Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Conformation-Variable PDI@β-Sheet Nanohelices Show Stimulus-Sensitive Supramolecular Chirality

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Contents

1. General Information.

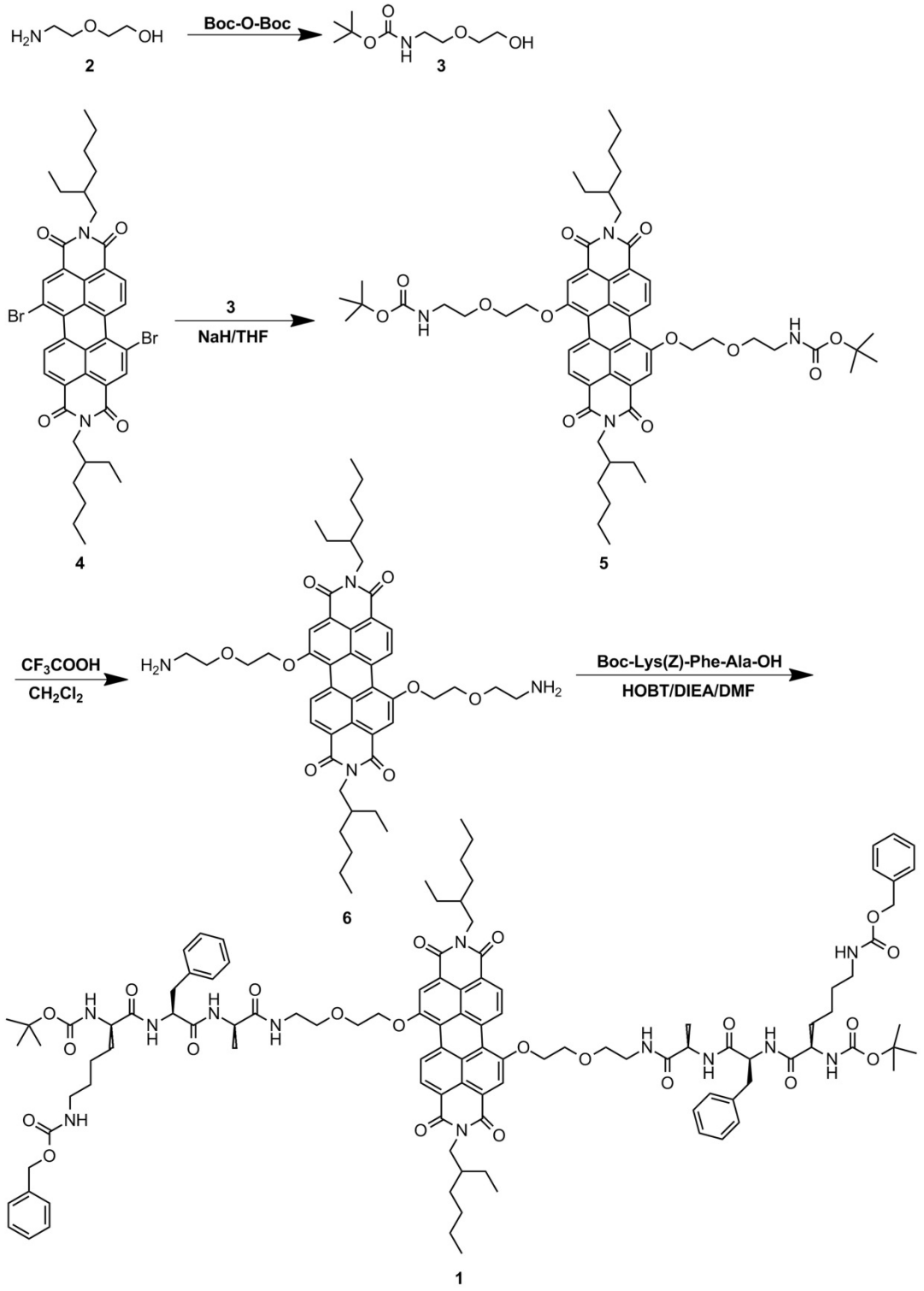
All the amino acid correlated compounds were purchased from GL Biochem (Shanghai) LTD and used as received. All the other chemical reagents were purchased reagent-grade from Acros or Aldrich Corporation and were used without further purification unless otherwise stated. All solvents were purified using standard procedures.

^{1}H and ^{13}C NMR spectra were recorded on a BrukerAVANCE400 or AVANCE600 spectrometer and referenced to solvent signals. ESI mass spectrometric were obtained on LC-MS 2010 and BRUKER Apex IV FTMS and MALDI-TOF mass spectrometric measurements were performed on BrukerBiflex □ MALDI-TOF spectrometer. High resolution mass spectra (ESI) were obtained on Bruker Apex IV Fourier transform mass spectrometer.

The SEM was recorded with a field emission scanning electron microscope (FESEM, Hitachi S-4800), operating at an accelerating voltage of 1.5 kV. The FT-IR spectra were performed with a Bruker TENSOR-27 spectrometer, using KBr plates as subtracts. CD spectra were obtained on a JASCO model J-815 spectropolarimeter. Each CD spectrum was obtained by integrating three repeated scans with a scan rate of 500 nm /min. The CD spectra of **1** in THF were background-corrected with a 1.0cm quartz cell. UV-visible spectra were recorded on HITACHI 3010 UV-vis spectrometer. Fluorescence spectra were obtained at using a HITACHI F-4600spectrometer.XRD measurements: XRD measurements were performed by using a X-ray powder diffraction (XRD, BRUKER D8 Focus) with Cu Kα as the radiation source (λ = 1.5418 Å) and operated at 40 kV and 40 mA.

2. Synthesis of Conjugate 1.

Compound **4** was prepared according to the known procedure.[1]



Scheme S1. Synthesis of Conjugate **1.**

Compound 3. A mixture of **2** (1.05 g, 10mmol), and di-*tert*-butyl dicarbonate (2.40 g, 11mmol) were stirred in THF (30 mL) for 2hours at 40°C. Then the mixture was removed under reduced pressure and the solid was purified by flash chromatography (silica gel, Petroleum ether/50% ethyl acetate) to afford the desired product. Yield: 95%. ^{1}H NMR (400M, $CDCl_3$, ppm) δ: 5.12 (1H, w), 3.70 (2H, s), 3.54 (4H, m), 3.30 (2H, d, 4.36 Hz), 2.72 (1H, s), 1.42 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ156.2, 172.3, 79.5, 72.4, 70.4, 61.8, 40.5, 28.5. Mass (ESI): m/z 228.1 ($M+Na^+$).

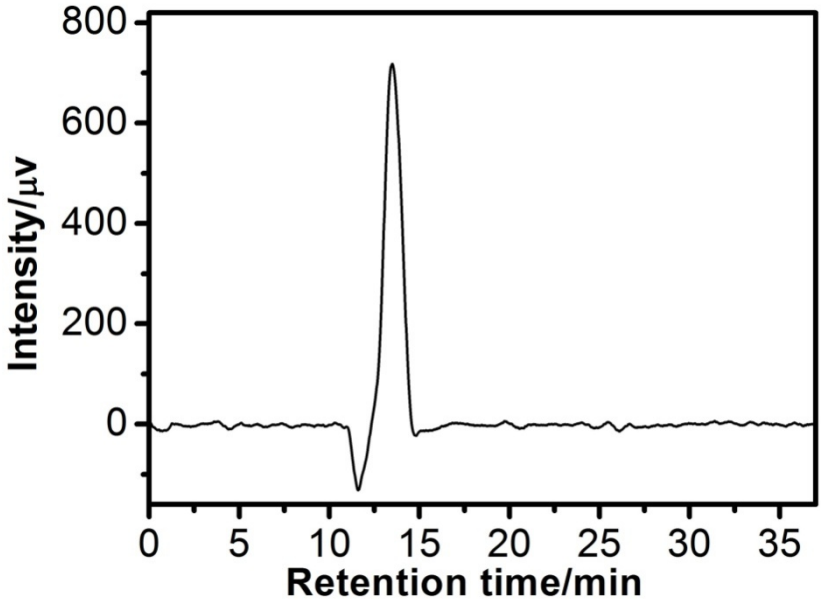
Compound 5. A mixture of **4** (122 mg, 0.16mmol), **3** (96.4 mg, 0.47mmol), and NaH (20 mg, 0.60mmol) were stirred in dried THF (25 mL) under N_2 at room temperature overnight. Then the solvent was removed under reduced pressure. The mixture was dispersed in 10 mL water and the aqueous phase was extracted with dichloromethane (3 ×10 mL). The organic phases were combined and dried over Na_2SO_4. The solvents were evaporated to give a crude product, which was purified by flash chromatography (silica gel, dichloromethane +10% ethyl acetate) to give the desired product. Yield: 92%.^{1}H NMR (400M, $CDCl_3$, ppm) δ: 9.30 (2H, d, 8.36 Hz), 8.29 (2H, d, 8.36 Hz), 8.08 (1H, s), 5.33 (2H, w), 4.47 (4H, s), 4.05 (8H, m), 3.76 (4H, t, 4.89 Hz), 3.47 (4H, s), 1.91 (2H, s), 1.46-1.28 (34H, m), 0.95 (6H, t, 7.18 Hz), 0.90 (6H, t, 6.80 Hz) .^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ163.7, 163.5, 156.2, 156.1, 133.2, 128.9, 128.6, 128.5, 123.2, 122.9, 121.2, 120.9, 116.9, 79.4, 70.8, 69.4, 69.1, 44.4, 40.7, 38.1, 31.0, 28.9, 28.5, 24.2, 23.2, 14.2, 10.7. Mass (MALDI-TOF): m/z 1020.8 ($M-e^-$). ESI-HRMS: calcd for [$M+K^+$] $C_{58}H_{76}KN_4O_{12}$ 1059.5097; found 1059.5068.

Compound 6.5 (175 mg, 0.17 mmol) was dissolved in dichloromethane (8mL), and 1.5 mL of TFA was added and stirred at room temperature. 2 hours later, 8mL×3 of saturated Na_2CO_3 aqueous and water were respectively used to wash the solution. Organic phase was collected and dried with Na_2SO_4. The solvents were removed to afford **6** as an oil-like solid. The residue was used for further synthesis without further purification.

Compound 1. 6 (55 mg, 0.067mmol) was dissolved in DMF (3 mL), and then 0.1 mL of DIEA was added and stirred for 10 minutes at room temperature. The peptide sequence Boc-Lys(Z)-Phe-Ala-OH (76 mg, 0.13mmol) were dissolved in DMF (1 mL) to obtain an transparent solution. Then 0.1 mL of DIEA was added and stirred at room temperature for 5minutes. 0.8 mL of HBTU (0.72 g/mL in DMF) was added to activate the peptide. After that, the activated peptide solution was added into **6** in DMF as prepared previously and then stirred overnight at room temperature. Then the mixture was removed under reduced pressure. The purple solid was dispersed in water. After centrifugation, the precipitation was purified by flash chromatography (silica gel, dichloromethane/2% ethanol) to give the desired product with a yield of 70%. Due to the low solubility, we can't get the NMR profiles with high resolution. However, together with HPLC experiment, we are sure that the final product is pure enough. ^{1}H NMR (600M, $CDCl_3$ and CD_3OD, ppm): δ9.60 (2H, d, 7.14 Hz), 8.48 (2H, m), 8.40 (2H, d, 7.80 Hz), 7.36 (8H, m), 7.20-7.04 (14H, m), 4.96 (4H, s), 4.49 (1H, w), 4.40 (2H, w), 4.32-3.98 (15H, m), 3.85 (3H, m), 3.68

(5H, w), 3.42 (4H, s), 3.00 (6H, w), 2.92 (2H, m), 1.88(2H, s), 1.54 (4H, w), 1.45 (4H, m), 1.36-1.11 (30H, m), 0.87 (8H, m), 0.82-0.74 (18H,m). ^{13}C NMR (151 MHz,$CDCl_3$ and CD_3OD, ppm): δ 171.2, 164.2, 163.9, 156.5,146.0, 136.4, 133.8, 129.0, 128.5, 128.3, 127.7,126.9, 126.7, 123.6, 123.0, 121.7, 121.1,117.8, 103.2, 80.0, 69.6, 69.3, 69.1, 66.3, 44.2, 39.2, 37.8, 37.0, 31.7, 30.6, 29.5, 29.3, 29.2, 29.0, 28.6, 28.0, 23.9, 22.9,13.8, 10.4. Mass (MALDI-TOF): m/z 2004.2 ($M+Na^+$). ESI-HRMS: calcd for [$M+Na^+$] $C_{110}H_{140}N_{12}NaO_{22}$2005.0136; found 2005.0110.

3. HPLC analysis of compound **1**.



HPLC conditions: 20×250 mm Buckyprep–M column; flow rate 6 mL/min; toluene as eluent.

4. Supporting figures.

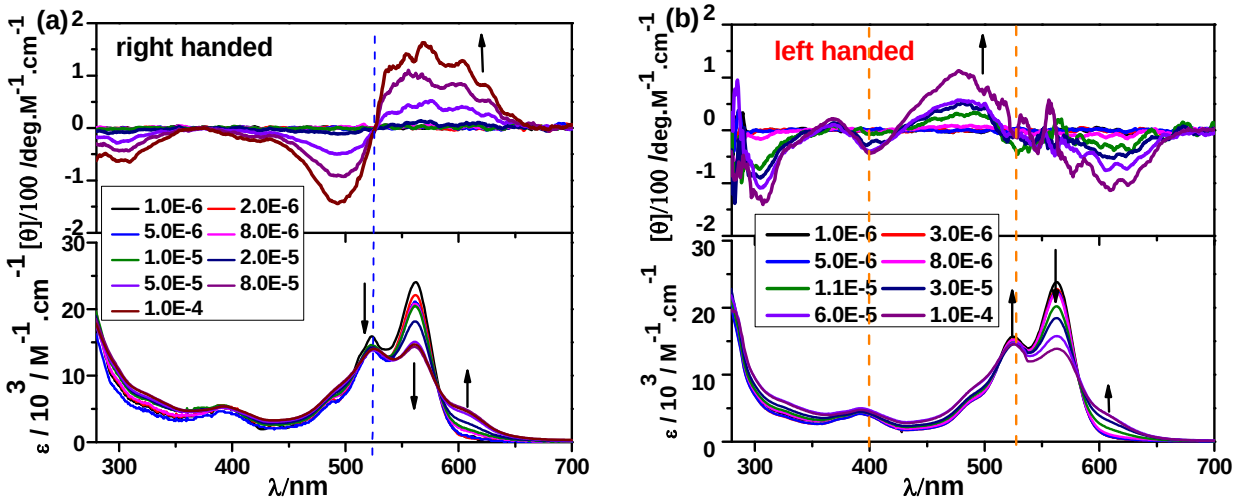


Figure S1. Concentration-dependent CD and UV-vis spectra of the right-handed (a) and left-hande (b) twist nanohelices formed from the heating-cooling and heating-sonication circles in THF.

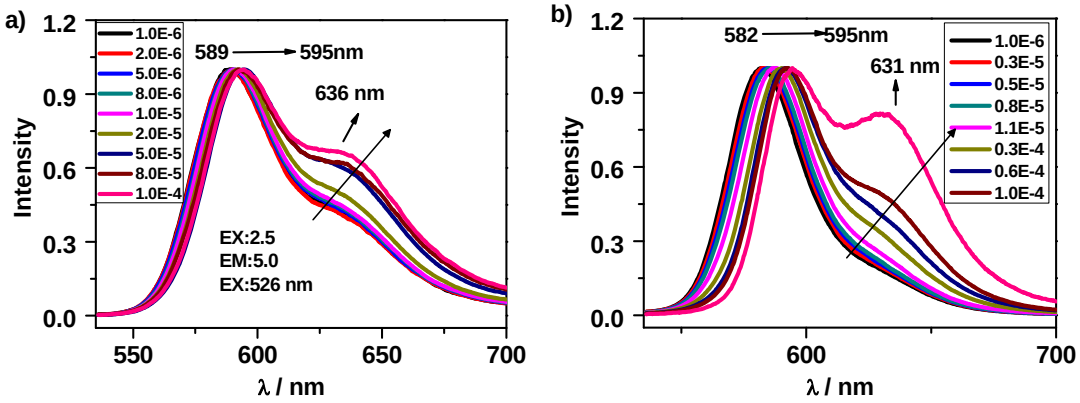


Figure S2. Concentration-dependent fluorescence spectra of the right-handed (a) and left-handed (b) nanohelices formed from the heating-cooling and heating-sonication circles in THF.

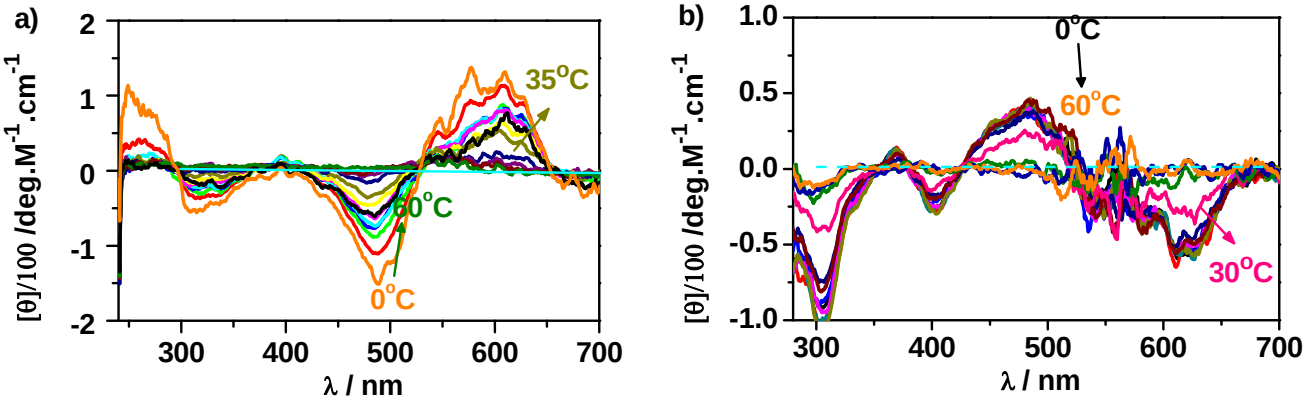


Figure S3. Temperature-variable CD of the right-handed (a) and left-handed (b) PDI@β-sheet nanohelices formed from the heating-cooling circle and heating-sonication circles, respectively.

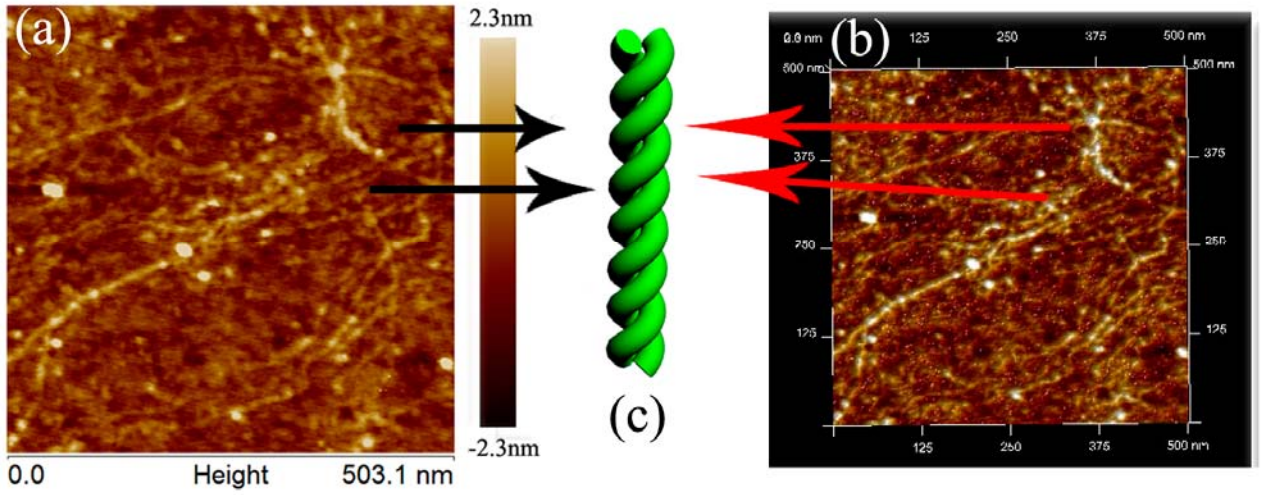


Figure S4. The atomic force microscopy (AFM) 2D images (a) and 3D height images (b) and the model (c) of the right-handed nanohelices, formed at [1]= 2.0×10^{-5} M, in THF and under the heating-cooling conditions.

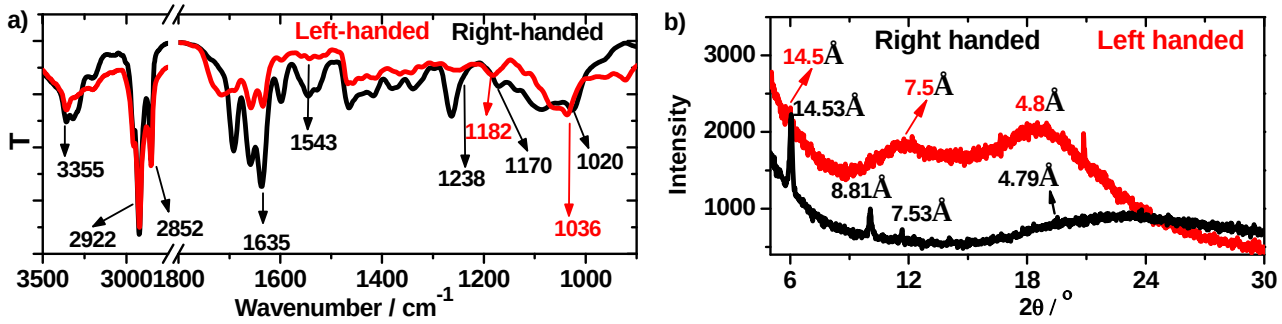


Figure S5. FTIR spectra (a) and XRD pattern (b) of the right- (black) and left-handed (red) nanohelices.

The values of the C-O-C stretching vibration around 1170, 1182 and 1020, 1036 $cm^{-1}$are assigned to the C-O-C asymmetrical and symmetrical stretching vibration, which are in accordance with the references.

The following equation was applied to estimate the vibrational frequency:

$$\bar{\upsilon} = \frac{1}{2\pi c}\sqrt{\frac{f}{(M_x M_y)/(M_x + M_y)}}$$

υ is vibrational frequency; c speed of light; f force constant of the bond; M_x and M_y mass of the atom x and y.

The increase of vibrational frequency will cause force constant increase. And the force constant partially depends on the bond patterns and bond intension. So the shifts of vibrational frequency in the right-handed nanohelices toward lower frequencies than that of the left-handed nanohelices indicated the conformation change of the 2-ethoxyethoxyl linkers.

5. **NMR data.**

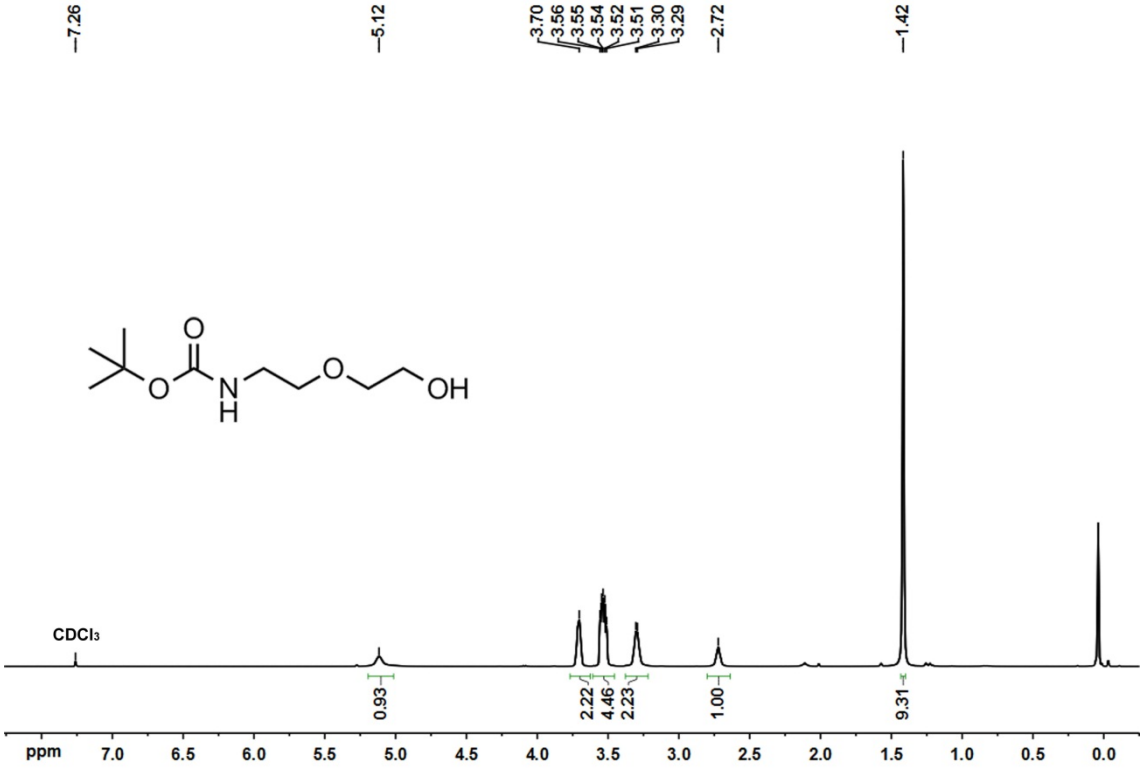


Figure S6. ^{1}H NMR spectra of **3** in $CDCl_3$.

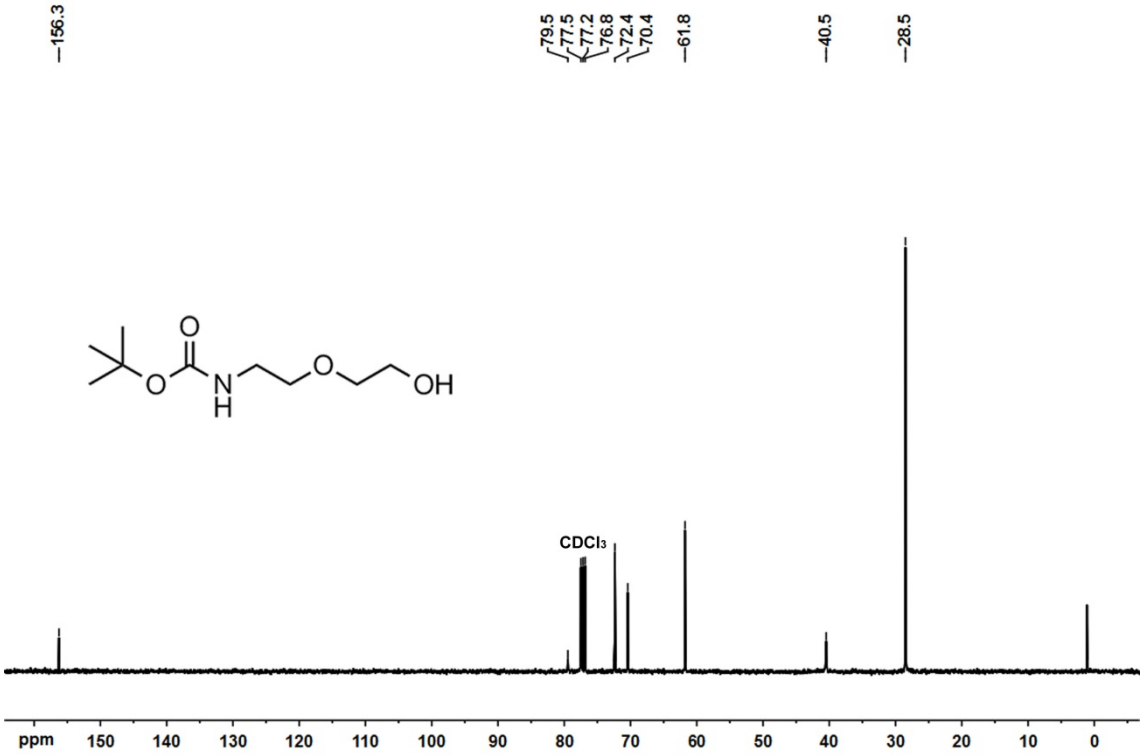


Figure S7. ^{13}C NMR spectra of conjugate **3** in $CDCl_3$.

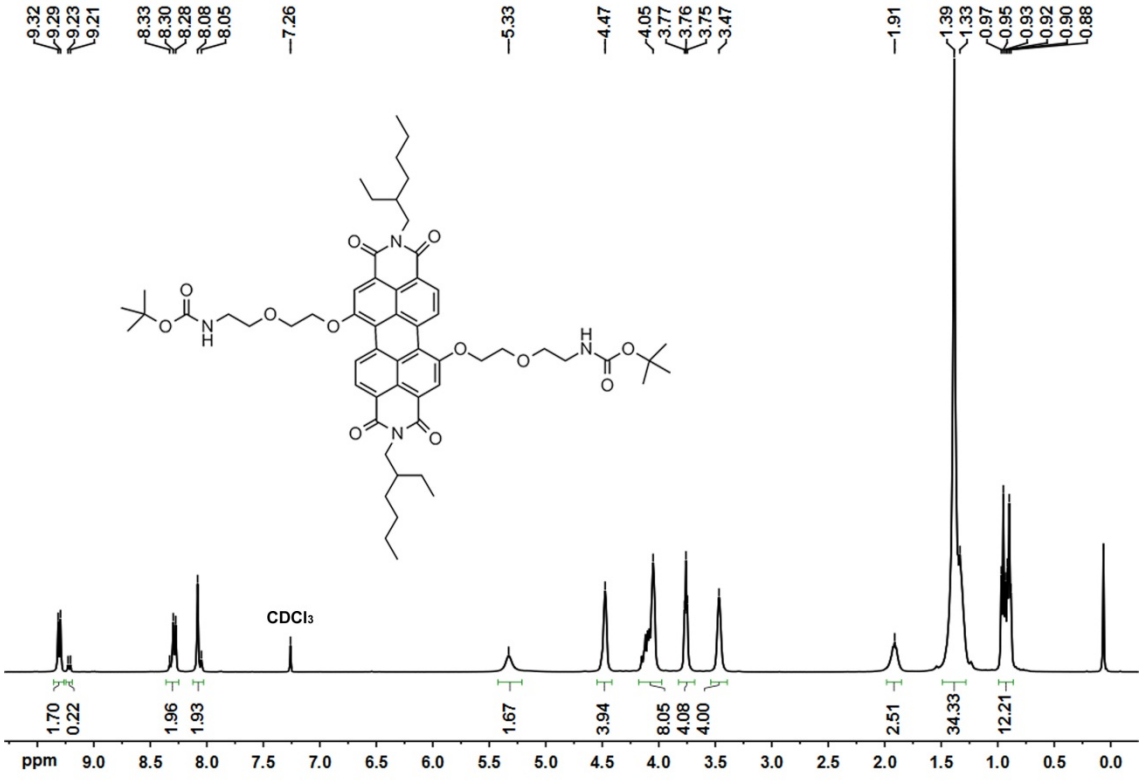


Figure S8. ^{1}H NMR spectra of **4** in $CDCl_3$.

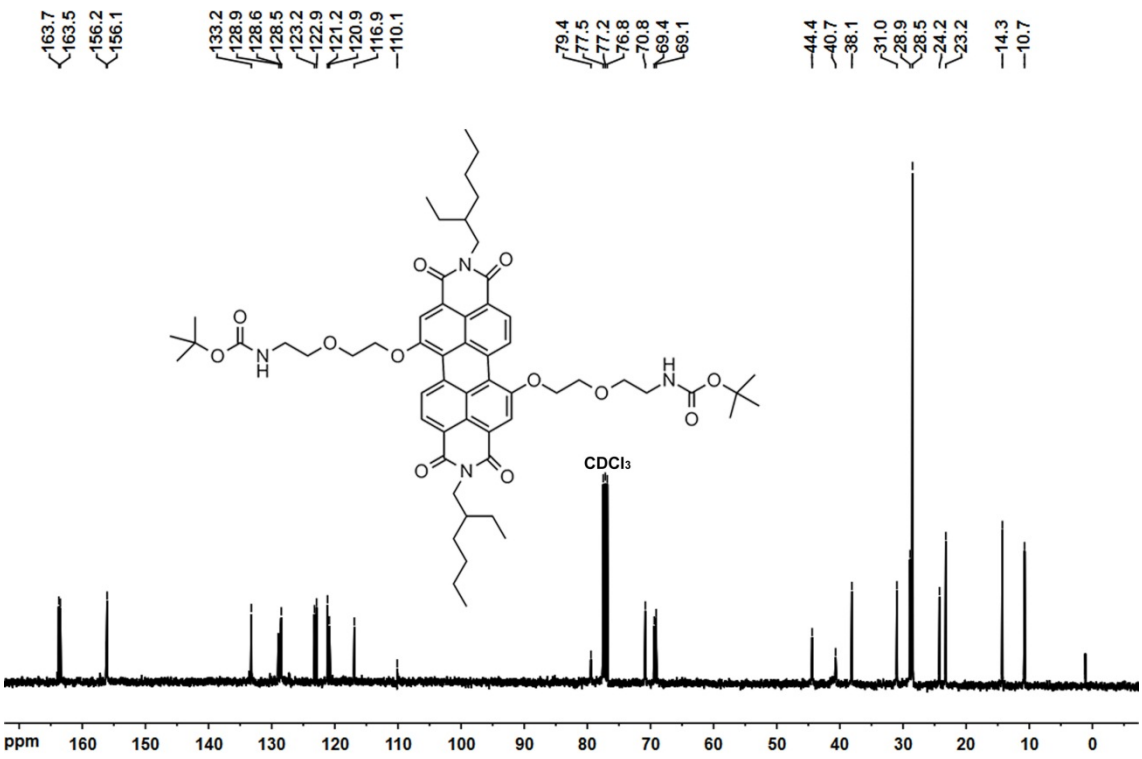


Figure S9. ^{13}C NMR spectra of conjugate **4** in $CDCl_3$.

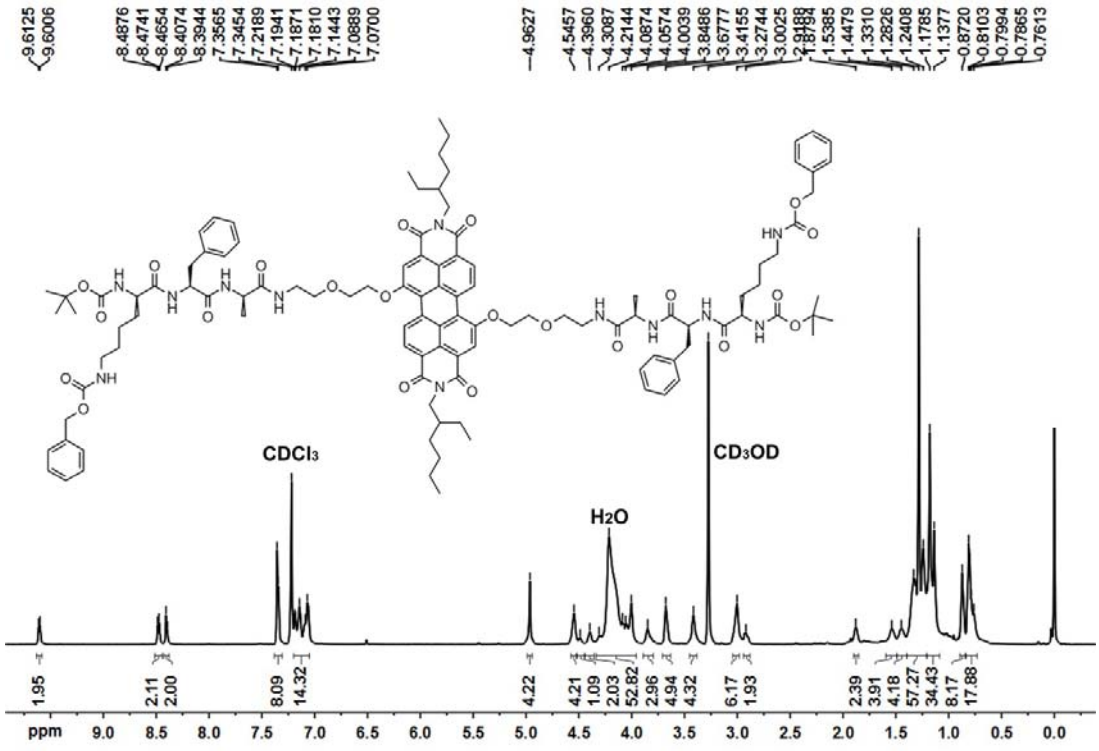


Figure S10. ^{1}H NMR spectra of **1** in $CDCl_3$and CD_3OD.

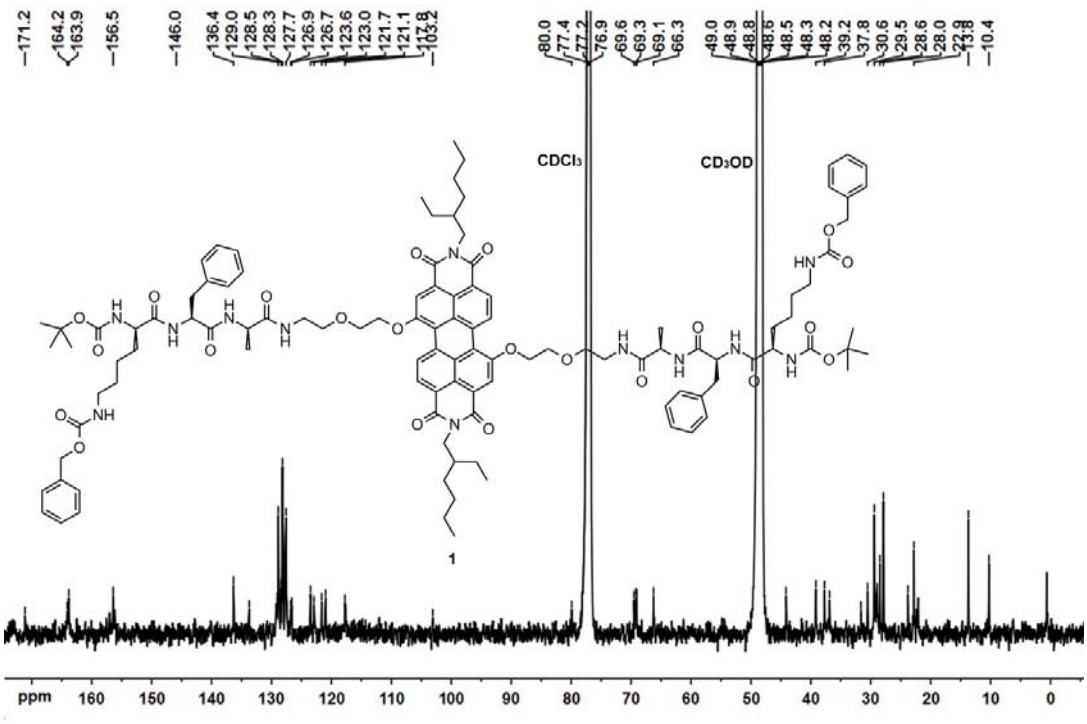


Figure S11. ^{13}C NMR spectra of conjugate **1** in $CDCl_3$ and CD_3OD.

Reference.

1. X. Zhang, S. F. Pang, Z. G. Zhang, X. L. Ding, S. L. Zhang, S. G. He, C. L. Zhan, *Tetrahedron Lett.* 2012, **53**, 1094–1097.