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Fine-controlled metal-assembling using a dendrimer reactor

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Abstract

We show that tinchlorides, $SnCl_2$ and $FeCl_3$ complexes to the imines groups of a spherical polyphenyl- azomethine dendrimer in a stepwise fashion according to an electron gradient, with complexation in a more peripheral generation proceeding only after complexation in generations closer to the core has been completed. The metal-assembly in a discrete molecule can be converted to a size-regulated metal cluster with a size smaller than 1 nm as a molecular reactor. Due to the well-defined number of metal clusters in the subnanometer size region, its property is much different from that of bulk or general metal nanoparticles.

Here we show that tin ions, Sn^{2+}, complex to the imines groups of a spherical polyphenylazo- methine dendrimer in a stepwise fashion according to an electron gradient, with complexation in a more peripheral generation proceeding only after complexation in generations closer to the core has been completed. By attaching an electron-withdrawing group to the dendrimer core, we are able to change the complexation pattern, so that the core imines are complexed last. By further extending this strategy, it should be possible to control the number and location of metal ions incorporated into dendrimer structures, which might and uses as tailored catalysts, building blocks, or fine-controlled clusters for advanced materials.

Many metal ions can be assembled inside the phenylazomethine dendrimer with a phenylene core(DPA) by the strong coordination ability of the imines in DPAs. During the complexation of DPA G4 with SnCl2, four shifts in the isosbestic point were observed in the spectra, which means that the complexation proceeds in four steps. The titration results show that SnCl2 molecules are assembled from the core to the terminals of DPA G4 in a stepwise fashion.

This radial stepwise complexation was also observed for the other dendrimers with phenylazomethine dendron skeletons. The basicity of the inner imines is enhanced by the electron-releasing effect of the outer imines, and the stepwise complexation is caused by the different basicity of the imines between the shells. This complexation behavior means that the number and the position of the metal ions in the dendrimers are controllable.

Biography

Kimihisa Yamamoto received his Ph.D. degrees from Waseda University in Polymer Chemistry in 1990, respectively. He was Research Associate and Associate Professor of Waseda University from 1989 to 1990 and from 1991 to 1996, respectively. He had been a professor of the Department of Chemistry at Keio University since 1997. He is now a professor of Chemical Resources Laboratory in Tokyo Institute of Chemistry. He received the Award for thead Young Chemist and the Divisional Award from the Chemical Society of Japan in 1996 and 2008, and the JSPS Wiley Award in 2005 from the Society of Polymer Science, Japan. He was also awarded the Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology, in 2012.