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# Azo...phenyl stacking: a persistent self-assembly motif guides the assembly of fluorinated *cis*-azobenzenes into photo-mechanical needle crystals†

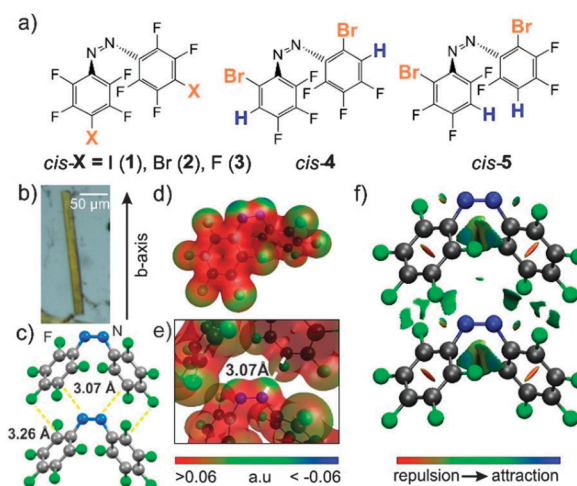
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We describe a novel, persistent motif of molecular assembly in photo-mechanical crystals and cocrystals of fluorinated *cis*-azobenzenes. The azo...phenyl stacking, preserved upon either chemical substitution or halogen-bonded cocrystallization, guides the assembly of fluorinated *cis*-azobenzenes into columnar stacks and drives the formation of crystals with needle-like morphologies optimal for photo-mechanical motion.

Control over molecular assembly in crystals is central to a range of applications for molecular materials, such as pharmaceuticals,<sup>1,2</sup> organic semiconductors,<sup>3</sup> and energy transduction and storage materials.<sup>4</sup> The latter have recently received much interest, as they include light-harvesting systems which can deform mechanically upon irradiation, and function as artificial muscles, photo-mechanical robots, and 'molecular machines'.<sup>5</sup> The understanding and prediction of solid-state molecular assembly, which is key to such designer crystalline materials, has been greatly advanced by an understanding of hydrogen-bonded supramolecular synthons<sup>6</sup> which, along with a variety of other interactions (*e.g.* halogen bonds,  $\pi$ - $\pi$  interactions), enable the design of crystals of high complexity and functional nature, including pharmaceuticals, explosives, or photo-switchable materials.<sup>7–10</sup> A recent development in the latter context is the discovery that azobenzenes, if obtained as sufficiently thin crystalline plates or needles, readily undergo large-scale light-induced photo-mechanical motion associated with photochemical switching of *trans*- and *cis*-geometries.<sup>11–13</sup> Specifically, crystals of *trans*-azobenzenes undergo rapid, reversible motion upon exposure to ultraviolet or visible light,<sup>11,13</sup> while fluorinated *cis*-azobenzenes, such as *cis*-1 and *cis*-2 (Fig. 1a),

undergo light-induced *cis*  $\rightarrow$  *trans* isomerization accompanied with irreversible bending.<sup>14,15</sup> Critical to both types of photo-mechanical motion is the formation of crystals sufficiently long and thin to permit macroscopic bending.

We now report a persistent, previously undescribed azo...phenyl stacking motif in crystalline fluorinated *cis*-azobenzenes, leading to columnar 'pringle chip'-like supramolecular architectures<sup>16</sup> and potentially driving the formation of crystals with thin needle-like morphologies (Fig. 1b and c, Fig. S2, ESI†) optimal for photo-mechanical motion. For the first time, this molecular assembly motif offers an opportunity to design crystal structures and ensure crystal morphologies ideal for photo-mechanical



**Fig. 1** (a) Fluorinated *cis*-azobenzenes synthesized in this work; (b) typical needle-like crystal morphology observed for fluorinated *cis*-azobenzenes; (c) stacking of *cis*-3 parallel to the long axis of crystal needle growth. Molecular electrostatic potential (MEP) calculated for: (d) a single *cis*-3 molecule and (e) for a pair of *cis*-3 molecules in an azo...phenyl stack (contours at 0.02 a.u.; red: repulsion; blue: attraction), highlighting the short contact between the azo nitrogen and a *meta*-positioned C–F bond. (f) The NCI plot for two molecules of *cis*-3 in an azo...phenyl stack (NCI contours at 0.5, electron density threshold 0.2), demonstrating notable areas of attraction and repulsion.

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behaviour, advancing applications in light-driven robotics, molecular machines, and artificial muscles.<sup>5</sup>

The azo...phenyl stacking in fact can be recognized from careful inspection of previously published<sup>14b</sup> crystal structures of *cis*-1 and two polymorphs of *cis*-2. These consist of one-dimensional molecular stacks with repeat distances 5.324(1) Å (*cis*-1, CSD code DOCCOP), 5.597(1) Å (*cis*-2, CSD code DOCCEF01) and 5.316(1) Å (*cis*-2, CSD code DOCCEF) along the crystallographic *b*-axis, respectively (Fig. S1, ESI†). Importantly, stacks exhibit unusually short N...C contacts between azo groups and fluorinated phenyl rings of neighbouring molecules (3.190(5) Å in *cis*-1, 3.210(3) Å and 3.157(3) Å in polymorphs of *cis*-2), compared to N...C separation of *ca.* 3.3 Å expected from van der Waals radii.<sup>17</sup> Importantly, almost identical stacking is seen in reported<sup>14a</sup> cocrystals of *cis*-1 and *cis*-2, but not in non-fluorinated *cis*-azobenzenes,<sup>18</sup> suggesting it may be characteristic for only the fluorinated derivatives. To verify the presence of a persistent stacking motif, we first prepared the fully fluorinated *cis*-3 (Fig. 1a).‡ Crystallization of *cis*-3 from hexane gave thin needles (Fig. 1b), established by single crystal X-ray diffraction to consist of one-dimensional stacks parallel to the crystallographic *b*-axis, resembling the stacks in *cis*-1 and -2. In *cis*-3, stacks are arranged in parallel, characterized by a short N...C separation (3.073(4) Å) and a repeat distance of 5.569(3) Å.

Formation of identical stacks independent of *para*-substituent is remarkable and points to a robust self-assembly motif. We undertook a computational analysis of interactions between molecules in stacks of *cis*-1, *cis*-2 (for one polymorph only, CSD code DOCCEF01) and *cis*-3 (see also ESI†). The molecular electrostatic potential (MEP) analysis revealed that stacking may be supported by two attractive interactions (Fig. 1c–e, Fig. S3 and S4, ESI†). One arises between the lone electron pair on each of the azo group nitrogen atoms and *meta*-carbon atoms in the fluorinated phenyl group of the neighbouring molecule. The other attractive interaction involves the negatively charged rim of the halogen *para*-substituents and the positively charged carbon atoms in perfluorinated phenyl groups of neighbouring molecules. We also evaluated these noncovalent interactions between two neighbouring molecules by calculating the non-covalent interactions (NCI) index using NCIPLOT,<sup>19</sup> which depicts intermolecular interactions by an electron density gradient isosurface. The NCI calculations (Fig. 1f, Fig. S3 and S4, ESI†) confirm that the above interactions are attractive and may help formation of molecular stacks.

In order to evaluate the importance of azo...phenyl stacking in the crystal packing of *cis*-3, we calculated intermolecular potentials using the UNI force field, implemented in MercuryCSD (version 3.5.1.).<sup>20,21</sup> Results reveal that stacking of *cis*-3 is the single most dominant stabilization factor in the crystal structure, with an intermolecular potential of  $-34 \text{ kJ mol}^{-1}$  (see ESI,† Fig. S5–S13). The next most negative intermolecular potential in crystal structure of *cis*-3 was at  $-16 \text{ kJ mol}^{-1}$ . Similar results were obtained for the published structure of *cis*-1 (CSD code DOCCOP), where molecular stacks provide a stabilization of  $-54 \text{ kJ mol}^{-1}$ , the next lowest intermolecular potential being  $-25 \text{ kJ mol}^{-1}$ . For both known *cis*-2 polymorphs (CSD codes DOCCEF and DOCCEF01),

azo...phenyl stacks provide a stabilization of  $-44 \text{ kJ mol}^{-1}$  and  $-50 \text{ kJ mol}^{-1}$ , with the next most negative intermolecular potential at  $-22 \text{ kJ mol}^{-1}$  (see ESI,† Fig. S5–S13). These calculations point to azo...phenyl stacking as the most stabilizing interaction in crystalline fluorinated *cis*-azobenzenes.

To explore the robustness of azo...phenyl stacking to modification of fluorinated *cis*-azobenzenes, we synthesized and grew single crystals of *cis*-4 and *cis*-5, in which the fluorinated phenyl rings bear a bromine atom in 2-position, and a hydrogen atom in positions 3 and 5, respectively (Fig. 1a). Both compounds form thin needle-shape crystals and crystal structure determination revealed antiparallel azo...phenyl stacks along the crystallographic *b*-direction, *i.e.* coincident with the crystal needle axis (Fig. 2). In *cis*-4 the molecules are arranged with a repeat distance of 5.661(3) Å within each stack. In *cis*-5 the repeat distance is 5.608(4) Å, with nearest-neighbour molecules in each stack mutually rotated by 90°.§

All herein explored fluorinated *cis*-azobenzenes, as well as previously reported *cis*-1, *cis*-2 and their cocrystals,<sup>14</sup> persistently form thin needle crystals from different solvents (CH<sub>2</sub>Cl<sub>2</sub>, acetonitrile, hexanes, ethyl acetate), with the needle axis always parallel to direction of molecular stacks, suggesting that azo...phenyl stacking can govern macroscopic crystal shape and, therefore, potential photo-mechanical behaviour.

Photo-mechanical properties were explored for needles of *cis*-3 which underwent bending under irradiation with visible (488 nm) laser light. In contrast to crystals of *cis*-1 and *cis*-2, that bend away from the light source, needles of *cis*-3 initially bend away and, after a few seconds of continuous irradiation, reverse the direction of motion and instead bend towards the light source (Fig. 3a–d). The maximum observed crystal tip deflection was *ca.* 5°. Similar to *cis*-1 and *cis*-2, irradiation of *cis*-3 leads to *cis*-*trans* isomerization, confirmed through reaction monitoring by powder X-ray diffraction (PXRD, Fig. 3e). Irradiation of bulk powder leads to disappearance of X-ray reflections of *cis*-3 and the appearance of new reflections, largely matching those for *trans*-3 which was also separately prepared and characterized by X-ray single crystal diffraction.‡

A tentative explanation for the unusual bending behaviour of *cis*-3 compared to *cis*-1 and *cis*-2 may be in the relative densities of corresponding *cis*- and *trans*-compounds. Whereas the structures of *trans*-1 and -2 exhibit densities only ~3% higher than those of *cis*-isomers, the density of *trans*-3 is >5% higher

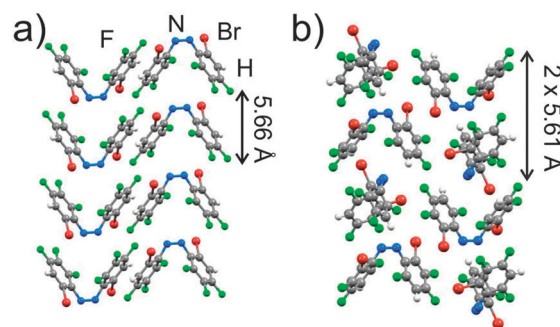
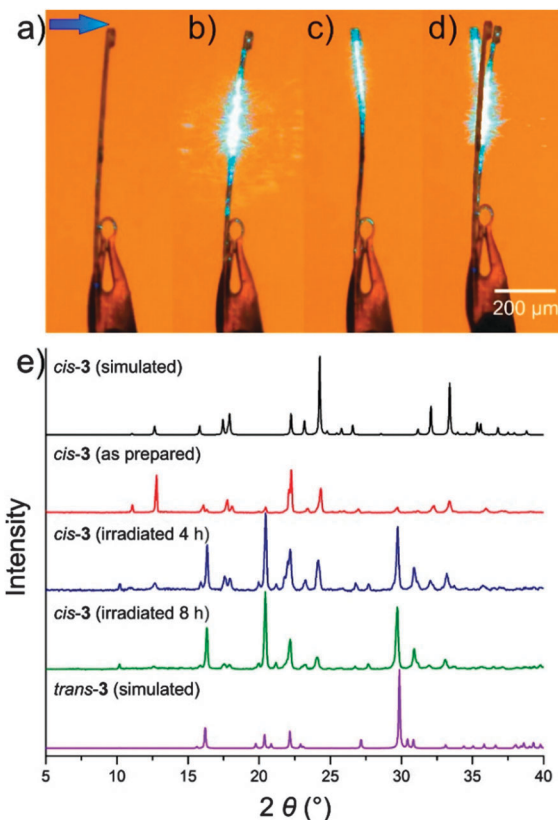


Fig. 2 Azo...phenyl molecular stacking in single crystals of: (a) *cis*-4 and (b) *cis*-5.

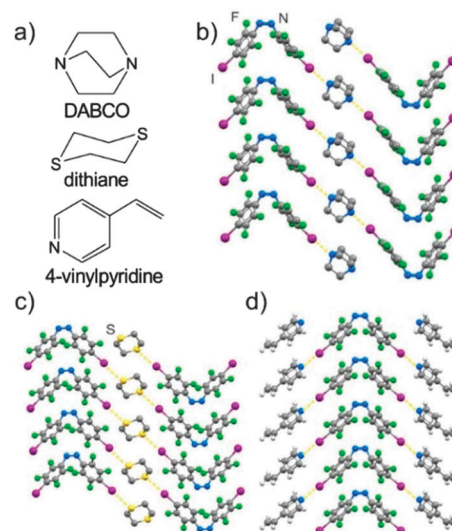




**Fig. 3** Bending of a single crystal of *cis*-3 upon irradiation with a 5 mW, 488 nm laser (arrow indicates direction of irradiation): (a) before irradiation; (b) after 10 seconds of irradiation; (c) after 30 seconds of irradiation; (d) image superimposing three snapshots of crystal motion. (e) PXRD patterns for bulk *cis*-3 at different irradiation times, demonstrating gradual conversion to *trans*-3.

than for *cis*-3 (Table S3, also see ESI†). Consequently, it may be that during photochemical transformation the density of irradiated material is first reduced due to amorphisation, resulting in photo-expansion and bending away from the light source, as indeed observed for irradiated single crystals and cocrystals of *cis*-1 and -2.<sup>14</sup> Subsequent crystallization of the more dense *trans*-3 could steer crystal motion in the opposite direction, towards the light. Importantly, *cis*-5 with a *trans*-isomer of notably higher density (~8%) than its *cis*-form demonstrates a similar photo-response, while *cis*-4 with ~3% denser *trans*-isomer exhibited a much weaker response to irradiation (Table S3, ESI†).‡ Whereas the Kobatake group recently demonstrated how varying the radiation wavelength can alter the direction of photo-mechanical motion for diarylethylene crystals,<sup>22</sup> in our case the course of bending did not change upon irradiation at 405 nm, 488 nm and 532 nm.

The stabilizing interaction of the fluorinated phenyl group with negatively charged rim of the iodine or bromine substituents (S3 and S4, ESI†) leaves the azo-phenyl stacks in *cis*-1 and *cis*-2 decorated with positive  $\sigma$ -holes potentially accessible for halogen bonding. Consequently, we tested if azo-phenyl stacking in *cis*-1 is retained upon halogen-bonded cocrystallization<sup>23,24</sup> with 1,4-diazabicyclo[2.2.2]octane (**dabco**), 1,4-dithiane and 4-vinylpyridine



**Fig. 4** (a) Herein explored halogen bond acceptors. Fragments of crystal structures of cocrystals of *cis*-1 with: (b) **dabco**; (c) dithiane and (d) 4-vinylpyridine, demonstrating halogen bond formation lateral to azo-phenyl stacking of *cis*-1. Molecular stacks are parallel to the crystallographic *b*-axis, i.e. the long axis of the needle-shaped crystal.

acceptors (Fig. 4a). Cocrystallization of *cis*-1 with **dabco** from dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) gave needle-like crystals of (*cis*-1)(**dabco**), consisting of antiparallel azo-phenyl stacks of *cis*-1 (repeat distance: 6.331(1) Å), laterally decorated by  $\text{I} \cdots \text{N}$  halogen bonds to **dabco** molecules ( $\text{I} \cdots \text{N}$  distance: 2.758(2) Å) that bridge neighbouring stacks. Cocrystallization of *cis*-1 and dithiane from  $\text{CH}_2\text{Cl}_2$  gave long needles of (*cis*-1)(dithiane), consisting of antiparallel stacks of *cis*-1 (repeat distance: 5.4079(4) Å) bridged by dithiane molecules connected via  $\text{I} \cdots \text{S}$  halogen bonds ( $\text{I} \cdots \text{S}$  distance: 3.2907(5) Å). Needles of (*cis*-1)(4-vinylpyridine)<sub>2</sub> were obtained from a  $\text{CH}_2\text{Cl}_2$ /4-vinylpyridine mixture (90:10, v/v) by slow evaporation. Single crystal X-ray diffraction revealed antiparallel stacks of *cis*-1 (stack repeat: 5.4157(7) Å) laterally decorated by halogen-bonded 4-vinylpyridine acceptors ( $\text{I} \cdots \text{N}$  distance: 2.780(2) Å). Synthesis and structures of (*cis*-1)(**dabco**), (*cis*-1)(dithiane) and (*cis*-1)(4-vinylpyridine)<sub>2</sub> demonstrate azo-phenyl stacking of fluorinated *cis*-azobenzenes as a persistent motif for crystal engineering: azo-phenyl stacks were in all cases aligned with the long needle axis of the crystal and evaluation of intermolecular potentials revealed azo-phenyl stacks as the most significant stabilizing motifs in all three cocrystals (Fig. S5–S13, ESI†).

In conclusion, we identified a new persistent supramolecular stacking motif based on fluorinated *cis*-azobenzene units. The azo-phenyl stacking has been observed for all herein described compounds, as well as all previously reported structures of fluorinated *cis*-azobenzene crystals and cocrystals. Stacking persists upon varying the type and position of substituents (H, F, Br, I) on the aryl rings, and upon halogen-bonded cocrystallization, which permitted the organisation of other molecules in one-dimensional fashion.<sup>24</sup> All fluorinated *cis*-azobenzene crystals and cocrystals explored herein and in previous work<sup>14</sup> appear as elongated needles, with azo-phenyl molecular stacks parallel



to the crystal long axis. We therefore believe that azo- $\pi$ -phenyl stacking of fluorinated *cis*-azobenzenes might allow both the predictable organization of these photo-mechanically active molecules into columnar 'pringle'-like supramolecular architectures, as well as encourage the growth of resulting crystals into needles, the ideal morphology for photo-mechanical effects and devices. Also described here is the unique observation of two distinct and opposite photo-mechanical regimes in the same crystal, resulting in bending either towards or away from visible light, depending on the time-scale of irradiation. We believe that azo- $\pi$ -phenyl stacking of fluorinated *cis*-azobenzenes may be developed into a rational tool to simultaneously control the crystal structure and permit ideal crystal morphologies for various applications.<sup>24</sup> In that context, we are now investigating photo-mechanical behaviour of the herein reported cocrystals.

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## Notes and references

- ‡ As *cis*-o-fluoro-azobenzenes exhibit long thermal half-lives, all herein prepared azobenzenes were nearly quantitatively converted into the *cis*-form by 532 nm laser irradiation and then crystallized in the dark.<sup>25</sup> *trans*-isomers were also prepared and structurally characterized by single crystal X-ray diffraction. Crystallographic data for all new structures is summarised in the ESI† and submitted in the CSD (CCDC codes 1431056–1431064).
- § Change in orientation of molecules in *cis*-5 azo- $\pi$ -phenyl stacks may be the result of C–H $\cdots$ N contacts in the stacks (Fig. S14, ESI†).
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