

Build-up enhancement of photoluminescence from phenylazomethine bismuth dendrimer using Bi(OTf)₃

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Abstract Metal assembly to a dendrimer can provide various functionalities based on the branched structure. Here, we researched assembly phenomena of bismuth salts in the phenylazomethine dendrimer and achieved enhancement of emission intensity per metal unit by using Bi(OTf)₃. This enhancement suggested increasing of Bi–N coordination bonds derived from the bismuth units in the dendrimer.

Keywords Phenylazomethine dendrimer · Bismuth · Photoluminescence · Optical nanomaterials

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Introduction

The precise arrangement of metals in organic polymers or macromolecules is an important objective considering natural materials, such as photosynthesis that control the direction and ratio of electron transfer. Various polymer-metal complexes have been reported, but the fine control of the nano-sized structure and the metal position is not available in conventional polymer-metal complexes due to the length distribution of the polymers (Ciardelli et al. 1995; Pittman et al. 1996).

Dendrimers, uniform three-dimensional branched polymers, are some of the most advantageous materials for fabricating controlled polymer-metal complexes (Tomalia et al. 1985; Newkome et al. 1985; Bosman et al. 1999; Grayson and Frechet 2001; Astruc and Chardac 2001). Various functional derivatives which contain metal complexes in the core and/or branches have been investigated (Newkome et al. 1995; Balzani et al. 1998). For example, introduction of metal ions or complexes in the core was utilized for organic light-emitting materials (Kawa and Frechet 1998; Hwang et al. 2008; Vicinelli et al. 2002; McClenaghan et al. 2003; Baudin et al. 2002). Catalytic and redox active metal complexes were also adopted for the functionalities (Bhyrappa et al. 1996; Knapen et al. 1994; Twyman et al. 2002; Nlate et al. 2000; Wang et al. 2014; Nijhuis et al. 2004; Suzuki et al. 2006). In addition, metal complexes at the periphery of the branches can be used for dendritic networks leading to the fabrication of macromolecules (Newkome et al. 1995, 1998).

The metal units of these metallodendrimers described above are incorporated into the skeletons. They have a merit of the high stability and can be novel building blocks for supramolecular structures. On the other hand, the assembly of the metal units into the dendrimer is another attractive strategy for metallodendrimers. Polyamidoamine (PAMAM) dendrimers can be metal complex dendrimers by the coordination of metal salts (Tomalia et al. 1985; 25 Esfand and Tomalia 2001; Lee et al. 2005; Tomalia et al. 2007; Lee et al. 2003). Such metal assembled dendrimers have been used as a nano-sized flask for the fabrication of size-controlled metal nanoparticles (Crooks et al. 2001; Zhao et al. 1998; Zhao and Crooks 1999). In this case, the shell-effect works for protection of the fabricated nanoparticles from the outer environment.

Among these dendrimers, we focused on dendritic polyphenylazomethines (DPAs) as a platform for metal assembly (Higuchi et al. 2001; Yamamoto et al. 2002; Takanashi et al. 2004; Enoki et al. 2006; Imaoka et al. 2013). The DPAs have imine-based coordination ligands in their branches. In addition, the π -conjugated skeleton produces an electronic potential gradient from the core to the periphery sites. It creates a different basicity of the imine sites and enables the stepwise controlled assembly of Lewis acidic units (e.g., metal salts, boron units, and organic molecules) (Yamamoto and Imaoka 2014; Yamamoto et al. 2005, 2009; Nakajima et al. 2004; Imaoka et al. 2005, 2006; Takanashi et al. 2007; Kambe et al. 2016a, b; Albrecht et al. 2013, 2016). The DPAs are also used for fabrication of metal particles and clusters (Yamamoto and Imaoka 2014; Yamamoto et al. 2009; Takahashi et al. 2017; Kambe et al. 2017; Inomata et al. 2018; Satoh et al. 2008).

Recently, we reported a luminous dendrimer based on the stepwise 1:1 complexation of BiCl_3 into the 4th generation DPA (DPAG4). This bismuth-assembled dendrimer showed orange-colored luminescence (broad emission peak centered around 600 nm). The stepwise 1:1 assembly enabled the fine intensity tuning of the photoluminescence. In addition, the photoluminescence was maintained even in the solid state whereas the corresponding mononuclear complex was quenched under the same condition. These specific features demonstrated effective shell protection of the DPAG4. Such a shell effect was also utilized for optical switching based on the reversible complexation (Kambe et al. 2016a). In this study, we

used bismuth salts different from BiCl_3 considering the effect of the coordination mode and achieved an increasing emission intensity per the assembled metal unit using the complexation behavior of $\text{Bi}(\text{OTf})_3$ (OTf: trifluoromethanesulfonate). The OTf ligand has excellent leaving group properties (Dixon et al. 1990). Therefore, it dissociates from the bismuth atom in a solvent and enables increasing coordination bonds between the Bi(III) and phenylazomethine units. We demonstrated the utility of this multiple coordination behavior for decreasing of the amount of the metal units which generated photoluminescence through an assembly process.

Experimental section

Materials

$\text{Bi}(\text{OTf})_3$, (Strem Chemicals), BiCl_3 ultra dry (Alfa Aesar), and bismuth 2-ethylhexanoate (Alfa Aesar) were purchased and used without any further purification. Dehydrated acetonitrile and triethylamine were obtained from Kanto Chemicals. Chloroform was obtained from Wako Pure Chemical Industries, Ltd. The DPAG4 was synthesized according to the literature (Enoki et al. 2006).

Characterization

The UV-vis spectra were recorded using Shimadzu UV-3600 and UV-3100PC spectrometer with a quartz cell having a 1-cm optical length at 20 °C. The photoluminescence spectra were obtained by a Jasco FP-8300 at room temperature.

Complexation between bismuth salts and DPAG4

In an Ar-filled glove box, an acetonitrile solution of $\text{Bi}(\text{OTf})_3$ (3.19 mM), or BiCl_3 (2.21 mM), and an acetonitrile/chloroform (1/1) mixed solution of the DPAG4 (0.64 μM) were prepared. Then, the appropriate amount of the bismuth salt solution was added to the DPAG4 solution (3.0 mL) and the solution was vigorously stirred. The reactions were monitored by using UV-vis absorption and photoluminescence spectroscopy.

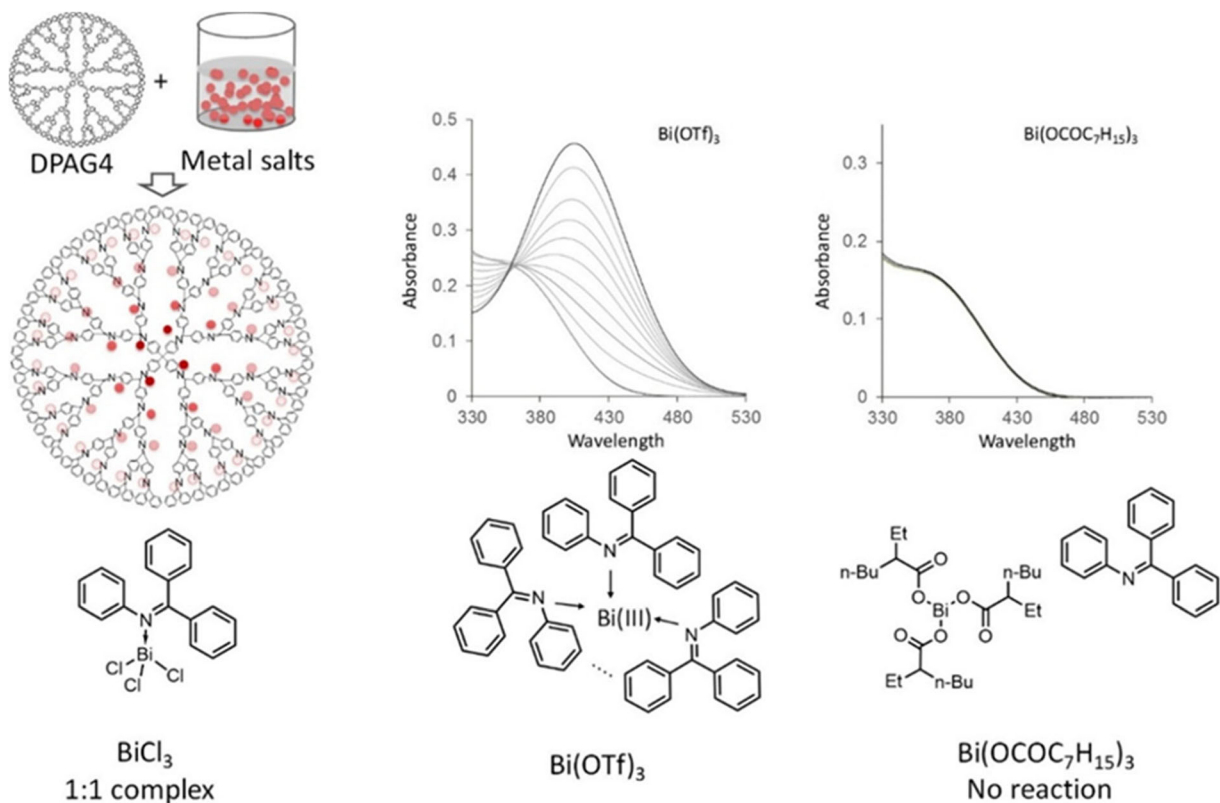


Fig. 1 Schematic illustration of assembly process of bismuth units into the DPAG4. BiCl_3 has a 1:1 coordination with the phenylazomethine part. On the other hand, bismuth trifluoromethanesulfonate shows increasing metal-imine complexes, while bismuth 2-ethylhexanoate does not react. Graphs

show the UV-vis titration results. The complexation of $\text{Bi}(\text{OTf})_3$ demonstrated saturation of the spectral change at the point of 20 equivalent bismuth units (middle up). No spectral change was observed in the case of bismuth 2-ethylhexanoate (right up)

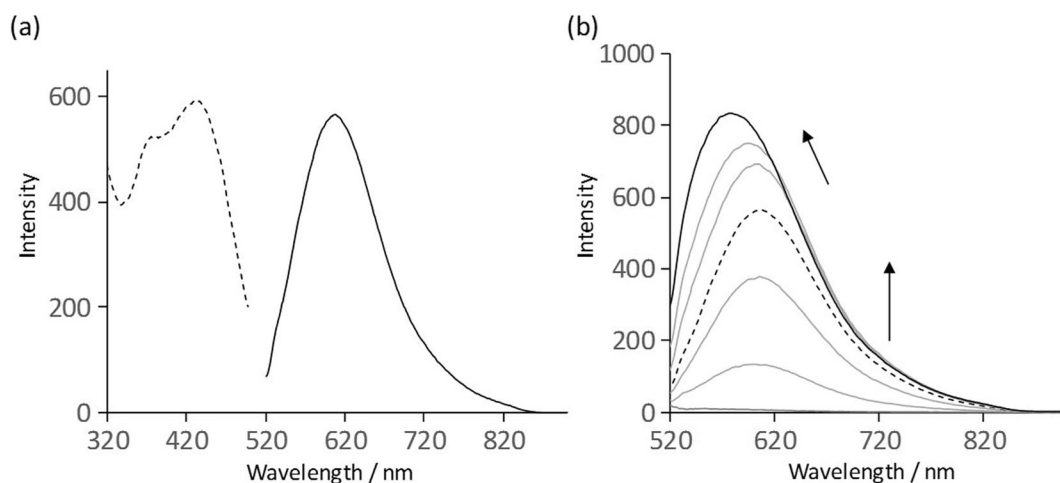


Fig. 2 a Excitation (dotted line; $\lambda_{em} = 600 \text{ nm}$) and emission (bold line; $\lambda_{ex} = 450 \text{ nm}$) spectra of $4\text{Bi}(\text{OTf})_3\text{-DPAG4}$. The solvent is a 1:1 mixed solution of acetonitrile and chloroform. **b**

Emission spectral change during the addition of $\text{Bi}(\text{OTf})_3$. Dotted and bold black lines correspond to the DPAG4 with 4 and 20 equivalents of $\text{Bi}(\text{OTf})_3$, respectively

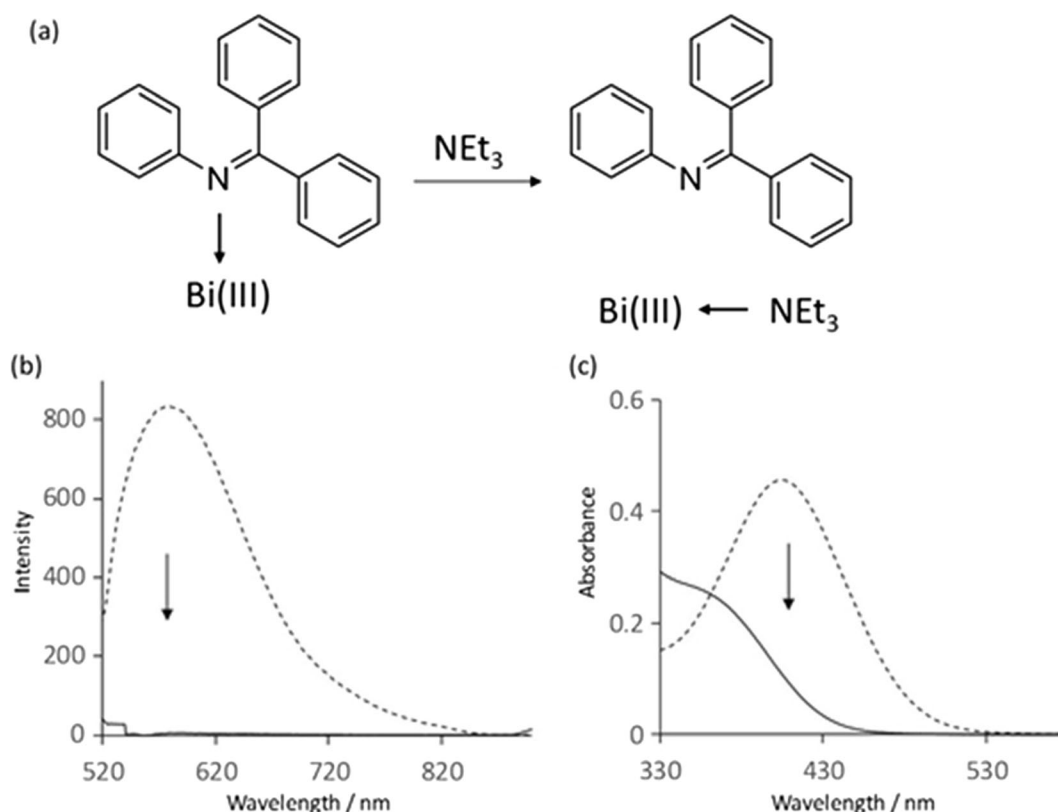


Fig. 3 a Chemical scheme of ligand exchange reaction using triethylamine (NEt₃). Spectral change in the **b** photoluminescence intensity and **c** absorbance

In the case of bismuth 2-ethylhexanoate, an acetonitrile solution of bismuth 2-ethylhexanoate (2.56 mM), and an acetonitrile/chloroform (1:1) mixed solution of the DPAG4 (0.47 μM) were used.

Removal of Bi(OTf)₃ from the DPAG4

This experiment was conducted by reference to the method in the case of BiCl₃ described in the previous literature (Kambe et al. 2016a). Triethylamine (1.0 μL) was added to the DPAG4 with Bi(OTf)₃ solution (0.64 μM , 3.0 mL; acetonitrile/chloroform = 1/1).

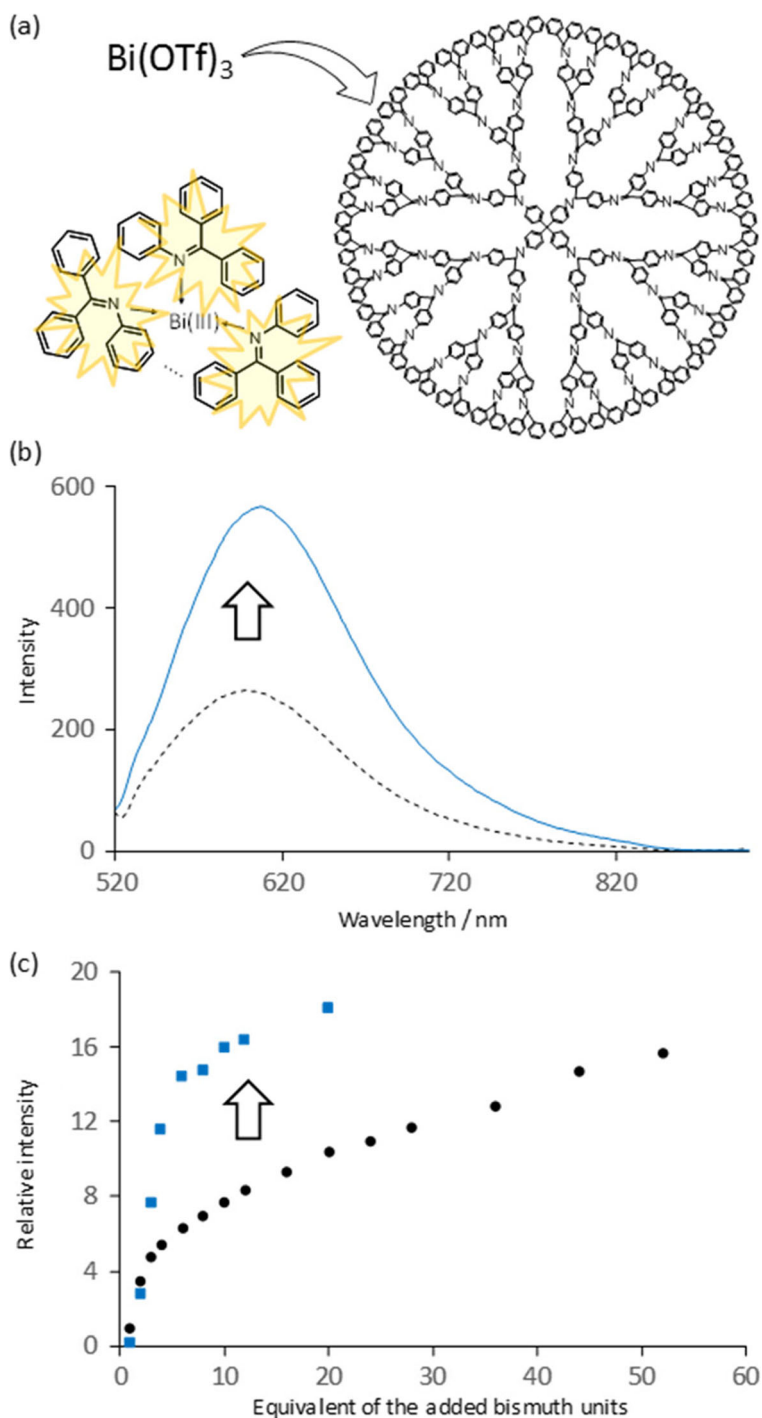
Results and discussion

Assembly of bismuth salts

A certain amount of the acetonitrile solution of Bi(OTf)₃ (3.19 mM) was stepwisely added to the mixed solution (acetonitrile/chloroform) of the

DPAG4 (0.64 μM). The spectral change was monitored by UV-vis spectroscopy. The absorption band around 410 nm increased during the addition of the Bi(OTf)₃ (from 1 to 20 equivalents). The peak shape and position were almost the same in the case of other metal units including BiCl₃ (Yamamoto and Imaoka 2014; Kambe et al. 2016a), suggesting similar coordination interaction between metals and the DPAG4. On the other hand, the amount of the absorption change was different. This spectral change was saturated around 20 equivalents of Bi(OTf)₃ whereas the DPAG4 possessed 60 phenylazomethine sites. After the saturation, the absorption peak shifted to the longer wavelength region when the Bi(OTf)₃ was continuously added to the solution containing the DPAG4 with 20Bi(OTf)₃ (Fig. S1). This spectral change is considered to be derived from decomposition of the azomethine parts in the DPAG4. These results suggest that the complexation between Bi(OTf)₃ and the phenylazomethine ligands in the DPAG4 was

Fig. 4 **a** The complexation of $\text{Bi}(\text{OTf})_3$ can increase number of the emissive bismuth complexes. **b** Photoluminescence spectra of the DPAG4 with 4 equivalents of $\text{Bi}(\text{OTf})_3$ (blue bold line) and BiCl_3 (black dotted line). The excitation wavelength is 450 nm. **c** Change in photoluminescence intensity during addition of the bismuth salts normalized by the peak area of BiCl_3 -DPAG4. The blue squares and black circles correspond to $\text{Bi}(\text{OTf})_3$ and BiCl_3 , respectively



multidentate, and the number of bismuth-coordinating phenylazomethine ligands per bismuth unit is greater than that in the case of BiCl_3 which behave in a 1:1 coordinating fashion (Kambe et al. 2016a). In contrast, bismuth 2-ethylhexanoate that

has carboxylate ligands was found not to be coordinated by the phenylazomethine ligands because the absorption spectra did not change. This means that the assembly feature could be changed by choice of the initial ligands on the bismuth atom (Fig. 1).

Table 1 Peak area of emission spectra (F) and the peak area per absorption (F/A) about the DPAG4 with bismuth units (4 equivalents)

	F	F/A
4Bi(OTf) ₃ -DPAG4	7.8×10^4	7.8×10^5
4BiCl ₃ -DPAG4	3.7×10^4	1.2×10^6

Photoluminescence properties

Assembly of Bi(OTf)₃ into the DPAG4 induced photoluminescence, and the emission intensity increased with the addition of the Bi(OTf)₃. The observed emission and excitation peaks were found to be similar to those of BiCl₃ (Fig. 2a). This suggested that the photoluminescence properties were maintained versus the change in the coordinating ligands. However, the emission peak was shifted to the shorter wavelength region after 4 equivalents of Bi(OTf)₃ (Fig. 2b). The reason is considered to be a multiple complexation among the dendrimers.

Reversible complexation

The complexation between Bi(OTf)₃ and the phenylazomethines is labile. Therefore, dissociation of the coordination bond using a base reagent is expected (Fig. 3a). Figure 3b and c shows the absorption and emission spectral change of the 20Bi(OTf)₃-DPAG4 solution with the addition of triethylamine which is a stronger base, respectively. We observed that the increased photoluminescence and absorption by the complexation with Bi(OTf)₃ was completely back to the initial state. The optical and chemical features that show the reversible complexation with photoluminescence are characteristic of the optical dendrimer based on the DPAG4.

Photoluminescence intensities

The use of Bi(OTf)₃ units enabled enhancement of the photoluminescence per bismuth unit (Fig. 4a). Figure 4b shows the emission spectra of 4Bi(OTf)₃-DPAG4 and 4BiCl₃-DPAG4 at the same concentration (0.64 μM). The higher intensity was clearly observed in the case of Bi(OTf)₃. Figure 4c shows the intensity change during the addition of the

bismuth units. The intensity was normalized by the peak area from BiCl₃-DPAG4. We found that the photoluminescence intensity was enhanced in the case of Bi(OTf)₃ at the low equivalents of the bismuth units. This result showed successful cut-down of the metal units that trigger the optical emission from the dendrimer. Table 1 shows a comparison of the parameters corresponding to the photoluminescence intensity (F) and quantum yield (F/A) (F : area of the emission spectra, and A : absorption at the excitation wavelength). Though 4Bi(OTf)₃-DPAG4 has high photoluminescence intensity, the F/A is smaller than that of 4BiCl₃-DPAG4. These results suggest that the increasing absorption affects the enhancement of the photoluminescence.

Conclusions

In conclusion, we revealed the coordination reactions of various kinds of bismuth units to the DPAG4 and achieved successful enhancement of the photoluminescence from the bismuth-coordinating dendrimers by utilizing the coordination fashion of Bi(OTf)₃. This complexation was revealed by the UV-vis absorption and photoluminescence spectra including the monitoring of the bond formation and dissociation reaction, suggesting multiple coordination bonds. We also revealed that this photoluminescence enhancement was affected by the increasing absorption from the metal-imine complexes in the DPAG4. These results demonstrate a certain application of this coordination behavior for the enhancement of the complex properties in the dendrimer.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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