

Luminescent Tags on Fullerenes: Eu^{3+} Complexes with Pendant Fullerenes**

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Novel fullerene-containing Eu (III) complexes are obtained by mixing a fullerene derivative bearing chelating pyridinyl groups with an Eu (III) complex possessing three coordinated 4,4,4-trifluoro-1-(2-naphthyl)-1,3-butanedione residues and two water molecules. One of the complexes designed is formed in water using a water-soluble fullerene derivative as a precursor material. We investigate the photophysical properties of this new type of highly soluble self-assembled fullerene-derivative Eu^{3+} coordination compounds. A strong emission line of the Eu^{3+} 4f–4f transition is recorded under excitation with UV irradiation. The behaviour of the complexes in organic matrices and water is studied as the first steps towards luminescence tagged fullerene derivatives for use in biomedicine and optoelectronics.

1. Introduction

In recent years, quite some research effort has been dedicated to complexes containing trivalent rare earth ions for luminescent applications such as fiber optic communication.^[1] The current interest in these materials is mainly due to their applications in optoelectronic devices such as OLEDs^[2–5] and optical amplifiers.^[6–8]

The 15 rare earth elements form a group of chemically rather similar atoms due to their open 4f shell with a closed xenon shell plus the 6s² configuration. The sharp absorption bands can be traced back to 4f–4f transitions, which are partly forbidden (LaPorte selection rule) and therefore rather weak. Breaking the symmetry by an external crystal and/or ligand field leads to allowed transitions. When coordinating the rare earth ion with organic ligands by complex formation, luminescent ions are achieved. Additionally, the ligands can act as sensitizers for the photoluminescence (PL) by donating absorbed energy to the ion via intramolecular energy transfer processes.^[9] Thus, the spectral width and intensity of the photoluminescence excitation (PLE) can be greatly enhanced due to the complex formation. Due to the shielding of the 4f

orbitals by the 5s5p6s orbitals rare earth ion complexes show characteristic atomic emission lines due to the transitions within the 4f shell with a high luminescence efficiency and a long luminescence lifetime.

By embedding the rare earth complexes in an energetically matching (polymeric) matrix, the energy transfer cascade can be extended by one step. The different transfer steps are sketched in Figure 1. Using these mechanisms, rare earth ion complexes can be doped into the active layer of a deep blue emitting organic LED which then shows the characteristic sharp emission lines of the rare earth ion in its electroluminescence spectrum.^[2]

Since the discovery and the first preliminary studies of buckminsterfullerene C_{60} ^[10,11] and the possibility to synthesize this material in large quantities by the arc discharge process^[12] a lot of research activity done by many groups worldwide resulted in the design of a large variety of functionalized fullerene derivatives.^[13–16] Films made of this fully conjugated molecule and most of its derivatives show n-type semiconducting behaviour,^[17] which lead to the usage of fullerene derivatives in organic field effect transistors.^[18,19] Their high electron affinity makes fullerenes useful as superior electron acceptors in organic solar cells.^[20,21]

In addition to the application of fullerenes in optoelectronic devices a lot of research has been dedicated to the application of fullerenes and their derivatives in biomedicine.^[22–24] Fullerenes absorb light in the ultraviolet and visible parts of the spectrum due to their extensive π -conjugation. Excitation of a fullerene results in the formation of singlet excited states which then undergo rapid inter system crossing to a long-lived triplet excited state. A triplet energy transfer from fullerene to molecular oxygen gives rise to highly reactive singlet oxygen with almost 100% quantum yield. This enables fullerenes to act as photosensitizers for photodynamic therapy.^[25] The photodynamic therapy applications for fullerenes are e.g. cancer

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[**] The authors acknowledge the financial support of the Austrian Science Foundation (FWF No. S9711-N08), the Austrian-Russian bilateral scientific collaboration funds and the Russian Foundation for Basic Research (project 07-03-01078).

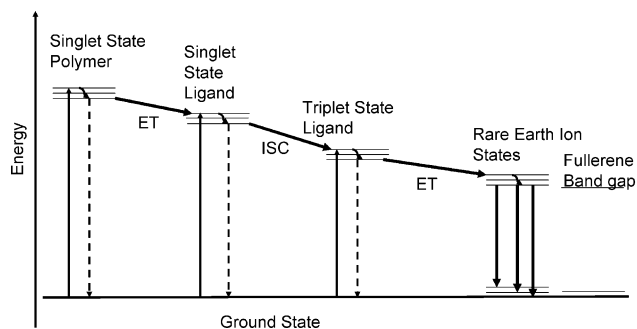


Figure 1. Schematic energy transfer cascade in a polymer matrix with rare earth ion complexes. The desired path of energy is indicated by full arrows. Dotted lines represent possible loss mechanisms.

therapy^[26–28] and dermatology.^[29] Photoinduced DNA cleavage by fullerenes also seems to be mediated by singlet oxygen production.^[30–33]

The capability of fullerenes to scavenge free radical species such as oxygen and hydroxide radicals and superoxide radical anion leads to implementation of fullerenes as efficient antioxidants or so-called ‘radical sponges’. The radical sponge action of fullerenes has been commercialized in new cosmetics.^[34] Most importantly, the radical scavenging activity of fullerenes and their derivatives makes them promising as neuroprotectors for *in vivo* applications.^[35–37] In particular, they were shown to be applicable for the prevention of Parkinson disease, the severest consequence of the neuronal disorder in the brain caused by excessive production of radical species.^[38] At the same time, fullerenes and their derivatives break the aggregation of amyloid peptides causing Alzheimer disease, another manifestation of human aging brain disorders.^[39]

Fullerene derivatives have also been shown to inhibit certain enzymes.^[42] The attraction of fullerenes to enzymes might be explained by the hydrophobic character and the high electron affinity of the C₆₀ cage.^[22] Friedman et al. reported that HIV-protease could be complexed and therefore inhibited by organic derivatives of C₆₀.^[40]

The development of biomedical chemistry of fullerenes is limited by their extremely low solubility in water. A lot of research has been done in this field to overcome this problem and to construct fullerene derivatives highly soluble in water.^[41–44] As a result, a number of fullerene-based water-soluble compounds was designed for use in biomedical research.

However, nowadays it is not sufficient just to observe some biological effects of fullerenes; some studies are urgently required to reveal the mechanism of their action *in vitro* and *in vivo*. In turn, for mechanistic studies there is a need for developing methods to monitor the fullerene behaviour and its distribution in tissues. Attachment of fluorescent tags to bioactive substances is typically used in detecting the substance in biological tissues. This proves to be very difficult in conjunction with fullerenes, as they are too strong electron acceptors capable of quenching fluorescence of virtually any

organic label attached via an efficient photoinduced electron transfer mechanism. Therefore, there is a challenge for chemists to design some labels that remain fluorescent when appended to fullerenes.

Here, we present the application of Eu³⁺ complexes as luminescent tags that associate with pyridinyl-substituted fullerene derivatives in organic solvents or in aqueous media and yield fullerene-metal assemblies that show characteristic Eu³⁺ emission lines.

2. Results and Discussion

The pyrrolidinofullerene (PyF) and the tetraaminofullerene (AmF) (Fig. 2) were prepared according to the literature procedures.^[43,45] The reference complex Eu(TFAcAcN)₃phen **1** was synthesized according to the conventional route^[46] as follows: by adding a solution of EuCl₃ in ethanol dropwise to a mixture of 4,4,4-trifluor-1-(2-naphthyl)-1,3-butandione and [1,10]phenanthroline in ethanol a precipitate of **1** is formed (Fig. 3).

In nearly the same way the precursor complex Eu(TFAcAcN)₃(H₂O)₂ **2** was obtained. The only difference to the above described synthesis was that no phenanthroline was added to the reaction mixture. The europium complex possessing two coordinated water molecules **2** Eu(TFAcAcN)₃(H₂O)₂ was used as a precursor in the ligand exchange reactions with fullerene derivatives PyF and AmF to form the fullerene containing complexes Eu(TFAcAcN)₃AmF **3a** and Eu(TFAcAcN)₃PyF **3b** (Fig. 3). It is reasonable to assume that pyridinyl nitrogen atoms in fullerene derivatives have stronger coordination affinity to the Eu³⁺ ion than water molecules. Therefore, it is expected that the water molecules are pushed away by the nitrogen-containing side groups of fullerene derivatives.

The AmF was shown to be convertible to highly water-soluble salts under dissolving in organic or inorganic acids such as trifluoroacetic acid or 37% aqueous hydrochloric acid.^[43] However, to obtain solid AmF · nHCl, the excess of hydrochloric acid must be removed at room temperature without additional heating (to avoid degradation of AmF), that usually takes quite a long time. Here, we developed an improved procedure for rapid conversion of AmF to water-soluble hydrochloride: for this purpose AmF was dissolved in acetic

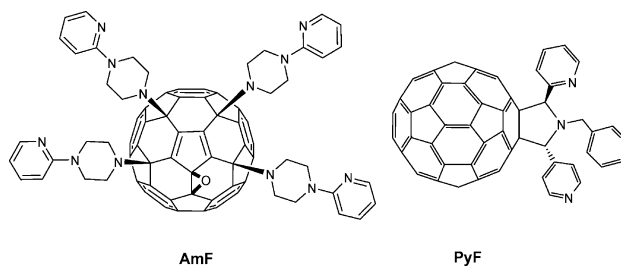


Figure 2. Chemical structures of AmF and 1',2',5'-trisubstituted PyF.

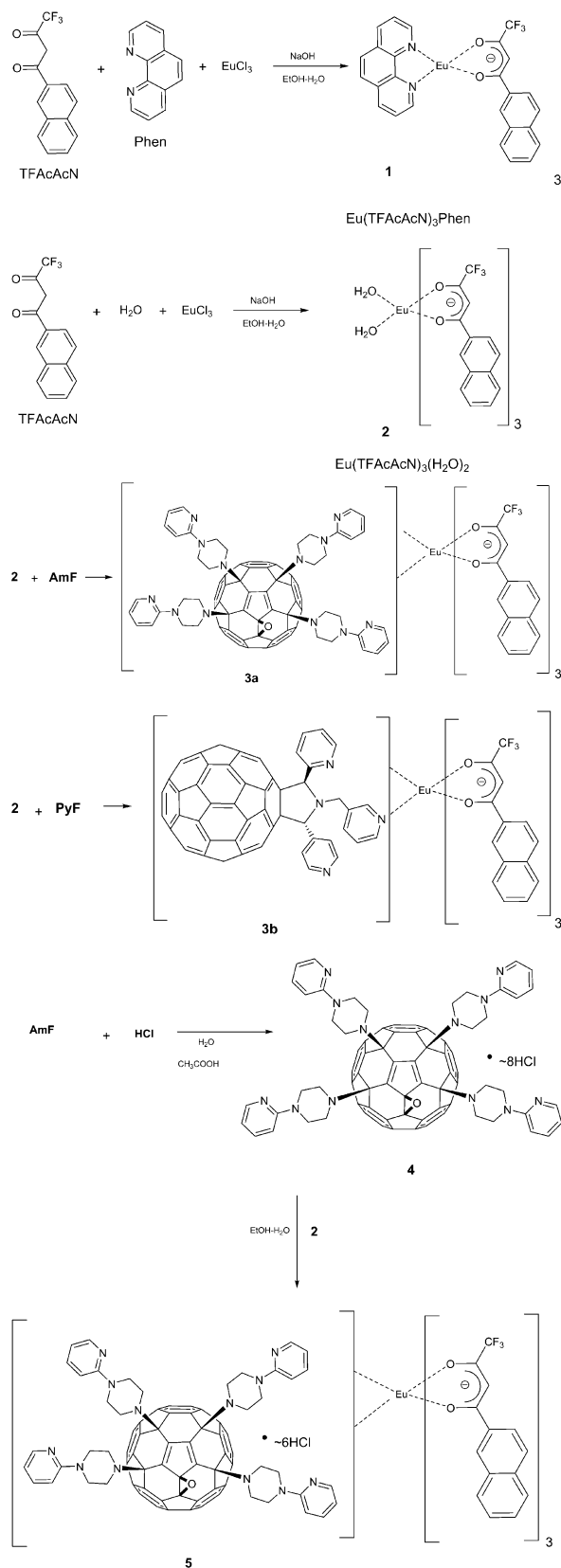


Figure 3. Reaction schemes illustrating preparation of all investigated compounds.

acid and then few drops of 37% aqueous hydrochloric acid were added. To obtain solid $\text{AmF} \cdot n\text{HCl}$ **4**, acetic acid used as a solvent and other volatile components were removed with a stream of N_2 . The composition of the salt obtained was assumed to be $\text{AmF} \cdot (\sim 8\text{HCl})$ as determined in previous studies (Fig. 3).^[43]

To obtain a water-soluble protonated $\text{AmF} \text{Eu}^{3+}$ complex a solution of **4** in water and a solution of **2** in ethanol were mixed in appropriate volumes (Fig. 3).

Note, that PyF has at least two pyridinyl groups sterically available for coordination with Eu^{3+} , while AmF has even four of them. Moreover, precursor **2** can exchange either one or both coordinated water molecules. In the case when two water molecules are replaced, these two coordination sites can be occupied by nitrogen-containing groups from either one or two different molecules of the fullerene derivative. In principle, since each of the reactants $\text{Eu}(\text{TFAcAcN})_3(\text{H}_2\text{O})_2$ **2** and the fullerene derivatives have at least two reactive coordination sites, their interaction can yield an enormous variety of products starting from monomeric species to oligomeric and polymeric assembles. Therefore, the exact chemical structures of **3a**, **3b** and **5** cannot be specified here.

Thus, here we do not draw any exact chemical structures of the complexes but just illustrate that metal-organic complexes have been formed. This is indicated by the brackets with coordination bonds in between on the drawings in Figure 3. The main goal of this work is to study spectroscopic properties of the diketonate- Eu^{3+} -fullerene coordination assembles.

First, the spectroscopic properties of the reference system have been investigated. The PL spectrum of **1** in chlorobenzene solution shows the characteristic sharp emission lines in the red part that are typical for Eu^{3+} ions (solid line in Fig. 4a). There are five bands in the PL spectra centered at 581, 593, 614, 654 and 706 nm. These lines can be attributed to the $^5\text{D}_0\text{-}^7\text{F}_0$, $^5\text{D}_0\text{-}^7\text{F}_1$, $^5\text{D}_0\text{-}^7\text{F}_2$, $^5\text{D}_0\text{-}^7\text{F}_3$ and $^5\text{D}_0\text{-}^7\text{F}_4$ transitions in the Eu^{3+} ion.

PL spectra of the fullerene-containing complexes **3a** (solid line in Fig. 4b) and **3b** (solid line in Fig. 4c) show the same bands with the same spectral positions. Figure 5 shows the PL spectra of **1** (divided by 3), **3a** and **3b** in chlorobenzene solution normalized to their molar concentration. It can be seen that the PL intensity in the case of reference complex **1** is higher. Compared with **1**, the PL intensities for **3a** and **3b** are decreased by factors of ~ 12 and ~ 19 , respectively. This clearly indicates that fullerene act as a quencher for fluorescent Eu^{3+} ion in its coordination surrounding.

As the PL intensities of **3a** and **3b** are not increased the fullerene does not seem to donate energy to the Eu^{3+} ion. The energy transfer cascade shows that the fullerene excited state energy is lower than the Eu^{3+} emission energy (Fig. 1). Thus, energy transfer from the Eu^{3+} ion to the fullerene molecule is possible and might be responsible for the observed quenching (Fig. 4). The phenanthroline can help in sensitizing the PL in **1** in contrast to the fullerenes in **3a** and **3b**.

There is a literature report on the quenching of the fluorescence coming from Eu^{3+} complexes by pristine C_{60} in solutions.^[47] The magnitude of such intermolecular PL

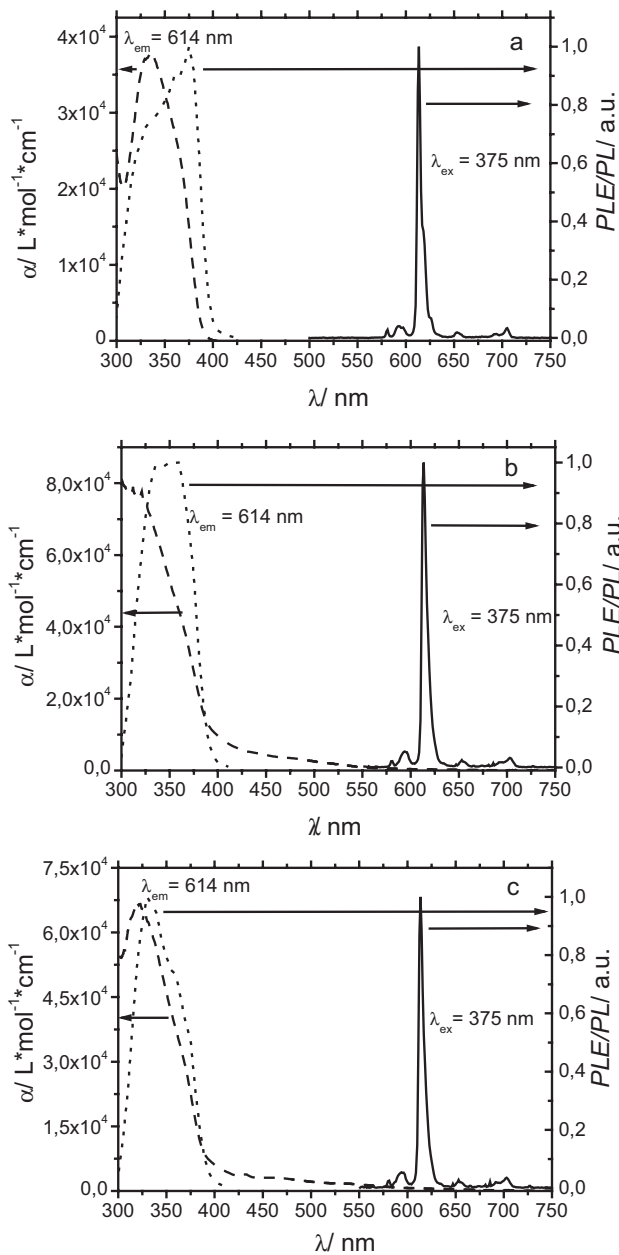


Figure 4. PL (solid line, $\lambda_{\text{ex}} = 375$ nm, 0.75 mW), PLE (dotted line) and absorption spectra (dashed line) of a) **1**, b) **3a** and c) **3b**.

quenching was smaller than we observed for **3a** and **3b**. This is reasonable because PL quenching in **3a** and **3b** goes through much more efficient intramolecular pathways.

The action of C_{60} and its derivatives as PL quenchers for Eu^{3+} complexes is probably due to the lower energy gap of fullerenes which can cause an energy transfer from the emitting state of the Eu^{3+} ion to the fullerene. In other words, fullerene takes part in the last stage of the energy transfer cascade illustrated in Figure 1.

The emission from **3a-b** is however still clearly visible even though the PL intensity is decreased for these compounds in comparison with **1**. Therefore compounds **3a** and **3b** are

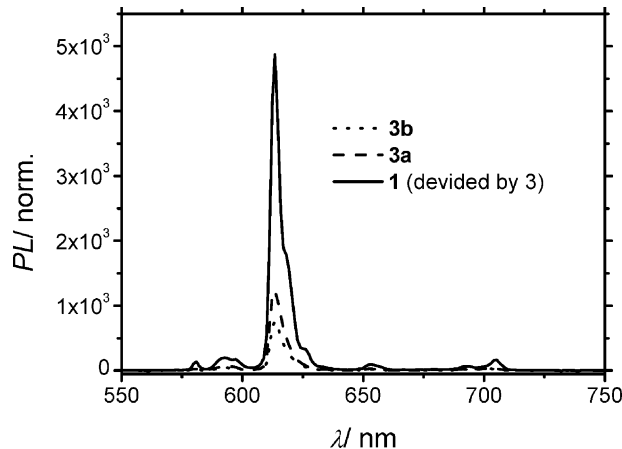


Figure 5. Comparison of PL intensities of **1** (solid line), **3a** (dashed line) and **3b** (dotted line) in chlorobenzene solution. $\lambda_{\text{ex}} = 375$ nm (0.75 mW).

fullerene derivatives with a red PL. To the best of our knowledge such luminescence labelling of fullerenes was never achieved before.

The absorption spectra of AmF (solid line) and PyF (dashed – dotted line) in chlorobenzene solution are shown in Figure 6. AmF and PyF both absorb light in the spectral region from 300–600 nm. Similar absorption features in this region are observed for solutions of **3a** (dashed line in Fig. 4b) and **3b** (dashed line in Fig. 4c) in chlorobenzene. The reference europium complex **1** does not show any absorption in the spectral region of $\lambda > 400$ nm. This is a further indication that the energy transfer should be expected from the Eu^{3+} complex to the fullerene but not vice versa.

The PLE spectra of **3a** (dotted line in Fig. 4b) and **3b** (dotted line in Fig. 4c) were shown to be very similar to the PLE spectrum for the reference complex **1**. In the case of **1** the PLE and the absorption spectra fit well to each other, however, for **3a** and **3b** there is a considerable mismatch. This mismatch comes from the fullerene counterpart in **3a** and **3b** which

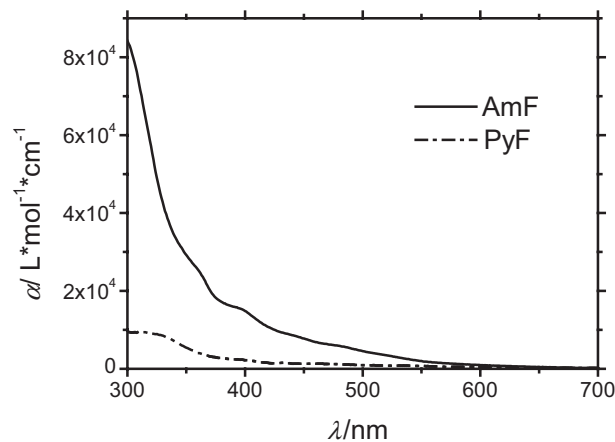


Figure 6. Absorption spectra of AmF (solid line) and PyF (dashed – dotted line) in chlorobenzene solutions.

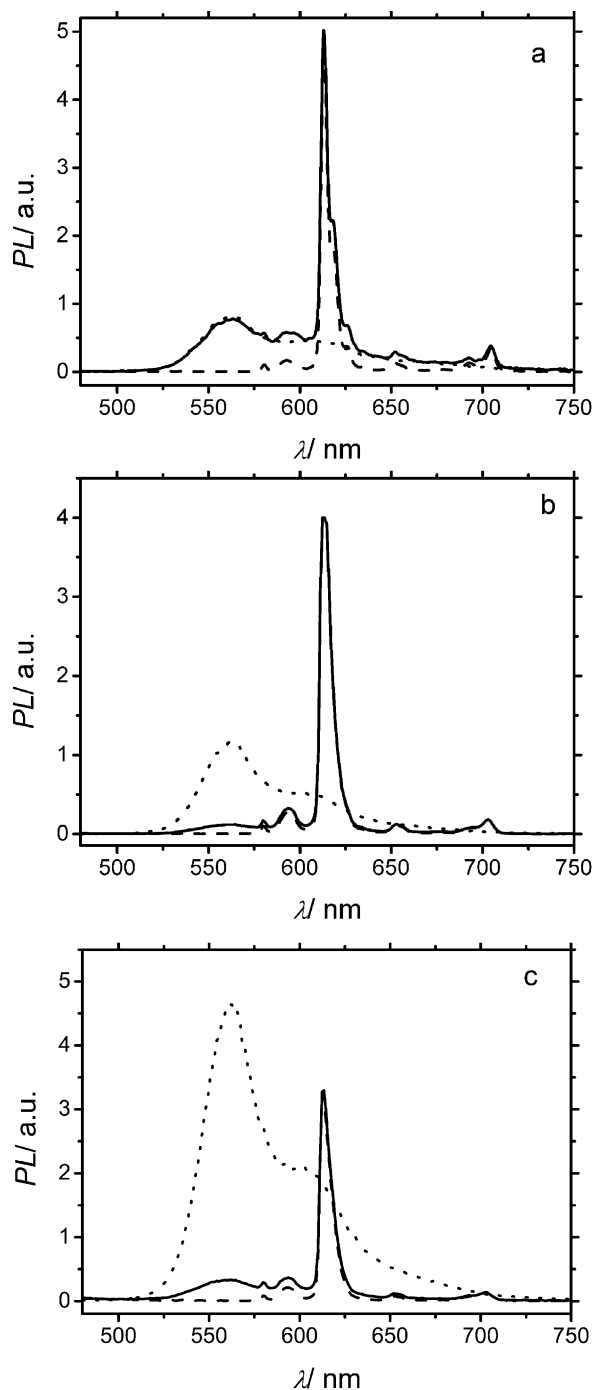


Figure 7. PL spectra of pristine materials MDMO-PPV (dotted line in a–c), **1** (dashed line in a), **3a** (dashed line in b) and **3b** (dashed line in c) compared to the PL spectra for the blend of MDMO-PPV with **1** (solid line in a), **3a** (solid line in b) or **3b** (solid line in c). All measurements were performed in chlorobenzene, $\lambda_{\text{ex}} = 350$ nm (0.5 mW).

contributes strongly to the absorption spectrum but is not active in the PLE spectrum.

Fullerene C_{60} and its derivatives are known as good quenchers of the PL of conjugated polymers such as poly[2-(3,7-dimethoxy)-5-methoxy]-*para*-phenylene-vinylene (MDMO-PPV). This quenching is due to a photoinduced

electron transfer from the π -conjugated polymer onto the C_{60} .^[48,49] After charge separation a positive polymer backbone and a negatively charged fullerene are formed. Figure 7 shows the PL spectra of MDMO-PPV (0.05 mg mL^{-1}) dissolved either alone or together with **1** (0.005 mg mL^{-1}), **3a** and **3b** (0.5 mg mL^{-1}) in chlorobenzene. The excitation was performed at 350 nm where both MDMO-PPV and the complexes are excited. The spectra demonstrate clearly that the PL of MDMO-PPV is quenched by complexes **3a–b** while no quenching is observed for **1**. The quenching rates are approximately the same for compounds **3a** and **3b** since they have similar molecular weights. Most likely the quenching is a result of a photoinduced charge transfer of an electron from the MDMO-PPV to the fullerene ligand. This leaves both transfer partners charged, the MDMO-PPV will be positively and the fullerene attached to the complex negatively charged. This means in our case that even though the fullerenes seem to be charged the complexes are still luminescent. The charging of the fullerene ligands in the complexes is a necessary condition for acquiring highly water-soluble complexes.

The fluorescent labelling of such compounds as PyF and AmF with Eu (III) species might be useful for biomedical studies, however, it is essential to mark fullerene derivatives soluble in water. We showed previously that AmF can be converted to highly water-soluble salts under treatment with acids. The organic groups appended to the fullerene cage in these salts bear positive charges that give hydrophilicity and hence water solubility for entire molecule. We obtained such water-soluble hydrochlorides of AmF and mixed it with a precursor Eu^{3+} complex **2**. As a result, complex **5** was formed that has considerably lower solubility in water comparing to $\text{AmF} \cdot (\sim 8\text{HCl})$ since some positive charges were removed as a result of the complexation.

Figure 8 shows the absorption, the PLE and PL spectra of **5** dissolved in water/EtOH 9:1 v/v mixture. The absorption profile of **5** resembles that of pristine AmF, while the PLE spectrum is similar to the spectrum of the reference complex **1**. The PL spectrum shows the same emission bands characteristic for the Eu^{3+} ion.

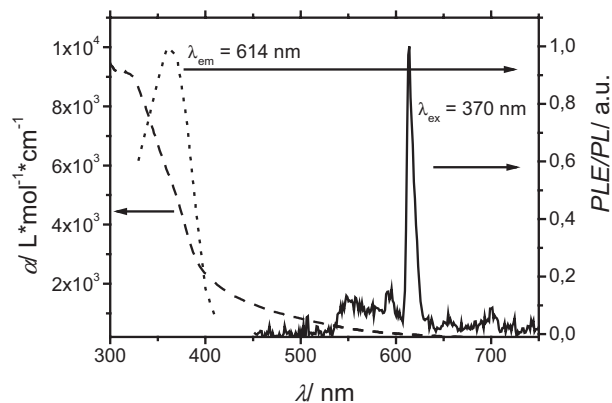


Figure 8. PL (solid line, $\lambda_{\text{ex}} = 370$ nm, 0.75 mW), PLE (dotted line) and absorption spectra (dashed line) of **5**.

3. Conclusions

We demonstrated an Eu(III) luminescence marker for labelling of soluble fullerene derivatives in organic or in aqueous media. Such labelling can be utilized extensively in biomedical research to investigate the mechanisms of action of fullerenes directly in vivo. It is, to the best of our knowledge, the first study where nitrogen-containing fullerene ligands and rare earth complexes are combined. The fullerene does not donate energy to the Eu^{3+} ion but the rare earth metal ion emission is quenched by the presence of fullerenes. This suggests that the energy is transferred from the Eu^{3+} ion to the fullerenes. Mixing this type of complexes into a π -conjugated polymer results in quenching of the PL of the polymer, indicating that the fullerene is still acting as an electron acceptor. The photophysics of such complexes using rare earth ions with organic semiconductors such as fullerenes and conjugated polymers is rich in interesting photoeffects such as photoinduced electron and energy transfer reactions which will be studied further.

4. Experimental

General: All chemicals were purchased from Sigma–Aldrich and used as received unless indicated otherwise. PyF and AmF (Fig. 2) were prepared according to the literature procedures [43,45].

Synthesis of Reference Complex $\text{Eu}(\text{TFAcAcN})_3\text{phen}$: $\text{Eu}(\text{TFAcAcN})_3\text{phen}$ **1** was synthesized according to the conventional route [46] as follows: 4,4,4,-Trifluor-1-(2-naphthyl)-1,3-butandione (160 mg, 0.6 mmol) and [1,10] phenanthroline (36 mg, 0.2 mmol) were dissolved in ethanol (10 mL) under stirring at room temperature. Then five drops of 2 M NaOH were added to adjust the pH level to ~ 8 . Afterwards a EuCl_3 (51 mg, 0.2 mmol) solution in ethanol (3.5 mL) was added dropwise. After complete addition the solution was stirred for 1 h to ensure a complete precipitation at room temperature. The precipitate was filtered out, washed repeatedly with ethanol and water and then dried overnight in vacuum (Fig. 3). Yield $\sim 80\%$. ^1H NMR spectrum for **1** (400 MHz, CDCl_3 , δ): 3.56 [s, 3H, C(O)-CH-C(O)], 7.43 (t, 3H, aromatic), 7.55 (m, 6H, aromatic), 7.70 (m, 3H, aromatic), 7.76 (m, 6H, aromatic), 7.92 (d, 3H, aromatic), 8.49 (d, 2H, aromatic), 9.33 (br. s, 2H, aromatic), 9.82 (s, 2H, aromatic), 10.41 (d, 2H, aromatic) ppm. ^{19}F NMR spectrum for **1** (280 MHz, CDCl_3 , δ): -78.91 (s) ppm.

Synthesis of Fullerene Containing Complexes $[\text{Eu}(\text{TFAcAcN})_3\text{AmF}$ **3a and $[\text{Eu}(\text{TFAcAcN})_3\text{PyF}$ **3b**]:** First, a precursor complex $\text{Eu}(\text{TFAcAcN})_3(\text{H}_2\text{O})_2$ **2** was prepared according to the standard procedure. In general, the synthesis was very similar to the method described above for $\text{Eu}(\text{TFAcAcN})_3\text{phen}$ complex. The only difference was that no [1,10]-phenanthroline was added to the reaction mixture.

^1H NMR spectrum for **2** (400 MHz, CDCl_3 , δ): 2.13 (br. s, 4H), 2.43 (s, 3H), 2.90 (br. s, 3H), 5.13 (br. s., 6H), 6.48 (br. m, 15H), 6.80 (br. s, 3H, aromatic), 7.66 (br. s, 6H, aromatic), 7.97 (br. m, 6H, aromatic), 8.20 (br. s, 3H, aromatic), 8.60 (br. s, 3H, aromatic) ppm. ^{19}F NMR spectrum for **2** (280 MHz, CDCl_3 , δ): -83.05 (m, 3F), -76.81 (br. s, 3F), -74.03 (br. s, 3F) ppm.

The fullerene-containing complexes were obtained via ligand exchange reactions. $\text{Eu}(\text{TFAcAcN})_3(\text{H}_2\text{O})_2$ **2** (29.6 mg, 0.03 mmol) was co-dissolved with 1 equiv. of AmF (41.5 mg, 0.03 mmol) or a 1',2',5'-trisubstituted pyrrolidinofullerene (30.2 mg, 0.03 mmol) in chloroform (Fig. 3). To ensure completion of the reaction, the reagents were stirred for 24 h at room temperature. Then the solutions were

concentrated in vacuum to dryness (on a rotary evaporator), the residues were washed with ethanol and dried in air (or in vacuum desiccator) to yield $\text{Eu}(\text{TFAcAcN})_3\text{AmF}$ **3a** and $\text{Eu}(\text{TFAcAcN})_3\text{PyF}$ **3b** (Fig. 3) as brownish solids with almost quantitative yields.

Synthesis of Water-Soluble Protonated Tetraaminofullerene Eu^{3+} Complex **5:** To obtain a water soluble AmF the fullerene needs to be converted in to a salt by organic or inorganic acids e.g. hydrochloric acid forms $\text{AmF} \cdot n\text{HCl}$. The excess of hydrochloric acid must be removed to obtain a solid salt. As the removal must be carried out at room temperatures to avoid degradation this process usually takes quite some time. We developed here an improved method for the conversion of AmF into solid $\text{AmF} \cdot n\text{HCl}$ **4**: for this purpose the AmF (25 mg, 0.02 mmol) was dissolved in of acetic acid (1 mL) and then few drops of 37% aqueous hydrochloric acid were added. To obtain solid $\text{AmF} \cdot n\text{HCl}$ **4**, acetic acid used as a solvent and other volatile components were removed with a stream of N_2 (alternatively, this can be done in vacuum). The composition of the salt obtained was assumed to be $\text{AmF} \cdot (\sim 8\text{HCl})$ as determined in previous studies [43].

To obtain a water-soluble protonated AmF Eu^{3+} complex **5**, 5 mL of a solution of **4** in water (2.5 mg mL^{-1}) and 2.95 mL of a solution of **2** (2.5 mg mL^{-1}) in EtOH were mixed together to achieve 1:1 molar ratio between the components (Fig. 3). The obtained solution was diluted with water (32 mL) and subjected afterwards to spectroscopic studies.

Photoluminescence, Photoluminescence Excitation and Absorption Measurements: The PL spectra were recorded using a M.U.T 'Tristan light' fibre spectrometer. The excitation source was a Xe-lamp (900 W) equipped with monochromator with a line width below 2 nm. The solution measurements were all performed in a 1 mm special optical glass cuvettes from Hellma.

The absorption spectra were measured using a Varian 3G UV-Vis spectrophotometer. The solution of **1** for the absorption measurements had a concentration of $8.10\text{--}5 \text{ mol L}^{-1}$. In the case of **3a** and **3b**, 1 mg of the material was dissolved in 1 mL of chlorobenzene. The solvent for the solutions of AmF and PyF (0.1 mg mL^{-1}) was chlorobenzene.

The solutions of **1**, **3a** and **3b** in chlorobenzene used for PL and PLE measurements were prepared by dissolving the substance (1 mg) in the solvent (1 mL). To ensure no undissolved particles are present the solutions were filtered through a $0.45 \mu\text{m}$ PTFE syringe filter. The excitation wavelengths for PL measurements were 350 nm (0.5 mW) or 375 nm (0.75 mW). The PLE spectra were obtained by measuring the PL spectra at different excitation wavelengths. Afterwards the maximum value from each spectrum was taken and plotted against the excitation wavelength. The excitation wavelength ranged in-between 300 and 420 nm.

The measurements for MDMO-PPV were performed using its solution in chlorobenzene (0.05 mg mL^{-1}). The solutions of **1** had a concentration of 0.005 mg in 1 mL, **3a** and **3b** had concentrations of 0.5 mg in 1 mL. In the mixture of MDMO-PPV and **3a-b** the concentration of MDMO-PPV was also 0.05 mg mL^{-1} and for **1**, **3a** and **3b** it was 0.005 mg mL^{-1} , respectively 0.5 mg mL^{-1} again. The solvent was chlorobenzene. The excitation wavelength was 350 nm (0.5 mW).

The solution of **5** in water/ethanol had a concentration of $2 \times 10\text{--}3 \text{ mol L}^{-1}$ for both absorption and PL/PLE measurements. The excitation wavelength for the PL measurements was 370 nm (0.75 mW)

Received: March 17, 2008

Revised: May 19, 2008

Published online: September 1, 2008

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