

Photoinduced reversible switching of porosity in molecular crystals based on star-shaped azobenzene tetramers

Massimo Baroncini^{1*}, Simone d'Agostino¹, Giacomo Bergamini¹, Paola Ceroni¹, Angiolina Comotti^{2*}, Piero Sozzani², Irene Bassanetti², Fabrizia Grepioni^{1*}, Taylor M. Hernandez¹, Serena Silvi¹, Margherita Venturi^{1,3} and Alberto Credi^{1*}

The development of solid materials that can be reversibly interconverted by light between forms with different physico-chemical properties is of great interest for separation, catalysis, optoelectronics, holography, mechanical actuation and solar energy conversion. Here, we describe a series of shape-persistent azobenzene tetramers that form porous molecular crystals in their *E*-configuration, the porosity of which can be tuned by changing the peripheral substituents on the molecule. Efficient *E* → *Z* photoisomerization of the azobenzene units takes place in the solid state and converts the crystals into a non-porous amorphous melt phase. Crystallinity and porosity are restored upon *Z* → *E* isomerization promoted by visible light irradiation or heating. We demonstrate that the photoisomerization enables reversible on/off switching of optical properties such as birefringence as well as the capture of CO₂ from the gas phase. The linear design, structural versatility and synthetic accessibility make this new family of materials potentially interesting for technological applications.

Photochromic compounds are very appealing for science and technology because they enable the implementation of light-induced functions within molecular, supramolecular and macromolecular species, biological constructs and bulk materials^{1,2}. Azobenzene is one of the most attractive photochromes because of its facile functionalization and its clean, fast and reversible photoisomerization between two isomers (*E* and *Z*) that exhibit some significantly different physico-chemical properties³. Current and prospective applications of research on azobenzene photoisomerization include holographic information storage⁴, optoelectronic devices⁵, magnetic memories⁶, nanomachines⁷, control of chemical reactivity⁸, responsive surfaces⁹ and materials^{10,11}, energy conversion¹² and drug design¹³.

In view of these applications, azobenzene photoisomerization in the solid state is attracting much interest, but the relatively large free volume change associated with this reaction^{14,15} poses a considerable challenge to its practical realization^{16,17}. The *E* → *Z* photoisomerization of azobenzene derivatives is well documented for azobenzene-containing polymers¹⁸, liquid crystals^{9,18–24}, thin films^{25–27} and crystals at the solid–liquid interface²⁸, and a limited number of examples are reported in porous materials^{29–33} (for example, metal–organic and covalent organic frameworks) and in molecular crystalline forms in which the azobenzene moiety is functionalized with polar substituents^{34–36}. Our strategy is based on the use of molecules containing a central node that imparts a star-like three-dimensional arrangement to azobenzene moieties for the fabrication of molecular crystals endowed with permanent porosity capable of promoting reversible *E/Z* isomerization in the solid state. Microporous molecular crystals^{37–40} may show substantial advantages in terms of preparation, processability, structural diversification and functional flexibility in comparison with porous

metal–organic⁴¹ and covalent⁴² frameworks. Moreover, the novel molecular crystals exhibit extrinsic porosity (that is, porosity resulting solely from the solid-state molecular packing), which is uncommon and challenging to design^{37–40}.

As an embodiment of these concepts we describe the preparation, structure and reversible photoisomerization in the solid state of porous tetra(azobenzene)methane compounds, which consist of four azobenzene units covalently linked to a tetrahedral carbon atom. We envisaged that the extended branches of the *E*-azobenzene units and the rigid tetrahedral structure of the molecule could prevent a tightly packed arrangement⁴³, resulting in a porous crystal structure in which the gained free volume, combined with the occurrence of weak van der Waals interactions, may allow photoswitching of the azobenzene units in the solid state.

Results and discussion

Synthesis and spectroscopic analysis in solution. Compounds ***E*₄-1a–c** (Fig. 1a), with their four azobenzene units in the *E* configuration and hydrogen, methyl and *tert*-butyl peripheral substituents, respectively, were synthesized in 70% yield by Mills coupling of tetra(4-aminophenyl)methane with four equivalents of the appropriately *para*-substituted nitrosobenzene in acetic acid. The products were isolated from the reaction mixture by filtration and purified easily by recrystallization (Supplementary Figs 1–6).

The absorption spectra of ***E*₄-1a–c** in CH₂Cl₂ (Supplementary Figs 14–16) show the typical features of *E*-azobenzene and are consistent with the presence of four such units, although they do not correspond exactly to the sum of the respective individual spectra. For example, the $\pi\pi^*$ band of ***E*₄-1c** ($\lambda_{\text{max}} = 345$ nm) is redshifted by 750 cm^{−1} in comparison with that of the 1,1'-dimethyl-*E*-azobenzene

¹Dipartimento di Chimica 'G. Ciamician', Università di Bologna, via F. Selmi 2, 40126 Bologna, Italy. ²Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, via R. Cozzi 55, 20125 Milano, Italy. ³Istituto per la Sintesi Organica e la Fotoreattività, Consiglio Nazionale delle Ricerche, via Gobetti 101, 40129 Bologna, Italy. *e-mail: massimo.baroncini@unibo.it; angiolina.comotti@mater.unimib.it; fabrizia.grepioni@unibo.it; alberto.credi@unibo.it

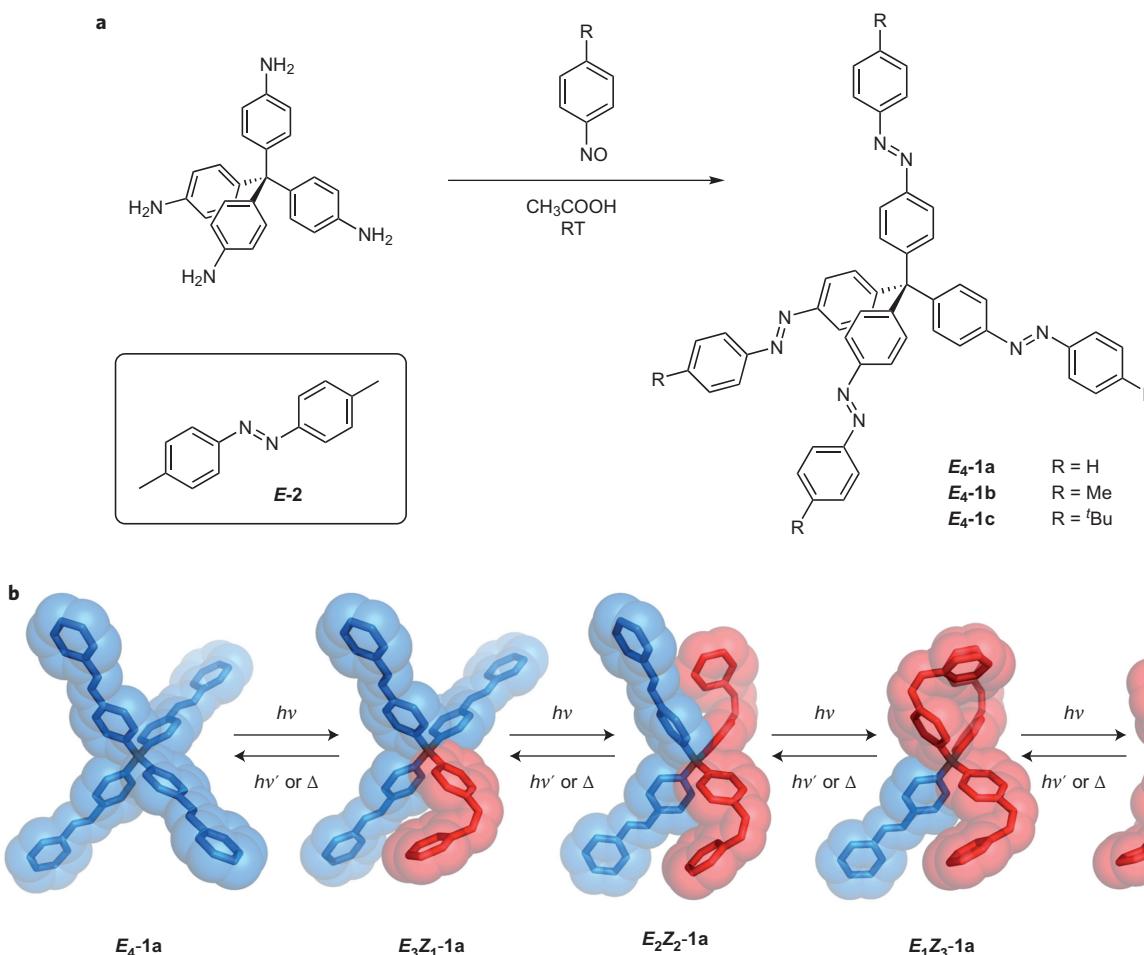


Figure 1 | Star-shaped azobenzene tetramers and their photochemical transformations. **a**, Synthetic route and molecular formula of **E₄-1a-c** and of model compound **E-2**. **b**, Molecular mechanics (MM3) optimized structure of the interconverting *E/Z* stereoisomers of **1a**. *E*- and *Z*-azobenzene units are blue and red, respectively, and hydrogen atoms are omitted for clarity. Compounds **1b** and **1c** exhibit similar behaviour. RT, room temperature.

model **E-2**, suggesting that the four units are not fully independent from an electronic point of view, possibly because of homoconjugation effects. Irradiation of **E₄-1c** at 365 nm causes the *E* → *Z* isomerization (Fig. 1b), with an initial quantum yield for azobenzene unit of $\Phi_{EZ} = 0.18$ (for **E-2**, $\Phi_{EZ} = 0.17$). The fact that isosbestic points in the absorption spectra are not precisely maintained and that the *E* → *Z* photoisomerization quantum yield decreases throughout the irradiation indicates that the four azobenzene units of **1c** exhibit similar but not identical photophysical and photochemical properties. Nevertheless, the *E* → *Z* conversion following exhaustive irradiation at 365 nm in CH_2Cl_2 is >95%. ¹H NMR analysis of the photostationary state (PSS) obtained in C_6D_6 under the same conditions shows that the composition is 89% **Z₄-1c**, 6% **E₁Z₃-1c**, 3% **E₂Z₂-1c**, <1% **E₃Z₁-1c** and <1% starting material, corresponding to an overall *E* → *Z* conversion of 97%. For the sake of simplicity, hereafter we will refer to the PSS obtained following 365 nm irradiation of **E₄-1c** in CH_2Cl_2 as **Z₄-1c**. Compounds **1a,b** exhibit a similar behaviour, as reported in Supplementary Figs 7–11 and 14–16.

Structure of the molecular crystalline solids. Compounds **E₄-1a-c** crystallize in the tetragonal system (Supplementary Table 2 and Supplementary Figs 21–30). In all solids the tetrahedral node lies on a -4 crystallographic axis, and the four azobenzene units are all mutually related by symmetry. The main structural motif observed in crystalline **E₄-1a-c** is the interlocking of adjacent molecules along the fourfold rotoinversion axes, which run parallel to the crystallographic *c*-axis direction (Fig. 2b). This

corresponds to the direction of maximum crystal growth and is apparent both in the ideal and experimental morphology of the crystals obtained from solution or constituting the deposited thin films (Supplementary Fig. 32). The ‘open’ molecular geometry determined by the four tetrahedrally arranged *E*-azobenzene units (Fig. 2a) combined with the presence of the bulky substituents, especially *tert*-butyl groups in **E₄-1c**, makes it particularly difficult to achieve an efficient space occupation in the solid state, as evidenced by a packing coefficient value of 0.59.

The molecular piles are placed side by side in the crystal, with shape taking control of the self-assembly. The resulting crystal packing (Fig. 2c) is characterized in **E₄-1c** by the presence of empty channels along the *c*-axis direction, with a 10.4% porosity (calculated as the ratio between the accessible volume by a 1.2 Å probe and the cell volume). A channel-like porosity is also observed, though less pronounced, in **E₄-1b** (8.1%), whereas for **E₄-1a** the porosity (6.7%) is confined to discrete, non-communicating regions along the pile (Supplementary Fig. 25). In the case of **E₄-1c**, the shape of the channels responsible for crystal porosity shows the periodic presence of necks (Fig. 2d), a feature that is unique to **E₄-1c**. A closer inspection of the structure reveals that the necks along the channels arise from the terminal *tert*-butyl substituents, and the widest sections of the channels are delimited by benzene moieties (Supplementary Fig. 33). ¹³C magic-angle spinning (MAS) NMR spectra of **E₄-1b** and **E₄-1c** show 10 and 11 resonances, respectively, in accordance with the highly symmetric arrangement of the molecule in the crystal structure.

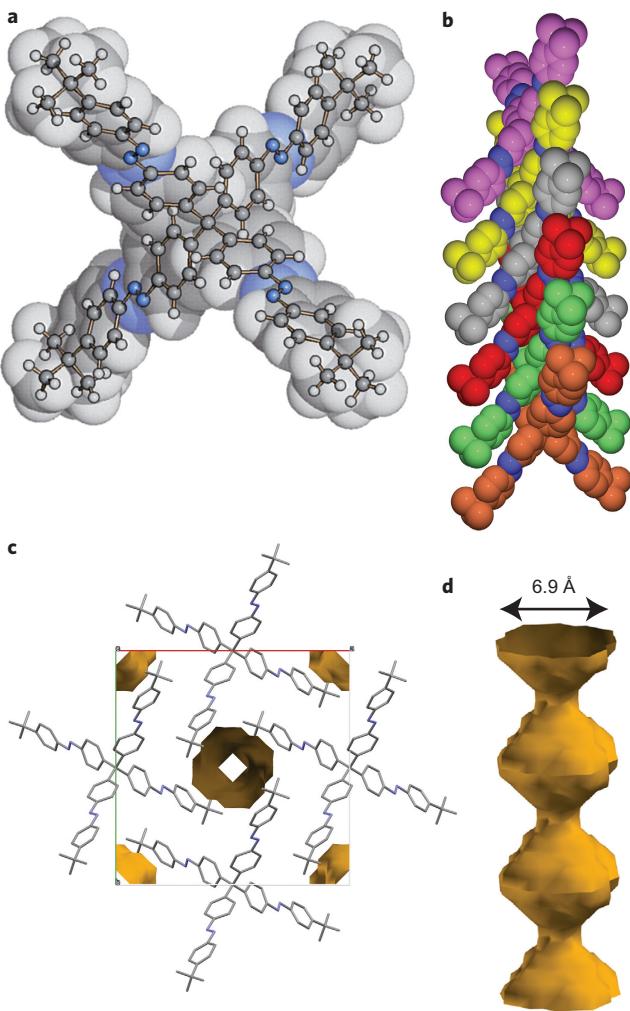


Figure 2 | Structural properties of *E*₄-1c in the crystalline state. **a**, Ball-and-stick and space-filling representations of the molecular structure of *E*₄-1c as observed in the solid state (colour code: blue, nitrogen; grey, carbon; white, hydrogen). The four azobenzene units are all equivalent by symmetry. **b**, Space-filling view of the interlocking of adjacent molecules along the *c*-axis direction. For the sake of clarity, hydrogen atoms are omitted and carbon atoms in different molecules are displayed with different colours. **c**, Relative arrangement of molecular piles in crystalline *E*₄-1c and representation of the empty channels extending along the *c*-axis direction. **d**, Side view of a channel segment.

(Supplementary Figs 12 and 13). No solvent molecules are observed in the spectra, as independently confirmed by thermogravimetric analysis (Supplementary Fig. 31).

Solid-state photoreactivity and photoinduced phase transitions. To investigate the photoreactivity in the solid state, powders of *E*₄-1a–c were subjected to 365 nm irradiation for 6 h in an NMR tube. ¹H NMR spectroscopic analysis performed on the irradiated solid dissolved in C₆D₆ showed, indeed, the presence of *Z*-azobenzene units (Supplementary Fig. 11). Quantitative information on the photoisomerization reaction was obtained from irradiation experiments carried out on dry films of 1a–c deposited on a quartz slide by spin-coating or drop-casting from solution. The X-ray powder diffraction (XRPD) pattern measured on drop-cast films of *E*₄-1a–c is superimposable on the pattern calculated on the basis of single-crystal data (Fig. 3a and Supplementary Figs 26–29), indicating that the layer contains crystalline particles. In the following we will describe in detail the

properties of 1c only, as compounds 1a and b exhibit a very similar behaviour (Supplementary Table 1 and Supplementary Figs 19, 20, 34 and 35).

The quality and homogeneity of the spin-coated thin films enabled characterization by transmission UV-visible absorption spectroscopy. The absorption spectra of *E*₄-1c (Fig. 3c) and *Z*₄-1c (Fig. 3d) in the solid film are similar to those recorded in solution and show the typical $\pi\pi^*$ (~350 nm) and $n\pi^*$ (~450 nm) bands of azobenzene.

Irradiation of the *E*₄-1c film at 365 nm brings about spectral changes (Fig. 3c) almost identical to those found in solution, indicating efficient *E* → *Z* isomerization. From a comparison of the spectra it can be estimated that, at the PSS, about 32% of the azobenzene unit of 1c is converted to the *Z* configuration. Conversely, no effect is detected when the same experiment is performed on a film of *E*-2, indicating that the rigid tetrahedral arrangement of the azobenzene moieties is crucial for their photoisomerization in the solid. Exposure of the irradiated sample, or a film of previously prepared *Z*₄-1c, to light of 436 nm causes *Z* → *E* photoisomerization, and a PSS enriched in *E*-azobenzene units is obtained (Fig. 3d). The absorption spectrum recorded before any irradiation is fully restored by heating the film at 130 °C for 10 min (Fig. 3c,d), indicating that (1) thermal *Z* → *E* isomerization occurs, (2) *E*₄-1c is the thermodynamically stable form of 1c in the solid state and (3) the photoreaction is a clean process (Fig. 3b).

The XRPD pattern obtained after 48 h irradiation of the film still corresponds to the pattern of *E*₄-1c, while the intensity of all peaks decreases and disappears after prolonged irradiation, indicating that the material has become amorphous (Fig. 3a). Notably, the XRPD signals of the *E*₄-1c crystals are recovered upon heating the irradiated film, showing that the phase change is reversible (Fig. 3a) and correlated to the *E/Z* interconversion. To gain more insight into the effect of light on solid *E*₄-1c, we imaged the crystals with a polarizing optical microscope. The crystals of *E*₄-1c exhibit a significant optical birefringence under cross-polarized light illumination (Fig. 4a,b), confirming an ordered arrangement of the molecules in the solid that gives rise to anisotropic crystals. It is important to note that the high yield of *E* → *Z* photoconversion for crystals of this size (roughly 1 μm) implies that the photoisomerization of *E*₄-1c upon irradiation in the 350–360 nm region is not limited to surface layers. Efficient bulk photoisomerization of azobenzene solid crystals is made possible, besides the high inherent photoreactivity of the material, because the *E* → *Z* conversion causes a decrease in the optical density at the irradiation wavelength (Fig. 3c), thus enabling photons to reach the core of the crystals. To the best of our knowledge, substantial *E* → *Z* photoisomerization of azobenzene-containing crystals has only been described in two recent reports on azobenzene cyclophanes bearing long alkyl substituents^{23,24}.

Upon near-UV irradiation of the crystals on the microscope slide, both the crystal morphology (Fig. 4c) and optical birefringence (Fig. 4d) disappear. Indeed, the crystals appear to melt and the material assumes the consistency of a viscous liquid (Supplementary Fig. 36). It is likely that the mixture of *E*- and *Z*-isomers leads to the formation of an eutectic^{16,24,44}. Consequently, the photogenerated material is amorphous, in agreement with XRPD data. Again, control experiments performed on *E*-2 crystals do not show light-induced effects. Birefringent crystals are formed on annealing the irradiated sample at 160 °C for 20 min as a consequence of *Z* → *E* thermal isomerization (Fig. 4e,f). The formation of crystals that are larger than the starting ones is consistent with crystallization from a melt phase under slow cooling. These findings also rule out the possibility that the transformation observed under UV irradiation is caused by local thermal effects and confirms that the observed phenomenon is in fact an isothermal photoinduced crystal–amorphous phase transformation taking place at ambient temperature^{19,21,23,24}. The photoinduced amorphization and thermal

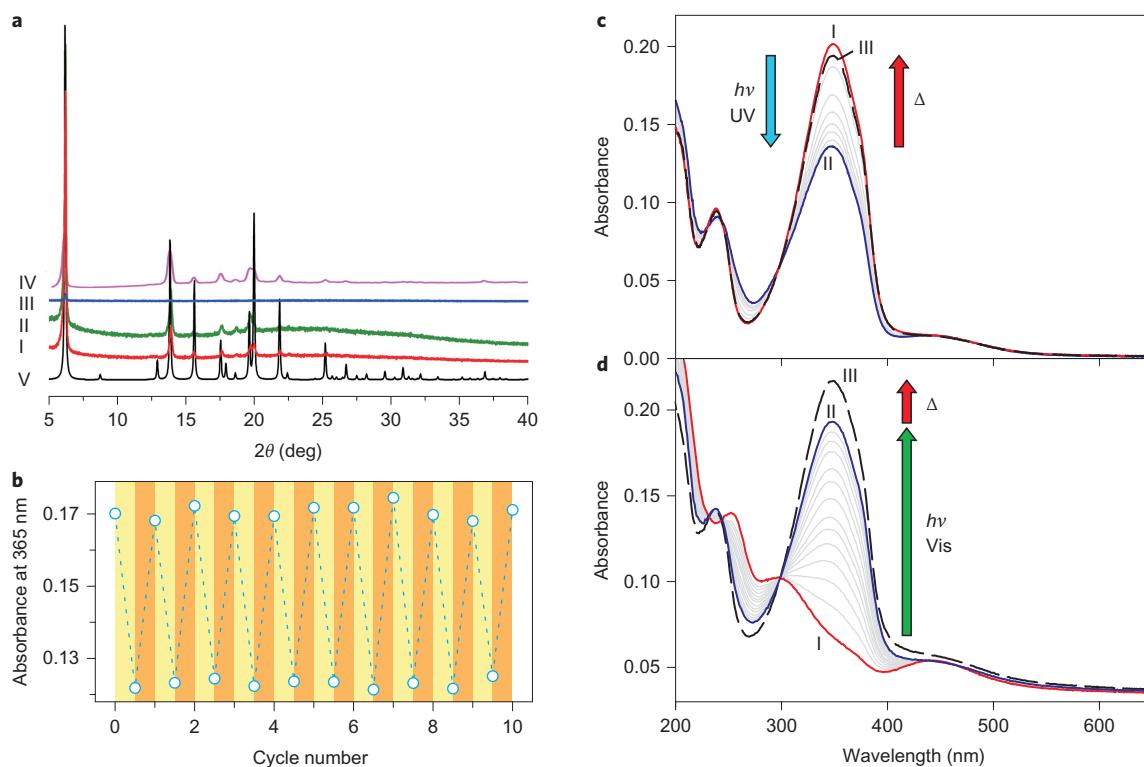


Figure 3 | Observation of the photoisomerization of 1c in a thin solid film by XRPD and UV-visible absorption spectroscopy. **a**, XRPD patterns obtained before (I) and after 48 h (II) and 96 h (III) of irradiation of a drop-cast film of **E₄-1c** at 365 nm. Curve III shows that crystallinity is lost upon prolonged irradiation. Curve IV is the pattern obtained after annealing of the irradiated film at 130 °C for 10 min and indicates that crystallinity is regained upon heating. The pattern calculated on the basis of single-crystal data (V) is also shown. **b**, Absorbance changes measured at 365 nm of a spin-coated thin film of **E₄-1c** subjected to UV irradiation and heating cycles. Yellow areas: irradiation at 365 nm for 20 min. Orange areas: heating at 180 °C for 20 min. The complete absorption spectra are reported in Supplementary Fig. 18. **c**, Absorption spectra of a spin-coated thin film of **E₄-1c** before (I) and after (II) irradiation at 365 nm for 6 min (photostationary state); spectra taken at intermediate times are shown in light grey. Curve III is the spectrum obtained after heating the film at 130 °C for 10 min. **d**, Absorption spectrum of a **Z₄-1c** thin film before (I) and after (II) irradiation at 436 nm for 34 min (photostationary state). Spectra taken at intermediate times are shown in light grey. Curve III (dashed line) is the spectrum obtained after heating the film at 130 °C for 10 min.

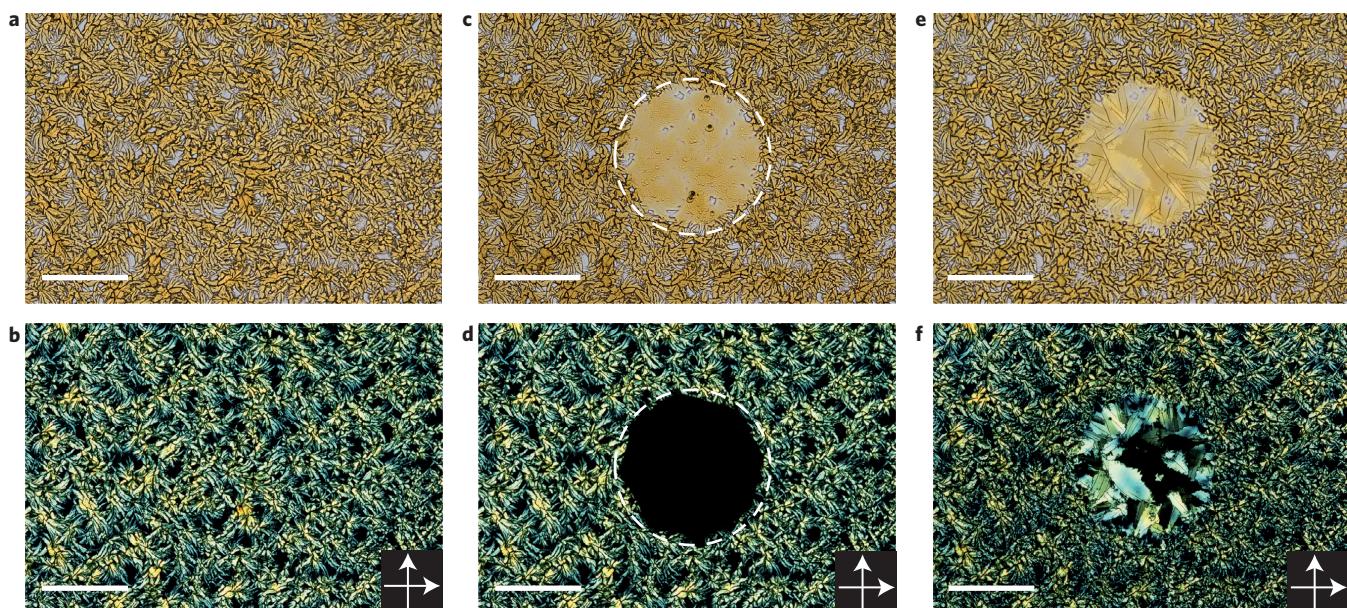


Figure 4 | Effect of photochemical and thermal stimulation on the 1c crystals. Polarizing optical photomicrographs of solid **E₄-1c** under bright field (top) and cross-polarized (bottom) light illumination. **a,b**, Before and **c,d**, after near-UV irradiation (330–380 nm) in a central spot (dashed line) for 10 min. **e,f**, Recrystallization of the irradiated sample is observed upon thermal annealing at 160 °C for 20 min. Scale bar, 100 μm. The white arrows in **b**, **d** and **f** represent the relative orientation of the polarizer and analyser.

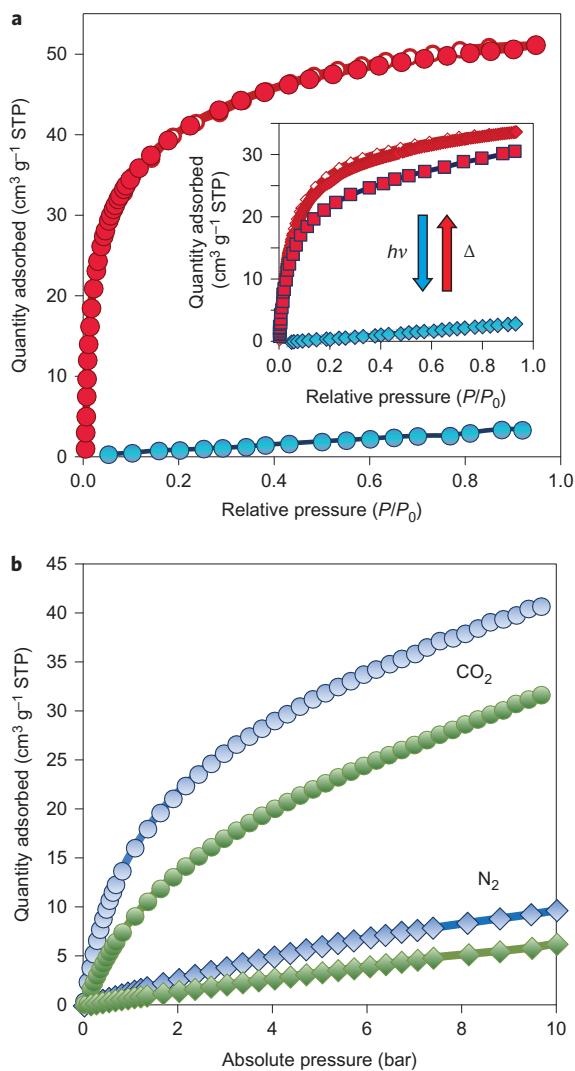


Figure 5 | Switching of gas adsorption properties and observation of CO₂/N₂ selectivity. **a**, CO₂ adsorption isotherms of **E₄-1c** (red circles) and **Z₄-1c** (blue circles) at 195 K. Inset: CO₂ adsorption isotherms at 195 K of **E₄-1b** (red diamonds), **Z₄-1b** (blue diamonds) and the **Z₄-1b** sample after heating at 160 °C for 2 h (red squares). **b**, CO₂ (circles) and N₂ (diamonds) adsorption isotherms of **E₄-1c** at 298 K (green) and 273 K (blue). The filled and open symbols refer to the adsorption and desorption isotherms, respectively.

recrystallization can be repeated on the same sample without degradation of the material (Fig. 3d, Supplementary Figs 18, 34 and 38).

A detailed examination of the effect of light on the **E₄-1c** crystals reveals an even more interesting behaviour, not observed for previously investigated azobenzene-containing crystals^{21,23,24}: exposure to UV light for a short time causes no significant change in morphology but affords a dramatic decrease in the birefringence, which is fully restored by heating (Supplementary Fig. 38). In other words, the loss of optical anisotropy does not require complete amorphization of the material. Such an observation supports the view, suggested by the XRPD and optical absorption results discussed above, that crystallinity is substantially maintained upon partial *E* → *Z* isomerization of **E₄-1c**. We hypothesize that *E* → *Z* isomerization in a relatively small population of **1c**, such as that afforded in the initial stages of irradiation, increases lattice disorder throughout the entire sample to an extent sufficient to disrupt long-range structural anisotropy, thus causing the loss of optical

birefringence⁴⁵. The solid, however, remains mostly ordered, and the crystal structure and morphology are not affected, as confirmed by the complete regeneration of the film upon thermal annealing (Supplementary Fig. 38).

Such a behaviour is interesting for optical information storage, because the thin film behaves as a one-input ternary switch under threshold control. Irradiation with a light dose below the threshold converts state ‘0’ (crystalline and birefringent; Fig. 4a,b and Supplementary Fig. 38a,b) to state ‘1’ (still crystalline but no longer birefringent; Supplementary Fig. 38c,d). Continued irradiation (that is, exposure to a dose of photons above the threshold) places the film into state ‘2’ (characterized by an amorphous structure; Fig. 4c,d). Clean and reversible switching among the three states can be performed by appropriate light and heat stimulation.

Gas adsorption experiments. The microporosity of the molecular crystals was demonstrated by gas adsorption measurements (Supplementary Figs 39–41). While **E₄-1a** exhibits negligible gas uptake properties, the CO₂ isotherm of **E₄-1c** at 195 K shows a Langmuir type-I profile that reaches the value of 52 cm³ g⁻¹ at standard temperature and pressure (STP), highlighting the open and accessible free volume in the compound (Fig. 5a). The maximum CO₂ uptake corresponds to the occupancy of four molecules per unit cell (that is, two molecules per cavity) and is consistent with the empty space as estimated from the crystallographic structure, suggesting a complete filling of the cavities by gas diffusion in the permeable crystal. Similarly, the maximum CO₂ sorption of **E₄-1b** compound results in a full loading of the available space (Fig. 5a, inset). In sharp contrast, the CO₂ adsorption isotherms of **Z₄-1b** and **Z₄-1c** samples obtained by precipitation from UV-irradiated solutions exhibit negligible CO₂ uptake, demonstrating that the all-*Z* isomers are not porous. However, upon heating, the samples are converted back to the porous forms, as shown in the inset of Fig. 5a. A reversible switching between the porous and non porous forms has therefore been realized⁴⁶, taking advantage of photoirradiation and thermal relaxation of the *E*- and *Z*-azobenzene moieties.

It is worth noting that very few cases of molecular solids in which porosity can be switched on and off reversibly have been reported^{47,48}. Such materials consist of cage or bowl-shaped molecules (that is, they exhibit intrinsic porosity)^{37–40} and their switching mechanism is based on solvation–desolvation effects, making them highly interesting from a structural viewpoint but less appealing for practical applications.

The porosity of the molecular crystals was further checked by CO₂ and N₂ adsorption measurements under mild conditions of temperature and up to 10 bar. The maximum CO₂ uptake values of 41 cm³ g⁻¹ and 32 cm³ g⁻¹ were found for the **E₄-1c** species at 10 bar and temperatures of 273 and 298 K, respectively (Fig. 5b). The pore size of ~7 Å guarantees an excellent interaction with the gas molecules. In fact, the compound exhibits an isosteric heat of adsorption (Q_{st}) equal to 28 kJ mol⁻¹, indicating the occurrence of favourable interactions of CO₂ with the aromatic groups exposed to the inner surface of the crystalline channels. Instead, N₂ adsorption experiments collected at 273 and 298 K for both **E₄-1b** and **E₄-1c** showed very limited uptake values even at high pressures, indicating a low affinity of the absorbent for nitrogen (Fig. 5b and Supplementary Fig. 39). This observation can be exploited for the selective capture of CO₂ in a mixture with N₂. In fact, ideal adsorbed solution theory (IAST) calculations indicated a CO₂/N₂ selectivity ratio as high as 80 for the **E₄-1b** compound. It is worth noting that this value exceeds the performances of most molecular crystals endowed with permanent porosity⁴⁹. Collectively, the gas adsorption data support the view that **E₄-1a–c** molecules pack inefficiently with one another because of their rigid star-like shape and the presence of bulky groups at the periphery. These features

generate a large free volume in the crystal, which enables $E \rightarrow Z$ photoconversion in the solid state.

Conclusions

A series of compounds based on a tetra(azobenzene)methane-type moiety with diversified end groups (H, Me or *t*-Bu) has been developed. The star-like shape and rigidity of the molecules prevent a close-packed arrangement in the crystals and promote low-density molecular self-assembly, affording porous molecular crystals in which azobenzene $E \rightarrow Z$ photoisomerization occurs in the solid state. The porosity of the crystals increases with the size of the terminal substituents introduced in the four azobenzene units. The porous crystals of **E₄-1b,c** adsorb CO₂ from the gas phase selectively with respect to N₂, whereas the corresponding *Z*-isomers, obtained by light irradiation at room temperature, are not porous. Crystallinity and porosity are restored upon *Z* \rightarrow *E* isomerization promoted by visible light irradiation or heating. These compounds—in particular **1b,c**—possess a number of valuable features, including synthetic accessibility, solution processability, high photoreactivity and tunability of the physico-chemical properties. These properties are key requirements for materials suitable for such technological applications as photoswitchable catalysts and membranes, solid-state photonic switches, substrates for holography and photolithography and photoresponsive adhesives.

The present study contributes to the design of novel microporous molecular solids in which photoreactive groups can be converted by light to high-energy molecular configurations, as the crystal porosity provides the space required for the photoinduced structural changes. It also paves the way to a better understanding of solid-state photochemical reactions and photoinduced phase transitions. The unique combination of porosity and photoactive moieties opens up intriguing perspectives in the field of responsive materials involving light irradiation, molecular movements and chemical stimuli.

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Author contributions

M.B., A.C. and An.C. conceived the project. M.B. and T.M.H. synthesized and characterized the compounds. S.d'A. and F.G. performed crystal growth experiments and X-ray diffraction studies. S.S. and M.B. carried out the spectroscopic, photochemical and microscopy experiments. I.B., An.C. and P.S. performed gas adsorption experiments, solid-state NMR spectra and preparation and characterization of the polymorphs. G.B., P.C., M.V. and all other authors analysed the data. A.C. wrote the paper.

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 M.B., A.C., F.G. and A.C.

Competing financial interests

The authors declare no competing financial interests.