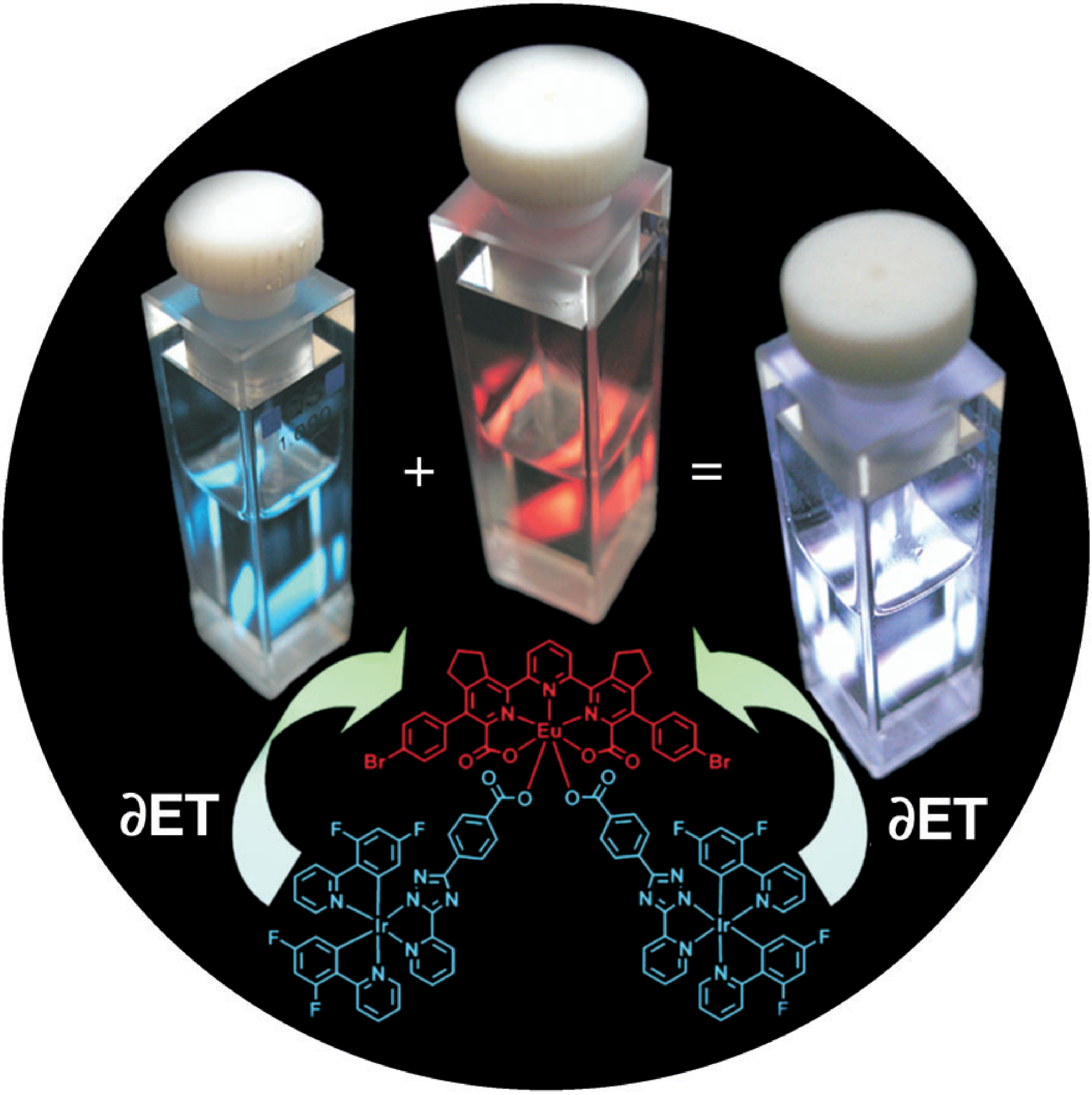
Zuschriften



Die partielle Übertragung der Anregungsenergie vom Ir^{III}- auf das Eu^{III}-Zentrum eines Komplexes aus diesen beiden Ionen führt zum Auftreten von weißem Licht. Mehr über die photophysikalische Untersuchung dieser Energieübertragungsprozesse finden Sie in der Zuschrift von L. De Cola et al. auf den folgenden Seiten.

DOI: 10.1002/ange.200461953

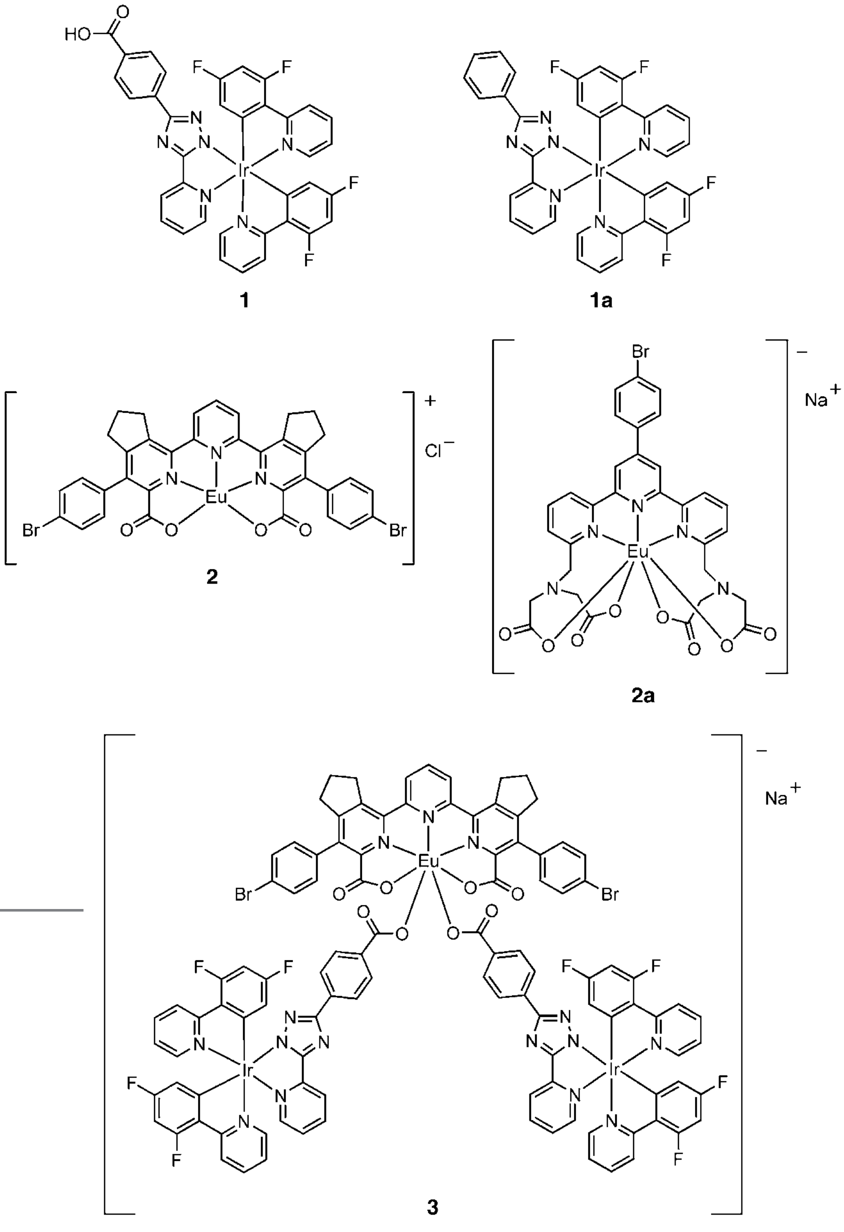
Luminescent Assemblies

White-Light Emission from an Assembly Comprising Luminescent Iridium and Europium Complexes**

*Paolo Coppo, Marco Duati, Valery N. Kozhevnikov, Johannes W. Hofstraat, and Luisa De Cola**

Europium(III) red emission receives increasing attention for application in bioassays and in sensors where its long-lived luminescence enables sensitive time-resolved or "gated" detection of the emission without interference from background or scattered excitation light.[1] Furthermore, the use of Eu^{III} complexes for applications in light-emitting devices has been described.[2] Eu^{III} complexes show little or no absorption in the visible region of the spectrum and often require the application of strongly absorbing "antennae" for light harvesting to obtain efficient photoluminescence.[3] Recently, energy transfer from transition metals to lanthanides to obtain near-IR (NIR) emission from Yb, Nd, and Er was reported.[4] The use of a light-harvesting unit based on a transition metal is extremely appealing for applications in luminescence and electro(chemi)luminescence owing to the addressability of the coordination-metal-based unit by both light and redox reactions. To the best of our knowledge, no transition-metal-based antennae have been reported for the photoexcitation of Eu^{III}. This absence is most likely due to the high triplet energy level required for the sensitization of this lanthanide which few metal complexes can provide. We have recently reported on the tuning of light emission in iridium(III) complexes in the "almost-blue" region of the visible spectrum.[5] Herein we discuss the application of such systems for the photoexcitation of a Eu^{III}—terpyridine-based complex. Emission of white light can be observed by the application of carefully designed systems that allow a partial transfer of energy from the excited Ir^{III} moiety to the Eu^{III} complex.

Complex **1** (see Scheme 1) was prepared according to procedures reported previously for similar systems, purified by column chromatography, and obtained as an amorphous yellow powder.[5,6] The UV/Vis absorption spectrum was consistent with the unsubstituted analogue **1a** and showed a MLCT (metal-to-ligand charge transfer) transition in the visible region and π–π^* bands that are attributed to transitions in the ligand in the UV region (see Figure 1). Complex **1** shows blue emission in CH$_2$Cl$_2$, MeOH, or CH$_3$CN with



Scheme 1. Structures of the investigated complexes.

---

[*] Dr. P. Coppo, Dr. M. Duati, Prof. Dr. L. De Cola
HIMS, Molecular Photonic Materials
University of Amsterdam
Nieuwe Achtergracht 166
1018 WV Amsterdam (The Netherlands)
Fax: (+31) 20-525-6456
E-mail: ldc@science.uva.nl

Dr. V. N. Kozhevnikov
Urals State Technical University
620002, Ekaterinburg (Russia)

Prof. Dr. J. W. Hofstraat
Philips Research
Prof. Holstlaan 4
5656 AA Eindhoven (The Netherlands)

[**] The authors acknowledge Roche Diagnostics, Philips Research, and the Dutch Foundation for Scientific Research (SENTER, Project No. TSGE3140) for funding the project. Dr. R. Williams and Dr. B. Göötz are acknowledged for their help with time-resolved and gated experiments. Dr. C. A. Schalley, Prof. F. Vögtle, and J. van Heyst are acknowledged for mass spectrometry analyses.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

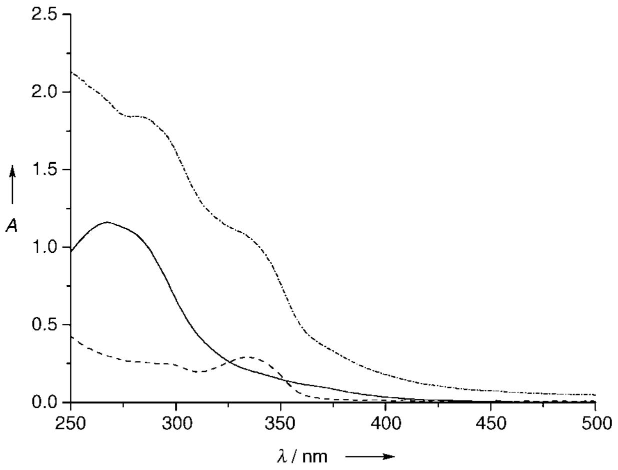


Figure 1. Absorption spectra of solutions (5×10^{-5} M in methanol) of complexes **1** (——), **2** (-----), and **3** (–•–•).

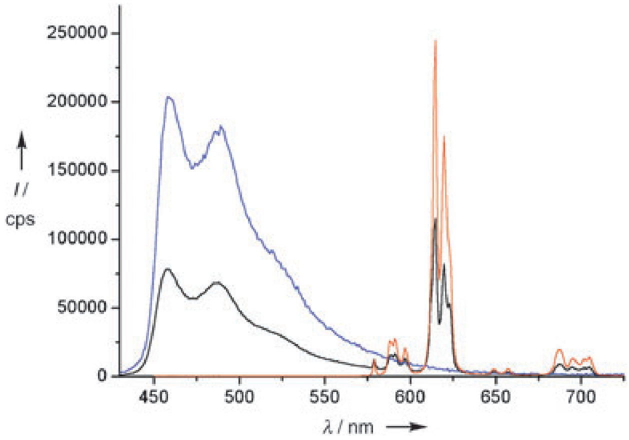


Figure 2. Relative steady-state emission spectra of solutions of complexes **1** (blue), **2** (red; *I*/6), and **3** (black) in CD_3OD upon excitation at $\lambda = 400$ nm (complex **2** was excited at $\lambda = 350$ nm as it shows negligible absorption at $\lambda = 400$ nm; cps = counts per second). The solutions all have identical absorption values at the excitation wavelength.

maxima centered at 460 nm and 491 nm (see Table 1) in similar fashion to the unfunctionalized analogue **1a**. The quantum yield of emission, Φ, of a deaerated solution of **1** in methanol is 17%, which is significantly lower than that for the unsubstituted analogue **1a** ($\Phi = 27\%$). The lifetime, τ, of the emitting species **1** is 1.4 μs.

Table 1: Emission maxima (λ_{em}), quantum yields of emission (Φ),[a] and lifetimes (τ) of the emitting species.[b]

Complex	λ_{em} [nm]	Φ	τ [μs]
1[c]	460, 491	0.17	1.4
1a[d]	461, 490	0.27	1.4
2[e]	615	0.33	1900
2a[c]	615	0.12	1900
3[c]	460, 491, 615	0.07	0.48 (Ir) 1900 (Eu)

[a] Quantum yields of complexes **1** and **1a** were measured by using quinine bisulfate in 0.5 M H_2SO_4 as a reference, whereas those of **2**, **2a**, and **3** were measured by using $[Ru(bpy)_3]Cl_2$ in distilled water as a reference (bpy = bipyridine). [b] A concentration of 5×10^{-5} M was used for steady-state experiments. A concentration of 10^{-4} M was used for time-resolved measurements. [c] Measurements performed in CD_3OD. [d] Measurements performed in dichloromethane. [e] Measurements performed in D_2O.

Complex **2** was prepared and purified according to reported procedures[7] and was isolated as a white powder. The complex shows absorption bands in the UV region (see Figure 1) and the characteristic, well-structured emission of Eu^{III} complexes (see Figure 2). Emission is mainly observed from the $^5D_0 \rightarrow {}^7F_2$ transition, centered at 615 nm (see Figure 2). This hypersensitive transition is an electric-dipole emission that is forbidden in the free ion. However, when the Eu^{III} ion experiences a strongly asymmetric or strongly interacting ligand field, this transition may be greatly enhanced.[1a] The quantum yield of emission of **2** in an air-equilibrated solution in D_2O was 33%. As can be seen by the schematic formula and as confirmed by spectroscopic investigation in water by comparing the excited-state lifetimes of **2** in D_2O ($\tau = 1.9$ ms) and in H_2O ($\tau = 0.25$ ms), the europium complex in which the Eu^{III} center is coordinated to a pentadentate cage-type ligand has a hydration number $q = 3.9$. Hence, complex **2** can bind up to 4 molecules of water or solvent to fill the coordination sphere. Such a situation is ideal for the assembly of a second metal complex through carboxylate or chelating units. Indeed, when complexes **1** and **2** were stirred in methanol at room temperature, the formation of an assembly of Eu^{III} and Ir^{III} moieties was established by spectroscopic investigations (see below). Its structure could not be determined by NMR spectroscopy owing to the paramagnetic properties of Eu^{III} and to the low solubility of the product. However, FT-IR spectroscopy of the sample in KBr matrix proved to be effective to highlight the formation of complex **3** (see Figure 3). The disappearance of the band at 1685 cm^{-1} in complex **3** which is associated with the stretch of the C=O bond in the Ar-COOH moiety of complex **1** suggests that the acid is coordinated to the europium ion. Indeed, the C=O stretching band in complex **3** can be detected at 1409 cm^{-1}, which is consistent with previous reports on Eu^{III} coordinated to four carboxylate groups.[8] Furthermore, the disappearance for complex **3** of the broad band at 3380 cm^{-1}, which is associated with the OH stretch of coordinated methanol molecules in the neat complex **2**, suggests that the solvent molecules have been displaced by the insertion of **1** as a coordinating unit. ESI-mass spectrometry confirmed **3** to be the main product with an Ir–Eu adduct and traces of Ir_3–Eu as byproducts (see Supporting Information).

Evidence of the formation of the adduct and of the absence of different equilibria in solution resulted from photophysical characterization. Irradiation of the assembly (diluted in CD_3OD) with monochromatic light at $\lambda = 400$ nm, where only the iridium moiety has appreciable absorption bands ($\varepsilon_{400} \approx 1000\,M^{-1}cm^{-1}$), resulted in the emission of almost-white light (Commission Internationale d'Eclairage, CIE coordinates: X: 0.28 Y: 0.30) owing to the combined

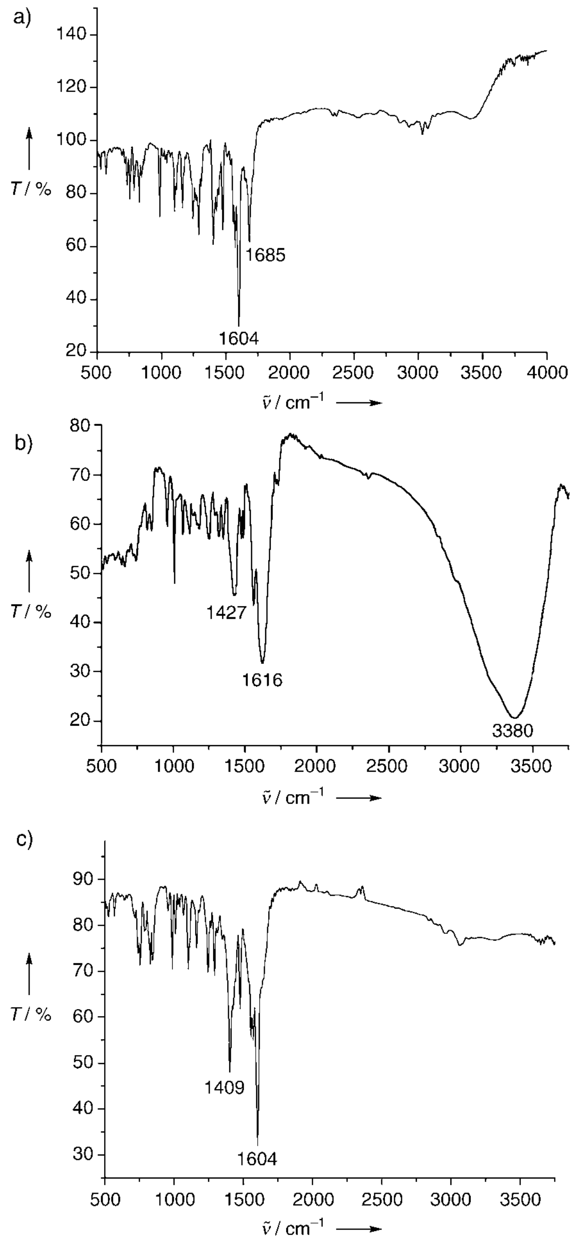


Figure 3. FT-IR spectra of complexes a) **1**, b) **2**, and c) **3** in KBr pellets.

presence of residual emission of the blue–green emitting Ir^{III} complex and the sensitized red emission of the Eu^{III} complex (see Figure 2). Measurement of the quantum yields of emission and time-resolved spectroscopy show that the excited-state lifetime of the Ir^{III} emitting species is strongly reduced ($\tau = 480$ ns, see Table 1) as compared to a deaerated solution of complex **1** alone in CD_3OD ($\tau = 1400$ ns). The sensitization of the Eu^{III} moiety suggests an energy-transfer process from the excited iridium moiety, which is the only component that absorbs light at $\lambda = 400$ nm, to the low-lying excited state ($^5D_0$) of the Eu^{III} center. If the emission of the bimetallic system is detected with a long delay on a millisecond scale by means of a streak camera, only the characteristic emission of the Eu^{III}-containing moiety is observed. By comparison of the steady-state emissions of complexes **1** and **3**, the efficiency of the energy transfer was determined to be 38 %. This value was calculated by assuming that the quantum yield of emission of the europium complex does not change upon coordination of the iridium moiety. By comparison of the lifetime of Eu^{III} emission in complex **3** in CD_3OD ($\tau = 1.9$ ms) and CH_3OH ($\tau = 0.7$ ms), a hydration number of $q = 0.78$ was calculated for complex **3** which is significantly lower than the q value for complex **2**.

The shape of the hypersensitive emission band of **2** at 615 nm changes slightly upon coordination of the Ir^{III} moiety and indicates a lower degree of symmetry. To establish the optimal stoichiometry of the adduct in solution through the carboxylate group that belongs to the iridium complex **1**, a titration of **1** against **2** was performed. It was immediately clear that the maximum intensity of the Eu^{III} moiety upon excitation of the Ir^{III}-based moiety at 400 nm was observed for a 1:2 stoichiometry of **1/2**. When the number of Ir^{III} centers in solution exceeds twice that of Eu^{III}, the emission is dominated by the blue–green signals that originate from the Ir^{III} complex.

To confirm that such a stable adduct can occur only with complexes with an unsaturated coordination sphere, complex **2a**[8] (see Scheme 1) was treated with complex **1** under analogous conditions. The resulting solution showed only Ir^{III}-based emission upon excitation at $\lambda = 400$ nm which suggests that no energy transfer to the europium moiety occurred. The difference in behavior is consistent with the hypothesis that the carboxylate group of **1** coordinates to the Eu^{III} ion in complex **2**, whereas for complex **2a** in which the Eu^{III} ion is already fully coordinated by the cage-type ligand ($q < 1$) no such assembly can be formed. Further evidence came by adding the unfunctionalized Ir^{III} complex **1a** (see Scheme 1), which lacks the carboxylate group, to a solution of complex **2**: Also in this case, no Eu^{III} emission was detected upon irradiation at $\lambda = 400$ nm.

In conclusion, we have reported the first example of sensitization of a Eu^{III} complex through the use of a transition-metal complex in a d–f bimetallic assembly which gives almost-white light emission. White electrophosphorescence is interesting for applications in electroluminescent displays and in lighting devices, both for illumination purposes and for backlights.[9] Investigations on electrically generated white-light emission from complex **3** are currently in progress as well as attempts to optimize the energy transfer process and improve the solubility.

Received: September 11, 2004
Revised: October 11, 2004

Keywords: energy transfer · europium · iridium · luminescence · time-resolved spectroscopy

---

[1] a) F. S. Richardson, *Chem. Rev.* **1982**, *82*, 541; b) H. Takalo, V.-M. Mukkala, H. Mikola, P. Liitti, I. Hemmilä, *Bioconjug. Chem.* **1994**, *5*, 278; c) S. Petoud, S. M. Cohen, J.-C. G. Bünzli, K. N. Raymond, *J. Am. Chem. Soc.* **2003**, *125*, 13324; d) G. Bobba, J. C. Frias, D. Parker, *Chem. Commun.* **2002**, 890; e) A. Beeby, S. W. Botchway, I. M. Clarkson, S. Faulkner, A. W. Parker, D. Parker, J. A. G. Williams, *J. Photochem. Photobiol. B: Biol.* **2000**, *57*, 83.

[2] a) M. A. Baldo, M. E. Thompson, S. R. Forrest, *Pure Appl. Chem.* **1999**, *71*, 2095; b) P.-P. Sun, J.-P. Duan, J.-J. Lih, C.-H. Cheng, *Adv. Funct. Mater.* **2003**, *13*, 683; c) T. Oyamada, Y. Kawamura, T. Koyama, H. Sasabe, C. Adachi, *Adv. Mater.* **2004**, *16*, 1082; d) J. W. Verhoeven, M. H. V. Werts, J. W. Hofstraat, US Pat. 2003012979.

[3] a) M. H. V. Werts, R. T. F. Jukes, J. W. Verhoeven, *Phys. Chem. Chem. Phys.* **2002**, *4*, 1542; b) C. Yang, L.-M. Fu, Y. Wang, J.-P. Zhang, W.-T. Wong, X.-C. Ai, Y.-F. Qiao, B.-S. Zou, L.-L. Gui, *Angew. Chem.* **2004**, *116*, 5120; *Angew. Chem. Int. Ed.* **2004**, *43*, 5010.

[4] a) T. A. Miller, J. C. Jeffery, M. D. Ward, H. Adams, S. J. A. Pope, S. Faulkner, *Dalton Trans.* **2004**, *10*, 1524; b) D. Imbert, M. Cantuel, J.-C. G. Bünzli, G. Bernardinelli, C. Piguet, *J. Am. Chem. Soc.* **2003**, *125*, 15698; c) S. J. A. Pope, B. J. Coe, S. Faulkner, *Chem. Commun.* **2004**, 1550; d) S. J. A. Pope, B. J. Coe, S. Faulkner, E. V. Bichenkova, X. Yu, K. T. Douglas, *J. Am. Chem. Soc.* **2004**, *126*, 9490; e) N. M. Shavaleev, L. P. Moorcraft, S. J. A. Pope, Z. R. Bell, S. Faulkner, M. D. Ward, *Chem. Eur. J.* **2003**, *9*, 5283; f) S. I. Klink, H. Keizer, H. W. Hofstraat, F. C. J. M. van Veggel, *Synth. Met.* **2002**, *127*, 213; g) S. I. Klink, H. Keizer, F. C. J. M. van Veggel, *Angew. Chem.* **2000**, *112*, 4489; *Angew. Chem. Int. Ed.* **2000**, *39*, 4319.

[5] P. Coppo, E. A. Plummer, L. De Cola, *Chem. Commun.* **2004**, 1774.

[6] a) M. Santus, *Polish J. Chem.* **1980**, *54*, 1067; b) M. Santus, *Polish J. Chem.* **1980**, *54*, 661.

[7] V. N. Kozhevnikov, D. N. Kozhevnikov, V. L. Rusinov, O. N. Chupakhin, B. König, *Synthesis* **2003**, *15*, 2400.

[8] a) V.-M. Mukkala, M. Helenius, I. Hemmilä, J. Kankare, H. Takalo, *Helv. Chim. Acta* **1993**, *76*, 1361; b) H. Takalo, V.-M. Mukkala, H. Mikola, P. Liitti, I. Hemmilä, *Bioconjugate Chem.* **1994**, *5*, 278.

[9] a) B. W. D'Andrade, J. Brooks, V. Adamovich, M. E. Thompson, S. R. Forrest, *Adv. Mater.* **2002**, *14*, 1032; b) B. W. D'Andrade, S. R. Forrest, *Adv. Mater.* **2004**, *16*, 1585; c) J. Slinker, D. Bernerds, P. L. Houston, H. D. Abruna, S. Bernhard, G. G. Malliaras, *Chem. Commun.* **2003**, 2392.