Electronic Supplementary Information

Modulating helicity through amphiphilicity-tuning supramolecular interactions for the controlled assembly of perylenes

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Experimental

1. Synthesis and characterization of PTCDI-HAG

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\begin{align*}
\text{NH}_4\text{OAc} & \quad \text{KOH} \quad \text{t-BuOH} \\
\text{NaBH}_3\text{CN} & \quad \text{imidazole}
\end{align*}
\]

1-hexylheptylamine (1)\(^1\)

2.50 g (12.6 mmol) 7-tridecanone, 10.0 g (129 mmol) NH\(_4\)OAc, and 0.56 g (8.9 mmol)NaBH\(_3\)CN were dissolved in 40 mL absolute MeOH and stirred at room temperature for 56h, until starting material was gone by TLC (R\(_f\) = 0.8 in CHCl\(_3\), dark blue with p-anisaldehyde). The mixture was quenched by added concentrated HCl dropwise (~2 mL), then concentrated with a rotary evaporator. The resulting white solid was taken up in 200 mL H\(_2\)O, taken to pH~10 with solid KOH, and extracted with 300 mL and then 150 mL of CHCl\(_3\). The CHCl\(_3\) fractions were combined and concentrated to give 2.3 g (90%) of pale yellow oil. \(^1\)H NMR (400 MHz,CDCl\(_3\)): \(\delta = 0.88\) (t, 6H), 1.18-1.33 (m, 16H), 1.37 (m, 4H), 2.67 (quint, 1H).

\(N,N'\)-bis(1-hexylheptyl)perylene-3,4,9,10-tetracarboxylbisimide (2)\(^1\)

1.44 g (3.7 mmol) perylene-3,4,9,10-tetracarboxylicdianhydride and 2.67 g (9.4 mmol) 1 in 6.0 g imidazole were stirred 3h at 130° C. The reaction mixture was cooled to room temperature, taken up in 100 mL ethanol, treated with 300 mL 2M HCl, and stirred overnight. The dark red precipitate was filtered and rinsed thoroughly with distilled water, and dried in vacuum at 60 °C to give 2.51g (90%) of red solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 0.83\) (t, 12H), 1.18-1.30 (m, 32H), 1.84 (m, 4H), 2.25 (m, 4H), 5.19 (m, 2H) , 8.67 (m, 8H).
N-(1-hexylheptyl)perylene-3,4,9,10-tetracarboxyl-3,4-anhydride-9,10-imide (3) \(^1\)

1.0 g (1.3 mmol) 2 was suspended in 60 mL \(t\)-BuOH and treated with 0.70 g solid 85% KOH. The reaction mixture was heated with vigorous stirring to reflux until the solution turned dark purple, ~1.5 h. The mixture was cooled to room temperature, treated with 30 mL acetic acid and stirred for 1 h, then added 20 mL 2M HCl and stirred overnight. The dark red precipitate was filtered, washed with distilled water, and dried in a vacuum oven at 60 °C. This solid was suspended in 50 mL 10% K\(_2\)CO\(_3\) solution and heated to reflux for 1 h. The mixture is cooled and filtered, the filter cake was rinsed with 10% K\(_2\)CO\(_3\) solution until the filtrate was clear, then stirred with 200 mL 2 M HCl overnight. The resulting solid was collected and rinsed with distilled water, then dried in vacuum at 60 °C. This solid was further purified by silica gel thin layer chromatography (TLC) (eluent CH\(_2\)Cl\(_2\)) to provide the title compound (0.15 g, 15%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 0.78\) (t, 6H), 1.18-1.30 (m, 16H), 1.75 (m, 2H), 2.15 (m, 2H, 5.18 (m, 1H) , 8.61 (m, 8H)

(4-Aminophenyl)-\(\alpha\)-D-glucopyranoside(4) \(^2\)

A catalytic amount of Pd/C (10 %) (ca.1.0mg) was added to a solution of (4-nitrophenyl)-\(\alpha\)-D-glucopyranoside (0.50 g, 1.66 mmol) in 50 mL THF/water (9:1) at ambient temperature under hydrogen atmosphere. After 24 h stirring under hydrogen atmosphere, the mixture was filtered and concentrated in vacuo to yield the amine (0.4 g, 88%) as a white solid. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) (ppm): \(\delta = 3.10\) (m, 1H), 3.23 (m, 1H), 3.57 (m, 4H), 4.44 (m, 1H), 4.67 (s, 2H), 4.82 (d, 1H, \(J = 4.8\) Hz), 4.90 (m, 2H), 5.04 (m, 1H), 6.44 (d, 2H, \(J = 4.5\) Hz), 6.76 (d, 2H, \(J = 6.3\) Hz).

N-(1-hexylheptyl)-\(N'\)-(4-aminophenyl)-\(\alpha\)-D-glucopyranoside-perylene-3,4:9,10-tetracarboxylibisimide (5)

0.115 g (0.2 mmol) 3 and 0.065 g (0.24 mmol) 4, 0.183 g Zn(OAc)\(_2\) in 6 g imidazole and stirred for 2h at 120° C under N\(_2\). The reaction mixture is cooled to room temperature, and then added 5 mL H\(_2\)O and 30 mL C\(_2\)H\(_5\)OH to the mixture. The dark red precipitate was filtered, washed with distilled water, and dried in vacuum at 60 °C. This solid was further purified by recrystallization with CHCl\(_3\)/n-C\(_6\)H\(_{14}\) to give the dark red solid (0.11 g, 64%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 0.831\) (s, 6H), 1.30-1.24 (m, 16H, \(J = 23.4\) Hz), 1.86 (s, 1H), 2.16 (s, 1H), 3.68-3.32 (m, 7H), 4.57 (s, 1H), 5.03 (m, 2H), 5.14 (d, 1H, \(J = 5.8\) Hz), 5.50 (s, 1H), 7.35 (dd, 4H, \(J = 7.2\) Hz), 8.18 (d, 2H, \(J = 26.9\) Hz). \(^{13}\)C NMR (solid, 400 MHz): \(\delta = 162.9\) , 131.6, 123.4, 102.7, 96.3 (br), 60.9, 55.2, 30.6, 23.4, 14.6. MS (MALDI-TOF): calcd for C\(_{40}\)H\(_{50}\)N\(_2\)O\(_{10}\), 826.35 m/z, found 826.3. Anal. Calcd for C\(_{40}\)H\(_{50}\)N\(_2\)O\(_{10}\): C, 71.17; H, 6.09; N, 3.39. Found: C, 69.73; H, 5.96; N, 3.68.
2. Methods

Circular dichroism (CD) measurements were conducted on a JASCOJ-810 spectrometer at room temperature. UV-Vis adsorption spectra were recorded on Perkin-Elmer Lambda 950 UV-Vis spectroscopy. Fluorescence spectra were recorded by using a Perkin-Elmer LS 55 luminescence spectrometer. X-ray diffraction measurements were carried out on a Japan Rigaku D/max-2500 rotation anode X-ray diffractometer quipped with graphite monochromatized Cu Kα radiation (λ = 1.5406 Å). The samples for X-ray diffraction measurement were prepared on glass cover slips by drop casting, followed by drying at room temperature. TEM measurement was acquired using a TECHNAI G² 20 S-TWIN transmission electron microscopy (200 KV). The sample was prepared by dropping the sample (1 µl) on carbon-film-covered 200 mesh grids, followed by drying in air. Contact angles were measured on an OCA20 machine at ambient temperature. The film samples for contact angles measurement were prepared by dropping the chloroform/n-octane (50/50, v/v) or tetrahydrofuran / water (50/50, v/v) solution containing helical nanowires, followed by drying in air, and annealed at 120 °C for 12 h before measured. ¹H NMR was acquired using a Bruker 400 MHz NMR spectrometer. Liquid-state ¹³C NMR was acquired using a Bruker 600 MHz NMR spectrometer. Solid-state ¹³C NMR was acquired using a Bruker AVANCE III 400 MHz NMR spectrometer.

References
Additional Figures

Figure S1. XRD patterns of PTCDI-HAG helical nanofibers obtained from CHCl₃/n-C₈H₁₈ and THF/H₂O

Figure S2. The fluorescence spectra of PTCDI-HAG in a) CHCl₃/C₈H₁₈ and b) THF/H₂O (Excitation wavelength λₑxc = 480 nm ).
Figure S3. Enlarge image of Figure 2 c and d.