Construction and Heterogeneous Photooxidization Reactivity of Cyclodextrin/Porphyrin Polyrotaxane Network

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Experimental Section.

General Methods. All chemicals were commercially available unless noted otherwise. *β*-Cyclodextrin of reagent grade (Shanghai Reagent Factory) was recrystallized twice from water and dried in vacuo at 95 °C for 24 h prior to use. N,N-Dimethylformamide (DMF) was dried over calcium hydride for 2 days and then distilled under a reduced pressure prior to use. p-phthaldehyde were commercially available and used without further purification. Compounds **1-2** were prepared according to the literature procedures. NMR spectra were recorded on a Varian Mercury VX400 instrument. Solid-state NMR experiments were performed on a Varian instrument at room temperature (25 °C) and at frequencies of 100.52 MHz for ^{13}C NMR. UV/vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer in a quartz cell (light path 10 mm) at 25 °C. Steady-state fluorescence emission spectra were recorded in a conventional quartz cell (10 × 10 × 45 mm) at 25 °C on a Varian Cary Eclipse equipped with a Varin Cary single-cell peltier accessory to control temperature. TEM images were acquired by a high-resolution transmission electronic microscope (Philips Tecnai G2 20 S-TWIN microscope) operating at an accelerating voltage of 200 keV. The samples were prepared by placing a drop of solution onto a carbon-coated copper grid and air-dried. The SEM images were recorded on a JEOL JSM-7500F scanning electronic microscope operating at an accelerating voltage of 30 keV. The zeta potential was recorded on NanoBrook 173Plus (Brookhaven company) at 25 °C. Thermal gravimetric analysis(TGA) were measured by using a NETZSCH TG209 under N_2 (15ml/min) atmosphere.

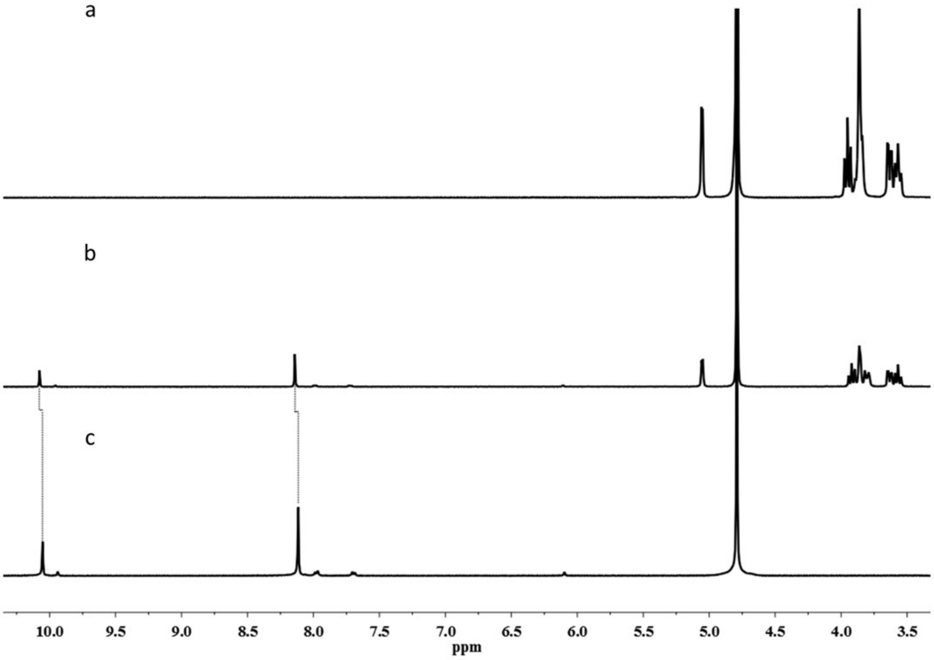
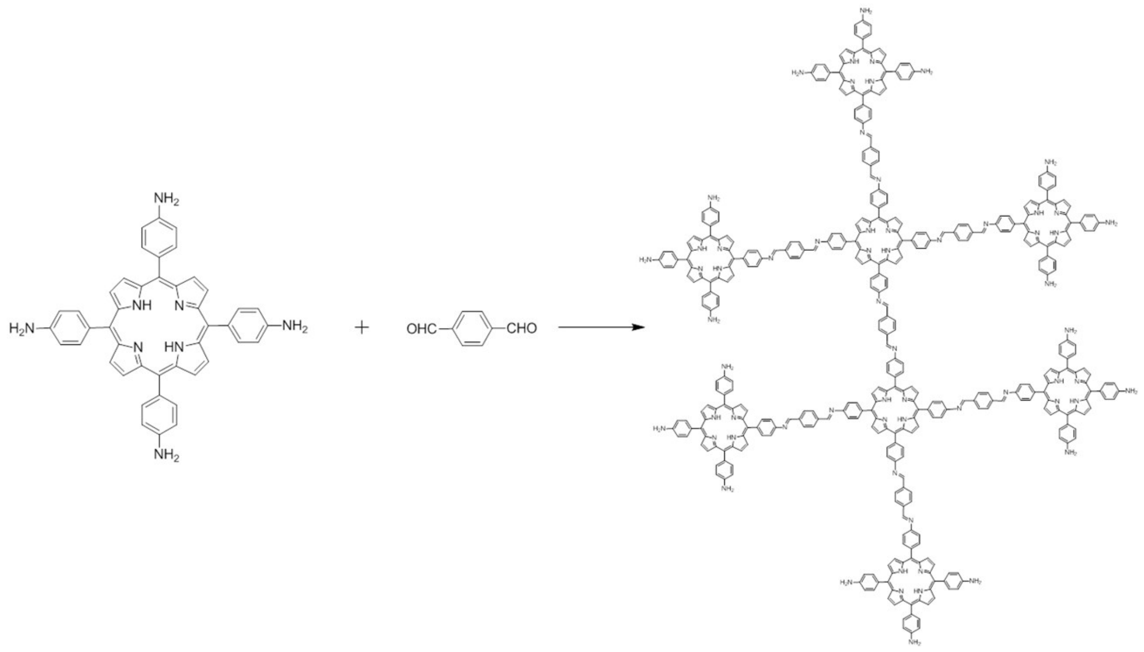


Figure S3. ^1H NMR (400 MHz) spectrum of (a) *β*-cyclodextrin, (b) the inclusion complexes 2 and (c) p-phthaldehyde in D_2O at 25 °C

Preparation of **3 and 4**.

1 (28.04 mg), *β*-cyclodextrin (157.3 mg), and CH_3COOH (0.5 mL) were dissolved in 3.5 mL of DMF. Then, a DMF solution (5 mL) of 2(105.5 mg) was added dropwise, and the resultant mixture was stirred in dark for 48 h at room temperature under nitrogen. After removing the solvent in vacuo, the residue was washed repeatedly with chloroform and water to remove the unreacted materials and possible byproducts. The crude product was dried in vacuo to give **3** (yield 35%).

1 (28.04 mg), and CH_3COOH (0.5 mL) were dissolved in 3.5 mL of DMF. Then, a DMF solution (5 mL) of p-phthaldehyde(11.15 mg) was added dropwise, and the resultant mixture was stirred in dark for 48 h at room temperature under nitrogen. After removing the solvent in vacuo, the residue was washed repeatedly with chloroform and water to remove the unreacted materials and possible byproducts. The crude product was dried in vacuo to give **4** (yield 43%).



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Scheme S1 Schematic illustration of **4**.

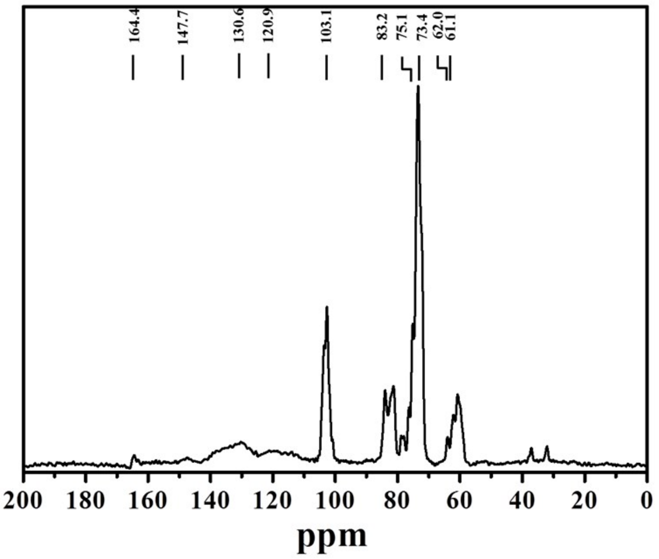

Figure S4. Solid state ^{13}C-NMR spectrum of **3**.

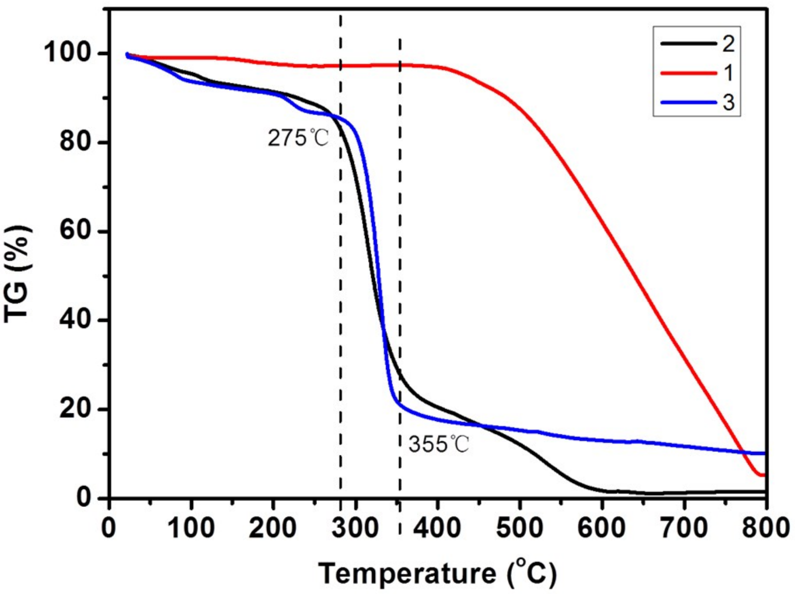

Figure S5. TG spectra of **1-3**.

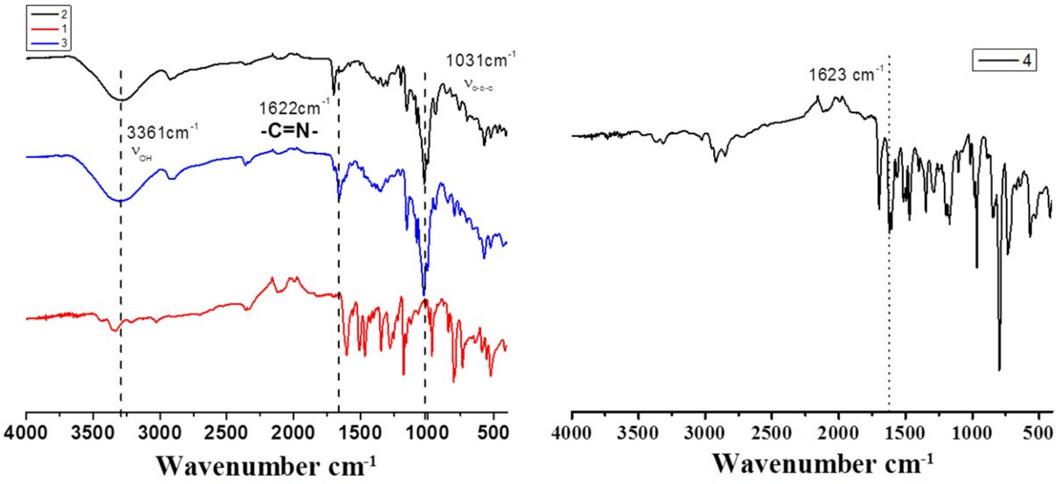

Figure S6 FT-IR spectra of **1-4**.

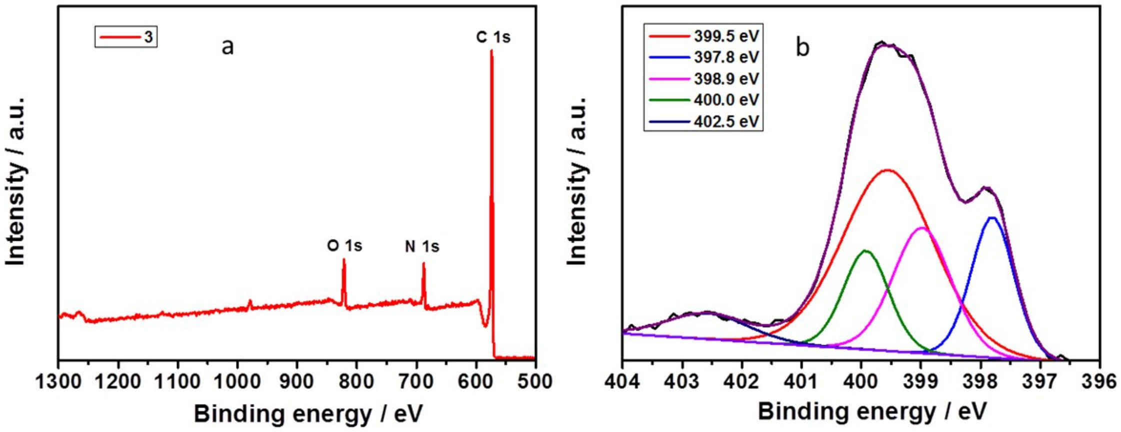

Figure S7. XPS spectrum (a) and nitrogen analysis (b) of **3**.

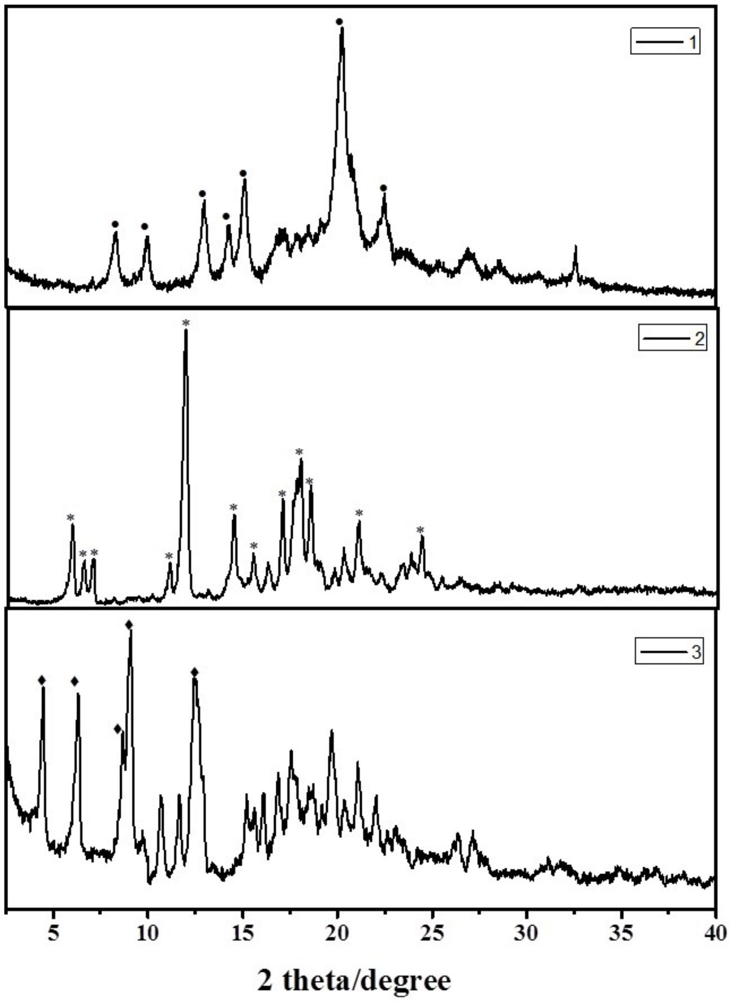

Figure S8. XRD spectra of (a) **1**, (b) **2** and (c) **3**.

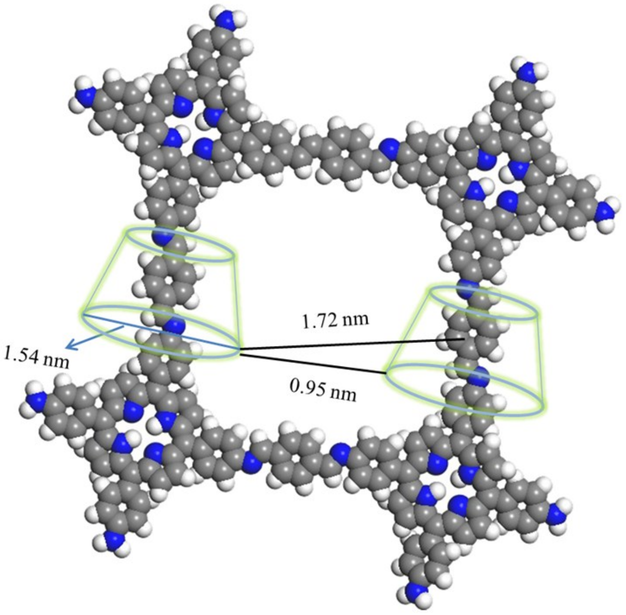

Figure S9. Molecular energy minimization structure through molecular modulation of **3** without *β*-CD.

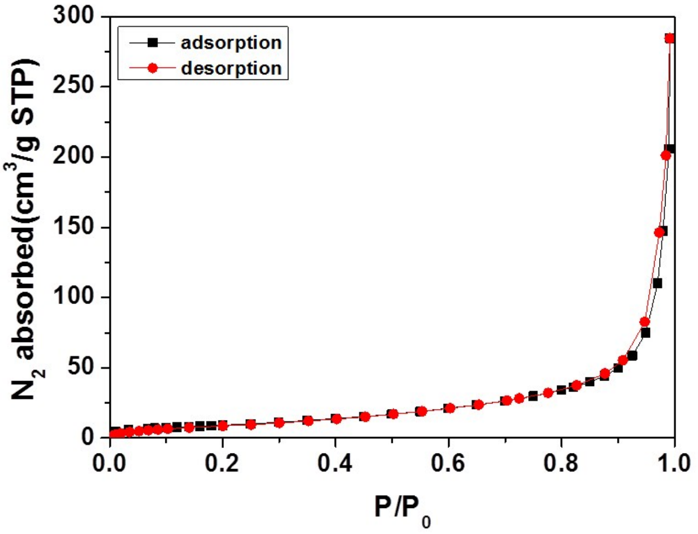

Figure S10. N_2 adsorption curve of **3** at 77 K.

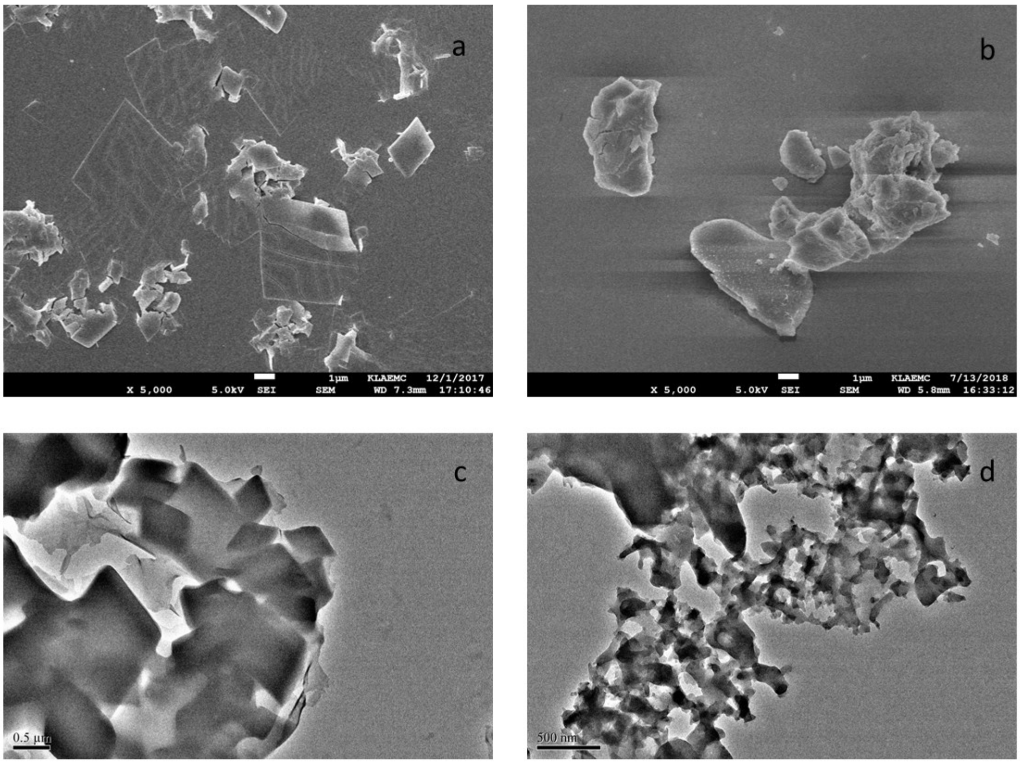

Figure S11. SEM images of (a) **2**, (b) **1** and TEM images of (c) **2**, (d) **1**.

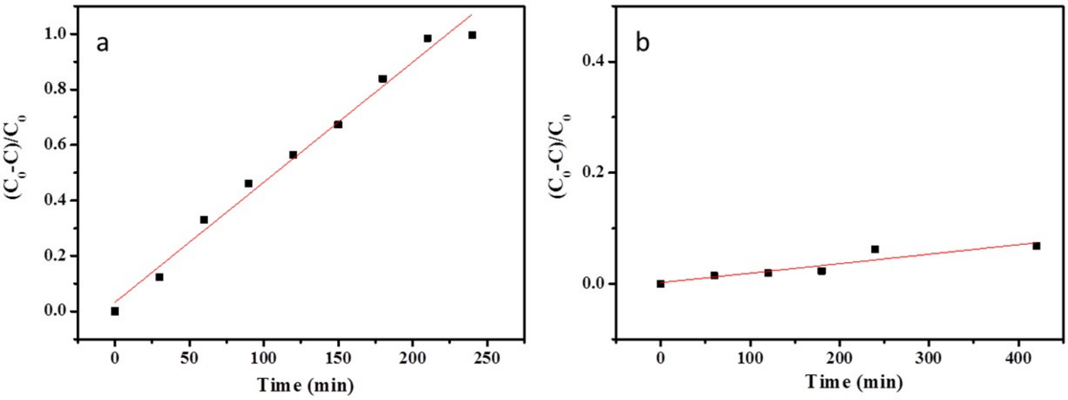

Figure S12. $(C_0\text{-}C) / C_0$ as functions of degradation time in the presence of (a) **3** or (b) **4**.