

Electronic Supporting Information (ESI)

Rational design and synthesis of covalent organic polymers with hollow structure and excellent antibacterial efficacy

Zhiyong Sun,^{a, b} Yangxue Li,^b Xingang Guan,^b Li Chen,^{a*} Xiabin Jing^b and Zhigang Xie^{b*}

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1. Instruments

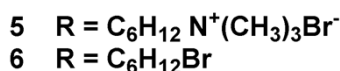
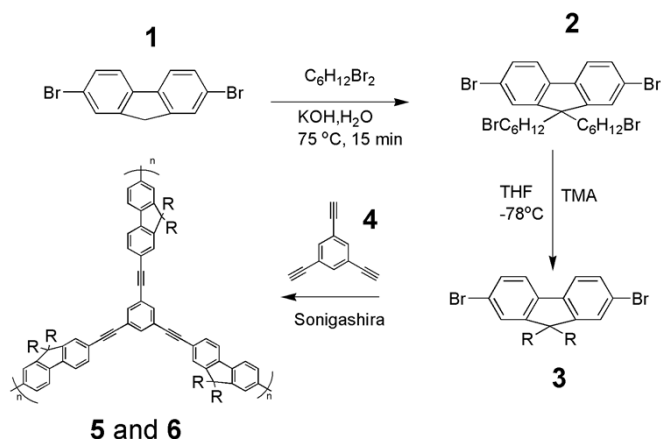
The thermogravimetric analysis (TGA) was performed using a Netzsch Sta 449c thermal analyzer system at the heating rate of 10° C/min in air atmosphere. The FTIR spectra were measured using a Nicolet Impact 410 Fourier transform infrared spectrometer. The nitrogen adsorption isotherm was measured on an Autosorb iQ2 adsorptometer, Quantachrome Instruments. The XRD was performed by a Riguku D/MAX2550 diffractometer using CuK α radiation, 40 kV, 200 mA with scanning rate of 0.4 ° /min. TEM micrographs was recorded using a FEI Tecnai G2F20 s-twin D573 with an acceleration voltage of 300 kV. SEM micrographs were performing on JEOL JXA- 840 under an accelerating voltage of 15 kV. The ¹H-NMR spectra were recorded at 400 MHz in CDCl₃ and DMSO-d₆ as internal standard with TMS, and the Solid-state ¹³C NMR spectra were recorded at 5KHz. DLS was applied on Beckman Coulter LS 13 320. Fluorescence spectra were recorded on a Perkin-Elmer LS55 spectrofluorometer. And optical density (OD) values were accorded on Biotech ELx808 with the absorbance at 600 nm.

2. Materials

All starting materials were purchased from commercial suppliers and used without further purification unless otherwise noted. The starting materials were urchased from sigma aldrich and TCI.

3. Synthesis

The general synthetic routes were presented in scheme S1



Scheme S1 General synthetic routes

3.1 Synthesis of 2 -- 2,7-dibromo-9,9-bis(6-bromo-hexyl)-9H-fluorene

2 was synthesized according to a literature published. 1.62 g **1** and 1,6-Dibromohexane were added in a round bottom flask with 50 ml 50% KOH solution, 0.33 g tetrabutylammonium bromide was added, the mixed solution was heated at 75 °C for 15 minutes.¹ After cooling to room temperature, the mixed solution was extracted with CH₂Cl₂, the combined organic layer was washed with water, 1M HCl, water, saline, then dried with anhydrous MgSO₄. After filtered and evaporation, the crude product was purified by silica gel column chromatography using hexane as the solvent. ¹H NMR (400 MHz, CDCl₃) : 0.60 -0.65 (m, 4H), 1.07 -1.21 (m, 8H), 1.54 -1.71 (m, 4H), 1.91 -1.99 (m, 4H), 3.26 -3.28 (t, 4H), 7.33 -7.36 (m, 2H), 7.45 -7.48 (m, 2H), 7.52 -7.60 (m, 2H).

3.2 Synthesis of 3

3 was prepared by dissolving **2** (1 g) in 10 ml THF in a flask, then trimethylammonium (1.5 ml) was added with stirring at -78 °C. After stirring for 12 h, the reaction was gradually warmed to room temperature and stirred for another 24 h. Then the THF and water were removed, and the residue was recrystallized from ethanol to yield the target monomer with yield of 75%. ¹⁻² ¹H NMR (400 MHz, D₂O, 90 °C) : 1.02 (m, 4H), 1.33- 1.35 (br, 8H), 1.76- 1.79 (m, 4H), 2.20 -2.30 (m, 4H), 2.45 (m, 4H), 3.39 -3.50 (m, 18H), 7.95 8.12 (m, 2 H), 8.39 -8.54 (m, 2H).

3.3 Synthesis of 5

3 (1g) and **4** (80 mg) were dissolved in a pressure flask in a mixed solution 20 ml of TEA: THF= 1:1, CuI (70 mg) was added, the mixture was degassed for 30 minutes, then Pd(PPh₃)₄ (70 mg) was added. After 48h reaction, the mixture was filtered and washed with THF, DMF, H₂O and ethanol for several times. Then dried in a heated oven at 70 °C, we got the polymer **5** with a yield of 56%. Further purification of the polymer was carried out by Soxhlet extraction with methanol for 24 h.

3.4 Synthesis of 6

The synthesis of **6** was followed by the preparation of **5**, **2** and **4** were added to the above mentioned condition. Then after the same procedure, we got the polymer **6** with a yield of 58%. Further purification of the as-synthesized polymer was carried out by Soxhlet extraction with methanol for 24 h.

4. FTIR for COP-H and COP-C

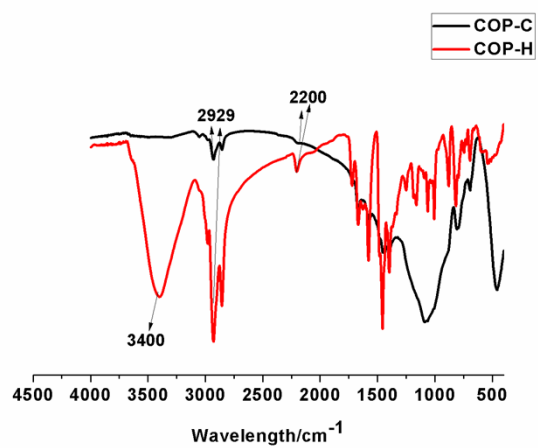


Fig. S1 FTIR of COP-H and COP-C

5. TGA for COP-H and COP-C

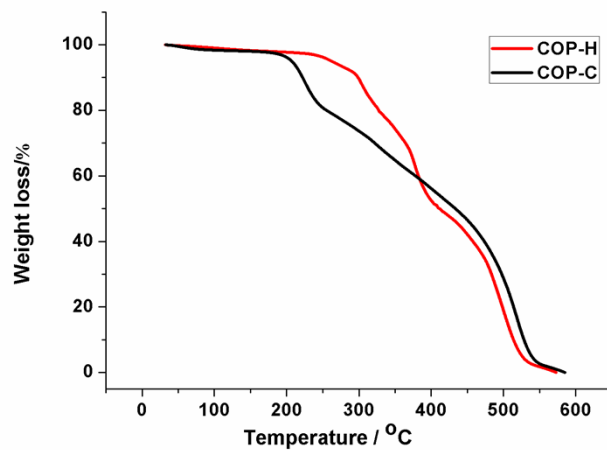


Fig. S2 TGA curve of COP-H and COP-C

6. Fluorescence emission spectroscopy of COP-H and COP-C

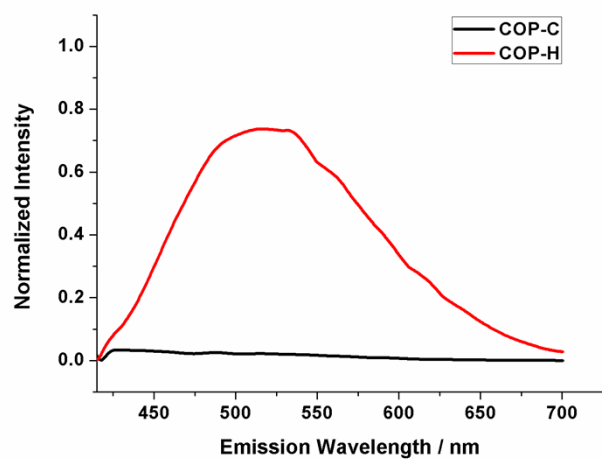


Fig. S3 Fluorescence emission spectroscopy of COP-H and COP-C

7. DLS

Dynamic light scattering (DLS) was employed to disperse the COP-H in water.

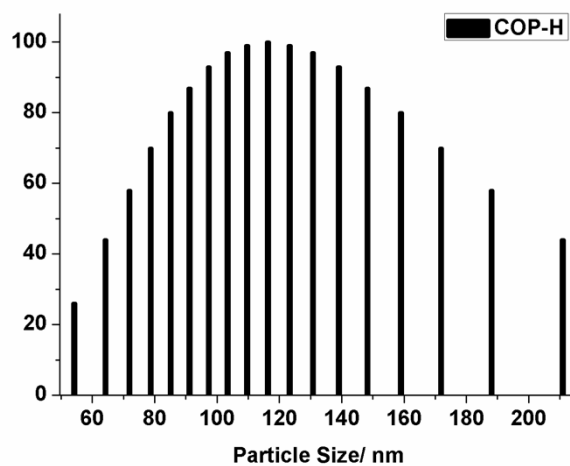


Fig. S4 DLS of COP-H

8. SEM and TEM of COP-C

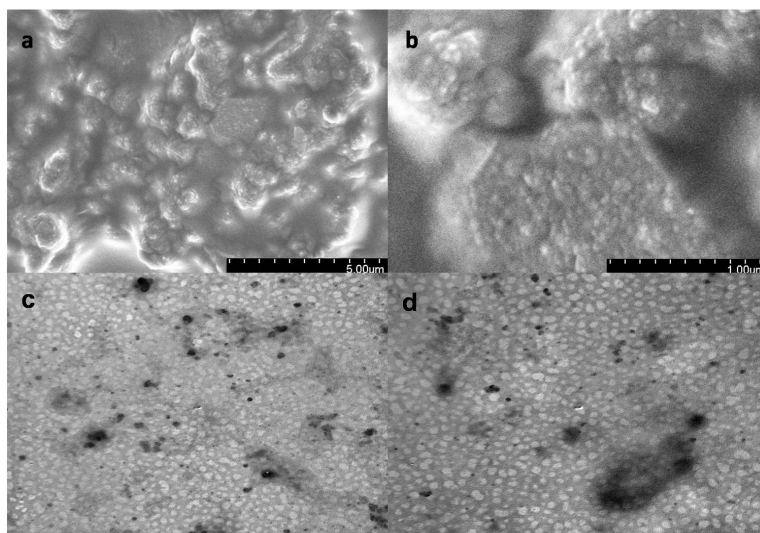


Fig. S5 SEM (a, b) and TEM (c, d) of COP-C

The scale bars are 5 μm for (a) and 1 μm for (b), and 1 μm for (c) and 500 nm for (d).

9. PXRD

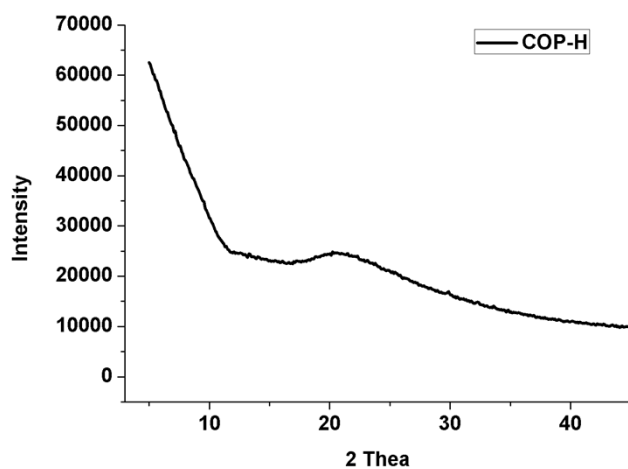


Fig. S6 PXRD of COP-H

10. Minimal inhibitory concentration (MIC) measurements

E. coli were reconstituted from its lyophilized form according to the manufacturer's protocol. Bacterial samples were cultured in Tryptic Soy Broth (TSB) solution at 37 °C under constant shaking of 100 rpm. The MICs of the polymers were measured using the broth microdilution method. Briefly, 100 ml of TSB broth containing a polymer at various concentrations (0, 0.033, 0.066, 0.125, 0.25, 0.5, 1, 2 mg/ml) was placed into each well of a 96-well tissue culture plate. An equal volume of bacterial suspension was added into each well. Prior to mixing, the bacterial sample was first inoculated overnight to enter its log growth phase. The concentration of bacterial solution was adjusted to give an initial optical density (O.D.) reading of 0.06- 0.07

at 600 nm wavelength on a microplate reader (Biotech ELx808, USA). The 96-well plate was kept in an incubator at 37 °C under constant shaking of 100 rpm for 16 h. The MIC was taken as the concentration of the antimicrobial polymer at which sample solution remains clear among the series and the microplate reader at the end of 16 h incubation. Broth containing microbial cells alone and COP-C were used as negative control, and each test was carried out in 4 replicates.³

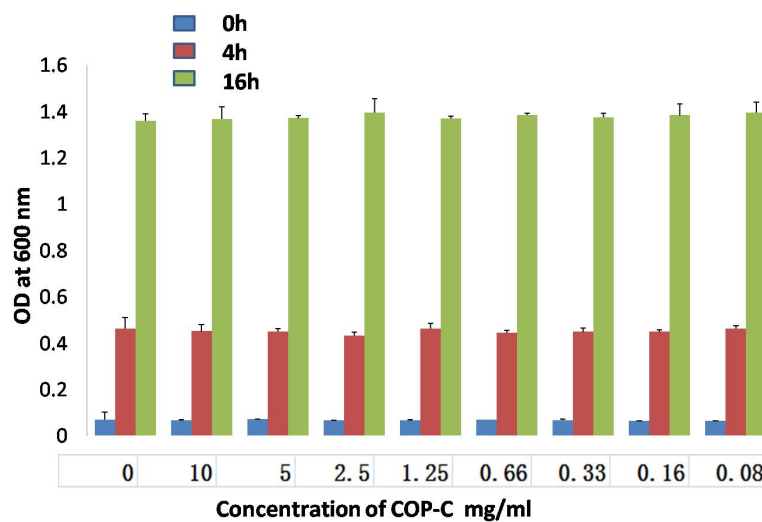


Fig. S7 OD values at 600 nm for the *E. coli* incubated with COP-H.

11. Reference

1. B. S. G. Bin Liu, Shu Wang, and Guillermo C. Bazan, *J. AM. CHEM. SOC.*, 2003, **125**.
2. S. W. Bin Liu, Guillermo C. Bazan, and Alexander Mikhailovsky, *J. AM. CHEM. SOC.*, 2003, **125**, 13306-13307.
3. Y. Qiao, C. Yang, D. J. Coady, Z. Y. Ong, J. L. Hedrick and Y. Y. Yang, *Biomaterials*, 2012, **33**, 1146-1153.