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Review Article

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Halogen Bonding beyond Crystals in Materials Science

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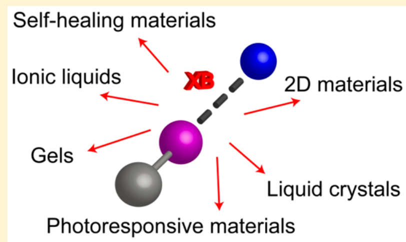
ABSTRACT: Halogen bonding has recently gained well deserved attention in present-day research for its importance in many fields of supramolecular science and crystal engineering. Although generally overlooked in comprehensive studies in the past, halogen bonding has become an important tool also in the field of materials science. An increased number of scientific reports are published every year where halogen bonding is exploited in soft materials rather than in crystal engineering. Here, we focus on a description of the most exciting contemporary developments in the field of halogen-bonded functional soft materials, assembled using the guiding principles of crystal engineering. We give a particular emphasis to those published in the past few years.



■ INTRODUCTION

Gaining precise control over the structure and dynamics of matter is still an open challenge, which can give access to architectures of ever-increasing complexity and, hence, to new functional materials with desired physicochemical properties.[1] To reach this goal, supramolecular chemistry as "chemistry beyond the molecule"[2] has proven to be a powerful tool for the design and synthesis of complex systems, whose structural and functional features are originated by the self-assembly trajectories of the constituent building blocks.[3] The geometrical arrangement of molecular monomers in higher-order assemblies is dictated by their molecular structure, their functionalities, the local chemical environment, and, ultimately, by specific sets of non-covalent interactions, which are driving the self-assembly processes to the free-energy minima, either kinetic or thermodynamic depending on the energy landscape shape and the height of the activation energy barriers of the system under consideration.[4] Intermolecular interactions play the key role in building supramolecular complexes, thanks to their strength, which can be high enough to drive the assembly of discrete and robust systems, to their inherent reversibility, and to the preservation of the chemical identity of the molecular precursors.[1] Thus, a careful selection of the supramolecular synthons, recurring supramolecular motifs based on specific non-covalent interactions which allow the *a priori* design of target materials through retrosynthetic strategies,[5] can give access to desired structural arrangements and, hence, tailored functional properties of the final product. There is a wide gamut of different intermolecular interactions at the disposal of chemists for the construction of supramolecular materials, which can be chosen depending on the required geometric and energetic features, e.g. hydrogen bonding,[6] halogen bonding,[7] π interactions,[8−10] and isotropic dispersive interactions (solvophobic effect, fluorous interaction, etc.).[11−13] Among them, halogen bonding (XB), defined as any interaction involving a halogen atom as an electrophilic site,[14] has recently attracted growing attention thanks to its unique features, such as directionality, strength, and tunability, which make it an ideal candidate as a structural tool for the design and synthesis of supramolecular functional materials.[15]

XB has been known for the last two centuries when the first halogen-bonded complexes were first reported by Colin in Gay-Lussac laboratories in 1814.[16,17] The first attempts to rationalize the findings related to the occurrence of these peculiar non-covalent interactions were made by Hassel and then by Bent, in the 1950s.[18,19] In the following decades, the paramount importance of XB in molecular recognition phenomena in the gas phase,[7] liquids,[15,20] and biological systems has been clearly emerging.[21,22] Solid state and, specifically, molecular crystals, as "supramolecules par excellence" as stated by Dunitz,[23] have been the ideal platform for the systematic studies of XB, which brought to its formal IUPAC definition.[14] The analysis of molecular crystals and the use of halogenated organic compounds in driving the self-assembly of crystalline materials in a controlled and predictable way via XB has comprehensively demonstrated the effectiveness of this intermolecular interaction as an architectural tool in designing and synthesizing new crystal forms. Subsequently, XB has been largely exploited in crystal engineering,[24,25] the branch of science devoted to the design and synthesis of solids with tailored properties via the study of non-covalent interactions and packing within crystalline lattices and their characterization.[26−31] In this context, XB-based synthons have been employed for the construction of a broad range of crystalline materials, e.g., novel optoelectronics,[32−35] drug formulation,[36] molecular machines,[37,38] magnetic and conductive materials,[39] and porous solids.[40]

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The concepts and ideas codified through crystal engineering can be generalized for other classes of materials. Among all, soft matters, defined as complex and flexible materials which can respond to a mild external stimulus with a drastic change of their physicochemical properties,[41] comprise a broad range of technologically relevant species, such as polymers, colloids, liquid crystals, biomacromolecules, among others, and they are attracting ever-increasing attention of the scientific community. They do not possess the long-range precise atomic disposition of crystals, but they are still based on flexible higher-order supramolecular lattices, whose structural organization relies on the nature of the intermolecular interactions driving the complex self-assembly and the molecular packing motifs.[42] The careful design of supramolecular synthons can give access to soft matters with tailored structural features and properties. In soft matter engineering, XB, thanks to its robustness and geometrical features, can play a key role in taking control over the hierarchical structure of this class of materials.

In this review, after a short pedagogical overview on the nature of XB, we present the paradigm shift of XB from a precious structural tool for the design of crystalline solids to its use to build novel functional soft matters, showing the generality of self-assembly phenomena, which go far beyond the traditional scope of crystal engineering.

■ PHYSICAL INSIGHTS ON HALOGEN BONDING

As explained previously, XB has emerged as a new phenomenon, or, more properly, a phenomenon studied more in detail, in the past 20 years. It is usually depicteded as R—X···Y, where X is a halogen and Y is an electron-rich moiety as in the hydrogen-bond (HB) case. Here, we give a simple model for XB which was shown to be valid for weak-to-moderate strength XB[43] and briefly comment at the end of this section on alternative models.

Halogen bonding arises from the substantial quadrupole moment of the halogen atom along the *z*-axis Q_{zz}, which we explain with a simple orbital model (Figure 1). When the halogen—bromine for example—is covalently bound to fluorine as in BrF, it has the configuration $4s^2 4p_x^2 4p_y^2 4p_z^1$ and the $4p_z$ electron is localized in the bond region, while the electron density of the outer lobe of the orbital is depleted. Thus, XB forms due to the complete occupancy of the p−π orbitals, but only partial occupancy of the p−σ orbitals, giving rise to the so-called "σ-hole".[44] The result is a positive electrostatic potential along the extension of the R−X bond beyond the X atom, which approaches the electron-rich region of the Y atom. The positive potential of this region increases if one increases the polarizability of the halogen (fluorine is the least polarizable) or the electron attracting capability of the moiety attached to the halogen, as is shown in Figure 1.

It is reasonable to expect that the XB geometry should be linear. Indeed, halogen bonds tend to be closer to linearity than hydrogen bonds. Here the main driving force is not the electrostatics but the flattened shape of bonded halogen atoms (polar flattening), because the X···Y distance is shorter when the R−X···Y is linear.[46]

The simple electrostatic model described above was brought up by Politzer, Murray, and Clark,[47] but it is not universally accepted. In recent years, several authors have proposed different models for XB, based on interaction energy decomposition schemes, where the interaction energy of a non-covalent complex (which is a physically observable quantity) is separated into a set of fundamental components,

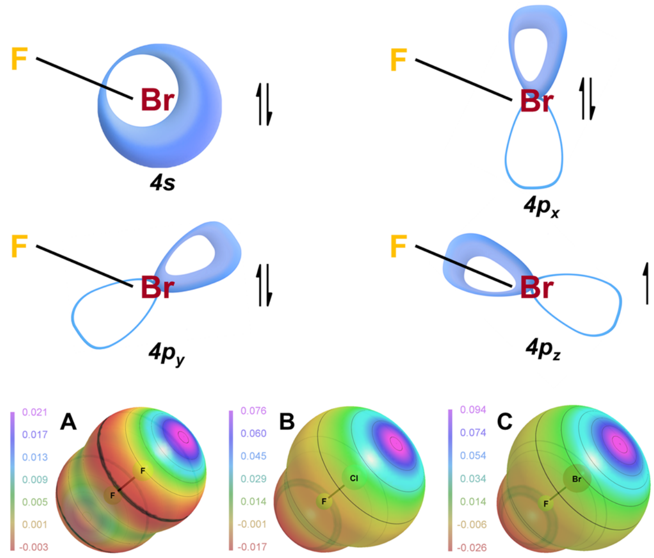


Figure 1. Top: Schematic view of the atomic orbitals of bromine in BrF. Bottom: Molecular electrostatic potential (all electron CCSD(T) _aug-cc-pV5Z-DK) of the F_2 molecule (A), ClF molecule (B), and BrF molecule (C) plotted on the 0.001 au contour of the electron density. The electrostatic potential on the halogen atom gets higher (more positive) as its polarizability is increased. The electrostatic potential was visualized using the software MoleCoolQt.[45]

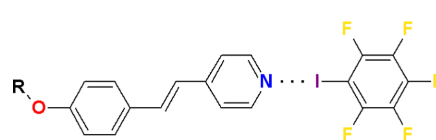
such as electrostatics, polarization, dispersion, exchange, charge transfer, repulsion, distortion, etc. These schemes such as SAPT,[48] NBO,[49] QTAIM,[50] EFL,[51] and others[52] were reviewed recently in the context of XB.[53,54] Here, we do not comment on the relative importance of the contributions calculated with the aforementioned methods (contributions which change upon changing the system under consideration), but we assume the electrostatic model, which can explain most, if not all, the properties of XB that are relevant in the context of soft materials.

■ LIQUID CRYSTALS

Liquid crystals (LCs), assembled by non-mesomorphic starting modules, which interact by means of specific non-covalent interactions, such as hydrogen bonding[55] and arene−perfluoroarene interactions,[56] have been known for a while.[57] Inspired by their previous work on phenol−stilbazole systems, Bruce et al. reported in 2004 the first XB-driven thermotropic LCs (Scheme 1). These dimeric systems feature iodopentafluorobenzene as the XB donor and alkoxystilbazoles as XB acceptors.

In this seminal work, Bruce et al. demonstrated that only the strong I···N_{pyr} interaction possesses the required rigidity and robustness to provide the LC phases. Since then, with only one exception,[58] all of the LCs driven by XB have been based on the I···N_{pyr} bonding. XB-driven LCs have been reviewed recently by Li et al.,[59] so we focus here on the most recent

Scheme 1. First Examples of XB-Driven LCs



R = C_4H_9, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$

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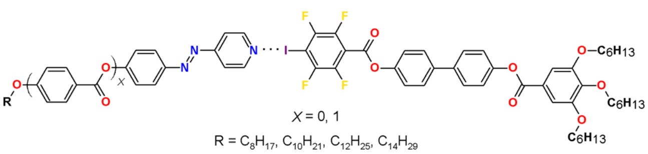
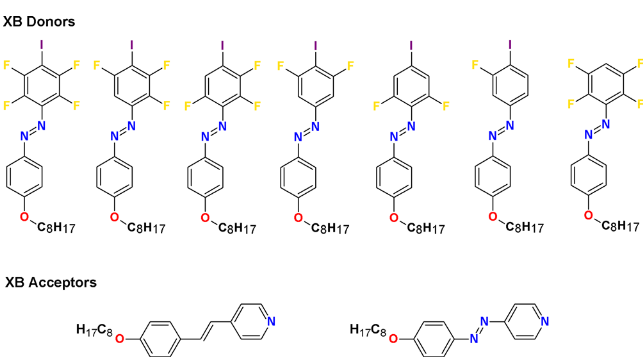
developments. Major advances in the field come from the work of Alaasar and Tschierske et al., who reported the first polycatenar XB-driven LCs (Scheme 2).[60]

Scheme 2. XB Photoresponsive Polycatenar LCs



In this study, a non-mesomorphic taper-shaped XB donor was combined with photoresponsive azopyridines to produce mesomorphic assemblies featuring broad smectic A (SmA) phases. The complexes featured fast and efficient LC-to-isotropic phase transitions upon irradiation with a laser pointer (405 nm). Comparison with analogous (nonfluorinated) hydrogen-bonded systems, based on benzoic acids and azopyridines, revealed the systematic lack of cubic (Cub) phases. This was attributed to the presence of fluorine atoms, which increased the cross-sectional area of the fluorinated core, leading to a reduction of the interface curvature between aromatic cores and aliphatic side chains. Similarly, the lower clearing points of the XB systems were explained with the relative weakness of the XB compared to HB. New physical insights on the reliability of iodofluorinated aromatic synthons for the assembly of XB-based mesogens were recently provided by Giese and Priimagi et al., who explored dimeric assemblies formed by stilbazoles and azopyridines—used as XB acceptors—and iodofluoroazobenzenes with different fluorine substitution patterns—used as XB donors (Scheme 3).[61]

Scheme 3. Role of Aromatic Fluorine Substitution in Photoresponsive XB Liquid Crystals



These authors found that at least three fluorine atoms are needed for the formation of the LC phases, giving rise to a sufficiently strong XB to support the supramolecular structure. Correlations between the mesophase width and the XB strength were thus unambiguously established. Furthermore, the aforementioned authors showed that stilbazoles are superior LC-phase inducers compared to azopyridines. All of the complexes featured a rich variety of phase transitions, in line with their previous studies (Figure 2).[62]

IONIC LIQUIDS

Ionic liquids (ILs) have attracted a considerable amount of attention in the past 20 years, due to their exceptional properties.[63] In 2016, Cavallo et al. reported the first XB IL,

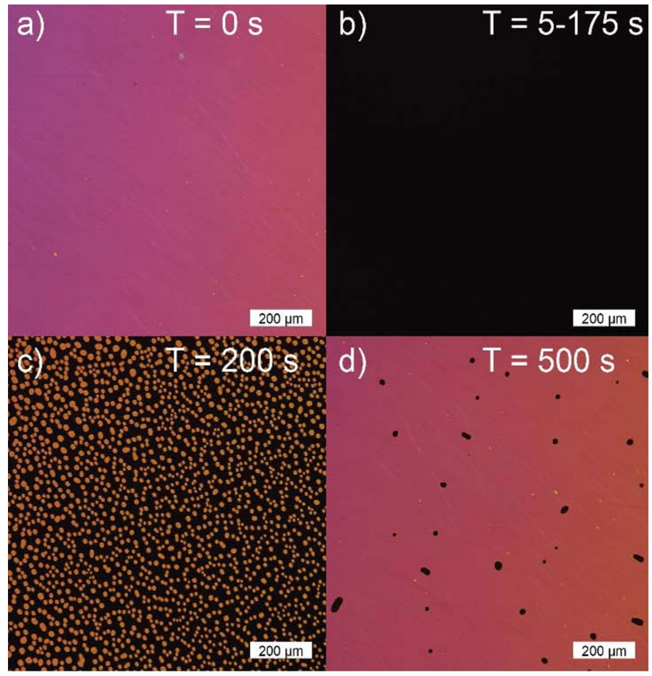
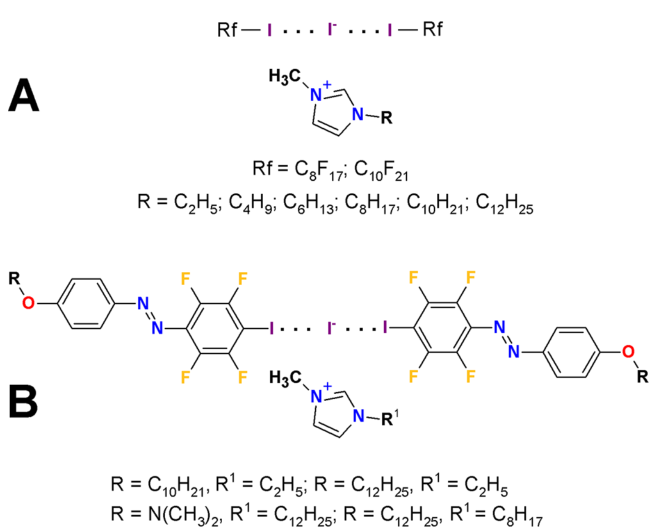


Figure 2. Photoinduced nematic-to-isotropic transition and the reverse transition for a stilbazole−iodofluoroazobenzene complex, observed under POM at 110 °C: (a) POM image before illumination, (b) POM image after illumination, (c) POM image at the onset of the isotropic-to-nematic transition, and (d) POM image after almost fully reversed transition. Reproduced with permission from ref 62. Copyright 2016 American Chemical Society.

assembled by commercially available alkylimidazolium iodide salts with iodoperfluoroalkanes (Scheme 4).[64]

These remarkable assemblies featured a supramolecular perfluorinated anion able to drive room temperature LC properties. Interestingly, the LC properties were sensitive to the properties of the supramolecular anion but quite insensitive to the alkyl chain on the imidazolium cation. In a follow-up study, the same authors reported on photoresponsive XB ILs

Scheme 4. (A) Ionic Liquids Formed by Iodoperfluoroalkanes and Lakylimidazolium Iodides; (B) Photoresponsive Ionic Liquids Showing LC → Iso Phase Transitions upon Light Irradiation



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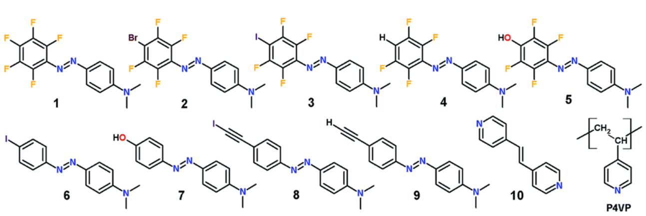
formed by replacing iodoperfluoroalkanes with a photoresponsive iodoperfluoroazobenzene (Figure 2).[65] The assemblies underwent photochemically induced irreversible LC-to-isotropic phase transitions and could be used as light-controllable ion transporters.

■ SUPRAMOLECULAR POLYMERS

The first XB-driven supramolecular polymer was reported in 2002 as a result of the self-assembly between poly(4-vinylpyridines) (P4VPs) and iodoperfluoroalkanes.[66] After this example, which demonstrated the reliability of the I···N_{pyr} interaction, several other supramolecular polymers and polymeric aggregates were reported on the basis of several supramolecular synthons.[67,68] The use of XB as an architectural tool in building new polymeric materials has then evolved from a merely academic curiosity to a solid design concept for the synthesis of new supramolecular functional polymers, as we will discuss in the following sections.

Photoresponsive Supramolecular Polymers. In recent years, XB has been used as a versatile tool to access a new class of photoresponsive supramolecular materials.[69] These can be divided into two broad classes, one based on crystalline assemblies[35] and the other one based on polymeric materials, for which we give a brief overview here. The first XB-driven photoresponsive polymers were reported by Priimagi, Metrangolo, and Resnati et al., who aimed at demonstrating the goodness of XB, compared to HB in driving the performances of azobenzene-based polymers for the inscription of surface-relief structures, SRG.[70] The superior directionality of XB as compared to HB was discovered to be the key factor for promoting the surface patterning efficiency. Recently, few other reports of XB photoresponsive polymers have appeared. Priimagi et al. have extended their studies to a broader range of photoresponsive molecules, to establish reliable structure−property relationships and a supramolecular hierarchy[71] among different XB and HB donors (Scheme 5).[72]

Scheme 5. Chemical Structures of Fluorinated Azobenzene Modules, Hydrogenated Azobenzene Modules, and Poly(4-vinyl pyridine) (P4VP) That Was Used as the Polymer Matrix for the Azobenzene Dyes[a]



[a]Reproduced with permission from ref 72. Copyright 2015 Royal Society of Chemistry.

It is worth noting that iodoethinyl compounds have recently attracted much attention for the development of supramolecular polymers.[73] The SRG formation developed in the order 8 > 3 > 5 (Scheme 5), and this was again attributed to the superior directionality of XB as compared to HB, despite their much weaker interaction with the polymer matrix. Furthermore, the iodoacetylene compound **8** outperformed the iodoperfluorophenyl compound **3** due to more favorable photochemical properties and the absence of fluorinated moieties which can promote phase separation and aggregation. These results were further confirmed in the report by Priimagi et al., who extended their investigation to much higher polymer−dye ratios, using the dyes **8** and **3** (Scheme 5).[74] Very recently, Gröschel and Giese et al. described supramolecular triblock terpolymers which self-assemble into microparticles under confinement.[75] The use of XB and HB donors with different binding affinity toward the polymer matrix allowed the volume and compatibility of the P4VP microphase toward the polystyrene and the polymethacrylate microphases to be studied with great detail. The HB donors were 8PAP (10 kcal/mol), LG (11 kcal/mol), and CHEMS (13 kcal/mol); the XB donors were XB C8 (5 kcal/mol) and XB A8 ≈ XB A12 ≈ XB A16 (6 kcal/mol). In general, the weaker donors lead to an increased volume of the P4VP domains. Interestingly, at f_{P4VP} = 17 wt %, the concentric lamella−sphere morphology transformed into axially stacked lamella−lamella when the strongest HB donor, CHEMS, was used (Scheme 6).

Self-Healing Polymers. Healable materials could have a tremendous technological impact thanks to extended functional lifetime and adaptation to external stimuli.[76] Intrinsic self-healing polymers, which heal through the reorganization of dynamic covalent bonds or non-covalent interactions, are the most promising candidates for real-world applications thanks to their high performances; e.g., they sustain a great number of healing cycles, mild conditions of the healing process, and mechanical robustness.[77] Recently, Hager and Schubert et al. reported the first example of self-healing supramolecular polymeric assembly based on XB.[78] The authors synthesized two different block copolymers bearing one XB donor (P4) and one XB acceptor (P6) moiety, respectively, as shown in Figure 3. As the XB donor, a halotriazolium unit was selected due to its well-known affinity to anions via charged-assisted XB,[79] while, as the XB acceptor, a methacrylate moiety was selected. The authors performed an extensive study to quantify the strength of XB interactions and their role in the self-assembly process by comparing the binding affinities of monomers, neutral derivatives, the hydrogen bonding donor analogue (P3), and the target charged systems through isothermal titration calorimetry. This analysis confirmed that the P4 and P6 self-assembly driving force is based on the formation of XB between the donor unit and the methacrylate acceptor unit. After ascertaining the binding behavior of the two species in solution, the supramolecular cross-linking based on XB of P4 and P6 was successfully confirmed by nanoindentation, Raman spectroscopy, and DFT calculations. The XB-based supramolecular polymeric architecture (P46) was deposited as film, and its self-healing ability was tested through scratch tests at 100 °C, revealing the self-healing behavior of the complex (Figure 3) thanks to the reversible and dynamic nature of the XB interactions within the supramolecular network.

The robustness of the design principle of using halotriazolium moieties to build XB-based cross-linked and self-healing supramolecular networks with ionomers was recently validated by the same authors, who reported a second example of self-healing polymeric adducts based on the same XB donor synthons.[80]

■ SUPRAMOLECULAR GELS

Low molecular weight supramolecular gels are attracting an ever increasing attention thanks to a plethora of possible applications, spanning from drug delivery systems, sensors, cell growth media, regenerative medicine, stimuli-responsive

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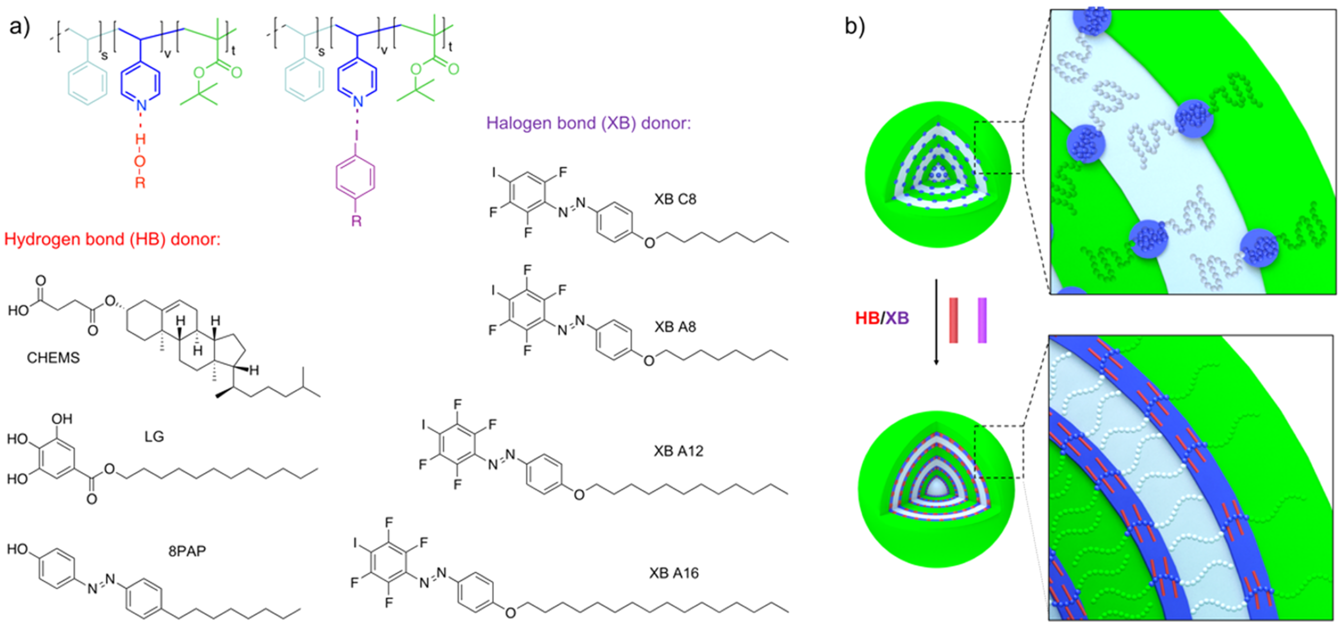
Scheme 6. (a) Chemical Structure of the XB and HB Donors Used by Gröschel and Giese et al.; (b) Tuning of the 4VP Volume with XB and HB Donors and Transition from Lamella−Sphere (ls) to Lamella−Lamella (ll) Morphology[a]



[a]Reproduced with permission from ref 75. Copyright 2018 MDPI.

materials, and catalysis, just to cite a few examples.[81] In this peculiar class of materials, the careful choice of the starting molecular building blocks and the individual supramolecular synthons dictates the overall self-assembly process, translating molecular information from the nanoscale up to macroscopic level, giving an unprecedented control over the physicochemical properties of the final materials.[82] Thanks to its unique features, XB is an ideal candidate as a self-assembly driving force able to guide the molecular-scale organization to the macroscale typical of gels.[83] Metrangolo, Resnati, and Steed et al. reported the first example of supramocular gel based on two components, bis(pyridil)urea derivative, as gelator and ditopic XB acceptor, and 1,4-diiodotetrafluorobenzene, as ditopic XB donor. The two separate components do not show any gelation, while their combination triggers the gelation process, providing evidence of the proclivity of XB to act as a gel-forming interaction.[84] Thanks to this latter feature together with the importance of XB in biological systems,[21,22,85−89] Metrangolo et al. studied in depth the effect of halogenation on peptidic fragments and its ability to promote hydrogel formation.[90−92] Interestingly, they observed that the modification of a single atom of the β amyloid core sequence KLVFF can bring an extremely rich self-assembly landscape, which in turn can give access to new amyloidal nano-architectures.[91] In particular, halogenation with highly polarizable halogen atoms (Br and I) of the p-position of the two phenylalanine residues was found to promote the gelation of aqueous solution at very low concentration compared to the wild-type fragment, as shown in Figure 4. Corroborated by crystal structure analysis and vibrational spectroscopy, they hypothesized the role of halogen bonding as the key self-assembly driving force of the final fibril architectures, once again highlighting the central role of this interaction in engineering novel molecular materials.

The same team recently reported how halogenation of phenylalanine in the amyloidogenic sequence DFNKF has a direct effect on the stabilization of the wet interface of the amyloid structures through XB with water molecules, depending on the polarizability of the halogens involved in the interactions, with the iodinated derivatives promoting the most stabilizing interactions.[93] Other authors further proved the efficiency of XB as a gel-forming interaction, using a broad range of organogelators and gelation conditions.[94−96] In the quest of building novel smart materials, a photoresponsive two-component supramolecular organogel has recently been reported, whose self-assembly driving force is a synergistic contribution of XB, hydrophobic interactions of long alkyl chains, and $\pi-\pi$ interactions (Figure 5).[97] The photoresponsive and XB acceptor component is an azopyridine derivative with long alkyl chains to hamper the crystallization process. The XB donor is 1,4-diiodotetrafluorobenzene, known for its strong XB donor character. Once the components are mixed in 2:1 (donor: acceptor) molar ratio in acetonitrile at 2 wt %, a robust gel is formed.

The supramolecular network undergoes a gel−sol transition under UV irradiation as a consequence of the *cis*−*trans* isomerization of the azopyridine derivative. The gel collapses after exposure to UV light due to several concomitant factors, namely, larger dipole moment of the photoresponsive moiety, poorer packing, and higher solubility in acetonitrile of the *cis*-azopyridine. This is the first report of a photoresponsive supramolecular gel based on XB, paving the way for the development of a new class of functional materials based on this non-covalent interaction.

NEW DIRECTIONS

In the near future, all of the designing principles of XB will probably be translated into low-dimensional systems to take control of 2D systems at the nanoscale. Taking control over 2D structures through self-assembly is of paramount importance for controlling surface materials properties such as corrosion resistance, molecular recognition, catalysis,

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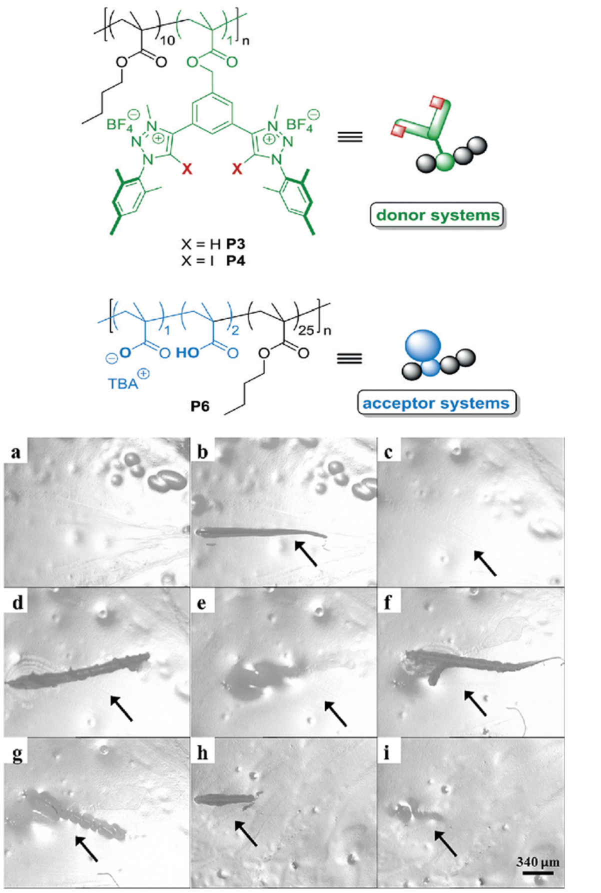

Figure 3. Top: The two copolymers bearing XB donor and XB acceptor units. Bottom: Self-healing behavior of P46: (a) pristine film, (b) first scratch, (c) healing after 17 h at 100 °C, (d) second scratch, (e) healing after 17 h at 100 °C, (f) third scratch, (g) partial healing after 4 h at 100 °C, (h) fourth scratch, (i) healing after 69 h at 80 °C. Reproduced with permission from ref 78 with permission. Copyright 2017 WILEY-VCH Verlag GmbH & Co.

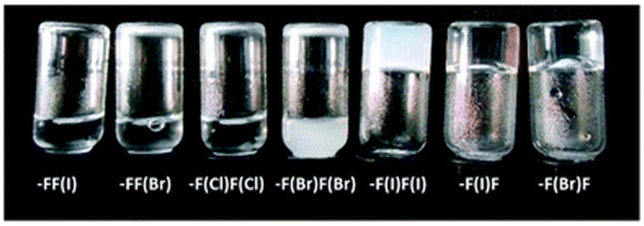

Figure 4. 15 mM peptide aqueous solutions after 48 h of aging at room temperature. Reproduced with permission from ref 91. Copyright 2017 Royal Society of Chemistry.

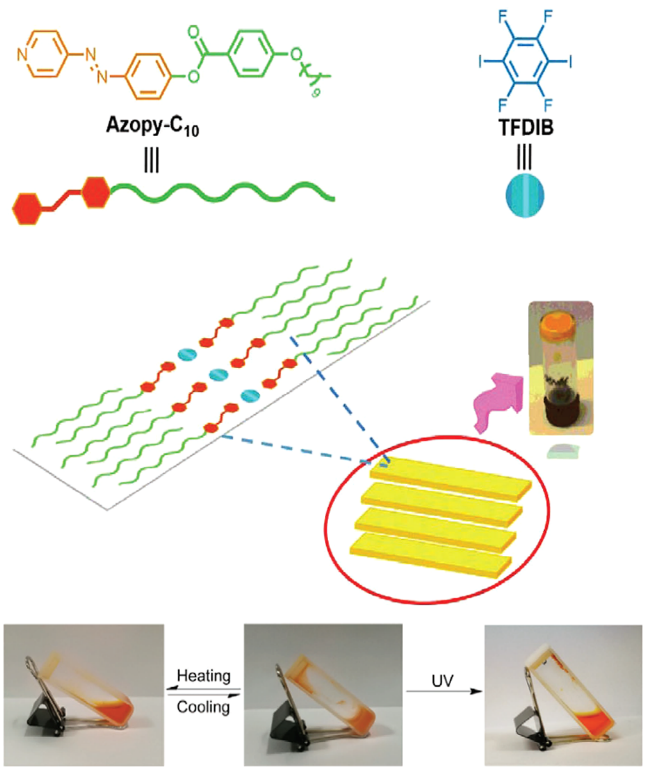

Figure 5. Illustrative strategy for preparing the supramolecular gel driven by halogen bond and the starting molecular building blocks (top). The response of the gel formed in acetonitrile to different stimuli, namely, temperature and light (bottom). Reproduced with permission from ref 97. Copyright 2019 WILEY-VCH Verlag GmbH & Co.

wettability, and optoelectronic features.[98−100] In this context, XB has recently been exploited as a structure-directing 2D self-assembly driving force thanks to its strength and directionality, giving access to a broad range of nanostructures depending on the chemical nature and geometry of the starting building blocks.[101−105] Wu, Ho, and co-workers have even reported the first direct observation of XB between halogenated benzene molecules on a silver surface via noncontact scanning tunneling microscopy.[106]

Recently, a supramolecular strategy based on the use of XB has proven to be effective in promoting microphase segregation in block copolymers, allowing the formation of complex surface nanostructures, a suitable feature for the implementation of an easy and accessible large-area fabrication method of nanopatterned surfaces.[107]

Haloperfluorinated monolayers are attracting a strong interest in the scientific community, thanks to their industrial relevance and their effectiveness in tuning the electronic properties of the functionalized surfaces.[108] For example, it has been reported that the surface supramolecular functionalization of photovoltaic devices based on hybrid lead halide perovskite via strong halogen bond donors (strongly interacting with the halide ions of the perovskite lattices) can electronically passivate the surface, reduce the number of intrinsic charge traps, and enhance the mobility of the charge carriers, bringing an overall increase of the efficiency and stability of the solar cells based on this class of materials.[109,110]

■ CONCLUSIONS

In this short review, we presented how the design principles of crystal engineering can be used to achieve halogen-bonded functional materials. In particular, when XB is turned on in the desired self-assembled materials, new properties are enabled, which are absent in the starting component of the material. Hierarchical steps in the history of halogen bonding started with XB as a tool for crystal engineering and proceeded through liquid crystals, polymers, micelles, and gels to 2D systems at the nanoscale and microscale to afford more and more complex structures. Our survey demonstrates that XB is now a mature tool for the design of functional materials and that its future is bright.

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Author Contributions

M.S. and L.C. conceived the work and wrote the paper.

Notes

The authors declare no competing financial interest.

Biographies

Marco Saccone was born and educated in Palermo, Italy. He obtained his Ph.D. from the Polytechnic University of Milano, Italy, studying materials for optoelectronics application assembled through halogen bonding, under the supervision of Pierangelo Metrangolo and Giuseppe Resnati. After two postdoctoral research appointments in Finland with Olli Ikkala and Arri Priimagi (at Aalto University and Tampere University of Technology, respectively), he joined the research group of Michael Giese at the University of Duisburg-Essen. In August 2019, he joined the engineering department at the University of Palermo as an assistant professor. Dr. Saccone's research interests cover specific non-covalent interactions, soft materials, fluorine chemistry, and crystal engineering.

Luca Catalano was born in Milan, Italy (1989). He received his Bachelor in Chemistry from University of Milan (2011) and his M.S. in Photochemistry and Molecular Materials from University of Bologna, working with Professor Dario Braga (2013). Then, he moved back to Milan, earning his Ph.D. in supramolecular chemistry from Polytechnic University of Milan under the supervision of Professor Pierangelo Metrangolo (2017). Currently, he is a postdoctoral associate at New York University Abu Dhabi working with Professor Panče Naumov. His research interests include design, synthesis, and characterization of crystalline systems and the study of stimuli-responsive materials.

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ABBREVIATIONS

XB, halogen bonding; HB, hydrogen bonding; LCs, liquid crystals; SmA, smectic A; Cub, Cubic; IL, ionic liquid

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