

# Supporting Information

## Porphyrin-containing hyperbranched supramolecular polymers: enhancing $^1\text{O}_2$ -generation efficiency by supramolecular polymerization

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### 1. Experimental Section

#### Synthesis of TPOR

5,10,15,20-Tetra(4-pyridyl)porphyrin (125 mg) and 2-(bromomethyl)naphthalene (1.0 g) were mixed in DMF and stirred at 90 °C for 12 hours in a nitrogen environment. The solution was then cooled and added dropwise into acetonitrile. Dark purple precipitate was filtered and washed with diethyl ether thoroughly then dried under vacuum.

<sup>1</sup>H-NMR (300M, DMSO-d<sub>6</sub>, 25 °C, δ): δ=9.72 (d, J=6.0 Hz, 8H), δ=9.22 (s, 8H), δ=9.04 (d, J=6.6 Hz, 8H), δ=8.45 (s, 4H), δ=8.19 (d, J=6.0 Hz, 4H), δ=8.09 (m, 8H), δ=8.00 (m, 4H), δ=7.68 (m, 8H), δ=6.40(s, 8H).

<sup>13</sup>C-NMR (400M, DMSO-d<sub>6</sub>, 25 °C, δ): δ=156.86, 143.6, 133.2, 132.9, 131.5, 129.3, 129.1, 128.2, 127.9, 127.2, 127.0, 126.7, 115.8, 63.4 ppm

MS: m/z=295.89, calculated for (C<sub>84</sub>H<sub>62</sub>N<sub>8</sub>)<sup>4+</sup> = 295.86

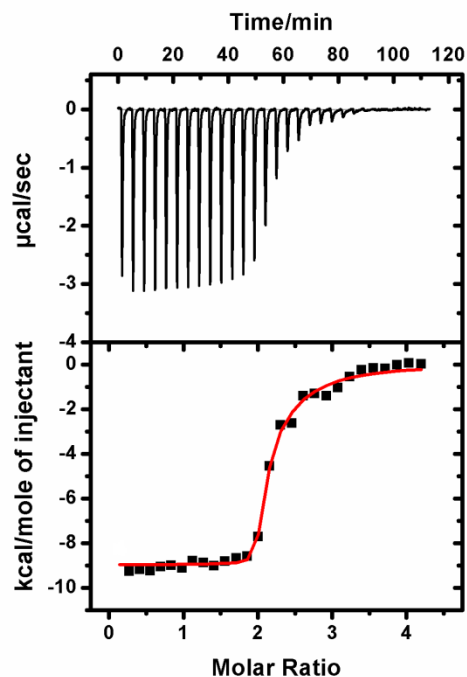
**ITC studies:** ITC was carried out with a Microcal VP-ITC apparatus at 298.15 K s in acetate buffer solution (pH 4.75).

**UV-Vis spectra and fluorescence emission spectra:** UV-Vis spectra were obtained using a HITACHI U-3010 spectrophotometer. Fluorescence spectra were obtained using a HITACHI F-7000 apparatus.

**NMR studies:** <sup>1</sup>H NMR spectra was recorded on a JOEL JNM-ECA300 apparatus (300 MHz). DOSY experiments were carried out with a BRUKER AVANCE 600 NMR Spectrometer.

**Singlet Oxygen Measurement:** The EPR spectroscopy was used to monitor the generation of singlet oxygen in aqueous solutions. Singlet oxygen was detected as TEMP-<sup>1</sup>O<sub>2</sub> adduct (TEMPO) using TEMP as a singlet oxygen trap. The EPR experiments were performed at room temperature on a JEOL JES-FA200 apparatus. The solution was saturated with oxygen, followed by addition of trace amount of TEMP and then irradiated by a xenon lamp with a sharp-cut filter (the cut off wavelength is 450 nm). The TEMPO signal was analyzed by EPR

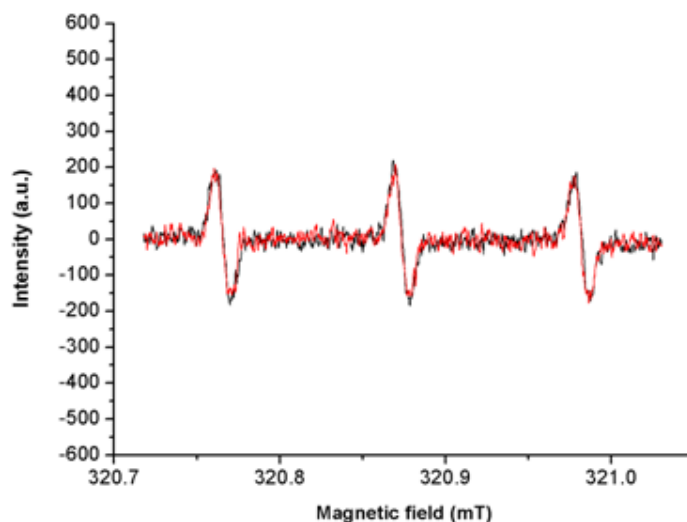
## 2. ITC Study of titration CB[8] with TPOR



Data: A20130314qnp\_NDH  
Model: TwoSites  
Chi<sup>2</sup> = 8.890E4  
N1 0.196 ± 0.480 Sites  
K1 5.08E4 ± 3.25E4 M<sup>-1</sup>  
ΔH1 -1.646E4 ± 4.61E4 cal/mol  
ΔS1 -33.7 cal/mol/deg  
N2 1.98 ± 0.0894 Sites  
K2 3.27E7 ± 3.89E7 M<sup>-1</sup>  
ΔH2 -8967 ± 93.6 cal/mol  
ΔS2 4.30 cal/mol/deg

**Fig. S1:** ITC data of titration CB[8] with TPOR. (TPOR 0.25 mM, CB[8] 0.05 mM). Here the TPOR was treated as four identical parts (using four times of TPOR's concentration as the concentration of the guest.) The binding stoichiometry of [0.25TPOR] with CB[8] can be read out to be 2:1, in other words, 1:2 for TPOR with CB[8].

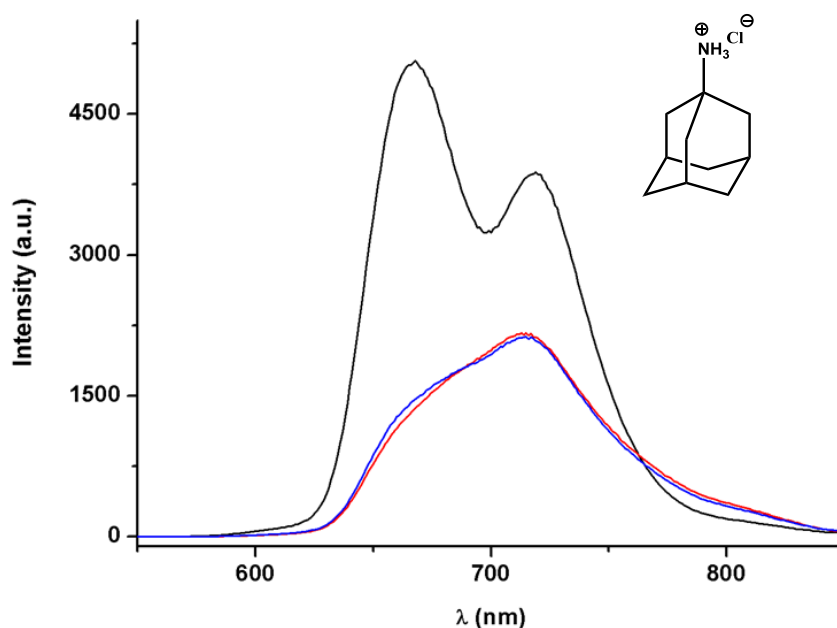
## 3. EPR spectra of TPOR-2CB[8] and TPOR without photoirradiation



**Fig. S2:** EPR spectra of 0.25 mM TPOR-2CB[8] (black) and 0.25 mM TPOR (red) without photoirradiation.

As shown in Fig. S2, TPOR-2CB[8] and TPOR show equal signals without photoirradiation.

#### 4. Fluorescence spectroscopy of TPOR, TPOR-2CB[8] and TPOR-2CB[8]-2AD



**Fig. S3:** Fluorescence spectroscopy of TPOR (red), TPOR-2CB[8] (black) and TPOR-2CB[8]-2AD (blue). The concentrations of all samples are set as 5.0  $\mu\text{M}$ .

Fig. S3 provides two points of view:

- 1) After adding CB[8] into the solution of TPOR, the fluorescence of TPOR enhances significantly. It indicates that the close stacking of the porphyrin moieties is disrupted, thus leading to the enhancement of the fluorescence.
- 2) After adding 2 equivalents of AD into the solution of TPOR-2CB[8], the fluorescence of the solution recovered to the quenched state as same as TPOR, indicating that the supramolecular hyperbranched polymers are depolymerised.