Dendrimers

Deutsche Ausgabe: DOI: 10.1002/ange.201607396
Internationale Ausgabe: DOI: 10.1002/anie.201607396

Bismuth Complexes in Phenylazomethine Dendrimers: Controllable Luminescence and Emission in the Solid State

*Tetsuya Kambe, Aiko Watanabe, Takane Imaoka, and Kimihisa Yamamoto**

Abstract: *Dendritic phosphors were obtained by the stepwise integration of $BiCl_3$ in phenylazomethine dendrimers. The bismuth-coordinated phenylazomethines displayed photoluminescence at 500–800 nm, and the intensity could be tuned by changing the stoichiometry of $BiCl_3$ and the dendrimer. This phosphor did not show serious luminescence quenching even though the local concentration of $BiCl_3$ in the dendrimer was as high as 20 M, and luminescence was also observed in the solid state. The absorption and emission properties could be reversibly switched by addition of a Lewis base or under electrochemical redox control, which induced the reversible complexation of $BiCl_3$ in the dendrimer.*

The precise control of photoluminescence plays a significant role in designing optical materials. Stimuli-responsive compounds, which change their emission intensity and wavelength in response to external stimuli, are particularly attractive. Various examples of such changes triggered by light, pH, mechanical forces, or the addition of chemicals have been reported,[1] and such compounds are expected to be utilized as sensors and optical standards. The changes in their optical properties are generally based on changes of their crystal conformation, molecular packing, or chemical structure. Therefore, the emission wavelength often changes differently from the intensity. Controlling the emission intensity of a phosphor molecule by simple means is still difficult. Herein, we assembled phosphors in a molecular dendrimer to control their luminescence intensity.

Assembling photoluminescent components within dendrimers is a suitable method for controlling the emission intensity. Dendrimers have three-dimensional skeletons derived from their branches.[2] Such unique structures can encapsulate chemical units, which is of particular interest for light harvesting, sensors with signal amplification, and understanding dendritic skeletons, for example.[3] However, a serious quenching effect generally prevents enhancement of the luminescence because the local concentration of the luminescent components is very high.[3a,4] Furthermore, typical dendrimers designed to capture multiple chemical units cannot assemble them precisely because various reactive positions are available in the dendrimer skeletons. This also complicates the control of the optical properties when ordinal dendrimers are used as nanocapsules.

Against this background, we designed luminous dendrimers of which the optical properties are finely tunable that are based on bismuth complexes in dendritic polyphenylazomethines (DPAs; Figure 1; see also the Supporting Information, Figure S1). The DPAs have an electronic potential gradient from the core to the periphery owing to the electron-donation effect of the phenylazomethine units, which enables the fine-controlled assembly of metal ions in a radial and stepwise fashion.[5] Furthermore, the DPAs have a semi-rigid skeleton,[6] which helps to maintain the optical characteristics of the metal complexes integrated in the DPAs by restricting the electronic interactions between the complexes. As an additional distinguishing feature from other emissive dendrimers, the luminescence of the complexes can be switched on and off through the formation of reversible coordination bonds. In our previous study, we reported that various metal chlorides, such as $PtCl_4$, $SnCl_2$, $GaCl_3$, $FeCl_3$, $AuCl_3$, $CuCl_2$, and VCl_3, could be integrated into DPAs with specific ratios;[5,7] however, their luminescence properties have not yet been investigated.

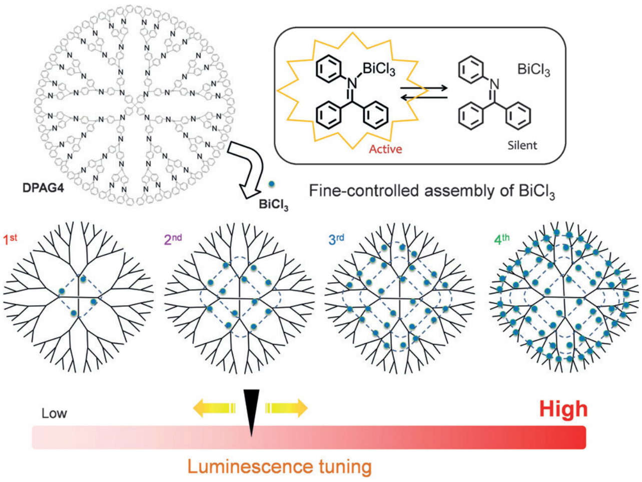

Figure 1. Luminescent dendrimers of DPAG4 with $BiCl_3$.

Bismuth, the heaviest atom without any toxicity or carcinogenicity, could also be integrated into such dendrimers, and it has attractive and unusual electronic, magnetic, catalytic, and optical properties.[8] The optical ones, in particular, which include emission and the possible use as a sensitizer for lanthanide atoms, are desirable for various

---

[*] Dr. T. Kambe, A. Watanabe, Dr. T. Imaoka, Prof. K. Yamamoto
Laboratory for Chemistry and Life Science
Tokyo Institute of Technology
4259 Nagatsuta Midori-ku, Yokohama 226-8503 (Japan)
E-mail: yamamoto@res.titech.ac.jp

Dr. T. Kambe, Dr. T. Imaoka, Prof. K. Yamamoto
ERATO Japan Science and Technology (JST)
4259 Nagatsuta Midori-ku, Yokohama 226-8503 (Japan)

Supporting information for this article can be found under:
http://dx.doi.org/10.1002/anie.201607396.

applications.[9–11] Despite the intriguing optical features, most of the research on bismuth has focused on inorganic solids.[8d,12] In this case, a detailed analysis of the optical properties is difficult because the structure of the luminous part is not clear. A few luminescent Bi complexes have been reported[13] but the fabrication of these complexes was difficult. Herein, we utilized Bi complexes to obtain finely controllable phosphors based on DPA and $BiCl_3$ (Figure 1). Furthermore, the strong emission in the solid state and approaches to switching the optical properties of the dendrimer capsules were investigated.

$BiCl_3$ was integrated into a fourth-generation DPA (DPAG4) with a potential gradient in the branches, which enabled stepwise complexation from the core to the periphery (Figure S1). This was confirmed by a UV/Vis titration analysis that we have established for various metal salts.[5,7] The addition of an acetonitrile solution of $BiCl_3$ changed the absorption spectrum of DPAG4 in a mixed solution of chloroform and acetonitrile (1:1 v/v; Figure S2). The absorption of the imine $BiCl_3$ complex at approximately $\lambda = 400$ nm increased in intensity while that of the free imine components decreased. This spectral change has an isosbestic point that shifts according to the coordinating phenylazomethine layers in the DPAG4. When 1–4 equiv of $BiCl_3$ were added, the isosbestic point was located at 367.5 nm. The isosbestic point then shifted to shorter wavelengths upon addition of a larger excess of $BiCl_3$ (6–12 equiv: 365.0 nm; 16–28 equiv: 361.5 nm; 36–60 equiv: 356.5 nm). This behavior confirms the finely controlled assembly of $BiCl_3$ in DPAG4 at a $BiCl_3$/phenylazomethine ratio of 1:1. The coordination to the nitrogen atoms was also confirmed by XPS. The N 1s peak shape changed upon coordination to the added $BiCl_3$ (Figure S3) while the N 1s peak corresponding to $N{-}BiCl_3$ increased in intensity and was located at a lower binding energy than that of the free azomethine. This shift to lower binding energies suggests that the $BiCl_3$ trapped the electrons of the nitrogen atoms, which were donated to the inner phenyl rings of DPAG4. Peak deconvolution clearly supported the change in the coordination ratio of the phenylazomethine parts. The $N{-}BiCl_3$/free azomethine ratios of DPAG4–4 $BiCl_3$, DPAG4–12 $BiCl_3$, and DPAG4–28 $BiCl_3$ were determined to be 4:56, 12:48, and 28:32, respectively. In the case of DPAG4 with 60 equiv of $BiCl_3$, the coordination ratio was lower than expected as the $BiCl_3$ units in the outermost layer were removed during evaporation. These peak ratios strongly corroborate the number-controlled integration of $BiCl_3$ into DPAG4. In addition, the 1:1 complexation was clearly confirmed by a Job plot[14] using a simple azomethine molecule, (diphenylmethylene)(phenyl)amine (G0; Figure S4). ^{1}H NMR spectra supported the complexation process. The ^{1}H resonances of electron-poor and electron-rich positions (7.80 and 6.80 ppm at 0 equiv, respectively) were shifted to lower and higher magnetic fields, respectively, during the complexation process (Figure S5). The ^{1}H NMR results confirm the inhibition of the π-electron-donating effect of the azomethine units upon coordination to $BiCl_3$. The precisely controlled integration of $BiCl_3$ into DPAG4 has thus been fully confirmed.

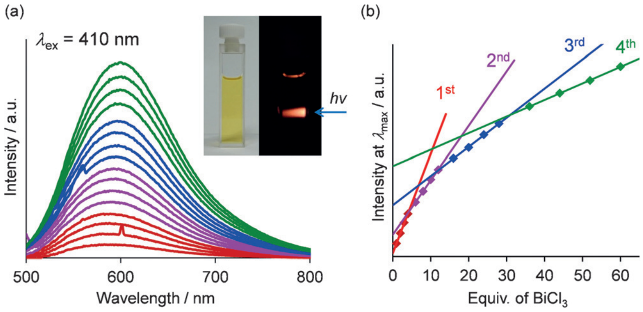

Figure 2. a) Luminescence spectra of DPAG4 with 0–60 equiv of $BiCl_3$ ($\lambda_{ex} = 410$ nm). The inset shows photographs of DPAG4–60 $BiCl_3$. b) Changes in the intensity at the maximum of the emissions.

The controlled assembly of $BiCl_3$ in DPAG4 enhanced the photoluminescence of the imine $BiCl_3$ complexes. Figure 2a shows the luminescence spectra of DPAG4 with 0–60 equiv of $BiCl_3$. The broad emission peak centered at $\lambda = 600$ nm (orange color) became more intense without a significant wavelength shift as the amount of $BiCl_3$ was increased. This phenomenon indicates the fine control of the luminescence intensity of each molecular dendrimer, which was achieved by the uniform integration of metal ions from the core site in a stepwise fashion.

Figure 2b shows the luminescence intensities at λ_{max} as $BiCl_3$ was added to the DPAG4 solution. The relative increases in intensity differed based on the coordination position of DPAG4 (from the 1st to the 4th layer). This suggests that the four dendritic layers derived from the flexibilities of the constituent phenylazomethine complexes have different quantum yields. In contrast, the almost linear increase for each layer suggests the same chemical environment for bismuth complexes in the same layer. It also demonstrates that the effect of concentration quenching is negligible in spite of the presence of many metal complexes in DPAG4 with diameters of about 2 nm. The local concentration of the integrated 60 $BiCl_3$ complexes is comparable to 20 M (Figure S6). General phosphors are quenched upon increasing the concentration.[15] For example, a mononuclear phenylazomethine $BiCl_3$ complex (G0–$BiCl_3$) shows concentration quenching at concentrations above 0.2 mM in the solution state, which corresponds to an average distance of about 50 nm between the complexes. Accordingly, the emission intensity of DPAG4 coordinated with 60 equiv of $BiCl_3$ (DPAG4–60 $BiCl_3$) was much higher than that of G0–$BiCl_3$ under the same conditions (Figure S7).

The restriction of luminescence quenching was critically effective in the solid state. Solid samples of DPAG4–60 $BiCl_3$ and G0–$BiCl_3$ were prepared on mica or glass substrates by drop casting. The absorption spectra demonstrated successful preparation of the solid samples (Figure S8). The luminescence of solid DPAG4-60 $BiCl_3$ was enhanced around 600 nm whereas that of solid G0–$BiCl_3$ was quenched (Figures 3 and S9).

To understand the luminescence properties of DPAG4–60 $BiCl_3$, the mononuclear complex (G0–$BiCl_3$) was studied. Figure S10 contains the emission, excitation, and absorption spectra of DPAG4–60 $BiCl_3$ and G0–$BiCl_3$. The absorption

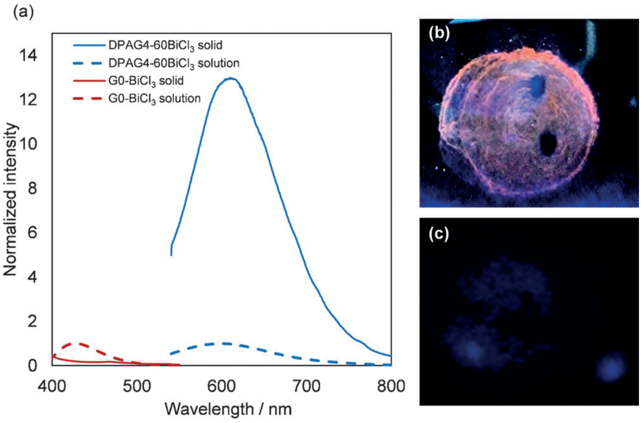

Figure 3. a) Luminescence spectra of solid (——) and solution (– – –) samples of DPAG4–60 BiCl$_3$ (blue) and G0–BiCl$_3$ (red). Photographs of b) DPAG4–60 BiCl$_3$ and c) G0–BiCl$_3$ in the dark under irradiation at b) $\lambda = 410$ nm and c) $\lambda = 380$ nm, respectively. The blue color observed in (b) and (c) is due to scattering light.

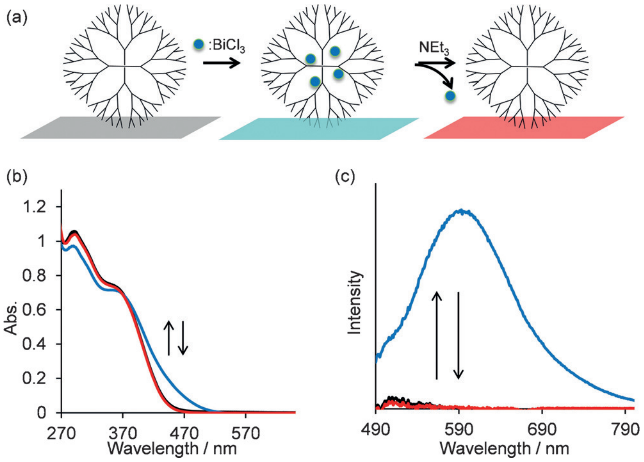

Figure 4. a) Switching the luminescence of DPAG4 by controlled integration and removal of BiCl$_3$ units. b, c) The spectral changes in UV/vis absorption and emission during the process illustrated in (a).

peaks were located at about 380 nm (DPAG4–60 BiCl$_3$) and 310 nm (G0–BiCl$_3$) in the long-wavelength region, and were considered to be due to interligand transitions as they are independent of the nature of the added metal salt.[7] These peaks are different from those observed in the excitation spectra, which suggests that the interligand transitions do not contribute to the emission, but that other weak transitions that are affected by the bismuth salt trigger the emission. Cyclic voltammograms of DPAG4 and G0 in the presence of BiCl$_3$ demonstrate that the LUMOs of the Bi complex dendrimers are located on the metal center (Figure S11) because the reduction of BiCl$_3$ was observed first. Therefore, the observed emission is due to a charge-transfer transition between metal and ligand. The broad shape of the emission peaks is also characteristic of a charge-transfer emission.

The lifetimes of the emissions of DPAG4–60 BiCl$_3$ and G0–BiCl$_3$ were measured using the Hamamatsu photonics C7700-ABS-N system ($\lambda_{ex} = 355$ nm). The lifetime of DPAG4–60 BiCl$_3$ was longer than that of G0–BiCl$_3$ (Figure S12a), which is presumably due to energy transfer between the bismuth complexes. Deconvolution of the lifetime spectrum of DPAG4–60 BiCl$_3$ revealed that the observed emission band clearly had two components located at approximately 600 and 680 nm. Their lifetimes were 0.12 and 0.70 μs, respectively (Figure S12b). The latter, longer-lifetime component was assigned to phosphorescence stemming from the heavy atom effect of bismuth.

The reversibility of the complexation enabled switching between photoluminescence and absorption in the visible region. Integrated BiCl$_3$ could be removed by addition of triethylamine as a stronger Lewis base, upon which the luminescence disappeared (Figure 4). A stepwise decrease in emission was also observed for DPAG4–60 BiCl$_3$ (Figure S13).

Furthermore, electronic reduction also triggered the desorption of BiCl$_3$, followed by luminescence quenching. A cyclic voltammogram of DPAG4–60 BiCl$_3$ is shown in Figure 5a. The observed waves were not simple, but reversible. The first reduction at −0.6 V was assigned to the reduction of 60 BiCl$_3$ coordinated by the phenylazomethine units because a similar reduction was also observed for G0–BiCl$_3$ and BiCl$_3$ without DPAG4 (Figures 5b and S11). The reduction of the bismuth complex led to the cleavage of the coordination bonds between the N and Bi atoms, resulting in the disappearance of the corresponding oxidation waves around −0.6 V. The oxidation wave of the reduced Bi was observed around −0.1 V; then the Bi^{III} was reassembled in DPAG4. In the cases of G0–BiCl$_3$ and BiCl$_3$, the first reduction waves were similar to that of DPAG4–60 BiCl$_3$, but the oxidation waves were different and irreversible. The oxidation current at 0.2 V increased with the number of sweep cycles (Figure S11). A possible reason is the precipitation of Bi^0 metal on an electrode. These results demonstrate that DPAG4 can be used as a capsule for switching between metal complexes and clusters (Figure 5c).

The formation of bismuth clusters in DPAG4 during this reduction process was revealed by HAADF-STEM analysis by using a mesoporous carbon support (Figure S14). The uniformity of the clusters confirms that the bismuth clusters were maintained in DPAG4, which constitutes a significant advantage for reversible switching.

This redox behavior in the presence of DPAG4 is associated with the reversible luminescence and absorption features. During the repeated reduction and oxidation processes, the emission and UV/Vis absorption spectra change reversibly. This was demonstrated for DPAG4–28BiCl$_3$ (Figures 5d–f). The spectral shapes of the emission and absorption were clearly assignable to the reversible coordination of Bi^{III} units. On the contrary, the absorption spectral change of G0–BiCl$_3$ upon electronic reduction was different from that induced by the complexation process, especially around 370 nm. This finding suggests partial decomposition (Figure S15).

In conclusion, we have investigated a photoluminescent dendrimer consisting of specific numbers of bismuth salts in a DPA. The precisely controlled assembly of BiCl$_3$ in DPAG4 provided a stepwise increase in the emission intensity at 500–800 nm. The features of the emission were revealed by the

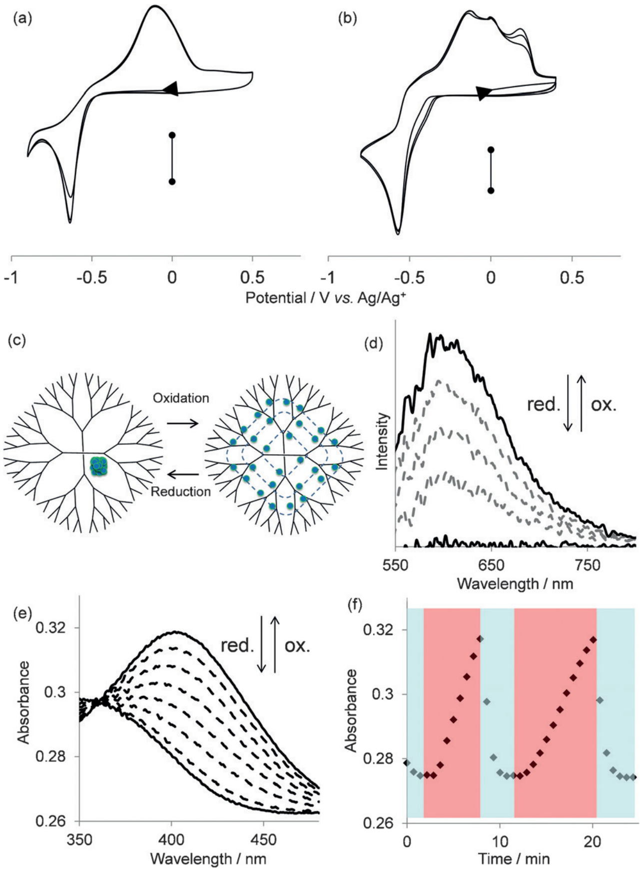

Figure 5. Cyclic voltammograms of a) DPAG4–60 $BiCl_3$ and b) G0–$BiCl_3$ in acetonitrile/chloroform (1:1). The bars in (a) and (b) demonstrate a current of 5 μA. Bu_4NPF_6 (0.1 M) was used as the electrolyte. c) Schematic illustration of the redox-induced switching between cluster and complex. d) Emission spectral change of DPAG4–60 $BiCl_3$ upon reduction at −1.0 V and oxidation at 1.0 V. e) Absorption spectral change of DPAG4–28 $BiCl_3$ upon reduction at −0.8 V and oxidation at 1.0 V. f) Reversibility of the changes in absorption at $\lambda = 410$ nm during the electrochemical measurements. Voltages of −0.8 and 1.0 V were applied in the blue and red areas, respectively.

luminescence spectra of DPAG4–60 $BiCl_3$ and G0–$BiCl_3$. Unlike G0–$BiCl_3$, DPAG4–60 $BiCl_3$ was luminescent even in the solid state. Furthermore, the optical properties of the DPAG4 complex could be switched by addition of a Lewis base or under redox control. The latter was found to be due to switching between metal complexes and metal clusters. This reversible switching was achieved by making use of the shell effect of DPAG4. Our investigations have thus significantly enhanced our knowledge of bismuth complexes and provided new functional phosphors.

Acknowledgements

This work was supported in part by Grants-in-Aid for Young Scientists (B) (15K17829) and for Scientific Research (S) (15H05757) from the Japan Society for the Promotion of Science (JSPS), and the ERATO program of the Japan Science and Technology (JST) Agency.

Keywords: bismuth · dendrimers · luminescence · optical properties · supramolecular chemistry

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 13151–13154
Angew. Chem. **2016**, *128*, 13345–13348

---

[1] a) M. Irie, *Chem. Rev.* **2000**, *100*, 1685–1716; b) F. Pina, A. Roque, M. J. Melo, M. Maestri, L. Belladelli, V. Balzani, *Chem. Eur. J.* **1998**, *4*, 1184–1191; c) R. Martínez-Máñez, F. Sancenón, *Chem. Rev.* **2003**, *103*, 4419–4476.
[2] a) D. A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder, P. Smith, *Polym. J.* **1985**, *17*, 117–132; b) A. C. Grimsdale, K. Müllen, *Angew. Chem. Int. Ed.* **2005**, *44*, 5592–5629; *Angew. Chem.* **2005**, *117*, 5732–5772; c) D. Astruc, E. Boisselier, C. Ornelas, *Chem. Rev.* **2010**, *110*, 1857–1959.
[3] a) M. Kawa, J. M. J. Fréchet, *Chem. Mater.* **1998**, *10*, 286–296; b) S.-H. Hwang, C. D. Shreiner, C. N. Moorefield, G. R. Newkome, *New J. Chem.* **2007**, *31*, 1192–1217; c) T. Sato, D.-L. Jiang, T. Aida, *J. Am. Chem. Soc.* **1999**, *121*, 10658–10659.
[4] V. Vicinelli, P. Ceroni, M. Maestri, V. Balzani, M. Gorka, F. Vögtle, *J. Am. Chem. Soc.* **2002**, *124*, 6461–6468.
[5] a) K. Yamamoto, M. Higuchi, S. Shiki, M. Tsuruta, H. Chiba, *Nature* **2002**, *415*, 509–511; b) K. Yamamoto, T. Imaoka, W.-J. Chun, O. Enoki, H. Katoh, M. Takenaga, A. Sonoi, *Nat. Chem.* **2009**, *1*, 397–402; c) K. Yamamoto, M. Higuchi, A. Kimoto, T. Imaoka, K. Masachika, *Bull. Chem. Soc. Jpn.* **2005**, *78*, 349–355; d) T. Imaoka, R. Tanaka, S. Arimoto, M. Sakai, M. Fujii, K. Yamamoto, *J. Am. Chem. Soc.* **2005**, *127*, 13896–13905; e) T. Imaoka, R. Tanaka, K. Yamamoto, *Chem. Eur. J.* **2006**, *12*, 7328–7336.
[6] T. Imaoka, Y. Kawana, T. Kurokawa, K. Yamamoto, *Nat. Commun.* **2013**, *4*, 2581.
[7] a) K. Takanashi, A. Fujii, R. Nakajima, H. Chiba, M. Higuchi, Y. Einaga, K. Yamamoto, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1563–1572; b) O. Enoki, T. Imaoka, K. Yamamoto, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 621–626; c) K. Yamamoto, Y. Kawana, M. Tsuji, M. Hayashi, T. Imaoka, *J. Am. Chem. Soc.* **2007**, *129*, 9256–9257.
[8] a) C.-Z. Chang et al., *Science* **2013**, *340*, 167–170; b) X.-L. Qi, S.-C. Zhang, *Rev. Mod. Phys.* **2011**, *83*, 1057–1110; c) C. Pan, J. Xu, Y. Wang, D. Li, Y. Zhu, *Adv. Funct. Mater.* **2012**, *22*, 1518–1524; d) Y. Fujimoto, M. Nakatsuka, *Jpn. J. Appl. Phys.* **2001**, *40*, L279–L281.
[9] a) W. J. Park, S. G. Yoon, D. H. Yoon, *J. Electroceram.* **2006**, *17*, 41; b) X. Y. Huang, X. H. Ji, Q. Y. Zhang, *J. Am. Ceram. Soc.* **2011**, *94*, 833–837.
[10] S. Ida, C. Ogata, U. Unal, K. Izawa, T. Inoue, O. Altuntasoglu, Y. Matsumoto, *J. Am. Chem. Soc.* **2007**, *129*, 8956–8967.
[11] M. N. Luwang, R. S. Ningthoujam, S. K. Srivastava, R. K. Vatsa, *J. Am. Chem. Soc.* **2011**, *133*, 2998–3004.
[12] a) F. Kang, M. Peng, Q. Zhang, J. Qiu, *Chem. Eur. J.* **2014**, *20*, 11522–11530; b) H.-T. Sun, Y. Matsushita, Y. Sakka, N. Shirahata, M. Tanaka, Y. Katsuya, H. Gao, K. Kobayashi, *J. Am. Chem. Soc.* **2012**, *134*, 2918–2921.
[13] a) P. J. Han, A. L. Rheingold, W. C. Trogler, *Inorg. Chem.* **2013**, *52*, 12033–12045; b) M. Imran, A. Mix, B. Neumann, H.-G. Stammler, U. Monkowius, P. Bleckenwegner, N. W. Mitzel, *Dalton Trans.* **2014**, *43*, 10956–10968.
[14] a) P. Job, *Ann. Chim.* **1928**, *9*, 113–203; b) W. C. Vosburgh, R. G. Cooper, *J. Am. Chem. Soc.* **1941**, *63*, 437–442; c) Z. D. Hill, P. MacCarthy, *J. Chem. Educ.* **1986**, *63*, 162–167.
[15] B. Valeur, *Molecular Fluorescence: Principle and Applications*, Wiley-VCH, Weinheim, **2002**.

Received: July 31, 2016