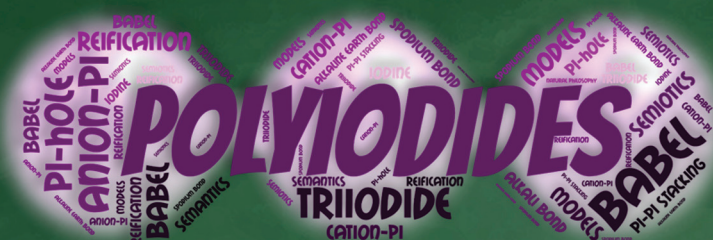


Dalton Transactions

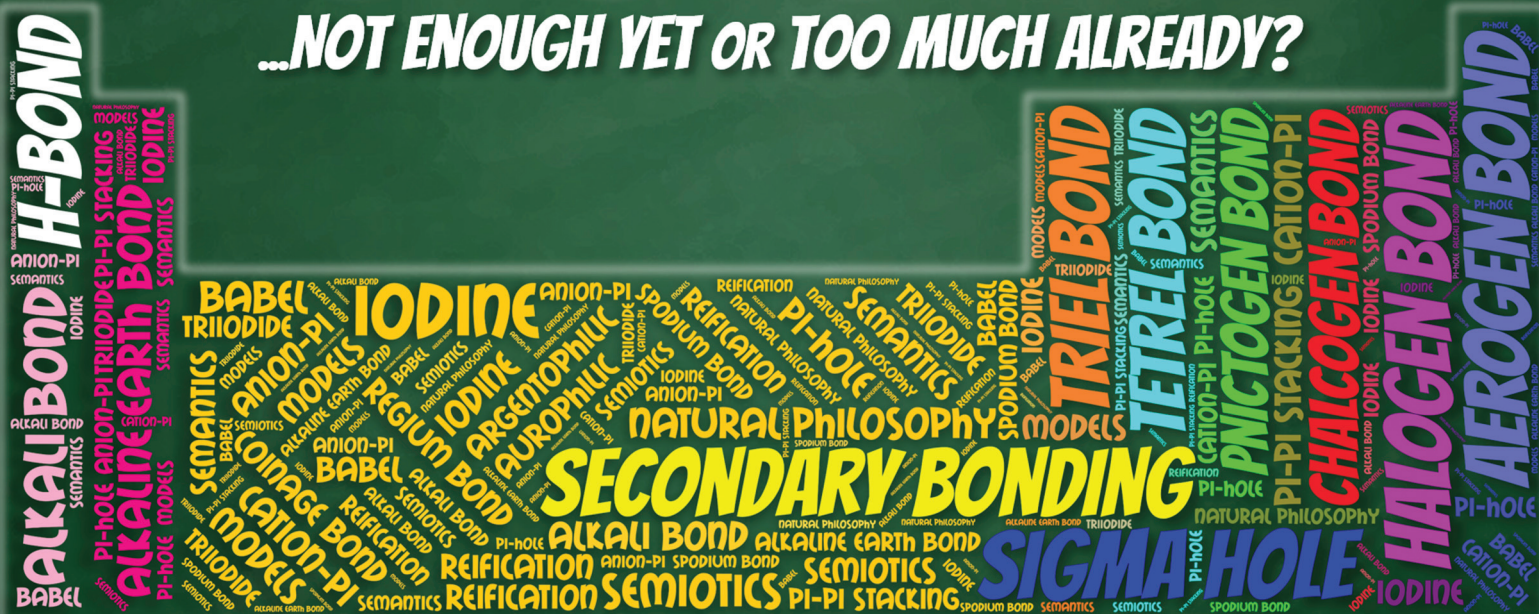
An international journal of inorganic chemistry

rsc.li/dalton

SUPRAMOLECULAR WORDS...



...NOT ENOUGH YET OR TOO MUCH ALREADY?



ISSN 1477-9226

Cite this: *Dalton Trans.*, 2021, **50**, 1142

Words in supramolecular chemistry: the ineffable advances of polyiodide chemistry

Matteo Savastano 

Polyiodide chemistry has a rich history deeply intertwined with the development of supramolecular chemistry. Technological and theoretical interest in polyiodides has not diminished in the last decade, quite the contrary; yet the advances this perspective intends to cover are muddled by the involution of supramolecular vocabulary, preventing their unbiased discussion. Herein we discuss the pressing necessity of ordering the current babel of novel – and less so – supramolecular terms. Shared decisions at the community level might be required to shape the field into a harmonious body of knowledge, dominated by concepts rather than words. Secondary, σ -hole and halogen bonding schools of thought are all addressed here, together with their respective impact on the field. Then, on the basis of a shared vocabulary, a discussion of polyiodide chemistry is presented, starting with a revisited view of triiodide. The contemporary fields of supramolecular caging and polyiodide networks are then discussed, with emphasis on how the terms we choose to use deeply affect scientific progress.

Received 30th November 2020,

Accepted 17th December 2020

DOI: 10.1039/d0dt04091f

rsc.li/dalton

Introduction†

“The fish trap exists because of the fish; once you’ve gotten the fish, you can forget the trap. The rabbit snare exists because of the rabbit; once you’ve gotten the rabbit, you can forget the snare. Words exist because of meaning; once you’ve gotten the meaning, you can forget the words. Where can I find a man who has forgotten words so I can have a word with him?”^{1,‡}

Iodine has an incredibly rich history,² telling of a fortuitous discovery in the evocative setting of Europe during the Napoleonic Wars and involving many scientific giants of the time: Gay-Lussac,³ Humphry Davy,⁴ and even Ampere. Polyiodide chemistry is just as old. Among the long-discovered peculiarities, we recall the famous blue starch–iodine complex, and reminisce about classic analytical methods (iodimetry, iodometry) and witty uses such as the Landolt iodine clock reaction.^{5,6} In 2016, *i.e.* 202 years after its discovery, insight into the nature of the starch–iodine complex still

granted publication on the cover of prestigious scientific journals,⁷ inviting reflection on the developments in this field of chemistry.

As we,^{8–10} and others before us,¹¹ have mentioned several times, the “feeble force” with which iodides retain molecular iodine, found in Gay-Lussac’s record,³ required the development of supramolecular chemistry to be properly understood.

Nowadays, as we recognize the importance of non-covalent interactions and can rely on unprecedented computational methods to cope with the issues of hypervalent polyiodides, polyiodide chemistry is blooming.

As oftentimes happens, this renewed interest is favoured by novel applications, namely solar cells^{12–17} and batteries,^{18,19} with noticeable efforts directed towards producing solid-state conductors based on a Grotthuss-like mechanism (we note here the chronological coincidence between Grotthuss’s original publication,²⁰ 1806, and iodine discovery, 1811). Polyiodide-based ionic liquids²¹ and iodine-containing polymers,¹⁹ which are outside the scope of this perspective (*vide infra*), are also growing fields of application.

One of the landmark publications in the field, to which we are much indebted, is the comprehensive 2003 review by Svensson and Kloo.²² Since 2003, the number of isolated I_3^- anions, the simplest of polyiodides, has increased from approximately 500 to over 1500 CSD²³ (Cambridge Structural Database) hits, signifying a noticeable expansion of the field.

Department of Chemistry “Ugo Schiff”, University of Florence, via della Lastruccia 3, 50019 Sesto Fiorentino, Italy. E-mail: matteo.savastano@unifi.it

† Maximum care has been taken in giving proper credit to the original authors and copyright holders for quoted text. Quotations do not imply that the original authors endorse the contents of this contribution. Contrasting previous statements has the sole purpose of rendering the reality of pluralistic scientific views, and stimulating reflection and scientific discussion.

‡ From ref. 1. Copyright © 2013. Reprinted with permission of Columbia University Press.

Despite our best efforts, while discussion of isolated polyiodides appears possible, elucidation of their supramolecular chemistry, and of I...I interactions specifically, poses peculiar issues. We were reminded of what can be considered the heritage and one of the greatest lessons of J. M. Lehn. Beyond high-quality science and beautiful examples (the list is long, we hope ref. 24 will suffice), Lehn forged most of the original supramolecular chemistry vocabulary, stressing the importance of language as a driving force for the imaginative development of the discipline, to the point of addressing the theme of reification.²⁵

Coming to the present case: should we propose a halogen bonding description for intermolecular interactions in polyiodides?²⁶ Should we refer to a more general electrostatic model based on σ -hole interactions?²⁷ What about a secondary bonding description?²⁸ Should we not require a pre-emptive definition of primary bonding in that case? If we can circumvent the issue for Au...Au or Ag...Ag interactions by introducing dedicated words (aurophilic/argentophilic interactions),²⁹ why should we not introduce one for I...I contacts as well? At the same time, anion- π interactions,³⁰⁻³² which we are very interested in,³³⁻³⁵ are becoming popular in polyiodide stabilization:^{9,10,36,37} what are they exactly? How could they remain counterintuitive for 4 decades? How do we prevent other supramolecular interactions from being perceived in the same controversial manner?

We are convinced it is not just us.

Should scientific journals feature advice columns, some related questions from the audience would be: What's in a name?^{38,39} Is a certain interaction a new molecular linker?⁴⁰ Or a rediscovered supramolecular force?⁴¹ An unnoticed metallophilic interaction?⁴² A new supramolecular force?⁴³ Do they, *i.e.* all manner of supramolecular forces, exist?⁴⁴⁻⁴⁶



Matteo Savastano

Matteo Savastano received his BS and MS degrees in Chemistry from the University of Florence, Italy. After stays at University of Jaén (Spain), 2014, and ICMol, University of Valencia (Spain), 2016, he received his Ph.D. in Chemical Sciences (Inorganic and Supramolecular Chemistry) from the Florentine Athenaeum (2018), under the supervision of Prof. Antonio Bianchi. He remained as a postdoctoral research fellow at the

Department of Chemistry "Ugo Schiff". His main interests are anion and cation coordination chemistry, supramolecular interactions and solution equilibria. A serendipitous encounter with polyiodides and a weakness for vintage literature led him to develop a taste for their chemistry.

Different from weekly magazines, the readership and authorship of scientific journals tend to coincide, hence the need to raise the issue in the hope of finding shared answers at the community level.

As we discussed elsewhere,³⁴ categorizing is an important process for organizing knowledge, yet we must be wary of "tag-words": we should prefer seeking a more advanced understanding, *i.e.* noticing peculiar differences from established interactions, rather than preferring an easy "labeling" of supramolecular forces. At the same time, while examining specificity, it could be worth looking for general trends. Choices we make today determine how we will present this chemistry tomorrow. Citing again the 2003 review by Svensson and Kloo²² as an example, the term "halogen bond" did not occur once! The concept of "secondary bonding" was used instead (this is not the only example, *cf.* ref. 47 and 48 for examples up to 2008). This is interesting proof of how the language of supramolecular chemistry has been evolving in recent years, especially if we consider that one of said authors (Prof. Lars Kloo) was, not much later (from 2009/2010 till 2013), part of the very IUPAC task group entrusted with defining the halogen bond itself.^{49,50}

A simple depiction of current affairs, visualising the trends shaping chemical literature, is presented in Fig. 1, from which the success of some concepts over others is manifest.

The success of some "keywords" does not mean they should become "*passe-partout* terms", as the abuse of some names might hinder recognition of other phenomena and slow down the development of other, much needed, supramolecular words.

As too many words are available to describe relevant interactions, preventing us from avoiding displeasing part of the readership by choosing some terms and avoiding others, we deemed it important to add the definition and scope of each keyword as a foreword to our polyiodide discussion.

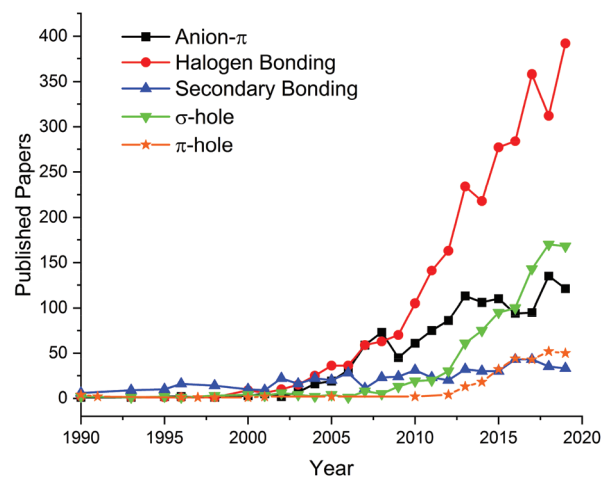


Fig. 1 Contemporary literature trends (scientific papers per year) for discussed supramolecular keywords. Source: Scifinder.⁵¹

Scope and definitions

Secondary bonding: Lewis acid/base theory and VSEPR model

“Nature’s task, at low temperatures, is how best to fit nucleophilic bumps into electrophilic hollows.”⁵²§

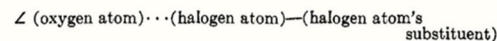
In 1960 Coulson summarized the state of intermolecular forces understanding in 3 words: wanted, new concepts;⁵³ arguably, we may find ourselves in the opposite situation, having developed redundant models with large overlap. Dissatisfied with available models and admittedly influenced by Lewis’s work, Bent produced a landmark review in 1968 analysing available structural data in search of patterns in non-covalent interactions.⁵² This is where the concepts of secondary donor–acceptor interactions as opposed to primary chemical bonds were introduced (we notice *en passant* how Bent’s discussion moves from iodine solutions) (Fig. 2). Later on, the concept was re-proposed in Alcock’s popular 1972 review.²⁸ The donor–acceptor part of the name became somewhat implicit and the concepts of primary and secondary bonds, exactly as we find them 31 years later in Svensson and Kloo’s review,²² were born. Some of the emphasis on Lewis acid/base theory was dropped by Alcock, either willingly or because of the implicit wide acceptance of Lewis’s work. What remained of it is the emphasis on the local geometry/orbital hybridization (we also recall here Bent’s involvement in such studies and the so-called Bent’s rule)⁵⁴ of involved atoms and its role in determining the directionality of secondary bonding, which at the time were mainly understood with VB theory and VSEPR considerations. While this can be easily relegated to the pre-density functional theory and pre-personal computer era, when current levels of theory and computing power were unthinkable, still in 2020 we can read novel studies advocating for a modern unified chemical model of secondary bonds,⁵⁵ where VSEPR inspired rules remain relevant. The periodic trends in halogen to tetrel bonding (*vide infra*) and in the underlying localization of σ -holes (*vide infra*) suggest that these seemingly far apart models are addressing common issues. For the sake of objectivity, both Bent⁵² and Alcock²⁸ had extremely slim datasets for polyiodides: Alcock discusses no more than a handful of cases and even the dedicated reviews he references (mostly 1960s work by Wiebenga *et al.*)^{56,57} contain datasets of negligible size in comparison to today’s possibilities.

Halogen bonding

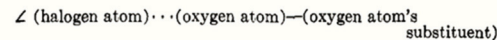
“A halogen bond occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity.”⁵⁸ ©IUPAC 2013.

Halogen bonding (Fig. 3) is, in relative terms, the easiest interaction to define. The reason for this is simple: a dedicated pool of international experts devoted itself to providing a definition, supported by theoretical and experimental data, in the

Table I lists several other examples of crystals that contain short interactions between oxygen-containing molecules and halogen-containing molecules.^{17,38} In each case the angle about the halogen acceptor atom, *i.e.*



is close to linear, while the angle about the oxygen donor atom, *i.e.*



is close to tetrahedral.

Fig. 2 An excerpt from Bent’s 1968 review. Deciding whether secondary or halogen bonding is being discussed is up to the reader. Reproduced from ref. 52 with permission from the American Chemical Society, copyright 1968.

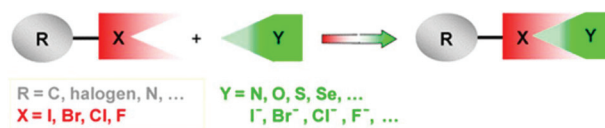


Fig. 3 Schematization of halogen bonding. Notice, for the sake of polyiodide chemistry, how anions are only presented as XB (halogen bond) acceptors and dihalogen molecules are presented as XB donors, a feature present also in the IUPAC recommendation.⁵⁸ Reproduced from ref. 26. With permission from the American Chemical Society, copyright 2016. <https://pubs.acs.org/doi/10.1021/acs.chemrev.5b00484>.

form of an IUPAC recommendation.^{49,50,58} This, within reasonable limits, has set a precise boundary on what can (*should*) be considered a halogen bond and what cannot (*should not*).

The history of halogen bonding has been briefly and brilliantly illustrated by Metrangolo and Resnati in their 2012 perspective,⁵⁹ to which the reader is referred (a more comprehensive version by the same main authors is also available).²⁶ The success of halogen bonding as a concept is manifest and unchallenged (*cf.* Fig. 1), yet three points from this history are relevant to the present discussion.

First, beyond the well-known key references cited as milestones in the development of halogen bonding,^{60–63} we also find Bent’s work,⁵² despite the fact that Bent’s and Alcock’s secondary bonding is a far broader concept element-wise.

Second, Metrangolo and Resnati make the shareable claim: “general conceptual frames are typically developed in chemistry only when a sufficiently wide and diverse set of single instances and occurrences relevant to the topic has been reported”.⁵⁹¶ Most of the historical findings cited in ref. 26 and 59 as starting points for the historical development of halogen bonding (from 1814 to the 50s, *e.g.* ref. 64) refer to iodine-based systems; the initial recognition of charge-transfer complexes by Benesi and Hildebrand,^{65,66} and their original interpret-

§ Reprinted with permission from ref. 52. Copyright 1968 American Chemical Society.

¶ Reprinted with permission from ref. 59. Copyright 2012 American Chemical Society.

ation by Mulliken⁶⁷ also involved iodine. As the most polarizable of halogens, iodine easily presents marked σ -holes (*vide infra*), giving strong halogen bonds. Could it be that the above “comprehensive set of instances” was mainly composed of halogen containing compounds (and iodine especially) because, for this kind of system, a general trend, at least as suggested by Bent⁵² and Alcock,²⁸ appears more manifest? How does the extension of the halogen bond concept to other groups and its declination (some would say fragmentation) into as many different interactions as there are groups in the periodic table (chalcogen,⁶⁸ pnictogen,⁴⁰ tetrel,⁴¹ triel, aerogen,⁴³ ...regium⁶⁹/coinage³⁸ ...spodium,⁷⁰ *etc.*) connect with old general models? Are we looking for many different interaction types, exalting differences, or for a comprehensive general model, as others advocate, exalting similarities? This is something for the community to decide: either choice will likely shape the field for years to come.

Third, they notice, as we are somewhat doing once more, that “single findings were understood within different conceptual frames and designated by different and erratic terms, varying from the imaginative “bumps in hollow” to the chemically meaningful “charge-transfer interaction”.”⁵⁹¶

Was a “bumps in hollow” description so whimsical?

This question, together with the extraordinary success of modern “holes”, both σ and π , leads us to the next section.

σ -Hole bonding

The term σ -hole refers to the asymmetric distribution of atomic charge, which generates electron-depleted regions of positive, or relatively so, electrostatic potential able to interact with electron rich species.^{27,71,72} This was indeed introduced as an explanation for the yet to be defined halogen bonding by Politzer, Murray and Clark.⁶³ This is considered a key passage for the understanding of halogen bonding: its implications are manifest in the IUPAC official halogen bond definition and its importance in the development of halogen bonding is acknowledged.⁵⁸ Over time, the concept of σ -hole interactions was expanded by the original authors.⁷² Today it encompasses, if not the whole periodic table, at least groups IV–VII, with all the group-by-group details rationalized according to a shared charge distribution model.

As stated by Politzer, Murray and Clark themselves, halogen bonding is but a subset of σ -hole interactions⁷² (curiously, the same claim is made also by the modern secondary bond school, though).⁵⁵ The original authors also referred to σ -hole bonds as a modern re-discovery, this time supported by contemporary high-level calculations, of the idea that these forces could be rationalized in a comprehensive general theory of intermolecular interactions which pays attention to the electrostatic surface potential (ESP) and the charge distribution of the interacting partners.⁷² The way Politzer, Murray and Clark presented σ -hole bonds (*cf.* the *Gibbs and Menedeleev* section of ref. 72) is that of a unifying theory of these types of forces potentially embracing the whole periodic table.

“It is remarkable how far modern structural data support Lewis’s view that an understanding of chemical affinity must be

sought in the localization of charges,⁷³ and how well that localization of charges is described by the graphic formulas of classical structural theory” wrote Bent in 1968.⁵²§

We ask the community: is there a conceptual difference between σ -hole and secondary bonding? Or have old ideas and hints based on incomplete data finally been rationalized in a conceptual framework? Could we finally fuse the VSEPR/VB views typical of the secondary bonding school with the modern σ -hole ESP/MO perspective (both of which, according to the two sides, explain halogen bonding) in one, if not *the*, comprehensive theory of non-covalent interactions?

Anion– π interactions

Definition:

To date there is no formal, official, and IUPAC recommended definition of anion– π interactions.

As a placeholder, anion– π interactions can be defined as stabilizing interactions between an anionic species and an aromatic ring. The interaction can be thought of as a combination of 3 different types of basic interactions: (i) electrostatic term: ion charge–ring quadrupole interaction (strongly affected by anion charge, charge density and the intrinsic polarization of the aromatic system); (ii) inductive term: ion charge–ion-induced ring dipole (the polarizability of the aromatic ring plays a role, ion polarization might contribute for large anions, *e.g.* polyiodides); (iii) van der Waals contacts.^{74–76}

In the solid state, anion– π interactions manifest themselves in individual structures in terms of short anion–ring contact distances.^{77,78} Recently it has been shown that they also bring about characteristic patterns in the fingerprint plots generated from Hirshfeld surface analysis of both aromatic ligands and anions.^{10,79,80} In statistical terms, anion– π interactions cause deviations from the ideal (random) distribution of anions around a given aromatic ring, *i.e.* they have a directionality that depends on the ring ESP.^{35,76} In solution, the joining of anion and ring surfaces requires their desolvation: entropic effects connected with the release of coordinated solvent molecules back into the bulk oftentimes act as a driving force for association in solution.^{33,77,81,82}

In a sense, recognition of the relevance of ESP, and of *in silico* calculations in order to understand it, somewhat connects anion– π forces with σ -hole interactions (and thus to the whole discussion) in terms of the underlying basic concepts and required tools. Yet again, we see the “classic” controversial “anion– π ” and “lone pair– π ” vocabulary shifting towards the new wave “ π -hole” interactions, calling for their synthesis and official collocation in a comprehensive view of supramolecular forces.⁸³

Beyond the issues connected with centered/off-centered interactions,⁷⁸ interactions with aromatic ring substituents, and the extent of the simple dipolar nature of the interaction in the case of popular perfluorinated derivatives (a research interest that has also benefited the development of the halogen bond concept),⁸⁴ we take the chance to underline here the necessity for a comprehensive definition. This is some-

thing that, we believe, no individual or research group can provide alone: it should ideally stem from a comprehensive review of the available evidence conducted by a plurality of international experts, representing different backgrounds and interests. In this sense, the route traced by the IUPAC commission for halogen bonding appears as an inspiring example of how we should develop the vocabulary of supramolecular chemistry: with a shared, pluralistic approach.

The anion- π lesson in chemical rhetoric

Anion- π interactions have known overhyped moments, followed by sharp criticism (“*Eenie, meenie, minie, mo—where does the anion go?*”),⁸⁵ and a recent resurgence backed by novel evidence. What is sure is that, through the years, we have read countless times about the counterintuitive nature of anion- π interactions.

How could an interaction first reported/theorised in the 80s remain counterintuitive for 40 years?

This is where we can learn a valuable lesson about language, something that invites reflection as we decide how to formulate and present novel supramolecular interactions to students (*e.g.* halogen/chalcogen/pnictogen.../spodium bonding *vs.* σ -hole *vs.* secondary bonding/extended acid-base or VSEPR theories).

We dare say here, for the first time, that anion- π interactions are intuitive.

They are intuitive provided we use a language that promotes our ability to understand them and inspire the next generation of chemists to do the same. Differences between different anions (and ions in general) have long been underappreciated. As there is no longer a poorly understood “Werner theory” to explain why spherical metal cations with different numbers of d electrons behave differently, or a “Pasteur handedness” in place of a fully developed chirality concept, differences between ions should be dragged out of the “Hofmeister” era. Speaking of language, the necessity of removing the “Hofmeister tag” and moving to a modern description has already been commented on, and the contemporary chosen name of “ion-specific effects”^{86,87} has been introduced. This name, placing emphasis on how different ions behave differently, somehow reveals how embarrassingly late chemists, as a community, started appreciating these aspects. Until textbooks show hydrated cations with water molecule dipoles pointing straight towards them, *i.e.* essentially ignoring the chemistry of the first solvation sphere, cations will appear more strongly hydrated than anions: the exact contrary of theoretical and experimental results.^{88,89} As for how such confusion affects the community, *cf.* how the widely accepted and long-lived extra-thermodynamic assumption for partitioning salt hydration free energies into the contributions of individual ions based on TPA/TPB (TPA = tetraphenyl arsonium, TPB = tetraphenyl borate) has been both contested⁹⁰ and supported⁹¹ by recent

studies appearing in the same journal and volume. Chances to meaningfully address anion coordination in solution decrease the less we understand their solvation, especially for those interactions, like anion- π ones, which are heavily influenced by solvent effects.^{33,77,81} At the same time, the polarity of heterocycles is not always well taught/understood either: we refer here to the clarification of Wheeler and Bloom regarding the π electron density of azines and to the misleading misuse we still make of the term “ π -acid”.⁹² It turns out that heterocycles popularly believed to be π electron deficient are actually π electron rich! Yet, as judging the electronic structure from the reactivity is an old habit, teaching courses are only marginally affected by these reports.

In this sense, we can foresee the success of “ π -hole” nomenclature,⁸³ as it suggests a local lack of electronic density, with respect to “anion- π ” which suggests direct interaction of anions with the π electron density, and is therefore counterintuitive: it is all about words and their perceived meaning!

As a matter of fact, if premade “tag words” are passed down to new generations, we might end up preventing proper understanding of phenomena, hindering the development of some portion of science. If the reader feels the need for a more convincing example, we refer her/him to the notorious case of π -distortivity and to how VB theory arguably got discarded for a MO approach on the basis of its flawed application to benzene.⁹³ Benzene, our shared model molecule, that with its electron-rich character makes cation- π interactions intuitive and anion- π ones counterintuitive.

We hope that the above invites reflection on how we, as a community, intend to name, present and teach novel supramolecular forces: whether with a unified model/theory (secondary bonding/VSEPR-type description/ σ -hole interactions), a group-by-group approach (halogen, chalcogen, pnictogen, ..., spodium bonds, ...), or a combination of the two, and how to address element-by-element specificity. Moreover, it is also worth remembering aurophilic and argentophilic interactions here, as they were already related to the case of polyiodides,²² as cases where specificity was introduced at the single element level from the start (to complicate the picture, “coinage-metal bonds”³⁸ and “regium bonds”⁶⁹ have also been defined with different meanings, *cf.* also Metrangolo and Resnati⁵⁹ signalling that “fluorine/chlorine/bromine/iodine bond” terms had already been used in the past to denote different interactions from halogen bonding).

The language and the words we choose to adopt have the power to shape the future of the field: for this reason, common and conscious choices must be promoted.

Ontology of triiodide

A large portion of the difficulties in describing the supramolecular chemistry of polyiodides can be elucidated by reducing the problem to the simplest member of the family (I_3^-) and asking ourselves: what is a triiodide?

|| Reprinted with permission from ref. 85. Copyright 2009 American Chemical Society.

It is tempting to dismiss the question as rhetorical, but we warn the reader that it is instead rather tricky.

I_3^- is the most commonly occurring and studied polyiodide, and as such it also possesses a highly prototypical function. Currently a search for isolated I_3^- anions in the CSD returns 1568 hits, ~ 3 times more than in 2003.²²

We believe we can work out a meaningful answer for our purposes in two different ways, *i.e.* by looking at what a triiodide is in itself and at how a triiodide is “perceived” by other polyiodides.

What is a triiodide in itself?

Regardless of our preference for one or the other model for supramolecular interactions, we need a way to tell covalent or primary interactions apart from non-covalent or secondary ones. As for most simple inorganic species, we tend to be convinced we know how I_3^- is made in terms of geometric parameters. Let us try to use the simplest of polyiodides to assess

the primary/covalent distance length and its standard deviation: an innocent task.

Fig. 4 presents the up to date version of Svensson and Kloo's plots²² for the structural features of I_3^- .

As shown in Fig. 4a, the I–I bond length in I_3^- has a curious profile, which is best fitted with a Lorentzian curve centred at 2.9179(1) Å and possessing a full width at half maximum of 0.0436(3) Å ($R^2 = 0.997$, $\chi^2 = 13.27$). In chemical terms, this means that if one considers the typical bond length for I_3^- as the distance range in which 90% of all I–I bonds fall (a forgiving assumption), we obtain a range of 2.865–2.975 Å, *i.e.* the I_3^- bond length is 2.92 ± 0.05 Å (*i.e.* $\pm 1.8\%$), which becomes 2.92 ± 0.085 Å ($\pm 2.9\%$) and 2.9 ± 0.2 Å ($\pm 6.9\%$) to include 95% and 99% of I_3^- , respectively. This large variability hinders a clear-cut definition of primary bonds, and consequently hampers definition of secondary ones, blurring the distinction between covalent and supramolecular contacts.

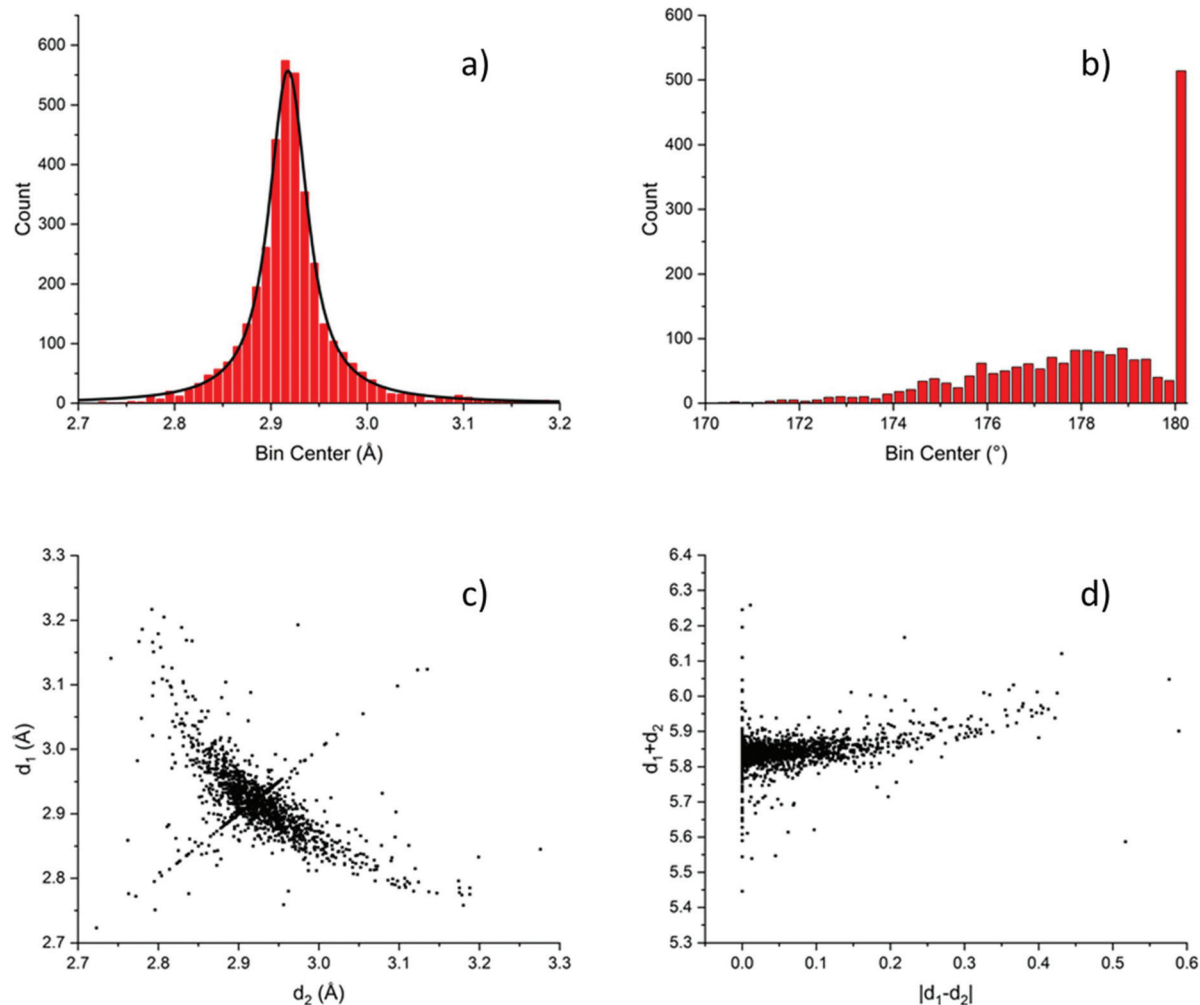


Fig. 4 Structural parameters for isolated I_3^- in the CSD. (a) Distribution and fitting of I–I bond lengths (bins of 0.01 Å); (b) distribution of I–I angles (bins of 0.25°); (c) relationship between the two I–I internal distances of I_3^- , d_1 and d_2 ; (d) relationship between total I_3^- length and $d_1 - d_2$ absolute difference. Adapted (*i.e.* re-drawn with contemporary data) from Fig. 10 of ref. 22 with permission from the American Chemical Society, copyright 2003.

In the face of this observation, both Bent (*"In the symmetrical I_3^- ion, one sees illustrated, again, an element or arbitrariness, from the structural point of view, in the terms "intermolecular" and "intramolecular", when applied to interactions in condensed systems, where it is not always possible, on the basis of interatomic distances, to define accurately the meaning of the word "molecule".*^{52§}) and Alcock (*"These compounds show great variations in bond lengths, and it is perhaps more difficult for secondary bonds to be distinguished from primary bonds than from van der Waals interactions."*^{28**}) show perplexity.

Another possibility to address the matter would be accounting for other structural parameters, such as those illustrated in the rest of Fig. 4. General tendencies, *i.e.* the preference for a linear arrangement (Fig. 4b), but again with an angular variability which is unthinkable for other elements, the tendency towards symmetry (Fig. 4c and d), and the propensity, when distorted, to simultaneously shorten one of the two I–I bonds as the other is lengthened, have been previously discussed.²²

Yet, in a sense, this is just the crystallized modern view.

There is general consensus (from Bent⁵² to Svensson and Kloo,²² passing through early work by Pimentel,⁹⁴ Hach and Rundle,⁹⁵ and others) about the fact that the fundamentally symmetric triiodide anion shows large deformations in the bond lengths in the solid state which are induced by nearby cations (especially if small and polarising) and/or the non-symmetric environment of the polyiodide within the crystal. Yet other chemists invited caution and cast doubt on the fundamentally symmetric nature of I_3^- and hence on the role of its surroundings. According to the prevailing view, the role of the I_3^- surroundings is to break its symmetry, making it deviate from the ideal symmetric geometry; according to the minority opinion, only when the I_3^- surroundings "push" the extremes of the asymmetric anion together under a certain critical distance can the symmetrisation of the anion happen.

This case is peculiar and deserves re-examination.

In 1959, Mooney-Slater reported one of the first I_3^- crystal structures and discussed the matter of I_3^- symmetry within the available structures.⁹⁶ Using theoretical tools discussed in the associated publication of her husband (J. C. Slater),⁹⁷ she showed that such symmetry is not obvious at all. In brief, Slater invoked H_3 as a model molecule for I_3^- .⁹⁷ What can be learned is that such a system would show a single energy minimum, *i.e.* the central atom would be equidistant from the extremes, if and only if the extreme atoms are close enough, or better, are closer than a certain critical distance. Otherwise, *i.e.* if the extreme atoms are too far apart, said minimum becomes a saddle point, and two minima arise, with the central atom closer to either of the extreme atoms. This explains the d_1 – d_2 relationship in Fig. 4c, *i.e.* the shortening of one I–I bond of I_3^- as the other is elongated, without the need for any interaction with an exogenous chemical species.

Within Slater's qualitative theoretical framework, Mooney-Slater computed values for the available triiodides and obtained rough approximations for the limiting values of d_1 (here the shortest I–I distance in I_3^-), *i.e.* about 2.7 Å, and d_2 (here the longest I–I distance in I_3^-), *i.e.* >3.5 Å. Today, these values appear to be extraordinarily accurate for being inferred based on merely 5 crystal structures. The black elements in Fig. 5 are a redrawing of Mooney-Slater's original graph.⁹⁶ It was believed at the time that this graph could possess some sort of predicting power, *i.e.* that since for certain D values ($D = d_1 + d_2$) it was observed that I_3^- was not symmetrical, the symmetric or asymmetric character of I_3^- could be predicted based on its total length. The red and blue dots in Fig. 5 are an attempt at populating Mooney-Slater's graph with contemporary I_3^- CSD data (isolated I_3^- only). At first, it would seem that the graph's predicting power is poor, being decent only in the large d_1 and d_2 zone and for a slim portion of the symmetric triiodides. However, re-examining Slater's H_3 model,⁹⁷ it is observed that the energy of the saddle point (corresponding to the fully symmetric structure) with respect to the global minima (corresponding to asymmetric structures) is a function of D : the less significantly the molecule is elongated, the lower the energy barrier. Thus, it should not be surprising that a certain portion of the graph, until d_1 and d_2 remain below ~3 Å, shows a certain degree of structural variability, surely influenced by the I_3^- surroundings. According to this view, however, the role of the lattice is not prominent, but a perturbation of an inherently distortive system. More difficult to explain are fully symmetric I_3^- species with both d_1 and d_2 in the 3.1–3.2 Å range. We learn from Wiebenga *et al.*⁵⁶ that in the first wave of XRD experiments on polyiodide crystals *"efforts have been made to prove that the symmetrical shape of the I_3^- ions is not simulated by a statistical distribution of triio-*

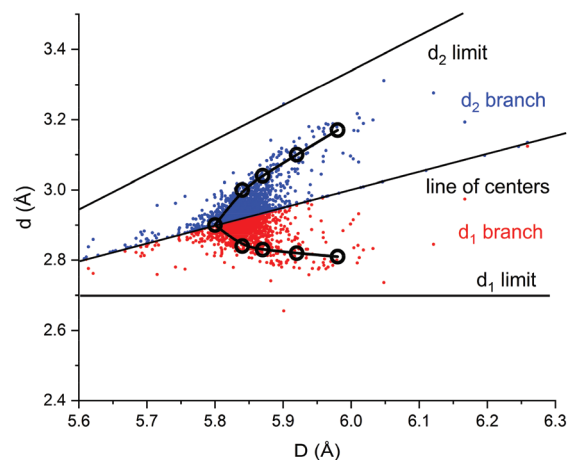


Fig. 5 Modern re-drawing of Mooney-Slater's graph (adapted from Fig. 5 in ref. 96 with permission from the International Union of Crystallography, copyright 1959). The original graph (black) based on 5 crystal structures shows a relationship between D , the distance between the terminal I atoms in I_3^- ions, and the shorter and longer bond lengths, d_1 and d_2 , respectively. The red and blue dots represent currently available CSD data for isolated I_3^- .

** Reprinted from ref. 28, Copyright 1972, with permission from Elsevier.

dide anions, in themselves asymmetrical"^{††} (such care is also manifested in individual original XRD reports of the time, *cf.* *e.g.* ref. 95). In this sense, one might question if we are still considering such issues as carefully, casting doubt on the quality of some odd data we possess today.

"The distinction between symmetrical and asymmetrical triiodide [sic] ions may not be significant, so far as the ion itself is concerned. The observed asymmetry of I_3^- in crystals may be produced entirely by neighboring cations" (Bent, 1968).^{52§} It may be so, or it is so? "It is believed that the large linear deformation of the I_3^- ion is a result of the different environments in the solid state" (Svensson and Kloo, 2003).^{22‡‡} It is believed so, or it is really so? The well-known calculations by Datta *et al.*,⁹⁸ referenced by most literature thereafter, clearly show that I_3^- is symmetrical. Yet, as Datta *et al.* focus on the theoretical minimum energy structure, there is no formal contradiction with Slater's model, which predicts fundamentally the same minimum. The Slaters' point of view is better described as being concerned with the nature of the solutions, rather than with minimum energy calculations (which they did not even attempt). Luckily, further contemporary discussion is available (*cf.* Aragoni *et al.*, ref. 99) as well as reliable contemporary data (computational tools have greatly evolved), which have recently been provided by Mealli and co-workers.¹⁰⁰ When calculating interaction energies for I_2 interacting with I^- at various distances to ultimately give fully symmetric triiodide, they found the following: (i) significant I_2 distortion (2.73 to 2.86 Å) is already observed when the approaching I^- is at 6.5 Å, with the energy of the $[(I_2) \cdot I]^-$ complex computed as $-7.1 \text{ kcal mol}^{-1}$; (ii) at 3.5 Å distance (I_2 internal distance 2.94 Å), the interaction energy is large, $-19.9 \text{ kcal mol}^{-1}$; (iii) from 3.5 Å distance all the way to symmetric I_3^- (I–I distance 3.04 Å), the further stabilization is very modest, computed as only $-4.7 \text{ kcal mol}^{-1}$. Whether we choose to believe that I_3^- is fundamentally distortive or not, the energy barrier to achieving strong distortion ($<5 \text{ kcal mol}^{-1}$) appears to be negligible compared to the ion–ion interaction energies in crystal lattices: this implies an intrinsic limitation of our ability to discriminate inter- and intra-molecular bonds.

A brief parenthesis should be opened here on CSD evaluation. The statistics can of course be altered if coordinated I_3^- or superior polyiodides are considered in the data pool. Most software possesses an intrinsic parameter to determine, depending on their nature and distance, if two atoms should be considered bonded or not. Setting the threshold for primary/covalent bonding to one value or another can alter the results; moreover, upon moving from one piece of software to another, borderline I–I bonds can formally become strong supramolecular interactions and *vice versa*. All these situations generally require manual attention with the associated annoyances. We close this digression, highlighting at the same time

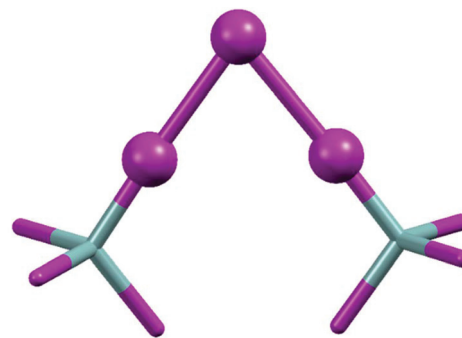


Fig. 6 The bent I_3^- acting as a μ_2 ligand in the QEPPAE crystal structure (tri-*t*-butylphosphonium (μ_2 -tri-iodo)-hexakis(iodo)-di-germanium).¹⁰¹

the importance of evaluating only non-bonded I_3^- as mentioned above and the colourful nature of polyiodide chemistry, with the illustrative case of QEPPAE¹⁰¹ (Fig. 6). QEPPAE contains an I_3^- acting as a μ_2 ligand on Ge(0) centres: this exotic I_3^- features an I–I–I angle of only 74.1° , setting a record, to the best of our knowledge, for I_3^- bending. The structure was reported by Jones and Ruthe as a private CSD communication in 2013¹⁰¹ with no further information; we hope that this explicit mention prompts the authors to share further insights.

Returning to our main point, the nature of the triiodide ion can be discussed even without statistics on the basis of bonding theories. Keeping the issue at the classical level, for now (*vide infra*), polyhalides received theoretical attention very early: we refer here to comprehensive reports by Wiebenga *et al.*^{56,57} Three types of explanation for the bonding in polyhalides are considered therein: fully electrostatic, localized covalent bonds and non-localized orbitals. The reason for referring to such old theoretical work is simple: it describes limit plain models, with strengths and shortcomings, in a very immediate manner. In brief, it was already concluded in the 60s that pure electrostatics has little applicability to polyhalides, while both localized and non-localized covalency work in certain cases but fail in others (*e.g.* the results of the fully localized description are unsatisfactory for I_5^- , I_7^- and polyiodides in general, while it succeeds at explaining polyhalides like IF_7 ; the reverse is also true).

These simple notions will prove important in the following discussion.

What is a triiodide according to other polyiodides?

This question is even more interesting in terms of supramolecular chemistry.

The best answer available at this time is depicted in Fig. 7. Fig. 7 is the "negative" image of a triiodide as defined by the $I \cdots I'$ contacts between a triiodide and an $I'-I-R$ probe (essentially I_2 molecules or polyiodides) built with the available CSD data. Interacting polyiodides are represented as violet $I'' \rightarrow I'$ vectors. The I–I covalent distances of individual triiodides are shown as black dots, representing the positions of the external I atoms in the individual triiodides composing the picture. Red vectors represent instead covalently bound I_2 fragments

^{††} Reprinted from ref. 56, Copyright 1961, with permission from Elsevier.

^{‡‡} Reprinted with permission from ref. 22. Copyright 2003 American Chemical Society

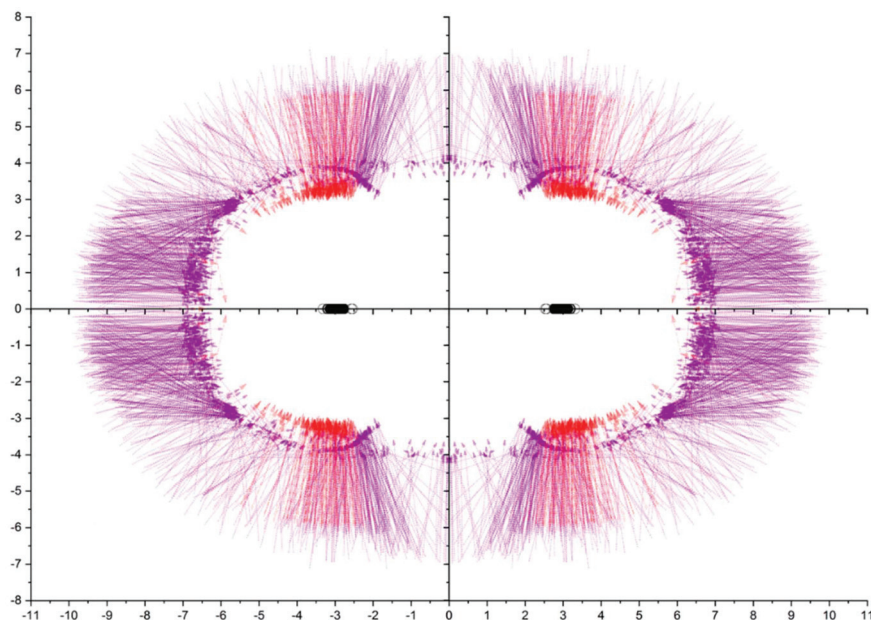


Fig. 7 Negative image of a triiodide as perceived by I–I–R interacting probes. Scales in Å.

belonging to I_5^- (the second most abundant polyiodide in the CSD, 162 hits). We notice here that, within possible I'–I'–R probes, I_3^- is also bound to be the most representative probe species, as it is the most abundant in the CSD (a general search for I–I–R, with R representing no atom or any atom, returns 2064 hits, of which 1849 hits (89.6%) are I–I–I; of these, 1586 hits correspond to isolated I_3^- , *i.e.* isolated I_3^- should account for >75% of the total contacts displayed in Fig. 7).

The existence of preferred directions and angles for interaction is already manifest from Fig. 7, yet thanks to the recent work by Esterhuysen and co-workers,¹⁰² we can be more explicit and present the data superimposed on the theoretical ESP of isolated I_3^- , as in Fig. 8.

It is manifest from Fig. 8 that the “bump in hollow”, “nucleophilic site in σ -hole” and “halogen bond” complexes correspond only to the regions highlighted in yellow, *i.e.* they are, statistically, minor interactions for these systems. We need

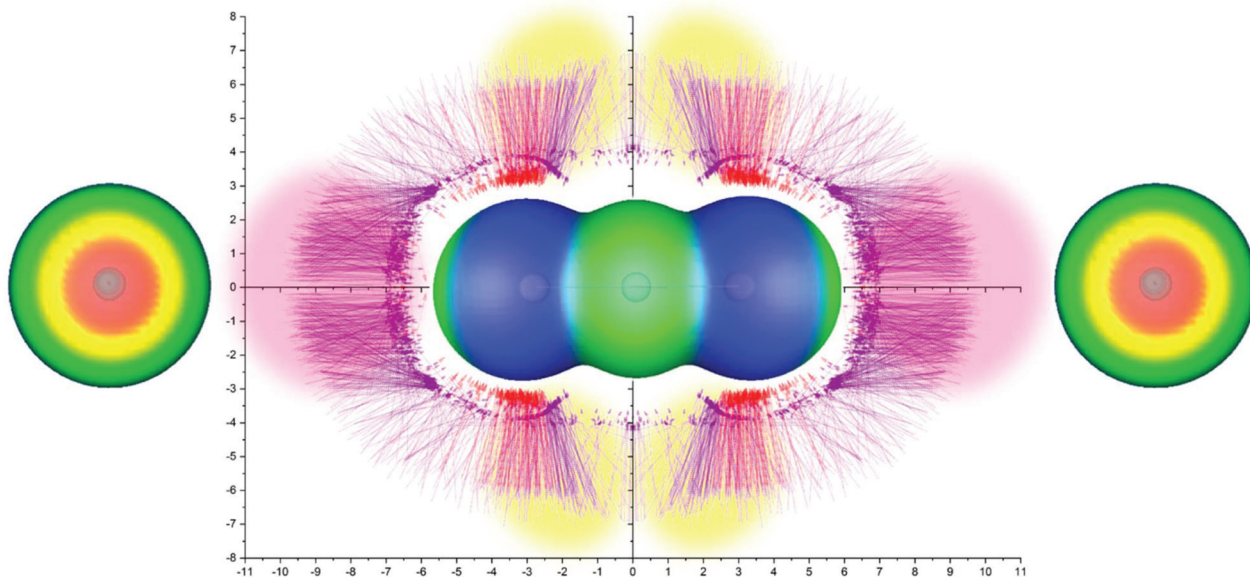


Fig. 8 Negative image of a triiodide as perceived by I–I–R interacting probes superimposed on the calculated ESP of I_3^- in the gas phase at the MP2 theory level. Zones corresponding to different interactions are highlighted in pink and yellow. Scales in Å. ESP data reproduced from Fig. 3 of ref. 102 with permission from Elsevier, copyright 2016.

to mention here that, on the contrary, these seem to be the main interactions for $I_2 \cdots I_2$ contacts.¹⁰³

For I_3^- the vast majority of the interactions are the counter-intuitive “hollow in hollow”, “ σ -hole in σ -hole” and “non-halogen” bonds found along the I_3^- axis, highlighted in pink.

How can such mismatched electrostatic interactions be favoured?

It is very simple: polyiodides pair these electrophilic regions and then share electrons among them.

Starting from Legon's ground-breaking reviews,^{62,104} which remain a landmark for halogen bonding and σ -hole development, the interest of the community has focused on what can be described as Mulliken outer complexes.⁶⁷ These complexes are held together by electrostatic forces, and show little (a few hundredths of an electronic charge) to no significant charge redistribution among the interacting partners, and hence there is no significant deviation of bond length in the complex with respect to the isolated species. Legon detailed this especially well; he also reported and discussed some inner Mulliken complexes, but he wisely held them in special consideration and avoided mixing them with outer Mulliken complexes, especially when attempting data modelling.¹⁰⁴ In inner Mulliken complexes, strong association and significant charge redistribution happen, the forces in play go beyond pure electrostatics and, as electrons are shared, a more marked dependence on the chemical nature of the interacting partners is introduced.

We believe, given the large variability in I_3^- bond length (*vide supra*), the difficulty in telling covalent and supramolecular contacts apart, and the manifest electrical conduction behaviour reported for some polyiodide networks (*vide infra*), that there is more than enough evidence to conclude that, in most of these systems, charge redistribution is non-negligible.

This brings us to the conclusion that polyiodide–polyiodide non-covalent interactions are fundamentally different from what we generally consider halogen bonding, for the simple reason that most of these descriptions were developed to describe outer Mulliken complexes, not inner ones.

The first step towards understanding and modelling these interactions lies in recognising this fundamental difference.

This is not to say that halogen bonding is not relevant to polyiodide...polyiodide interactions, but to remark that, despite its popularity, the term should not be abused. Thankfully, we were provided with a formal definition, which clearly talks about “*net attractive interaction between an electrophilic region [...] and a nucleophilic region.*”⁵⁸ When two electrophilic regions are interacting, according to the definition, the term halogen bonding is improperly used.

There is another point that must be stressed here.

Even the “bump in hollow”, “negative site in σ -hole” and “halogen bond” polyiodide–polyiodide interactions are not classical most of the time. The yellow portions of Fig. 8 are dangerously near to the red zones defined by covalently bound polyiodides (I_5^-). Not only are they dangerously near, but it can be shown that there is partial overlap between what is considered covalent and what is considered non-covalent

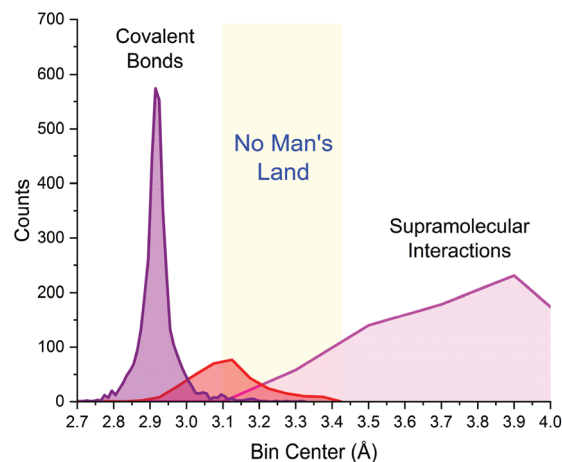


Fig. 9 I–I covalent bond distances in I_3^- (violet, cf. Fig. 4a) and I_5^- (red) compared to the shortest I...I supramolecular interactions from the dataset used to generate Fig. 7 and 8 (magenta). A ~ 0.3 Å shell, approximately from 3.1 to 3.4 Å, exists where interactions cannot be assigned as properly covalent or properly supramolecular.

in the CSD (Fig. 9) (*cf.* Alcock's¹⁰⁴ and Bent's quoted statements above).

Attributing our manifest inability to distinguish intra- and inter-molecular interactions for these systems to data quality, or assignments made by single crystallographers, *etc.* is only a partial excuse. The truth is, very different from the opinion of the software we use daily, that for interacting polyiodides there is not a well-defined threshold distance value under which the interaction is fully covalent and above which it is fully supramolecular. Charge redistribution happens also for the interactions in the yellow areas of Fig. 8 and 9, and, due to fractional bond orders, it is inherently difficult to distinguish covalent and non-covalent interactions. This is where a certain degree of freedom of choice in interpretation still exists, and, as everyone exerts this freedom, how statistics and distinctions tend to become more and more blurred.

Politzer, Murray and Clark made a case for the purely semantic distinction between $n-\sigma^*$ charge transfer and polarization for σ -hole bonded systems. “*The difference is more semantic and definition than reality*”,⁷²§§ they wrote, *vs.* “*Le langage est une législation, la langue en est le code*”,²⁵¶¶ Lehn's take on the supramolecular chemistry lexicon (originally formulated in a broader sense by the semiotician Roland Barthes¹⁰⁵): perhaps chemical semantics would make for a good field of study. Their observation, also discussed by others in the literature,^{106,107} is fully agreeable for the cases they discuss, but less so in the specific case of polyiodides. It is true that attempting to reduce the complexity of polyiodides into σ -hole bonding, aiming to solve the issue with a simple electrostatic model, is extremely tempting. However, the shortcomings of a pure electrostatic model for polyiodides have been demon-

§§ Reproduced from ref. 72 with permission from the PCCP Owner Societies.

¶¶ Copyright 2006 Wiley. Used with permission from ref. 25.

strated in the 60s, together with those of localized and non-localized covalent models.^{56,57} The truth, according to a good share of the literature evidence – we mention here again the detailed work by Mealli *et al.* on I_3^- , I_4^{2-} and $I \cdots I-R^-$ systems,¹⁰⁰ substantiating the negligible importance of σ -holes in their formation and, on the contrary, the remarkable σ electron sharing – lies somewhere in the middle, in a conceptually difficult realm where “orbital overlap”, “rehybridization”, “hypervalency” and “fractional bond order” are the keywords. What is important, to foster future understanding, is to embrace such complexity and not be scared away from it. Hence, in this specific context, we must make careful use of “secondary bonding” and especially of the popular “halogen bonding” and “ σ -hole bonding” terms: we must learn to use such terms within the limits of their respective definitions and strongly refuse their usage as *passé-partout* “tag-words” allowing us to dismiss complex matters in need of further investigation. The central idea we want to pass on is that, under the appropriate light, the no man’s land in Fig. 9 is nothing but a land of opportunity for further supramolecular chemistry development.

One is also tempted to plant his own flag, introducing his own term in the new-wave supramolecular chemistry vocabulary (such seems to be the trend in the current supramolecular literature): iodophilic interactions could be the one (not particularly original either, as the similarities between I and Au have been addressed elsewhere²² and the *philia* and *neikos* understanding of chemistry is arguably better left to Empedocles’s writings – around 400 BC). We decide to pass, deeming the appreciation of the underlying meaning more important than the establishment of novel words.

We also refrain here from any other statistical evaluation of more complex polyiodides for three reasons.

First, we hope to have pointed out that, even for the simplest polyiodide, the situation is inherently complex. Some misconceptions exist, at times impeding recognition of the nature of the underlying interactions: these need to be fixed in order to meaningfully prosecute studies in the field. Moreover, I_3^- is always referenced as one of the fundamental building blocks of polyiodides: since the situation is not trivial for I_3^- , it cannot be but more complex for the others.

Second, starting from pentaiodide, polyiodides start to exist as different isomers, denoting different hybridization/electronic distribution (V and L for I_5^- , pyramidal and Z-shaped for I_7^- , and so on). This adds a further layer of complexity that prevents presentation of a comprehensive view in a single image.

Lastly, no other polyiodide is equally represented in the CSD: when the available data is of the order of a few tens of structures or less (*e.g.* I_7^- returns only 24 CSD hits, ideally to be separately analysed for pyramidal (11) and Z-shaped (13) I_7^-), extraction of statistically meaningful information is not yet possible (*i.e.* the community needs more data and structures for superior polyiodides, a conclusion we share with essentially the whole reference list).

Now-affable advances in polyiodide chemistry

As discussed above, polyiodides have the ability to foster broad scientific interest, resulting somewhat in fragmentation of knowledge into different schools of thought. The same is also true from an experimental viewpoint, where several divisions can be envisaged.

The first choice concerns the phase under study. Most studies deal with either liquid or solid phases.

Liquid phase studies can employ either organic solvents, polymers or even molten I_2 as a medium.²² These studies can generally only access non-extended polyiodides, either due to dilution (solvents), incorporation in a pre-formed matrix (polymers) or due to the required temperature (molten I_2). This field is not covered in the present review, for the sole reason that the finer discussion of supramolecular forces is better accomplished in crystalline solids. Moreover, we believe that better framing in terms of secondary/halogen/ σ -hole bonding can be given, maintaining the crystal engineering focus that led to the development of these concepts in supramolecular chemistry.

The relevant crystalline phase studies can be divided, again, into three main categories.

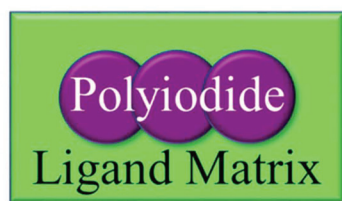
A first body of work, too classical to be covered here, corresponds to the period of scientific curiosity towards polyiodides and the initial/growing availability of diffraction techniques: there was a time when examples of complex polyiodides were rarely, if at all, reported, and it was still possible to steadily isolate “odd” species with a certain ease. This was already systematically described by Svensson and Kloo,²² who also took the time to review critically, illustrating such cases where exotic individual species were claimed but could be rather interpreted as familiar building blocks held together by weaker, clearly non-covalent, interactions.

Beyond these early efforts, it became manifest that series of compounds with systematic structural variations are required to extract meaningful trends:²² difficulties connected with synthesis and crystallization (which should also be conducted in a controlled manner so as not to alter the results) slowed down further progress.

There were two long-lasting questions in the field:

- (i) How can we achieve selective synthesis of one specific polyiodide over the others?
- (ii) How can we produce extended polyiodide networks and what are their properties?

This resulted in two different branches, which use fundamentally different tools and produce crystalline phases that lie at opposite poles in terms of iodine density: these go by the broad names of “supramolecular caging” and “iodine-dense frameworks”, with some crossbreed systems also being reported. A pictorial view of the main differences is displayed in Fig. 10.



Supramolecular Caging of Polyiodides

Discrete polyiodides embedded in ligand matrices

Shape/Size/Stereoelectronic templating effect of the ligands environment

Ligand-polyiodide contacts dominate



Iodine-dense Polyiodide Networks

Polyiodide clathrates engulfing ligands

Ligands as 3D moulds for polyiodides

Polyiodide-polyiodide contacts dominate

Fig. 10 Schematization of current approaches to polyiodide chemistry: supramolecular caging vs. polyiodide frameworks.

Supramolecular caging of polyiodides

The concept of caging was developed as an answer to question (i).

It is possible to achieve selective synthesis of polyiodides by applying a sort of Supramolecular Darwinism, *i.e.* survival of the fittest, to complex mixtures of polyiodides. This is achieved with a clever use of supramolecular tectons that tend to form polycationic networks with cavities of desired and controllable size in the presence of anions. When their spontaneous assembly happens in the presence of Γ^-/I_2 mixtures, the best fitting polyiodide is preferentially included in the solid, leading to an entirely selective self-assembly process. This is commonly known as dimensional caging of polyiodides, since size complementarity is the first and foremost discriminating factor in play. Over time, shape, angles, the disposition of the charged groups, the directionality of the forces in play, and the tectons' intermolecular packing tendencies have also come into use. The resulting crystalline phases tend to be relatively iodine-dilute: this is because each polyiodide is generally encapsulated in a ligand matrix, with few to no opportunities to contact and interact with other polyiodides. In other words, the main contacts in these systems are expected to be of the polyiodide–lattice type: this is the realm where halogen, secondary and σ -hole bonding are fully relevant concepts, of capital importance for understanding the resulting phases. The better the concepts of halogen and σ -hole bonding were understood, the more possible it became to effectively implement finer host/guest stereoelectronic complementarity criteria in designing such systems.

Many types of ligand molecules have been employed in this context, selected according to either their structural features and/or their amenability to different supramolecular forces. Lately this became a matter of preference, often tied to the desired results in terms of the target polyiodide and/or the final properties of the resulting lattices.

The idea of selective stabilization of discrete polyiodides based on supramolecular interactions existed in the chemical literature for a long time. Until recently, this was formulated in classic supramolecular terms, *e.g.* by referring to the obtained phases as “complexes of complexes” obtained with well-established intermolecular forces. As an example, we can cite the study by Ilioudis and Steed,¹⁰⁸ where a protonated azacyclophane, **1** (Fig. 11), with a cavity matching the iodide anion in size, was used to obtain polyiodide complexes. Not only did the ligand display effective iodide binding, but it also effectively promoted the formation of the elusive I_4^{2-} species by insertion of a bridging I_2 molecule in between two ligand-bound iodides.

The shaping of this area of supramolecular chemistry into the sub-field of supramolecular caging of polyiodides was pioneered by Svensson and Kloo, together with Gorlov.⁴⁸ Their study promoted the ideas of selective spatial confinement of polyiodides through a hierarchical use of different supramolecular interactions.

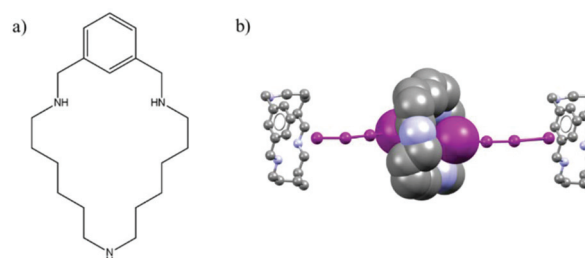


Fig. 11 Stabilization of the I_4^{2-} anion (b) through the protonated azacyclophane **1** (a). CSD refcode: NABWOD.¹⁰⁸ Space-filling representation used to highlight the good complementarity between **1** and the hosted I^- anion.

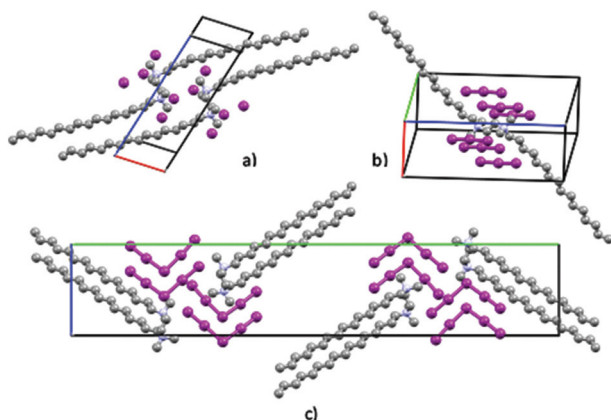


Fig. 12 Overview of the solid phases formed by the HA^{2+} ligand and I^-/I_2 mixtures (CSD refcodes: (a) LOQMAG; (b) LOQMEK; (c) LOQMIO).⁴⁸

The initial idea was to use ligands composed of a central couple of separated quaternized ammonium groups possessing long alkyl side chains: in such a way the spontaneous assembly of long alkyl chains into a lamellar-type structure would result in the confinement of the necessary polyiodide counteranions in close proximity to the ammonium groups. In fact, using the dication $(\text{C}_{12}\text{H}_{25})(\text{CH}_3)_2\text{N}(\text{C}_2\text{H}_4)\text{N}(\text{CH}_3)_2(\text{C}_{12}\text{H}_{25})^{2+}$ (DA^{2+}), I^- and I_3^- complexes could be isolated, while using the larger $(\text{C}_{16}\text{H}_{33})(\text{CH}_3)_2\text{N}(\text{C}_2\text{H}_4)\text{N}(\text{CH}_3)_2(\text{C}_{16}\text{H}_{33})^{2+}$ (HA^{2+}) ligand, I^- , I_3^- and I_5^- complexes were obtained (Fig. 12). The resulting phases are indeed composed of the expected lamellar arrangement of alkyl chains with confinement of polyiodides: the small iodide ion and the linear triiodide (matching the arrangement of the diammonium ligand) can always be accommodated. Pentaiodide binding interestingly results in transition of the ligand from an extended conformation to a U conformation, affecting the overall lattice properties and giving rise to polyiodide chains rather than full encapsulation of the polyiodide as in the other cases.

Metrangolo, Resnati, Rissanen and coworkers reported instead a different take on selective polyiodide stabilization, demonstrating that it is possible to access the elusive I_4^{2-} species selectively by using a very simple dicationic receptor: bis(trimethylammonium)hexane (Fig. 13).¹⁰⁹ This molecule possesses a precise dimensional matching with I_4^{2-} : once the ligand is in contact with an I^-/I_2 mixture, 2 I^- ions are coordinated and a perfectly fitting cavity for an I_2 molecule remains between them, leading to selective I_4^{2-} formation (Fig. 13a). The more easily formed I_3^- and I_5^- can also be stabilized with some compromises: due to the imperfect anion/ligand size match, I_3^- organizes in infinite ribbons (Fig. 13b), while I_5^- , owing to its bent structure, requires a major rearrangement of the packing, now featuring a zig-zag pattern of ligand-defined cages (Fig. 13c).

In the same year Rissanen, Albrecht and co-workers introduced anion- π interactions as directional forces for stabilization of polyiodides and other related trihalides, such as Br_3^- .³⁶

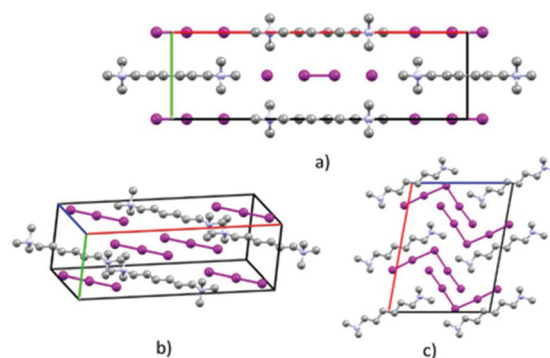


Fig. 13 (a) Perfect caging of I_4^{2-} (displayed as $[\text{I}_2\text{I}_2]^{2-}$) by the bis(trimethylammonium)hexane ligand. Imperfect matching with I_3^- and I_5^- leads to I_3^- infinite chains (b) and to a ligand zig-zag pattern to accommodate I_5^- (c). CSD refcodes: (a) NUTSOL; (b) NUTTAY; (c) NUTSUR.¹⁰⁹

As displayed in Fig. 14a, through a quinoline-based ligand functionalized with a pentafluorophenyl appendage, the tribromide anion can be effectively surrounded by 4 aromatic moieties (2 quinolines, 2 pentafluorophenyl moieties), stabilizing it through anion- π interactions. 2 additional quinoline rings complete the aromatic cage around the anion, interacting *via* $\text{CH}\cdots\text{I}$ and $\text{NH}\cdots\text{I}$ contacts.

The same concept is successfully applied to polyiodides with pentafluorobenzylidibenzylammonium as counterion. In this case, encapsulation of I_3^- and I_4^{2-} anions is simultaneously achieved within the same crystal through anion- π interactions (Fig. 14b).

An attempt to use a biphosphonium cation functionalized with pentafluorophenyl appendages still resulted in I_4^{2-} caging in a mixed $\text{I}^-/\text{I}_4^{2-}$ crystal. Control of I_4^{2-} formation in this case seems to be due to the spacing of the cation charges

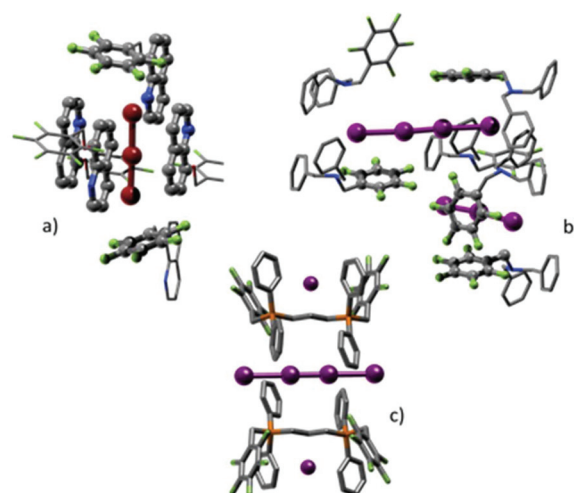


Fig. 14 (a) Aromatic cage around the Br_3^- anion as found in the LAGGEH crystal structure;³⁶ (b) similar anion- π -based stabilization achieved for polyiodides in the LAGFEG crystal structure;³⁶ (c) caging of I^- and I_4^{2-} with anion- π interactions and $\text{CH}\cdots\text{I}$ contacts, respectively, using a biphosphonium derivative (CSD refcode LAGFOQ).³⁶

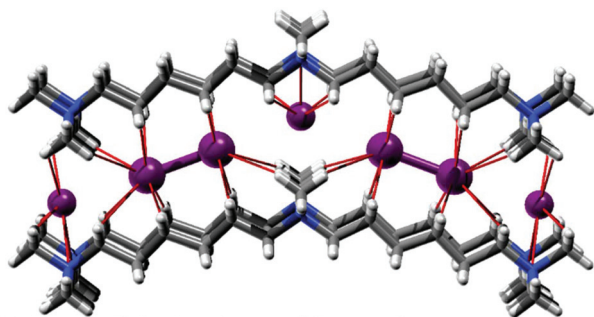


Fig. 15 Supramolecular alkylammonium cage stabilizing the I_7^{3-} anion (here formally displayed as an $[(I)_3(I)_2]^{3-}$ complex for clarity). The main short $CH\cdots I$ contacts are highlighted in red. CSD refcode: PEKKEX.¹¹⁰

and $CH\cdots I$ interactions, while anion- π contacts remain relevant only for the iodide anion, effectively sandwiched in between pentafluorophenyl rings (Fig. 14c).

In 2012 Metrangolo and Resnati returned to the idea of polyiodide stabilization with structurally matching cations, illustrating this time how the cation's shape, and especially angular parameters, can also lead to stabilization of exotic species not commonly isolated otherwise, such as I_7^{3-} .¹¹⁰ Caging of such species is achieved through a network of charge assisted $CH\cdots I$ contacts involving an alkyl ammonium trication (*N,N,N',N'*-pentamethyl-*N'*-(6-(trimethylammonio)hexyl)hexane-1,6-diaminium) as shown in Fig. 15.

Meanwhile, in 2011, halogen bonds were also introduced in the number of supramolecular tools available in the supramolecular caging of polyiodides.¹¹¹ This was achieved by modular preparation of 4,4'-bipyridinium salts possessing different substituents, including fluorinated and iodinated ones. It was demonstrated that methylpyridinium is not suitable for caging purposes (Fig. 16a), leading instead to polyiodide ribbons. Functionalization with benzylic appendages resulted in much better results, with cages being formed due to ligand-ligand π - π stacking forces, thus allowing for effective polyiodide incorporation (Fig. 16b). When these appendages featured iodo-substituted aromatic rings, the formation of directional halogen bonds was observed, further assisting the selective incorporation of the best fitting polyiodide in the crystal matrix (Fig. 16c).

It is worth noticing here that the almost linear (163.5°) interaction (1 in Fig. 16c) is no more than a van der Waals-type contact ($I\cdots I$ distance 4.04 Å) with non-stringent interaction geometry. The other $I\cdots I$ interaction in the same figure, 2, is much stronger ($I\cdots I$ distance 3.63 Å) and is in line with the expected geometric parameters for proper halogen bonding: it is observed to be collinear with the $C\cdots I$ bond at the electrophilic/ σ -hole site, and the angle at the nucleophilic site is relatively close to tetrahedral ($I-I\cdots I$ angle 120.9° , cf. Fig. 2).

Reiss and van Megen partially revisited some of the above systems. They reported additional members of the 4,4'-bipyridinium I_2/I^- family of complexes¹¹² and reconsidered ammonium-based receptors: usage of 1,8-diaminooctane (longer with respect to bis(trimethylammonium)hexane,

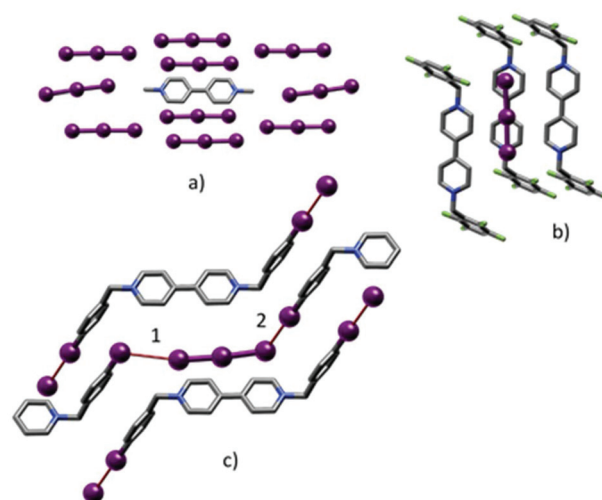


Fig. 16 Simple bipyridinium cations and their influence on supramolecular caging of polyiodides: (a) no caging observed; (b) effective caging due to appended benzylic substituents; (c) effective caging reinforced by $I\cdots I$ halogen bonds with iodo-substituted aromatic appendages. CSD refcodes: (a) SOXHET01; (b) SAZZAW; (c) SAZYUP.¹¹¹

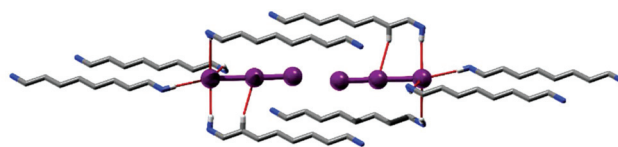


Fig. 17 Caging of I_6^{2-} (shown as an $[(I)_2]^{2-}$ complex for clarity) with protonated 1,8-diaminooctane. The main hydrogen bond pattern is highlighted in red. CSD refcode: PUXWEM.¹¹³

observed to stabilize I_4^{2-})¹⁰⁹ led to selective formation of I_6^{2-} complexes as shown in Fig. 17.¹¹³ As a protonated primary amine is used instead of a quaternized ammonium, a dialogue between the $I\cdots I$ interactions holding the I_6^{2-} together and the H-bonding to the receptor is established.

Even simple coordination compounds, like $[Cu(DMSO)_6]^{2+}$, have been demonstrated to be able to pack, leaving suitable cavities for polyiodide caging.¹¹⁴ In the specific case of this Cu(II) complex, multiple $CH\cdots I$ contacts stabilize I^- coordination in the proximity of the Cu(II) complex (Fig. 18). As weakly bound I^- ions are found at the periphery of each Cu(II) complex, their close packing is somewhat hindered by charge-charge repulsion. The system is observed to solve the issue by inserting bridging I_2 molecules in between each pair of I^- anions, resulting in effective stabilization of I_4^{2-} .

In conclusion, supramolecular caging of polyiodides effectively applies complementarity and preorganization principles to the selective stabilization of polyiodides. While simpler criteria based on size and shape considerations were among the first ideas to be implemented, effective usage of stereoelectronic complementarity has been demonstrated with a plethora of different underlying interactions (hydrogen bonds, anion- π interactions, halogen bonds). As $I\cdots I$ contacts tend to be of secondary importance here, since polyiodides tend to exist as iso-

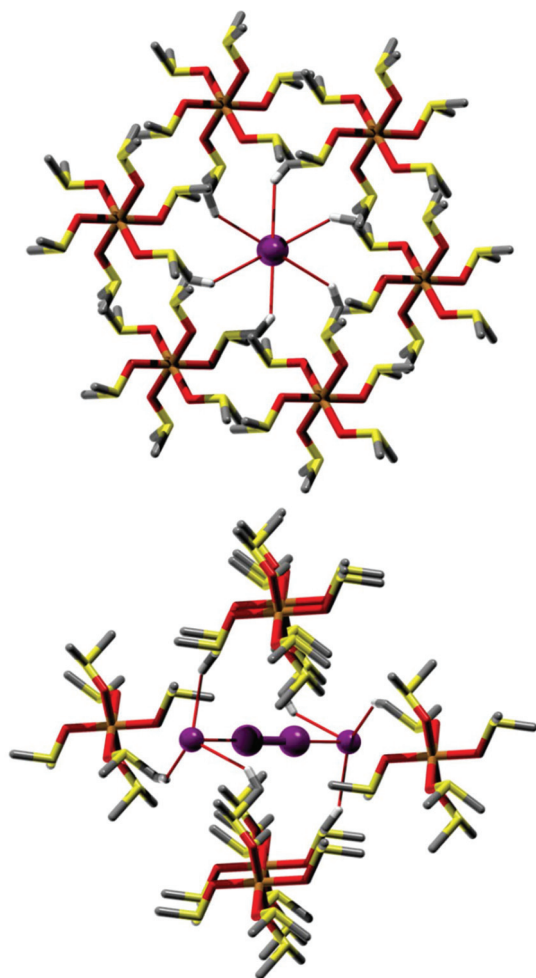


Fig. 18 Top and side views of I_4^{2-} caging by $[Cu(DMSO)_6]^{2+}$ cations. Red lines represent short $CH\cdots I$ interactions. CSD refcode: FILDAH.¹¹⁴

lated entities within the crystals, most of the novel vocabulary of supramolecular chemistry is of full relevance.

From cages to unintended moulds and proper cage/mould systems

As we shift the focus of our discussion from isolated caged polyiodides to polyiodide networks, it is useful to emphasize a relevant fact: the distinction between the two subfields at times is more dependent on the mindset and scope of the investigators than on the actual outcome of polyiodide crystallization.

With the best intention to achieve solely selective supramolecular caging of the target polyiodide, many of the above described ligands led to the formation of solid phases with different polyiodides. Some of them can be rightfully classified as polyiodide networks. To name some examples, bis(trimethylammonium)hexane does selectively cage I_4^{2-} , but can still form I_3^- and I_5^- complexes as shown in Fig. 13.¹⁰⁹ While the I_5^- complex still features polyiodide confinement, the I_3^- complex presents infinite triiodide chains instead.

Effective salt-bridge bonding stabilization of I^- leading to I_4^{2-} confinement, as demonstrated by Ilioudis and Steed, is

but one of the possibilities offered by their cyclophane (**1**, Fig. 11). If crystallization is conducted more slowly, allowing for aging and aerobic oxidation, a more iodine rich phase can be isolated where the interaction of **1** with iodide remains relevant, but ribbons of I_8^{2-} anions are instead stabilized between the charged rims of neighbouring cyclophanes, resulting in a network.¹⁰⁸

In general, it is well known that crystallization of polyiodides is strongly dependent on the conditions, and heavily influenced by several different effects so that the overall results are difficult to predict. These include the solubility of possible solid phases and the crystallization time (especially if iodide containing solutions are left exposed to air), together with the parameters that can influence the general $nI^- + mI_2 = I_{2m+n}^{n-}$ equilibrium, such as solvent/crystallization medium and temperature.²²

In a sense, the nice progress achieved in the supramolecular caging of polyiodides testifies to a profound understanding of supramolecular chemistry principles and skilful ligand design, as selective stabilization can indeed be achieved. Yet even a perfect ligand for a target polyiodide is easily defied by a totally different, or time dependent, I^-/I_2 stoichiometry in the crystallization mixture. This means that, in sub-optimal conditions, ligands intended as caging agents for discrete polyiodides can instead stabilize polyiodide networks by unintentionally moulding the formation of polyiodide frameworks around them.

As the parameters in play can be many and their individual effects difficult to assess, the exact process through which an intended supramolecular cage becomes an unintended supramolecular mould remains unclear most of the time.

Bianchi and co-workers recently reported the case of a system behaving as a cage or mould in different conditions, along with a new collection of 8 crystal structures at increasing iodine content, and tried to shed light on the underlying processes.^{9,10,80}

The renowned tetracation cyclobis(paraquat-*p*-phenylene)¹¹⁵ (also known as Stoddart's Blue Box, BB in the following discussion) crystallizes in the presence of iodide anions, giving crystal structures with the expected $[BB(I)_4]$ general formula. The obtained crystals are hybrid organic-inorganic salts held together by charge-charge, anion- π and dipolar $CH\cdots I^-$ interactions arranged in 3D ordered porous networks, with cavities defined by the arrangement of I^- -bridged BB pillars (Fig. 19).⁸⁰ Since none of these interactions are as directional as coordination, covalent or H-bonds, used respectively to achieve the predetermined porous architectures of MOFs, COFs and SOFs (Metal, Covalent and Supramolecular Organic Frameworks, respectively), the system behaves as a ball-jointed three-dimensional assembly, showing global packing re-organization dependent on the crystallization conditions (Fig. 19). According to the unprecedented flexibility of such networks and their controlled but stimuli-responsive assembly, this has led to the definition of POFs, permutable organized frameworks, as a novel type of porous material.⁸⁰

When the BB/I^- system is allowed to come into contact with I_2 , different situations are encountered depending on the solvent (Fig. 20).

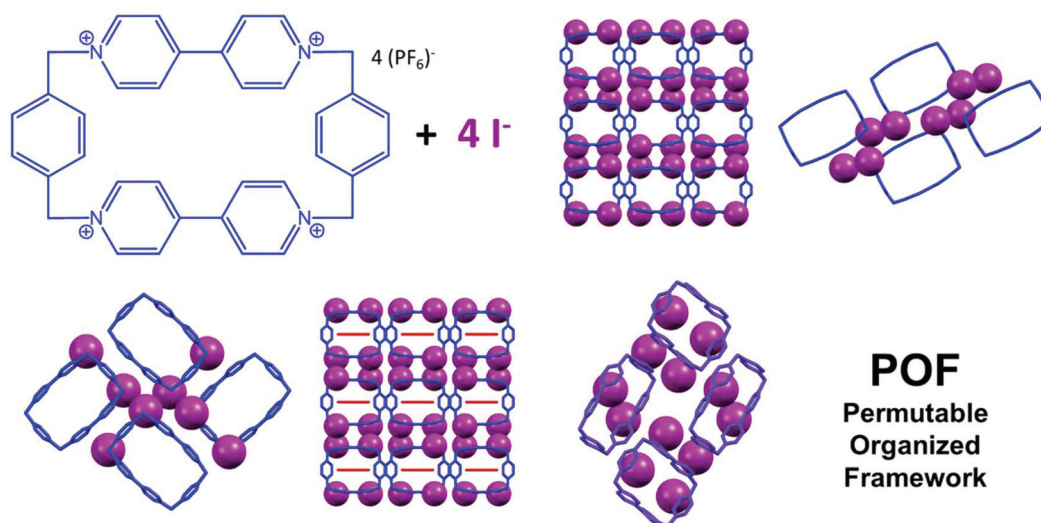


Fig. 19 Examples of the unprecedented structural variability of the [BB(I)₄] system in forming porous architectures, leading to the definition of POFs. Colour code: BB, blue; iodide, violet; hosted naphthalene molecules, red; co-crystallized solvent molecules omitted. Full details in ref. 80. Partially adapted from ref. 80 with permission from Wiley, copyright 2020.

In DMSO solution in the presence of an excess 1:2 $\Gamma^- : I_2$ mixture, BB behaves as a cage, resulting in a [BB(I₃)₄] type complex featuring replacement of the 4 I^- ions bridging BB pillars with two I_3^- . A third I_3^- is effectively hosted in the BB cavity (Fig. 20a) and the fourth is hosted in a binding site located in between BB pillars. This can be thought of as a caging process, where the BB cavity effectively hosts isolated polyiodides and governs crystal packing.¹⁰

By adding an excess of iodine, isolated [BB-I₅] complexes were observed in DMSO *via* Raman spectroscopy, showing I_5^- in its asymmetric L configuration.¹⁰

Using the same excess iodine conditions in acetonitrile instead leads to stabilization of a polyiodide framework.⁹ The resulting complex has the [I₅@BB(I₃)₃] formula. Each BB hosts an I_5^- anion leading to a rearrangement of individual BB pillars into twin columns held together by short $I \cdots I$ contacts and $BB \cdots BB$ π - π stacking interactions. This leads to the for-

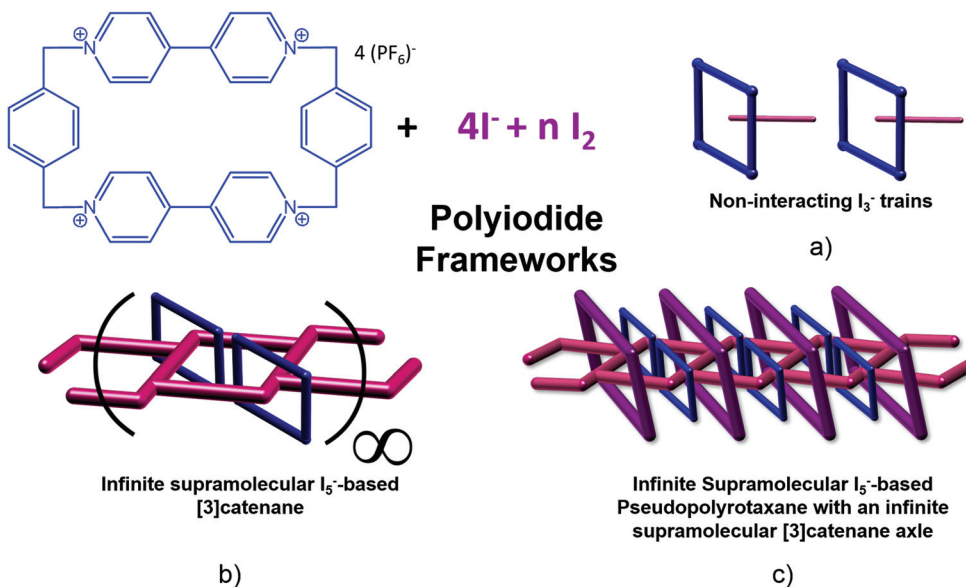


Fig. 20 Schematic evolution of the BB ligand (blue) from a supramolecular cage encapsulating polyiodides (pink/violet) (a), to a supramolecular mould templating a polyiodide network passing inside (b), and outside (c), its cavity depending on the nature and I_2 content of the crystallization medium. Full details in ref. 9 and 10. Partially adapted from ref. 80 with permission from Wiley, Copyright 2020. Partially adapted from ref. 9 with permission from The Royal Society of Chemistry, copyright 2020.

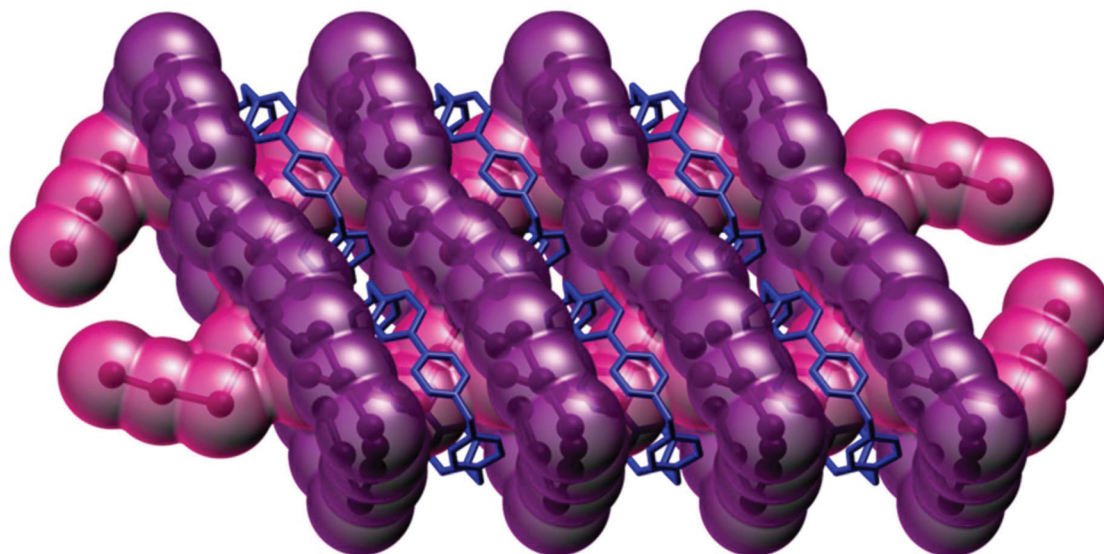


Fig. 21 "Interlocked polyiodides", the 1st Italian national finalist in Wiki Science Competition 2019¹¹⁶ (non-photographic media category), represents a portion of the $[I_5@BB@(I_5)(I_3)_2]$ crystal structure.¹¹⁷ The image is free to share under a CC 4.0 international licence.

mation of an infinite chain of fused 14-membered polyiodide rings encompassing 2 BB molecules each, *i.e.* to the formation of an infinite supramolecular [3]catenane (Fig. 20b). In this solid phase, the I_5^- anion is observed (XRD, Raman) to regain its full V-shaped symmetry. In this case BB promotes the formation of a polyiodide framework that nevertheless remains somewhat confined within the BB cavity, transitioning from a fully caging function to a certain degree of templating.

The full moulding ability of BB emerges at even larger iodine excess. In such conditions the core internal $I_5^-@BB$ interaction and the twinned columns survive, but the system can now also take full advantage of the BB external surface for the stabilization of a polyiodide network surrounding it (Fig. 20c). By incorporation of a further I_2 molecule per BB, $[I_5@BB@(I_5)(I_3)_2]$, a complexes of complexes type of adduct, is produced in the solid state: the former [3]catenane structure observed for $[I_5@BB(I_3)_3]$ is converted into the axle of an infinite pseudopolyrotaxane as very large (22-membered, *i.e.* $[(I_5)_2(I_3)_4]^{6-}$) polyiodide rings are templated by the external surface of each pair of catenated BB molecules (Fig. 21).⁹

This not only results in one of the most intricate (and perhaps beautiful) recent examples of interlocked polyiodides, but overall shows that several parameters, including stoichiometry and the nature of the solvent, play a major and not easily addressed role in determining the caging or moulding function, even for exactly the same ligand molecule.

Polyiodide frameworks

Extended polyiodide frameworks received early interest in view of some of the material properties they may bring about. A famous example is that known as $(TTT)_2I_3$ (TTT = tetrathiotetracene). This system, also known as TETTRI (from the CSD refcode of the crystal structure) (Fig. 22), has been called a one

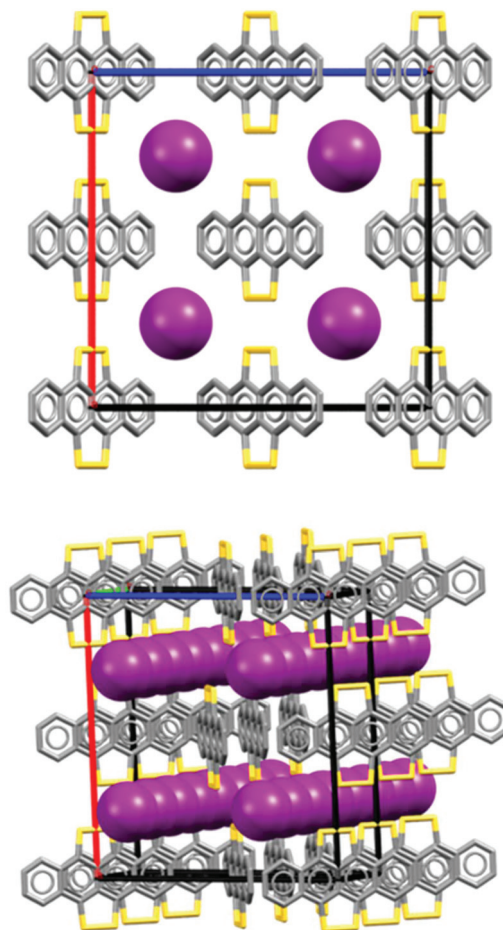


Fig. 22 Front and side views of the cell content and polyiodide wires of TETTRI (CSD refcodes: TETTRI to TETTRI12).

dimensional organic metal,¹¹⁸ due to its trains of interacting triiodides, and features a reported electrical conductivity close to that of elemental In.²² Despite intense scientific consideration in the late 70s and early 80s, as testified by the 12 CSD depositions (TETTRI to TETTRI12) and related publications,^{118–122} it was not possible, to the best of our knowledge, to fully elucidate the structure of the I_3^- trains, a fact that was, to some extent, also viewed as a consequence of the limited I–I bond localization of the interacting triiodides.

A certain fascination and supramolecular interest in extended polyiodide frameworks has long existed in the literature. Although this perspective intends to cover the latest contributions, which have a rather different focus (*vide infra*), a brief mention of earlier work is due. Pioneering and well-known contributions to the field have been made by a collaboration between Lippolis,^{123–125} Blake and Schröder.^{126–132}

Blake, Lippolis, Schröder and co-workers reported several beautiful examples of extended polyiodide networks, demonstrating very interesting ideas concerning templating through organic ligands or metal complexes as structured counterions. Their work resulted in some of the first examples of polyiodide systems of superior complexity, including supramolecular belts, helices and even cross-linked double helices (Fig. 23).

We make only a brief mention of these studies here, as these authors have already produced a remarkable review illustrating their ideas for moulding polyiodide frameworks around ligands or metal complexes designed for the task: the reader is gladly directed to this first-hand account.¹³³ As the number of noteworthy supramolecular polyiodide architectures expands, the influence of these reports in our own and other research groups' latest contributions^{134,135} is manifest.

To better frame the latest trends in the field, as well as stressing the importance of a deep understanding of I...I inter-

actions (hence the above discussion on supramolecular interactions), a few facts must be noted.

First, contrary to supramolecular caging, the crystal structures of polyiodide frameworks tend to be dominated by I...I contacts. As we transition from halogen/ σ -hole/secondary I...I lattice interactions typical of supramolecular caging to I...I contacts, detailed understanding of the nature of such interactions becomes of paramount importance: subtleties are no more semantics as they affect material properties. Recent attention has been given to iodine-dense systems as solid-state conductor candidates based on a Grotthuss-like mechanism.²⁰ It is implicit that proper understanding of the chemical bonding in such systems and tailoring of the material properties are different faces of the same problem.

When the issue is approached with applications in mind, the Grotthuss-like mechanism is reported to have qualitative and quantitative requirements. In terms of the quality of I...I interactions, maintenance of a certain degree of orbital overlap is required to allow electron jumping: structures with uninterrupted trains of polyiodides with short intermolecular distances are generally more effective. This is where detailed understanding of I...I supramolecular interactions would come in play. On a quantitative level, experimental results indicate that conductivity tends to increase with increased iodine density.^{22,137,138} On a rough material level, one could think that the more conducting wires (*i.e.* trains of polyiodides) per volume unit there are, the better the conductor. Yet, chemically, higher iodine density generally implies not only shorter (on average) I...I distances, but also increased I...I connectivity. In the end, the nature of the I...I contacts and macroscopic parameters such as iodine density end up being intertwined and difficult to disentangle.

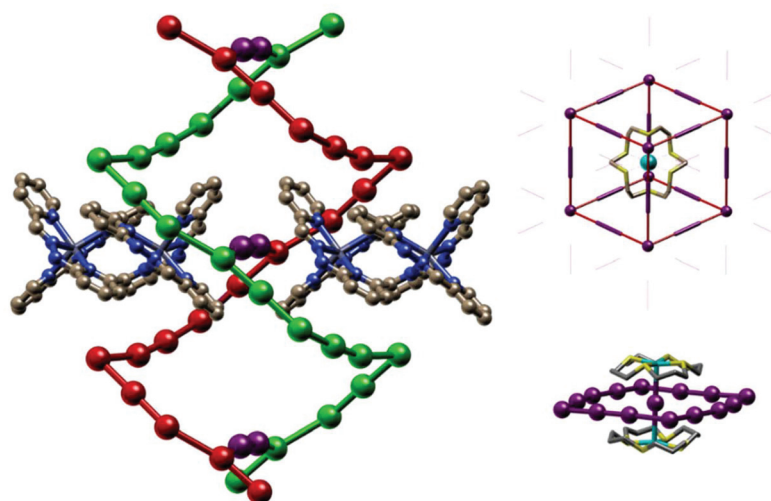


Fig. 23 Self-assembly examples, selected from ref. 133, directed towards polyiodide framework stabilization using *ad hoc* molecules and metal complexes. Left, polyiodide double helix (red/green) cross-linked by I_2 bridges (violet) templated by a Zn(II) helicate complex (CSD refcode: UJEGAR);¹³¹ top right, polyiodide $[I(I_2)_3]^-$ cubic lattice developed around a $[Ag([18]aneS_6)]^+$ metal complex (CSD refcodes: ZIFBIZ/ZIFBIZ01);^{128,136} bottom right: molecular belts around I^- bridged $[Pd([16]aneS_4)]^{2+}$ complexes (CSD refcode: TOHIG).¹²⁶

In 2017, Bianchi and Melguizo reported some peculiar polyiodide complexes organized in a lamellar fashion (Fig. 24)³⁷ (*cf.* Englert, Espinosa *et al.*¹³⁹ for a further report of layered cation–polyiodide assembly and I⋯I bond investigation). This peculiar organization was made possible by the s-tetrazine-based ligand L2, exploiting the strong anion– π interactions of this family of ligands^{35,81,82,140} to stabilize polyiodide sheets.

This invited reflection and comparison with structures such as TETTRI, which features separate “wires” of polyiodide and is, at first sight, much less iodine dense than the L2 layered complexes.

Yet there was no simple universal method to directly and quickly compare the iodine density of different polyiodide networks. Such a parameter might be of use in the arduous but coveted case where we manage not only to prepare ligands with systematic structural variations, crystallize their polyiodide complexes and determine their structures (already mentioned as a demanding task by Svensson and Kloo),²² but also obtain crystals of suitable size, quantity and quality to allow experimental access to their conduction properties (to this day a parameter that is seldom reported, but also one that tends to grant prestigious publication).⁷ In the long run, perhaps, this will give us the chance to unravel structure–property relationships and achieve tailoring of solid-state polyiodide conductors and semiconductors.

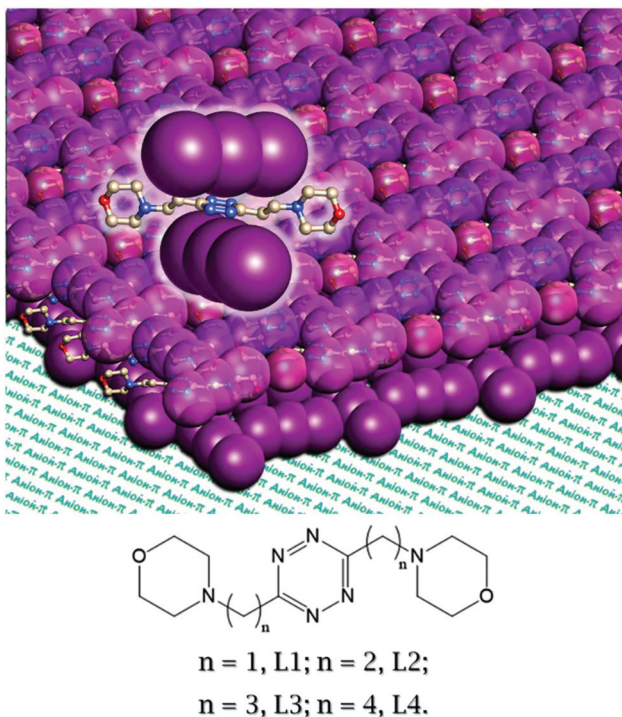


Fig. 24 Unused cover art suggestion for *Dalton Transactions*, showing polyiodide layers stabilized by the tetrazine based ligand L2. The $[H_2L_2(I_3)_2]$ anion– π complex is viewed from above the plane. The formula of L_n ($n = 1–4$) is given below the picture. Full information and the official artwork are found in ref. 37.

A parameter fit for the task was introduced in 2019: it is the iodine number (I_N).⁸ The iodine number is simply the ratio of the experimental iodine number density (number of I atoms per \AA^3) in the discussed crystal structure and the same parameter for crystalline (orthorhombic) I_2 (*i.e.* 0.02346 I atoms per \AA^3), where crystalline I_2 is assumed as a reference ($I_N(I_2) = 1$). At this point all possible polyiodide structures can be characterized and quickly compared in terms of iodine density by the convenient I_N parameter, ranging from 0 (no iodine atoms in the crystals) to 1 (same iodine density as crystalline I_2) (the scale can theoretically extend above 1, should such extreme densities be accessible, *e.g.* in high-pressure experiments).

The first application of the novel I_N descriptor was demonstrated for a class of azacyclophanes and their *N*-methylated derivatives, used in their protonated form as small counteranions for polyiodide growth.⁸ With a modular approach in mind we first assessed successive methylation of the ligand, diminishing the importance of $NH^+ \cdots I^-$ hydrogen bonds. Due to complementarity reasons, polyiodide-based clathrate-like structures were produced, *e.g.* resulting in cubic boxes (POJWET, Fig. 25) reminiscent of previous literature in the field (*cf.* ZIFBIZ01, Fig. 23, top right).¹²⁸ While the two structures feature a manifestly different iodine density (both are composed only of polyiodides and counteranions, with the monovalent cation $[Ag([18]aneS_6)]^+$ bigger than the divalent $H_2L_2-Me_3^{2+}$), I_N fulfils the purpose of allowing quick comparison of any crystal structures in terms of iodine density. It allows us to say that ZIFBIZ01¹²⁸ has an I_N of 0.393, while POJWET⁸ has an I_N of 0.589, *i.e.* POJWET is about 1.5 times more iodine dense than ZIFBIZ01. While to this day our ability to draw bonding information from iodine density is limited, we notice that in ZIFBIZ01 the original authors correctly formulated I_7^- as an $[I(I_2)_3]^-$ complex (formal $I^- \cdots I_2$ distance 3.356 \AA);¹²⁸ while in the case of POJWET molecular I_7^- with shorter bond distances (formal $I^- \cdots I_2$ distances in the 3.061–3.233 \AA range) are formed.⁸ In order to be able to extract precise information, rather than pointing out hints, better

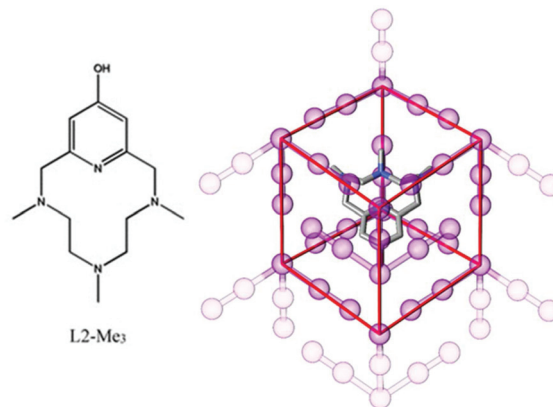


Fig. 25 Hepta-iodide cubic boxes in the POJWET crystal structure. Partially adapted from ref. 8.

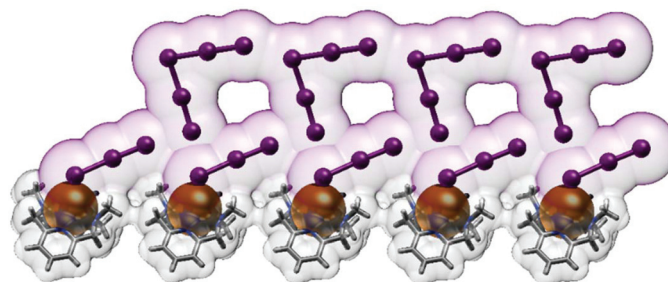


Fig. 26 Infinite chains of fused 11-membered I_5^-/I_3^- polyiodide rings decorated by $Cu(II)$ complexes *via* direct I_3^- coordination on the metal centres. Partially adapted from ref. 146 with permission from The Royal Society of Chemistry, copyright 2020.

understanding of the correlation between iodine density and the nature of the $I\cdots I$ bonding must be sought.

The availability of new tools (I_N ,⁸ but also Hirshfeld surface analysis^{141–143} must be mentioned here) is among the reasons we took an interest in BB and its transition from supramolecular cage to supramolecular mould depending on I_2 content (*vide supra*), despite the fact that the molecule itself, due to its synthesis/availability/market price, hardly allows us to envisage massive usage around the corner.

In the wake of this renewed interest in conduction properties, metals have been reconsidered on two different grounds.

The first viewpoint is tied to materials chemistry and is perfectly exemplified in a study by Zeng and co-workers.¹⁴⁴ As commented above, the possible templating role of discrete metal complexes had been explored and commented on. Yet, as the community gained expertise far more rapidly in MOFs (fastest growing metal–organic family of structures in the CSD)¹⁴⁵ than in supramolecular templates for polyiodide frameworks, it became possible to employ 3D preformed architectures to stabilize polyiodide networks. In this way, the self-assembly process concerns only the polyiodide portion of the framework, while the cations are pre-emptively organized in a 3-dimensional array. The abovementioned study demonstrated a MOF-based polyiodide 3D framework with superior thermal stability, iodine release and recovery as well as properties (conductivity, optical) dependent on iodine content. These promising results are likely to promote further exploration of this parallel access route to polyiodide networks.¹⁴⁴

The second approach is perhaps further away from such goals as it addresses direct metal–polyiodide interactions. Bianchi and García-España have just reported a series of coordinatively unsaturated $Cu(II)$ azacyclophane complexes, differing only by the degree of *N*-methylation, where the progressive removal of NH H-bond donor sites progressively shifts the packing control of the resulting phases from hydrogen bonding to $I\cdots I$ interactions, causing the $Cu(II)$ centres to take part in polyiodide chains (Fig. 26).¹⁴⁶ The working hypothesis, to be verified and developed, is that direct involvement of unsaturated metal centres *via* iodine–metal coordination bonds might result in superior mechanical properties and

potentially alter the conduction properties (*cf.* the interesting recent communication by Hu, Zhou and Cao¹⁴⁷ for further insights).

In closing our overview of current advances in polyiodide chemistry, we recall that the study of metal–polyiodide interactions in 3D frameworks is potentially of interest also for the hot topic of iodine-based perovskites. Several prestigious reports about iodine migration or the nature of defective sites addressed the properties of metal polyiodides:^{148,149} *cf.* the QEPPAE case (Fig. 6) which demonstrates the room for improvement in our understanding of such chemistry.

Conclusions

“When I use a word,” Humpty Dumpty said, in rather a scornful tone, “it means just what I choose it to mean—neither more nor less.”

“The question is,” said Alice, “whether you can make words mean so many different things.”

“The question is,” said Humpty Dumpty, “which is to be master—that’s all.”¹⁵⁰

The prime objective of this review was to present an updated record of the advances in polyiodide chemistry, mainly covering its long-term goals leading to the contemporary branches of supramolecular caging of polyiodides and iodine-dense polyiodide frameworks. Both topics are exquisitely supramolecular in nature. The former is mainly concerned with polyiodide–lattice interactions, while the latter focuses on $I\cdots I$ interactions, calling attention to the nature of such forces. Referencing well over 100 studies in the field, we hope to have provided a reasonably good service.

Yet, perhaps the higher purpose of this perspective was to invite reflection and promote discussion on the nature of polyiodides, on the language we employ to render in words the physical reality of their supramolecular complexes, and on the effectiveness of the terms we choose to employ in conveying such corporeality to others. Concepts like ontology, reification and rhetoric, provided we manage to address any of these, polarised natural philosophy debate for ages: possibly, their sporadic discussion in scientific journals can still be beneficial for the community.

Beyond their different views on supramolecular interactions (secondary/ σ -hole/halogen bonding), all schools of thought converge in recognising the pivotal role of iodine and polyiodides in the historical development of the state-of-the-art understanding of supramolecular forces. We can confidently predict here that the prominent role of iodides is not bygone yet, as further theoretical advances, together with many pragmatic applications, are to be expected for years to come.

Shaping the future rests with the scientific community as a whole. This does not prevent us from using these last lines to envisage, and share, what we believe to be the most desirable course of action.

As brilliantly discussed elsewhere,^{151,152} *lex parsimoniae*/Occam's razor has been oftentimes used in chemistry, yet evidence for the supposed simplicity of the world remains scant. The coming to light of different theories addressing the same phenomena is no novelty: here it is not a matter of cutting branches, it is all about realizing that they stem from the same trunk. Consolidation of the available material in one single, mature, and unifying view, including interactions that traditionally fall by the wayside and featuring a harmonization of both MO and VB perspectives, would be a major accomplishment and a strong legacy for the future. Group by group systematization would remain relevant and could easily find a home in a general theory, with the significant advantage of avoiding excessive fragmentation. Organizing knowledge is precisely what science (from *scientia*, literally knowledge) is all about. Serendipitous leaps aside, technology generally stems from scientific understanding. Once such conciliation is accomplished, it would tremendously help in focalizing those areas which elude its boundaries, like bonding in superior polyiodides and polyiodide networks, where satisfactory descriptions are still needed. This is what we deem required to break into the material properties of these systems and foster long-term development of the field.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Beyond the abovementioned Scifinder⁵¹ and CSD²³ databases, the author acknowledges the usage of the academic software CCDC Conquest¹⁵³ and Mercury,¹⁵⁴ as well as UCSF Chimera.¹⁵⁵ The world famous "The School of Athens" by Raffaello Sanzio, about 1510, Apostolic Palace, Vatican City and "The Tower of Babel" by Pieter Bruegel "the Elder", 1563, Kunsthistorisches Museum, Vienna (Austria) were adapted by the author for the graphical abstract image.

Notes and references

1 B. Watson, *The Complete Works of Zhuangzi*, Columbia University Press, 2013, ch. 26.

- A. Dronsfield, P. Ellis and P. S. June, 2011, Discovering iodine, <https://edu.rsc.org/feature/discovering-iodine/2020126.article> (accessed July 29, 2020).
- J. L. Gay-Lussac, *Mémoire sur l'iode*, 1815.
- H. Davy, *Philos. Trans. R. Soc. London*, 1814, **104**, 74–93.
- H. Landolt, *Ber. Dtsch. Chem. Ges.*, 1887, **20**, 745–760.
- H. Landolt, *Ber. Dtsch. Chem. Ges.*, 1886, **19**, 1317–1365.
- S. Madhu, H. A. Evans, V. V. T. Doan-Nguyen, J. G. Labram, G. Wu, M. L. Chabinyk, R. Seshadri and F. Wudl, *Angew. Chem., Int. Ed.*, 2016, **55**, 8135–8135.
- M. Savastano, Á. Martínez-Camarena, C. Bazzicalupi, E. Delgado-Pinar, J. M. Llinares, P. Mariani, B. Verdejo, E. García-España and A. Bianchi, *Inorganics*, 2019, **7**, 48.
- M. Savastano, C. Bazzicalupi, C. Gellini and A. Bianchi, *Chem. Commun.*, 2020, **56**, 551–554.
- M. Savastano, C. Bazzicalupi, C. Gellini and A. Bianchi, *Crystals*, 2020, **10**, 387.
- G. Jones, *J. Phys. Chem.*, 1930, **34**, 673–691.
- H. Wang, H. Li, B. Xue, Z. Wang, Q. Meng and L. Chen, *J. Am. Chem. Soc.*, 2005, **127**, 6394–6401.
- H. Wang, J. Li, F. Gong, G. Zhou and Z.-S. Wang, *J. Am. Chem. Soc.*, 2013, **135**, 12627–12633.
- J. Li and Z.-S. Wang, *RSC Adv.*, 2015, **5**, 56967–56973.
- J. Wu, Z. Lan, J. Lin, M. Huang, Y. Huang, L. Fan and G. Luo, *Chem. Rev.*, 2015, **115**, 2136–2173.
- F. Bella, S. Galliano, M. Falco, G. Viscardi, C. Barolo, M. Grätzel and C. Gerbaldi, *Chem. Sci.*, 2016, **7**, 4880–4890.
- E. Pulli, E. Rozzi and F. Bella, *Energy Convers. Manage.*, 2020, **219**, 112982.
- Q. Abbas, H. Fitzek, H. Schröttner, S. Dsoke and B. Gollas, *Nanomaterials*, 2019, **9**, 1413.
- Z. Meng, H. Tian, S. Zhang, X. Yan, H. Ying, W. He, C. Liang, W. Zhang, X. Hou and W.-Q. Han, *ACS Appl. Mater. Interfaces*, 2018, **10**, 17933–17941.
- T. von Grothhuss, *Mémoire sur la décomposition de l'eau et des corps qu'elle tient en dissolution à l'aide de l'électricité Galvanique par C.J.T. de Grothhuss*, 1805.
- V. K. Thorsmølle, J. C. Brauer, S. M. Zakeeruddin, M. Grätzel and J.-E. Moser, *J. Phys. Chem. C*, 2012, **116**, 7989–7992.
- P. H. Svensson and L. Kloo, *Chem. Rev.*, 2003, **103**, 1649–1684.
- C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.*, 2016, **72**, 171–179.
- The Nobel Prize in Chemistry 1987, <https://www.nobel-prize.org/prizes/chemistry/1987/summary/>, (accessed July 29, 2020).
- J.-M. Lehn, in *Supramolecular Chemistry*, John Wiley & Sons, Ltd, 2006, pp. 1–9.
- G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati and G. Terraneo, *Chem. Rev.*, 2016, **116**, 2478–2601.
- P. Politzer, J. S. Murray, T. Clark and G. Resnati, *Phys. Chem. Chem. Phys.*, 2017, **19**, 32166–32178.

- 28 N. W. Alcock, in *Advances in Inorganic Chemistry and Radiochemistry*, ed. H. J. Emeléus and A. G. Sharpe, Academic Press, 1972, vol. 15, pp. 1–58.
- 29 H. Schmidbaur and A. Schier, *Chem. Soc. Rev.*, 2012, **41**, 370–412.
- 30 A. Frontera and P. Ballester, in *Aromatic Interactions*, 2016, pp. 39–97.
- 31 X. Kan, H. Liu, Q. Pan, Z. Li and Y. Zhao, *Chin. Chem. Lett.*, 2018, **29**, 261–266.
- 32 Y. Zhao, Y. Cotellet, L. Liu, J. López-Andarias, A.-B. Bornhof, M. Akamatsu, N. Sakai and S. Matile, *Acc. Chem. Res.*, 2018, **51**, 2255–2263.
- 33 P. Arranz-Mascarós, C. Bazzicalupi, A. Bianchi, C. Giorgi, M.-L. Godino-Salido, M.-D. Gutiérrez-Valero, R. Lopez-Garzón and M. Savastano, *J. Am. Chem. Soc.*, 2013, **135**, 102–105.
- 34 M. Savastano, C. Bazzicalupi, C. García-Gallarín, M. D. L. de la Torre, A. Bianchi and M. Melguizo, *Org. Chem. Front.*, 2019, **6**, 75–86.
- 35 M. Savastano, C. García-Gallarín, M. D. López de la Torre, C. Bazzicalupi, A. Bianchi and M. Melguizo, *Coord. Chem. Rev.*, 2019, **397**, 112–137.
- 36 M. Müller, M. Albrecht, V. Gossen, T. Peters, A. Hoffmann, G. Raabe, A. Valkonen and K. Rissanen, *Chem. – Eur. J.*, 2010, **16**, 12446–12453.
- 37 M. Savastano, C. Bazzicalupi, C. García, C. Gellini, M. D. L. de la Torre, P. Mariani, F. Pichierri, A. Bianchi and M. Melguizo, *Dalton Trans.*, 2017, **46**, 4518–4529.
- 38 A. C. Legon and N. R. Walker, *Phys. Chem. Chem. Phys.*, 2018, **20**, 19332–19338.
- 39 A. J. Edwards, C. F. Mackenzie, P. R. Spackman, D. Jayatilaka and M. A. Spackman, *Faraday Discuss.*, 2017, **203**, 93–112.
- 40 S. Zahn, R. Frank, E. Hey-Hawkins and B. Kirchner, *Chem. – Eur. J.*, 2011, **17**, 6034–6038.
- 41 A. Bauzá, T. J. Mooibroek and A. Frontera, *Angew. Chem., Int. Ed.*, 2013, **52**, 12317–12321.
- 42 J. Echeverría, *Chem. Commun.*, 2018, **54**, 6312–6315.
- 43 A. Bauzá and A. Frontera, *Angew. Chem., Int. Ed.*, 2015, **54**, 7340–7343.
- 44 D. Quiñero, C. Garau, C. Rotger, A. Frontera, P. Ballester, A. Costa and P. M. Deyà, *Angew. Chem., Int. Ed.*, 2002, **41**, 3389–3392.
- 45 M. Yáñez, P. Sanz, O. Mó, I. Alkorta and J. Elguero, *J. Chem. Theory Comput.*, 2009, **5**, 2763–2771.
- 46 M. D. Esrafil, F. Mohammadian-Sabet and M. Solimannejad, *Chem. Phys. Lett.*, 2016, **659**, 196–202.
- 47 L. Kloo, J. Rosdahl and P. H. Svensson, *Eur. J. Inorg. Chem.*, 2002, **2002**, 1203–1209.
- 48 P. H. Svensson, M. Gorlov and L. Kloo, *Inorg. Chem.*, 2008, **47**, 11464–11466.
- 49 Project Details: categorizing halogen bonding and other noncovalent interactions involving halogen atoms, <https://iupac.org/projects/project-details/>, (accessed July 29, 2020).
- 50 IUPAC Project No.: 2009-032-1-100, P. Metrangolo and G. Resnati chairs, *Chem. Int.*, 2010, **32**, 20–21.
- 51 SciFinder, <https://www.cas.org/products/scifinder>, (accessed October 1, 2020).
- 52 H. A. Bent, *Chem. Rev.*, 1968, **68**, 587–648.
- 53 C. A. Coulson, *Rev. Mod. Phys.*, 1960, **32**, 170–177.
- 54 H. A. Bent, *Chem. Rev.*, 1961, **61**, 275–311.
- 55 B. Silvi, E. Alikhani and H. Ratajczak, *J. Mol. Model.*, 2020, **26**, 62.
- 56 E. H. Wiebenga, E. E. Havinga and K. H. Boswijk, in *Advances in Inorganic Chemistry and Radiochemistry*, ed. H. J. Emeléus and A. G. Sharpe, Academic Press, 1961, vol. 3, pp. 133–169.
- 57 E. H. Wiebenga and D. Kracht, *Inorg. Chem.*, 1969, **8**, 738–746.
- 58 G. R. Desiraju, P. S. Ho, L. Kloo, A. C. Legon, R. Marquardt, P. Metrangolo, P. Politzer, G. Resnati and K. Rissanen, *Pure Appl. Chem.*, 2013, **85**, 1711–1713.
- 59 P. Metrangolo and G. Resnati, *Cryst. Growth Des.*, 2012, **12**, 5835–5838.
- 60 N. Ramasubbu, R. Parthasarathy and P. Murray-Rust, *J. Am. Chem. Soc.*, 1986, **108**, 4308–4314.
- 61 G. R. Desiraju and R. Parthasarathy, *J. Am. Chem. Soc.*, 1989, **111**, 8725–8726.
- 62 A. C. Legon, *Chem. – Eur. J.*, 1998, **4**, 1890–1897.
- 63 T. Clark, M. Hennemann, J. S. Murray and P. Politzer, *J. Mol. Model.*, 2007, **13**, 291–296.
- 64 F. Guthrie, *J. Chem. Soc.*, 1863, **16**, 239–244.
- 65 H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 1948, **70**, 2832–2833.
- 66 H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703–2707.
- 67 R. S. Mulliken, *J. Phys. Chem.*, 1952, **56**, 801–822.
- 68 D. J. Pascoe, K. B. Ling and S. L. Cockcroft, *J. Am. Chem. Soc.*, 2017, **139**, 15160–15167.
- 69 J. H. Stenlid, A. J. Johansson and T. Brinck, *Phys. Chem. Chem. Phys.*, 2018, **20**, 2676–2692.
- 70 I. Alkorta, J. Elguero and A. Frontera, *Crystals*, 2020, **10**, 180.
- 71 P. Politzer, J. S. Murray and T. Clark, *Phys. Chem. Chem. Phys.*, 2010, **12**, 7748–7757.
- 72 P. Politzer, J. S. Murray and T. Clark, *Phys. Chem. Chem. Phys.*, 2013, **15**, 11178–11189.
- 73 G. N. Lewis, *Valence and the Structure of Atoms and Molecules*, Chemical Catalog Company, Incorporated, 1923.
- 74 D. Quiñero, C. Garau, A. Frontera, P. Ballester, A. Costa and P. M. Deyà, *Chem. Phys. Lett.*, 2002, **359**, 486–492.
- 75 C. Garau, A. Frontera, D. Quiñero, P. Ballester, A. Costa and P. M. Deyà, *ChemPhysChem*, 2003, **4**, 1344–1348.
- 76 A. Frontera, P. Gamez, M. Mascal, T. J. Mooibroek and J. Reedijk, *Angew. Chem., Int. Ed.*, 2011, **50**, 9564–9583.
- 77 M. Savastano, C. Bazzicalupi, C. García-Gallarín, C. Giorgi, M. D. L. de la Torre, F. Pichierri, A. Bianchi and M. Melguizo, *Dalton Trans.*, 2018, **47**, 3329–3338.
- 78 B. L. Schottel, H. T. Chifotides and K. R. Dunbar, *Chem. Soc. Rev.*, 2008, **37**, 68–83.

- 79 Á. Martínez-Camarena, M. Savastano, C. Bazzicalupi, A. Bianchi and E. García-España, *Molecules*, 2020, **25**, 3155.
- 80 M. Savastano, C. Bazzicalupi and A. Bianchi, *Chem. – Eur. J.*, 2020, **26**, 5994–6005.
- 81 M. Savastano, C. Bazzicalupi, C. Giorgi, C. García-Gallarín, M. D. López de la Torre, F. Pichierri, A. Bianchi and M. Melguizo, *Inorg. Chem.*, 2016, **55**, 8013–8024.
- 82 M. Savastano, C. García-Gallarín, C. Giorgi, P. Gratteri, M. D. López de la Torre, C. Bazzicalupi, A. Bianchi and M. Melguizo, *Molecules*, 2019, **24**, 2247.
- 83 J. S. Murray, P. Lane, T. Clark, K. E. Riley and P. Politzer, *J. Mol. Model.*, 2012, **18**, 541–548.
- 84 S. E. Wheeler and K. N. Houk, *J. Phys. Chem. A*, 2010, **114**, 8658–8664.
- 85 B. P. Hay and R. Custelcean, *Cryst. Growth Des.*, 2009, **9**, 2539–2545.
- 86 P. Jungwirth and P. S. Cremer, *Nat. Chem.*, 2014, **6**, 261–263.
- 87 H. I. Okur, J. Hladílková, K. B. Rembert, Y. Cho, J. Heyda, J. Dzubiella, P. S. Cremer and P. Jungwirth, *J. Phys. Chem. B*, 2017, **121**, 1997–2014.
- 88 J. W. Steed and J. L. Atwood, in *Supramolecular Chemistry*, John Wiley & Sons, Ltd, 2009, pp. 223–284.
- 89 *Anion Coordination Chemistry*, ed. K. Bowman-James, A. Bianchi and E. Garcia-España, Vch Verlagsgesellschaft Mbh, Weinheim, 2011.
- 90 T. T. Duignan, M. D. Baer and C. J. Mundy, *J. Chem. Phys.*, 2018, **148**, 222819.
- 91 T. P. Pollard and T. L. Beck, *J. Chem. Phys.*, 2018, **148**, 222830.
- 92 S. E. Wheeler and J. W. G. Bloom, *Chem. Commun.*, 2014, **50**, 11118–11121.
- 93 S. Shaik, A. Shurki, D. Danovich and P. C. Hiberty, *Chem. Rev.*, 2001, **101**, 1501–1540.
- 94 G. C. Pimentel, *J. Chem. Phys.*, 1951, **19**, 446–448.
- 95 R. J. Hach and R. E. Rundle, *J. Am. Chem. Soc.*, 1951, **73**, 4321–4324.
- 96 R. C. L. Mooney-Slater, *Acta Crystallogr.*, 1959, **12**, 187–196.
- 97 J. C. Slater, *Acta Crystallogr.*, 1959, **12**, 197–200.
- 98 S. N. Datta, C. S. Ewig and J. R. Van Wazer, *J. Mol. Struct.*, 1978, **48**, 407–416.
- 99 M. C. Aragoni, M. Arca, F. A. Devillanova, A. Garau, F. Isaia, V. Lippolis and A. Mancini, *Bioinorg. Chem. Appl.*, 2007, **2007**, 017416.
- 100 G. Manca, A. Ienco and C. Mealli, *Cryst. Growth Des.*, 2012, **12**, 1762–1771.
- 101 P. G. Jones and F. Ruthe, CCDC 926016: Experimental Crystal Structure Determination, 2013, DOI: 10.5517/cc102lh5.
- 102 F. Groenewald, C. Esterhuysen and J. Dillen, *Comput. Theor. Chem.*, 2016, **1090**, 225–233.
- 103 A. Yu. Rogachev and R. Hoffmann, *J. Am. Chem. Soc.*, 2013, **135**, 3262–3275.
- 104 A. C. Legon, *Angew. Chem., Int. Ed.*, 1999, **38**, 2686–2714.
- 105 R. Barthes, *Leçon : Leçon inaugurale de la chaire de sémiologie littéraire du Collège de France, prononcée le 7 janvier 1977*, Seuil, Paris, 1978.
- 106 A. J. Stone and S. L. Price, *J. Phys. Chem.*, 1988, **92**, 3325–3335.
- 107 A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899–926.
- 108 C. A. Ilioudis and J. W. Steed, *CrystEngComm*, 2004, **6**, 239–242.
- 109 A. Abate, M. Brischetto, G. Cavallo, M. Lahtinen, P. Metrangolo, T. Pilati, S. Radice, G. Resnati, K. Rissanen and G. Terraneo, *Chem. Commun.*, 2010, **46**, 2724–2726.
- 110 J. Lin, J. Martí-Rujas, P. Metrangolo, T. Pilati, S. Radice, G. Resnati and G. Terraneo, *Cryst. Growth Des.*, 2012, **12**, 5757–5762.
- 111 M. D. García, J. Martí-Rujas, P. Metrangolo, C. Peinador, T. Pilati, G. Resnati, G. Terraneo and M. Ursini, *CrystEngComm*, 2011, **13**, 4411–4416.
- 112 G. J. Reiss and M. van Megen, *Z. Naturforsch., B: J. Chem. Sci.*, 2012, **67**, 5–10.
- 113 M. Van Megen and G. J. Reiss, *Inorganics*, 2013, **1**, 3–13.
- 114 L. Garzón-Tovar, Á. Duarte-Ruiz and K. Wurst, *Inorg. Chem. Commun.*, 2013, **32**, 64–67.
- 115 B. Odell, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1547–1550.
- 116 Wiki Science Competition – The Wikipedia photo contest around science, <http://www.wikisciencecompetition.org/>, (accessed September 25, 2020).
- 117 M. Savastano, C. Bazzicalupi, C. Gellini and A. Bianchi, *Interlocked Polyiodides*, Wikimedia Commons, https://commons.wikimedia.org/wiki/File:Interlocked_Polyiodides.png, 2019.
- 118 D. L. Smith and H. R. Luss, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1977, **33**, 1744–1749.
- 119 L. I. Buravov, G. I. Zvereva, V. F. Kaminskii, L. P. Rosenberg, M. L. Khidekel, R. P. Shibaeva, I. F. Shchegolev and E. B. Yagubskii, *J. Chem. Soc., Chem. Commun.*, 1976, 720–721.
- 120 R. P. Shibaeva and V. F. Kaminskii, *Kristallografiya*, 1978, **23**, 5.
- 121 C. Lowe-Ma, R. Williams and S. Samson, *J. Chem. Phys.*, 1981, **74**, 1966–1979.
- 122 A. Filhol, J. Gaultier, C. Hauw, B. Hilti and C. W. Mayer, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1982, **38**, 2577–2589.
- 123 M. C. Aragoni, M. Arca, C. Caltagirone, C. Castellano, F. Demartin, A. Garau, F. Isaia, V. Lippolis, R. Montis and A. Pintus, *CrystEngComm*, 2012, **14**, 5809–5823.
- 124 M. C. Aragoni, M. Arca, F. Demartin, F. A. Devillanova, A. Garau, F. Isaia, V. Lippolis, S. Rizzato and G. Verani, *Inorg. Chim. Acta*, 2004, **357**, 3803–3809.
- 125 M. C. Aragoni, M. Arca, F. A. Devillanova, M. B. Hursthouse, S. L. Huth, F. Isaia, V. Lippolis and A. Mancini, *CrystEngComm*, 2004, **6**, 540–542.
- 126 A. J. Blake, V. Lippolis, S. Parsons and M. Schröder, *Chem. Commun.*, 1996, 2207–2208.

- 127 A. J. Blake, R. O. Gould, W.-S. Li, V. Lippolis, S. Parsons, C. Radek and M. Schröder, *Angew. Chem., Int. Ed.*, 1998, **37**, 293–296.
- 128 A. J. Blake, R. O. Gould, W.-S. Li, V. Lippolis, S. Parsons, C. Radek and M. Schröder, *Inorg. Chem.*, 1998, **37**, 5070–5077.
- 129 A. J. Blake, R. O. Gould, W.-S. Li, V. Lippolis, S. Parsons and M. Schröder, *Cryst. Eng.*, 1999, **2**, 153–170.
- 130 C. J. Horn, A. J. Blake, N. R. Champness, A. Garau, V. Lippolis, C. Wilson and M. Schröder, *Chem. Commun.*, 2003, 312–313.
- 131 C. J. Horn, A. J. Blake, N. R. Champness, V. Lippolis and M. Schröder, *Chem. Commun.*, 2003, 1488–1489.
- 132 A. J. Blake, W.-S. Li, V. Lippolis, S. Parsons and M. Schröder, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2007, **63**, 81–92.
- 133 A. J. Blake, W.-S. Li, V. Lippolis, M. Schröder, F. A. Devillanova, R. O. Gould, S. Parsons and C. Radek, *Chem. Soc. Rev.*, 1998, **27**, 195–206.
- 134 Z. Wang, Y. Cheng, C. Liao and C. Yan, *CrystEngComm*, 2001, **3**, 237–242.
- 135 J. Short, T. J. Blundell, S. Yang, O. Sahin, Y. Shakespeare, E. L. Smith, J. D. Wallis and L. Martin, *CrystEngComm*, 2020, **22**, 6632–6644.
- 136 A. J. Blake, R. O. Gould, S. Parsons, C. Radek and M. Schröder, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2374–2376.
- 137 H. Stegemann, A. Rohde, A. Reiche, A. Schnittke and H. Füllbier, *Electrochim. Acta*, 1992, **37**, 379–383.
- 138 S. Kusabayashi, H. Mikawa, S. Kawai, M. Uchida and R. Kiriya, *Bull. Chem. Soc. Jpn.*, 1964, **37**, 811–817.
- 139 K. Lamberts, P. Handels, U. Englert, E. Aubert and E. Espinosa, *CrystEngComm*, 2016, **18**, 3832–3841.
- 140 M. Savastano, C. García, M. D. López de la Torre, F. Pichierri, C. Bazzicalupi, A. Bianchi and M. Melguizo, *Inorg. Chim. Acta*, 2018, **470**, 133–138.
- 141 M. A. Spackman and P. G. Byrom, *Chem. Phys. Lett.*, 1997, **267**, 215–220.
- 142 M. A. Spackman and J. J. McKinnon, *CrystEngComm*, 2002, **4**, 378–392.
- 143 J. J. McKinnon, M. A. Spackman and A. S. Mitchell, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2004, **60**, 627–668.
- 144 Z. Yin, Q.-X. Wang and M.-H. Zeng, *J. Am. Chem. Soc.*, 2012, **134**, 4857–4863.
- 145 H. Furukawa, K. E. Cordova, M. O’Keeffe and O. M. Yaghi, *Science*, 2013, **341**, 974.
- 146 Á. Martínez-Camarena, M. Savastano, J. M. Llinares, B. Verdejo, A. Bianchi, E. García-España and C. Bazzicalupi, *Inorg. Chem. Front.*, 2020, **7**, 4239–4255.
- 147 J. Hu, J. Zhou and S. Cao, *Dalton Trans.*, 2018, **47**, 17216–17220.
- 148 C. Eames, J. M. Frost, P. R. F. Barnes, B. C. O’Regan, A. Walsh and M. S. Islam, *Nat. Commun.*, 2015, **6**, 7497.
- 149 J. L. Minns, P. Zajdel, D. Chernyshov, W. van Beek and M. A. Green, *Nat. Commun.*, 2017, **8**, 15152.
- 150 L. Carrol, *Through the looking-glass and what Alice found there*, Dodge publishing company, New York, 1909.
- 151 P. Politzer, K. E. Riley, F. A. Bulat and J. S. Murray, *Comput. Theor. Chem.*, 2012, **998**, 2–8.
- 152 R. Hoffmann, V. I. Minkin and B. K. Carpenter, *HYLE-Int. J. Philos. Chem.*, 1997, 3–28.
- 153 I. J. Bruno, J. C. Cole, P. R. Edgington, M. Kessler, C. F. Macrae, P. McCabe, J. Pearson and R. Taylor, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, **58**, 389–397.
- 154 C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. Platings, G. P. Shields, J. S. Stevens, M. Towler and P. A. Wood, *J. Appl. Crystallogr.*, 2020, **53**, 226–235.
- 155 E. F. Pettersen, T. D. Goddard, C. C. Huang, G. S. Couch, D. M. Greenblatt, E. C. Meng and T. E. Ferrin, *J. Comput. Chem.*, 2004, **25**, 1605–1612.