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Synthesis of a Dendrimer Reactor for Clusters with a Magic Number

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A new type of phenylazomethine dendrimer (DPA) that has one more coordination site compared to the tetraphenylmethane core DPA was synthesized for the "magic number 13" metal cluster template that has cubic or hexagonal densely packed structures. The stepwise complexation property was revealed, and this property is expected to be the "magic number 13" metal cluster template.

It is well known that properties of metal clusters, which are different from bulk materials, change with the number of atoms or the size.[1] In particular, metal clusters that consist of the "magic number" 13, 55, 147, 309, etc., of metal atoms are known as especially stable clusters that have cubic or hexagonal densely packed structures with the complete, regular outer geometry of a cuboctahedron.[2] With the evolution of the field of nanotechnology, the function of "magic number" clusters has received much attention, and the synthesis of a finely size-controlled cluster is strongly desired for advanced nanomaterials.[3]

In particular, dendrimers, such as the poly(amidoamine) dendrimer (PAMAM) incorporating metal ions, have received much attention as the cluster template for synthesizing clusters and nanocatalysts.[4] However, metal clusters using traditional dendrimers have a statistical cluster size distribution.[5] On the other hand, the dendritic poly(phenylazomethine) (DPA) shows a stepwise radial complexation with metal ions from the core imines to the terminal imines based on the gradients in the basicity of the imine groups.[6] Therefore, it is possible to control the number and location of metal ions incorporated into the dendrimers, and DPA can be used as the size-controlled cluster template.[7]

We have already reported that dendrimer-encapsulated platinum clusters consisting of 12 platinum atoms can be synthesized using the tetraphenylmethane core DPA (TPM dendrimer) which has a dense-shell structure and an internal cavity.[8] However, the finely controlled synthesis of the "magic number 13" cluster cannot be achieved with this dendrimer. Therefore, in this paper, we report a new type of phenylazomethine dendrimer, Py-DPA G4, which has one more coordination site at the core compared to the traditional DPA, and revealed the stepwise complexation (Figure 1).

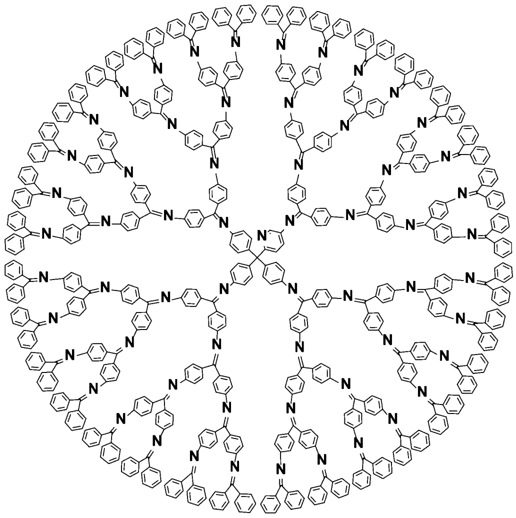
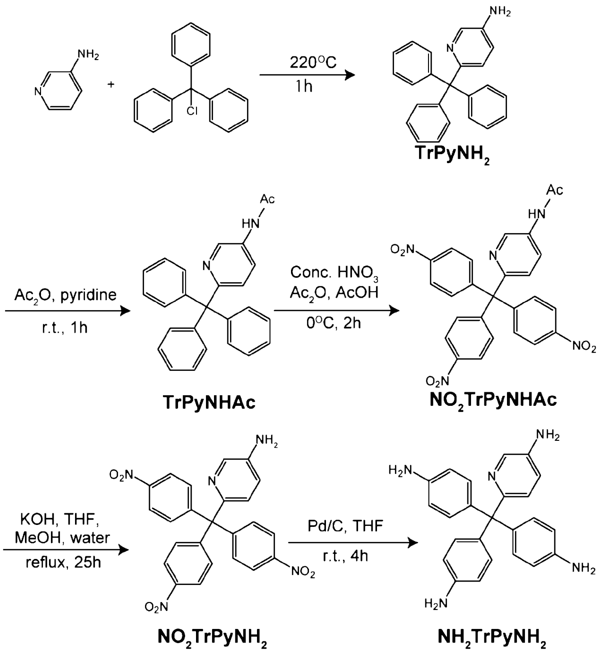


Figure 1. Structure of the Py-DPA G4 dendrimer.



Scheme 1. Synthesis of the core of Py-DPA (NH$_2$TrPyNH$_2$).

We designed a new kind of core molecule, (5-aminopyridin-2-yl)tris(4-aminophenyl)methane (NH$_2$TrPyNH$_2$), which has one position altered in the pyridine of tetrakis(*p*-aminophenyl)methane, as an additional coordination site for synthesis of the "magic number 13" cluster template. The strategy for the preparation of the core of Py-DPA, NH$_2$TrPyNH$_2$, is outlined in Scheme 1 (Schemes S1–S5, see the Supporting Information for details[11]). Similarly to the synthesis of tetrakis(*p*-aminophenyl)methane,[9] the pyridine-substituted tetraphenylmethane backbone (TrPyNH$_2$) was synthesized by heating 3-aminopyridine and trityl chloride at 220 °C without a solvent, and the structure was identified by an X-ray single-crystal analysis (Figure S1[11]). The other amine groups were added by the nitration reaction of the phenyl group followed by a hydrogenation reaction.

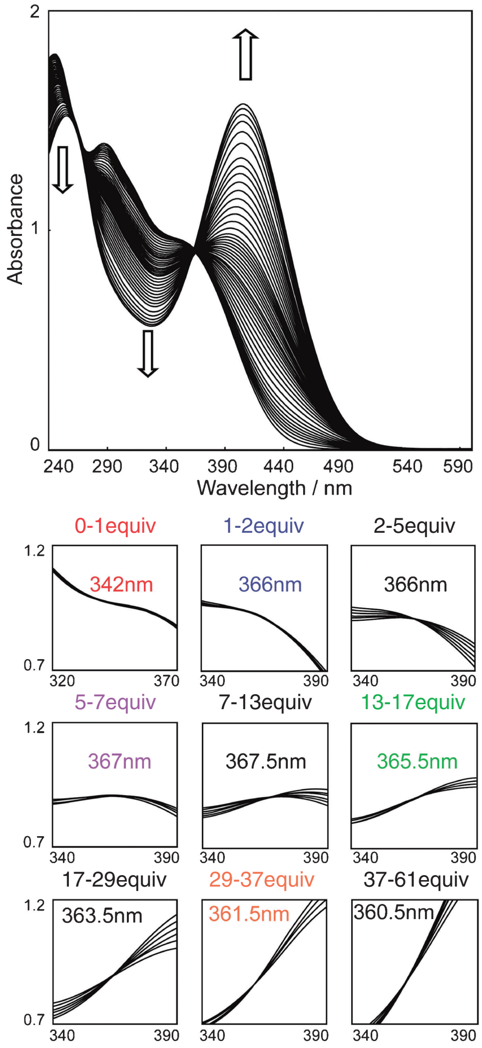
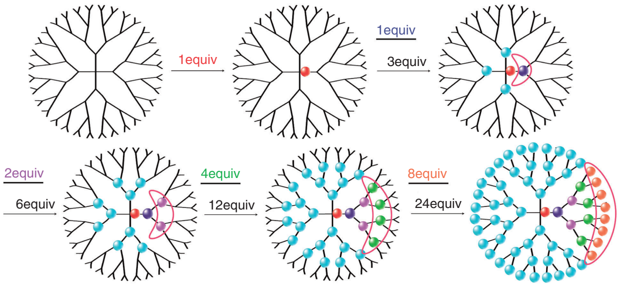


Figure 2. UV–vis spectra of Py-DPA G4 (2.5×10^{-6} M, in acetonitrile/chloroform = 1:1) upon the addition of $GaCl_3$ (2.1×10^{-3} in acetonitrile) at 293 K.

The phenylazomethine (DPA) dendrons, G1–G4, were synthesized according to a literature method.[10] The Py-DPA dendrimers were obtained by the same dehydration reaction between the core and the dendrons (Py-DPA G1 and G4, Scheme S6[11]). All products were identified by ^{1}H NMR, ^{13}C NMR, MALDI-TOF MS, and elemental analysis, and the purity of Py-DPA G1 and G4 was verified by an HPLC (SEC) analysis (Figure S2[11]).

The coordination chemistry of the dendrimer was confirmed by UV–vis titration with $GaCl_3$. Upon the addition of $GaCl_3$ to the Py-DPA dendrimer solution, the spectra gradually changed until the stoichiometry with the added $GaCl_3$ was equal to the number of coordination sites in the dendrimer. This means that the $GaCl_3$ and the coordination site of the Py-DPA dendrimer quantitatively form a 1:1 complex. When the Py-DPA G4 was used, nine isosbestic points were observed during the titration. Each isosbestic point shifted stepwise, as 342 (0–1 equiv), 366 (1–2 equiv), 366 (2–5 equiv), 367 (5–7 equiv), 367.5 (7–13 equiv), 365.5 (13–17 equiv), 363.5 (17–29 equiv), 361.5 (29–37 equiv), and 360.5 nm (37–61 equiv) (Figure 2).



Scheme 2. Stepwise radial complexation of Py-DPA G4 with $GaCl_3$.

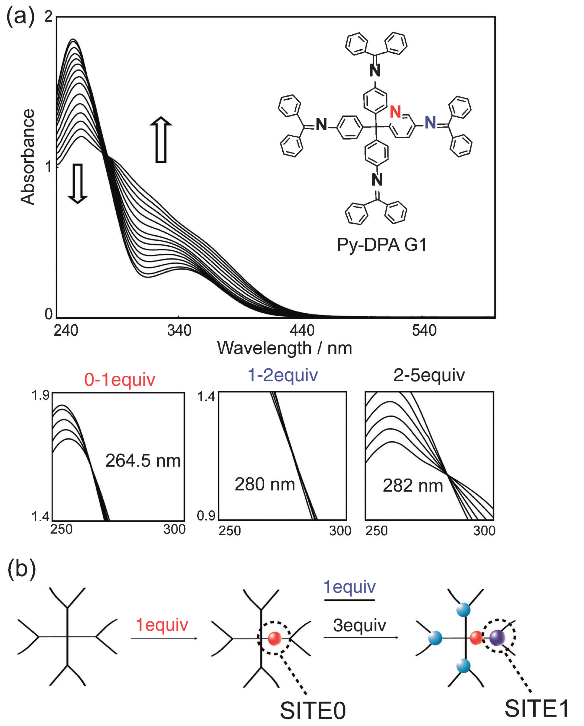


Figure 3. (a) UV–vis spectra of Py-DPA G1 (2.1×10^{-5} M, in acetonitrile/chloroform = 1:1) upon the addition of $GaCl_3$ (6.5×10^{-3} in acetonitrile) at 293 K. (b) Stepwise radial complexation of Py-DPA G4 with $GaCl_3$.

The number of added equivalents of $GaCl_3$ that induced the shifts in the isosbestic points is in good agreement with the number of coodination sites in the Py-DPA G4. This means that the complexing process proceeds in a stepwise fashion from the coordination site of the core to the terminal coordination site of the Py-DPA G4, and this indicated that the order of coordination in the same layer is first to the coordination site of the dendrons, which was attached to the pyridine site of the core, then to the other coordination sites of the same layer dendron (Scheme 2).

When a UV–vis titration was similarly performed by the addition of $GaCl_3$ to the Py-DPA G1, three isosbestic points were observed during the titration. Each isosbestic point shifted stepwise, as 264.5 (0–1 equiv), 280 (1–2 equiv), 282 nm (2–5 equiv) (Figure 3a). As a result, a similar stepwise radial complexation was also observed for the Py-DPA G1 (Figure 3b).

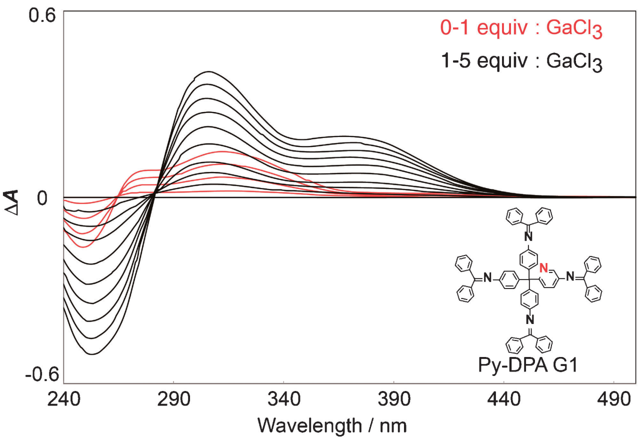


Figure 4. Differential spectra during the UV–vis titration of Py-DPA G1 with $GaCl_3$.

Furthermore, to confirm the complexation of the core (SITE0) and the first layer dendron, which is attached to the pyridine site of the core (SITE1), the differential spectra during the UV–vis titration of the Py-DPA G1 with $GaCl_3$ were analyzed. These spectra show distinctly different between SITE0, SITE1, and the other coordination sites (Figure 4). This result indicated that $GaCl_3$ is first coordinating to SITE0, then $GaCl_3$ coordinates to SITE1 between 0 and 2 equiv of $GaCl_3$, and then $GaCl_3$ coordinates to the other coordination sites of the same layer dendron between 2 and 5 equiv of $GaCl_3$.

Therefore, these results suggested that $GaCl_3$ first coordinates to SITE0, and then $GaCl_3$ coordinates to SITE1 between 0 and 2 equiv of $GaCl_3$. After that, the order of coordination in the same layer is first to the coordination site of the dendrons which were attached to the pyridine site of the core, then the other coordination sites of the same layer dendron in the case of the Py-DPA dendrimers. In addition, these results obviously suggested that the core of the Py-DPA G4 formed a 1:1 complex and the Py-DPA G4 become the "magic number 13" metal cluster template. Furthermore, the Py-DPA G4 showed a stepwise radial complexation with metal ions and quantitatively formed a 1:1 complex.

In conclusion, a new type of the poly(phenylazomethine) dendrimer, Py-DPA, with a new core that has one more coordination site compared to the core of the TPM dendrimer was synthesized and clearly revealed the stepwise complexation. Therefore, by using Py-DPA G4 as the metal cluster template, it would be possible to synthesize "magic number 13" metal cluster in the near future.

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