



Feature Article

Synthesis and functionality of dendrimer with finely controlled metal assembly

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ABSTRACT

Integrated research on the synthesis and functionality of macromolecular metal complexes has suggested that dendritic structures exhibiting a geometrical density gradient also impart a potential gradient within the constituent molecules. Focusing on dendritic π -conjugated macromolecules containing azomethine (imine) as a metal assembly site, the stepwise radial complexation of metal ions in a dendritic phenylazomethine structure has been identified for the first time. Using this discovery, the first macromolecules with precision control of the number and position of metal molecules have been synthesized. A series of new physicochemical discoveries have followed from this success, related to stepwise radial complexation, one-step multi-electron transfer, and potential gradients. The usefulness of these new macromolecules as a nano-material has also been demonstrated through application to (1) polymer electroluminescent devices, (2) organic solar cells with high energy conversion efficiency, and (3) the storage and release of metals in a manner similar to ferritin protein.

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1. Introduction

Recent developments in nanotechnology and precision synthesis have accelerated the demand for a technology to place metal molecules precisely within organic nanostructures. This demand has yet to be met in reality. The conventional metal-organic hybrid materials, typified by macromolecular complexes, are nothing more than results of statistical complexation with metal [1,2]. Conventional macromolecules have a straight-chain structure, a distributed molecular weight, and flexible backbone, and thus exhibit a statistical distribution in terms of molecular structure (Fig. 1). However, from the observation that proteins display advanced functionality attributable to the singular structure [3–6], the precise control of higher-order structures of macromolecules is of substantial technological importance.

Dendrimers are macromolecules with a complete, and precisely controlled, branch structure, representing a type of nano-material that has attracted great interest in recent years [7–10]. Tomalia et al. synthesized a single-core dendrimer with a regular structure by repeating polymerization under precise branching control [11]. This procedure is known as the divergent method [10]. As branches become denser with increasing distance from the center of the molecule, the molecular shape becomes increasingly spherical with the degree of polymerization. Fréchet and Hawker proposed a convergent method for the synthesis of dendrimers through the

creation of a dendron step by step from the ends in a sequence opposite to that of the divergent method [12]. Multiple dendrons are then combined with a core to complete the dendrimer. This facilitates the synthesis of a dendrimer without missing branches, and also allows for the introduction of functional groups. In both of these methods, the core molecule, branch chain, and ends can be chosen according to the application, and the desired macromolecule can be synthesized under precise structural control. This allows for a great diversity of molecular designs to serve a wide variety of purposes. The synthesis procedure, however, is more complicated than that required for conventional polymers. Dendrimers synthesized in this way, those with molecular weights exceeding 10 000, have a single molecular weight, and are therefore expected to exhibit similar precision functionality to proteins. A number of such dendrimers are now commercially available, and many studies examining the application of these materials in photoelectronics [13–15], drug delivery [16–23], and other areas [24–32] are in progress.

One of the interesting characteristics of a dendrimer is the shell effect [7,8,33–35], by which the branches become denser with increasing distance from the core as a feature of the geometrical structure. A high-generation dendrimer thus has highly dense branches near the outer surface, functioning as a wall to restrict the transfer between into and out of the dendrimer. Dendrimers thus contain nano-scale space in a capsule-like structure. This space can contain an organic functional molecule, or a metal particle, for example. Dendrimers containing a metal assembly are attractive candidates for metal-organic hybrid nano-materials [14,15,24–30]. Taking advantage of the characteristics of metals and organic

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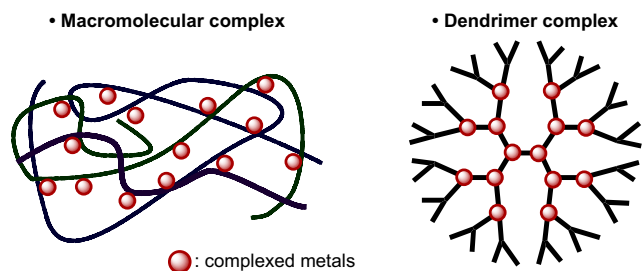


Fig. 1. (a) Macromolecular complex; (b) metal-assembling macromolecule using a dendrimer.

substances, which allow for very flexible design, multiple functions can be expected to emerge out of such dendrimers in the future. With conventional materials, however, complexation of metal and an organic substance is statistical, as no methods for precision

positioning of the metal are currently available. For this reason, the full potential functionality of such materials has yet to be realized. In the recent accelerated progress of nanotechnology, “precision control” has become an indispensable keyword. The development of a method for metal assembly in which the number of metal molecules and positions can be controlled precisely would improve the strength and efficiency of the desired functionality. Such precision metal-organic hybrid nano-materials are thus the topic of much research, not just as a source of artificial metal proteins and other life functional materials, but also of materials for use in fuel cells, environmental catalysts, and new medicines. Precision hybrid nano-materials are expected to find their way into a great diversity of applications, ranging from electronics to medicine.

2. Establishing a new method to synthesize dendrimers

To synthesize a dendritic macromolecule of azomethine (Figs. 2 and 3), the CN bond must be formed repeatedly, requiring efficient

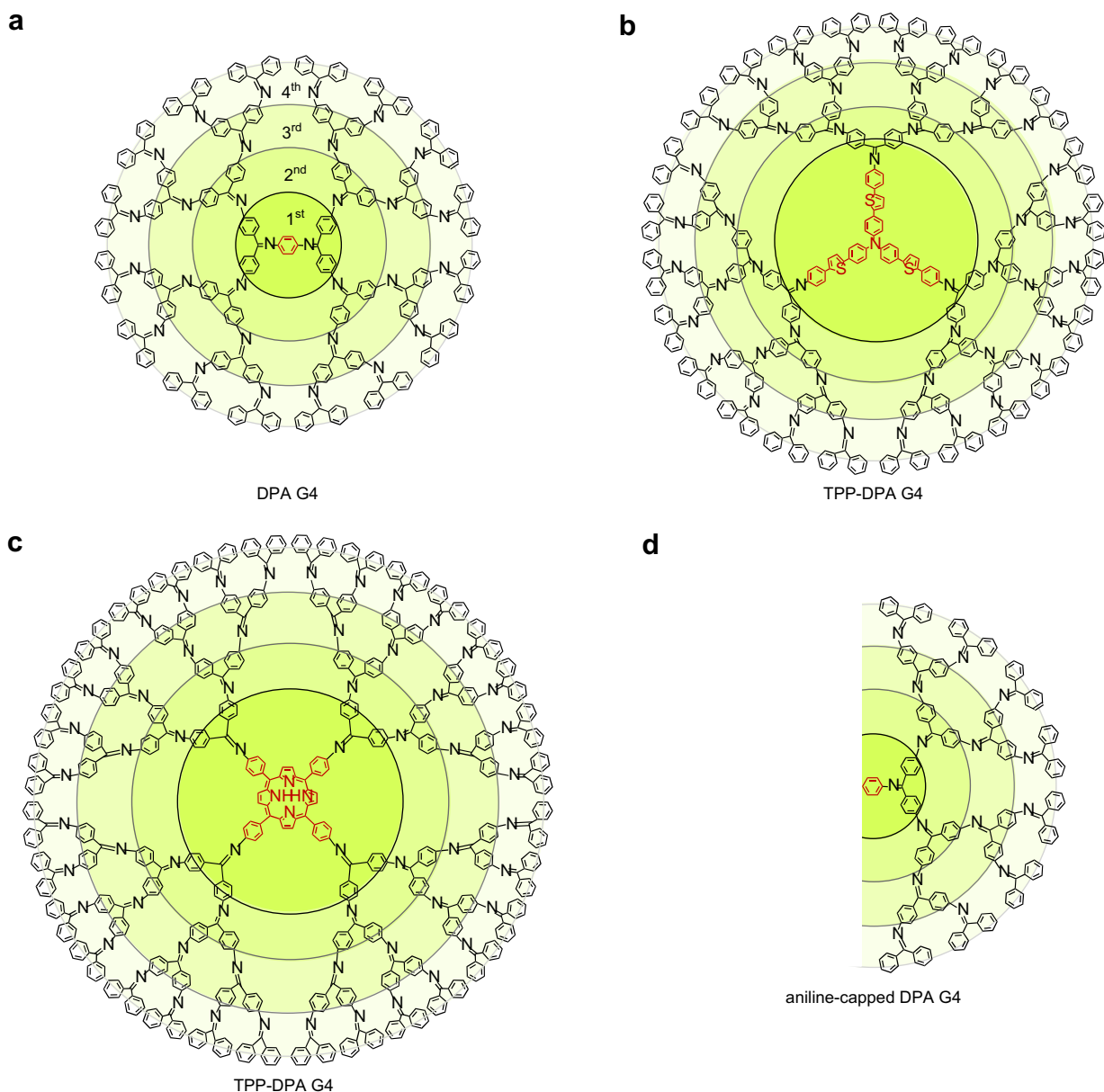


Fig. 2. Structure of the fourth generation phenylazomethine dendrimers: (a) Phenyl core (DPA G4); (b) triphenylamine core (TPP-DPA G4); (c) tetraphenylporphyrine core (TPP-DPA G4); (d) aniline-capped DPA G4.

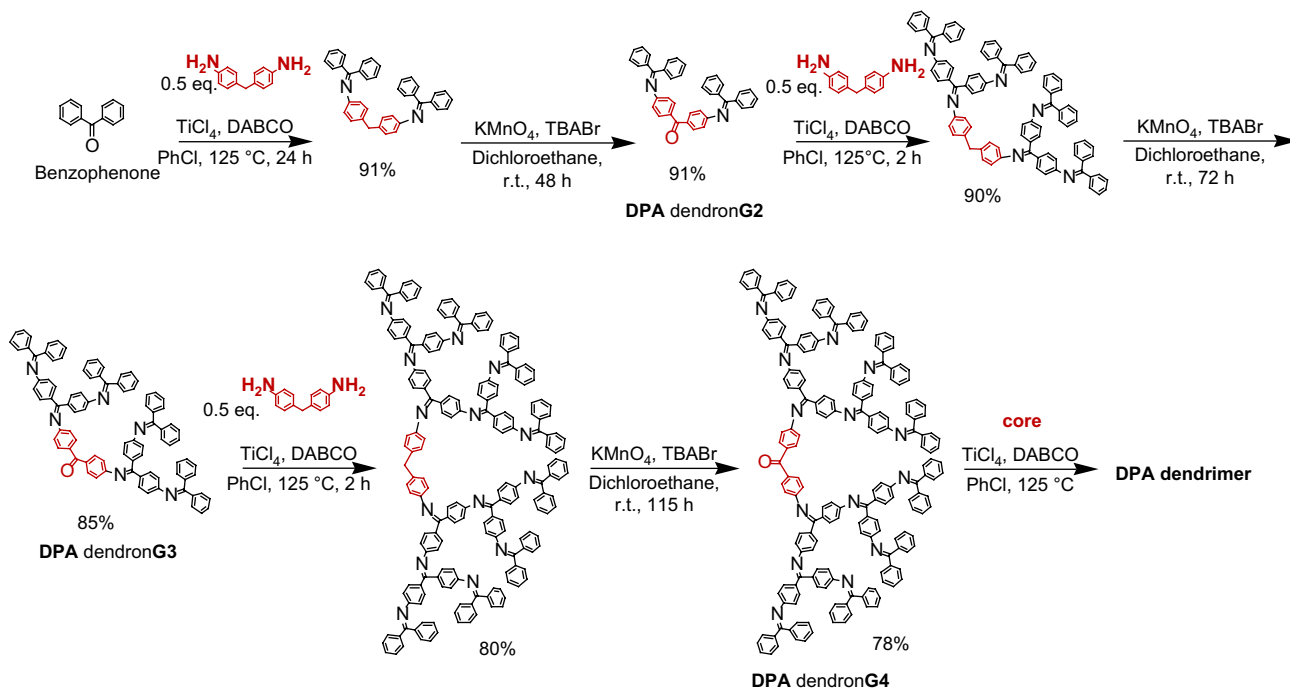


Fig. 3. Synthesis of DPA dendrons. DPA dendrons were synthesized by repetitions of a condensation reaction of an aromatic amine and an aromatic carbonyl involving titanium tetrachloride and an oxidation reaction of methylene to carbonyl by potassium permanganate.

imine formation. Our group has recently discovered a condensation reaction involving titanium tetrachloride, in which an aromatic amine and an aromatic carbonyl are employed to promote imine formation [36,37]. Further, a benzyl methylene was oxidized to carbonyl [38]. These afford a very efficient method for the synthesis of phenylazomethine dendrons and dendrimers (Fig. 3). Employing the convergent method, a core suitable for use with many different functional molecules has been developed, and more than 20 kinds of phenylazomethine dendrimer derivatives have been synthesized in the last five years (Fig. 4) [39–50].

Many of the conventional dendrimers, consisting of a flexible backbone with single bonds, easily flatten on a substrate, rendering

it difficult to achieve regular assembly of molecules [40,51]. A characteristic of high-generation (e.g., G4) dendrimers with a phenylazomethine backbone is the inflexible π -conjugated backbone that the dendrimers form on a substrate while maintaining a spherical shape with diameter of 2–5 nm (Fig. 5) [40,42,45,59]. In case of DPA G4, the combination of TEM and AFM measurements gives direct information about the molecule [40]. In general, the TEM image of a dendrimer shows the two-dimensional figure of the molecule. The DPA G4 molecule was confirmed by TEM to have a round shape with a 2.3 ± 0.3 nm diameter (Fig. 5a). Additionally, the height of the DPA G4 molecule was estimated from the AFM image to be at least 2.0 ± 0.1 nm (Fig. 5b). This indicates that the DPA G4 molecules are assembled on a plate without deformation.

Phenylazomethine dendrimers can be readily formed even as films by the solvent cast method, and are also heat resistant when treated as raw materials. The 10% weight loss temperature of these materials is 500 °C or higher, comparable to super engineering plastics (Fig. 6) [52]. The ease of film formation and heat resistance make these dendrimers excellent nano-materials for electronic devices.

3. As-desired fine assembly of metal

3.1. Establishing fine metal assembly

A fourth-generation phenylazomethine dendrimer (DPA G4, Fig. 2a) has 30 imine sites and can contain 30 ions of tin dichloride (SnCl_2) [39]. The gradual addition of tin chloride to phenylazomethine causes a strengthening of visible absorption around 420 nm by coordination to imine nitrogen. Interestingly, the addition of tin chloride to a G4 phenylazomethine dendrimer resulted in four shifts of the isosbestic points, from 375 nm upon addition of 2 equiv. SnCl_2 , to 364 nm with a further 4 equiv., 360 nm with a further 8 equiv., and 355 nm with a further 16 equiv. (Fig. 7). A random metal coordinating to the 30 imine sites should result in

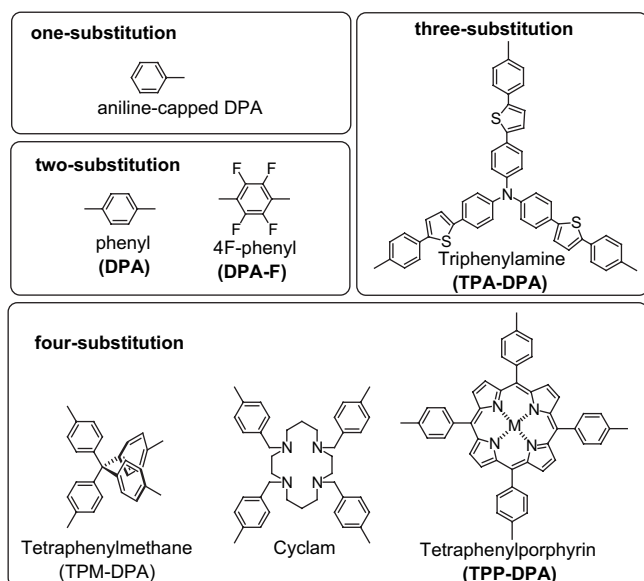


Fig. 4. Core structure of phenylazomethine dendrimers.

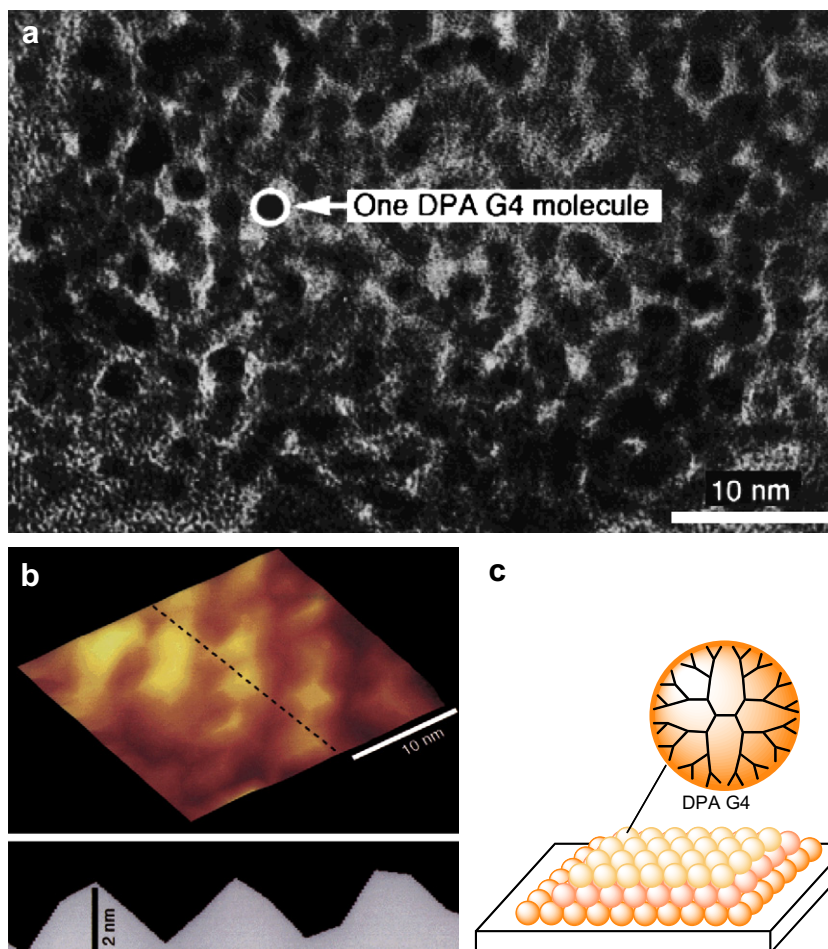


Fig. 5. (a) TEM image of DPA G4 stained by RuO₄. The DPA G4 molecule was round in shape with a 2.3 ± 0.3 nm diameter; (b) AFM images of DPA G4. Lower is a crosssection at the dotted line. The height of the DPA G4 molecule was at least 2.0 ± 0.1 nm; (c) the assembling structure of DPA G4 on a substrate. DPAs form films by the solvent cast method and the DPA molecules are assembled on a plate without deformation.

a single position of the isosbestic point. These experiments thus suggest that this particular complexation progresses in four stages. As the quantity of SnCl₂ added during each of the four stages matched well with the number of imine nitrogen molecules (2, 4, 8,

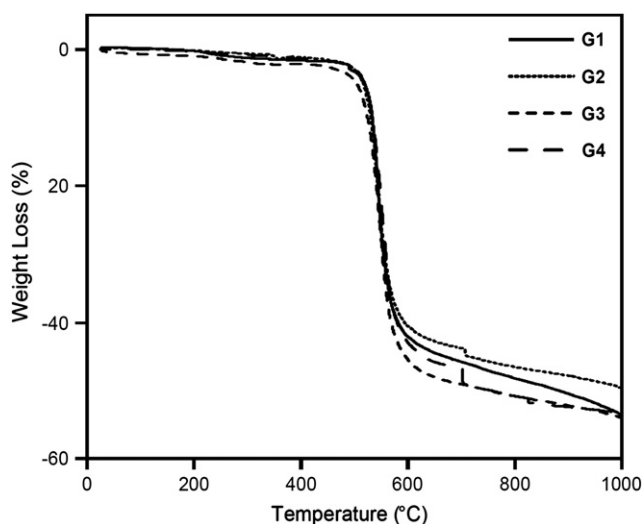
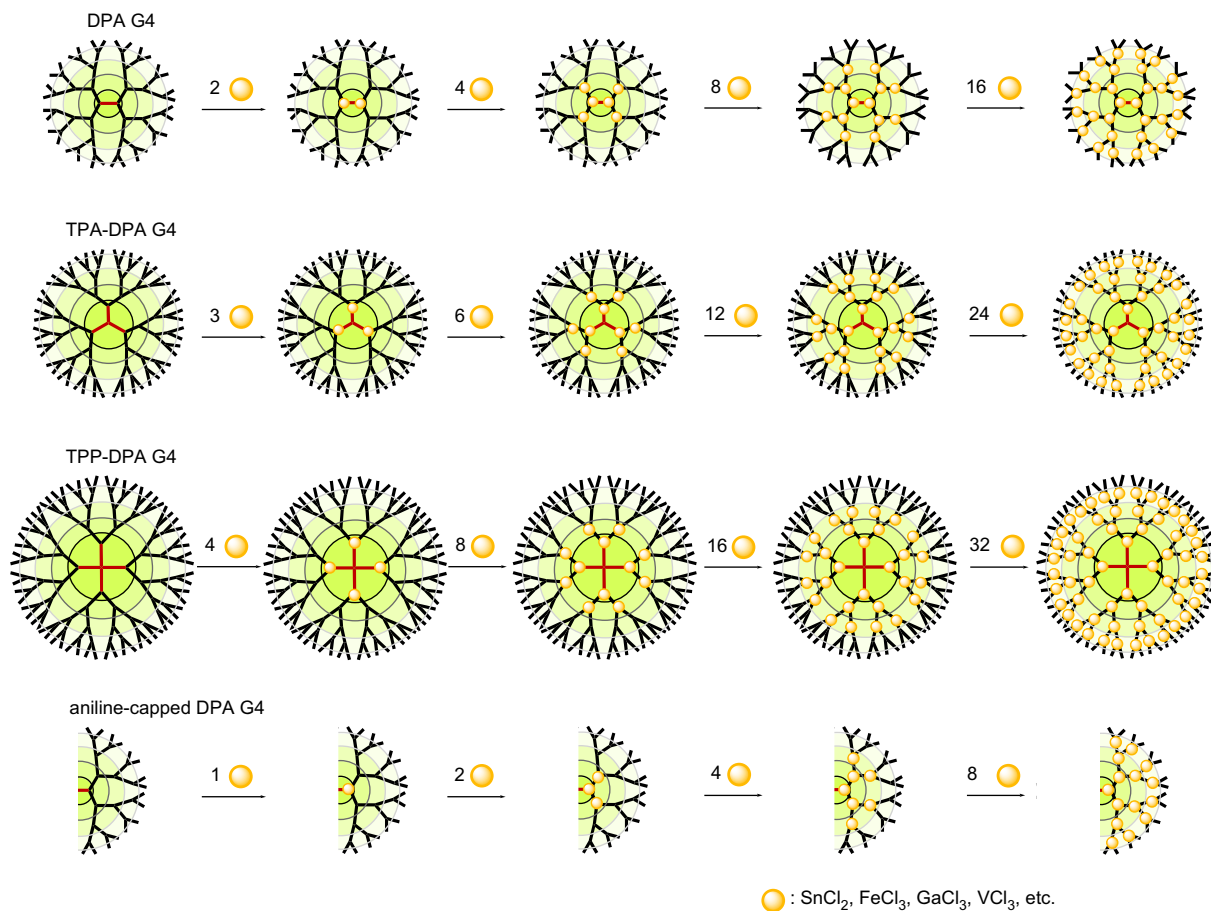
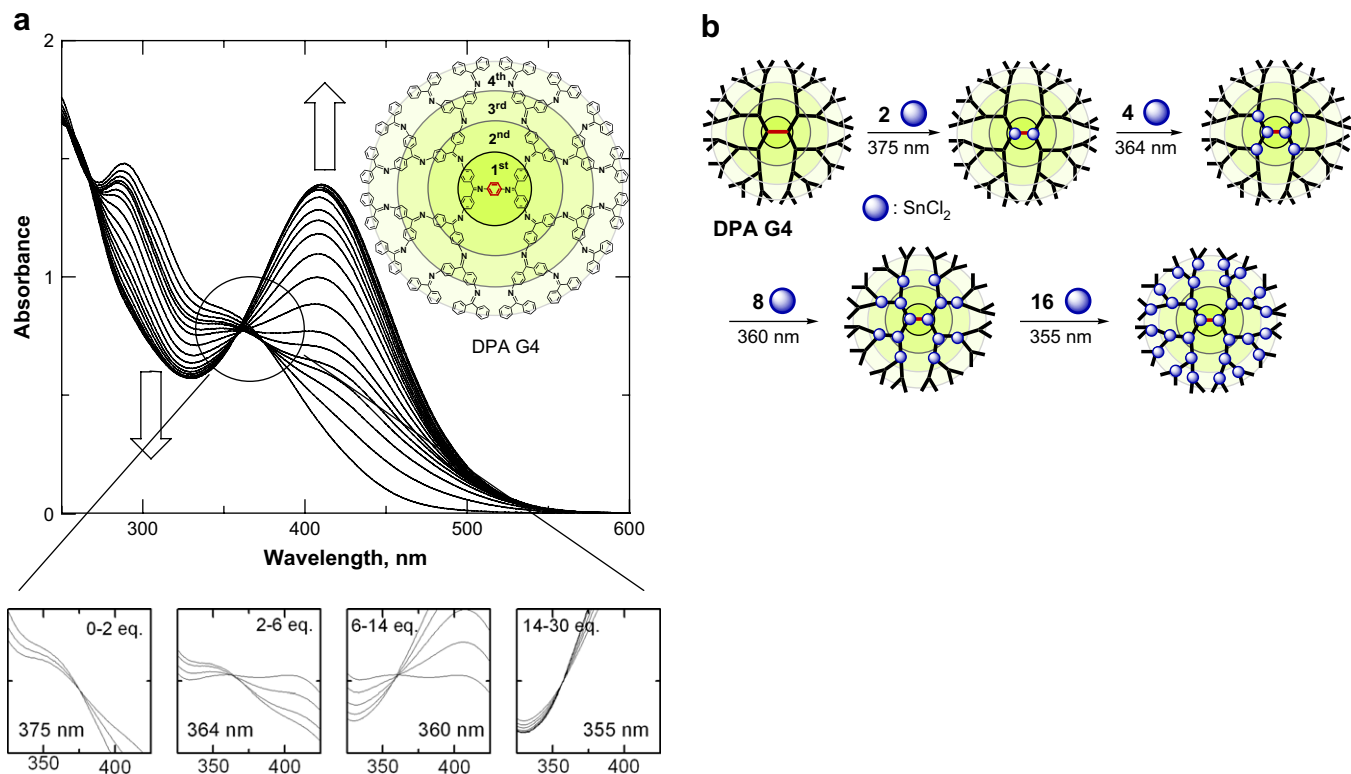


Fig. 6. The 10% weight decreasing temperatures of TPP-DPAs (solid: G1, dash-dot-dot: G2, dash-dot-dot-dot: G3, short-dash: G4).

and 16 of each generation, 1 through 4) of DPA G4, the metal ions are considered to assemble gradually and radially from the inner part to the outer part of the molecule.

This gradual radial complexation behavior is also observed in many different derivatives with the phenylazomethine dendron structure (Fig. 8). For example, the four-stage shift of the isosbestic point takes place with the addition of a metal ion of $3 \rightarrow 6 \rightarrow 12 \rightarrow 24$ equiv. to TPA-DPA G4 (Fig. 2b) with a three-substituted core [42], $4 \rightarrow 8 \rightarrow 16 \rightarrow 32$ equiv. to TPP-DPA G4 (Fig. 2c) with a four-substituted core [43], and $1 \rightarrow 2 \rightarrow 4 \rightarrow 8$ equiv. to aniline-capped DPA G4 (Fig. 2d), which has a one-substituted core [46]. As the equivalent weights of metals in each stage and the number of imines in each layer match in all of these cases, the complexation is considered to proceed via the gradual assembly of metal, beginning with the innermost generation. This unusual complexation behavior suggests that metal can be assembled with molecules in the number and positions desired.

In addition to spectroscopy, evidence of this phenomenon has also been obtained by transmission electron microscopy (TEM) and chemical reduction [39,41]. Dendrimers containing 14 and 30 tin ions were examined by TEM observation of the metal sites. If the 14 ions were randomly coordinated, the dendrimer should have the same area as that containing 30 ions. However, the dendrimer containing 14 ions is smaller in area than the 30-ion dendrimer, suggesting that the assembly of metal begins at the center of the dendrimer. The imines coordinated with tin alone are selectively reduced to amine by sodium hydroborate (Fig. 9a). Observation of



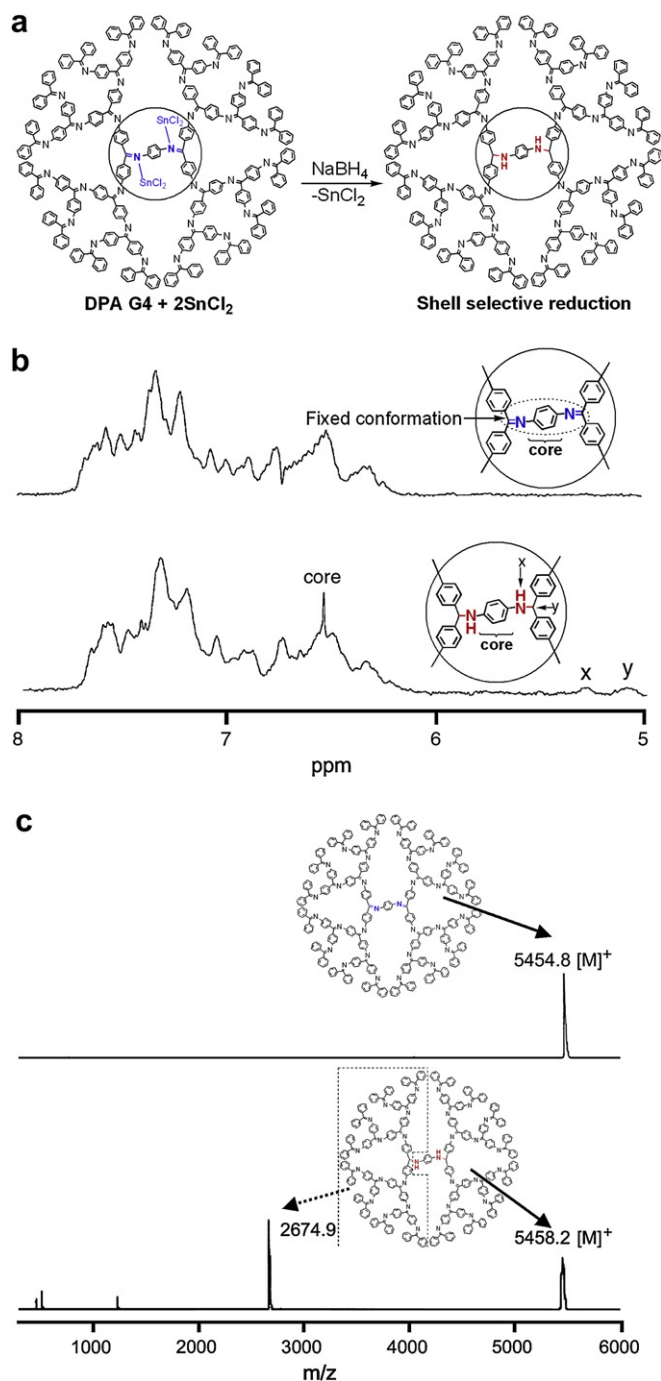


Fig. 9. (a) Shell-selective reduction of imines in DPA G4 complexed with 2 equiv. SnCl₂. Imines on the first layer were selectively reduced to amines; (b) ¹H NMR spectra (400 MHz, DMSO-*d*₆) of DPA G4 (upper) and the product obtained by reduction of DPA G4 complexed with 2 equiv. SnCl₂ (DPA-red G4, lower). In the spectrum of DPA G4, a singlet peak attributed to the core protons did not appear due to the fixed conformation of the core by the bulky G4 dendrons. On the other hand, a singlet peak attributed to the core protons appeared in the spectrum of the DPA-red G4; (c) MALDI-TOF MS spectrum of DPA G4 (upper) and DPA-red G4 (lower). In the spectrum of DPA-red G4, the fragment peak at *m/z* 2674.9 shows the cleavage of the C–N single bond at the first shell.

amine protons by nuclear magnetic resonance (NMR) has confirmed the coordination of tin ions (Fig. 9b). Using this reaction, dendrimers containing 2 ions of tin were reduced, and it was confirmed by NMR that the core imine was the ion reduced. In other words, the two tin ions always assemble first in the first

generation on the core. The MALDI-TOF MS measurement is also useful in determining the positions of the amine groups in DPA-red G4, because the fragment peak based on the cleavage of the C–N single bond appears in the spectrum. In the spectrum of DPA-red G4, the fragment peak shows the cleavage of the C–N single bond at the first shell (Fig. 9c).

This gradual radial complexation represents metal assembly behavior in which the complexation does not begin with an outer generation until the inner generations closer to the core have been populated. This behavior reflects the electronic gradient of imine [43,46]. Imine basicity (*K*) is $1.5 \times 10^7 \text{ M}^{-1}$ in the first (innermost) layer, and decreases with each successive (outer) generation, to $3.0 \times 10^5 \text{ M}^{-1}$ in the second layer, $1.4 \times 10^4 \text{ M}^{-1}$ in the third layer, and $1.2 \times 10^3 \text{ M}^{-1}$ in the fourth layer. This gradual gradient in basicity (i.e., potential gradient) is responsible for the gradual radial complexation. This dendrimer is regularly branched at the imines and the number of imines on the outer layer is greater than that on the inner layer. Because imines on the outer layer act as electron donors to the imines on the inner layer, the imines on the inner layer become electron-rich compared to those on the outer layer. This causes the basicity gradient on the DPA.

3.2. Control of fine metal assembly

Applying this principle, control of the potential gradient was attempted [39,41]. The generation in the gradual complexation is considered to be determined by the basicity of each generation of imines. Using a dendrimer with an electron-withdrawing fluorine group introduced into the core (DPA-F G3), the complexation pattern was successfully modified by reversing the electron density on the imine nitrogen atoms in successive generations (Fig. 10). In DPA-F G3, metals complex with 4 imines in the second layer, then with 8 in the third layer, and finally with those in the first layer. Introducing the electron-withdrawing group changes the order of assembly, providing control of the metal position within the dendrimer.

4. Applying macromolecules with a finely controlled metal assembly to nano-materials

4.1. Catalyst to reduce carbon dioxide under normal temperature and pressure conditions

For carbon dioxide reduction, which requires the transfer of many electrons, the catalytic potency of a dendrimer (CoTPP–DPA G3) with cobalt porphyrin core was electrochemically confirmed [43]. It was discovered that the use of a dendrimer with an assembly of 60 Tb³⁺ ions as an electrode catalyst promotes the reduction of carbon dioxide at a voltage of -0.7 V (vs. NHE, 1 V reduction of the excess voltage from conventional porphyrin). This can be compared with the case for a homogeneous catalyst, data for which are available in the literature [53,54]. The one-step transfer of multiple electrons accompanying the Tb³⁺/Tb²⁺ redox is considered to carry forward a multi-electron process with carbon dioxide, which in turn causes reduction at high voltage.

4.2. High-intensity light-emitting device

As a high-performance electroluminescent (EL) device, an organic EL device consisting of two layers was prepared (Fig. 11) [42]. One of the layers is a hole transport layer made of a dendrimer (TPP–DPA, Fig. 2b) with arylamine in the core, and the other is an electronic transport light-emitting layer employing Alq₃ (aluminium tris(8-hydroxyquinolate)). The assembly of tin chloride in the dendrimer improved the light emission efficiency by more than 20 times, and reduced the turn-on voltage by almost 5 V.

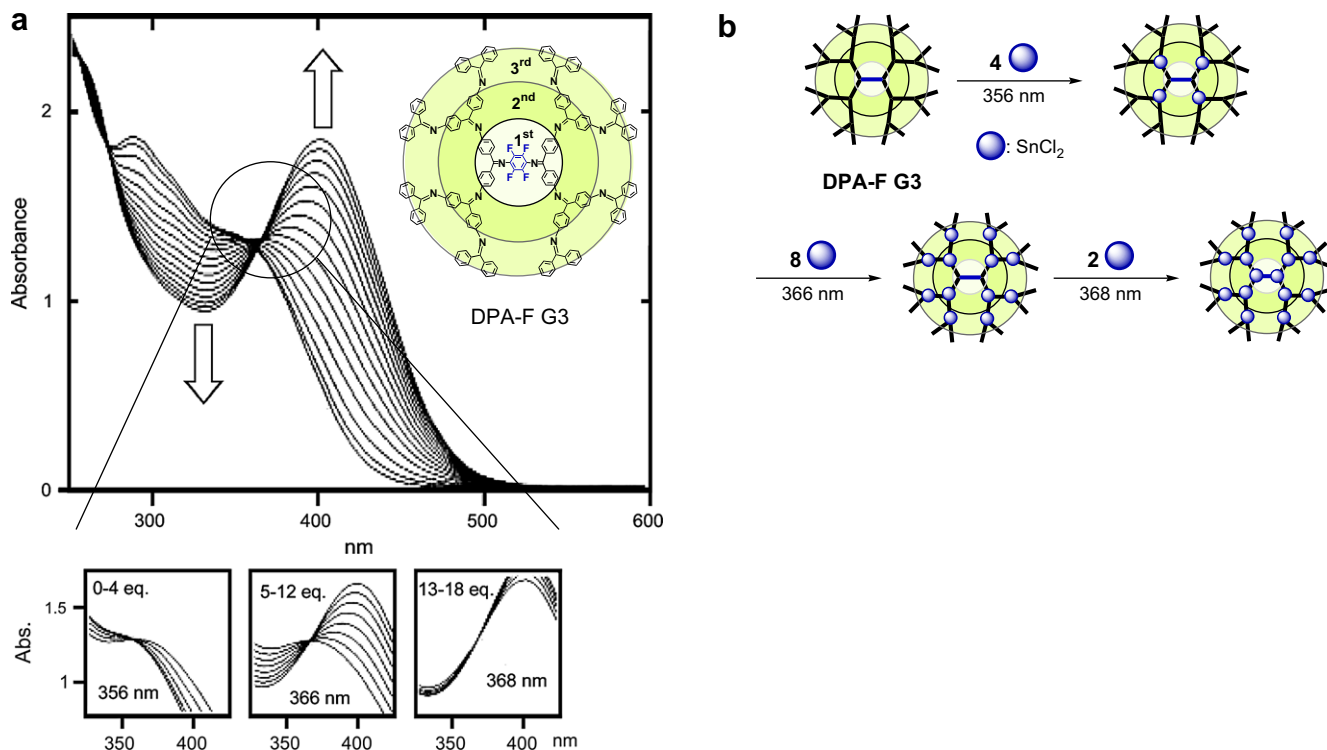


Fig. 10. (a) Change in the UV-vis absorption spectra of DPA-F G3 with coordination to tin chloride; (b) schematic representation of the stepwise radial complexation of the DPA-F G3 with tin chloride.

The device characteristics were thus significantly improved. This is a new type of hole transport material, the luminance of which is effectively enhanced by metal assembly.

Using a derivative of polyphenylenevinylene or polyfluorene as the light-emitting layer and a dendrimer as the hole transport layer, polymer EL devices can be manufactured by a wet method. The

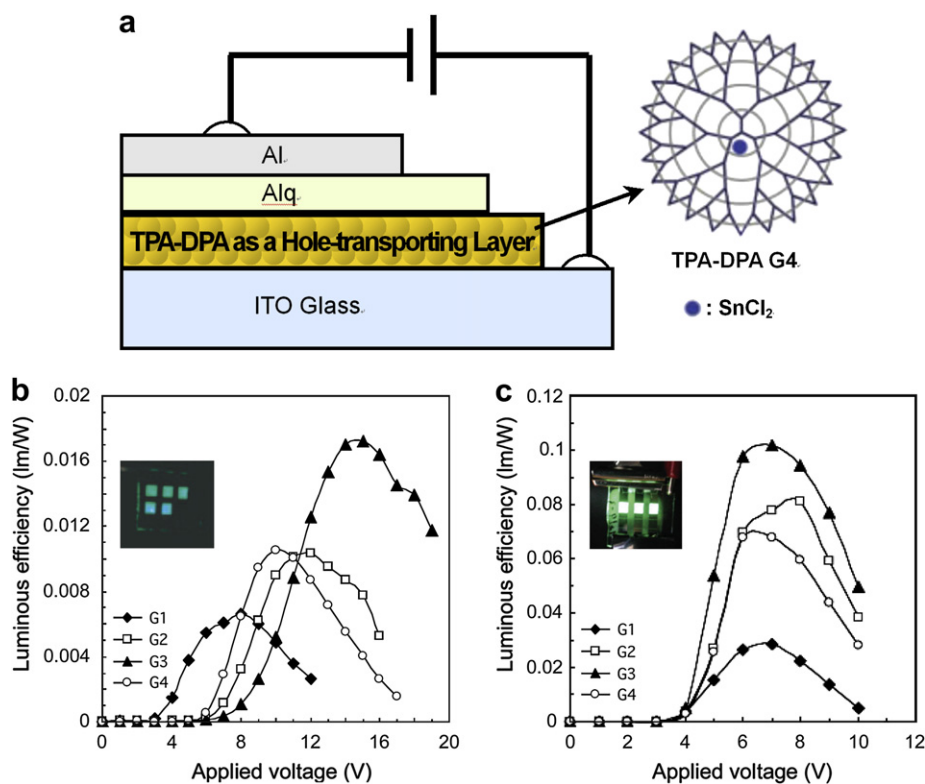


Fig. 11. (a) EL device with a dendrimer-based hole transport layer; (b) luminous efficiency of OLEDs using TPA-DPAs without SnCl_2 ; (c) with 1 equiv. SnCl_2 . Inner photographs are emitting OLEDs using TPA-DPA G4 with each condition. The assembly of tin chloride in the dendrimer improved the light emission efficiency.

dendrimer has also been confirmed to work with all devices for RGB light emission.

4.3. Efficient organic solar cell

A dye-sensitized solar cell is theoretically thought to be capable of generating nearly 1 V with energy conversion efficiency of 15% [55]. In practice, however, the back-transfer of electrons from the titanium oxide back into I_3^- or the dye reduces the energy efficiency of such a cell. Gratzel et al. took a decade to improve the energy conversion efficiency of solar cells by just 1% [56–58].

The shielding provided by a dendrimer was examined using a dye-sensitized solar cell in which the dye was coated with TPA-DPA G5 (Fig. 12) [59]. The open voltage and energy conversion efficiency of the cell were successfully improved. Coating with TPA-DPA, accompanied by the generational increase from G1 to G5, suppressed the back-transfer of electrons and raised the open voltage from 700 to 830 mV. In addition, the complexation with SnCl_2 promoted electron transfer, resulting in an increase in current density. An operation as simple as coating the existing device with a dendrimer is thus capable of improving the energy conversion efficiency by almost 30%. This was the first case of a solar cell employing a dendrimer to enhance cell performance through the effect of shielding and the metal assembly.

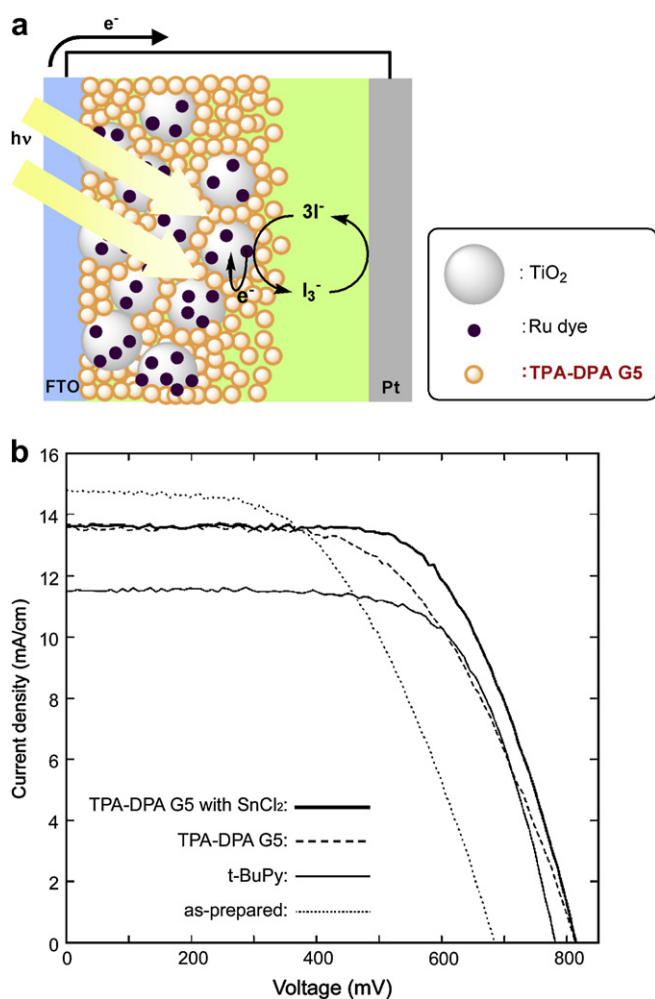


Fig. 12. (a) Organic dye-sensitized solar cell with dendrimer coating; (b) photocurrent density and voltage characteristics of dye-sensitized solar cells using TPA-DPA G5 with SnCl_2 (bold solid line), TPA-DPA G5 (dashed line), and *t*-BuPy (thin solid line) for comparison with the as-prepared device (dotted line). The coating of dye with TPA-DPA G5 with SnCl_2 enhanced the cell performance.

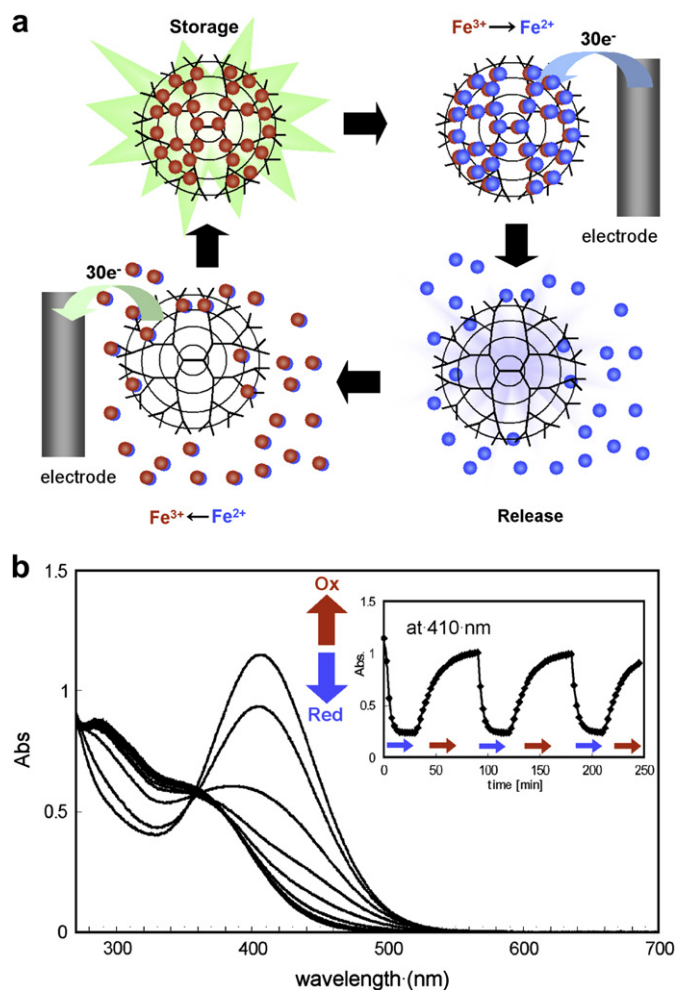


Fig. 13. Storage and release of a precise number of ferric ions in DPA G4 controlled by the redox of ferric ions ($\text{Fe}^{2+}/\text{Fe}^{3+}$): (a) Schematic representation of storage/release cycle of ferric ions; (b) UV-vis spectral change during the redox of ferric acid and the storage/release cycle monitored at 410 nm (inset).

4.4. Metal delivery system

Ferritin in the living body stores and releases iron in nano-sized spaces formed by proteins [60]. A phenylazomethine dendrimer was examined as a 3 nm capsule suitable for the precise storage and release of a predetermined number of ferric ions (Fig. 13) [61]. With a dendrimer containing 30 trivalent ferric ions, a voltage of -0.5 V (vs. Ag/Ag^+) was applied and ferric ions were successfully and completely reduced to the bivalent state. This reduction of valence also significantly lowers the Lewis acidity, resulting in release of the ions. Oxidizing back to the trivalent state assembles the ferric ions. Thus, by changing the voltage, ferric ions can be stored and released reversibly. This functionality was also successfully reproduced using a capsule almost 1/50 the size of ferritin.

5. Conclusion

Metal polymer composite materials, typified by macromolecular complexes, have the characteristics of both metal and organic frameworks, allowing for highly customizable design. Such materials are anticipated to provide multiple functionality. Although macromolecular complexes are not new, most existing complexes combine metal and organic substances statistically, and do not allow for precision metal placement. This situation has thus far

prevented the functionality of such materials from being fully developed and utilized.

Using a dendrimer with a hard dendritic structure, our group has achieved precise control of the number of metal atoms introduced, and have successfully created a new metal-organic hybrid nano-material with arbitrarily customizable number of metal atoms. This new material has been demonstrated to be usable in high-intensity light-emitting devices and solar cells. In addition, the functionality of ferritin proteins has been successfully reproduced using a phenylazomethine dendrimer, opening pathways to new drug delivery systems capable of precise control of the storage and release of metal. Beyond these basic studies, the new material was shown to be applicable in energy and molecular conversion, providing control such as stepwise radial complexation, potential gradient, and precise control of the number of atoms.

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