

Synthesis and Photoluminescence Properties of Heteroleptic Europium(III) Complexes with Appended Carbazole Units

Youxuan Zheng,^{[a],‡} Francois Cardinali,^[a] Nicola Armaroli,^[a] and Gianluca Accorsi^{*,[a]}

Keywords: Europium / Photoluminescence / Carbazoles / Chromophores

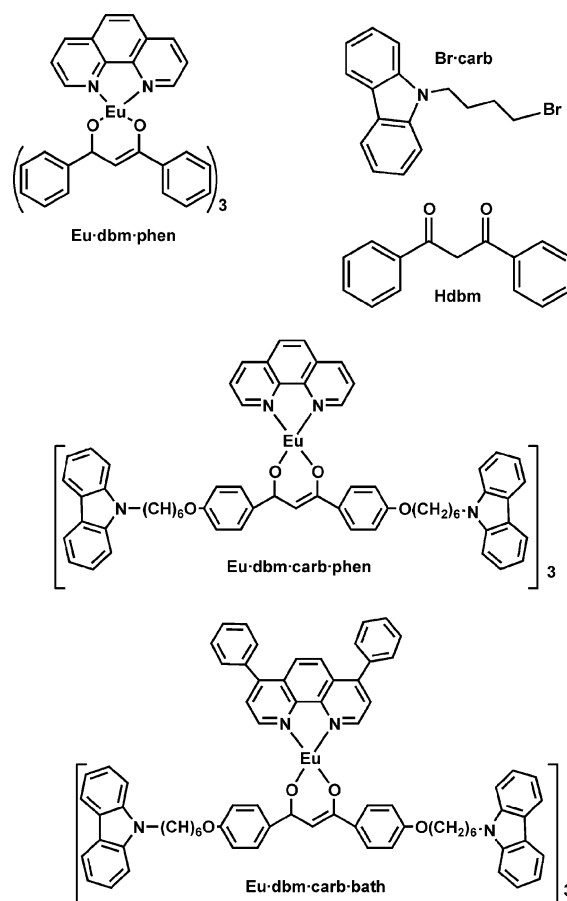
Two europium complexes {Eu·dbm·carb·phen = tris[1-([6-(9*H*-carbazol-9-yl)hexoxy]phenyl)-3-([6-(9*H*-carbazol-9-yl)hexoxy]phenyl)propane-1,3-dione](1,10-phenanthroline)-europium(III), Eu·dbm·carb·bath = tris[1-([6-(9*H*-carbazol-9-yl)hexoxy]phenyl)-3-([6-(9*H*-carbazol-9-yl)hexoxy]phenyl)propane-1,3-dione](bathophenanthroline)europium(III)} and their reference compounds were synthesized and characterized. Each complex contains three different chromophores: carbazole (carb), phenanthroline (phen) (or bathophenanthroline, bath) and dibenzoylmethane (dbm) units. The luminescence properties investigated in dichlorometh-

ane solution and in solid matrix show that the carbazole moiety is a better sensitizer for the metal-centred emitting states of the Eu^{III} ion compared to the dibenzoylmethane and phenanthroline units. Furthermore, the charge-transporting properties of the carbazole moieties appear to be appealing when integrated into the emitting units. Finally, the high number of appended carbazole units confers a strong light-harvesting character to the structure.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2008)

Introduction

Organic light-emitting diodes (OLEDs)^[1] are extensively studied for their potential application in next generation full-colour flat panel displays and light sources.^[2–12] Eu^{III} complexes are suitable luminescent materials for red OLEDs^[13–16] owing to their quasimonochromatic red-light emission. Furthermore, the multiplet nature of the electronic transitions (f–f) leads to an efficient energy conversion in electroluminescence.^[17] However, in spite of the excellent photoluminescence (PL) properties of Eu^{III} materials, bright-red europium-containing electroluminescent (EL) devices with satisfying performance are hardly obtainable because of the poor charge-transporting ability of the lanthanide complexes and the luminescence quenching by matrix vibrations through nonradiative pathways.^[18,19] To improve the charge-transporting properties of Eu^{III} complexes to be used in electroluminescent devices, a suitable strategy would involve doping with electron/hole-transporting molecules, such as biphenyl-*p*-(*tert*-butyl)phenyl-1,3,4-oxadiazole (PBD), *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) or 4,4'-*N,N'*-



Scheme 1. Chemical structures of the studied compounds.

[a] Molecular Photoscience Group, Istituto per la Sintesi Organica e la Fotoreattività, Consiglio Nazionale delle Ricerche (CNR-ISOF),

Via P. Gobetti 101, 40129 Bologna, Italy

E-mail: gianluca.accorsi@isof.cnr.it

[‡] Current address: State Key Laboratory of Coordination Chemistry, Nanjing University, 210093 Nanjing, P. R. China

E-mail: yxzheng@nju.edu.cn

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

dicarbazolebiphenyl (CBP). Unfortunately, this method usually leads to phase separation during device manufacturing, (i.e. sublimation). An alternative approach is given by covalent linking of charge-transporting moieties with lanthanide complexes, as proposed by Zheng et al.,^[20] Bazan et al.,^[21] Tian et al.^[7] and Huang et al.,^[22] who reported efficient OLEDs by using oxadiazole- or carbazole-functionalized lanthanide complexes. In contrast, to enhance the molar extinction coefficients of the complex and limit the vibronic luminescence quenching by the matrix, light-harvesting multichromophoric ligands have been proposed.^[7] These systems have the ability to collect and transfer the excitation energy from the periphery of the complex to the emitting lanthanide ion core and, at the same time, protect the central ion by parasite quenching processes.

In this paper, the synthesis and photophysical properties of two multichromophoric europium complexes and their reference compounds (Scheme 1) are described. The appended carbazole moieties, which widen the absorption profile and act as light-harvesting units, are expected to improve the hole-transporting ability, prevent the crystallization of complexes and increase the solubility in common organic solvents.

Results and Discussion

Synthesis

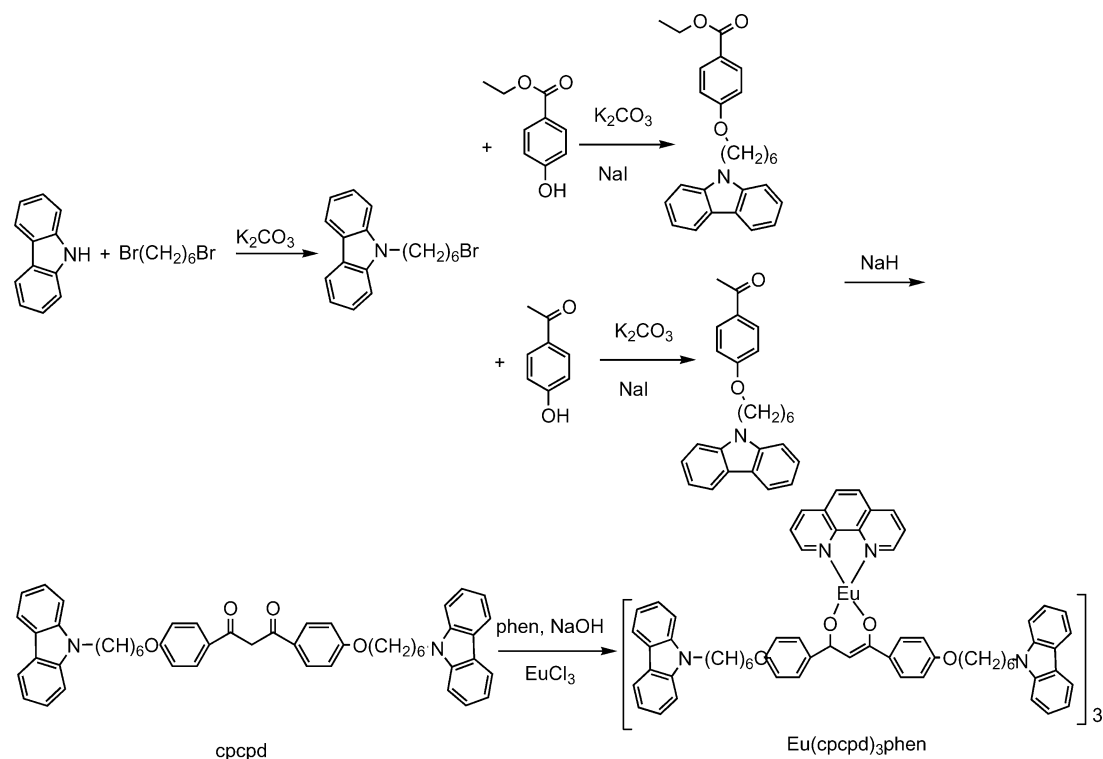
The structural basis and model complex of the present study was the strongly luminescent complex (1,10-phenanthroline)tris(dibenzoylmethanato)europium(III), which was

first reported by Bauer et al.^[23] and is now commercially available.

We developed an approach in which two carbazole units were appended to the dibenzoylmethane^[24] unit through a synthetic method described in Scheme 2. Carbazole was treated with 1,6-dibromohexane in the presence of potassium carbonate to give 6-(9H-carbazol-9-yl)-1-bromohexane. This product was then treated on the one hand with ethyl 4-hydroxybenzoate to give the corresponding ether through classical conditions (potassium carbonate, NaI), and on the other hand, 6-(9H-carbazol-9-yl)-1-bromohexane was treated with 1-(4-hydroxyphenyl)ethanone to give the corresponding ether. Reaction of the two building blocks in the presence of a strong base (NaH) yielded the desired ligand 1-{[6-(9H-carbazol-9-yl)hexoxy]phenyl}-3-{[6-(9H-carbazol-9-yl)hexoxy]phenyl}propane-1,3-dione (cpcpd). This synthetic route provided the ligand in gram-scale quantities, which was essential for the purpose of further preparative scale up. The two complexes involving three units of cpcpd with europium and the nitrogen-bearing ligands 1,10-phenanthroline and bathophenanthroline were then prepared through classical conditions.^[25]

Absorption and Emission Properties

The electronic absorption spectra of Eu·dbm·carb·phen, Eu·dbm·carb·bath and those of related reference compounds (i) Eu·dbm·phen [tris(dibenzoylmethane)mono-(1,10-phenanthroline)europium(III)], (ii) Br·carb {9-(6-bromohexyl)-9H-carbazole} and (iii) Hdbm (1,3-diketone



Scheme 2. Synthetic route to the Eu·dbm·carb·phen complex (an identical process was used for Eu·dbm·carb·bath).

dibenzoylmethane) were recorded in CH_2Cl_2 solution (Figure 1). Five peaks at 240, 264, 294, 332 and 347 nm were attributed to $\pi\text{--}\pi^*$ transitions of the carbazole moieties by comparison with Br·carb. The electronic transitions of the β -diketonate (peak at ca. 350 nm) and the phenanthroline (peak at ca. 230 and 260 nm) units are overlapped with the much stronger carbazole features.^[26] However, although in the high-energy spectral region ($\lambda < 300$ nm) carbazole-selective excitation may be accomplished ($>90\%$, Figure 1), the light partitioning around 350 nm is approximately 65 and 35% for the carbazole and β -diketonate moieties, respectively.

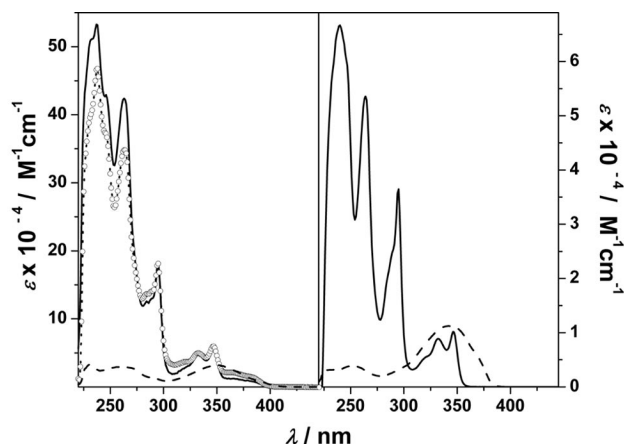


Figure 1. UV/Vis electronic absorption spectra recorded in CH_2Cl_2 solution. Left: Eu·dbm·carb·phen (—), Eu·dbm·carb·bath (○) and Eu·dbm·phen (---). Right: Br·carb (—) and Hdbm (---).

For both Eu·dbm·carb·bath and Eu·dbm·carb·phen, the typical Eu^{III} ion luminescence spectrum peak at 612 nm was detected in dichloromethane solution upon exciting at 264 and 350 nm (Table 1), respectively. For these two compounds, which also exhibit the same emission quantum yield, the lack of residual carbazole fluorescence (peak at 340 and 360 nm, $\Phi_{\text{em}} = 0.24$) suggests an efficient energy-transfer (EnT) process between the appended fragment and the central metal ion. By contrast, Eu·dbm·phen can be selectively excited on both the phenanthroline (≈ 260 nm) and the β -diketonate (≈ 350 nm) moieties. In the first case, a relatively intense metal-centred (MC) luminescence was detected ($\Phi = 0.05$), whereas the excitation at 350 nm afforded an almost 10-fold weaker emission spectrum (Table 1, Figure 2), which points to an inefficient sensitization of the Eu^{III} excited states by the dbm units (Table 1). Even lower

luminescence intensity from Eu·dbm·phen was detected in solvents bearing --OH quenching groups,^[19] such as CH_3OH (Table 1), which suggests that the phen and dbm coordinating ligands do not provide efficient shielding of the metal core towards external quenching.

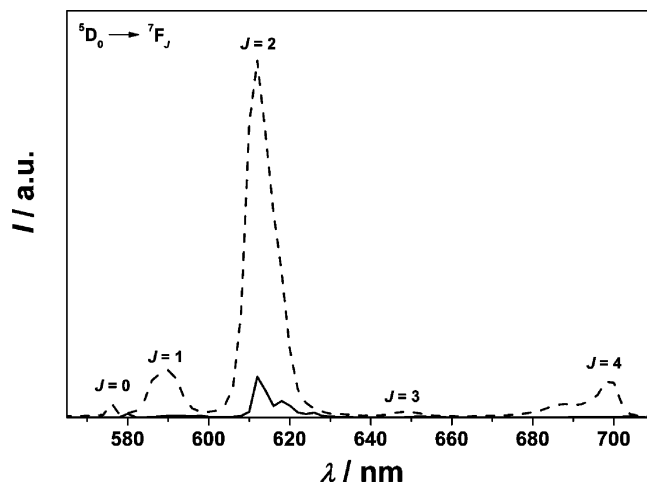


Figure 2. Luminescence spectra of Eu·dbm·carb·phen (---) and Eu·dbm·phen (—) obtained at room temperature in CH_2Cl_2 ($O.D. = 0.2$, $\lambda_{\text{exc}} = 350$ nm) under the same experimental conditions. The radiative transitions from the emitting ($^5\text{D}_0$) to the ground ($^7\text{F}_J$) states were assigned and depicted.

Measurements in solid state matrices (6% doped polycarbonate) were performed for Eu·dbm·phen, Eu·dbm·carb·phen and Eu·dbm·carb·bath (Table 1). A remarkable enhancement in the luminescence intensity relative to that in solution was detected. This shows that the quenching observed in solution, mainly attributable to --OH and --CH vibrations of the solvent molecules, is severely limited in the rigid solid medium. In polycarbonate matrix, the absolute emission quantum yields are difficult to assess with acceptable accuracy, but the measured lifetimes (consistent with values reported in the literature for Eu^{III} complexes in rigid media)^[27] can provide quantitative information. Indeed, it is possible to evaluate the emission quantum yield by means of Equation (1), where τ_{obs} and τ_0 are the observed and the radiative^[18,28,29] lifetimes, respectively. Notably, quantum yields as high, as 0.18 and 0.14 are estimated for Eu·dbm·carb·phen and Eu·dbm·carb·bath, respectively.

$$\Phi_{\text{em}} = \tau_{\text{obs}}/\tau_0 \quad (1)$$

Table 1. Photophysical data collection (CH_2Cl_2 , room temp.) and rigid matrix and solid state.

	MC Luminescence (CH_2Cl_2 , 298 K)			Spin-coated thin film ^[d]		
	λ_{max} ^[a] [nm]	Φ_{em} [%]	τ [ms]	λ_{max} ^[a] [nm]	Φ_{em} [%] ^[e]	τ [ms]
Eu·dbm·phen	614	0.5 ^[b] 0.06 ^[c] 0.02 ^[c,f]	1.0 ^[b] 0.1 ^[c] 0.08 ^[c,f]	612	10	0.5
Eu·dbm·carb·phen	614	1.0 ^[c]	0.6 ^[c]	612	18	0.9
Eu·dbm·carb·bath	614	1.0 ^[b]	0.50 ^[b]	612	14	0.7

[a] Emission maxima from uncorrected spectra. [b] $\lambda_{\text{exc}} = 264$ nm. [c] $\lambda_{\text{exc}} = 350$ nm. [d] 6% in polycarbonate. [e] Estimated by Equation (1), see text. [f] CH_3OH solution.

The emitting states of the Eu^{III} complexes involving π -conjugated ligands are usually populated by intramolecular EnT process through the triplet excited state of the ligand(s).^[30,31] For Eu^{III} and lanthanide complexes in general, the intramolecular energy migration efficiency from the chelating and/or appended ligands to the central Ln^{3+} ion is the most important step influencing their luminescence output.^[30] The intersystem-crossing efficiency and the intrinsic luminescence quantum yield of the Ln^{III} ion are the other steps regulating the overall efficiency of Ln^{III} -sensitized emission. Generally, a large ($>1500\text{ cm}^{-1}$) energy gap

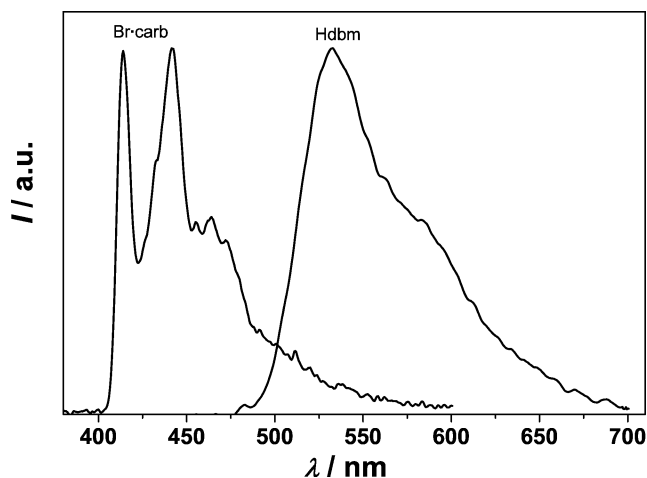


Figure 3. Normalized phosphorescence spectra of Br-carb (left, $\lambda_{\text{exc}} = 294\text{ nm}$) and Hdbm (right, $\lambda_{\text{exc}} = 350\text{ nm}$) in 77 K rigid matrix (CH_2Cl_2).

between the lowest triplet ligand centred donor level and the acceptor level of the lanthanide ion ($^5\text{D}_0$ for Eu^{III}) favours an efficient EnT process,^[32] which prevents the formation of a thermal equilibrium (back-energy-transfer process) between the involved levels. In order to determine the ligand-centred triplet energy levels of the dbm and carbazole subunits in the complexes, 77 K phosphorescence spectra of Hdbm and Br-carb reference fragments were recorded (Figure 3).

The maxima of the highest-energy emission features are located at 19500 (Hdbm) and 24000 (Br-carb) cm^{-1} . Thus, the energy gap between the Eu^{III} core ($^5\text{D}_0 \approx 17500\text{ cm}^{-1}$)^[30] and the donor ligand units turns out to be ca. 2000 and ca. 6500 cm^{-1} for Hdbm and Br-carb, respectively. This suggests that although the triplet state of the carbazole unit is energetically compatible with an efficient EnT process, the lower-lying dbm level may undergo thermal back-energy transfer from the central core.^[19] Furthermore, the $^5\text{D}_1$ Eu^{III} emitting state, located at approximately 18800 cm^{-1} , is critically close to the triplet energy level of dbm (19500 cm^{-1}). A schematic representation of ligand-centred and metal-centred energy levels is depicted in Figure 4.

For $\text{Eu}\cdot\text{dbm}\cdot\text{carb}\cdot\text{phen}$ and $\text{Eu}\cdot\text{dbm}\cdot\text{carb}\cdot\text{bath}$, the apparently large distance between the carbazole units and the central ion due to the alkyl spacer chains (Scheme 1) would seem to suggest a Förster-type mechanism^[33] for the energy-transfer process. However, in solution, the floppy nature of the spacer is likely to allow close vicinity between the carbazole and the metal centre, which supports a short-distance mechanism (Dexter)^[34] for the sensitization process.

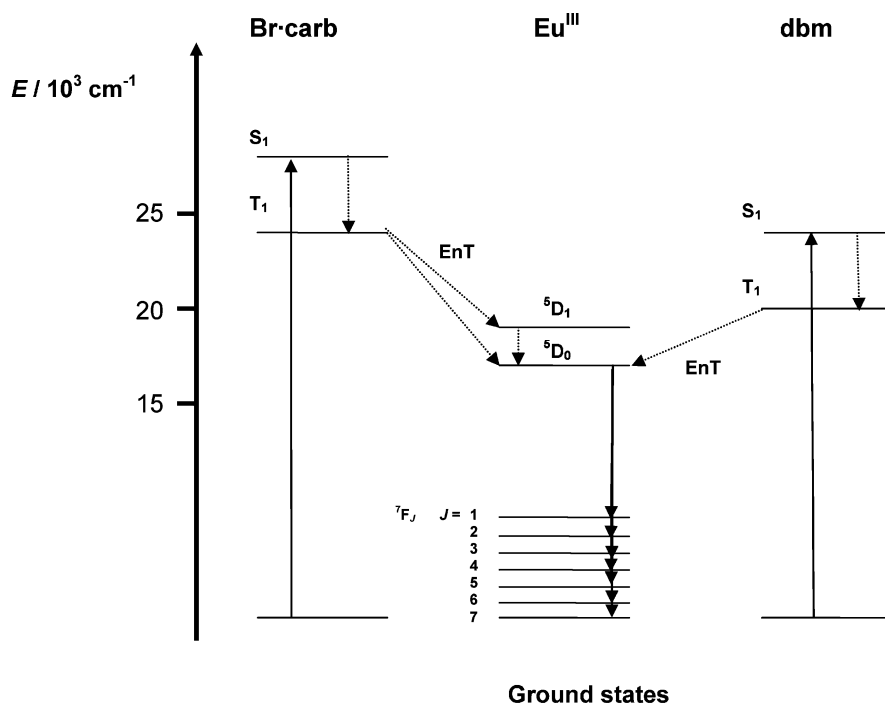


Figure 4. Energy level diagram of Br-carb, dbm and Eu^{III} and radiative (—) and nonradiative (····) deactivation pathways in related complexes investigated here.

Conclusions

We synthesized two multichromophoric europium complexes containing appended carbazole units. These compounds contain three different types of chromophores, namely phenanthroline (phen), dibenzoylmethane (dbm) and carbazole itself (carb); an almost selective excitation ($\approx 90\%$) was possible only for the latter moiety. The PL properties of Eu·dbm·carb·phen in solution in comparison to those of Eu·dbm·phen showed that an efficient population of the Eu^{III} emitting states by energy transfer occurs from the carbazole units. In contrast, the dbm units turned out to be poor sensitizers for the metal centre, which points to the importance of the relative position of the ligand lowest triplet levels relative to the metal-centred accepting state ($^5\text{D}_0$). Notably, in both cases, a strong enhancement in the MC luminescent intensity was detected in solid matrix, which provides evidence for the limited action of the vibrational quenchers under these conditions.

The ability of the carbazole units to act as light-harvesting systems, sensitize and protect the metal emitting states, together with their intrinsic charge-transporting capability, make such molecules potentially interesting for the fabrication of electroluminescent devices.^[35,36]

Experimental Section

General Information: Carbazole, 1,6-dibromohexane, K_2CO_3 , ethyl 4-hydroxybenzoate, NaI, NaH, 4-hydroxyacetophenone, dimethoxyethane, $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, 1,10-phenanthroline and bathophenanthroline were commercially available and used without further purification. Elemental analysis was carried out with a CE-440 and Carlo Erba Elemental Analysers.

Spectroscopic Measurements: Absorption spectra were recorded with a Perkin–Elmer $\lambda 9$ spectrophotometer. For luminescence experiments, the samples were placed in fluorimetric 1-cm path cuvettes and, when necessary, purged from oxygen by bubbling with argon. Uncorrected emission spectra were obtained with an Edinburgh FLS920 spectrometer equipped with a Peltier-cooled Hamamatsu R928 photomultiplier tube (185–850 nm). Corrected spectra were obtained by a calibration curve supplied with the instrument. Luminescence quantum yields (Φ_{em}) obtained from spectra on a wavelength scale (nm) were measured according to the approach described by Demas and Crosby^[37] by using air-equilibrated $[\text{Ru}(\text{bpy})_3\text{Cl}_2]$ in water solution, $\Phi_{\text{em}} = 0.028$,^[38] as standard. The luminescence lifetimes in the microsecond–millisecond scales were measured by using a Perkin–Elmer LS-50B spectrofluorometer equipped with a pulsed xenon lamp with variable repetition rate and elaborated with standard software fitting procedures (Origin 6.1). To record the 77-K luminescence spectra, the samples were put in glass tubes (2 mm diameter) and inserted into a special quartz dewar filled up with liquid nitrogen. Experimental uncertainties are estimated to be $\pm 8\%$ for lifetime determinations, $\pm 20\%$ for emission quantum yields and ± 2 nm and ± 5 nm for absorption and emission peaks, respectively.

9-(6-Bromohexyl)-9H-carbazole (Br·carb): A mixture of carbazole (10.0 g, 0.06 mol), 1,6-dibromohexane (58.6 g, 0.24 mol) and K_2CO_3 (25.0 g, 0.18 mol) in dimethylformamide (DMF; 100 mL) was stirred at room temperature for 24 h before pouring into water. After extraction with dichloromethane (3×15 mL), the organic

layer was washed with water and dried with Na_2SO_4 . Solvent was removed by evaporation, and then the resulting residue was purified by chromatography (SiO_2 ; dichloromethane/hexane, 2:3) to obtain the product (10.3 g, 52%). M.p. 50–51 °C. ^1H NMR (400 MHz, CDCl_3): δ = 1.32–1.45 (m, 4 H, CH_2), 1.72–1.87 (m, 4 H, CH_2), 3.32 (t, J = 6.67 Hz, 2 H, $-\text{CH}_2\text{Br}$), 4.46 (t, J = 7.08 Hz, 2 H, $-\text{NCH}_2-$), 7.22 (t, J = 7.52 Hz, 2 H, ArH), 7.36 (d, J = 8.23 Hz, 2 H, ArH), 7.45 (t, J = 7.54 Hz, 2 H, ArH), 8.01 (d, J = 7.62 Hz, 2 H, ArH) ppm. $\text{C}_{18}\text{H}_{20}\text{BrN}$ (330.27): calcd. C 65.46, H 6.10, N 4.24; found C 64.92, H 6.13, N 4.31.

Ethyl 6-(9H-Carbazol-9-yl)hexoxybenzoate: A mixture of 9-(4-bromohexyl)-9H-carbazole (3.3 g, 10 mmol), ethyl 4-hydroxybenzoate (1.66 g, 10 mmol), potassium carbonate (1.52 g, 11 mmol) and NaI (1 g) in anhydrous acetone (60 mL) was stirred vigorously and heated at reflux for 48 h under the protection of a nitrogen atmosphere. The solvent was removed by evaporation, and the resulting solid was recrystallized from ethanol to give white needles (2.91 g, 70.1%). M.p. 107–108 °C. ^1H NMR (500 MHz, CDCl_3): δ = 1.37 (m, 3 H, CH_3), 1.85–2.12 (m, 8 H, CH_2), 3.98 (m, 2 H, $-\text{OCH}_2-$), 4.32 (m, 2 H, $-\text{NCH}_2-$), 4.40 (m, 2 H, $-\text{OCH}_2-$), 6.84 (d, J = 8.8 Hz, 2 H, ArH), 7.23 (t, J = 7.0 Hz, 2 H, ArH), 7.43 (d, J = 8.1 Hz, 2 H, ArH), 7.47 (t, J = 7.2 Hz, 2 H, ArH), 7.96 (d, J = 8.7 Hz, 2 H, ArH), 8.10 (d, J = 7.6 Hz, 2 H, ArH) ppm. $\text{C}_{27}\text{H}_{29}\text{NO}_3$ (415.53): calcd. C 78.04, H 7.04, N 3.37; found C 77.95, H 7.07, N 3.42.

6-(9H-Carbazol-9-yl)hexoxyphenone: A mixture of 9-(4-bromohexyl)-9H-carbazole (3.3 g, 10 mmol), 4-hydroxyacetophenone (1.36 g, 10 mmol), potassium carbonate (1.52 g, 11 mmol) and NaI (1 g) in anhydrous acetone (60 mL) was stirred vigorously and heated at reflux for 48 h under the protection of a nitrogen atmosphere. The solvent was removed by evaporation, and the resulting solid was recrystallized from ethanol to give white needles (3.18 g, 85.3%). ^1H NMR (500 MHz, CDCl_3): δ = 1.35 (m, 3 H, CH_3), 1.84–2.11 (m, 8 H, CH_2), 4.30 (m, 2 H, $-\text{NCH}_2-$), 4.37 (m, 2 H, $-\text{OCH}_2-$), 6.84 (d, J = 8.8 Hz, 2 H, ArH), 7.23 (t, J = 7.0 Hz, 2 H, ArH), 7.43 (d, J = 8.1 Hz, 2 H, ArH), 7.47 (t, J = 7.2 Hz, 2 H, ArH), 7.96 (d, J = 8.7 Hz, 2 H, ArH), 8.10 (d, J = 7.6 Hz, 2 H, ArH) ppm. $\text{C}_{26}\text{H}_{27}\text{NO}_2$ (385.51): calcd. C 81.00, H 7.06, O 8.30, N 3.63; found C 79.54, H 7.09, O 8.35, N 3.68.

1-[[6-(9H-Carbazol-9-yl)hexoxy]phenyl]-3-[[6-(9H-carbazol-9-yl)-hexoxy]phenyl]propane-1,3-dione (cpcpd): Ethyl 6-(9H-carbazol-9-yl)hexoxybenzoate (1.68 g, 4.05 mmol), 6-(9H-carbazol-9-yl)-hexoxyphenone (1.53 g, 4.1 mmol) and NaH (0.12 g, 5 mmol) were put in a dry flask. Dry dimethoxyethane (30 mL) was added, and the solution was heated at reflux for 24 h. Then, the solution was poured into water and acidified to pH ~ 2 by using HCl solution. The solid collected was purified by column chromatography (SiO_2 ; acetone/hexane, 1:8) to obtain a white solid (0.9 g, 29.5%). ^1H NMR (400 MHz, CDCl_3): δ = 1.49 (m, 8 H, CH_2), 1.77 (m, 4 H, CH_2), 1.93 (m, 4 H, CH_2), 3.96 (t, J = 6 Hz, 4 H, CH_2), 4.34 (t, J = 6 Hz, 4 H, CH_2), 6.88 (d, J = 8.4 Hz, 4 H, ArH), 7.23 (m, 6 H, ArH and diketone CH_2), 7.45 (m, 8 H, ArH), 8.04 (d, J = 8 Hz, 4 H, ArH), 8.11 (d, J = 8 Hz, 4 H, ArH) ppm. $\text{C}_{51}\text{H}_{50}\text{N}_2\text{O}_4$ (754.97): calcd. 81.13, H 6.68, O 8.48, N 3.71; found C 81.01, H 6.71, O 8.39, N 3.75.

Eu(cpcpd)₃phen (Eu·dbm·carb·phen): The cpcpd ligand (0.45 g, 0.6 mmol) and 1,10-phenanthroline (0.036 g, 0.2 mmol) were dissolved in hot ethanol (15 mL, 60 °C). A solution of NaOH (1 N, 0.6 mL) was added to neutralize the cpcpd ligand. Then, $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (0.073 g, 0.2 mmol) was dissolved in ethanol (2 mL) and added dropwise to the above solution. The solution was stirred at 60 °C for 5 h. Then, the solvent was removed under reduced pressure, and the solid was washed with water several times. After

drying, the solid was dissolved in chloroform (5 mL) and then a lot of hexane was added down the wall of the flask carefully. After 1 d, the light-brown solid $\text{Eu}(\text{cpcpd})_3\text{phen}$ crystallized. Yield: 63%. M.p. 99–100 °C. $\text{C}_{165}\text{H}_{155}\text{EuO}_{12}\text{N}_8$ (2594.05): calcd. C 76.39, H 6.02, O 7.40, N 4.32; found C 76.31, H 6.13, O 7.46, N 4.47.

$\text{Eu}(\text{cpcpd})_3\text{bath}$ (Eu-dbm-carb-bath): The same procedure as that above was followed by replacing 1,10-phenanthroline with bathophenanthroline. Yield: 67%. M.p. 108–109 °C. $\text{C}_{177}\text{H}_{163}\text{EuO}_{12}\text{N}_8$ (2746.25): calcd. C 77.41, H 5.98, O 6.99, N 4.08; found C 77.02, H 6.06, O 7.08, N 4.29.

Supporting Information (see footnote on the first page of this article): ^1H NMR spectrum of the cpcpd ligand.

Acknowledgments

We thank the EC (IST-2002-004607, OLLA) and the CNR (PM.P04.010, MACOL) for financial support; we also thank Roberto Cortesi for technical help.

- [1] K. Müllen, U. Scherf, *Organic Light Emitting Devices: Synthesis Properties and Applications*, Wiley-VCH, Weinheim, **2006**.
- [2] M. A. Baldo, M. E. Thompson, S. R. Forrest, *Pure Appl. Chem.* **1999**, *71*, 2095–2106.
- [3] B. W. D'Andrade, S. R. Forrest, *Adv. Mater.* **2004**, *16*, 1585–1595.
- [4] R. C. Evans, P. Douglas, C. J. Winscom, *Coord. Chem. Rev.* **2006**, *250*, 2093–2126.
- [5] R. U. A. Khan, C. Hunziker, P. Gunter, *J. Mater. Sci. Mater. Electron.* **2006**, *17*, 467–474.
- [6] J. P. Leonard, T. Gunnlaugsson, *J. Fluoresc.* **2005**, *15*, 585–595.
- [7] S. F. Li, G. Zhong, W. H. Zhu, F. Y. Li, J. F. Pan, W. Huang, H. Tian, *J. Mater. Chem.* **2005**, *15*, 3221–3228.
- [8] T. X. Li, H. Fukuyama, Y. Yamagata, H. L. Lan, J. Kido, *Polym. Adv. Technol.* **2004**, *15*, 302–305.
- [9] E. F. Schubert, J. K. Kim, *Science* **2005**, *308*, 1274–1278.
- [10] Y. R. Sun, N. C. Giebink, H. Kanno, B. W. Ma, M. E. Thompson, S. R. Forrest, *Nature* **2006**, *440*, 908–912.
- [11] D. L. Tao, Y. Z. Xu, J. Feng, T. Zhang, Z. H. Xu, H. Shen, J. G. Wu, Z. Xu, X. R. Xu, D. F. Xu, *J. Mater. Chem.* **2004**, *14*, 1252–1256.
- [12] J. B. Yu, L. Zhou, H. J. Zhang, Y. X. Zheng, H. R. Li, R. P. Deng, Z. P. Peng, Z. F. Li, *Inorg. Chem.* **2005**, *44*, 1611–1618.
- [13] C. Adachi, M. A. Baldo, S. R. Forrest, *J. Appl. Phys.* **2000**, *87*, 8049–8055.
- [14] J. F. Fang, D. G. Ma, *Appl. Phys. Lett.* **2003**, *83*, 4041–4043.
- [15] C. J. Liang, D. Zhao, Z. R. Hong, D. X. Zhao, X. Y. Liu, W. L. Li, J. B. Peng, J. Q. Yu, C. S. Lee, S. T. Lee, *Appl. Phys. Lett.* **2000**, *76*, 67–69.
- [16] Y. X. Zheng, Y. H. Zhou, J. B. Yu, Y. N. Yu, H. J. Zhang, W. P. Gillin, *J. Phys. D-Appl. Phys.* **2004**, *37*, 531–534.
- [17] J. Kido, Y. Okamoto, *Chem. Rev.* **2002**, *102*, 2357.
- [18] G. Accorsi, N. Armaroli, A. Parisini, M. Meneghetti, R. Marega, M. Prato, D. Bonifazi, *Adv. Funct. Mater.* **2007**, *17*, 2975–2982.
- [19] N. Armaroli, G. Accorsi, F. Barigelletti, S. M. Couchman, J. S. Fleming, N. C. Harden, J. C. Jeffery, K. L. V. Mann, J. A. McCleverty, L. H. Rees, S. R. Starling, M. D. Ward, *Inorg. Chem.* **1999**, *38*, 5769–5776.
- [20] J. F. Wang, R. Y. Wang, J. Yang, Z. P. Zheng, M. D. Carducci, T. Cayou, N. Peyghambarian, G. E. Jabbour, *J. Am. Chem. Soc.* **2001**, *123*, 6179–6180.
- [21] M. R. Robinson, M. B. O'Regan, G. C. Bazan, *Chem. Commun.* **2000**, 1645–1646.
- [22] M. Guan, Z. Q. Bian, F. Y. Li, H. Xin, C. H. Huang, *New J. Chem.* **2003**, *27*, 1731–1734.
- [23] H. Bauer, J. Blanc, D. L. Ross, *J. Am. Chem. Soc.* **1964**, *86*, 5117–5125.
- [24] K. Binnemans, "Rare-Earth Beta-Diketonates" in *Handbook on the Physics and Chemistry of Rare Earths* (Eds.: K. A. Gschneidner Jr, J.-C. Bünzli, V. K. Pecharsky), Elsevier, Amsterdam, **2005**, vol. 35, pp. 107–272.
- [25] S. Biju, D. B. A. Raj, M. L. P. Reddy, B. M. Kariuki, *Inorg. Chem.* **2006**, *45*, 10651–10660.
- [26] D. Nie, Z. Chen, Z. Bian, J. Zhou, Z. Liu, F. Chen, Y. Zhaob, C. Huang, *New J. Chem.* **2007**, *31*, 1639–1646.
- [27] H. Liang, B. Chen, Q. J. Zhang, Z. Q. Zheng, H. Ming, F. Q. Guo, *J. Appl. Pol. Sci.* **2005**, *98*, 912.
- [28] G. Stein, E. Wurzburg, *J. Chem. Phys.* **1975**, *62*, 208.
- [29] M. H. V. Werts, R. T. F. Jukes, J. W. Verhoeven, *Phys. Chem. Chem. Phys.* **2002**, *4*, 1542.
- [30] S. Quici, M. Cavazzini, G. Marzanni, G. Accorsi, N. Armaroli, B. Ventura, F. Barigelletti, *Inorg. Chem.* **2005**, *44*, 529–537.
- [31] S. Quici, G. Marzanni, A. Forni, G. Accorsi, F. Barigelletti, *Inorg. Chem.* **2004**, *43*, 1294–1301.
- [32] S. Sato, M. B. Wada, *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1955.
- [33] T. Förster, *Discuss. Faraday Soc.* **1959**, *27*, 7.
- [34] D. L. Dexter, *J. Chem. Phys.* **1953**, *21*, 836–850.
- [35] J. P. Lu, P. F. Xia, P. K. Lo, Y. Tao, M. S. Wong, *Chem. Mater.* **2006**, *18*, 6194–6203.
- [36] J. Q. Ding, J. Gao, Y. X. Cheng, Z. Y. Xie, L. X. Wang, D. G. Ma, X. B. Jing, F. S. Wang, *Adv. Funct. Mater.* **2006**, *16*, 575–581.
- [37] J. N. Demas, G. A. Crosby, *J. Phys. Chem.* **1971**, *75*, 991–1024.
- [38] K. Nakamaru, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697–2705.

Received: November 22, 2007
Published Online: March 4, 2008