

Supplementary Information

Controlling Molecular Assembling by Photons: Reversible Light-Powered Monomer-Aggregates Interconversion of Porphyrins

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Chemicals.

All other chemicals (reagent grade) were purchased by Sigma-Aldrich and used as received. All solvents used were spectrophotometric grade.

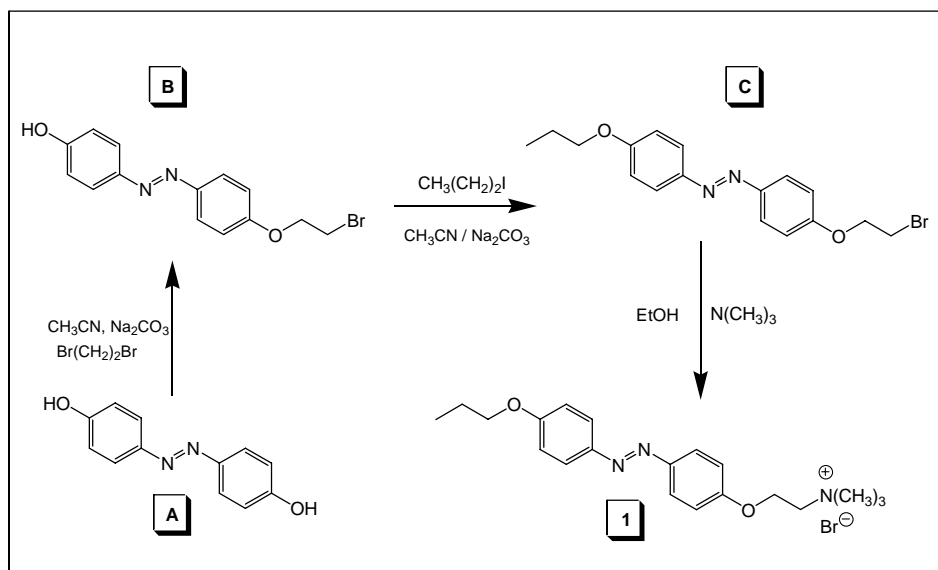
Instrumentation.

¹H NMR spectra were recorded on a VARIAN INOVA 200 spectrometer, using TMS as internal standard. ESI-MS spectra were recorded on an Agilent 1100 Series ESI/MSD spectrometer. Experimental conditions were as follows: capillary voltage, 3.5 KV; fragmentor, 100 V; source temperature, 350 °C; drying gas, N₂ (10 L/min), carrier solvent, methanol (0.4 mL/min). The samples were dissolved in a mixture methanol:acetonitrile. UV/vis absorption spectra were recorded with a Jasco V 560 spectrophotometer. Fluorescence excitation and emission spectra and Resonance Light Scattering experiments were recorded with a Spex Fluorolog-2 (mod. F-111) spectrofluorimeter.

Conductivity measurements were performed using a TOA Electronics Ltd. electroconductance meter CM-40S. Irradiation was carried out in quartz cuvettes (10 mm pathlength) using UV/Vis irradiation was performed, under ambient conditions, by using the monochromatic radiations of a fluorimeter Fluorolog-2 (mod. F-111).

Synthetic procedures.

N,N,N-trimethyl-2-{4-[(*E*)-(4-propoxyphenyl)diazenyl]phenoxy}ethanaminium bromide (**1**) was synthesized in a three step synthesis, as reported in Scheme 1S, starting from 4,4'-(*E*)-diazene-1,2-diylidiphenol (**A**) which was prepared according to the procedure described in the literature.^{1S,2S} All syntheses were carried out under a low intensity level of visible light.



Scheme 1S

(E)-4-(2-(4-(2-bromoethoxy)phenyl)diazenyl)phenol (B)

A mixture of **A** (1.18 g, 5.5 mmol), 1,2 dibromoethane (430 μ L, 4.94 mmol) and sodium carbonate (7.42 g, 70 mmol) were refluxed in 100 ml of acetonitrile for 6 days. After cooling down to ambient temperature the resulting suspension was filtered. The organic solution was concentrated under reduced pressure and purified by column chromatography (dichloromethane 100%) to give **B** (yield 32 %) as a yellowish powder. Anal. Calcd (%) for $C_{14}H_{13}N_2O_2Br$ (321.17): C, 52.25; H, 4.08; N, 8.72; found: C, 52.86; H, 4.13; N, 8.66;. ESI-MS m/z : $[M]^+$ 321.2. H^1 -NMR $CDCl_3-d_1$ (200 MHz) δ (ppm) = 7,881 (d, 2H, $J=9$ Hz, =N-C(CH₂)₂(CH)₂C-O-(CH₂)₂Br); 7,843 (d, 2H, $J=9$ Hz, =N-C(CH₂)₂(CH)₂C-OH); 7,008 (d, 2H, $J=9$ Hz, =N-C-(CH)₂(CH₂)₂C-O-(CH₂)₂Br); 6,945 (d, 2H, $J=8,5$ Hz, =N-C-(CH)₂(CH₂)₂C-O-H); 4,365 (t, 2H, $J=6,2$ Hz, -O-CH₂-); 3,671 (t, 2H, $J=6,2$ Hz, -CH₂-Br).

(E)-1-[4-(2-bromoethoxy)phenyl]-2-(4-propoxyphenyl)diazene (C)

A mixture of **B** (0.19 g, 0.6 mmol), 1-iodopropane (590 μ L, 6 mmol) and sodium carbonate (0.9 g, 8.4 mmol) were refluxed in 100 ml of acetonitrile for 3 days. After cooling down to ambient temperature the resulting suspension was filtered. The organic solution was concentrated under reduced pressure and purified by column chromatography (dichloromethane 100%) to give **C** (yield 35 %) as a yellowish powder. Anal. Calcd (%) for $C_{17}H_{19}N_2O_2Br$ (363.26): C, 56.21; H, 5.27; N, 7.71; found: C, 56.68; H, 5.48; N, 7.54; ESI-MS m/z : $[M]^+$ 363.2. H^1 -NMR $CDCl_3-d_1$ (200 MHz) δ = 7,902 (d, 4H, $J=9$ Hz, -(CH)₂C-N=N-C(CH)₂-); 6,998 (d, 4 H, $J= 8$, -(CH)₂(CH)₂C-N=N-C(CH)₂(CH)₂-); 4,324 (t, 2H, $J= 7$ Hz, Br-CH₂-CH₂-O-); 4,003 (t, 2H, $J= 6,5$ Hz, CH₃-CH₂-CH₂-O-); 3,451 (t, 2H, $J= 6,8$ Hz, Br-CH₂-CH₂-O-); 1,85 (m, 2H, CH₃-CH₂-CH₂-O-); 1,063 (t, 3H, $J= 7,5$, CH₃-CH₂-CH₂-O-).

N,N,N-trimethyl-2-{4-[(E)-4-(2-bromoethoxy)phenyl]diazenyl}phenoxy}ethanaminium bromide (1)

Compound **C** was dissolved in ethanol and was allowed to react with an excess of trimethylamine at 60° C for one week. After cooling at room temperature, the mixture was concentrated under reduced pressure to afford **1** (yield 95%) as a yellowish powder. Anal. Calcd (%) for $C_{20}H_{28}N_3O_2Br$. C, 56.87; H, 6.68; N, 9.95; found: C, 56.68; H, 6.42; N, 9.87; ESI-MS m/z : $[M]^+$ 342.3. H^1 -NMR $CDCl_3-d_1$ (200 MHz) δ (ppm) 7,88 (dd, 4H, $J=9$ Hz 3,4 Hz, -(CH)₂C-N=N-C(CH)₂-), 7,2 (d, 2H, $J=9$ Hz, -(CH)₂C-O-(CH₂)₂-N(CH₃)₃⁺), 7,09 (d, 2H, $J= 9$ Hz, CH₃-(CH₂)₂-O-C(CH)₂-), 4,78 (m,

2H, $-(\text{CH}_2)_2\text{-O-CH}_2\text{-CH}_2\text{-N}(\text{CH}_3)_3^+$, 4,23 (t, 2H, $J=4,7$ Hz, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-O-C}(\text{CH}_2)_2-$), 4,06 (t, 2H, $J=6,5$ Hz, $-(\text{CH}_2)_2\text{-O-CH}_2\text{-CH}_2\text{-N}(\text{CH}_3)_3^+$), 3,59 (s, 9H, $-\text{N}(\text{CH}_3)_3$), 1,8 (m, 2H, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-O-C}(\text{CH}_2)_2-$), 1,04 (t, 3H, $J=7,4$ Hz, $-\text{CH}_2\text{-CH}_3$)

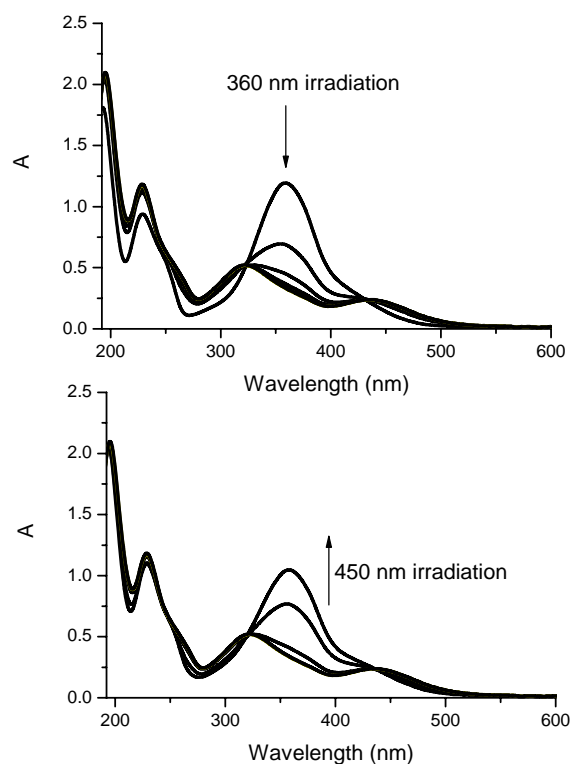


Figure S1. Absorption spectra of an aqueous solution of **1** recorded upon intervals of irradiation with 360 nm light (top) and afterwards with 450 nm light (bottom). The spectra were recorded under ambient conditions using a quartz cell with an optical pathway of 10 mm.

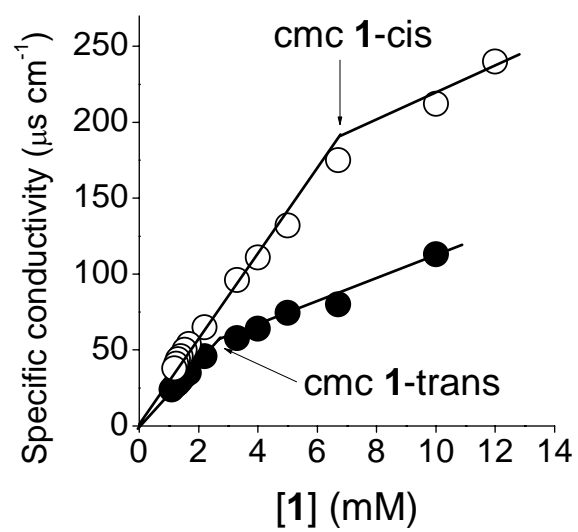


Figure S2. Specific conductivity of aqueous solutions of 1-trans (●) and 1-cis (○) as a function of surfactant concentration.

References

- (1S) J. Y. Shin and L. N. Abbot, *Langmuir*, 1999, **15**, 4404
- (2S) B. M. Bogoslawsky, *Gen. Chem.*, 1946, **16**, 193.