Supporting Information for:

Nanoporous Films with Photoswitchable Absorption Kinetics Based on Polymerizable Columnar Discotic Liquid Crystals

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Experimental methods

Methods-Sample preparations
Clean glass substrates (3 x 3 cm) were prepared by washing with acetone and isopropanol and finally dried. The nanoporous materials were made by making a solution of 4-((2,3,4-tris(undec-10-en-1-yloxy)phenyl)diazeyln)-benzoic acid 3 (3.2 equivalents) and 1,10-decane di thiol (4.8 equivalents) in CHCl3/MeOH (9:1 v/v) and adding this solution to the required amount of 1,3,5-tris(5-methyl-1H-benzo[d]imidazol-2-yl)benzene (McTB, 1 equivalent) (50 mg mL-1). Finally, Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (Irgacure 819, 3 wt%) was added as photo-initiator. 100/200 µL of the solution was casted on a clean glass substrate of 3 x 3 cm and spin coated at 2000 rpm for 30 seconds. The temperature was then raised to 70°C and the sample was photo-polymerized using an EXFO Omnicure S2000 lamp with 8 mW/cm2 of intensity, for 10 minutes, resulting in a bright orange non-soluble polymer. Then, the sample was placed in DMSO and shaken for 3h to remove the template. Lastly, the DMSO was extracted and the sample was dried in a vacuum oven at 40°C.

Methods-UV-VIS switching experiment
The photoinitiated switching between trans and cis was measured by making a solution of 3 in 10 mL chloroform (93.01 µM). The UV-VIS spectrum was measured with a baseline set for chloroform. Trans to cis switching was measured by irradiating with 365 nm UV-light (700 mA) for respectively 5, 10, 15, 30, 60 seconds and measuring a new UV-VIS spectrum after each irradiation time. Cis to trans switching was measured by first irradiating the sample for 2 minutes with UV-light (365 nm) and then irradiating the sample 5, 10, 15, 30 and 60 seconds with blue light of 450 nm (350 mA) and measuring the UV-VIS spectra.

The photo and back isomerization between trans and cis of the polymer were measured in solid state onto glass substrates via UV-VIS spectroscopy. The baseline is set for the clean glass. Trans to cis switching was measured by irradiating with 365 nm UV-light (700 mA) for 4h and then a new UV-VIS spectrum every 5, 10 or 20 minutes in the end due to the stabilization. Cis to trans back switching was measured by first irradiating the sample for 4 hours with UV-light (365 nm) and then in the dark a spectrum was taken every 30 minutes for 9 hours.

Methods-Cis to trans decay experiment
Cis to trans decay experiments were performed by irradiating a solution of 3 (13.8 mg) in CDCl3 (0.7 mL) with UV-light of 365 nm (700 mA) for 5 minutes. Then a 1H-NMR was measured after 0, 5, 22 and 27 hours. Integrals were compared to the single proton peak on the benzene ring.

Half-life determination
The graph data of Figure S15 was fitted with the equation for half-life (1):

\[ N(t) = N_0 \times (0.5)^{t/t_{0.5}} \]  

Where \( N(t) \) represents the amount of cis at time = t, \( N_0 \) the amount at t = 0 (3.92 mM), t the time (h) and \( t_{0.5} \) represents the half-life time (h) at a specific temperature.

Dye-Selectivity tests
Measurements were done in a quartz cuvette and stirred at 400 rpm. Concentrations were calculated from the molar extinction coefficient of Rhodamine 6G at 474 nm using Lambert-Beer’s Law in water. The mass of the films was weighed on a microbalance before the measurement. The volume was kept constant at 3 mL. For absorption measurements, the initial concentration of the dye was 10 µM (40 mg/L) and the absorbance was measured every minute during 10 h. Measurements were done upon time at room temperature for a sample before irradiation (trans isomer) and after irradiated with UV-light during 6 hours (cis isomer).

Fickian diffusion model fitting
Dye uptake for the full-time scale was directly fitted using the Fickian transport model (Equation 2), which correlates the absorption profile of the dye, in this case Rhodamine 6G in a single pore of the porous material with the decrease in concentration in solution.
\[ C_b(t) = \int_{x=0}^{x=l/2} C_0 \left( 1 - erf \frac{x}{\sqrt{4 \mathcal{D} t}} \right) dx \]  

With \( C_b \) as concentration of the dye (mg/L) in the solution at \( y(t) \), \( C_0 \) concentration dye at \( t(0) \), \( t \) time (s), \( x \) the pore length (\( \mu m \)) and \( \mathcal{D} \) the absorption coefficient of the adsorbate.

Eq. 1 was fitted to the batch absorption curves obtained for the cis and the trans isomers (Figure S18) by applying a range of diffusion coefficients. The best fit value was determined by minimizing the sum \( S \) of absolute weighted difference between the measured and fitted data points (Eq. 3)

\[ S = \sum_{i=1}^{N} \left| \frac{y_i - f(x_i)}{y_i} \right| \]  

With \( y_i \) as concentration of the dye (mg/L) in the solution at \( t \), \( f(x_i) \) concentration dye calculated according to Eq.2, and \( S \) the sum of absolute weighted deviations between \( f(x_i) \) and \( y_i \).

The fitting procedure was performed on a reduced number of data points (20 from initial 100) to shorten the fitting time. The equilibrium concentration of the dye (\( C_{eq} \)) was obtained by extrapolating Eq. 2 to infinite time \( C_0 \) (\( t=\infty \)). Best fit for trans and cis isomers are presented in the report.
Supporting figures and tables

NMR Spectra

**Figure S1.** $^1$H-NMR spectrum of alkene ester 2 in CDCl$_3$

**Figure S2.** $^{13}$C-NMR spectrum of alkene ester 2 in CDCl$_3$
Figure S3. $^1$H-NMR spectrum of azobenzoic acid 3 in CDCl$_3$. 
Figure S4: $^{13}$C-NMR spectrum of azobenzoic acid 3 in CDCl$_3$

Figure S5. COSY spectrum of alkene ester 2 in CDCl$_3$
Figure S6. COSY spectrum of azobenzoic acid 3 in CDCl₃

Figure S7: COSY spectrum of azobenzoic acid 3 in CDCl₃

Figure S8. HSQC spectrum of azobenzoic acid 3 in CDCl₃
Figure S9. HMBC spectrum of alkene ester 2 in CDCl₃

Figure S10. HMBC spectrum of azobenzoic acid 3 in CDCl₃
Figure S11. FT-IR spectrum of alkene ester 2

Figure S12. DSC trace and POM image of azobenzoic acid 3 at 75°C
Figure S13. DSC 2nd cycle of TB·Azoac₃ complex in a 3.2:1 mixture heating and cooling at 10°C/min

Figure S14. MAXS and WAXS diffractogram of complex TB·Azoac₃ at RT.
Figure S15. $^1$H-NMR spectra after 0, 5, 22 and 27 hours of thermal relaxation in CDCl$_3$.

| Time (h) | Area | Concentration (mM) |
|----------|------|-------------------|
| 0        | 0.17 | 3.92              |
| 5        | 0.14 | 3.31              |
| 22       | 0.07 | 1.76              |
| 27       | 0.06 | 1.53              |

Table S1: Area of $^1$H-NMR converted to concentrations after different relaxation times

Figure S16. Plot of the concentration for the $cis$ isomer at different relaxation times (black) and plot of the half-life time fitted model (red).
Figure S17: Cis-trans back-isomerization of the polymer accelerated using blue light of 455 nm.

Figure S18: MAXS of the 3:1 polymer before and after UV irradiation corresponding to the Trans and Cis state respectively at room temperature.

Figure S19: Plot of absorption Rhodamine 6G upon time for trans and cis porous polymers.
