Neighbour-sensitized near-infrared emission of new Nd(III) and Er(III) complexes with 1-(anthracene-2-yl)-4,4,4-trifluoro-1,3-butanedione†

Jung-Soo Kang, Kam Tong Leung, Min-Kook Nah, Jung-Sik Shin, Myung-Hyun Kang, Bonggeun Shong, Jun-Gill Kang, Jisuk Lee and Youngku Sohn

The photophysical properties of Nd(2-ATFB)₃ and Er(2-ATFB)₃ (2-ATFB = 1-(anthracene-2-yl)-4,4,4-trifluoro-1,3-butanedione) were investigated in various organic solvents. The Nd(III) and Er(III) complexes excited by near-UV light emitted near-infrared (NIR) emission from the lanthanide ions via energy transfer from the singlet excited states of the anthracene moiety to the resonance levels of the metal ions. The quantum yields of the sensitized NIR luminescence were estimated from the observed lifetimes of NIR luminescence. The efficiency of the sensitized NIR luminescence increased with increasing polarity of the solvent except for methanol: the OH group of methanol acted as a quencher. Quantum mechanical calculations were performed on the optimization of the model Gd(2-ATFB)₃ molecule and the configurational interaction singlet (CIS) using a coordinate 2-ATFB anion adapted from the optimized structure. The nature of the excited state of the 2-ATFB ligand as an energy donor in the complex was proposed.

Introduction

Recently, near-infrared (NIR) emitting Ln(III) ions, such as Er(III), Nd(III) and Yb(III), have attracted considerable interest for their optical applications, solar energy conversion, and fluororimmuno assays. These ions have characteristic luminescence at wavelengths close to 980, 1300, and 1500 nm, which are quite attractive for optical communication. On the other hand, their absorption cross sections are intrinsically low owing to the partially allowed f → f transitions. To achieve the efficient luminescence of Ln(III), the complexes are functionalized with a strong absorbing chromophore as an antenna. Anthracene-functionalized ligands have been used widely for the main group metal complexes because anthracene provides the versatility for studying the inter- and intra-interactions of these complexes. Anthracene induces metal-to-ligand-charge-transfer (MLCT) due to the large π-conjugated system, which might provide the opportunity to understand the photophysical properties and photoreactivity of the complexes. In addition, anthracene-functionalized antennas play a key role in energy transfer as either an energy donor or acceptor correlated with other coordinated chromophores in the transition metal complex. In this case, the singlet and triplet excited states of anthracene act as energy donating and receiving levels, respectively. A previous study investigated the NIR luminescence properties of Nd(III) complex with 1-(anthracene-9-yl)-4,4,4-trifluoro-1,3-butanedione (9-ATFBH) dissolved in three different organic solvents, N,N-dimethylformamide (DMF), chloroform (CF) and 2-methyltetrahydrofuran (mTHF). The sensitized NIR luminescence of Nd(III) and Er(III) via energy transfer from the singlet excited state of anthracene to the lanthanide ions was observed. For a given lanthanide ion, the quantum yield of the sensitized NIR luminescence was almost independent of the solvent. In this work, we extended this investigation to 1-(anthracene-2-yl)-4,4,4-trifluoro-1,3-butanedione (2-ATFBH). We synthesized three Ln(2-ATFB)₃ (Ln = Gd, Nd and Er) complexes (Chart 1) and comprehensively characterized their photophysical properties, such as luminescence and excitation, quantum yield, and lifetime, in various organic solvents. The visible and the NIR luminescence properties of the Nd(III) and Er(III) complexes were found to be in very good accordance with the nature of the organic solvent. In particular, the photophysical properties of visible emission from the ligand in the Gd(III) complex were...
affected by the solvent polarity. Complementing the experimental procedures, quantum mechanical calculation of the molecular orbitals and excited states of the coordinated 2-ATFB anion was performed to characterize the absorbing and emitting states for the visible luminescence. The energy-transfer processes for the NIR luminescence of the Nd(III) and Er(III) complexes are proposed.

**Experimental**

**Synthesis and composition analysis**

Hexahydrated lanthanide chlorides, ethyl trifluoroacetate, sodium hydride, 2-acetylanthracene, magnesium sulfate, chloroform-d (CDCl₃), N,N-dimethylformamide (DMF), and 2-methyltetrahydrofuran (mTHF) were purchased from Sigma-Aldrich. Acetonitrile (MeCN), methanol (MeOH), and chloroform (CF) were obtained from Samchun Chemical Co. All materials and solvents used in this study were of chemically pure grade and used as received.

The apparatus for chemical composition analyses was described previously. The ¹H nuclear magnetic resonance (NMR, 400 MHz) spectra were recorded on a JEOL JNM-LA400. The chemical shifts are reported in δ ppm referenced to an internal tetramethylsilane standard for ¹H NMR. The 2-ATFBH ligand and its lanthanide complexes were synthesized using a previously reported method. 2-ATFBH. Ethyl trifluoroacetate (1.43 mL, 12 mmol) was slowly added to a solution containing sodium hydride (0.72 g, 30 mmol) in benzene (30 mL). After stirring for 5 min, 2-acetyl anthracene (2.20 g, 10 mmol) was added and stirred overnight at room temperature under N₂(g). The resulting solution was quenched with 3 M hydrochloric acid (50 mL), extracted twice with ethyl acetate (70 mL). The organic layer was dried over MgSO₄, filtered, and evaporated to dryness. The product was obtained as a yellow solid (3.0 g, 95% yield). ¹H NMR (400 MHz, CDCl₃): δ 15.1 (s, 1H, OH), 8.66 (s, 1H, anthracene), 8.01–7.95 (m, 3H, anthracene), 7.80–7.77 (dd, 1H, anthracene), 7.50–7.46 (m, 2H, anthracene), 6.68 (s, 1H, CH). FTIR (cm⁻¹): 1603 (vs, νC=O,keto-form), 1276 (vs), 1200, 1185, 1145 (s, νC–F), 797, 754 (m, νC–CF₃), 474 (w, νC–O–O).

Ln(2-ATFB)₃·xH₂O·yNaCl (Ln = Nd, Er and Gd). 2-ATFP (0.60 mmol) in acetonitrile (80 mL) was added dropwise to 0.20 mmol of lanthanide (Ln) chloride in 5 mL of water. The pH of the resulting solution was adjusted to 6–7 with a 0.05 M NaOH solution and stirred overnight. After filtering, the yellow precipitate was washed several times with water and ethanol, alternately, and dried in a vacuum oven at 50 °C. For Gd, found: C 56.3, H 3.4, O 9.2, Gd 12.4, Na 0.8%. Calculd for Gd(C₁₈H₁₁O₂F₃)₃·H₂O·0.5NaCl: C 55.9, H 3.6, O 9.6, Gd 13.5, Na 1.0%. For Nd, found: C 58.3, H 3.3, O 8.6, Nd 12.0, Na 0.7%. Calculd for Nd(C₁₈H₁₁O₂F₃)₃·0.5H₂O·0.25NaCl: C 57.8, H 3.6, O 9.3, Nd 12.6, Na 0.5%. For Er, found: C 56.3, H 2.8, O 9.0, Er 13.7, Na 1.2%. Calculd for Er(C₁₈H₁₁O₂F₃)₃·0.25H₂O·0.5NaCl: C 56.1, H 3.4, O 8.7, Er 14.5, Na 1.0%.

**Synthesis and composition analysis**

For the measurements of photophysical properties, the prepared ligand and Ln(III) complexes were dissolved at a concentration of 1.0 × 10⁻⁵ M in various solvents. The instrumentation used for the photophysical measurements is described elsewhere. Briefly, the UV-visible absorption spectra were recorded on a Shimadzu UV-2401PC spectrophotometer. The luminescence and excitation spectra were measured using an Edinburgh FS920 Fluorescence Photometer equipped with a PMT system (Hamamatsu R955) for the visible spectrum or a Ge-detector (Edinburgh Instruments EI-L) cooled with liquid nitrogen for the NIR spectrum. The NIR-luminescence lifetime was determined using a PTI-3300 N₂ Laser (337.1 nm). The signal detected using an Acton SpectraPro 2300i instrument (Acton, MA, USA) equipped with a cooled Hamamatsu H9170-75 photomultiplier tube was recorded using an Agilent 54832B DSO oscilloscope and the final result consisted of an average of 500 signals to improve the signal-to-noise ratio. The luminescence decay curves were fitted to a single exponential curve with high Pearson’s correlation coefficients (≥ 0.999). The relative quantum yield of the visible luminescence for each sample (Φv) was determined using a reference solution of quinine bisulfate in a 1 N H₂SO₄ solution (Φv = 0.546).

**Results and discussion**

**Absorption, luminescence and excitation spectra**

Fig. 1(a) shows the absorption spectra of the free 2-ATFBH and 9-ATFBH ligands, and their model Gd(III) complexes dissolved in DMF. In the present study, the Gd(III) complexes were introduced as a model system to support the NIR energy transfer processes in Nd(2-ATFB)₃ and Er(2-ATFB)₃. For 9-ATFBH introduced for comparison, there was no difference in the spectral shape between the free ligand and the Gd(III) complex: two apparent absorption bands, spanning over the 340–420 nm and the 280–340 nm regions (hereafter, referred to as A and B, respectively). The fine structures of the A band at 352.7, 370.4 and 390.2 nm correspond to the characteristic absorption band of anthracene. The spacing wavenumbers between the two adjacent peaks were 1356 and 1370 cm⁻¹. Compared to the A-band of the unsubstituted anthracene in ethanol, the number of split peaks was reduced due to substitution at the 9th position and...
the barycenter was red-shifted to 370.4 nm from 356.4 nm. For
the B-absorption band, the difference in the peak position
between 9-ATFBH (\(\lambda_{\text{peak}} = 304 \text{ nm}\)) and anthracene (\(\lambda_{\text{peak}} =
250 \text{ nm}\)) was quite large compared to the A-absorption band.
This indicates that the B-band transition is affected significantly
by the substituted group. For the 2-ATFBH ligand, however, the
fine vibronic splitting was removed and the peak positions of
the A and B bands showed a slight blue shift to 355 nm for the
free ligand and to 340 nm for the Gd(III) complex from 370 nm
for those of the 9-ATFBH ligand. As shown in the inset in
Fig. 1(a), the A-band absorption band was resolved into two
Gaussian components, peaking at 346.5 and 385.5 nm (here-
after, referred to as A1 and A2 components, respectively). As
shown in Fig. 1(b), the solvent had a negligible effect on the
spectral shape of Gd(2-ATFB)3 except for CF. In CF, an additional
band (hereafter, referred to as A’) appeared at a low-energy,
compensating for the intensity of the A1 component. [Gd(9-
ATFBH)3]3− dissolved in CF did not produce an additional A’ band.

The luminescence spectra of Gd(2-ATFB)3 in different solvents
were measured upon A-band excitation. As shown in Fig. 2(a), the peak position and intensity of the A-band emission from the
2-ATFB ligand in the complex were dependent on the solvent.
Among the selected solutions, the CF solution and MeCN solution
produced the strongest and weakest intensity, respectively. As
listed in Table 1, the peak position of the A-band emission varied
from 522 nm to 450 nm depending on the solvent. The mTHF
solution excited at 337 nm produced two emission bands,
peaking at 513 nm as the main peak and 432 nm as the minor
peak. Note that the phosphorescence process is forbidden. As
shown in Fig. 2(b), the excitation spectrum of the A-band
emission produced a well-resolved structure compared to that
appeared at 397 and 340 nm, respectively. This shows that the
vibronic interaction of the excited state is more effective than
the case for the ground state. Although the absorbance of the A2
component was larger than that of the A1 component, the visible emission from the ligand 2-ATFB in MeCN and DMF
was produced by A1-band excitation. In contrast, for mTHF
and CF the visible emission was produced mainly by A2-band
excitation. In MeOH, the intensities of the A1 and A2 excitations
were similar. Because the excitation and fluorescence spectra
appear as a mirror-image, the emitting centers in MeCN and
DMF are associated with the A1 excited state and those in
MeOH, mTHF and CF are with the A2 excited state. The A’ absorption component did not appear for the mTHF solution. Table 1 lists
some physical data of the solvents. Among them, the polarity of
the solvent was strongly correlated with the observed photophysical properties of the 2-ATFB ligand in the Gd(III) complex.
For both CF and mTHF solutions, the additional excitation A’
band appeared more strongly in the excitation spectrum, compared
to the case of absorption. Here, the additional A’ absorption component did not appear for the mTHF solution. Table 1 lists
some physical data of the solvents. Among them, the polarity of
the solvent was strongly correlated with the observed photophysical properties of the Gd(III) complex because CF and mTHF
have a lower dielectric constant (<10), while the other solvents
have a higher dielectric constant (> 30). In a strong polar solvent, the low-energy A1 excited state is more efficient as an emitting level, whereas in a weak polar solvent, the high-energy A2 excited state is more efficient and is accompanied by the additional A’-band excitation. Here, the Stokes shift of the A2 band was much larger than that of the A1 band. The strong vibronic splitting in the absorption and excitation spectra of the A2 component suggests that the large Stokes shift could be due to the strong dynamic Jahn–Teller (DJT) stabilization of the A2 excited state, coupling to a vibrational mode. Note that the JT stabilization energy (ΔEJT) is approximately a half the Stokes shift, ΔEJT ≈ 1490 cm⁻¹ for the A1 state and ΔEJT ≈ 5090 cm⁻¹ for the A2 state. The exceptionally large DJT stabilization of the A2 excited state resulted in the A2 relaxed excited state (RES) being lower than the A1 RES [Fig. 3].

The luminescence and the excitation spectra of Nd(2-ATFB)₃ and Er(2-ATFB)₃ in the selected solvents were measured in the visible-NIR range. Fig. 4(a) shows the luminescence spectra of the three Ln(2-ATFB)₃ complexes in MeCN spanning the 380–1640 nm range. For all solvents, the A-band excitation produced both visible emission and NIR emission from the two complexes. For Nd(2-ATFB)₃, the observed 888, 1064, and 1332 nm bands were associated with the 4F3/2 → 4I(J = 9/2, 11/2 and 13/2) transitions, respectively, and the observed 1536 nm band for Er(2-ATFB)₃ was attributed to the 4I13/2 → 4I15/2 transition. Fig. 4(b) shows the excitation spectra of the visible and NIR emission from the two complexes in MeCN. The solvent effect on the spectral shapes of the visible emission and its excitation from the two complexes were the same as that for Gd(2-ATFB)₃, as shown in Fig. S1 (ESI†). As shown in Fig. S2 (ESI†), however, for all solvents, the excitation spectra of the NIR emission from the two complexes appeared at 340 nm as the main peak and at 400 nm as the minor peak; these two bands correspond to the A2- and A1-absorption components, respectively. These results showed that energy transfer took place predominantly upon excitation of the A2 excited state of the 2-ATFB ligand.

Fig. 5 shows the spectral overlap between the A emission (A2 and A1) and the absorption of the aqueous Nd(III) or Er(III) solutions. The hypersensitive absorption bands, corresponding to the 4I13/2 → 4G5/2 transition (peaking at 574.8 nm) for Nd(III) and Er(III) solutions, overlap strongly with the A2 excited state.

### Table 1: Observed photophysical properties and their assignments of model Gd(2-ATFB)₃ in some organic solvents with their physical parameters

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Excitation/nm (absorbing state)</th>
<th>Emission/nm (emitting state)</th>
<th>Dielectric constant</th>
<th>Dipole moment/D</th>
<th>Refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeCN</td>
<td>397 (A1)</td>
<td>458 (A1)</td>
<td>37.5</td>
<td>3.92</td>
<td>1.344</td>
</tr>
<tr>
<td>DMF</td>
<td>397 (A1)</td>
<td>450 (A1)</td>
<td>38</td>
<td>3.82</td>
<td>1.4305</td>
</tr>
<tr>
<td>MeOH</td>
<td>340 (A2) 397 (A1)</td>
<td>504 (A2) 33</td>
<td>33</td>
<td>1.70</td>
<td>1.3284</td>
</tr>
<tr>
<td>mTHF</td>
<td>338 (A2) 423 (A’)</td>
<td>432 (A1, w) 513 (A2, s)</td>
<td>6.97</td>
<td>1.38</td>
<td>1.406</td>
</tr>
<tr>
<td>CF</td>
<td>340 (A2) 423 (A’)</td>
<td>522 (A2)</td>
<td>4.81</td>
<td>1.04</td>
<td>1.4459</td>
</tr>
</tbody>
</table>

Fig. 3: Relaxed excited states (RESs) accountable for the A emission from 2-ATFB of Gd(2-ATFB)₃. For strong polar solvents the A1 emission is more efficient than the A2 emission.
and the \( ^4I_{15/2} \rightarrow ^2H_{11/2} \) transition (peaking at 523.0 nm) for Er(III),\(^7\) overlapped more with the A2 emission band than the cases with the A1 emission band. The large Stokes shift of the A2 excited state is a key factor as the energy donor level.

Fig. 6 presents a model for the energy transfer process. All the energy levels are described using the term symbols of Nd(III) and Er(III). When induced by near-UV excitation, the main energy transfer begins with the singlet A2 RES of the 2-ATFB ligand to the closely underlying \( ^4G_{7/2} (J=9/2, 7/2, 5/2) \) levels for Nd(III) or the \( ^4F_{7/2} \) and \( ^4H_{11/2} \) levels for Er(III). Subsequently, the nonradiative transitions occur from the receiving levels to the emitting levels, the \( ^4F_{3/2} \) level for Nd(III) or the \( ^4I_{13/2} \) level for Er(III), followed by emitting NIR photons with characteristic energies.

**Quantum yield and lifetime**

The dependence of the intensity of the visible emission is due to the extent of energy transfer from the 2-ATFB ligand to the Nd(III) or Er(III) ions. Note that energy transfer from 2-ATFB to Gd(III) does not take place because the emitting \( ^6P_{7/2} \) level of Gd(III) (32 200 cm\(^-1\)) is much higher than the singlet A2 excited state of 2-ATFB. The relative quantum yields of visible emission from the Ln(III) complexes in different solvents were measured using a standard quinine sulfate solution. As listed in Table 2, for the Gd(III) complex, A2 emission from the mTHF and CF solutions was more efficient than A1 emission from the MeCN and DMF solutions because of the larger absorbance of the A2 component. For the Nd(III) and Er(III) complexes, the quantum yields of the visible emission from the ligand were significantly lower in the MeCN and DMF solutions. Although the emission from the MeOH solution was produced by both excitations, the quantum yield was not high as those of the other A2 emissions, possibly because the OH group partially quenched the fluorescence.

Fig. 7 shows the relative intensities of the NIR emission from Nd(III) and Er(III). The solvent effect on the NIR emission intensities of the Nd(III) and Er(III) complexes was significant. For the two complexes, the MeCN solution produced the strongest intensity compared to the other solutions. With respect to the NIR luminescence of the MeCN solutions, the CF solution produced only 1/20 of luminescence for the Nd(III) complex and the MeOH solution yielded only 1/2000 of the luminescence for the Er(III) complex (Table 2).

The time-profiles of NIR emission from Nd(2-ATFB)\(_3\) and Er(2-ATFB)\(_3\) by excitation of the 2-ATFB ligand (\( \lambda_{\text{exn}} = 337 \text{ nm} \)) were also measured in different solvents. A typical time-profile of the 1060 nm emission from Nd(III) is shown in Fig. S3 (ESI†). Table 2 lists the lifetimes \( (\tau_{\text{obs}}) \) fitted by one exponential decay component. Using \( \tau_{\text{obs}} \) and the natural lifetime \( (\tau_0) \), which is the reciprocal of the radiative transition and independent of the environment, respectively, the quantum yields of the sensitized NIR luminescence were estimated using the following expression:8

\[
\phi_{\text{sens}} = \frac{\tau_{\text{obs}}}{\tau_0}
\]

where \( \tau_0 = 0.27 \text{ ms for Nd(III) and } \tau_0 = 8.0 \text{ ms for Er(III).} \) The sensitized NIR luminescence of the Ln(III) complexes began with the A2-band excitation of the 2-ATFB ligand, followed by energy transfer from the A2 RES of 2-ATFB to the near resonance state of Ln(III) and subsequent relaxation to the emitting levels of Ln(III). As shown in Fig. 6, the main energy-receiving levels were the \( ^4G_{7/2} \) and \( ^4G_{5/2} \) states of Nd(III), and the \( ^2H_{11/2} \) and \( ^4F_{7/2} \) states of Er(III). Considering this pathway, the quantum yield of the sensitized NIR luminescence can be expressed as

\[
\phi_{\text{sens}} = \phi_{\text{antenna}} \phi_{\text{ET}} \phi_{\text{Ln}}
\]

where the quantum yield of the Gd(2-ATFB)\(_3\) complex is taken as \( \phi_{\text{antenna}} \) and \( \phi_{\text{Ln}} \) is the relaxation efficiency strongly associated with radiative and non-radiative transitions from the receiving...
Table 2  Quantum yields and luminescence lifetimes of Ln(2-ATFB)3 dissolved in various solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Ln</th>
<th>NIR integral</th>
<th>$\Phi_{\text{vis}}$</th>
<th>$\eta_{\text{ET}}$</th>
<th>$\Phi_{\text{sens}}$</th>
<th>$\Phi_{\text{Ln}}$</th>
<th>$\tau_{\text{obs}}$ (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeCN</td>
<td>Gd</td>
<td>$1.93 \times 10^6$ (1.0)</td>
<td>0.0133</td>
<td>0.6767</td>
<td>$5.0 \times 10^{-3}$</td>
<td>0.56</td>
<td>1.35</td>
</tr>
<tr>
<td></td>
<td>Nd</td>
<td>$4.51 \times 10^5$ (1.0)</td>
<td>0.0047</td>
<td>0.6466</td>
<td>$2.6 \times 10^{-4}$</td>
<td>0.03</td>
<td>2.05</td>
</tr>
<tr>
<td>DMF</td>
<td>Gd</td>
<td>$3.80 \times 10^3$ (0.20)</td>
<td>0.0292</td>
<td>0.7637</td>
<td>$2.9 \times 10^{-3}$</td>
<td>0.13</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>Nd</td>
<td>$1.61 \times 10^3$ (0.42)</td>
<td>0.0069</td>
<td>0.6986</td>
<td>$1.6 \times 10^{-4}$</td>
<td>7.8 $\times 10^{-3}$</td>
<td>1.30</td>
</tr>
<tr>
<td>MeOH</td>
<td>Gd</td>
<td>$1.90 \times 10^5$ (0.10)</td>
<td>0.0230</td>
<td>0.6565</td>
<td>$6.3 \times 10^{-4}$</td>
<td>0.042</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>Er</td>
<td>$2.17 \times 10^5$ (4.8 $\times 10^{-4}$)</td>
<td>0.0120</td>
<td>0.4783</td>
<td>$1.3 \times 10^{-5}$</td>
<td>1.2 $\times 10^{-3}$</td>
<td>0.10</td>
</tr>
<tr>
<td>mTHF</td>
<td>Gd</td>
<td>$5.07 \times 10^3$ (0.26)</td>
<td>0.0375</td>
<td>0.2533</td>
<td>$9.6 \times 10^{-4}$</td>
<td>0.10</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>Nd</td>
<td>$5.91 \times 10^4$ (0.13)</td>
<td>0.0280</td>
<td>0.0666</td>
<td>$1.5 \times 10^{-5}$</td>
<td>6.0 $\times 10^{-3}$</td>
<td>0.12</td>
</tr>
<tr>
<td>CF</td>
<td>Gd</td>
<td>$9.23 \times 10^4$ (0.048)</td>
<td>0.2160</td>
<td>0.0134</td>
<td>$6.7 \times 10^{-4}$</td>
<td>0.23</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>Nd</td>
<td>$7.35 \times 10^4$ (0.16)</td>
<td>0.1407</td>
<td>0.3486</td>
<td>$1.9 \times 10^{-4}$</td>
<td>2.5 $\times 10^{-4}$</td>
<td>0.15</td>
</tr>
</tbody>
</table>

*a* The values in parentheses represent the relative integral values for the NIR emission with respect to the case of the MeCN solution.

![Fig. 7](image-url)  
Solvent effect on the intensities of the NIR emission from Nd(2-ATFB)3 (a) and Er(2-ATFB)3 (b): 1; MeCN, 2; DMF, 3; MeOH, 4; mTHF, 5; CF. 

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from the 2-ATFB ligand to the Ln(III) ion was calculated by defining $\eta_{\text{ET}} = (\Phi_{\text{vis,Gd}} - \Phi_{\text{vis,Ln}})/\Phi_{\text{vis,Gd}}$. $\Phi_{\text{Ln}}$ was calculated by substituting the values of $\Phi_{\text{antenna}}$, $\eta_{\text{ET}}$ and $\Phi_{\text{sens}}$ to eqn (2). As listed in Table 2, at a given solvent, the sensitized NIR emission of the Nd(m) complex was much more efficient than that of the Er(m) complex. This is because the energy difference between the A2 RES of 2-ATFB and the emitting level of the $^4F_{3/2}$ level of Nd(m) was smaller than that for the $^4I_{13/2}$ level of Er(m). For a given Ln(m) ion, the solvent with a larger dielectric constant may produce a more effective quantum yield. For the MeOH solution, however, the quantum yield of the sensitized NIR luminescence of both Nd(m) and Er(m) was the lowest among the solvents tested. This indicates that the O–H vibration ($\approx 3490$ cm$^{-1}$) is much more efficient in deactivating the emissive state than the C–H vibration ($\approx 2950$ cm$^{-1}$).

**Structural optimizations and electronic transitions**

Quantum mechanical calculations were performed to characterize the observed optical properties of Gd(2-ATFB)3. First, the molecular geometry of the complex molecule was optimized using density functional theory (DFT) at B3LYP using the GEN basis functions (MWB28 for Gd, and 3-21G for H, C, O and F atoms). Fig. S4 (ESI†) shows the molecular geometry optimized to the 1D-4 convergence criteria. The dihedral angles between the anthracene frame and the plane formed by the 1-C(O)–CH group were optimized to be in the 0.411–0.694° range, indicating that 2-substituted anthracene and 1-C(O)CH formed a planar geometry. On the other hand, the dihedral angles between the two carbonyl groups were 0.716–1.438°, indicating that the 3-C(O) was slightly tilted with respect to 1-C(O). A configurational interaction singlet (CIS) calculation was performed for the electronic structures of the excited states of the optimized molecule but the convergence failed because of the huge molecular size. Assuming that the linear combinations between the orbitals of the Gd atom and the orbitals of the other atoms in the ligand were neglected for some high-lying occupied molecular orbitals and some low-lying unoccupied molecular orbitals, the geometry of the 2-ATFB anion coordinated to the Gd atom (hereafter, referred to as the coordinate-form) was adapted as a model molecule for the CIS calculations. Fig. S5 (ESI†) compares the optimized geometries of the coordinate and the free 2-ATFB anions.
The next two high-lying MOs corresponded to the π-electron orbitals of the C atoms in the anthracene moiety, resulting from the linear combinations of the p_z orbitals of the four C atoms and the two O atoms in the butanedione group. Therefore, they corresponded to π_CO(2z;1) and π_O(2z;3), respectively. Here, the p_z orbital of the O atom at 1-C also participated in the linear combination but its contribution was very low. The next two high-lying MOs, l1–l3, resulted from a linear combination of the p_z orbitals of the 2-C atom, which is referred to as π_C(2z;1). The two MOs were characterized by the two and three nodes, respectively, along the short axis of the anthracene moiety; these two MOs were specified as π_C(2z;2) and π_C(2z;3), respectively. The other p_z orbital of the C atom at 1-C also participated in the linear combination but its contribution was very low. The next two high-lying MOs, l1–l3, resulted from a linear combination of the p_z orbitals of the C atoms in the anthracene moiety. The two MOs were characterized by the two and three nodes, respectively, along the short axis of the anthracene moiety; these two MOs were specified as π_C(2z;2) and π_C(2z;3), respectively. Therefore, they corresponded to π_C(2z;2) and π_C(2z;3), respectively. The lowest unoccupied molecular orbital (LUMO) and the next two high-lying MOs, l1–l3, resulted from a linear combination of the p_z orbitals of the C atoms in the anthracene moiety, corresponding to π_C^*(2z;1)–π_C^*(2z;3), respectively. As shown in Fig. 8, the l1 MO was characterized by four nodes along the short axis, and the l2 MO was characterized by three nodes along the short axis and one node along the long axis across the entire frame of anthracene, whereas the l3 MO was characterized by two cross nodes of two separated benzene frames and one node along the long axis. The l4 MO was composed of the p_z orbitals from some of the C atoms in the anthracene moiety and the butanedione group, which is referred to as π_C^*(2z;4).

Table 3 lists the first ten excited states of the coordinate-form 2-ATFB anion. The CIS calculations showed that the A-band transitions were partially due to ICT from the butanedione group as an electron donor to the anthracene moiety as an electron acceptor. The absorption and emission properties of the coordinate-form 2-ATFB anion could be affected by the twisted geometry between the anthracene plan and the butadiene frame. The electronic transitions of the 2-ATFB anion were calculated as a function of the dihedral angle (φ) between the C2–C1 bond of the butadiene and the C2–C1 bond of the anthracene moiety.

For the latter, the two carbonyl groups were positioned opposite to each other.

Fig. 8 shows some high-lying occupied and low-lying unoccupied molecular orbitals of the coordinate-form anion. The highest occupied molecular orbital (HOMO), h1, resulted from a linear combination of the p_x orbitals of the two O atoms and the p_x orbitals of the 2-C atom, which is referred to as π_CO(2z;1). The next two high-lying MOs, h2 and h3, corresponded to the π-bonding orbitals of the butanedione moiety, resulting from the linear combinations of the p_z orbitals of the 2-C atom, which is referred to as π_C(2z;1). The two MOs were characterized by the two and three nodes, respectively, along the short axis of the anthracene moiety; these two MOs were specified as π_C(2z;2) and π_C(2z;3), respectively. Therefore, they corresponded to π_C(2z;2) and π_C(2z;3), respectively. The other p_z orbital of the C atom at 1-C also participated in the linear combination but its contribution was very low. The next two high-lying MOs, l1–l3, resulted from a linear combination of the p_z orbitals of the C atoms in the anthracene moiety, corresponding to π_C^*(2z;1)–π_C^*(2z;3), respectively. As shown in Fig. 8, the l1 MO was characterized by four nodes along the short axis, and the l2 MO was characterized by three nodes along the short axis and one node along the long axis across the entire frame of anthracene, whereas the l3 MO was characterized by two cross nodes of two separated benzene frames and one node along the long axis. The l4 MO was composed of the p_z orbitals from some of the C atoms in the anthracene moiety and the butanedione group, which is referred to as π_C^*(2z;4).

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Fig. 9 shows the dependence of the dihedral angle on the oscillator strength for the 1A, 2A and 3A excited states. For the 1X → 1A transition, the oscillator strength increased with increasing dihedral angle, reaching a maximum at φ = 30° (f = 0.0914). Above φ = 30°, with increasing φ, the f value decreased and at φ = 90°, f = 0.002. Compared to the value of the optimized geometry (f = 0.0291 at φ = 6.657°), the maximum oscillator strength was more than three time larger; thus, the 1X → 1A transition could appear as an additional band. Note that above φ = 45°, with increasing φ, the contribution of the ant-based π transition became active instead of the π (π-1) and π (π-3) transitions. For the 1X → 1A transition, with increasing φ, the oscillator strength decreased slightly and the wavelength blue-shifted up to λ = 45° (f = 0.6529 and λ = 69.41 nm). Above this angle, the oscillator strength increased to 0.7606 and the wavelength red-shifted to 69.3 nm at φ = 90°. For the optimized geometry (φ = 6.657°), the 1X → 1A transition consisted of ICT from the carbonyl groups to the anthracene moiety and the direct transition of the anthracene moiety. Above φ > 30°, the direct transition of the anthracene moiety became predominant. The φ dependence of the 1X → 3A transition exhibited different behaviors in the oscillator strength. At φ = 0°, the oscillator strength was 1.6114. With increasing φ, the f value decreased slightly up to 60° but it decreased rapidly above this angle; at φ = 90° f = 0.2369. This is because at φ > 30°, ICT became more predominant than the π → π* transition in the anthracene moiety. The CIS calculations showed that CIT was affected by the twisted angle between the anthracene moiety and the substituted group, i.e., the oscillator strength of ICT reached a maximum at φ = 30°. In contrast, the π → π* transition of the anthracene moiety was almost unaffected by the rotation of the butadiene group with respect to the anthracene plane. Taking the CIS calculation results into account, the 1A, 2A and 3A excited states were responsible for the A’, A1 and A2 absorption, respectively. In particular, the rotation of the butadiene group was suppressed by the polar solvation, which inhibited the A*-absorption component. On the other hand, in the nonpolar or weak polar solvents, the interaction between the 2-ATFB ion and the solvent was weak, meaning the rotation of the butadiene group was more probable, resulting in the appearance of the A*-absorption component. In contrast, the solvatochromic effect on the A1 and A2 absorption components was negligible because the oscillator strengths of the 1X → 1A and 1A transitions were insensitive to rotation below φ = 90°.

Conclusions

The Nd(III) and Er(III) complexes with 1-(anthracene-2-yl)-4,4,4-trifluoro-1,3-butane (2-ATFB) produced sensitized NIR luminescence via energy transfer from the ligand to the lanthanide ions. Two or three absorption components were observed in the 300–500 nm range depending on the solvent polarity. The lowest-energy A*-absorption component appeared as an additional band at 425 nm only in the weak-polar solvent. The CIS calculation suggested that charge transfer from the butanedione to the anthracene moiety was partially responsible for the A’ band. The other two A1 and A2 absorption components, peaking at 390 and 335 nm, respectively, appeared in all the solvents tested. The A1 excited state resulted from a combination of charge transfer from the two carbonyl groups to the anthracene moiety and the π → π* transition of the anthracene moiety. Among the A-absorption components, the A2 component was strongest, predominantly due to the π → π* transition of the anthracene moiety. The excitation spectra of the sensitized NIR luminescence showed that the energy transfer process took place predominantly via excitation to the singlet 2A excited state. The estimated quantum yield of the sensitized NIR luminescence showed that for the Er(III) complex, energy loss during relaxation from the resonance level to the emitting level was much greater than that for the Nd(III) complex because of the larger energy gap between the receiving level and the emitting level of the Er(III) ion.

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Notes and references


