

Highly Efficient Sensitized Red Emission from Europium (III) in Ir–Eu Bimetallic Complexes by ³MLCT Energy Transfer

Fang-Fang Chen, Zu-Qiang Bian,* Zhi-Wei Liu, Dao-Bo Nie, Zhu-Qi Chen, and Chun-Hui Huang*

Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, China

Received September 14, 2007

Two novel iridium–europium bimetallic complexes, $\{[(dfppy)_2Ir(\mu\text{-phen5f})_3EuCl]Cl_2\}$ and $\{[(dfppy)_2Ir(\mu\text{-phen5f})Eu(TFAcA)_3]\}$ [dfppy represents 2-(4',6'-difluorophenyl)-pyridinato-N,C^{2'}, phen5f stands for 4,4,5,5,5-pentafluoro-1-(1',10'-phenanthroline-2'-yl)-pentane-1,3-dionate and TFAcA represents trifluoroacetylacetonate], were successfully synthesized. The novel ligand Hphen5f with four coordination sites was designed as a bridge to link the Ir^{III} center and the Eu^{III} center. The X-ray diffraction data shows that the nonbonding distances for Eu···Ir are 6.028, 5.907, and 6.100 Å in the bimetallic complex $\{[(dfppy)_2Ir(\mu\text{-phen5f})_3EuCl]Cl_2\}$. Photophysical studies implied that the high efficient red luminescence from the Eu^{III} ion was sensitized by the ³MLCT (metal-to-ligand charge transfer) energy based on an Ir^{III} complex-ligand in a d-f bimetallic assembly. The excitation window for the new bimetallic complex $\{[(dfppy)_2Ir(\mu\text{-phen5f})_3EuCl]Cl_2\}$ extends up to 530 nm (1×10^{-3} M in EtOH), indicating that this bimetallic complex can emit red light under the irradiation of sunlight.

Introduction

Europium(III) complexes are attracting an increasing amount of attention as analytical sensors¹ and are widely used in immunoassays,² imaging techniques,³ and organic light-emitting diodes.⁴ In general, the excitation wavelength of a Eu^{III} complex is in the UV region because of its weak absorption in the visible region, which may lead to damage to organisms, though two-photon excitation can be used to

extend the excitation wavelength up to 800 nm.⁵ There are two strategies for solving this problem. One is to try to modify the ligands,^{6,7} and the other is to use a “complexes as ligands” approach.⁸ For example, to achieve longer-wavelength sensitization of Eu^{III} emission, Wang and co-workers incorporated an *N,N*-dialkyl aniline moiety into a

* To whom correspondence should be addressed. E-mail: chhuang@pku.edu.cn (C.-H.H.), bianzq@pku.edu.cn (Z.-Q.B.). Phone: (+86)10-6275-7156. Fax: (+86)10-6275-7156.

- (1) (a) Terai, T.; Kikuchi, K.; Iwasawa, S.-Y.; Kawabe, T.; Hirata, Y.; Urano, Y.; Nagano, T. *J. Am. Chem. Soc.* **2006**, *128*, 6938–6946. (b) Gunnlaugsson, T.; Leonard, J. P.; Sénéchal, K.; Harte, A. J. *Chem. Commun.* **2004**, 782–783. (c) Gunnlaugsson, T.; Leonard, J. P.; Sénéchal, K.; Harte, A. J. *J. Am. Chem. Soc.* **2003**, *125*, 12062–12063. (d) Bazzicalupi, C.; Bencini, A.; Bianchi, A.; Giorgi, C.; Fusi, V.; Masotti, A.; Valtancoli, B.; Roque, A.; Pina, F. *Chem. Commun.* **2000**, 561–562. (e) Lowe, M. P.; Parker, D. *Chem. Commun.* **2000**, 707–708. (f) Charbonnière, L. J.; Ziessel, R.; Montalti, M.; Prodi, L.; Zaccaroni, N.; Boehme, C.; Wipff, G. *J. Am. Chem. Soc.* **2002**, *124*, 7779–7788.
- (2) (a) Mathis, G. *Clin. Chem.* **1995**, *41*, 1391–1397. (b) Yuan, J.-L.; Wang, G.-L.; Kimura, H.; Matsumoto, K. *Anal. Biochem.* **1997**, *254*, 283–287.
- (3) (a) Vereb, G.; Jares-Erijman, E.; Selvin, P. R.; Jovin, T. M. *Biophys. J.* **1998**, *74*, 2210–2222. (b) Weibel, N.; Charbonnière, L. J.; Guardigli, M.; Roda, A.; Ziessel, R. *J. Am. Chem. Soc.* **2004**, *126*, 4888–4896.

- (4) (a) Kido, J.; Hayase, H.; Hongawa, K.; Nagai, K.; Okuyama, K. *Appl. Phys. Lett.* **1994**, *65*, 2124–2126. (b) Adachi, C.; Baldo, M. A.; Forrest, S. R. *J. Appl. Phys.* **2000**, *87*, 8049–8055. (c) Hong, Z.-R.; Liang, C.-J.; Li, R.-G.; Li, W.-L.; Zhao, D.; Fan, D.; Wang, D.-Y.; Chu, B.; Zang, F.-X.; Hong, L.-S.; Lee, S.-T. *Adv. Mater.* **2001**, *13*, 1241–1245. (d) Sun, M.; Xin, H.; Wang, K.-Z.; Zhang, Y.-A.; Jin, L.-P.; Huang, C.-H. *Chem. Commun.* **2003**, 702–703. (e) Liang, F.-S.; Zhou, Q.-G.; Cheng, Y.-X.; Wang, L.-X.; Ma, D.-G.; Jing, X.-B.; Wang, F.-S. *Chem. Mater.* **2003**, *15*, 1935–1937. (f) Oyamada, T.; Kawamura, Y.; Koyama, T.; Sasabe, H.; Adachi, C. *Adv. Mater.* **2004**, *16*, 1082–1086. (g) Sun, P.-P.; Duan, J.-P.; Lih, J.-J.; Cheng, C.-H. *Adv. Funct. Mater.* **2003**, *13*, 683–691.
- (5) (a) Fu, L.-M.; Wen, X.-F.; Ai, X.-C.; Sun, Y.; Wu, Y.-S.; Zhang, J.-P.; Wang, Y. *Angew. Chem., Int. Ed.* **2005**, *44*, 747–750. (b) Werts, M. H. V.; Nerambourg, N.; Pélégry, D.; Le Grand, Y.; Blanchard-Desce, M. *Photochem. Photobiol. Sci.* **2005**, *4*, 531–538.
- (6) Werts, M. H. V.; Duin, M. A.; Hofstra, J. W.; Verhoeven, J. W. *Chem. Commun.* **1999**, 799–800.
- (7) Yang, C.; Fu, L.-M.; Wang, Y.; Zhang, J.-P.; Wong, W.-T.; Ai, X.-C.; Qiao, Y.-F.; Zou, B.-S.; Gui, L.-L. *Angew. Chem., Int. Ed.* **2004**, *43*, 5010–5013.
- (8) (a) Shavaleev, N. M.; Bell, Z. R.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **2002**, 3925–3927. (b) Shavaleev, N. M.; Moorcraft, L. P.; Pope, S. J. A.; Bell, Z. R.; Faulkner, S.; Ward, M. D. *Chem. Commun.* **2003**, 1134–1135.

dipyrazolyltriazine system to obtain a new ligand for Eu^{III} .⁷ Thus, the excitation window for the Eu^{III} complex could be extended to 460 nm when the concentration was increased to 1×10^{-2} M. As regards the second strategy, most of the energy levels (13000–18000 cm^{-1}) of the d-block chromophores based on related transition metals such as Ru, Pt, Re, Os, Pd, and Cr^{8-11} are too low to sensitize Eu^{III} of which the $^5\text{D}_1$ and $^5\text{D}_0$ states are 19000 and 17500 cm^{-1} , respectively. As far as we know, only Pt and Ir based antennae have been reported for the sensitization of Eu^{III} ions.^{11,12} However, the photoluminescence efficiency of Eu^{III} sensitized by the ³MMLCT (metal-metal-to-ligand charge transfer) excited-state based on Pt^{II} complexes was very low (<3%).¹¹ De Cola and co-workers first reported the transfer of excited-state energy from an Ir^{III} center to a Eu^{III} center in a d→f bimetallic assembly.¹² Since the energy transfer is incomplete, white light emission was observed instead of pure red light emission.

In this work, we introduced an Ir^{III} -based chromophore to Eu^{III} -containing complexes using the “complexes as ligand” approach with a novel bridge ligand. Then, the emission of pure red light from Eu^{III} can be observed under the irradiation of visible light through a “d→f” energy-transfer course, and the excitation window can extend up to 530 nm. Moreover, the single crystal structure of the novel bimetallic complex containing Ir and Eu was determined by X-ray crystallography.

Experimental Section

The ^1H NMR and ^{13}C NMR spectra were recorded on an ARX-400 NMR spectrometer. Chemical shift data for each signal were reported in ppm units with tetramethylsilane as the internal reference. Elemental analyses (C, H, N) were performed on a VARIO EL instrument. Mass spectra were recorded on a ZAB-HS mass spectrometer and an Ultraflex tandem time-of-flight (TOF) mass spectrometer. IR spectra were recorded on a Bio-Rad FTS-65A/896 FTIR system. UV–vis absorption spectra were measured on a Shimadzu UV-3100 spectrometer. The photoluminescence (PL) spectra were recorded on an Edinburgh Analytical Instruments FLS920 spectrometer. The emission quantum yields of the complexes were measured in CH_2Cl_2 solutions, using $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ in degassed water solution as the standard. Solvents for reactions were distilled prior to use. Solvents used in photophysical experiments were of spectroscopic grade.

- (9) (a) Klink, S. I.; Keizer, H.; van Veggel, F. C. J. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4319–4321. (b) Pope, S. J. A.; Coe, B. J.; Faulkner, S.; Bichenkova, E. V.; Yu, X.; Douglas, K. T. *J. Am. Chem. Soc.* **2004**, *126*, 9490–9491. (c) Miller, T. A.; Jeffery, J. C.; Ward, M. D.; Adams, H.; Pope, S. J. A.; Faulkner, S. *Dalton Trans.* **2004**, 1524–1526. (d) Guo, D.; Duan, C.-Y.; Lu, F.; Hasegawa, Y.; Meng, Q.-J.; Yanagida, S. *Chem. Commun.* **2004**, 1486–1487. (e) Pope, S. J. A.; Coe, B. J.; Faulkner, S. *Chem. Commun.* **2004**, 1550–1551. (f) Sambrook, M. R.; Curiel, D.; Hayes, E. J.; Beer, P. D.; Pope, S. J. A.; Faulkner, S. *New J. Chem.* **2006**, *30*, 1133–1136. (g) Beeby, A.; Dickins, R. S.; FitzGerald, S.; Govenlock, L. J.; Maupin, C. L.; Parker, D.; Riehl, J. P.; Siligardi, G.; Gareth Williams, J. A. *Chem. Commun.* **2000**, 1183–1184. (h) Imbert, D.; Cantuel, M.; Bünzli, J.-C. G.; Bernardinelli, G.; Piguet, C. *J. Am. Chem. Soc.* **2003**, *125*, 15698–15699.
- (10) Shavaleev, N. M.; Moorcraft, L. P.; Pope, S. J. A.; Bell, Z. R.; Faulkner, S.; Ward, M. D. *Chem.—Eur. J.* **2003**, *9*, 5283–5291.
- (11) Xu, H.-B.; Shi, L.-X.; Ma, E.; Zhang, L.-Y.; Wei, Q.-H.; Chen, Z.-N. *Chem. Commun.* **2006**, 1601–1603.
- (12) Coppo, P.; Duati, M.; Kozhevnikov, V. N.; Hofstraat, J. W.; De Cola, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 1806–1810.

X-ray Crystallography. The X-ray diffraction data were collected on a Rigaku MicroMax-007 CCD diffractometer by the ω scan technique at 131 K using graphite-monochromated $\text{Mo}/\text{K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. An absorption correction by multiscan was applied to the intensity data. The structures were solved by the direct method, and the heavy atoms were located from the E-map. The remaining nonhydrogen atoms were determined from the successive difference Fourier syntheses. The nonhydrogen atoms were refined anisotropically, whereas the hydrogen atoms were generated geometrically with isotropic thermal parameters. The structures were refined on F^2 by full-matrix least-squares methods using the SHELXTL-97 program package.¹³ Because the crystal structure of $\{[(\text{dfppy})_2\text{Ir}(\mu\text{-phen5f})_2]\text{GdCl}\}\text{Cl}_2$ contained solvent that was highly disordered, PLATON/SQUEEZE¹⁴ was used to correct the data for the presence of the disordered solvent. A summary of the refinement details and the resulting factors is given in Table 1. Full crystallographic data are provided in CIF files as Supporting Information and are available from the Cambridge Crystallographic Data Centre (CCDC-626219, 631670, 651603).

Synthesis. 2-Acetyl-1,10-phenanthroline¹⁵ and 2-(4',6'-difluorophenyl)pyridine¹⁶ were prepared and purified according to the previously published procedures. The Ir^{III} chloro-bridged dimer $(\text{dfppy})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{dfppy})_2$ was synthesized according to the Nonoyama route by refluxing $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ with 2.2 equiv of 2-(4',6'-difluorophenyl)pyridine in a 3:1 mixture of 2-ethoxyethanol and water.¹⁷

4,4,5,5,5-Pentafluoro-1-(1',10'-phenanthrolin-2'-yl)pentane-1,3-dione (Hphen5f). 2-Acetyl-1,10-phenanthroline (13.9 mmol, 3.10 g) and ethyl 2,2,3,3,3-pentafluoro-propanoate (28.0 mmol, 5.38 g) were mixed in a round-bottomed flask (50 mL), and 20 mL of benzene was added. When the mixture was cooled to 273 K, sodium (28.0 mmol, 0.644 g) was added. The mixture was stirred at room temperature for 12 h and poured into ice-water. It was then acidified with diluted hydrochloric acid. The crude product was extracted with CHCl_3 . After evaporation of the solvent, the residue was recrystallized in CHCl_3/n -hexane (1:1) and a pale yellow powder was obtained (1.80 g, yield 40%). ^1H NMR(400 MHz, $\text{DMSO}-d_6$): δ , ppm 12.5–13.5 (1H, hydroxyl), 9.17 (dd, 1H, $J = 4.3, 1.7$ Hz), 8.84 (d, 1H, $J = 8.4$ Hz), 8.57 (dd, 1H, $J = 8.1, 1.7$ Hz), 8.46 (d, 1H, $J = 8.4$ Hz), 8.17 (d, 1H, $J = 8.9$ Hz), 8.10 (d, 1H, $J = 8.9$ Hz), 7.87 (dd, 1H, $J = 8.1, 4.3$ Hz), 6.51 (s, 1H). ^{13}C NMR(100 MHz, $\text{DMSO}-d_6$): δ , ppm 185.3 (C), 161.1 (C), 150.5 (CH), 149.8 (C), 143.7 (C), 142.3 (C), 139.9 (CH), 136.8 (CH), 130.9 (C), 129.7(CH), 129.0 (C), 125.9 (CH), 124.4 (CH), 122.2 (CH), 118.3 (C), 109.7 (C), 99.6 (CH). EI-MS: m/z : 368 [M^+]. Anal. Found for $\text{C}_{17}\text{H}_9\text{F}_5\text{N}_2\text{O}_2$: C, 55.35; H, 2.75; N, 7.60. Calcd. C, 55.45; H, 2.46; N, 7.61. FT-IR: $\nu = 3100\text{--}3000$ (w, aromatic C–H); 1630 (s, C=O stretch); 1602 (m); 1562 (m); 1443 (m); 1412(m); 1196 (vs) cm^{-1} .

$\text{Ir}(\text{dfppy})_2(\text{phen5f})$ (1). $(\text{dfppy})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{dfppy})_2$ (0.50 mmol), Hphen5f (1.1 mmol), and anhydrous sodium carbonate (5.0 mmol) were refluxed in 2-ethoxyethanol under a N_2 atmosphere for 12 h. After cooling to room temperature, the mixture was poured into water. The crude product was obtained by filtration and then dissolved in CHCl_3 . The solution was dried in anhydrous sodium sulfate overnight. After evaporation of the solvent, the residue was purified via chromatography, using an acetone/petroleum ether

- (13) Sheldrick, G. M. *SHELXTL*, version 5.1; Bruker Analytical X-ray System, Inc.: Madison, WI, 1997.
- (14) van der Sluis, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194–201.
- (15) Zong, R.-F.; Thummel, R. P. *Inorg. Chem.* **2005**, *44*, 5984–5986.
- (16) Coppo, P.; Plummer, E. A.; De Cola, L. *Chem. Commun.* **2004**, 1774–1775.
- (17) Nonoyama, M. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 767–768.

Table 1. Crystallographic Data and Structure Refinement for **1**, **2**, and **3**

	1	2	3
empirical formula	C _{40.50} H ₂₃ F ₉ IrN ₄ O _{3.13}	C _{127.50} H _{91.50} Cl ₃ EuF ₂₇ Ir ₃ N ₁₂ O _{11.50}	C ₁₁₇ H ₆₀ Cl ₃ F ₂₇ GdIr ₃ N ₁₂ O ₆
fw	978.83	3323.54	3082.97
temperature	113(2) K	113(2) K	113(2) K
wavelength	0.71073 Å	0.71070 Å	0.71070 Å
crystal system	monoclinic	triclinic	monoclinic
space group	C2/c	P $\bar{1}$	P2 ₁ /n
unit cell dimensions	<i>a</i> = 29.352(6) Å <i>b</i> = 16.412(3) Å <i>c</i> = 19.288(4) Å	<i>a</i> = 16.153(10) Å <i>b</i> = 16.598(12) Å <i>c</i> = 28.10(2) Å	<i>a</i> = 15.6984(10) Å <i>b</i> = 30.5430(15) Å <i>c</i> = 28.2430(17) Å
volume	7866(3) Å ³	6556(8) Å ³	13291.2(13) Å ³
Z	8	2	4
density (calculated)	1.655 g cm ⁻³	1.684 g cm ⁻³	1.541 g cm ⁻³
absorption coefficient	3.481 mm ⁻¹	3.669 mm ⁻¹	3.637 mm ⁻¹
<i>F</i> (000)	3826	3241	5932
crystal size	0.10 × 0.08 × 0.08 mm	0.06 × 0.04 × 0.02 mm	0.12 × 0.10 × 0.06 mm
theta range for data collection	2.13 to 30.05°	1.37 to 25.00°	1.52 to 25.00°
reflections collected/unique	32273/11467 [<i>R</i> (int) = 0.0358]	46076/22330 [<i>R</i> (int) = 0.1078]	99586/23405 [<i>R</i> (int) = 0.0943]
transmission factors	min/max ratio: 0.940	min/max ratio: 0.871	min/max ratio: 0.825
refinement method	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²
data/restraints/parameters	11467/224/629	22330/237/1732	23405/86/1559
goodness-of-fit on <i>F</i> ²	1.048	1.182	1.085
final <i>R</i> indices [<i>I</i> > 2σ (<i>I</i>)]	<i>R</i> 1 = 0.0447, <i>wR</i> 2 = 0.1040	<i>R</i> 1 = 0.1203, <i>wR</i> 2 = 0.2222	<i>R</i> 1 = 0.0639, <i>wR</i> 2 = 0.1210
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0569, <i>wR</i> 2 = 0.1101	<i>R</i> 1 = 0.1713, <i>wR</i> 2 = 0.2597	<i>R</i> 1 = 0.0913, <i>wR</i> 2 = 0.1341
largest diff. peak and hole	1.113 and -1.245 e. Å ⁻³	2.154 and -1.602 e. Å ⁻³	1.121 and -1.310 e. Å ⁻³

(2:1) mixture for the elution. The pure product was obtained as a yellow powder (0.52 g, yield 55%). ¹H NMR (400 MHz, DMSO-*d*₆): δ, ppm 8.75–8.90 (m, 2H), 8.03–8.45 (m, 6H), 7.92–7.96 (m, 2H), 7.79–7.88 (m, 1H), 7.17–7.61 (m, 2H), 6.83–6.98 (m, 3H), 6.63–6.69 (m, 1H), 5.35–5.56 (m, 2H), 4.28–4.42 (m, 1H). Anal. Found for C₃₉H₂₀F₉IrN₄O₂·0.5CH₃COCH₃·1.25H₂O: C, 49.13; H, 2.42; N, 5.83; Calcd. C, 49.07; H, 2.59; N, 5.65. TOF-MS: observed 939.17; calculated for C₃₉H₂₀F₉IrN₄O₂ 939.80. FT-IR: ν = 3100–3000 (w); 1607 (vs); 1575 (s); 1539 (s); 1431 (m); 1182 (m) cm⁻¹.

[[**(dfppy)**₂**Ir(μ-phen5f)**]₃**EuCl**]**Cl**₂ (**2**). Ir(dfppy)₂(phen5f) (0.3 mmol) and EuCl₃·6H₂O (0.1 mmol) were dissolved in ethanol and refluxed for 6 h. The ethanol solution was evaporated slowly (over more than 15 days), and yellow crystals were obtained. Anal. Found for C₁₁₇H₆₀Cl₃EuF₂₇Ir₃N₁₂O₆·2H₂O: C, 44.90; H, 1.92; N, 5.36; Calcd. C, 45.13; H, 2.07; N, 5.40. FT-IR: ν = 3500–3200 (m); 3100–3000 (w); 1606 (vs); 1575 (m); 1531 (m); 1446 (m); 1188 (m) cm⁻¹.

[[**(dfppy)**₂**Ir(μ-phen5f)**]₃**GdCl**]**Cl**₂ (**3**). Ir(dfppy)₂(phen5f) (0.15 mmol) and GdCl₃·6H₂O (0.050 mmol) were dissolved in ethanol and refluxed for 6 h, and pale yellow crystals were obtained from the EtOH solution by slow diffusion of Et₂O. Anal. Found for C₁₁₇H₆₀Cl₃F₂₇GdIr₃N₁₂O₆·4H₂O: C, 44.52; H, 2.58; N, 5.19; Calcd. C, 44.54; H, 2.17; N, 5.33. FT-IR: ν = 3500–3200 (m); 3100–3000 (w); 1605 (vs); 1575 (m); 1530 (m); 1447 (m); 1189 (m) cm⁻¹.

(dfppy)₂**Ir(μ-phen5f)Eu(TFAcA)**₃ (**4**). Ir(dfppy)₂(phen5f) (0.20 mmol) was dissolved in ethanol. Eu(TFAcA)₃·2H₂O (TFAcA = trifluoroacetylacetonate, 0.20 mmol) was also dissolved in ethanol and then added in portions to the Ir(dfppy)₂(phen5f) solution. The mixture was refluxed for 6 h under stirring. The yellow solution was cooled to room temperature, and the solvent was evaporated under reduced pressure. The crude product was recrystallized from CHCl₃/*n*-hexane to give **(dfppy)**₂**Ir(μ-phen5f)Eu(TFAcA)**₃ as a light yellow amorphous powder (0.16 g, yield 52%). Anal. Found for IrEuC₅₄H₃₂N₄O₈F₁₈: C, 41.52; H, 2.51; N, 3.59; Calcd. C, 41.82; H, 2.08; N, 3.61. FT-IR: ν = 3100–3000 (w); 1628 (vs); 1607 (vs); 1576 (m); 1526 (m); 1432 (m); 1191 (s) cm⁻¹.

Ir(dfppy)₂**(acac)**. Ir(dfppy)₂(acac) as a reference sample was prepared and purified according to a previously published procedure.¹⁸

Eu(TFAcA)₃·**2H**₂**O** and **Eu(phen5f)**₃·**4H**₂**O**. Eu(TFAcA)₃·2H₂O and Eu(phen5f)₃·4H₂O were prepared according to the following similar methods. Three equivalents of β-diketone were dissolved in ethanol, and 3 equiv of NaOH was added to the solution. After refluxing, the mixture was added dropwise to 1 equiv of EuCl₃·6H₂O in ethanol. The mixture was then refluxed for a few hours. After removal of the solvent, the crude product was recrystallized by appropriate solvents (CH₃OH/H₂O for Eu(TFAcA)₃·2H₂O and CHCl₃/*n*-hexane for Eu(phen5f)₃·4H₂O), and a pure product was obtained. Anal. Found for C₁₅H₁₆EuF₉O₈ [Eu(TFAcA)₃·2H₂O]: C, 27.84; H, 2.36; Calcd. C, 27.84; H, 2.49. Anal. Found for C₅₁H₃₂EuF₁₅N₆O₁₀ [Eu(phen5f)₃·4H₂O]: C, 45.79; H, 2.25; N, 6.12; Calcd. C, 46.20; H, 2.43; N, 6.34.

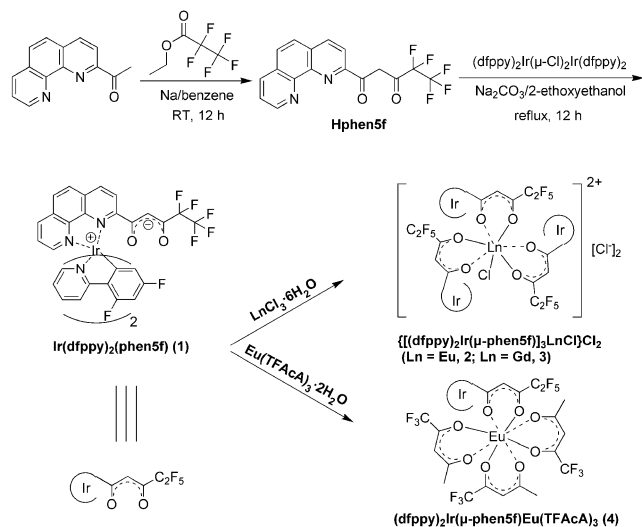
Results and Discussion

Synthesis and Structure. Synthetic routes for the ligand and complexes are outlined in Scheme 1. The novel bridge ligand Hphen5f was designed for connecting the Ir^{III} and Ln^{III} centers. The complex **1** Ir(dfppy)₂(phen5f) was prepared from the reaction of the chloride-bridged Ir(III) dimer (dfppy)₂Ir(μ-Cl)₂Ir(dfppy)₂ and the ligand Hphen5f under similar conditions as those for the synthesis of Ir(C[^]N)₂(O[^]O).¹⁹ However, the chelating sites are nitrogen atoms instead of oxygen atoms in the resulting Ir(III) complex. This fact reflects that the affinity between the transition metal ion and the former is stronger than that between the transition metal ion and the latter. So in the [Ir(dfppy)₂]⁺ unit, the iridium ion is coordinated to the phenanthroline site (N, N) of phen5f, and the diketone site (O, O) is free for Ln^{III} ion.

(18) Li, J.; Djurovich, P. I.; Alleyne, B. D.; Yousufuddin, M.; Ho, N. N.; Thomas, J. C.; Peters, J. C.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2005**, *44*, 1713–1727.

(19) Lamansky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzaq, F.; Lee, H.-E.; Adachi, C.; Burrows, P. E.; Forrest, S. R.; Thompson, M. E. *J. Am. Chem. Soc.* **2001**, *123*, 4304–4312.

Scheme 1. Synthetic Routes of Hphen5f, Ir(dfppy)₂(phen5f) (1), {[dfppy]₂Ir(μ-phen5f)]₃LnCl₂]Cl₂ (Ln = Eu, 2; Ln = Gd, 3), and (dfppy)₂Ir(μ-phen5f)-Eu(TFAcA)₃ (4).



Single crystals of complex **1** were grown from a slowly evaporating solution of acetone/*n*-hexane. The X-ray crystal structures of **1**, **2**, and **3** are shown in Figure 1, and selected bond lengths and angles are shown in Table 2. From the crystal structure of **1**, one can see that the central ion Ir^{III} is six coordinated by two carbon atoms and four nitrogen atoms. Herein, two carbon atoms and two nitrogen atoms are offered by the two cyclometalated ligands dfppy, and the other two nitrogen atoms are contributed by the ancillary ligand phen5f. The two carbonyl groups in the β-diketone fragment of phen5f are in the trans form and uncoordinated. The overall molecule is electrically neutral. In the tetranuclear complex **2**, the Eu^{III} ion is seven coordinated by six oxygen atoms and one chloride ion. The former are offered by the three β-diketone fragments while the chloride ion comes from the starting material EuCl₃·6H₂O. It is noteworthy that the configuration of the two carbonyl groups in the β-diketone has been changed from the trans form to the cis form upon coordination. The nonbonding distances for Eu⋯Ir are 6.028, 5.907, and 6.100 Å, revealing that effective energy transfer may exist in the donor-bridge-acceptor system because the short distances all are around 6 Å (<10 Å).²⁰

Photophysical Properties. The UV–vis absorption spectrum of complex **1** shows π–π* bands that are attributed to intraligand transitions in the UV region and to an MLCT (metal-to-ligand charge transfer) transition in the visible region. Compared to Ir(dfppy)₂(acac),¹⁸ the ¹MLCT transition in complex **1** cannot be identified in detail because it is submerged in the absorption of the ancillary ligand phen5f, in the range 350–400 nm. However, the weaker absorption tail from 440 to 480 nm in complex **1** should be mainly assigned to the ³MLCT transition in the Ir(dfppy)₂²⁺ moiety²¹ (Figure 2 and Table 3) because the ligand Hphen5f does not exhibit absorption at wavelengths longer than 440 nm, and

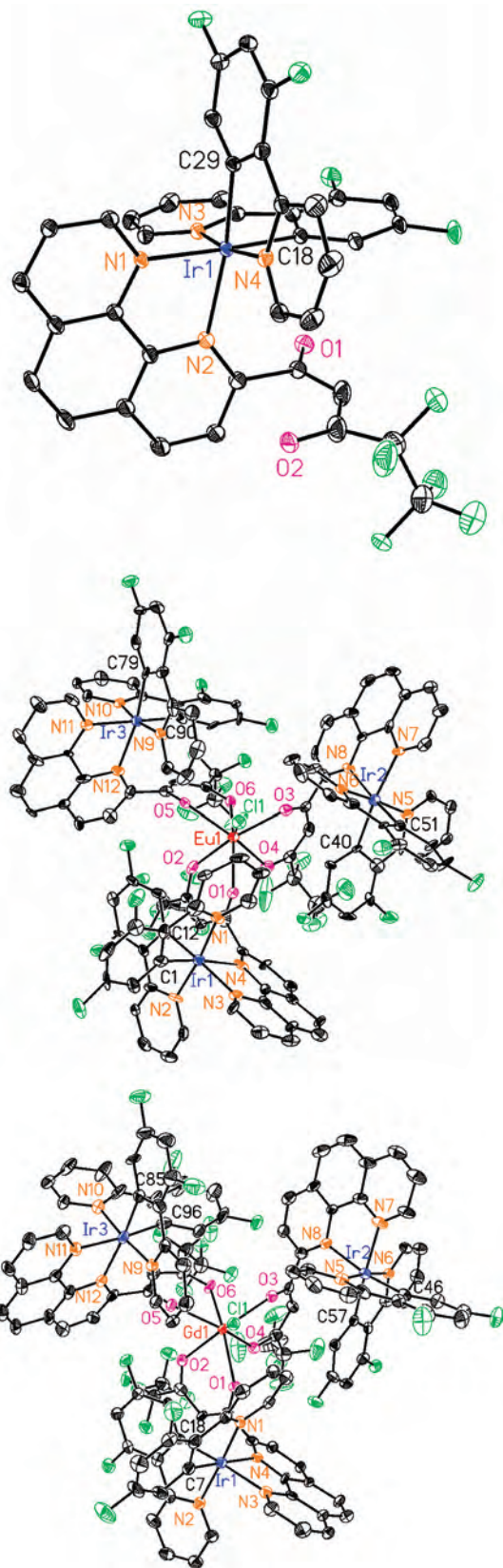


Figure 1. ORTEP (Oak Ridge thermal ellipsoid plot) diagrams of complexes **1** (top), **2** (middle), and **3** (bottom, thermal ellipsoids shown at the 20% probability level). The hydrogen atoms, counterions, and solvent molecules are omitted for clarity.

the possible ³MLCT transition on Ir^{III} to the N^N ligand phen5f was not obviously distinguished. The photolumines-

(20) Montes, V. A.; Pérez-Bolívar, C.; Agarwal, N.; Shinar, J.; Anzenbacher, P., Jr. *J. Am. Chem. Soc.* **2006**, *128*, 12436–12438.

(21) Laskar, I. R.; Hsu, S.-F.; Chen, T.-M. *Polyhedron* **2006**, *25*, 1167–1176.

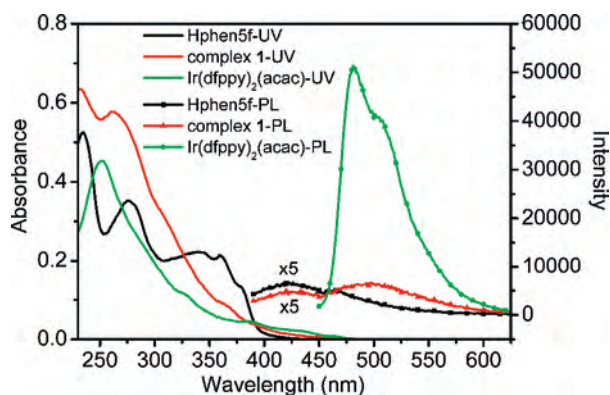
Table 2. Selected Bond Lengths and Angles for **1**, **2**, and **3**

1		2		3	
Selected Bond Lengths [Å]					
Ir(1)–C(29)	2.018(4)	Eu(1)–O(5)	2.372(13)	Gd(1)–O(2)	2.348(6)
Ir(1)–C(18)	2.024(4)	Eu(1)–O(3)	2.377(13)	Gd(1)–O(5)	2.352(6)
Ir(1)–N(4)	2.053(4)	Eu(1)–O(1)	2.382(13)	Gd(1)–O(3)	2.353(6)
Ir(1)–N(3)	2.066(4)	Eu(1)–O(2)	2.392(15)	Gd(1)–O(1)	2.363(6)
Ir(1)–N(1)	2.136(4)	Eu(1)–O(4)	2.405(14)	Gd(1)–O(6)	2.374(6)
Ir(1)–N(2)	2.216(4)	Eu(1)–O(6)	2.406(12)	Gd(1)–O(4)	2.374(6)
		Eu(1)–Cl(1)	2.610(6)	Gd(1)–Cl(1)	2.597(2)
Selected Angles [degrees]					
C(18)–Ir(1)–N(3)	80.30(18)	O(5)–Eu(1)–O(6)	72.0(4)	O(2)–Gd(1)–O(1)	72.5(2)
C(29)–Ir(1)–N(4)	80.37(18)	O(1)–Eu(1)–O(2)	72.1(5)	O(5)–Gd(1)–O(6)	72.4(2)
N(1)–Ir(1)–N(2)	76.88(15)	O(3)–Eu(1)–O(4)	72.0(5)	O(3)–Gd(1)–O(4)	72.4(2)

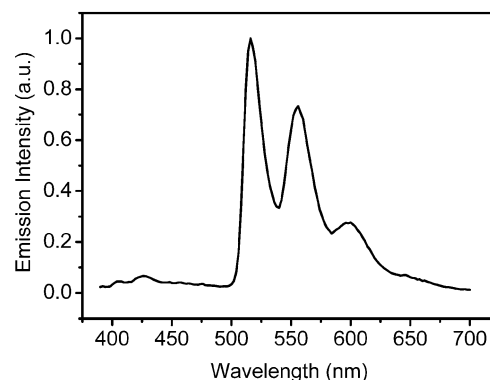
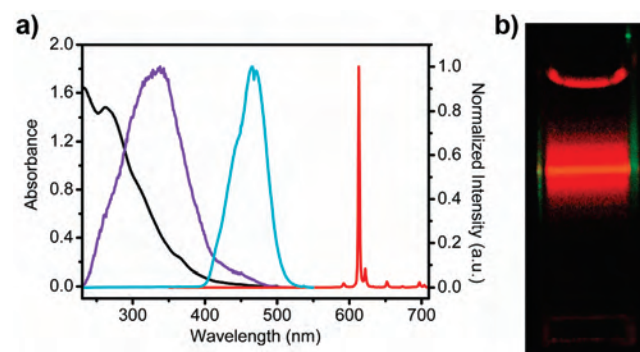
cence spectra of Hphen5f and complex **1** are both very weak compared to that of Ir(dfppy)₂(acac) at room temperature upon excitation at 326 nm. Herein, the weak emission of complex **1** around 415 nm should originate from the fluorescence of the ancillary ligand phen5f. On the other hand, the strong phosphorescence emission detected around 483 nm in the visible region for the Ir(dfppy)₂⁺ moiety is largely quenched in complex **1**. According to the literature method,²² Gd(Hphen5f)Cl₃ was prepared, and the low temperature emission spectrum was recorded (Figure 3). The triplet energy level of Hphen5f was calculated to be 2.41 eV, which is lower than the Ir-based ³MLCT excited-state energy level, 2.64 eV.²³ Therefore, the energy from the ³MLCT transition in the Ir(dfppy)₂⁺ moiety might mostly transfer to the ³LC (ligand centered) excited-state of phen5f. Thus, complex **1** has its excited-state localized predominantly on the phen5f ligand, leading to the very weak light emission at room temperature.¹⁹

To determine whether a Eu^{III} ion can be sensitized by the complex-ligand Ir(dfppy)₂(phen5f), the photophysical proper-

ties of complex **2** were examined. The absorption spectrum of complex **2** is obviously similar to that of complex **1** at room temperature because of the weak absorption from EuCl₃, and the extinction coefficients of complex **2** are about three times those of complex **1** as expected (Table 3). In Figure 4a, the excitation spectrum of complex **2** (monitored at 613 nm) is in agreement with its ground-state absorption spectrum. Its excitation window (1 × 10⁻⁵ M in EtOH) has been extended to 470 nm, and the 1 × 10⁻³ M solution can be excited by the light up to 530 nm. It can therefore be effectively excited by daylight (Figure 4b). As expected, characteristic emission bands from a Eu^{III} ion are observed for complex **2** at about 592, 613, 652, and 697 nm corresponding to the transitions ⁵D₀→⁷F₁, ⁷F₂, ⁷F₃, ⁷F₄, respectively, with the dominant band at 613 nm. This

**Figure 2.** UV–vis absorption and PL spectra of Hphen5f, complex **1**, and Ir(dfppy)₂(acac) in EtOH (1 × 10⁻⁵ M) at room temperature.**Table 3.** Photophysical Data for Hphen5f, Ir(dfppy)₂(acac), and Complexes **1**, **2**

compound	absorption features, nm (ε, 10 ³ cm ⁻¹ M ⁻¹)	λ _{em} , nm
Hphen5f	235 (52.5), 275 (35.3), 338 (22.3), 359 (21.5)	415 (weak)
Ir(dfppy) ₂ (acac)	252 (45.3), 387 (4.5), 462 (0.8)	483
complex 1	231 (63.5), 263 (57.7), 361 (9.2), 451 (0.6)	415 (weak), 490 (weak)
complex 2	232 (164.3), 262 (148.5), 366 (23.3), 448 (1.7)	592, 613, 652, 697

**Figure 3.** Emission spectrum of Gd(Hphen5f)Cl₃ in an EtOH rigid matrix at 77 K.**Figure 4.** (a) UV–vis absorption (black line), and normalized excitation (λ_{em} = 613 nm) (violet line 1 × 10⁻⁵ M, cyan line 1 × 10⁻³ M) and photoluminescence (λ_{ex} = 326 nm) (red line) spectra of complex **2** in EtOH at room temperature; (b) red emission of complex **2** in EtOH (1 × 10⁻³ M) upon excitation at 532 nm laser.

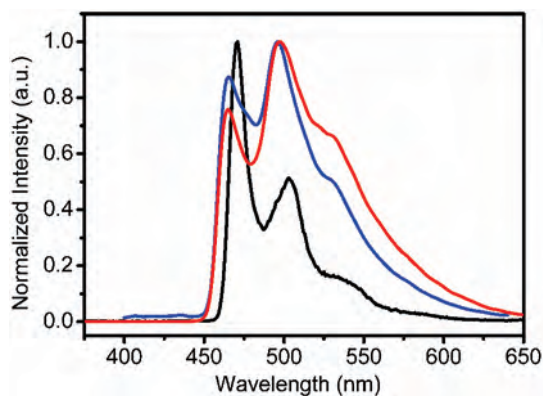


Figure 5. Normalized emission spectra of complex **1** (blue line), complex **3** (red line) and Ir(dfppy)₂(acac) (black line) in an EtOH rigid matrix (1×10^{-5} M) at 77 K.

hypersensitive $^5D_0 \rightarrow ^7F_2$ transition is an electric-dipole emission which is forbidden in the free ion. However, this transition has been greatly enhanced because the Eu^{III} ion experiences a strongly asymmetric ligand field. The intensity ratio $I_{5D_0 \rightarrow 7F_2} / I_{5D_0 \rightarrow 7F_1}$ reaches as high as 50, which is much higher than the values reported in the literature.²⁴ The high color purity could not only greatly decrease the background interference in biological detection, but also improve the monochromatic red emission of Eu^{III} complex based organic light-emitting diodes. The lifetime of the Eu^{III}-centered emission is 313 μ s.

To study the origin of the energy on the Ir^{III} complex-ligand, which sensitizes the Eu^{III} ion, low-temperature emission spectra of complex **1**, complex **3** and Ir(dfppy)₂(acac) were recorded in an EtOH rigid matrix at 77 K (Figure 5). For Ir(dfppy)₂(acac), the higher emission around 471 nm, which is in good agreement with that reported in literature,¹⁸ is assigned to the Ir-based ³MLCT excited-state energy level (2.64 eV, 2.12×10^4 cm⁻¹) from Ir(dfppy)₂²⁺ moiety. A similar behavior, with a small difference in the individual emission intensities around 465 and 497 nm, was observed for complex **1** at 77 K. It should be noted that the increase in emission intensity of complex **1** around 497 nm and after 500 nm compared to that of Ir(dfppy)₂(acac) might be attributed to the ³LC excited-state of phen5f around 516 nm (Figure 3) and the ³MLCT excited-state of Ir^{III} to the N[^]N ligand phen5f.²⁵ Namely, the phosphorescence spectra in Figure 5 showed the superimposition of the mainly ³MLCT emission from the Ir(dfppy)₂²⁺ moiety, the ³LC emission of phen5f and the ³MLCT emission from Ir^{III} to the N[^]N ligand phen5f. Furthermore, when complex **1** was coordinated to Gd^{III} ion as a whole complex-ligand, the emission bands of complex **3** showed a surprising similarity to those of complex **1** except for a small difference in the emission profile. Therefore, as a complex-ligand, the triplet energy level of

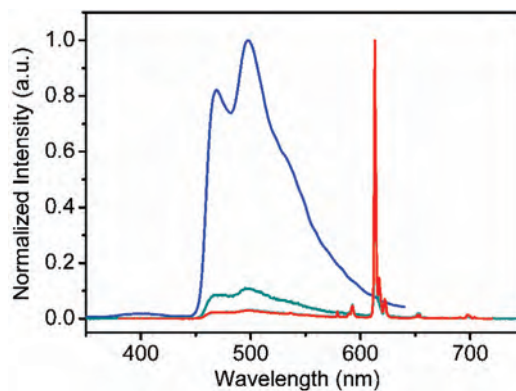


Figure 6. Normalized emission spectra of complex **1** (blue line) and mixtures of complex **1** and EuCl₃ with different proportions [4:1 (dark cyan line), 2:1 (cyan line), 1:1 (red line)] in an EtOH rigid matrix at 77 K.

Table 4. Emission Maxima (λ_{em}) and Lifetimes (τ) of Solutions with Different Proportions of Ir^{III} and Eu^{III} Centers

proportion of Ir ^{III} /Eu ^{III}	λ_{em} [nm]	τ [μ s]
1:0	469, 498	24.46 μ s, 134.08 μ s (469 nm)
4:1	469, 497 613	18.25 μ s, 95.67 μ s (469 nm) 418.9 μ s (613 nm)
2:1	469, 498 613	15.82 μ s, 82.23 μ s (469 nm) 413.59 μ s (613 nm)
1:1	469, 498 613	14.46 μ s, 62.17 μ s (469 nm) 413.83 μ s (613 nm)

complex **1** is 2.67 eV (2.15×10^4 cm⁻¹), which is the same as that of the Ir-based ³MLCT excited-state energy level from Ir(dfppy)₂²⁺ moiety, within experimental error. Moreover, the triplet energy 2.15×10^4 cm⁻¹ is very suitable for sensitizing the low-lying excited state (⁵D₀, 1.75×10^4 cm⁻¹) of Eu^{III}, making energy transfer highly efficient and irreversible.²⁶ Interestingly, under the same experimental conditions, the emission from the Ir^{III} moiety was evidently decreased with an increasing concentration of EuCl₃ at 77 K when the EtOH solution of EuCl₃·6H₂O was titrated stepwise into a 2×10^{-5} M solution of complex **1** in EtOH (Figure 6). At the same time, the emission life times were measured. They are 134.08 and 24.46 μ s (double-exponential decay), 62.17 and 14.46 μ s for the solutions when complex **1** and EuCl₃ with a 1:0 ratio and 1:1 ratio, respectively (Table 4), which implies that there might be at least two intermediate excited states, and that energy transfer from the Ir^{III} moiety to the Eu^{III} center takes place.

The bimetallic complex **4** was synthesized to further support that the energy, which makes the Eu^{III} center sensitized emission, comes from the Ir^{III} center and mainly belongs to the ³MLCT excited state. Because both of the

(22) Xu, H.; Wang, L.-H.; Zhu, X.-H.; Yin, K.; Zhong, G.-Y.; Hou, X.-Y.; Huang, W. *J. Phys. Chem. B* **2006**, *110*, 3023–3029.

(23) Welter, S.; Lafalet, F.; Cecchetto, E.; Vergeer, F.; De Cola, L. *ChemPhysChem* **2005**, *6*, 2417–2427.

(24) (a) Bünzli, J.-C. G.; Moret, E.; Foiret, V.; Schenk, K. J.; Wang, M.; Jin, L. *J. Alloys Compd.* **1994**, *207–208*, 107–111. (b) Brito, H. F.; Malta, O. L.; Felinto, M. C. F. C.; Teotonio, E. E. S.; Menezes, J. F. S.; Silva, C. F. B.; Tomiyama, C. S.; Carvalho, C. A. A. *J. Alloys Compd.* **2002**, *344*, 293–297.

(25) According to the references (such as Watts, R. J.; Crosby, G. A. *J. Am. Chem. Soc.* **1971**, *93*, 3184; *J. Am. Chem. Soc.* **1972**, *94*, 2606; Ayala, N. P.; Flynn, C. M., Jr.; Sacksteder, L.; Demas, J. N.; DeGraff, B. A. *J. Am. Chem. Soc.* **1990**, *112*, 3837), the emission around 450 nm for Ir(phen)₃³⁺ was assigned to the π - π^* ligand-localized phosphorescence (similar to the free ligand phen) and the emission around 470 nm for [Ir(phen)₂Cl₂]⁺ was assigned to the d- π^* MLCT emission. It might be concluded that the ³MLCT state on Ir to N[^]N should be lower than the ³LC state on N[^]N ligand. That is to say, the ³MLCT emission from Ir^{III} to the N[^]N ligand phen5f should exist after the ³LC emission of phen5f, but it cannot be distinguished under the present experimental conditions. Studies using time-resolved spectroscopy and transient absorption spectroscopy are currently in progress.

(26) Steemers, F. J.; Verboom, W.; Reinhoudt, D. N.; van der Tol, E. B.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 9408–9414.

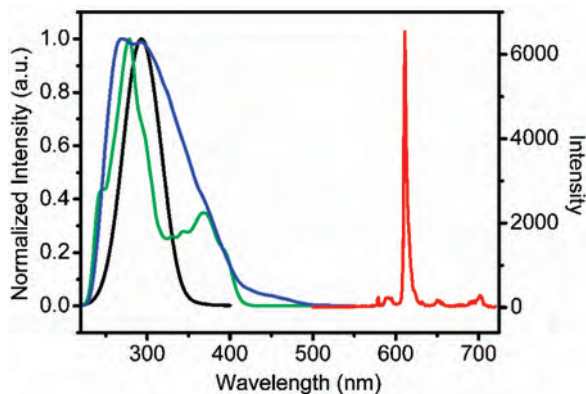


Figure 7. Normalized excitation spectra of $\text{Eu}(\text{TFACa})_3 \cdot 2\text{H}_2\text{O}$ (black line), $\text{Eu}(\text{phen5f})_3 \cdot 4\text{H}_2\text{O}$ (green line), and complex **4** (blue line) and photoluminescence spectrum ($\lambda_{\text{ex}} = 480 \text{ nm}$) of complex **4** (red line) in CH_2Cl_2 ($1 \times 10^{-5} \text{ M}$) at room temperature.

ligands TFACa and phen5f could sensitize the Eu^{III} ion, a comparison of the photophysical properties of $\text{Eu}(\text{TFACa})_3 \cdot 2\text{H}_2\text{O}$ and $\text{Eu}(\text{phen5f})_3 \cdot 4\text{H}_2\text{O}$ to those of complex **4** is meaningful. All the excitation spectra of the three complexes were recorded (Figure 7). It is worth noting that $\text{Eu}(\text{TFACa})_3 \cdot 2\text{H}_2\text{O}$ cannot be strongly excited at wavelengths longer than 350 nm, whereas $\text{Eu}(\text{phen5f})_3 \cdot 4\text{H}_2\text{O}$ cannot be excited at wavelengths longer than 430 nm. Therefore, the use of an excitation wavelength longer than 430 nm will result in essentially selective excitation of the Ir-based chromophore in complex **4**.¹⁰ The experimental results show that a bright red emission centered at 613 nm is observed when complex **4** is excited at 480 nm, and this should be mainly sensitized by the $^3\text{MLCT}$ energy of the Ir-based chromophore. Moreover, we measured the quantum efficiencies of the three complexes using $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ in a degassed water solution as a reference (Φ

$= 4.2\%$).²⁷ The quantum yield of complex **4** reached 17.7%, whereas the quantum efficiencies of $\text{Eu}(\text{TFACa})_3 \cdot 2\text{H}_2\text{O}$ and $\text{Eu}(\text{phen5f})_3 \cdot 4\text{H}_2\text{O}$ were both lower than 3%. This implies not only that the d→f energy transfer occurs between the Ir^{III} center and the Eu^{III} center but also that the energy transfer is very efficient.

Conclusions

Two classes of new Ir–Eu bimetallic complexes were successfully synthesized. The novel ligand with four coordination sites was designed as a bridge to link the Ir^{III} center and the Eu^{III} center, making the nonbonding distances all around 6 Å. Photophysical studies implied that the highly efficient pure red luminescence from the Eu^{III} ion was sensitized by the $^3\text{MLCT}$ energy based on an Ir^{III} complex- ligand in a d-f bimetallic assembly. Remarkably, the excitation window for the bimetallic complexes $\{[(\text{dfppy})_2\text{Ir}(\mu\text{-phen5f})_3\text{EuCl}]\text{Cl}_2$ ($1 \times 10^{-3} \text{ M}$ in EtOH) extended up to 530 nm. Investigations into and applications of the Ir–Eu bimetallic complexes, as well as the design of new bridging ligands to make the energy transfer more effective, are currently in progress.

Acknowledgment. The authors thank the National Basic Research Program (2006CB601103) and the NNSFC (20221101, 20471004, 50372002, 20671006) for financial support.

Supporting Information Available: The CIF files of complexes **1**, **2**, **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC701817N

(27) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 4853–4858.