Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Formation and photoinduced processes of the host-guest complexes of a β-cyclodextrin-conjugated aza-BODIPY and tetrasulfonated porphyrins

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Fig. S10 (a) Fluorescence spectra of mixtures of **1** and **2** with different mole fractions in H_2O (λ_{ex} = 515 nm). The total concentration of **1** and **2** was fixed at 4.0 μM. (b) The corresponding Job's plot by monitoring the change in fluorescence intensity at 641 nm.

Fig. S11 (a) Fluorescence spectra of mixtures of **1** and **3** with different mole fractions in H_2O (λ_{ex} = 556 nm). The total concentration of **1** and **3** was fixed at 4.0 μM. (b) The corresponding Job's plot by monitoring the change in fluorescence intensity at 604 nm.

Fig. S12 DAF spectra of (a) **1·2** and (b) **1·3** in water upon excitation of **1** at 650 nm. The inset of (b) shows the normalised spectra. The concentration of all the components was fixed at 5 μM.

Fig. S13 Transient absorption spectra of **1·3** in water at different delay times upon excitation of (a) **1** at 650 nm and (b) **3** at 556 nm. The decay of the induced absorption of the radical anion of **1** at 820 nm is shown in (c).

Fig. S14 Transient absorption spectra of **1·2** in water at different delay times upon excitation of (a) **1** at 650 nm and (b) **2** at 515 nm. The decay of the induced absorption of the radical anion of **1** at 820 nm is shown in (c).

Fig. S15 ^1H NMR spectrum of **1** in $CDCl_3$.

Experimental Section

Materials and methods. All the reactions were performed under an atmosphere of nitrogen. *N*,*N*-Dimethylformamide (DMF) was distilled from barium oxide. Deionised water without fluorescent impurities was used for the spectroscopic measurements. Chromatographic purification was performed on a silica gel (Macherey-Nagel 230-400 mesh) column with the indicated eluent. Size exclusion chromatography was carried out on Bio-Beads S-X1 beads (200-400 mesh) with tetrahydrofuran (THF) as the eluent. All other solvents and reagents were of reagent grade and used as received. Compounds **3**,[1] **4**[2] and **5**[3] were prepared as described.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer (^{1}H, 400; ^{13}C, 100.6 MHz) in $CDCl_3$. Spectra were referenced internally using the residual solvent (^{1}H: δ 7.26) or solvent (^{13}C: δ 77.2) resonances relative to $SiMe_4$. Electrospray ionisation (ESI) mass spectra were recorded on a Thermo Finnigan MAT 95 XL mass spectrometer. UV-Vis and steady-state fluorescence spectra were taken on a Cary 5G UV-Vis-NIR spectrophotometer and a Hitachi F-7000 spectrofluorometer respectively. The fluorescence quantum yields of the samples [$\Phi_{F(sample)}$] were determined by the equation: $\Phi_{F(sample)} = (F_{sample}/F_{ref})(A_{ref}/A_{sample})(n_{sample}^2/n_{ref}^2)\Phi_{F(ref)}$,[4] 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. *meso*-Tetraphenylporphyrin in DMF was used as the reference [$\Phi_{F(ref)} = 0.12$] for porphyrins **2** and **3**.[5]

[5-(4-Methoxyphenyl)-3-phenyl-1*H*-pyrrol-2-yl][5-(4-methoxyphenyl)-3-phenyl-pyrrol-2-ylidene]amine in $CHCl_3$ was used as the reference [$\Phi_{F(ref)}$ = 0.36] for aza-BODIPY **1**.[6]

Preparation of aza-BODIPY 1. A mixture of aza-BODIPY **4** (50.0 mg, 83 μmol), cyclodextrin **5** (0.71 g, 0.49 mmol), $CuSO_4 \cdot 5H_2O$ (21 mg, 84 μmol) and sodium ascorbate (33 mg, 0.17 mmol) in CH_2Cl_2/EtOH/H_2O (6 mL/0.5 mL/0.5 mL) was reflux for 15 h. CuI (50 mg, 0.26 mmol) was then added and the mixture was further refluxed overnight. After cooling, CH_2Cl_2 (50 mL) was added into the mixture. It was then washed with water (50 mL). The aqueous phase was extracted with CH_2Cl_2 (50 mL × 2). The combined organic portions were dried over anhydrous Na_2SO_4, and then evaporated *in vacuo*. The residue was purified by column chromatography with CH_2Cl_2/MeOH (50/1 v/v) as the eluent. The crude product was further purified by size exclusion chromatography with THF as the eluent to give a dark green solid (80.6 mg, 28%). ^{1}H NMR: δ 8.09 (d, *J* = 8.8 Hz, 4 H, ArH), 8.05 (d, *J* = 7.6 Hz, 4 H, ArH), 7.76 (s, 2 H, triazole-H), 7.39-7.47 (m, 6 H, ArH), 7.09 (d, *J* = 8.8 Hz, 4 H, ArH), 7.03 (s, 2 H, pyrrole-H), 5.23-5.26 (m, 6 H, OCH_2 & CD-H_1), 5.12-5.15 (m, 12 H, CD-H), 4.99 (d, *J* = 12.4 Hz, 2 H, CD-H_5), 4.75 (dd, *J* = 6.4 and 14.4 Hz, 2 H, CD-H_4), 4.14 (t, *J* = 6.4 Hz, 2 H, CD-H_3), 3.03-3.98 (m, 198 H, CD-H). ^{13}C{^{1}H} NMR: δ 160.6, 158.0, 145.4, 143.4, 142.9, 132.4, 131.7, 129.4, 129.3, 128.6, 125.3, 124.7, 118.7, 114.9, 99.3, 98.9, 98.8, 98.3, 82.9, 82.1, 82.0, 81.9, 81.8, 81.7, 81.2, 80.3, 79.9, 79.3, 71.5, 71.4, 71.3, 71.0, 70.9, 70.8, 70.7, 70.3, 62.1, 61.8, 61.5, 61.4, 59.2, 59.1, 59.0 (some

of the signals are overlapped). MS (ESI): *m*/z 1766 (100%, $[M+2Na]^{2+}$). HRMS (ESI): *m*/z calcd for $C_{162}H_{244}BF_2N_9Na_2O_{70}$ $[M+2Na]^{2+}$ 1765.7851, found 1765.7880.

Molecular dynamics simulation. The CHARMM sugar force field was adopted for β-cyclodextrin and the CHARMM force field for heme-porphyrin was modified to describe the porphyrin molecule. All the simulations were performed by using the NAMD programme[7] with CHARMM General Force Field.[8] The timestep was set as 2 fs, non-bond interactions were cut off at 12 Å and electrostatic interactions were computed with the Particle Mesh Ewald method. The system temperature was controlled by Langevin dynamics. The figures were prepared with the VMD programme. The porphyrin molecule was put in the centre of the two β-cyclodextrin molecules. Then it was solvated in a 60*60*60 TIP3P water box. The total system was heated to 300 K by five steps: 500 steps energy minimisation and 50 ps molecular dynamics simulation were performed at 50K, 100K, 150K, 200K and 250K respectively. Then the system energy was minimised for 500 steps at 300 K and 5 ns NPT molecular dynamics simulation was performed.

Electrochemical measurements. Cyclic Voltammograms were recorded on a BAS CV-50W voltammetric analyser. The cell comprised inlets for a platinum-sphere working electrode, a platinum-wire counter electrode and a silver-wire pseudo reference electrode. All measurements were carried out in deoxygenated DMF with

0.1 M $[Bu_4N][PF_6]$ as the supporting electrolyte at a scan speed of 50 mV s^{-1}. Ferrocene was used as an internal standard.

Time-resolved fluorescence spectroscopy. The experimental setup was described previously.[9] A pulsed, frequency-doubled, linear polarised radiation of a Nd:VO_4 laser (Cougar, Time Bandwidth Products) with a wavelength of 532 nm, a pulse width of 12 ps and a repetition rate of 60 MHz was used directly for excitation of the samples or to synchronously pump a dye laser (Model 599, Coherent) tuneable in the range from 610 to 670 nm. Fluorescence was detected under a "magic" polarisation angle[10] relative to excitation with a thermo-electrically cooled micro-channel plate (R3809-01, Hamamatsu). Detection wavelength was chosen by a computer-controlled monochromator (77200, Lot-Oriel). Electrical signals were processed by a PCI TCSPC controller card (SPC630, Becker & Hickl). The instrument response function was 42 ps, as measured at an excitation wavelength with Ludox. Data were analysed by a home-made programme by applying a variable projection algorithm to the global fitting problem.[11] The Nelder-Mead simplex algorithm[12] was used for optimisation of the nonlinear parameters, and the support plane approach[10] to compute error estimates of the decay times.

Picosecond transient absorption spectroscopy. To measure the transient absorption spectra, a white light continuum was generated as a test beam in a cell with a D_2O/H_2O mixture using intense 25 ps pulses from a Nd^{3+}:YAG laser (PL2143A,

Ekspla) at 1064 nm. Before passing through the sample, the continuum radiation was split to obtain a reference spectrum. The transmitted as well as the reference beams were focused into two optical fibers and were recorded simultaneously at different traces on a cooled CCD-matrix (Lot-Oriel, Instaspec IV). Tuneable radiation from an OPG/OPA (Ekspla PG 401/SH, tuning range 200–2300 nm) pumped by the third harmonic of the same laser was used as an excitation beam. The mechanical delay line allowed the measurement of light-induced changes of the absorption spectrum at different delays up to 15 ns after excitation. Analysis of experimental data was performed using the compensation method.[13]

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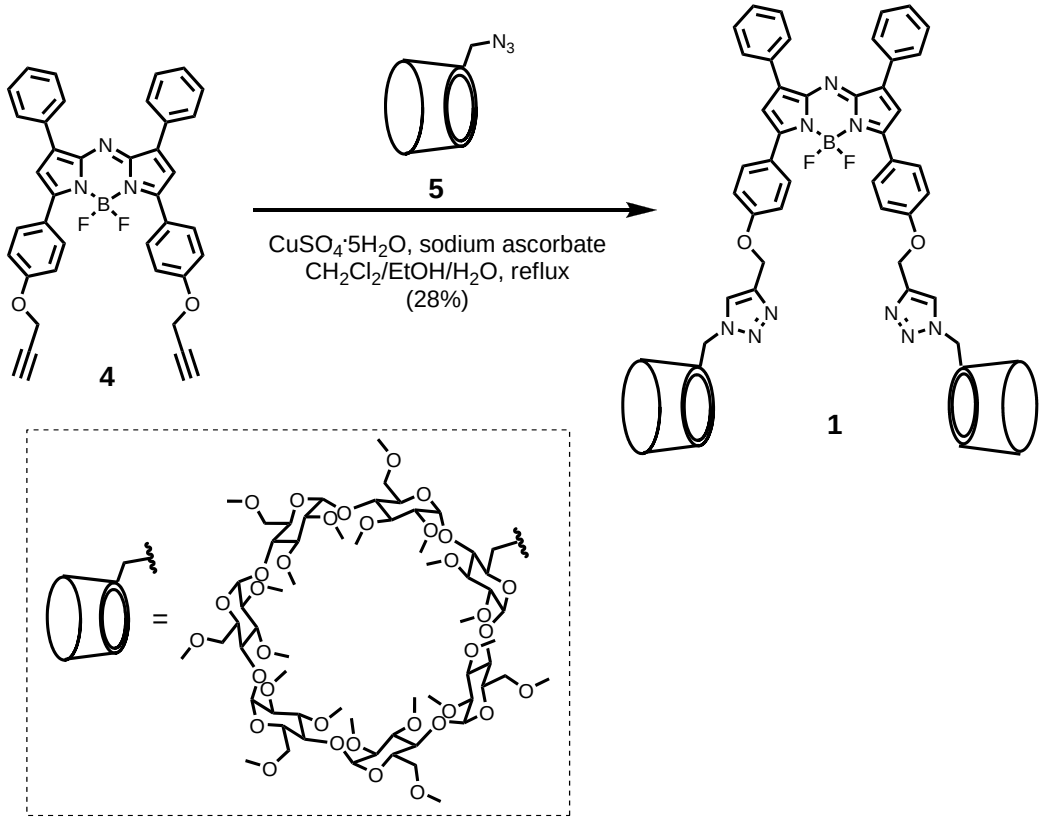


Scheme S1 Preparation of aza-BODIPY **1**.

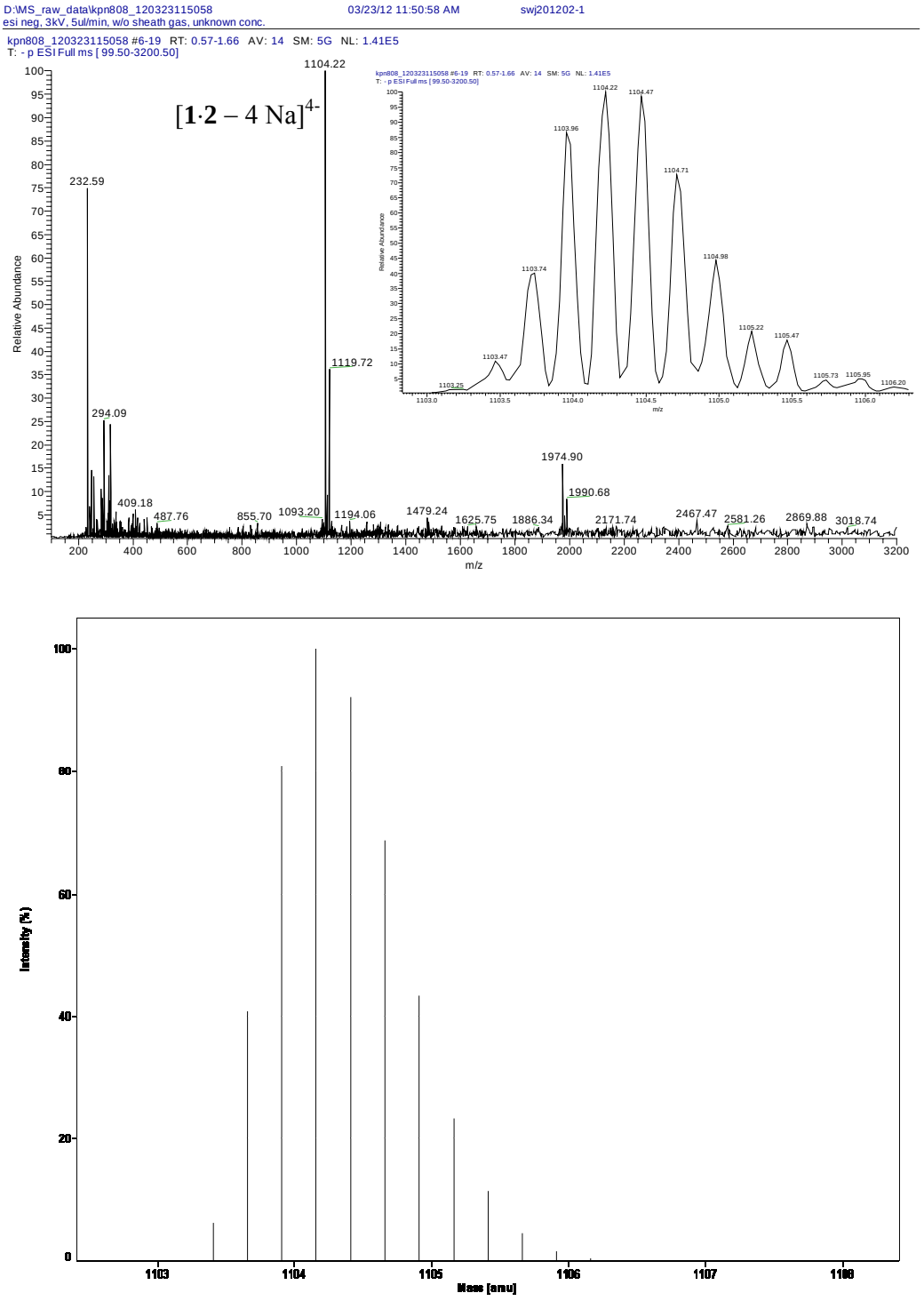


Fig. S1 (a) Electrospray ionisation mass spectrum of a 1:1 mixture of **1** and **2** in water. The inset shows the enlarged isotopic pattern for the base peak. (b) The simulated isotopic pattern for $[\mathbf{1}\cdot\mathbf{2} - 4\ Na]^{4-}$.

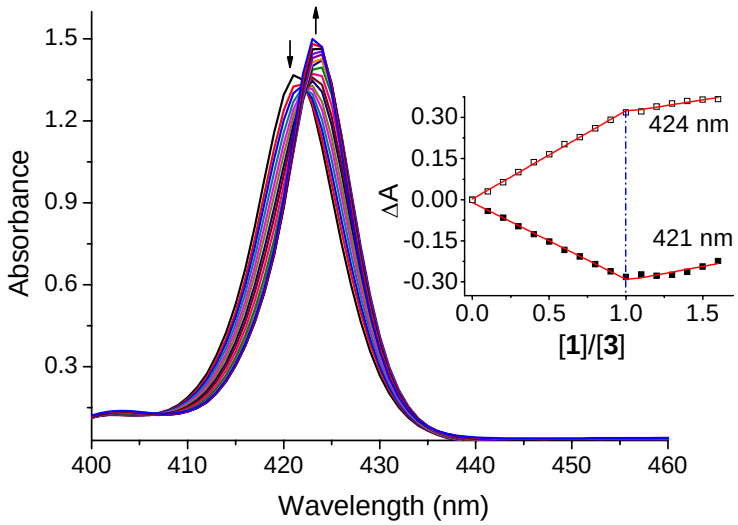


Fig. S2 Change in UV-Vis spectrum of **3** (2.0 μM) upon addition of **1** (0-3.2 μM) in water. The inset plots the change in absorbance of the B bands at 421 and 424 nm versus the concentration ratio [**1**]/[**3**].

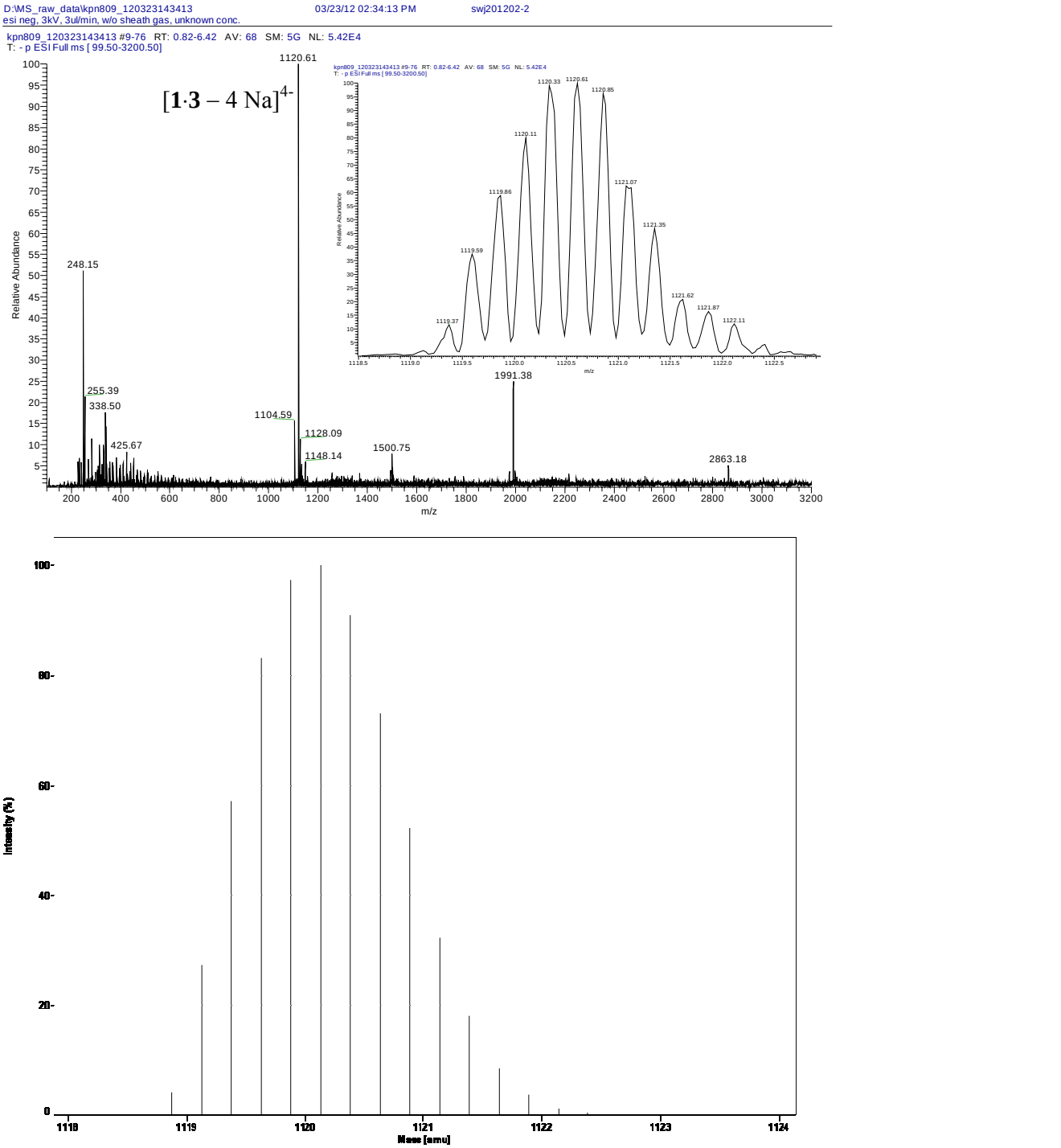


Fig. S3 (a) Electrospray ionisation mass spectrum of a 1:1 mixture of **1** and **3** in water. The inset shows the enlarged isotopic pattern for the base peak. (b) The simulated isotopic pattern for $[\mathbf{1}\cdot\mathbf{3} - 4\ \mathrm{Na}]^{4-}$.

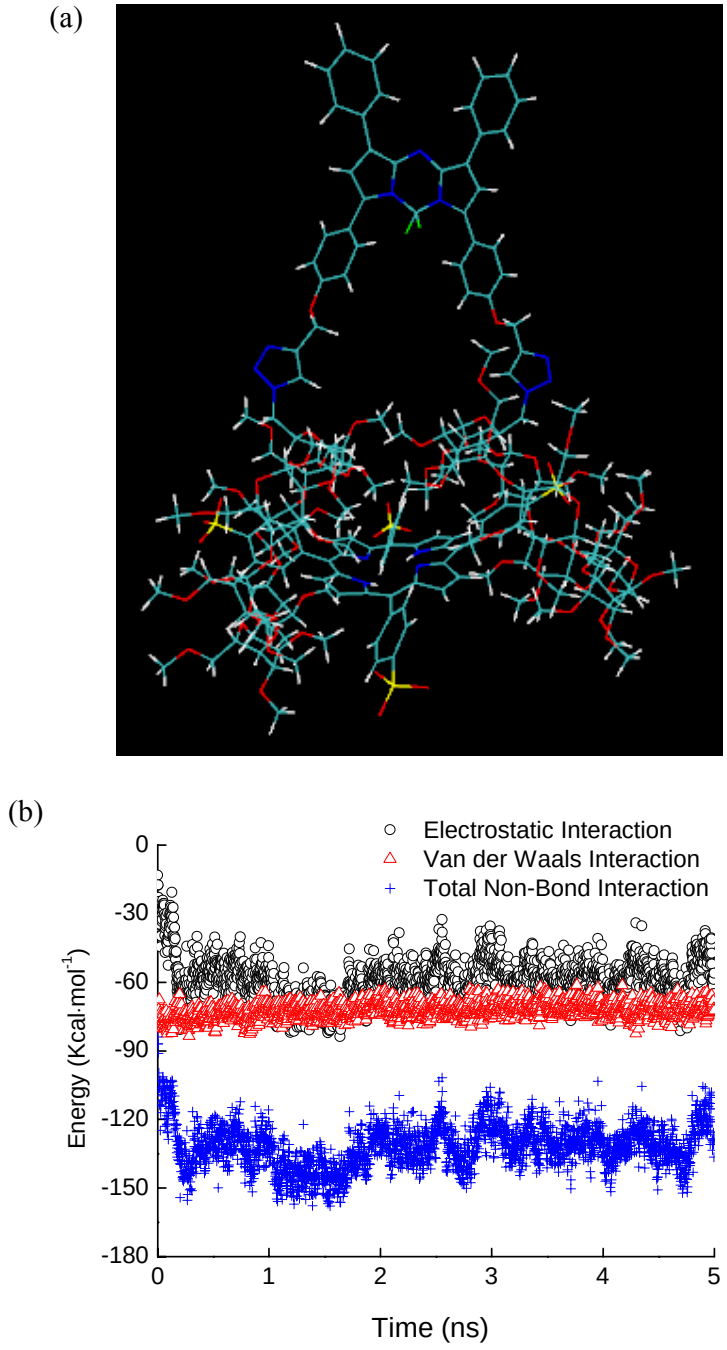


Fig. S4 (a) Molecular structure of **1**·**2** obtained by molecular dynamics simulation. (b) Variations of the electrostatic, Van der Waals and total non-bonding interaction energies of **1**·**2** with time.

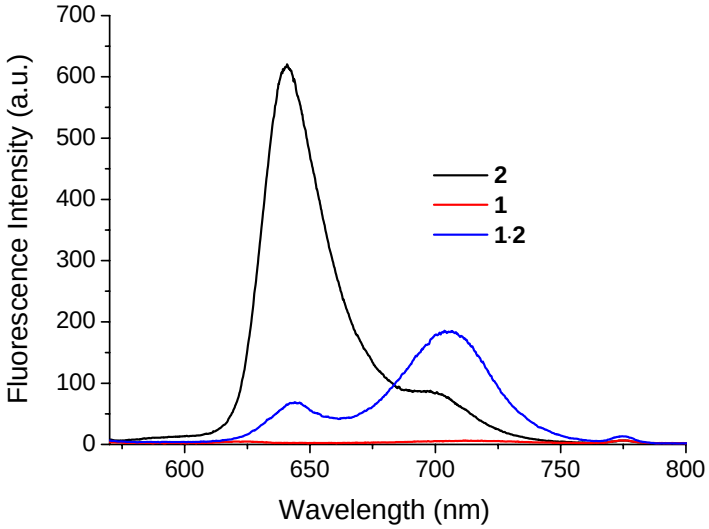


Fig. S5 Steady-state fluorescence spectra of **1**, **2** and their 1:1 mixture (both at 2.0 μM) in H_2O (λ_{ex} = 515 nm).

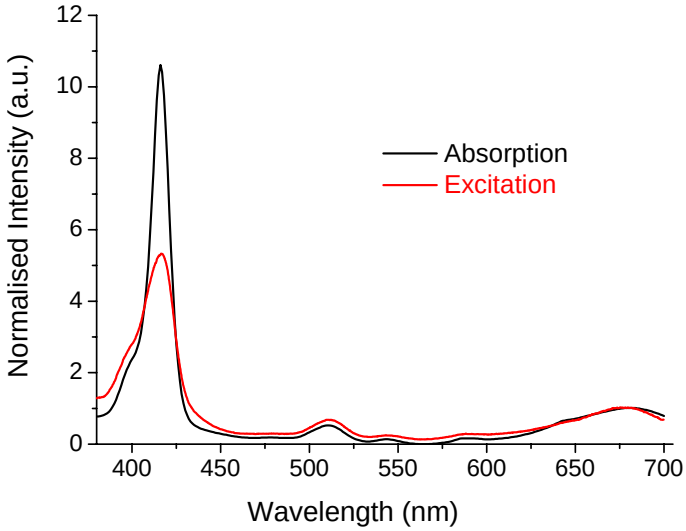


Fig. S6 Normalised (at 684 nm) UV-Vis and excitation (monitored at 706 nm) spectra of a 1:1 mixture of **1** and **2** (both at 2.0 μM) in H_2O.

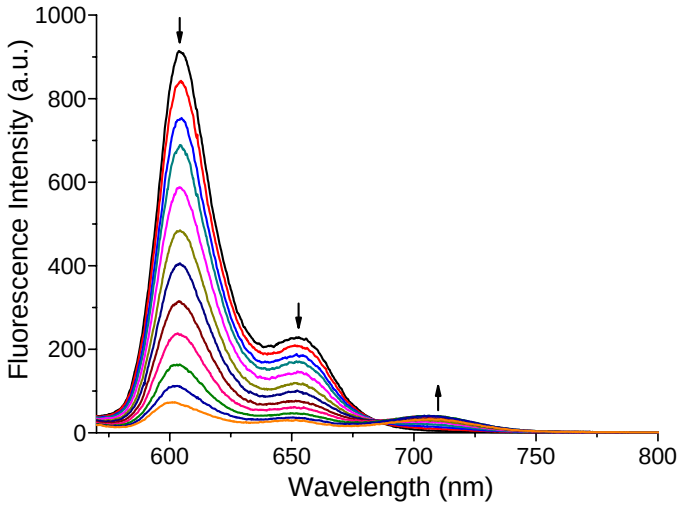


Fig. S7 Change in fluorescence spectrum of **3** (2.0 μM, λ_{ex} = 556 nm) upon addition of **1** (0-2.0 μM) in water.

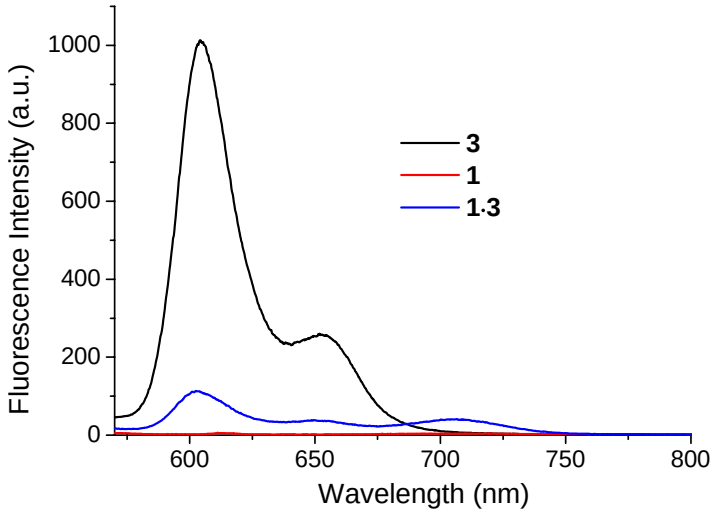


Fig. S8 Steady-state fluorescence spectra of **1**, **3** and their 1:1 mixture (both at 2.0 μM) in H_2O (λ_{ex} = 556 nm).

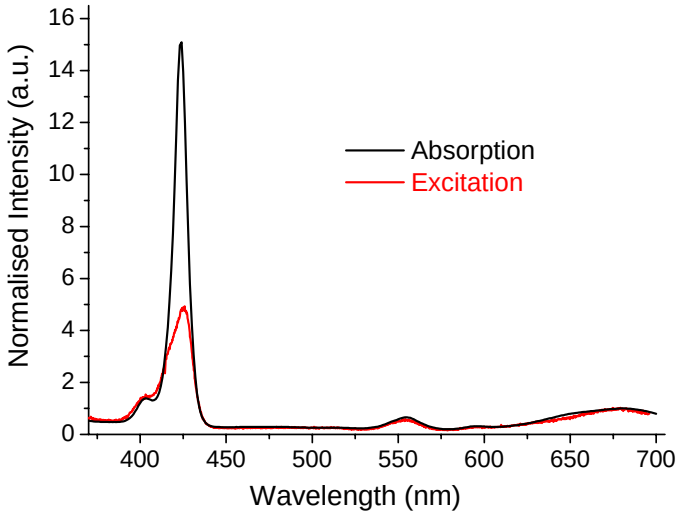
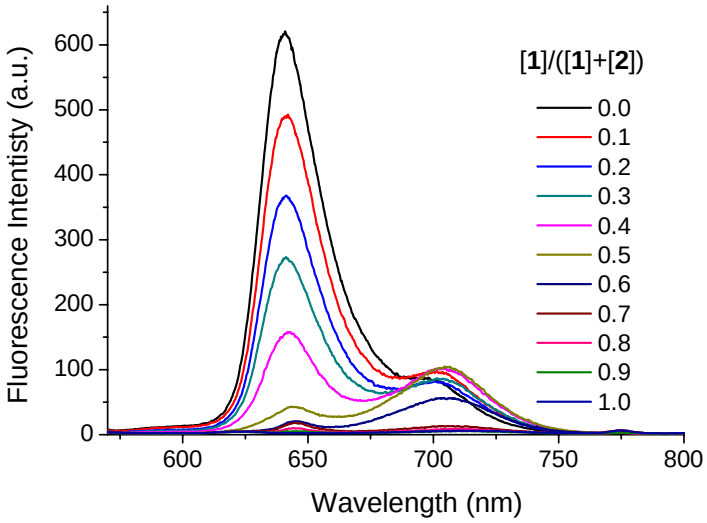


Fig. S9 Normalised (at 681 nm) UV-Vis and excitation (monitored at 708 nm) spectra of a 1:1 mixture of **1** and **3** (both at 2.0 μM) in H_2O.

(a)



(b)

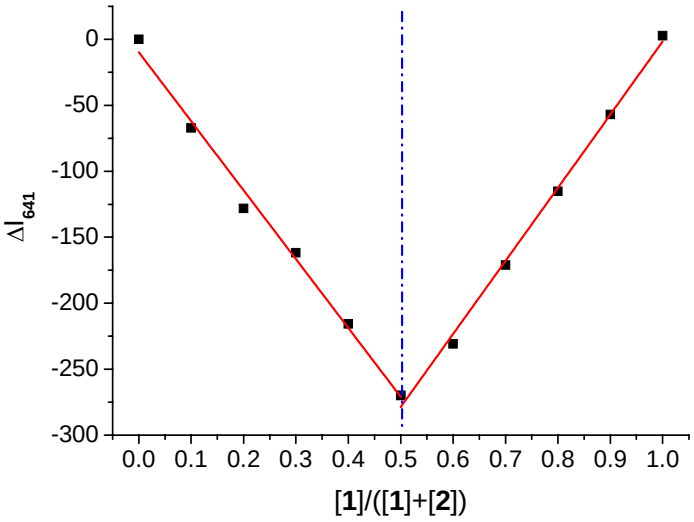
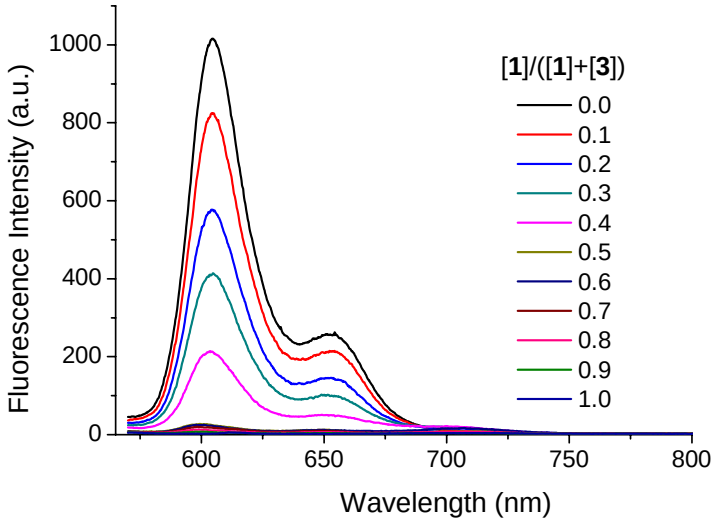


Fig. S10 (a) Fluorescence spectra of mixtures of **1** and **2** with different mole fractions in H_2O (λ_{ex} = 515 nm). The total concentration of **1** and **2** was fixed at 4.0 μM. (b) The corresponding Job's plot by monitoring the change in fluorescence intensity at 641 nm.

(a)



(b)

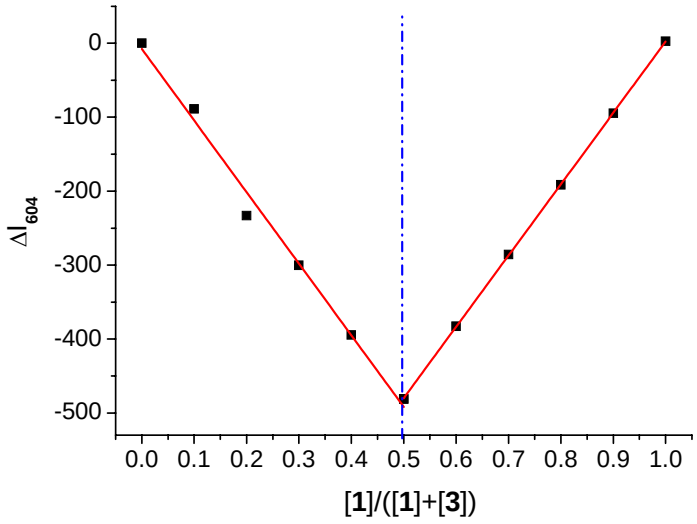


Fig. S11 (a) Fluorescence spectra of mixtures of **1** and **3** with different mole fractions in H_2O (λ_{ex} = 556 nm). The total concentration of **1** and **3** was fixed at 4.0 μM. (b) The corresponding Job's plot by monitoring the change in fluorescence intensity at 604 nm.

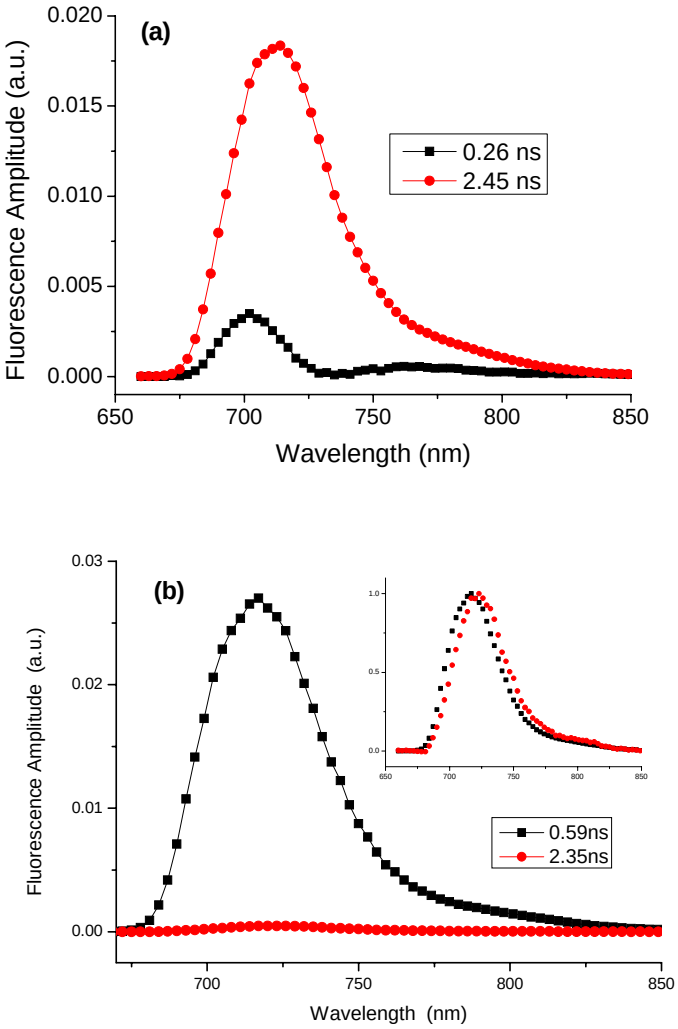


Fig. S12 DAF spectra of (a) **1**·**2** and (b) **1**·**3** in water upon excitation of **1** at 650 nm. The inset of (b) shows the normalised spectra. The concentration of all the components was fixed at 5 μM.

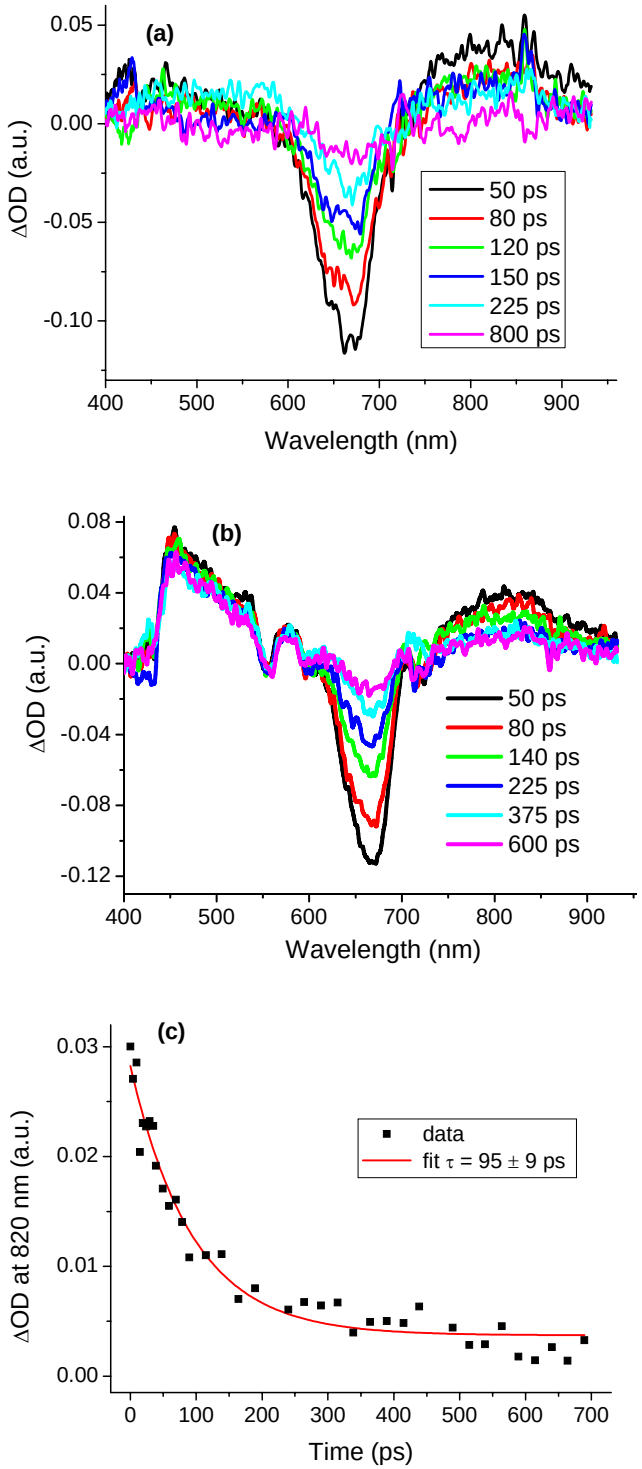


Fig. S13 Transient absorption spectra of **1**·**3** in water at different delay times upon excitation of (a) **1** at 650 nm and (b) **3** at 556 nm. The decay of the induced absorption of the radical anion of **1** at 820 nm is shown in (c).

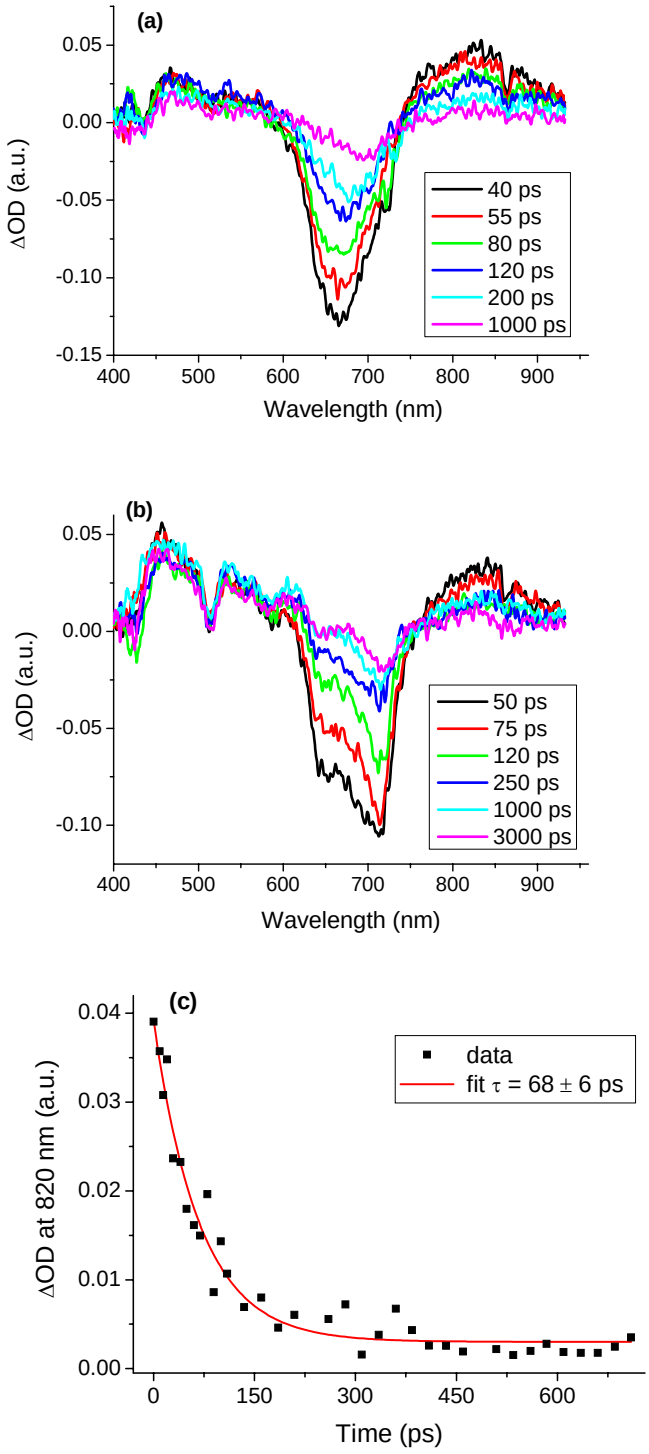


Fig. S14 Transient absorption spectra of **1**·**2** in water at different delay times upon excitation of (a) **1** at 650 nm and (b) **2** at 515 nm. The decay of the induced absorption of the radical anion of **1** at 820 nm is shown in (c).

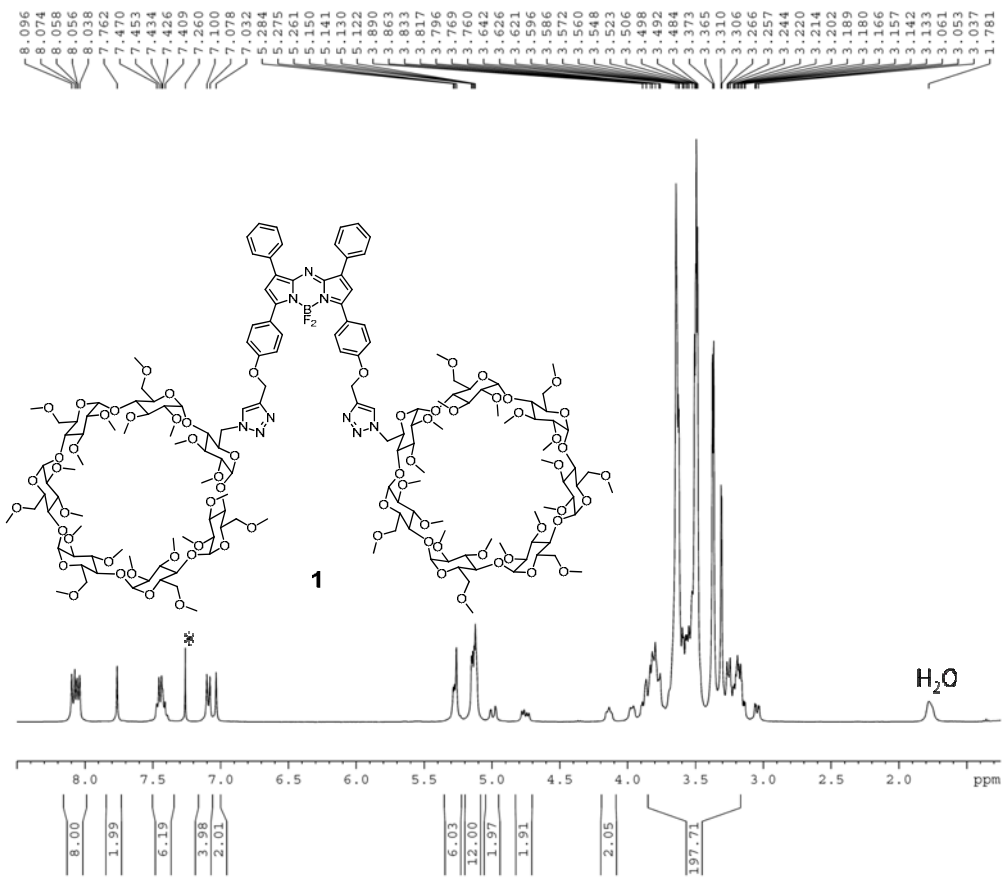


Fig. S15 ^{1}H NMR spectrum of **1** in $CDCl_3$.

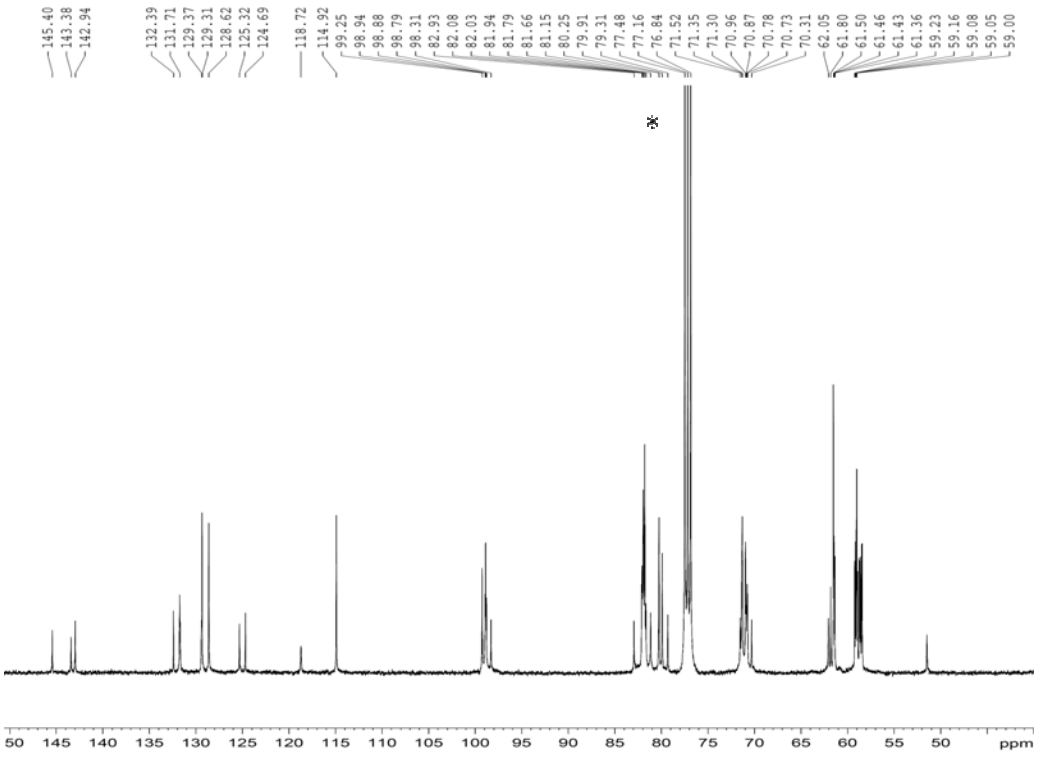
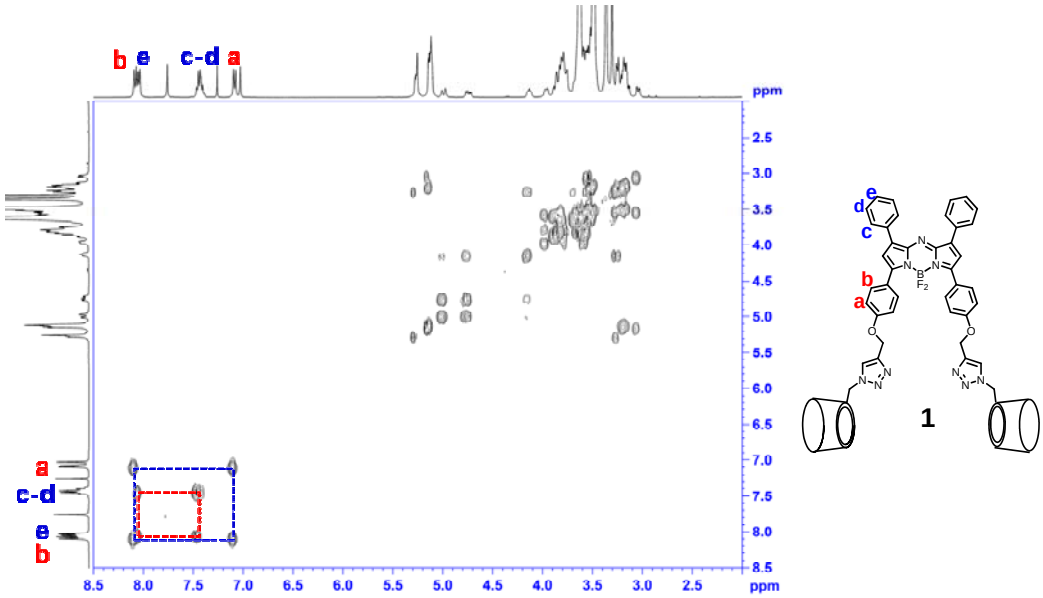


Fig. S16 $^{13}C\{^{1}H\}$ NMR spectrum of **1** in $CDCl_3$.

(a)



(b)

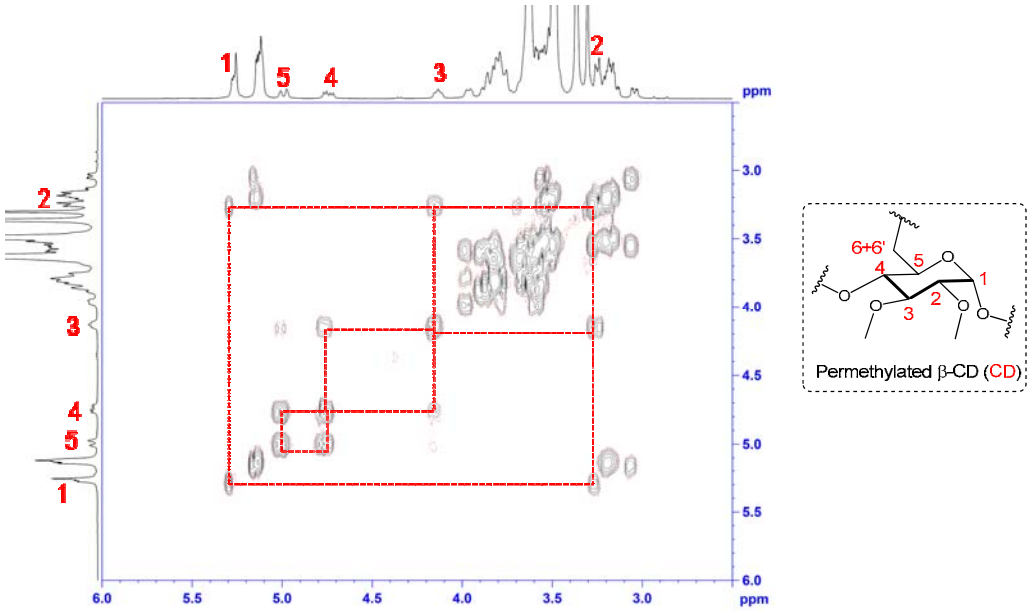
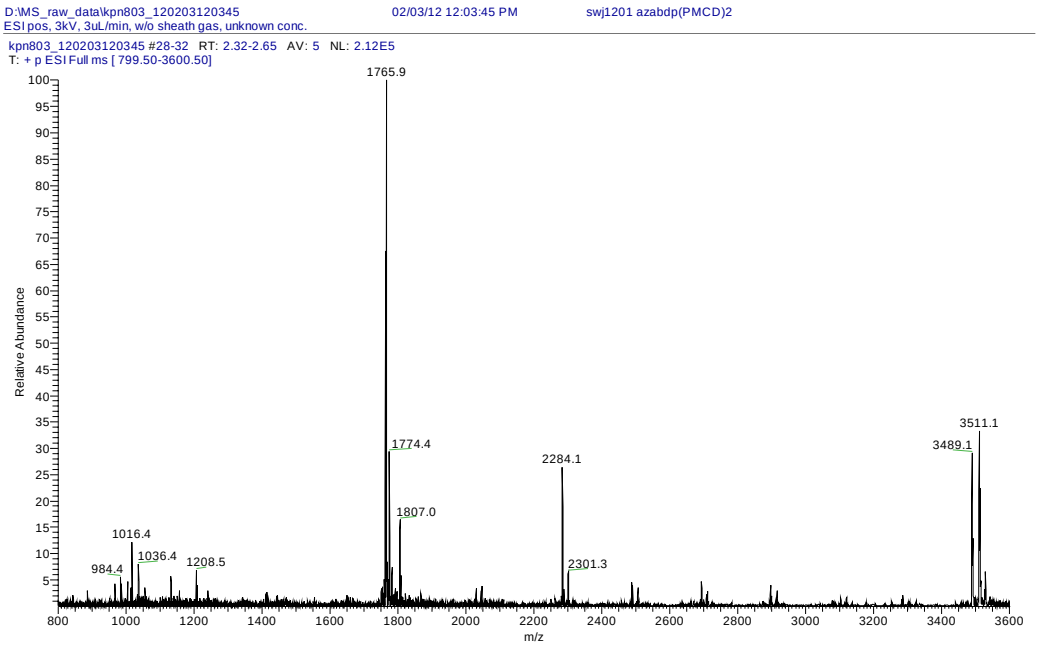


Fig. S17 (a) ^{1}H-^{1}H COSY spectrum of **1** in $CDCl_3$ and (b) an enlarged spectrum in the region of δ 2.5-6.0.

(a)



(b)

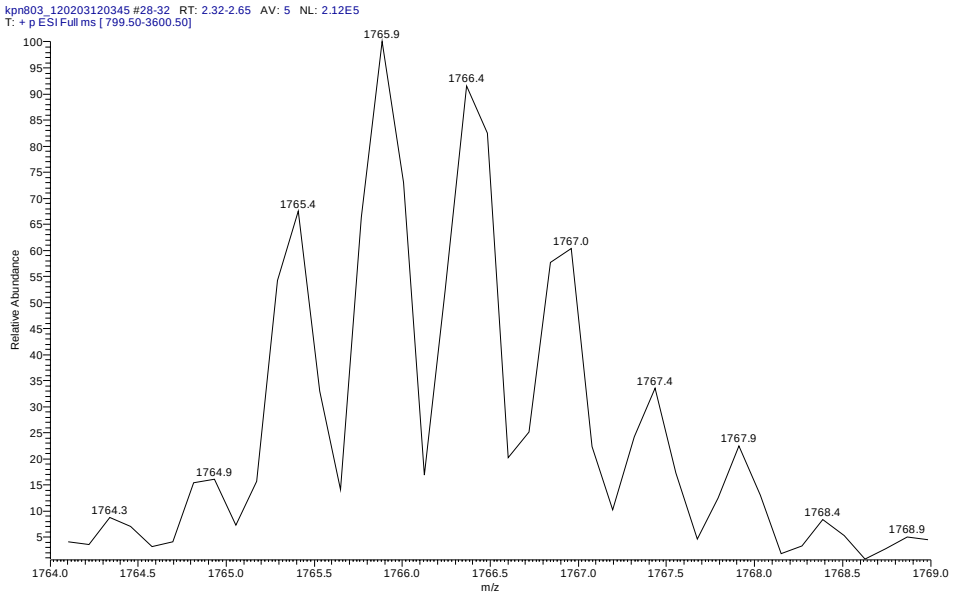


Fig. S18 (a) Electrospray ionisation mass spectrum of **1** and (b) an enlarged isotopic pattern for the base peak.

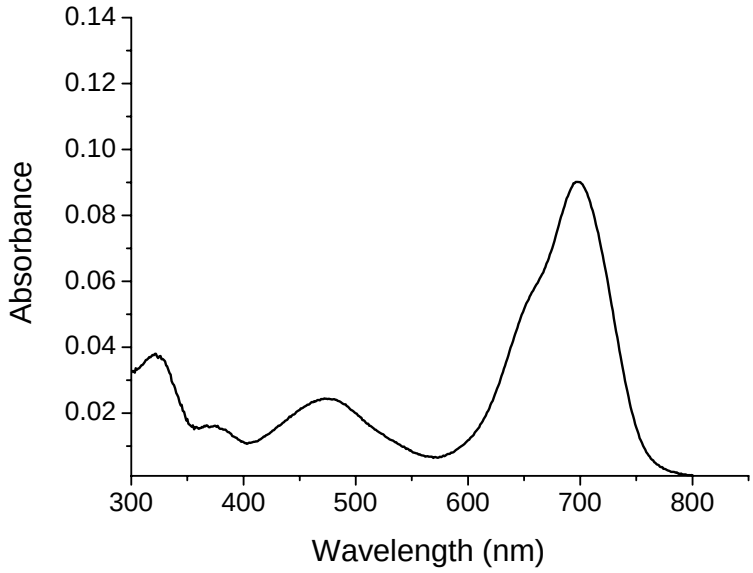


Fig. S19 UV-Vis spectrum of **1** (2.0 μM) in water.

Table S1 Half-wave redox potentials for **1-3** in DMF and the free energy change of charge separation for **1·2** and **1·3** upon porphyrin- or aza-BODIPY-part (data in brackets) excitation.

Compound	$E_{1/2}$ (oxd) (V)[a]	$E_{1/2}$ (red) (V)[a]	$\Delta G_0^{D(A)}$ (eV)[b]
1	---	-0.81	---
2	0.60	-1.57	---
3	0.36	-1.80	---
1·2	---	---	-0.54 (-0.31)
1·3	---	---	-0.89 (-0.59)

[a] Recorded with $[Bu_4N][PF_6]$ (0.1 M) as the electrolyte and ferrocene (Fc) as an internal standard ($E_{1/2}$ = 0.00 V) in DMF at ambient temperature. Potentials were obtained by cyclic voltammetry with a scan rate of 50 mV s^{-1} and are expressed in V *vs.* Fc^+/Fc. [b] $\Delta G_0^{D(A)} = e[E_{1/2}(D/D^{\bullet+}) - E_{1/2}(A/A^{\bullet-})] - \Delta E_{0,0}^{D(A)}$, where D and A are the porphyrin (**2** or **3**) and **1** respectively, and $\Delta E_{0,0}^{D(A)}$ is the energy of $S_0 \rightarrow S_1$ transition of **1** (1.76 eV), **2** (1.95 eV) or **3** (2.06 eV).