Fluorophores

DOI: 10.1002/ange.200901266

A Color-Tunable Europium Complex Emitting Three Primary Colors and White Light**

*Guangjie He, Dong Guo, Cheng He, Xiaolin Zhang, Xiuwen Zhao, and Chunying Duan**

The manufacture of new full-color displays is one of the main tasks in flat-panel display systems and lighting technology.[1] Different applications place different demands on emitted light: in some cases a white-light source is needed,[2] and in others pure colors are necessary.[3] Thus, white emission should ideally be composed of three (blue, green, and red) or two (blue and yellow) primary colors and cover the whole visible range from 400 to 700 nm, and the emitter should have the ability to emit the primary colors simultaneously with equal intensities to produce white light and the pure colors separately in a tunable way.[4] Considerable interest exists for such color-tunable materials, which can be used to define or modify environments, moods, and brands.[5] Traditional methods of such white light generation typically rely on mixing various primary colors from different emitting materials.[6] An alternative approach for the generation of efficient (white) light sources is to use a single-component emitter, which can have advantages such as greater stability, better reproducibility, no phase separation, and simpler fabrication processes.[7,8] Although a few materials show white-light emission as a single-emitting component, none has been reported to produce well-separated blue, green, and red emissions beside white light.[8a] Since energy transfer typically quenches one or more of the emission pathways and thereby restricts the transitions that define the output spectrum,[9] the design of color tunable single-component emitters requires readily tailorable different fluorophores and fine-tuning of the energy-transfer processes between the different fluorophores.

On the other hand, lanthanide-containing materials, which exhibit excellent sharp-emission luminescence properties with suitable sensitization, have attracted considerable interest and been effectively used in designing white-emitting nanoparticles.[10] With judiciously chosen red- (Eu^{III}, Pr^{III}, Sm^{III}), green- (Tb^{III}, Er^{III}), and blue-emissive (Tm^{III} , Ce^{III}, Dy^{III}) ions doped in an suitable host, it is possible to obtain phosphors which emit across the entire visible spectrum with high color purity.[11] Specifically, an Eu^{III}-containing single-component complex has been reported to offer white-light emission in a carefully designed system which only allows partial energy transfer between the sensitizing fluorophore and the Eu^{III} center.[12] Herein we report the design and synthesis of a new fluorophore that exhibits tunable emission of three primary colors (blue, green, and red) and white light, by combining an Eu^{III} moiety as the origin of red light with an organic ligand that comprises a blue-emitting coumarin fluorophore and a green-emitting Rhodamine 6G fluorophore.

Coumarin-Rhodamine **CR1** was synthesized by reaction of 7-diethylamino-2-oxo-2*H*-chromen-3-carboxylic chloride and *N*-(Rhodamine-6G)lactamethylenediamine and recrystallized from ethanol as yellow crystals. Single-crystal X-ray structural analysis confirms the coexistence of two fluorophores in **CR1** (Supporting Information Figure S1), whereby the Rhodamine 6G moiety is in a luminescence-inactive ring-closed tautomeric form.[13] Europium compound **CR1-Eu** (**1**) was prepared by refluxing ligand **CR1** and [Eu(tta)$_3$] in THF (tta = 1,1,1-trifluoro-3-(2-thenoyl)acetone) and purified by recrystallization as an amorphous yellow powder. Elemental analysis and ^{1}H NMR spectroscopic characterization suggest the chemical formula [Eu(tta)$_2$(**CR1**)$_2$](tta) for **1** (Figure 1).

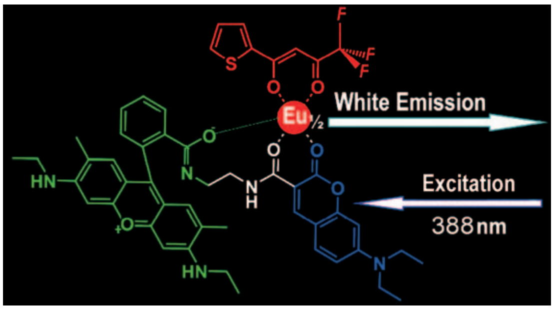

Figure 1. Proposed structure of the white-emitting dye **1** showing the fragments of the coumarin (blue), Rhodamine 6G (green), and Eu^{III}-based (red) primary-color-emitting fluorophores.

Fourier transform IR spectroscopic studies on **1** and **CR1** (Supporting Information Figure S3) showed a significant change in the stretching bands of the carbonyl group at 1699 and 1685 cm^{-1}, which suggests participation of the carbonyl groups in coordination to Eu^{III}. Additionally, the ESI-MS spectrum of **1** (Supporting Information Figure S4) exhibited only one intense peak at *m*/*z* 1993.61, which was assigned to the [Eu(tta)$_2$(**CR1**)$_2$]$^+$ cation according to the exact comparison of the intense peak with the simulation based on natural isotopic abundances, which indicates formation of complex **1** and its stability in solution.

---

[*] G. He, Dr. D. Guo, Dr. C. He, Dr. X. Zhang, X. Zhao, Prof. C. Duan
State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, 116012 (P. R. China)
Fax: (+86) 411-8370-2355
E-mail: cyduan@dlut.edu.cn

[**] This work is supported by the National Natural Science foundation of China (20571041 and 20501016) and the Start-up Fund of The Dalian University of Technology.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200901266.

The absorption spectra of **1**, **CR1**, [Eu(tta)$_3$], and acidified *N*-(Rhodamine-6G)lactamethylenediamine are shown in Figure 2. Free **CR1** displays an intensive absorption band in the visible region centered at 415 nm that arises from the coumarin chromophore (Supporting Information Figure S5.1) and a weak band at about 302 nm, which is attributed to absorption of the ring-closed tautomeric form of the Rhodamine 6G moiety (Supporting Information Figure S5.2). The UV/Vis absorption spectrum of **1** displays three main absorption bands centered at 345, 415, and 525 nm. By comparison of the absorption spectra of [Eu(tta)$_3$], **CR1**, and **1**, the first two were mainly assigned to the characteristic absorption maxima of the Eu-TTA moiety and the coumarin chromophore, respectively. The last band, which is absent in **CR1**, should be assigned to the absorption of the ring-opened tautomer of the Rhodamine 6G chromophore,[14] that is, the carbonyl group of the Rhodamine 6G moiety is coordinated to the Eu center and the attached spiro ring has opened to make green emission of **1** possible.

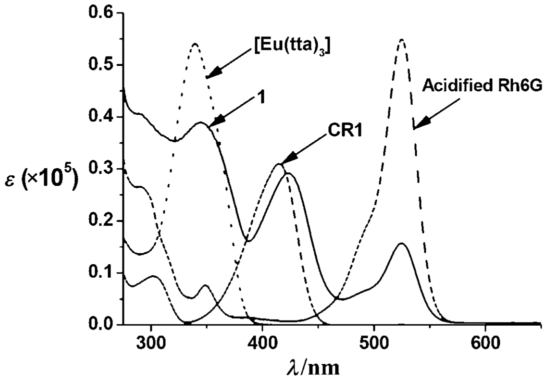

Figure 2. UV/Vis absorption spectra of free [Eu(tta)$_3$] (dotted), **CR1** (dash-dotted), *N*-(rhodamine-6G)lactamethylenediamine with *p*-toluenesulfonic acid (dashed), and **1** (solid line) in CH$_3$CN solution.

Thus, **1** exhibits characteristic blue emission of the coumarin fluorophore centered at 460 nm, green Rhodamine emission centered at 550 nm, and typical red emission of the Eu^{III} ion with dominant peak at 612 nm when its solution in acetonitrile (50 μM) is excited at 415, 525, and 360 nm, respectively (Figure 3). The quantum yields of the blue, green, and red emissions are about 0.056, 0.085 and 0.005, respectively.[15] While a few organic dyes have been reported that exhibit tunable emissive properties,[8a] the generation of pure blue, green, and red emissions in a single-component dye by simply changing the excitation wavelengths is extremely appealing and significant. Such color-tunable materials may be promising candidates for emitting "pure" white light by controllably tailoring blue, green, and red primary colors that fully span the entire visible spectrum.[5]

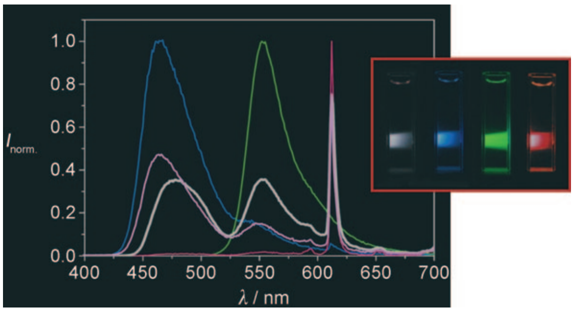

Figure 3. Emission spectra of **1** in acetonitrile solution (50 μM) showing the three individual blue (blue line), green (green line), red (red line), and nearly white (pink line) emissions when excited at 415, 525, 360, and 388 nm, respectively. The right picture shows the three primary colors and nearly white color corresponding to each case. The white line shows the pure white emission of **1** (0.2 mM) when excited at 388 nm in acetonitrile solution.

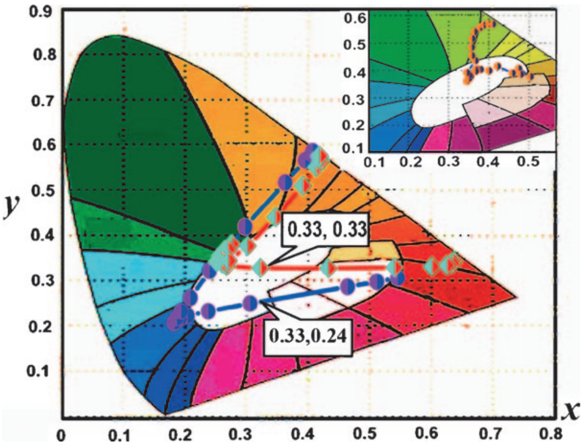

Figure 4. Luminescence spectra of **1** in acetonitrile solution plotted on a CIE diagram with excitation wavelengths varying from 360 to 500 nm (step size 5 nm) showing tunable chromaticity of visual emission image. The red and blue lines represent concentrations of 0.20 mM and 50 μM, respectively. Insert: CIE diagram of a solid thin film of **1** with excitation wavelengths varying from 360 to 500 nm (step size 5 nm).

As expected, the CIE chromaticity diagram[16] of 50 μM **1** (Figure 4, blue line) exhibited a color shift from red to blue and then to green when the excitation wavelength varied from 360 to 500 nm (Supporting Information Figure S6). Clearly, **1** is able to create a nearly white emission to the eye with CIE coordinates of (0.33, 0.24), which fall well within the white region of the 1931 CIE diagram (for pure white $x = 0.33$, $y = 0.33$), the quantum yield of the whitest emission spanning the entire visible spectrum is calculated as 0.025 when excited at 388 nm.[15] To the best of our knowledge, it is the first example of a single-component dye that can emit blue, green, and red primary colors as well as nearly white light.

Detailed emission and excitation spectra of **1** were extensively examined to elucidate the energy-transfer mechanisms in this system (Supporting Information Figures S6–S9). The typical Eu^{III} emission at 612 nm with lifetime of 0.55 ms when excited at 360 nm can be assigned to the excitation of the auxiliary organic ligand followed by energy transfer to the Eu^{III} ion. Excitation of TTA at 360 nm also triggered the characteristic coumarin blue emission and Rhodamine 6G green emission, beside the Eu^{III} emission, through multichannel energy transfer.[17] Moreover, the excitation at 415 nm has the potential to cause the characteristic Rhodamine 6G green emission, besides the major coumarin blue emission, through fluorescence resonant energy transfer.[18] In this regard, the nearly white emission should be attributed mainly to the equilibrium of these multichannel energy-transfer processes, rather than simple overlap of the emission spectra, when the sample was excited at 388 nm, the middle point between 360 (red Eu^{III} emission) and 415 nm (blue coumarin emission). These multichannel energy-transfer processes thus act as significant balancers that diminish the emission band edges for white-light emission. The considerably shorter lifetime (0.28 ns) of the emission at 460 nm of **1** compared to reference material *N*-butyl-7-diethylamino-2-oxochromen-3-carboxamide (0.46 ns) under the same experimental condition (excited at 388 nm) suggests the possibility of energy transfer from the coumarin moiety to the Rhodamine 6G moiety.

Interestingly, the quality of white emission could be improved by increasing the concentration of **1** in acetonitrile solution, which gave a better-balanced pure-white emission with the chromaticity coordinate exactly positioned at (0.33, 0.33) when it was excited at 388 nm (Supporting Information Figure S10). The spectrum of the pure white emission (Figure 3, white line) comprises the three primary colors (blue, green, and red) and covers the whole visible range from 400 to 700 nm. The large Stokes shift and broad emission spectrum spanning the whole visible range demonstrate the advantages of using single-component emitters for white organic light-emitting devices. Whereas increasing dye concentration could cause concentration quenching of the blue emission and thus lower the efficiency of white light emission),[19] the pure-white emission could be ultimately achieved by fine-tuning the multichannel energy-transfer processes within such a system. **1** also showed good photostability without obvious photobleaching decay (< 5 %) over 2 h (Supporting Information Figure S11). Furthermore, solid thin films of **1**, fabricated by the spin-coating method, also exhibited tunable luminescent properties, and the best chromaticity with coordinates of (0.35, 0.36), when the thin film was excited at 388 nm, lies within the white region of the 1931 CIE diagram (inset of Figure 4), demonstrating its potential applications in full-color display devices.

In summary, a new Eu^{III} complex acting as a single-component white-light-emitting fluorophore with tunable emission colors has been prepared. By tailoring the excitation energies, the synthetic dye can exhibit three individual primary colors (blue, green, and red) as well as white emission. Our future research will focus on the optimization of energy-transfer processes in such small-molecule three-primary-color systems to permit tuning of the emission color with high quantum yield, and ultimately the fabrication of emitting devices.

Received: March 6, 2009
Revised: May 19, 2009

Keywords: chromophores · dyes/pigments · fluorescence · lanthanides

[1] a) C. D. Müller, A. Falcou, N. Reckefuss, M. Rojahn, V. Wiederhirn, P. Rudati, H. Frohne, O. Nuyken, H. Becker, K. Meerholz, *Nature* **2003**, *421*, 829 – 833; b) L. D. Carlos, R. A. S. Ferreira, J. P. Rainho, V. D. Bermudez, *Adv. Funct. Mater.* **2002**, *12*, 819 – 823.

[2] a) J. Kido, M. Kimura, K. Nagai, *Science* **1995**, *267*, 1332 – 1334; b) R. H. Frient, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Brédas, M. Lögdlund, W. R. Salaneck, *Nature* **1999**, *397*, 121 – 128.

[3] a) C.-T. Chen, *Chem. Mater.* **2004**, *16*, 4389 – 4400; b) A. van Dijken, J. J. A. M. Bastiaansen, N. M. M. Kiggen, B. M. W. Langeveld, C. Rothe, A. Monkman, I. Bach, P. Stössel, K. Brunner, *J. Am. Chem. Soc.* **2004**, *126*, 7718 – 7727; c) L. Chan, R. Lee, C. Hsieh, H. Yeh, C. Chen, *J. Am. Chem. Soc.* **2002**, *124*, 6469 – 6479.

[4] a) R. Abbel, C. Grenier, M. J. Pouderoijen, J. W. Stouwdam, P. E. L. G. Leclère, R. P. Sijbesma, E. W. Meijer, A. P. H. J. Schenning, *J. Am. Chem. Soc.* **2009**, *131*, 833 – 843; b) J. Luo, X. Li, Q. Hou, J. Peng, W. Yang, Y. Cao, *Adv. Mater.* **2007**, *19*, 1113 – 1117; c) A. Ajayaghosh, V. K. Praveen, S. Srinivasan, R. Varghese, *Adv. Mater.* **2007**, *19*, 411 – 415; d) J. H. Kim, P. Herguth, M.-S. Kang, A. K.-Y. Jen, Y.-H. Tseng, C. F. Shu, *Appl. Phys. Lett.* **2004**, *85*,1116 – 1118; e) A. C. A. Chen, S. W. Culligan, Y. Geng, S. H. Chen, K. P. Klubek, K. M. Vaeth, C. W. Tang, *Adv. Mater.* **2004**, *16*, 783 – 788.

[5] B. Kokuoz, J. R. DiMaio, C. J. Kucera, D. D. Evanof, Jr., J. Ballato, *J. Am. Chem. Soc.* **2008**, *130*, 12222 – 12223.

[6] a) H. Su, H. Chen, F. Fang, C. Liu, C. Wu, K. Wong, Y. Liu, S. Peng, *J. Am. Chem. Soc.* **2008**, *130*, 3413 – 3419; b) X. Yu, H. Kwok, W.-Y. Wong, G. Zhou, *Chem. Mater.* **2006**, *18*, 5097 – 5103; c) B. W. D'Andrade, R. J. Holmes, S. R. Forrest, *Adv. Mater.* **2004**, *16*, 624 – 628; d) R. H. Jordan, A. Dodabalapur, M. Strukelj, T. M. Miller, *Appl. Phys. Lett.* **1996**, *68*, 1192; e) Y. Z. Wang, R. G. Sun, F. Meghdadi, G. Leising, A. J. Epstein, *Appl. Phys. Lett.* **1999**, *74*, 3613; f) Y. Liu, J. Guo, H. Zhang, Y. Wang, *Angew. Chem.* **2002**, *114*, 190 – 192; *Angew. Chem. Int. Ed.* **2002**, *41*, 182 – 184.

[7] a) J. Liu, Y. Cheng, Z. Xie, Y. Geng, L. Wang, X. Jing, *Adv. Mater.* **2008**, *20*, 1357 – 1362; b) J. Liu, Z. Xie, Y, Cheng, Y. Geng, L. Wang, X. Jing, F. Wang, *Adv. Mater.* **2007**, *19*, 531 – 535; c) G. Tu, C. Mei, Q. Zhou, Y. Cheng, Y. Geng, L. Wang, D. Ma, X. Jing, F. Wang, *Adv. Funct. Mater.* **2006**, *16*, 101 – 106; d) J. Jiang, Y. Xu, W. Yang, R. Guan, Z. Liu, H. Zhen, Y. Cao, *Adv. Mater.* **2006**, *18*, 1769 – 1773; e) S. K. Lee, D. H. Hwang, B. J. Jung, N. S. Cho, J. Lee, J. D. Lee, H. K. Shim, *Adv. Funct. Mater.* **2005**, *15*, 1647 – 1655.

[8] a) Y. Yang, M. Lowry, C. M. Schowalter, S. O. Fakayode, J. O. Escobedo, X. Xu, H. Zhang, T. J. Jensen, F. P. Fronczek, I. M. Warner, R. M. Strongin, *J. Am. Chem. Soc.* **2006**, *128*, 14081 – 14092; b) Y. Liu, M. Nishiura, Y. Wang, Z. Hou, *J. Am. Chem. Soc.* **2006**, *128*, 5592 – 5593; c) P. T. Furuta, L. Deng, S. Garon, M. E. Thompson, J. M. J. Fréchet, *J. Am. Chem. Soc.* **2004**, *126*, 15388 – 15389; d) J. Y. Li, D. Liu, C. Ma, O. Lengyel, C. S. Lee, C. H. Tung, S. T. Lee, *Adv. Mater.* **2004**, *16*, 1538 – 1541.

[9] a) X. L. Zhang, Y. Xiao, X. H. Qian, *Org. Lett.* **2008**, *10*, 29 – 32; b) C. Hippius, F. Schlosser, M. O. Vysotsky, V. Böhmer, F. Würthner, *J. Am. Chem. Soc.* **2006**, *128*, 3870 – 3871.

[10] a) G. Glaspell, J. Anderson, J. R. Wilkins, M. S. El-Shall, *J. Phys. Chem. C* **2008**, *112*, 11527 – 11531; b) S. Sivakumar, F. C. J. M. van Veggel, M. Raudsepp, *J. Am. Chem. Soc.* **2005**, *127*, 12464 – 12465.

[11] a) P. Escribano, B. Julián-López, J. Planelles-Aragó, E. Cordoncillo, B. Viana, C. Sanchez, *J. Mater. Chem.* **2008**, *18*, 23 – 40; b) R. C. Evans, L. D. Carlos, P. Douglas, J. Rocha, *J. Mater. Chem.* **2008**, *18*, 1100 – 1107; c) J. Kido, Y. Okamoto, *Chem. Rev.*

2002, *102*, 2357–2368; d) R. Shunmugam, G. N. Tew, *Polym. Adv. Technol.* **2007**, *18*, 940–945.

[12] P. Coppo, M. Duati, V. N. Kozhevnikov, J. W. Hofstraat, L. D. Cola, *Angew. Chem.* **2005**, *117*, 1840–1844; *Angew. Chem. Int. Ed.* **2005**, *44*, 1806–1810.

[13] Crystal data for **CR1**: $C_{42}H_{45}N_5O_5 \cdot C_2H_5OH$; $M_r = 745.90$, monoclinic; $P21/c$; $a = 19.1515(5)$, $b = 12.9911(4)$, $c = 15.9890(5)$ Å, $\beta = 95.423(2)°$, $V = 3960.2(2)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.251\ \text{g cm}^{-3}$; $T = 293(2)$ K. The final refinement gave $R1 = 0.0585$, $wR2 = 0.1541$, and GOF = 1.004 for 3626 observed reflections with $I > 2\sigma(I)$. CCDC 720202 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[14] The absorption of the related ring-opened tautomer of the Rhodamine 6G chromophore shown in Figure 2 was recorded in an acidified solution of the subunit. Y. K. Yang, K. J. Yook, J. Tae, *J. Am. Chem. Soc.* **2005**, *127*, 16760–16761.

[15] The quantum yield was measured in accordance with M. Fischer, J. Georges, *Chem. Phys. Lett.* **1996**, *260*, 115–118.

[16] Colorimetry: Commission Internationale de L'éclairage (CIE), Paris, **1986**.

[17] S. Samanta, M. B. Roy, S. Ghosh, *Chem. Phys.* **2006**, *328*, 392–402.

[18] a) K. E. Sapsford, L. Berti, I. L. Medintz, *Angew. Chem.* **2006**, *118*, 4676–4704; *Angew. Chem. Int. Ed.* **2006**, *45*, 4562–4588; b) A. E. Albers, V. S. Okreglak, C. J. Chang, *J. Am. Chem. Soc.* **2006**, *128*, 9640–9641.

[19] C. E. Wheelock, *J. Am. Chem. Soc.* **1959**, *81*, 1348–1349.
