Electronic Supplementary Information (ESI) for:

Chemical Energy Assisted Self-Assembling of A Porphyrin-Substituted Benzoic Acid in Complex Environments

Bingxu Ma, Bowen Pang, Wang Zeng*, Huimin Fu, Yi Jiang, Shenglin Yao, Yida Yang, Kaisheng Zhu, Wei Zhang*

South China Advanced Institute for Soft Matter Science and Technology, School of Emergent Soft Matter and Guangdong Provincial Key Laboratory of Functional and Intelligent Hybrid Materials and Devices, South China University of Technology, Guangzhou 510640, China

*Correspondence: zengwang@scut.edu.cn; weizhang@scut.edu.cn

Table of contents

1. General

Unless otherwise noted, ^{1}H NMR spectra were recorded at 25°C using a JEOL model JNM-ECZ500R spectrometer, operating at 500 MHz, where chemical shifts (δ in ppm) were determined with respect to non-deuterated solvent residues as internal references. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was acquired using a Waters model Synapt G2-Si MALDI-TOF mass spectrometer. Ultraviolet-visible (UV-vis) absorption spectra were recorded on the SHIMADZU model UV-3600 Plus UV-vis spectrophotometer using a quartz cell with 1 mm optical path length. Fourier transform infrared (FT-IR) spectra were recorded on a Thermo Scientific Nicolet iS5 spectrometer equipped with iD1 Transmission accessory and scanned between 900 to 4000 cm^{-1} at a resolution of 4 cm^{-1}. Transmission electron microscope (TEM) images were recorded on a JEOL model JEM-1400 electron microscope operating at 120 kV, each of the samples was deposited on a specimen Cu grid covered with thin polymer and carbon support films manufactured by Zhongjingkeyi Technology Co., Ltd. Atomic force microscope (AFM) images were recorded using an Oxford Instruments Asylum Research model Cypher VRS AFM microscope with Olympus AC160TS-R3 probe for gas phase scanning and Olympus BL-AC40TS-C2 probe for liquid phase scanning. The samples tested for gas phase scanning wre deposited on mica substrates. Scanning electron microscope (SEM) images were recorded on a JEOL model JSM-7900F SEM microscope operating at 5 kV. Each of the samples was deposited on a mica substrate followed by sputtering with Pt. Dynamic light scattering (DLS) was conducted on a Brookhaven model Omni particle size tester using a cell with 10 mm optical path length. Wide-angle X-ray diffraction (WAXD) spectrum was measured using a Rigaku Ultima IV WAXD instrument equipped with an Cu Kα radiation (λ = 0.154 nm). Each of the samples was filled into a gasket and tested in the transmission mode. Polarized light microscopy images were recorded using Leica model DM4P optical microscope. Confocal laser scanning microscope (CLSM) images were recorded using Zeiss model LSM 880 NLO confocal laser scanning microscope.

2. Materials

Unless otherwise noted, all commercial chemicals and reagents were obtained from commercial sources (Sigma-Aldrich, TCI or Titan Chemicals) and used as received without further purification. Deionized water was used throughout all experiments. Compounds **POR-COOH** and **POR-COOMe**

were prepared according to the reported procedures.[1-2] The dehydrated solvents were used as received from Titan Chemicals.

3. Fabrication of Thin Film Sample

3.1. Fabrication of the film of amorphously aggregated **POR-COOH** ($\mathbf{AA_{POR\text{-}COOH}}$)

50 μL of **POR-COOH** solution (0.01 M in THF-DCM (1/1, v/v)) was drop-casted on a silicon substrate first, and then followed by a spin-coating process (50 rpm for 10 seconds and 3000 rpm for 50 seconds).

3.2. Fabrication of the film of randomly co-aggregated **POR-COOH**&**POR-COOMe**

50 μL of solutions (solvent: THF/DCM (1/1, v/v)) containing **POR-COOH** and **POR-COOMe** mixture (total concentration 0.01 M) with different molar ratio (2/8, 4/6, 6/4, and 8/2) was drop-casted on silicon substrates, respectively. Then a spin-coating process (50 rpm for 10 seconds and 3000 rpm for 50 seconds) was applied for each sample to fabricate a thin film.

4. Preparation of Polyacrylamide Hydrogel

The polyacrylamide hydrogel used in the experiment was prepared according to the reported methods.[3] An aqueous solution containing 1.28 M acrylamide (monomer), 2.95 mM *N,N*'-methylenediacrylamide (Bisacrylamide, crosslinking agent), and 0.50 mM 2,2-Dimethoxy-2-phenylacetophenone (photoinitiator) was irradiated by UV light (3 mW, 2 h) to generate a transparent hydrogel. Later, this hydrogel was soaked with DMSO-H_2O (6/4, v/v) for 72 h, to replace the solvent inside and cutted into the desired shape for the next step.

5. Supporting References

1. Xia, R.; Zheng, X.; Hu, X.; Liu, S.; Xie, Z., Photothermal-Controlled Generation of Alkyl Radical from Organic Nanoparticles for Tumor Treatment. *ACS Appl. Mater. Interfaces* **2019**, *11*, 5782.

2. Matile, S.; Berova, N.; Nakanishi, K.; Novkova, S.; Philipova, I.; Blagoev, B., Porphyrins: Powerful Chromophores for Structural Studies by Exciton-Coupled Circular Dichroism. *J. Am. Chem. Soc.* **1995**, *117*, 7021.

3. Wirthl, D.; Pichler, R.; Drack, M.; Kettlguber, G.; Moser, R.; Gerstmayr, R.; Hartmann, F.; Bradt, E.; Kaltseis, R.; Siket, C. M.; Schausberger, S. E.; Hild, S.; Bauer, S.; Kaltenbrunner, M., Instant Tough Bonding of Hydrogels for Soft Machines and Electronics. *Sci. Adv.* **2017**, *3*, e1700053.

6. Supporting Figures

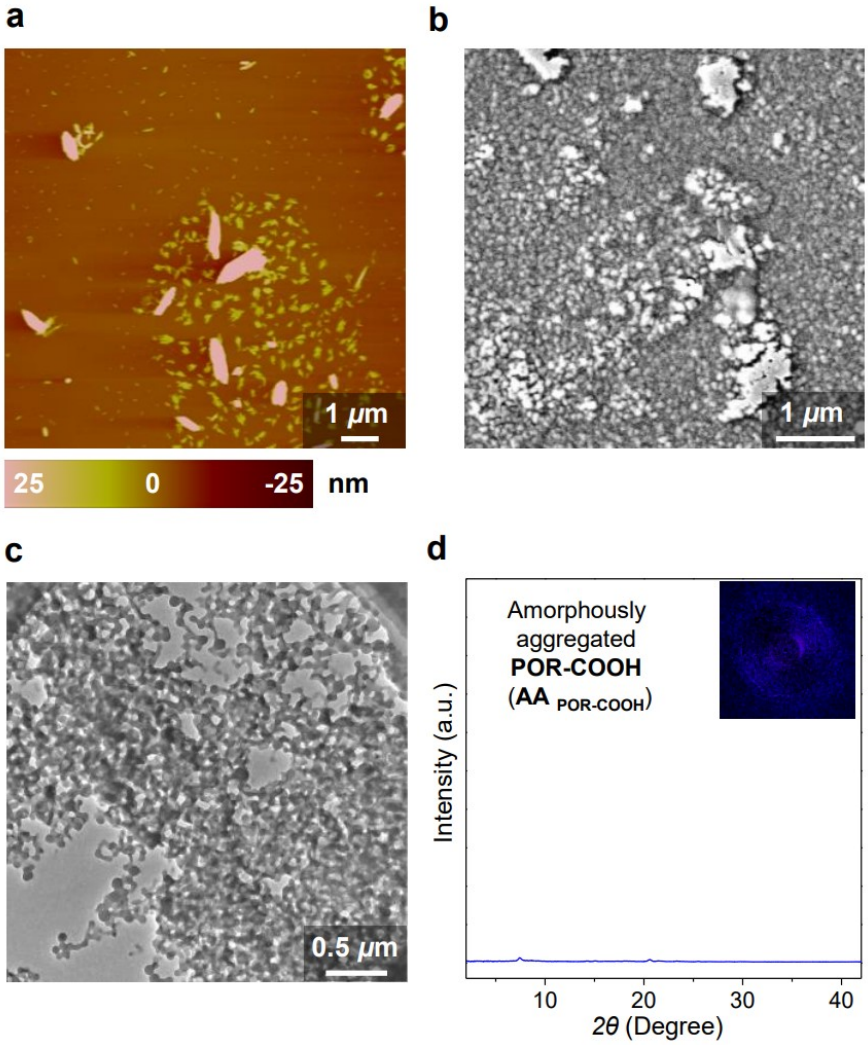

Fig. S1 (a) AFM, (b) SEM, and (c) TEM micrographs of the air-dried suspension of $\mathbf{AA_{POR\text{-}COOH}}$. (d) WAXD profile of $\mathbf{AA_{POR\text{-}COOH}}$ and its 2D WAXD pattern (inset).

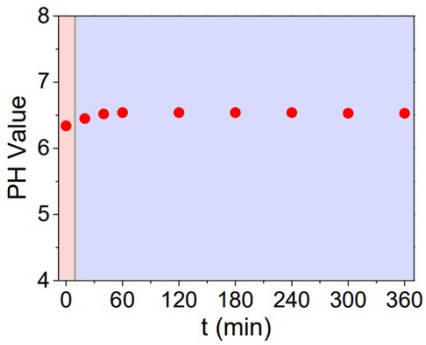

Fig. S2 Time-dependent pH values after the addition of **EDC**.

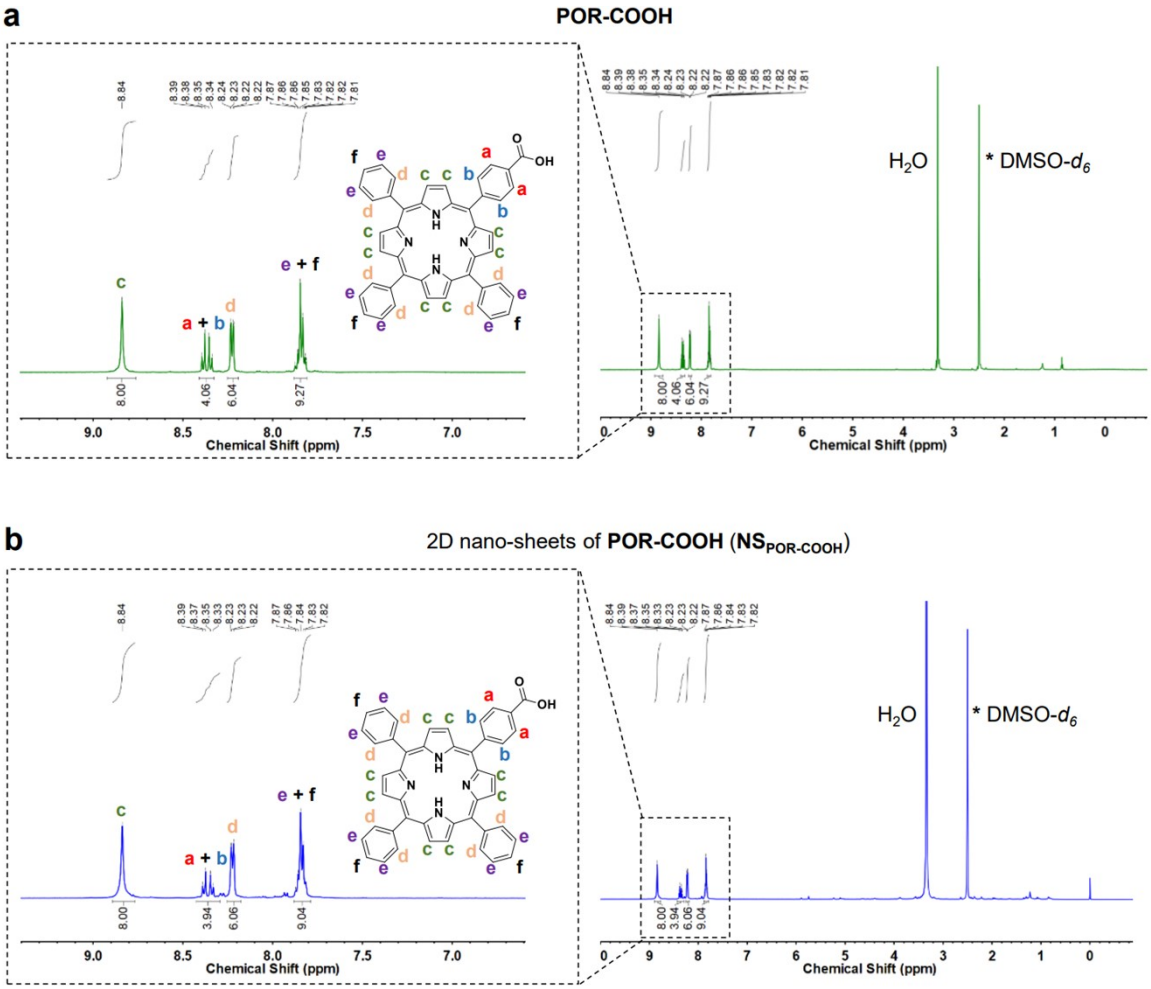

Fig. S3 ^{1}H NMR spectra of (a) **POR-COOH** and (b) the 2D nano-sheets of **POR-COOH** ($\mathbf{NS_{POR\text{-}COOH}}$) dissolved in DMSO-$d_6$.

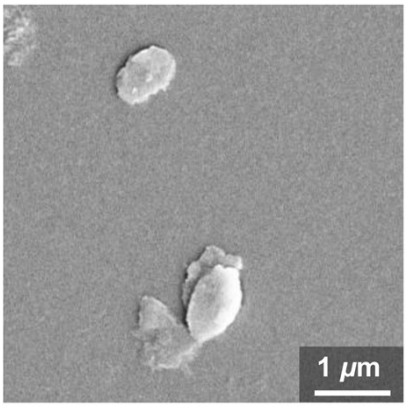

Fig. S4 SEM micrograph of an air-dried dispersion of $\mathbf{NS_{POR\text{-}COOH}}$.

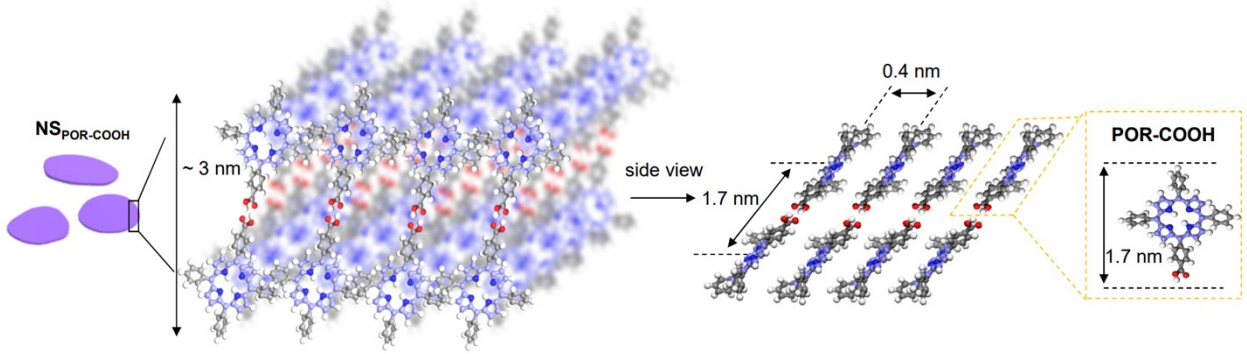

Fig. S5 Proposed packing modle of $\mathbf{NS_{POR\text{-}COOH}}$.

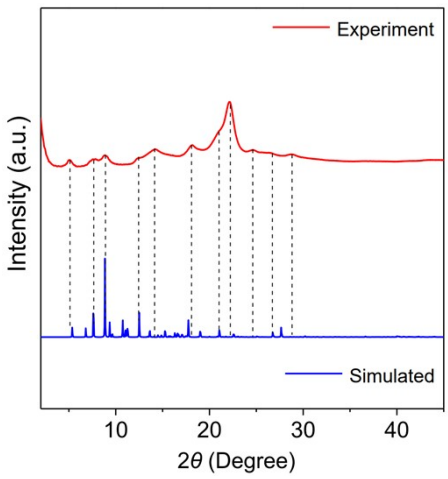

Fig. S6 Simulated integrated WAXD pattern (blue curve) according to the proposed structure of $\mathbf{NS_{POR\text{-}COOH}}$ and the comparison with experimental result (red curve).

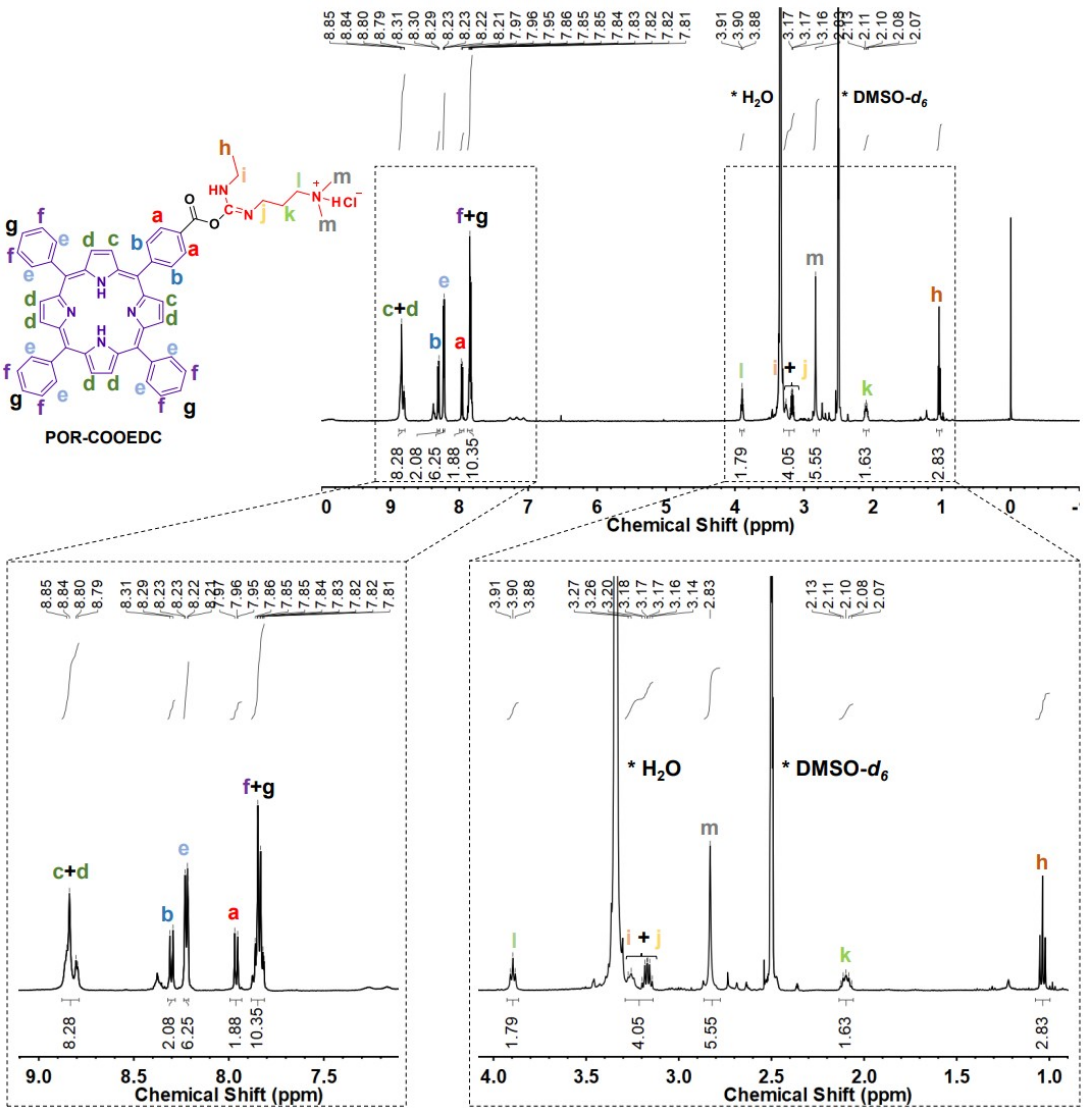

Fig. S7 ^{1}H NMR spectrum of **POR-COOEDC** dissolved in DMSO-d_6.

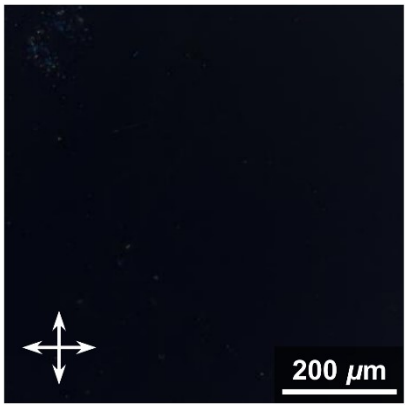

Fig. S8 Polarized light microscopy image of $\mathbf{AA_{POR\text{-}COOH}}$ under crossed polarizers.

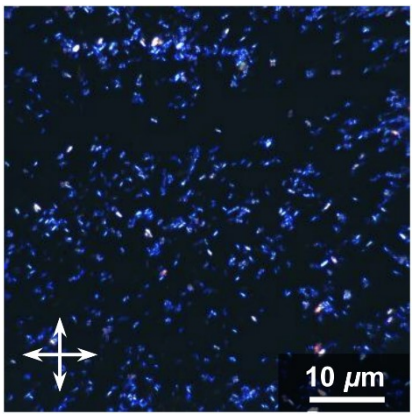

Fig. S9 Polarized light microscopy image of $\mathbf{NS_{POR\text{-}COOH}}$ under crossed polarizers.