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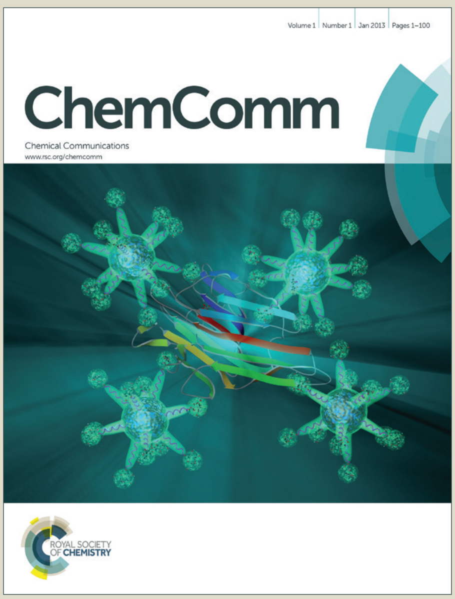

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Conductive Porphyrin Helix from Ternary Self-assembly Systems

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The helix with ternary components of $TPPS_4$, $Zn(NO_3)_2$ and C_{14}DMAO is easily obtained in aqueous solution. It retains characteristic fluorescence of porphyrin and can be conductive when bridges on gold electrode that provides the potential application in photochemistry and electrical devices.

Helix is ubiquitous in nature and has exclusive biological functions in living system.[1] These helical structures represent ordered structures and are consist of multiple components,[2] such as DNA, peptides and proteins, which are precisely arranged with multi-conponent.[3] To achieve these fantastic helical structures, self-assembly is developed as one of the vital important approaches.[4] Self-assembled helices[5] are particularly popular for their applications in biomaterials,[6] optoelectronics,[7] and catalysis.[8] Although some reports related to artificial helix, most of them are concerning mono-[9] or bi-component[10] systems which are distinguishing with the natural multi-component helices. Therefore, it is still a great challenge to build ternary or multi-component helices by supramolecular chemistry.

Porphyrins have attracted considerable interest in functional molecular assemblies because of the diverse utilization in catalysis,[11] photomedicine[12] and material science.[13] Especially, some porphyrin structures have constructed for photoconductors[14] and photovoltaics.[15] Schwab and co-workers researched on porphyrin nanorods which could generate photoconductivity upon light exposure.[16] Wasielewski et al. synthesized modified zinc porphyrin that produced long-lived charge separation in the segregated π-stacks and charge migration through the columnar structure.[17] However, little attention has been paid to the conducting properties of these self-assembled nanostructures.

Herein we report a helical structure based on ternary molecular self-assembly of tetrasodium meso-tetra(sulfonatophenyl)porphine ($TPPS_4$), zinc ions and tetradecyldimethylamine oxide (C_{14}DMAO) in aqueous solution. As shown in the scanning electron microscopy (SEM) images (Fig. 1), both left-handed and right-handed helix have single stranded (Fig. 1a, 1b), double stranded (Fig. 1c, 1d) and even multi-stranded (Fig. 1e, 1f) structures. The low magnification image indicates that they are hundreds of micrometers in length, 150 - 950 nm in diameter (averagely 440 nm, Fig. S1). The transmission electron microscopy (TEM) image also confirms helical structure formation in $TPPS_4$/$Zn(NO_3)_2$/C_{14}DMAO system (Fig. S2). However, any two components of $TPPS_4$, $Zn(NO_3)_2$ and C_{14}DMAO could not form helix in solution but stable and clear solution, which reveals the key role of each component to assemble into the ordered helical structure.

The helices retain the fluorescent properties of porphyrin. Confocal laser scan microscopy (CLSM) offers the optical and fluorescent images of the helical structures in solution which possessed red fluorescence (Fig. 1g, 1h and S3). The fluorescent intensity of the solution, with addition of C_{14}DMAO, increased firstly until the maximum reached at about 4.0 equiv. C_{14}DMAO, probably due to the enhancement of $TPPS_4$/$Zn(NO_3)_2$/C_{14}DMAO aggregation (Fig. S4). After adding more than 4.0 equiv. C_{14}DMAO, the fluorescence intensity decreased accompanied with the destruction of aggregation. The turbidity had the similar variation trend with the fluorescent intensity (Fig. S5).

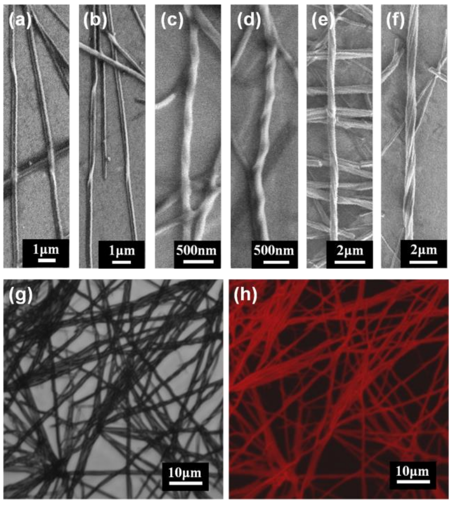

Fig. 1. SEM images of $TPPS_4$/$Zn(NO_3)_2$/C_{14}DMAO deposited from the solution on silicon slice: (a), (b) the single stranded helices, scale bar = 1 μm; (c), (d) the double stranded helices, scale bar = 500 nm; and (e), (f) the multi-stranded helices, scale bar = 2 μm. (g) The optical image and (h) fluorescent image of $TPPS_4$/$Zn(NO_3)_2$/C_{14}DMAO deposited

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onto glass slide. Helices were achieved in the solution of $TPPS_4$ (1.0 × 10^{-4} M), $Zn(NO_3)_2$ (1.0 × 10^{-4} M) and C_{14}DMAO (2.0 × 10^{-4} M).

Current-voltage (*I-V*) measurement was performed to measure the conductivity of the helix. The device was designed with one helix bridging two Au electrodes (Fig. 2a and 2b). The resulted *I-V* curve exhibited a nearly linear correlation (Fig. 2c) in which larger current was generated when higher voltage applied. The conductivity (σ) of a single helix calculated by the following formula:

$$\sigma = \frac{I}{V}\frac{L}{S} \qquad (1)$$

Here, *V* is the voltage, *I* is the current, *S* is the average cross sectional area which is estimated by assuming that the cross section of the helix is a cylinder, and *L* is the length of a helix between electrodes. For the device measured, the conductivity of the helix is about 3.95 × 10^{-5} S cm^{-1}, which is comparatively higher than those of porphyrin structures.[16,18] The conductivity of helix is attributed to overlap of molecular HOMO and LUMO orbits.[9,19] Therefore, the molecular arrangement of the helices is supposed that each porphyrin has interactions and forms helical alignment. These helices are anticipated to meet the special structural requirements for electronic and sensor device fabrication.

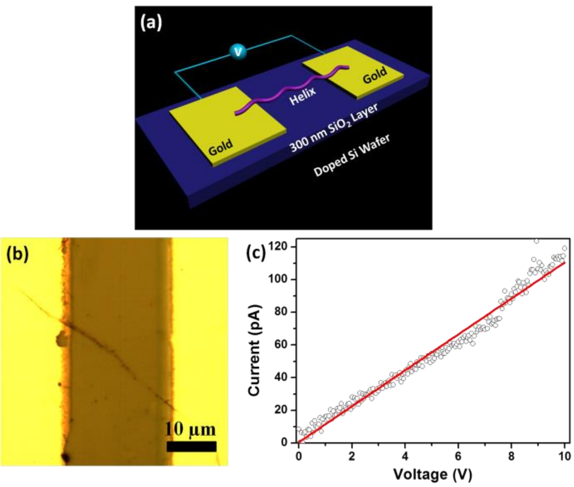

Fig. 2. (a) Scheme and (b) optical image of electrodes connected by a helix, where the silicon wafer acted as a global back-gate, scale bar = 10 μm; and (c) *I-V* curve of a helix deposited across a pair of Au electrodes separated by ~20 μm at a gate bias of 0 V.

UV-Vis spectroscopy and X-ray photoelectron spectroscopy (XPS) were employed to access the molecular arrangement within helices. Concretely, the formation of zinc porphyrin was demonstrated by UV-Vis spectrum (Fig. 3a). The Q band of $TPPS_4$ (557 nm and 596 nm) corresponding to the $S_0 \rightarrow S_1$ transition is essentially ascribed to the formation of $TPPS_4/Zn(NO_3)_2$ that zinc ion occupies central cavity of porphyrin.[20] The enhancement of Soret band is attributed to the Mie effect.[21] In the XPS spectra (Fig. 3b), 2p spectrum of zinc in $TPPS_4/Zn(NO_3)_2$ suggests that the spin-orbit pair with the 2p3/2 component appearing at 1022.36 eV is due to the zinc oxidation state. In $TPPS_4/Zn(NO_3)_2/C_{14}$DMAO, a large chemical shift to lower binding energy was observed in the Zn 2p spectrum at 1021.25 eV,[22] indicating the zinc ion was coordinated to oxygen of C_{14}DMAO as well as the Zn-O coordination was based on axial ligand to metal porphyrin. Besides, no obvious porphyrin-porphyrin stacking peak was appeared in UV-Vis spectrum since the affinity of zinc porphyrin to C_{14}DMAO would lead to a weak π-π interaction among each porphyrin.

For the construction of the ternary component helix, C_{14}DMAO was added to the aqueous solution of $TPPS_4$ and $Zn(NO_3)_2$ in molar ratio of $TPPS_4/Zn(NO_3)_2/C_{14}$DMAO = 1/1/2. Isothermal titration calorimetry (ITC) measurement was performed to confirm this optimal ratio and the binding curve (Fig. 3c) provided the binding ability of C_{14}DMAO with $TPPS_4/Zn(NO_3)_2$. The binding stoichiometry between $TPPS_4/Zn(NO_3)_2$ and C_{14}DMAO was calculated to be 1/2, suggesting that each $TPPS_4/Zn(NO_3)_2$ planar was connected with two C_{14}DMAO molecules. X-ray diffraction (XRD) measurement was taken to reveal information of molecular arrangement. In figure 3d and S6, the diffraction peak 2θ was 2.64°, suggesting that the unit-to-unit distance (~33.44 Å) might be the distance of each porphyrin planar.

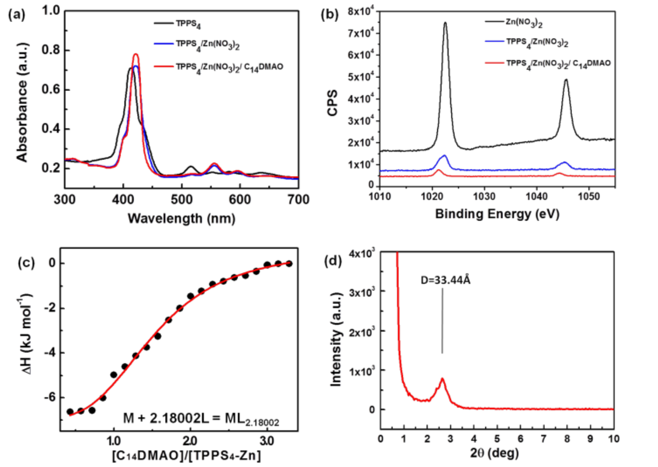

Fig. 3. (a) The UV-Vis spectra of $TPPS_4/Zn(NO_3)_2/C_{14}$DMAO system. $TPPS_4$ solution (5.0 × 10^{-6} M) (black); $TPPS_4$ solution with the addition of $Zn(NO_3)_2$ (5.0 × 10^{-6} M) (blue), and the $TPPS_4/Zn(NO_3)_2/C_{14}$DMAO at the ratio of 1/1/2 ($C_{C14DMAO}$ = 1.0 × 10^{-5} M) (red) at 25°C. (b) The XPS measurement of Zn 2p peak for $Zn(NO_3)_2$ (black), $TPPS_4/Zn(NO_3)_2$ (blue) and the helices of $TPPS_4/Zn(NO_3)_2/C_{14}$DMAO (red) deposited on the silicon substrate, respectively. (c) Fitted binding isotherms for calorimetric titration of $TPPS_4/Zn(NO_3)_2$ (x_{TPPS4} = 0.5) with C_{14}DMAO. (d) XRD patterns of the helices on glass sheet.

Combined with the results of UV-Vis, XPS, ITC, and XRD measurements, we speculate the structure model for the ternary-component helix of $TPPS_4/Zn(NO_3)_2/C_{14}$DMAO (Fig. S7). The coordination interaction plays a key role in self-assembly which leads to zinc ion coordinated with $TPPS_4$ and two C_{14}DMAOs, correspondingly. There are still some uncoordinated C_{14}DMAOs existing in aggregations besides the C_{14}DMAOs coordinated with zinc porphyrin. Hydrophobic interaction plays as a driving force for self-assembly. The cooperative effect of coordination, π-π and hydrophobic interactions is believed to trigger the ordered self-assemble of ternary components helical structure. Furthermore, the similar helical structure can be acquired by replacing C_{14}DMAO with C_{12}DMAO (Fig. S8).

Conclusions

In summary, the helical structure is successfully fabricated by the ternary components of $TPPS_4$, $Zn(NO_3)_2$ and C_{14}DMAO in aqueous solution. The unit of $TPPS_4/Zn(NO_3)_2/C_{14}$DMAO is constructed through the coordination of zinc ion to porphyrin and

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zinc ion to amiphiphilic molecules. The delicately cooperative effect of coordination, π-π and hydrophobic interactions are accounted for the helical structure. Moreover, the helices retain characteristic fluorescence of porphyrin and exhibit high conductive feature compared with other porphyrin tubes and ribbons reported previously. It is anticipated that the assembling helix with ternary components might have potential application in photochemistry and electrical devices.

Notes and references

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