Supporting information

A Reversible Helical Chirality of Perylene Bisimide Aggregates: Amino Acid-Directed Chiral Transfer and Chiral Inversion

Yizhi Liu, [a] Xinpei Gao, [a] Fei Lu, [a] Mei Hu, [c] Lijuan Shi [b] and Liqiang Zheng [a]

a. Key laboratory of Colloid and Interface Chemistry, Shandong University, Ministry of Education, Jinan, 250100, P. R. China
b. Key Laboratory of Coal Science and Technology of Ministry of Education and Shanxi Province, Taiyuan University of Technology
c. Shandong Institute for Food and Drug Control, Jinan 250100, China.

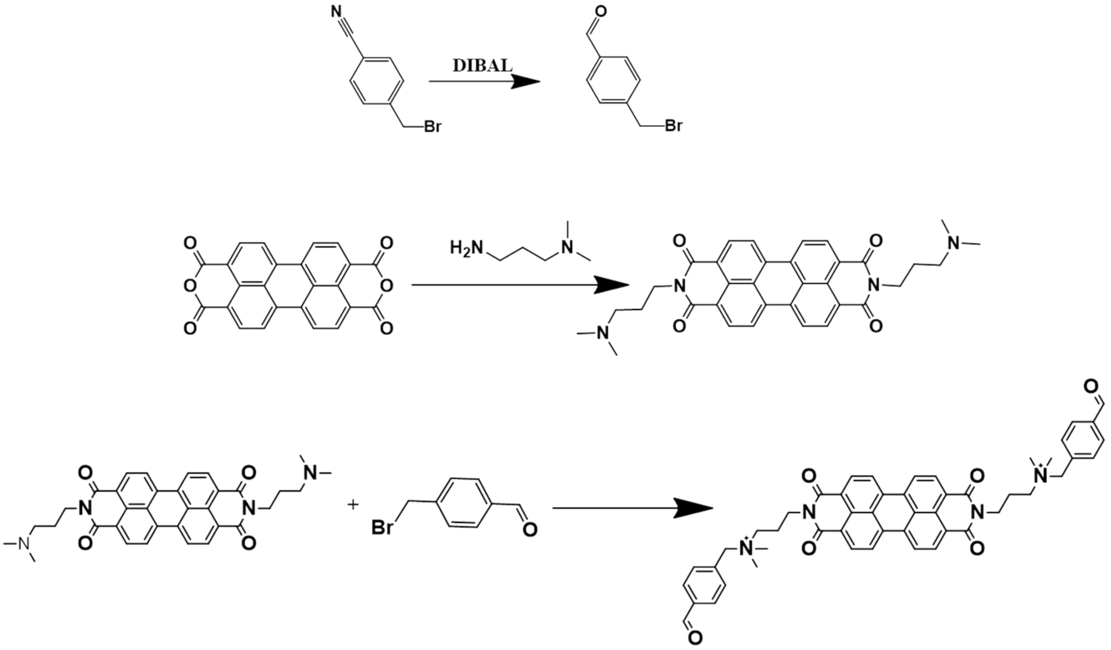
Materials. Perylene-3,4,9,10-tetracarboxylic dianhydride (98%), N,N-dimethyl-1,3-propanediamine (98%), diisobutylaluminiumhydride (DIBAL), *L*-/*D*-phenylalanine (98%), *L*-/*D*-tyrosine (98%), *L*-alanine (98%), *L*-leucine (98%), *L*-valine (98%), *L*-aspartic acid (98%), *L*-glutamic acid (98%), (S)-(-)-1-phenylethylamine (98%), (S)-1-(4-methoxyphenyl)ethylamine (98%) and (S)-(+)-1-cyclohexylethylamine (98%) were purchased from J&K Scientific Ltd. sodium hydroxide, acetone and dimethylformamide methanol ethanol were purchased from Shanghai Chemical Co. All the above materials were used without further purification. Milli-Q water (18.25 MΩ·cm) was used in all cases.

Synthesis of 4-(Bromomethyl)benzaldehyde.[1] 4-

(bromromethyl)benzonitrile (10.00 g, 51.0 mmol) was dissolved in dry toluene (200 mL) and cooled to 0 °C. 1.2 M DIBAL in toluene (64 mL, 7.65 mmol) was added dropwise and the reaction mixture was stirred at 0 °C for 1 hour. Then, 10% HCl (200 mL) were added and the reaction mixture was stirred at room temperature overnight. The organic layer was extracted three times with water, dried over magnesium sulfate, filtered, and evaporated to afford the crude product. Needle-like crystal was obtained by recrystallizing with hexane 8.55 g (84.2%).

Synthesis of N,N'-Bis(propanedimethylamine)-3,4,9,10-perylenediimide (PBIPr). N,N'-Bis(propanedimethylamine)-3,4,9,10-perylenediimide (PBIPr) was synthesized according to a reported procedure.[2] 3,4,9,10-perylenetetracarboxylic acid dianhydride (PTCDA, 1.18 g, 3 mmol) was added to 50 mL N,N-dimethyl-1,3-propanediamine and stirred at 90 °C for 24 h under nitrogen atmosphere. The reaction mixture was allowed to cool to room temperature and the crude product was filtered and washed with deionized water and ethanol. The obtained residue was suspended in 5% aqueous NaOH solution to remove the unreacted PTCDA. The suspension was filtered and washed with water and ethanol, dried under vacuum to give PBIPr as a dark red solid (1.43g, 84.8%).

Synthesis of BAPBI. 4-(bromomethyl)benzaldehyde (0.40 g, 2.0 mmol) and PBIPr (0.112g, 20.2 mmol) were mixed in 15 mL MeCN and refluxed for 24 h in a nitrogen environment. The reaction mixture was filtered and refluxed for 30 min with MeOH to remove PBIPr. The residue was filtered, washed with chloroform and dried under vacuum to give 0.74g black powder (0.14 g, 73.1%). ^{1}H-NMR (300M, DMSO-d_6, 25 °C): δ (ppm) 10.04 (s, 2H), 9.03 (d, J = 8.1, 4H), 8.65 (d, J = 8.1, 4H), 7.97 (d, J = 8.2 Hz, 4H), 7.74 (d, J = 8.2 Hz, 4H), δ = 4.61 (4H, CH_2), δ = 4.19 (4H, CH_2), δ = 2.99 (12H, CH_3), δ =2.73 (4H, CH2), δ =2.27 (4H, CH_2). m/z: Calcd for $C_{50}H_{46}N_4O_6^{2+}$: 399.6725; Found: 399.6707.



Characterization. UV− vis spectroscopy measurements were carried out using a U-4100 UV–vis spectrophotometer. Circular dichroism (CD) measurements were performed on a JASCO J-810 spectropolarimeter, which was flushed with constant nitrogen flow during operation to purge the ozone generated by the light source of the instrument. The spectra were smoothed by using the noise-reducing option in the operating software of the instrument. Three scans were averaged per spectrum to improve the signal-to-noise ratio. Wavelength scans were recorded at 1 nm intervals from 700 to 200 nm. The solution was determined using a 0.1 mm path-length quartz cuvette at 25 °C. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker ALPHA-T with a wavenumber resolution of 4 $cm{\cdot}S^{-1}$ at room temperature. Morphology and size was characterized using a JEOL JEM-100CX II transmission electron microscope (TEM) and a JEOL JSM-6700F field-emission scanning electron microscope (SEM). Atomic force microscopy (AFM) with a Nanoscope IIIA (Digital Instruments, USA) in tapping mode was used.

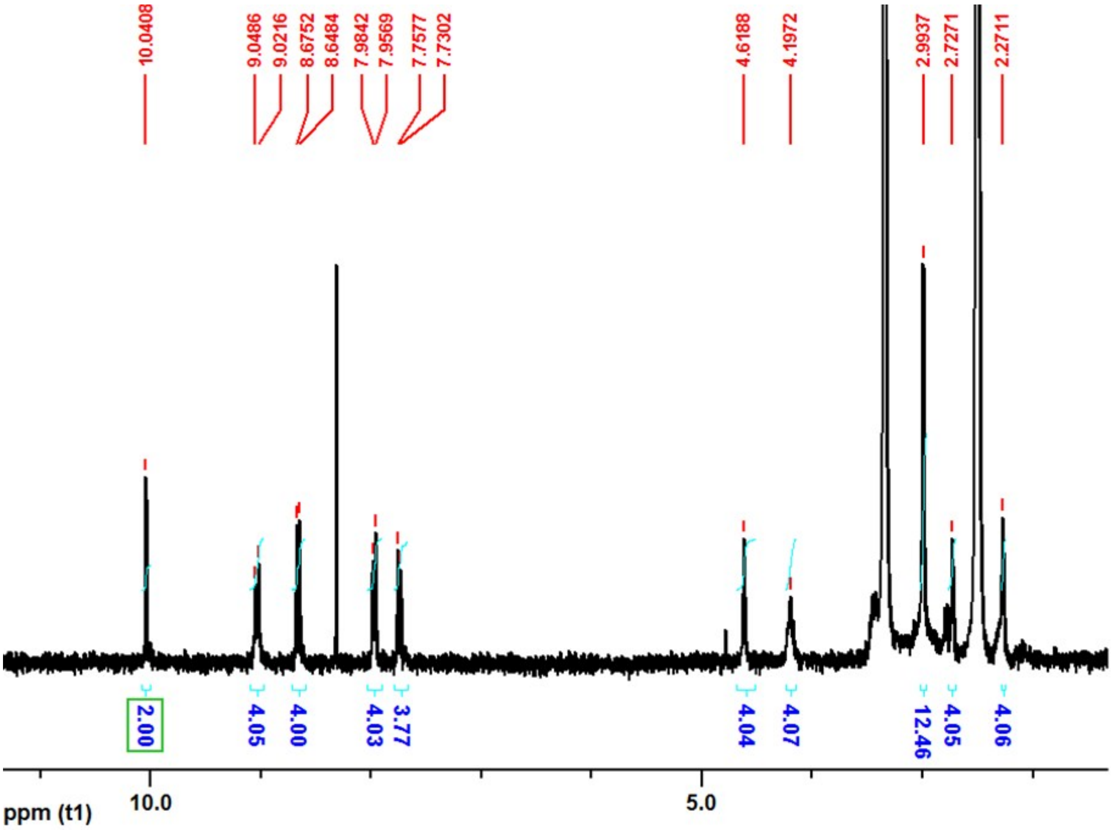


Fig. S1 ^{1}HNMR of BAPBI (300 MHz) in DMSO-d_6.

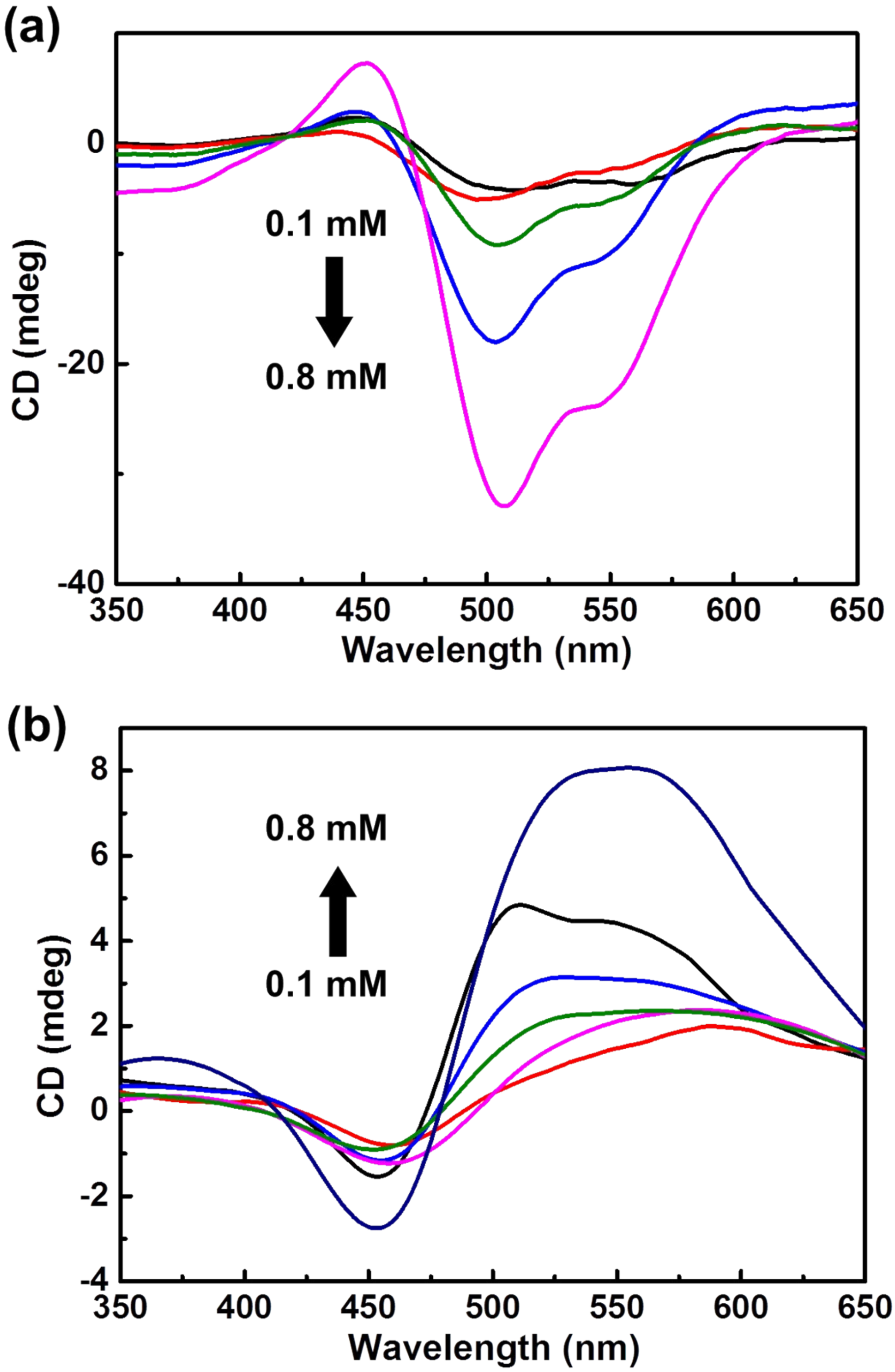


Fig. S2 (a) CD spectra of BAPBI (0.1 mM) in the presence of *L*-Phe of increasing concentration in pH = 12.0 Na_3PO_4 aqueous solution; (b) CD spectra of BAPBI (0.1 mM) in the presence of *L*-Tyr of increasing concentration in pH = 7.0 aqueous solution.

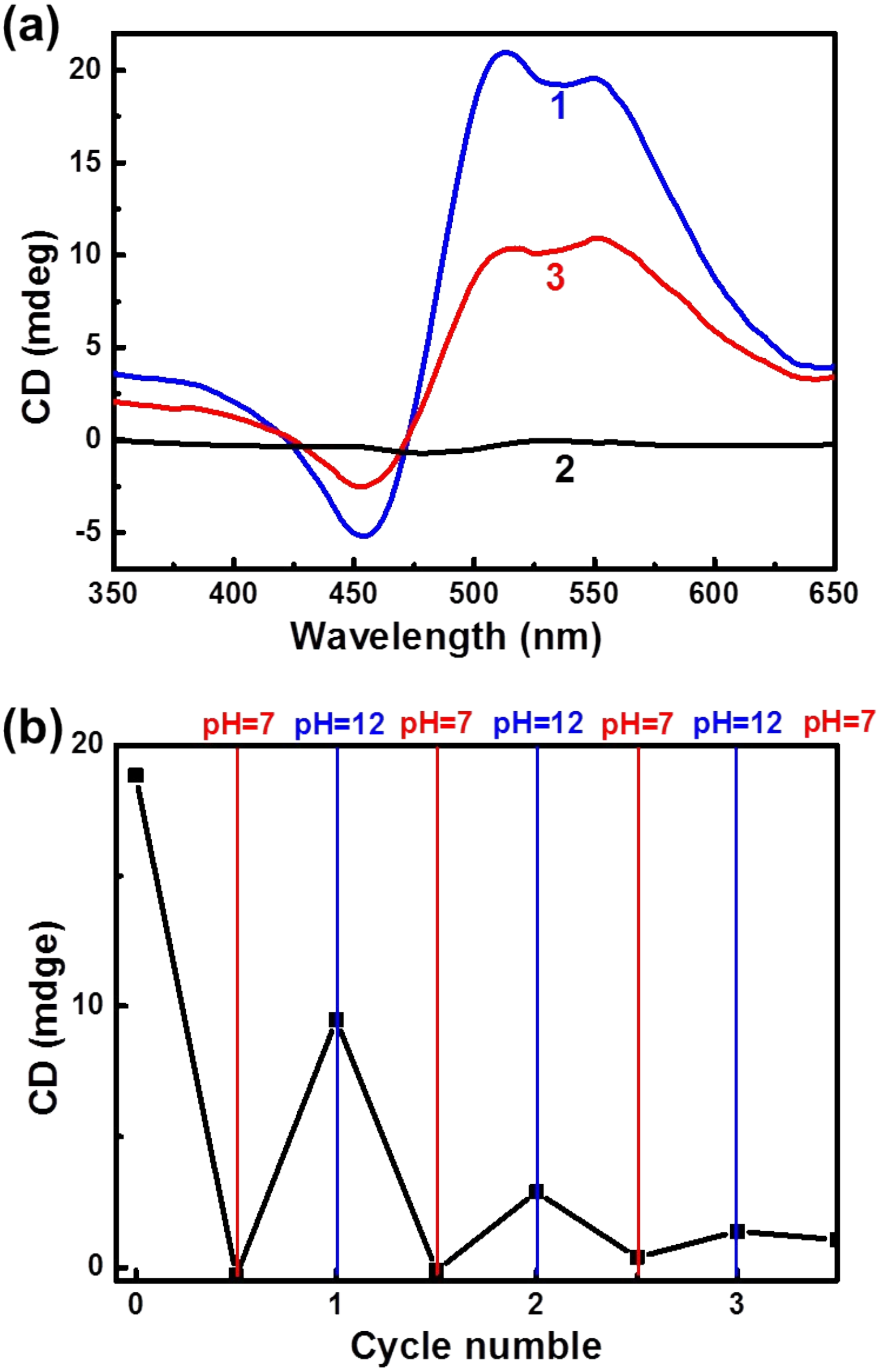


Fig. S3 (a) CD spectra of the BAPBI/D-Phe with the acid–base response. (b) Plot of CD signals at 504 nm upon four cycles of alternate conditions of pH=7 or pH=12. The pH values are adjusted by adding HCl or NaOH. The numbers in (a) represent: 1. BAPBI/D-Phe; 2. BAPBI/D-Phe/HCl; 3. BAPBI/D-Phe/HCl/NaOH.

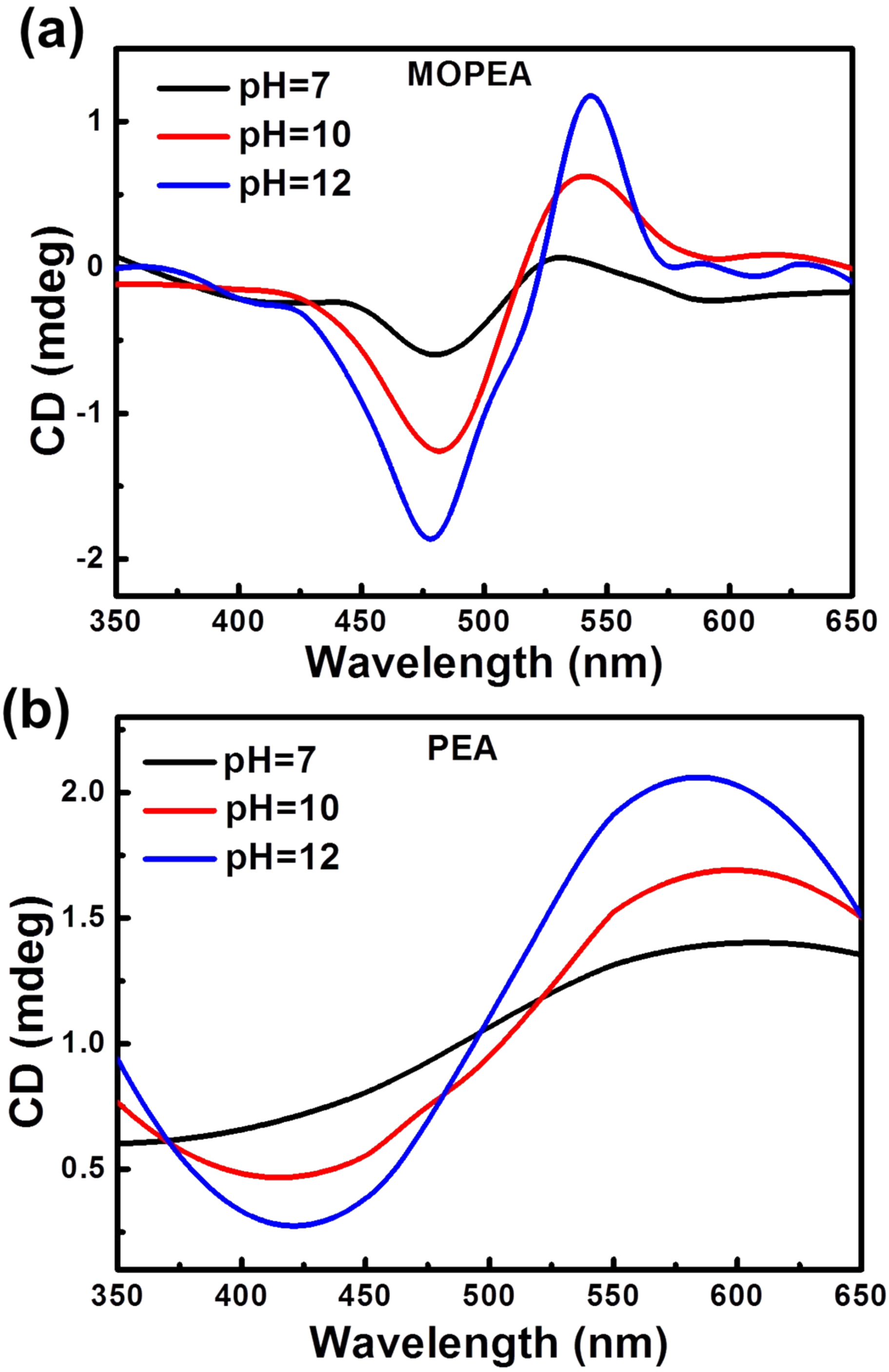
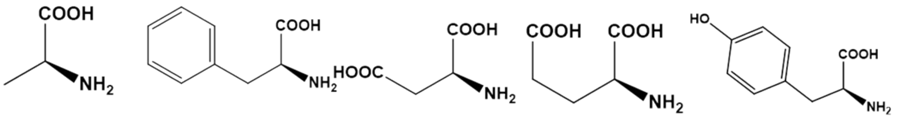
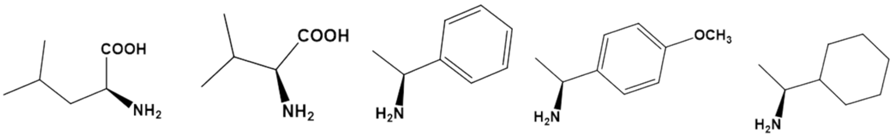


Fig. S4 CD spectra of (a) BAPBI/*S*-MOPEA complexes and (b) BAPBI/-*S*-PEA at different pH values.

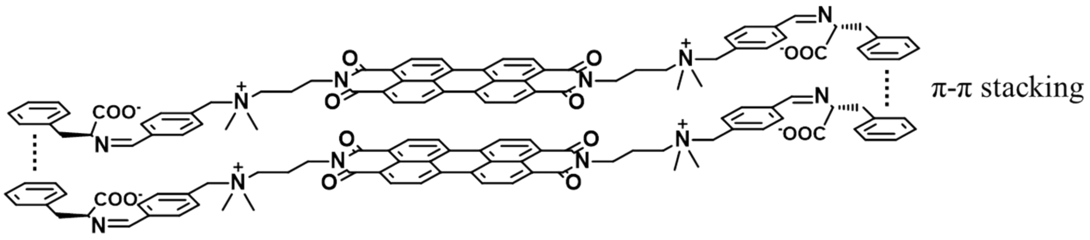
Chart S1. Structures of chiral primary amines and the corresponding Cotton effects in induced chiral BAPBI aggregates.



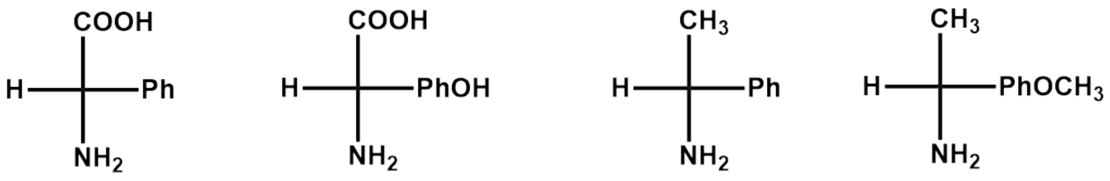
chiral amine	Ala	*L*/*D*-Phe	Asp	Glu	*L*/*D*-Tyr
Cotton effect	none	negative/ positive	none	none	positive/ negative



chiral amine	Leu	Val	*S*-PEA	*S*-MOPEA	*S*-EACYH
Cotton effect	none	none	positive	positive	none

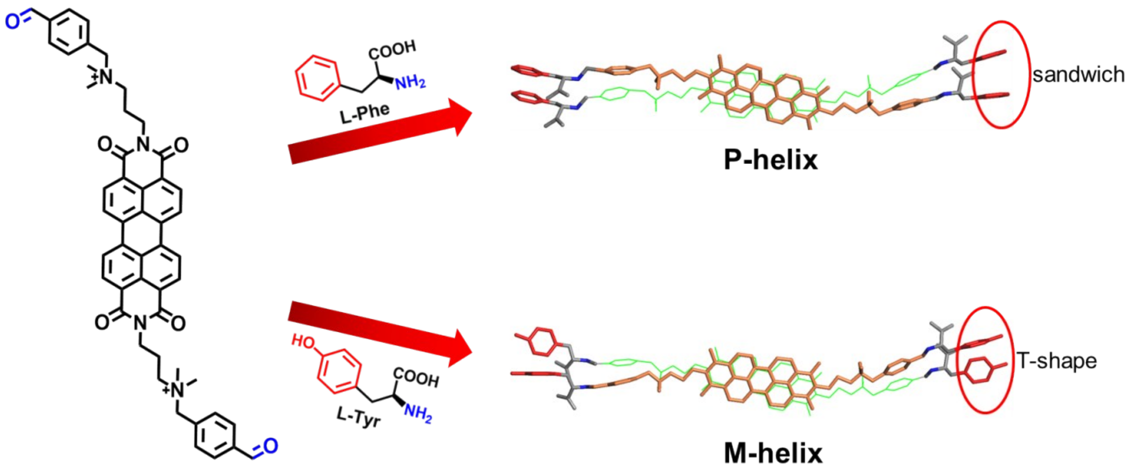


Scheme S1. Proposed structures for the BAPBI/*L*-Phe.



D-Phe D-Tyr S-PEA S-MOPEA

Fig. S5 Fischer projection of D-Phe, D-Tyr, S-PEA and S-MOPEA.



Scheme S2. Proposed mechanism of the formation of opposite helical arrangements induced by *L*-Phe and *L*-Tyr.

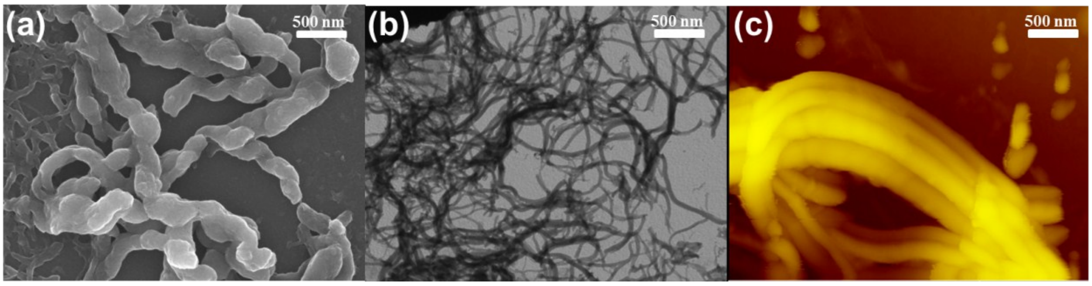


Fig. S6 SEM (a), TEM (b) and AFM (c) image taken from a sample prepared from a solution of BAPBI (0.1 mM) and Phe (1.0 mM).

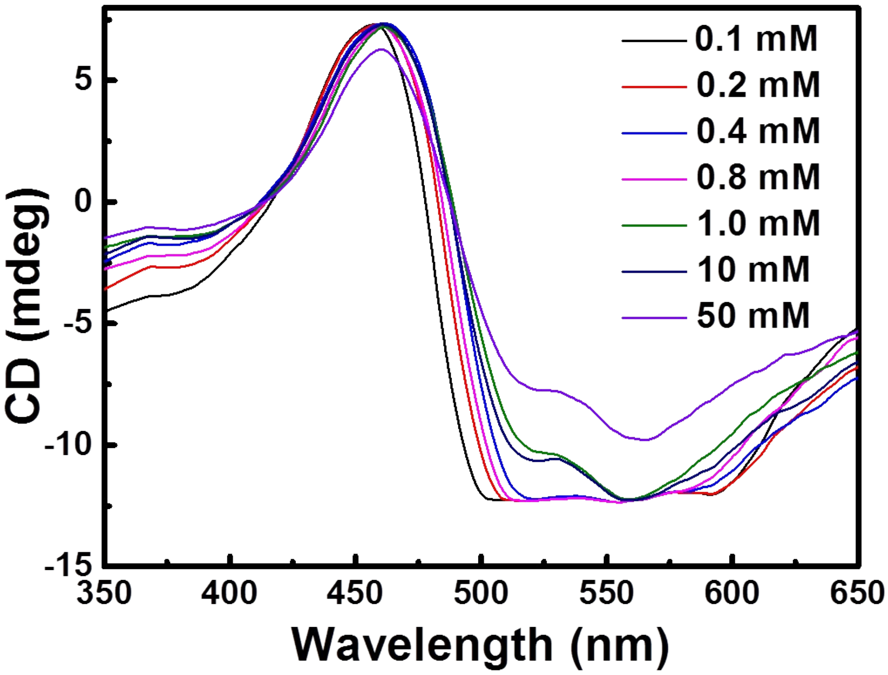


Fig. S7 CD spectra of BAPBI/L-Phe with the presence of different concentration of aniline. BAPBI (0.1 mM) and Phe (1.0 mM)

Reference

1. O. Iliashevsky, L. Amir, R. Glaser, R. S. Marks, N. G. Lemcoff, *J. Mater. Chem.*,2009, **19**, 6616.

2. K. Liu, Y. X. Yao, Y. T. Kang, Y. Liu, Y. C. Han, Y. L. Wang, Z. B. Li, X. Zhang, *Sci. Rep.*, 2013, **3**, 2372.