Thermo-switchable Imaging Medium Achieving Both Emissive Reflective Modes

Kazuki Nakamura, Yukino Kobayashi, Kenji Kanazawa, Norihisa Kobayashi
Department of Image & Materials Science, Graduate School of Advanced Integration Science, Chiba University,
1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

Abstract

A multifunctional composite film that exhibited thermoresponsive absorption and emission was fabricated using a thermochromic leuco dye, its developer, and a luminescent Europium(III) complex. The emissions from and coloration of this composite film could be reversibly changed and maintained via the thermochromic reaction taking placing within the leuco dye-developer system. The coloration and decoloration of the composite film were caused by thermoresponsive control of the nanoscale aggregation of structures of the leuco dye and its developer, whose molecular structure consisted of a long alkyl chain. The control of the phenomenon of photoluminescence could also be achieved via thermochromism, which was induced by intermolecular energy transfers from the Eu(III) ions in the excited states to the leuco dye.

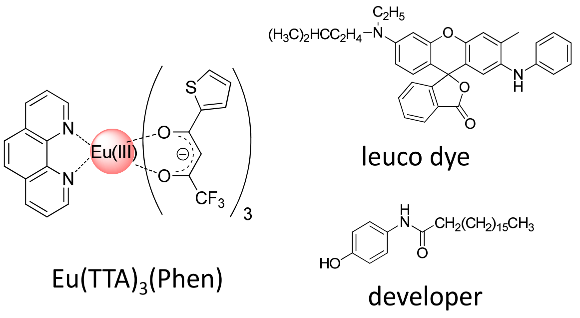

Figure 1. *Chemical structures of Eu(tta)3(Phen), leuco dye, and developer.*

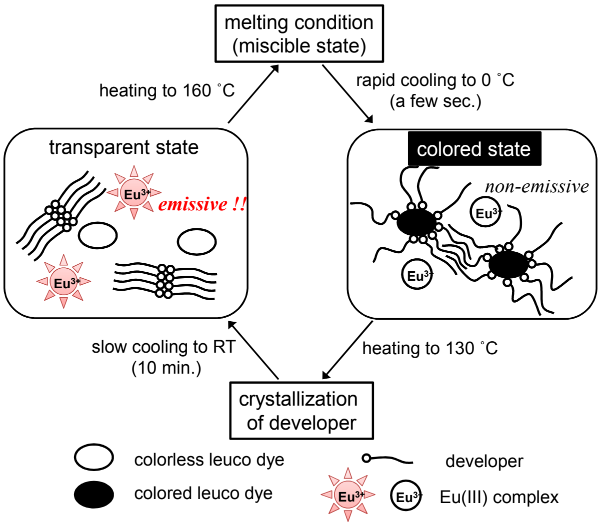

Figure 2. *Schematic illustration of coloring and decoloring process.*

Introduction

Recently, multifunctional materials enabling control of dual emission and coloration in response to external stimuli such as light irradiation, the application of an electrical voltage have attracted considerable research interest since they can be successfully applied to the development of efficient chemical sensors[1], biochemical labels[2], molecular logic gates[3], molecular memories[4], and display devices[5]. Photoactive multifunctional materials were reported by combinating photochromic and fluorescent functions[6]. Eleectroactive multifunctional materials were investigated by using electroluminescent system, electrohemicSal luminescence system, and electrochromic system[5,7]. Concerning with thermoseisitive systems, a lot of color-changing materials by thermal stimuli (thermochromic materials) have been reported[8-10]. Thermosensitive fluorescent switchings have also been reported as crystal structure changes of low molecular dye[11], columnar liquid crystals[12], and intermolecular energy transfer from fluorescent dyes to leuco dyes induced by phase transition[13]. However, the multifunctional material enabling vivid color change and fluorescent switching were hardly reported, because the fluorescent moieties often showed large absorption band in visible region. In order to utilize the multifunctional optical switching as displaying systems, achievement of clear transparent state is essentially required in addition to large color contrast.

The purpose of this study was to fabricate a thermoresponsive multifunctional material that allowed for the dual control of its emission and coloration. We focused on a luminescent Eu(III) complex to obtain a multifunctional material that exhibited a clear transparent state. Eu(III) complexes have unique luminescent properties such as line-like red emissions, long luminescence lifetimes, a large Stokes shift, and high emission quantum efficiencies. These properties have resulted in their widespread use in phosphors, bioassays, and sensor development[14]. In particular, the large Stokes shift (>300 nm) seen in these complexes can enable one to achieve a material with a transparent, colorless state in the visible region. Therefore, the fabrication of highly transparent multifunctional stimuli-responsive media should be feasible by introducing luminescent Eu(III) complexes into leuco dye-developer systems.

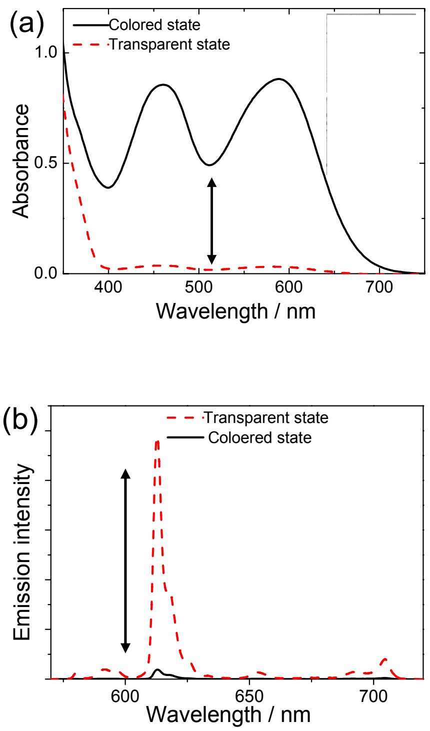

Figure 3. *Absorption spectra (a) and emission spectra (b) of the composite film at transparent state and colored state. Inset shows the photographs of each state. Excited wavelength was 350 nm.*

In this paper, we report novel polymeric composite material based on leuco dye, developer and luminescent Europium(III) complex, whose emission and coloration can be reversibly changed and maintained by thermocromic reaction of the leuco dye system. Coloration and de-coloration of the composite film were caused by thermo-responsive control of nanoscale aggregation of a leuco dye and a developer with a long alkyl chain. the leuco dye and developer. Photoluminescence control was also achieved by the thermochromism via intermolecular energy transfers from the excited states of Eu(III) ions to colored leuco dye.

Experimental method

We employed (1,10-phenanthroline)tris[4,4,4-trifluoro-1- (2-thienyl)-1,3-butanedionato] europium(III) (Eu(tta)3(Phen)) as luminescent material, 2-anilino-3-methyl-6-(N-ethyl-N-isoamylamino)leuco as coloration material, and 1-(4-hydroxyphenyl)-3-octadecylurea as developer (Fig. 1). The leuco dye, 2-anilino-3-methyl-6-(N-ethyl-N- isoamylamino)leuco, was purchased from Yamada kagaku Co. Ltd.. Developer molecule of 1-(4-hydroxyphenyl)-3- octadecylurea was synthesized by literature method. Europium(III) complex, (1,10-phenanthroline)tris[4,4,4- trifluoro-1-(2-thienyl)-1,3-butanedionato] europium(III), was also synthesized according to literature method by using europium(III) acetate (Wako Chemical), 4,4,4-trifluoro-1-(2- thienyl)-1,3-butanedionato (Tokyo Kasei) and 1,10- phenanthroline (Tokyo Kasei).8 The host matrix of polymethyl metacrylate (PMMA, Wako Chemical) was used as received. The composite films were fabricated by spin-coating dimethylformamide solution containing leuco dye (100 mmol/L), developer (200 mmol/L), Eu(III) complex (5 mmol/L), and PMMA (10 wt%) on glass substrate. The film thickness was approximately 2.0 μm.

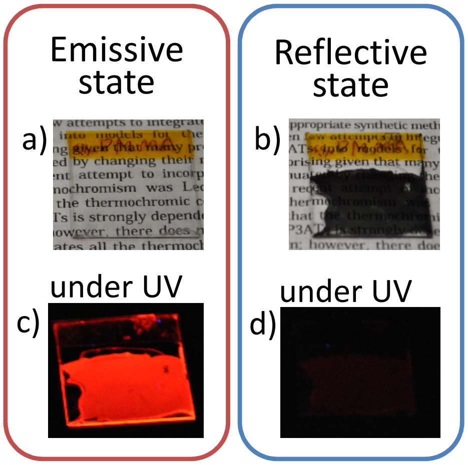

Figure 4. *Photographs of the composite films.*

The coloration of the composite film was carried out by heating the film to 160 °C, which was melting point of the developer, for 10 seconds and subsequently rapid cooling to 0 °C. The bleaching of the colored film occurred upon heating to a temperature 110 °C, which was above the Tg (glass-transition temperature) of the polymer but a little below the melting point of the developer, for 10 seconds and then cooling to room temperature in 10 minutes (Fig. 2).

Results and Discussions

Fig. 3a shows absorption spectra of the composite film under transparent state and colored state. At the transparent state, absorbance in visible region was less than 0.05, resulting in highly transparent film as indicated in inset photo. After the coloration of the film, large absorption bands with the peak at 460 nm and 590 nm were appeared; the film changed to black color. The absorption bands of the colored film were nearly same as those of the colored film without Eu(III) complex, indicating that these absorption peaks were attributed to colored leuco dye which was open-ringed structure induced by protonation of the lactone ring. In order to analyze aggregation structure of the composite film, X-ray diffraction measurements of the films in each state were carried out. When the film was colored state, broad diffraction peak was observed at around 20 °, indicating that there is disorder among the long alkyl groups and that they are slightly miscible with the amorphous polymer matrix. In contrast, the two tiny diffraction peaks were appeared on the broad peak at around 20 ° in the colorless state. Those peaks were ascribed to segregation of the developer. The results were consistent with reported thermocromic system in polymer matrix. Those results suggested that the novel composite film works well as thermosensitive color changing material. Then, we measured emission spectra of the composite film at transparent state and colored state (Fig. 3b). Strong red emissions were observed from the Eu(III) complex

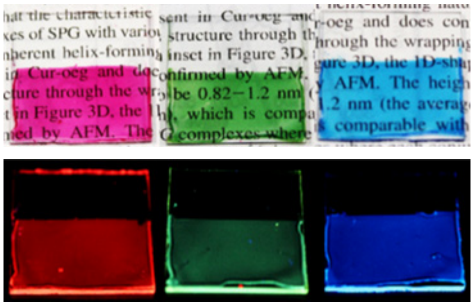

Figure 5. *Photographs of the multi-color DMD films.*

under the excitation of tta ligands (350 nm) when the composite film was transparent state (Fig. 3b dashed line and Fig. 4).

Whereas, the red emission from the Eu(III) complex was almost quenched when the composite film was colored (Fig. 3b solid line). The emission intensity was recovered after bleaching of the black color. The emission quantum efficiency of the film at transparent state was 41.4%, besides that at colored state was 3.4% under tta ligand excitation (350 nm). The estimated quenching efficiency was 92%, resulting in good emission switching property. On the other hand, the energy transfer efficiency was found to be 80%. Those results indicated that the emission quenching was mainly due to the excited energy transfer from excited state of the Eu(III) complex to colored leuco dye. The absorption band of the colored leuco dye appeared at around 600 nm, and this overlapped well with the emission band of the Eu(III) complex. Such an overlapping of the absorption and emission bands enable efficient energy transfers from the excited states of the Eu(III) complex to the ground states of colored leuco dye. In addition to the excited energy transfer, the absorption of the emitted light by colored leuco dye would be the alternative cause of the Eu(III) emission quenching. The absorbance changes of the film were stably repeated between 0.05 (colorless state) and 0.9 (colored state). On the other hand, the emission intensities also repeatedly changed depending on the absorbance changes.

Finally, we demonstrated multicolor representation by introducing suitable materials in the film. As can be seen in Fig. 5, the film showed RGB emission and RGB coloration. Those films are expected to be potential candidate for full-color DMD representation.

Conclusion

In this paper, we successfully demonstrated the thermo-switchable emission and coloration by using composite film containing luminescent Eu(III) complex, leuco dye, and developer molecule. whose emission and coloration can be reversibly changed and maintained by thermocromic reaction of the leuco dye system. Coloration and de-coloration of the composite film were caused by thermo-responsive control of nanoscale aggregation of a leuco dye and a developer with a long alkyl chain. the leuco dye and developer. Photoluminescence control was also achieved by the thermochromism via intermolecular energy transfers from the excited states of Eu(III) ions to colored leuco dye. We are expecting that our thermo-switchable system will contribute to development of the novel displaying medium such as rewritable card, electric paper, and security systems.

This work was supported in part by a Grants-in-Aid grant for Scientific Research (No. 23750208) from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) Japan; the CASIO Science Promotion Foundation; the Konica Minolta Science and Technology Foundation; and the Futaba Electronics Memorial Foundation.

References

[1] K. Niikura, A. Metzger and E.V. Anslyn, J. Am. Chem. Soc., 120, 8533 (1998).

[2] M. A. Rizzo, G. H. Springer, B. Granada and D. W. Piston, Nat. Biotechnol., 22, 445 (2004).

[3] A. P. De Silva and N. D. McClenaghan, Chem.–Eur. J., 2004, 10, 574 (2004).

[4] M. Irie, Chem. Rev., 100, 1685 (2000).

[5] Y. Watanabe, K. Nakamura and N. Kobayashi, Chem. Lett., 1309, (2010); X. J. Wang, W. M. Lau and K. Y. Wong, Appl. Phys. Lett., 87, 113502 (2005).

[6] Y. Hasegawa, T. Nakagawa and T. Kawai, Coord. Chem. Rev., 254, 2643 (2010); A. Fernández-Acebes, J. –M. Lehn, Chem. –Eur. J., 5, 3285 (1999).; T. Nakagawa, Y. Hasegawa and T. Kawai, Chem. Commun., 37, 5630 (2009).

[7] M. Tropiano, N. L. Kilah, M. Morten, H. Rahman, J. J. Davis, P. D. Beer and S. Faulkner, J. Am. Chem. Soc., 133, 11847 (2011); K. Nakamura, K. Kanazawa and N. Kobayashi, Chem. Commun., 47, 10064 (2011); K. Kanazawa, K. Nakamura, and N. Kobayashi, Chem. –Asia. J., 7, 2551 (2012); B. Wang, L. -H. Bi, L. –X. Wu, J. Mater. Chem., 21, 69 (2011).

[8] I. Sage, Liq. Cryst., 38, 1551 (2011).

[9] O. Inganäs, W. R. Salaneck, J. –E. Österholm, J. Laakso, Synth. Met., 22, 395 (1988).

[10] S. M. Burkinshaw, J. Griffiths, A. D. Towns, J. Mater. Chem., 8, 2677 (1998); S. Yamamoto, H. Furuya, K. Tsutsui, S. Ueno and K. Sato, Cryst.Growth Des., 8, 2256 (2008).

[11] T. Mutai, H. Satou and K. Araki, Nat. Mater., 4, 685 (2005).

[12] A. Kishimura, T. Yamashita, K. Yamaguchi and T. Aida, Nat. Mater., 4, 546 (2005).

[13] S. Hirata, K. –S. Lee and T. Watanabe, Adv. Funct. Mater., 18, 2869 (2008).

[14] J. C. G. Bunzli and C. Piguet, Chem. Soc. Rev., 34, 1048 (2008); D. Parker, Coord. Chem. Rev., 205, 109 (2000); K. Binnemans, Chem. Rev., 109, 4283 (2009); S. Faulkner, S. J. A. Pope and B. P. Burton-Pye, Appl. Spectrosc. Rev., 40, 1 (2005); N. Weibel, L. J. Charbonniere, M. Guardigli, A. Roda and R. Ziessel, J. Am. Chem. Soc., 126, 4888 (2004); E. G. Moore, G. Szigethy, J. Xu, L.-O. Palsson, A. Beeby and K. N. Raymond, Angew. Chem., Int. Ed., 47, 9500 (2008).

[15] K. Nakamura, Y. Hasegawa, H. Kawai, N. Yasuda, N. Kanehisa, Y. Kai, T. Nagamura, S. Yanagida and Y. Wada, J. Phys. Chem. A, 111, 3029 (2007); Y. Kuramochi, T. Nakagawa, T. Yokoo, J. Yuasa, T. Kawai and Y. Hasegawa, Dalton Trans., 41, 6634 (2012).

[16] L. J. Charbonnière, N. Hildebrandt, Eur. J. Inorg. Chem., 3241 (2008).

Author Biography

Dr. Kazuki Nakamura received his PhD from Osaka University, Japan, for the study on phtotophysical properties of luminescent Lanthanide(III) complex in 2007. From 2007 to 2009, he worked at Advanced Technology R & D Center, Mitsubishi Electric Corporation. Since April 2009 he works in Graduate School of Advanced Integration Science, Chiba University. His research interest focused on luminescent materials based on organic and organometallic compounds especially on Lanthanide(III) compounds.

Prof. Norihisa Kobayashi received his PhD in 1988 from Waseda University, Japan. He worked as Assistant Professor in Department of Image Science, Chiba University (1987–1995). He was also Visiting Associate, California Institute of Technology, USA (1992-1993). He has worked as a Associate professor in Department of Image Science, Chiba University (1995-2004). Since 2004, he held a position of professor in current position of Graduate School of Advanced Integration Science, Chiba University. His research interest primarily focused on photoelectronic-functional molecules including polymer for development of photoconductive materials, materials with high electronic carrier mobility, highly emissive materials, light emitting materials, ionic conductive materials, electroactive materials, chromogenic materials and so on.