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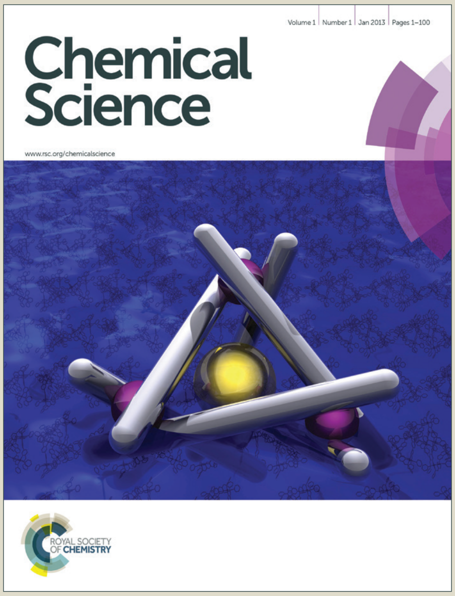

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Photo-mechanical azobenzene cocrystals and *in situ* X-ray diffraction monitoring of their optically-induced crystal-to-crystal isomerisation

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We demonstrate the first supramolecular cocrystallisation strategy to generate crystalline azobenzene materials with a range of photo-mechanical and thermochemical properties: from those that exhibit isomerisation without any change in crystal shape to those that undergo a crystal-to-crystal *cis-trans* isomerisation accompanied by large scale bending. The latter permitted the use of variable temperature single crystal X-ray diffraction for the first *in situ* monitoring of structural changes behind the *cis-trans* isomerisation in the solid-state, which revealed a topotactic process mediated by an amorphous phase. While the design of photo-mechanical azobenzene solids has so far focused on polymer matrices and gels, the herein presented cocrystallisation approach represents the first methodology for generating new photo-mechanical azobenzene crystals from a limited number of photo-active building blocks, opening a route to potential bio-mimetic and light-harvesting materials based on crystalline solids.

Introduction

Photo-mechanical materials, that undergo light-induced changes in shape[1-5] or even exhibit motion[6,7] are being extensively explored for applications in light-harvesting, molecular robotics, and in the design of nano-actuators and bio-mimetic artificial muscles.[8,9] Azobenzenes are a prominent family of photo-mechanical molecules whose *cis-trans* isomerisation (Figure 1a)[10,11] causes large-scale changes in molecular shape. This change was used in the design of photo-mechanical liquid crystals[12,13] and polymer-based[14] solids, some of which have been likened to molecular muscles capable of exerting force on objects several times their weight.[15] Due to their close-packed structure, crystalline photo-mechanical systems offer access to faster energy transfer than their polymer-based counterparts and, in principle, should also allow the direct structural studies of the photo-mechanical effect by X-ray diffraction.[7,16] However, the development of photo-mechanical azobenzene (azo) crystals has only just begun: photo-induced bending of a thin azo crystal under ultraviolet irradiation was first reported in 2009[17] and, recently, rapid photo-mechanical bending[18] induced by visible light was observed in pseudostilbenes, *i.e.* azo compounds containing complementary electron-donating and withdrawing groups. While a molecular-level mechanistic understanding of photo-mechanical effect in azo crystals is not yet accessible, a mathematical description of crystal bending and associated kinetics of isomerisation have recently been reported.[19,20] An exciting development in photo-mechanical azo crystals has been provided by perfluorinated azo compounds,[21] whose *cis*-isomers have sufficiently long thermal half-lives to be isolated as single crystals. Single crystals of the perfluorinated azobenzene *cis*-**1** and its iodo-analogue *cis*-**2** (Figure 1b) undergo apparently

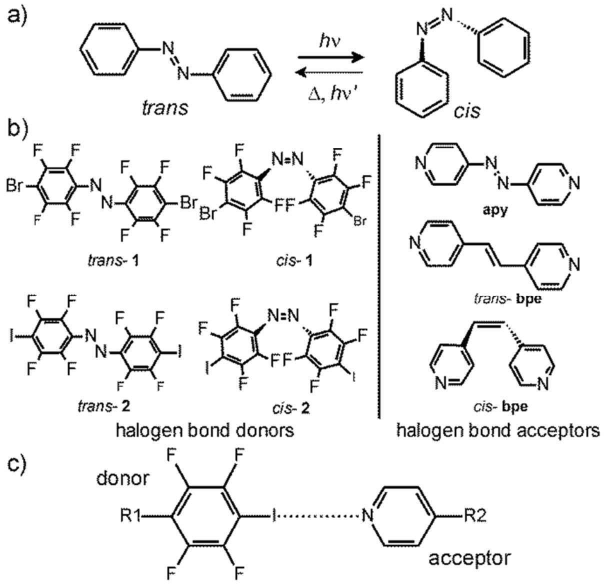


Figure 1. Schematic representation of: a) azo-isomerisation; b) herein studied halogen bond donors (left) and acceptors (right) and c) a general halogen bonding motif.

irreversible photo-mechanical bending[22] caused by light-induced *cis*→*trans* azo isomerisation. Irreversibility of this transformation permitted the deliberate shaping of micrometer-sized crystals and was explained by the higher density of the *trans*-crystal which hinders the opposite transformation to the *cis*-form. This photo-mechanical transformation proceeded in a crystal-to-crystal manner, which transformed a single crystal of *cis*-**1** into polycrystalline *trans*-**1**, suggesting X-ray diffraction could be utilised to study the azo photo-mechanical bending.

However, further studies and the design of photo-mechanical azo crystals are inherently limited by the number of available chromophores, challenges of their synthesis and, ultimately, their crystal morphology.[23] In principle, all of these limitations can be circumvented by crystal engineering, that allows the modification of a number of solid-state properties through the formation of multi-component crystals (cocrystals). Cocrystallisation has previously been employed to tune solid-state physicochemical properties of molecules, especially for pharmaceutical applications and photochemical synthesis.[24,25] Whereas the formation of azo cocrystals was previously explored through π··π-stacking,[26,27] molecular inclusion,[28,29] hydrogen[30-33] and halogen-bonding,[34-36] there have been no reports of photo-mechanical activity in the resulting solids. Moreover, there have not yet been any reports of design or structural characterisation of cocrystals of *cis*-azobenzenes, most likely due to often short lifetimes preventing the isolation of single crystals.

We now demonstrate halogen bond-driven cocrystallisation as a simple, rapid strategy to deliberately generate a diversity of azo-based crystalline materials involving *cis*- or *trans*-azo moieties or their combination, with different photo-mechanical and thermal properties. Most importantly, we report a halogen-bonded *cis*-azo cocrystal that undergoes large-scale irreversible photo-mechanical bending in crystal-to-crystal fashion. We have used this photo-mechanically active cocrystal for the first *in situ* single crystal X-ray diffraction study of solid-state azo isomerisation. The *in situ* studies at different temperatures revealed that the transformation of the *cis*- to the *trans*-cocrystal is topotactic and mediated by an amorphous phase.

Results and discussion

Preparation of cocrystals

Cocrystallisation is enabled by the highly polarizable bromine or iodine atoms on the electron-deficient perfluorphenyl moiety in **1** and **2** (Figure 1b,c), making them potentially suitable as halogen bond[37] donors. The halogen bond donors are expected to form a linear interaction with acceptor pyridine nitrogen atoms.[38] By pairing of either the *cis*- or the *trans*-isomer of **1** or **2** with suitable azo- or olefin-based pyridine derivatives (Figure 1c), we aimed to obtain first crystalline solids containing diverse combinations of azo and/or olefin geometric isomers. Cocrystals were prepared by slow evaporation of solutions containing equimolar amounts of a halogen bond donor (**1** or **2**) in *cis*- or *trans*-form and one of the following acceptors: *cis*- and *trans*-1,2-bis(4-pyridyl)ethylene (*cis*- and *trans*-**bpe**, respectively) and *trans*-4,4'-azopyridine (**apy**) (see ESI, Section 1). Attempts to synthesize *cis*-4,4'-azopyridine as a potential cocrystallisation partner by photochemical isomerization of **apy** in solution were not successful. Furthermore, none of the attempts to obtain the cocrystal (*cis*-**1**)(*cis*-**bpe**) was successful. As revealed by single crystal X-ray diffraction, all prepared cocrystals exhibit the expected Br···N (with **1**) and I···N (with **2**) halogen bonds with donor···acceptor distances below 3.2 Å (see ESI, Section 2).[39]

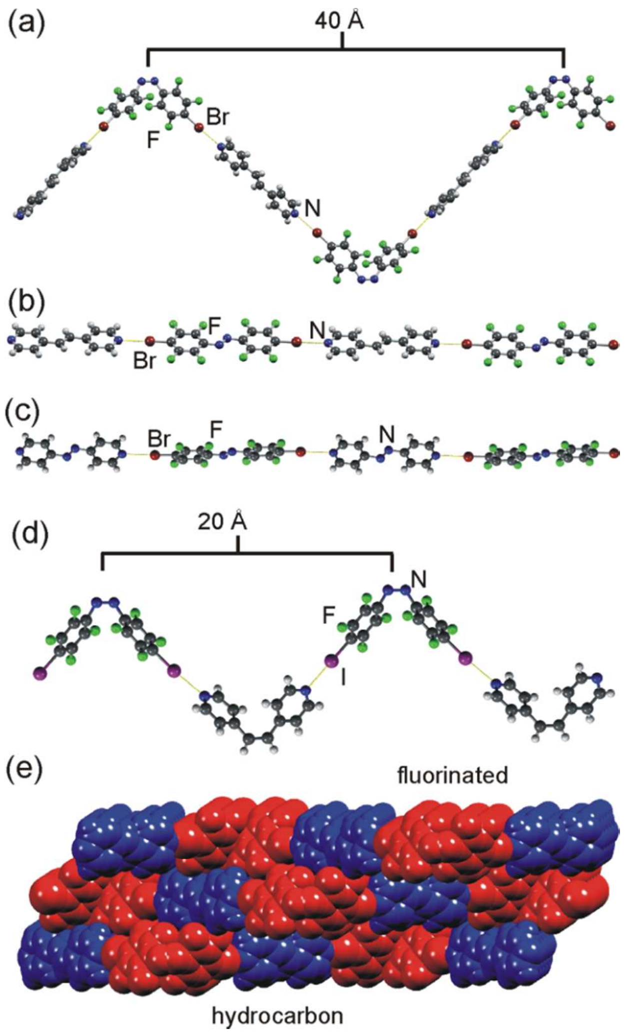


Figure 2. (a) Zigzag structure of a supramolecular chain in the (*cis*-**1**)(*trans*-**bpe**) cocrystal, with the repeat distance of the chain undulation indicated. Linear structure of supramolecular chains in the: (b) (*trans*-**1**)(*trans*-**bpe**) cocrystal and (c) (*trans*-**1**)(**apy**) cocrystal. Chain components in (*trans*-**1**)(*trans*-**bpe**) are coplanar, while in (*trans*-**1**)(**apy**) the best planes drawn through molecules of *trans*-**1** and **apy** are rotated by 66°.(d) In the zigzag structure of a (*cis*-**2**)(*cis*-**bpe**) chain the repeat distance of undulation is roughly half of that seen in cocrystals of *cis*-**1** or -**2** with *trans*-halogen bond donors. (d) The spacefill representation of molecular packing in (*cis*-**1**)(**apy**) illustrates the segregation of hydrocarbon (blue) and perfluorocarbon (red) residues into columns.

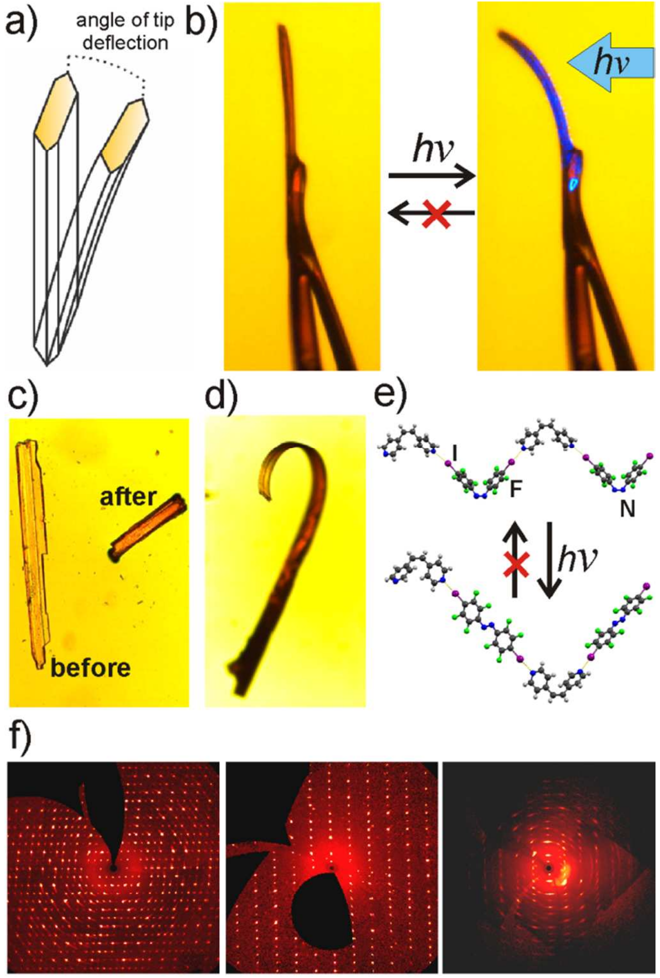
The halogen bonds associate cocrystal components into infinite one-dimensional chains of alternating halogen bond donors and acceptors, whose topology is dictated by the choice of their geometric isomer. The bent "V-shape" of *cis*-**1**, *cis*-**2** or *cis*-**bpe** dictates a zigzag geometry of the chains with a chain undulation distance of ca. 40 Å (Figure 2a). Chains involving *trans*-components only are linear, with adjacent molecules in each chain being either coplanar (in cocrystals with *trans*-**bpe**, Figure 2b) or rotated around the chain direction by 66.0° for (*cis*-1)(**apy**) (Figure 2c) and 65.2° for (*cis*-2)(**apy**). Two *cis*-building blocks in (*cis*-**2**)(*cis*-**bpe**) dictate the undulation of the supramolecular chain to be twice that found in cocrystals composed of *cis*- and *trans*-molecules (Figure 2d, wavelength 20.3 Å). Another important structural distinction between (*cis*-**2**)(*cis*-**bpe**) and other prepared cocrystals is the absence of face-to-face π-stacking, suggesting an explanation for the inability to obtain the analogous (*cis*-**1**)(*cis*-**bpe**). Presumably, the Br···N interactions expected in (*cis*-**1**)(*cis*-**bpe**) would be too weak to hold together a cocrystal in the absence of π···π interactions.[40] In all cocrystals the supramolecular chains assemble so as to segregate perfluorinated and hydrocarbon residues, as often observed in halogen-bonded cocrystals (Figure 2e).[41]

Photo-mechanical behaviour

Cocrystallisation of *cis*-**1** and *cis*-**2** with all explored pyridines gave materials with very different photo-mechanical properties in terms of: 1) the power of irradiation required to induce bending and 2) of the magnitude of resulting deformation expressed as the deflection angle of the crystal tip. Upon irradiation with a 532 nm laser all prepared *cis*-azo cocrystals underwent a colour change from orange to red, consistent with solid-state isomerisation.[†] However, an overview of the photo-mechanical properties of the cocrystals (Table 1) reveals that photo-mechanical behavior of a *cis*-azobenzene is significantly modified by the choice of a cocrystallisation partner. Photo-mechanical characteristics of cocrystals follow the differences in the efficiency of their crystal packing, given as calculated volume per non-hydrogen atom in the unit cell. As planar *trans*-molecules are expected to more readily achieve a close-packed structure than their V-shaped *cis*-analogues,[22] there might also be a tentative relationship between cocrystal composition and photo-mechanical activity. Indeed, the only cocrystal in our study based only on *cis*-molecules, (*cis*-**2**)(*cis*-**bpe**), also exhibits the highest calculated volume per non-hydrogen atom of 16.6 Å^3. Crystals of (*cis*-**2**)(*cis*-**bpe**) readily bend at a low irradiation power of 5 mW/cm^2, with the deflection angle of the crystal tip exceeding 90^o (Figure 3, see also ESI Section 3, Table S2 and video S1). The cocrystals of *cis*- and *trans*-components, such as (*cis*-**1**)(*trans*-**bpe**) and (*cis*-**2**)(*trans*-**bpe**), are more closely packed with respective volumes of 15.4 Å^3 and 15.8 Å^3 per non-hydrogen atom. These cocrystals require an irradiation power of at least 60 mW/cm^2 for deflection. The cocrystals (*cis*-**1**)(**apy**) and (*cis*-**2**)(**apy**), which exhibit similar volumes per non-hydrogen atom as their *trans*-analogues (Table 1), are photo-mechanically inactive up to the irradiation power of 200 mW/cm^2 and even then undergo only a minimal deformation of the crystal shape (Table S2 in the ESI). Variation in crystal thickness between different samples (ranging between 15 μm and 20 μm) was too small to play a significant role in the described differences in photo-mechanical behaviour. No photo-mechanical bending was observed in cocrystals involving *trans*-**1** and -**2**. This is consistent with the report that pure *trans*-**1** and *trans*-**2** do not exhibit photo-mechanical behavior, explained by the much more efficient molecular packing compared to their *cis*-analogues.[22] As it was not possible to induce photochemical switching of **apy** in solution, it is not surprising that pure **apy** and its cocrystals with *trans*-**1** and **2** did not exhibit bending.

Crystal-to-crystal photo-mechanical bending in (*cis*-2)(*cis*-bpe)

Photo-mechanical bending of thin (ca. 20 μm) needles of (*cis*-**2**)(*cis*-**bpe**) was accompanied by a change in crystal color from yellow to brick-red (Figure 3b, ESI video S1), consistent with



(*cis*-**2**)(*cis*-**bpe**) (*trans*-**2**)(*cis*-**bpe**) (*cis*-**2**)(*cis*-**bpe**) (after irradiation)

Figure 3. a) Schematic illustration of the deflection of crystal tip upon photo-mechanical motion. b) Permanent photo-mechanical change in shape of a (*cis*-**2**)(*cis*-**bpe**) cocrystal upon photochemical transformation into (*trans*-**2**)(*cis*-**bpe**), the blue arrow indicates the direction of irradiation. c) Comparison of a (*cis*-**2**)(*cis*-**bpe**) cocrystal before and after irradiation with 532 nm laser, the photochemical *cis*→*trans* isomerisation is indicated by the colour change of the

irradiated cocrystal. d) A highly bent crystal of (*cis*-**2**)(*cis*-**bpe**) with a tip deflection angle >90°. e) Fragments of cocrystal structures of the parent (top) and the daughter (bottom) phase involved in the photochemical transformation (*cis*-**2**)(*cis*-**bpe**)→ (*trans*-**2**)(*cis*-**bpe**). f) Composite diffraction images of the *h0l* plane for the starting (*cis*-**2**)(*cis*-**bpe**) cocrystal (left), the (*trans*-**2**)(*cis*-**bpe**) cocrystal (center) and (*trans*-**2**)(*cis*-**bpe**) obtained by irradiation of (*cis*-**2**)(*cis*-**bpe**) (right). Analogous composite images for (*0kl*) and (*hk0*) planes are given in the ESI, Figures S2 and S3. For a video of the photo-mechanical bending of (*cis*-**2**)(*cis*-**bpe**) see ESI, video S1.

Table 1. Photo-mechanical behaviour of prepared cocrystals[a,b]

Cocrystal	Irradiation power, mW/cm^2	Deflection angle, °	Volume per non-H atom in the unit cell, Å^3	Volume per non-H atom in the unit cell for corresponding cocrystal of *trans*-**1** or -**2**, Å^3
(*cis*-**2**)(*cis*-**bpe**)	5	> 90	16.6	16.1
(*cis*-**2**)(*trans*-**bpe**)	60	10	15.8	15.1
(*cis*-**1**)(*trans*-**bpe**)	60	9	15.4	15.0
(*cis*-**2**)(**apy**)	200	4	15.4	15.4
(*cis*-**1**)(**apy**)	200	3	14.8	14.8

a) the thickness for all crystals ranged between 15 µm and 20 µm; b) cocrystals of *trans*-**1** and -**2** were not photo-mechanically active; c) for comparison, previously reported irreversible transformation in single-component crystals of *cis*-**1** reliably generated deflection angles of > 90° at an irradiation power of 200 mW/cm^2.[22]

cis→*trans* isomerisation of *cis*-**2**. After irradiation the crystal exhibited an X-ray diffraction pattern of sufficient quality for crystal structure determination, revealing the crystal structure of (*trans*-**2**)(*cis*-**bpe**) identical to that obtained from separately grown crystals. Although this transformation did not take place in a single-crystal-to-single-crystal[42,43] fashion, the majority (ca. 75%) of the X-ray reflections collected from the irradiated crystal could be indexed to only two crystalline domains of (*trans*-**2**)(*cis*-**bpe**), and the rest to several smaller crystalline domains of (*trans*-**2**)(*cis*-**bpe**) (ESI Section 4). Such photochemical behavior is significantly more susceptible to structural studies by X-ray diffraction than the previously investigated pure *cis*-**1** which, upon irradiation, typically produced five or more crystalline domains that were difficult or impossible to index. In contrast, the presence of only two major crystalline domains in irradiated (*cis*-**2**)(*cis*-**bpe**) enabled indexing and structure solution using conventional protocols.‡

Photochemical transformation underlying crystal bending is apparent from the comparison of composite diffraction images of the *h0l* diffraction planes for the (*cis*-**2**)(*cis*-**bpe**) cocrystal before irradiation, the separately grown (*trans*-**2**)(*cis*-**bpe**) cocrystal and the (*cis*-**2**)(*cis*-**bpe**) cocrystal after irradiation (Figure 3f, also ESI Section 4, Figs S2, S3). The reaction also proceeds in the bulk powder, as confirmed by powder X-ray diffraction (PXRD), which revealed the transformation of the powder diffractogram of (*cis*-**2**)(*cis*-**bpe**) into one consistent with (*trans*-**2**)(*cis*-**bpe**) upon irradiation. (ESI Section 5, Fig. S5). The high quality of X-ray diffraction patterns observed from single crystals of (*cis*-**2**)(*cis*-**bpe**) irradiated *ex situ* encouraged us to explore the mechanism of this apparent crystal-to-crystal transformation by *in situ* monitoring of changes in the X-ray reflections in the reciprocal (001) plane of a single crystal of (*cis*-**2**)(*cis*-**bpe**) during irradiation. Importantly, *in situ* diffraction studies on azo crystals undergoing photoisomerisation have never previously been reported. The intensity of the reflections was found to rapidly diminish upon irradiation with 532 nm laser at 5 mW/cm^2, with concomitant appearance and strengthening of reflections consistent with (*trans*-**2**)(*cis*-**bpe**) (Figure 4a). Disappearance of reflections of the starting phase and appearance of those of the product suggests a transformation mediated by amorphisation and recrystallisation. To verify the appearance of an amorphous intermediate, we conducted an analogous experiment with the crystal cooled to 200 K. Irradiation of a (*cis*-**2**)(*cis*-**bpe**) single crystal produced the expected change in crystal color and shape, but also led to a complete loss of features in the diffraction image, consistent with amorphisation (Figure 4b). Presumably, 200 K is a sufficiently low temperature to hinder the crystallisation of the product (*trans*-**2**)(*cis*-**bpe**) from the amorphous phase generated by photochemical transformation.

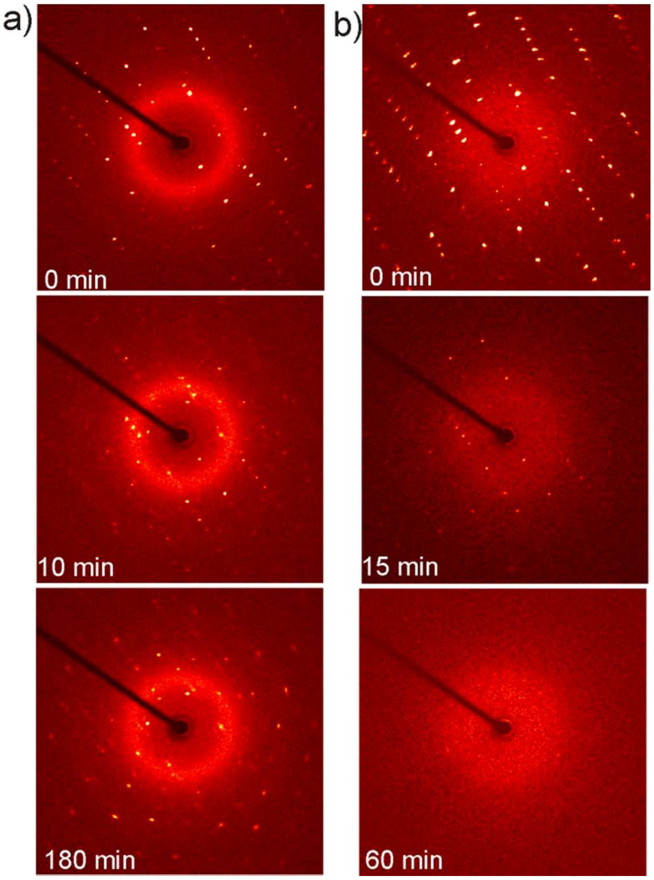


Figure 4. X-ray diffractograms collected *in situ* on single crystals of (*cis*-**2**)(*cis*-

bpe) while being irradiated with a 532 nm laser. (a) A single crystal of (*cis*-**2**)(*cis*-**bpe**) being irradiated at room temperature at 5 mW/cm^2. (b) A single crystal of (*cis*-**2**)(*cis*-**bpe**) being irradiated at 200 K at 15 mW/cm^2. These images reveal that room-temperature irradiation leads to the disappearance of parent (*cis*-**2**)(*cis*-**bpe**) and simultaneous formation of (*trans*-**2**)(*cis*-**bpe**). In contrast, low-temperature irradiation leads only to the appearance of an amorphous material, as evidenced by the loss of diffraction spots. The *in situ* diffraction data strongly indicates that "crystal-to-crystal" (*cis*-**2**)(*cis*-**bpe**)→(*trans*-**2**)(*cis*-**bpe**) transformation is mediated by an amorphous phase.

The reflections of the nascent daughter phase do not correspond to any simple (*e.g.* *h0l*, *hk0* or *0kl*) diffraction planes of (*trans*-**2**)(*cis*-**bpe**). However, repeating the experiment on a different crystal of (*cis*-**2**)(*cis*-**bpe**), with the same positioning of the laser source and the identical initial crystal orientation, yielded the same product diffraction pattern, indicating an identical orientation of the (*trans*-**2**)(*cis*-**bpe**) daughter phase (ESI, Figure S4). Repeating the experiment with a different position of the laser source, but retaining the initial crystal orientation again provided the same diffraction pattern.

Modification of the incident laser light polarisation also did not have any noticeable effect on the diffraction pattern and, therefore, crystallographic orientation of the product.

The described experiments indicate that the solid-state photoisomerisation of (*cis*-**2**)(*cis*-**bpe**) is a topotactic reaction,[43] *i.e.* the molecular arrangement of the parent phase appears to, at least partially, determine the crystallographic orientation of the daughter (*trans*-**2**)(*cis*-**bpe**) phase.

Thermochemical behavior of *cis*-azo cocrystals

Cocrystallisation also affected the thermal behavior of *cis*-**1** and -**2** in the solid state. Thermal analysis by combined differential scanning calorimetry and thermogravimetric analysis (DSC/TGA) revealed that *cis*-**1** and -**2** exhibit different solid-state thermal properties as pure solids than in the form of cocrystals. DSC thermograms of pure *cis*-**1** and -**2** display an endothermic event, immediately followed by a broad exotherm (Figure 5a, ESI Section 6). The two events are not associated with a loss of sample weight (ESI, Figs. S6,7) and are interpreted as endothermic melting, followed by exothermic isomerisation into the *trans*-isomer (it was previously calculated that the *cis*-forms of **1** and **2** are ca. 37 kJ mol^{-1} higher in energy than the corresponding *trans*-isomer).[22] Thermal isomerisation is confirmed by another endothermic event at a higher temperature, corresponding to the melting point of *trans*-**1** or -**2**. In contrast, DSC thermograms of all prepared halogen-bonded cocrystals of *cis*-**1** and -**2** display an exothermic event first, (Figure 5a, also ESI Section 6) taking place at a significantly lower temperature (130 °C-160 °C) than any other endothermic signal or weight loss detected in the combined DSC/TGA measurement.

We conclude that the exothermic *cis*→*trans* isomerisation in prepared cocrystals can take place in the solid state, *i.e.* without prior melting observed for pure *cis*-**1** and -**2**. Interpretation of the first exothermic event as the *cis*→*trans* isomerisation is supported by the measured enthalpy change which is consistent with the previously calculated[22] differences in energy between *cis*- and *trans*-forms of **1** and **2**, *e.g.* 37 kJ mol^{-1} for (*cis*-**1**)(*trans*-**bpe**) and 33 kJ mol^{-1} for (*cis*-**2**)(*cis*-**bpe**).

Next, we undertook a more detailed study of thermal behavior of (*cis*-**2**)(*cis*-**bpe**) and (*cis*-**1**)(*trans*-**bpe**) cocrystals (Figure 5b,c), as well as pure solid *cis*-**2** (Figure 5d,e) *via* thermal hot-stage microscopy (ESI Section 6, videos S2-S4). The cocrystals underwent slight mechanical bending upon heating to 140 °C and 120 °C, respectively, followed by thermal decomposition above 200 °C. In contrast, pure *cis*-**2**, as anticipated from bulk DSC measurements, underwent melting accompanied with color change and solidification, both due to the formation of *trans*-**2**. The combined DSC and hot-stage microscopy data on cocrystals clearly show that cocrystallisation enabled the thermochemical *cis*→*trans* isomerisation to take place in the solid, without prior melting, potentially explaining the thermo-mechanical bending of cocrystals that was not observed in pure *cis*-**1** or -**2** crystals.[¶]

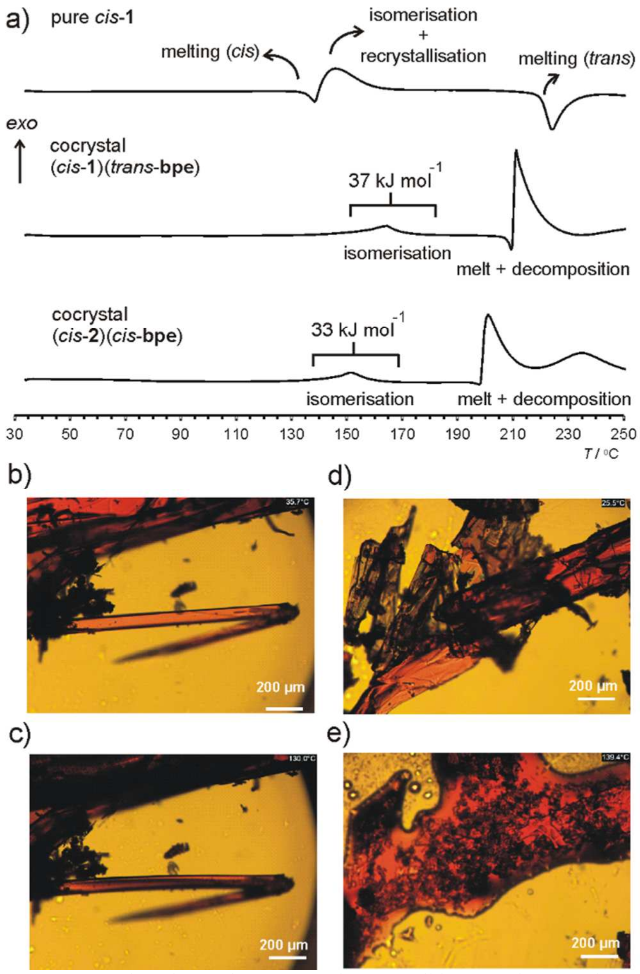


Figure 5. a) Overlay of DSC thermograms for pure solid *cis*-**1** and cocrystals (*cis*-**1**)(*trans*-**bpe**) and (*cis*-**2**)(*cis*-**bpe**). b) A selected elongated crystal of (*cis*-**1**)(*trans*-**bpe**) on the hot-stage microscope at 37 °C and c) the same crystal at 130 °C. These two images, extracted from the ESI video S4, demonstrate the slight thermomechanical bending of the (*cis*-**1**)(*trans*-**bpe**) cocrystal, followed by chemical decomposition upon further heating. d) Image of an aggregate of crystals of pure *cis*-**1** at 25 °C; e) image of the same sample at 139 °C, demonstrating partial melting of the sample and f) image of the same sample at 205 °C, demonstrating the recrystallisation of the sample. The images d) and e)

have been extracted from the ESI video S2, which demonstratea that pure *cis*-**1** does not undergo solid-state *cis*→*trans* isomerisation and thermomechanical bending, but instead melts and then undergoes *cis*→*trans* isomerisation.

Conclusion

We demonstrated the first solid-state supramolecular strategy to generate new photo-mechanical azo crystals. Halogen bond-driven cocrystalisation enabled modification of the photo-mechanical behavior of a particular azobenzene in a crystalline solid, and permitted the first use of single crystal X-ray diffraction for *in situ* study of azo isomerisation. Using only one photo-mechanically active component (*e.g.* *cis*-**2**), cocrystallisation yielded one cocrystal exhibiting crystal-to-crystal photo-mechanical motion, several cocrystals that exhibited lesser photo-mechanical activity, and several cocrystals that displayed no photo-mechanical bending at all, demonstrating a means to modify the photo-mechanical response of a crystal to solid-state azo isomerisation. Thermal measurements reveal that cocrystallisation also allows decoupling of thermal isomerisation and melting, leading to new crystalline solids that can undergo thermal azo isomerisation in the solid state. This is a novel observation in the solid-state chemistry of azobenzenes, also resulting from the ability to form new azobenzene crystals by cocrystallisation. The facile crystal-to-crystal azo isomerisation in (*cis*-**2**)(*cis*-**bpe**) enabled the use of X-ray single crystal diffraction to follow the structural changes behind photo-mechanical bending, revealing that the apparent crystal-to-crystal reactivity is topotactic and proceeds *via* an amorphous phase.[45] The presented cocrystallisation strategy offers rapid access to new structurally and photo-mechanically diverse azo crystals, including those susceptible to fundamental structural studies by X-ray single crystal diffraction. Complemented by the ongoing development of detailed kinematic studies,[7,19] this will be of paramount importance for understanding the structure-property relationships and, therefore, the design and optimisation of azo crystals for energy harvesting and transduction of light into mechanical motion. In that context, the demonstrated ability to synthesise photomechanically active cocrystals opens up the opportunity to design materials in which photomechanical behavior could be based on more than one type of chromophore. Our particular interest lies in exploring the potential of irreversible photo-mechanical behavior for precise shaping of materials at the micrometer scale.

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Notes and references

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Electronic Supplementary Information (ESI) available: details of experimental procedures, selected PXRD, FTIR-ATR and thermal (TGA/DSC) data, summary of crystallographic data and indexing of the **(*cis*-2)(*cis*-bpe**) cocrystal after irradiation, crystallographic data for all prepared cocrystals (CCDC code 984291-984300) and videos photo-mechanical bending and hot-stage microscopy experiments. See DOI: 10.1039/b000000x/

† Spectral characterisation of *cis*-**1** and -**2**, as well as *trans*-**1** and -**2** was reported previously.[22] Irradiation wavelengths were selected according to solid-state UV/Vis absorption profiles for *cis*-**1**/*trans*-**1** and *cis*-**2**/*trans*-**2** systems, which effectively coincide and allow irradiation with wavelengths up to 550 nm for irreversible solid-state *cis*→*trans* transformation. Fourier-transform infrared attenuated total reflectance spectroscopy (see ESI, Figs S23-39) confirms the presence of both components in all prepared cocrystals.

‡ The differences between photo-mechanical behaviour of previously reported single crystals of *cis*-**1**[22] and the herein investigated cocrystal (*cis*-**2**)(*cis*-**bpe**) merit some discussion. While both materials undergo photo-mechanical crystal-to-crystal transformation, a crucial difference was observed in the quality of the irradiated crystals as measured by single crystal X-ray diffraction. Irradiation of *cis*-**1** crystals[22] always yielded multiple domains, which allowed for structural characterisation only in select few *ex situ* irradiated crystals. For the (*cis*-**2**)(*cis*-**bpe**) cocrystal nearly any specimen irradiated *in situ* produced a diffraction pattern of sufficient quality for routine indexing and structure determination. Crystalss of (*cis*-**2**)(*cis*-**bpe**) more readily accommodated the structural changes in the material upon photoisomerization and bending, and were less brittle upon irradiation than single-component crystals of *cis*-**1;** thus, cocrystallization allowed study of the process *in situ*.

¶ We consider it unlikely that the difference in thermal behavior of pure *cis*-**1** or *cis*-**2** and corresponding cocrystals would affect the mechanism of their photo-indiced bending, as the low irradiation powers are not likely to significantly increase the temperature of the irradiated crystal.

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