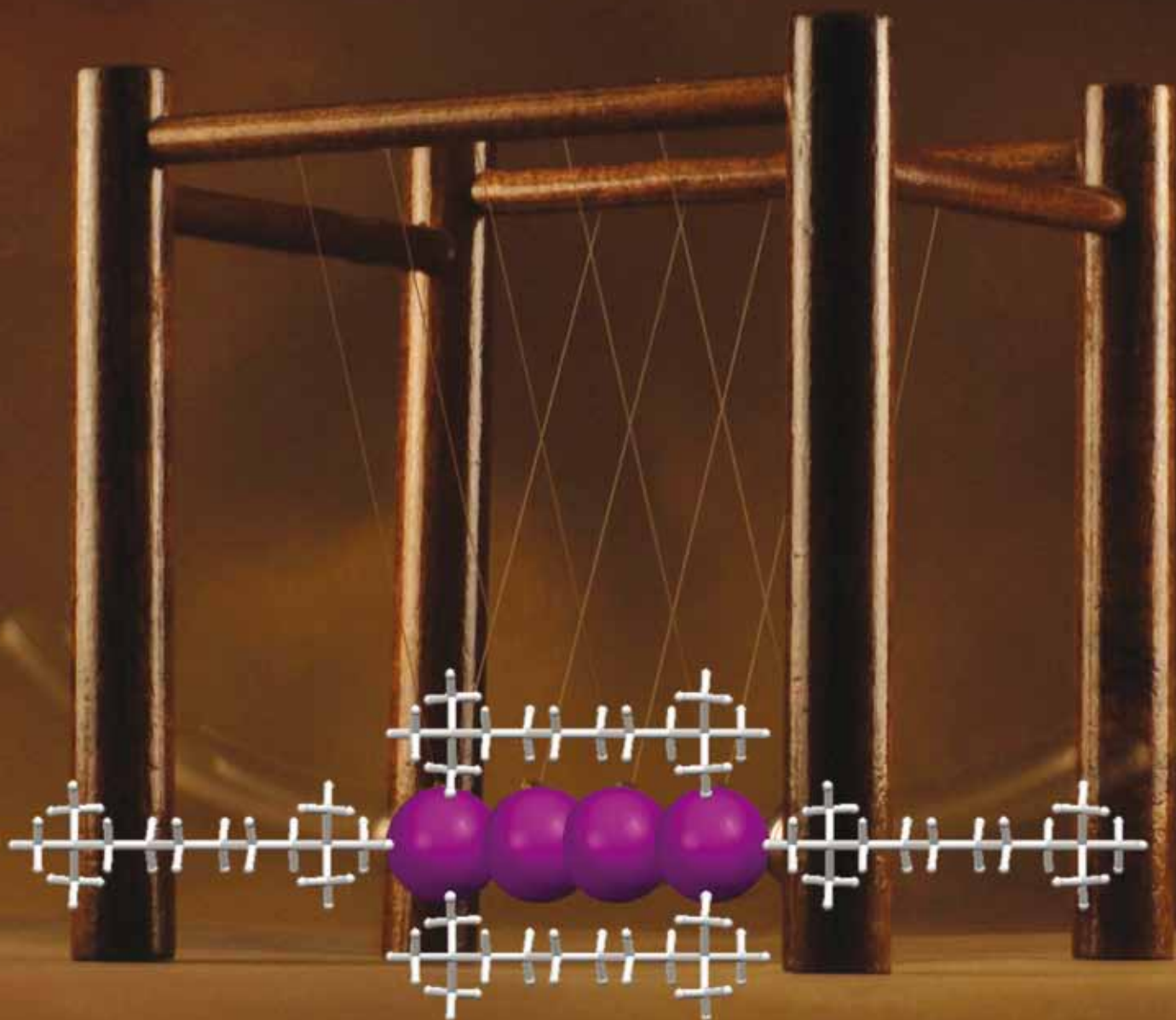


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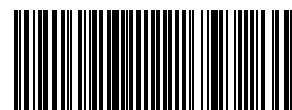
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FEATURE ARTICLE

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Dimensional encapsulation of $I^- \cdots I_2 \cdots I^-$ in an organic salt crystal matrix†

Antonio Abate,^a Manuel Brischetto,^a Gabriella Cavallo,^a Manu Lahtinen,^b Pierangelo Metrangolo,^{*a} Tullio Pilati,^c Stefano Radice,^d Giuseppe Resnati,^{*ac} Kari Rissanen^e and Giancarlo Terraneo^a

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Bis(trimethylammonium)hexane diiodide encapsulates iodine from solution and through a gas/solid reaction yielding in a predictable and controllable manner the selective formation of the rare polyiodide species $I^- \cdots I-I \cdots I^-$, which matches in length to the chosen dication.

Polyiodides give rise to a particularly wide variety of structures that are assembled starting from I^- , I_2 and I_3^- building blocks, where I^- and I_3^- may be considered as electron-donor moieties and I_2 as electron-acceptor. It has been already demonstrated that the rich structural chemistry of polyiodides depends strongly on the nature of the nearest neighbours in the structure. Therefore, the I^- counterion plays a key role in determining both the stoichiometry and geometry of the assembled polyiodide chain.¹ For example, the use of long-chain hydrocarbon dications proved to be effective in the control of the synthesis of polyiodide species by dimensional caging of I_3^- and I_5^- ions.² On the other hand, a search in the Cambridge Structure Database (CSD)³ revealed that there are only eight crystal structures containing the symmetric polyiodide I_4^{2-} as a discrete unit.⁴ The symmetric I_4^{2-} species may be described as an I_2 molecule bound at both ends each to one I^- ion through linear halogen bonding,⁵ that is the intermolecular interaction involving halogen atoms as electrophilic species,⁶ with the central I–I bond length ~ 2.8 Å and the external I–I \cdots I $^-$ distances ~ 3.4 Å. Theoretical investigations proved that the linear I_4^{2-} ion is unstable;⁷ hence, it is not surprising that I_4^{2-} ions coordination to or stabilization by the surrounding environment is observed in many of the reported systems.

In our ongoing interest in the optimization of charge transport mechanisms in I^-/I_3^- -based electrolytes for dye sensitized solar cells (DSSCs),⁸ we were interested in the isolation and characterization of the symmetric I_4^{2-} polyiodide species. It is in

fact considered that charge transport in DSSCs electrolytes occurs by the following Grotthuss-like process:⁹ I^- approaches I_3^- from one end and forms the unstable encounter complex $[I^- \cdots I-I \cdots I^-]$, from which I^- is released at the other end. In this fashion, the I^- is displaced by the length of one I–I bond, ~ 2.8 Å, without having to cross that distance. The bond exchange occurs immediately on formation of the encounter complex, rendering the process diffusion-controlled. The identification of the exact nature of the polyiodide species in the electrolyte solution is therefore crucial for the full understanding of the conduction mechanism in electrolytes for DSSCs based on the I^-/I_3^- redox couple.

In this communication we show the application of supramolecular and crystal engineering principles to the selective and reversible encapsulation of the symmetric I_4^{2-} species by ionic organic solids. The method we applied is general and can be extended to the predictable obtainment of other uncommon polyiodide species. This has the potential for significantly augmenting our knowledge of polyiodide species, as well as providing a novel approach to the field of their design and synthesis. In particular, as electrostatic binding is largely dependent on structural complementarity of the interacting charged moieties,¹⁰ we reasoned that matching the symmetric I_4^{2-} polyiodide species with a dication wherein the space separation of the two positive charges is similar to the size of the I_4^{2-} dianion, should increase the strength of electrostatic interactions in the ionic lattice, thus driving forcefully the selective formation of the target polyiodide species. For this purpose, we selected the bis(trimethylammonium)hexane diiodide salt **1**. In fact, the $N^+ \cdots N^+$ intramolecular distance in the chloride salt structure of bis(trimethylammonium)hexane is 8.853 Å,¹¹ which nicely matches the $I^- \cdots I^-$ distance in the $I^- \cdots I_2 \cdots I^-$ superdianion (~ 9.6 Å) as found in the CSD.³ The diiodide salt of the dication $(CH_3)_3N^+(CH_2)_6N^+(CH_3)_3$ **1**, hereafter abbreviated BTMAH²⁺, selectively encapsulates in solution one molecule of I_2 (Scheme 1) and forms crystals containing the unstable polyiodide species I_4^{2-} , which is trapped in the crystal matrix of organic BTMAH²⁺ dications (Fig. 1). Remarkably, the solid-state salt **1** can also selectively capture one I_2 molecule from the vapour phase, yielding the same dynamically porous product **2** formed from solution. This occurs despite the non-porous lattice structure of the starting organic salt, as is common for the salts of bis(trimethylammonium)alkanes.^{11,12} The complex BTMAH²⁺· I_4^{2-} **2** has been fully characterized by DSC, IR and Raman. The size-selective entrapment of the I_4^{2-} species has also been confirmed by the characterization of the mismatched complex **3** containing two I_3^- anions.

^a NFMLab and CNST-IIT@POLIMI, D.C.M.I.C. "Giulio Natta", Politecnico di Milano, Via L. Mancinelli 7, 20131 Milan, Italy.

E-mail: pierangelo.metrangolo@polimi.it, giuseppe.resnati@polimi.it; Fax: +39 02 2399 3080;

Tel: +39 02 2399 3041 (P. M.), 3032 (G. R.)

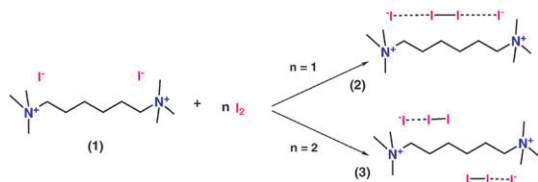
^b Department of Chemistry, University of Jyväskylä, P.O. Box 35, Jyväskylä, FI-40014, Finland

^c ISTM-CNR, Università di Milano, Via Venezian 21, 20133 Milan, Italy

^d Solvay-Solexis S.p.A., Viale Lombardia 20, 20121 Bollate (MI), Italy

^e Department of Chemistry, Nanoscience Center, University of Jyväskylä, P.O. Box 35, Jyväskylä, FI-40014, Finland

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Scheme 1 Bis(trimethylammonium)hexane diiodide **1** reacted with one equivalent of iodine yields in a predictable and controllable way the supramolecular complex **2** containing the symmetric polyiodide species I_4^{2-} . When **1** is reacted with two equivalents of iodine, the supramolecular complex **3** containing the polyiodide species I_3^- is obtained quantitatively.

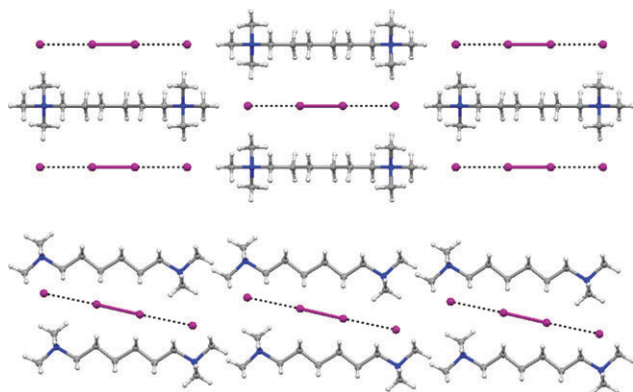


Fig. 1 The structure of complex **2** viewed along c (top) and b (bottom) crystallographic axes. The polyiodide species $I^- \cdots I_2 \cdots I^-$ is allocated in specific cavities surrounded by four dications of **1**. No contacts occur between different polyiodide species. Colours are as follows: C, gray; H, light gray; N, sky blue; I, magenta.

Particularly, upon slow isothermal diffusion of $CHCl_3$ vapour into an CH_3CN solution containing equimolar amounts of $BTMAH^{2+} \cdot 2I^-$ **1** and I_2 , good-quality yellow–red plate-like crystals were obtained. These crystals were submitted to single-crystal X-ray analysis. The crystal structure of **2** revealed that $BTMAH^{2+} \cdot 2I^-$ and I_2 are present in a 1 : 1 ratio. In particular, four alkyl dications define a rectangular parallelepiped-shaped cavity that encapsulates one molecule of I_2 , trapped by strong halogen bonds to the two I^- ions at either end. The structure of the complex **2** confirmed our initial hypothesis: The distance between the intramolecular N atoms of $BTMAH^{2+}$ in the complex is within 1 Å (0.852 Å) of the iodide ions' spacing in the superanion $I^- \cdots I_2 \cdots I^-$. The $I^- \cdots I_2$ distance of 3.440(2) Å is noticeably shorter than the sum of vDW and Pauling radii for I and I^- , respectively (4.14 Å, 17% reduction),¹³ while the $I-I \cdots I^-$ angle is 178.84(5)°. These geometric parameters are perfectly consistent with those observed in other halogen-bonded structures.¹⁴

As a likely consequence of the strong $n \rightarrow \sigma^*$ character of halogen bonding,¹⁵ the covalent I–I bond is significantly elongated (2.829(2) Å) in **2** compared to the distance observed in elemental iodine (2.72 Å).¹⁶ As a result of the optimized binding resulting from the structural complementarity of the interacting charged moieties and the matching sizes of $BTMAH^{2+}$ and I_4^{2-} , complex **2** shows quite a high melting point of 194 °C (mp **1** = 285 °C; mp I_2 = 113 °C) and a very low solubility in organic solvents if compared to the pure starting materials.

Intrigued by the structure of the complex **2**, we considered whether the solid-state salt **1** could selectively capture one I_2 molecule directly from the vapour phase, yielding the same structure **2** formed from solution,¹⁷ despite its non-porous salt lattice structure. We, therefore, exposed finely powdered **1** in a sealed vessel to an equimolar amount of I_2 vapour. After one day at ambient pressure and temperature, the solid-state salt **1** transformed into a 1 : 1 complex exhibiting the same lattice structure observed from solution crystallization (Fig. 2, top, C). However, in these reaction conditions some organic salt **1** remained unchanged. Interestingly, also grinding equimolar amounts of **1** and I_2 in a mortar and pestle for 5 min yielded quantitatively a 1 : 1 complex corresponding to the same crystal phase of **2** (Fig. 2, top, D).

The importance of size-matching of the interacting partners in the formation of complex **2** was further confirmed by the analysis of two crystal structures reported in the CSD that are closely related to that of the complex **2**. In fact, when bis(ammonium)-alkane diiodides longer than **1** were co-crystallized with I_2 , no sign of formation of the I_4^{2-} species was detected. Specifically, the structure of the complex bis(decane-1,10-diammonium) diiodide bis(triiodide) shows only isolated linear and asymmetric I_3^- species.^{2b} On the other hand, when nonane-1,9-diammonium bis(iodide) was co-crystallized with I_2 , an infinite zigzag polyiodide chain was obtained, which was comprised of alternating linear and asymmetric I_3^- species and I_2 molecules.^{2c}

In order to study the influence of solution stoichiometry over crystal stoichiometry and in particular on the nature of the polyiodide species that could be obtained upon complexation of I_2 by $BTMAH^{2+} \cdot 2I^-$ **1**, we prepared solutions having different $BTMAH^{2+} \cdot 2I^- : I_2$ stoichiometries. By using a 1 : 2 ratio of the starting materials with the same experimental set-up used for the

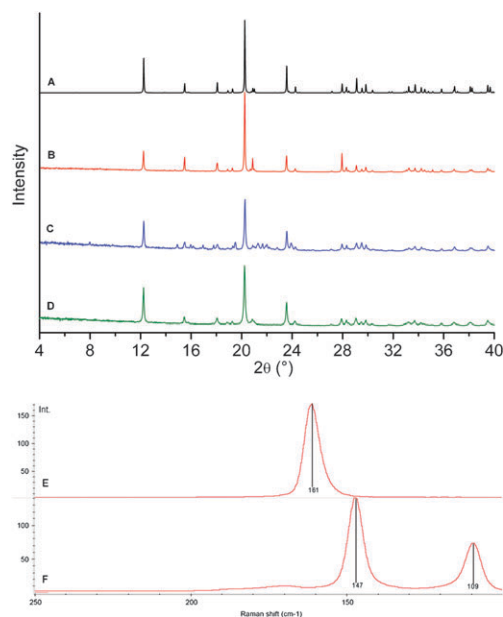


Fig. 2 Top: PXRD patterns of the complex **2** (A) simulated from single-crystal X-ray data, (B) experimental pattern acquired after solution crystallization, (C) acquired after gas–solid reaction, and (D) after grinding. In (C) it can be noted that some organic salt **1** remains unchanged. Bottom: Raman spectra in the region 250–100 cm^{-1} of the complexes **2** (E) and **3** (F).

synthesis of **2**, we obtained quantitatively and in pure form the 1 : 2 complex **3** as red plate-like crystals (Scheme 1). Different from **2**, the single-crystal X-ray structure of **3** revealed the presence of couples of I_3^- ions weakly interacting with each other through a twofold axis. Moreover, the overall crystal packing of the mismatched complex BTMAH[I_3]₂ **3** is completely different from the matched structure **2**. In fact, there is no cavity to trap one I_2 molecule; instead the structure of **3** consists of alternating cation and I_3^- anion layers. The iodine atom spacings in the I_3^- species are I1–I2 2.8590(8) Å and I1–I3 2.9827(8) Å, with an [I3–I1–I2][–] angle of 179.48(2)°; these geometric features are typical of discrete linear and asymmetric I_3^- species.¹⁹ Two I_3^- ions are subsequently organized into pairs as a result of short type I–I···I interactions (3.7595(11) Å; the I1–I3···I3_{–x,y,z} angle is 151.14(2)°), with a good interpenetration of the vDW radii (corresponding to a 5% reduction of the sum of the VDW radii for two I atoms).¹³ The complex **4**, containing V-shaped I_5^- ions, could also be obtained as single crystals, but was not further characterized.¹⁸

Raman spectroscopy is a powerful tool for the structural identification of polyiodide species, but their inherent instability may cause decomposition and the appearance of spurious peaks.²⁰ It is thus desirable that the identification of the diagnostic vibrations of a species is made on a stable polyiodide salts with known crystal structures, and the demand for a stable sample is particularly strong for the rare and poorly characterized I_4^{2-} species. Moreover, the *in situ* spectro-electrochemical study of iodide salts of ionic liquid electrolytes doped with iodine has demonstrated clearly that I_3^- , I_4^{2-} and I_5^- are the polyiodide species, the formation of which is correlated with an enhanced ionic conductivity in DSSCs,^{21,22} thanks to the established relay-type Grotthus-like mechanism.²³ For all of these reasons, we undertook a detailed study of the complexes **2** and **3** by Raman spectroscopy.

In the region 250–100 cm^{–1}, the Raman spectrum of the complex **2** shows only one intense band at 161 cm^{–1}, attributable to the ν_{1-I} vibration of the iodine molecule perturbed as a consequence of the interaction with the two iodide electron donors. As far as the Raman spectrum of the complex **3** is concerned, the same region (250–100 cm^{–1}) is dominated by two bands at 147(s) and 109(m) cm^{–1}. These vibrations can be assigned to the ν_3 antisymmetrical and ν_1 symmetrical stretching modes, respectively, of discrete, linear asymmetric triiodide ions.^{20,24}

In conclusion, we present here that the nonporous organic salt bis(trimethylammonium)hexane diiodide (**1**) shows a size-matching dynamic response to I_2 , leading to quantitative formation of the unstable and rare I_4^{2-} polyiodide species. Despite bis(trimethylammonium)alkanes being typically nonporous materials, I_2 is readily transported through the solid **1** until a thermodynamically stable porous structure is achieved. The obtained I_4^{2-} has been fully characterized and Raman vibrations assigned with certainty. The results described in this paper are a significant proof that templating agents can effectively control the synthesis of unstable polyiodide species and networks.²⁵ At present our laboratories are studying the behaviour of I_4^{2-} containing crystalline species under extreme conditions (*e.g.* high pressure), as well as the technological exploitation of compound **1** in the handling and recovery of radioactive I_2 .

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- Similarly to **3**, starting from a 1 : 4 BTMAH²⁺·2I[–] : I_2 stoichiometry, the complex **4** (Scheme S1, ESI†) was isolated in the form of deep red prismatic crystals. The single-crystal X-ray structure of **4** shows the presence of discrete V-shaped I_5^- ions. The inner iodine atoms I2–I1 and I2–I4 bond distances are 3.0800(10) and 3.0642(11) Å, respectively, while the outer ones show the distances I4–I5 and I1–I3 of 2.8093(11) and 2.7955(10) Å, respectively; the angle of the symmetric V-shaped I_5^- ion structure is 98.49(3)°; based on these geometric features the I_5^- ions found in **4** can be described as an I[–] ion coordinating two I_2 molecules.¹⁹ The crystal packing of **4**, similarly to **3**, roughly consists of sheets of alternating cations and I_5^- ions layers.
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