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Article

Visible-Light Excitable Europium(III) Complexes with 2,7-Positional Substituted Carbazole Group-Containing Ligands

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Two novel carbazole-based β-diketones with 2- or 2,7-substituted groups in the carbazole ring, 2-(4′4′4′-trifluoro-1′3′-dioxobutyl)-carbazole (2-TFDBC) and 2,7-bis(4′4′4′-trifluoro-1″3′-dioxobutyl)-carbazole (2,7-BTFDBC), and their europium(III) ternary complexes Eu(2-TFDBC)$_3$phen and Eu$_2$(2,7-BTFDBC)$_3$(phen)$_2$ were synthesized via a dexterously designed routine, where phen is 1,10-phenanthroline. The Eu(III) complexes were characterized by elementary analysis, IR and UV−visible absorption spectroscopy, thermogravimetric analysis (TGA), and photoluminescence (PL) measurements. TGA shows that the decomposition temperatures of the complexes are 361.4 and 367.3 °C, respectively. PL measurement results indicated that suitably expanded π-conjugation in the complex molecules makes the excitation band redshift to the visible region, and both the Eu(III) complexes exhibit intense red emission under blue-light excitation. The triplet state energy levels of 2-TFDBC and 2,7-BTFDBC in the complexes are higher than that of the lowest excited level of Eu^{3+} ion, $^5D_0$, so the photoluminescence mechanism of the Eu(III) complexes was proposed as a ligand-sensitized luminescence process. All of the results indicate that Eu(2-TFDBC)$_3$phen and Eu$_2$(2,7-BTFDBC)$_3$(phen)$_2$ are promising candidates as visible-light excitable red phosphor for luminescence applications.

Introduction

Europium(III) β-diketonate complexes have been widely studied because of their excellent photoluminescent properties with high color purity and environment-independent emission wavelength.[1−9] One of the most famous complexes is [Eu(tta)$_3$(phen)] (where tta is a short denotation for 2-thenoyltrifluoroacetonate and phen is 1,10-phenanthroline) as a red-emitting europium-based molecular phosphor.[10] These europium(III) β-diketonate complexes give a wide excitation band in the near-ultraviolet (UV) region, and a strong red emission, high quantum yield, and suitable thermal stability. However, they also show a major disadvantage, namely, low photochemical stability under UV irradiation.[10]

There are two ways to solve this problem. One of the approaches is to introduce a 4d- or 5d- transition metal ion such as Ir(III) into the Eu(III) complex molecule. Unfortunately, photoluminescence efficiency of this kind of Eu(III) complexes based on the ^{3}MMLCT (metal−metal-to-ligand charge transfer) or ^{3}MLCT (metal-to-ligand charge transfer) was always very low.[11−13] Another method is to modify the ligand molecule with a suitable expanded π-conjugated system to shift the excitation band of its Eu(III) complex to

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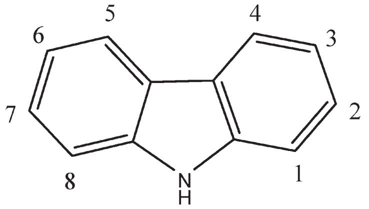

Figure 1. Structure of a carbazole ring system.

the visible region, and this expanded π-conjugated system cannot be either too small to absorb visible light or too big to rise the triplet state (singlet state in some complexes) of the ligand to a degree higher than $^5D_0$, the lowest excited state energy level of the central Eu^{3+} ion. Examples of such ligands are Michler's ketone,[14] phenalenone[15] and tridentate ligands.[16,17]

The carbazole group is a attractive unit with interesting photoconducting and charge-transporting properties and was introduced widely to poly(*N*-vinylcarbazole) (PVK) and numerous side-chain polymers.[18−22] Carbazole exhibits distinguished advantages to the application because of inexpensive starting material, good chemical and environmental stability, and being tailored with a wide variety of functional groups to tune the optical and electrical properties.[18]

Carbazole-containing β-diketones and their Eu(III) complexes have been investigated intensively.[23−28] These carbazole-containing β-diketones are generally synthesized by a direct routine through Friedel−Crafts acylation and Claisen condensation from a carbazole molecule (Figure 1), and this synthesis method only can locate 1′3′-dioxobutyl at *N*-, 3-, and 6-positions in the carbazole ring and cannot synthesis directly to the positions of 2,7-carbons because of the orientation effect of the nitrogen atom in the carbazole ring. Importantly, the Eu(III) complexes with this kind of β-diketonates containing 1′3′-dioxobutyl linked at the 3- and 6- positions failed to extend their excitation band to the visible region. Introduction of 1′3′-dioxobutyl linked at the 2- and 7-positions in carbazole ring should lead to a longer π-conjugation length;[28] therefore, the resulting bathochromic shift in the excitation band is expected, though this kind of synthesis faces a big challenge. Many papers on synthesis of β-diketones containing 1′3′-dioxobutyl linked at the 3- and 6-positions of the carbazole ring were reported; however, to our best knowledge, there is no report on the synthesis of β-diketones containing a carbazole ring with 2- and 7-positional substituted groups and their Eu(III) complexes.

In this article, we report an indirect synthesis method of 2- and 7-positional linked β-diketonate ligands and their Eu(III) complexes. Two novel carbazole-based β-diketone ligands, 2-(4′4′4′-trifluoro-1′′3′-dioxobutyl)-carbazole (2-TFDBC) and 2,7-bis(4′4′4′-trifluoro-1′3′-dioxobutyl)-carbazole (2,7-BTFDBC), have been designed and synthesized, and then their europium(III) ternary complexes Eu(2-TFDBC)$_3$phen and Eu$_2$(2,7-BTFDBC)$_3$(phen)$_2$ were also prepared. Photoluminescence (PL) measurements show that the ligands successfully extend the excitation bands of the Eu(III) complexes to the blue-light region, and the Eu(III) complexes exhibit strong red emission under blue-light excitation.

Experimental Section

All reagents and materials are analytical grade. Solvents were freshly distilled and dried by standard methods.

Elemental analysis for the synthesized ligand and the Eu(III) complexes was carried out with an Elementar vario EL elemental analyzer. Electron impact-mass spectrometer (EI-MS) spectra were determined on a Thermo DSQ EI-mass spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400. Photoluminescence excitation (PLE) and emission (PL) spectra for solid samples and DMF solution samples were measured on an EDINBURGH FLS 920 combined fluorescence lifetime and steady state spectrophotometer equipped with thermo-electric cooled red sensitive PMT (Edinburgh Instruments). The silts of this equipment are controlled for a suitable output display range of intensity and are fixed for the series of samples in the whole measurement process. UV−visible absorption spectra were recorded on a UV-2501PC UV−visible spectrophotometer. IR spectra were recorded on a Nicolet Avatrar 330 FT-IR spectrometer. Thermogravimetric analysis (TGA) was carried out up to 930 °C with a heating speed of 10.0 K/min in atmosphere on an NETZSCH TG-209 thermogravimetric analyzer. The quantum yield of the complexes were measured with an EVERFINE PMS-80 PLUS UV−vis-near IR.

The synthesis routines for the ligands and their Eu(III) ternary complexes, 2-TFDBC and Eu(2-TFDBC)$_3$phen, 2,7-BTFDBC and Eu$_2$(2,7-BTFDBC)$_3$(phen)$_2$, are shown in Figure 2 and Figure 3, respectively.

1-(2′-Nitrobiphenyl-4-yl)ethanone (NBP-4-EN) and 1,1′-(2-nitrobiphenyl-4,4′-diyl) diethanone (NBP-4,4-EN) were synthesized via the Suizuki−Miyaura cross-coupling reaction.[29−31] 1-Bromo-2-nitrobenzene or 1-(4-bromo-3-nitrophenyl)ethanone (10 mmol), 4-acetylphenyl boronic acid (1.5 equi), K_2CO_3 aqueous solution (2 mol/L 15 mL), and Pd(PPh$_3$)$_4$ (0.4 g) were solved in toluene (50 mL) and heated at 110 °C for 2 days. The crude products were extracted with CH_2Cl_2 and purified by column chromatography (ethyl acetate - petroleum ether) to give NBP-4-EN and NBP-4,4-EN (86% yield for NBP-4-EN and 84% yield for NBP-4,4-EN).

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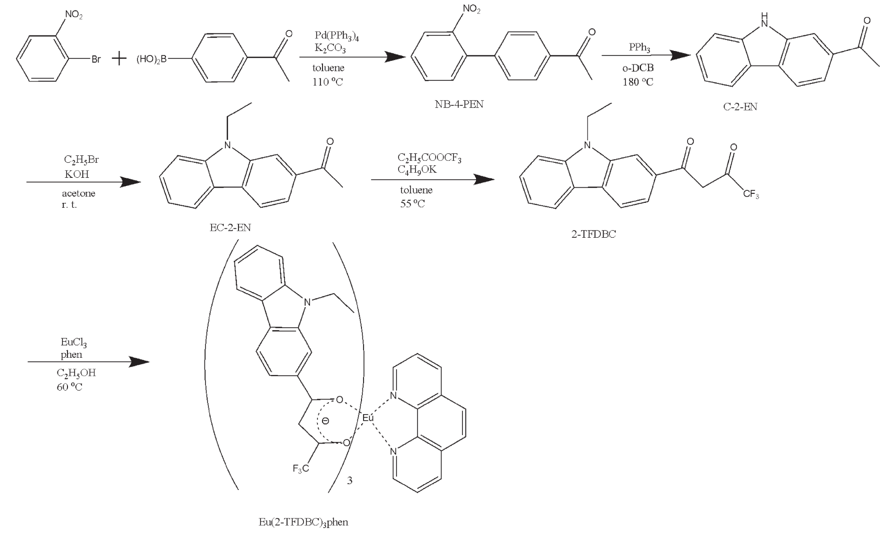

Figure 2. Synthesis routine of 2-TFDBC and complex Eu(2-TFDBC)$_3$phen.

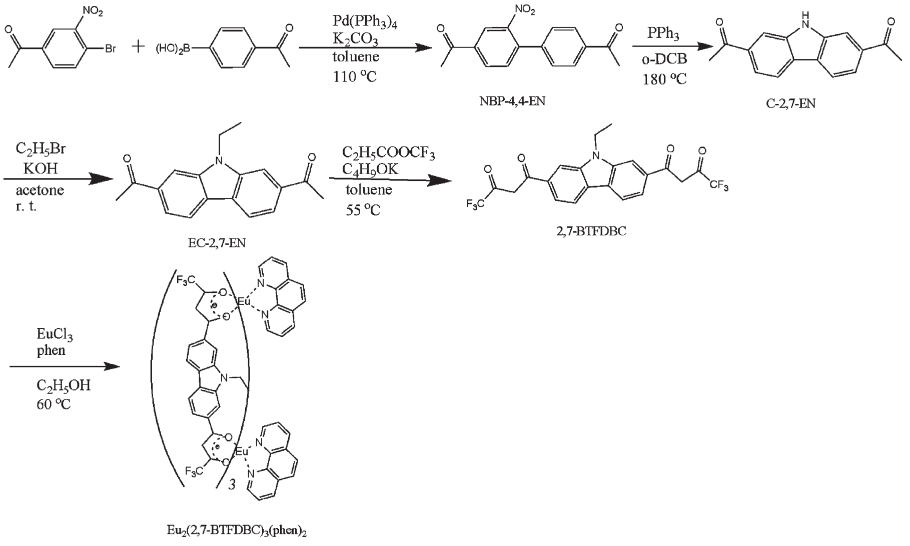

Figure 3. Synthesis routine of 2,7-TFDBC and complex Eu$_2$(2,7-BTFDBC)$_3$(phen)$_2$.

NBP-4-EN. ^{1}HNMR (CDCl$_3$): δ 2.64 (s, 3H, -CH$_3$); δ 7.41−7.45 (t, 3H ,PhH); δ 7.52−7.56 (t, 1H ,PhH); δ 7.64−7.68(t, 1H, PhH); δ 7.93−7.95(d, 1H, PhH); δ 8.01−8.03(d, 2H, PhH). MS (EI) *m*/*z*: 241(M$^+$), 226(M$^+$ − CH$_3$). The elemental analysis data for C$_{14}$H$_{11}$NO$_3$ were found (calculated) %: C, 69.82 (69.70); H, 4.67 (4.60); N, 5.60 (5.81).

NBP-4,4-EN. ^{1}HNMR (CDCl$_3$): δ 2.67 (s, 3H, -CH$_3$); δ 2.72 (s, 3H, -CH3); δ 7.44−7.47(d, 2H, PhH); δ 7.58−7.60(d, 1H, PhH); δ 8.05−8.07(d, 2H, PhH); δ 8.22−8.25(q, 1H, PhH); δ 8.49−8.49(d, 1H, PhH). MS (EI) *m*/*z*: 283(M$^+$), 268(M$^+$ − CH$_3$); 255(M$^+$ − 2CH$_3$ + 2H); 238(M$^+$ − NO$_2$). The elemental analysis data for C$_{16}$H$_{13}$NO$_4$ were found (calculated) %: C, 67.98 (67.84); H, 4.693 (4.63); N, 4.834 (4.94).

The synthesis method of 1-(9H-carbazol-2-yl)ethanone (C-2-EN) and 1,1′-(9H-carbazole-2,7-diyl)diethanone (C-2,7-EN) is commonly referred to as the Cadogan cyclization.[32] NBP-4-EN or NBP-4,4-EN (10 mmol) and PPh$_3$ (2.5 equi) was added into *o*-dichlorobenzene (*o*-DCB) (30 mL) and refluxed for 6.5 h. The most byproducts and impurities have been removed by precipitation from hexane. No further purification was executed, considering that the major impurity, PhPh$_3$ and PPh$_3$O, can be readily removed by chromatography in the last products,and would not influence the next reactions.

C-2-EN. MS (EI) *m*/*z*: 209(M$^+$), 194(M$^+$ − CH$_3$), 166(M$^+$ − COCH$_3$).

C-2,7-EN. MS (EI) *m*/*z*: 251(M$^+$), 236(M$^+$ − CH$_3$), 208(M$^+$ − COCH$_3$); 193(M$^+$ − COCH$_3$ − CH$_3$); 164(M$^+$ − 2COCH$_3$ − H).

C-2-EN or C-2,7-EN (all amounts achieved from the above experiment) and C$_2$H$_5$Br (2 mL) were added into the mixture of KOH (0.4 g) and acetone (30 mL). The reaction solutions were refluxed for 3 days. The solution was poured into deionized water and stirred continuously until a white precipitate was deposited completely. The precipitate was then filtered, washed with deionized water, and recrystallized from alcohol to remove C-2-EN or C-2,7-EN, which have not reacted. 1-(9-Ethyl-9H-carbazol-2-yl)ethanone (EC-2-EN) and 1,1′-(9-ethyl-9H-carbazole-2,7-diyl)diethanone (EC-2,7-EN) were achieved. No further purification was executed.

EC-2-EN. MS (EI) *m*/*z*: 237(M$^+$), 222(M$^+$ − methyl), 166 (M$^+$ − ethyl).

EC-2,7-EN. MS (EI) *m*/*z*: 279(M$^+$), 264(M$^+$ − methyl), 236(M$^+$ − COCH$_3$), 221(M$^+$ − COCH$_3$ − CH$_3$); 193(M$^+$ − 2COCH$_3$); 178(M$^+$ − 2COCH$_3$ − CH$_3$); 164(M$^+$ − 2COCH$_3$ − ethyl).

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2-TFDBC and 2,7-TFDBC were synthesized via a Claisen condensation reaction from ketone and esters with a similar method described in our earlier work.[33] A mixture of EC-2-EN or EC-2,7-EN (all amounts achieved from the above experiment), toluene (30 mL), $CF_3COOC_2H_5$ (3 equiv for EC-2-EN or 6 equiv for EC-2,7-EN)and C_4H_9OK (2 equiv for EC-2-EN or 4 equiv for EC-2,7-EN) was stirred under room temperature and refluxed for 6 h in a N_2 atmosphere. Then the mixture was treated with diluted hydrochloric acid and extracted with toluene. The solvent was evaporated in vacuum. The 2-TFDBC crude product was purified by recrystallization in a mixture solution of ethyl acetate and petroleum ether (1:5) after separation by column chromatography (dichloromethane–petroleum ether), and 2,7-TFDBC was just washed in ethanol to gain purified product because of its small solubility (36% yield for 2-TFDBC and 42% yield for 2,7-TFDBC calculated from NBP-4-EN and NBP-4,4-EN).

2-TFDBC. ^{1}HNMR ($CDCl_3$): δ 1.46–1.49 (t, 3H, $-CH_3$); δ 4.41–4.46 (q, 2H, $-CH_2-$); δ 6.72 (s, H, enol-γ-CH–); δ 7.25–7.30 (m, 1H, ArH); δ 7.44–7.58 (m, 2H, ArH); δ 7.75–7.78 (q, 1H, ArH); δ 8.06–8.15 (m, 3H, ArH). ^{13}CNMR($CDCl_3$): δ_c 187.3, 176.5, 176.1, 141.7, 139.5, 129.7, 127.9, 127.8, 122.0, 121.5, 120.5, 119.8, 118.2, 109.1, 108.2, 92.5, 37.7, 13.9. MS (EI) *m*/*z*: 333(M^+), 318($M^+ - CH_3$), 264($M^+ - CF_3$). The elemental analysis data for $C_{18}H_{14}F_3NO_2$ were found (calculated)%: C, 64.81(64.86); H, 4.34(4.23); N, 4.08(4.20).

2,7-BTFDBC. ^{1}HNMR ($CDCl_3$): δ 1.39–1.42 (t, 3H, $-CH_3$); δ 4.72–4.77 (q, 2H, $-CH_2-$); δ 5.75 (s, H, enol-γ-CH–); δ 7.29 (s, 1H, ArH); δ 8.02–8.04 (q, 2H, ArH); δ 8.47 (s, 1H, ArH); δ 8.49 (s, 1H, ArH); δ 8.52 (s, 1H, ArH). ^{13}CNMR($CDCl_3$): δ_c 186.4, 141.2, 131.6, 126.6, 121.8, 118.8, 108.8, 92.8, 38.1, 14.1. MS (EI) *m*/*z*: 471(M^+), 456($M^+ - CH_3$), 402($M^+ - CF_3$); 360($M^+ - CH_2COCF_3$); 248($M^+ - 2COCF_3$ – ethyl). The elemental analysis data for $C_{22}H_{15}F_6NO_4$ were found (calculated)%: C, 56.36(56.06); H, 3.32(3.21); N, 3.05(2.97).

Preparation and IR Absorption Spectral Analysis of Eu(2-TFDBC)$_3$phen and Eu(2,7-BTFDBC)$_3$(phen)$_2$. 2-TFDBC, phen and $EuCl_3$ were mixed with a molar ratio of 3:1:1 in alcohol, stirred, and heated at 60 °C for 6 h. A yellow precipitate was obtained. The precipitate was washed with alcohol and dried at at 50 °C in a vacuum drying oven, and Eu(2-TFDBC)$_3$phen powder was obtained. Eu(2,7-BTFDBC)$_3$(phen)$_2$ was prepared with a similar method. 2,7-BTFDBC, phen, and $EuCl_3$ were mixed with a molar ratio of 3:2:2 in *N*,*N*-dimethylformamide (DMF) and stirred at room temperature for 6 h, and then deionized water was added into the solution to precipitate the complex when the reaction finished. The precipitate was recrystallized in the mixture solution of DMF and triethylamine, washed with alcohol, dried at 50 °C in a vacuum drying oven, and Eu(2,7-BTFDBC)$_3$(phen)$_2$ yellow powder was obtained. Comparison of the IR absorption spectra of 2-TFDBC and Eu(2-TFDBC)$_3$phen, 2,7-BTFDBC and Eu(2,7-BTFDBC)$_3$-(phen)$_2$ (KBr method) shows that the peaks at 1570 cm^{-1} in 2-TFDBC spectrum and 1587 cm^{-1} in 2,7-BTFDBC spectrum were shifted to 1562 and 1562 cm^{-1} in the spectra of their complexes, and a strong stretching vibration peak of C=C appeared respectively on 1523 and 1527 cm^{-1}. This is the characteristic of β-diketonate coordinated with rare earth ions because the C=O bond was converted into the vibrating structure of C–O–Eu bond and C=O–Eu bond.

Data for Eu(2-TFDBC)$_3$phen and Eu$_2$(2,7-BTFDBC)$_3$(phen)$_2$. The elemental analysis data for Eu(2-TFDBC)$_3$phen ($C_{66}H_{47}EuF_9N_5O_6$) were found (calculated) %: C, 59.36 (59.64); N, 5.26 (5.27); H, 3.59 (3.56). FT-IR (KBr): v = 1607(s); 1562(m); 1523(s); 1493(w); 1474(m); 1453(w); 1344(w); 1327(w); 1290(s); 1241(m); 1327(w) cm^{-1}. ^{1}HNMR for Eu(2-TFDBC)$_3$phen ($CDCl_3$): δ 1.68–1.70 (t, 9H, $-CH_3$); δ 3.80 (s, 3H, enol-γ-CH–); δ 4.61–4.64 (q, 6H, $-CH_2-$); δ 6.19–6.21 (d, 3H, ArH); δ 7.26–8.47 (m, 22H, ArH); δ 10.06 (s, 2H, ArH); δ 10.53–10.55 (d, 2H, ArH). The elemental analysis data for Eu$_2$(2,7-BTFDBC)$_3$(phen)$_2$ ($C_{90}H_{55}Eu_2F_{18}N_7O_{12}$) were found (calculated) %: C, 51.88 (52.16); N, 4.46 (4.73); H, 2.80(2.68). FT-IR (KBr): v = 1668(m); 1606(s); 1562(s); 1527(s); 1471(s); 1383(m); 1285(s); 1187(s); 1135(s); 1074(w) cm^{-1}.

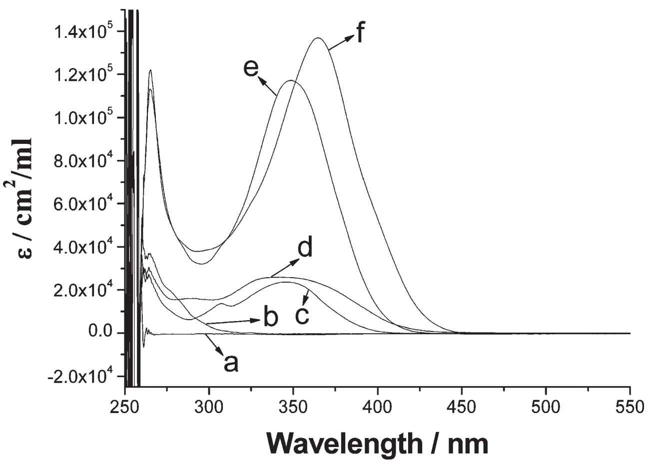

Figure 4. UV–visible absorption spectra of the ligands and Eu^{3+} complexes in DMF solutions (1 × 10^{-5} mol/L): (a) $EuCl_3$, (b) phen, (c) 2-TFDBC, (d) 2,7-BTFDBC, (e) Eu(2-TFDBC)$_3$phen, and (f) Eu$_2$-(2,7-BTFDBC)$_3$(phen)$_2$.

For measuring the lowest triplet state energy level of the ligand 2-TFDBC and 2,7-BTFDBC, gadolinium(III) binary complexes, Gd(2-TFDBC)$_3$·2H$_2$O and Gd(2,7-BTFDBC)$_3$·4H$_2$O, were also synthesized with a similar procedure except using phen. The elemental analysis data for Gd(2-TFDBC)$_3$·2H$_2$O ($C_{54}H_{43}GdF_9N_3O_8$) were found (calculated) %: C, 54.22-(54.49); H, 3.78(3.64); N, 3.31(3.53). The elemental analysis data for Gd(2,7-BTFDBC)$_3$·4H$_2$O ($C_{66}H_{47}Gd_2F_{18}N_3O_{16}$) were found (calculated) %: C, 44.26(44.43); H, 2.93(2.66); N, 2.61(2.36).

Results and Discussion

The key points in the synthesis routines (Figure 2 and Figure 3) were to synthesize 1-(2′-nitrobiphenyl-4-yl)-ethanone (NBP-4-EN) and 1,1′-(2-nitrobiphenyl-4,4′-diyl) diethanone (NBP-4,4-EN) via a the Suizuki–Miyaura cross-coupling reaction first and then to synthesize 1-(9H-carbazol-2-yl)ethanone (C-2-EN) and 1,1′-(9H-carbazole-2,7-diyl)diethanone (C-2,7-EN) via a Cadogan cyclization. In this way, the difficulty of 2,7-positional substitution in the carbazole ring was overcome. More importantly, the 2,7-positions in C-2-EN and C-2,7-EN molecules could be bound with other groups using the same way as mentioned above, so this synthesis method may find more application for synthesis of similar compounds.

High thermal stability is an essential requirement for most applications. Thermogravimetric analysis for Eu(2-TFDBC)$_3$phen and Eu(2,7-BTFDBC)$_3$(phen)$_2$ showed that the decomposition temperatures of the complexes are 361.4 and 367.3 °C in air, respectively, which are high enough for the luminescence application.

The UV–visible absorption spectra of Eu(2-TFDBC-BD)$_3$phen, Eu$_2$(2,7-BTFDBC)$_3$(phen)$_2$, 2-TFDBC, 2,7-BT-FDBC, phen, and $EuCl_3$ in DMF solution (1 × 10^{-5} mol/L) are shown in Figure 4. The absorption band of the complexes

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[33] Xiang, N.; Leung, L. M.; Sob, S.; Gong, M. *Spectrochim. Acta Part A* **2006**, *65*, 907–911.

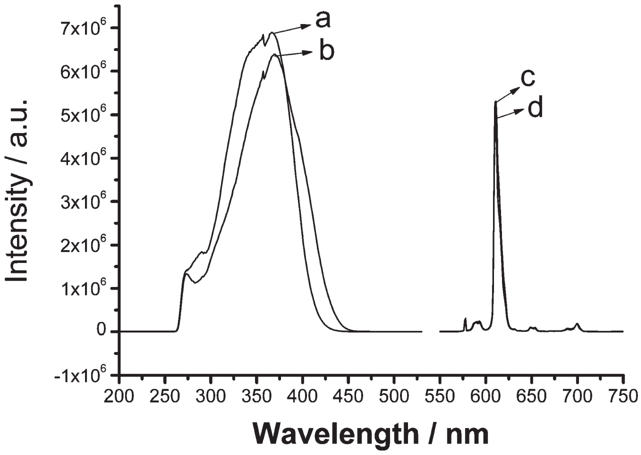

Figure 5. PLE and PL spectra of Eu(2-TFDBC)$_3$phen (a and c, respectively) (λ_{ex} = 367 nm and λ_{em} = 611 nm, respectively) and Eu$_2$(2,7-BTFDBC)$_3$(phen)$_2$ (b and d, respectively) (λ_{ex} = 370 nm and λ_{em} = 611 nm, respectively) as solutions in DMF (1 × 10−5 mol/L).

from 300 to 400 nm is mostly attributed to the absorption of principal ligand 2-TFDBC and 2,7-BTFDBC. The existence of the second ligand phen not only enhances the absorption intensity but also satisfies the high coordination number of the central Eu^{3+} ion and, thus, improves the coordination stability and thermal stability of the complexes. Compared to 2-TFDBCBD and 2,7-BTFDBC, the absorption bands of Eu(2-TFDBCBD)$_3$phen and Eu$_2$(2,7-BTFDBC)$_3$(phen)$_2$ exhibited some redshift. With a suitably expanded π-conjugation system, the absorption bands of both complexes have been extended to the visible region, and this is favorable to being excited by visible light for the complexes.

To search the PL properties of the complexes in solutions, the PLE and PL spectra of Eu(2-TFDBC)$_3$phen and Eu$_2$(2,7-BTFDBC)$_3$(phen)$_2$ in DMF solutions (1 × 10^{-5} mol/L) were measured as shown in Figure 5. The PLE spectrum band of the Eu$_2$(2,7-BTFDBC)$_3$(phen)$_2$ is broader than that of Eu(2-TFDBC)$_3$phen, which was consistent with the extension of π-conjugated systems in the two complex molecules.

The PLE and PL spectra of Eu(2-TFDBC)$_3$phen and Eu$_2$(2,7-BTFDBC)$_3$(phen)$_2$ powder samples are shown in Figure 6. Compared with the similar β-diketonate complexes linked at 3- and 6- positions in the carbazole ring in our earlier work,[26,27] the excitation bands of Eu(2-TFDBC)$_3$phen and Eu$_2$(2,7-BTFDBC)$_3$(phen)$_2$ showed remarkable redshift by about 30 nm and were extended to 500 nm because of the larger π-conjugation in the molecules. This redshift would make the complexes avoid much UV irradiation-induced photodecomposition in photoluminescence applications. Excited by blue light, both the complexes showed intense and narrow red emission peaking at 613 nm, which was attributed to the $^5D_0 \rightarrow {}^7F_2$ transition of the central Eu^{3+} ion.

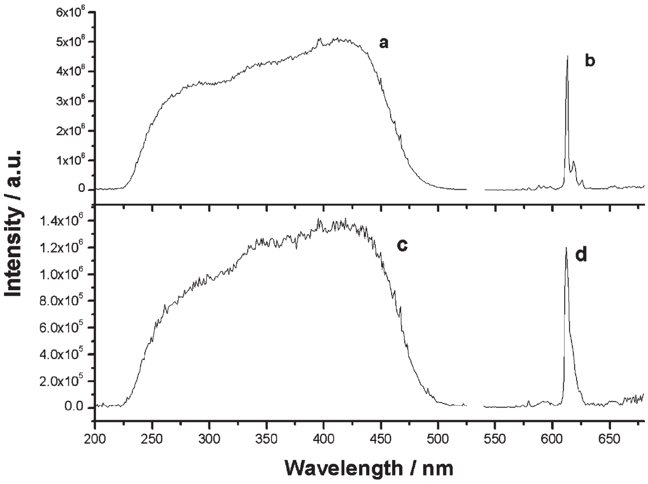

Figure 6. PLE and PL spectra of Eu(2-TFDBC)$_3$phen (a and b, respectively) and Eu$_2$(2,7-BTFDBC)$_3$(phen)$_2$ (c and d, respectively) in the solid state (λ_{ex} = 429 nm and λ_{em} = 613 nm, respectively).

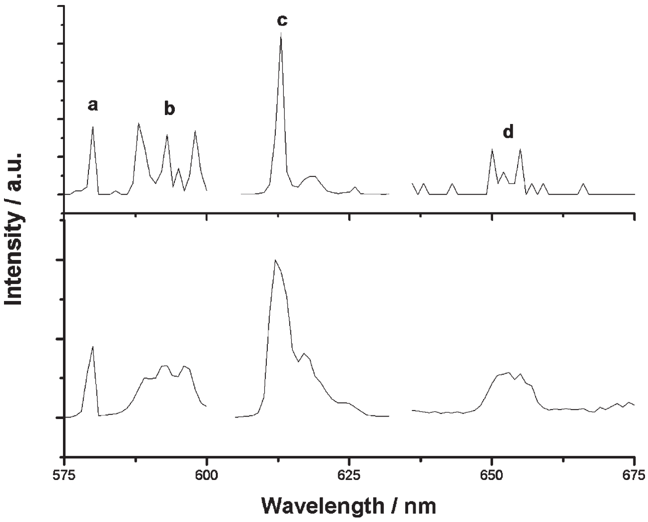

Figure 7. Emission spectra of Eu(2-TFBDC)$_3$phen (up) and Eu$_2$(2,7-DTFDBC)$_3$(phen)$_2$ (down) at 23 K with transitions (a) $^5D_0 \rightarrow {}^7F_0$, (b) $^5D_0 \rightarrow {}^7F_1$, (c) $^5D_0 \rightarrow {}^7F_2$, and (d) $^5D_0 \rightarrow {}^7F_3$; ($\lambda_{ex}$ = 419 nm). Bands below 600 nm have been magnified 10 times, and bands above 636 nm have been magnified 30 times.

To find the details of the fluorescence properties of both complexes clearly, their emission spectra were measured at 23 K as shown in Figure 7. The transitions from the lowest excited state $^5D_0$ to the different J-levels of the lower ^7F_J states of Eu^{3+} ion were observed (J = 0−3, and the longer wavelength is lying outside of the measuring range of the detection system): $^5D_0 \rightarrow {}^7F_0$ at 17241 cm^{-1} (580 nm), $^5D_0 \rightarrow {}^7F_1$ at 16863 cm^{-1} (593 nm), $^5D_0 \rightarrow {}^7F_2$ at 16313 cm^{-1} (613 nm), and $^5D_0 \rightarrow {}^7F_3$ at at 15337 cm^{-1} (652 nm). The strongest emission peak is due to the $^5D_0 \rightarrow {}^7F_2$ transition at 613 nm, revealing the lack of inversion symmetry for the Eu^{3+} ion.[34] The luminescence decay time of the $^5D_0$ states in Eu(2-TFDBC)$_3$phen and Eu$_2$(2,7-BTFDBC)$_3$(phen)$_2$ are 323 and 106 μs, respectively, both fit with a single exponential function, indicating that the two Eu^{3+} ions in Eu$_2$(2,7-BTFDBC)$_3$(phen)$_2$ molecule are located in the same parity sites.

The CIE chromaticity coordinates for both complexes are calculated to be the same, x = 0.677 and y = 0.323, on the basis of their emission spectra, which are very close to the NTSC standard CIE values for red (x = 0.67, y = 0.33).[35] The quantum yield of the complexes was measured in solid state using an integrating sphere according to the method

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(34) Kim, T.; Kang, S. *J. Lumin.* **2007**, *122–123*, 964–966.

(35) Wang, Z.; Liang, H.; Zhou, L.; Wu, H.; Gong, M.; Su, Q. *Chem. Phys. Lett.* **2005**, *412*, 313–316.

described by Lin.[36] The quantum yields are 0.28 for Eu(2-TFDBC)$_3$phen and 0.10 for Eu$_2$(2,7-BTFDBC)$_3$(phen)$_2$. This quantum yield reduction may be caused by the closer Eu^{3+}−Eu^{3+} distance in the Eu$_2$(2,7-BTFDBC)$_3$(phen)$_2$ molecule than that in Eu(2-TFDBC)$_3$phen, and thus, the concentration quenching more easily happens for the former. Compared with the other europium(III) complexes already published,[37]they are in a normal region.

To investigate the photoluminescence mechanism of the complexes, the phosphorescence spectra of the Gd(2-TFDBC)$_3$·2H$_2$O and Gd$_2$(2,7-BTFDBC)$_3$·4H$_2$O solid samples were measured at 23 K. Because the coordination environments for Gd^{3+} ion (radius 94 pm) and Eu^{3+} ion (radius 95 pm) are similar and the energy absorbed by the ligands could not be transferred to the lowest excited state of Gd^{3+} ion (high to about 32 000 cm^{-1}), the triplet states of 2-TFDBC and 2,7-BTFDBC were determined by the shortest wavelength of the phosphorescence peak of the Gd (III) complexes to be about 18115 cm^{-1} (552 nm) and 18051 cm^{-1} (554 nm), both of which are higher than the lowest excited state of Eu^{3+}, $^5D_0$ (17 267 cm^{-1}). Therefore, the photoluminescence mechanism of the Eu(III) complexes is proposed as a ligand-sensitized luminescence process (antenna effect).[38,39] The overall photoluminescence process is described as the following: (1)After the ligands absorb the exciting-light energy, electrons in the ground state S_0 transit to the excited state S_n. (2) Excited electrons fall to the S_1 state through quick nonradiative transitions. (3) Excited electrons transit to the lowest triplet state of the ligand [T_1(L)] via an intersystem-cross (ISC). (4) Energy is transferred to the lowest excited state ($^5D_0$) of the central Eu^{3+} ion in the complex. (5) Radiative transitions $^5D_0 \rightarrow {}^7F_J$ (J = 0−6) happen, and the characteristic and narrow fluorescence peaks of the Eu^{3+} ion appear. The photophysical process in the Eu(III) complexes is schematically represented in Figure 8. The triplet state of phen (22100 cm^{-1})[40] is much higher those of 2-TFDBC and 2,7-BTFDBC, which makes the energy transfer from phen to the europium ion limited because of the existence of many energy levels between the triplet state of phen and the lowest excitation energy level of Eu^{3+}and $^5D_0$ (about 580 nm, 17200 cm^{-1}), so the major pathway of the energy transfer is through the triplet state of the principal ligand, 2-TFDBC and 2,7-BTFDBC.

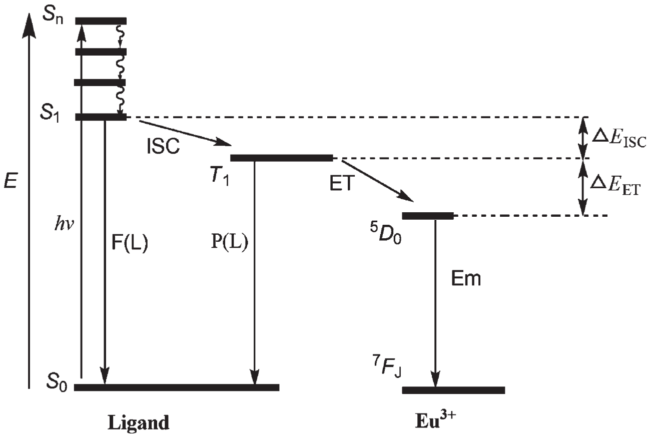

Figure 8. Schematic representation of the photophysical process of the Eu(III) complexes.

Conclusions

Two novel carbazole-based β-diketones with 2- or 2,7-substituted groups in the carbazole ring, 2-TFDBC and 2,7-BTFDBC, and their europium(III) ternary complexes Eu(2-TFDBC)$_3$phen and Eu$_2$(2,7-BTFDBC)$_3$(phen)$_2$ were synthesized via a dexterously designed routine. These complexes show high thermal stability. Suitably expanded π-conjugation in the complex molecules makes the excitation band redshift to the visible region, and both the Eu(III) complexes exhibit intense red emission under blue-light excitation. Measurements of the triplet state energy level of the ligands confirmed the photoluminescence mechanism of the Eu(III) complexes was a ligand-sensitized luminescence process. All of the results indicate that Eu(2-TFDBC)$_3$phen and Eu$_2$(2,7-BTFDBC)$_3$(phen)$_2$ are promising candidates as visible-light excitable red phosphor for luminescence applications.

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