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Rare-Earth Complexes of Ferrocene-Containing Ligands: Visible-Light Excitable Luminescent Materials

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The ferrocene-derivatives bis(ferrocenyl-ethynyl)-1,10-phenanthroline (Fc$_2$phen) and ferrocenoyltrifluoroacetone (Hfta) have been used to synthesize ferrocene-containing rare-earth β-diketonate complexes. The complexes [Ln(tta)$_3$(Fc$_2$phen)] and [Ln(fta)$_3$(phen)] (where Ln = La, Nd, Eu, Yb) show structural similarities to the tris(2-thenoyltrifluoroacetonate)(1,10-phenanthroline)lanthanide(III) complexes, [Ln(tta)$_3$(phen)]. The coordination number of the lanthanide ion is 8, and the coordination sphere can be described as a distorted dodecahedron. However, the presence of the ferrocene moieties shifts the ligand absorption bands of the rare-earth complexes to longer wavelengths so that the complexes can be excited not only by ultraviolet radiation but also by visible light of wavelengths up to 420 nm. Red photoluminescence is observed for the europium(III) complexes and near-infrared photoluminescence for the neodymium(III) and ytterbium(III) complexes. The presence of the ferrocene groups makes the rare-earth complexes hydrophobic and well-soluble in apolar organic solvents.

Introduction

Luminescent molecular materials based on rare-earth (or lanthanide) complexes are presently very popular study objects.[1−11] Possible applications are luminescent polymer films,[12,13] active optical fibers for data transmission,[14−18] and light-emitting devices.[19−22] The emission spectra of trivalent lanthanide ions contain linelike transitions. If one of these transitions dominates the emission spectrum, a very pure emission color is observed. The emission wavelength depends on the lanthanide ions but shows only limited dependence on the local environment of the lanthanide ions. Provided that a suitable ligand coordinates to the lanthanide ion, ultraviolet emission can be observed for gadolinium(III),

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blue emission for thulium(III), green emission for terbium(III), red emission for europium(III), and near-infrared emission for neodymium(III), erbium(III), and ytterbium(III). Because the absorption coefficients of the lanthanide ions are very small, stronger light absorption can be achieved in molecular complexes by ligand absorption, and the excitation energy is transferred from the ligands to the lanthanide ions, which transform it into electromagnetic radiation. The shell of organic ligands also protects the lanthanide ion from interaction with the environment and especially from interaction with small molecules like water that can efficiently depopulate the excited states of the metal by radiationless deactivation.

Well-known luminescent rare-earth compounds are the β-diketonate complexes.[23−36] In fact, the complex [Eu(tta)$_3$(phen)] (where tta = 2-thenoyltrifluoroacetonate and phen = 1,10-phenanthroline) is one of the most efficient red-emitting rare-earth-based molecular phosphors.[23] These complexes have been incorporated into sol−gel glasses,[37] inorganic−organic hybrid materials,[38−41] mesoporous silica,[42] polymer matrices,[28,43,44] and even liquid crystals.[45−50] A major disadvantage of the rare-earth β-diketonates is their low photochemical stability.[23] This low photochemical stability becomes apparent when luminescence of these materials is studied under ultraviolet irradiation in conventional molecular solvents. In ionic-liquid solvents, the photochemical stability is significantly higher.[51] Rare-earth β-diketonate complexes often show intense luminescence when ultraviolet radiation is used as the excitation source, because of the position of the ligand absorption bands in this spectral region. However, one could benefit from shifting the excitation wavelength to longer wavelengths and even to the visible region. Less photodecomposition is expected for excitation of the luminescent compounds by electromagnetic radiation of lower energy. Light sources like ultraviolet- and blue-emitting LEDs could be used as the excitation source instead of the conventional ultraviolet lamps.

Different approaches for shifting the excitation wavelength toward longer wavelengths are possible. For instance, one can design complexes of ligands (or coligands) with strongly delocalized π-systems. Examples of such ligands are the phenalenones[52] and Michler's ketone.[53] An alternative method is to make use of the light absorption by transition metal ions. Complexes of 4d- and 5d-transition metals such as platinum(II), rhenium(I), or ruthenium(II) have been applied as antennas in near-infrared-emitting heterometallic f−d systems and exhibit an efficient energy transfer to the rare-earth ion.[54−60] The use of ferrocene as a photosensitizer for the near-infrared luminescence of neodymium(III) and ytterbium(III) has already been reported by van Veggel et al., but the excitation maximum of the ferrocene antenna was situated in the ultraviolet region.[61,62] The incorporation of conjugated ethynyl backbones containing a ferrocene moiety into the molecular framework has gained considerable

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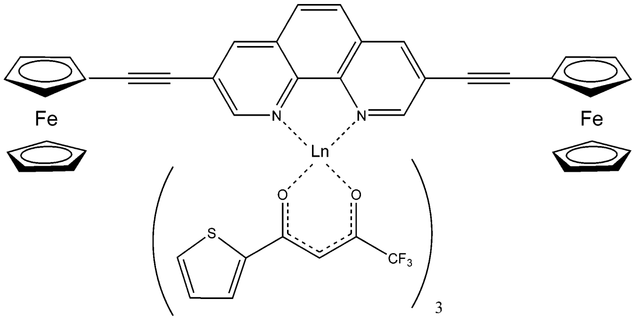

Figure 1. Structure of the complexes of type [Ln(tta)$_3$(Fc$_2$phen)], with Ln = La, Nd, Eu, or Yb.

attention due to their potential application as materials for molecular wires and electronics.[63−65] Ferrocene-containing lanthanide complexes received so far only limited interest from the scientific community.[66−71]

In this Article, we report how the [Ln(tta)$_3$(phen)] complexes can be functionalized by ferrocene moieties to shift the excitation wavelength from the ultraviolet to the visible region. Two different approaches have been followed: attaching ferrocene groups to 1,10-phenanthroline or replacing the thiophene group in 2-thenoyltrifluoroacetone by ferrocene. This will be illustrated for the red emission of the europium(III) complex and for the near-infrared emissions of the neodymium(III) and ytterbium(III) complexes.

Results and Discussion

The first type of ferrocene-containing ligand that we considered was 3,8-bis(ferrocenyl-ethynyl)-1,10-phenanthroline (Fc$_2$phen), which was recently described by Schmittel and Kishore.[72] The ligand Fc$_2$phen was synthesized by a Sonogashira cross-coupling reaction of ferrocenylacetylide and 3,8-dibromo-1,10-phenanthroline. The ethynyl bridges expand the π-system of the phenanthroline ring. This results in a red shift of the excitation wavelength, like it has already been reported for other 3,8-substituted derivatives of 1,10-phenanthroline.[73] Complexes of the type [Ln(tta)$_3$(Fc$_2$phen)], with Ln = La, Nd, Eu, Yb (Figure 1), were obtained by adding an equimolar solution of 3,8-bis(ferrocenyl-ethynyl)-1,10-phenanthroline (Fc$_2$phen) to a solution of [Ln(tta)$_3$]·2H$_2$O in 1,2-dichloroethane. The second type of ligand was ferrocenoyltrifluoroacetone (Hfta). This ligand is comparable with 2-thenoyltrifluoroacetone (Htta), but in Hfta, the thiophene ring of Htta has been replaced by a ferrocene group. Complexes of the type [Ln(fta)$_3$(phen)], with Ln = La, Nd, Eu, Yb (Figure 2), were obtained after adding 1,10-phenanthroline to a solution of [Ln(fta)$_3$]·2H$_2$O in 1,2-dichloroethane. Both the [Ln(tta)$_3$(Fc$_2$phen)] and the [Ln(fta)$_3$(phen)] complexes have a higher solubility in organic solvents like chloroform, dichloromethane, and toluene than the corresponding [Ln(tta)$_3$(phen)] complexes.

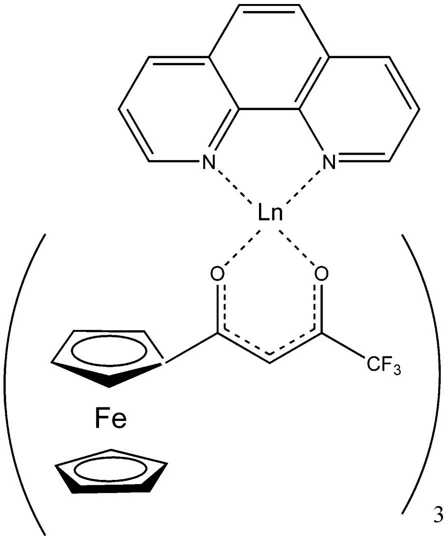

Figure 2. Structure of the complexes of type [Ln(fta)$_3$(phen)], with Ln = La, Nd, Eu, or Yb.

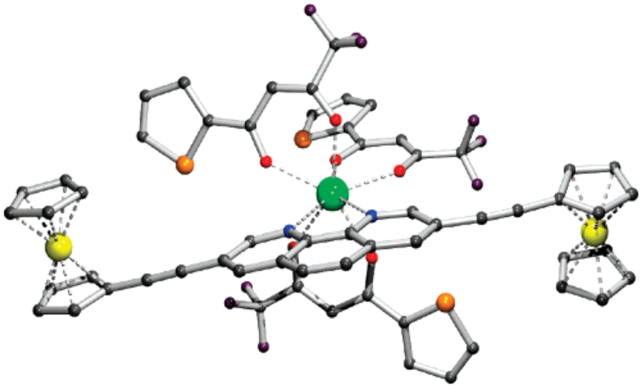

Figure 3. Molecular structure of [Nd(tta)$_3$(Fc$_2$phen)].

The crystal structure of [Nd(tta)$_3$(Fc$_2$phen)] has been determined and shows the coordination of three bidentately coordinating 2-thenoyltrifluoroacetonate ligands and one bidentately coordinating 3,8-bis(ferrocenyl-ethynyl)-1,10-phenanthroline ligand (Figure 3). The coordination number of the neodymium(III) ion is 8, and the coordination polyhedron can be described as a distorted dodecahedron. No solvent molecules are coordinated to the neodymium(III) ion. The two attached ferrocene moieties are oriented opposed to each other with respect to the axis along the ethynyl bridges. The crystal structure of [Nd(fta)$_3$(phen)] could also be determined and shows the coordination of three

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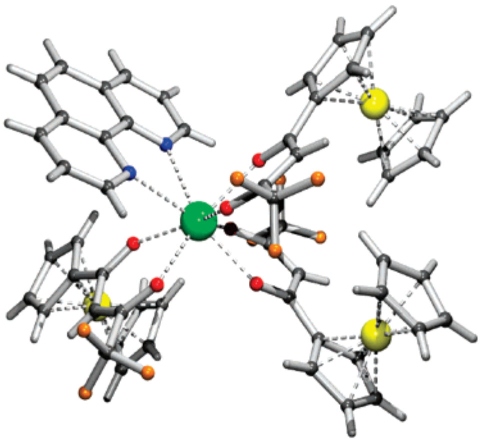

Figure 4. Molecular structure of [Nd(fta)$_3$(phen)].

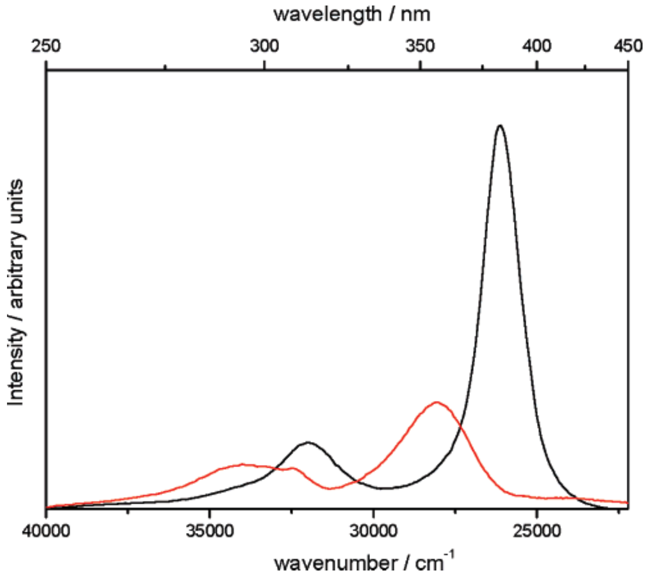

Figure 5. Excitation spectra of [Eu(tta)$_3$(Fc$_2$phen)] (black line) and [Eu(fta)$_3$(phen)] (red line) (both monitored at 612 nm).

bidentately coordinating ferrocenoyltrifluoroacetonate ligands and one bidentately coordinating 1,10-phenanthroline ligand (Figure 4). The coordination number of the neodymium(III) ion is 8 with an irregular coordination polyhedron. No solvent molecules are coordinated to the neodymium(III) ion. $\pi-\pi$-stacking interactions of the ferrocene units of two different molecules can be observed (centroid-to-centroid distance = 3.495 Å).

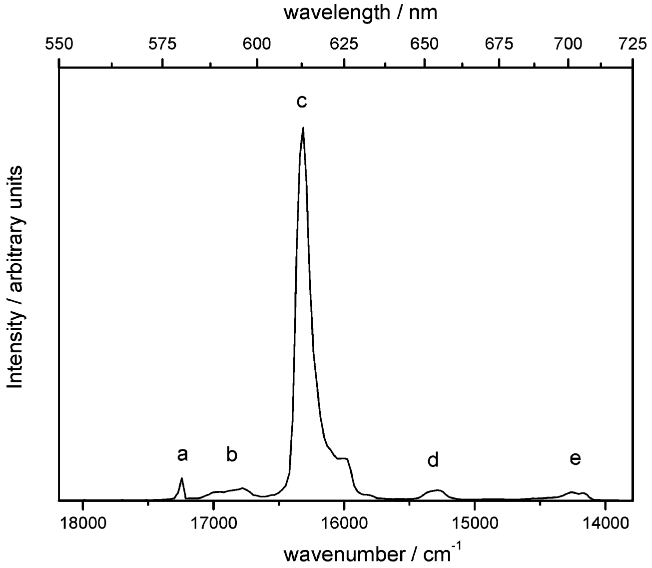

Figure 6. Emission spectrum of [Eu(tta)$_3$(Fc$_2$phen)] with the transitions (a) $^5D_0 \rightarrow {}^7F_0$, (b) $^5D_0 \rightarrow {}^7F_1$, (c) $^5D_0 \rightarrow {}^7F_2$, (d) $^5D_0 \rightarrow {}^7F_3$, (e) $^5D_0 \rightarrow {}^7F_4$ (excited at 403 nm).

The complex [Eu(tta)$_3$(Fc$_2$phen)] exhibits an intense, characteristic red europium(III) emission upon excitation with a wavelength of 420 nm. Two bands can be distinguished in the excitation spectrum of the compound: one excitation band with a maximum at about 30 770 cm^{-1} (325 nm) and one intense band with a maximum at about 25 640 cm^{-1} (390 nm) (Figure 5). No f−f transitions were observed in the excitation spectrum; all transitions have to be attributed to the β-diketonate and Fc$_2$phen ligands. Transitions from the excited $^5D_0$ state to the different J-levels of the lower ^7F state were observed in the emission spectrum (Figure 6) ($J = 0-4$; the transitions to the $J = 5$ and $J = 6$ levels are lying outside of the measuring range of the detection system): $^5D_0 \rightarrow {}^7F_0$ at 17 241 cm^{-1} (580 nm); $^5D_0 \rightarrow {}^7F_1$ at 16 778 cm^{-1} (596 nm); $^5D_0 \rightarrow {}^7F_2$ at 16 340 cm^{-1} (612 nm); $^5D_0 \rightarrow {}^7F_3$ at 15 291 cm^{-1} (654 nm); and $^5D_0 \rightarrow {}^7F_4$ at 14 265 cm^{-1} (701 nm). The emission spectrum is dominated by the hypersensitive transition $^5D_0 \rightarrow {}^7F_2$; the intensity ratio $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ is 16.5. Such a large intensity ratio is typical for europium(III) β-diketonate complexes.[23] The luminescence decay time of the $^5D_0$ state is 264 μs (determined by monitoring the $^5D_0 \rightarrow {}^7F_2$ line). The quantum yield of the [Eu(tta)$_3$(Fc$_2$phen)] complex has been determined with respect to standards leading to $Q_F = (1.75 \pm 0.15)\%$. The solution spectra have been recorded in chloroform, which is a noncoordinating solvent and can therefore not compete with the ligands for coordination to the lanthanide ion. The luminescence decay curves are single-exponential curves. This indicates that only one species is present in solution and that this is the nondissociated complex. Complex dissociation would result in a distribution of different species in solution, and these species would have each their own luminescence decay time.

The excitation spectra of the near-infrared emitting neodymium(III) and ytterbium(III) complexes are analogous to that of europium(III). These infrared emitters exhibit intense emission lines upon excitation with a wavelength of 420 nm. In the emission spectrum of the neodymium(III) complex, the following transitions were observed: $^4F_{3/2} \rightarrow {}^4I_{9/2}$ at 11 442 cm^{-1} (874 nm); $^4F_{3/2} \rightarrow {}^4I_{11/2}$ at 9443 cm^{-1} (1059 nm); and $^4F_{3/2} \rightarrow {}^4I_{13/2}$ at 7519 cm^{-1} (1330 nm) (Figure 7). The luminescence decay time of the $^4F_{3/2}$ excited state is 0.83 μs (determined by monitoring the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ line). For the ytterbium(III) complex, the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition is at 10 235 cm^{-1} (977 nm). The luminescence decay time of the $^2F_{5/2}$ excited state is 14 μs. The quantum yields of the complexes were determined with respect to standards, leading to (0.09 ± 0.02)% for [Yb(tta)$_3$(Fc$_2$phen)] and (0.013 ± 0.003)% for [Nd(tta)$_3$(Fc$_2$phen)].

The excitation spectrum of [Eu(fta)$_3$(phen)] (Figure 5) shows two broad bands: one with a maximum at about

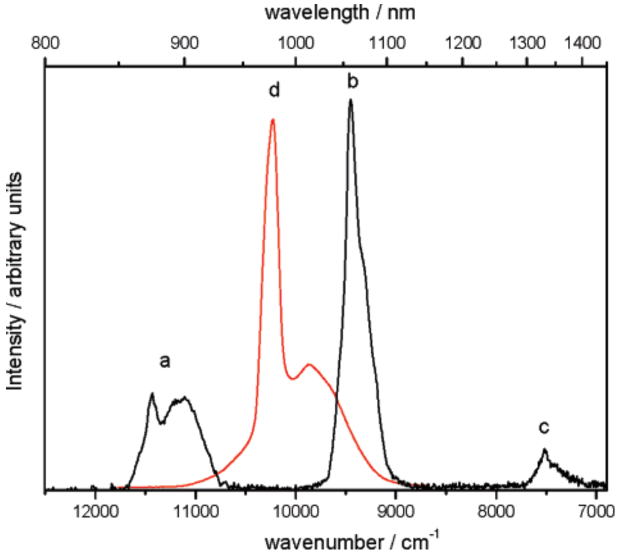

Figure 7. Emission spectra of [Nd(tta)$_3$(Fc$_2$phen)] (black line) with the transitions (a) $^4F_{3/2} \rightarrow {}^4I_{9/2}$, (b) $^4F_{3/2} \rightarrow {}^4I_{11/2}$, (c) $^4F_{3/2} \rightarrow {}^4I_{13/2}$ and [Yb(tta)$_3$(Fc$_2$phen)] (red line) with the transition (d) $^2F_{3/2} \rightarrow {}^2F_{7/2}$ (both excited at 403 nm).

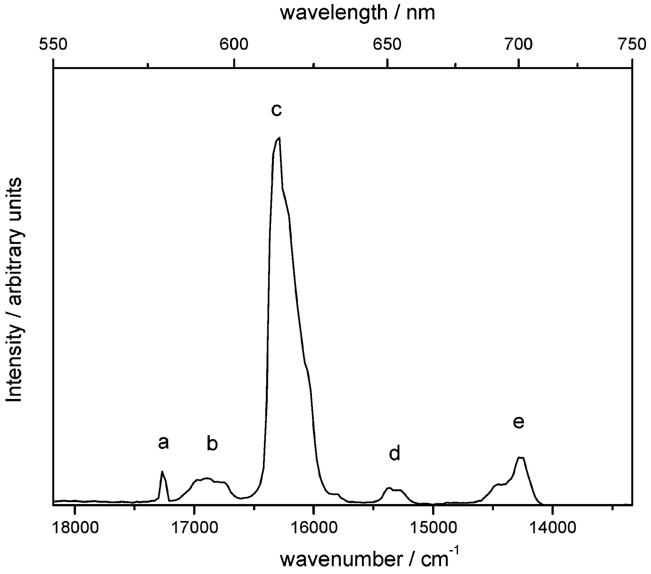

Figure 8. Emission spectrum of [Eu(fta)$_3$(phen)] with the transitions (a) $^5D_0 \rightarrow {}^7F_0$, (b) $^5D_0 \rightarrow {}^7F_1$, (c) $^5D_0 \rightarrow {}^7F_2$, (d) $^5D_0 \rightarrow {}^7F_3$, (e) $^5D_0 \rightarrow {}^7F_4$ (excitation at 360 nm).

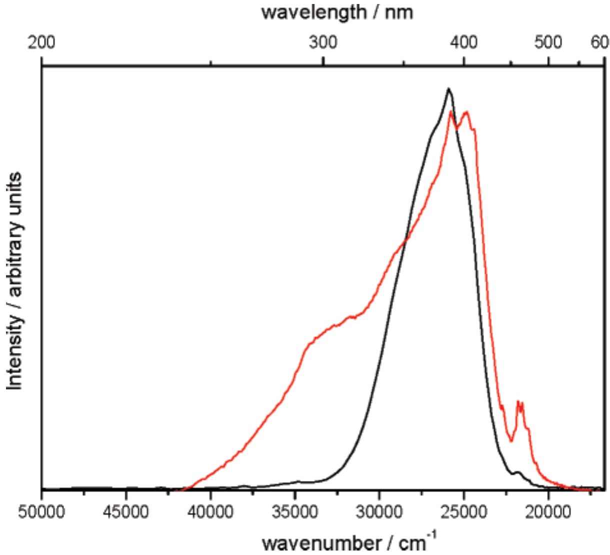

Figure 9. Excitation spectra of [Nd(fta)$_3$(phen)] (black line) and [Yb(fta)$_3$(phen)] (red line) (monitored at 1064 and 978 nm, respectively).

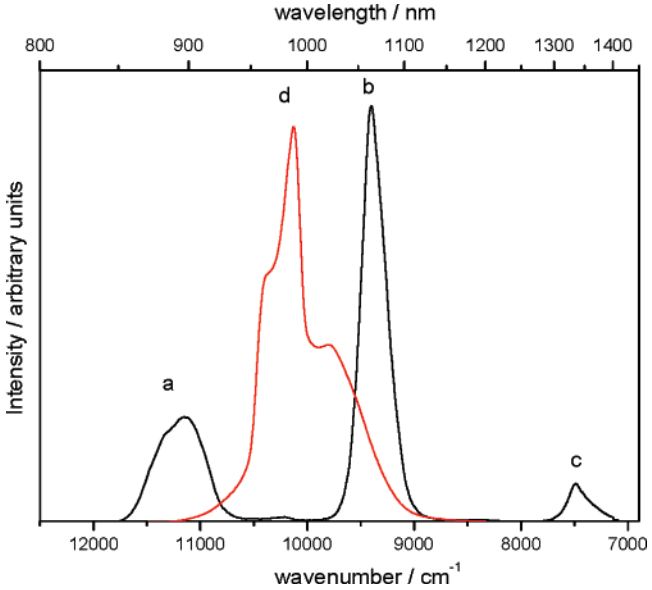

Figure 10. Emission spectra of [Nd(fta)$_3$(phen)] (black line) with the transitions (a) $^4F_{3/2} \rightarrow {}^4I_{9/2}$, (b) $^4F_{3/2} \rightarrow {}^4I_{11/2}$, (c) $^4F_{3/2} \rightarrow {}^4I_{13/2}$ and [Yb(fta)$_3$(phen)] (red line) with the transition (d) $^2F_{3/2} \rightarrow {}^2F_{7/2}$ (both excited at 400 nm).

33 300 cm^{-1} (300 nm) and one band with a maximum at about 28 100 cm^{-1} (356 nm). Therefore, the [Eu(fta)$_3$(phen)] complex cannot be excited with long wavelength radiation like [Eu(tta)$_3$(Fc$_2$phen)], and excitation has to be done with UV radiation of a wavelength shorter than 370 nm. The compound exhibits the characteristic red europium(III) emission (Figure 8). The following transitions were observed: $^5D_0 \rightarrow {}^7F_0$ at 17 007 cm^{-1} (588 nm); $^5D_0 \rightarrow {}^7F_1$ at 16 556 cm^{-1} (604 nm); $^5D_0 \rightarrow {}^7F_2$ at 15 924 cm^{-1} (628 nm); $^5D_0 \rightarrow {}^7F_3$ at 14 993 cm^{-1} (667 nm); and $^5D_0 \rightarrow {}^7F_4$ at 14 045 cm^{-1} (712 nm). The intensity ratio $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ is 12.3. The luminescence decay time of the $^5D_0$ state is rather short with 100 μs (determined by monitoring the $^5D_0 \rightarrow {}^7F_2$ line). The excitation spectra of the near-infrared emitting complexes [Nd(fta)$_3$(phen)] and [Yb(fta)$_3$(phen)] are significantly different from that of [Eu(fta)$_3$(phen)] (see Figures 5 and 9). These infrared emitters exhibit intense emissions upon excitation at 25 000 cm^{-1} (400 nm) (Figure 10). In the emission spectrum of [Nd(fta)$_3$(phen)], the following transitions were observed: $^4F_{3/2} \rightarrow {}^4I_{9/2}$ at 11 135 cm^{-1} (898 nm); $^4F_{3/2} \rightarrow {}^4I_{11/2}$ at 9398 cm^{-1} (1064 nm); and $^4F_{3/2} \rightarrow {}^4I_{13/2}$ at 7485 cm^{-1} (1336 nm). The luminescence decay time of the $^4F_{3/2}$ excited state is 0.79 μs (determined by monitoring the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ line). For the ytterbium complex [Yb(fta)$_3$(phen)], the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition is at 10 132 cm^{-1} (987 nm). The decay time of the $^2F_{5/2}$ excited state is 9 μs. The different excitation spectra can be attributed to different energy transfer pathways from the ligands to [Nd(fta)$_3$(phen)] and [Yb(fta)$_3$(phen)] as compared to the [Eu(fta)$_3$(phen)] complex. The [Ln(fta)$_3$(phen)] complexes have unfortunately a limited photostability in solution. This

is evident from a color change of the complexes to a greenish color upon irradiation with an UV source.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 (operating at 300 MHz for ^{1}H) or on a Bruker AMX-400 spectrometer (operating at 400 MHz for ^{1}H). FTIR spectra were recorded on a Bruker IFS-66 spectrometer, using the KBr pellet method. Elemental analyses (C, H, N) were obtained on a CE Instruments EA-1110 elemental analyzer. Mass spectra were recorded on a Thermo Finnigan LCQ mass spectrometer. The samples were dissolved in methanol/dichloromethane mixtures (80/20) and inserted using electrospray ionization (ESI).

All commercially available reagents and starting materials were used without further purification unless otherwise stated. Chemicals were purchased from Acros Organics or from Aldrich. Absolute THF, diethyl ether, and anhydrous DMF were purchased from Fluka Chemika. Diisopropylamine (DIPA) was dried over KOH for several days and distilled from KOH before use. For chromatography, ICN silica 32-63 (60 Å, ICN Biomedicals GmbH, Germany) was used. TLC was carried out on silica gel coated 5 cm × 20 cm glass plates (Macherey-Nagel GmbH SIL G-25 UV254).

Spectroscopy. The luminescence spectra in the visible spectral range have been recorded on an Edinburgh Instruments FS-900 spectrofluorimeter. Luminescence lifetime measurements were made on the same instrument. This instrument is equipped with a xenon arc lamp, a microsecond flash lamp, and a red-sensitive photomultiplier (300−850 nm). The spectra were corrected for variations in the output of the excitation source and for variations in the detector response. The emission spectra in the near-infrared region were recorded with an Edinburgh Instruments FS920P spectrofluorimeter. This instrument is equipped with a 450 W xenon lamp, a double excitation monochromator with 1800 lines/mm, an emission monochromator with 600 lines/mm, and a liquid nitrogen cooled Hamamatsu R5509-72 near-infrared photomultiplier tube. For luminescence decay time measurements, the setup includes a Continuum Minilite Nd:YAG laser, equipped with second, third, and fourth harmonic crystals, allowing excitation at 1064, 532, 355, and 266 nm. The repetition rate was 10 Hz, and the pulse width was 3−5 ns. Standard quartz 1 cm fluorescence cuvets (Hellma type QS-111) were used. Chloroform and DMSO were used as solvents for all spectra. The quantum yields of the europium compounds were determined with respect to two organic dyes, 9,10-phenylanthracene (undegassed, in cyclohexane, $Q_F = (70 \pm 4)\%$) and quinine bisulfate (QBS, in 1 N H_2SO_4, $Q_F = 54.6\%$), used as standards.[74] The excitation wavelength was set to 340 nm for the standards and the samples. For the measurements of the near-infrared luminescent complexes, samples of $[Yb(tta)_3(H_2O)_2]$ (in toluene, 0.35%) and $[Yb(tta)_3(phen)]$ (in toluene, 1.1%) were used as standards.[75] The quantum yields of the $[Ln(fta)_3(phen)]$ (Ln = Eu, Yb, Nd) complexes were measured but are not reported because of a low accuracy due to the limited photostability. The quantum yields were measured and calculated according to the reported conventional methods.[76,77]

Synthetic Procedures. Synthesis of 3,8-Bis(ferrocenyl-ethynyl)-1,10-phenanthroline (Fc_2phen). The synthesis of the ligand 3,8-bis(ferrocenyl-ethynyl)-1,10-phenanthroline (Fc_2phen) was carried out following a modified route reported by Schmittel and Kishore.[72] In a Schlenk flask under argon atmosphere, 3,8-dibromo-1,10-phenanthroline (0.65 g, 1.92 mmol) was mixed with ferrocenylacetylide (1.16 g, 5.52 mmol), $[Pd(PPh_3)_2Cl_2]$ (77.5 mg, 0.11 mmol), CuI (42 mg, 0.22 mmol), and diisopropylimide $(i\text{-}Pr)_2NH$ (0.78 mL). Dry *N*,*N*-dimethylformamide (50 mL) was added, and the mixture was heated under stirring for 48 h at 83 °C. After cooling to room temperature, an aqueous solution of potassium cyanide (KCN) was added. The organic phase was separated, washed with water, and dried on $MgSO_4$, and the solvent was removed under reduced pressure. The product was purified on a silica column. A CH_2Cl_2/CH_3OH (v/v 100/1) mixture was used as the eluent. Yield: 0.52 g (45%). $R_f = 0.38$ (CH_2Cl_2/CH_3OH 15:1). δ_H ($CDCl_3$, 300 MHz): 4.28 (s, 10H, C_5H_5), 4.30 (s, 4H, β,β'-C_5H_4), 4.56 (s, 4H, α,α'-C_5H_4), 7.75 (s, 2H, 5,6-phen), 8.30 (s, 2H, 4,7-phen), and 9.20 (s, 2H, 2,9-phen).

Synthesis of $[Ln(tta)_3(Fc_2phen)]$ complexes (Ln = La, Nd, Eu, Yb). A solution of $[Ln(tta)_3(H_2O)_2]$ (0.084 mmol) and 3,8-bis(ferrocenyl-ethynyl)-1,10-phenanthroline (Fc_2phen) (50 mg, 0.084 mmol) in 25 mL of 1,2-dichloroethane was refluxed for 42 h. After cooling to room temperature, the solution was filtered. The solvent was removed under reduced pressure. The $[Ln(tta)_3(Fc_2phen)]$ compounds were obtained as dark red crystals.

Data for $[La(tta)_3(Fc_2phen)]$. Yield: 73%. Mp: 207 °C. δ_H ($CDCl_3$, 400 MHz): 4.27 (s, 10H, C_5H_5), 4.32 (s, 4H, β,β'-C_5H_4), 4.57 (s, 4H, α,α'-C_5H_4), 6.16 (s, 3H, −CH of tta), 6.96 (s, 3H, H^4-thiophene ring of tta), 7.41 (s, 3H, H^3-thiophene ring of tta), 7.54 (s, 3H, H^5-thiophene ring of tta), 7.67 (s, 2H, 5,6-phen), 8.26 (s, 2H, 4,7-phen), and 9.65 (s, 2H, 2,9-phen). δ_C ($CDCl_3$, 100 MHz): 69.48, 70.21, 71.84, 92.29, 126.74, 128.08, 129.73, 132.03, 132.45, 133.75, 138.10, and 153.65. IR (KBr, cm^{-1}): 2211 (m), 1604 (vs, $\nu_{C=O}$), 1535 (s, $\nu_{C=C}$), 1409 (s, ν_{C-O} /δ_{C-H}), 1353 (m), 1300 (vs, $\nu_{C=C,}$ ν_{C-CF3}), 1228 (w), 1183 (s), 1135 (vs), 1060 (w), 930 (w), 783 (s), 714 (s), 676 (w), 639 (m), 578 (m), 482 (m). ESI-MS (methanol, *m*/*z*): 1415.9 $\{La(tta)_3(Fc_2phen) + H\}^+$. Elemental analysis calcd (%) for $C_{60}H_{36}F_9Fe_2LaN_2O_6S_3 \cdot 2H_2O$ (1434.74): C, 50.23; H, 2.81; N, 1.95. Found: C, 50.17; H, 2.84; N, 1.91.

Data for $[Nd(tta)_3(Fc_2phen)]$. Yield: 79%. IR (KBr, cm^{-1}): 2209 (m), 1625, 1595 (vs, $\nu_{C=O}$), 1537 (s, $\nu_{C=C}$), 1411 (s, ν_{C-O} /δ_{C-H}), 1353 (m), 1305 (vs, $\nu_{C=C}$,ν_{C-CF3}), 1229 (m), 1186 (s), 1138 (vs), 1060 (m), 933 (w), 860 (w), 820 (w), 787 (s), 719 (s), 681 (w), 641 (m), 580 (m), 486 (m). ESI-MS (methanol, *m*/*z*): 1421.8 $\{Nd(tta)_3(Fc_2phen)(H_2O) + H\}^+$. Elemental analysis calcd (%) for $C_{60}H_{36}F_9Fe_2N_2NdO_6S_3 \cdot H_2O$ (1422.06): C, 50.68; H, 2.69; N, 1.97. Found: C, 50.80; H, 2.76; N, 1.98.

Data for $[Eu(tta)_3(Fc_2phen)]$. Yield: 81%. IR (KBr, cm^{-1}): 2212 (m), 1722 (m), 1602 (vs, $\nu_{C=O}$), 1538 (s, $\nu_{C=C}$), 1410 (s, ν_{C-O} ,δ_{C-H}), 1355 (m), 1307 (vs, $\nu_{C=C}$,ν_{C-CF3}), 1229 (m), 1187 (s), 1138 (vs), 1063 (m), 787 (s), 721 (s). ESI-MS (methanol, *m*/*z*): 1410.0 $\{Eu(tta)_3(Fc_2phen) + H\}^+$. Elemental analysis calcd (%) for $C_{60}H_{36}EuF_9Fe_2N_2O_6S_3 \cdot H_2O$ (1429.79): C, 50.40; H, 2.68; N, 1.96. Found: C, 50.38; H, 2.73; N, 1.95.

Data for $[Yb(tta)_3(Fc_2phen)]$. Yield: 73%. IR (KBr, cm^{-1}): 2212 (s), 1735 (m), 1601 (vs, $\nu_{C=O}$), 1541 (s, $\nu_{C=C}$), 1412 (s, ν_{C-O}, δ_{C-H}), 1353 (m), 1313 (vs, $\nu_{C=C,}$ ν_{C-CF3}), 1229 (m), 1189 (s), 1142 (vs), 1063 (w), 934 (w), 914 (m), 860 (w), 823 (w), 788 (s), 718 (s), 684 (w), 641 (m), 584 (w), 498, 483 (m). ESI-MS (methanol, *m*/*z*): 1432.5 $\{Yb(tta)_3(Fc_2phen) + H\}^+$. Elemental analysis calcd (%) for $C_{60}H_{36}F_9Fe_2N_2O_6S_3Yb \cdot 4H_2O$ (1504.91): C, 47.89; H, 2.95; N, 1.86. Found: C, 47.88; H, 2.61; N, 1.88.

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Synthesis of Ferrocenoyltrifluoroacetone (Hfta). Sodium ethoxide (3.4 g, 50 mmol) was added to a stirred solution of acetylferrocene (10.94 g, 48 mmol) in anhydrous diethyl ether (50 mL) under argon atmosphere. After 20 min of stirring, ethyl trifluoroacetate (6.82 g, 48 mmol) was added, and the reaction mixture was stirred at room temperature for another 12 h. The resulting orange-red precipitate was filtered off, and crude Hfta was obtained as a dark-purple solid. The compound was purified by complex formation with copper(II) as follows: to a solution of Hfta (25 mmol) in acetone (20 mL), a solution of copper(II) acetate (10.7 g, 54 mmol) and sodium acetate (2.2 g, 27 mmol) in water (120 mL) was added. After 45 min of stirring at room temperature, the copper(II) complex of Hfta precipitated. The precipitate was filtered off and washed with water and heptane, respectively. The solid was dissolved in chloroform (80 mL). Liberation of the free Hfta was accomplished by shaking the chloroform solution with an equal volume of HCl (6 N), washing with water, and evaporation to dryness under reduced pressure. Pure Hfta was obtained as a purple solid (3.2 g, 41.2%). δ_H ($CDCl_3$, 300 MHz): 4.22 (s, 5H, C_5H_5), 4.66 (s, 2H, C_5H_4), 4.85 (s, 2H, C_5H_4), 6.07 (s, 1H, CH). Elemental analysis calcd (%) for $C_{14}H_{11}O_2F_3Fe$ (324.07): C, 51.85; H, 3.40. Found: C, 51.90; H, 3.41.

Synthesis of [Ln(fta)$_3$(phen)] Complexes (Ln = La, Nd, Eu, Yb). First the [Ln(fta)$_3$]$\cdot n$H$_2$O complexes were prepared as precursors. Ferrocenoyltrifluoroacetone (Hfta) (118 mg, 0.364 mmol) was dissolved in 30 mL of ethanol. NaOH (0.2225 N, 1.64 mL, 0.364 mmol) and a solution of $LnCl_3\cdot 6H_2O$ (0.121 mmol) in 10 mL of water were successively added to the solution of ferrocenoyltrifluoroacetone. The mixture was stirred overnight at room temperature and evaporated to dryness under reduced pressure. The residue was extracted with chloroform. The chloroform solution of the complexes was evaporated to dryness in vacuo. Pure complexes were obtained in high yield (>70%).

A solution of [Ln(fta)$_3$]$\cdot$2H$_2$O (0.085 mmol) and 1,10-phenanthroline (15.37 mg, 0.085 mmol) in 25 mL of 1,2-dichloroethane was refluxed for 2 days. After cooling to room temperature, the reaction mixture was filtered. The solvent was evaporated under reduced pressure to yield [Ln(fta)$_3$(phen)] as red crystals.

Data for [Nd(fta)$_3$(phen)]. Yield: 83%. Mp: 139 °C. IR (KBr, cm^{-1}): 1602 (vs, $\nu_{C=O}$), 1520 (s, $\nu_{C=C}$), 1432 (s, ν_{C-O},δ_{C-H}), 1377 (m), 1292 (vs, $\nu_{C=C}$ /ν_{C-CF3}), 1254 (m), 1183 (s), 1133 (vs), 1093 (w), 1019 (vw), 944 (s), 844 (w), 794 (s), 727 (m), 665 (s), 581 (w), 546 (w), 493 (s). ESI-MS (methanol, *m*/*z*): 1315.7 {Nd(fta)$_3$(phen)(H$_2$O) + H}$^+$. Elemental analysis calcd (%) for $C_{54}H_{40}F_9Fe_3O_6Nd$ (1299.69): C, 49.90; H, 3.41; N, 2.16. Found: C, 50.28; H, 3.27; N, 2.28. R_f (CH$_2$Cl$_2$/MeOH 100:2 v/v) = 0.42.

Data for [Eu(fta)$_3$(phen)]. Yield: 78%. Mp: 165 °C. IR (KBr, cm^{-1}): 1604 (vs, $\nu_{C=O}$), 1521 (s, $\nu_{C=C}$), 1434 (m, ν_{C-O},δ_{C-H}), 1377 (m), 1297 (vs, $\nu_{C=C}$ /ν_{C-CF3}), 1252 (m), 1182 (vs), 1134 (vs), 1094 (w), 1000 (vw), 945 (s), 820 (m), 792 (s), 730 (s), 668 (s), 583 (w), 547 (m), 490 (s). ESI-MS (methanol, *m*/*z*): 1324.2 {Eu(fta)$_3$(phen)(H$_2$O) + H}$^+$. Elemental analysis calcd (%) for $C_{54}H_{40}F_9Fe_3O_6Eu$ (1307.42): C, 49.61; H, 3.39; N, 2.14. Found: C, 50.28; H, 3.27; N, 2.28. R_f (CH$_2$Cl$_2$/MeOH 100:2 v/v) = 0.38.

Data for [Yb(fta)$_3$(phen)]. Yield: 80%. Mp: 149 °C. IR (KBr, cm^{-1}): 1637, 1606 (sh, vs, $\nu_{C=O}$), 1522 (s, $\nu_{C=C}$), 1439 (m, ν_{C-O}, δ_{C-H}), 1378 (m), 1297 (vs, $\nu_{C=C,}$ ν_{C-CF3}), 1254 (m), 1183 (s), 1137 (vs), 1099 (w), 1003 (vw), 944 (s), 843 (w), 792 (s), 727 (s), 665 (s), 584 (w), 552 (w), 496 (s). ESI-MS (methanol, *m*/*z*): 1345.8 {Yb(fta)$_3$(phen)(H$_2$O) + H}$^+$. Elemental analysis calcd (%) for $C_{54}H_{40}F_9Fe_3O_6Yb$ (1328.49): C, 48.82; H, 3.34; N, 2.11. Found: C, 49.28; H, 3.27; N, 2.28. R_f (CH$_2$Cl$_2$/MeOH 100:2 v/v) = 0.40.

Crystallography. Dark red single crystals of [Nd(tta)$_3$(Fc$_2$phen)] and [Nd(fta)$_3$(phen)] were obtained by slow diffusion of a hexane/ethyl acetate mixture into a solution of the compounds in chloroform after 3 days. X-ray intensity data were collected on a SMART 6000 diffractometer equipped with CCD detector using Cu Kα radiation (λ = 1.541 78 Å). The images were interpreted and integrated with the program SAINT from Bruker.[78]

Crystallography Data for [Nd(tta)$_3$(Fc$_2$phen)]. $C_{60}H_{36}F_9Fe_2N_2NdO_6S_3$, $M = 1404.06$ g mol^{-1}, triclinic, $P\bar{1}$ (No. 2), $a = 14.5049(2)$ Å, $b = 15.6998(2)$ Å, $c = 15.9769(3)$ Å, $\alpha = 119.147(1)°$, $\beta = 114.041(1)°$, $\gamma = 90.289(1)°$, $V = 2805.96(9)$ Å^3, $T = 100(2)$ K, $Z = 2$, $\rho_{calc} = 1.662$ g cm^{-3}, μ(Cu Kα) = 12.814 mm^{-1}, $F(000) = 1398$, crystal size 0.3 mm × 0.2 mm × 0.1 mm, 9536 independent reflections ($R_{int} = 0.0834$). Final $R = 0.0547$ for 8522 reflections with $I > 2\sigma(I)$ and ωR2 = 0.1147 for all data.

Crystallography Data for [Nd(fta)$_3$(phen)]. $C_{54}H_{38}F_9Fe_3N_2NdO_6$, $M = 1293.66$ g mol^{-1}, triclinic, $P\bar{1}$ (No. 2), $a = 10.0642(10)$ Å, $b = 14.7923(15)$ Å, $c = 19.532(2)$ Å, $\alpha = 85.012(4)°$, $\beta = 82.825(4)°$, $\gamma = 70.490(4)°$, $V = 2716.2(5)$ Å^3, $T = 100(2)$ K, $Z = 2$, $\rho_{calc} = 1.582$ g cm^{-3}, μ(Cu Kα) = 14.162 mm^{-1}, $F(000) = 1286$, crystal size 0.4 mm × 0.15 mm × 0.15 mm, 7282 independent reflections ($R_{int} = 0.1196$). Final $R = 0.0658$ for 4795 reflections with $I > 2\sigma(I)$ and ωR2 = 0.1641 for all data. One disordered CF$_3$ group (C41, F7−9, F10−12) is observed.

Both structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program package.[79] Non-hydrogen atoms were anisotropically refined, and the hydrogen atoms in the riding mode with isotropic temperature factors were fixed at 1.2 times *U*(eq) of the parent atoms (1.5 times for methyl groups). CCDC-643250 ([Nd(tta)$_3$(Fc$_2$phen)]) and CCDC-643251 ([Nd(fta)$_3$(phen)]) contain the supplementary crystallographic data for this paper and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk).

Conclusions

In order to shift the excitation wavelength of rare-earth β-diketonate complexes to longer wavelengths, the ferrocene-derivatives bis(ferrocenyl-ethynyl)-1,10-phenanthroline (Fc$_2$phen) and ferrocenoyltrifluoroacetone (Hfta) have been synthesized and used to prepare two ferrocene-containing rare-earth β-diketonate complexes. The complexes [Ln(tta)$_3$(Fc$_2$phen)] and [Ln(fta)$_3$(phen)] (where Ln = La, Nd, Eu, Yb) show structural similarities to the parent [Ln(tta)$_3$(phen)] complexes. The presence of the ferrocene moiety improves the solubility of the complexes in organic solvents like dichloromethane, chloroform, and toluene. The best luminescence properties were found for the [Ln(tta)$_3$(Fc$_2$phen)] complexes of the ferrocene-substituted 1,10-phenanthroline ligand. Here, visible light with a wavelength up to 420 nm (blue light) could be used for excitation of europium(III) (red emission) and of neodymium(III) and ytterbium(III) (both near-infrared emission). The optical absorption properties of the [Ln(fta)$_3$(phen)] are less favorable for visible-light sensitization. Unfortunately, prob-

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(78) *SAINT*, manual version 5/6.0; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.

(79) *SHELXTL-PC*, manual version 5.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.

lems with the photochemical stability of the latter complexes were observed for solutions of the complexes in organic solvents.

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Supporting Information Available: Crystallographic data for [Nd(tta)$_3$(Fc$_2$phen)] and [Nd(fta)$_3$(phen)] in CIF format and checkCIF/PLATON report for [Nd(fta)$_3$(phen)]. This material is available free of charge via the Internet at http://pubs.acs.org.

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