

Modulation of porosity in a solid material enabled by bulk photoisomerization of an overcrowded alkene.

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Abstract: Incorporation of photoswitchable molecules into solid state materials holds promise for fabrication of the responsive materials, the properties of which can be controlled on-demand. However, the possible applications of these materials are limited, due to the restrictions imposed by the solid state environment on the incorporated photoswitches, which render the photoisomerization inefficient. Here we present responsive porous switchable framework materials based on a bistable chiroptical overcrowded alkene incorporated in the backbone of the rigid aromatic framework. As a consequence of the high intrinsic porosity, the resulting framework readily responds to a light stimulus as demonstrated by solid-state Raman and reflectance spectroscopies. Solid state ¹³C NMR spectroscopy highlights efficient and quantitative bulk photoisomerization of the incorporated light-responsive overcrowded olefins in the solid material. Taking advantage of the quantitative photoisomerization, the porosity of the framework, and as a consequence gas adsorption, can be reversibly modulated in response to light and heat.

Inspired by biological systems, a vast number of artificial molecular machines and switches, capable of elaborate structural dynamics, have been developed.¹⁻⁴ However, in solution stimulated molecular motion is inevitably overwhelmed by isotropic thermal noise which thereby precludes any form of collective action and the extraction of macroscopic work, since the molecules behave independently from one another.⁵⁻⁷ On the contrary, solid state organization can translate stimuli-controlled nanoscopic changes into useful material properties and precludes to practical outputs. Thus, a challenging endeavour of current research is to organize molecular machines and switches in the solid state to impede random, thermal motion and amplify mechanical effects along multiple length scales: this effort requires reliable strategies, allowing for restricting random motion and limiting the degrees of freedom to selected modes, without impairment of the rotary or switching functions.⁸⁻¹⁰

One strategy to achieve these goals is the use of solid porous materials¹¹⁻¹⁵ which can incorporate switchable moieties and provide the free volume essential for unhindered dynamics, thereby serving

as a static scaffold for the flexible components. Indeed, it was demonstrated recently that molecular rotors^{16–23}, shuttles²⁴, switches²⁵ and motors²⁶ can display their designed motion while incorporated in porous architectures. The incorporation of photoresponsive molecular switches in solid materials, on the other hand, opens new opportunities to enrich the properties of these materials in a non-invasive manner with high spatiotemporal precision.^{27,28} This notion was illustrated in pioneering studies on photoresponsive porous solids functionalized with azobenzenes^{29–39}, dithienylethenes^{40–48} or spiropyrans^{49–51} showing photomodulation of gas uptake, diffusion, or guest release. However, bulk photoisomerization in solids suffers from poor efficiency due to geometrical constraints and scarce light penetration depth and is therefore limited to near-surface region while the bulk of the material remains unaffected. So far, photoswitching in bulk of solid materials has only been reported for rare cases of porous molecular crystals sustained by soft interactions²⁹ and dithienylethene-based MOFs^{42,45} which, because of minimal structural arrangement, were shown to undergo efficient photoisomerization even in densely packed molecular crystals.⁴⁸ Hence, attaining bulk photoresponsivity, involving large structural motion triggering significant changes in properties, in robust solid materials remains a fundamental challenge.

Chiral overcrowded alkenes constitute a unique class of molecular photoswitches which exhibit a stereogenic centre in the vicinity of the olefinic bond. The steric congestion present in the system forces the molecule to adopt helical chirality, which is inverted in the photochemically generated metastable isomer (Figure 1a).^{52,53} With appropriate structural modification the thermal stability of the metastable isomer can be increased by many orders of magnitude up to the point that unidirectional rotation is inhibited and the molecule can be operated as a chiroptical bistable switch.⁵⁴ Previously, incorporation of overcrowded alkenes in soft matter matrixes^{55–60}, or their anchoring to a surface⁶¹ allowed for fabrication of materials showing unique, dynamic properties. Here we report incorporation of an overcrowded alkene bistable chiroptical switch in highly porous and stable organic frameworks sustained by covalent bonds, herein referred to as porous switchable frameworks (PSFs), allowing for the switching of porosity and hence gas uptake. The overcrowded alkene was integrated into the framework backbone via its fluorenyl (stator) moiety, leaving the naphthyl moiety (rotor) as pendant (Figure 1b). In the resulting architecture, the PSF backbone serves as a scaffold for the switchable unit without preventing the light-controlled large amplitude motion of the naphthyl moiety of the photoswitch. The high intrinsic porosity of the PSF-type materials alleviates the constraints imposed by the solid environment on the molecular motion and allows for bulk photoisomerization in the solid state as well as photomodulation of the materials porosity. This transformation probably involves cooperative rearrangement of the flexible, yet constrained framework, and carries the local strain and conformational changes into conformational

restructuring of the framework, thus enabling on-command and non-invasive modulation of the observed porosity.

Figure 1.

Synthesis of Porous Switchable Frameworks. The fabrication of robust porous materials with overcrowded alkene-based chiroptical switch **1_{st}** directly inserted into the framework through covalent bonds was realized by a Yamamoto cross-coupling reaction. The reaction between a network-forming tri-dimensional monomer, tetra-*p*-bromo-phenylmethane (**TPM-Br₄**), and an overcrowded alkene-based chiroptical switch **1_{st}-Br₂** bearing two bromide substituents afforded the desired frameworks (Figure 2a). The choice of the tetraphenyl methane (**TPM**) building block was motivated by the very high pore capacity and BET surface area up to ~5000 m²/g of the **TPM**-based framework^{23,62}, which we envisaged to be suitable to provide a sufficient free volume for the isomerization of overcrowded alkene **1** embedded in the solid material. Two porous switchable frameworks (**PSFs**) were synthesized by varying the molar fraction of building blocks (**TPM** and **1**) used during the synthesis of the materials denoted as **PSF-1** and **PSF-2** (10:1 and 4:1 of **TPM-Br₄** to **1_{st}-Br₂** for **PSF-1** and **PSF-2**, respectively, for synthetic details and characterization, see method section and supplementary information). The resulting **PSFs** were stable up to 450 °C, as determined by thermogravimetric analysis (Figure 2d). The porosity of the materials was established by N₂ adsorption isotherms at 77 K (Figure 2c). The Langmuir and BET surface areas were as large as 4545 and 3948 m²/g for **PSF-1** and 1330 and 1177 m²/g for **PSF-2** with pore capacity of 2.39 and 0.66 cm³/g, respectively, while the pore size distribution was centred at about 1.4 nm for **PSF-1** and 1.2 nm for **PSF-2**, as calculated by non-Local Density Functional theory (Supplementary Fig. 12, Table 2). The hysteretic loops are indicative of the framework swellability.⁶²⁻⁶⁴ The homogeneity of the samples and the molecular composition of the frameworks were established by elemental analysis (Supplementary Table 1) and quantitative ¹³C MAS NMR (Figures 2b and S6): the results correspond to the fractions of the building blocks used in the synthesis of the frameworks. Thus, the fraction of the switch unit in the **PSFs** can be modulated at will, and **PSF-1** and **PSF-2** were used for further experiments.

Figure 2.

Photochemical and thermal isomerization in solution. The photochemical isomerization behaviour of **1_{st}-Br₂** in solution was studied with ¹H and ¹³C NMR, UV/Vis absorption and Raman spectroscopies. In the ¹H NMR spectrum, irradiation of **1_{st}-Br₂** at 365 nm in CD₂Cl₂ solution resulted in appearance of a new set of ¹H downfield shifted resonances, indicating the formation of the metastable isomer (**1_{mst}-Br₂**) with almost quantitative yield (PSS₃₆₅ 94:6 of **1_{mst}-Br₂**:**1_{st}-Br₂**) (Figure 3a, see Methods Section for details). Likewise, in the ¹³C NMR spectrum, a new set of upfield shifted resonances for carbons C_a (35.6 → 34.6 ppm), and C_c (30.0 → 28.5 ppm) was observed, in line with the formation of **1_{mst}-Br₂** (Figure 3b). In the UV/Vis absorption spectrum, irradiation at 365 nm led to a gradual bathochromic shift of the absorption band centred at 366 nm. This shift of absorption is consistent with the formation of the metastable twisted isomer of the overcrowded alkene-based photoswitch. During the photo-isomerization, an isosbestic point was maintained at 385 nm, indicating a unimolecular process (Figure 3c). In the Raman spectrum of **1_{st}-Br₂**, a band centred at 1582 cm⁻¹ is present, characteristic of the stretching of the olefinic bond of the photoswitch **1_{st}-Br₂**. Upon irradiation of the sample at 365 nm, this band disappeared, while a new broad band centred at 1542 cm⁻¹, characteristic of the stretching of the olefinic bond of the metastable overcrowded alkene **1_{mst}-Br₂** appeared. The reverse **1_{mst}-Br₂** → **1_{st}-Br₂** isomerization in solution could be achieved by irradiation of the **1_{mst}** at 470 nm upon which the ¹H NMR resonances of **1_{st}-Br₂** reappeared (PSS₄₇₀ 97:3 **1_{st}-Br₂** to **1_{mst}-Br₂**) (Supplementary Fig. 2,3) and the original UV/Vis absorption and Raman spectra were recovered (Figure 3c,d).

Figure 3

Photochemical isomerization in the solid state. The photochemical isomerization behaviour (Figure 4a,b) of the switch **1** embedded in the solid **PSF-1** and **PSF-2** frameworks was studied with Diffuse-Reflectance UV/Vis (DR UV/Vis) and Raman spectroscopies (Figure 4c-f). Upon exposure to light irradiation, spectral changes almost identical to those found in solution were detected for both porous materials (**PSF-1** and **PSF-2**) indicating facile photoisomerization of the overcrowded alkene embedded in the PSFs. In the DR UV/Vis spectra of **PSF-1** and **PSF-2**, bathochromic shifts were observed upon irradiation at 365 nm and hypsochromic shifts upon irradiation at 470 nm in line with the light reversible **1_{mst}** ↔ **1_{st}** photoisomerization (Figure 4c and d, respectively). Additionally, the evident colour change from white to yellow of the material exposed to 365 nm light was readily visible, which is consistent with the bathochromic shift of the absorption spectra of the material (Figure 4b). For both materials, the alternating cycles of the UV and Visible light irradiations could be repeated for several cycles without any noticeable sign of fatigue indicating

high stability of the material (Figure 4c and d insets for **PSF-1** and **PSF-2**, respectively). The Raman spectra of both solid **PSFs** were dominated by the intense broad band centred at 1610 cm^{-1} characteristic of the benzene rings stretching mode, associated with the relatively large fraction of **TPM** building blocks in both frameworks. Nevertheless, irradiation of the porous materials at 365 nm resulted in the expected decrease in Raman intensity at 1582 cm^{-1} and the appearance of a distinctive new band at 1542 cm^{-1} . Irradiation at 470 nm fully reverted these changes for the **PSF-1** framework as the band characteristic of the **1_{mst}** isomer could not be detected in the Raman spectrum, clearly demonstrating the reversible photoisomerization of **1** incorporated in the solid material (Figure 4e). Conversely, **1** incorporated in the **PSF-2** framework showed only a partial back-isomerization to **1_{st}** upon irradiation at 470 nm, as indicated by the incomplete disappearance of the band at 1542 cm^{-1} . Complete reversibility occurred by thermal treatment as shown below (160°C, 15 h [see Methods for details](#)).

Figure 4

Solid state ^{13}C MAS NMR proved to be an invaluable tool to highlight the structural changes occurring to the individual components of the framework at a molecular level, thus providing a precise and quantitative measure of the extent of photoisomerization in the material bulk. For the solid state NMR studies the **PSF-2** framework was chosen as a starting point owing to its higher content of the photoswitch **1**, which facilitated quantitative analysis of the spectra. To this end, the **PSF-2** material was irradiated at 365 nm with low power density ($\sim 3\text{ mW/cm}^2$ for 54 h) and ^{13}C MAS NMR spectra were recorded. Upon irradiation of **PSF-2** at 365 nm similar changes to those observed in solution were recorded, that is, the upfield shift of the resonances of the carbons C_a ($35.0 \rightarrow 34.1\text{ ppm}$), and C_c ($29.2 \rightarrow 28.0\text{ ppm}$) (Figure 5b). This similarity to the solution studies allowed us to unequivocally ascribe these changes to photochemical formation of the metastable isomer (**1_{mst}**) embedded in the framework, in agreement with DR UV/Vis and Raman spectral data (Figure 4). Deconvolution of the spectrum and integration of the resonances originating from the respective diastereoisomers (Figure 5b middle panel, [Supplementary Table 5](#)) showed that the photostationary state achieved upon irradiation of the bulk material (93:7 of **1_{mst}**:**1_{st}**) is as high as that in solution (94:6 of **1_{mst}**:**1_{st}**). These results are remarkable as quantitative photoswitching of solid materials have been previously reported only for flexible MOFs containing dithienylethenes derived struts^{42,45} and porous molecular crystals sustained by weak van der Waals interactions.²⁹

Furthermore, similar quantitative results were obtained for three distinct samples, thus demonstrating reproducibility of these data within a small error margin (Supplementary Fig. 16).

Upon irradiation at 470 nm, the metastable form reverted only partially to the stable form as determined by solid state NMR (Supplementary Fig. 17, Table 5) and in accordance with Raman spectroscopy. Conversely, complete reversibility was achieved by thermal treatment: indeed, owing to the noticeable thermal stability, the samples were cured at 160°C (15 h) and 200°C (2 h), the **1_{mst}** isomer could be quantitatively converted back to **1_{st}** isomer, as shown by the recovery of the original ¹³C MAS NMR spectrum (Figure 5b right panel). Accordingly, the **PSF-1** material showed the same, nearly quantitative, light and heat induced isomerization cycle which could be followed and quantified by MAS NMR, despite the moderate switch fraction in the framework (Supplementary Fig. 19 and 20). This intriguing trend confirms the virtually unhindered confinement in which the switch function was preserved by insertion in the low-density framework.

Figure 5

Gas adsorption experiments. We anticipated that the accessible volume of the framework would be reversibly changed during the overall stable-metastable-stable isomerization sequence and therefore, gas adsorption experiments were performed. Indeed, N₂ adsorption isotherms at 77 K revealed the striking reduction of the pore volume between pristine and irradiated **PSF-2** material, which accounts for 20% at $p/p^{\circ}=0.6$ (Figure 6). Furthermore, this phenomenon was nearly fully reversible after heating of the irradiated material, as demonstrated by N₂ adsorption isotherm (Figure 6c, Supplementary Table 3). Conversely, only a partial recovery of the surface area (approximately 40% of the initial value) was observed for the **PSF-2** material upon prolonged irradiation at 470 nm, in line with the incomplete back-isomerization of the **1_{mst}** to **1_{st}** under these conditions as determined by solid state NMR (Supplementary Fig. 17,18). In addition, the light and heat induced switching cycle of **PSF-1** yielded N₂ adsorption isotherm behaviour consistent with that of **PSF-2**, although a smaller reduction was observed, in line with the lower switch concentration and the larger pore volume of the sample (Supplementary Fig. 19). The 20% reduction of pore volume on 365-nm irradiated **PSF-2** was corroborated by CO₂ adsorption isotherms at 195 K (from 500 to 402 cm³/g STP, Supplementary Fig. 13). This decrease in the adsorption capacity upon irradiation of almost 100 cm³/g STP is a benchmark and exceeds the values so far reported of about 33 cm³/g (STP) for the dithienylethene-based MOF⁴⁵ and 52 cm³/g (STP) for the porous star-shaped azobenzene tetramer molecular crystal²⁹ and is comparable to the

value of the MOF with azobenzene pendants.⁶⁵ The similar relative drop in adsorption for both probe gases (approximately 20% for N₂ and CO₂) and negligible changes in the dipole moment of the switch **1** upon photoisomerization (Supplementary Fig. 20) indicate that the electrostatic interactions do not play a dominant role in the change of sorption capacity of the **PSF-2** framework.^{65,66} Indeed, the CO₂ adsorption isotherms at variable temperature (273 K, 283 K and 298 K, Supplementary Fig. 14) analysed by van t'Hoff equation gave the isosteric heat of adsorption at low coverage of 27.1 and 27.9 kJ/mol at 0.2 mmol/g for **PSF-2** with **1_{st}** and **1_{mst}**, respectively, indicating that the frameworks exhibit similar interactions with CO₂. Hence, the differences in the observed porosity of the material upon isomerization of **1** most likely originate from structural change of the switch and the framework upon photoisomerization. The structures and geometries of both stable and metastable isomers were optimized by DFT on the B3LYP 6-31G(d,p) level of theory. While the stable isomer adopts a folded conformation in which both methyl and naphthyl substituents are located on the same side of the central olefinic bond, the steric congestion in the metastable isomer forces the molecule to adopt a twisted conformation. As a result the dihedral angles between substituents of the central double bond increase from 13.4° and 14.4° in **1_{st}** to 25.2° and 27.3° for **1_{mst}**. When the switch is inserted covalently in the framework, it bears two *p*-phenyl substituents, which belong to the **TPM** unit and interact with naphthyl moiety at shorter distances in the stable than the metastable configuration (Supplementary Fig. 21). Owing to the flexibility and hyper-cross-linked nature of the 3D framework, the differential local interactions between the switch and the comonomeric unit presumably trigger an extensive rearrangement of the architecture, generating the remarkable impact on the pore volume and the gas uptake.

Figure 6

Conclusions In summary, we have developed a successful strategy to fabricate light-responsive porous materials in which overcrowded alkene based photoswitches are covalently incorporated in a solid and robust framework. Our approach is unique since it realizes a continuous covalent framework by a copolymerization process involving the functionalized switch and a comonomer, which sustains the architecture and promotes the porosity. Two porous switchable frameworks consisting of a tetraphenylmethane moiety (**TPM**) and various amounts of photoswitch were obtained by the formation of carbon-carbon bonds, such that the switch is an intrinsic part of the framework itself. The great stability of the solid state framework, combined with the dynamics of the light-responsive switches were proven to modulate gas sorption, yet retaining high porosity in

each respective geometry. Such unique prerogative of high porosity for both states of the bi-stable switch provided by our strategy, was crucial to achieve unhindered reversible photoisomerization in the solid state. The proposed synthetic strategy is simple and straightforward, yet, it guarantees the full incorporation of the light-responsive switch as a functional component in a controlled amount with respect to a pore-forming unit. By combination Diffuse-Reflectance UV/Vis and Raman spectroscopies, it was demonstrated that the chiroptical switch embedded in the porous framework maintains its function and can undergo wavelength-dependent isomerization upon exposure to light. Furthermore, solid-state NMR studies performed on the framework with higher photoswitch content showed that the photostationary state ratio of the chiroptical switch **1** inserted in the framework, as established in the solid sample upon exposure to UV irradiation, is essentially the same as the one reached in solution. These findings are highly remarkable since the values of the photostationary state previously reported for bulk solid materials had never been as high as in solution. Furthermore, the porosity and gas uptake of the porous switch frameworks can be reversibly modulated with light and heat owing to the unique quantitative photoisomerization in the bulk of the porous material. Furthermore, these extensive aromatic frameworks entail exceptional thermal and chemical stability, which make them usable for many cycles. The novel prototypical materials allow us to envision the generation of responsive properties of practical utility, such as the regulation of adsorption on command. Our findings open up also opportunities to design responsive porous organic frameworks containing rotors, motors and switches exhibiting specialized functions beyond controlled gas uptake and release such as switchable size-based or enantiomer-based⁶⁷ separation technologies.

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Author contributions

W.D., F.C., S.J.W., P.S. and B.L.F. conceived the project. W.D. synthesized bistable switch **1-Br₂**, F.C. synthesized **PSF** materials. W.D. performed photoisomerization studies in solution, Raman and DR UV/Vis studies on PSFs. J.P. performed gas adsorption isotherms and evaluation of adsorption energy. S.B. and A.C. performed SS NMR studies on synthesized materials. F.C. performed DSC, TGA and gas uptake experiments. W.D. performed DFT studies. S.J.W., A.C. and B.L.F. guided the project. W.D., A.C., S.J.W., P.S., B.L.F. wrote the manuscript. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

Figure legends

Figure 1. Photoisomerization of overcrowded olefin-based bistable switch. **a** Schematic representation of the structural changes upon photochemical E/Z isomerization of bistable overcrowded alkene **1** and top view of the DFT (B3LYP/631-G(d,p)) optimized structures of stable (**1_{st}**, left) and metastable (**1_{mst}**, right) isomers. **b** Schematic representation of photoswitching of overcrowded alkene **1** in pores of the PSF framework. In both panels stable isomer was coloured with yellow and metastable isomer in beige.

Figure 2. Synthesis, structure, sorption and thermal properties of PSF materials. **a** Schematic representation of synthesis of the **PSF-1** and **PSF-2** materials from tetra-*p*-bromo-phenyl methane (**TPM-Br₄**) and photoswitch **1_{st}-Br₂** via Yamamoto coupling. **b** Solid state ¹³C MAS NMR (75.04 MHz, 12.5 kHz, recycle delay=100 s) spectrum of **PSF-2** material. The peaks highlighted in blue correspond to the cyclohexene ring. **c** N₂ gas adsorption isotherms (77 K) of activated **PSF-1** (green trace) and **PSF-2** (blue isotherm). Filled and empty symbols denote adsorption and desorption, respectively. Additional N₂ adsorption isotherms for **PSF-2** are shown in Figure 6. **d** TGA profiles show the stability of **PSF-1** (green line) and **PSF-2** (blue line) up to 450°C.

Figure 3. Photochemical isomerization of bistable switch 1-Br₂ in solution. **a** Schematic representation of the structural change upon photochemical E/Z isomerization of overcrowded alkene based bistable switch **1-Br₂**. **b** Comparison of aliphatic part of ¹³C NMR (CD₂Cl₂, 400 MHz, See Figure 3a for atom labelling) spectra of **1_{st}-Br₂** (black spectrum, bottom) and **1_{mst}-Br₂** (as a PSS₃₆₅ mixture obtained upon sufficient irradiation at 365 nm, red spectrum, top). **c** Changes in UV/Vis absorption spectra of **1_{st}-Br₂** (8 μM, DCM, black spectrum) upon irradiation at 365 nm resulting in a large bathochromic shift of the absorption bands characteristic of the metastable isomer (red spectrum) and subsequent irradiation at 470 nm leading to a recovery of the initial spectrum (red, dashed spectrum). Grey lines indicate intermediate states, while black arrows direction of spectral changes upon irradiation at 365 nm. Note that isosbestic points were maintained throughout isomerizations indicating that both isomerizations are unimolecular. **d** Comparison of changes in Raman (785 nm, 50 mW, solutions were drop-casted on quartz substrate) spectra of **1_{st}-Br₂** (black solid line), upon irradiation at 365 nm resulting in appearance of new broad band at 1542 cm⁻¹ characteristic of **1_{mst}-Br₂** (red solid line, PSS₃₆₅), and subsequent irradiation at 470 nm leading to recovery **1_{st}-Br₂** and initial spectrum (red dashed line, PSS₄₇₀). Relevant bands corresponding to stretching modes characteristic of metastable (1542 cm⁻¹) and stable (1582 cm⁻¹) isomers were indicated with arrows.

Figure 4. Photochemical isomerization studies in the solid state, **a** Schematic representation of light-induced structural changes in the PSFs upon isomerization of **1** from stable to metastable

isomer. **b** Pictures of the **PSF-2** material before (left panel) and after (right panel) irradiation at 365 nm for 30 min (power density ~ 20 mW/cm²). **c,d** Changes in the diffuse-reflectance UV/Vis spectra of the PSFs (**PSF-1** - panel **c**, **PSF-2** - panel **d**) materials upon consecutive irradiation at 365 nm followed by irradiation at 470 nm for 45 min (power density ~ 8 mW/cm²). Pristine materials (black, solid lines, pristine), photostationary state reached upon irradiation at 365 nm (red, solid line, PSS₃₆₅), and photostationary state reached upon subsequent irradiation of the material at 470 nm (red, dashed lines, PSS₄₇₀). The insets show changes in the Kubelka-Munk function at 470 nm over alternative irradiation cycles. **e,f** Changes in the Raman spectra (785 nm, 50 mW) of PSFs (**PSF-1** - panel **e**, **PSF-2** - panel **f** materials upon consecutive irradiation at 365 nm followed by irradiation at 470 nm. Pristine materials (black, solid lines, pristine), photostationary state reached upon irradiation at 365 nm (red, solid lines, PSS₃₆₅), and photostationary state reached upon subsequent irradiation of the material at 470 nm (red, dashed lines, PSS₄₇₀). The insets show changes in the area of the band centred at 1547 cm⁻¹ over alternative irradiation cycles.

Figure 5. Solid-state NMR observations of the reversible structural switching in PSF-2. **a** Schematic representation of the structural changes of **1** (**1_{st}**) (left) incorporated in the **PSF-2** framework, upon irradiation at 365 nm (**1_{mst}**) (middle) and subsequent heating (**1_{st}**) (right). **b** Changes in the ¹³C{¹H} CP-MAS NMR spectra of the **PSF-2** framework at each stage of the structural transformations, pristine (left), after photoisomerization (middle) and thermal annealing (right). In the stable isomer the cyclohexene ring and the corresponding NMR resonances are highlighted in blue while in the metastable isomer they are highlighted in red. After photoisomerization a minor amount of the stable state was detected, as indicated by blue coloured peaks (middle spectrum).

Figure 6. Switching of the gas adsorption properties. N₂ adsorption isotherms of the **PSF-2** framework at 77 K of the pristine material (**a**, blue isotherm), after irradiation at 365 nm for 54 h (**b**, red isotherm) and heating (**c**, blue isotherm). The filled and open circles denote adsorption and desorption isotherms, respectively. The arrows indicate the adsorbed gas amount at p/p°=0.6. The isotherm of the pristine material is an enlargement of the isotherm reported in Figure 2c.

Methods

Synthesis of 4-(2,7-dibromo-9H-fluoren-9-ylidene)-3-methyl-1,2,3,4-tetrahydrophenanthrene. A two-neck round bottom flask equipped with reflux condenser was charged with 2,7-dibromofluorenone **3**, (340 mg, 1.0 mmol, 1.0 eq.), Lawessons reagent (814 mg, 2.0 mmol, 2.0 eq.) and dry toluene (20 mL) was added and the reaction mixture was heated at 100 °C for 2 h. Next, the reaction mixture was cooled to room temperature, filtrated over a plug of cotton, concentrated *in vacuo* and the residue was purified by column

chromatography (SiO₂, pentane/DCM 5:1) and concentrated *in vacuo* to afford thioketone 4 as a brown oil (135 mg, 0.38 mmol, 38%), which was used immediately in the next step. A separate flask was charged with hydrazone 2 (85 mg, 0.38 mmol, 1.00 eq.) and DMF (5 mL) was added. Next, the reaction mixture was cooled to -40 °C, and a solution of PIFA ([Bis(trifluoroacetoxy)iodo]benzene) (172 mg, 0.40 mmol, 1.05 eq.) in DMF (2 mL) was added dropwise. The reaction mixture was stirred at -40 °C for 5 min during which the color of the reaction mixture changed to pink. Next, the solution of previously prepared thioketone 4 in DCM (10 mL) was added dropwise. The reaction mixture was allowed to warm up to room temperature overnight, and HMPT (Tris(dimethylamino)phosphine) (186 mg, 1.14 mmol, 207 μL, 3.00 eq.) was added and stirring was continued at room temperature for 24 h. Next the reaction mixture was diluted with EtOAc (60 mL), washed two times with water (2x30mL), brine (30 mL), dried over MgSO₄, filtrated and concentrated in *vacuo*. The crude product was purified by flash column chromatography (SiO₂, pentane/DCM) to afford 1 as a yellow solid (133 mg, 0.26 mmol, 68%). ¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, J = 1.6 Hz, 1H), 7.92 (dd, J = 12.3, 8.2 Hz, 2H), 7.79 (d, J = 8.5 Hz, 1H), 7.63 (d, J = 8.1 Hz, 1H), 7.54 (dd, J = 8.1, 1.7 Hz, 1H), 7.52 – 7.36 (m, 3H), 7.26 – 7.21 (m, 1H), 7.17 (dd, J = 8.1, 1.8 Hz, 1H), 5.96 (d, J = 1.7 Hz, 1H), 4.20 (p, J = 7.0 Hz, 1H), 2.87 – 2.74 (m, 1H), 2.66 – 2.40 (m, 2H), 1.36 – 1.12 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 147.7, 140.0, 139.4, 139.1, 138.4, 137.0, 132.2, 132.1, 131.6, 131.2, 130.0, 129.5, 129.2, 128.3, 128.1, 127.9, 127.0, 125.7, 125.0, 124.2, 120.9, 120.7, 120.4, 119.8, 34.8, 30.4, 29.4, 20.5. HRMS (ESI pos.) calcd C₂₈H₂₀Br₂ [M⁺] 516.9926 found 519.9921.

Synthesis of PSFs. 1 (32.4 mg, 0.063 mmol) and 5 (400 mg, 0.63 mmol) were transferred in an oven-dried 50 ml two-neck round-bottom flask. The flask was closed with a silicon septum and three vacuum-nitrogen cycles were performed. Then, dry THF (30 ml) was transferred by means of a syringe and the mixture was stirred at RT under N₂ until complete dissolution of the solids. Meanwhile, inside a glovebox, Ni(COD)₂ (1 g, 3.64 mmol) and 2,2'-bipyridyl (570 mg, 3.65 mmol) were transferred to an oven-dried 250 ml three neck flask equipped with a nitrogen inlet. One of the necks was sealed with a silicon septum. The closed flask was brought outside the glovebox, covered with aluminium foil and quickly put under fluxing N₂. Then, dry DMF (90 ml), dry THF (20 ml) and cyclooctadiene (COD) (0.5 ml, 4.08 mmol) were added by means of a syringe. The violet mixture was stirred at RT for a few seconds, before cooling it to 0 °C with an ice bath. As the mixture was cooling down, an oven-dried 50 ml pressure-equilibrating dropping funnel was mounted on the last neck of the flask, flushed with N₂ and finally sealed with a rubber septum. The solution of 1 and 5 previously prepared was transferred to the dropping funnel by means of a syringe and added to the violet mixture over 15-20 min. At the end of the addition, the resulting mixture was stirred at 0 °C for an additional 15 min, then it was allowed to cool at RT and left to react under N₂ for 48 h. Subsequently, the flask was opened to air and diluted aq. HCl was added (10 ml, 2.5% wt); the mixture was stirred at RT until it turned to a bright blue color. At this point, the suspended white solid was recovered by filtration and washed with THF (2 x 30 ml), water (3 x 30 ml), chloroform (2 X 30 ml) and acetone (2 x 30 ml). PSF-1 was obtained as pale yellow powder (156 mg, 70 % yield). PSF-2 was synthesized following the same procedure described for PSF-1. The following quantities were used: 1 (75 mg, 0.145 mmol), 5 (370 mg, 0.581 mmol), Ni(COD)₂ (1g,

3.64 mmol), COD (0.5 ml, 4.08 mmol), 2,2'-bipyridyl (570 mg, 3.65 mmol), DMF (90 ml), THF (20+30 ml). PSF-2 was obtained as deep yellow powder (183.6 mg, 78%).

UV/Vis absorption and reflectance spectroscopy. Solution UV/Vis absorption spectra were collected on Hewlett-Packard 8453 diode array spectrometer in a 1 cm quartz cuvette. A 1-Br₂ solution (8 μM, DCM) was irradiated at 365 nm for 10 min until no further changes were observed (i.e. PSS₃₆₅ was reached). Next, the PSS₃₆₅ nm mixture was irradiated at 470 nm for 20 min until no further changes were observed in the UV/Vis spectrum. Throughout the irradiation experiments an isosbestic point was maintained at 385 nm. Solid state DR UV/Vis spectra were collected on Jasco V-570 UV/Vis NIR spectrophotometer equipped with Jasco ISN-470 integrating sphere. Prior to the measurement the samples of either PSF-1 or PSF-2 (2 mg) were ground with a pestle in a mortar with BaSO₄ (100 mg). The resulting samples were put on the sample holder closed with a quartz window and spectra were collected. Samples were irradiated at either 365 nm or 470 nm for 5 min with LEDs placed 10 cm from the sample holder window.

Raman spectroscopy. Raman spectra were collected on Perkin Elmer Raman Station connected to the Olympus BX51M microscope equipped with a 785 nm 50 mW laser. For solution studies, samples of either 1-Br₂ or 1-Br₂-PSS₃₆₅ were drop-casted from a DCM solution (10⁻³ M) on a quartz slide and Raman spectra were recorded. For PSF-1 or PSF-2, samples were placed on a quartz substrate and irradiated at 365 nm and subsequently 470 nm and Raman spectra were recorded.

NMR Spectroscopy in solution. For ¹³C and ¹H NMR spectra of both PSS₃₆₅ and PSS₄₇₀ mixtures a sample of 1-Br₂ (10 mM, DCM-*d*₂) was irradiated at 365 nm for 30 min at RT and spectra were recorded. Subsequently, the same sample was irradiated at 470 nm for 1 h to reach PSS₄₇₀.

IR spectroscopy. ATR FT-IR spectroscopy was performed on a PerkinElmer FT-IR Nexus spectrometer in the range 400-4000 cm⁻¹. Compound 1-Br₂ was drop-casted from a 10⁻³ M solution in DCM directly on the ATR crystal. Compound 1-Br₂-PSS₃₆₅ was obtained by irradiation of a 10⁻³ M solution at 365 nm for 20 min, then the sample was drop-casted on the ATR crystal and analysed. PSF-1 and PSF-2 were irradiated while deposited on the ATR crystal, then spectra of PSF-1-PSS₃₆₅ and PSF-2-PSS₃₆₅ were collected.

Solid state NMR. ¹³C Magic Angle Spinning (MAS) NMR experiments were carried out at 75.5 MHz with a Bruker Avance 300 instrument operating at a static field of 7.04 T equipped with high-power amplifiers (1 kW) and a 4 mm double resonance MAS probe. ¹³C{¹H} ramped-amplitude Cross Polarization (CP) experiments were performed at a spinning speed of 12.5 kHz using a contact time of 2 ms, a 90° pulse for proton of 2.9 μs and a recycle delay of 5 s. Spectral profiles, recorded with 30840 scans, were simulated by mixed Gaussian/Lorentzian line shapes in the ratio of 0.5 : 0.5. Quantitative ¹³C Single-Pulse Excitations (SPE) MAS NMR experiments were performed at a spinning speed of 12.5 kHz with a recycle delay of 100 s and a 90° pulse of 3.6 μs length. The simulation analyses could provide the quantification of TPM (78%) and switch (22%) units in PSF-2 architecture and TPM (89%) and switch (11%) in PSF-1, in agreement with the synthetic procedure. Crystalline polyethylene was taken as an external reference at 32.8 ppm relative TMS.

N₂ and CO₂ sorption isotherms at 77K. N₂ adsorption/desorption isotherms were collected at liquid nitrogen temperature (77 K) while and CO₂ adsorption/desorption isotherms were carried out at solid carbon

dioxide temperature (195K), 273 K, 283 K and 298K and up to 1 bar of pressure by means of a Micromeritics ASAP 2020 HD analyzer. All samples were degassed by heating at 130°C for 5 h under vacuum (approx. 10^{-3} mmHg) before carrying out the analysis. Specific surface area values were calculated from the N₂ isotherms using the Brunauer, Emmett, and Teller (BET) model and the Langmuir model. Pore size distributions were calculated from nitrogen adsorption curves considering a slit pore geometry and the Non-Local Density Functional Theory (NLDFT). The isosteric heat of adsorption was calculated by applying van t'Hoff equation.

Irradiation procedure in the solid state. Irradiation experiments for solid-state NMR and gas adsorption analyses were performed using a Spectroline ENF-20C/FE lamp (6W) for 365 nm irradiation and a home-made LED lamp built with 9 LEDs (3W each) for 470 nm irradiation. About 40 mg of sample were distributed over a Petri dish ($\varnothing = 4$ cm) and thoroughly mixed every 60 min. The lamps were set at approximately 3 cm from the sample. The PSF-2 material has been irradiated for 54 h at 365 nm and 72 h at 470 nm while PSF-1 material for 74 h at 365 nm. Heat-promoted back-switching experiments were performed heating the samples at 200 °C or 160°C for 15 h under vacuum by means of a Buchi B-585 glass oven.

DFT calculations. Density functional theory (DFT) calculations were carried out with the Gaussian 09 program (rev. D.01).⁶⁸ All of the calculations were performed on systems in the gas phase using the Becke's three-parameter hybrid functional⁶⁹ with the LYP correlation functional^{70,71} (DFT B3LYP/6-31G(d,p)). Each geometry optimization was followed by a vibrational analysis to determine that it represents a minimum on the potential energy surface.

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Data availability. The data associated with the reported findings are available in the manuscript or the Supplementary Information. Other related data are available from the corresponding author upon request.

Additional information

Supplementary information and chemical compound information are available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to S.J.W., A.C., or B.L.F.

