Supporting Information

Controlled Self-Assembly of Helical Nano-ribbons Formed by Achiral Amphiphiles

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The aqueous solution with self-assembled structures of TPP-11 was casted onto silicon substrate and investigated by powder X-ray diffractometer (XRD) (X'pert-pro MRD produced by Panalytical, Netherlands). As shown in Fig S1a, two peaks appear at $2\theta = 5.01°$, and 7.05°, which correspond to the distance of 1.76 and 1.26 nm, respectively. These two distances match well with the lengths of pyridinium alkyl chain and the aromatic part of the TPP-11, as illustrated in Fig S1c. As known that the strong diffraction happens at area where the electron density changes abruptly. This appearance of the two peaks suggest that the molecules are paralell packed in the helical nanostrcutures.

The above prepared sample was also analyzed by Grazing incidence small angle X-ray scattering (GISAXS) (SAXSESS mc2 manufactured by Anton Paar, Austria). As shown in Fig S1b, the GISAXS pattern has a relatively strong diffraction signal at the vertical direction, whereas the diffractions at the other directions are weak. This result indicates that the helical nanostructures absorbed on the silicon substrates are likely lying on the surface. And the the diffraction at the other directions imply the the helicity of the nanostructures.

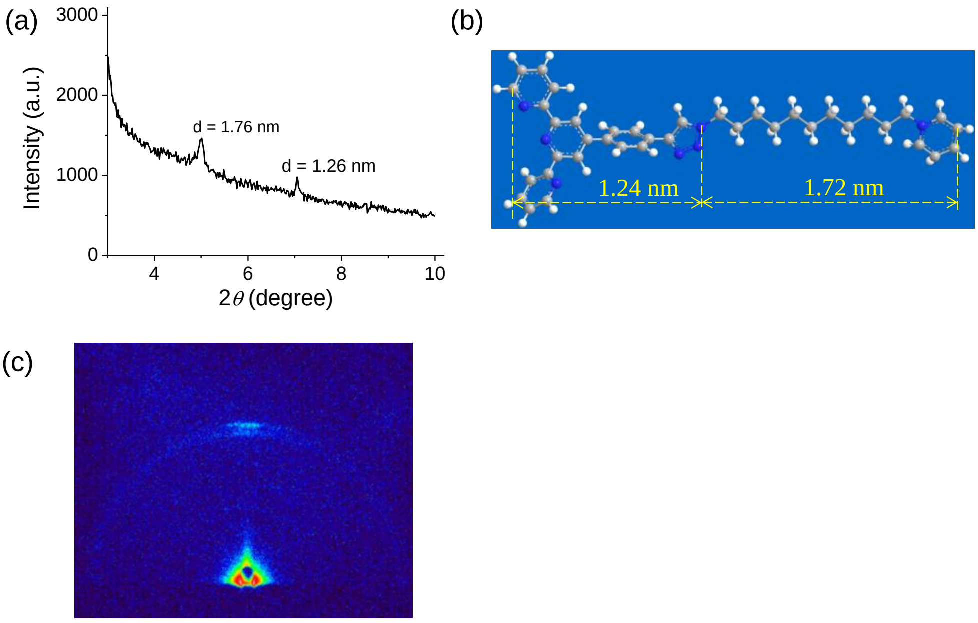

Fig. S1 XRD (a) and GISAXS (b) patterns of the self-assemblies formed by TPP-11. (c) Scheme of TPP-11 molecule and scale estimation.

Concentration effect on the self-assembled structures.

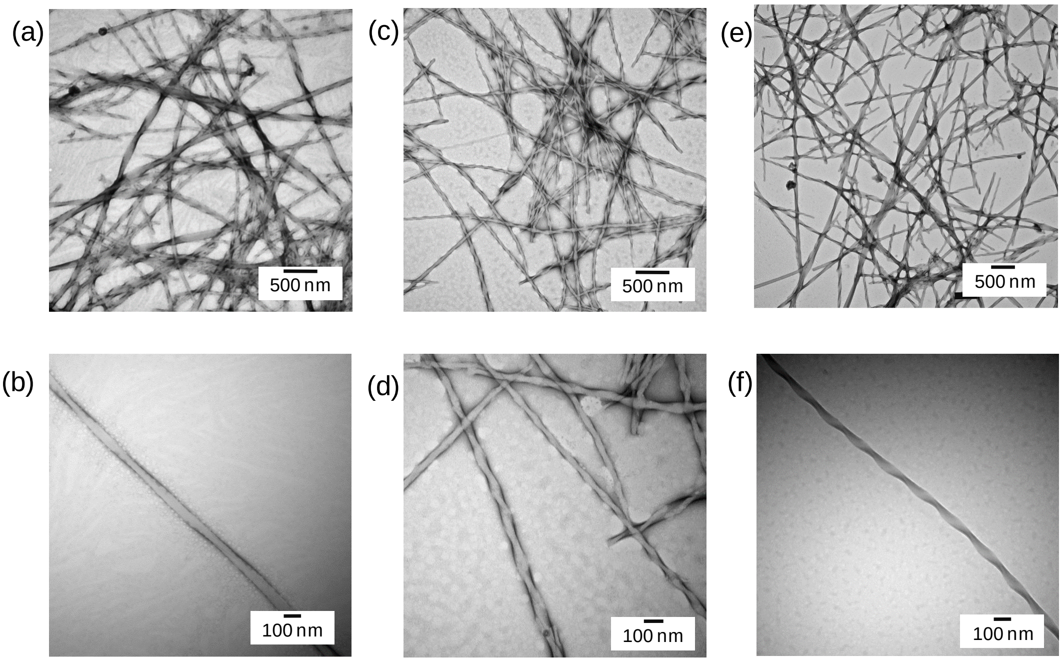

Fig. S2 TEM images of the self-assembled structures of TPP-11 with different concentrations: (a) (b), 1.0×10^{-4} mol/L; (c) (d), 2.0×10^{-4} mol/L; (e) (f), 5.0×10^{-4} mol/L.The pitches of the helical ribbons are 590, 210 and 210 nm when the concentration varies as 1.0×10^{-4} mol/L, 2.0×10^{-4} mol/L and 5.0×10^{-4} mol/L, respectively.

The NMR responses upon addition of sodium tosylate and zinc tosylate.

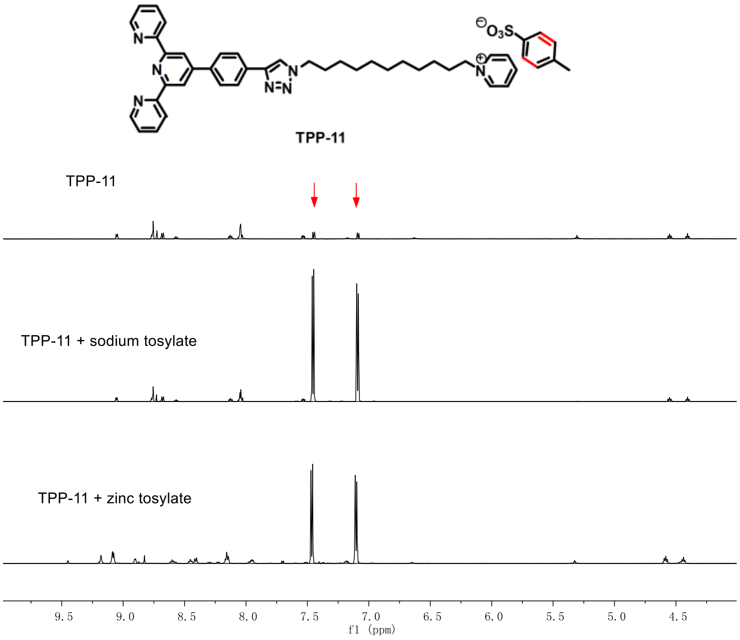

Fig. S3 The NMR spectra of TPP-11. The highlight (marked with red arrows) corresponds to the protons on tosyl group

Experiments

Materials: *N*,*N*-Diisopropylethylamine (DIPEA), CuI, $Pd(PPh_3)_4$ and pyridine were purchased from Aldrich and used without further purification. Toluene and triethylamine were distilled from sodium benzophenone ketyl immediately and potassium hydroxide, respectively.

4'-(4-bromophenyl)-2,2':6',2"-terpyridine and 11-azidoundecyl 4-methylbenzenesulfonate[1] was synthesized according to literature procedures. Milli Q water with resistivity more than 18 MΩ·cm was used all through the experiment.

Instruments: ^{1}H NMR spectra were recorded at room temperature with a Bruker Avance instrument. ^{1}H NMR spectra in $CDCl_3$ were referenced to tetramethylsilane ($\delta = 0.00$ ppm) as an internal standard. Mass spectra were recorded on a PE Sciex API 3000 spectrometer (ESI mode). UV-vis spectra were measured with a HITACHI U-3010 spectrometer. Corrected steady-state emission spectra were obtained by using a HITACHI F7000 fluorescence spectrophotometer. The critical micelle concentration (CMC) was determined by the inflection point of solution conductivity versus concentration. The conductivities were measured at 25°C with a digital conductivity instrument (DDS-307, Shanghai Precision & Scientific Instrument Co. Ltd.). Circular Dichroism (CD) was measured with Pistar π-180, Applied Photophysics Ltd.

Transmission electron microscopy (TEM) was performed on a HITACHI H-7650B operating at an accelerating voltage of 80 kV. 10 μL of aqueous solution was applied to a carbon-coated copper grid for 10 min. After removal of excess solution with filter paper, the grid was dried in the air for 15 min and then negatively stained with 10 μL of 1.5% (w/w) uranyl acetate aqueous solution for 1 min. The excess solution was wicked by filter paper. The resultant grid was dried in the air for at least 2 hour.

The atomic force microscope (AFM) images were taken on a commercial multimode Nanoscope IV (Bruker). AFM images were obtained with tapping mode in air with Si cantilevers (RTESPA, purchased from Bruker). The sample preparation in AFM observation was similar as that inthe TEM measurement, only without using uranyl acetate aqueous solutionfor staining the sample. The data shown in the paper were processed with first order flatten and no more modification.

Synthesis of 4-(4-([2,2':6',2"-terpyridin]-4'-yl)phenyl)-2-methylbut-3-yn-2-ol (compound A)[2-3]*:* 2-Methyl-3-butyn-2-ol (3.08 mL, 30 mmol) was added to a solution of $Pd(PPh_3)_4$ (800 mg, 0.7 mmol), CuI (134 mg, 0.7 mmol), and 4'-(4-bromophenyl)-2,2':6',2"-terpyridine (3.87 g, 10 mmol) in triethylamine (10 mL) and toluene (100 mL) under a nitrogen atmosphere. The mixture was heated at 80°C for 8 h. After the solvent being removed under reduced pressure, the residue was extracted three times with H_2O/CH_2Cl_2. The combined organic extracts were dried over anhydrous Na_2SO_4, and then the solvent was removed by a rotavapor. The crude product was purified bysilicacolumn chromatography using a mixture of petroleum ether/ethyl acetate (2:1 v/v) as eluent to give a yellow solid (compound ***A***). Yield: 58%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.74 (d, 4H), 8.68 (d, J = 8.0 Hz, 2H), 7.91 (d, J = 8.0 Hz, 2H), 7.87 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.37 (dd, J = 5.4 Hz, 2H), 1.66 (s, 6H).

Synthesis of 4'-(4-ethynylphenyl)-2,2':6',2''-terpyridine (compound B): Sodium hydroxide (1.00 g, 25 mmol) was added under stirring into a solution of compound ***A*** (1.96 g, 5 mmol) in toluene (80 mL) under argon protection. The reaction mixture was then refluxed for 0.5 h. After cooling to room temperature, the solid was filtered.The filtrate was concentrated and extracted three times with H_2O/CH_2Cl_2. The combined organic extracts were dried over anhydrous Na_2SO_4, and then the solvent was removed by a rotavapor. The crude product was purified by silicacolumn chromatography using a mixture of petroleum ether/ethyl acetate (4:1 v/v) as eluent to give a yellow solid (compound ***B***). Yield: 45%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.67 (d, 4H), 8.61 (d, J = 8.0 Hz, 2H), 7.83 (dd, 4H), 7.30 (dd, J = 5.6 Hz, 2H), 3.13 (s, 1H).

Synthesis of 11-(4-(4-([2,2':6',2''-terpyridin]-4'-yl)phenyl)-1H-1,2,3-triazol-1-yl)undecyl4-methyl-benzenesulfonate (compound C): CuI (76 mg, 0.4 mmol) and DIPEA (103 mg, 0.8 mmol) was added into compound ***B*** (333 mg, 1 mmol) and 1-azidoundecyl 4-methylbenzenesulfonate (367 mg, 1 mmol) in 20 mL of $(CH_2)_2Cl_2/H_2O$ (1:1 v/v). The mixture was stirred at room temperature for 24 h, then diluted with 20 mL of water and extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous Na_2SO_4. After the solvent being removed under reduced pressure, the residue was purified by silica column chromatography (CH_2Cl_2/CH_3OH 10:1 v/v)) to afford the desired product compound ***C*** (623 mg) as a light yellow solid. Yield: 89%. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.78 (d, 2H), 8.74 (d, J = 4.1 Hz, 2H), 8.68 (d, J = 8.0 Hz, 2H), 7.99 (d, 2H), 7.91 (t, J = 7.8 Hz, 2H), 7.84 (s, 1H, 5-H of 1*H*-[1,2,3]triazol ring), 7.78 (d, J = 8.2 Hz, 2H), 7.37 (t, J = 5.0 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 4.21 (t, J = 7.2 Hz, 2H), 4.01 (t, J = 6.5 Hz, 2H), 2.43 (s, 3H, CH_3 of Tos), 1.97 (m, 2H), 1.71 (m, 2H), 1.22 (m, 14H).

Synthesis of 1-(11-(4-(4-([2,2':6',2''-terpyridin]-4'-yl)phenyl)-1H-1,2,3-triazol-1-yl)undecyl)pyridin-1-ium4-methylbenzenesulfonate (TPP-11): Compound ***C*** (70 mg, 0.1 mmol) was dissolved in 3 mL pyridine. The solution was stirred at 70°C for 48 h under argon protection. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was dissolved in 1 mL methanol and then added dropwise to 30 mL diethyl ether to give the precipitation. The dissolution–precipitation process was repeated at least three times to afford the brown solid. The brown solid were further purified by using ion-exchange methods. An ion-exchange column was filed with Dowex 1×8 200-400 mesh (Merck). After regeneration with sodium tosylate, the column was washed with 3 L of water and then 0.5 L of methanol. The obtained brown solid was dissolved in 1 mL of methanol and then introduced on the column. The purple product was fractionally collected, and then the solvent was evaporated using a rotavapor. Finally the compound (TPP-11) was freeze-dried overnight. Yield: 65%. ^{1}H NMR (300 MHz, CH_3OD, δ): 8.94 (d, J = 4.1 Hz, 2H), 8.66 (d, J = 3.0 Hz, 2H), 8.59 (t, J = 3.0 Hz, 2H), 8.52 (t, J = 6.0 Hz, 2H), 8.39 (s, 1H, 5-H of 1*H*-[1,2,3]triazol ring), 8.04 (t, J = 5.5 Hz, 2H), 7.94 (m, 6H), 7.70 (d, J = 6.1 Hz, 2H), 7.40 (m, 2H), 7.21 (d, J = 6.1 Hz, 2H), 4.55 (t, J = 5.5 Hz, 2H), 4.43 (t, J = 5.5 Hz, 2H), 2.34 (s, 3H, CH_3 of Tos), 1.94 (m, 4H), 1.30 (m, 14H). I-MS *m/z* (%): 608.35 (100) [$M^+ - Ts$]; 171.01 (100) [Ts^-].

References:

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