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N···I halogen bonding supported stabilization of a discrete pseudo-linear polyiodide [I₁₂]²⁻ †

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Two different dicationic N-donors, based on the DABCO diamine, have been studied as templates for polyiodides. The results present a new strategy for polyiodide stabilization, which involves both N···I halogen bonding and cation-anion
10 **interactions. This is highlighted by the self-assembly of an unprecedented discrete pseudo-linear dodecaiodide species.**

Polyiodides present a fascinating group of compounds with rich structural chemistry and many useful physical properties such as high conductivity and redox behaviour suitable for
15 electrochemical applications.[1] The structural diversity of polyiodides can be accounted for the ability of iodine to concatenate through I··· I halogen bonding (XB) interactions using I^-, I_2 and I_3^- subunits of which I^- and I_3^- are generally considered as nucleophilic (Lewis base, XB acceptor) and I_2
20 electrophilic (Lewis acid, XB donor) species. These subunits are able to organize in several different ways, often in unpredictable manner, and thus generate structures that span from discrete polyiodide units to extended three-dimensional networks.[2] Especially, controlled synthesis of discrete polyiodide motifs
25 presents a significant challenge as it requires the termination of the polyiodide species thus inhibiting its propagation throughout the crystal lattice.

One formidable strategy of polyiodide design involves regulating the composition and geometrical features of the
30 polyiodide chain by I^- templating. In this scheme, the I^- anions are spaced out in a suitable manner to obtain a polyiodide species of specific composition. The most important part of this approach is to work out a way to dictate the spatial arrangement of the I^- anions accurately. Supramolecular and crystal engineering tools,
35 including ionic (cation···I^-) interaction,[3] hydrogen bonding (HB)[4] and halogen bonding via iodoorganic[5] or metal iodide species,[6] have been successful in this regard resulting in characterization of various discrete polyiodide species, such as I_5^-, I_4^{2-}, I_6^{2-}, I_7^{3-} and I_8^{2-} in addition to I_3^-. Ammonium cations, separated by alkyl
40 spacers, in particular, have been shown to serve as effective templates for "dimensional caging"[7] of polyiodides as their length, and thus the positions of the cationic centres, can be easily modulated.[3a,3c,4]

Recently, we have demonstrated that monocationic N-donors
45 based on monoalkylated DABCO (DABCO = 1,4-diazabicyclo[2.2.2]octane) are efficient halogen bond acceptors toward I_2.[8] We reckoned that N···I_2 halogen bonding interactions, used together with the concept of stabilizing polyiodides via
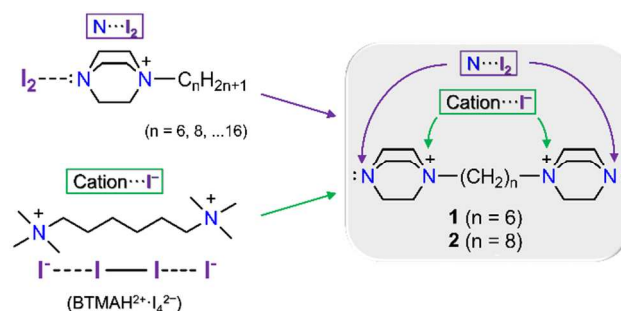
50 **Scheme 1** Left: previous investigations on N···I_2 and I^-···I_2··· I^- systems employing cationic N-donors and bis(trimethylammonium)hexane (BTMAH²⁺),[3a] respectively. Right: dicationic N-donors, reported in the present investigation, which incorporate the crystal engineering principles of both N···I_2 halogen bonding and cation···I^- interactions for
55 stabilization of polyiodides.
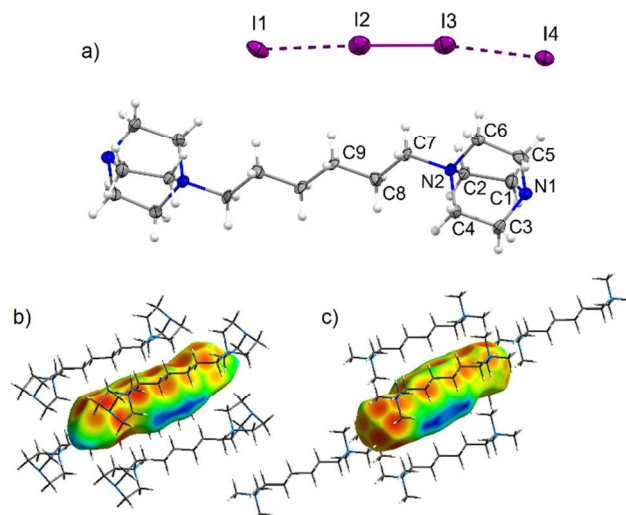
Fig. 1 a) The asymmetric unit of $\mathbf{1}\cdot I_4^{2-}$ with labels of the crystallographically unique atoms shown. The displacement ellipsoids are shown at the 50% probability level. Visualization of the d_e-mapped
60 Hirshfeld surfaces of I_4^{2-} anions in the crystal structures of b) $\mathbf{1}\cdot I_4^{2-}$ and c) BTMAH²⁺·I_4^{2-} (CSD ref.code: NUTSOL).[3a] List of interatomic distances (Å): (I1–I2) = 3.3786(16), (I2–I3) = 2.8180(15), (I3–I4) = 3.2920(13). List of interatomic angles (°): (I1–I2–I3) = 177.46(5) and (I2–I3–I4) = 170.95(5).

65 cation···I^- interactions, could be a route to a new interesting polyiodide species. Therefore, we have extended the structural features of our prior cationic N-donors to resemble diammonium alkyl dications, which have been effective in stabilizing

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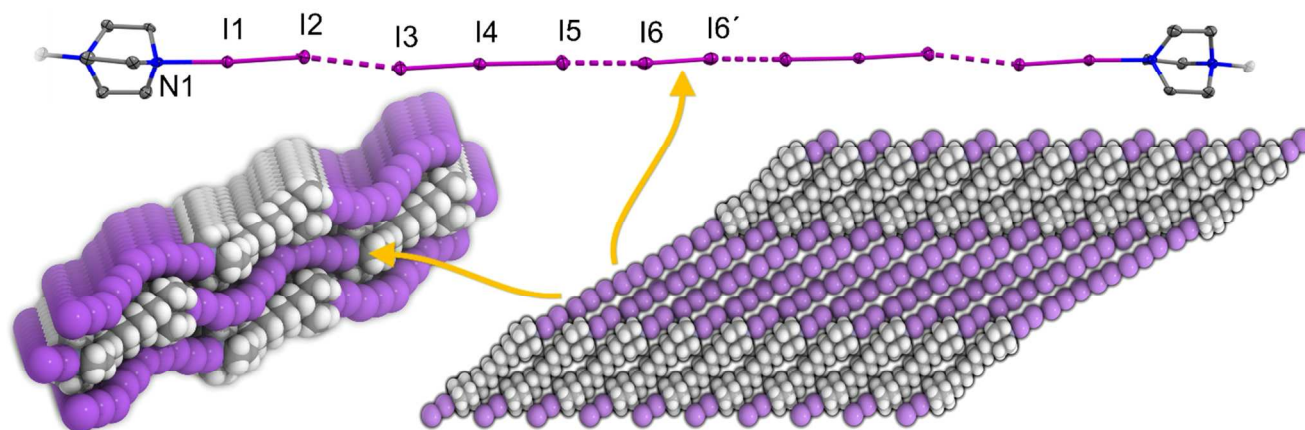
Fig. 2 Illustration of the structural ordering of the anions and cations in the structure of $2 \cdot I_{12}^{2-}$ showing sheet-like packing of the neighbouring infinite chains (bottom right) which are stacked on top of each other (left). A numbering scheme for a part of the asymmetric unit is presented at the top (H atoms are omitted from the picture). List of interatomic distances (Å): (N1–I1) = 2.528(7), (I1–I2) = 2.7869(8), (I2–I3) = 3.5711(8), (I3–I4) = 2.8577(8), (I4–I5) = 3.0074(8), (I5–I6) = 3.4421(8) and (I6–I6′) = 2.7444(8). List of interatomic angles (°): (N1–I1–I2) = 175.9(2), (I1–I2–I3) = 168.10(3), (I2–I3–I4) = 164.81(3), (I3–I4–I5) = 177.24(3), (I4–I5–I6) = 160.03(3) and (I5–I6–I6′) = 173.25(3). The displacement ellipsoids are drawn at the 50% probability level. Symmetry code (′) = –x, –y, –z.

polyiodides such as I_5^-, I_4^{2-} and I_6^{2-}.[3a,4b-c,9] More specifically, these dicationic N-donors, derived from DABCO, incorporate two ammonium and tertiary amine centres, separated with an alkyl spacer (Scheme 1). Dication **1** was designed to possess the same separation of the ammonium centres as bis(trimethylammonium)hexane ($BTMAH^{2+}$), which has been previously used by Metrangolo et al. for stabilization of I_4^{2-} species,[3a] whereas **2** offers 2.6 Å of an additional space between the DABCO groups, thus being a theoretical size match for I_6^{2-} (i.e. $2I_3^-$).[4c]

Due to the size equivalence of the alkyl spacers between **1** and $BTMAH^{2+}$, it was not entirely unexpected that an addition of one equivalent of I_2 (in acetonitrile) into a methanol solution of iodide salt of **1** affords a polyiodide with I_4^{2-} composition (compound $1 \cdot I_4^{2-}$). Single crystal X-ray analysis shows that the anion in $1 \cdot I_4^{2-}$ adopts an asymmetric and non-linear conformation whereas in $BTMAH^{2+} \cdot I_4^{2-}$ the anion lies at a two-fold rotation axis and is symmetric and approximately linear (Fig. 1). Such differences in geometrical features of the I_4^{2-} anion can be attributed to differences in cationic surroundings.[10] A closer analysis of the crystal structure of $1 \cdot I_4^{2-}$ shows the I_4^{2-} anion surrounded by four adjacent cations "side-on" in respect of the $I^- \cdots I_2 \cdots I^-$ axis. On the contrary, in $BTMAH^{2+} \cdot I_4^{2-}$, the anion is enclosed by six cations which interact with the anion both "side-on" and "head-on". These differences are evident in the Hirshfeld surfaces of the two distinct I_4^{2-} anions mapped with the property d_e which describes the distance of external nuclei to the surface (Fig. 1).[11] Both d_e-decorated surfaces appear similar at the I_2 regions showing a number of "side-on" contacts from the external nuclei (C-H$\cdots$I). However, only the surface corresponding to the I_4^{2-} anion in $BTMAH^{2+} \cdot I_4^{2-}$ exhibits significant "head-on" C–H$\cdots$I$^-$ contacts. Also, the shapes of the two surfaces at the terminal I^-

are very distinct and correspond to the space taken by the anions in the crystal lattice, again, underlining the different cationic environments in these two structures. The observed differences in packing can be explained by the reluctance of cation **1** to face the negatively charged terminal iodide of the I_4^{2-} anion due to the presence of lone pairs of electrons on the DABCO moiety.

The importance of size matching in the stabilization of I_4^{2-} anion via diammonium alkanes becomes evident when the reaction described above is repeated with cation **2**. Both 1:1 and 1:2 reactions between iodide salt of **2** and I_2 resulted in formation of triiodide salt, $2 \cdot 2I_3^-$, while no I_4^{2-} species was observed. This is in sharp contrast to the behaviour of cation **1** which can stabilize either I_4^{2-} species, as discussed earlier, or two I_3^- anions depending on the reaction stoichiometry (see ESI for details). However, **1** shows clear preference towards the I_4^{2-} species as was demonstrated by diffusing I_2 vapours into a solution containing iodide salt of **1**. This reaction selectively yields crystals of $1 \cdot I_4^{2-}$, without any indication of $1 \cdot 2I_3^-$ forming, whereas in the case of **2**, the sole product was found to be $2 \cdot 2I_3^-$. Structure and bonding of triiodide species is widely studied and discussed in earlier literature and since $1 \cdot 2I_3^-$ and $2 \cdot 2I_3^-$ do not offer any new insights to this discussion their detailed characterization is not presented here (see ESI). However, it is noteworthy that the composition of the anionic species in $2 \cdot 2I_3^-$ can be formally described as I_6^{2-}, since the two encapsulated triiodide units exhibit a relatively short $I_3^- \cdots I_3^-$ distance $[d(I_3^- \cdots I_3^-) = 3.5904(13)$ Å].[12]

As our aim in the present investigation is to explore the effects of tertiary amine functionality (incorporated into the cationic species) on polyiodide formation it is worth noting that none of the reactions presented above yield structures that exhibit $N \cdots I_2$ halogen bonding interactions. The reason lies in the competition

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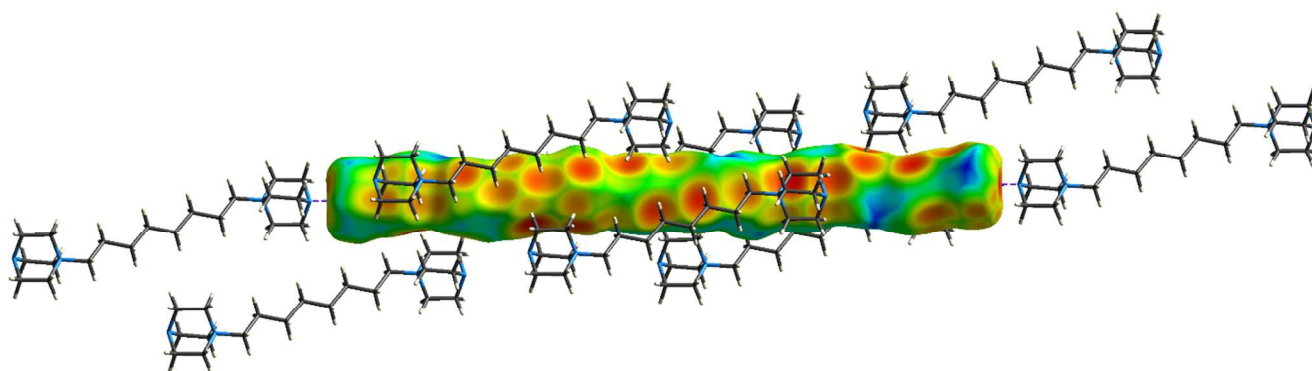
Fig. 3 Hirshfeld surface of the I_{12}^{2-} anion, mapped with the property d_e, which demonstrates the high number of cation-anion ($C-H\cdots I_{12}^{2-}$) contacts. Iodine atoms external to the surface are omitted for clarity.

between two halogen bond acceptors, monoalkylated DABCO and I^-, from which the I^- possesses a higher affinity toward I_2 and
5 can thus suppress the formation of $N\cdots I_2$ halogen bonds (although N-donors are prominent XB acceptors, in general[13]). In fact, systems, where I_2 is bonded to an N-donor via XB interactions in the presence of "free" iodide species (I^- or I_3^-), are
10 unknown according to CSD which merely shows the tendency of I^- and I_2 to concatenate and form polyiodides. Alternatively, the $N\cdots I_2$ complex could be generated prior to the addition of the polyiodide subunits. Fortunately, a review of earlier literature revealed alternative pathways to obtain polyiodides without the
15 use of an iodide starting material.[14] One of such strategies involves reacting molecular I_2 with a BF_4^- or PF_6^- salt of the desired cationic template in acetonitrile (MeCN),[14a] which can promote the heterolytic dissociation of I_2 by stabilizing the I^+ cation.[15] Hence, instead of using the iodide salts of **1** and **2**
20 directly as above, we exchanged the I^- anion to a weakly coordinating PF_6^- and reacted the respective PF_6^- salts with I_2.

The addition of two equivalents of I_2 to the PF_6^- salts of either **1** or **2** in MeCN afforded, in both cases, light orange crystals which could be isolated and structurally characterized. Single
25 crystal X-ray analysis of the crystals revealed analogous complexes of $[I_2\cdots\mathbf{1}\cdots I_2][PF_6]_2$ and $[I_2\cdots\mathbf{2}\cdots I_2][PF_6]_2$, in which the iodine molecules are bonded to the terminal DABCO groups in similar fashion to what was observed earlier for complexes of I_2 and monocationic DABCOs (Figures S1 and S2 ESI).[8]
30 However, in the reaction between **2**[PF_6]_2 and an excess (10 equivalents) of I_2, dark brownish red (black to the naked eye) crystals with a metallic lustre were obtained. Structural analysis of these crystals confirmed the formation of a polyiodide salt consisting of two asymmetric I_3^- anions and three I_2 molecules:
35 one and a half I_2 and one I_3^- along with half of the cation **2** in the asymmetric unit (Fig. 2). These subunits concatenate by "head-on" $I_2\cdots I_3^-$ contacts to form a pseudo-linear $[\angle(I-I-I) \geq 160°]$ polyiodide species, with a formal composition of I_{12}^{2-}, which is capped by $N\cdots I_2$ halogen bonding interactions at both ends
40 (compound **2**·I_{12}^{2-}).[16] Together, these form infinite one-

dimensional chains of alternating I_{12}^{2-} and **2**, via $N\cdots I_2$ and $I_2\cdots I_3^-$ interactions, which pack into sheets along the crystallographic *b*-axis (Fig. 2). These sheets are stacked in a way that the cations and anions are on top of each other.

45 A deeper analysis of the structural characteristics of **2**·I_{12}^{2-} shows a remarkable interplay of $N\cdots I_2$ and cation-anion interactions which work in cooperation to stabilize the unusual I_{12}^{2-} species. From these two types of interactions, the relatively short $N\cdots I_2$ halogen bonds are fairly obvious to the keen eye,
50 whereas the stabilizing effects of the cation-anion interactions are more visually accessible by observing the d_e-mapped Hirshfeld surface of the anion, as above (Fig. 3). Visual inspection of the surface shows multiple $C-H\cdots I$ contacts throughout the anion, especially at the I_3^- subunit regions. Also, an interesting detail is
55 the spatial ordering of the cations which exhibit a helical arrangement parallel to the I_{12}^{2-} anion. Altogether, the number of cations encapsulating the whole of the I_{12}^{2-} anion is eight, including the two $N\cdots I_2$ bonded cations.

The probable mechanism for the formation of the **2**·I_{12}^{2-}
60 structure is by a template effect of the cationic species preceded by the formation of the $[I_2\cdots\mathbf{2}\cdots I_2]$ complex and the heterolytic dissociation of I_2. The importance of using this route for the synthesis of **2**·I_{12}^{2-} became evident when our efforts to crystallize the corresponding dodecaiodide salt, starting from the iodide salt
65 of **2**, proved to be unsuccessful. Instead of single crystals, the reaction between **2**·2I^- and I_2 afforded a poorly soluble dark brown precipitate, which elemental analysis was consistent with the **2**·I_{12}^{2-} species. However, this poorly crystalline product (denoted as **2**(5I_2)·2I^-) is not crystallographically identical to
70 **2**·I_{12}^{2-}, as shown by a powder X-ray diffraction analysis (Fig. S8 in ESI). Hence, the mixing of **2**·2I^- with an excess of I_2 results in a chemical composition equivalent to **2**·I_{12}^{2-}, but a different solid state structure and, most likely, a different polyiodide unit.

Similar synthesis of polyiodides using **1**[PF_6]_2 proved more
75 challenging as attempts frequently resulted in the formation of the $[I_2\cdots\mathbf{1}\cdots I_2][PF_6]_2$ complex, which seems to be the favoured product. Eventually, a small batch of crystals were obtained that

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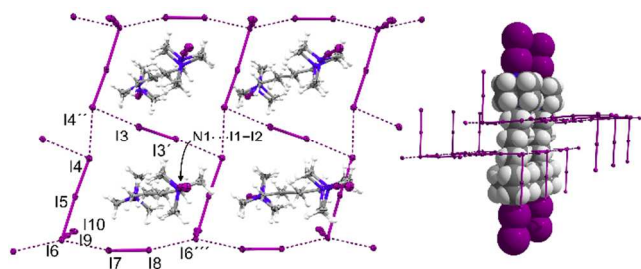
Fig. 4 Left: illustration of one of the 1D polyiodide networks observed in crystal structure of $[I_2\cdots\mathbf{1}\cdots I_2]\cdot I_{16}{}^{2-}$ viewed perpendicular to the network plane. Right: Another view along the network plane which shows the
[5] $[I_2\cdots\mathbf{1}\cdots I_2]$ complexes shared between two stacked polyiodide networks. Naming scheme of the I-atoms on the left correspond to the crystallographically unique atoms of the polyiodide. The displacement ellipsoids are shown at the 50% probability level. List of interatomic distances (Å): (N1–I1) = 2.528(6), (I1–I2) = 2.7680(7), (I3–I3′) =
[10] 2.7242(9), (I3–I4′) =3.5107(7), (I4′′–I4) = 3.6648(9), (I4–I5) = 2.8100(6), (I5–I6) = 3.0974(6), (I6–I7) = 3.3054(7), (I6–I9) = 3.1700(7), (I7–I8) = 2.7555(7), (I8–I6′′′) = 3.3418(7) and (I9–I10) = 2.7681(8). Symmetry codes: (′) = –x, y–2, –z; (′′) = 1–x, 2–y, –z; (′′′) = x–1, y, z.

exhibited dark brown colour with a metallic lustre similar to the
[15] crystals of $\mathbf{2}\cdot I_{12}{}^{2-}$. Instead of a discrete polyiodide unit, these crystals consist of a one-dimensional (1D) planar polyiodide networks composed of I_5^- ($I_2\cdots I^-\cdots I_2$) and I_2 subunits (Fig. 4). The polyiodide is templated by $[I_2\cdots\mathbf{1}\cdots I_2]$ cationic complexes, each of which occupy two trapezoidal meshes of two parallel
[20] polyiodide networks, thus, stacking two distinct 1D nets on top of each other (Fig. 4). As each polyiodide network consists of two rows of cations, the cation templated stacking extends throughout the crystal lattice. In contrary to the $[I_2\cdots\mathbf{2}\cdots I_2]$ units in $\mathbf{2}\cdot I_{12}{}^{2-}$, the $[I_2\cdots\mathbf{1}\cdots I_2]$ XB complexes do not exhibit significant I$\cdots$I
[25] contacts (<4.0 Å) to the polyiodide network. Thus, a suitable formulation for this polyiodide species would be $[I_2\cdots\mathbf{1}\cdots I_2]\cdot I_{16}{}^{2-}$.

In summary, we have demonstrated the use of dicationic N-donors, based on DABCO, as host for various polyiodides. These
[30] cationic hosts can stabilize polyiodides either solely by cation-anion interactions or additionally by N$\cdots I_2$ XB interactions. The structure of the resulting polyiodide species is reflected by the synthesis method and the length of the alkyl spacer. Controlled synthesis of I_4^{2-} and I_6^{2-} polyiodides was possible using a method
[35] reported earlier for dications of similar size. More complex iodide species could be obtained by disproportionation of I_2 in MeCN and in the presence of PF_6^- salts of $\mathbf{1}$ and $\mathbf{2}$. Especially, the stabilization of a linearly arranged $I_{12}{}^{2-}$ anion is a remarkable example of dimensional caging of an unprecedented polyiodide
[40] species via cooperation between both N$\cdots I_2$ halogen bonding and cation-anion interactions. It is expected that the presented strategy allows the design of even more intricate polyiodide species by further modification of the cationic backbone.

Acknowledgements

Notes and references

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1 F. C. Küpper, M. C. Feiters, B. Olofsson, T. Kaiho, S. Yanagida, M. B. Zimmermann, L. J. Carpenter, G. W. Luther III, Z. Lu, M. Jonsson and L. Kloo, *Angew. Chem. Int. Ed.*, 2011, **50**, 11598.

2 a) 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; b) P. H. Svensson and L. Kloo, *Chem. Rev.*, 2003, **103**, 1649.

3 a) 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; b) M. Müller, M. Albrecht, V. Gossen, T. Peters, A. Hoffmann, G. Raabe, A. Valkonen and K. Rissanen, *Chem. Eur. J.* 2010, **16**, 12446; c) J. Lin, J. Martí-Rujas, P. Metrangolo, T. Pilati, S. Radice, G. Resnati and G. Terraneo, *Cryst. Growth Des.*, 2012, **12**, 5757; d) J. Martí-Rujas, L. Meazza, G. Keat Lim, G. Terraneo, T. Pilati, K. D. M. Harris, P. Metrangolo and G. Resnati, *Angew. Chem. Int. Ed.*, 2013, **52**, 13444.

4 a) G. J. Reiss and M. van Megen, *Z. Naturforsch., B: Chem. Sci.*, 2012, **67**, 5; b) G. J. Reiss and M. van Megen, *Z. Naturforsch., B: Chem.Sci.*, 2012, **67**, 447; c) M. van Megen, and G. J. Reiss, *Inorganics*, 2013, **1**, 3; d) M. van Megen, A. Jablonka and G. J. Reiss, Z. Naturforsch. **2014**, *69b*, 753.

5 Y. Kuwatani, E. Ogura, H. Nishikawa, I. Ikemoto and M. Iyoda, *Chem. Lett.*, 1997, **26**, 817.

6 a) X. Bu. and P. Coppens, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1992, **C48**, 1565; b) R. Hernández-Molina, I. V. Kalinina, P. A. Abramov, M. N. Sokolov, A. V. Virovets, J. G. Platas, R. Llusar, V. Polo, C. Vicent and V. P. Fedin, *Inorg. Chem.*, 2008, **47**, 306.

7 P. H. Svensson, M. Gorlov and L. Kloo, *Inorg. Chem.*, 2008, **47**, 11464.

8 A. Peuronen, A. Valkonen, M. Kortelainen, K. Rissanen and M. Lahtinen, *Cryst. Growth Des.*, 2012, **12**, 4157.

9 a) G. J. Reiss, Private Communication, 2010 (CSD ref.code: UJOMAI); b) G. J. Reiss and S. Konieczka, Private Communication, 2010 (CSD ref.code: UJOMEM).

10 For an extensive investigation of the effects of charge distribution along the I_4^{2-} anion, see a recent paper by Mealli et al.; G. Manca, A. Ienco, and C. Mealli, *Cryst. Growth Des.*, 2012, **12**, 1762.

11 J. J. McKinnon, M. A. Spackman and A. S. Mitchell, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2004, **B60**, 627.

12 M. K. Meyer, J. Graf and G. J. Reiss, *Z. Naturforsch.*, 2010, **65b**, 1462.

13 See, for example: a) R. D. Bailey, G. W. Drake, M. Grabarczyk, T. W. Hanks, L. L. Hook and W. T. Pennington, *J. Chem. Soc., Perkin Trans. 2*, 1997, 2773; b) R. D. Bailey, M. Grabarczyk, T. W. Hanks and W. T. Pennington, *J. Chem. Soc., Perkin Trans. 2*, 1997, 2781; c) R. B. Walsh, C. W. Padgett, P. Metrangolo, G. Resnati, T. W. Hanks and W. T. Pennington, *Cryst. Growth Des.*, 2001, **1**, 165; d) W. T. Pennington, T. W. Hanks and H. D. Arman, in *Halogen bonding – Fundamentals and Applications*, ed. P. Metrangolo and G. Resnati, Springer-Verlag, Berlin, 2008, pp. 65–104 and references therein.

14 a) A. J. Blake, R. O. Gould, W.-S. Li, V. Lippolis, S. Parsons and M. Schröder, *Cryst. Eng.* 1999, **2**, 153; b) M. García-Castro, A. Martín, M. Mena, J.-M. Poblet and C. Yélamos, *Eur. J. Inorg. Chem.* 2006, 1155.

15 In addition to other Lewis bases, the disproportionation of I_2 is known to occur also in acetonitrile where the I^+ cation can be stabilized as a $[MeCN-I-NCMe]^+$ or $[MeCN-I\ ]^+$ species. See, for example: a) W. S. Hua, S. I. Ajiboye, G. Haining, L. McGhee, R. D. Peacock, G. Peattie, R. M. Siddique and J. M. Winfield, *J. Chem. Soc., Dalton Trans.*, 1995, 3837; b) M.-J. Crawford, M. Göbel, K. Karaghiosoff, T. M. Klapötke and J. M. Welch, *Inorg. Chem.* 2009, **48**, 9983.

16 Alternatively, by emphasizing the relatively short N$\cdots I_2$ bonds (2.53 Å), this unusual structure can also be described as an $[I_3^-\cdots I_2\cdots I_3^-]$ octaiodide capped by two $I_2\cdots\mathbf{2}\cdots I_2$ complexes.