Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary information

Light-fuelled reversible expansion of spiropyran-based vesicles in water

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1. General methods

Materials and characterization methods. Reagents and solvents were purchased from commercial sources and used without further purification unless stated otherwise. 1,3,3-Trimethylindolino-6'-bromobenzopyrylospiran (**2**) was purchased from TCI. ^{1}H- and ^{13}C- NMR were recorded at 400 and 100.6 MHz, respectively. Chemical shifts are reported in δ = units (ppm) relative to the residual protonated solvent signals of CD_3CN (^{1}H NMR: δ = 1.94 ppm). Thin-layer chromatography (TLC) was carried out using Merck silica gel 60 on aluminum sheet, with visualization by UV light. Column chromatography was carried out using Merck silica gel 60 (230-400 Mesh). ESI-MS spectra were obtained for samples dissolved in DCM-MeOH at low μM concentrations.

UV-visible spectroscopy. The solutions were prepared at µM range concentrations. They were prepared at least 12 hours before the irradiation experiments from a concentrated stock solution in water. All the solution were kept under dark. UV-visible spectra were recorded at room temperature (20 °C) with a Perkin Elmer Lambda 850 UV-visible spectrometer in 1-cm quartz cells.

Critical aggregation concentration determination. Critical aggregation concentration (CAC) was determined by pyrene 1:3 ratio method as described elsewhere.[1] Briefly, pyrene at a concentration of 1 µM in milliQ water was used as a fluorescent probe. The pyrane solution was used to prepare appropriate dilutions of **1** that were further incubated at room temperature for at least 15 min. Fluorescence emission spectra between 350-500 nm were recorded using a fluorescence spectrophotometer (Perkin Elmer LS55) at an excitation of 340 nm. The decrease of the fluorescence intensity ratio between the first and the third peak with changing concentration of the **1** was used to determine the CAC value.

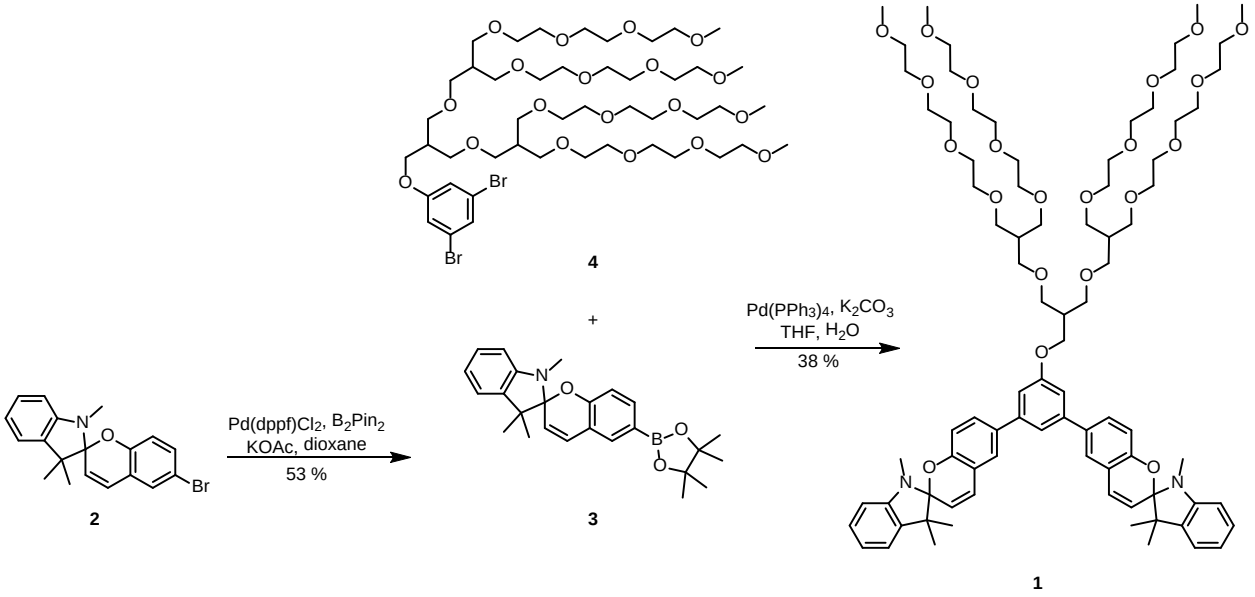
Transmission electron microscopy (TEM) measurements. The samples for TEM measurements were prepared by drop-casting a solution of compound **1** on carbon grids (Formvar/Carbon 200 mesh, Copper) and stained by Uranyl acetate. TEM micrographs were recorded using a Philips CM300ST - FEG TEM equipment.

Measurements of the diameter of vesicles. ImageJ 1.46 software was used to analyze TEM micrographs in order to determine the diameter of vesicles.

Visible light irradiation. The samples were irradiated with visible light using Edmund MI-150 high-intensity illuminator incorporating a tungsten lamp and without using any additional filters. Such a setup generates broad spectrum white light.

2. Synthesis and characterization

Compound **1** was synthesized according to the **Scheme 1**. Compound **4** was synthesized according to previously reported procedures.[2]



Scheme S1. Synthesis of the target molecule **1**.

1',3',3'-trimethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)spiro[chromene-2,2'-indoline] (3)

6-bromo-1',3',3'-trimethylspiro[chromene-2,2'-indoline] **2** (350 mg, 0.98 mmol), 4,4,4′,4′,5,5,5′,5′-octamethyl-2,2′-bi(1,3,2-dioxaborolane) (B_2Pin_2) (349 mg, 1.37 mmol), potassium acetate (KOAc) (289 mg, 2.95 mmol), and [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) ($Pd(dppf)Cl_2$) (36 mg, 0.05 mmol) in anhydrous dioxane (15 mL) was stirred at 90 °C under N_2 atmosphere for 24 h. After cooling down to room temperature, 15 mL of water was added to the mixture. The crude product was extracted into CH_2Cl_2 and dried over anhydrous Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using 2% EtOAc in hexane as an eluent initially and followed by a gradual increase

of the polarity to 1:1 EtOAc/hexane mixture to yield compound **3** as an orange solid (210 mg, 53%).

^{1}H-NMR (400 MHz, CD_3CN) δ 7.47 (d, J = 1.4 Hz, 1H), 7.45 (dd, J = 8.1, 1.6 Hz, 1H), 7.14 (td, J = 7.7, 1.2 Hz, 1H), 7.09 (dd, J = 7.3, 0.8 Hz, 1H), 6.99 (d, J = 10.3 Hz, 1H), 6.81 (td, J = 7.5, 0.9 Hz, 1H), 6.59 (d, J = 8.1 Hz, 1H), 6.55 (d, J = 7.7 Hz, 1H), 5.77 (d, J = 10.3 Hz, 1H), 2.69 (s, 3H), 1.30 (s, 12H), 1.24 (s, 3H), 1.13 (s, 3H). ^{13}C-NMR (100.3 MHz, CD_3CN) δ 158.01, 149.15, 137.64, 137.31, 134.43, 130.29, 128.56, 122.48, 120.19, 120.16, 119.58, 115.09, 107.82, 105.91, 84.56, 52.48, 29.09, 26.09, 25.11, 20.09. ESI-MS (*m/z*) calculated for $[C_{25}H_{31}BNO_3]^+$ 404.24, found: 404.28.

Spiropyran amphiphile (1)

Compound **4** (137 mg, 0.124 mmol) was dissolved in 16 mL of degassed mix solvent THF/water (7:1), then added to a mixture of compound **3** (150 mg, 0.37 mmol), potassium carbonate (103 mg, 0.74 mmol), and tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) (29 mg, 0.025 mmol) under N_2 atmosphere. The reaction mixture was heated at 100 °C for 48 h. After cooling down to room temperature, the mixture was quenched with water and extracted 3 times with EtOAc. The combined organic extract was dried over anhydrous Na_2SO_4. Evaporation of solvents left a crude product which was purified by column chromatography with EtOAc/MeOH (10:1) as eluent to afford compound **1** as an orange liquid (71 mg, 38%).

^{1}H-NMR (400 MHz, CD_3CN) δ 7.52 (d, J = 2.3 Hz, 2H), 7.47 (dd, J = 8.4, 2.3 Hz, 2H), 7.37 (s, 1H), 7.16 (td, J = 7.7, 1.2 Hz, 2H), 7.11 (d, J = 7.3 Hz, 2H), 7.09 (d, J = 1.5 Hz, 2H), 7.04 (d, J = 10.2 Hz, 2H), 6.82 (td, J = 7.5, 0.9 Hz, 2H), 6.69 (d, J = 8.4 Hz, 2H), 6.57 (d, J = 7.7 Hz, 2H), 5.83 (d, J = 10.2 Hz, 2H), 4.16 (d, J = 5.7 Hz, 2H), 3.55–3.40 (m, 64H), 3.26 (s, 12H), 2.73 (s, 6H), 2.33 (quin, J = 5.9 Hz, 1H), 2.05 (quin, J = 5.9 Hz, 2H), 1.29 (s, 6H), 1.15 (s, 6H). ^{13}C-NMR (101 MHz, CD_3CN) δ 161.05, 155.13, 149.23, 143.16, 137.69, 133.83, 130.31, 129.33, 128.58, 126.60, 122.51, 120.84, 120.15, 115.70, 112.05, 107.84, 105.80, 72.54, 71.26, 71.14, 71.08, 70.98, 70.94, 70.11, 70.03, 69.77, 67.06, 58.84, 52.56, 41.26, 40.89, 29.20, 26.12, 20.23. ESI-MS (*m/z*) calculated for $[C_{84}H_{121}N_2O_{21}]^+$ 1493.85, found: 1493.7

NMR spectra

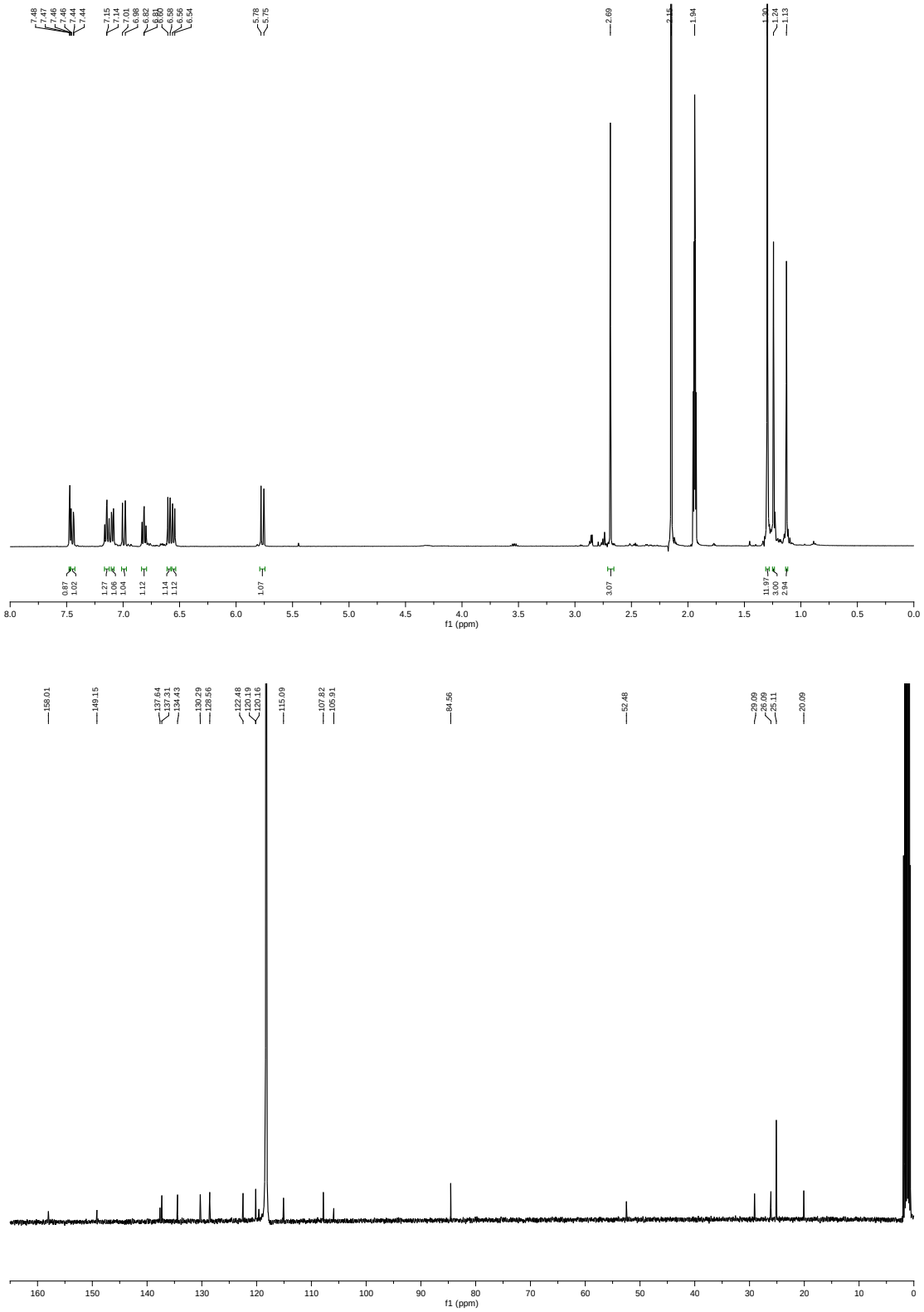


Figure S1. ^{1}H-NMR (top) and ^{13}C-NMR (bottom) spectra of **3** in CD_3CN.

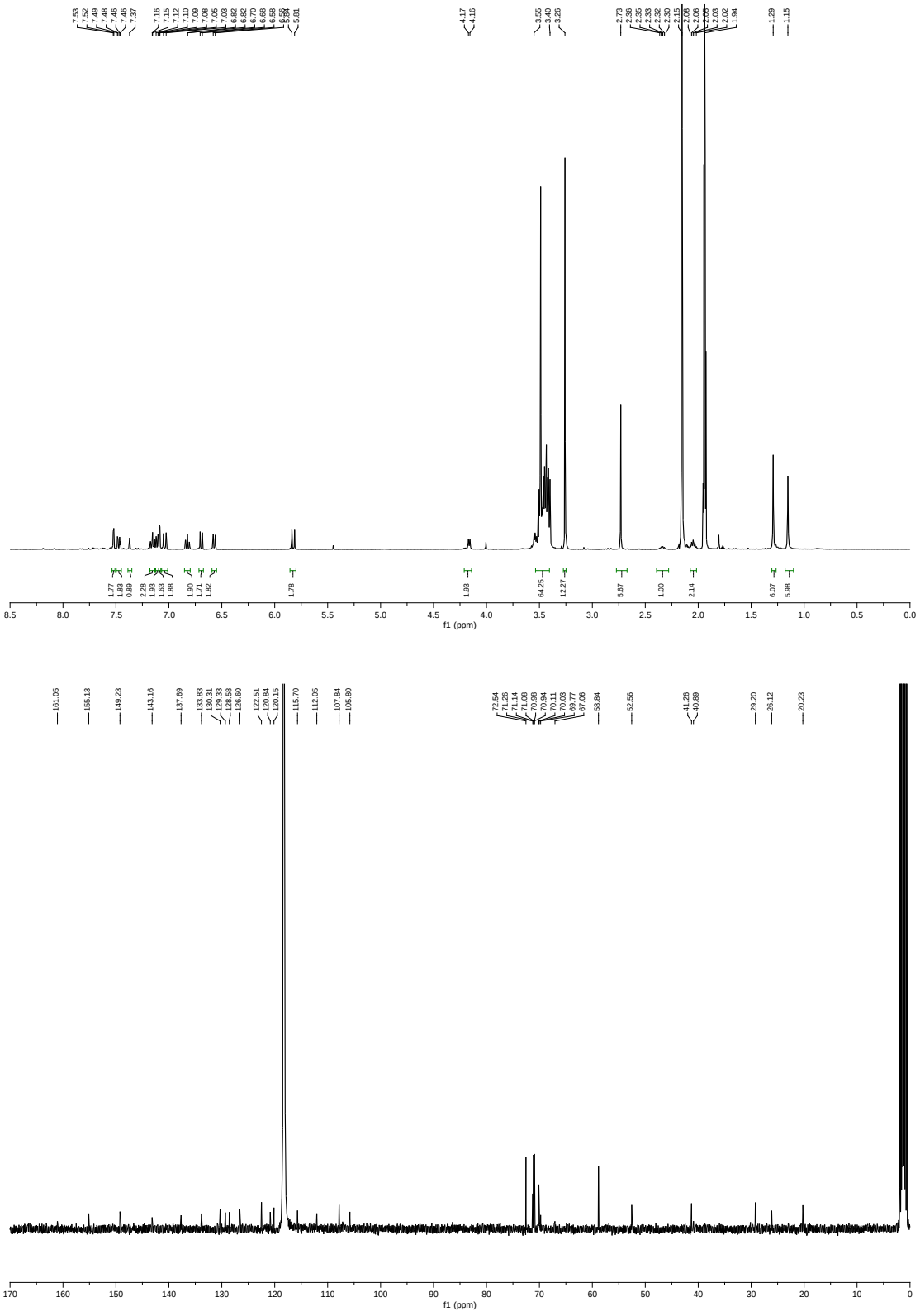


Figure S2. ^{1}H-NMR (top) and ^{13}C-NMR (bottom) spectra of **1** in CD_3CN.

3. Supporting experiments

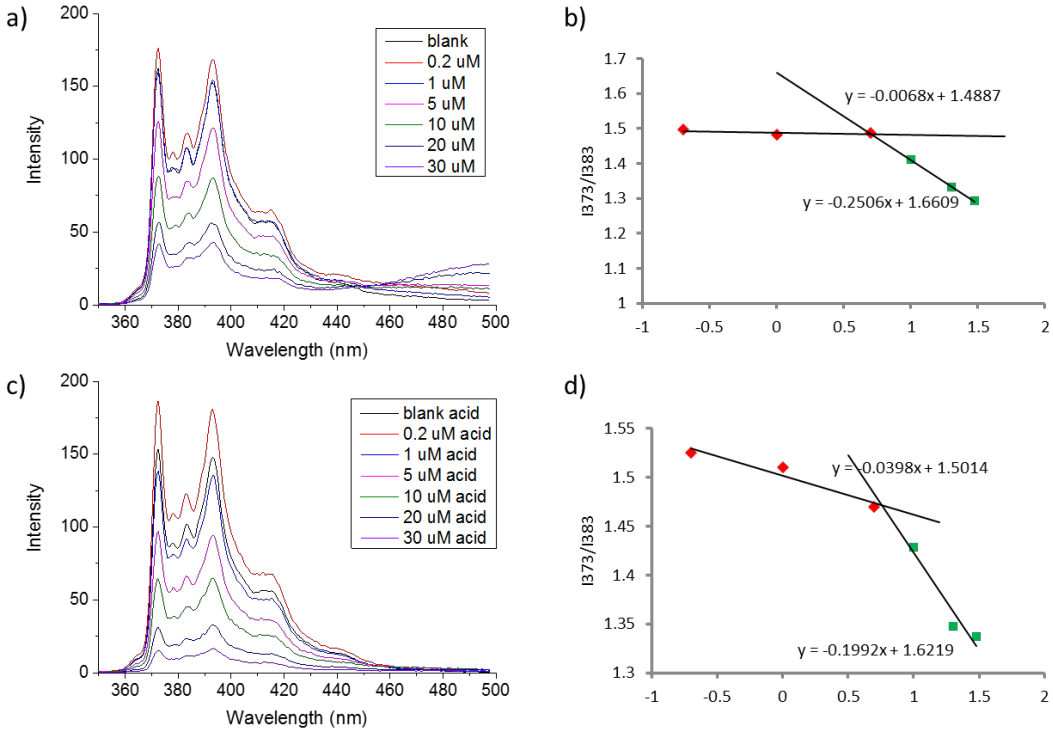


Figure S3. Critical aggregation concentration (CAC) of compound **1** determined by the fluorescence response of pyrene to changing concentration of **1** causing its transition into the hydrophobic environment of formed vesicles. The CAC in each condition was determined by the intersection of two trend lines from the plot between the ration of the first and the third band maxima (I_{373}/I_{383}) of the fluorescence and log concentration. The determined CAC values are; (a) and (b) at 5.1 μM under the neutral condition, pH = 7; (c) and (d) at 5.7 μM under the acidic condition, pH = 2.

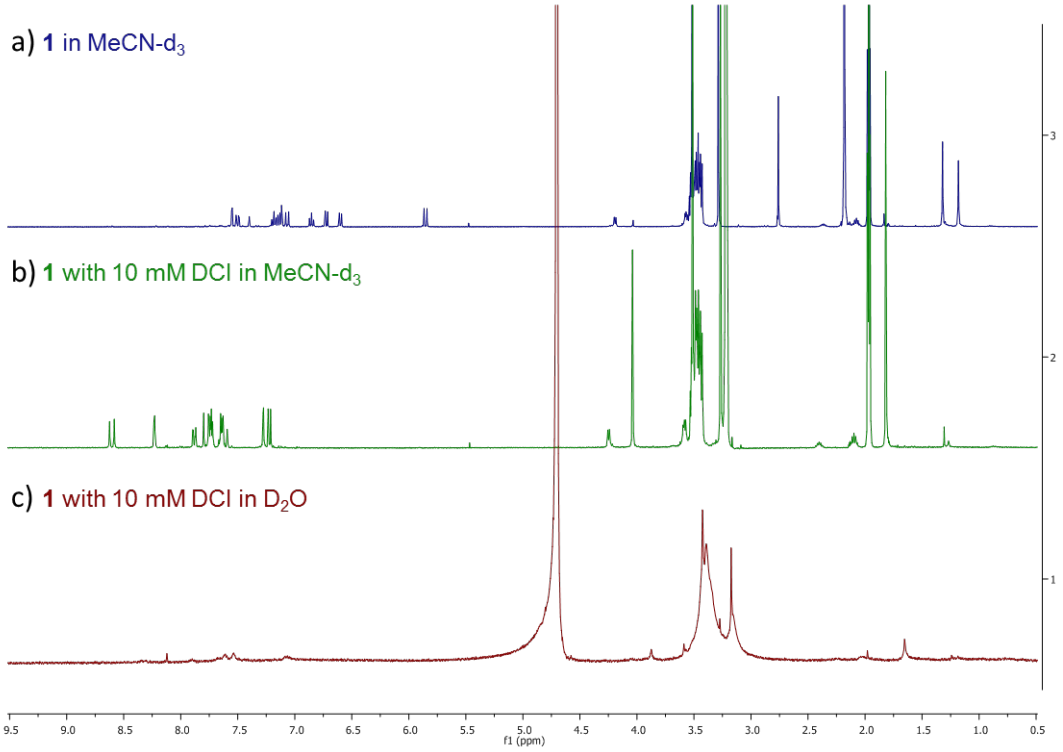


Figure S4. ^{1}H-NMR of **1** at different conditions. (a) In CD_3CN. (b) With 10 mM DCl in CD_3CN. (c) With 10 mM DCl in D_2O. Compound **1** is fully converted into its MCH^+ form in CD_3CN and under acidic conditions (green). Broadening of the spectrum in D_2O (red) does not allow for determination of the SP and MCH^+ ratio.

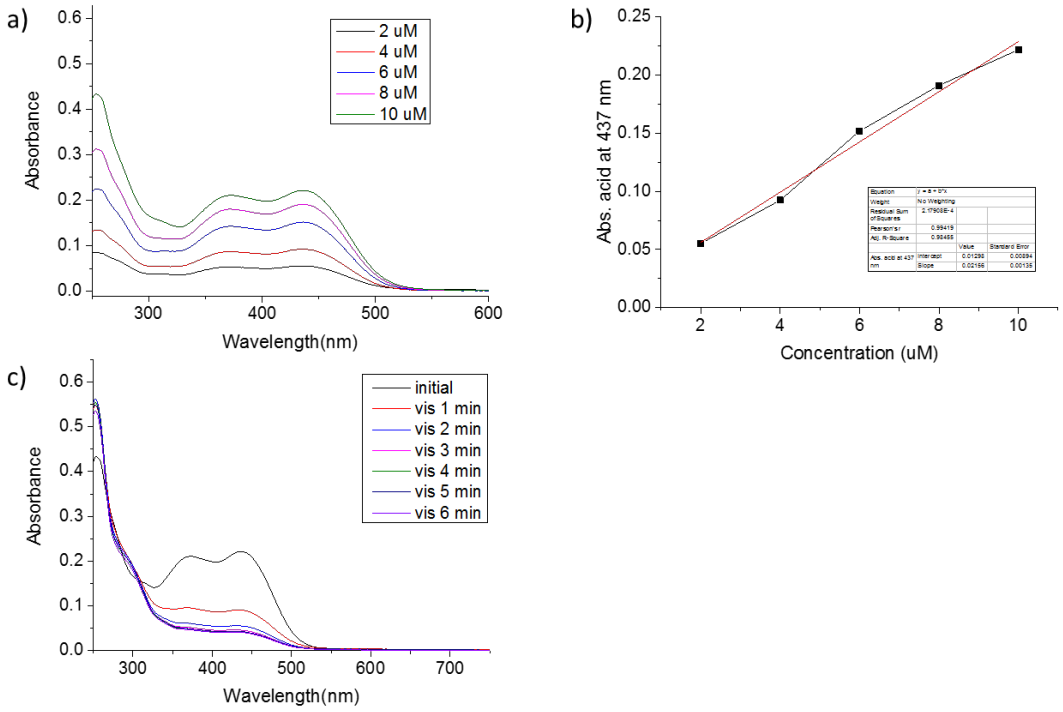


Figure S5. Determination of SP/MCH$^+$ ratio at the photostationary state. (a) Absorption spectra of compound **1** under neutral condition (pH = 7) at varying concentration. (b) Calibration curve of compound **1** using absorbance at 437 nm. (c) Absorption spectrum of compound **1** at 10 μM under acidic condition (pH = 2) and visible light irradiation.

Table S1. Calculation of the SP/MCH$^+$ ratio at pH = 2 after visible light irradiation

Abs at 437 nm = 0.02156 (concentration in μM) + 0.01298 (equation S1)

Condition	Absorbance at 437 nm	Conc. (μM) calculated from eq. S1	% of the MCH$^+$→SP	MCH$^+$/SP
initial	0.222	9.67	0	100/0
vis 1 min	0.091	3.61	58.96	41/59
vis 2 min	0.055	1.95	75.12	25/75
vis 3 min	0.046	1.51	79.46	21/79
vis 4 min	0.042	1.37	80.86	19/81
vis 5 min	0.043	1.38	80.68	19/81
vis 6 min	0.041	1.30	81.54	18/82

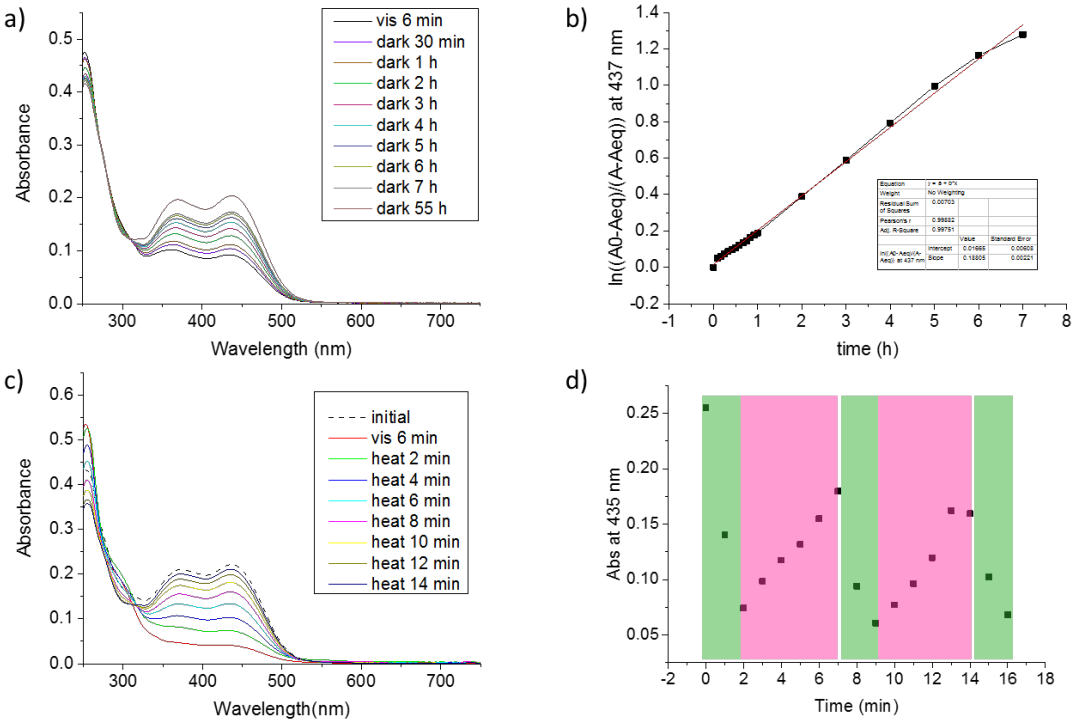


Figure S6. Relaxation of compound **1** at 10 µM (pH = 2) after 6 minutes of visible light irradiation. (a) Absorption spectra showing the relaxation of MCH^+ in the dark. (b) First order plot for the relaxation in the dark. (c) Absorption spectra showing the relaxation upon heating at 60 °C. (d) Switching cycles between visible light irradiation for 2 minutes (green) and relaxation upon heating at 60 °C for 5 minutes (pink).

Half-life time of the relaxation reaction in the dark was calculated from first order reaction kinetics;

$$ln\left(\frac{A_0 - A_{eq}}{A - A_{eq}}\right) = (k_1 + k_2)t$$

$$t_{1/2} = \frac{0.693}{k}$$

From plot; y = mx + c

Slope (m) ≡ (k_1+k_2) = 0.188 ; $t_{1/2}$ = 0.693/0.188 = 3.69 h

4. References

1. J. Aguiar, P. Carpena, J. A. Molina-Bolívar and C. Carnero Ruiz, *J. Colloid Interface Sci.*, 2003, **258**, 116-122.
2. I.-S. Park, Y.-R. Yoon, M. Jung, K. Kim, S. Park, S. Shin, Y.-b. Lim and M. Lee, *Chemistry – An Asian Journal*, 2011, **6**, 452-458.