Electronic Supplementary Information

Remote Electron and Energy Transfer Sensitized Photoisomerization of Encapsulated Stilbenes

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1. General Information

All commercially available materials were used as supplied without further purification, unless otherwise noted. ^{1}H NMR characterization, NMR titration studies and diffusion experiment were performed on Bruker Avance 500 spectrometer equipped with cryoprobe. Chemical shifts are reported in parts-per-million (ppm). Deuterated solvent was used as a lock and residual protonated solvent peak was used as reference. Absorption spectra were recorded on a Shimadzu UV - 3150 spectrophotometer. Steady-state luminescence spectra were recorded using a FS920CDT fluorometer (Edinburgh Analytical Instruments).

2. Materials:

2.1 Synthesis of Host and Guest molecules

Host octa acid (OA) was synthesized and characterized according to the reported procedure[1]. The stilbene guest molecules were synthesized according to the literature[2]. bis-N-methylacridiniumnitrate was purchased from Aldrich and used as received.

2.2 Synthesis of N,N,N-trimethyl-4-(phenylcarbonyl)benzenaminiumiodide (4-TMABP)

Added dropwise methyl iodide (0.93 mL, 1.5 mmol) to a stirred solution of 4-aminobenzophenone (10 mmol) in DMF (5 mL) at room temperature, stirred the resulting solution for 24 h at 50°C after that reaction mixture cooled to RT and added diethyl ether (15 mL) to the solution. Kept the resulting mixture aside for 12 hours, and filtered the precipitates, then washed the solid with ether and dried, finally it was crystallized at room temperature from methanol to afford 4-TMABP as a

pale gray powder. Pure product (490 mg, 25%) was obtained and characterized by ^{1}HNMR, ^{13}C NMR and Mass spectrometry.^{1}H NMR (500 MHz, D_2O): δ 7.97 (s, 4H), 7.79 (d, 2H), 7.72 (t, 1H), 7.56 (t, 2H), 3.67 (s, 9H). ^{13}C NMR (125 MHz, D_2O): δ 198.93, 149.54, 138.68, 135.97, 134.11, 132.02, 130.37, 128.73 120.20, 56.97. HRMS (ESI): calcd for $C_{16}H_{18}NOI^{+}$ $[M - I]^{+}$ 240.14, found 240.1394.

3. Complexation of Guest Molecules studied by ^{1}H NMR

General procedure:

To a D_2O (10 mM borate buffer) solution of OA (1 mM) 5 μL of 60 mM of guest solution was added in gradual increments. After each addition, NMR spectrum was recorded. Observed changes were taken as an indication of inclusion of guest within OA

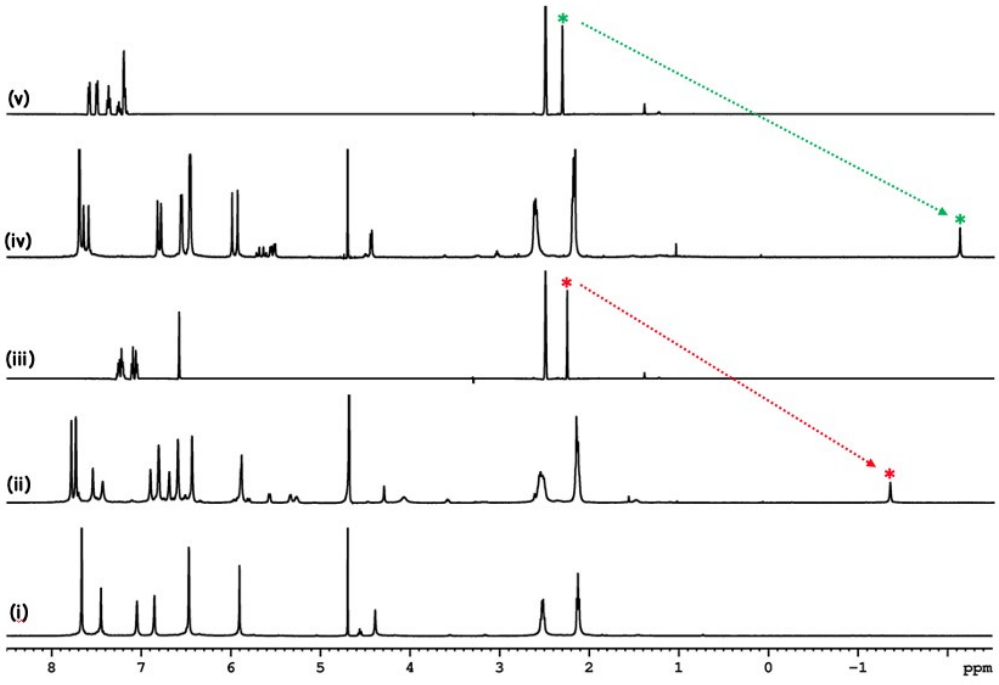

Figure S1. ^{1}H NMR spectra (500 MHz, D_2O) of (i) 1 mM OA in borate buffer (ii) *cis*-**1**@$(OA)_2$ (iii) *cis*-**1** in DMSO-d_6 (iv) *trans*-**1**@$(OA)_2$ (v) *trans*-**1** in DMSO-d_6. (* & *) – represent the bound methyl protons of (*) *cis* and (*) *trans* respectively.

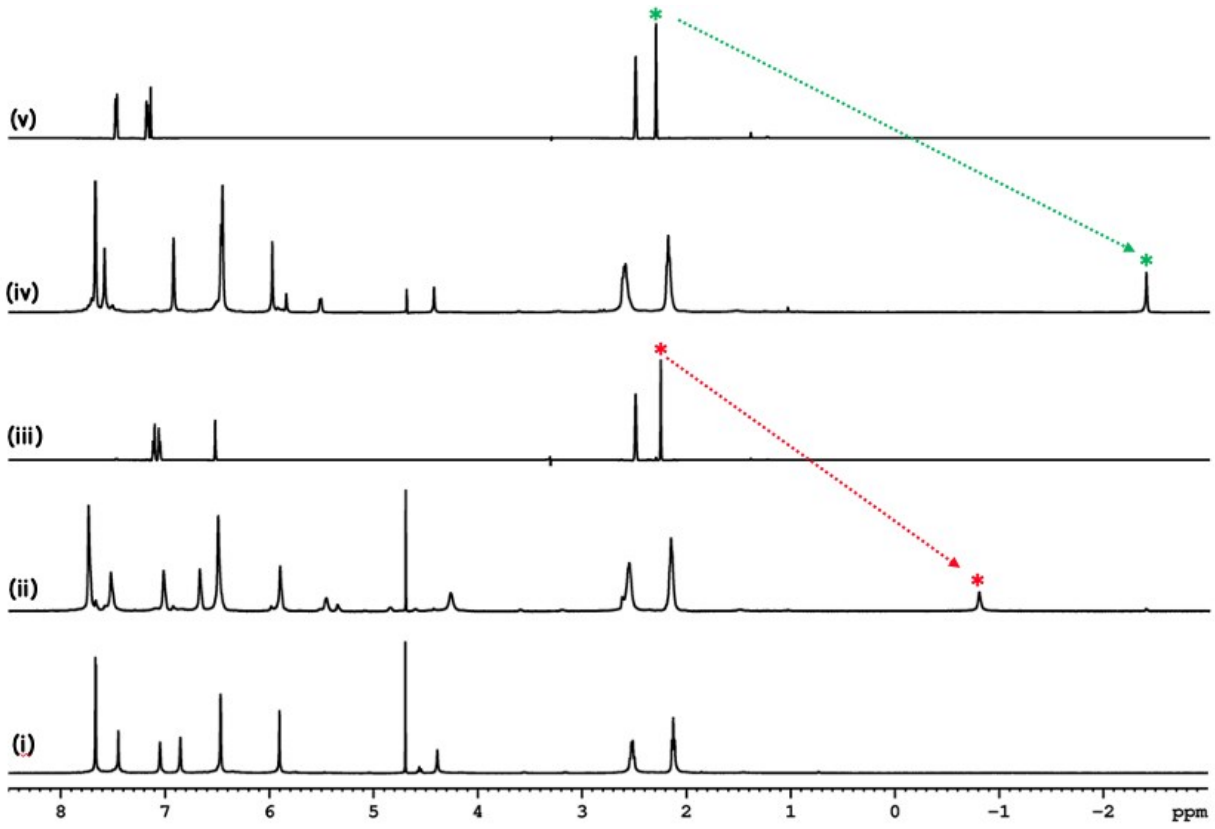

Figure S2. ^{1}H NMR spectra (500 MHz, D_2O) of (i) 1 mM OA in borate buffer (ii) *cis*-**2**@$(OA)_2$ (iii) *cis*-**2** in DMSO-d_6 (iv) *trans*-**2**@$(OA)_2$ (v) *trans*-**2** in DMSO-d_6. (* & *) – represent the bound methyl protons of (*) *cis* and (*) *trans* respectively.

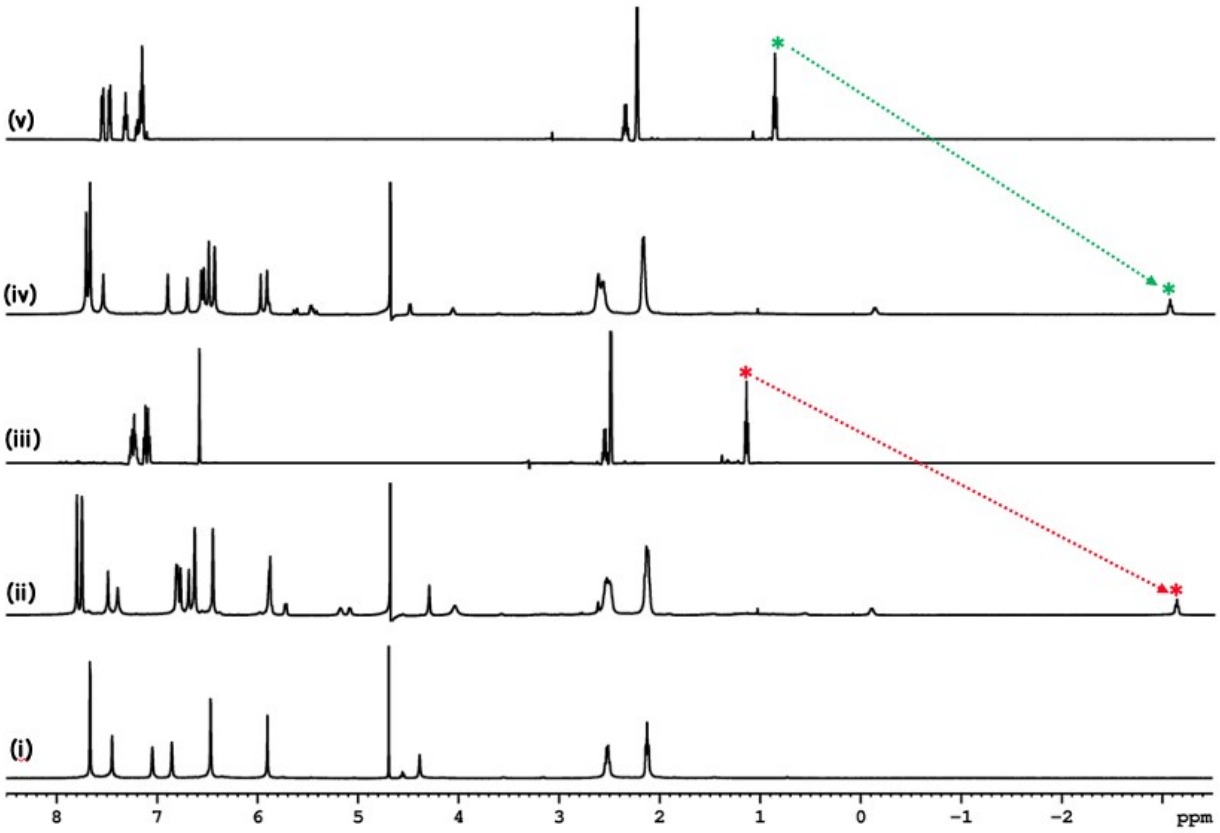

Figure S3. ^{1}H NMR spectra (500 MHz, D_2O) of (i) 1 mM OA in borate buffer (ii) *cis*-**3**@$(OA)_2$ (iii) *cis*-**3** in DMSO-d_6 (iv) *trans*-**3**@$(OA)_2$ (v) *trans*-**3** in DMSO-d_6. (* & *) – represent the bound methyl protons of (*) *cis* and (*) *trans* respectively.

4. Identification of the location of the sensitizers:

4.1 Titration studies of 4-TMABP with *trans*-**1**@$(OA)_2$

To locate the sensitizers BMAN and 4-TMABP in presence of stilbene@OA_2, buffer solutions containing the capsules of *cis*-**1**@$(OA)_2$ and *trans*-**1**@$(OA)_2$ were prepared by adding 5 µL of 60 mM standard guest solution to 0.6 mL of 1 mM of OA in 10 mM of borate buffer solution. To this 60 µL of 20 mM of BMAN or 4-TMABP solution were added in a step wise manner. After each addition, NMR spectrum was recorded. From the changes in spectra the sensitizers were identified to be present close to the capsule in water.

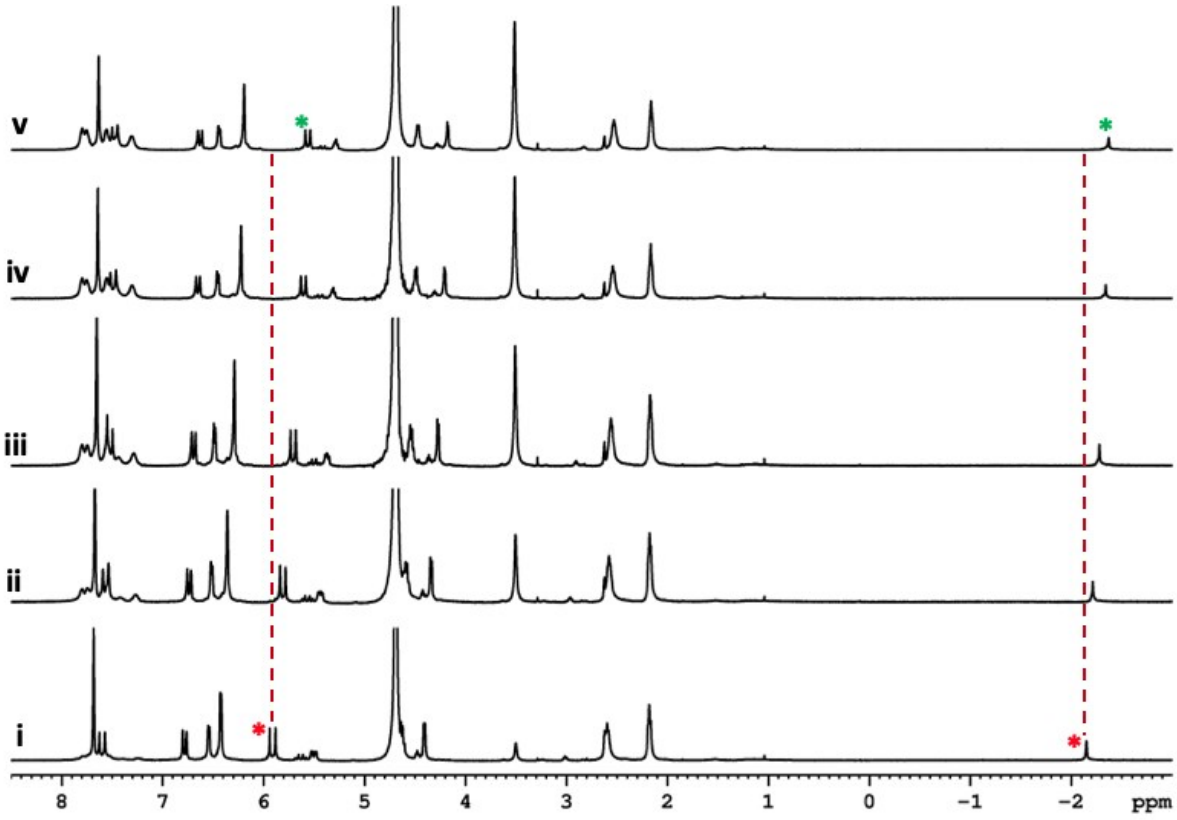

Figure S4. ^{1}H NMR spectra (500 MHz) of *trans*-**1**@$(OA)_2$ encapsulated within OA (1 X 10^{-3} M) in buffered D_2O with slow addition of 4-TMABP **(i)** *trans*-**1**@$(OA)_2$ only **(ii)** addition of 0.33 mM of 4-TMABP **(iii)** addition of 0.99 mM of 4-TMABP **(iv)** addition of 1.66 mM of 4-TMABP **(v)** addition of 2.0 mM of 4-TMABP. (*) – represent the *trans*-**1**@$(OA)_2$ and (*) – represent the *trans*-**1**@$(OA)_2$ with 4-TMABP

4.2 Titration studies of BMAN with *cis*-**1**@$(OA)_2$

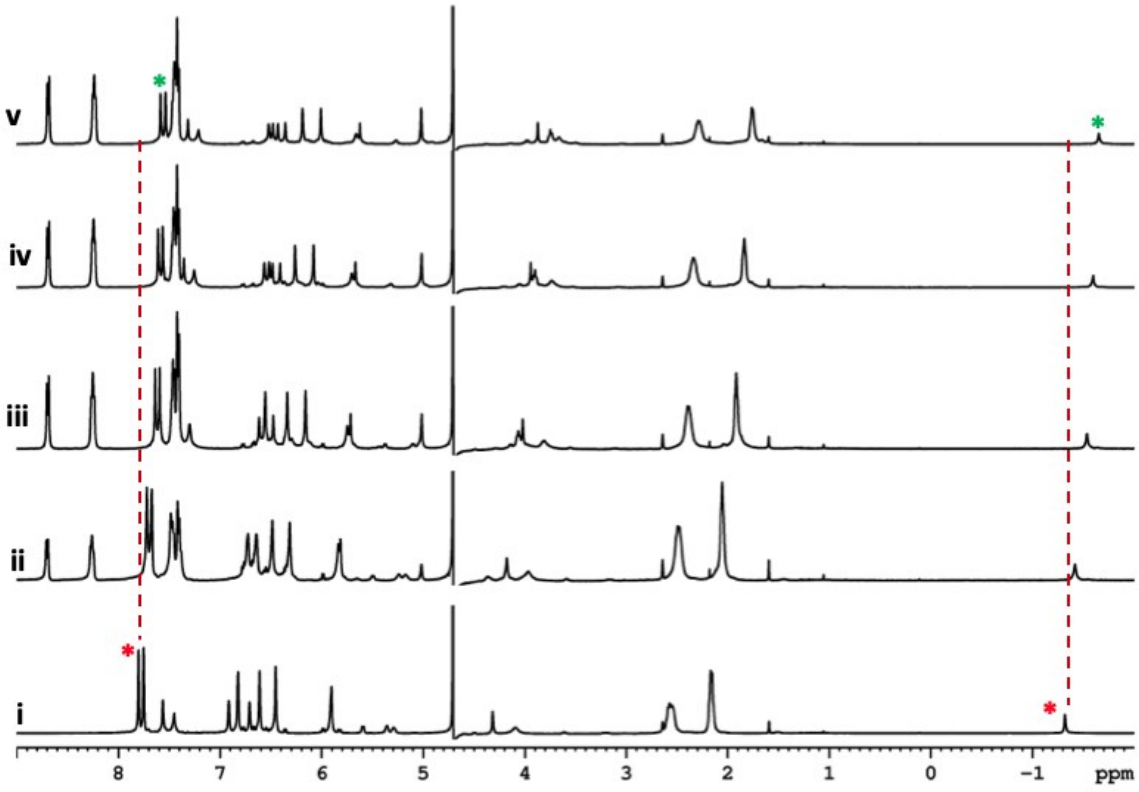

Figure S5. ^{1}H NMR spectra (500 MHz) of *cis*-**1**@$(OA)_2$ encapsulated within OA (1 X 10^{-3} M) in buffered D_2O with slow addition of photo catalyst BMAN (i) *cis*-**1**@$(OA)_2$ only (ii) addition of 0.33 mM of BMAN (iii) addition of 0.99 mM of BMAN (iv) addition of 1.66 mM of BMAN (v) addition of 2.0 mM of BMAN. (*) – represent the cis-**1**@$(OA)_2$ and (*) – represent the *cis*-**1**@$(OA)_2$ with BMAN.

5. Diffusion experiments

General Procedure.

Diffusion NMR studies with guests@(OA): 600 μL of a D_2O solution of host OA (1 mM OA in 10 mM $Na_2B_4O_7$) was taken in a NMR tube and to this 0.5 equivalent increment of guest (5 μL of a 60 mM solution in DMSO-d_6) was added. Further, diffusion experiments were carried out to characterize capsular assemblies.

S.No.	Experiment	Diffusion Constant (10^{-6} cm^2/s)
1	OA only	1.84
2	*cis*-**1**@$(OA)_2$	1.50
3	*trans*-**2**@$(OA)_2$	1.34
4	BMAN (2 mM)	4.35
5	4-TMABP (2 mM)	5.50
6	*cis*-**1**@$(OA)_2$ + 2.00 mM of BMAN	1.29
7	*trans*-**2**@$(OA)_2$ + 2.00 mM of 4-TMABP	1.88

Table-S1. Diffusion constant values of the host OA, cationic sensitizers and OA complexes with guest molecules.

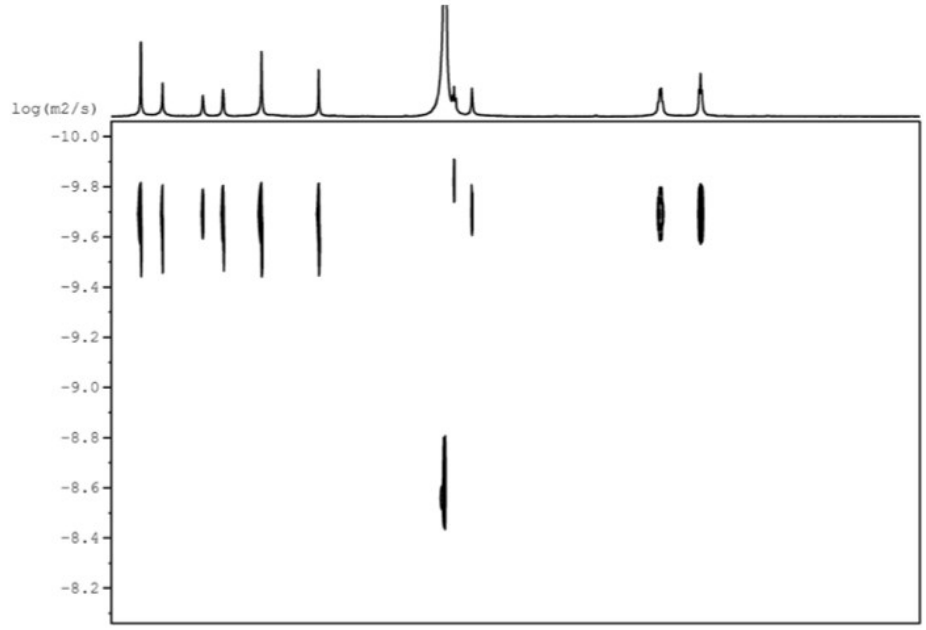

Figure S6. 2D-DOSY spectra of Octa acid 500 MHz, [OA] = 1 mM, buffer 10 mM).

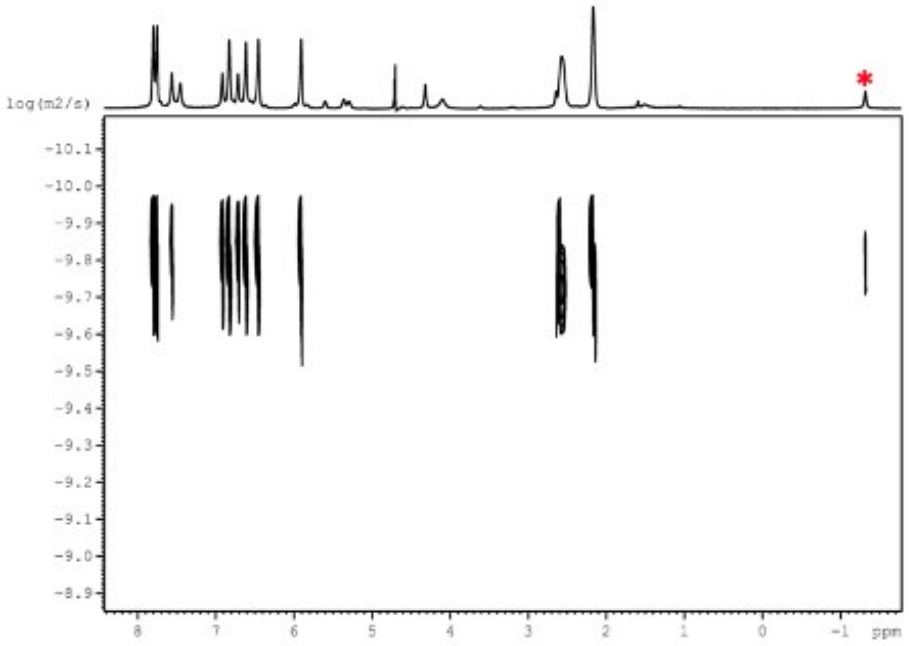

Figure S7. 2D-DOSY spectra of *cis*-**1**@$(OA)_2$ (500 MHz, [OA] = 1 mM, buffer 10 mM). (*) – represent the bound methyl protons *cis* -**1**@$(OA)_2$

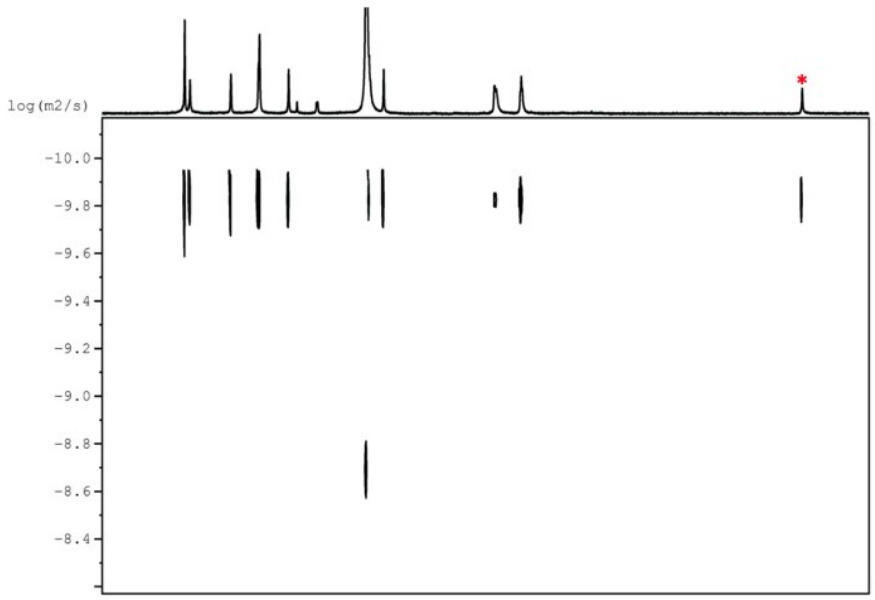

Figure S8. 2D-DOSY spectra of *trans*-**2**@$(OA)_2$ (500 MHz, [OA] = 1 mM, buffer 10 mM). (*) – represent the bound methyl protons *trans* -**2**@$(OA)_2$

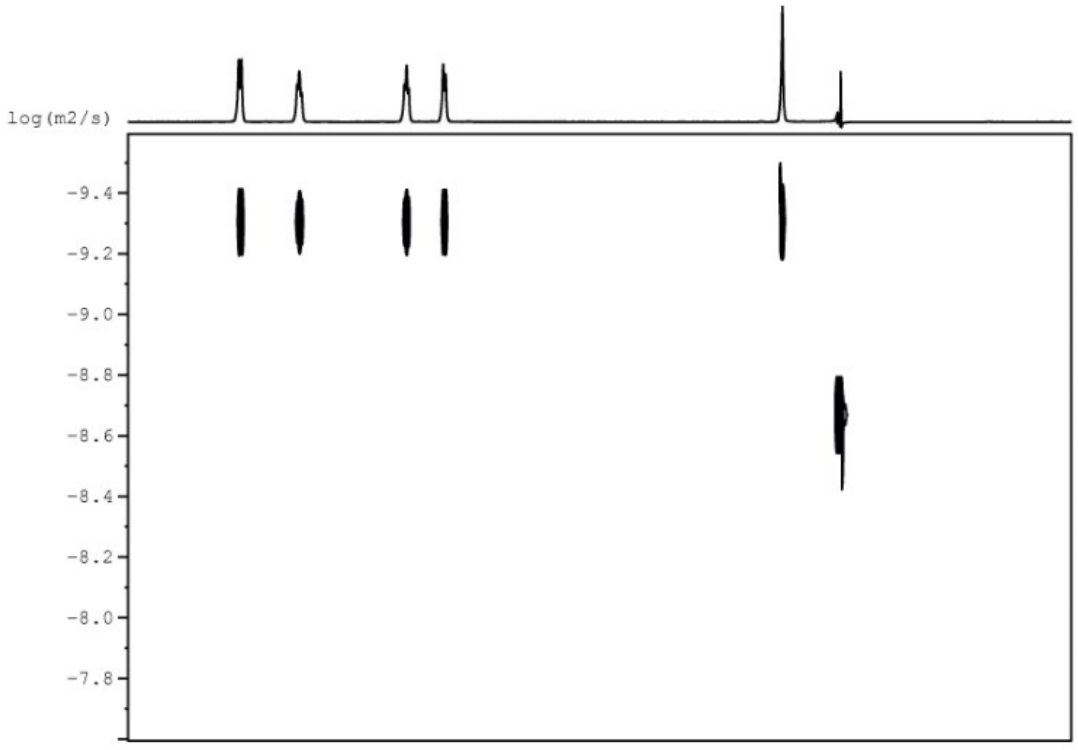

Figure S9. 2D-DOSY spectra of **BMAN** (500 MHz, 2 mM).

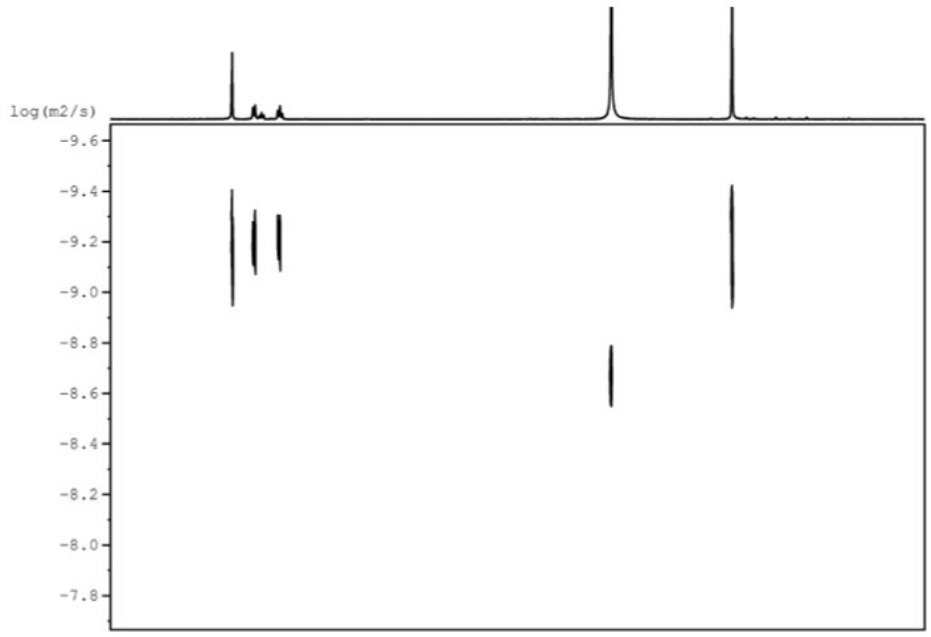

Figure S10. 2D-DOSY spectra of **4-TMABP** (500 MHz, 2 mM).

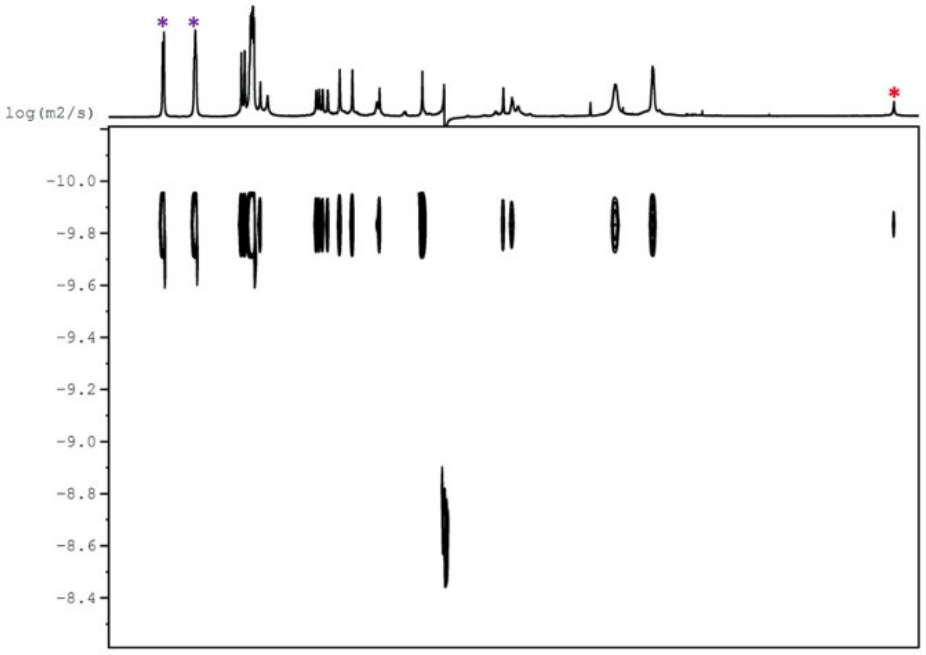

Figure S11. 2D-DOSY spectra of *cis*-**1**@$(OA)_2$ (500 MHz, [OA] = 1 mM, buffer 10 mM) with **BMAN** (2 mM). (*) – represent the *cis* -**1**@$(OA)_2$ and (*) – represent the BMAN .

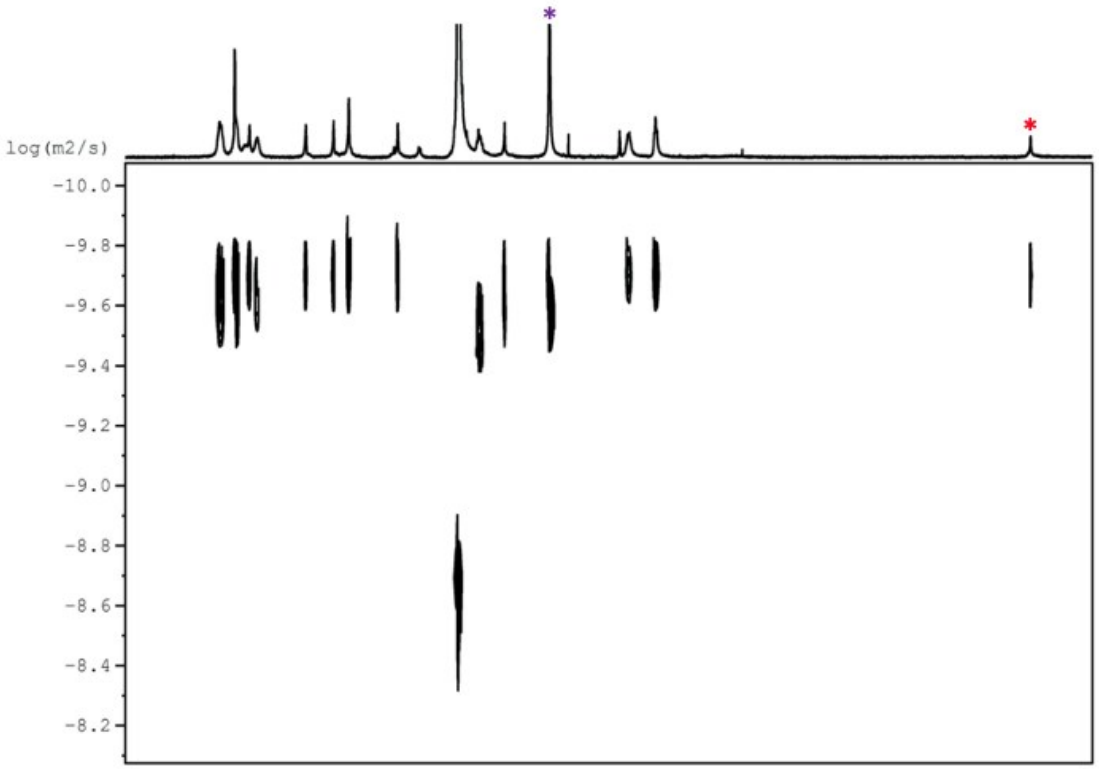

Figure S12. 2D-DOSY spectra of *trans*-**2**@$(OA)_2$ (500 MHz, [OA] = 1 mM, buffer 10 mM) with 4-TMABP (2 mM). (*) – represent the *trans* -**2**@$(OA)_2$ and (*) – represent the 4-TMABP.

6. UV-Visible absorption spectra

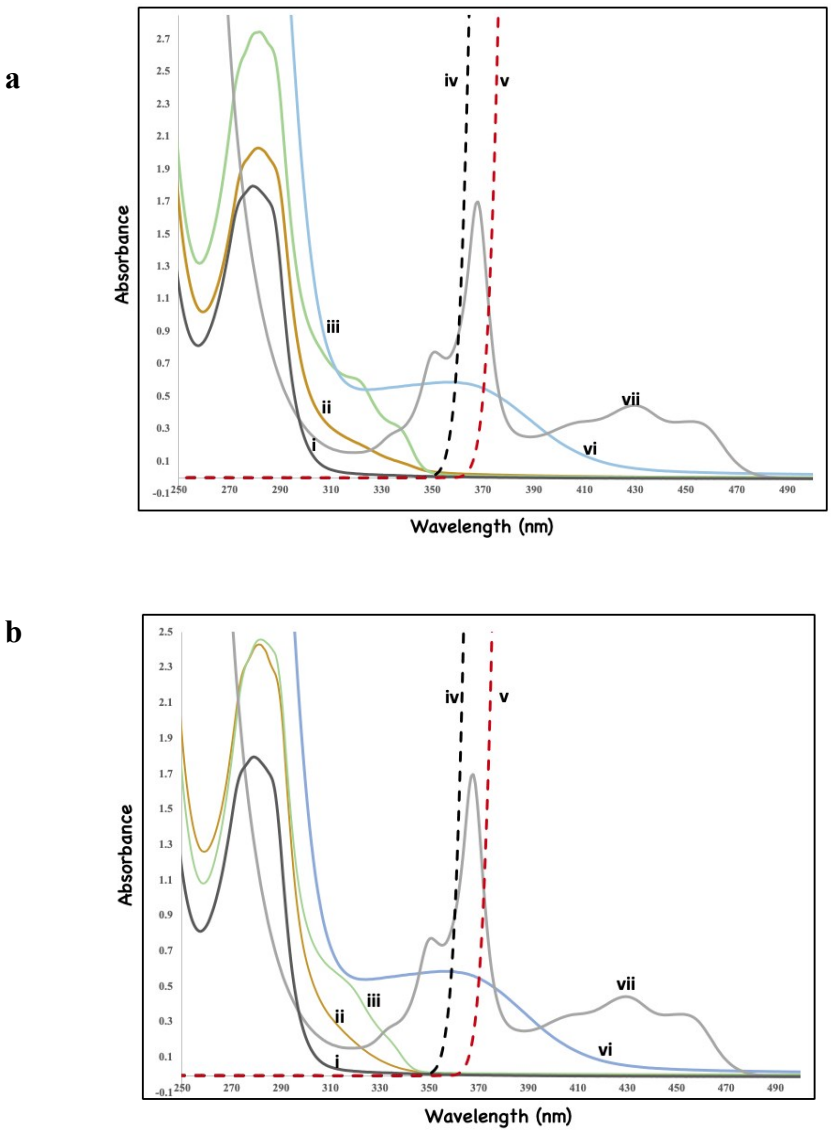

Figure S13. (**a**) Absorption spectra of (i) OA ([OA] = 1 X 10^{-4} M) (ii) *cis*-***2***@$(OA)_2$ ([*cis*-**2**] = 1 X 10^{-4} M : [OA] = 2 X 10^{-4} M) (iii) *trans*-**2**@$(OA)_2$ ([*trans*-**2**] = 1 X 10^{-4} M : [OA] = 2 X 10^{-4} M) (iv) Filter 0-51(v) Filter 3-75 (vi) 4-TMABP ([4-TMABP] = 0.5 X 10^{-4} M) and (vii) BMAN ([BMAN] = 0.5 X 10^{-4} M) (**b**) Absorption spectra of (i) OA ([OA] = 1 X 10^{-4} M) (ii) *cis*-**3**@$(OA)_2$ ([*cis*-**3**] = 1 X 10^{-4} M : [OA] = 2 X 10^{-4} M) (iii) *trans*-**3**@$(OA)_2$ ([*trans*-**3**] = 1 X 10^{-4} M : [OA] = 2 X 10^{-4} M) (iv) Filter 0-51(v) Filter 3-75 (vi) 4-TMABP ([4-TMABP] = 0.5 X 10^{-4} M) and (vii) BMAN ([BMAN] = 0.5 X 10^{-4} M)

7. Emission studies

7.1 Fluorescence quenching of BMAN with *cis*-**2**@OA_2 complex.

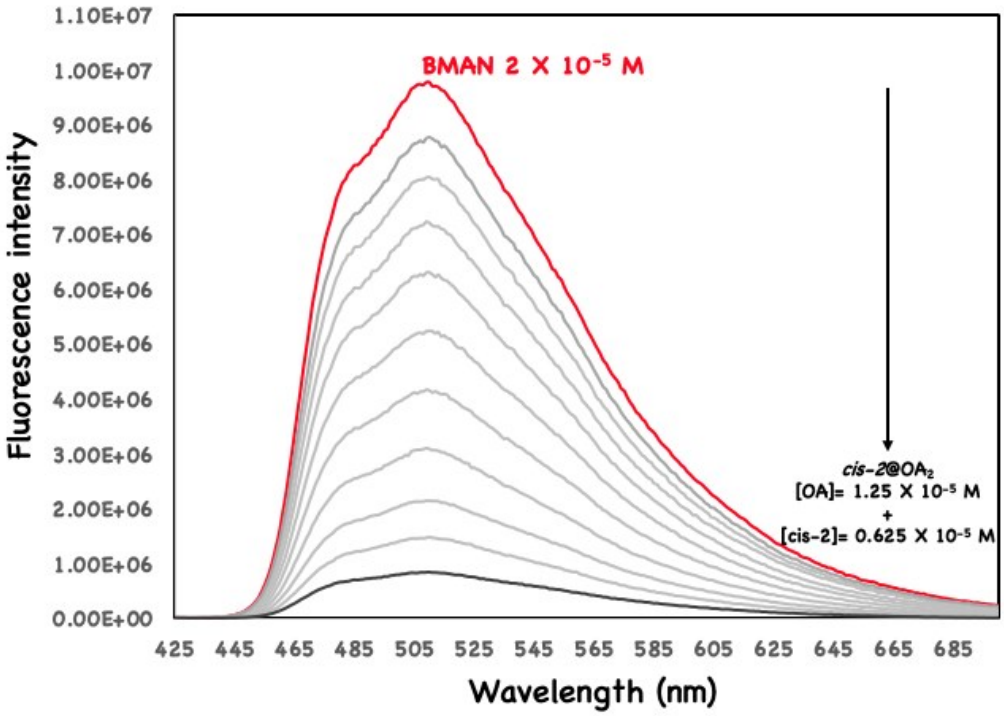

Figure S14. Emission spectra (λ_{exc} = 420 nm) of acceptor BMAN (red), and BMAN (black) as function of the donor (*cis*-**2**@OA) concentration ;([BMAN] = 2.0 x 10^{-5} M, [*cis*-**2**]= 0 – 0.625 x 10^{-5} M + [OA]= 0 – 1.25 x 10^{-5} M in buffer/H_2O, pH = 8.7).

7.2 Fluorescence quenching of BMAN with *cis*-**3**@OA_2 complex.

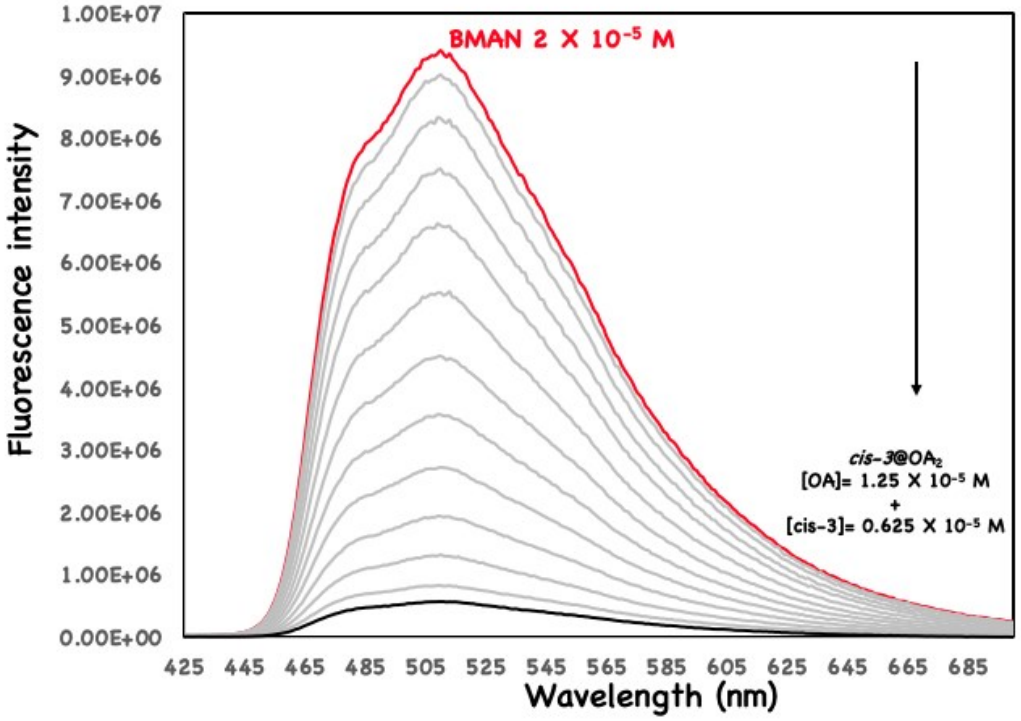

Figure S15. Emission spectra (λ_{exc} = 420 nm) of acceptor BMAN (red), and BMAN (black) as function of the donor (*cis*-**3**@OA) concentration ;([BMAN] = 2.0 x 10^{-5} M, [*cis*-**3**]= 0 – 0.625 x 10^{-5} M + [OA]= 0 – 1.25 x 10^{-5} M in buffer/H2O, pH = 8.7).

7.2 Emission spectra of 4-TMABP

7.2.1. Emission spectra of 4-TMABP (0.5 X 10^{-4} M) in water was recorded

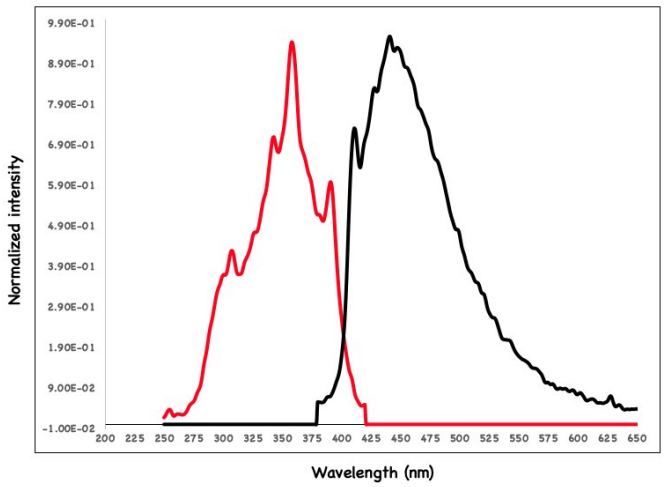

Figure S16. Emission and excitation spectra of 4-TMABP (excitation wavelength = 360 nm)

7.2.2. Quenching with Oxygen

The 4-TMABP (0.5×10^{-4} M) solution was prepared in three cuvettes. The Emission was recorded for 1) with N_2 purging 2) O_2 purging 3) without purging and emission results are compared in Figure S17.

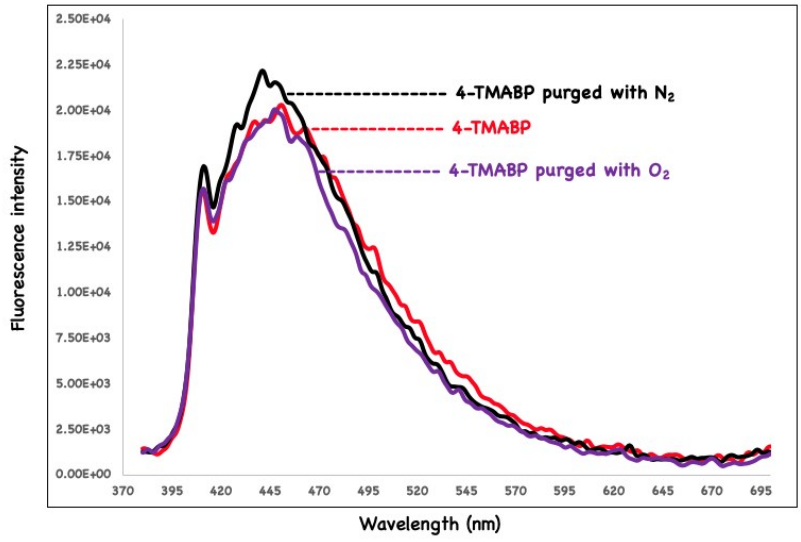

Figure S17. Comparison of emission spectra of 4-TMABP (excitation wavelength = 360 nm) in three different conditions.

8. Energy transfer studies of stilbenes with 4-TMABP

For energy transfer experiments, a solution containing *cis*-**1**@$(OA)_2$, *cis*-**2**@$(OA)_2$ and *cis*-**3**@$(OA)_2$ were prepared by adding 5 µL of 60 mM standard solutions to 0.6 mL of 1 mM of OA in 10 mM of borate buffer solution. To this 60 µL of 20 mM 4-TMABP solution was added and the solution was purged with nitrogen for 20 mins and then solution irradiated using filter (0-51, cut off wavelength 360 nm) and monitored over a period of time by recording ^{1}H NMR spectra. Experiments with corresponding *trans*-isomers were also repeated by following a similar procedure.

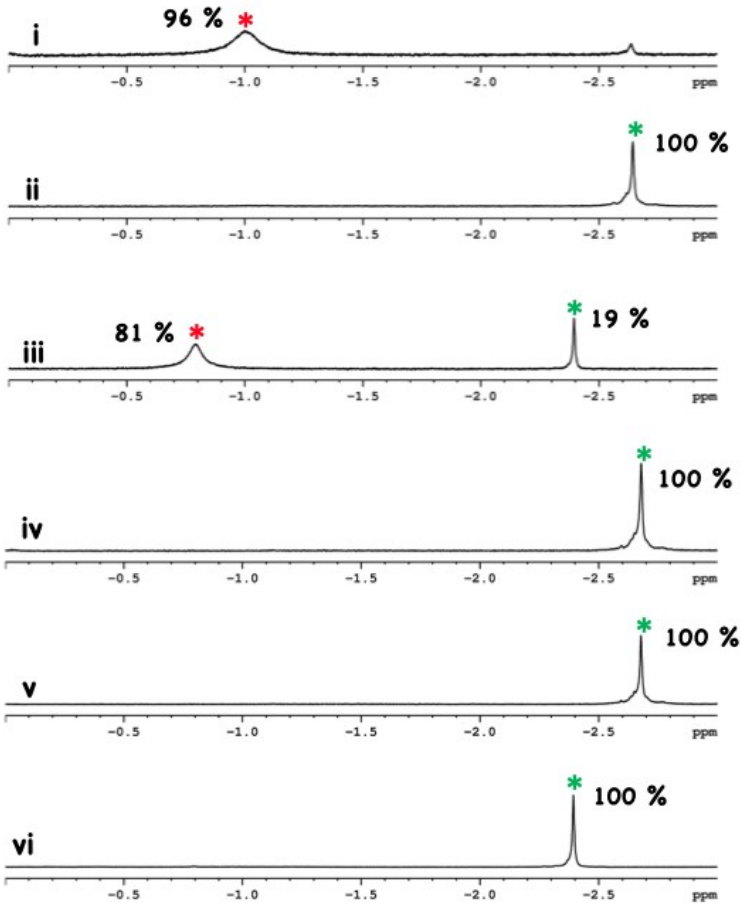

Figure S18. Partial ^{1}H NMR spectra (500 MHz) of *cis*-**2**@$(OA)_2$ and *trans*-**2**@$(OA)_2$ encapsulated within OA (1 X 10^{-3} M) in buffered D_2O after added sensitizer 4-TMABP **(i & iv)** initial (**ii & v)** after 72 hour irradiation **(iii & vi)** without 4-TMABP after 24 hour irradiation (control). (* & *) – represent the bound methyl protons of (*) *cis* and (*) *trans* respectively.

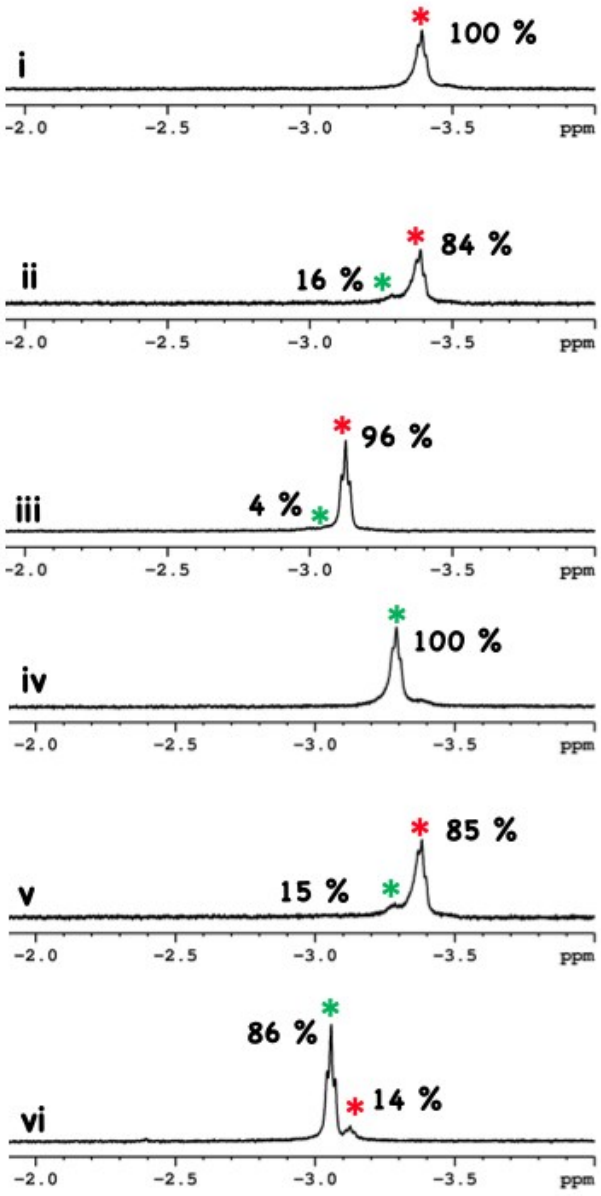

Figure S19. Partial ^{1}H NMR spectra (500 MHz) of *cis*-**3**@$(OA)_2$ and *trans*-**3**@$(OA)_2$ encapsulated within OA (1 X 10^{-3} M) in buffered D_2O after added sensitizer 4-TMABP **(i & iv)** initial (**ii & v)** after 72 hour irradiation **(iii & vi)** without 4-TMABP after 72 hour irradiation (control). (* & *) – represent the bound methyl protons of (*) *cis* and (*) *trans* respectively.

9. Electron transfer studies of stilbenes with BMAN

For electron transfer experiments, a solution containing *cis*-**1**@$(OA)_2$, *cis*-**2**@$(OA)_2$ and *cis*-**3**@$(OA)_2$ were prepared by adding 5 μL of 60 mM standard solutions to 0.6 mL of 1 mM of OA in 10 mM of borate buffer solution. To this 4 μL of 15 mM BMAN solution was added and the solution was purged with nitrogen for 20 mins. The solution was irradiated using filter (3-75, cut off wavelength 375 nm) and monitored over a period of time by recording ^{1}H NMR spectra.

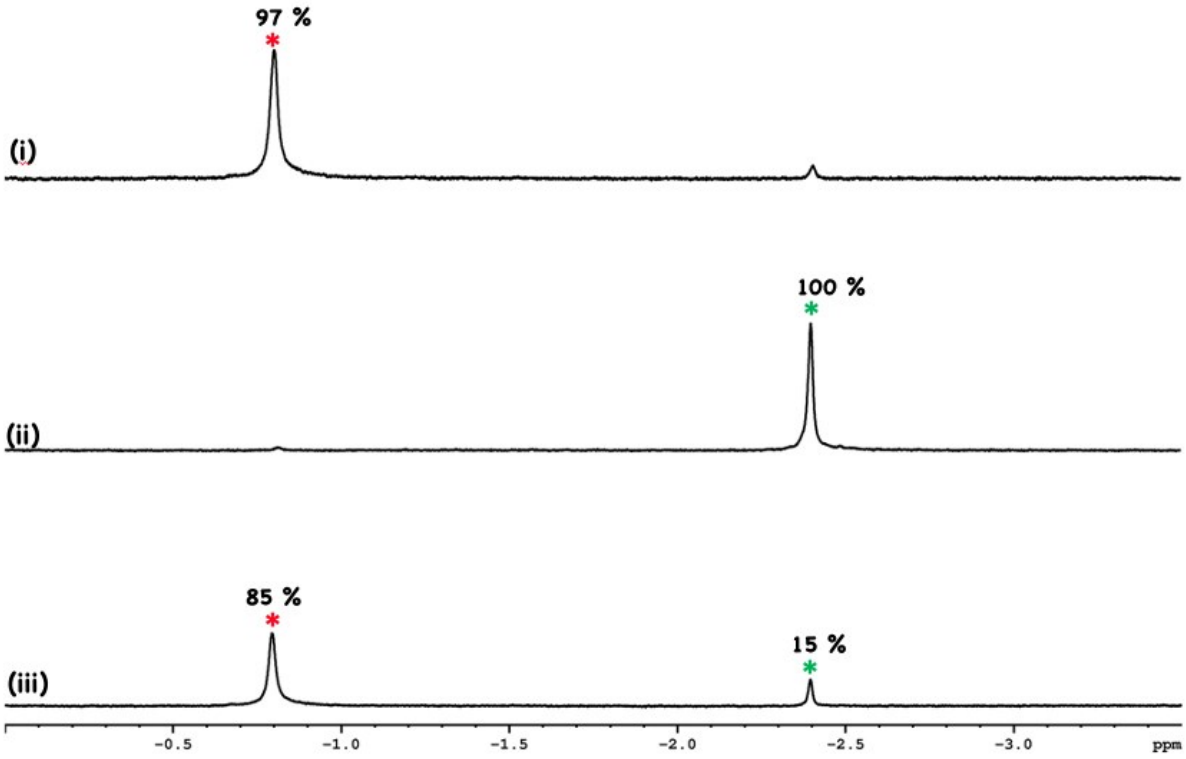

Figure S20. Partial ^{1}H NMR spectra (500 MHz) of *cis*-**2**@$(OA)_2$ encapsulated within OA (1X 10^{-3} M) in buffered D_2O after added photo catalyst BMAN **(i)** initial **(ii)** after 8 hour irradiation **(iii)** without BMAN after 24 hour irradiation (control). (* & *) – represent the bound methyl protons of (*) *cis* and (*) *trans* respectively.

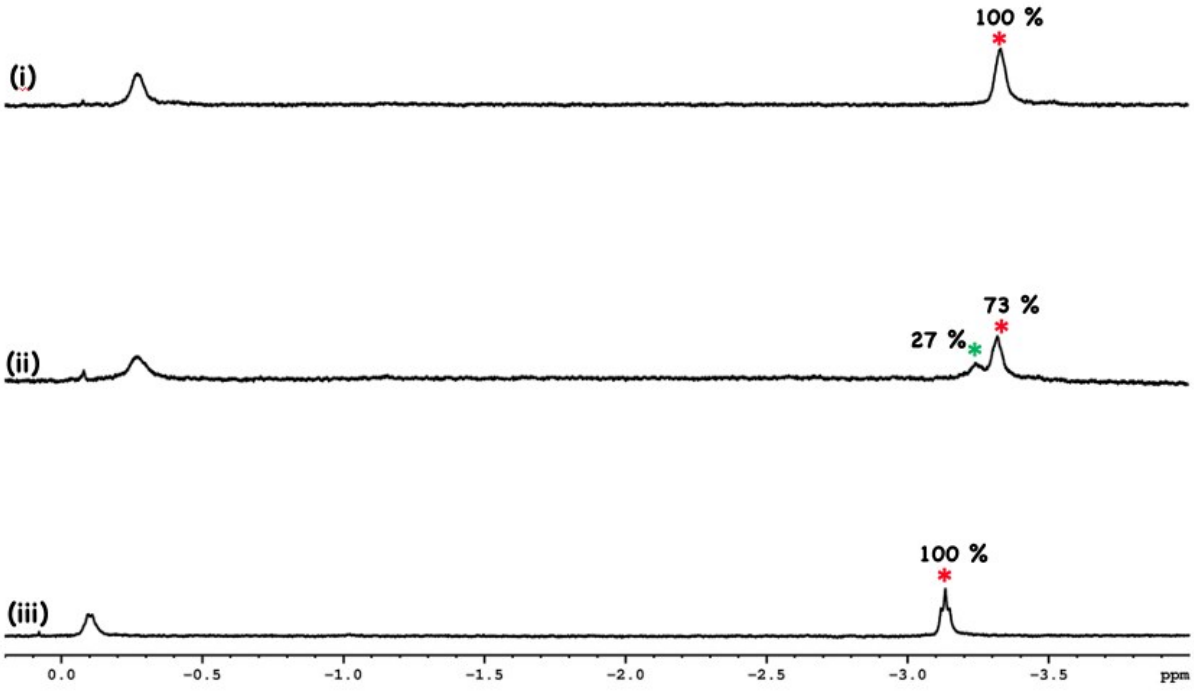

Figure S21. Partial ^{1}H NMR spectra (500 MHz) of *cis*-**3**@$(OA)_2$ encapsulated within OA (1X 10^{-3} M) in buffered D_2O after added photo catalyst BMAN **(i)** initial **(ii)** after 10 hour irradiation **(iii)** without BMAN after 24 hour irradiation (control). (* & *) – represent the bound methyl protons of (*) *cis* and (*) *trans* respectively.

10. ^{1}H, ^{13}C and Mass for 4-TMABP sensitizer

10.1. ^{1}H NMR

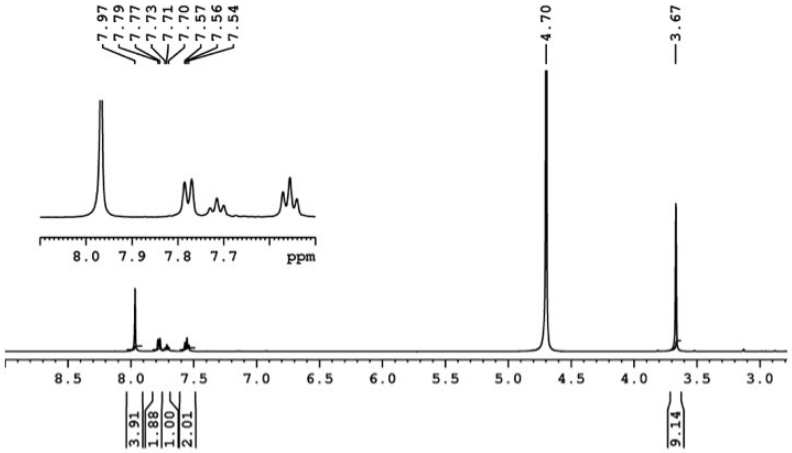

Figure S22. ^{1}H NMR (D_2O, 500 MHz) spectrum of N,N,N-trimethyl-4-(phenylcarbonyl)benzenaminiumiodide (4-**TMABP**)

10.2. ^{13}C NMR

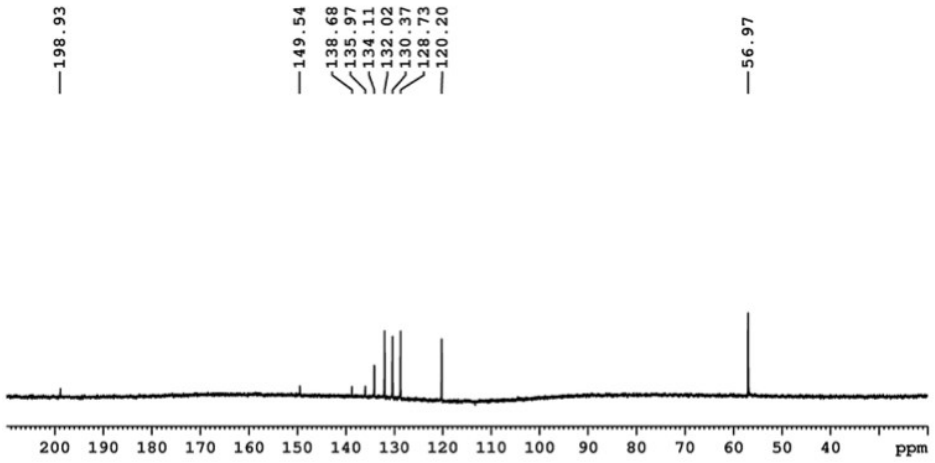

Figure S23. ^{13}C NMR (D_2O, 500 MHz) spectrum of N,N,N-trimethyl-4-(phenylcarbonyl)benzenaminiumiodide (4-**TMABP**)

10.3. Mass Spectra

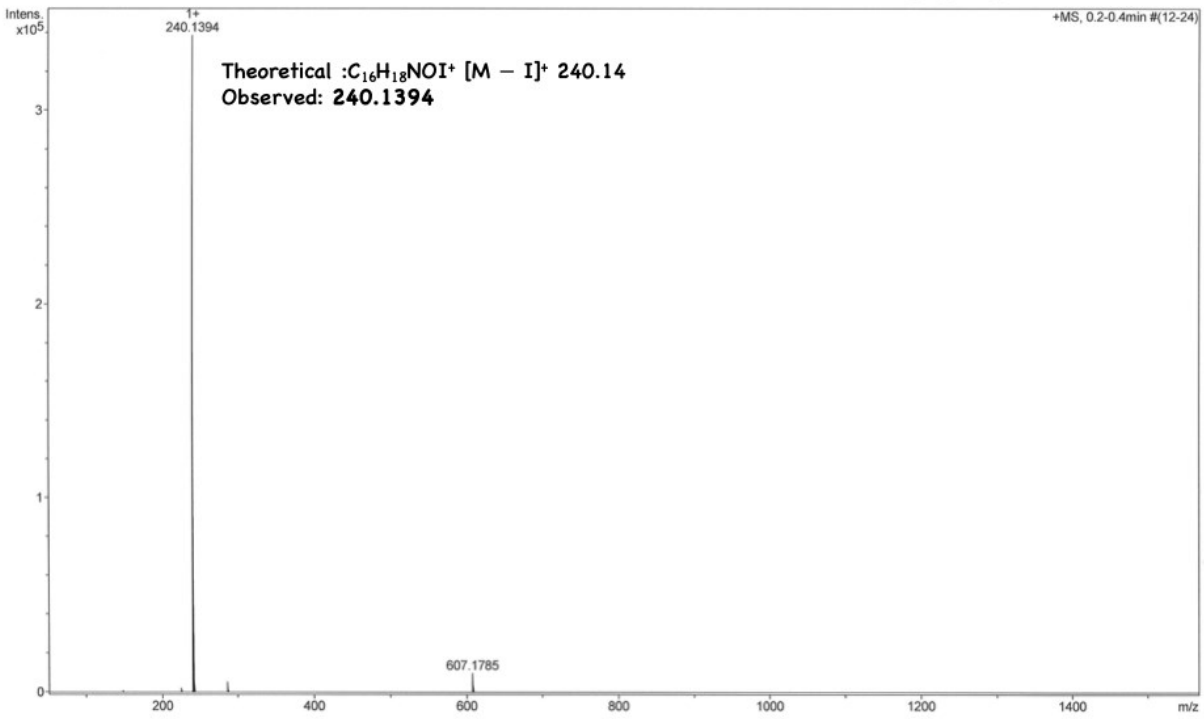

Figure S24. MS of N,N,N-trimethyl-4-(phenylcarbonyl)benzenaminiumiodide (4-**TMABP**)

References:

1. Gibb, C. L.; Gibb, B. C. *J. Am. Chem. Soc*. **2004,** *126*, 11408.
2. Parthasarathy, A.; Ramamurthy, V. *Photochem. Photobiol. Sci*. **2011**, *10*, 1455 & Samanta, S. R.; Parthasarathy, A.; Ramamurthy, V. *Photochem. Photobiol. Sci*. **2012**, *11*,1652.