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Preparation of cationic silsesquioxanes that can stably retain triiodide ion

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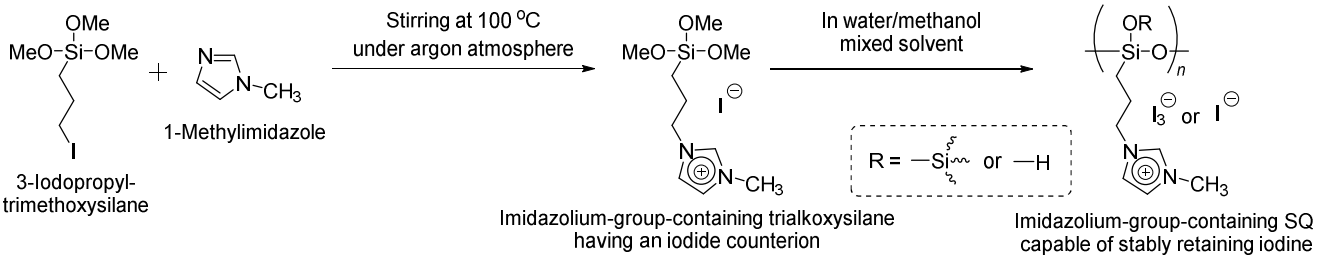
Abstract

Iodine is known as an excellent dopant (electron acceptor) for improving the conductivity of π-conjugated polymers, such as polyacetylene and polythiophene.[1] However, since iodine is volatile, practical application of iodine-doped π-conjugated polymers indicating high conductivity is difficult. Meanwhile, it has been reported that iodine is stably retained as triiodide ion and/or polyiodide ion in organic polymers, such as starch, polyvinyl alcohol, and a polymer containing imidazolium side-chain groups. Since triiodide ion also functions as an electron acceptor, it may have a possibility as a dopant for π-conjugated polymers. As mentioned above, most of the materials capable of retaining iodine are organic polymers. If iodine can be retained stably with inorganic materials, we believe that the application of materials will expand due to the durability of inorganic materials.

So far, we have found that cationic ladder-like polymeric silsesquioxanes (SQs)[2] and polyhedral oligomeric SQs (POSSs)[3] as soluble inorganic materials were successfully prepared by the hydrolytic condensation of organotrialkoxysilanes containing functional groups convertible to cationic substituents during the reaction.

In this study, we investigated the preparation of cationic SQs capable of stably retaining iodine. Such a SQ could be prepared by hydrolytic condensation (sol-gel reaction) of an imidazolium-funtionalized trialkoxysilane having an iodide counterion in a water/methanol mixed solution of iodine (Scheme 1). Based on UV-Vis and EDX measurements, it was found that this SQ contained triiodide ions. Furthermore, even when this was heated at 100 °C, the content of iodine did not decrease so much. Furthermore, the counterion of imidazolium-group-containing POSS, which was prepared according to our previous report,[4] was converted into triiodide ion. Consequently, even when this product was heated at 100 °C, the triiodide ion was also retained stably.



Scheme 1. Preparation of imidazolium-group-containing SQ capable of stably retaining iodine.

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