Supporting Information

Light-triggered self assembly of a dichromonyl compound in water

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Photoswitching Experiments Irradiation experiments were performed with a spectroline ENB-280C/FE UV lamp (365 nm) and Thor Labs OSL1-EC Fiber Illuminator (white light).

Synthesis. *General.* For synthesis all chemicals were obtained from commercial sources and used as received unless stated otherwise. Solvents were reagent grade. Thin-layer chromatography (TLC) was performed using commercial Kieselgel 60, F254 silica gel plates. Flash chromatography was performed on silica gel (Silicycle Siliaflash P60, 40-63 μ m, 230-400 mesh). Drying of solutions was performed with MgSO₄. Solvents were removed from the produced solutions with a rotary evaporator. Chemical shifts for NMR measurements were determined relative to the residual solvent peaks ($\delta_{\rm H}$ 7.26 for CHCl₃ and 2.50 for DMSO, $\delta_{\rm C}$ 77.16 for CDCl₃ and 39.52 for DMSO). The following abbreviations are used to indicate signal multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; brs, broad signal; appt, apparent triplet. HRMS (ESI) spectra were obtained on a Thermo scientific LTQ Orbitrap XL. Melting points were recorded using a Buchi melting point B-545 apparatus. UV/Vis absorption spectra were recorded on an Agilent 8453 UV-Visible Spectrophotometer using Uvasol grade solvents.



Figure S1 Reversible photochromism of compound **1** in water at a concentration of 128 μ M. Switching was realized by irradiating the sample with 365 nm light and white light (390 – 750 nm) consecutively.



Figure S2 Cryo-TEM image of *cis*-**1** in water at a concentration of 10 mg/mL. Small, micelle-like structures were observed.



Figure S3 Cryo-TEM image of *trans*-**1** in water at a concentration of 10 mg/mL, obtained by illuminating the same sample as Fig. S2 with white light. Fibers were observed throughout the sample.



Figure S4 Cryo-TEM image of *trans*-**1** in water at a concentration of 4 mg/mL. Some small fibers were observed.



Figure S5 Cryo-TEM image of *trans*-**1** in aqueous 100 mM NaCl at a concentration of 4 mg/mL. A highly branched network of fibers were observed.



Figure S6 The ratio between absorbance at λ_{max}^{trans} of *trans*-1 and absorbance at λ_{max}^{trans} of *cis*-1 at different concentrations. When the ratio is large, there is efficient switching between *trans*-1 and *cis*-1, whereas the ratio around 1 means no switching. Switching from *trans*-1 to *cis*-1 is efficient in DMSO, even at high concentrations. Switching from *cis*-1 to *trans*-1 in water is also efficient at high concentrations. However, switching from *trans*-1 to *cis*-1 in water at high concentrations is inhibited. This is probably due to tight stacking of *trans*-1 molecules at these concentrations. At high concentrations the samples were diluted in the dark after irradiation to measure UV-absorbance.



Scheme S1: Synthesis of compound 1.

Methyl 5-hydroxy-4-oxo-4H-chromene-2-carboxylate (2) 2,6-Dihydroxyacetophenone (1.50 g, 9.90 mmol) and dimethyloxalate (5.80 g, 49.3 mmol) were dissolved in 0.5 M MeONa/MeOH (100 mL) and the mixture was heated at reflux overnight. The solvent was removed in vacuo and the slurry was dissolved in water (100 mL) and subsequently acidified with concentrated HCl. The precipitate was filtered off and dissolved in a mixture of MeOH (50 mL) and concentrated HCl (10 mL). This solution was heated at reflux for 2 h after which the crude product was purified by flash chromatography (Silicagel, 40-63 μ m, pentane/AcOEt, 9:1, v/v) yielding 762 mg (33%) of a yellow powder.

¹H-NMR (400 MHz, CDCl₃): δ 7.61 (appt, J=8.4 Hz, 1H), 7.03-7.06 (m, 2H), 6.85 (d, J=8.3 Hz, 1H), 4.02 (s, 3H). ¹H-NMR spectrum in agreement with published data.¹

1-Methyl-3-nitrosobenzene (3) 3-Methylaniline (708 mg, 6.61 mmol) was dissolved in DCM (20 mL), a solution of oxone (8.10 g, 13.2 mmol) in water (80 mL) was added and the resulting biphasic mixture was stirred at room temperature for 30 min. The organic layer was separated and the aqueous layer was extracted twice with DCM. The

combined organic layers were washed with 1 M aq. HCl, saturated NaHCO₃ and brine and dried (MgSO₄). The crude product was purified by flash chromatography (Silicagel, 40-63 μ m, pentane/AcOEt, 4:1, v/v), yielding 430 mg (54%) of a light green solid.

¹H-NMR (400 MHz, CDCl₃): δ 7.77 (d, J=6.4 Hz, 1H), 7.63 (s, 1H), 7.48-7.54 (m, 2H), 2.50 (s, 3H). ¹H-NMR spectrum in agreement with published data.²

3,3'-Dimethylazobenzene (4) Compound 3 (500 mg, 4.13 mmol) and 3-methylaniline (369 mg, 3.44 mmol) were dissolved in glacial acetic acid (33 mL) and the mixture was stirred overnight. The solution was diluted with water and extracted with ethyl acetate. The organic phase was washed four times with water and once with brine and dried (MgSO₄). The crude product was filtered through silica yielding 400 mg (55%) of an orange solid. ¹H-NMR (400 MHz, CDCl₃): δ 7.70-7.74 (m, 4H), 7.41 (appt, J=8.0 Hz, 2H), 7.29 (d, J=7.6 Hz, 2H), 2.46 (s, 6H). ¹H-NMR spectrum in agreement with published data.³

3,3'-Bis(bromomethyl)azobenzene (5) To a solution of compound 4 (1.30 g, 6.18 mmol) in 60 mL of CCl₄ was added NBS (2.50 g, 14.2 mmol) and AIBN (80 mg, 0.48 mmol). The resultant solution was stirred overnight at 70°C, then filtered and the filtrate was washed with hot water and brine and dried (MgSO₄). After evaporation the product was recrystallized from acetonitrile yielding 800 mg (35%) of an orange solid. Mp. 140-141 °C.

¹H-NMR (400 MHz, CDCl₃): δ 7.95 (m, 2H), 7.87 (m, 2H), 7.52 (m, 4H), 4.59 (s, 4H). ¹H-NMR spectrum in agreement with published data.³

(*E*)-Dimethyl5,5'-(((diazene-1,2-diylbis(3,1-phenylene)))bis(methylene)))bis(oxy)))bis(4oxo-4H-chromene-2-carboxylate) (6) To a solution of compounds 2 (638 mg, 2.73 mmol) and 5 (400 mg, 1.09 mmol) in 80 mL acetonitrile was added K_2CO_3 (451.93 mg, 3.27 mmol) and the resulting mixture was stirred overnight at 65 °C. The solution was concentrated in vacuo and the crude product was purified using flash chromatography (Silicagel, 40-63 μ m, DCM/Methanol, 95:5, v/v) yielding 520 mg (70%) of a light orange solid. ¹H-NMR (400 MHz, CDCl₃): δ 8,06 (s, 2H), 7.90-7.85 (m, 4H), 7.56-7.61 (m, 4H), 7.18 (d, J = 8.5 Hz, 2H), 7.02 (s, 2H), 6.91 (d, J = 8.3 Hz, 2H), 5.38 (s, 4H), 4.00 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 177.6, 161.1, 158.4, 158.0, 152.7, 150.1, 137.5, 134.7, 129.7,

129.4, 122.6, 120.7, 116.7, 113.8, 111.1, 108.9, 70.6, 53.4.

HR-MS (ESI, $[M+H]^+$): Calcd. for $C_{36}H_{27}N_2O_{10}$: 647.1660 ; Found: 647.1603.

Sodium (E)-5,5'-(((diazene-1,2-diylbis(3,1-phenylene))bis(methylene))bis(oxy))

bis(4-oxo-4H-chromene-2-carboxylate) (1) To a solution of compound 6 (100 mg, 0.15 mmol) in ethanol (5 mL) was added aq. NaOH (2.5 M, 186 μ L) dropwise at 0°C. The reaction mixture was heated at reflux for 2 h after which the insoluble product was filtered off yielding

85 mg (86%) of an orange solid.

¹H-NMR (400 MHz, Methanol-d₄): δ 8.12 (s, 2H), 7.86 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.63 (m, 4H), 7.26 (d, J = 8.4 Hz, 2H), 7.06 (d, J = 8.4 Hz, 2H), 6.88 (s, 2H), 5.42 (s, 4H).

¹³C-NMR (100 MHz, Methanol-d₄): δ 180.4, 164.7, 158.3, 158.1, 157.9, 152.7, 138.3, 134.5, 129.1, 121.2, 113.8, 112.5, 110.9, 108.5, 69.9.

HR-MS (ESI, $[M+Na]^+$): Calcd. for $C_{34}H_{22}N_2O_{10}Na$: 641.1167 ; Found: 641.1140.

References

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