Thermally Activated Photophysical Processes of Organolanthanide Complexes in Solution

Waygen Thor, Hei-Yui Kai, Yonghong Zhang, Ka-Leung Wong,* and Peter A. Tanner*

ABSTRACT: The effect of temperature upon the lanthanide luminescence lifetime and intensity has been investigated in toluene solution for the complexes LnPhen(TTA)₃ (Ln = Eu, Sm, Nd, Yb; Phen = 1,10-phenanthroline; TTA = thenoyltrifluoroacetonate). Thermally excited back-transfer to a charge transfer state was found to occur for Ln = Eu and can be explained by lifetime and intensity back-transfer models. The emission intensity and lifetime were also quenched with increasing temperature for Ln = Sm, and the activation energy for nonradiative decay is similar to that for the thermal population of Sm³⁺ excited states. Unusual behavior for lifetime and intensity was found for both Ln = Nd, Yb. The usually assumed equivalence of \( \frac{r}{\tau_0} = I/I_0 \) (where \( r \) is lifetime and \( I \) is intensity) does not hold for these cases. We infer that for these lanthanide systems the intensity decreases with temperature in the stage prior to population of the luminescent state. The lifetime changes are discussed.

For many decades, the unique sharp emission bands and long lifetimes of trivalent lanthanide ions (Ln³⁺) have received attention in diverse fields of application, including light emitting diodes (LEDs) and imaging probes for the biomedical field. More recently, the use of Ln³⁺ ions in thermal sensing, employing homonuclear or heteronuclear complexes, has been a burgeoning field of study. To further this application, the mechanism of thermal quenching needs to be thoroughly investigated and understood. This present work utilizes different Ln³⁺ ions in the same organometallic complex in order to understand and compare the temperature quenching mechanisms.

In organolanthanide complexes, the sensitization of Ln³⁺ is often taken to follow the \( S_0 \rightarrow S_1 \rightarrow T_1 \rightarrow \text{Ln}^{3+} \) pathway, although other mechanisms have been put forward. Emission from a lanthanide ion is observed when the excited state relaxes with the radiative rate \( k_r \) and nonradiative rate \( k_{nr} \) with \( k_r > k_{nr} \). The increase of nonradiative rate with temperature may be due to (i) increased vibrational relaxation to a lower state, (ii) thermally induced energy transfer, or (iii) electron transfer processes. In addition, other processes such as those affecting excitation may change the intensity of emission. It is important to distinguish temperature-dependent and -independent nonradiative losses—whether the quenching occurs before or after the excitation reaches the luminescent state—and this may be possible by comparing emission intensity with lifetime measurements to see if they follow a similar trend.

The emission quenching can be modeled by a simple Arrhenius process with activation energy \( E \) to a higher state such as a triplet in the case of Tb³⁺. Alternatively, a scenario for thermal quenching of luminescence lifetime \( \tau \) or intensity \( I \) due to a single-barrier back-transfer to a triplet state, conduction band, or a charge-transfer (CT) state (Figure 1a) has been modeled by eqs 1 and 2:

\[
\tau(T) = \frac{1}{k_r + \Gamma_0 \exp\left(-\frac{E}{kT}\right)} \tag{1}
\]

and assuming that \( \frac{r(T)}{\tau_i} = \frac{I(T)}{I_0} \) where \( \tau_i = 1/k_i \):

\[
\frac{I(T)}{I_0} = \frac{1}{1 + \frac{k_r}{k_i} \exp\left(-\frac{E}{kT}\right)} \tag{2}
\]

where \( \Gamma_0 \) is the attempt nonradiative rate, \( k \) is the Boltzmann constant, and \( T \) is the temperature.

Various strategies have been applied to optimize the antenna design for the triplet state in light-harvesting for lanthanide ions. These include the chemical variation of the triplet state energy of the lanthanide complex and the tuning of the location of the CT energy level. Since eqs 1 and 2 describe single-barrier back-energy transfer, the location of the triplet state or the CT state energy level can in principle be estimated using thermal quenching experiments.

In this work, by using the same complex LnPhen(TTA)₃ (Phen = 1,10-phenanthroline; TTA = thenoyltrifluoroacetato-...
nate), we enquire how the mechanisms of thermal quenching properties vary for different Ln3+ ions. The relevant energy level diagrams for the ions are included in Figure S1. The luminescence lifetime and intensity have been recorded at different temperatures for each complex dissolved at low concentration in toluene solution. We have chosen this complex because it is well-researched21 and gives efficient luminescence for Ln3+.22–24 The materials, syntheses, and instrumental details are presented in the Supporting Information.

Our complexes have been characterized spectroscopically (Figure 1b) and by DFT25 (Figure 1c). The FTIR spectra of solid LnPhen(TTA)3 (Figure 1b) are similar and show that the coordination of the antennae to the Ln3+ does not change.
across the series. The calculated vibrational frequencies of SmPhen(TTA)$_3$ are in agreement with the experimental data (Figure S2). The electronic absorption spectra of LnPhen(TTA)$_3$ (Ln = Eu, Sm, Yb, and Nd) decreases with increasing temperature. The ligand singlet level lies below the lanthanide energy levels for Ln = Y, La, and Gd, and hence, ligand–metal ion energy transfer does not occur in those cases. We now discuss the results from individual lanthanide ions in turn, starting with Eu$^{3+}$, for which the $^5D_0$ level is situated at more than 11 900 cm$^{-1}$ above the next-lowest level, $^7T_{6}$ so that multiphonon relaxation is slow. The dominant mechanism for temperature quenching should then involve back-energy transfer to an excited state. The variation of the emission intensity of $^{3}D_0$ to $^{3}F_0$ is shown in Figure S5b. Presumably, the lower activation energy in this temperature range corresponds to back-transfer to $^5D_1$ and to the triplet state. The nature of this excited level is now considered. Figure S7 shows that for Ln = Gd, Y, and La, the ligand triplet state is located at $\sim$488 nm (20 480 $\pm$ 50 cm$^{-1}$). The energy gap from $^3D_0$ at 17242 cm$^{-1}$ is only 3238 cm$^{-1}$, which is considerably smaller than the calculated activation energy. Back-energy transfer to $^3D_1$ (at 4180 cm$^{-1}$) is also discounted. Berry et al. have attributed the back-energy transfer in solid-state europium tris(2,2,6,6-tetramethyl-3,5-heptanedionato) (hereafter abbreviated to Eu(thd)$_3$) to a charge transfer state. We plot their data according to the simple Arrhenius model in Figure S8a. The $^3D_0$ nonradiative rate is very small and constant up to 236 K, and it increases. We fitted the rising linear portion to give the activation energy of 4076 $\pm$ 41 cm$^{-1}$. There is no evidence for dominant back-transfer to a second state above the temperature of 290 K. The analogous plot of our lifetime data is presented in Figure S8b, and a linear fitting with an activation energy of 4712 $\pm$ 50 cm$^{-1}$ is obtained above 297 K. The portion to lower temperature in this figure exhibits a lower activation energy (roughly 2580 $\pm$ 166 cm$^{-1}$ from five data points), just like the portion between 236–290 K in Figure S8a. Presumably, the lower activation energy in this temperature range corresponds to back-transfer to $^5D_1$ and to the triplet state.

Generally, although other parameters may be involved, the charge transfer energy can be related to the electric dipole/magnetic dipole ratio of the emission spectrum, since the $^3D_0$ $\rightarrow$ $^3F_1$ Eu$^{3+}$ emission intensity can be enhanced, whereas $^3D_0$ $\rightarrow$ $^3F_1$ is not, to first order. The degree of enhancement is inversely proportional to the energy separation of the CT band from that of $^3D_0$. Taking the ratio $(^3D_0 \rightarrow ^3F_2)/(^3D_0 \rightarrow ^3F_1) = R$ as an illustration, the value of $R$ for Eu(thd)$_3$ is 19.9, whereas it is 13.0 for EuPhen(TTA)$_3$. The charge transfer band is therefore expected at higher energy in the present case than for Eu(thd)$_3$.

The charge transfer vertical transition state for EuPhen(TTA)$_3$ is estimated at 385 nm (25 974 cm$^{-1}$) from the subtraction of the EuPhen(TTA)$_3$ and GdPhen(TTA)$_3$.

Figure 3. (a) Visible and (b) NIR emission spectra of 10 $\mu$M SmPhen(TTA)$_3$ in toluene as a function of temperature after a Jacobian correction to energy scale. The insets show the integrated area of $^4G_{5/2} \rightarrow ^6H_{15/2}$ (visible) and $^4G_{5/2} \rightarrow ^6F_{5/2}$ (NIR) Sm$^{3+}$ emission with temperature. The fits using eq 2 are displayed in olive. Purple: lowest temperature; red: highest temperature, as in Figure 2.
As noted by Blasse et al.,

the location of the vertical charge transfer transition energy may differ appreciably from that of the intersection of the \(4f^{6}7F_j\) level manifold with the charge transfer state given by \(E\).

We move on to the quenching of \(\text{Sm}^{3+}\) emission in both the visible (below 565 nm) and near-infrared (below \(\sim 880\) nm) regions, which occurs from the same luminescent state, \(4G_{5/2}\), at \(\sim 17\,700\) cm\(^{-1}\). The emission spectra of \(\text{SmPhen(TTA)}_3\) in toluene are displayed in Figure 3 a,b as a function of temperature. The charge transfer state of \(\text{SmPhen(TTA)}_3\) is calculated to lie at \(9103\pm1231\) cm\(^{-1}\) above that of \(\text{EuPhen(TTA)}_3\) so that back-energy transfer to this state does not occur at the temperatures investigated. The next-lowest level, at \(\sim 9200\) cm\(^{-1}\) below \(4G_{5/2}\), is \(6F_{9/2}\) and using the equation for the temperature dependence of multiphonon relaxation rate for weak coupling

\[
k_{nr} = k_{nr}(0)[1 + n_{eff}]^p \tag{3a}
\]

\[
n_{eff} = (e^{\hbar\nu/kT} - 1)^{-1} \tag{3b}
\]

where \(\nu\) is an effective phonon frequency and \(p\) is the order of the process, it is not possible to obtain a data fit using sensible values for \(\nu\) and \(p\). The \(4F_{3/2}\) and \(4G_{7/2}\) levels of \(\text{Sm}^{3+}\) are situated at \(\sim 1000\) and \(\sim 2000\) cm\(^{-1}\) above \(G_{5/2}\) respectively,

so that, just as for the following case of \(\text{Nd}^{3+}\), the multiphonon decay rates from these states to \(G_{5/2}\) are very high. The Arrhenius plot of the variation of nonradiative rate with temperature (Figure S10) shows that the activation energy changes with temperature, with the slope of the red line for the highest temperatures measured in Figure S10 giving the activation energy of \(866\pm93\) cm\(^{-1}\). The insets show the integrated areas of the emission transitions \(4F_{3/2} \rightarrow 4I_{13/2}\) and \(2F_{5/2} \rightarrow 2F_{7/2}\) respectively, with temperature with fits using eq 2. The decay curves of \(10\,\mu M\) (b) \(\text{NdPhen(TTA)}_3\), and (d) \(\text{YbPhen(TTA)}_3\) emission in toluene with varying temperature. The insets show the variation in lifetime with temperature with fits by eq 1. Purple: lowest temperature; red: highest temperature, as in Figure 2.

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example, \(Y_{\text{Al}_{2}O_{3}}\) \(\text{Nd}^{3+}\) (1 at. %), where the radiative and measured lifetimes are 250 and 228 \(\mu\text{s}\), respectively,\(^{34}\) because the \(\approx 5100 \text{ cm}^{-1}\) gap to \(4^1\text{I}_{15/2}\) can be spanned by three \(\approx 1600 \text{ cm}^{-1}\) vibrations in the present case. The decrease in emission intensity and yet increase in lifetime is intriguing, because they follow the same trend in Figure S11a but in fact work in opposite directions (Figure S11b). The excitation wavelength is similar in these experiments: 349 nm for the intensity measurement and 355 nm for the lifetime measurement. The difference between these lifetime and intensity plots shows an energy loss prior to entering the \(4^3\text{I}_{15/2}\) state, presumably during transfer from the ligand. The state above \(4^3\text{I}_{15/2}\) (i.e., \(4^3\text{F}_{7/2}\)) has a greater oscillator strength for the emission transition to the electronic ground state and a shorter luminescence lifetime than \(4^3\text{F}_{7/2}\) (for example, see refs 35 and 36). In fact, the decrease in \(4^3\text{F}_{7/2}\) lifetime with decreasing temperature has been found by other authors, particularly in crystals with a higher concentration of \(\text{Nd}^{3+}\), and attributions to cross-relaxation, self-absorption, and multisite effects have been discounted as the major reason by Turri et al.\(^{37}\) We consider that the change in lifetime with temperature could result from (i) thermalization within the two Kramers doublets of \(4^3\text{F}_{7/2}\) and/or (ii) back-energy transfer to \(\text{Nd}^{3+}\) \(4^3\text{F}_{3/2}\) from a trap, such as \(\text{Yb}^{3+}\) present in the sample. The lifetime of the \(2^3\text{F}_{7/2}\) state of \(\text{Yb}^{3+}\) in \(\text{YbPhen(TTA)}_3\) (see below) is longer than that of the \(4^3\text{I}_{15/2}\) \(\text{Nd}^{3+}\) state in \(\text{NdPhen(TTA)}_3\) and it is situated at \(\approx 1150 \text{ cm}^{-1}\) to lower energy (i.e., \(-1150 \text{ cm}^{-1}\)). The three-parameter single-barrier fit eq 1 to the lifetime data in Figure 4b in the inset gives the values \(k_i = (9.6 \pm 0.1) \times 10^8 \text{ s}^{-1}\), \(\Gamma_0 = 22 \pm 34 \text{ s}^{-1}\), and \(E = -1699 \pm 293 \text{ cm}^{-1}\). However, the adjusted coefficient of determination, \(R^2_{\text{adj}} = 0.99072\) and the value of \(k_i\) would infer a quantum yield around 90%. Restraining the quantum yield to less than 50% and using separate fits to the two fairly linear portions of the curve gives much smaller values of \(E\) around \(-150 \text{ cm}^{-1}\).

The \(4^3\text{F}_{7/2}\) system \(\text{Yb}^{3+}\) comprises only two \(2^1\text{I}_{15/2}\) multiplet terms: the ground state term \(2^3\text{F}_{7/2}\) (comprising four Kramers doublets) and the excited \(2^3\text{F}_{5/2}\) term at \(\approx 10,200 \text{ cm}^{-1}\) (comprising three Kramers doublets) (Figures S1 and S12a). The temperature variation of the \(\text{YbPhen(TTA)}_3\) emission spectrum and lifetime are displayed in Figure 4c,d. The spectrum has previously been reported at slightly higher resolution, with an estimated quantum yield of 0.16%.\(^{38}\) The lifetime does not show a significant change when the concentration in toluene is increased by a factor of 10 (Figure S12b) showing that solvent quenching effects may not be very important. Although the trends of intensity and lifetime are similar in Figure S12c, over the temperature range studied, the lifetime only increases by a factor of 1.01, whereas the intensity decreases by a factor of 1.38 (Figure S12d). The single-barrier quenching model, eq 2, gives the activation energy for Figure 4c of \(954 \pm 210 \text{ cm}^{-1}\), with the fit shown in the inset. Similar to the trap in \(\text{NdPhen(TTA)}_3\), this is in reasonable agreement with the separation of \(\approx 1150 \text{ cm}^{-1}\) from the \(4^3\text{I}_{15/2}\) level of \(\text{Nd}^{3+}\). However, the fit of lifetime data in Figure 4d using eq 1 gives the activation energy of \(-1663 \pm 331 \text{ cm}^{-1}\), with a quantum yield of nearly 100%. Using the above quantum yield to estimate \(k_i\) in an Arrhenius equation gives a poor fit \((R^2_{\text{adj}} = 0.955)\) with \(E = -17 \text{ cm}^{-1}\).

In conclusion, we have investigated the occurrence of thermally activated processes occurring near room temperature for \(\text{LnPhen(TTA)}_3\) complexes. Dominant back-transfer from \(\text{Eu}^{3+}\) to a charge-transfer state has been demonstrated for \(\text{Ln} = \text{Eu}\), analogous to the solid-state study of Berry et al.\(^{26}\) The derived energies from the back-transfer model for \(\text{Ln} = \text{Sm}\), \(\text{Nd}\), and \(\text{Yb}\) cannot be linked to the ligand or charge transfer states. \(\text{Ln} = \text{Sm}^{3+}\) exhibits quenching of intensity and lifetime with increasing temperature, and this has been associated with thermal occupation of higher levels. By contrast, \(\text{Ln} = \text{Nd}, \text{Yb}\) exhibit intensity quenching and lifetime lengthening with increasing temperature. The two effects cannot be consistently modeled using the common back-transfer models. We infer that the intensity decrease with increasing temperature is related to the population mechanism from the ligand, whereas the lifetime change with temperature subsequently occurs in the lanthanide excited state. A detailed investigation of the ligand–lanthanide energy transfer is therefore required for these cases.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.2c01350.

**Syntheses; instruments; calculations; energy level diagrams; FT-IR spectra; absorption spectra of \(\text{LnPhen(TTA)}_3\) in toluene; trends in intensity and lifetime for \(\text{EuPhen(TTA)}_3\); fitting of \(\text{EuPhen(TTA)}_3\) lifetime and intensity data vs temperature; emission spectra of \(\text{LnPhen(TTA)}_3\) in 10 \(\mu\text{M}\) toluene; Arrhenius plots of \(\text{Eu(phen)}_3\) and \(\text{EuPhen(TTA)}_3\) absorption spectra of \(\text{LnPhen(TTA)}_3\); plots of functions of lifetime and integrated intensity data as a function of temperature and inverse temperature for \(\text{NdPhen(TTA)}_3\); 77 K emission spectrum of \(\text{YbPhen(TTA)}_3\) luminescence decay of \(\text{YbPhen(TTA)}_3\) in toluene; spectral data plots of \(\text{YbPhen(TTA)}_3\) versus temperature and inverse temperature (PDF)

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