Electronic Supplementary Information

β-Cyclodextrin-conjugated phthalocyanines as water-soluble and recyclable

sensitisers for photocatalytic applications

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 1H and $^{13}C\{^1H\}$ NMR and MALDI-TOF mass spectra of all the new compounds

Experimental Section

General

All the reactions were performed under an atmosphere of nitrogen. DMF and *n*-pentanol were dried over barium oxide and sodium respectively and distilled under reduced pressure. All other solvents and reagents were used as received. Chromatographic purification was performed on silica gel (Macherey-Nagel 230-400 mesh) with the indicated eluents. Size-exclusion chromatography was carried out on Bio-Beads S-X1 beads (200-400 mesh) with THF as eluent. The mono-tosylated permethylated β -cyclodextrin (**3**)^{R1} and adamantane-functionalised silica nanoparticles^{R2} were prepared as described.

¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker AVANCE III 700 spectrometer (¹H, 700; ¹³C, 176 MHz) in CDCl₃ or CDCl₃ with a trace amount of pyridine-d₅. Spectra were referenced internally by using the residual solvent (¹H: δ 7.26) or solvent (¹³C: δ 77.2) resonances relative to SiMe₄. Matrix-assisted laser desorption/ionisation time-of-flight (MALDI-TOF) mass spectra were recorded on a Bruker Daltonics Autoflex III spectrometer with α -cyano-4-hydroxycinnamic acid as the matrix. TEM images were obtained on a FEI Tecnai G2 Spirit transmission electron microscope operated at 120 keV acceleration voltage. The images were digitised and analysed using the TEM image and analysis software (v421). Dynamic light scattering measurements were performed with a Malvern Zetasizer Nano ZS90 analyser.

Electronic absorption and steady-state fluorescence spectra were recorded on a Gary 5G UV-Vis-NIR spectrophotometer and a Hitachi F-7000 spectrofluorometer respectively. The fluorescence quantum yields $[\Phi_{F(sample)}]$ were determined by the equation: $\Phi_{F(sample)} =$

 $(F_{\text{sample}}/F_{\text{ref}})(A_{\text{ref}}/A_{\text{sample}})(n_{\text{sample}}^2/n_{\text{ref}}^2) \Phi_{F(\text{ref})}$, R³ where F, A and n are the measured fluorescence (area under the emission peak), the absorbance at the excitation position and the refractive index of the solvent respectively. The unsubstituted ZnPc in DMF ($\Phi_F = 0.28$)^{R4} was used as the reference. For the determination of singlet oxygen quantum yields, mixtures of DPBF (30 μ M) and the phthalocyanines (2 μ M) in DMF were prepared in the dark and then irradiated with red light coming from a 100 W halogen lamp after passing through a water tank for cooling and a colour glass filter (Newport) cut-on at $\lambda = 610$ nm. The absorbance of DPBF at 415 nm was recorded immediately after irradiation for every 5 seconds. The singlet oxygen quantum yield (in DMF) was determined by the equation: $\Phi_{\Delta}(\text{sample})$ = $\Phi_{\Delta}(\text{ref})[W_{\text{sample}}I_{\text{abs}}(\text{ref})]/[W_{\text{ref}}I_{\text{abs}}(\text{sample})], \text{ in which } W \text{ and } I \text{ are the DPBF photobleaching rate}$ and the rate of light absorption respectively.^{R5} The unsubstituted ZnPc in DMF was used as the reference ($\Phi_{\Delta} = 0.56$).^{R6}

Preparation of phthalonitrile 5

A mixture of β -cyclodextrin **3** (600 mg, 0.38 mmol), 3,6-dihydroxyphthalonitrile (**4**) (24 mg, 0.15 mmol) and K₂CO₃ (525 mg, 3.8 mmol) in DMF (10 mL) was stirred at 120 °C for 24 h. The solvent was then removed under reduced pressure. The residue was redissolved in CHCl₃ (150 mL) and the mixture was filtered to remove the unreacted salt. The filtrate was evaporated *in vacuo* and the residue was purified by column chromatography with CHCl₃/MeOH (100:1, v/v) as eluent to yield a white solid (124 mg, 28%). ¹H NMR (CDCl₃): δ 7.28 (s, 2 H, Ar-H), 5.04-5.18 (m, 14 H, CD-H), 4.58-4.62 (m, 2 H, CD-H), 4.40-4.42 (m, 2 H, CD-H), 4.05-4.08 (m, 2 H, CD-H), 3.73-3.88 (m, 30 H, CD-H), 3.51-3.68 (m, 120 H, CD-H), 3.32-3.40 (m, 32

H, CD-H), 3.16-3.23 (m, 16 H, CD-H). ¹³C {¹H} NMR (CDCl₃): δ 155.4, 119.4, 113.0, 105.2, 99.6, 99.4, 99.1, 99.0, 98.9, 98.7, 82.1, 82.0, 81.9, 81.7, 81.4, 81.0, 80.5, 80.2, 79.5, 72.0, 71.5, 71.4, 71.3, 71.0, 70.9, 70.8, 70.5, 70.2, 61.8, 61.5, 61.4, 59.2, 59.1, 59.0, 58.9, 58.7, 58.6, 58.5, 58.3, 34.2, 30.3 (some of the cyclodextrin signals were overlapped). MS (MALDI-TOF): *m/z* calcd for C₁₃₂H₂₂₀N₂O₇₀Na [M+Na]⁺: 2977.3643, found: 2977.3611.

Preparation of phthalocyanines 1 and 2

A mixture of phthalonitrile 5 (200 mg, 68 µmol) and the unsubstituted phthalonitrile 6 (17 mg, 0.13 mmol) in *n*-pentanol (10 mL) was heated to 90 °C. Li (30 mg, 4.3 mmol) was then added to the mixture and the temperature was quickly raised to 150 °C. After 2 h, Zn(OAc)₂ (36 mg, 0.20 mmol) was added and the green mixture was kept stirring at 150 °C for further 3 h. The mixture was cooled briefly and then evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with CHCl₃/MeOH (50:1, v/v) as eluent, followed by size-exclusion chromatography with THF as eluent. The crude products were further purified by recrystallisation from CHCl₃/n-hexane to yield 1 (21 mg, 9%) and 2 (13 mg, 6%) both as a greenish solid. 1: ¹H NMR (CDCl₃ with a trace amount of pyridine-d₅): δ 9.69 $(d, J = 7.2 Hz, 2 H, Pc-H_{\alpha}), 9.46-9.48 (m, 4 H, Pc-H_{\alpha}), 8.14-8.23 (m, 8 H, Pc-H_{\beta}), 5.63 (d, J =$ 3.0 Hz, 2 H, CD-H), 5.59 (d, J = 3.0 Hz, 2 H, CD-H), 5.43 (d, J = 8.3 Hz, 2 H, CD-H), 5.23-5.24 (m, 2 H, CD-H), 5.16-5.17 (m, 2 H, CD-H), 5.13-5.15 (m, 2 H, CD-H), 5.08-5.12 (m, 6 H, CD-H), 5.00-5.03 (m, 2 H, CD-H), 4.84 (d, J = 9.1 Hz, 2 H, CD-H), 4.36-4.38 (m, 2 H, CD-H), 3.10-4.04 (m, 188 H, CD-H), 2.78 (s, 6 H, CD-H). ¹³C{¹H} NMR (CDCl₃ with a trace amount of pyridine-d₅): δ 166.5, 154.2, 154.1, 153.3, 150.5, 150.2, 149.7, 138.8, 138.6, 138.4,

135.8, 129.4, 129.3, 127.6, 124.1, 123.5, 122.9, 122.7, 122.5, 119.8, 114.3, 99.4, 99.3, 99.1, 99.0, 98.9, 98.8, 98.0, 82.6, 82.3, 82.2, 82.1, 82.0, 81.9, 81.8, 81.7, 81.5, 80.9, 80.6, 80.5, 80.3, 80.2, 79.7, 78.9, 72.0, 71.5, 71.4, 71.3, 71.2, 71.0, 70.9, 70.8, 70.7, 68.5, 62.2, 61.8, 61.7, 61.6, 61.5, 61.4, 61.3, 61.2, 59.9, 59.2, 59.1, 59.0, 58.9, 58.8, 58.6, 58.5, 58.4, 58.3, 58.2, 57.5 (some of the signals were overlapped). MS (MALDI-TOF): m/z calcd for C₁₅₆H₂₃₃N₈O₇₀Zn [M+H]⁺: 3404.4267, found: 3404.4699; C₁₅₆H₂₃₂N₈NaO₇₀Zn [M+Na]⁺: 3426.4087, found: 3426.3390. 2: ¹H NMR (CDCl₃ with a trace amount of pyridine-d₅): δ 9.65 (pseudo s, 4 H, Pc-H_a), 8.19 (pseudo s, 4 H, Pc-H_{β}), 7.62 (pseudo s, 4 H, Pc-H_{β}), 5.61-5.63 (m, 8 H, CD-H), 5.43 (d, J = 8.2Hz, 4 H, CD-H), 5.24-5.27 (m, 4 H, CD-H), 5.11-5.18 (m, 16 H, CD-H), 5.02-5.03 (m, 4 H, CD-H), 4.81 (d, *J* = 8.8 Hz, 4 H, CD-H), 4.33 (d, *J* = 8.8 Hz, 4 H, CD-H), 3.12-4.03 (m, 374 H, CD-H), 2.73 -2.78 (m, 18 H, CD-H). ¹³C {¹H} NMR (CDCl₃ with a trace amount of pyridined₅): δ 168.7, 154.2, 153.3, 150.5, 149.6, 141.4, 138.6, 135.9, 135.8, 134.1, 132.9, 129.2, 127.5, 123.7, 123.5, 123.4, 114.1, 99.5, 99.1, 98.9, 97.9, 82.6, 82.3, 82.2, 82.1, 82.0, 81.9, 81.8, 81.7, 81.5, 80.9, 80.7, 80.5, 80.4, 79.7, 78.9, 72.0, 71.6, 71.4, 71.3, 71.1, 71.0, 70.7, 68.4, 62.2, 61.8, 61.6, 61.5, 61.3, 60.0, 59.3, 59.1, 59.0, 58.9, 58.6, 58.5, 58.4, 58.3, 57.4, 36.7, 34.8, 34.7, 34.5, 29.4 (some of the signals were overlapped). MS (MALDI-TOF): m/z calcd for C₂₈₀H₄₄₉N₈O₁₄₀Zn [M+H]⁺: 6232.7643, found: 6232.7856.

Preparation of 1@SiO₂ and 2@SiO₂

A mixture of adamantane-functionalised silica nanoparticles and **1** or **2** (0.1 mg mL^{-1}) in water was stirred at ambient temperature for 24 h. After leaving it for 15 min, the green precipitate on the bottom was abandoned and the suspension was centrifuged at 10000 rpm for 3 min. The green solid obtained was washed thoroughly with water until the supernatant was colourless to give $1@SiO_2$ and $2@SiO_2$.

Determination of the loading of phthalocyanines

 $1@SiO_2 \text{ or } 2@SiO_2 \text{ was suspended in DMF}$ and sonicated for 30 min. The suspension was centrifuged at 10000 rpm for 3 min and the supernatant was collected. The extraction was repeated for four times until a white solid was obtained after centrifugation. The amount of phthalocyanines in the combined DMF solution was quantified by comparing the absorbance at 692 nm for 1 and 717 nm for 2.

Photooxygenation reactions

All of the reactions were carried out in a test tube with an oxygen inlet apparatus at ambient temperature. The concentration of all the substrates was fixed at 0.1 M. Mixtures of the substrates and photosensitisers were irradiated with a halogen lamp at 100 W or 300 W placed at *ca*. 10 cm from the reactor with continuous bubbling of oxygen unless otherwise stated. A glass filter was used to cut off the light at $\lambda < 610$ nm. The reactions were monitored by TLC. For the photooxygenation of 1-naphthol, the conversion efficiency and isolated yield were calculated based on the starting material recovered and the product isolated by column chromatography using the equations: % Conversion = $(n_0-n_1)/n_0 \times 100\%$ and % Yield = $n_p/(n_0-n_1) \times 100\%$ respectively, where n_0 and n_1 are the number of mole of the starting material before and after the reaction respectively, and n_p is the number of mole of the product.^{R7} For the photooxygenation of 2-furoic acid, the conversion efficiency and yield were determined using

¹H NMR spectroscopy with 2,5-dimethylfuran as an internal standard.^{R8} An example is given in Fig. S7 (see below).

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Fig. S1 (a) Electronic absorption and (b) fluorescence ($\lambda_{ex} = 610$ nm) spectra of 1 and 2 in DMF and in water (both at 2 μ M).



Fig. S2 Electronic absorption spectra of (a) **1** and (b) **2** in water at different concentrations. The inset of each figure plots the Q-band absorbance versus the concentration of the phthalocyanine.



Fig. S3 Comparison of the rates of decay of DPBF sensitised by 1, 2, $1@SiO_2$ and $2@SiO_2$ in DMF and in water using ZnPc in DMF as the reference.



Fig. S4 Change in the Q-band absorbance of (a) 1 and (b) 2 (both at 5 μ M) in various solvents upon irradiation with a 100 W halogen lamp equipped with a colour glass filter cut-on at 610 nm at ambient temperature.



Fig. S5 TEM images of (a) $1@SiO_2$ and (b) $2@SiO_2$.



measurements.

^b PDI: polydispersity index

Fig. S6 Dynamic light scattering analysis of 1@SiO₂ and 2@SiO₂.



Fig. S7 A typical ¹H NMR spectrum of the mixture after photooxygenation of 2-furoic acid in CDCl₃.

Photosensitiser	Solvent	Conv. (%)	Yield (%)	
1	CHCl ₃	85	92	
1	THF	88	85	
1	CH ₃ CN	89	86	
1	H ₂ O with 1% CH ₃ CN	88	95	
2	CHCl ₃	88	94	
2	THF	84	80	
2	CH ₃ CN	87	83	
2	H ₂ O with 1% CH ₃ CN	90	91	

Table S1 Photooxygenation of 1-naphthol using 1 and 2 (0.1 mol%) as the photosensitisers in different solvents^a

^a The mixtures were bubbled with O₂ and irradiated with a 100 W halogen lamp equipped with a colour glass filter cut-on at 610 nm at ambient temperature for 1 h.

Entry	Photosensitiser	Loading (mol%)	Time (h)	Conv. (%)	Yield (%)
1	1	0.1	4	36	80
2	1	2	2	50	89
3	1	2	4	54	84
4	2	0.1	4	40	81
5	2	2	2	55	89
6	2	2	4	57	85

Table S2 Photooxygenation of 2-furoic acid using 1 and 2 as the photosensitisers in water^a

^a The mixtures were bubbled with O_2 and irradiated with a 100 W halogen lamp equipped with a colour glass filter cut-on at 610 nm at ambient temperature. The conversion efficiency and percentage yield were determined by ¹H NMR spectroscopy with 2,5-dimethylfuran as an internal standard.

Table S3 Recycling of $1@SiO_2$ and $2@SiO_2$ in photooxygenation of 1-naphthol and 2-furoicacid in water (with 0.2% CH₃CN)^a

Photosensitiser	Substrate	Cycle/yield (%)				
		1	2	3	4	5
1@SiO ₂	1-Naphthol	94	90	90	88	85
2 @SiO ₂	1-Naphthol	92	89	89	86	86
1@SiO ₂	2-Furoic acid	85	80	78	73	69
2 @SiO ₂	2-Furoic acid	89	85	81	75	66

^a The mixtures containing the photosensitisers (at 1 mol% of phthalocyanine) were bubbled with O_2 and irradiated with a 100 W halogen lamp equipped with a colour glass filter cut-on at 610 nm at ambient temperature for 1 h (for 1-naphthol) or 8 h (for 2-furoic acid).



1H and $^{13}C\{^1H\}$ NMR spectra of phthalonitrile **5** in CDCl₃:

MALDI-TOF mass spectrum of phthalonitrile 5:





 1H and $^{13}C\{^1H\}$ NMR spectra of 1 in CDCl3 with a trace amount of pyridine-d5:

MALDI-TOF mass spectrum of 1:





 1H and $^{13}C\{^1H\}$ NMR spectra of ${\bf 2}$ in CDCl3 with a trace amount of pyridine-d5:

MALDI-TOF mass spectrum of **2**:

