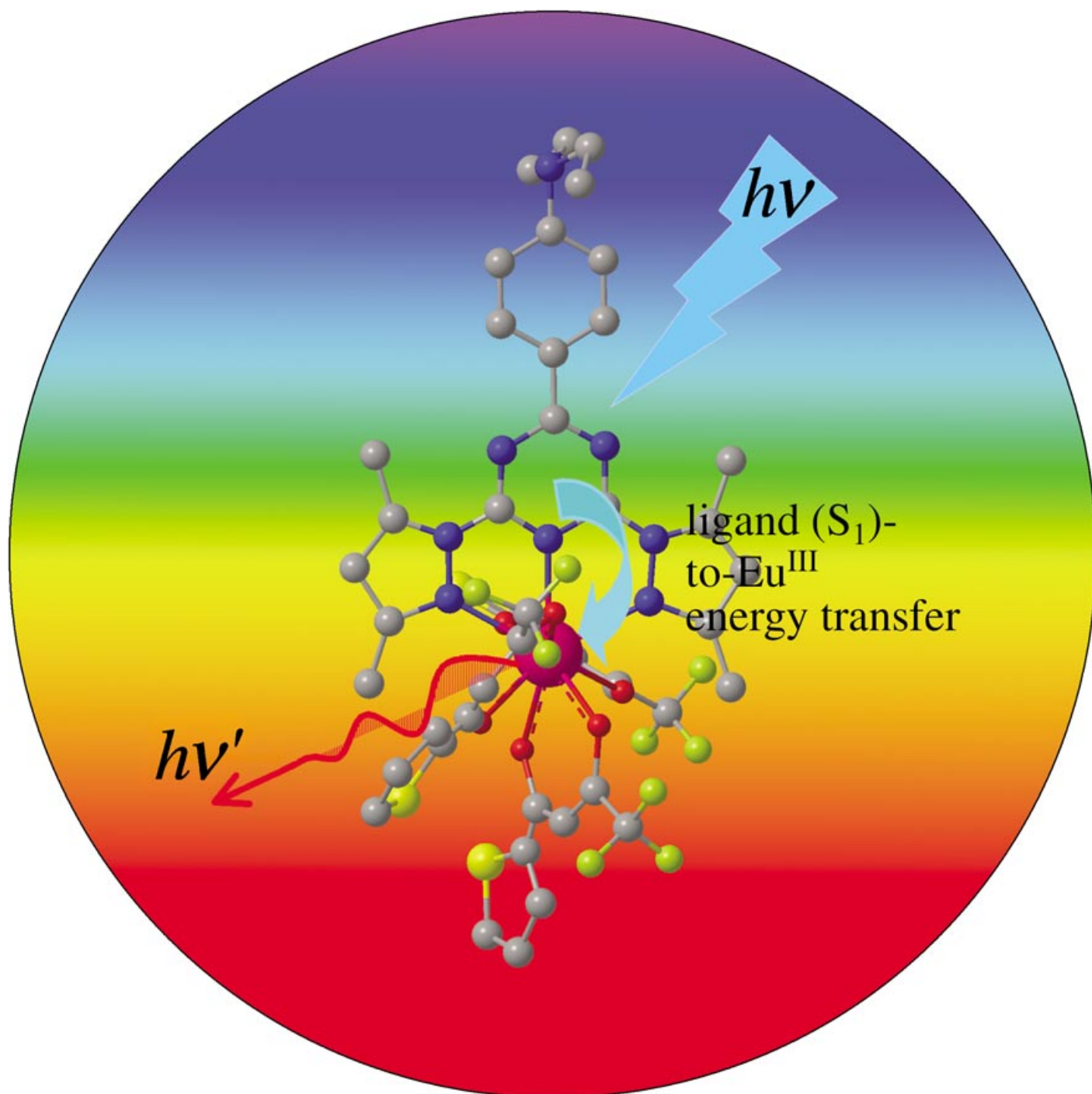# *Communications*

Visible-light excitation of the europium complex shown leads to characteristic red emission from the Eu^{III} center. A spectroscopic study shows the nature of the sensitization process and accounts for why the complex can be excited at these longer wavelengths. For more information see the Communication by Y. Wang, J.-P. Zhang, W.-T. Wong et al. on the following pages.

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Communications

A Highly Luminescent Europium Complex Showing Visible-Light-Sensitized Red Emission: Direct Observation of the Singlet Pathway**

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A challenge in the chemistry of the lanthanide ions is to develop luminescent Eu complexes that can be sensitized by visible light and to determine the energy-transfer mechanisms in these systems. Recently, this field has become much more important because of the demand for less-harmful labeling reagents in the life sciences and low-voltage-driven pure-red emitters in optoelectronic technology.[1] The commonly

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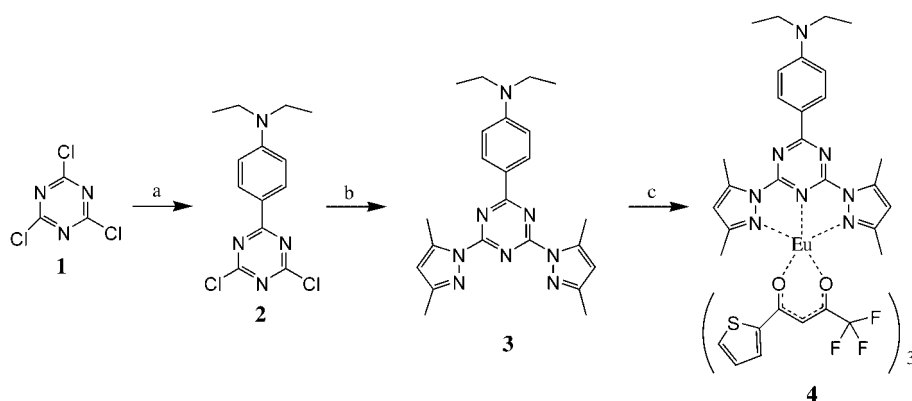Guangdong University of Technology, Guangzhou 510090 (China)

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observed sensitization mechanism for luminescent europium complexes involves a triplet pathway, in which the transfer of the energy absorbed by the ligand to the Eu^{III} ion takes place from the ligand-centered triplet excited state (T_1). In this case, the optical excitation window for luminescent Eu complexes appears to be limited to < 385 nm owing to the energetic constraints highlighted by Reinhoudt and co-workers.[2] With the use of 'antenna' chromophoric groups, which have a smaller energy gap between the lowest singlet excited state (S_1) and the T_1 state (e.g. acridone, diaryl ketones), it has been demonstrated by several research groups that the excitation wavelength for Eu complexes can be extended into the visible region through the usual triplet pathway.[3–4] Another promising means of longer-wavelength sensitization of Eu^{III} emission is through the singlet pathway, in which the excited-state energy of a chromophore is directly transferred from its S_1 state to the luminescent states of the Eu^{III} center. In this way the energetic constraints from the T_1 state of the ligand can be avoided.

The singlet pathway for the sensitization of lanthanide luminescence was first proposed by Kleinerman in 1969.[5] Horrocks and co-workers later examined the energy-transfer processes in lanthanide-ion-binding proteins and assumed that it was the singlet excited state of the chromophore that sensitized the lanthanide emission.[6] However, owing to the lack of information regarding the emission from the excited states of the coordinated ligand and the difficulties in the determination of the ligand-localized triplet–triplet absorption spectra for lanthanide chelates, it has been very difficult to prove for certain which state is responsible for the energy-transfer process.[7] All the experimental work conducted on the sensitization of lanthanide–chelate luminescence seems to support the triplet pathway, whereas the singlet pathway for the sensitization of the Eu complex has not been observed experimentally.[7] Herein, we report the successful extension of the excitation window to the visible region for a Eu complex, which subsequently exhibits highly efficient Eu^{III}-centered luminescence. The sensitization mechanism is shown to take place through the singlet pathway by means of time-resolved luminescence spectroscopic studies.

We have previously demonstrated that dipyrazolyltriazine derivatives are good chromophores for the efficient sensitization of lanthanide ion luminescence.[8] To achieve longer-wavelength sensitization of the Eu^{III} emission, we explored the effect of incorporating *N,N*-dialkyl aniline moieties into the dipyrazolyltriazine systems. The new ligand **3** was prepared by heating **2** and the potassium salt of 3,5-dimethylpyrazole in dry THF at reflux for 12 h (Scheme 1). The reaction of **3** and europium thenoyltrifluoroacetonate [Eu(tta)$_3$·3H$_2$O] in THF yielded a yellow solution of the complex **4**, which showed a bright red emission under daylight illumination. After evaporation of the solvent, the residue was taken up in dry diethyl ether, and the solution was triturated with *n*-hexane; the complex Eu(tta)$_3$L (**4**) was obtained as a bright orange powder (Scheme 1).

The photophysical properties of a solution of complex **4** in toluene were investigated systematically. Upon the coordination of **3** to Eu^{III}, the ligand charge-transfer (CT) absorption band is shifted from 387 nm ($\varepsilon = 38000$ cm M^{-1}) to 406 nm

Scheme 1. Synthesis of the complex **4**. a) *N,N*-diethylaniline; b) potassium 3,5-dimethylpyrazolate; c) ([Eu(tta)$_3$]·3 H$_2$O).

($\varepsilon = 55\,000$ cm M^{-1}) owing to the stabilization of the very polar excited states (Figure 1). The excitation spectrum of complex **4** (emission monitored at 614 nm) is in agreement with its
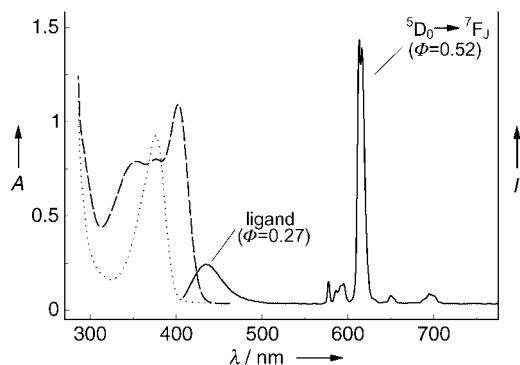
Figure 1. The room temperature UV/Vis absorption spectra of the Eu complex **4** (dashed line) and the ligand **3** (dotted line) as solutions in toluene, and the fluorescence emission spectrum of complex **4** (solid line, $\lambda_{ex} = 402$ nm) at ~1.0×10^{-5} M. Luminescence quantum yields (Φ) for **4** are given in parentheses.

ground-state absorption spectrum. The excitation window for complex **4** can be extended beyond 460 nm when the concentration is increased up to 1×10^{-2} M. Upon selective excitation at the ligand CT band at room temperature, the emission spectrum of complex **4** displays a broad band centered at 430 nm, derived from the coordinated ligand, and the characteristic sharp peaks associated with the $^5D_0 \rightarrow {}^7F_J$ transitions of the Eu^{III} ion (Figure 1). The five expected components of the $^5D_0 \rightarrow {}^7F_{0-4}$ transitions are well resolved and the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition is very intense, which reflects a low symmetry of the Eu^{III} site. The overall luminescence quantum yields for the emissions from the Eu^{III} ion and the coordinated ligand in **4** in toluene are 0.52 and 0.27, respectively ($\lambda_{ex} = 402$ nm, room temperature). The observed quantum yield for the Eu^{III} emission is the highest reported value for such visible-light-sensitized Eu complexes. When the temperature was reduced to 77 K, the ligand

emission band at 430 nm vanished completely to leave only the intense $^5D_0 \rightarrow {}^7F_{0-4}$ emission of Eu^{III}. This indicates that the Ligand-to-Eu^{III} energy transfer is more efficient at lower temperatures.
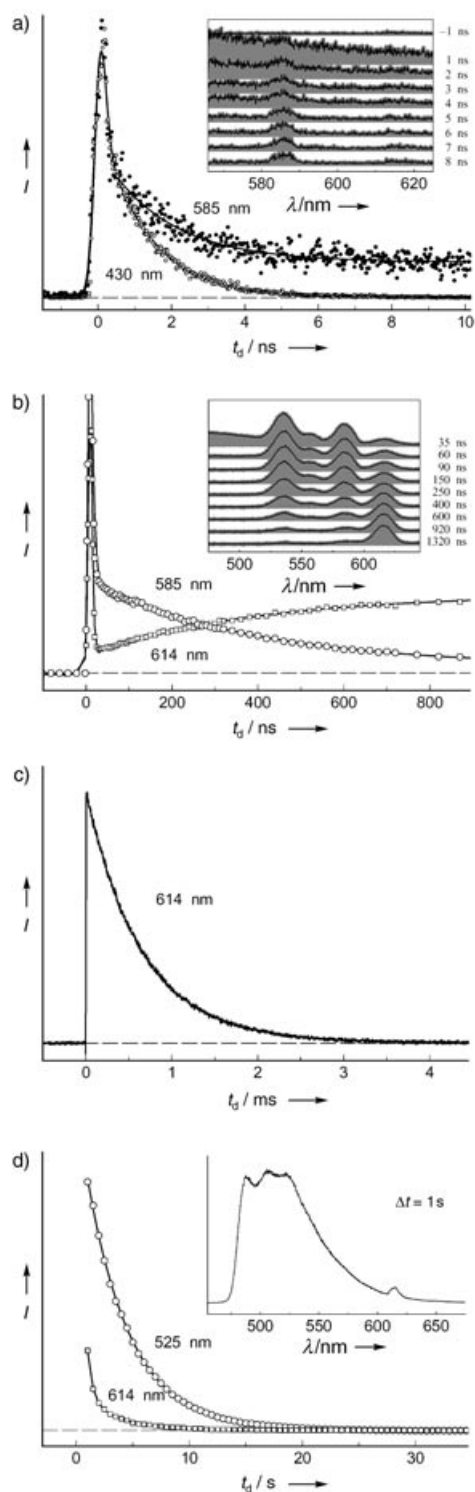
The kinetics and the time-resolved spectra of the luminescence from **4** were recorded on different timescales as shown in Figures 2a–d. On the nanosecond timescale (Figure 2a) and immediately following the pulsed excitation at 400 nm, broad spectra which extend up to 620 nm were observed (inset, 1–4 ns). These broad signals arise from the red edge of the $S_1 \rightarrow S_0$ fluorescent emission of the coordinated ligand that is centered at ≈ 430 nm. Simultaneously, the emission from the $^5D_1 \rightarrow {}^7F_3$ transition of the Eu^{III} ion at 585 nm is also clearly seen. The intensities of these signals vary upon increasing the delay time. The decay-time constant of the ligand S_1-state emission exhibits a weak wavelength dependence, that is, 1.3 ns at 430 nm and 1.8 ns at 605 nm. On the other hand, the rise-time constant of the $^5D_1$ luminescence at 585 nm is found to be 1.8 ns. This decay-to-rise correlation strongly suggests direct energy transfer from the S_1 state of the coordinated ligand **3** to the $^5D_1$ state of Eu^{III}.

On the sub-microsecond timescale (Figure 2b), a tight correlation between the decay of the $^5D_1 \rightarrow {}^7F_{1-3}$ luminescence signals at 535, 555, and 585 nm (decay constant, 387 ns) and the rise of the $^5D_0 \rightarrow {}^7F_2$ luminescence at 614 nm (rise constant, 392 ns) can be established; this indicates the transfer of the excited-state population from the $^5D_1$ state to the $^5D_0$ state of the Eu^{III} ion. The kinetics of the $^5D_0 \rightarrow {}^7F_2$ luminescence of Eu^{III} at 614 nm was examined on the millisecond timescale (Figure 2c). The lifetimes of the excited state are 0.48 and 0.65 ms at room temperature and 77 K, respectively.

To determine the energy of the T_1 state of the coordinated ligand **3**, we performed time-resolved phosphorescence measurements at 77 K (Figure 2d). The emission spectrum reveals an asymmetric broad phosphorescence band centered at ≈ 525 nm (19048 cm^{-1}) with a weak reminiscent $^5D_0 \rightarrow {}^7F_2$ emission band at 614 nm. Most importantly, the lifetime of the T_1-state of the coordinated ligand is determined to be 3.9 s, which is significantly longer than the lifetime of the $^5D_0$ state of the Eu^{III} metal center (0.65 ms). Therefore the excitation-energy transfer from the triplet state of the coordinated ligand **3** to the emissive states of the Eu^{III} ion ($^5D_1$ and $^5D_0$), if any, would have a very low probability ($< 10^{-3}$).[9–10] On the basis of the above observations, we conclude that the sensitization of the Eu^{III} emission in complex **4** proceeds through the singlet pathway, whereas the triplet pathway is essentially inactive (Figure 3).

In conclusion, we have demonstrated the first observable case of excitation-energy transfer from the ligand to the luminescent states of Eu^{III} ion through the singlet pathway in a visible-light-sensitized europium complex. The excitation window for this complex has been extended up to 460 nm.

Figure 2. The time-resolved luminescence spectra of complex **4** in toluene on different timescales recorded at room temperature (a, b) and 77 K (c, d). a) Kinetics curves at 430 (○) and 585 nm (●) with an excitation pulse at 400 nm (130 fs); the inset shows the luminescence spectra at different delay times (t_d). b) Kinetics curves at 585 (○) and 614 nm (□) with an excitation pulse at 417 nm (5 ns); the inset shows the luminescence spectra at different delay times. c) Kinetics curves at 614 nm with an excitation pulse at 417 nm (5 ns). d) Kinetics curves at 525 (○) and 614 nm (□); the inset shows the phosphorescence spectrum of complex **4** after a delay time of 1 s.
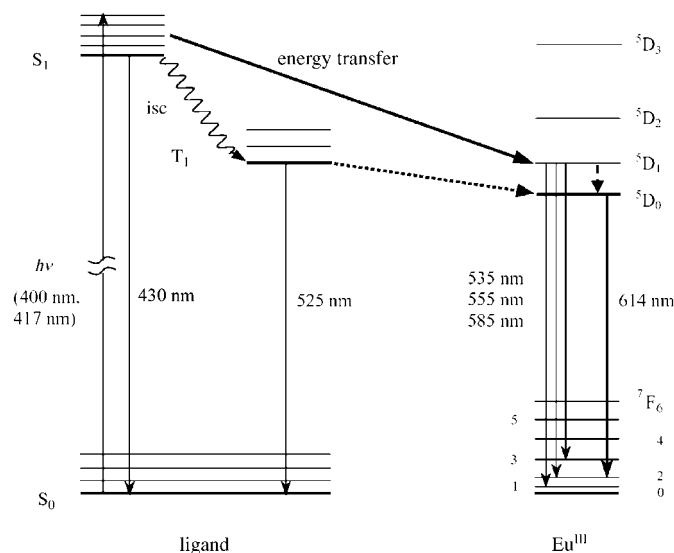
Figure 3. Energy-level diagram showing the energy-transfer pathways in complex **4**; isc denotes intersystem crossing.

Experimental Section

3: Potassium (0.08 g, 2.07 mmol) was added to a stirred solution of 3,5-dimethylpyrazole (0.288 g, 3.0 mmol) in dry THF (30 mL) under N_2 at 70 °C. After the metal dissolved, the colorless solution was cooled to ≈ 10 °C and **2** (0.297 g, 1.0 mmol) was added. The reaction mixture was stirred at room temperature for 0.5 h and then heated at reflux for 5 h. The solution was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel with a mixture of petroleum ether and benzene as eluent to afford **3** (0.36 g, 86 %). M.p. 235–236 °C; ^{1}H NMR (CDCl$_3$, 300 MHz, 25 °C, TMS): $\delta = 8.39$ (d, $^3J(H,H) = 9.2$ Hz, 2H; Ph-H), 6.72 (d, $^3J(H,H) = 9.1$ Hz, 2H; Ph-H), 6.08 (s, 2H; Pz-H), 3.46 (q, $^3J(H,H) = 7.0$ Hz, 4H; NC*H$_2$*CH$_3$), 2.85 (s, 6H; Pz-CH$_3$), 2.35 (s, 6H; Pz-CH$_3$), 1.23 ppm (t, $^3J(H,H) = 6.9$ Hz, 6H; NCH$_2$*CH$_3$*); ^{13}C NMR (300 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 173.37$, 163.98, 152.48, 151.59, 143.95, 131.57, 121.23, 111.35, 110.68, 44.64, 16.06, 14.06, 12.60 ppm; IR (KBr): $\tilde{\nu} = 2983$, 2955, 2893, 2863 (C-H), 1587 (C=N), 1560 (C=N), 1537, 1509 (C=N), 1409 (C=N), 1389, 1355, 1338, 1268, 1184, 1067, 970, 803, 747 cm^{-1}; FAB MS (nba): m/z : 417$[M+1]$; elemental analysis: calcd for C$_{23}$H$_{28}$N$_8$: C 66.32, H 6.78, N 26.90; found: C 66.28, H 6.78, N 26.81 %.

4: A solution of Eu(tta)$_3$·3H$_2$O (87 mg, 0.1 mmol) in THF (10 mL) was added to a solution of **3** (41.6 mg, 0.1 mmol) in THF (10 mL) to give instantaneously a yellow solution with very bright red luminescence in daylight. After evaporation of the solvent, the residue was redissolved in a small amount of diethyl ether. Addition of n-hexane to the solution led to the precipitation of the ternary complex of [Eu(tta)$_3$(**3**)] (**4**) as an orange powder (≈ 86 %). M.p. 138–139 °C; ^{1}H NMR (CDCl$_3$, 300 MHz, 25 °C, TMS): $\delta = 25.54$ (s, 3H; CH), 12.22 (s, 2H; Pz-H), 7.43 (d, $^3J(H,H) = 8.2$ Hz, 2H; Ph-H), 6.91 (s, 3H; Th-H), 6.05 (s, 3H; Th-H), 5.90 (d, $^3J(H,H) = 8.2$ Hz, 2H; Ph-H), 5.03 (s, 3H; Th-H), 4.82 (s, 6H; Pz-CH$_3$), 3.31 (q, $^3J(H,H) = 6.9$ Hz, 4H; NCH$_2$CH$_3$), 0.95 (t, $^3J(H,H) = 6.6$ Hz, 6H; NCH$_2$*CH$_3$*), −0.06 ppm (s, 6H; Pz-CH$_3$); IR (KBr): $\tilde{\nu} = 2978$, 2931 (C-H), 1612, 1591, 1559 (C=N), 1538, 1502, 1415 (C=N), 1393, 1353, 1304, 1185, 1140, 1037, 808 (C=N), 783, 751, 716, 692, 641, 580 cm^{-1}; FAB MS: m/z: 1232 $[M^+]$; elemental analysis: calcd for EuC$_{47}$H$_{40}$N$_8$F$_9$O$_6$S$_3$: C 45.82, H 3.27, N 9.10, S 7.81; found: C 45.35, H 3.28, N 9.03, S 7.59 %.

Steady-state UV/Vis absorption and photoluminescence (PL) measurements were carried out on an absorption spectrometer (U-

3310, Hitachi) and a fluorescence spectrophotometer (F-2500, Hitachi), respectively. Luminescence quantum yields were determined by the method described by Demas and Grosby,[11] with 4-dicyanomethylene-2-methyl-6-p-dimethylaminostyryl-4H-pyran ($\Phi = 0.71$) as the reference.[12]

Time-resolved PL spectroscopy on the nanosecond timescale was performed on a photon-counting type streak camera (C2909, Hamamatsu) combined with a polychromator (Chromex 250is, Chromex); the excitation pulses were provided by a regenerative amplifier (Spitfire, Spectra Physics), whose output wavelength was converted to 400 nm with the second-harmonic generation (≈ 200 nj, 120 fs, 1 KHz). The time-resolution was 30 ps. For the sub-microsecond PL measurements, a gated linear photodiode-array detector (1420, EG&G; gate width 5 ns) attached to a polychromator was employed; the excitation pulses (417 nm, 1 mj, 5 ns) were obtained with a hydrogen-charged Raman shifter (2 MPa) which was pumped by the third harmonics of a Nd:YAG laser (355 nm, 1 Hz, 40 mJ/pulse). The PL kinetics on a millisecond timescale were recorded on a PMT (R298, Hamamatsu) detector attached to a monochromator. The time-resolved phosphorescence measurements were carried out at 77 K. Excitation was realized with the aforementioned 400 nm laser beam, which was chopped by an electric shutter; phosphorescence emissions were sent to a polychromator (Spectropro 550i, Acton) equipped with a liquid-nitrogen cooled CCD detector (SPEC-10-400B/LN, Roper Scientific). A delay-pulse generator (DG535, Stanford Research System) was used to trigger the CCD detection (exposure time 0.1 s) at various delay times with intervals of 0.5 s.

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