The stable polyiodides: Experimental and theoretical studies of formation mechanism
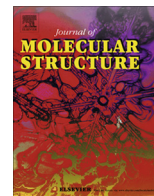
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The stable polyiodides: Experimental and theoretical studies of formation mechanism

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HIGHLIGHTS

- We synthesized tetraethylammonium polyiodides with different ratios of reactants.
- The regularities of syntheses and characteristics of sable polyiodides were analyzed.
- The molar standard Gibbs free energy changes of possible reactions were calculated.
- We explained the abnormal phenomena in solvent and solid syntheses of Et_4NI_5.
- We interpreted the formation mechanism of polyiodides.

GRAPHICAL ABSTRACT
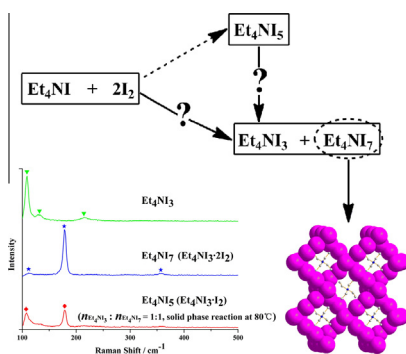
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ABSTRACT

The structures of polyiodides have been extensively studied for long time, but it was rarely involved of the mechanism of polyiodide species formation in preparation. The tetraethylammonium polyiodides were chosen as model chemicals and prepared with different molar ratios of reactants in ethanol solvent, the products were analyzed by titration, Raman spectra and TGA/DTG/DSC analysis, with the increase of the molar ratios of reactants, the iodine contents of the products reached a constant value. Finally, only two stable structures, Et_4NI_3 (**1**, space group *Cmca*) and Et_4NI_7 (**2**, space group *Cmca*), were isolated by recrystallization of slow evaporating solvent(s). The thermal analysis of tetraethylammonium polyiodides showed that all tetraethylammonium polyiodides lost I_2 together to become Et_4NI_3 firstly and then continue to decompose. The decomposition of Et_4NI_3 was not a simple process which Et_4NI_3 lost one iodine molecule and then became Et_4NI. In addition, the thermodynamical properties of species (I_2 and Et_4NI_x, $x = 1, 3, 5, 7$) and the molar standard Gibbs free energy changes of reactions ($\Delta_r G_m^0$), as well as the mechanism of tetraethylammonium polyiodides formation were interpreted by density functional theory (DFT) calculations. The calculations show that the solvent effects have impact on the reactions. Accordingly, a comparative study was carried out on the solid phase synthesis of Et_4NI_5 at 80 °C and at molten state. Furthermore, the solid synthesis of Et_4NI_5 was characterized by variable temperature (-25 °C $\sim$ 150 °C) Raman Spectrometer. The polyiodide components interconversion showed the discrete I_5^- could be formed in molten state. In short, what species of polyiodides crystallized from reactions in solutions are decided by the synergy between $\Delta_r G_m$ of reactions and Coulombic interactions etc. of polyiodide crystals.

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Introduction

Polyiodides have been extensively studied in the solid and liquid state, which constitutes a class of long known, yet relatively poorly understood, materials. Up to now, applications of polyiodides on electronics, batteries, optical devices and medicine have drawn people's attention [1–3]. A large number of polyiodide structures which have been characterized may contain small, discrete polyiodides or large, extended anionic networks of interconnected units, ranging from simple I_3^- through linear I_4^{2-} [4], V-shaped I_5^- [5], three-pronged structures of I_7^- [6], I_9^- [7], even to the highest iodine content I_{29}^{3-} [8]. Typically, these structures can be described as three "building blocks" construction: I^-, I_2, and I_3^-, where the I^- and I_3^- ions may be considered as donors, while the I_2 molecules surrounding I^- and I_3^- ions are considered as acceptors. The diversity of polyiodide structures is a consequence of strong tendency of iodine to catenate through donor–acceptor interactions combined with the influence of counter-ions. Polyiodide materials with different polymerization degrees may have different properties (a general formula is $mI_2 + nI^- \rightarrow I_{2m+n}^{n-}$, where m and n integers > 0, $n = 1–4$ [9]. Herein, we define the number $2m + n$ as the apparent "polymerization degree" of polyiodides, although polyiodides are different from polymers). Furthermore, technically useful polyiodide materials exhibit interesting structural transformations which are hard to understand and control, especially in its degree of polymerization.

In the long history of polyiodides research, the polymerization degree of polyiodides change laws in the preparation processes have not been in-depth studied. For the existing synthesized polyiodides, people were primarily interested in what kind of structures by selecting different cations and iodo reactants with 2–3 stoichiometric ratios. But no one except Horn et al. [10] have made great achievements in some polyiodide species occurred with the same cationic reactants according to many different ratios. Due to the linear flexibility of the triiodide ion which is sensitive to the influence of the nearest neighbors in the structures, polyiodide assemblies are often a matter of taste and follows self-made rules [7], mostly based on distances among cations and polyanions or any other interactions we up to now unknown by which polymorphism with various crystal packing might occur. As a matter of fact the nature of polyiodides and the template effect of the counter-cation have been elucidated by some authors, including for example Blake et al. [11]. This can be considered as the general characteristics of stable polyiodides, but this does not explain the formation mechanism of polyiodide species in the reactions.

Tetraethylammonium polyiodides is a class of representative polyiodides and the above problems also exist. Although Migchelsen et al. [12] and Tebbe et al. [13] have prepared polyiodides by using Et_4NI and I_2 with one stoichiometric ratio respectively. Nevertheless, the stable forms of the polyiodides, the regularities of polymerization degree of the polyiodides prepared by different reactants ratios, and the formation mechanism of the tetraethylammonium polyiodide species has not been clarified. Moreover, it is also unclear why Et_4NI_5 has not been prepared out so far. In this paper, the first part describes the experiments that the preparation of tetraethylammonium polyiodides in EtOH solvent at different reactants ratios. The products were precipitated from the solutions and characterized by titration, Raman spectra and TGA/DTG/DSC analysis. In addition, it is well known that the phase transformation can occur in the classical manner of dissolution and recrystallization in some circumstances. Recrystallization makes the metastable substances dissolved and more stable in precipitation. Therefore, in order to get relatively stable polyiodide products at room temperature, we have used a method that combines redissolution and recrystallization by slow evaporation solvents [14].

The products after recrystallization would be characterized by X-ray analysis. In the second part, the thermodynamical properties of species and the possible formation mechanism of the tetraethylammonium polyiodides would be also investigated by DFT calculations. Based on the theoretical and experimental analysis, two sets of solid phase synthesis experiments were designed, and the Raman spectra changes of the products both at room temperature and in the range of −25 °C ∼ 150 °C were also reported. This research work might provide somewhat guidance for solid polyiodides in practical applications.

Experimental section

Materials and methods

Chemicals (AR) and solvents (AR) were received from commercial resources and used without further treatment. The TGA and DSC spectra were carried on a Q600 thermogravimetric analyzer (TA, USA) and a Q2000 differential scanning calorimeter (TA, USA) respectively. All samples were under nitrogen atmosphere and at the heating rate of 10 °C/min, with initial temperature of 25 °C and end temperature of 800 °C. The Raman spectra at room temperature (25 °C) were recorded on a Laser Confocal Microprobe Raman Spectrometer (Renishaw in via, the UK). The laser intensity was 0.05% with 514 nm wavelength and 2400 grating slit. The Raman shift range was 500–100 cm^{-1} and the exposure time was 10 s. The Raman spectra at various temperatures (from −25 °C to 150 °C) were recorded on a HR800 Laser Confocal Microprobe Raman Spectrometer (Jobin Yvon, France). The laser intensity was 0.1 mW with 532 nm wavelength and 1800 grating slit. The Raman shift range and the exposure time were the same as the former.

Preparation

The tetraethylammonium polyiodides were prepared with different molar ratios of reactants and details of the procedures are:

Experiments 1–7. In the solvent phase reaction method, to a suspension of Et_4NI (3 mmol, 0.7715 g) in absolute alcohol (15 mL) was added dropwise a solution of I_2 (3 mmol, 0.7614 g; 6 mmol, 1.5229 g; 9 mmol, 2.2843 g; 12 mmol, 3.0457 g; 15 mmol, 3.8071 g respectively) in absolute alcohol (35 mL) with stirring and refluxed for 3 h. (in Exp. 6, to a stirred solution of Et_4NI (0.5 mmol 0.1286 g) in absolute alcohol (5 mL) was added dropwise I_2 (5 mmol, 1.2690 g) in absolute alcohol (25 mL) and refluxed for 3 h). The mixture was allowed to warm to room temperature for 4 h and then slowly cooled to room temperature. Then, when the molar ratio $n(I_2): n(Et_4NI) = 1$, the solution precipitated brown needle-like crystals; When the molar ratio $n(I_2): n(Et_4NI) = 2$, the solution precipitated mixture of brown and black needle or plate-like crystals; While the molar ratio $n(I_2): n(Et_4NI) > 2$, all the ethanol solutions precipitated black flake crystals. The crystals were separated by filtration and washed with small aliquots of cold alcohol with yields averaging 50% over the all experiments. Products were redissolved in solutions specified in Table 1, and left undisturbed for slow evaporation of the solvents. Large red-brown (Exp. 1, Et_4NI_3 (**1**)) or black (Exp. 3–7, Et_4NI_7 (**2**)) block crystals were collected after several days. However, in Exp.2, in addition to many large black block crystals, few small strip brown crystals were also collected.

Experiment 9. In the solid phase method, a mixture of Et_4NI_3 crystals (0.2 mmol, the recrystallized product form Exp. 1) and Et_4NI_7 (0.2 mmol, the recrystallized product form Exp. 3) crystals was ground by agate mortar at room temperature for 10 min and then placed in a sealed container at 80 °C-water bath for 3 h. The

Table 1
Crystallisation experiments yielding tetraethylammonium polyiodides.

Exp.	Solvent system	Mole ratio I_2: Et_4NI	Product	Space group
1	C_2H_5OH:CH_3CN 1:1	1:1	Et_4NI_3	Cmca
2[a]	C_2H_5OH:CH_3CN 1:1	2:1	Et_4NI_3	Non single crystal
			Et_4NI_7	Cmca
3	C_2H_5OH:CH_3CN 1:1	3:1	Et_4NI_7	Cmca
4	C_2H_5OH:CH_3CN 1:1	4:1	Et_4NI_7	Cmca
5	C_2H_5OH:CH_3CN 1:1	5:1	Et_4NI_7	Cmca
6	C_2H_5OH:CH_3CN 1:1	10:1	Et_4NI_7	Cmca
7	C_2H_5OH	3:1	Et_4NI_7	Cmca
8[b]	C_2H_5OH	3:1	Et_4NI_7	Aba2

[a] From the redissolved solution, a small amount of brown stripe crystalline compounds and Et_4NI_7 (Cmca) crystals grew concurrently. We speculated the brown stripe compounds was Et_4NI_3.

[b] The first crop of crystals by slow diffusion [13].

mixture was allowed to cool to room temperature. In the reaction the mixture was not molten and the color changed from brown to dark brown during the heating course.

Experiment 10. In the solid phase method, a mixture of Et_4NI_3 crystals (0.2 mmol, the recrystallized product form Exp. 1) and Et_4NI_7 (0.2 mmol, the recrystallized product form Exp. 3) crystals was ground by agate mortar at room temperature for 10 min and then placed in a sealed container ca. 150 °C and stirred for 15 min. The color of mixture changed from brown to dark brown during the heating course. The mixture was converted into homogeneous molten liquid and warmed to room temperature. The final product was solidified into a piece of hard solid and ground by agate mortar. Then it was observed by a microscope and found that it was a mixture of black crystals and brown crystals.

Experiment 11. In the solid phase method, a mixture of Et_4NI_3 crystals (0.2 mmol, the recrystallized product form Exp. 1) and Et_4NI_7 (0.2 mmol, the recrystallized product form Exp. 3) crystals was ground by agate mortar at room temperature for 10 min. Take a little mixture into a capillary (long ca. 8 mm) and seal it by alcohol blast burner. The capillary characterized by Raman spectra from −25 °C to 175 °C.

Crystal structure determination

Suitable single crystals of all samples were carefully selected under an optical microscope and glued to thin glass fibers. Structural measurements were performed on a computer-controlled Oxford Xcalibur E diffractometer with graphite-monochromated Mo/Kα radiation ($\lambda_{Mo/K\alpha}$ = 0.71073 Å) at T = 293(2) K. Absorption corrections were made using the SADABS program [15]. The structures were solved using the direct method and refined by full-matrix least-squares methods on F^2 by using the SHELX-97 program package [16]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms attached to carbon atoms were geometrically placed and refined using a riding model. Crystal data, as well as details of data collection and refinements of all samples are summarized in Table S1, and selected bond lengths and angles are given in Table S2.

Computational details

The widely used density functional method B3LYP with 6-31G (3df, 3pd) and LanL2DZ basis set were tested for many cases, such as iodine or iodides [17]. All calculations were performed at 1.0 atmospheres and 298.15 K with GAUSSIAN 09 quantum chemistry package [18]. The solvent effects of all calculations were on the conditions of without any solvents participation (i.e. in gas phase) and with in ethanol respectively. In the process of structural optimization, tetraethyl ammonium cations and polyiodide/iodide anions were designated as the different molecular fragments. Each

geometry was firstly optimized by B3LYP/3-21G in order to reduce the overall calculation and time. Then the geometries were fully calculated by B3LYP/GenECP with the job type of "opt + freq". The 6-31G (3df, 3pd) basis set was used for C, H and N. Iodine was treated using the effective core potential (ECP) LanL2DZ relativistic procedure. The keyword of every calculation was scf = (maxcycle = 9999, conver = 6).

Results and discussion

General

From Table 1, similar to the literature reported by Migchelsen et al. [12], the iodine content of the first crop in Exp. 1 was determined with the direct iodine quantity method by $Na_2S_2O_3$ [19] corresponding to the formula Et_4NI_3. As can be seen in the Fig. 1, the Raman spectra at room temperature and with 514 nm wavelength, the peaks of the first crop at 108 cm^{-1} (vs), 214 cm^{-1} (w) and 129 cm^{-1} (w) could be assigned to I_3^-. The first crop in Exp. 1 was recrystallized in EtOH/CH_3CN (v/v 1:1) mixed solvents and **1** crystallized with the space group Cmca from the solution. It is noteworthy that, when $n(I_2)$: $n(Et_4NI)$ = 2, the first crop of the reaction is a mixture of brown and black needlelike crystals, which iodine content roughly matched the formula Et_4NI_5 (anal. found: 60.6%, calcd.: 66.4%). Nour et al. [20] characterized that was the Et_4NI_3 and Et_4NI_7 mixture by Raman spectra. Here, the first crop of Exp. 2 was characterized by Raman spectrometer. The peaks at 108 cm^{-1} was assigned to I_3^- and the peaks at 178 cm^{-1} and 355 cm^{-1} could be assigned to I_2. Then we recrystallized the first crop of crystals to precipitate a large amount of black bulk crystals. However, the result of X-ray single crystal diffraction analysis showed they were not Et_4NI_5, but Et_4NI_7 (Cmca). This can be seen as the first direct identification evidence of Et_4NI_5 product. Meanwhile, a small amount of brown stripe crystalline compounds were also deposited concomitant with Et_4NI_7 crystals, and we speculated that was Et_4NI_3.

This was not an isolated phenomenon. Analogously, Blake et al. [21] prepared [Ag([18]aneS$_6$)]I$_5$ unsuccessfully, and they considered that [Ag([18]aneS$_6$)]I$_5$ may automatically converted into other substances. Can the hypothesised reaction of Et_4NI_5 occur as Eq. (1)?

$$2Et_4NI_5 = Et_4NI_3 + Et_4NI_7 \qquad (1)$$

When $n(I_2)$: $n(Et_4NI)$ = 3 (Exp. 3), the product was Et_4NI_7 titrated by $Na_2S_2O_3$. Unlike the Raman spectra of Et_4NI_7 reported by Nour et al.
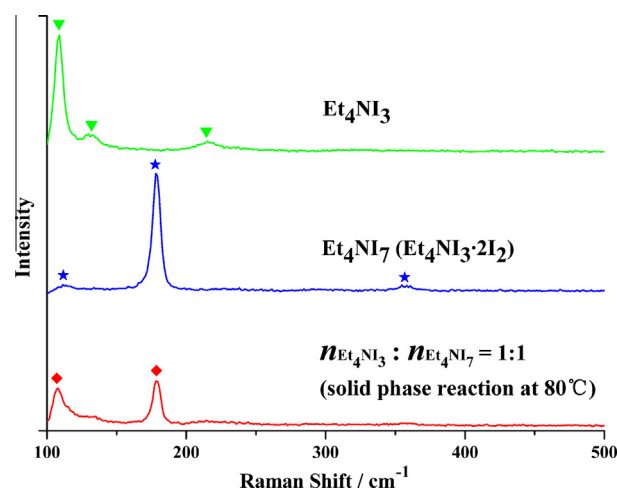

Fig. 1. The Raman spectra of tetraethylammonium polyiodides at 25 °C (λ = 514 nm).

[20], the intensity of the peak at 178 cm^{-1} was much higher than the ones at 108 cm^{-1} and 355 cm^{-1} through the modern instruments. Therefore, according to the results of Raman analysis, the more suitable chemical formula of tetraethylammonium polyiodides should be described as $Et_4NI_3 \cdot nI_2$ (n = 0, 1, 2). When the ratio of $n(I_2)$: $n(Et_4NI) \geqslant 4$ (Exp. 4–6), the polyiodides with more higher polymerization degree such as Et_4NI_9 cannot be prepared. Through titration with sodium thiosulfate, it was found that the iodine contents of the first crops in Exp. 3–6 were almost same. The Raman spectra peaks of these first crops were similar to that found in Exp. 3. These products were redissolved in $EtOH/CH_3CN$ (v/v 1:1) mixture and by slow evaporation at room temperature to give a new polymorph of Et_4NI_7, with space group *Cmca*. In Exp. 8, Tebbe et al. [13] used ethanol in H-type tube by slow diffusion of the reactants to obtain Et_4NI_7 (*Aba2*) and can be regarded as the kinetically stable product. In Exp. 7, we also used ethanol solvent and recrystallization by slow evaporation, obtaining Et_4NI_7 (*Cmca*) product. This can be regarded as the thermodynamically stable product, as same as in $EtOH/CH_3CN$ (v/v 1:1) mixed solvent (Exp. 3). Interestingly, in the structure of Et_4NI_7 (*Cmca*) prepared by different molar ratios, all tetraethyl groups were disordered in a ratio of 0.5 to 0.5 (Fig. 2).

Thermal property

TGA/DTG/DSC measurements were performed for reactant (Et_4NI, Fig. 3(a)) and the first crops of Exp.1 (analyzed by the direct iodine quantity method by $Na_2S_2O_3$, i.e. Et_4NI_3, Fig. 3(b)), Exp. 2 (Fig. 3(b)) and Exp. 3 (analyzed by the direct iodine quantity method by $Na_2S_2O_3$, i.e. Et_4NI_7 ($Et_4NI_3 \cdot 2I_2$), Fig. 3(c)) in the temperature range of 25–800 °C. In Fig. 3(a), there was one platform in the TGA curve of Et_4NI. It began from 237 °C and ended with 326 °C. At 308 °C it reached to the maximum amount of decomposition loss. It can be seen from the TGA curves of tetraethylammonium polyiodides (Fig. 3(b–d)) that with the iodine content increasing, the initial decomposition temperature decreased, while the final decomposition temperatures was all the same (355 °C). The tetraethylammonium polyiodides lost I_2 all together to become Et_4NI_3 firstly and then continued to decompose. This showed that with the increasing of polymerization degree results in the decrease of thermal stability. The initial decomposition temperature (239 °C) of Et_4NI_3 was higher than Et_4NI. Generally, the TGA curve of Et_4NI_3 had only one decomposition platform, but its DTG curve showed

that there were two obvious loss inflection points. Their peaks were 274 °C and 332 °C. Curiously, the total loss in the range of 239–309 °C of the first platform in TGA curve was 70.2%, which was greater than the iodine content of Et_4NI_3 (calcd.: 49.7%). Furthermore, when the temperature was higher than 355 °C, comparing the DSC curve of Fig. 3(b) with Fig. 3(a), Et_4NI_3 had a flat exothermic peak in Fig. 3(b). Putting these phenomena together illustrated that the decomposition of Et_4NI_3 was not a simple process which Et_4NI_3 lost one iodine molecule and then became Et_4NI. In Fig. 3(d), the substance loss in the range of 25–239 °C was 49.3%, which corresponded to the percentage of two iodine molecules in Et_4NI_7 ($Et_4NI_3 \cdot 2I_2$) (calcd.: 49.8%). It should be noted that the experimental iodine content (60.6%) of the first crop in Exp. 2 was less than the calculated value (66.4%). The iodine loss (25.5%) of the first platform was much lower than the percentage of one iodine molecule in Et_4NI_5 ($Et_4NI_3 \cdot I_2$) (calcd.: 33.2%), indicating that the proportion Et_4NI_3 and Et_4NI_7 in the first crop of Exp. 2 was greater than 1:1 (Fig. 3(c)). In other words, according to the hypothesis (Eq. (1)), due to the solubility differences, although the proportion of the product Et_4NI_3 and Et_4NI_7 was 1:1, they were not crystallized out in an equal proportion.

Description of the crystal structures

In Fig. 4, the single-crystal structure of **2** shows the $[Et_4N]^+$ ion is embedded in a three-dimensional polymeric polyiodide matrix. The molecules around center N1 atom are centrosymmetric. The polyiodide component in crystal lattice, with formal stoichiometry I_7^-, can be regarded as some combinations of I_3^- and I_2. Take the relative position of I_3^- and I_2 as an example to illustrate the symmetrical differences between two polymorphs of Et_4NI_7 (Fig. 5). I_3^- in the two polymorphs with minor differences which the bond angle of one is 180° (*Cmca*) and the other is 179° (*Aba2*), and I–I of I_3^- (2.9172(3) Å) in **2** are shorter than the ones (2.9223(10) Å) in Et_4NI_7 (*Aba2*). Clearly, in Fig. 5(a), the bond distances of $I_2 \cdots I_3^-$ are unequal (3.4790(38) Å, 3.4942(38) Å), the angles between I_2 and I_3^- ions (81.037(34)° and 80.498(30)°) are as unequal as their distances. Compared with the polymorph *Aba2*, Fig. 5(b) accompanied by a subtle adjustment, both the bond lengths and bond angles of $I_2 \cdots I_3^-$ in **2** are equal (3.4818(2) Å, 80.700(1)°), leading to a conclusion that polymorph *Cmca* is more symmetrical than polymorph *Aba2*. In **2**, all polyiodide ions wrap tetraethyl ammonium ion and form a distorted cubic box with missing two edges. Meanwhile, the entire structure is stabilized by fourteen pairs of halogen-hydrogen bonds which lengths ranged from 3.3557(2)–3.8839(3) Å (Fig. 4, for clarity, the symmetrical halogen-hydrogen bonds from disorded tetraethyl groups are omitted). The disorded tetraethyl groups, 28 pairs of I···H bonds and the torsion angle (I3A-I2A-I2AA-I3B or I3C-I2C-I2AC-I3BD) of 19.753(57)° are the overall result of the cooperative effects. In the matrix, the distance of I3AD···I3A is equal to I3AD···I3AC (7.3706(5) Å). This gap cannot be stuffed into one iodine molecule (I–I 2.715 Å [22] plus twice the van der Waals radius of iodine (2.2 Å), making 7.1115 Å). So the $[Et_4N]^+$ cation makes the fullest use of I_2 and I_3^- in order to enwrap the $[Et_4N]^+$ cation.

As the experiment shows, **1** has lower iodine saturation. Once the molar ratio of the cation to iodine is higher than that of the tri-iodide forms, system tends to form one of the more steady-state polymerization degrees. The polyiodide anions around N cation to form optimal static equilibrium, seems like four ethyl "shuttle" in the polyiodide-box which "encapsulate" the tetraethylammonium cation. This phenomenon can also be considered as a separately second-coordination of polyiodide anions around center N cation [23], which the chemical nature of these effect are Coulombic potential energy and strongest halogen bonds (such as I···I or I···H interactions).
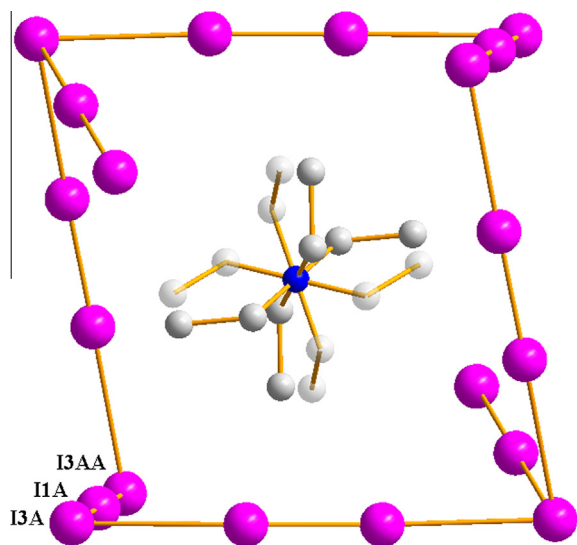

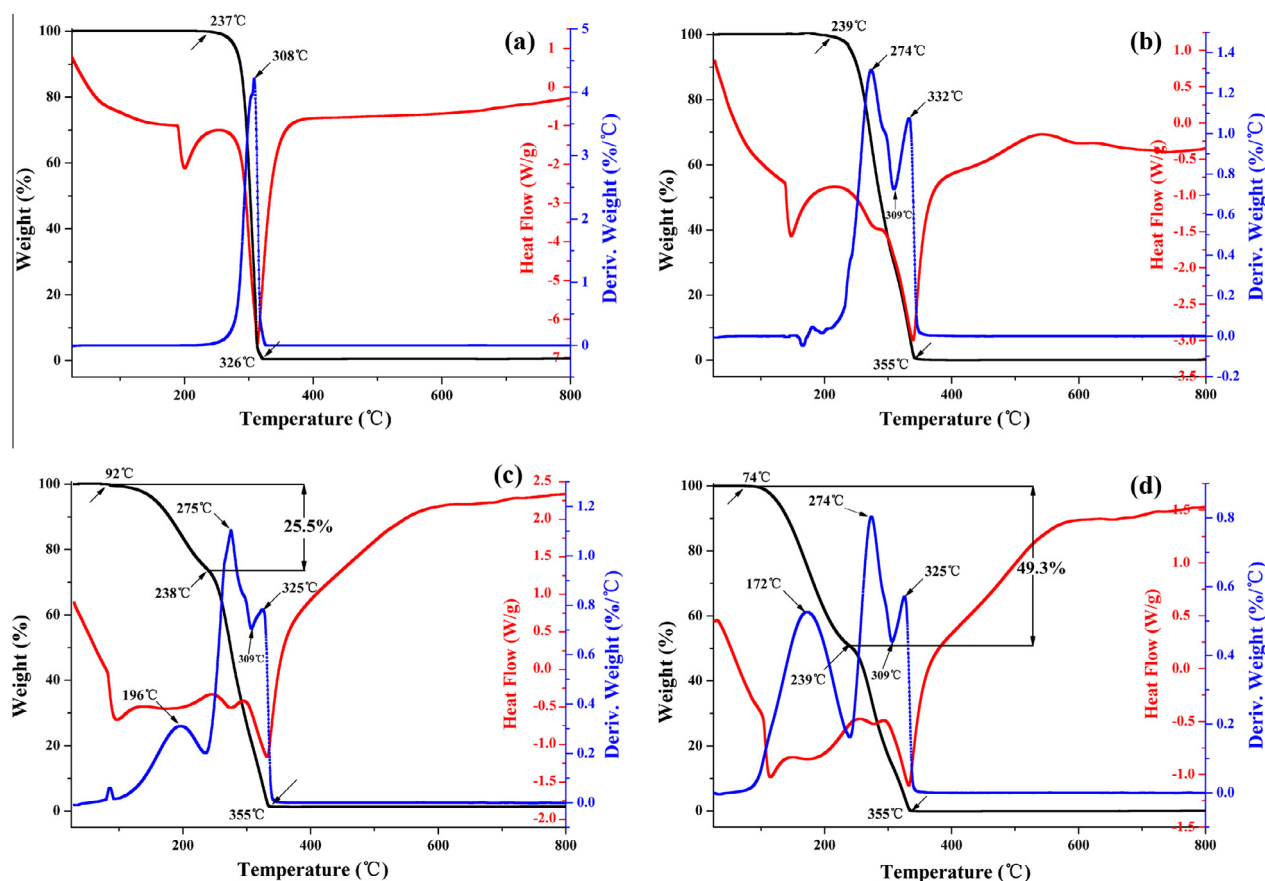**Fig. 2.** The disordering of $[Et_4N]^+$ in polyanion matrix.

Fig. 3. The TG (black)/DTG (blue)/DSC (red) spectra of (a) Et_4NI, the first crops of (b) Exp.1, (c) Exp. 2 and (d) Exp. 3. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
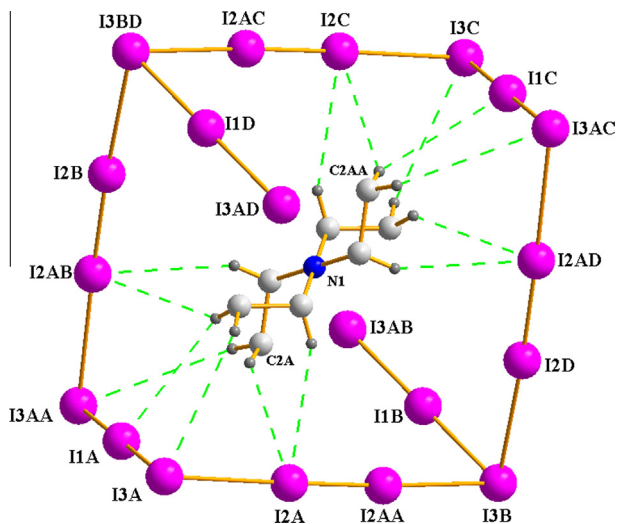

Fig. 4. View of the $[Et_4N]^+$ cation is wrapped by polyiodide ions in Et_4NI_7 (*Cmca*), the green dashed lines are the hydrogen bonds between polyanion and cation (disordered tetraethyl groups omitted for clarity). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Theoretical studies on polyiodides

Geometry optimization and energy calculations

$Et_4NI_3^*$ We optimized the tetraethylammonium triiodide structure with the linear I_3^- as initial configuration, the $Et_4NI_3^*$ (the symbol * denotes optimized structures to distinguish with

the ones from experiments) was obtained (Fig. 6(a)). Compared with **1**, $Et_4NI_3^*$ containing an asymmetric I_3^-, and three iodine atoms are arranged approximately 172.3°, while the three iodine atoms of **1** is 180°. The energy values and the standard Gibbs free energy of optimized species are presented in Tables 2 and 3 as below.

$Et_4NI_5^*$ Then we constructed tetraethylammonium pentaiodide with linear and V-shaped configuration as initial geometries, what is surprising is that they eventually get a V-shaped $Et_4NI_5^*$ (Fig. 6(b)). I_5^- in $Et_4NI_5^*$ can be seen as two iodine molecules (I1-I2, I4-I5) combining with an iodide ion (I3) which forms two arms of an approximately straight line, and the angle between the arms is about rectangular ($\angle I2–I3–I4 = 92.5°$).

$Et_4NI_7(P)^*$ and $Et_4NI_7(L)^*$ Finally on the basis of $Et_4NI_5^*$, we constructed two configurations of $Et_4NI_7^*$. One is the three iodine molecules sharing one iodide ion, after optimization and pyramidal $Et_4NI_7(P)^*$ was obtained (Fig. 6(c)). The angles between three arms are approach to right. The other is the linear initial configuration, after optimization get $Et_4NI_7(L)^*$ (Fig. 6(d)). The I_7^- in $Et_4NI_7(L)^*$ can be regarded as the two ends of a I_3^- (I3–I4–I5) connecting molecular iodine (I1–I2, I6–I7). It is interesting that we can see two types of I_7^- from Fig. 3, however, compare the energy of optimized structure (Tables 2 and 3), $E(Et_4NI_7(P)^*) > E(Et_4NI_7(L)^*)$, indicates the linear- I_7^- is more stable.

Possible mechanism of tetraethylammonium polyiodides formation

As can be observed in Table 2, the energy of all the optimized polyiodides structures mentioned above was lower than that of the sum of corresponding ammonium iodide and iodine as reactants ($E(Et_4NI_{2n+1}) < E(Et_4NI) + nE(I_2)$, $n = 1, 2, 3$). With polymerization degree increases, single point energy (E) of these optimized

(a) Polymorph *Aba2*
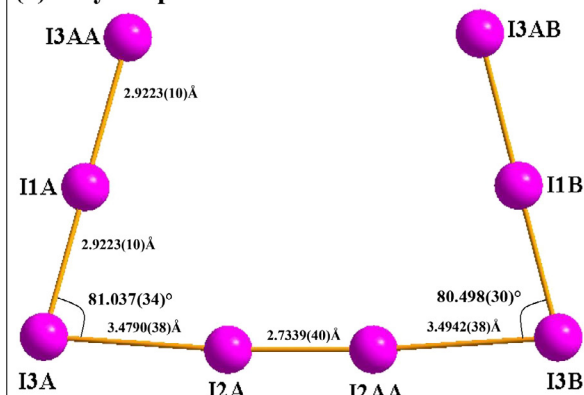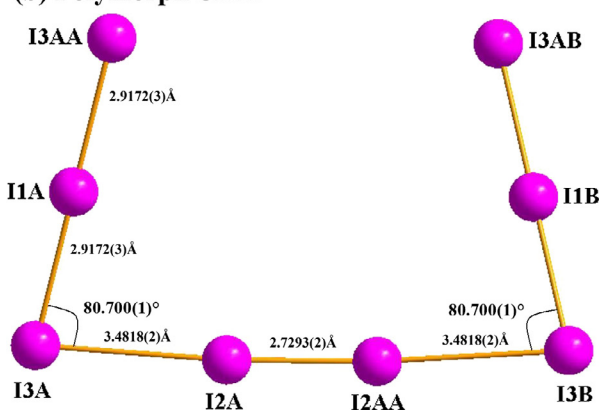

(b) Polymorph *Cmca*

Fig. 5. View of the difference in the relative position between (a) Et$_4$NI$_7$ (*Aba2*) and (b) Et$_4$NI$_7$ (*Cmca*).
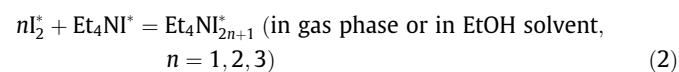
Table 2
Energy (E) and Gibbs free energy (G^θ) for optimized structures of separated tetraethylammonium polyiodides molecules with no solvents.

Molecular formula	E (kcal/mol)	$^a E'/I_2$ (kcal/mol)	G^θ (kcal/mol)
I$_2^*$	−14288.010417	–	−14304.040147
Et$_4$NI*	−240370.403029	–	−240223.062543
Et$_4$NI$_3^*$	−254687.772105	−14317.369076	−254547.223782
Et$_4$NI$_5^*$	−268994.255146	−14311.926059	−268859.577175
Et$_4$NI$_7$(P)*	−283287.807727	−14305.801566	−283160.783489
Et$_4$NI$_7$(L)*	−283289.082826	−14306.226390	−283161.619959

^{a} $E' = [E(\text{Et}_4\text{NI}_{2n+1}^*) - E(\text{Et}_4\text{NI}^*)]/n, n = 1, 2, 3.$

structures gradually decreased. However, average energy E' (E' is the average energy of two iodine atoms in the polyiodides, which can be regarded as the average energy of one iodine molecule in the polyiodides) of I$_2$ molecules in every tetraethylammonium polyiodide from Et$_4$NI$_3^*$ (E' = −14317.369076 kcal/mol) to Et$_4$NI$_7$(L)* (E' = −14306.226390 kcal/mol) increases with the polymerization degree increases, which suggest that the increase in the E' with successive addition of I$_2$ is obviously decreased. Therefore, much larger polyiodides formation of this type may not be impossible. These regularities are the same as the results of simulations of polyiodides ions in aqueous solution [24]. The similar trends of E(EtOH solvent) and E'(EtOH solvent) of polyiodides which calculated in ethanol solution can be seen in Table 3.

The possibility of related Eqs. (2)–(10) examined through the Gibbs free energy data in the tables, which G^θ and G^θ (EtOH solvent) of the polyiodides isomers adopted the ones of optimized geometries with its lowest single point energy.

$$nI_2^* + \text{Et}_4\text{NI}^* = \text{Et}_4\text{NI}_{2n+1}^* \text{ (in gas phase or in EtOH solvent,}$$
$$n = 1, 2, 3) \tag{2}$$
$$\Delta_r G_m^\theta (2) < 0$$
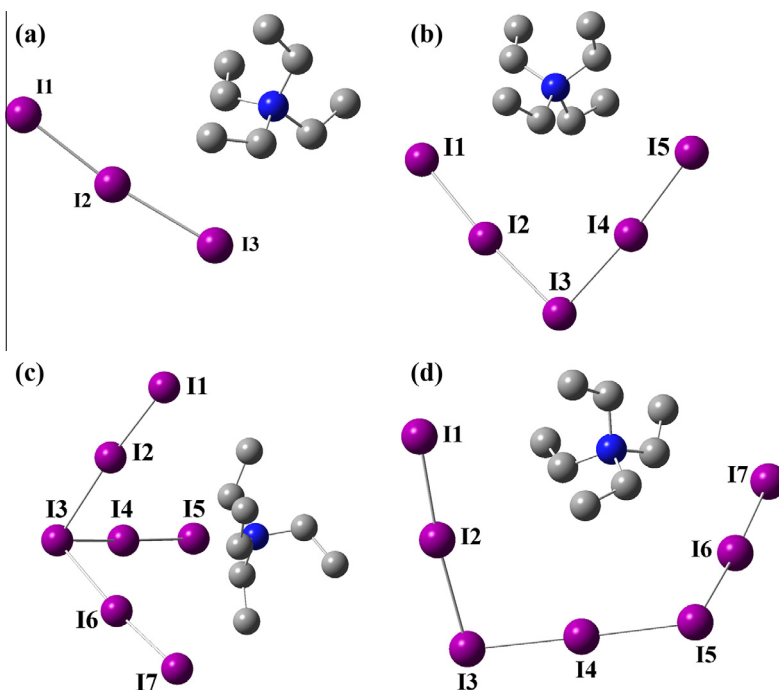
Fig. 6. Optimized structures of (a) Et$_4$NI$_3^*$, (b) Et$_4$NI$_5^*$, (c) Et$_4$NI$_7$(P)* and (d) Et$_4$NI$_7$(L)*. The optimization was done at the B3LYP/6-31G (3df, 3pd)/(ECP) LanL2DZ level by using the Gaussian 09 series of programs. All hydrogen atoms of tetraethyl groups omitted for clarity.

Table 3
Energy (E(EtOH solvent)) and Gibbs free energy (G^0 (EtOH solvent)) for optimized structures of separated tetraethylammonium polyiodides molecules in EtOH solvent.

Molecular formula	E (EtOH solvent) (kcal/mol)	[a]E' (EtOH solvent)/I_2 (kcal/mol)	G^0 (EtOH solvent) (kcal/mol)
I_2^*(EtOH solvent)	−14289.172564	–	−14305.205432
Et_4NI^*(EtOH solvent)	−240399.966256	–	−240253.918440
$Et_4NI_3^*$(EtOH solvent)	−254710.921558	−14310.955302	−254571.618841
$Et_4NI_5^*$(EtOH solvent)	−269009.696273	−14304.864694	−268876.996839
$Et_4NI_7(P)^*$(EtOH solvent)	−283304.579801	−14301.537639	−283180.749586
$Et_4NI_7(L)^*$(EtOH solvent)	−283305.374855	−14301.803075	−283178.998207

[a] E'(EtOH solvent) = $[E(Et_4NI_{2n+1}^*$(EtOH solvent)) − $E(Et_4NI^*$(EtOH solvent))$]/n, n = 1, 2, 3.$

$$nI_2^* + Et_4NI_3^* = Et_4NI_{2n+3}^* \text{ (in gas phase, } n = 1, 2; \text{ in EtOH solvent,}$$
$$n = 1) \tag{3}$$
$$\Delta_r G_m^\theta \ (3) < 0$$

$$I_2^* + Et_4NI_{2n+1}^* = Et_4NI_{2n+3}^* \text{ (in gas phase or in EtOH solvent,}$$
$$n = 1, 2) \tag{4}$$
$$\Delta_r G_m^\theta \ (4) < 0$$
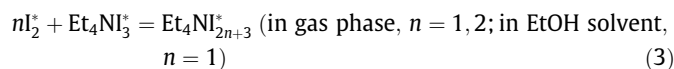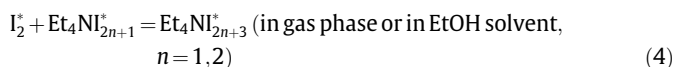
$$2Et_4NI_3^* = Et_4NI_5^* + Et_4NI^*$$
$$\Delta_r G_m^\theta \ (5) = 11.807846 \text{ kcal/mol} > 0 \tag{5}$$

$$3Et_4NI_3^* = Et_4NI_7(L)^* + 2Et_4NI^*$$
$$\Delta_r G_m^\theta \ (6) = 33.926301 \text{ kcal/mol} > 0 \tag{6}$$

$$2Et_4NI_3^*(\text{EtOH solvent}) = Et_4NI_5^*(\text{EtOH solvent}) + Et_4NI^*$$
$$(\text{EtOH solvent}) \tag{7}$$
$$\Delta_r G_m^\theta \ (7) = 12.322403 \text{ kcal/mol} > 0$$
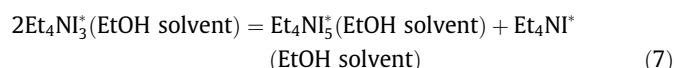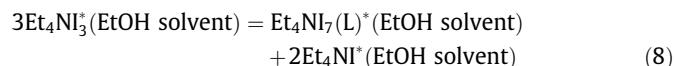
$$3Et_4NI_3^*(\text{EtOH solvent}) = Et_4NI_7(L)^*(\text{EtOH solvent})$$
$$+ 2Et_4NI^*(\text{EtOH solvent}) \tag{8}$$
$$\Delta_r G_m^\theta \ (8) = 28.021436 \text{ kcal/mol} > 0$$

Both in the absence of solvents and in ethanol, all tetraethyl polyiodides can be prepared by nI_2^*, Et_4NI^* or nI_2^*, $Et_4NI_3^*$ in gas phase directly (Eqs. (2), (3)). However, neither in the absence of solvents nor in ethanol Et_4NI_7 can be prepared by polyiodides with lower polymerization degree ($Et_4NI_5^*$) and I_2^* (Eq. (4)). Unlike the reversibly disproportionation reaction of I_3^- ($(n + 1)$ $I_3^- = I_3(I_2)_n^- + nI^-$) to prepare polyiodides reported by Svensson and Kloo [25], the Gibbs free energy changes of Eqs. (5)–(8) indicate that $Et_4NI_5^*$ and $Et_4NI_7^*$ cannot be formed by the disproportionation of $Et_4NI_3^*$ directly.

In Exp. 2, when the ratio of reactants $n(I_2)$: $n(Et_4NI) = 2$, the product was prepared in accordance with the stoichiometric ratio of Et_4NI_5 can be obtained, but the actual solid were a mixture of Et_4NI_3 and Et_4NI_7.

$$2Et_4NI_5^* = Et_4NI_3^* + Et_4NI_7(L)^* \quad \Delta_r G_m^\theta \ (9)$$
$$= 10.310609 \text{ kcal/mol} > 0 \tag{9}$$
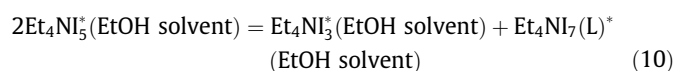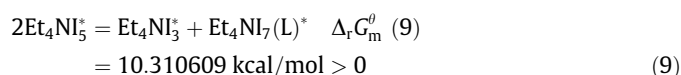
$$2Et_4NI_5^*(\text{EtOH solvent}) = Et_4NI_3^*(\text{EtOH solvent}) + Et_4NI_7(L)^*$$
$$(\text{EtOH solvent}) \tag{10}$$
$$\Delta_r G_m^\theta \ (10) = 3.37663 \text{ kcal/mol} > 0$$

It is can be seen from the $\Delta_r G_m^\theta$ of Eqs. (2)–(10) that the solvent effects have a certain influence on the reactions. Some polyiodide species (Et_4NI_7 in Eq. (3)) cannot form from the solutions. In the absence of solvents, the calculation of reaction 9 show that $\Delta_r G_m^\theta$ of the reaction is 10.310609 kcal/mol, the reaction 9 cannot occur. The $\Delta_r G_m^\theta$ of the reaction 10 is greater than zero unexpectedly. That is to say, Et_4NI_3 and Et_4NI_7 do not come from the spontaneous decomposition of Et_4NI_5 in EtOH solvent. Through the Eqs. (9) and (10), we can conclude that either in the gas phase and in ethanol

solvent, Et_4NI_5 exists in theory, while it can be prepared by I_2 and Et_4NI at molar ratio 2:1 or the disproportionation reaction of Et_4NI_3 and Et_4NI_7 spontaneously. This also explains the experiments whose product was accordance with the stoichiometric ratio of Et_4NI_5.

In order to reduce the solvent effects and investgate the possibility of existence of the reaction 1 in the solid state reaction, we designed Exp. 9 and Exp.10. In Exp. 9, Et_4NI_3 and Et_4NI_7 did not reach the melting point at 80 °C, the color of the reaction mixture changed from brown to dark brown with the increase of both heating temperature and time. The Raman spectra showed that the ratio of the intensity at 108 cm^{-1} and 178 cm^{-1} of the product was between Et_4NI_3 and Et_4NI_7 ($Et_4NI_3 \cdot 2I_2$) (Fig. 1). We consider that the iodine molecules in the entire reaction system tended to distributed uniformly, due to the reason that the iodine molecules with weak bonding in Et_4NI_7 came off and gradually diffused to Et_4NI_3 molecule lattices. Therefore, the resulting product of Exp. 9 was Et_4NI_5 ($Et_4NI_3 \cdot I_2$). In Exp. 10, at high temperature, Et_4NI_3 and Et_4NI_7 ($Et_4NI_3 \cdot 2I_2$) with the molar ratio 1:1 formed molten liquid (we can regard I_2 itself as the solvent) whose stoichiometric equation was Et_4NI_5 ($Et_4NI_3 \cdot I_2$). After cooling to room temperature, a mixture of brown and black particles observed under the microscope was obtained. Meanwhile, Raman tests confirmed the two components of the product were Et_4NI_3 and Et_4NI_7 ($Et_4NI_3 \cdot 2I_2$). This also indicated that the reverse reaction of Eq. (1) through the molten state cannot occur.

To further explore the component change rules of tetraethylammonium polyiodides in the absence of solvents and at various temperatures, we designed Exp. 11. The mixture of Et_4NI_3 and Et_4NI_7 with the molar ratio 1:1 was characterized by variable temperature Raman Spectrometer (Fig. 7). Since HR800 Laser Confocal Microprobe Raman Spectrometer did not equip 514 nm wavelength laser, in order to facilitate comparison, we chose 532 nm which was relatively close to 514 nm to be served as the test wavelength. Fig. 7(a) was the Raman spectra of Et_4NI_3 and Et_4NI_7 ($Et_4NI_3 \cdot 2I_2$) at room temperature at 532 nm. Compared with Fig. 1, their absorption peak positions and relative intensities were consistent with the one characterized at 514 nm. Fig. 7(b) was the Raman spectra change chart of the mixture from −25 °C to 150 °C. At −25 °C, the mixture had three peaks, which 108 cm^{-1} (vs) and 211 cm^{-1} (w) were assigned to I_3^-, while 179 cm^{-1} (w) was assigned to I_2. When the temperature rose to 50 °C, I_2 vibration peak at 179 cm^{-1} disappeared due to the diffusion of iodine into the capillary. When the temperature rose to 80 °C, a new weak peak emerged at 423 cm^{-1}, which could be assigned to double frequency vibration peak of 211 cm^{-1}. At 150 °C, the mixture became molten liquid, the intensity of 423 cm^{-1} strengthened to a maximum, the peak intensity of 108 cm^{-1} reduced to a minimum, while a new peak appeared at 163 cm^{-1} which was assigned to the discrete I_5^- [20,26]. This was the result that the disproportionation of Et_4NI_3 according to Eq. (5).

It is a fundamental in inorganic ionic crystals that small cations tend to fill smaller interstices or [27], in other words, large anions fill smaller interstices surrounding cations to the maximum extent
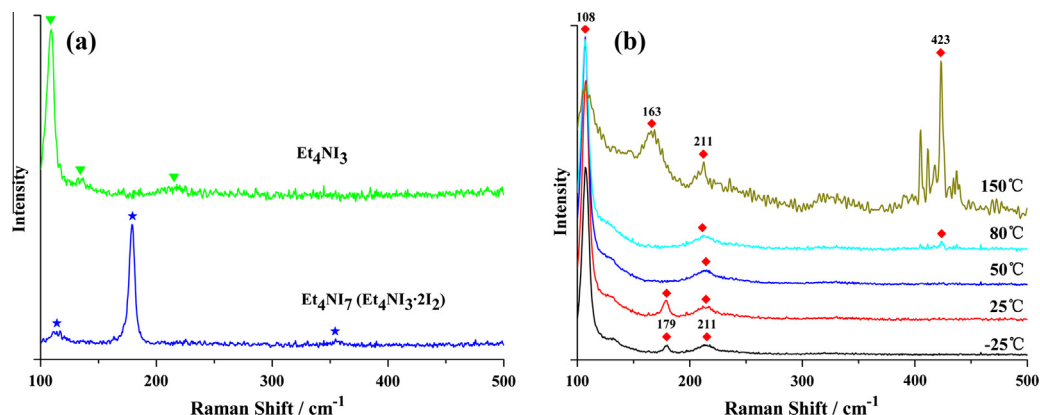
Fig. 7. The Raman spectra of (a) Et_4NI_3 and Et_4NI_7 ($Et_4NI_3·2I_2$) at room temperature and (b) the mixture of Et_4NI_3 and Et_4NI_7 ($Et_4NI_3·2I_2$) with the molar ratio 1:1 in a sealed capillary. (λ = 532 nm).

possible if space permits, due to the lower Coulombic potential energy in such interstices. As the reaction ratio increases, the iodine content of products is bound to a constant value.

From what have been discussed above, the reaction in solution and the solid crystallization from solution are two different processes. The components change of the product in Exp. 2 from Et_4NI_5 in EtOH solvent to the mixture of Et_4NI_3 and Et_4NI_7 solids occurred in the crystallization process. In other words, the crystallization of tetraethylammonium polyiodides is an independent self-assembling process. What species of polyiodides crystallized from the solutions is both decided by $\Delta_r G_m$ of the reactions and by Coulombic potential energy of the polyiodide crystals. The solution of polyiodide with stoichiometric ratio of Et_4NI_5 crystalized into a mixtures of Et_4NI_3 crystals with the lowest E' and Et_4NI_7 crystals with lower Coulombic potential energy. When the ratio of reactants $n(I_2)$: $n(Et_4NI) > 2$, then the reaction solutions were only precipitated Et_4NI_7 crystals, whose tetraethylammonium cation was completely wrapped by polyiodide anions with the highest iodine content and the minimum Coulombic potential energy. Moreover, our future work will focus on the theoretical calculations of solid phase structures of polyiodide compounds such as Eq. (11) (l: liquid; s: solid;).

$$2Et_4NI_5(l) = Et_4NI_3(s) + Et_4NI_7(s) \qquad (11)$$
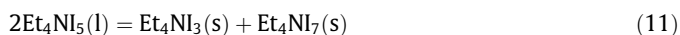
Discussion of the stable polyiodides formation

According to the formation mechanism of tetraethylammonium polyiodides above mentioned, the general formation mechanism of polyiodides will be discussed below. Polyiodides formation are mainly based on $\Delta_r G_m$ of the reactions, stable polyiodide solids are anions attract around the cations as much as possible to form position balanced "ion pairs". It can be inferred that: the reaction system may forms some metastable polyiodides with different polymerization degrees, due to steric hindrance, the minimum electrostatic potential and other reasons, some metastable polyiodide crystals cannot be formed directly such as Et_4NI_5. However, two types of stable polyiodides will be formed after recrystallization. One is when $n(I_2)$: $n(I^-) \leqslant 1$ in the reaction system, the iodine and iodide ions can form stable oligomeric polyiodides, such as I_3^-; alternatively, when the system $n(I_2)$: $n(I^-) \geqslant 2$, basing on $\Delta_r G_m$, the formed I_3^- and the excess involved iodine atoms preferentially in tend to form a number of high polymerization degree polyiodides which encapsulate the cations (the specific number may largely depend on structural complementarity of the interacting charged moieties). So it will cause the following similar scenario: polyiodide with a much higher polymerization degree may decompose into a mixture of relatively stable oligomeric states by recrystallization;

if the amount of I_3^- through the process of re-oligomerization is remaining, I_3^- will be co-crystallized with the mixture of relatively stable oligomeric states. For example, FcI_3 (Fc^+: ferrocenium ion) and I_2 can synthesize Fc_3I_{29}, while after recrystallization, only FcI_7 or FcI_{16} were precipitated [8]. If a larger excess of I_2 reacted with Me_4NI in alcohol solution and Me_4NI_9 precipitated, while a small excess yielded some Me_4NI_3 [5]. Indeed, metastable polyiodides from the first crop through recrystallization can disproportionation for these two types of the stabilized polyiodides in different proportions instantaneously. Polyiodides with different polymerization degrees have solubility difference, after recrystallization, the metastable polyiodides with high solubility general remain in the solution, and relatively stable polyiodides will be crystallized. This is because the template effect of the cation and second-sphere coordination of the polyiodide anions that can form stable polyiodides have relatively symmetrical structures with the poor solubility in the solvent. After repeat recrystallization, the final product have constant polymerization degree and the polyiodide ions completely "encapsulate" the counter-ions, which is controlled by a process akin to Ostwald's rule [28]. Therefore, the limit of the polymerization degree in polyiodides is associated with the geometry morphology and charge distribution of counter-ion, the highest polymerization degree of stable polyiodides has the maximum iodine content which encapsulates the counter-ion completely.

Conclusion

The experimental and theoretical results show that not each polyiodide specimen with various polymerization degrees can be synthesized by changing molar ratios of reactants in solvents. In the case of tetraethylammonium polyiodides which prepared with different molar ratios of reactants, the products were analyzed by Raman spectra and titration, only two stable structures, Et_4NI_3 (*Cmca*) and Et_4NI_7 (*Cmca*), were isolated by recrystallization of slow evaporating solvent(s). The structure optimization and frequency calculation of the tetraethylammonium polyiodides were calculated by density functional theory. With iodine content increases, single point energy (E) of the optimized structures gradually decreased, while average energy E' of I_2 molecules in the polyiodides increases. That is to say the greater the polymerization degree is, the lower the stability of the polyiodide has. The possible mechanism of tetraethylammonium polyiodides formation are as follows: either in the absence of solvents or in ethanol solvent, Et_4NI_5 can also be formed, the components change of the product in Exp. 2 from Et_4NI_5 in EtOH solvent to the mixture of Et_4NI_3 and Et_4NI_7 solids occurred in the crystallization process instantaneously and self-assembley; what is more, according to the Raman spectra of the products prepared by solid phase synthesis, Et_4NI_5

could be prepared by Et_4NI_3 and Et_4NI_7 with the molar ratio of 1:1 at 80 °C, while at the same ratio, compared with the starting material, there were not any Raman spectra changes after the molten liquid cooled to room temperature; furthermore, the solid synthesis of Et_4NI_5 was characterized by variable temperature (-25 °C $\sim$ 150 °C) Raman Spectrometer as well, the polyiodide components interconversion showed that the peak intensity of 108 cm^{-1} which assigned to I_3^- reduced and the discrete I_5^- formed in molten state; what species of polyiodides crystallized from reactions in solutions are decided by the synergy between $\Delta_r G_m$ of reactions and Coulombic interactions etc. of polyiodide crystals.

Acknowledgements

Appendix A. Supplementary material

Tables of selected bond lengths, bond angles, crystal data and structure refinement, as well as X-ray crystallographic files in CIF format for two compounds **1** and **2** are available in supporting material section. The CCDC reference numbers are CCDC 902957 for **1** and 902958 for **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2014.05.062.

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