Supporting Information

Polysilsesquioxane Nanowire Networks as an “Artificial Solvent” for Reversible Operation of Photochromic Molecules

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1. Materials and methods

All chemicals were of analytical grade and were used as received. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance III 400 MHz (for the characterization of 3) or a Bruker Avance III HD 500 MHz (for determining the compositions of the photostationary states) NMR spectrometer. Chemical shifts (δ) in the $^1$H NMR spectra are reported in parts per million (ppm) relative to residual solvent resonances (2.51 ppm for DMSO-d$_6$ or 7.26 ppm for CDCl$_3$). Multiplicities in the $^1$H NMR spectra are reported as s (singlet), d (doublet), t (triplet), and m (multiplet). Chemical shifts (δ) in the $^{13}$C NMR spectra are reported in ppm relative to TMS relative to residual solvent resonances (77.16 ppm for CDCl$_3$). For determining the compositions of photostationary states on PNN-coated substrates, the substrates were washed extensively with CDCl$_3$ or DMSO-d$_6$ in the dark and the NMR spectra of the resulting solutions were rapidly recorded. For all azo compounds, we verified (by monitoring thermal back-isomerization in solution) that the delay between washing the substrates and recording the spectrum did not cause changes in the compositions of the photostationary states. Electrospray ionization mass spectrometry (ESI-MS) measurements were carried out on a Waters Micromass Q-TOF spectrometer. Scanning electron microscopy (SEM) was carried out on a Zeiss Ultra-55 scanning electron microscope and on a Thermo Fischer Scientific Quattro S Environmental scanning electron microscope. Solution and solid-state UV/Vis absorption spectra were recorded on a Shimadzu UV-2700 spectrophotometer. For all the solid-state absorption spectra, glass slides derivatized with thin layers of polysilsesquioxane nanowire networks (PNNs) were used as the baseline. For photoirradiation experiments, we used a 365 nm UVP UVGL-25 lamp (light intensity ~0.7 mW/cm$^2$) as the UV light source, a 420 nm Prizmatix Mic-LED light-emitting diode and a 460 nm Prizmatix Mic-LED light-emitting diode as blue light sources (both light-emitting diodes had a collimated power of 400 mW), and a 520 nm Prizmatix Ultra High Power light-emitting diode (collimated power of 900 mW) as the green light source.

2. Synthesis of photochromic compounds

Compound 1 was purchased from Sigma-Aldrich. Compounds 2, 4, 5, 6, 7, 8, and 9 were synthesized based on previously reported procedures. Compound 3 was synthesized in one step from the previously reported 2,2,2′,2′-tetrafluoro-4-hydroxyazobenzene as described below.

2,2,2′,2′-tetrafluoro-4-methoxyazobenzene (3): A solution of 2,2,2′,2′-tetrafluoro-4-hydroxyazobenzene (135 mg; 0.5 mmol), iodomethane (1 mL), and potassium tert-butoxide (67 mg; 0.6 mmol) in dry THF (10 mL) was refluxed overnight in a sealed tube. Then, the solvent was evaporated in vacuo and the solid residue was dissolved in dichloromethane (50 mL). The resulting solution was washed with deionized water (100 mL × 2), dried over MgSO$_4$, and concentrated in vacuo. The obtained crude product was purified using silica gel column chromatography (eluent: hexane/dichloromethane = 3:1) to afford 95 mg of 3 (yield = 72%).

$^1$H NMR (400 MHz, CDCl$_3$): δ = 7.35–7.27 (m, 1H), 7.03 (t, 2H), 6.61–6.58 (d, 2H), 3.88 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 162.78 (t, $^3$J$_{CF}$ = 14.0 Hz), 157.61 (dd, $^1$J$_{CF}$ = 259.9 Hz, $^3$J$_{CF}$ = 7.1 Hz), 155.63 (dd, $^1$J$_{CF}$ = 257.6 Hz, $^3$J$_{CF}$ = 4.3 Hz), 132.25 (t, $^2$J$_{CF}$ = 10.0 Hz), 130.52 (t, $^1$J$_{CF}$ = 10.3 Hz), 126.17 (t, $^2$J$_{CF}$ = 9.4 Hz), 112.65 (m), 99.07 (dd, $^2$J$_{CF}$ = 24.0 Hz, $^4$J$_{CF}$ = 3.1 Hz), 56.34 (s). HRMS calcd for C$_{15}$H$_9$F$_4$N$_2$O [M + H]$^+$, m/z = 285.0651; found, 285.0645.
Figure S1. $^1$H NMR spectrum of 3 (400 MHz, CDCl$_3$).
Figure S2. $\text{^13C NMR}$ spectrum of 3 (100 MHz, CDCl$_3$).
Figure S3. HR ESI-MS spectrum of 3.
3. Derivatizing glass slides with polysilsesquioxane nanowire networks (PNNs)

Glass slides (26 mm × 56 mm) were derivatized with PNNs using the dip-coating method reported before. A glass slide was immersed in a vigorously stirred solution of trichloromethylsilane in toluene (c = 0.3%, v/v) in humid air (relative humidity ≈ 35%). After 30 min, the slide was removed from the solution, washed consecutively with toluene, ethanol, and water, and finally dried with a stream of nitrogen. This procedure resulted in a 1.6-μm-thick layer of PNNs (based on SEM imaging). The same procedure was used to prepare PNNs on silicon wafer (coated with a native oxide film), indium tin oxide (ITO), aluminum, and stainless steel. To prepare a sample of freestanding PNNs, the same procedure was performed without any solid substrate. To prepare a layer of PNNs on polypropylene, the substrate was treated with oxygen plasma for 3 min before being subjected to the same coating procedure.

BET surface area of freestanding PNNs was determined in the laboratory of Prof. Cafer T. Yavuz at the Korea Advanced Institute of Science and Technology (KAIST). The sample (50 mg) was degassed overnight at 150 °C and the surface area was calculated from N₂ isotherms measured at 77 K (Figure S4a) using BET theory, in the range of relative pressure determined by the Rouquerol plots (Figure S4b; 0.1–0.25).

**Figure S4.** (a) N₂ physisorption isotherms of PNNs at 77 K (STP = standard temperature and pressure). (b) Rouquerol plot for PNNs.
To determine the thermal stability of PNNs, we subjected them to heating experiments while inspecting the sample in-situ using environmental scanning electron microscopy. First, we grew layer of PNN on silica-coated Si wafers (thickness of the silica layer = 300 nm). In-situ heating was carried out on a Quattro S environmental SEM equipped with an in-situ heating stage and operating at 20 kV under 200 Pa (~0.002 atm) of water vapor. In a representative experiment, a series of 475 images (available upon request) was recorded within 120 min during heating from 30 °C to 800 °C at a heating rate of 8 °C/min (see Figure S5 for the temperature vs. time plot). Video S1 shows the evolution of the structure of the PNNs subjected to heating under these conditions.

Figure S5. Temperature–time profile in the in-situ heating experiments.
4. Depositing photochromic compounds onto PNN-derivatized surfaces

A PNN-derivatized glass slide was immersed in a toluene solution of a photochromic compound \((c = 12 \text{ mM unless stated otherwise})\) for 1 s and then dried in air. Longer immersion times did not increase the amount of photochromic compound deposited within the PNNs.

PNN-derivatized glass slides doped with photochromic compounds were characterized by UV/Vis absorption spectroscopy (PNN-derivatized glass slides prior to dipping in a solution of a photochromic compound were used as the baseline). Figure S6a shows a solid-state absorption spectrum of a PNN-derivatized slide after dipping in a 12 mM solution of 1. A sharp peak (centered at the same wavelength as 1 in toluene solution) and no absorption in the high-wavelength region are indicative of efficient dispersion of 1 within the PNNs. For comparison, an identical glass slide but without a PNN layer was immersed in the same solution of 1. Solid-state absorption spectrum of this slide features a much broader and red-shifted band centered at \(\lambda_{\text{max}} \approx 350 \text{ nm}\), indicative of H-aggregation, and increased absorption throughout the spectrum is due to light scattering by the crystallized 1. The amount of adsorbed 1 is significantly lower than that within PNN-roughened glass.

The amount of photochromic compound deposited on PNN-roughened glass slides was estimated by washing the slides with toluene and analyzing the resulting solution by UV/Vis absorption spectroscopy. Surface coverage, \(\sigma\), was calculated assuming that a 1.6 \(\mu\)m thickness of the PNN layer covers both sides of each glass slide. We found that the \(\sigma\) value of all the photochromic compounds scaled linearly with the concentration of their toluene solutions, in which the slides were immersed (see, e.g., Figure 1d for compound 1).

To verify that washing with toluene quantitatively removes the absorbed compound from the PNN-roughened glass, we recorded UV/Vis spectra of the slides after washing. We found that the absorption of these slides was identical to that before the deposition of the photochromic compound (i.e., baseline absorption, as shown in Figure S6b for 1 as an example). Importantly, desorbing a photochromic compound with a good solvent regenerated the original PNN-coated glass slide, which could subsequently be used for the deposition of another compound. We verified that repeated absorption-desorption cycles did not affect the quality of the PNN layers.

**Figure S6.** (a) Solid-state UV/Vis absorption spectra of a bare glass slide dipped in a 12 mM toluene solution of 1 (red) and a PNN-roughened glass slide dipped in the same solution (blue). (b) Blue: UV/Vis absorption spectrum of a PNN-roughened glass slide dipped in a 12 mM toluene solution of 1. Red: UV/Vis spectrum of the same slide after washing with toluene.
5. Photoswitching of azobenzenes on PNN-roughened glass

Experimental data supporting the results in Figure 2 of the main text are shown in Figure S7 below. Thermal half-lives of cis-1, $\tau_{1/2}$, showed relatively little dependence on the solvent; in contrast, a drastic reduction of $\tau_{1/2}$ was observed on PNN-roughened glass (Figure S7a).

Figure S7. (a) Solvent-dependent kinetics of thermal back-isomerization of cis-1 ($A = \text{absorbance at 343 nm; } \tau_{1/2} = 2.0 \text{ h for PNN-coated glass, 31.7 h for hexane, 34.1 h for toluene, 48.5 h for DMSO, and 65.4 h for methanol; red lines represent linear fits; } R^2 = 0.990 \text{ for PNN-roughened glass and 0.999 for all the liquid solvents).}$ (b) Ten cycles of reversible photoisomerization of 1 on PNN-roughened glass (3 min of UV light, followed by 2 min of blue light were applied in each cycle). (c) NMR spectra of solutions obtained by washing 1-doped, PNN-roughened glass with CDCl$_3$ after exposure to UV (top) and blue light (bottom).

We also studied the behavior of several other azobenzenes on PNN-roughened glass. For all the azobenzenes except the red-shifted compounds 2 and 3, UV light (365 nm) was used for the trans$\rightarrow$cis isomerization. For 2 and 3, green light (520 nm light-emitting diode) was used instead. The cis$\rightarrow$trans back-isomerization for all azobenzenes was accomplished with blue light or was allowed to proceed thermally in the dark. Detailed data for compounds 2, 3, 4, and 7 are shown in Figs. S8–S11 below.
Figure S8. Isomerization of azobenzene 2 on PNN-roughened glass ($\sigma = 23.8$ nmol/cm$^2$). (a) UV/Vis absorption spectra of a PNN-roughened glass slide doped with 2 before exposure to light (gray trace; overlaps with the blue trace), after exposure to green light (520 nm; green trace), and after subsequent exposure to blue light (420 nm; blue trace). (b) Changes in absorbance at 303 nm (proportional to the content of $\text{trans-2}$) as a function of green (0→180 s) and blue light (180→360 s) irradiation time. (c) Ten cycles of reversible photoisomerization of 2 on PNN-roughened glass (15 s of green light followed by 15 sec of blue light were applied in each cycle). (d) Kinetics of the thermal back-isomerization of $\text{cis-2}$ on PNN-roughened glass ($A =$ absorbance at 330 nm; red line = linear fit; $R^2 = 0.993$). (e) NMR spectra of solutions obtained by washing 2-doped, PNN-roughened glass with DMSO-$d_6$ after exposure to green (top) and blue light (bottom).
Figure S9. Isomerization of azobenzene 3 on PNN-roughened glass (σ = 20.3 nmol/cm²). (a) UV/Vis absorption spectra of a PNN-roughened glass slide doped with 3 before exposure to light (gray trace), after exposure to green light (520 nm; green trace), and after subsequent exposure to blue light (420 nm; blue trace). (b) Changes in the absorbance at 327 nm (proportional to the content of trans-3) as a function of green (0→120 s) and blue light (120→240 s) irradiation time. (c) Ten cycles of reversible photoisomerization of 3 on PNN-roughened glass (10 s of green light followed by 15 sec of blue light were applied in each cycle). (d) Kinetics of thermal back-isomerization of cis-3 on PNN-roughened glass (A = absorbance at 327 nm; red line = linear fit; R² = 0.919). (e) NMR spectra of solutions obtained by washing 3-doped, PNN-roughened glass with CDCl₃ after exposure to green (top) and blue light (bottom).
Figure S10. Isomerization of azobenzene 4 on PNN-roughened glass (σ = 22.1 nmol/cm²). (a) UV/Vis absorption spectra of a PNN-roughened glass slide doped with 4 before exposure to light (gray trace), after exposure to UV (365 nm; purple trace), and after subsequent exposure to blue light (460 nm; blue trace). (b) Changes in the absorbance at 343 nm (proportional to the content of trans-4) as a function of UV (0→150 s) and blue light (150→240 s) irradiation time. (c) Ten cycles of reversible photoisomerization of 4 on PNN-roughened glass (2 min of UV light followed by 15 sec of blue light were applied in each cycle). (d) Kinetics of thermal back-isomerization of cis-4 on PNN-roughened glass (λ = absorbance at 343 nm; red line = linear fit; R² = 0.999). (e) NMR spectra of solutions obtained by washing 4-doped, PNN-roughened glass with CDCl₃ after exposure to UV (top) and blue light (bottom).
Figure S11. Isomerization of azobenzene 7 on PNN-roughened glass ($\sigma = 18.8 \text{ nmol/cm}^2$). (a) UV/Vis absorption spectra of a PNN-roughened glass slide doped with 7 before exposure to light (gray trace), after exposure to UV (365 nm; purple trace), and after subsequent exposure to blue light (460 nm; blue trace). (b) Changes in the absorbance at 345 nm (proportional to the content of trans-7) as a function of UV (0→300 s) and blue light (300→480 s) irradiation time. (c) Ten cycles of reversible photoisomerization of 7 on PNN-roughened glass (2 min of UV light followed by 15 sec of blue light were applied in each cycle). (d) Kinetics of thermal back-isomerization of cis-7 on PNN-roughened glass ($A =$ absorbance at 345 nm; red line = linear fit; $R^2 = 0.991$). (e) NMR spectra of solutions obtained by washing 7-doped, PNN-roughened glass with CDCl$_3$ after exposure to UV (top) and blue light (bottom).
Figure S12. (a) Kinetics of thermal back-isomerization of cis-1 in DMSO vs. on PNN-roughened glass (A = absorbance at 343 nm; red lines = linear fits; $R^2 = 0.999$ for DMSO and 0.996 for PNN). Acceleration factor, $\chi = 24.8$. (b) Kinetics of thermal back-isomerization of cis-2 in DMSO vs. on PNN-roughened glass (A = absorbance at 330 nm; red lines = linear fits; $R^2 = 0.981$ for DMSO and 0.993 for PNN); $\chi = 27.0$. (c) Kinetics of thermal back-isomerization of cis-4 in DMSO vs. on PNN-roughened glass (A = absorbance at 343 nm; red lines = linear fits; $R^2 = 0.999$ for DMSO and 0.999 for PNN); $\chi = 4.53$. (d) Kinetics of thermal back-isomerization of cis-5 in DMSO vs. on PNN-roughened glass (A = absorbance at 345 nm; red lines = linear fits; $R^2 = 0.999$ for DMSO and 0.992 for PNN); $\chi = 2.29$. (e) Kinetics of thermal back-isomerization of cis-6 in DMSO vs. on PNN-roughened glass (A = absorbance at 345 nm; red lines = linear fits; $R^2 = 0.999$ for DMSO and 0.995 for PNN); $\chi = 1.95$. (f) Kinetics of thermal back-isomerization of cis-7 in DMSO vs. on PNN-roughened glass (A = absorbance at 345 nm; red lines = linear fits; $R^2 = 0.999$ for DMSO and 0.991 for PNN); $\chi = 1.67$. 
The thermal half-life of cis-3 at room temperature is very long. To estimate it, we first determined the rate constants at several different temperatures in the range 65–96 °C (Figure S13a-e). Next, we extrapolated the results to room temperature (23 °C) using the Arrhenius equation (Figure S13f) as described previously for other compounds with long thermal half-lives.\textsuperscript{7,10}

**Figure S13.** (a-e) Kinetics of thermal back-isomerization of cis-3 in DMSO at different temperatures (black lines = linear fits; $R^2$ = 0.996 (a), 0.996 (b), 0.990 (c), 0.987 (d), and 0.998 (e)). (f) Determination of the rate constant for thermal back-isomerization of cis-3 at 23 °C (dashed line = linear fit; $R^2$ = 0.999 both with and without the 23 °C point). $A$ = absorbance at 336 nm.
6. Effect of oxygen plasma on azobenzene switching on PNN-roughened glass

To investigate the effect of PNN surface polarity on the kinetics of the thermal relaxation of azobenzene, we compared the behavior of 1 on native PNN-roughened glass slides vs. the same slides treated with oxygen plasma. Oxygen plasma generates Si–OH species on the surfaces of polysilsesquioxane nanowires, thereby significantly increasing their surface polarity. The high-polarity environment can stabilize the polar, cis isomer of azobenzene, as reported previously, consequently, the spontaneous (dark) back-isomerization reaction is expected to proceed slower. Indeed, we found that treating PNN-roughened glass slides with oxygen plasma dramatically increased the \( \tau_{1/2} \) value of 1 from 2.0 h to 16.5 h (Figure S14).

**Figure S14.** Kinetics of thermal back-isomerization of cis-1 in DMSO (gray markers; red line = linear fit; \( R^2 = 0.999 \)), on PNN-coated glass (white markers; red line = linear fit; \( R^2 = 0.999 \)), and on the same PNN-coated glass treated with oxygen plasma for 3 min (green markers; red line = linear fit; \( R^2 = 0.986 \)). \( A = \) absorbance at 343 nm.

7. Photoswitching of spiropyran on PNN-roughened glass

Additional data on 8-doped PNN layers (see Figure 4) are shown in Figure S15 below.

We found that the thermal decay of 8′ significantly deviated from the first-order kinetics (Figure S15e), which can be attributed to the dimerization or oligomerization of the zwitterionic merocyanine species, as reported before. To confirm this hypothesis, we followed the decay of 8′ generated in 8-doped, PNN-roughened glass slides by exposing them to UV light for two different amounts of time (30 sec and 10 min; Figure S15f), assuming that 8′ in the slide exposed to prolonged UV irradiation would have more time to diffuse to form the relatively stable 8′ aggregates. Indeed, 8′ in the sample exposed to 10 min of UV light decayed considerably slower (Figure S15f).

Unfortunately, it has proven impossible to determine the compositions of the 8/8′ photostationary states within PNN layers using the method we adapted for the azo compounds – in all the solvents we tested for desorbing 8/8′ from PNN-coated substrates, the 8′→8 back-isomerization proceeded rapidly.
Figure S15. (a) Evolution of solid-state UV/Vis spectra of a PNN-roughened glass slide doped with 8 (σ = 18.2 nmol/cm$^2$) upon exposure to UV light (λ = 365 nm). (b) Evolution of UV/Vis spectra of a UV-adapted PNN-roughened glass slide doped with 8 upon exposure to green light (λ = 520 nm). (c) Five cycles of reversible photoisomerization of 8 on PNN-roughened glass. (d) Spontaneous disappearance of an image created in 8-doped, PNN-roughened glass by exposing it to 0.1 mW/cm$^2$ UV light for 10 min. (e) Kinetics of the thermal back-isomerization of 8' on PNN-roughened glass (A = absorbance at 554 nm). 8' was generated by exposing 8-doped, PNN-roughened glass to 0.1 mW/cm$^2$ UV light for 10 min. (f) Kinetics of the thermal back-isomerization of 8' generated by exposing 8-doped, PNN-roughened glass slides to 0.7 mW/cm$^2$ UV light for 30 sec vs. 10 min.
8. Photoswitching with sunlight

Experiments with PNN-roughened glass slides doped with azobenzene 1 were carried out during early afternoon on December 15, 2018. Experiments with PNN-roughened glass slides doped with spiropyran 8 were carried out during early afternoon on February 4, 2019 (all experiments were carried out in Rehovot, Israel). On both days, the weather was sunny, with a temperature of ~24 °C. As the “visible filter”, we used a combination of a UVP 98-0118-02 filter (allowing light of 250–400 nm and >700 nm to pass through) and polyethylene terephthalate (UV filter with a ~320 nm cutoff). Together, these filters allowed UVA light (320–400 nm) to pass through (in addition to NIR light, which none of the photochromic compounds tested here absorbs; Figure S16). For the UV filter, we used polycarbonate (~400 nm cutoff; Figure S16). We determined the UV intensity of sunlight as ~0.5 mW/cm² with our “visible filter” and ~1.8 mW/cm² without any filter.

Figure S16. UV/Vis transmittance of sunlight through visible and UV filters used in this work.

Figure S17. (a) Solid-state UV/Vis spectra of a 1-doped, PNN-roughened glass slide following exposure to sunlight through a visible filter (transparent to UVA light, 320-400 nm) for 3 min and subsequent exposure to sunlight through a UV filter (400 nm cutoff) for 1 min. (b) Changes in absorbance at 343 nm as a function of sunlight exposure time. (c) NMR spectra of solutions obtained by washing 1-doped, PNN-roughened glass slides with CDCl₃ after exposing the slides to sunlight through a visible filter (top) and a UV filter (bottom).
We also verified that efficient switching between photostationary states featuring ~20% and >80% of trans-1 using sunlight could be achieved within PNNs fabricated on other materials, such as indium tin oxide (ITO), aluminum, and stainless steel (Figure S18). The compositions of the photostationary states

![Figure S18](image1)

**Figure S18.** Representative SEM images of PNNs on ITO (left), aluminum (center), and steel (right) and the compositions of photostationary states of 1 under sunlight exposure with visible and UV filters.

![Figure S19](image2)

**Figure S19.** (a) Photograph of an initially transparent 8-doped PNN-roughened glass slide following exposure to sunlight for 30 s. (b) Photographs of four PNN-roughened glass slides doped with 8, following exposure to sunlight for increasing amounts of time.

9. Photoswitching of azopyrazole on PNN-roughened glass

Phenylazotrimethylpyrazole 9 (Figure S20) was prepared by modifying a previously published procedure. The compound was donated by Mr. Anton I. Hanopolskyi.

First, we determined the thermal half-life of 9 in DMSO solution as ~173 h:

![Figure S20](image3)

**Figure S20.** Kinetics of thermal back-isomerization of cis-9 in DMSO (A = absorbance at 330 nm; red line = linear fit; R² = 0.995).
Photoswitchable properties of $9$ on PNN-roughened glass were then studied and the results are shown in Figure S21. We found that the thermal half-time of $9$ within PNNs = 15.2 h, i.e., 11.4 times faster than the solution (DMSO) value. Our results show that the PNN-induced acceleration of the thermal relaxation of azopyrazole $9$ was smaller than for azobenzenes 1–3, for which acceleration factors in the range 23.5–27 were found (Figure 3c).

**Figure S21.** Isomerization of pyrazole $9$ on PNN-roughened glass ($\sigma = 20.6$ nmol/cm$^2$). (a) UV/Vis absorption spectra of a PNN-roughened glass slide doped with $9$ before exposure to light (gray trace), after exposure to UV light (purple trace), and after subsequent exposure to green light (green trace). (b) Changes in absorbance at 343 nm (proportional to the content of trans-$9$) as a function of UV (0→300 s) and green light (300→360 s) irradiation time. (c) Ten cycles of reversible photoisomerization of $9$ on PNN-roughened glass (2 min of UV light followed by 10 sec of green light were applied in each cycle). (d) Kinetics of thermal back-isomerization of cis-$9$ on PNN-roughened glass ($A =$ absorbance at 330 nm; red line = linear fit; $R^2 = 0.990$). (e) NMR spectra of solutions obtained by washing $9$-doped, PNN-roughened glass with CDCl$_3$ after exposure to UV (top) and green light (bottom).
10. Supporting references


