Supporting Information

Conductive Porphyrin Helix from Ternary Self-assembly Systems

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Experimental Section

Materials and Methods. The tetrasodium meso-tetra(sulfonatophenyl)porphine (TPPS₄, >97.0%) and dodecyldimethylamine oxide (C₁₂DMAO, 95.0%) were purchased from Alfa Aesar. Tetradecyldimethylamine oxide (C₁₄DMAO) 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. TPPS₄ (1.0 × 10⁻⁴ M), Zn(NO₃)₂ (1.0 ×
$10^{-4}$ M) and C$_{14}$DMAO ($2.0 \times 10^{-4}$ 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 deionized water were used. The ITC test was taken in a TAM 2277-201 microcalorimetric system with a 1 mL sample at the desired temperature $T \pm 0.01$°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.
**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 TPPS₄/Zn(NO₃)₂/C₁₄DMAO 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 $1.18 \times 10^{-13}$ m², respectively. Meanwhile, the value of $I/V$ is calculated to be $1.75 \times 10^{-9}$ S from figure 2c. Hence, the room temperature conductivity of TPPS₄/Zn(NO₃)₂/C₁₄DMAO helix is supposed to be $\sigma_{RT} = 3.95 \times 10^{-5}$ S cm⁻¹.

Supplementary 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 TPPS₄/Zn(NO₃)₂/C₁₄DMAO at the ratio of 1/1/2 (C_{TPPS₄} = 1.0 × 10⁻⁴ M).

2. TEM image of helix.

![TEM image of helix](image)

Figure S2. The TEM image of helices in the solution of TPPS₄/Zn(NO₃)₂/C₁₄DMAO without negative staining. Scale bar = 3 µm. The ratio of TPPS₄/Zn(NO₃)₂/C₁₄DMAO is 1/1/2 (C_{TPPS₄} = 1.0 × 10⁻⁴ M).

3. CLSM image of helix in aqueous solution.

![CLSM image of helix](image)
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°C, TPPS$_4$/Zn(NO$_3$)$_2$ = 1/1, C$_{TPPS4}$ = 1.0 × 10$^{-4}$ M.

5. Turbidity of helix.
Figure S5. (a) The photo under the daylight, and (b) turbidity changes at 700 nm of TPPS₄ and TPPS₄/Zn(NO₃)₂ upon addition of C₁₄DMAO (0 - 5.0 × 10⁻⁴ M) in aqueous solution at 25°C, TPPS₄/Zn(NO₃)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 TPPS₄/Zn(NO₃)₂/C₁₄DMAO solution.
7. Structure model for molecular arrangement of helix.

Figure S7. A possible model for the molecular arrangement of TPPS₄/Zn(NO₃)₂/C₁₄DMAO helical nanostructure.

8. Properties of helix in TPPS₄/Zn(NO₃)₂/C₁₂DMAO 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°C. 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).