Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Supramolecular 2D Monolayered Nanosheets Constructed by Using Synergy of Non-covalent Interactions

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Contents

1. General information

All raw materials were obtained from commercial suppliers and used without any further purification. The drying solvents used were purchased from Energy Chemical and Aladdin Co. All water used in the experiment was ultrapure water. All reactions were monitored by thin layer chromatography (TLC) visualizing with ultraviolet light (UV), column chroma-tography purifications were carried out using silica gel (SiO_2, 200-300 mesh).

Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on the Bruker AVANCEIII 500 instrument with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts for proton and carbon are referenced to solvent residual peak in the NMR solvent ($CDCl_3$ = δ 7.26 ppm, DMSO = δ 2.5 ppm for ^{1}H NMR spectrum; $CDCl_3$ = δ 77.16 ppm, DMSO = δ 39.52 ppm for ^{13}C NMR spectrum). NMR data are presented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in Hertz (Hz), integration. Mass spectra were recorded on the Agilent1290-micrOTOF Q II.

The measurements of Ultraviolet-Visible (UV-vis) absorption spectra were recorded on a Shimadzu UV-2450 3100 UV spectrophotometer. The measurements of fluorescence spectra were performed on a Shimadzu RF-5301 PC spectrofluorimeter.

The measurements of atomic force microscopy (AFM) were performed on Nanoscope III a controller, Veeco Metrology, Santa Barbara, CA using the tapping mode with a SiN_4 tip with a radius of 10~20 nm. Samples were prepared by depositing a droplet (*ca.* 2 μL) of the solutions of target molecule **1** and control molecule **2** (in chloroform, *ca.* 10^{-7} M) on silicon wafers surface followed by drying in air, respectively.

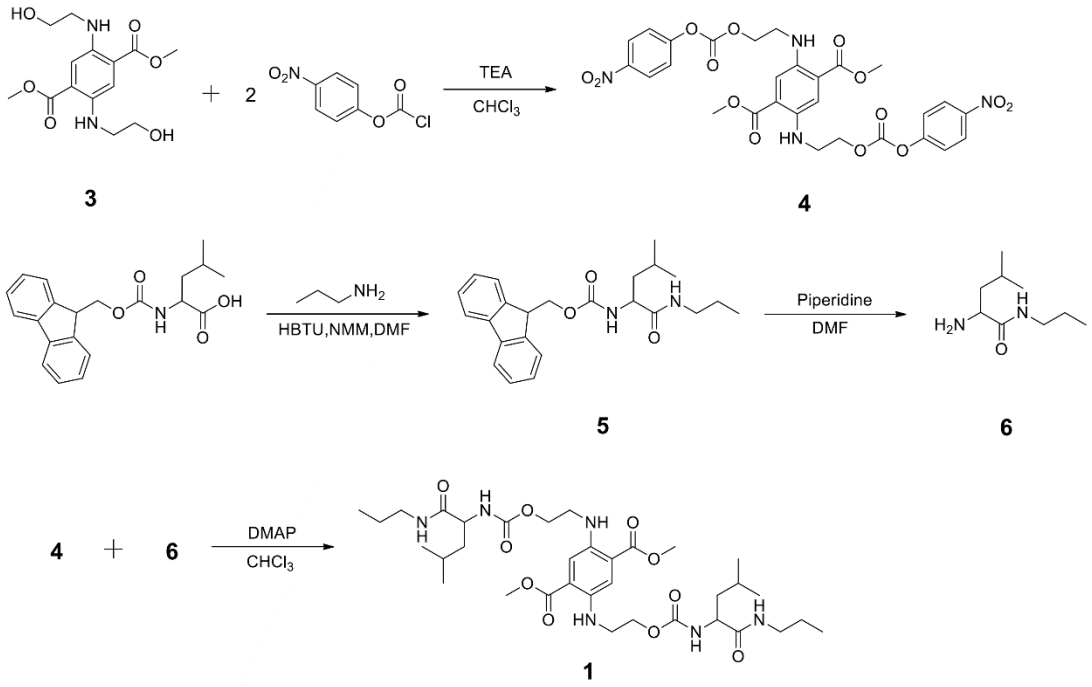
Transmission electron microscopy (TEM) images were observed by using FEI Talos 200c from a FEI company, operating at an accelerating voltage of 120 kV. Depositing a droplet (*ca*. 2 μL) of the solution of compound **1** (in chloroform, *ca*. $2*10^{-8}$ M) on a freshly formvar carbon-coated copper surface.

Scanning electron microscopy (SEM) images were recorded with a JEOL JSM-6700F instrument. A drop of the stock solution was dripped onto a silicon wafer and air-dried.

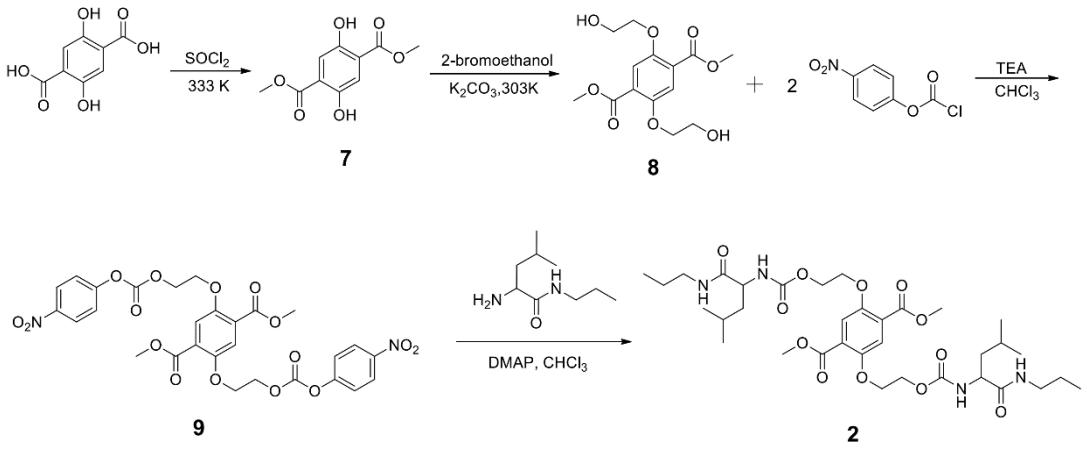
Wide-angle X-ray scattering (WAXS) pattern of a self-assembled nanosheet powder sample in the solid state. The d values of the interplanar crystal spacing are calculated according to Bragg's Law $2d\sin\theta=n\lambda$.

2. Synthesis Schemes

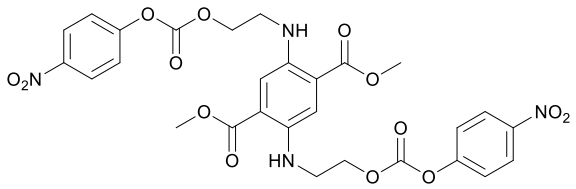
Scheme S1. Synthetic routes of compound **1**.



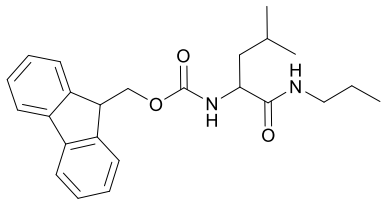
Scheme S2. Synthetic routes of compound **2**.



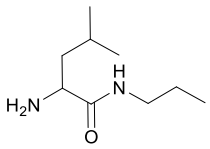
3. Synthetic Procedures



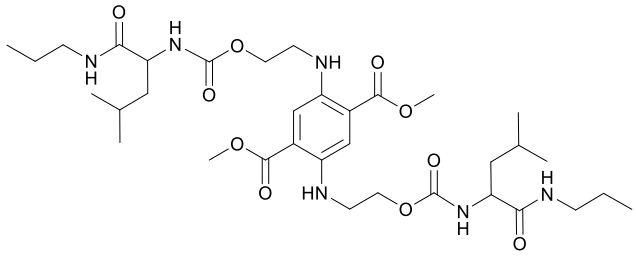
Dimethyl 2,5-bis((2-(((4-nitrophenoxy)carbonyl)oxy)ethyl)amino)terephthalate (4). To a mixture of dimethyl 2,5-bis((2-hydroxyethyl)amino)terephthalate (0.2 g, 0.64 mmol), 4-nitrophenyl carbonochloridate (0.3 g, 1.47 mmol) and triethylamine (0.44ml, 3.20mmol), added 3ml of dry chloroform, the reaction mixture under the protection of nitrogen was stirred for 4h at room temperature. Then the solvent was evaporated to dryness and the residue was purified by column chromatography (silica gel, dichloromethane/ methanol =500/1) to obtain **4** as a dark red powder (0.33g, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, J = 9.1 Hz, 4H), 7.40 (dd, J = 17.8, 10.9 Hz, 6H), 7.18 (s, 2H), 4.55 (t, J = 5.3 Hz, 4H), 3.93 – 3.89 (m, 6H), 3.66 – 3.59 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ=168.14, 155.49, 152,54, 140.80, 126.14, 125.31, 121.83, 115.64, 114.25, 67.63, 52.12, 42.30; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{26}N_4O_{14}$ 643.1518; found 643.1511.



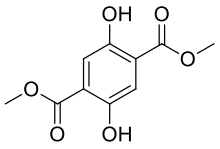
(9H-fluoren-9-yl)methyl (4-methyl-1-oxo-1-(propylamino)pentan-2-yl)carbamate (5). To a mixed solution of Fmoc-Leu-OH (2.00 g, 5.66 mmol), O-Benzotriazole-N,N,N',N'-tetramethyl-uronium-hexafluorophosphate (4.3 g, 11.33 mmol), 1-Hydroxybenzotriazole (1.53 g,11.33 mmol), N-methylmorpholinz(1.27ml,11.33mmol)in dry N,N-Dimethylformamide,then propylamine (0.56ml,6.79mmol) was added and the solution was stirred overnight at room temperature. After vacuum distillation, the residue was dispersed into the methanol. The solid was filtered and fully washed with methanol, then the filter liquor was evaporated to dryness and the pure white product (2.1 g, 94%) was obtained by column chromatography (silica gel, dichloromethane/methanol =200/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 7.5 Hz, 2H), 7.60 (d, J = 7.5 Hz, 2H), 7.43 (t, J = 7.4 Hz, 2H), 7.34 (t, J = 7.4 Hz, 2H), 5.96 (s, 1H), 5.19 (d, J = 8.1 Hz, 1H), 4.44 (s, 2H), 4.23 (t, J = 6.7 Hz, 1H), 4.14 (s, 1H), 3.23 (s, 2H), 1.68 (s, 2H), 1.53 (d, J = 7.0 Hz, 3H), 0.94 (dd, J = 16.5, 9.0 Hz, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.15, 156.33, 143.78, 141.31, 127.74, 127.09, 125.03, 120.00, 66.99, 53.64, 47.16, 41.56, 41.24, 24.73, 22.73, 22.13,11.31; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{30}N_2O_3$ 395.2329; found 395.2325.



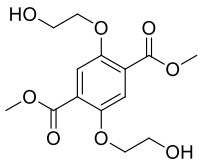
2-amino-4-methyl-N-propylpentanamide (6). Compound **5** (2 g, 5.07 mmol) was added to the 20% DMF solution of piperidine(20 ml), the mixture was stirred 0.5h at room temperature. After reduced pressure distillation, the product was extracted with ethyl acetate and 0.1mol HCl aqueous solution. Then, sodium bicarbonate ($NaHCO_3$) solution was added to the aqueous phase, the solution was adjusted to weak alkalinity, and DCM was added to extract the product. Anhydrous sodium sulfate (Na_2SO_4) solution was dried, filtered, the residue was purified by column chromatography (silica gel, dichloromethane/ methanol =50/1) and the product was obtained as a colorless liquid (0.6g, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.38 (dd, J = 9.8, 3.2 Hz, 1H), 3.21 (dd, J = 13.6, 6.6 Hz, 2H), 1.75– 1.67 (m, 2H), 1.53 (dd, J = 14.6, 7.3 Hz, 2H), 1.45 (s, 2H), 1.37–1.30 (m, 1H), 0.97–0.91 (m, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ =175.46, 53.53, 44.13, 40.71, 24.87, 23.40, 22.84, 21.36, 11.36; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_9H_{20}N_2O$ 173.1648; found 173.1649.



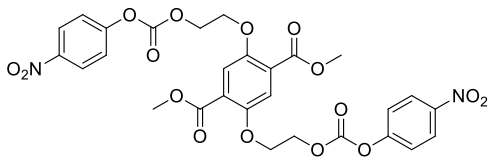
Dimethyl 2,5-bis ((2-(((4-methyl-1-oxo-1-(propyl amino) pentan-2-yl) carbamoyl) oxy) ethyl) amino) terephthalate (1). The compound **6** (0.045g, 0.26mmol) was added to the mixture of compound **4** (0.07g, 0.11mmol), 4-dimethylaminopyridine (0.032g, 0.26mmol) and dry chloroform (3ml), then the reaction mixture under a nitrogen atmosphere was sealed and stirred at room temperature for 24h. The solvent was removed by reduced pressure distillation and the residue was purified by column chromatography (silica gel, dichloromethane/ methanol =70/1) to obtain compound **1** as an orange solid (0.04g, 51%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (s, 2H), 7.05 (s, 2H), 6.04 (s, 2H), 5.20 (s, 2H), 4.31 (s, 4H), 4.11 (s, 2H), 3.89 (s, 6H), 3.44 (s, 4H), 3.22 – 3.16 (m, 4H), 1.50 (s, 6H), 1.25 (s, 4H), 0.92 (t, J = 11.2 Hz, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ =171.96, 156.18, 140.96, 133.72, 129.68, 114.24, 63.77, 62.69, 42.79, 41.32, 41.17, 29.63, 24.63, 22.66, 21.96, 11.21; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{34}H_{56}N_6O_{10}$ 709.4131; found 709.4114.



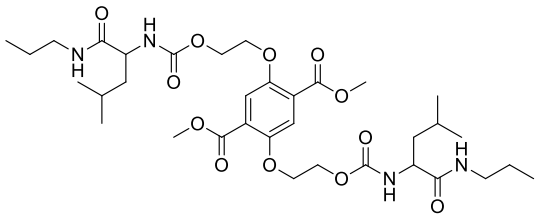
Dimethyl 2,5-dihydroxyterephthalate (7). 1g 2,5-Dihydroxytelephthalic acid was dissolved in 20 ml methanol, then 4.5ml dichlorosulfoxide was slowly added, the solution was allowed to stir at 60 °C in oil bath for overnight under a stream of nitrogen and then the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, dichloromethane) to obtain **7** as a yellow powder (0.95 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 10.08 (s, 2H), 7.49 (s, 2H), 4.00 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, δ): 169.48, 152.92, 118.33, 117.77, 52.80; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{10}H_{10}O_6$ 227.0550; found 227.0549.



Dimethyl 2,5-bis(2-hydroxyethoxy)terephthalate (8). A solution of the compound **7** (0.2g, 0.9 mmol), potassium carbonate (0.27g, 1.98 mmol) and 2-bromoethanol (0.14 ml, 1.98mmol) in N,N-dimethylformamide (10 mL) was boiled in oil bath and stirred overnight at 303K. The solution was evaporated to dryness and the residue was purified by column chromatography (silica gel, dichloromethane/ methanol =50/1) to obtain **8** as a white powder (0.18 g, 63%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.45 (s, 2H), 4.22 – 4.20 (m, 4H), 3.92 – 3.89 (m, 10H), 3.58 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$, δ): 165.48, 152.84, 125.10, 118.92, 72.93, 61.00, 52.62; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{18}O_8$ 315.1074; found 315.1072.



Dimethyl 2,5-bis(2-(((4-nitrophenoxy)carbonyl)oxy)ethoxy)terephthalate (9). To a mixture of compound **8** (0.2 g, 0.64 mmol), 4-nitrophenyl carbonochloridate (0.3 g, 1.47 mmol) and triethylamine (0.44ml, 3.20mmol), added 3ml of dry chloroform, the reaction mixture under the protection of nitrogen was stirred for 4h at room temperature. Then the solvent was evaporated to dryness and the residue was purified by column chromatography (silica gel, dichloromethane/ methanol =100/1) to obtain **9** as a white powder (0.33 g, 81%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.29 (d, J = 8.5 Hz, 4H), 7.51 – 7.38 (m, 6H), 4.68 (s, 4H), 4.35 (s, 4H), 3.89 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$, δ): 165.36, 155.50, 152.46, 151.92, 145.50, 125.46, 125.33, 121.85, 118.21, 68.10, 67.10, 52.50; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{24}N_2O_{16}$ 645.1199; found 645.1204.



Dimethyl 2,5-bis (2-(((4-methyl-1-oxo-1-(propyl amino) pentan-2-yl) carbamoyl) oxy) ethoxy) terephthalate (2). The compound **9** (0.05g, 0.08mmol) was added to the mixture of compound **4** (0.03g, 0.19mmol), 4-dimethylaminopyridine (amount of catalyst) and dry chloroform (3ml), then the reaction mixture under a nitrogen atmosphere was sealed and stirred at room temperature for 24h. The solvent was removed by reduced pressure distillation and the residue was purified by column chromatography (silica gel, dichloromethane/ methanol = 50/1) to obtain compound **2** as a white solid (0.046 g, 83%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.41 (s, 2H), 6.06 (s, 2H), 5.24 (s, 2H), 4.43 (m, 4H), 4.22 (t, J = 4.3 Hz, 4H), 4.11 (dd, J = 13.3, 8.5 Hz, 2H), 3.90 (s, 6H), 3.22 (dd, J = 19.9, 13.5 Hz, 4H), 1.66 (d, J = 6.1 Hz, 6H), 1.53 – 1.48 (m, 4H), 0.92 (m, 18H); ^{13}C NMR (126 MHz, $CDCl_3$, δ): 175.04, 171.92, 165.68, 156.02, 151.98, 118.24, 68.96, 63.61, 53.55, 52.48, 43.96, 41.24, 24.71, 23.39, 22.88, 22.75, 11.29; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{34}H_{54}N_4O_{12}$ 711.3811; found 711.3798.

4. Spectroscopic analyses

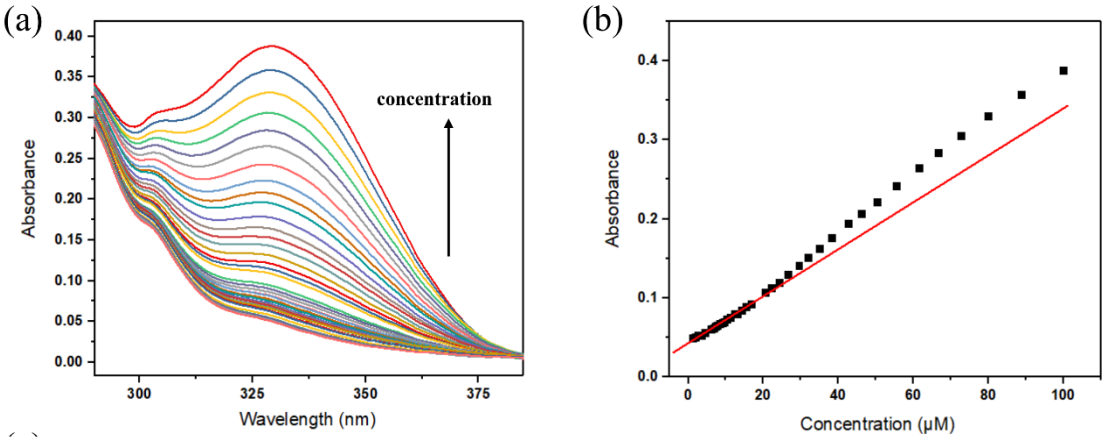


Figure S1. (a) The ultraviolet-visible (UV-Vis) spectra of **2** in chloroform ($CHCl_3$) at 298K at different concentrations (0-100μM); (b) Plots of absorbance at 330 nm versus concentrations.

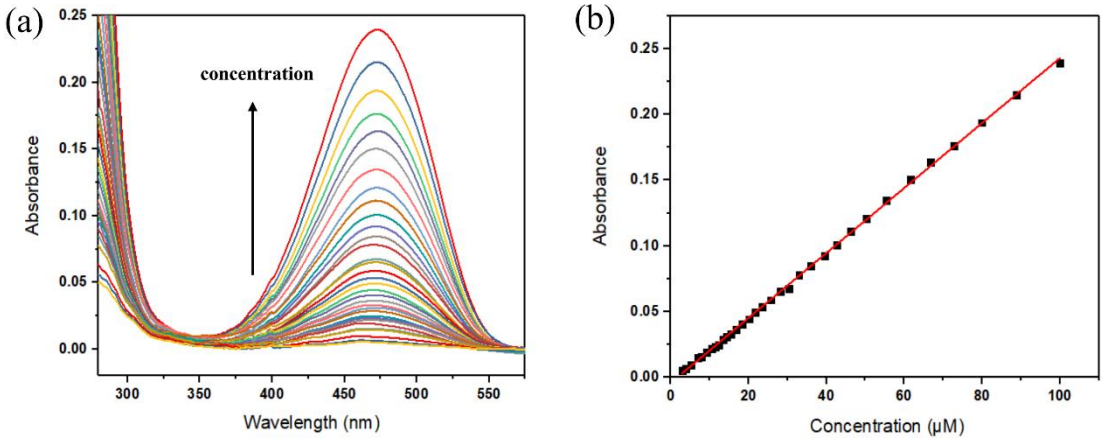


Figure S2. (a) The ultraviolet-visible (UV-Vis) spectra of **1** in $CHCl_3$ at 298K at different concentrations (0-100μM); (b) Plots of absorbance at 472 nm versus concentrations.

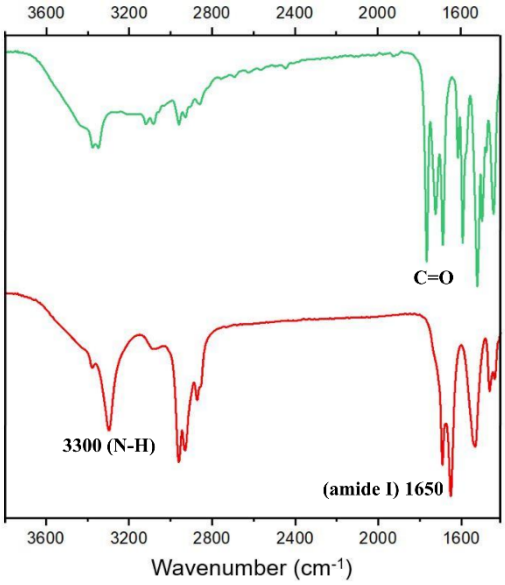


Figure S3. FT-IR spectrum of **4** (green) and **1** (red). The shift of vibration peak for C=O and the appearance of peak at 1650 cm^{-1} (amide I) indicate the formation of hydrogen-bonding interactions.

5. Morphology characterization of assemblies

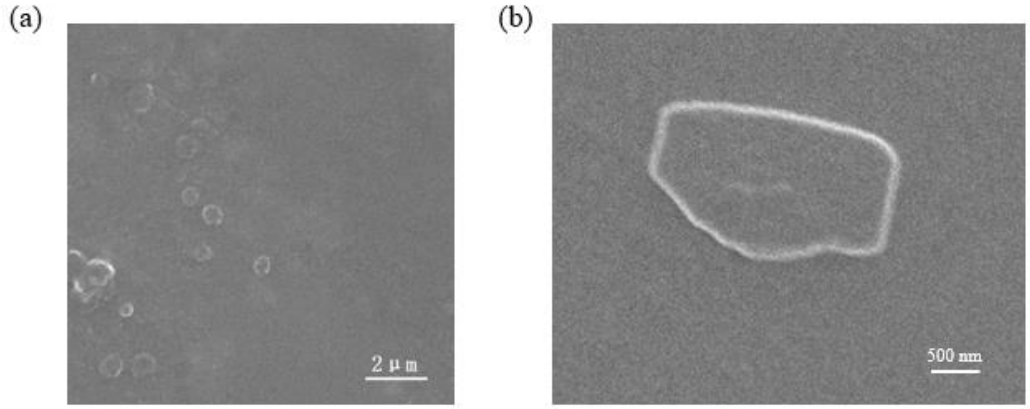


Figure S4. SEM images of nanosheets of self-assembled **1**.

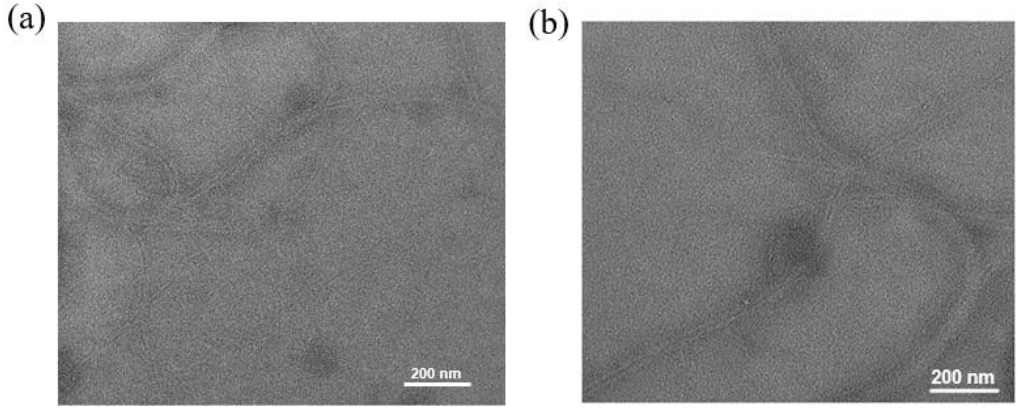


Figure S5. TEM images of nanowires of self-assembled **2**.

6. Supplementary Figures

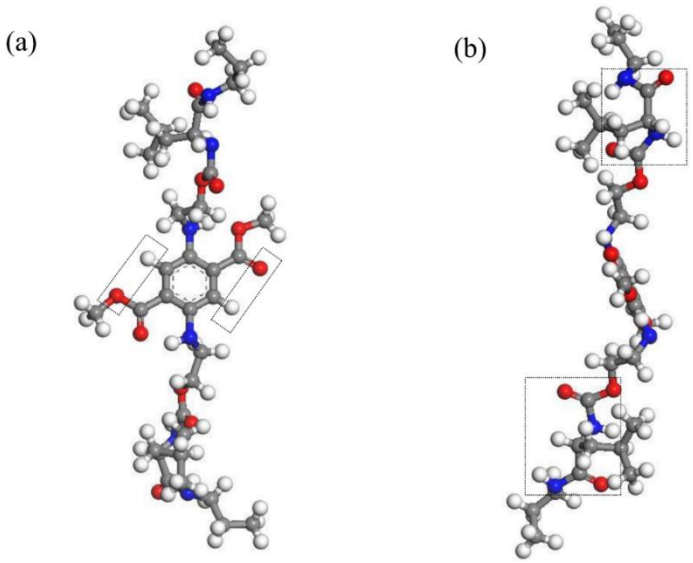


Figure S6. Energy minimized conformation of **1**.

7. ^{1}H NMR and ^{13}C NMR spectra

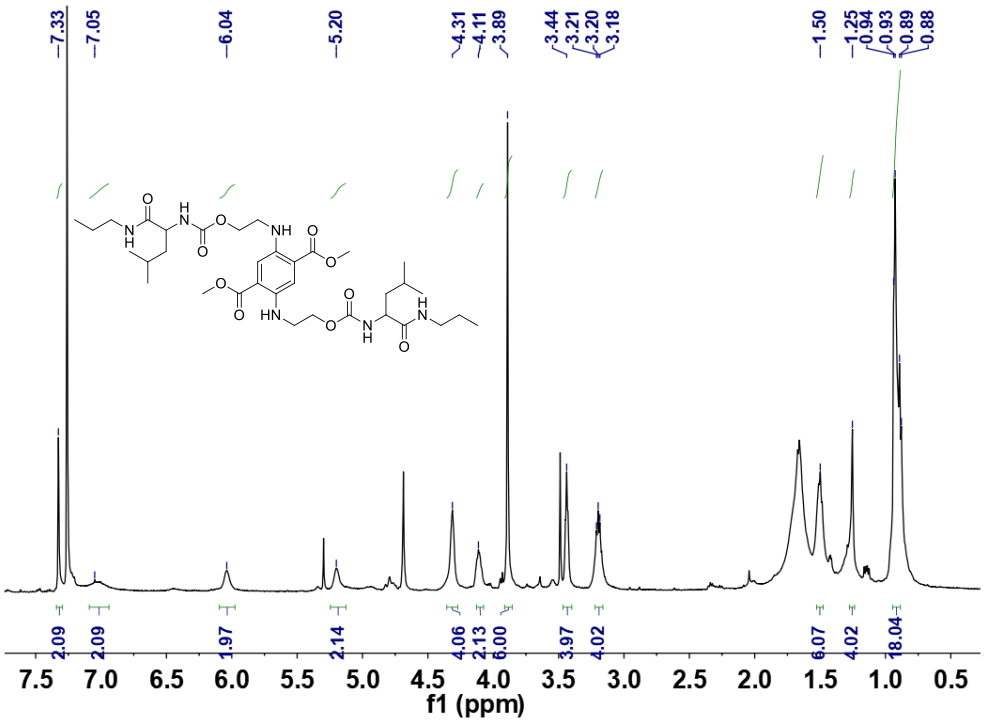


Figure S7. ^{1}H NMR spectrum (500MHz, $CDCl_3$) of compound **1**.

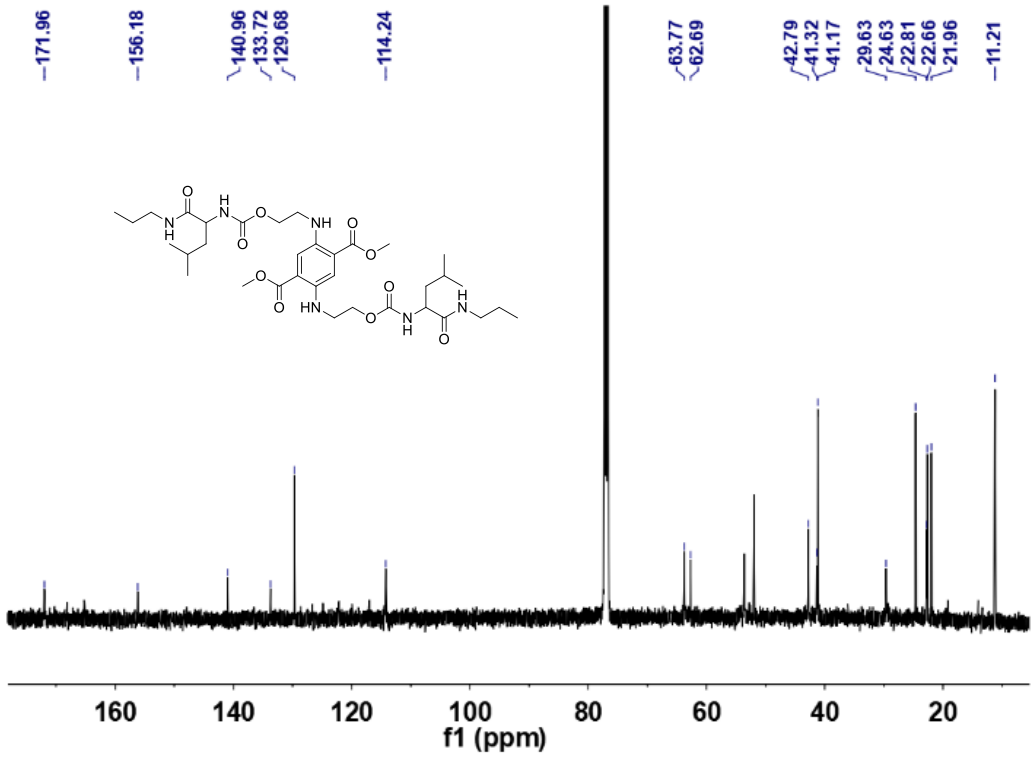


Figure S8. ^{13}C NMR spectrum (126MHz, $CDCl_3$) of compound **1**.

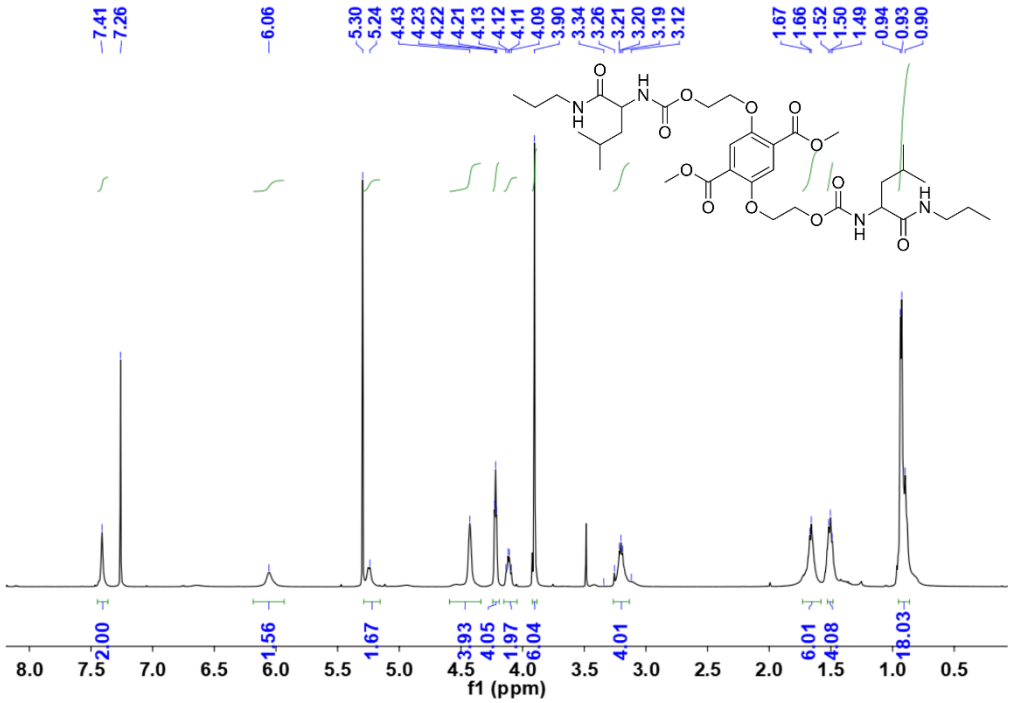


Figure S9. ^{1}H NMR spectrum (500MHz, $CDCl_3$) of compound **2**.

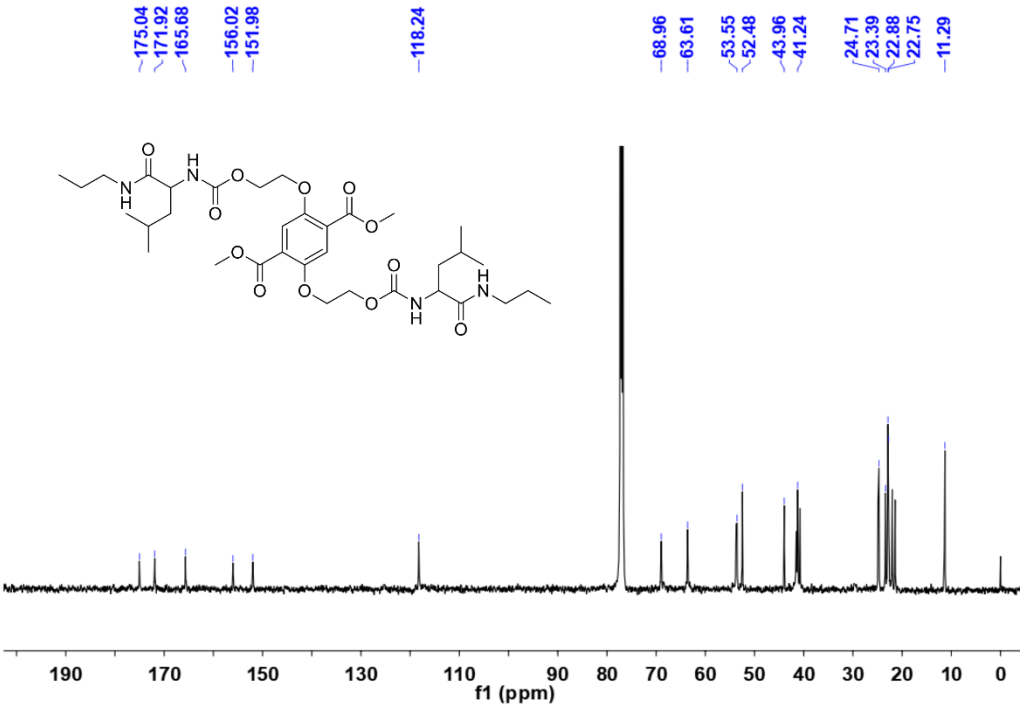


Figure S10. ^{13}C NMR spectrum (126MHz, $CDCl_3$) of compound **2**.

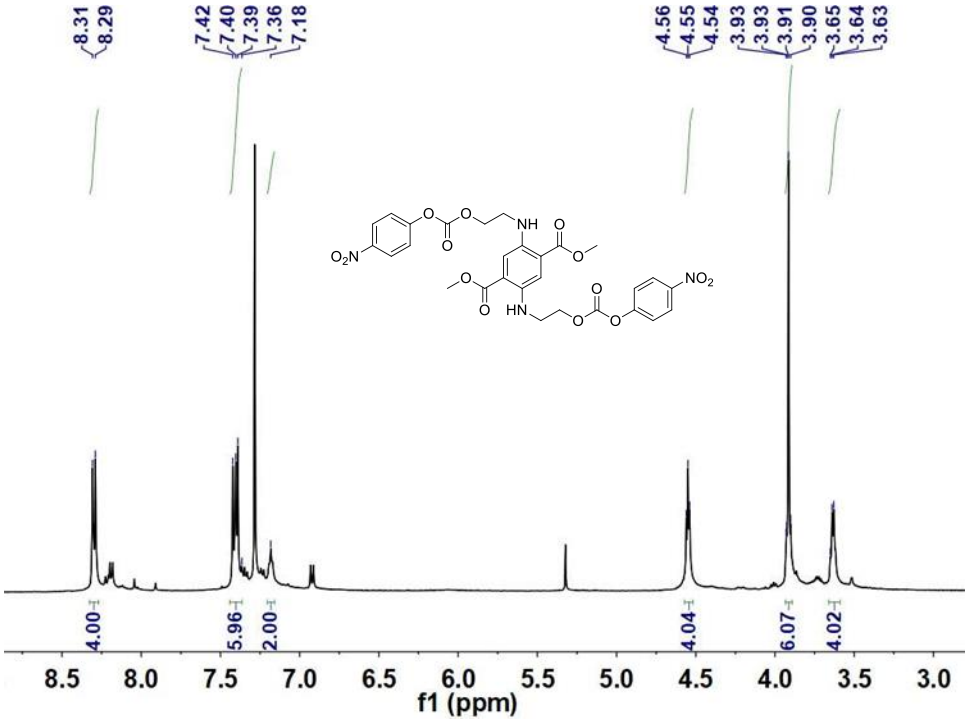


Figure S11. ^{1}H NMR spectrum (500MHz, $CDCl_3$) of compound **4**.

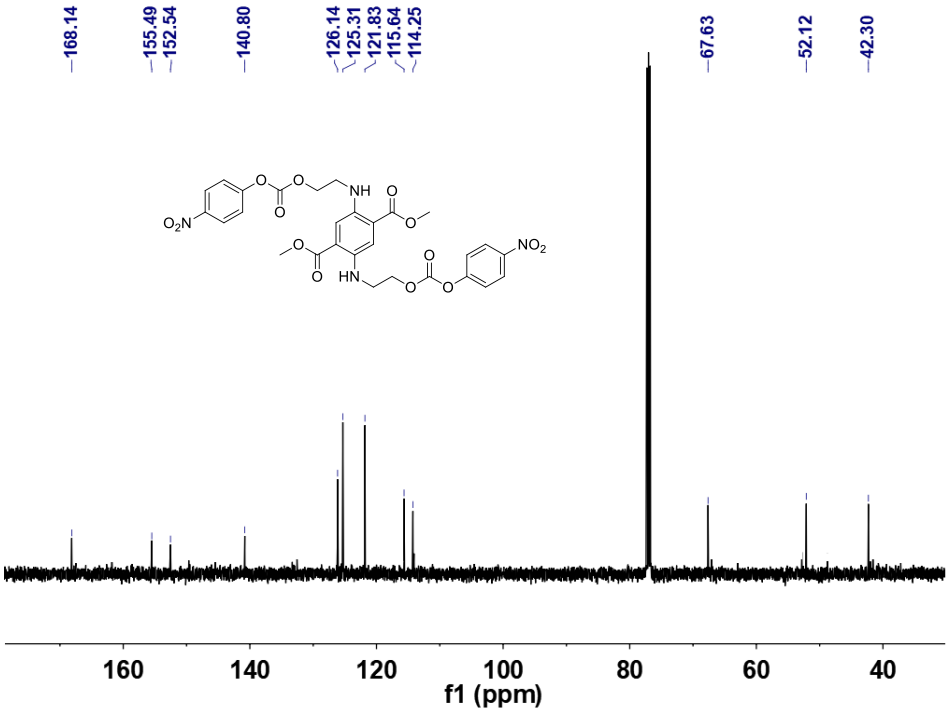


Figure S12. ^{13}C NMR spectrum (126MHz, $CDCl_3$) of compound **4**.

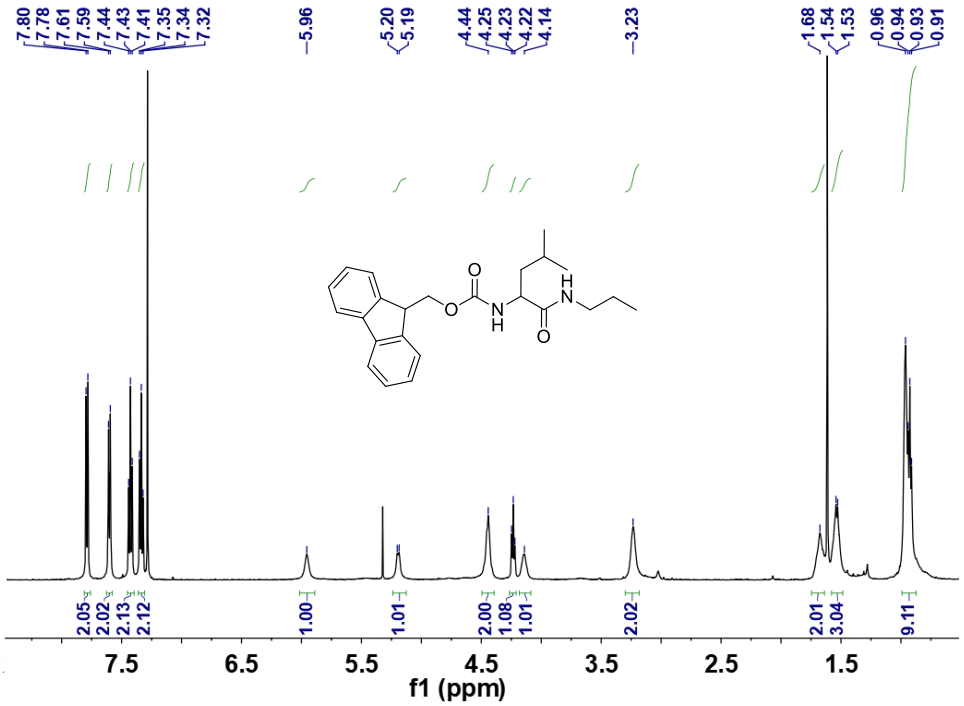


Figure S13. ^{1}H NMR spectrum (500MHz, $CDCl_3$) of compound **5**.

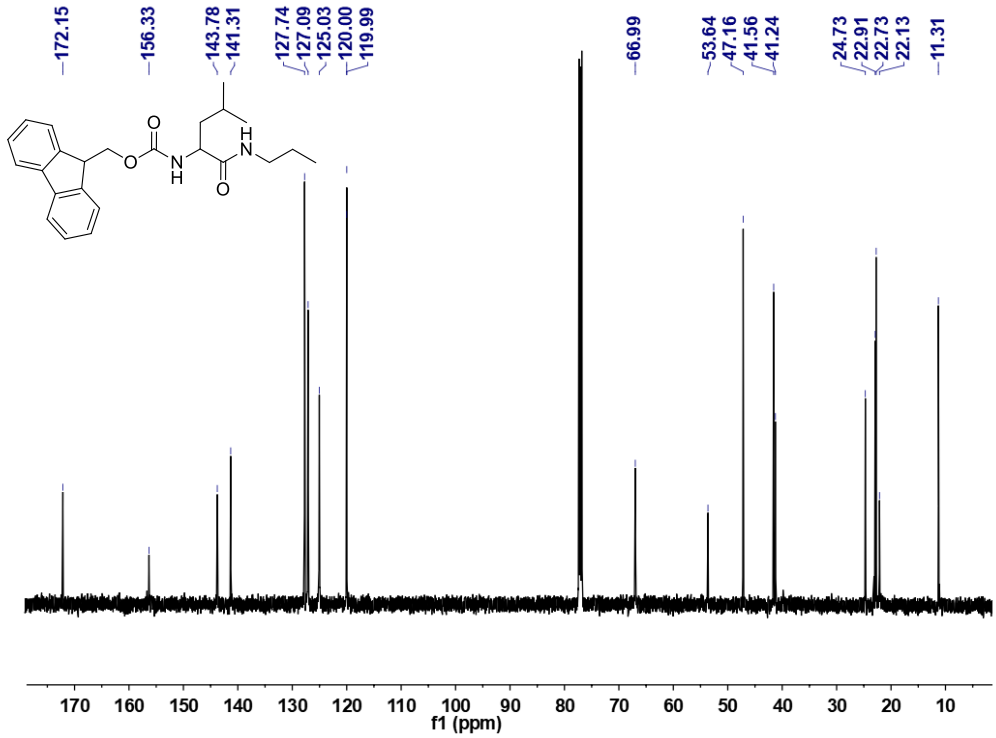


Figure S14. ^{13}C NMR spectrum (126MHz, $CDCl_3$) of compound **5**.

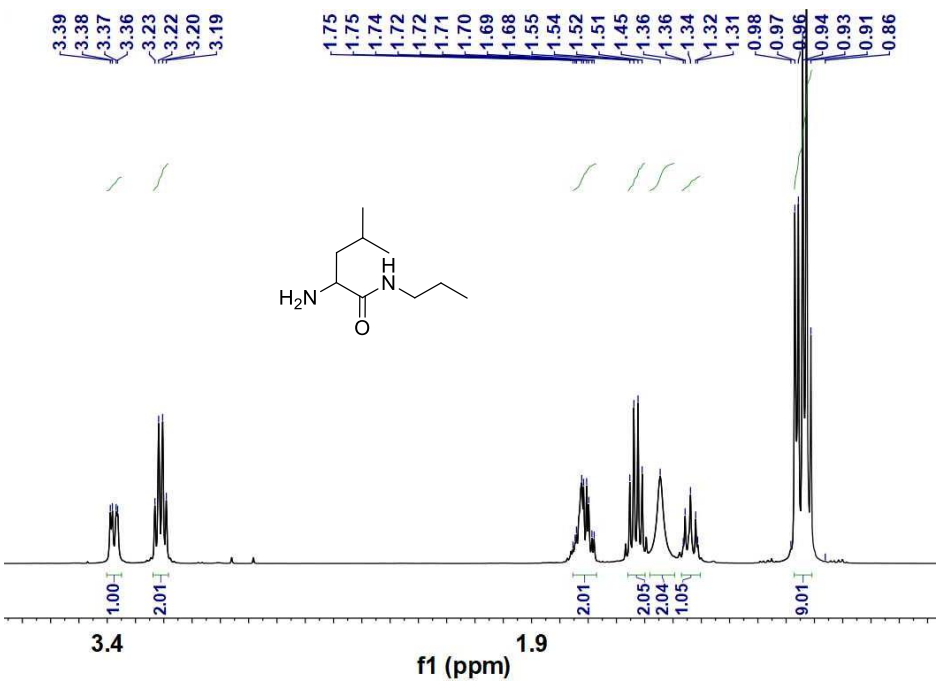


Figure S15. ^{1}H NMR spectrum (500MHz, $CDCl_3$) of compound **6**.

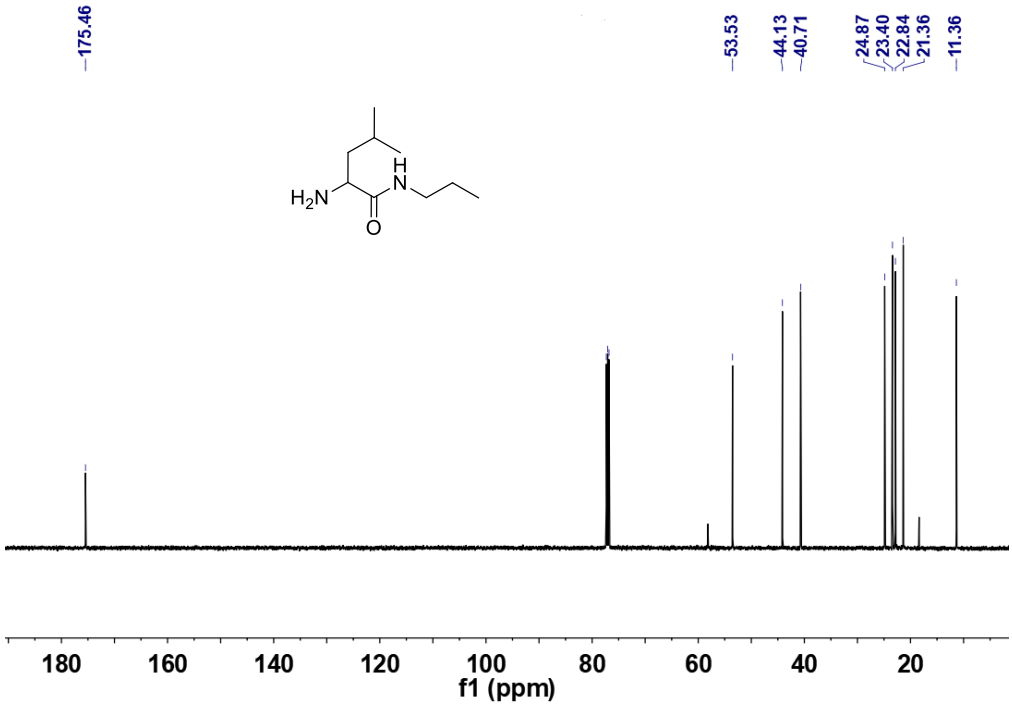


Figure S16. ^{13}C NMR spectrum (126MHz, $CDCl_3$) of compound **6**.

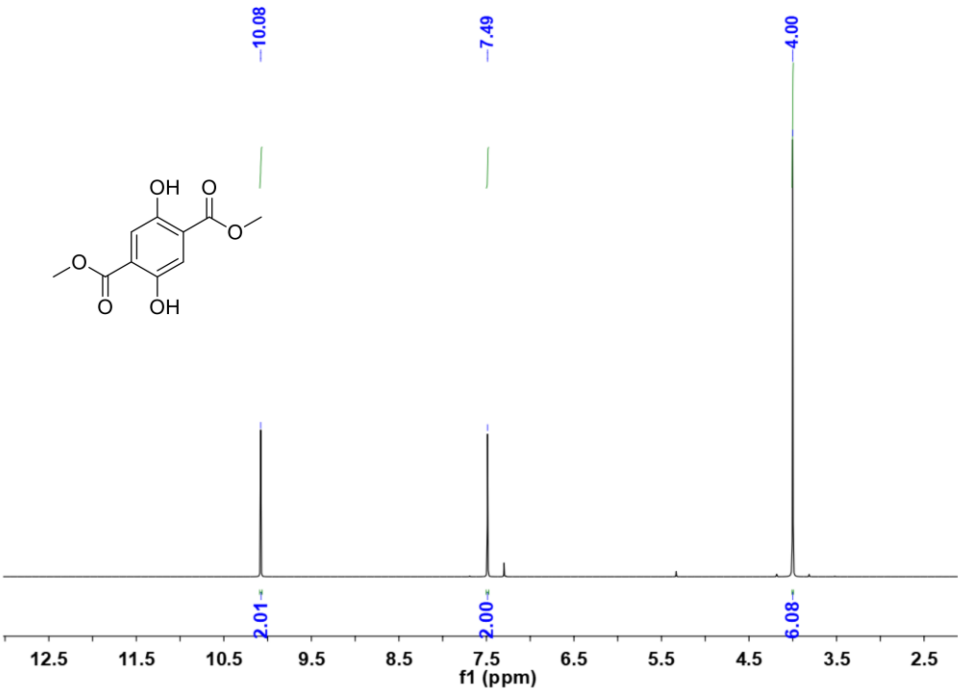


Figure S17. ^{1}H NMR (400MHz, $CDCl_3$) of compound **7**.

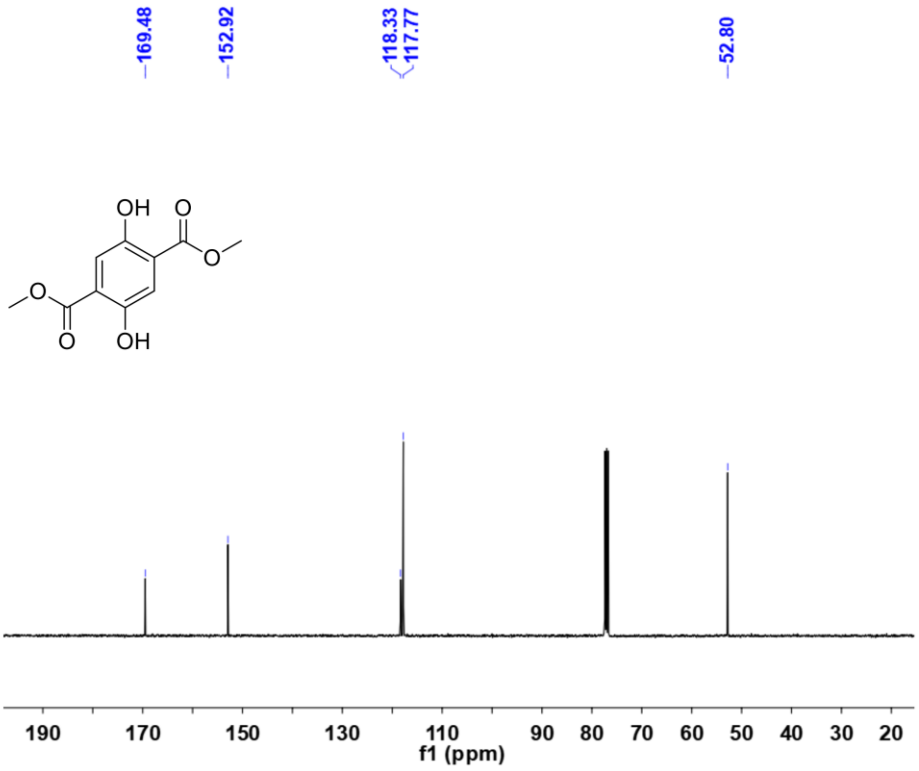


Figure S18. ^{13}C NMR (101MHz, $CDCl_3$) of compound **7**.

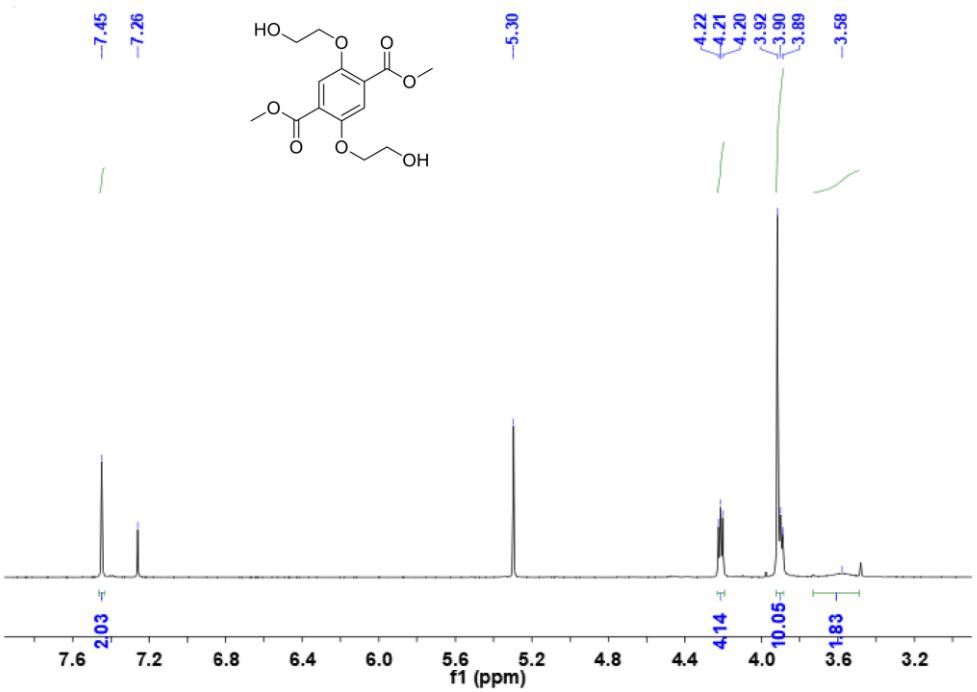


Figure S19. ^{1}H NMR spectrum (400MHz, $CDCl_3$) of compound **8**.

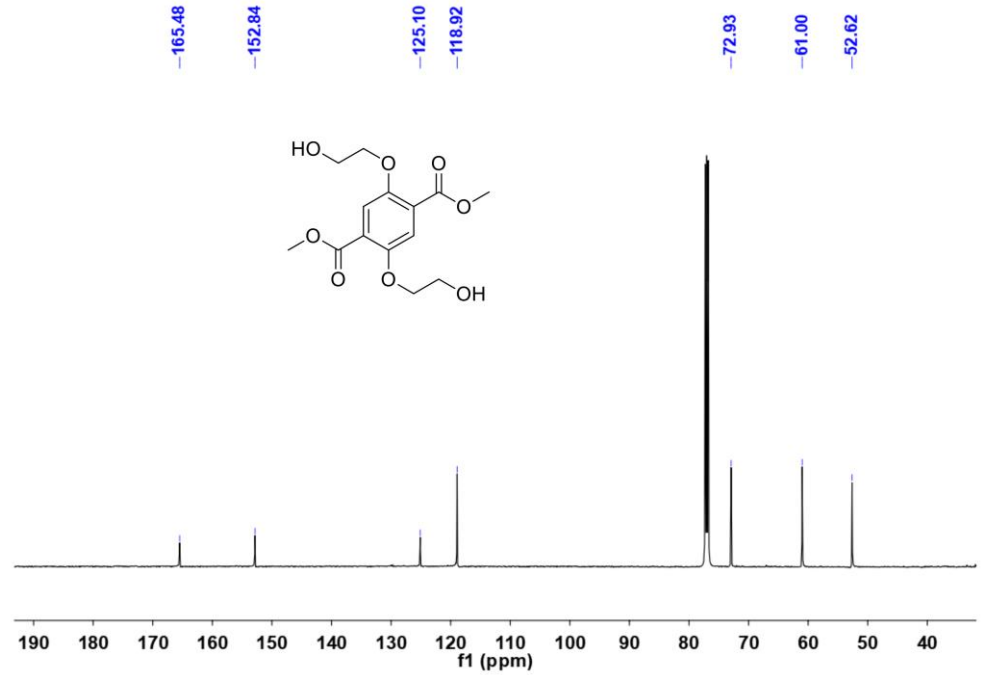


Figure S20. ^{13}C NMR spectrum (126MHz, $CDCl_3$) of compound **8**.

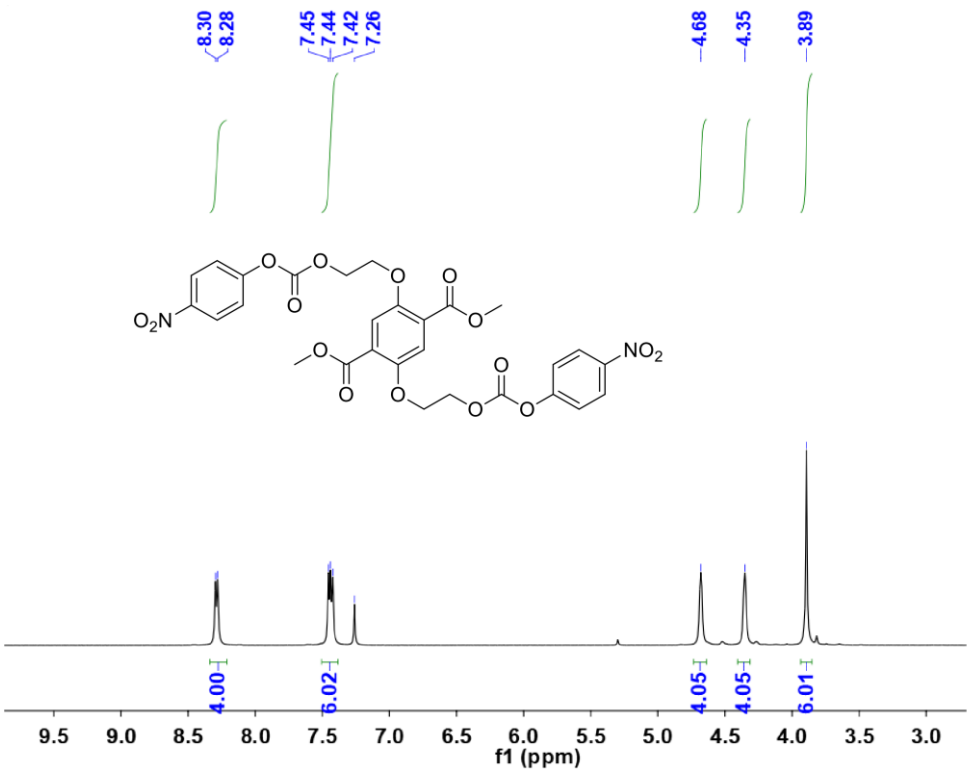


Figure S21. ^{1}H NMR spectrum (500MHz, $CDCl_3$) of compound **9**.

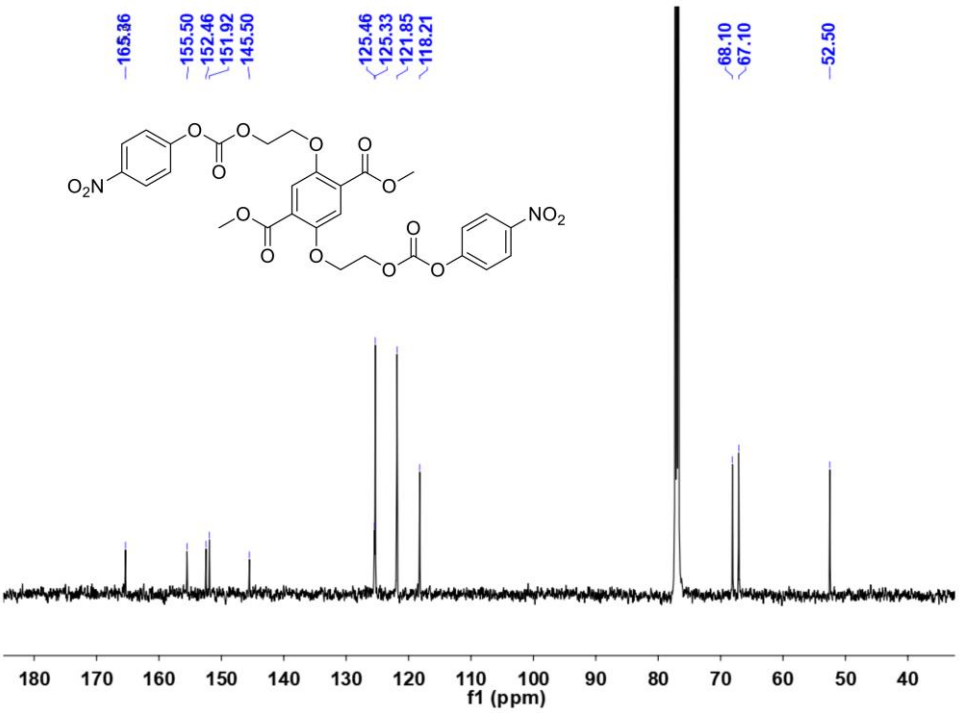


Figure S22. ^{13}C NMR spectrum (126MHz, $CDCl_3$) of compound **9**.