Electronic Supporting Information (ESI)

Light-driven control of the composition of a supramolecular network

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General methods and materials

The DTE derivative 1 was prepared by a modified published procedure (see below). All chemicals for the synthesis were used as received without further purification, unless stated otherwise. CH$_2$Cl$_2$ was distilled over CaH$_2$. $^1$H NMR (400 MHz) and $^{13}$C NMR (101 or 125 MHz) spectra for the characterization of 1 and its precursor were recorded on Varian Unity 400 or 500 spectrometers at 25 °C. In the $^1$H and $^{13}$C NMR spectra, chemical shifts ($\delta$/ppm) are referenced to the residual solvent peak: CDCl$_3$, 7.26 ppm ($^1$H NMR) and 77.20 ppm ($^{13}$C NMR); D$_2$O, 4.80 ($^1$H NMR); MeOH-d$_4$, 49.00 ppm ($^{13}$C NMR). Thin-layer chromatography to monitor the reactions was performed on silica gel plates (Merck Kieselgel 60, F$_{254}$).

All measurements (at room temperature) were done in water (miliQ quality) or in deuterium oxide (D$_2$O, >99 atom% D) at pH or pD 5.0, respectively. The pH/pD was adjusted by additions of HCl/DCl or NaOH/NaOD. The pD values were obtained after correction for isotope effects ($pD = pH^* + 0.4$).\textsuperscript{1} Cucurbit[7]uril (CB7) was prepared by following a published procedure.\textsuperscript{2} The water content was taken as 20 weight-%, determined by $^1$H NMR spectroscopy using malonic acid as internal standard. Cucurbit[8]uril (CB8; 20 weight-% water) and geranylamine (2) are commercial products and were used in the highest quality available.

$^1$H NMR experiments to characterize the network were done with a Varian Mercury 500 MHz NMR spectrometer. For the irradiation two light sources were used: 365-nm light was generated by a UVP handheld UV lamp (Model VL-4.LC, 4 W) and light at $\lambda > 590$ nm by a 150 W Xenon lamp (Oriel GmbH & Co.KG), using a long-pass optical filter.

Note: For the four-component mixture (1, 2, CB7, and CB8; all at 500 $\mu$M) a small amount of precipitate was observed on prolonged standing of the solution. This can be re-dissolved by heating gently with a hairdryer.
Experimental procedure for the synthesis of 1

Scheme S1. Synthesis of 1.

Synthesis of 1,2-bis(2-methyl-5-(4-pyridyl)-3-thienyl)cyclopentene

A published method was modified to synthesize 1,2-bis(2-methyl-5-(4-pyridyl)-3-thienyl)cyclopentene. 1,2-Bis(5-chloro-2-methyl-3-thienyl)cyclopentene (493 mg, 1.5 mmol), 4-pyridinylboronic acid (406 mg, 3.3 mmol), Na$_2$CO$_3$ (720 mg, 3 mmol) and Pd(PPh$_3$)$_4$ (174 mg, 0.15 mmol) were placed in a flask under Ar. Dimethoxyethane (DME, 20 mL, degassed) and water (5 mL, degassed) were subsequently added and the reaction mixture was refluxed (90 °C) for 48 h under argon. After cooling to room temperature, the reaction was quenched with water (40 mL) and Et$_2$O (100 mL). The organic layer was separated, and the water phase was extracted with Et$_2$O (2 × 100 mL). The combined organic phases were dried (Na$_2$SO$_4$), filtered, and the solvent was evaporated in vacuo. The crude product was purified by column chromatography (SiO$_2$, MeOH/CH$_2$Cl$_2$ = 2:98) to afford the product (173 mg, 28% yield). The $^1$H and $^{13}$C NMR data are in agreement with the published data.

$^1$H NMR (400 MHz, CDCl$_3$): 8.53 (m, 4H, pyridine-H), 7.35 (m, 4H, pyridine-H), 7.22 (s, 2H, thiophene-H), 2.86 (t, $J = 7.4$ Hz, 4H, CH$_2$), 2.18-2.06 (m, 2H, CH$_2$), 2.03 (s, 6H, CH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$): 150.4, 141.5, 137.5, 137.3, 136.9, 135.0, 126.5, 119.5, 38.7, 23.2, 14.8.

Synthesis of 1

2-Bis(2-methyl-5-(4-pyridyl)-3-thienyl)cyclopentene (69 mg, 0.093 mmol) was dissolved in dry CH$_2$Cl$_2$ (3 mL) under argon and CH$_3$I (0.3 mL) was injected. The solution was stirred at room temperature for 3 h. The greenish precipitate was collected by filtration, washed repeatedly with dry CH$_2$Cl$_2$ afforded the NMR-pure 1 (55 mg, 55% yield). The $^1$H NMR data are in agreement with the published data.

$^1$H NMR (400 MHz, D$_2$O): 8.50 (d, $J = 6.8$ Hz, 4H, pyridine-H), 7.97 (d, $J = 7.2$ Hz, 4H, pyridine-H), 7.84 (s, 2H, thiophene-H), 4.22 (s, 6H, CH$_3$), 2.88 (t, $J = 7.4$ Hz, 4H, CH$_2$), 2.18-2.06 (m, 2H, CH$_2$), 2.05 (s, 6H, CH$_3$).

$^{13}$C NMR (125 MHz, MeOH-d$_4$): 150.1, 146.4, 145.9, 140.4, 136.8, 134.6, 134.3, 122.8, 47.8, 39.5, 24.0, 15.2.
$^1$H and $^{13}$C NMR spectra

Figure S1. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 1,2-bis(2-methyl-5-(4-pyridyl)-3-thienyl)cyclopentene.

Figure S2. $^{13}$C NMR spectrum (101 MHz, CDCl$_3$) of 1,2-bis(2-methyl-5-(4-pyridyl)-3-thienyl)cyclopentene.
Figure S3. $^1$H NMR spectrum (400 MHz, D$_2$O) of 1.

Figure S4. $^{13}$C NMR spectrum (125 MHz, MeOH-$d_4$) of 1.
UV/vis absorption spectra of the four-component mixture on irradiation with light

Figure S5. UV/vis absorption spectra of the four-component mixture (1, 2, CB7, and CB8; all at 15 μM) at pH 5 before (red) and after (black) irradiation at 365 nm.
NMR spectra for the different binding and switching state situations

Note: The protons \( b \), \( c \), and \( d \) (Figure 1 in main text) were assigned to aid fast identification of the binding situation. These protons define the structural frame of the symmetric DTE. They are color-coded: \( 1_o \) – black; \( 1_o\text{-CB7} \) – blue; \( 1_o\text{-CB8} \) – red; \( 1_c \) – gray; \( 1_c\text{-CB7} \) – green; \( 1_c\text{-CB8} \) – magenta.

Figure S6. \(^1\)H NMR spectra (all at pD 5.0) of (a) \( 1_o \) (500 \( \mu \text{M} \)); (b) \( 1_o \) in the presence of CB7 (both at 500 \( \mu \text{M} \)); (c) \( 1_o \) in the presence of CB8 (both at 500 \( \mu \text{M} \)); (d) \( 1_o \) in the presence of CB8 and CB7 (all at 500 \( \mu \text{M} \)). \( 1_o \) binds preferably to CB8.

Figure S7. \(^1\)H NMR spectra (all at pD 5.0) of (a) \( 1_c \) (500 \( \mu \text{M} \)); (b) \( 1_c \) in the presence of CB7 (both at 500 \( \mu \text{M} \)); (c) \( 1_c \) in the presence of CB8 (both at 500 \( \mu \text{M} \)); (d) \( 1_c \) in the presence of CB8 and CB7 (all at 500 \( \mu \text{M} \)). \( 1_c \) binds preferably to CB8.
**Figure S8.** $^1$H NMR spectra (all at pD 5.0) of (a) 2 (1 mM); (b) 2 in the presence of CB7 (both at 500 µM); (c) 1c (500 µM); (d) 1c in the presence of CB7 (both at 500 µM); (e) mixture 1c and 2 in the presence of CB7 (all at 500 µM). 2 displaces 1c completely from CB7.

**Figure S9.** $^1$H NMR spectra (all at pD 5.0) of (a) 2 (1 mM); (b) 2 in the presence of CB7 (both at 500 µM); (c) 1c (500 µM); (d) 1c in the presence of CB7 (both at 500 µM); (e) mixture of 1c and 2 in the presence of CB7 (all at 500 µM). 2 displaces 1c completely from CB7.
Figure S10. \(^1\)H NMR spectra (all at pD 5.0) of (a) 2 (1 mM); (b) 2 in the presence of CB8 (both at 500 µM); (c) 1\(_o\) (500 µM); (d) 1\(_o\) in the presence of CB8 (both at 500 µM); (e) mixture 1\(_o\) and 2 in the presence of CB8 (all at 500 µM). 2 displaces 1\(_o\) completely from CB8.

Figure S11. \(^1\)H NMR spectra (all at pD 5.0) of (a) 2 (1 mM); (b) 2 in the presence of CB8 (both at 500 µM); (c) 1\(_c\) (500 µM); (d) 1\(_c\) in the presence of CB8 (both at 500 µM); (e) mixture of 1\(_c\) and 2 in the presence of CB8 (all at 500 µM). 2 displaces 1\(_c\) partially from CB8.
References