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Isolation of methylammonium room temperature reactive polyiodide melt into a new starch complex

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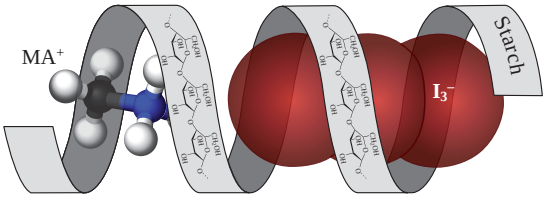
Recently discovered room temperature methylammonium reactive polyiodide melts (RPM) known as perspective precursors for hybrid perovskite solar cells were completely isolated for the first time into a new RPM–starch complex. This complex is of interest both for the study of polyiodide structure and the development of a new and scalable technology of hybrid perovskite synthesis as a photoactive material for perovskite solar cells.



Polyiodides are attracting permanent interest due to a great diversity of their chemical structures and properties.[1] In particular, recent trends in the research and development activity in this field are closely related to new ionic liquids and, more importantly, to the discovery and operation of the first generation of inexpensive Graetzel type solar cells. Recently, a new wave of interest to polyiodides has arisen due to the discovery of highly-reactive polyiodide melts (RPM) based on $MeNH_3I$ (MAI) and I_2.[2] This RPM turned out to be a new effective precursor for a direct synthesis of hybrid organic-inorganic lead halide perovskite $MeNH_3PbI_3$ (MAPI) widely used as a revolutionary light-absorbing material in solar cells.[3,4] MAI–I_2 RPM is a dark brown liquid formed from MAI and I_2 powders at room temperature. Liquid phase boundaries were found to be inside the MAI : I_2 ratio from 1 : 1 (MAI_3) to 1 : 3 (MAI_7).[2] Along with the change of MAI : I_2 ratio, the polyiodide structure, such as polyiodide chain length (I_3^-, I_5^-, or I_7^-) of RPM is also expected to vary.

In order to either provide a more precise analysis of the MAI–nI_2 structure or prepare new potential precursors for lead conversion into MAPI, MAI_3 and MAI_5 (MAI : I_2 ratio of 1 : 2), RPMs were intercalated into starch, which has a well-known capability of forming stable complexes with iodine molecules and polyiodide ions.[5] According to published data, polyiodide I_n^- (n = 3, 5, *etc.*) ions could be intercalated inside amylose helixes in the form of linear chains parallel to the helical axis or random associates with amylopectin branches stabilized by hydrogen bonds.[6,7] This feature of starch can be used in different ways including fundamental investigations of RPM–starch complex structure, analytical chemistry, and, still hypothetically, for the development of potentially new and scalable technologies of perovskite synthesis *via* RPM.

MAI_3–starch and MAI_5–starch complexes were prepared by direct mixing of liquid RPMs with an excessive amount of starch resulted in brown dry powders. Interestingly, no additional solvents were needed for the reaction between the starch and RPM. This is a rare example of such a kind. The I_2–starch complex was prepared by mixing iodine solution in isopropanol with aqueous suspension of starch. The prepared complexes were dried at room temperature. RPM–starch complexes and all the precursors (MAI, I_2, starch, MAI_3, MAI_5, I_2–starch) were studied by X-ray powder diffraction (XRD), UV-VIS optical absorption, and Raman spectroscopy.

According to the XRD pattern in Figure 1(*b*), there was no significant amount of any crystalline phase such as MAI or I_2 in the mixture of starch and MAI_3. Starch is a quite usual admixture in XRD allowing one to increase the volume of analyzed powder mixtures since it is transparent for XRD and gives no substantial background in such experiments. Therefore, the absence of XRD pattern indicated that both polyiodide ions and methylammonium cations (MA^+) were completely intercalated by starch forming the new XRD-amorphous RPM–starch complex. The possible structure of RPM–starch complex is shown in Figure 1(*a*) where I_3^- (or probably I_5^-) anions associated with MA^+ cations are embedded into amylose helixes in the form of linear pairs parallel to the helical axis. Since MA^+ has an even smaller size than I_3^- (3.6 *vs.* 4.12 Å), intercalation of MA^+ into amylose helixes is

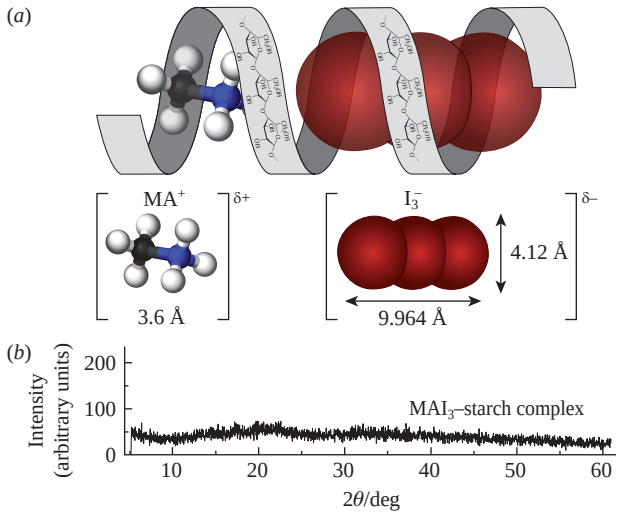


Figure 1 (*a*) Amylose helix in starch and a possible model of the MAI_3–starch complex; (*b*) XRD pattern of MAI_3–starch complex demonstrates the absence of ordered structures.

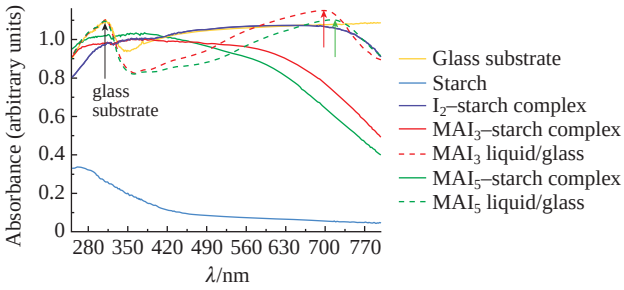


Figure 2 UV-VIS absorption spectra of the MAI_3–starch and MAI_5–starch complexes compared with absorption of the liquid MAI_3 and MAI_5 polyiodide melts.

highly expected to compensate the negative charge of polyiodide anions. At the same time, hydrogen bonds are expected to be an additional driving force for such a process since the MA^+ cation also contains hydrogen atoms and is positively charged.

More details about the structure of RPM–starch complexes were provided by spectroscopic studies (Figures 2–4). According to UV-VIS absorption spectra of both liquid MAI_3 and MAI_5 RPMs, as well as dry powders of MAI_3–starch and MAI_5–starch complexes, the change in optical properties of polyiodide melts was observed (see Figure 2). While liquid RPMs showed wide absorption maxima at about 700 nm (MAI_3) and 720 nm (MAI_5) as would be connected with iodine molecules solvating triiodide ions and MA^+ cations, RPM–starch complexes did not demonstrate such maxima. This difference can be possibly explained by shortening polyiodide/polyiodine chains embedded inside helixes in the latter case as compared with polyiodide chains in the liquid RPM. According to the published data, the length of amylose/amylopectin helixes depends on the degree of polymerization and defines the potential length of polyiodide/polyiodine chains which could be intercalated inside the helixes.[8] One more possible reason for the absence of any absorbance

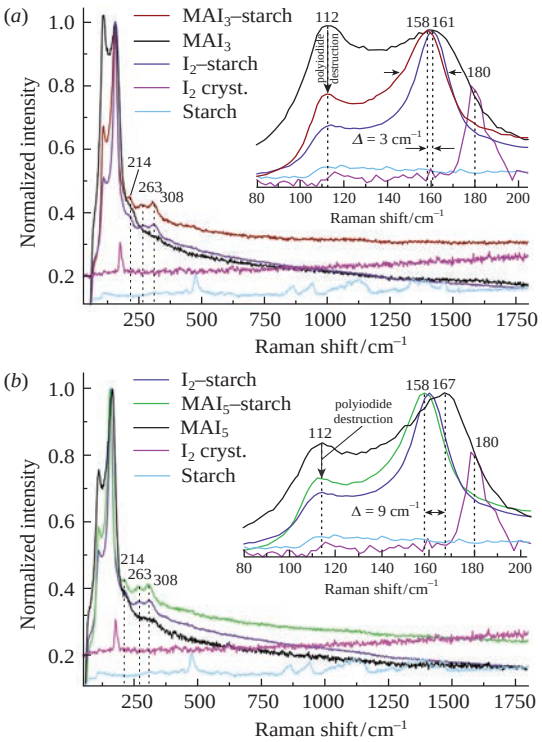


Figure 3 Raman spectra of precursors and (*a*) MAI_3–starch and (*b*) MAI_5–starch complexes in comparison with liquid MAI_3 and MAI_5 RPMs. The insets show the enlarged low-frequency regions; the intensity of starch and I_2 lines in both insets was increased for better visualization. All the spectra were recorded with 633 nm laser beam.

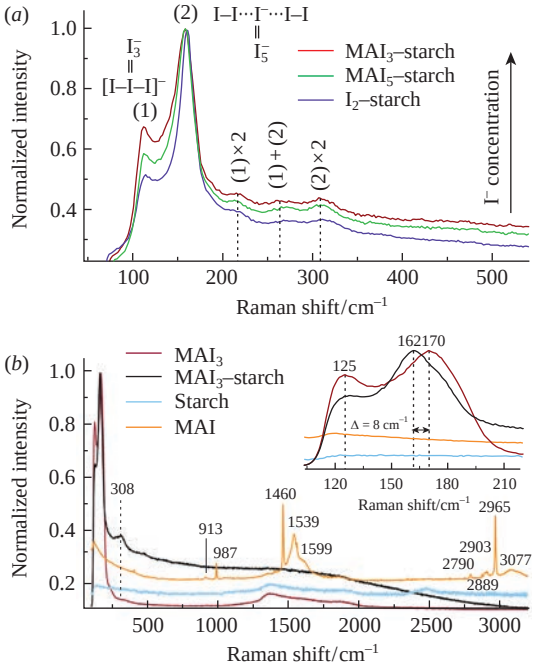


Figure 4 (*a*) A part of Raman spectra of I_2–starch, MAI_3–starch, and MAI_5–starch complexes with assigned vibration modes in a high-energy region; (*b*) Raman spectrum of MAI_3–starch complex and its precursors recorded using infrared 785 nm laser beam. Inset shows enlarged 105–215 cm^{-1} region of the initial spectrum.

maximum is a variable amount of amylose–RPM and amylopectin–RPM complexes which are known to reveal absorption peaks at different wavelengths, and also different forms and intensity of peaks.[9–11] To further clarify the complex structure, an investigation of characteristic vibration states of the molecules using Raman spectroscopy was needed.

Figure 3 shows Raman spectra of MAI_3 and MAI_5 systems. In both cases, intensive lines in the high-energy region for liquid RPMs, RPM–starch and I_2–starch complexes indicating strong vibration modes of polyiodide ions are observed. Two most intensive peaks at 112 and 158 cm^{-1} are commonly assigned to polyiodide I_3^- and I_5^- species, respectively [see Figure 4(*a*)].[1,12] Less intensive peaks at 208, 263, and 308 cm^{-1} are considered to be overtones of the intensive 112 and 158 cm^{-1} peaks [see Figures 3 and 4(*a*)]. Comparing MAI_3 and MAI_5 systems, one can see notable difference in the relative intensities of I_3^- peak (112 cm^{-1}) in liquid RPMs indicating the difference in I_2 and I^- concentrations. Indeed, I_3^- ion concentration in liquid MAI_3 with the $I^-:I_2$ ratio of 1:1 is much higher than that in MAI_5 RPM where $I^-:I_2$ ratio is 1:2, and I_5^- ion is in excess or solvating iodine is present as noted.[1] One significant feature observed during RPM–starch complex formation is a decreasing of the I_3^- peak intensity in both the systems (see Figure 3). This points out the I_3^- polyiodide ion destruction into I^- and I_2 components during RPM intercalation into amylose or amylopectin helixes. We propose that I^- anion electrostatically couples with the MA^+ cation inside helix while I_2 forms together with other I_2 molecules and deficient I^- ions infinite $[I_5^-]_n$ chains which are also intercalated inside the helixes. Actually, the I_3^- ion does not disappear completely during RPM–starch complex formation so relatively weak I_3^- peaks can still be detected in Raman spectra. Furthermore, a small amount of I_3^- ions was also present in the I_2–starch complex despite the fact that this complex was prepared without KI or NaI addition. This can be explained by partial oxidation of isopropanol, used in the I_2–starch preparation procedure, to acetone by I_2 according to reaction (1).[13]

$$Me_2CHOH + I_2 = HI + I^- + Me_2C{=}O \qquad (1)$$

Comparing Raman spectra of starch complexes, one can see a gradual I_3^- peak intensity weakening in the row MAI_3^- > MAI_5^- > > I_2–starch indicating the decrease of I_3^- concentration, which is in agreement with the previous discussion [see Figure 4(*a*)].

The other characteristic features in Raman spectra of both the systems are a notable narrowing of the second peak (158 cm^{-1}) and the growth of its intensity after intercalation of liquid RPM into amylose/amylopectin helixes (see Figure 3). It can be caused by the decrease in the extent of polyiodide species freedom in rigid amylose helixes as compared to liquid RPM where random iodine molecules solvate triiodide ions. The I–I bond length can hardly vary inside a rigid amylose helix but can easily be changed due to I_2 interaction with ions in the liquid RPM. This usually leads to Raman modes widening for such disordered systems. It is also worth pointing out that widths of solid I_2 and I_2–starch powder Raman peaks are almost the same as well as those of RPM–starch complexes.

For the peaks of I_5^- (158–167 cm^{-1}), one can also observe a notable shift to lower frequencies for RPM–starch complexes in comparison with liquid RPMs. Interestingly, while the value of this shift is small for the MAI_3 system (3 cm^{-1}), for the MAI_5 system, it increases up to 9 cm^{-1} (see Figure 3). This feature can be explained by different forms of polyiodide ions in MAI_3 and MAI_5 RPMs since MAI_3 contains mostly I_3^- ions while MAI_5 may include I_5^- ions with longer and weaker I–I bonds or a larger amount of solvating iodine.[1] As soon as polyiodides are embedded into the amylose matrix, they lose their initial structure and form standard complexes with neutral iodine chains and ions close to I_3^-. This is a reasonable explanation of why the Raman frequency of MAI_3–starch and MAI_5–starch complexes remains the same (158 cm^{-1}). We can also conclude that iodine inside the starch complex has a different I–I bond length and energy as compared with the elemental I_2 in crystals. It indicates that amylose molecules affect on the internal structure of iodine and polyiodide arrays making them more strongly bonded, probably due to the hydrogen bond association.

Polyiodides demonstrate resonant Raman scattering since the red laser agitates electronic structure of these species. This causes domination of polyiodide Raman modes among other vibrations. Thus, in order to see organic molecules (MA^+, starch) inside RPM–starch complex, a Raman spectroscopy study was conducted using an infrared 785 nm laser [Figure 4 (*b*)]. Along with the similar behavior of polyiodide peaks inside the high energy region, weak Raman modes were also observed in the region about 1250 cm^{-1} and further, which could be assigned to organic components inside liquid RPM and solid RPM–starch complex. Again, an analogous behavior was observed for the molecular iodine lines around 160–170 cm^{-1} (see the inset in Figure 4) indicating some shortening of polyiodide chains in the complexes.

The MA^+ cation in the reference pure crystalline MAI demonstrates two series of peaks, narrow and wide ones. Most of narrow peaks correspond to valence vibrations [913 cm^{-1} (Me–NH_3^+ rocking), 987 cm^{-1} (C–N stretching), 1460 cm^{-1} (sym. NH_3^+ bending), 2790 cm^{-1} (N^+–H stretching), 2889 cm^{-1} (sym. Me stretching), 2995 cm^{-1} (asym. Me stretching)],[14] while the widening of other peaks [1539 cm^{-1} (asym. NH_3^+ bending), 1599 cm^{-1} (NH_3^+ twisting), 3077 cm^{-1} (NH_3* sym. stretching)][14] reflects, most probably, intermolecular interactions, in particular, *via* hydrogen bonding in the crystal of MAI. In contrast, MA^+ in RPM exhibits wider and smaller vibration peaks mostly in the region of 1450–1800 cm^{-1} [see Figure 4(*b*)] since the liquefied system becomes highly disordered due to the presence of only separated MA^+ ions solvated with iodine molecules in RPM. Even a deeper effect of the same origin was demonstrated by the RPM–starch complexes since the further lowering of the MAI peaks would be related to strong hydrogen bonding of MA^+ cations with either amylose helix or amylopectin branches in the starch.

From a practical point of view, the reported findings provide some hints for the new fabrication techniques development of the hybrid perovskite. This comes from the understanding of the unique origin of the discovered complexes. The complexes seem to serve as a new precursor for possible binary synthesis of perovskites with controlled activity of iodine as oxidizer and also containing MAI in a form of intercalated cations MA^+ with iodide ions stacked to the chains of iodine. The starch matrix could be prepared in a form of films thus allowing MAI and iodine to be released over large contacting areas in the possible binary synthesis. It would be also hypothesized that such films would be a suitable source for either storage or the use-on-demand of such active reagents distributed homogeneously in the film. Starch as a biopolymer would be transferred in a gel state by swelling in proper solvent environment followed by diffusion-controlled release of MAI or its polyiodides to the interface of chemically forming film of perovskites followed by careful peeling of the residual starch matrix. All these concepts should be experimentally verified in the future; however, the new precursors ensure new possibilities in the preparation of active layers for various optoelectronic devices.

Therefore, we have for the first time found that a new starch–polyiodide complex can be prepared by a direct interaction of starch with room temperature RPMs of methylammonium iodide and molecular iodine. The complex contains both MA^+ and polyiodide ions shortened with respect to disordered RPM structure containing triiodides and solvating iodine. This starch complex either plays a fundamental role in refining the RPMs structure or may be potentially applicable for new methods of perovskite layer deposition in solar cells.

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