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### PAPER

## Dimensional caging of polyiodides: cation-templated synthesis using bipyridinium salts<sup>†</sup>

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The potential of bipyridinium derivatives in the cation templated synthesis of polyiodides has been explored by applying the strategy of size-matching between cations and anions. Bipyridinium cations **1–4**, bearing benzyl and functionalized benzyl pendants at nitrogen atoms, are able to template the selective formation of  $I_4^{2-}$  and  $I_3^{-}$  species. Thanks to the supramolecular space compartmentation induced by the benzyl pendants, the formation of  $I_4^{2-}$  and  $I_3^{-}$  is independent of the stoichiometry adopted in the crystallization procedure. Bipyridinium cation **5**, bearing methyl pendants, is unable to induce space compartmentation and different polyiodides are obtained depending on the stoichiometry used in the crystallization process as the cation–anion size-matching alone does not control the polyiodide formation.

#### Introduction

Polyiodides are extended structures with the general formula  $I_{2m+n}^{n-}$  (*m* and *n* integers > 0, n = 1-4).<sup>1</sup> They form from the building blocks  $I^{-}/I_{3}^{-}$  and  $I_{2}$ , which self-assemble as a consequence of the well-known tendency of the heavier halogen atoms (especially iodine) to catenate. The exact nature of the connections between these building blocks in polyiodide species has long been debated. In a large number of cases, the connection in polyiodides can be rationalized in terms of halogen bonding,<sup>2</sup> with  $I^{-}/I_{3}^{-}$  subunits functioning as halogen bonding-acceptors (Lewis bases, electron-donors) and molecular  $I_{2}$  functioning as halogen bonding-donor (Lewis acid, electron-acceptor).<sup>3</sup>

The availability of general, selective, and robust synthetic protocols for solid polyiodides is of great importance as the study of their properties impacts in many applicative fields due to their peculiar electric properties spanning from conduction values typical of insulators to those of metals.<sup>14,4</sup> Moreover, the

unstable species  $I_4^{2-}$  has been postulated to be the charge-transfer intermediate responsible for the charge-transport mechanism in  $I^-/I_3^-$ -based electrolytes of dye sensitized solar cells (DSSCs),<sup>5</sup> following a Grotthuss-like process.<sup>6</sup>

The most common approach for the systematic study of polyiodide species is the preparation and characterization of simple model systems: *i.e.* stable polyiodide salts with known crystal structures. One of the major drawbacks of this approach is the lack of synthetic control over the system as a subtle and unpredictable balance of a large number of parameters frequently influences the composition and structure of solid polyiodides formed in a given synthesis (e.g. stoichiometry of the reagents, nature of the cation, crystallization solvent(s), etc.).<sup>1</sup> To circumvent this problem, metal complexes containing  $I^-$  and  $I_3^$ ions have been extensively used in cation-templated synthesis of higher polyiodides.<sup>1</sup> However, the design of metal ion complex is rather difficult and metal coordination may strongly modify the nature of the interactions involving  $I^-/I_3^-$  and  $I_2$  building blocks in the polyiodide chain.<sup>7</sup> For all of these reasons, the general and selective preparation of organic polyiodide salts by using the reliable principles of supramolecular chemistry and crystal engineering is a unique and fascinating goal.

Long-chain alkyl ammonium cations have been successfully used for the dimensional caging of polyiodides. In fact, the known tendency of these cations to organize into lamellar structures, forces the polyiodide anions to be confined in the vicinity of the positive charges.<sup>8</sup> Consistent with this approach, some of the present authors have shown that 1,6-bis(trimethylammonium)hexane diiodide (BTMAH·2I<sup>-</sup>) selectively encapsulates iodine and yields the rare polyiodide species  $I_4^{2-}$  thanks to the size-matching between the N<sup>+</sup>–N<sup>+</sup> separation in the dication unit (~8.9 Å) and the separation between the terminal iodine

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<sup>&</sup>lt;sup>*d*</sup>*ISTM-CNR*, Università di Milano, Via Venezian 21, 20133 Milan, Italy † Electronic supplementary information (ESI) available: Synthetic and crystallization protocols, spectroscopic characterization of compounds **1–3**·2I<sup>-</sup>, **1**·I<sub>4</sub><sup>2-</sup>, **2–4**·2I<sub>3</sub><sup>-</sup>; synthesis and X-ray crystallographic data for structures **5**·2I<sub>3</sub><sup>-</sup>, **5**·I<sup>-</sup>·I<sub>3</sub><sup>-</sup>, **5**·I<sub>3</sub><sup>-</sup>·J<sub>2</sub>I<sub>8</sub><sup>2-</sup>, **5**·I<sub>5</sub><sup>-</sup>·J<sub>2</sub>I<sub>8</sub><sup>2-</sup> relevant geometrical data, extra figures and PXRD data. CCDC reference numbers 794577–794584. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0ce00860e

atoms in the self-assembled  $I_4^{2-}$  unit (~9.6 Å). Moreover, ongoing investigations of some of the authors are proving 4, 4'-bipyridinium salts (*i.e.* viologens) as useful building blocks in supramolecular chemistry<sup>9</sup> and crystal engineering.<sup>10</sup>

We thus decided to explore the potential of viologen derivatives in the cation templated synthesis of polyiodides by applying the strategy of the size-matching between the cation and anion. A wide diversity of viologen derivatives is easily available by changing either the spacer connecting the two pyridine rings or the alkyl pendants quaternarizing the pyridine nitrogen atoms. We reasoned that the connecting spacer is crucial in tuning the  $N^+-N^+$  separation, that is, in identifying the size-matching polyiodide which is preferentially templated. The alkyl pendant is crucial in allowing for tailored space compartmentation, namely in caging the size-matching polyiodide and hampering catenation which leads to the formation of complex and diverse polyiodides.

The (*E*)-1,2-bis(4,4'-bypyridiumium)ethylene cation was identified as a particularly convenient candidate for the templated synthesis of the uncommon  $I_4^{2-}$  anions as the intramolecular N<sup>+</sup>–N<sup>+</sup> separation (typically ~9.3 Å)<sup>1b</sup> matches very well with the expected  $I_4^{2-}$  length (~9.6 Å).<sup>5</sup> For the templated formation of  $I_3^-$  anions (~5.8 Å), the smallest polyiodide, we chose the 4,4'-bipyridinium cation (~6.9 Å), the shortest viologen. Benzyl pendants were selected to quaternarize the pyridine nitrogen atoms as a search in the Cambridge Structure Database (CSD)<sup>11</sup> showed that dibenzyl viologens frequently adopt a *Z*-like conformation<sup>12</sup> (where the benzyl pendants are on opposite sides of the planar bipyridinium unit) and organize into columns or layers,<sup>13</sup> so that effective space compartmentation occurs.<sup>14</sup>

Moving from a comparison of the crystal packings in N,N'-bisbenzyl-4,4'-bipyridinium iodide<sup>15</sup> and in the three polymorphs of N,N'-bis-methyl-4,4'-bipyridinium iodide,<sup>16</sup> we reasoned that when the pendants used for quaternarizing the nitrogen give no  $\pi$ - $\pi$  interactions and no steric hindrance on the bipyridinium core, space compartmentation becomes less efficient and stoichiometry dependent formation of extended polyiodides is likely to occur. The behaviour of methyl substituted viologens was thus studied as a negative proof of the relevance of space compartmentation in the cation templated synthesis of polyiodides.

In this paper we describe how the N,N'-bis(tetrafluorobenzyl)-(*E*)-1,2-bis(4,4'-bipyridinium)ethylene cation (1) (Fig. 1) templates so effectively the formation of the  $I_4^{2-}$  anion that the generation of  $1 \cdot I_4^{2-}$  is secured independent of the  $1 \cdot 2I^-$ :  $I_2$  ratio adopted in the crystallization solution. Similarly, the N,N'-bisbenzyl-4,4'-bipyridinium cations (2–4) template the formation of the  $I_3^-$  anion and the salts 2–4·2 $I_3^-$  are formed once again independently of the starting materials' ratios adopted in the crystallization. In all cases anions are confined in parallelepipeds



Fig. 1 Chemical diagrams of the bipyridinium derivatives 1-5.

where four bispyridinium cations are the sides and the benzyl pendants the bases of the cage. Finally, when the N,N'-bismethyl-4,4'-bipyridinium cation (5) is challenged with iodine, new polymorphs of known polyiodides or mixed, highly complex and extended polyiodides are obtained as a function of the stoichiometry adopted in the crystallization.

#### **Results and discussion**

### Structure of *N*,*N*'-bis(tetrafluorobenzyl)-(*E*)-1,2-bis(4,4'-bipyridinium) ethylene $(1 \cdot I_4^{2^-})$

Addition of a concentrated methanol solution of  $I_2$  (0.1 mmol) to a concentrated solution of the dipyridylethylene derivative  $1 \cdot 2I^-$ (0.1 mmol) resulted in the immediate formation of a redbrownish microcrystalline precipitate.<sup>17</sup> Acetone was added until the precipitate re-dissolved and the resulting homogenous system was allowed to slowly evaporate at room temperature. After 1–2 days, dark reddish crystals were obtained which were shown by X-ray crystallography to be  $1 \cdot I_4^{2-}$ . By using the procedure described above, crystals with the same colour, shape and exhibiting similar DSC thermograms were obtained when excess iodine was used, namely when the  $1 \cdot 2I^-$ :  $I_2$  molar ratio in the methanol/acetone solution was 1 : 2 and 1 : 3.

The intramolecular distance between the N atoms in the dication 1 is 9.323 Å and templates the formation of the dianion  $I_4^{2-}$  wherein the distance between the external iodine atoms is 9.321 Å. The structural features of the  $I_4^{2-}$  dianion in  $1 \cdot I_4^{2-}$  are typical for these types of halogen-bonded adducts<sup>18</sup> and are in good agreement with previously reported data in other  $I_4^{2-}$  salts. The  $I_4^{2-}$  anion is symmetric and nearly linear ( $\angle I_{-1}...I_{-} = 179.11$  (1)°), displaying an  $I^-...I_2$  distance of 3.2534(6) Å (21% shorter than the sum of van der Waals and Pauling radii for I and  $I^-$ , 198 and 216 pm, respectively). Consistent with the strong  $n \rightarrow \sigma^*$  character of halogen bonding involving dihalogens, <sup>19</sup> the covalent I–I bond (2.81 Å) is significantly elongated in the complex  $1 \cdot I_4^{2-}$ , compared to molecular iodine (2.72 Å).

The formation of the rare  $I_4^{2-}$  dianion independent of the stoichiometry in the crystallization solution is also a result of the effective space compartmentation provided by the dication which adopts the expected Z-like conformation. The overall crystal packing is characterized by the presence of alternating layers (Fig. 2). One layer is composed of bispyridinium cations and the  $I_4^{2-}$  anions which are held together by strong



**Fig. 2** Crystal packing of the salt  $1 \cdot I_4^{2-}$  viewed approximately along the *b* axis showing the effective space compartmentation. Halogen bond indicated as dashed lines. Colour code: grey, carbon; blue, nitrogen; green, fluorine; violet, iodine. Hydrogen atoms are not shown for clarity.

electrostatic interactions. The other layer is composed of segregated tetrafluorophenyl rings which stack *via*  $\pi$ - $\pi$  interactions in an offset face-to-face (OFF) fashion ( $d_{\text{planes}} = 3.4093(3)$  Å,  $d_{\text{centroid}} = 4.011(1)$  Å). This allows for an effective caging of single I<sub>4</sub><sup>2-</sup> anions by dication molecules (Fig. 3).

Bipyridinium ethylene moieties adopt a nearly coplanar conformation and four of them are the sides of a parallelepiped cage which is self-capped by the phenyl rings of fluorobenzyl pendants functioning as the bases of the cage. Any short contact between neighbouring diiodides is prevented, the shortest distance between polyiodides in the layers being 6.1713(8) Å. Probably this crystal packing of the cations is robust enough to prevent the formation of extended polyiodides when starting from excess iodine as its disruption would be required.

### Structure of *N*,*N*-bis-benzyl-4,4'-bipyridinium bis-triiodides $(2-4 \cdot 2I_3^{-})$

Starting from 0.2 mmol of  $I_2$  and 0.1 mmol of bipyridinium iodides  $2-4 \cdot 2I^-$  and using the protocol described above for the preparation of  $1 \cdot I_4^{2-}$ , the triiodides  $2-4 \cdot 2I_3^-$  were obtained in nearly quantitative yields as dark red crystals.

The substitution pattern of benzyl pendants in the three bipyridinium triiodides  $2-4 \cdot 2I_3^-$  differs substantially from each other and this might translate into differences in the overall crystal packings. On the contrary, single crystal analyses of  $2-4 \cdot 2I_3^-$  reveal numerous similarities among the three packings and with  $1 \cdot I_4^{2-}$ . The size-matching between the bispyridinium cation and the triiodide anion controls effectively the packing and allows  $2-4 \cdot 2I^-$  to template triiodide formation independent of the substitution pattern in benzyl pendants. Here too, the crystal packing consists of a layering of cations and anions held together by electrostatic interactions. These layers alternate with layers composed of the benzyl groups held together by  $\pi-\pi$  interactions in an OFF fashion (Fig. 4).<sup>17</sup>

Pairs of triiodide anions are caged in cavities where the sides are four 4,4'-bipyridinium systems and the caps of the cage are the phenyl rings of the benzyl pendants (Fig. 5).<sup>17</sup> The volume of these cages is larger than that of cages in  $1 \cdot I_4^{2-}$  and self-capping, occurring in  $1 \cdot I_4^{2-}$ , is no more efficient. The participation of phenyl rings bound to viologens of nearby cages is required. Moreover, differences in the substitution patterns on phenyl rings of dications 2–4 translate into differences in the capping mode of cages in 2–4  $\cdot 2I_3^{-}$ . Four phenyls of surrounding cages



**Fig. 3** A  $I_4^{2-}$  dianion caged in  $1 \cdot I_4^{2-}$  by four bispyridinium dications.



**Fig. 4** Crystal packing of the triiodides  $2 \cdot 2I_3^-$  (top) and  $4 \cdot 2I_3^-$  (bottom) approximately along *a* axis. Halogen bond indicated as dashed lines. Colour codes as in Fig. 2. Hydrogen atoms are not shown for clarity.

(two per side) contribute to the formation of the cage bases in  $2 \cdot 2I_3^-$  and  $3 \cdot 2I_3^-$  via a net of  $\pi - \pi$  interactions in an OFF fashion.

In  $4 \cdot 2I_3^-$  only two phenyls of surrounding cages (one per side) contribute to the formation of the cage bases as a consequence of the different interactions given by these incoming phenyl rings. In fact, in addition to the above mentioned  $\pi - \pi$  interactions, strong halogen bonds contribute to the caps formation in  $4 \cdot 2I_3^-$ . The iodine atoms of two *p*-iodophenyl residues of neighbouring cages are close to the outer iodines of the two  $I_3^-$  in the cage, and  $I^-\cdots I$ -C halogen bonds with standard properties are formed (I<sup>-</sup>…I distance 3.629 Å, I<sup>-</sup>…I-C angle 176.57°).



**Fig. 5** A pair of  $I_3^-$  anions caged in  $3 \cdot 2I_3^-$  (top) and  $4 \cdot 2I_3^-$  (bottom). Halogen bonds are indicated as dashed lines. Colour codes as in Fig. 2. Hydrogen atoms are not shown for clarity.

Interestingly, powder X-ray diffraction (PXRD) and DSC experiments showed that  $2-4 \cdot 2I_3^-$  are also formed when excess of  $I_2$  is used in the crystallization (*i.e.*, when the  $2-4 \cdot 2I^-$ :  $I_2$  molar ratio in the solution was 1:4 and 1:6). Moreover, triiodides  $2-4 \cdot 2I_3^-$  were obtained when methanol solutions of  $2 \cdot 2I^-$  (1 mmol),  $3 \cdot 2I^-$  and  $4 \cdot 2I^-$  (0.1 mmol) were exposed to vapours of  $I_2$  (excess) in sealed vessels.

These results prompted us to attempt the templated synthesis of pure triiodide ions *via* gas–solid conditions.<sup>5,20,21</sup> We exposed finely ground  $3 \cdot 2I^-$  to vapours of I<sub>2</sub> (excess) in a sealed vessel. After 3 hours, the PXRD pattern was in good agreement with a partial conversion into  $3 \cdot 2I_3^-$  as the peaks of the pattern simulated from single crystal data of  $3 \cdot 2I^-$  were still present (Fig. 6). A clean and complete conversion was obtained after two days of gas–solid reaction, and one extra day in which the obtained brown-reddish powder was left in the open air at room temperature.<sup>17</sup>

### Structure of N,N'-bis-methyl-4,4'-bipyridinium polyiodides $5 \cdot I^-I_3^-, 5 \cdot 2I_3^-, 5 \cdot I_3^{-1/2}I_8^{2-}$ , and $5 \cdot I_5^{-1/2}I_8^{2-}$

On recrystallization from acetone/MeOH mixture of the precipitate obtained upon adding a methanol solution of  $I_2$  (0.2 mmol) to a water/MeOH (1:10) solution of  $5 \cdot 2I^-$  (0.1 mmol), the unusual mixed salt  $5 \cdot I^- \cdot I_3^-$  (*Pnma*) was obtained. The packing of this crystal shows no caging of triiodide anions. On the contrary, it is characterized by the presence of



**Fig. 6** PXRD study of  $3 \cdot 2I^-$  exposed to  $I_2$  at different times: experimental pattern of the starting  $3 \cdot 2I^-$  (A); pattern acquired after 3 hours (B) and 2 days (C) of gas–solid reaction; simulated pattern of  $3 \cdot 2I_3^-$  from single crystal X-ray data (D).



**Fig. 7** Top: crystal packing of  $5 \cdot I^- \cdot I_3^-$  along the *c* axis (top) and of  $5 \cdot 2I_3^-$  along *a* axis (bottom). Halogen bonds are shown in dashed lines. Colour codes as in Fig. 2. Hydrogen atoms have been omitted for clarity.

alternating cationic and anionic layers (Fig. 7, top). Catenation of triiodide anions affords loosely bound infinite polyiodide chains as the external iodine of a triiodide unit enters the central iodine of another triiodide  $(d_{I-I(-I)\cdots I-I-I} = 3.9390(4) \text{ Å}, \ \angle_{I-I(-I)\cdots I-I-I} = 89.25(1)^\circ, 91.54(1)^\circ).$ 

Slow diffusion of methanol into a mixture of I<sub>2</sub> (0.2 mmol) and  $5 \cdot 2I^-$  (0.1 mmol) dissolved in DMSO, produced a polymorph of  $5 \cdot 2I_3^-$  different from the polymorphs already reported in the CSD (Fig. 7, bottom).<sup>22</sup> Differences between the crystal packing of  $5 \cdot 2I_3^-$  prepared by us and that reported in the literature are considerable. For instance type-I iodide–iodine contacts<sup>23</sup> are 3.8192(8) Å long in our polymorph and 4.024 Å long in the already reported structure.

On increasing the amount of I<sub>2</sub> in the MeOH/DMSO experimental protocol described above, polyiodides containing increased amounts of catenated I<sub>2</sub> are obtained. Specifically, starting from MeOH/DMSO solutions containing 0.1 mmol of  $5 \cdot 2I^-$  and 0.3 mmol or 0.4 mmol of  $I_2$ , polyiodides  $5 \cdot I_3^- \cdot \frac{1}{2}I_8^{2-}$ , or  $5 \cdot I_5^{-1/2} I_8^{2-1}$  were isolated, respectively. In  $5 \cdot I_3^{-1/2} I_8^{2-1}$ , the  $I_3^{-1/2} I_8^{2-1}$  the  $I_3^{$ anions have quite standard arrangement and are not involved in short iodine-iodine contacts. I822 dianions adopt a usual outstretched Z-shaped conformation and consists of two I<sub>3</sub><sup>-</sup> ions connected through the end atoms by a rotationally disordered I<sub>2</sub> molecule  $[I_3^- \cdot I_2 \cdot I_3^-]$ . A net of iodine-iodine interactions catenate  $I_8^{2-}$  dianions into infinite two-dimensional (2D) nets (Fig. 8, top). In  $5 \cdot I_5^{-1/2} I_8^{2-}$ , the  $I_8^{2-}$  dianions are similar to those in  $5 \cdot I_3^{-1/2} I_8^{2-}$ , the disorder of the connecting  $I_2$  molecule being translational rather than rotational. The I<sub>5</sub><sup>-</sup> anions consist of two  $I_2$  molecules bound to an iodide anion and adopt a nearly linear conformation. Short iodine-iodine contacts further catenate the external atoms of the  $I_8^{2-}$  dianion to one external atom of  $I_5^-$  anion and the  $I_5^- \cdot I_8^{2-} \cdot I_5^-$  complex is formed (Fig. 8, bottom).

The obtained structures evidence that in the absence of  $\pi$ - $\pi$  interactions and steric hindrance associated with the pendants quaternarizing viologen nitrogens, the size matching between the



**Fig. 8** Top: ball and stick representation of  $5 \cdot I_3^{-1/2} I_8^{2-}$  evidencing the 2D net formed by  $I_8^{2-}$  dianions; one bipyridinium unit and one triiodide unit are reported (sticks representation); I(17A) and I(17B) are splitted over two positions optimized with a 66.5 and 33.5 population, respectively. Bottom: crystal packing of  $5 \cdot I_5^{-1/2} I_8^{2-}$ ,  $I_5^{-}$  and  $I_8^{2-}$  is in ball and stick representation, bipyridinium units are reported in sticks representation; I(19A) and I(19B) are splitted over two equally populated positions. Colour codes as in Fig. 2. Hydrogen atoms have been omitted for clarity.

cation and the anion in viologen iodides is unable to direct unambiguously the stoichiometry of the obtained polyiodide. The strong tendency of polyiodides to catenate prevails over the templating ability of viologens and the stoichiometry of the formed polyiodide is controlled by the stoichiometry in the crystallization solution.

### Conclusions

The N<sup>+</sup>–N<sup>+</sup> intramolecular distance in viologen-type cations can be easily tuned by using the different extended bipyridinium scaffolds that are easily available. This offers a unique opportunity to pursue the selective formation of a given polyiodide by combining the metric engineering strategy (based on the cation– anion size-matching principle) with the space compartmentation induced by  $\pi$ – $\pi$  stacking interactions. In this paper, we have shown that if benzyl pendants are used to quaternarize the pyridine nitrogens, effective supramolecular space compartmentation occurs and the resulting anion caging controls the formation of the targeted polyiodides.

The bis-benzyl bis(pyridinium)ethylene  $1 \cdot 2I^-$  templates the selective formation of  $1 \cdot I_4^{2-}$  via the matching between the intramolecular N<sup>+</sup>–N<sup>+</sup> separation in the cation and the separation of the external iodine atoms in the dianion  $I_4^{2-}$ .  $1 \cdot I_4^{2-}$  is formed independent of the amount of iodine present in the crystallization solution thanks to the cooperation between this size-matching and the space compartmentation produced by the cations. The bis-benzyl bis(pyridinium)ethylene moieties adopt a *Z*-like conformation and stack via  $\pi$ – $\pi$  interactions affording

supramolecular parallelepipeds wherein the metastable  $I_4^{2-}$  anion is effectively caged. Similarly, the bis-benzyl bipyridiniums **2**–**4**·2I<sup>–</sup> template the formation of  $I_3^-$  anions thanks to the cation–anion size matching and pairs of  $I_3^-$  anions are caged into parallelepipeds formed by four Z-shaped bis-benzyl bipyridinium units.

A negative proof of the importance of the synergy of cationanion size-matching and anion caging come from experiments conducted with the bis-methyl dipyridinium  $5 \cdot 2I^-$ . This compound cannot give rise to space compartmentation and different polyiodide species are formed as a function of the experimental setup and the stoichiometry of the reacting species in solution.

In conclusion, we have shown that if controlled cation templated synthesis of viologen polyiodides is pursued, the synergistic effect of size-matching and space compartmentation can be used as an effective strategy to develop a general and reliable protocol where the crystal stoichiometry is independent of the stoichiometry in the crystallization solution. The results described in this paper demonstrate the successful exploitation of viologen derivatives for the cation-templated synthesis of polyiodides species. The method we applied may be extended to the predictable preparation of other polyhalide species. This has the potential for significantly augmenting the knowledge on polyhalides, as well as providing a novel approach to their design and synthesis. Furthermore, considering the very rich electrochemical behaviour<sup>24</sup> and electronic properties<sup>25</sup> of these bipyridinium cations, their combination with polyiodide species could result in a new class of materials with unique and interesting electronic properties.

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