Supporting Information

Conductive Porphyrin Helix from Ternary Self-assembly Systems

Qiang Zhao,[a,b] Yao Wang,[a,c] Yan Qiao,[a,b] Xiaolong Wang,[a,b] Xuefeng Guo,[a,b] Yun Yan[a,b] and*

Jianbin Huang[a,b]

*[a] Beijing National Laboratory for Molecular Sciences (BNLMS), College of Chemistry
and Molecular Engineering, Peking University, Beijing 100871, People's Republic of
China, E-mail: JBHuang@pku.edu.cn;*

*[b] State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Peking
University, Beijing 100871, People's Republic of China;*

*[c] Key Laboratory of Polymer Chemistry and Physics of the Ministry of Education, Peking
University, Beijing 100871, People's Republic of China.*

Experimental Section

Materials and Methods. The tetrasodium meso-tetra(sulfonatophenyl)porphine (TPPS$_4$, >97.0%) and dodecyldimethylamine oxide (C$_{12}$DMAO, 95.0%) were purchased from Alfa Aesar. Tetradecyldimethylamine oxide (C$_{14}$DMAO) was prepared by freeze drying 70.0% aqueous solution, followed by recrystallizing more than five times from acetone. All the other reagents were purchased from Beijing Chemical Reagents (Beijing, China, >99.0%). The purities of the surfactants were examined by the lack of minima in their surface tension curves. Aqueous solutions were prepared using Milli-Q water (Millipore, 18 MΩ/cm resistivity). The helical structures were prepared through mild process. TPPS$_4$ (1.0×10^{-4} M), Zn(NO$_3$)$_2$ ($1.0 \times$

10^{-4} M) and $C_{14}DMAO$ (2.0×10^{-4} M) were mixed together in aqueous solution. After 3 days undisturbed in dark at 25°C, the precipitate suspended in solution were collected.

Characterization of Helical Nanostructures. The helical structures were characterized by scanning electron microscopy (SEM, Hitachi S4800, 5 kV), confocal laser scan microscopy (CLSM, Nikon A1R-si), transmission electron microscopy (TEM, JEM-100CX, 100 kV), ultraviolet-visible spectrophotometry (UV-Vis, Beijing Purkinje General Instrument Co., LTD. TU-1810), fluorescence spectrophotometer (Hitachi F7000), X-ray photoelectron spectroscopy (XPS, Axis Ultra, Kratos Analytical Ltd.), isothermal titration microcalorimetry (ITC, Thermometric AB, Jarfalla, Sweden), fourier transform infrared spectrophotometry (FT-IR, Bruker Tensor 27) and X-ray diffraction (XRD, Rigaku Dmax-2000, Ni-filtered Cu Kα radiation). Except ITC test, all the other measurements were conducted under ambient conditions at room temperature.

For SEM and TEM measurements, a drop of suspension was placed on clean silicon sheets or copper grids and then dried freely under ambient conditions. For UV-Vis measurements, the precipitates in deioned water were used. The ITC test was taken in a TAM 2277-201 microcalorimetric system with a 1 mL sample at the desired temperature T ± 0.01°C. For FT-IR, dry powder of precipitates was examined with micro-attenuated total reflection (ATR) method. For XPS and XRD measurements, several drops of the suspension were dropped on a clean glass slide, followed by drying in the air.

2

Preparation of Gold Electrodes. The gold electrodes were prepared by thermal evaporation of gold through a shadow mask on silicon wafer. The silicon wafer was doped with 300 nm thick oxidized silicon on the surface. The gold electrodes were separated by ~20 μm (Figure 2b). Then a drop of $TPPS_4/Zn(NO_3)_2/C_{14}DMAO$ solution was poured over the electrodes, and the solvent evaporated at room temperature. This process transferred single helix onto substrate, some of which bridged across the micro-fabricated gold electrodes.

For the calculation of conductivity, as shown in figure 2c, the helix length L and cross sectional area S are 26.6 μm and 1.18×10^{-13} m^2, respectively. Meanwhile, the value of I/V is calculated to be 1.75×10^{-9} S from figure 2c. Hence, the room temperature conductivity of $TPPS_4/Zn(NO_3)_2/C_{14}DMAO$ helix is supposed to be $\sigma_{RT} = 3.95\times10^{-5}$ S cm^{-1}.

Supplymental Results

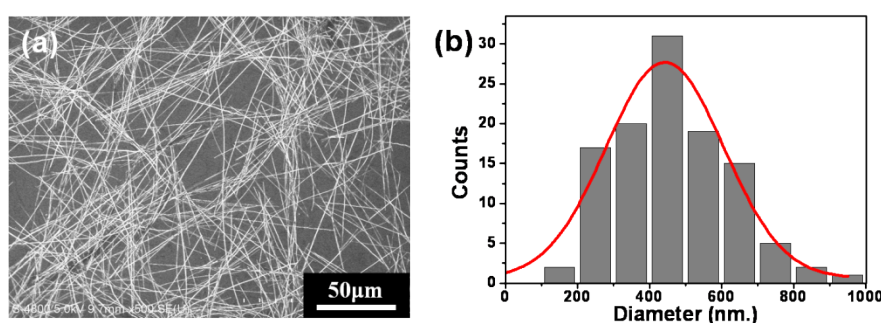**1. SEM image and diameter distribution of helix.**

Figure S1. (a) SEM images of complex deposited from solution onto silicon slice. Scale bar = 50 μm. (b) Distribution of helices in diameter. Helices were achieved in the solution of TPPS$_4$/Zn(NO$_3$)$_2$/C$_{14}$DMAO at the ratio of 1/1/2 (C$_{TPPS4}$ = 1.0 × 10^{-4} M).
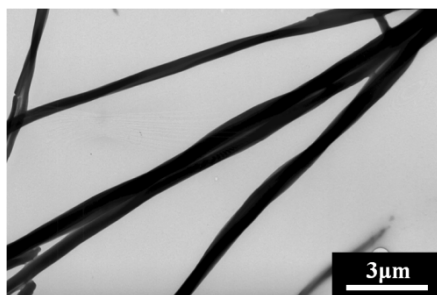
2. TEM image of helix.

Figure S2. The TEM image of helices in the solution of TPPS$_4$/Zn(NO$_3$)$_2$/C$_{14}$DMAO without negative staining. Scale bar = 3 μm. The ratio of TPPS$_4$/Zn(NO$_3$)$_2$/C$_{14}$DMAO is 1/1/2 (C$_{TPPS4}$ = 1.0 × 10^{-4} M).

3. CLSM image of helix in aqueous solution.

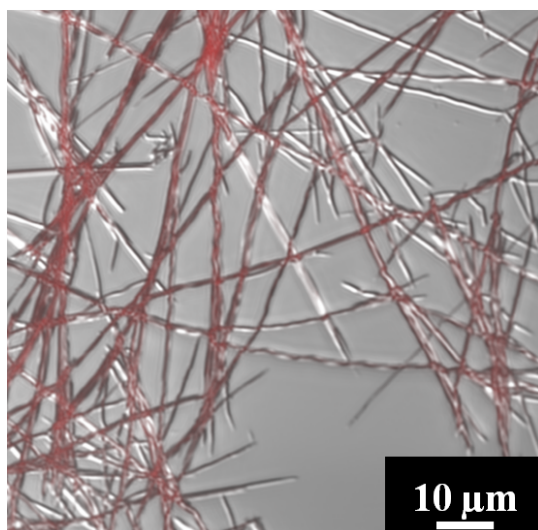**Figure S3.** Optical and fluorescent overlapping image of helix in aqueous solution. Scale bar

= 10 μm. The ratio of TPPS$_4$/Zn(NO$_3$)$_2$/C$_{14}$DMAO is 1/1/2 (C$_{TPPS4}$ = 1.0 × 10^{-4} M).
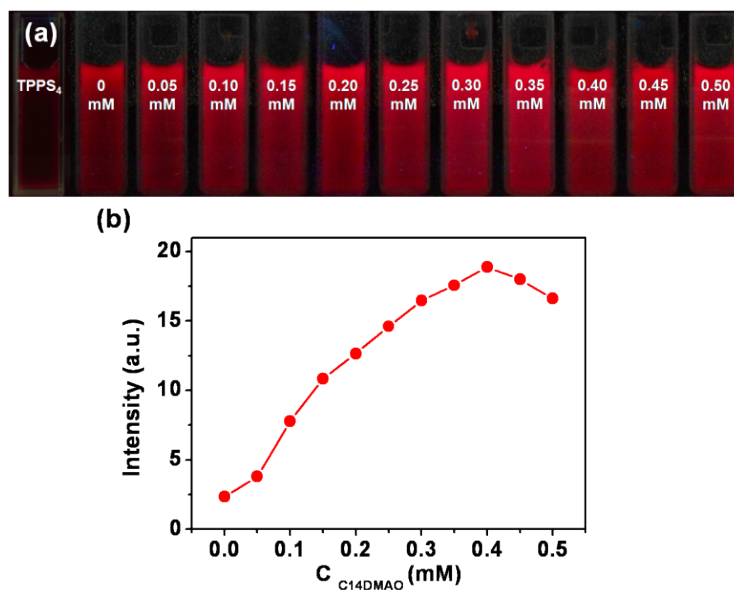
4. Fluorescent properties of helix.

Figure S4. (a) The photo under UV-light irradiation of TPPS$_4$ and TPPS$_4$/Zn(NO$_3$)$_2$ upon

addition of C$_{14}$DMAO (0 - 5.0 × 10^{-4} M) at 365 nm. (b) The fluorescent intensity changes at

648 nm of TPPS$_4$/Zn(NO$_3$)$_2$ upon addition of C$_{14}$DMAO (0 - 5.0 × 10^{-4} M) in aqueous

solution at 25℃, TPPS$_4$/Zn(NO$_3$)$_2$ = 1/1, C$_{TPPS4}$ = 1.0 × 10^{-4} M.

5. Turbidity of helix.

5
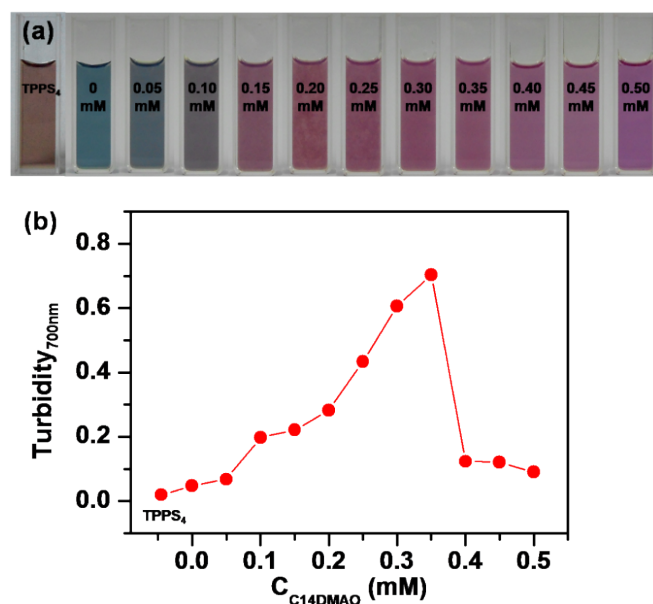
Figure S5. (a) The photo under the daylight, and (b) turbidity changes at 700 nm of TPPS$_4$ and TPPS$_4$/Zn(NO$_3$)$_2$ upon addition of C$_{14}$DMAO (0 - 5.0 × 10^{-4} M) in aqueous solution at 25℃, TPPS$_4$/Zn(NO$_3$)$_2$ = 1/1, C$_{TPPS4}$ = 1.0 × 10^{-4} M.
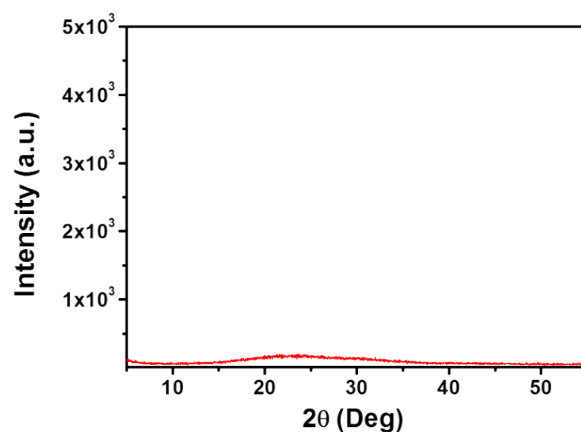
6. XRD patterns.

Figure S6. XRD patterns of the helix at 2theta ranging from 5° to 55° on glass sheet. The helix was made in TPPS$_4$/Zn(NO$_3$)$_2$/C$_{14}$DMAO solution.
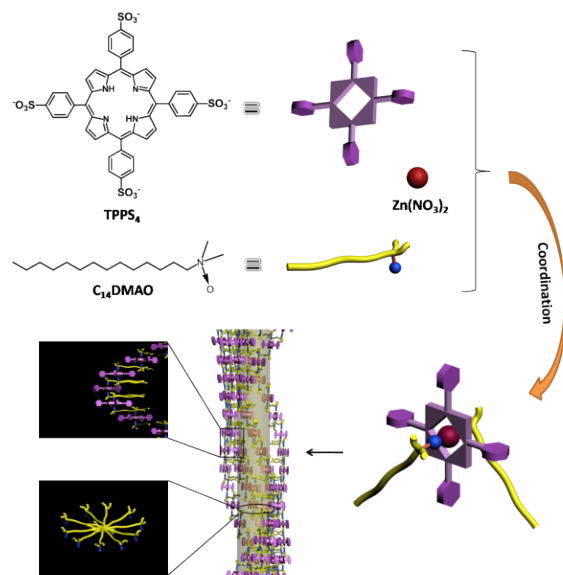
7. Structure model for molecular arrangement of helix.

Figure S7. A possible model for the molecular arrangement of TPPS$_4$/Zn(NO$_3$)$_2$/C$_{14}$DMAO helical nanostructure.

8. Properties of helix in TPPS$_4$/Zn(NO$_3$)$_2$/C$_{12}$DMAO system.
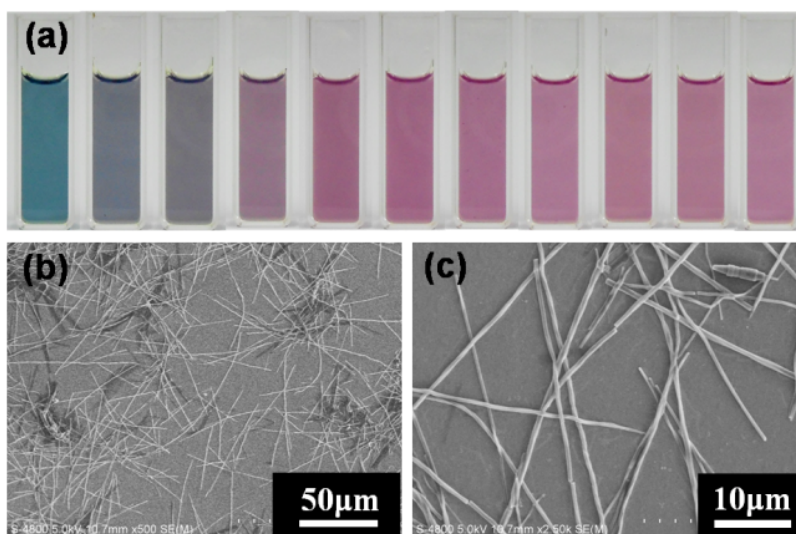
Figure S8. (a) The photo of $TPPS_4$/$Zn(NO_3)_2$ upon addition of $C_{12}DMAO$ ($0 - 5.0 \times 10^{-4}$ M)

in aqueous solution under the daylight at 25℃. $TPPS_4$/$Zn(NO_3)_2 = 1/1$, $C_{TPPS4} = 1.0 \times 10^{-4}$ M.

(b), (c) SEM images for $TPPS_4$/$Zn(NO_3)_2$/$C_{12}DMAO$ helices. Helices were achieved in the

solution of $TPPS_4$/$Zn(NO_3)_2$/$C_{12}DMAO$ system. The ratio of $TPPS_4$/$Zn(NO_3)_2$/$C_{12}DMAO$ is

1/1/2 ($C_{TPPS4} = 1.0 \times 10^{-4}$ M).