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Review

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Halogen-Bonded Cocrystals as Optical Materials: Next-Generation Control over Light−Matter Interactions

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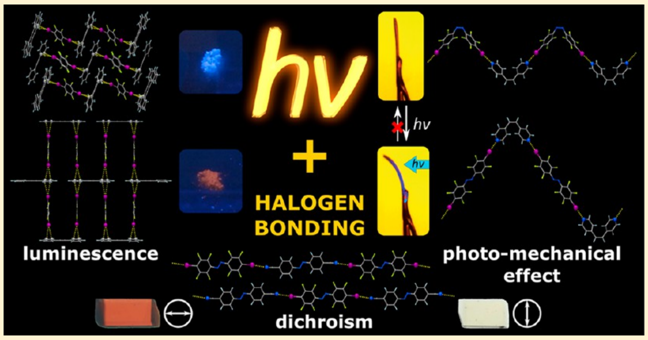
ABSTRACT: This review summarizes the recent advances in utilizing halogen bond-driven cocrystal formation as a design element in the creation of optical or photoresponsive materials, notably cocrystals and liquid crystals. The extensive work over a relatively short time has demonstrated halogen bonding as a versatile supramolecular interaction capable of creating libraries of fluorescent, phosphorescent, dichroic, photoswitchable, as well as photomechanical crystals and liquid crystals. Such rapid development, and the diversity of materials properties that have been designed or fine-tuned with success, signal the emergence of halogen-bonded cocrystallization as an exciting new playground for crystal engineers, chemists, and physicists to develop next-generation optical materials.



1. INTRODUCTION

The field of halogen bonding has grown remarkably over the past two decades.[1−5] While the initial interest in this exciting and now rapidly growing area of supramolecular chemistry was first sparked due to similarities with hydrogen bonding, the focus has slowly but certainly shifted toward the unique nature of halogen bonds, their complementarity to hydrogen bonding, and new opportunities offered by halogen bonding in the assembly of a wide range of materials. Halogen bonding has found clear applications in organic and metal−organic synthesis,[5] and the implications for a possible role in biological systems[6,7] have also been newly acknowledged. While many of these topics have already been visited in high-impact and extensive reviews,[8−13] here we highlight the still relatively small but promising and rapidly growing area of halogen bond-driven cocrystallization for generating materials that can interact with light in controllable ways.[14,15] The past 5 years have witnessed the emergence of many new reports describing crystalline or liquid-crystalline materials in which halogen bonding involving molecular building blocks with interesting optical or emissive properties has been employed to generate materials exhibiting novel or improved optical properties or light-responsive behavior, for example, photomechanical effects or photochemical reactivity. Such materials, upon further development, hold strong promise for the design of next-generation optical materials, such as sensors, optical filters, and waveguides, as well as propulsion, light-upconverting and light-harvesting systems. Consequently, we believe now is the right time to highlight, describe, and encourage the development of halogen-bonded cocrystallization as a strategy for generating and investigating optical and photoresponsive materials.

1.1. Halogen Bonding: A σ-Hole Interaction.

Whereas this review is focused on the emergence of halogen-bonded cocrystals as optical materials, it is worthwhile to highlight the recent developments in the understanding of halogen bonds, as well as their characteristics and potential in crystal engineering. Halogen bonding is considered to be a primarily electrostatic interaction between an electron donor (i.e., a halogen bond acceptor) and a region of positive electrostatic potential (ESP) that is generated on a polarized halogen atom (i.e., the halogen bond donor) attached to electron-withdrawing groups (Figures 1A,B).[16,17] Such an area of positive ESP is termed the σ-hole due to spatial overlap with the σ* orbital associated with the covalent bond adjoining the polarized halogen atom to the electron-withdrawing substituent.[18] The σ-hole is particularly pronounced for heavier, more readily polarized halogen atoms, such as bromine and iodine, and is observed in molecular halogens, as well as in compounds of halogens connected to fluoro- or nitro-substituted aromatic rings, perfluoroalkyl groups, alkynes, and electron-deficient heterocycles such as succinimide, saccharin, etc. (Scheme 1). With polarization at its core, halogen bond strength increases with an increase in the size of the halogen donor atom, i.e., F < Cl < Br < I. A plethora of electron-rich species have been employed as halogen bond acceptors (Scheme 1), most of which are also well-known hydrogen bond acceptors, such as amines, ethers, amine and phosphine oxides, π-systems, and various anions ranging from monoatomic halides to more complex oxoanions and cyanometallates.

A special case of halogen bonding arises between two halogens interacting through the respective areas of the positive σ-hole, and the negative equatorial region, leading to Type II halogen−halogen contacts (Figure 1C).[19] Together with the

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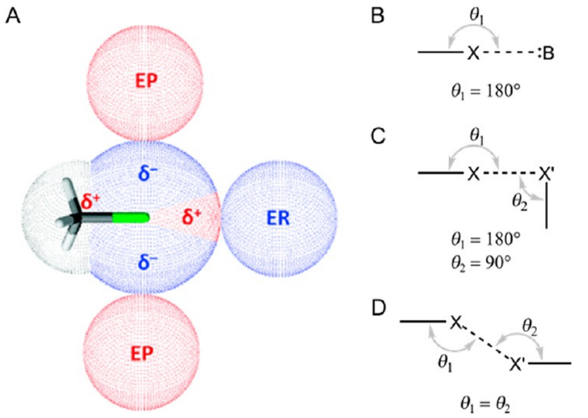


Figure 1. (A) Representation of the distribution of positive (∂^+) and negative (∂^-) electrostatic potential for a simple halomethane molecule, indicating the preferred sites of interactions with electron-poor (EP) and -rich (ER) moieties. (B) Schematic views of a typical halogen bond with X as the halogen and B as the Lewis base; (C) type II and (D) type I halogen···halogen interaction. Panel A is modified with permission from Mooibroek et al.[20] Copyright 2013 Royal Society of Chemistry.

similar but non-halogen bonding Type I contacts (Figure 1D), they are a class of interactions inherent to most crystalline halogenated organic compounds that has been utilized extensively in crystal engineering, but has not been a tool for the rational assembly of halogen-bonded cocrystals.

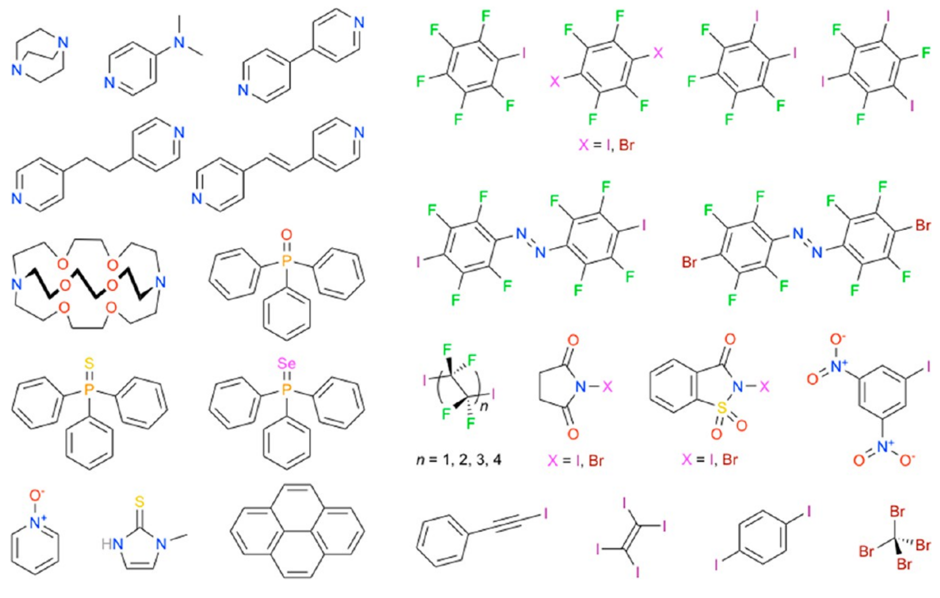
1.2. Halogen Bonds in Crystal Engineering and Materials Design. Halogen bonding is a versatile design element for the construction and control over the structure of a wide range of materials, from single- or multicomponent (i.e., cocrystals) organic solids and frameworks, to metal−organic solids, host−guest polymers, liquid crystals, and more. Halogen bonding was shown to be not only energetically competitive, but sometimes also stronger than hydrogen bonding, providing superior directionality, as well as orthogonality to hydrogen bonding, and can be fine-tuned by either varying the halogen bond donors or acceptors, or by varying the proximal functional groups. For example, Cinčić and co-workers have shown the possibility to vary between I···N, I···S, I···O, Br···N, Br···O, and Br···S halogen bond donor···acceptor combinations in cocrystal synthesis, affecting thermal or morphological properties of the materials, but without any notable changes to overall cocrystal structure.[21]

Although halogen bond-driven cocrystal formation has been known since the 1950s,[22] its utility in cocrystal design has only begun to be systematically exploited over the past 20 years. The early work in that direction was pioneered by the group of Resnati and Metrangolo, who demonstrated the assembly of α,ω-diiodoperfluoroalkanes with nitrogen-based electron-rich species, such as diazabicyclo[2.2.2]octane (dabco) and related molecules, to be a highly robust and reproducible supramolecular reaction.[23,24] Moreover, the formation of halogen-bonded cocrystals was then found not to be limited only to perfluorinated iodoalkanes, as demonstrated by efficient cocrystal formation between nitrogen-based halogen bond acceptors and simple organic iodides, such as 1,4-diiodobenzene, 1,4-diiodotetrafluorobenzene, tetraiodoethylene, or organic bromides, such as 1,4-dibromotetrafluorobenzene. Indeed, 1,4-diiodotetrafluorobenzene is now an almost ubiquitous component of halogen-bonded cocrystals.[25,26]

An important advance in validating halogen bonding in cocrystal design was the demonstration that it can compete well with, and sometimes even supersede, the formation of hydrogen bonds.[27] Aakeröy et al. have elucidated various methods to tune the strength of halogen bonds and provided a means to quantitatively analyze their strengths[28] and determine a hierarchy of halogen and hydrogen bond donors. Recently, Robertson et al. used competitive cocrystallization of 1,4-bis(4-pyridyl)ethane with 1,4-hydroquinone derivatives or 1,4-diiodotetrafluorobenzene to demonstrate how cocrystal formation can be driven either by hydrogen or by halogen bonding, depending on the solvent (Figure 2).[29]

Halogen bonding can engage a wide range of functional groups in molecular recognition and self-assembly. For example, organic sulfur or selenium, which do not often

Scheme 1. A Variety of Halogen Bond Acceptors (Left) and Donors (Right) Commonly Encountered in Halogen Bond-Driven Cocrystal Formation



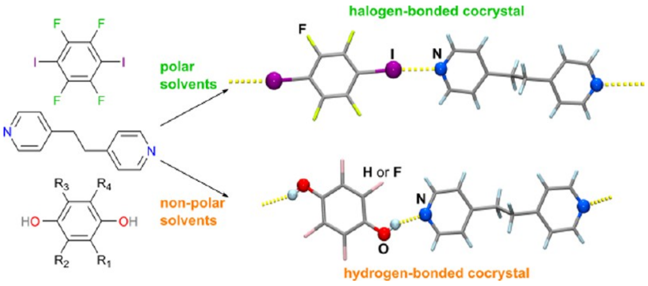


Figure 2. Role of solvent in the formation of halogen- or hydrogen-bonded cocrystals of 1,2-bis(4-pyridyl)ethane, as described by Robertson et al.[29]

partake in hydrogen bonding, readily form halogen bonds, as shown by Kosaka et al., who explored sulfur acceptors in the design of organic conductors,[30] or by the Pennington group, who used thioamides as acceptors for hydrogen and halogen bonds.[31] Sulfur acceptors readily form bifurcated halogen bonds, involving multiple halogen bond donors (Figure 3A).[32] Whereas bifurcation on the halogen bond acceptor atom is fairly common, the formation of halogen bonds involving bifurcated donors is more unusual. Recent examples of bifurcated halogen bond donors were provided by Nemec et al., who observed a bifurcated iodine donor in the cocrystal of 1,4-diiodotetrafluorobenzene and 4-nitroaniline,[33] and by Zbačnik et al., who reported on the propensity of *ortho*-vanillin derivatives to act as acceptors in forming halogen bonds with bifurcated donors (Figure 3B).[34,35]

Other electron donors, namely, selenium atoms, can also act as halogen bond acceptors (Figure 3C),[36] providing crystal engineers with a rich variety of intermolecular geometries and interactions for use in materials design. Halogen bonds can also involve π-systems as acceptors. The formation of such halogen bonds is relevant to biological systems[37] and was observed in metal–organic,[38] and organic cocrystals.[39] Shen et al. have shown that cocrystallization via C–I···π halogen bonds can be used to modify pyrene luminescence, and similar observations were made by d'Agostino et al., who explored the effect of halogen bonding on the luminescence of tolane and stilbene (Figure 3D).[40] Cocrystal formation by C–Br···π and C–I···π halogen bonding interactions was used to modify a wide range of light-emission properties of diphenylanthracene, including light upconversion and chemiluminescence.[41] A systematic exploration of halogen bonding to π-systems has recently been reported by the Jin group, using flouranthene as a π-based halogen bond acceptor, and iodo- or bromo-substituted perfluorinated arenes as σ- and π-hole donors (Figure 4).[42]

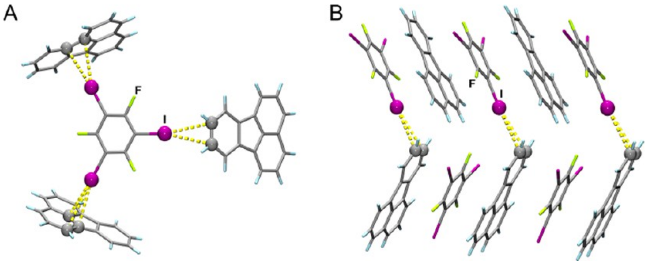


Figure 4. Views of the crystal structure of the cocrystal of 1,3,5-triiodotrifluorobenzene and fluoranthene reported by the Jin group,[42] illustrating (A) C–I···π halogen bonding environment of a single 1,3,5-triiodobenzene molecule and (B) the molecular stacking along the crystallographic *c*-axis.

Halogen bonding also permits the synthesis of more complex, elaborate solid-state structures and networks, as shown by Frausto et al., who reported that I···N interactions are key for the formation of two-dimensional "bricklayer" structures of asymmetric diphenylacetylenes[43] with a possible role in developing organic semiconductors. Yamamoto et al. have utilized halide anions[44] as nodes in the formation of anionic frameworks based on a node-and-linker approach. Liantonio et al. used such an approach to achieve interpenetrated anionic networks with honeycomb (Figure 5A),[45] as well as Borromean ring[46] topologies (Figure 5B).[47,48] Similar designs have been utilized by Yamamoto et al. in creating materials containing insulated conducting wires, with the anionic halogen-bonded molecular networks acting as insulating hosts for conductive stacks of tetrathiafulvalene-based cations.[49] Halogen-bonded ribbon motifs, often involving bi-

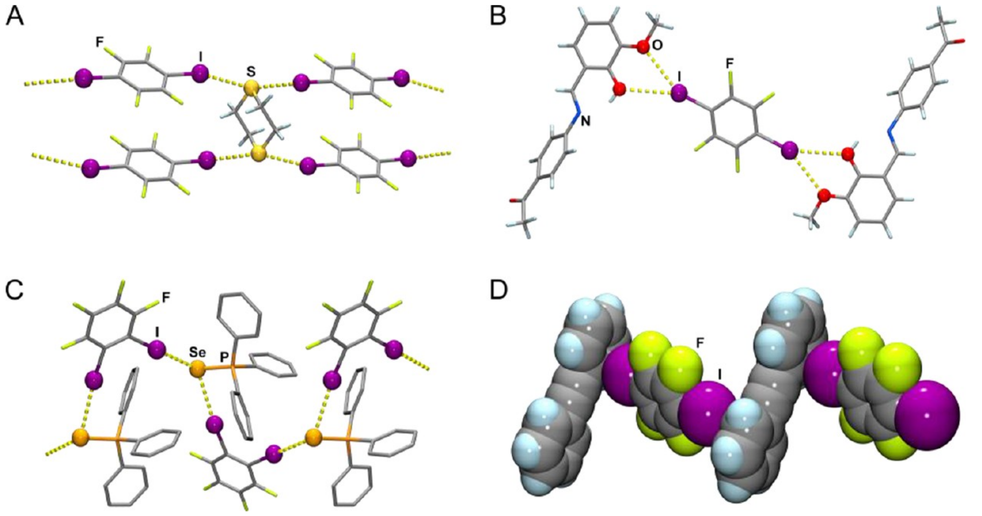


Figure 3. Fragments of crystal structures of halogen-bonded cocrystals, illustrating (A) bifurcated halogen bond acceptor sulfur atoms (B) a bifurcated halogen bond donor; (C) selenium atoms in triphenylphosphine selenide acting as halogen bond acceptors, and (D) the assembly of tolane and 1,4-diodotetrafluorobenzene via C–I···π halogen bonds.

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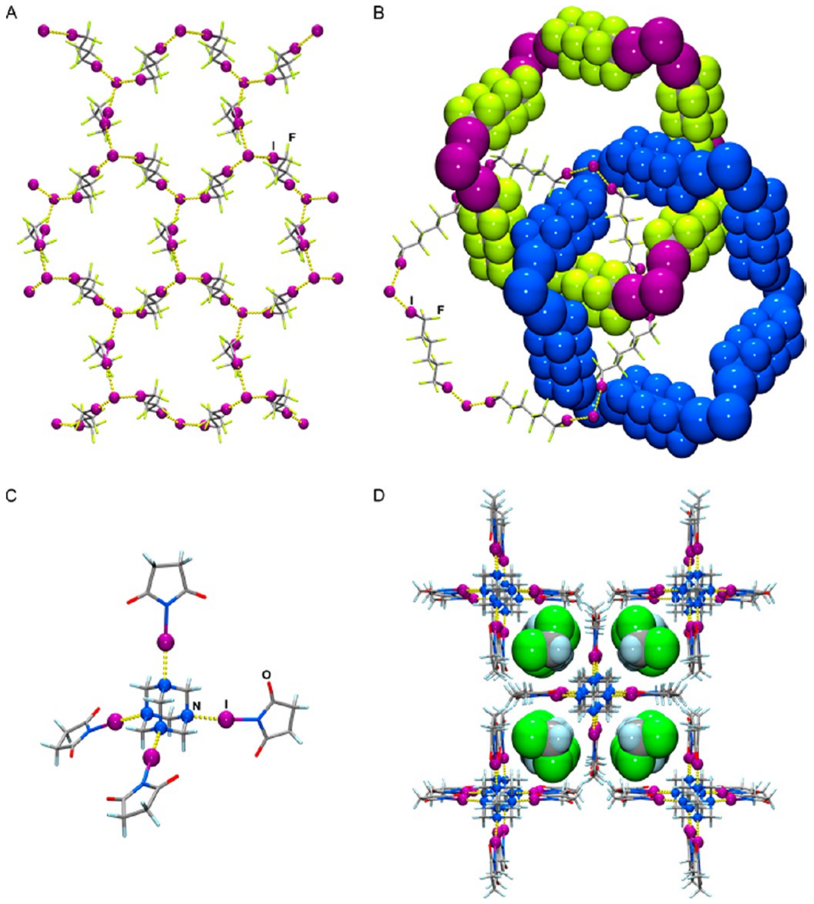

Figure 5. Fragments of the (A) honeycomb-topology network[45] and (B) interpenetrated Borromean ring topology[46] observed in cocrystals of *α*,*ω*-diiodoperfluoroalkanes halogen bond donors with iodide anions as acceptors. Cations are omitted for the sake of clarity. (C) A halogen-bonded tetrahedral building block based on hexamethylenetetramine, which assembles by weak hydrogen bonds into open structures incorporating different guests, for example, (D) dichloromethane.[52,53]

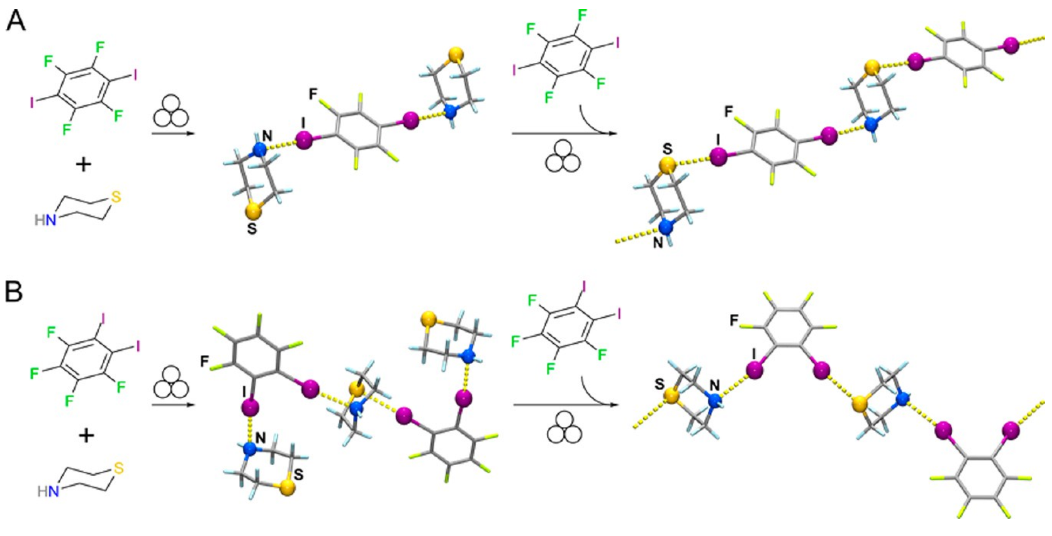

Figure 6. (A, B) Stepwise mechanism of mechanochemical cocrystallization by halogen bonding, described by the Jones group.[56]

and tridentate halogen bond donors have also been reported in the design of host systems,[50] where the use of "soft" sulfur halogen bond acceptors provides increased flexibility for potential guest uptake.[51]

That halogen bonding can lead to microporous frameworks was noted by Raatikainen et al.[52] upon cocrystallization of hexamethylenetetramine with *N*-iodosuccinimide, with the shape of framework channels depending on the choice of solvent for cocrystallization.[53] Such frameworks, built of halogen-bonded building blocks (Figure 5C) connected through weak hydrogen bonds, were demonstrated to be robust enough to undergo solvent exchange and accompanying framework reorganization (Figure 5D) in a single-crystal-to-single-crystal (SCSC)[54,55] manner.

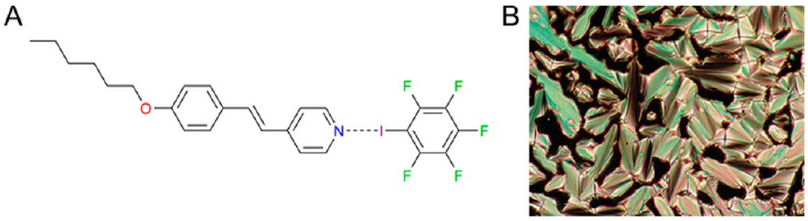

Figure 7. (A) Molecular components and (B) plane-polarized light microscopy image of a halogen-bonded liquid crystal reported by Bruce and co-workers. Panel B is adapted with permission from Bruce et al.[61] Copyright 2004 American Chemical Society.

Halogen-bonded cocrystals are readily prepared through conventional solution-based processes, as well as by solvent-free methods based on mechanochemistry and gas–solid reactions.[56,57] Mavračić et al. demonstrated that using mechanochemistry enables the clean synthesis of halogen-bonded cocrystals of *N*-bromosuccinimide, avoiding the possible side-reactions that might take place in solution, such as bromination.[58] Halogen-bonded cocrystal formation also provided one of the early examples of a stepwise reaction mechanism in a mechanochemical process, as cocrystal formation involving a heteroditopic halogen bond acceptor, such as thiomorpholine, leads first to cocrystals involving stronger I⋯N halogen bonds, which subsequently convert to stoichiometrically different materials involving stronger I⋯N and weaker I⋯S bonds (Figure 6).[56] Pennington and co-workers also investigated halogen bonding in pharmaceutical cocrystals, focusing upon the presence of X⋯S interactions and their impact on the structure.[51]

Halogen bonds have also been used to synthesize liquid crystals, as shown by Bruce et al.,[59] who demonstrated the formation of liquid crystalline phases in cocrystallization of pentafluoroiodobenzene and a range of 4-alkoxystilbazoles, as well as of alkoxystilbazoles with ditopic α,ω-diiodoperfluoroalkanes.[60] Studies of liquid crystal formation with 1,4-diiodotetrafluorobenzene as the halogen bond donor revealed liquid crystalline behavior over a range of ca. 1 °C. However, the use of appropriate alkoxystilbazoles enabled the range to be increased to >10 °C, demonstrating how the variation of halogen bond acceptors (or donors) can be used to modify liquid crystal properties (Figure 7).[61] More recently, molecules containing iodoethynyl (IC_2-) substituents have been used as halogen bond donors, forming liquid crystals over a wide range of temperatures.[62]

2. HALOGEN BOND-DRIVEN COCRYSTALLIZATION IN THE DESIGN OF LIGHT–MATTER INTERACTIONS

The use of halogen bonding to steer the organization of molecules in materials that interact with or respond to light stimuli is an emergent field. In principle, such materials incorporate chemical functionalities capable of halogen bonding, as well as functionalities that carry particular optical or emissive properties, e.g., chromophores, fluorophores, or photoreactive groups, etc. Although such systems can involve many currently popular chromophores or fluorophores (e.g., BODIPY molecules, diarylethylenes,[63,64] anthracenes,[65,66] etc.), the field has so far focused largely on the readily accessible, versatile, and ubiquitous azobenzene (azo) chromophores.[67] Covalent modification of azo chromophores can often be quite tedious, making the ability to generate materials rapidly through cocrystallization particularly attractive for uses in multi-component systems and devices.

Azobenzenes are highly popular in the design of colored and/or photoresponsive materials,[68,69] as they undergo reversible, light-induced *trans* → *cis* geometric isomerization (Figure 8a). The isomerization leads to significant changes in molecular shape and electronic structure, and many other

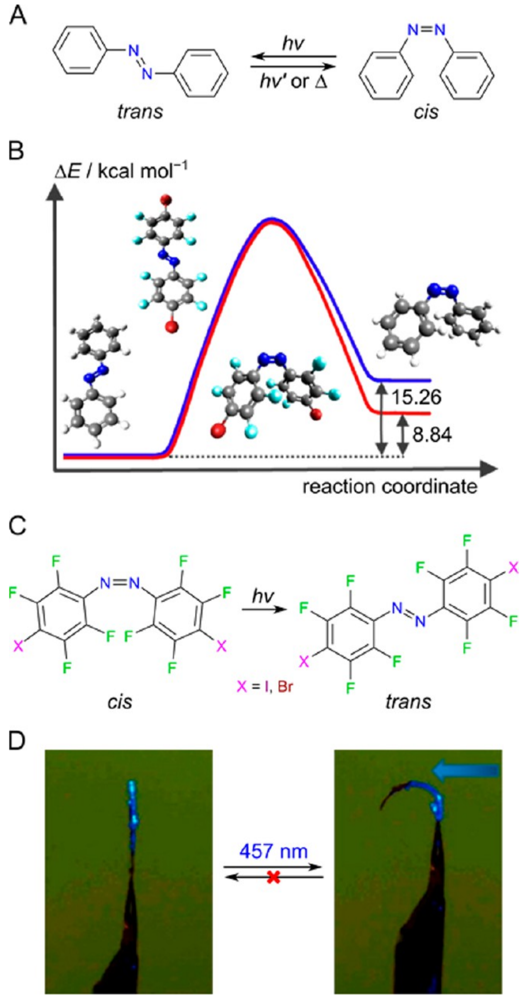

Figure 8. (A) Schematic illustration of the *cis*–*trans* azobenzene isomerization; (B) relative calculated energies of *cis*- and *trans*-isomers of azobenzene (blue) and 4,4′-dibromooctafluoroazobenzene (red), demonstrating the relative stabilization of the *cis*-form in case of the fluorinated compound; (C) schematic representation of the irreversible solid-state *cis* → *trans* isomerization of *cis*-4,4′-diiodooctafluoroazobenzene and its bromo analogue; and (D) images of a thin crystal of *cis*-4,4′-dibromooctafluoroazobenzene before (left) and after (right) exposure to visible 457 nm light.[74] The blue arrow indicates the direction of irradiation. Panels A, B, and D adapted with permission from ref 76. Copyright 2013 American Chemical Society.

optical and physical properties as a result. The conversion is fast, robust, and can be effected by low-power light in the visible or near-UV regions, making azo chromophores well-suited for a wide variety of efficient photoswitching materials applications. If contained in a solid-state or liquid crystal architecture, the photoinduced change in molecular geometry of the azo chromophore can also lead to significant macroscopic changes in the shape of the host material. Such photomechanical behavior, which enables the direct transformation of light into macroscopic mechanical motion, has been extensively demonstrated and explored in polymers or gels. In crystalline organic solids, photomechanical behavior of azo compounds has only been demonstrated recently, by Koshima et al., who reported the bending of thin crystals of *trans*-4-(dimethylamino)azobenzene upon exposure to ultraviolet (UV) light.[70] Photomechanical motion upon exposure of crystalline azobenzenes to visible light has been demonstrated by our group, through the use of pseudostilbenes, i.e., azo molecules substituted with a combination of electron-donating and -withdrawing functionalities.[71] The photomechanical motion of a pseudostilbene has been recently utilized by the Naumov group in the development of a general kinetic model describing the light-induced bending of slender crystals.[72]

2.1. Halogen-Bonded Cocrystals Involving Azobenzene Chromophores. The use of azo functionality in crystalline halogen-bonded architectures was explored early by the Aakeröy group, who used 4,4′- and 3,3′-azopyridines as halogen bond acceptors in combination with perfluorinated halogen bond donors.[73] The inverse strategy, the use of an azobenzene as a halogen bond donor in cocrystallization, was reported by Saccone et al.,[74] who employed *trans*-4,4′-diiodooctafluoroazobenzene as a halogen bond donor in combination with nitrogen- or oxygen-based acceptors. Whereas these reports demonstrated a new strategy to incorporate azo chromophores into readily designed and predictable halogen-bonded architectures, no optical or light-responsive properties were reported for the resulting cocrystals.

2.2. Photomechanical Effects in Halogen-Bonded Azobenzene Cocrystals. The design of photomechanical crystals based on azo chromophores was enabled by the observation that the lifetimes of *cis*-azobenzenes are greatly increased by fluorination. The Hecht group noted that introduction of fluorine substituents leads to significant stabilization of the *cis*-azobenzene structure relative to the thermodynamically favorable *trans*-isomer,[75] with the half-lives of fluorinated *cis*-azobenzenes found to be unusually long, ranging from days to months (Figure 8b). In contrast, half-lives of nonfluorinated and nonconstrained *cis*-azobenzene structures are much shorter, typically minutes or just seconds. This stabilization strategy enabled Bushuyev and co-workers to isolate a number of fluorinated *cis*-azobenzenes in the form of crystalline solids. On one hand, this provided an entry into tantalizing X-ray diffraction studies of *cis*-azobenzene crystals, previously impossible.[76] On the other hand, it led to the discovery of an unexpected, irreversible photomechanical effect, as thin crystals of *cis*-4,4′-diiodo- and *cis*-4,4′-dibromooctafluoroazobenzene were found to readily undergo photochemical solid-state *cis* → *trans* isomerization accompanied by a significant macroscopic bending of the crystal (Figure 8c,d).

Importantly, the irreversible photomechanical effect was found to be retained both upon covalent introduction of diverse substituents onto the fluorinated azobenzene core, as well as upon cocrystallization.[77−79] The latter was demonstrated by Bushuyev and co-workers, who used *cis*-4,4′-diiodo- and *cis*-4,4′-dibromooctafluoroazobenzenes as photomechanical cocrystal components in the synthesis of a family of cocrystals with nitrogen-based halogen bond acceptors (Figure 9A,B).[79] In that way, the use of only two photomechanically active building blocks enabled the preparation of a library of five photomechanically active crystalline materials, each with a different response to visible (532 nm) light, expressed in terms of the deflection angle of the crystal tip (Figure 9C). The cocrystal of *cis*-4,4′-diiodooctafluoroazobenzene with *cis*-bis(4-pyridyl)ethylene exhibited particularly extensive bending upon exposure to visible light, with deflection angles >90° (Figure 9D). Importantly, the cocrystal was found to undergo photochemical *cis* → *trans* isomerization in a crystal-to-crystal fashion, enabling the process to be monitored *in situ* by single crystal X-ray diffraction. Real-time X-ray diffraction experiments on a cocrystal irradiated at room temperature revealed the concomitant disappearance of Bragg reflections of the starting

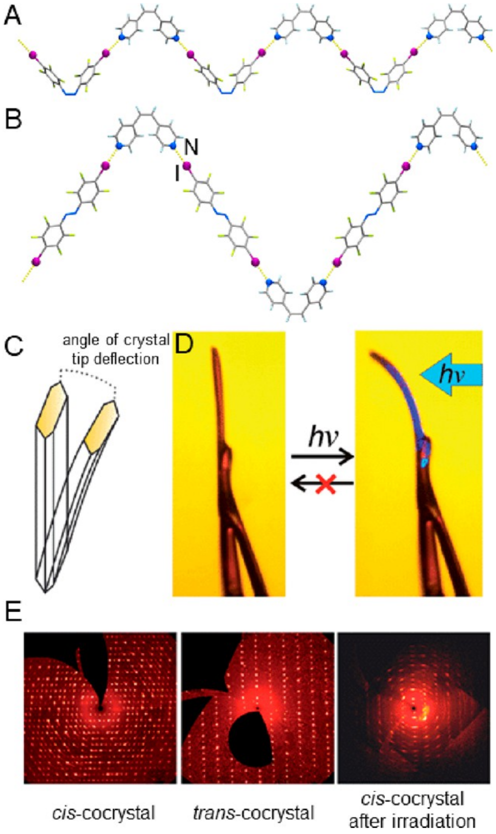

Figure 9. Fragment of crystal structures of halogen-bonded cocrystals based on (A) *cis*-4,4′-diiodooctafluoroazobenzene and (B) *trans*-4,4′-diiodooctafluoroazobenzene.[79] (C) Illustration of the crystal tip deflection angle, used as a measure of photomechanical crystal bending. (D) Photomechanical bending of the cocrystal of *cis*-4,4′-diiodooctafluoroazobenzene with *cis*-bis(4-pyridyl)ethylene upon exposure to 532 nm visible radiation, with the direction of irradiation indicated by the blue arrow and (E) composite X-ray diffraction images for the crystallographic (*h*0*l*) plane of (from left to right): the cocrystal of *cis*-4,4′-diiodooctafluoroazobenzene with *cis*-bis(4-pyridyl)ethylene; the corresponding cocrystal of *trans*-4,4′-diiodooctafluoroazobenzene and the cocrystal of *cis*-4,4′-diiodooctafluoroazobenzene after irradiation, demonstrating the crystal-to-crystal *cis* → *trans* isomerization.[79] Adapted with permission from ref 79. Copyright 2014 Royal Society of Chemistry.

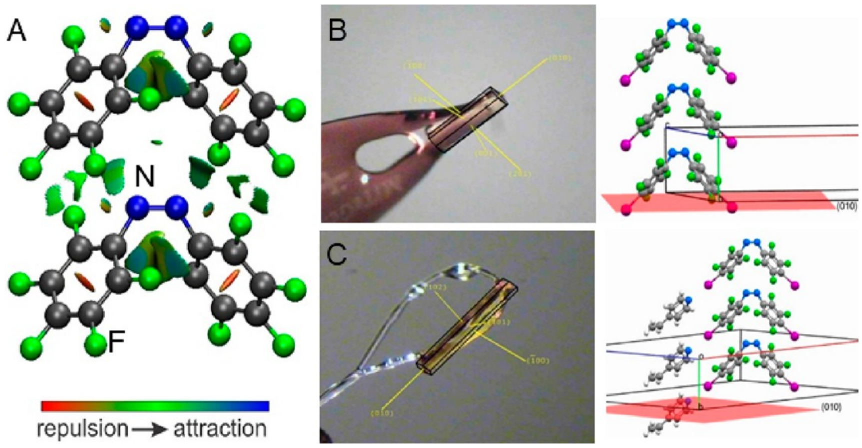

Figure 10. (A) Stacking of molecules in a crystal of *cis*-decafluorazobenzene, illustrating the azo···phenyl interactions. The azo···phenyl stacking directs the needle-like growth of crystals and persists regardless of substitution on the azobenzene or formation of halogen-bonded cocrystals, as shown by crystal images (left) and illustration of molecular stacking (right) in (B) *cis*-4,4′-diiodooctafluoroazobenzene and (C) its cocrystal with 4-vinylpyridine. In all cases, the crystal is elongated along the crystallographic *b*-axis, which is parallel to the azo···phenyl stacking.[78] Adapted with permission from ref 78. Copyright 2016 Royal Society of Chemistry.

cis-4,4′-diiodooctafluoroazobenzene cocrystal, and the appearance of reflections consistent with the analogous cocrystal of *trans*-4,4′-diiodooctafluoroazobenzene (Figure 9E).[79] In contrast, studies at a temperature of 200 K revealed only the disappearance of the Bragg reflections of the starting cocrystal, indicating the formation of a nondiffracting, amorphous material. Such behavior was interpreted as evidence of an amorphous intermediate during the photoisomerization process, indicating that the photomechanical activity was mediated by an amorphous phase.

2.3. Supramolecular Chemistry for Large Photomechanical Bending of Perfluorinated *cis*-Azobenzenes.

A key factor in the optimization and investigation of photomechanical bending is the ability to obtain sufficiently thin, micrometer-width crystals. In that respect, the electronic structure and the characteristic shape of perfluorinated *cis*-azobenzene molecules are particularly important, as they enable the formation of one-dimensional molecular stacks, held together by strong electrostatic interactions between the electron-deficient perfluorinated aromatic rings and electron-rich azo nitrogen atoms in neighboring molecules.[78] Such azo···phenyl "pringle chip-like" stacking (Figure 10A) was observed in all so far determined structures of perfluorinated azobenzenes by Bushuyev and co-workers. With a calculated energy of ca. 50 kJ mol^{-1}, the azo···phenyl stacking was evaluated to be the single most important interaction contributing to crystal structure stability. Because of this strong, directional stacking motif, perfluorinated azobenzenes show a high tendency to grow in the form of long and thin needles, highly desirable for photomechanical bending (Figure 10B). Importantly, the azo···phenyl stacking persists in combination with halogen bonding, providing the ability to direct the structure and macroscopic shape of halogen-bonded cocrystals involving a range of cocrystallization partners (Figure 10C,D). Fluorination of both benzene rings of the azo moiety appears important for azo···phenyl stacking motif: the presence of electron-rich alkoxyphenyl substituent in nonsymmetrical 4-iodotetrafluorophenyl-4′-dodecyloxyphenylazobenzene hinders the azo···phenyl stacking in the solid state and presumably facilitates the formation of I···N halogen bonds to azo nitrogen atoms, as observed by Saccone and co-workers.[80] The latter is particularly notable, having in mind that formation of halogen bonds between *trans*-azopyridine and *α*,*ω*-diiodoperfluorohexane- and -octane takes place selectively through pyridine nitrogen atoms as acceptors.[81]

2.4. Toward Halogen-Bonded Crystals with Nonlinear Optical Response.

Early theoretical work, combined with solution-based measurements, showed that self-complementary halogen-bonding molecules based on a push–pull design, i.e., molecules designed to simultaneously act as halogen bond donors and acceptors, respectively, through strongly electron-withdrawing (i.e., 4-iodotetrafluorophenyl) and strongly electron-donating (e.g., *N*,*N*′-dimethylamino) substituents, might offer a route to tune and optimize second order nonlinear optic (NLO) effects.[82] Extended analogues of these self-complementary halogen-bonding molecules, based on butadiene, 1,4-divinylbenzene, and 2,5-divinylthiophene fragments separating the electron-donating and -withdrawing moieties were later investigated experimentally and were established to form linear head-to-tail chains in the solid state and exhibit high molecular hyperpolarizability and nonlinear response in solution.[83] Whereas this work has not yet led to overall non-centrosymmetric crystal structures required for solid-state NLO behavior, it nevertheless provides a strong basis for the use of halogen-bonded materials in the field of organic nonlinear optics.

2.5. Photo- and Thermochromism in Halogen-Bonded Cocrystals.

Thermochromism is defined as the reversible change in color of a material due to a temperature change.[84] By extension, the photochromic effect corresponds to analogous reversible color switching behavior induced by light and is of particular importance for modern light-responsive eyewear and other types of variable-transmittance "smart windows".[85] A recent entry into exploration of photo- and thermochromic behavior of halogen-bonded cocrystals was reported by Carletta et al., who explored light- and heat-induced changes in optical absorption spectra of three *N*-salicylideneanilines based on 3-pyridyl, 4-bromophenyl, and 4-iodophenyl substituents, and their respective cocrystals with 1,4-diiodotetrafluorobenzene (Figure 11A–D).[86] All single-component *N*-salicylideneaniline solids and all derived cocrystals were found to be thermochromic, effectively demonstrating the persistence of

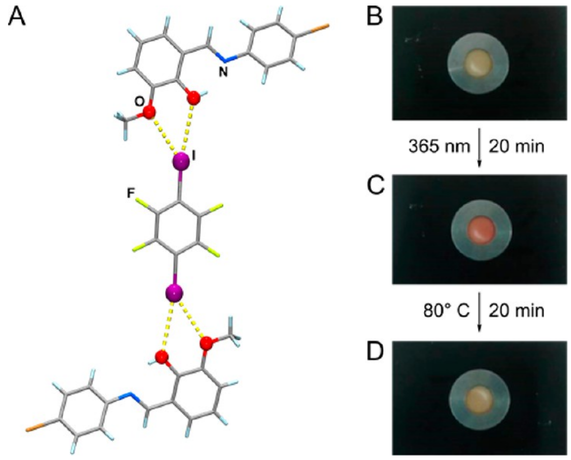

Figure 11. (A) Halogen-bonded assembly in the crystal structure of a photochromic cocrystal of 1,4-diiodotetrafluorobenzene with an *o*-vanillin Schiff base derivative, also illustrating bifurcation of a halogen bond donor site. Optical images of a KBr pellet containing the same cocrystal: (B) before irradiation, (C) after irradiation at 365 nm for 20 min, and (D) after thermal recovery. Panels B−D adapted with permission from Carletta et al.[86] Copyright 2017 John Wiley & Sons.

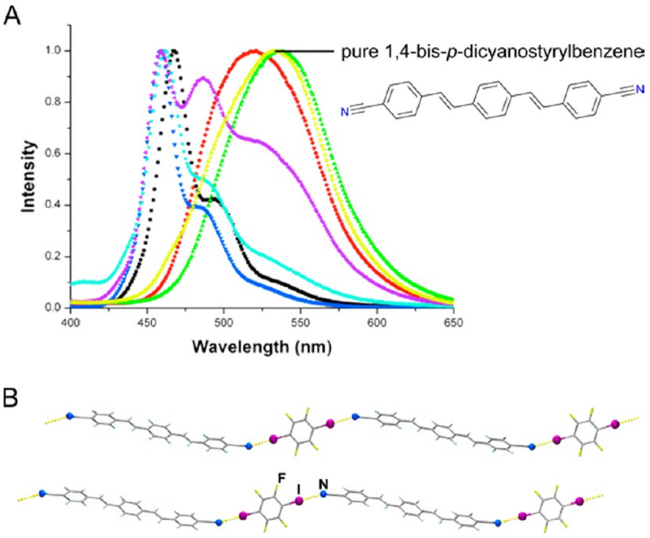

Figure 12. (A) Solid-state fluorescence emission spectra of pure 1,4-bis(4-cyanostyryl)benzene (yellow) and its halogen- or hydrogen-bonded cocrystals with 4-bromotetrafluorobenzoic acid (light blue), pentafluorophenol (purple), 1,4-dibromotetrafluorobenzene (dark blue), 1,4-diiodotetrafluorobenzene (black), 1,4-diiodobenzene (red) and resorcinol (green). (B) View of halogen-bonded chains in the crystal structure of the cocrystal of 1,4-bis(4-cyanostyryl)benzene and 1,4-diiodotetrafluorobenzene. Panel A adapted with permission from Yan et al.[89] Copyright 2011 John Wiley & Sons.

thermochromism upon cocrystallization, albeit with some difference in colors between the pure *N*-salicylideneanilines and the cocrystals. On the other hand, the photochromic effect was only observed in one of the pure *N*-salicylideneaniline solids and in two of the prepared cocrystals. Specifically, no photochromism was observed for 3-pyridyl-substituted *N*-salicylideneaniline or its halogen-bonded cocrystal, whereas 4-bromophenyl-substituted *N*-salicylideneaniline exhibited photochromism both as a pure solid, and as a cocrystal with 1,4-diiodotetrafluorobenzene. Interestingly, 4-iodophenyl-substituted *N*-salicylideneaniline formed crystalline solvate that was not photochromic, but its cocrystal with 1,4-diiodotetrafluorobenzene exhibited significant change in solid-state absorption spectrum upon irradiation with 365 nm light. Although a clear correlation between the structures of investigated solids and their thermo- or photochromic behavior is still not accessible, this work provides a strong demonstration that cocrystal formation through halogen bonds can be used to obtain new thermo- and photochromic crystalline solids.

2.6. Controlling Solid-State Luminescence. Halogen bond-based cocrystallization is an effective method for tuning the solid-state luminescence of crystals, i.e., tuning of the emission of light as a response to stimuli other than heat.[87] For the purpose of this review, we have decided to focus on luminescence via singlet−singlet and triplet−singlet electronic relaxation, or fluorescence and phosphorescence, respectively. A particularly well-investigated family of luminescent halogen-bonded cocrystals is based on the fluorescent linear ditopic halogen bond acceptor 1,4-bis(4-cyanostyryl)benzene and its isomers 1,4-bis(2-cyanostyryl)benzene and 1-(2-cyanostyryl)-4-(4-cyanostyryl)benzene.[88] Specifically, Yan et al. showed[89] that the formation of halogen-bonded cocrystals with a variety of structurally and chemically diverse halogen bond donors enabled the modification of solid-state optical properties of 1,4-bis(4-cyanostyryl)benzene, including UV/vis absorption, color, and fluorescence emission. The notable changes in the emission properties of 1,4-bis(4-cyanostyryl)benzene (Figure 12A) were explained in terms of changes to the geometric arrangement of molecules in the solid state.[89] The light absorption and fluorescence of the cocrystals could also be manipulated through crystal size, as demonstrated by the observed difference between the emission of the microsized particles of the cocrystal of 1,4-bis(4-cyanostyryl)benzene with 1,4-diiodotetrafluorobenzene (Figure 12B), compared to corresponding nanococrystals obtained by sonication. Besides a change in fluorescence emission profile, the nanococrystals also exhibited an extended fluorescence lifetime, which was explained through a reduction in cocrystal aggregation, which is expected to decrease excited-state nonradiative relaxation.[90] The nanococrystals of (1,4-bis(4-cyanostyryl)benzene)(1,4-diiodotetrafluorobenzene) also exhibited partially reversible changes in fluorescence emission with temperature, which was tentatively ascribed to changes in the length of halogen-bonding interactions due to thermal expansion of the material. The formation of I···N and Br···N halogen bonds was used to modify the emissive properties of the luminescent molecule 2,5-diphenyloxazole by cocrystallization,[13,91] resulting in changes to the solid-state emission profile and upconversion behavior. Interestingly, the cocrystals of 2,5-diphenyloxazole with 1,4-dibromotetrafluorobenzene and 4-bromotetrafluorobenzoic acid also exhibited a mechanochromic response, evidenced by partially reversible changes in emission profiles upon mechanical grinding. The effect of grinding on solid-state fluorescence emission was rationalized through mechanically induced structural changes, including amorphization. Other luminescent molecules whose solid-state emission properties were modulated through formation of halogen-bonded cocrystals include 9-acetylanthracene and 2-(2′-hydroxy-5′methylphenyl)benzotriazole.[92] In the latter case,[93] formation of a halogen-bonded cocrystal with 1,4-diiodotetrafluorobenzene led to a modification of the energy barrier associated with excited-state keto−enol tautomerization. Specifically, the tautomerization process in the cocrystal is essentially

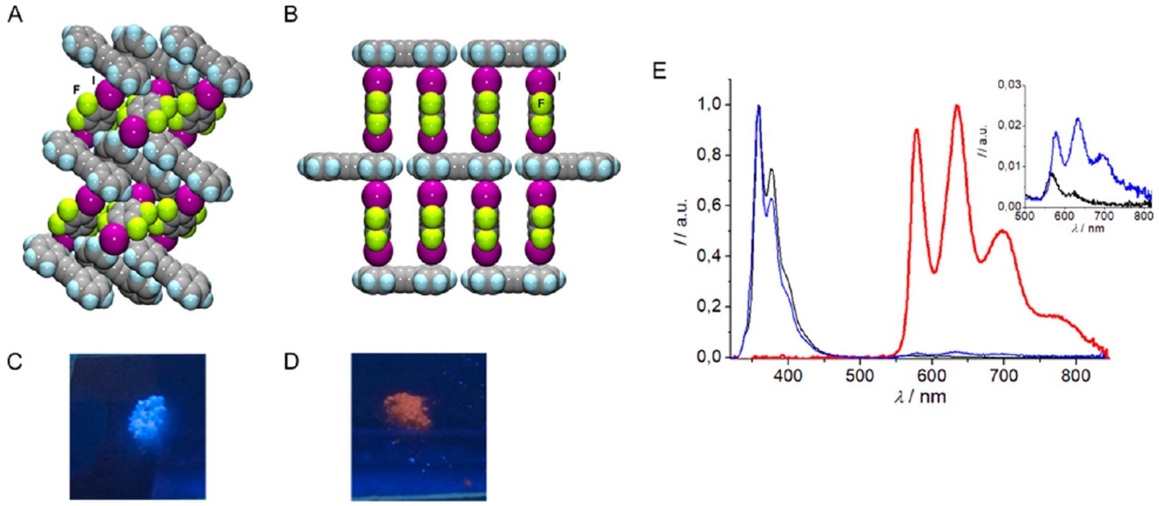

Figure 13. Controlling luminescence by halogen bonding. View of the crystal structures of two cocrystals of tolane and 1,4-diiodotetrafluorobenzene with respective: (A) 1:1 and (B) 1:2 stoichiometric compositions. Optical luminescence images for the (C) (tolane)(1,4-diiodotetrafluorobenzene) cocrystal and (D) (tolane)(1,4-diiodotetrafluorobenzene)$_2$ cocrystal. (E) Normalized solid-state emission spectra of tolane (black), the (tolane)(1,4-diiodotetrafluorobenzene) cocrystal (blue) and the (tolane)(1,4-diiodotetrafluorobenzene)$_2$ cocrystal (red), taken at room temperature, with an excitation wavelength of 315 nm. Inset shows a magnified range of 500−800 nm for tolane (black) and the cocrystal (tolane)(1,4-diiodotetrafluorobenzene) (blue). Panels C−E adapted with permission from d'Agostino et al.[40] Copyright 2015 American Chemical Society.

barrierless, which eliminated the fluorescence of the enol tautomer from the solid-state emission spectrum.

Further investigations on the relationship between luminescent properties and structure[94] of halogen-bonded cocrystals have shown that modifications to the molecular stacking can promote triplet−triplet annihilation, resulting in delayed fluorescence emission.[95]

Halogen bonding has been recognized as a particularly valuable design element in creating phosphorescent materials, as the close interaction between the bromine or iodine atoms of halogen bond donor can enhance or induce phosphorescence in selected acceptor molecules via heavy atom-induced spin−orbit coupling. This was demonstrated by Bolton and coworkers for brominated carbonyl compounds in the solid state. Whereas carbonyl groups are amenable to singlet−triplet intersystem crossing required for phosphorescent behavior, the emission is usually negligible. This limitation was overcome for differently substituted 4-bromobenzaldehyde derivatives by formation of solid solutions with 1,4-dibromobenzene. The formation of short halogen-bonded Br···O contacts in these solid solutions led to heavy atom-induced, highly efficient (up to 55% quantum yield) fluorescence emission in blue, green, yellow, and orange, depending on the carbonyl compound used.[96] Similarly, the formation of I···π halogen bonds between 1,4-diiodotetrafluorobenzene and carbazole,[97] as well as fluorene, dibenzofurane, and dibenzothiophene as halogen bond acceptors led to phosphorescent cocrystals.[98] The halogen bond donor in such I···π systems[9] was proposed to both provide a source of heavy atom-induced spin−orbit coupling, but also to hinder emission quenching by spatially separating emissive molecules. Similarly, Br···π halogen bond formation was utilized as a means to induce solid-state phosphorescence of phenanthrene by forming a cocrystal with 1,4-dibromotetrafluorobenzene.[99] Cocrystal formation with halogen bond donor diiodotetrafluorobenzenes was utilized by Shen to induce solid-state phosphorescence in pyrene,[39] while d'Agostino et al. demonstrated how changing the stoichiometric composition of cocrystals based on I···π halogen bonds can be utilized to control the preference for fluorescence or phosphorescence of diphenylacetylene (tolane) in the solid state. Whereas the cocrystal of tolane and 1,4-diiodotetrafluorobenzene in a 1:1 stoichiometric ratio exhibited both fluorescence and phosphorescence, a corresponding cocrystal of 1:2 stoichiometry exhibited phosphorescent emission only (Figure 13).[40] Very recently, Liu et al. demonstrated a family of phosphorescent cocrystals based on bifurcated I···N halogen bonds involving 1,4-diiodotetrafluorobenzene as the halogen bond donor and differently 4,7-disubstituted 1,10-phenanthrolines as acceptors.[100] Importantly, the color of phosphorescent emission was found to be readily modified by variation of the substituents on the halogen bond acceptor. An in-depth review of the tunability of luminescence through polymorphism and formation of multicomponent solids, including halogen-bonded materials, was provided by Yan and Evans.[101]

2.7. Control of Crystal Dichroism. A dichroic material is one which exhibits different absorptions at a single or over a range of wavelengths, depending upon its orientation relative to a source of plane-polarized light.[102,103] The presence of dichroism and tuning of its strength can also be achieved by halogen bonding; the use of halogen bonding to control dichroism of molecular materials was described by Bushuyev and co-workers,[103] who observed that, despite high similarity of molecular structures, single crystals of *trans*-4,4′-diiodo- and 4,4′-dibromoperfluoroazobenzene exhibit very different dichroic properties (Figure 14A). Specifically, whereas single crystals of 4,4′-dibromooctafluoroazobenzene exhibited a noticeable change in transmission color upon rotation in polarized light, the effect was hardly, if at all, observable for the corresponding iodo-derivative (Figure 14A). The difference was ascribed to crystal packing, as the structure of 4,4′-dibromooctafluoroazobenzene exhibited azo chromophore groups aligned in parallel, compared to the 4,4′-diiodooctafluoroazobenzene structure, which exhibited a herringbone-like arrangement of molecules (Figure 14A). Consequently, the control over dichroic properties of a material reduces to avoiding the formation of herringbone structures, which is a well-known problem of crystal engineering in context of

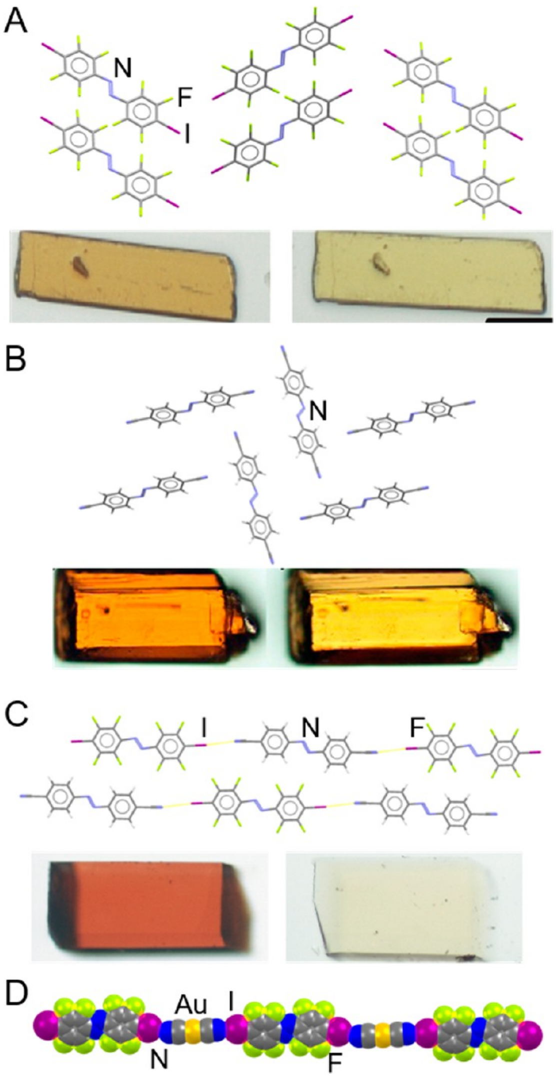

Figure 14. Controlling dichroic properties in halogen-bonded cocrystals.[103,109] Fragments of crystal structures (top) and polarized light images of crystals in two mutually perpendicular orientations (bottom) for the poorly dichroic single-component crystals of (A) *trans*-4,4′-diiodooctafluoroazobenzene and (B) *trans*-4,4′-dicyanoazobenzene, as well as for the strongly dichroic cocrystal (C) (*trans*-4,4′-diiodooctafluoroazobenzene)(*trans*-4,4′-dicyanoazobenzene). (D) A single halogen-bonded anionic chain, involving *trans*-4,4′-diiodooctafluoroazobenzene donors and dicyanoaurate(I) acceptors, as found in the dichroic metal−organic salt solvate crystals reported by Christopherson et al.[109] Figures adapted with permission from Bushuyev et al.[103] Copyright 2015 American Chemical Society.

photoactive or conductive organic materials.[104−108] Two strategies have been described for inducing dichroic behavior via halogen-bonded cocrystal formation, using 4,4′-diiodooctafluoroazobenzene as a chromophoric building block and halogen bond donor.

One strategy relied on the use of linear ditopic halogen bond acceptors, such as *trans*-4,4′-dicyanoazobenzene, which form linear halogen-bonded chains with 4,4′-diiodooctafluoroazobenzene. Parallel alignment of such supramolecular chains and, therefore, azobenzene chromophores, leads to highly dichroic materials (Figure 14A−C).[96] This strategy was subsequently expanded toward the design of metal−organic dichroic materials, by using dicyanoaurate(I) ion, Au(CN)$_2^-$, as a linear ditopic halogen bond acceptor (Figure 14D).[109] Cocrystallization of 4,4′-diiodooctafluoroazobenzene with KAu(CN)$_2$ in the presence of the crown ether 15-crown-5 led to the formation of a four-component cocrystal salt solvate, consisting of expected halogen-bonded anionic chains of 4,4′-diiodooctafluoroazobenzene and Au(CN)$_2^-$.[109] The second demonstrated strategy for the design of dichroic halogen-bonded cocrystals of 4,4′-diiodooctafluoroazobenzene involves the use of monotopic halogen bond acceptors substituted with long alkyl chains, such as 4-cyano-4′-*n*-pentylbiphenyl. In such a design, the halogen bond acceptor forms discrete complexes with 4,4′-diiodooctafluoroazobenzene, whose parallel arrangement in the crystal is dictated by the interdigitation of alkyl chains.[103]

Halogen bonding is also likely to be of importance in an area related to crystal dichroism, specifically the understanding and design of X-ray birefringence in molecular solids. Pioneering work in X-ray birefringence imaging of solids has been reported by the Harris group,[110] who demonstrated that polarized X-rays can be sensitive to the parallel and directional alignment of chemical bonds, notably those involving heavy atoms such as bromine or iodine, in highly anisotropic crystals. This enables the direct X-ray imaging and mapping of molecular orientation and ordering in solids, through a high-energy radiation analogy of the optical polarizing microscope. As both bromine and iodine are central to crystal engineering via halogen bonds, further development of this novel imaging technique is likely to be of considerable use in the field. Conversely, the ability to design new materials and molecular ordering via halogen bonding offers a route to develop and fine-tune new polarizing filters for X-rays.[110]

2.8. Directing Solid-State Photochemical Reactions via Halogen Bonds. Similar to hydrogen bonds,[111] halogen bonds can also be utilized to direct the assembly of organic molecules into geometric arrangements suitable for topochemical [2 + 2] photodimerization. This was first demonstrated elegantly by the group of Caronna and coworkers, who utilized a 4-iodotetrafluorophenyl-substituted pentaerythritol derivative as a halogen bond donor template for the assembly of pairs of *trans*-1,2-bis(4-pyridyl)ethylene molecules into parallel, and at a separation of less than 4 Å (Figure 15A).[112] Such organization of olefins was within the range of Schmidt's topochemical postulates for photodimerization[113] and, consequently, the exposure of the resulting cocrystals to ultraviolet (UV) light led to the stereoselective formation of the cyclobutane dimer, *rctt*-1,2,3,4-tetrakis(4-pyridyl)butane. Importantly, the geometry of the resulting cyclobutane product was in agreement with the organization of the olefin reactant molecules imposed by the halogen bond donor template.[113] The inverse template-directed strategy, in which the template is a pyridine-based halogen bond donor, and the reactant is a halogen bond acceptor, has been demonstrated by the MacGillivray group, who employed 1,8-bis(4-pyridyl)naphthalene to align molecules of *trans*-1,2-bis(4-iodotetrafluorophenyl)ethylene into discrete photoreactive assemblies. Exposure of the halogen-bonded cocrystals to UV light led to quantitative and stereoselective formation of the cyclobutane dimer *rctt*-1,2,3,4-*tetrakis*(4-iodotetrafluorophenyl)cyclobutane (Figure 15B).[114] A similar design, using 1,8-bis(iodoethynyl)anthracene as a halogen bond donor template, was utilized by the Aakeröy group to steer molecules of *trans*-1,2-bis(4-pyridyl)ethylene into rectangle-shaped tetramolecular assemblies.[115]

Halogen bond-driven cocrystallization was used by Zhu and co-workers[116] to enable a green [2 + 2] photodimerization

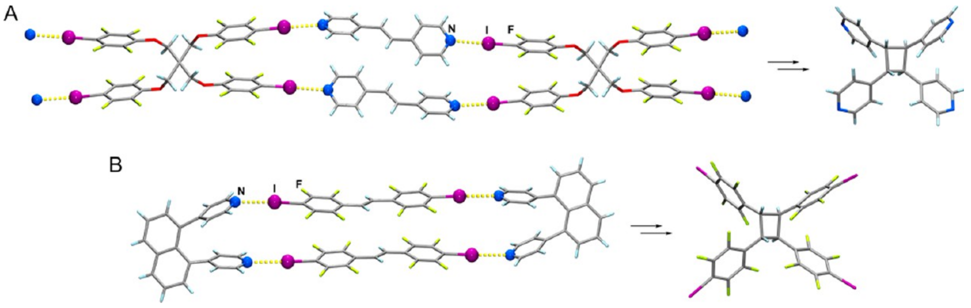

Figure 15. Examples of template-directed solid-state [2 + 2] olefin photodimerization[113] in halogen-bonded cocrystals reported by (A) Caronna and co-workers, who utilized a template acting as a halogen bond donor,[112] and (B) Sinwell and MacGillivray, who utilized a halogen bond acceptor linear template.[114]

process involving vitamin K_3 as the reactant (Figure 16). Cocrystal formation involving vitamin K_3 with either 1,4-diiodo- or 1,4-dibromotetrafluorobenzene leads to the formation of linear halogen-bonded chains whose stacking brings the carbon−carbon double bond (C=C bond) in orientations suitable for [2 + 2] photodimerization. Upon exposure of cocrystals to UV light, the *syn*-dimer of vitamin K_3 is formed stereospecifically. Importantly, whereas previously reported approaches for cocrystal-directed photodimerization require additional operations and auxiliary reagents to remove the template and isolate the dimeric photoproduct, in this case the vitamin K_3 dimer was readily obtained by simple heating of the cocrystal after photodimerization, leading to solvent-free removal of the halogen bond donor by sublimation.[113] The obtained donor could be used in the next cycle of photochemical dimerization by mechanochemical grinding with fresh reactant.[116]

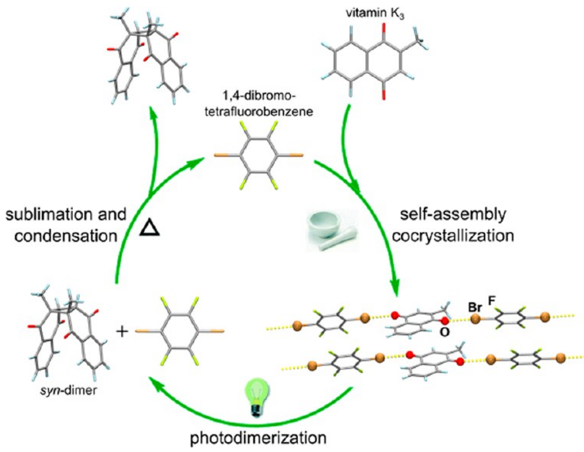

Figure 16. Photochemical [2 + 2] dimerization of vitamin K_3 in a cocrystal with 1,4-dibromotetrafluorobenzene, reported by Zhu and co-workers. Following photodimerization, the halogen bond donor is readily removed by sublimation and recycled for the next [2 + 2] photodimerization step by grinding cocrystallization with fresh reactant.[116]

3. EXAMPLES OF OTHER TYPES OF SOLID-STATE REACTIVITY IN HALOGEN-BONDED COCRYSTALS

Whereas the focus of this overview is constrained to opportunities in controlling light-matter interactions, halogen bond-driven cocrystal formation also offers an entry into other types of solid-state reactivity, sometimes even producing novel, otherwise difficult to make materials. One example is the selective formation of halogen-bonded ionic cocrystals by a solid−gas reaction of alkylammonium iodides and terminal α,ω-diiodoperfluoroalkanes (Figure 17A).[3] The gas−solid reactions enable the otherwise tantalizing separation of iodoperfluoroalkanes of different molecular sizes, as the cocrystal salt formation is controlled by a size match between alkylammonium cation of the salt and the α,ω-diiodoperfluoroalkane in the gas phase. The excellent selectivity achieved through this process provides an exciting new opportunity for resolving the challenge of industrial separation of fluoroalkanes.

A particularly exciting example of novel solid-state reactivity enabled by halogen bonding has been provided by the Goroff and Lauher groups, who prepared a library of cyano-substituted ditopic oxalamide derivatives to organize molecules of 1,4-diiododiacetylene for a topochemical diacetylene polymerization (Figure 17B).[117−119] Analysis of the prepared cocrystals confirmed the ability of the self-assembled oxalamide hosts to organize 1,4-diiododiacetylene for the reactions, and, in case of one of the host templates, structural analysis of the cocrystals revealed spontaneous single-crystal-to-single-crystal polymerization into the poly(diacetylene) product. The formation of poly(1,4-diiododiacetylene) was also achievable in the case of other oxalamide templates, upon exposure of the cocrystals to pressures above 300 bar, and was readily observable optically and spectroscopically in a diamond anvil cell.[120] So far, the topochemical polymerization controlled by halogen bonds appears to be the only route for the synthesis of this simple, fully conjugated polymer with composition $[C_2I]_n$.

4. PHOTORESPONSIVE HALOGEN-BONDED LIQUID COCRYSTALS

While most studies of halogen bonding in liquid crystals design focus on the ability to induce or control liquid crystal formation by halogen bonds, the introduction of photoactive moieties into halogen bond donors or acceptors now enables chemically driven changes and switching in such systems. A notable recent example is a photoresponsive halogen-bonded liquid crystal which combines properties of photoalignment and photoinduced mass transfer for the formation of surface relief gratings, achieved by halogen bond-driven complexation between a nonsymmetrical azobenzene acting as the halogen bond donor, with a nonsymmetrical stilbazole as the acceptor.[121] It was subsequently shown that analogous cocrystals in which long alkyl chains are attached to the noninteracting end of the azobenzene moiety can exhibit the same effect, with as little as 4% *trans* → *cis* conversion leading to a transition between a liquid crystal and an isotropic liquid (Figure 18).[122]

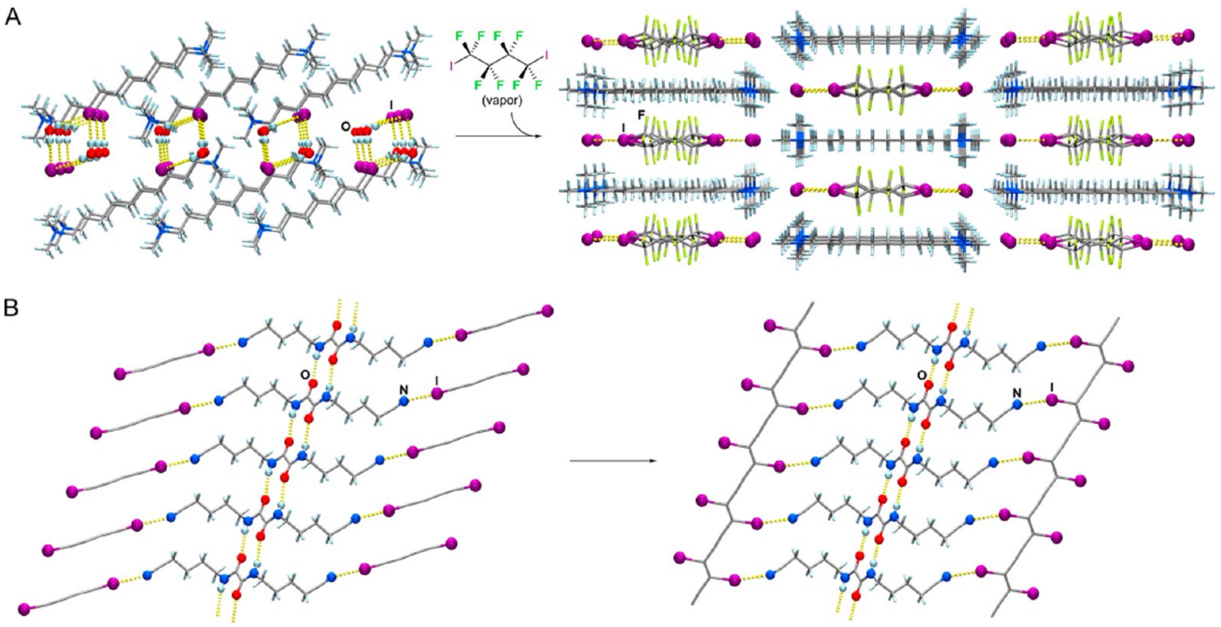

Figure 17. (A) Example of a gas−solid reaction between α,ω-diiodoperfluorinated alkanes and solid alkylammonium salts leading to the formation of halogen-bonded salt cocrystals.[3] The reaction is highly selective to perfluoroalkane chain length, controlled by size matching to the length of the alkylammonium cations; (B) spontaneous polymerization of 1,4-diiododiacetylene in a halogen-bonded cocrystal with a self-assembled template, reported by the Lauher and Goroff groups.[117−119]

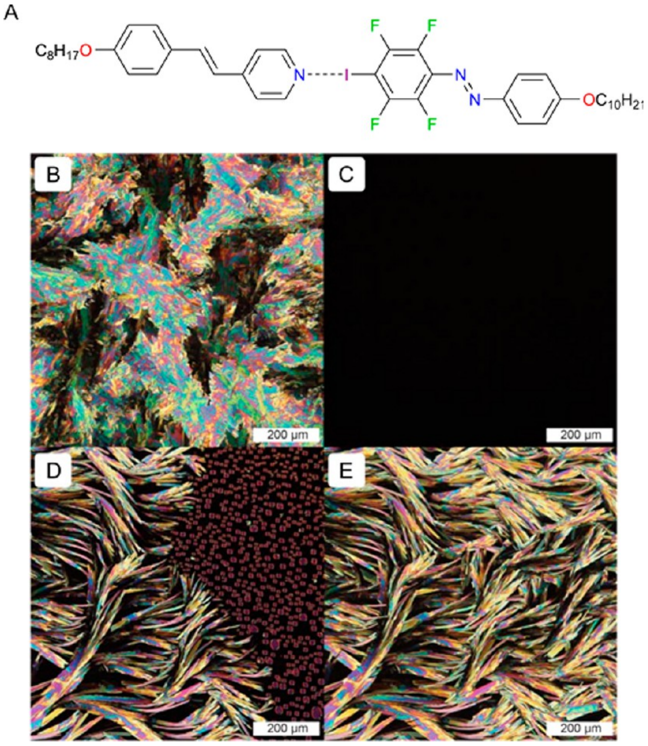

Figure 18. Photoresponsive halogen-bonded liquid crystalline system described by Fernandez-Palacio et al.: (A) cocrystal components; (B) initial crystalline material during melting; (C) crystals immediately after irradiation; (D) formation of partial nematic liquid cocrystal phase; and (E) final fully crystalline material (E). Panels B−E adapted with permission from Fernandez-Palacio et al.[122] Copyright 2016 American Chemical Society.

Rather than synthesizing bulk stoichiometric cocrystal phases to act as novel liquid crystals, Vapaavuori et al. have shown how small amounts of carefully selected halogen-bonding additives can be used to modify the ordering and develop new optical properties of a known liquid crystalline phase.[123] As established by a wide range of techniques, including differential scanning calorimetry, polarized absorption spectroscopy, and optical diffraction, addition of small amounts (between 0.3% and 1%) of halogen bond donor dyes to the nematic liquid crystalline material 4-cyano-4′-*n*-pentylbiphenyl resulted in significant modification of both the temperature of the isotropic-to-nematic transition, and also introduced optical response to the otherwise colorless material. Comparing the effect of iodo-, bromo-, and hydrogen-substituted dye derivatives on the order parameter of the liquid crystals revealed that stronger, more directional halogen-bonding interactions help the alignment of dye molecules with the director axis of the 4-cyano-4′-*n*-pentylbiphenyl matrix.

An inverse halogen bond-based design was also shown to be possible, in which the azobenzene molecular photoswitch acts as a halogen bond acceptor to molecular dihalogens as donors (I_2 or Br_2). In this case, liquid crystals containing iodine could be reversibly photoisomerized to switch between a liquid crystal and an isotropic phase. Interestingly, such behavior was not observed with bromine-based analogues.[124] Following the initial reports of halogen-bonded ionic liquid crystals,[125] Saccone et al. very recently reported a related system incorporating azobenzene halogen bond donors and iodide anions acting as bidentate halogen bond acceptors. Irradiation with UV light induced the photoisomerization of the azo moiety, resulting in the transition from a liquid crystal phase to an isotropic material,[126] opening the possibility of using halogen-bonded ionic liquid crystals as photoactuated anion transport materials.

5. OUTLOOK

In this review, we have attempted to summarize the tremendous recent activity in using halogen bonding to design and develop light-responsive and optically active materials.

Admittedly, in the preparation of this review even the authors ourselves were somewhat surprised with the current extent of this rapidly growing field, with new reports outlining clever new designs for a wide range of properties, not only for photoreactive or photomechanical solids, but also for generating fluorescent, phosphorescent, dichroic, and upconverting materials. It appears, at least in the context of experimental studies, that the area of halogen-bonded optical cocrystals is rapidly achieving maturity, opening new opportunities for solid-state materials design. We expect that the potential of halogen-bonded molecular association for the design and synthesis of photoresponsive or optically active materials and, subsequently, devices will be further augmented through the development and implementation of periodic density functional theory (DFT) theoretical approaches,[127] not only to model but also to predict and design solid-state properties of such materials, as was recently demonstrated for microporous organic solids.[128] Whereas the herein illustrated examples represent only the very first entries of halogen bonding into engineering functional optical crystals, it is not early to highlight that similar successes and maybe even different opportunities for materials design can be expected by exploration of other σ-hole interactions, notably chalcogen, pnictogen, and tetrel bonds.[129−132] We hope that this overview will provide an inspiration for further development of crystal engineering by halogen bonding and other σ-hole interactions, bolstering their use in the development of an exciting and powerful new class of self-assembled designer optical and photoresponsive materials.

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Notes

The authors declare no competing financial interest.

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