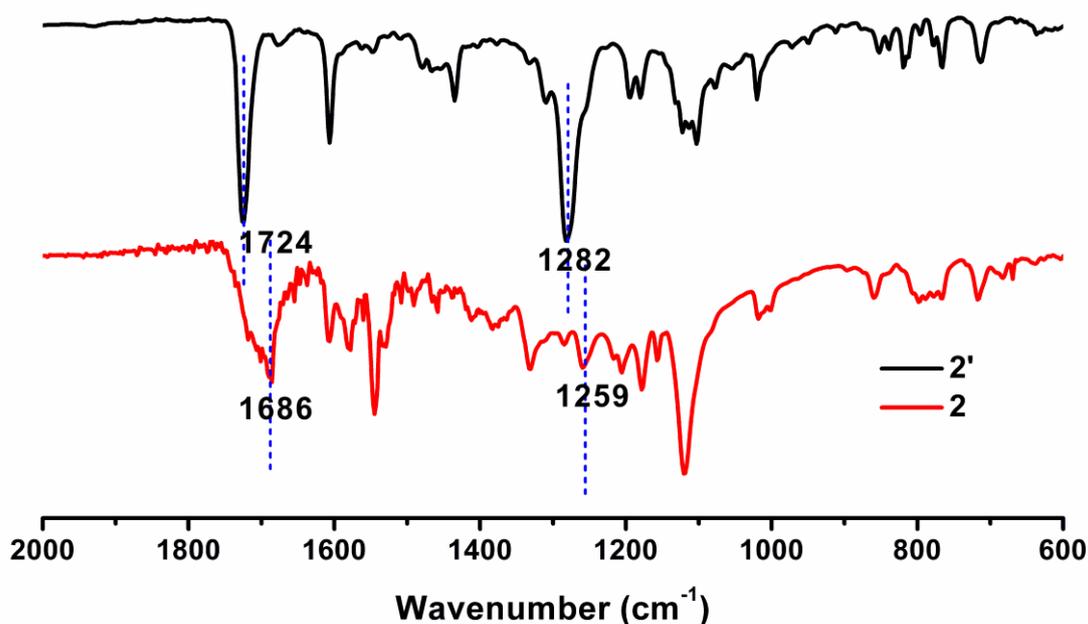


Fig. S15 FT-IR Spectra of **2'** (red) and **2** (black).

Attribution and analysis of FT-IR spectra:

- (a) 1600-1400 cm^{-1} for aromatic system stretching frequency;
- (b) 830-810 cm^{-1} for 1, 4-disubstituted benzene bending vibration frequency out of plane;
- (c) $\sim 1100 \text{ cm}^{-1}$ for C-N stretching frequency;
- (d) as a result of intermolecular hydrogen bonds, the C=O (1686 cm^{-1}) and CO-O-C (1259 cm^{-1}) stretching frequency for **2** are less than those (1724 cm^{-1} , 1282 cm^{-1}) for **2'**, respectively.

References:

- 1 Y. Li and Z. Wang, *Org. Lett.*, 2009, **11**, 1385; Y. Li, L. Hao, H. Fu, W. Pisula, X. Feng and Z. Wang, *Chem. Commun.*, 2011, **47**, 10088.
- 2 C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.*, 1990, **112**, 5525; J. E. Anthony, *Chem. Rev.*, 2006, **106**, 5028.