

Electronic Supplementary Information

Formation and energy transfer property of a subphthalocyanine- porphyrin complex held by host-guest interactions

Hu Xu, Eugeny A. Ermilov, Beate Röder and Dennis K. P. Ng*

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Experimental Section

General. All the reactions were performed under an atmosphere of nitrogen. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. *N,N*-Dimethylformamide (DMF) and *p*-xylene were distilled from barium oxide and sodium, respectively, under reduced pressure. Triethylamine was dried over anhydrous Na₂SO₄ prior to use. All other solvents and reagents were of reagent grade and used as received. Mono-6-hydroxy permethylated β -cyclodextrin was prepared according to literature procedure.^{R1}

¹H and ¹³C{¹H} NMR spectra were recorded on Bruker DPX 300 (300 MHz) and AVANCE II 400 (100.6 MHz) spectrometers, respectively, in CDCl₃. Spectra were referenced internally by using the residual solvent (¹H: δ 7.26) or solvent (¹³C: δ 77.0) resonances relative to SiMe₄. ESI mass spectra were measured on a Thermo Finnigan MAT 95 XL mass spectrometer.

Photophysical studies. Ground-state absorption spectra were taken on a Cary 5G UV-Vis-NIR spectrophotometer. Steady-state fluorescence spectra were measured by using a combination of a cw-xenon lamp (XBO 150) and a monochromator (Lot-Oriel, bandwidth 10 nm) for excitation and a polychromator with a cooled CCD matrix as the detector system (Lot-Oriel, Instaspec IV).^{R2} Fluorescence quantum yields were determined by the equation: $\Phi_{F(\text{sample})} = (F_{\text{sample}}/F_{\text{ref}})(A_{\text{ref}}/A_{\text{sample}})(n_{\text{sample}}^2/n_{\text{ref}}^2)\Phi_{F(\text{ref})}$,^{R3} where F , A and n are the integrated fluorescence intensity, the absorbance at the excitation wavelength and the refractive

index of the solvent respectively. *meso*-Tetraphenylporphyrin in DMF [$\Phi_{F(\text{ref})} = 0.11$]^{R4} and rhodamine 6G in ethanol [$\Phi_{F(\text{ref})} = 0.95$]^{R5} were used as the references. Time-resolved fluorescence spectroscopic studies were carried out by using the set-up described previously.^{R6}

Electrochemical studies. Electrochemical measurements were carried out with a BAS CV-50W voltammetric analyser. The cell comprised inlets for a platinum-sphere working electrode, a platinum-plate counter electrode and a silver-wire pseudo-reference electrode. Typically, a 0.1 M solution of [Bu₄N][PF₆] in DMF containing the sample was purged with nitrogen for 15 min, then the voltammograms were recorded at ambient temperature. Potentials were referenced to saturated calomel electrode (SCE) by using ferrocene as an internal standard ($E_{1/2} = +0.38$ V vs. SCE).^{R7}

Subphthalocyanine 1. A mixture of boron(III) subphthalocyanine chloride (*ca.* 90% in purity, 30 mg, 0.06 mmol), mono-6-hydroxy permethylated β -cyclodextrin (0.30 g, 0.21 mmol) and Et₃N (0.5 mL) in *p*-xylene (5 mL) was heated under reflux for 3 days. After cooling, the volatiles were removed under reduced pressure. The residue was then loaded onto a silica gel (Macherey-Nagel, 70-230 mesh) column and eluted with CHCl₃/MeOH (50:1 v/v). The crude product obtained was further purified by size exclusion chromatography with Bio-Beads S-X1 beads using THF as the eluent, followed by recrystallisation from acetone/hexane. The product was isolated as a violet solid (5.8 mg, 5%). ¹H NMR: δ 8.82-8.84 (m, 6 H), 7.87-7.90 (m, 6 H), 5.13 (virtual t, $J = 3.3$ Hz, 2 H), 5.08 (d, $J = 3.3$ Hz, 2 H), 5.03 (d, $J = 3.3$ Hz, 1

H), 4.60 (d, $J = 3.3$ Hz, 1 H), 4.18 (d, $J = 3.3$ Hz, 1 H), 3.00-3.83 (m, 96 H), 2.77-2.82 (m, 2 H), 2.55-2.61 (m, 2 H), 2.17 (d, $J = 11.7$ Hz, 1 H), 1.61 (d, $J = 11.7$ Hz, 1 H); $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 151.4, 131.0, 129.6, 122.0, 121.9, 96.9-99.1 (7 resolved signals for C_1), 77.2-82.0 (C_2 , C_3 and C_4), 70.2-71.2 (C_5 and C_6), 61.0-61.5 (one of the methyl groups), 58.3-59.1 (the remaining two methyl groups); HRMS (ESI) calcd for $\text{C}_{86}\text{H}_{121}\text{BN}_6\text{NaO}_{35}$ ($[\text{M} + \text{Na}]^+$) 1831.7858, found: 1831.7850; UV-Vis (EtOH) [λ_{max} nm (log ϵ)]: 302 (4.66), 507 (4.42), 559 (4.95); UV-Vis (H_2O) [λ_{max} nm (log ϵ)]: 303 (4.53), 510 (4.35), 566 (4.88).

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- R6 S. Tannert, E. A. Ermilov, J. O. Vogel, M. T. M. Choi, D. K. P. Ng and B. Röder, *J. Phys. Chem. B*, 2007, **111**, 8053.
- R7 R. T. Boéré, K. H. Moock and M. Parvez, *Z. Anorg. Allg. Chem.*, 1994, **620**, 1589.

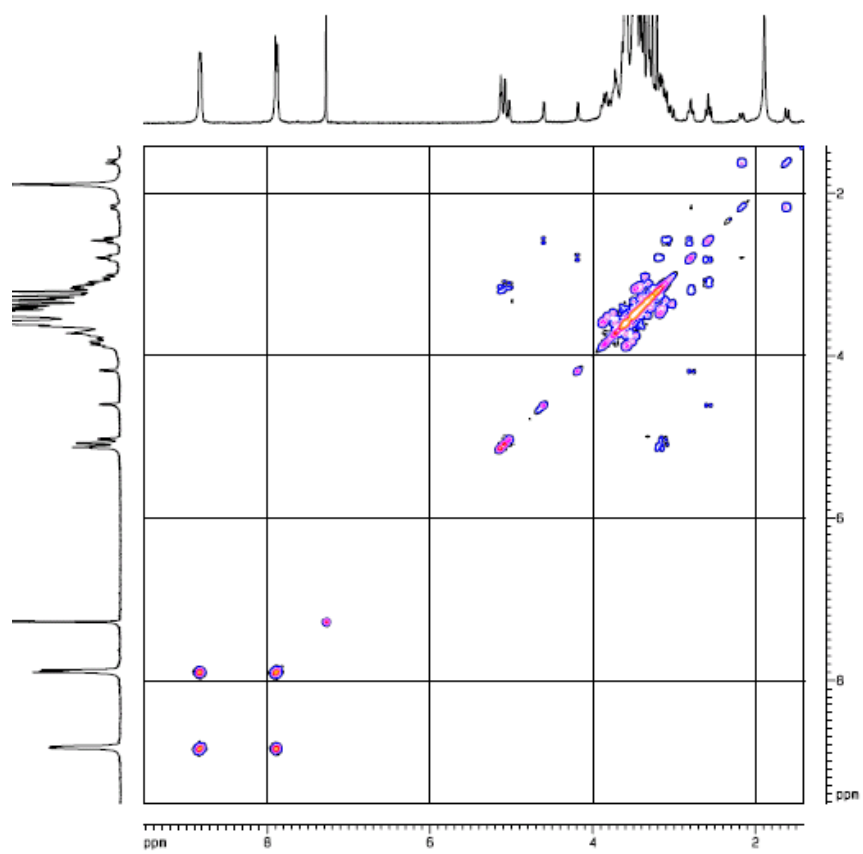


Fig. S1 ^1H - ^1H COSY spectrum of **1** in CDCl_3 .

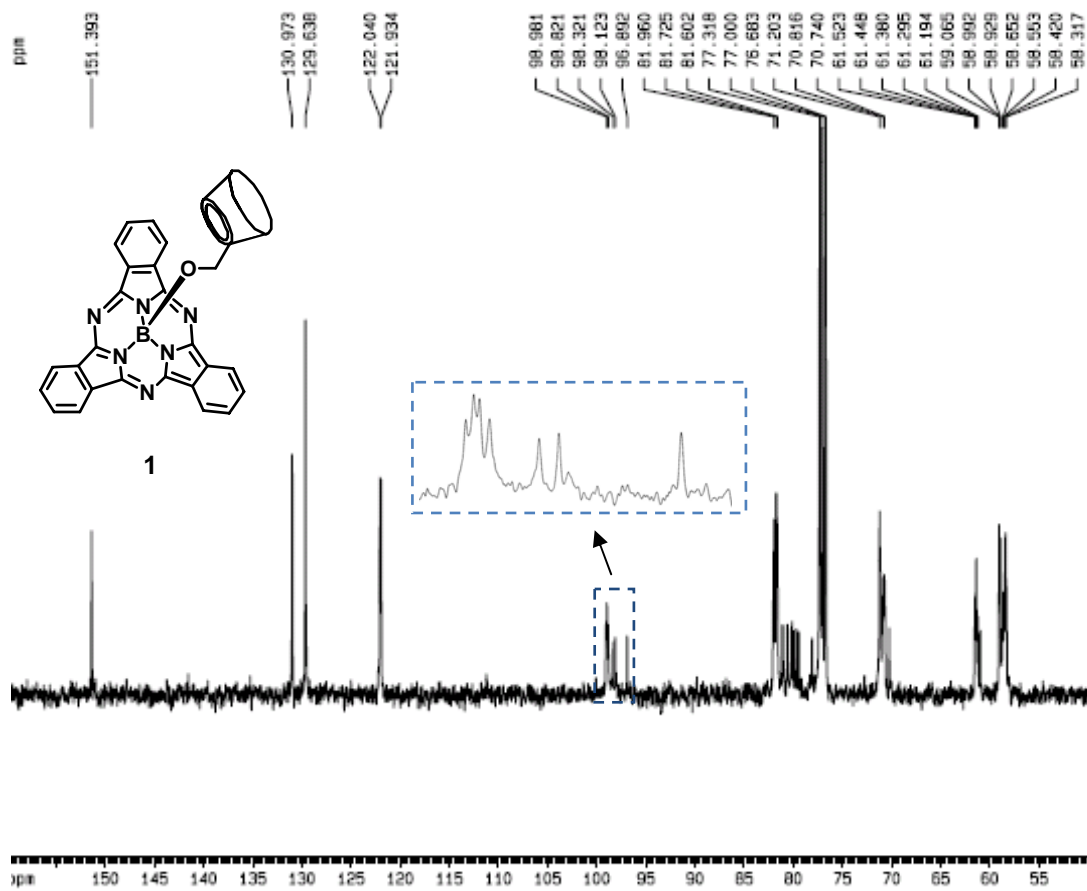
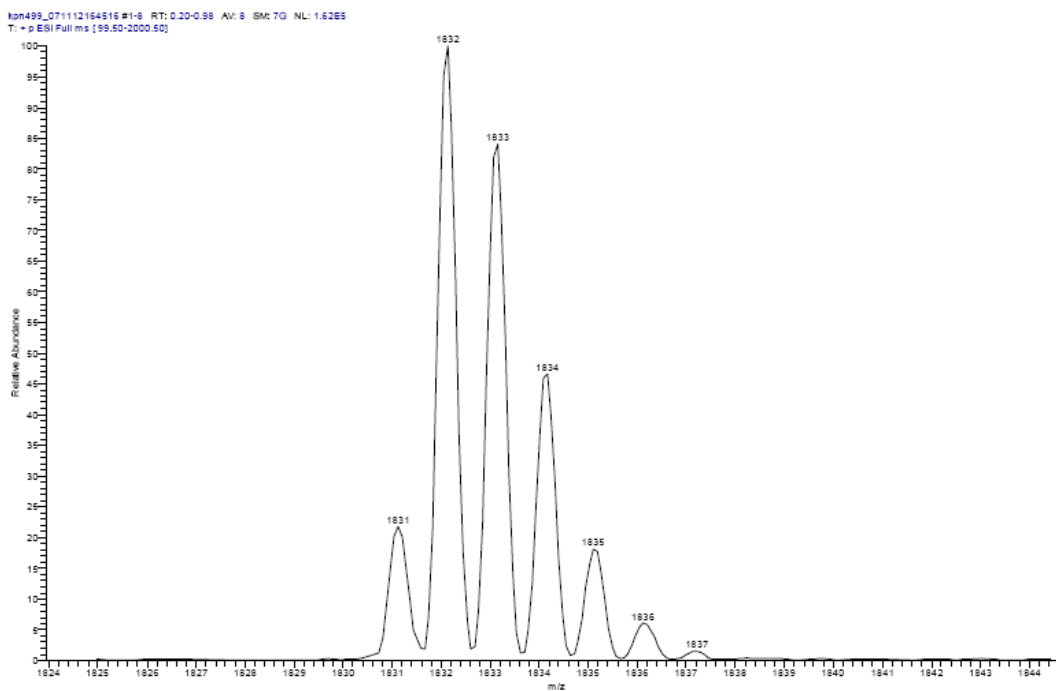


Fig. S2 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** in CDCl_3 .

(a)



(b)

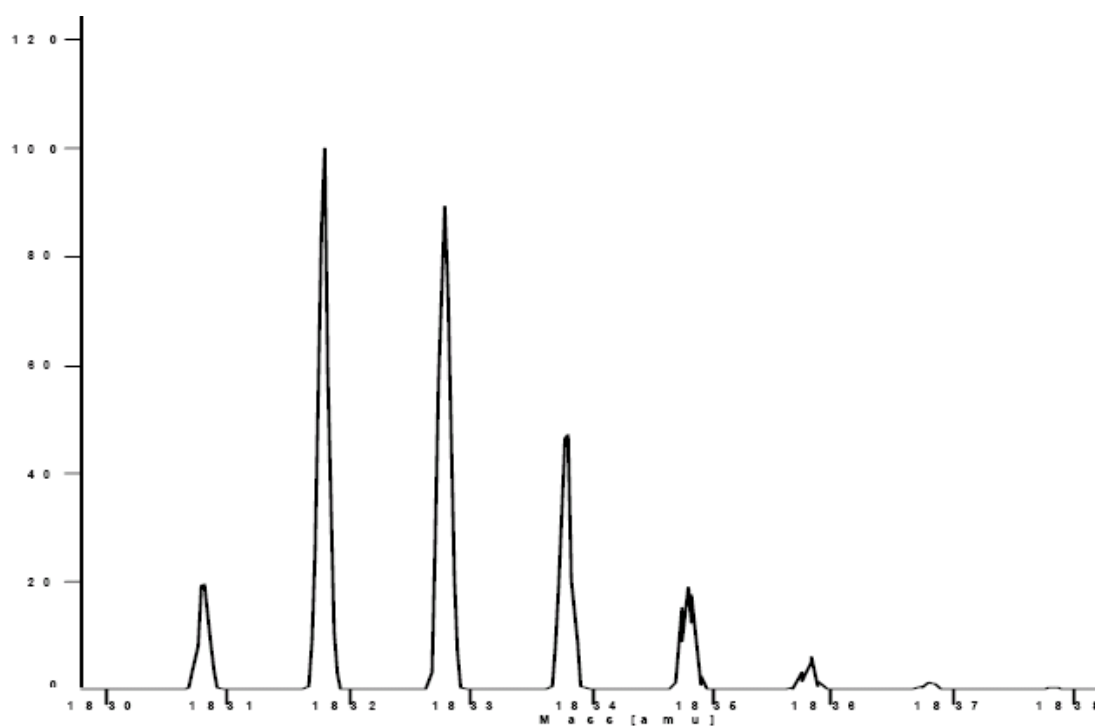
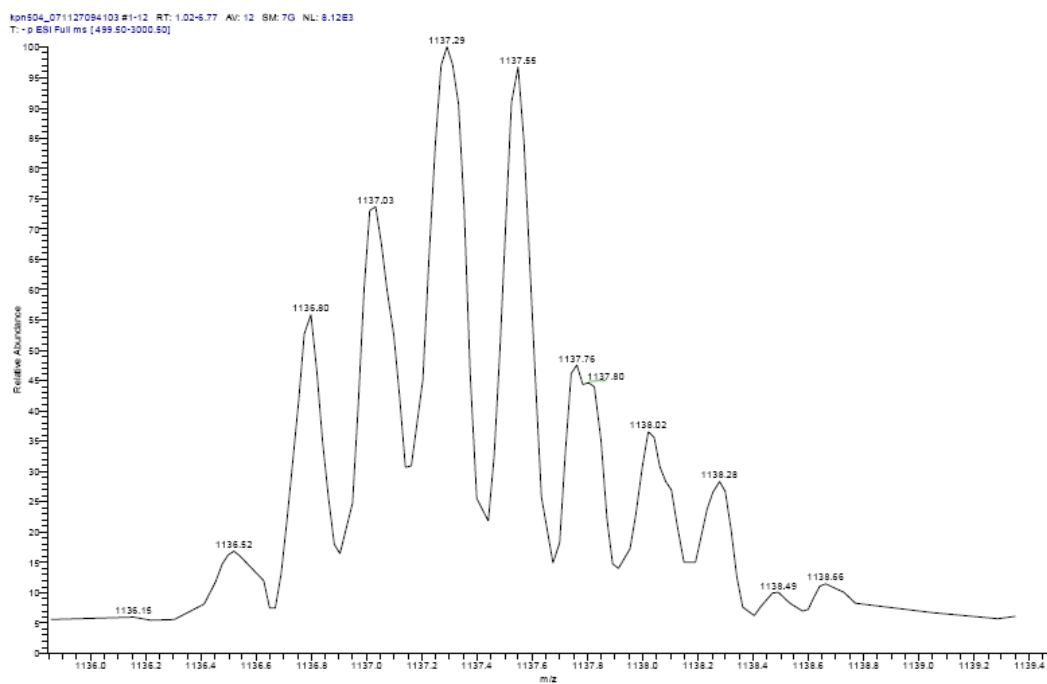


Fig. S3 The observed (a) and simulated (b) isotopic envelope for the $[M + Na]^+$ ion in the ESI mass spectrum of **1**.

(a)



(b)

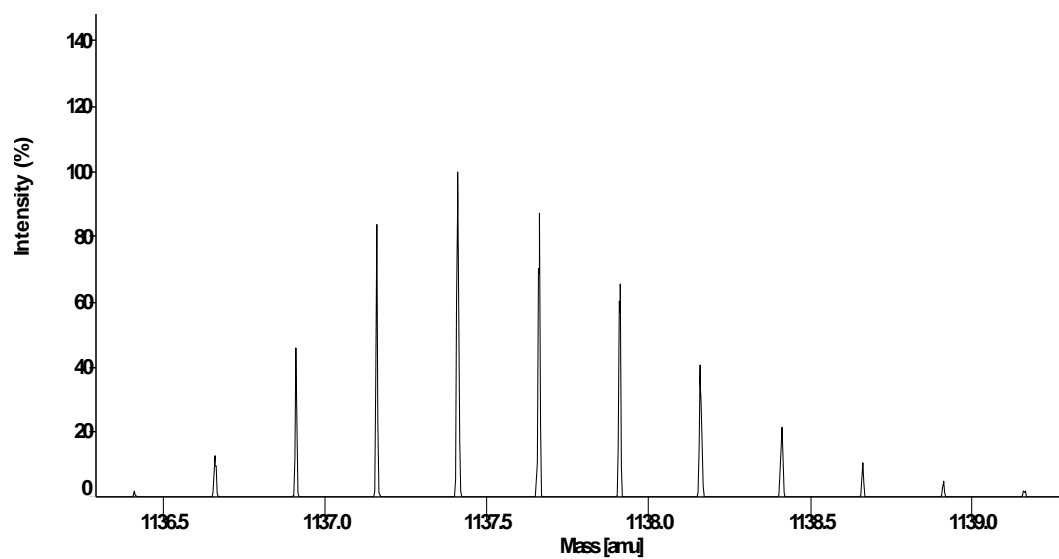


Fig. S4 The observed (a) and simulated (b) isotopic envelope for the $[M - 4 Na]^{4+}$ ion in the ESI mass spectrum of a 2:1 mixture of **1** and **2** in water.

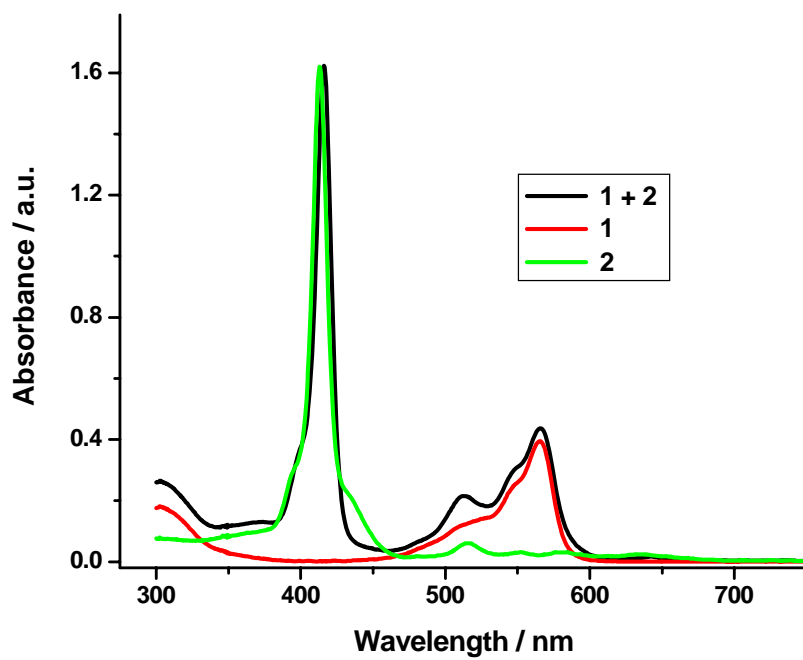


Fig. S5 Electronic absorption spectra of **1**, **2** and a 2:1 mixture of **1** and **2** in water.

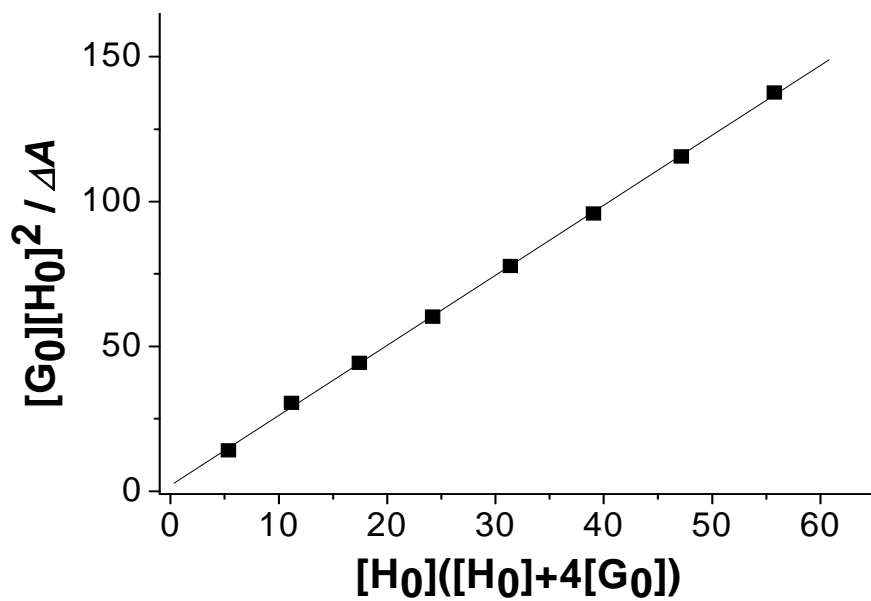


Fig. S6 Plot of $[G_0][H_0]^2/\Delta A$ vs. $[H_0]([H_0] + 4[G_0])$ for the titration of **2** (as the guest G) with **1** (as the host H) in water. A linear least-squares analysis determines the association constant K of the complex $(\mathbf{1})_2\cdot\mathbf{2}$.

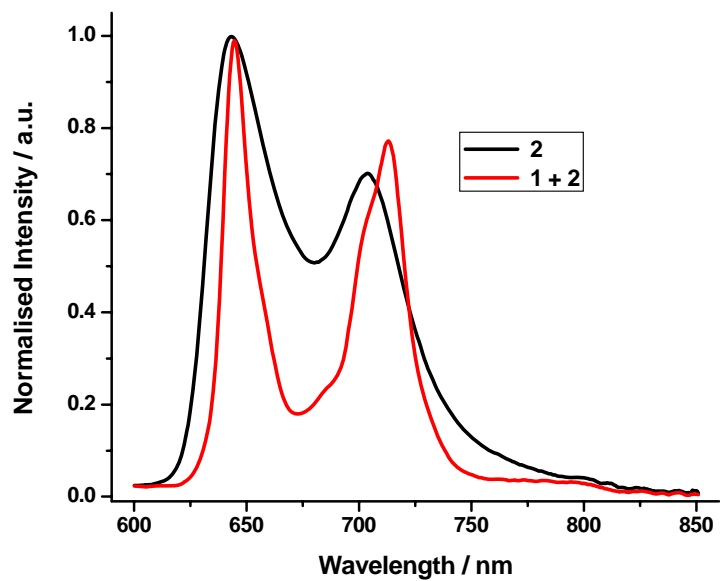


Fig. S7 Fluorescence spectra of **2** (3.0 μM) and a mixture of **1** (6.0 μM) and **2** (3.0 μM) in water ($\lambda_{\text{ex}} = 400 \text{ nm}$).

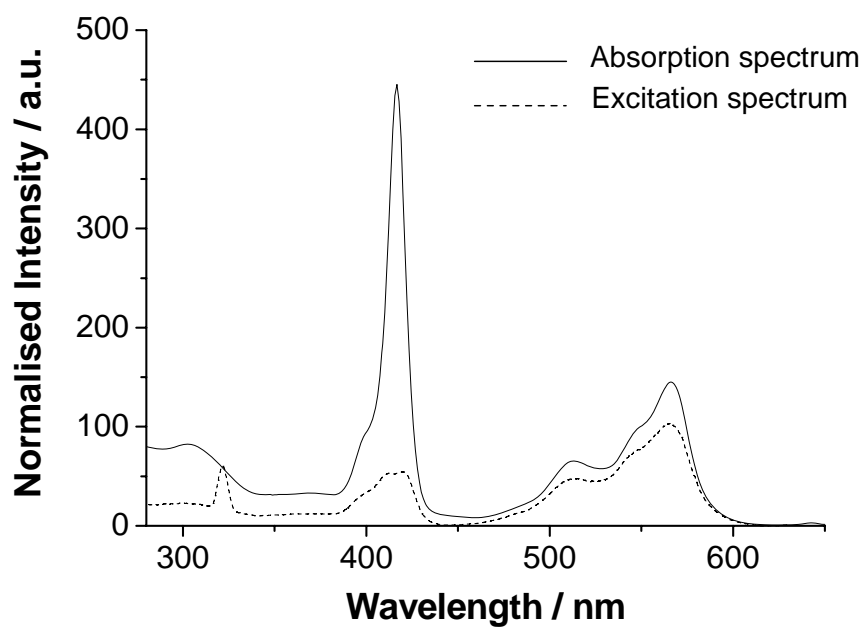
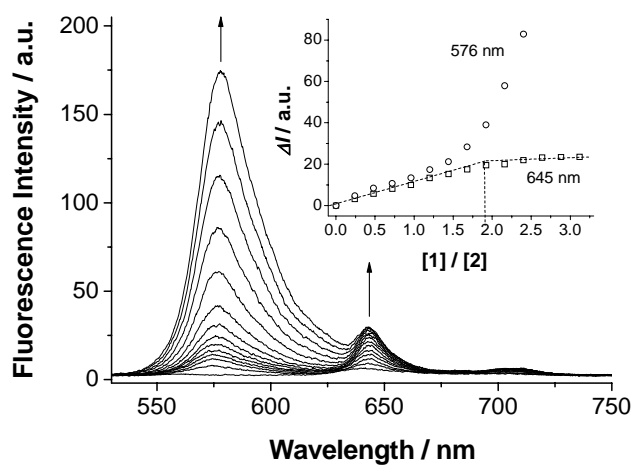


Fig. S8 Normalised (at 630 nm) absorption and excitation spectra (monitored at 645 nm) of a 2:1 mixture of **1** and **2** in water.

(a)



(b)

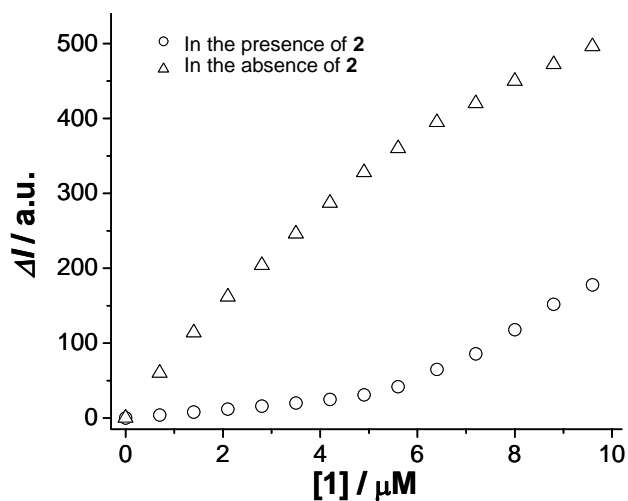


Fig. S9 (a) Change in fluorescence spectrum of **2** (3.0 μM) upon addition of **1** (up to 9.6 μM) in water ($\lambda_{\text{ex}} = 470$ nm). The inset shows the change in fluorescence intensity at 576 and 645 nm during the titration process. (b) Comparison of the changes in fluorescence intensity at 576 nm for **1** in the absence and presence (3.0 μM) of **2**.