

# Visible-Light Excitation of Infrared Lanthanide Luminescence via Intra-Ligand Charge-Transfer State in 1,3-Diketonates Containing Push-Pull Chromophores

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A new 1,3-diketonato ligand containing both an electron-donor [4-(dimethylamino)benzene] and an electron-acceptor (4-nitrobenzene) group and its lanthanide complexes have been prepared. They display an intense intra-ligand charge-transfer absorption transition in the visible region of the spectrum

at 400–550 nm which was utilized to achieve visible-light excitation of metal-centred infrared luminescence of Nd<sup>III</sup>, Er<sup>III</sup> and Yb<sup>III</sup> ions.

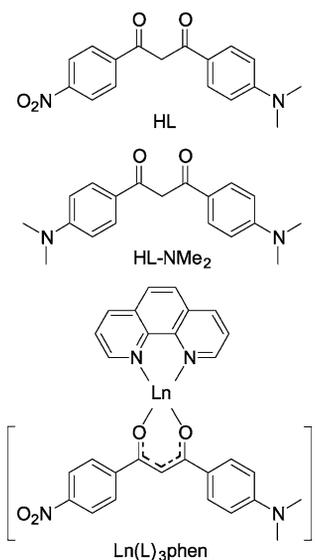
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## Introduction

An ever growing attention is being given to the lanthanide ions Nd<sup>III</sup>, Er<sup>III</sup> and Yb<sup>III</sup> which display a long-lived metal-centred luminescence in the near-infrared (NIR) range of the spectrum at 800–2000 nm.<sup>[1–3]</sup> This interest is stirred by potent applications in telecommunications, bioanalyses, and medicine. The forbidden nature of the f-f transitions in trivalent lanthanide ions results in a very weak intensity of the metal-centred absorption bands. As a result one has to coordinate a suitable chromophore to the lanthanide ion and to rely on energy transfer in order to achieve efficient excitation of the metal ion.<sup>[4]</sup> Whereas energy transfer from the triplet state of the chromophore moiety is often a preferred (and commonly invoked) pathway for the sensitization of the metal ion luminescence, several other mechanisms can be operative, which involve the ligand singlet state,<sup>[5,6]</sup> metal-to-ligand charge-transfer (MLCT) states,<sup>[4]</sup> or intra-ligand charge-transfer (ILCT) states.<sup>[7–9]</sup> One of the challenges in the design of luminescent lanthanide tags, particularly those aimed at bioanalyses and bioimaging, is to shift the excitation wavelength from the UV to the visible range, for both an intrinsic reason, since biomolecules are usually damaged by UV light, and a practical one, visible excitation requiring cheaper optical cells and optics. Several strategies have been proposed towards this goal, for instance excitation through d-metal ions,<sup>[2,4,10]</sup> by multiphoton excitation,<sup>[11–14]</sup> or via ILCT states<sup>[7–9,15]</sup> which may have relatively low energy. For instance, we recently showed that energy can be transferred from bodipy (a boradiazaindacene-appended terpyridine

with maximum absorption at 529 nm) to Nd<sup>III</sup>, Er<sup>III</sup>, and Yb<sup>III</sup>.<sup>[16]</sup>

1,3-Diketones form stable lanthanide complexes and display intense absorption transitions, and thus have been extensively used to prepare luminescent lanthanide materials.<sup>[17]</sup> However, most of the 1,3-diketones employed so far with lanthanides absorb light mostly in the UV range, at wavelengths < 400 nm.<sup>[17–19]</sup> Only a few examples of lanthanide 1,3-diketonates are reported in which the absorption spectrum of the donor ligand and the energy of its triplet state are redshifted by incorporation of a condensed aromatic group,<sup>[20,21]</sup> ferrocene,<sup>[22]</sup> or a conjugated polyene chain.<sup>[23]</sup> Herein we adopt a simple approach for redshifting the absorption spectrum of the 1,3-diketonato ligand by incorporating both an electron-donor and an electron-



Scheme 1. Structures of the new 1,3-diketones and the lanthanide complexes with L<sup>-</sup>.

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acceptor group into the ligand. This creates a low-energy absorption having an intra-ligand charge-transfer character. To illustrate the concept, two new 1,3-diketones, HL and HL-NMe<sub>2</sub> (Scheme 1) and the lanthanide complexes with ligand HL are prepared, characterized, and their photo-physical properties reported.

## Results and Discussion

### Synthesis

The ligand HL was obtained as a bright red solid in 33% yield by Claisen condensation of 4-(dimethylamino)acetophenone with methyl 4-nitrobenzoate. It is present mainly as enol form (>95%) in solutions in chloroform and dmsol. The lanthanide complexes [LnL<sub>3</sub>phen] (phen = 1,10-phenanthroline) were obtained as dark red solids in 70–85% yield by a known procedure.<sup>[24]</sup> <sup>1</sup>H NMR spectroscopy of the diamagnetic La<sup>III</sup> complex recorded in dmsol solution confirmed the 3:1 (L<sup>-</sup>/phen) ratio and also indicated that the ternary ligand phen is not coordinated to metal ions in this solvent; the complex is therefore present as a solvate, [LnL<sub>3</sub>(dmsol)<sub>n</sub>].

The symmetrical ligand HL-NMe<sub>2</sub> was obtained as a bright yellow solid in 70% yield by Claisen condensation of 4-(dimethylamino)acetophenone with ethyl 4-(dimethylamino)benzoate. It is present as 80% enol and 20% ketone in solutions in chloroform and dmsol. Attempts to prepare lanthanide complexes [Ln(L-NMe<sub>2</sub>)<sub>3</sub>phen] were unsuccessful (the synthetic procedure is provided in the Supporting Information). This may be the result of low acidity of ligand HL-NMe<sub>2</sub> due to the presence of electron-rich dimethylamino groups. Further discussion of HL-NMe<sub>2</sub> will be limited to a comparison of its spectroscopic properties with ligand HL.

### Crystal Structures

The structures of the ligand HL and its Nd<sup>III</sup> complex were determined by X-ray crystallography. The ligand HL is nearly planar (Figure 1). The angles between the planes defined by the 1,3-diketone central moiety and the benzene rings of either the nitrophenyl or (dimethylamino)phenyl groups are 3.58° and 7.64°, respectively. These planar molecules are packed in a column-like structure running along the crystallographic *a*-axis. Within the column, the 1,3-diketone moieties of the molecules are oriented in the same

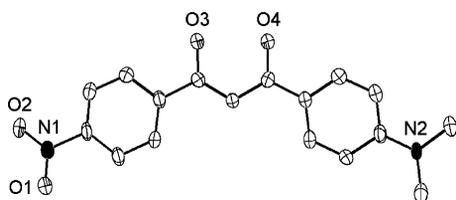


Figure 1. Structure of the ligand HL (50% probability ellipsoids, H atoms omitted).

direction, while the electron-rich (dimethylamino)phenyl group of one molecule is situated above the electron-deficient nitrophenyl group of another molecule resulting in an aromatic  $\pi$ - $\pi$  interaction (the molecules in the neighbouring layers are almost parallel with an average interplanar distance of around 3.39 Å).

In the structure of the complex, the Nd<sup>III</sup> ion is octacoordinated by six oxygen atoms from three ligands L<sup>-</sup> and two nitrogen atoms from phen. The Nd–O bond lengths are in the range 2.369(6)–2.420(6) Å (mean 2.386 Å), while the Nd–N bond lengths are 2.662(7) Å and 2.683(7) Å (Figure 2). The coordination polyhedron around Nd<sup>III</sup> can be best described as a square antiprism with two square faces comprised of atoms N(1), N(2), O(4), O(3) and O(1), O(2), O(5), O(6), respectively. The Nd<sup>III</sup> is situated out of the plane of the 1,3-diketonato ring, the angles between the planes defined by Nd–O–O and O–C–C–O atoms (where C and O atoms belong to a given 1,3-diketonato ring) are 12.99°, 20.18° and 20.91° for the three ligands. The Nd<sup>III</sup> ion also lies out of the plane of the 1,10-phenanthroline chelate ring, the angle between the planes defined by Nd–N(1)–N(2) and N(1)–N(2)–C(56)–C(57) atoms being 13.54°.

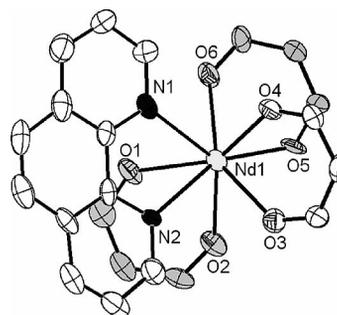
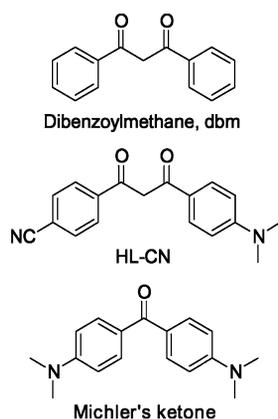


Figure 2. Structure of the complex [NdL<sub>3</sub>phen] as viewed down the square face of a square-antiprismatic coordination polyhedron of Nd<sup>III</sup> centre (50% probability ellipsoids, H atoms, co-crystallized solvent molecules and phenyl groups of the 1,3-diketonato ligands omitted). Selected bond lengths [Å] and angles [°]: Nd(1)–O(3) 2.369(6), Nd(1)–O(6) 2.371(6), Nd(1)–O(2) 2.373(6), Nd(1)–O(5) 2.386(6), Nd(1)–O(4) 2.397(6), Nd(1)–O(1) 2.420(6), Nd(1)–N(1) 2.662(7), Nd(1)–N(2) 2.683(7); O(2)–Nd(1)–O(1) 69.3(2), O(3)–Nd(1)–O(4) 70.06(18), O(6)–Nd(1)–O(5) 70.27(19), N(1)–Nd(1)–N(2) 61.1(2).

Only one of the three 1,3-diketonato ligands is relatively planar. It is involved in an aromatic  $\pi$ - $\pi$  interaction with the “planar” 1,3-diketonato ligand of another molecule; the corresponding plane-to-plane distance is 3.401 Å [the planes were calculated by including all atoms in the ligand apart from the NO<sub>2</sub> and N(CH<sub>3</sub>)<sub>2</sub> groups]. The interacting pair of “planar” 1,3-diketonato ligands are related by a centre of inversion so that an electron-rich (dimethylamino)-phenyl group of one ligand is situated above an electron-deficient nitrophenyl group of another, similar to the situation observed in the structure of ligand HL. The ligand phen is nearly planar and is involved in aromatic  $\pi$ - $\pi$  interaction with a phen ligand of another molecule; the corresponding plane-to-plane distance is 3.502 Å. The “planar”

1,3-diketonato ligand is found in “*trans*” position to the phen ligand in the coordination sphere of Nd<sup>III</sup>. The aromatic  $\pi$ - $\pi$  interactions that both of these ligands are involved in, results in the packing of molecules in a chain-like structure running along the crystallographic *c*-axis (Figure S1, Supporting Information). The inter-chain interaction is supported by weaker aromatic  $\pi$ - $\pi$  interactions between “non-planar” 1,3-diketonato ligands.

Comparison of the structure of [NdL<sub>3</sub>phen] with that reported for a model complex [Nd(dbm)<sub>3</sub>phen] (dbm = dibenzoylmethane, Scheme 2)<sup>[25]</sup> reveals somewhat slightly longer bonds in the case of [Nd(dbm)<sub>3</sub>phen], which are in the range 2.379–2.425 Å for Nd–O bonds (mean: 2.393) and 2.692 Å and 2.699 Å for Nd–N bonds. However, in sharp contrast to [NdL<sub>3</sub>phen], the chelate rings in [Nd(dbm)<sub>3</sub>phen] are much closer to planarity, the corresponding angles are 4.99°, 7.13° and 8.91°, for 1,3-diketonato chelate rings, and 8.98° for the phen chelate ring.



Scheme 2. Structures of the known ligands discussed in the paper.

At last, it may be noted that intermolecular interaction observed in the crystal structures of ligand HL and its Nd<sup>III</sup> complex may explain the low solubility of these compounds in common organic solvents.

### Photophysical Properties

The absorption spectrum of ligand HL (Figure 3) displays two bands with maxima at 339 (log  $\epsilon$  = 4.25) and 442 nm (log  $\epsilon$  = 4.38). The low-energy band at 442 nm, which determines the intense red colour of the ligand, is likely a transition with intra-ligand charge-transfer character, wherein the dimethylamino group serves as an electron donor and both 1,3-diketonone and nitro groups serve as electron acceptors. The charge-transfer absorption band of ligand HL is redshifted by 25 nm compared to the one reported for the 4-cyanophenyl analogue HL-CN (Scheme 2,  $\lambda_{\text{max}}$  = 417 nm in polar solvents),<sup>[26]</sup> probably due to the stronger electron-acceptor properties of the nitro substituent relative to the cyano group. The role of the 1,3-diketonato moiety as an electron acceptor in a charge-transfer transition in ligand HL was confirmed by comparison with HL-NMe<sub>2</sub>. The ligand HL-NMe<sub>2</sub>, which lacks the nitro group,

still displayed a low-energy absorption at 436 nm due to a charge transfer from the dimethylamino group to the 1,3-diketonato moiety (Figure S2, Supporting Information). One may consider HL-NMe<sub>2</sub> as an analogue of Michler's ketone (Scheme 2) – a push-pull chromophore, which was shown to be an excellent sensitizer of lanthanide luminescence.<sup>[27]</sup>

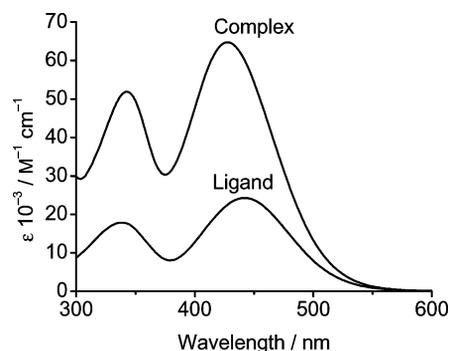


Figure 3. Absorption spectra of the ligand HL ( $2.69 \times 10^{-4}$  M) and the complex [YbL<sub>3</sub>phen] ( $1.26 \times 10^{-4}$  M) in dmso solution.

In fact, similar 1,3-diketones containing 4-(dialkyl- or diarylamino)phenyl groups reported in the literature<sup>[15,26,28–32]</sup> also display a low-energy absorption band which was shown by spectroscopic measurements<sup>[26,28]</sup> and calculations<sup>[31]</sup> to be of a charge-transfer nature. In comparison, the lowest-energy absorption transition in dibenzoylmethane and bis(*p*-nitrobenzoyl)methane – model 1,3-diketones which do not contain donor groups – occurs in the onset of the UV range at 352 nm and 362 nm,<sup>[17]8</sup> respectively (Figure S2, Supporting Information).

Upon coordination to a lanthanide ion, the visible absorption band of the ligand HL is blueshifted by 14–19 nm (Figure 3, Figure S3 in the Supporting Information), while the UV band at 334 nm experiences no spectral shift. The intensity of the UV band in the complexes [ $\epsilon$  =  $(5.2–5.6) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ] is about threefold higher than its intensity in the neutral ligand [ $\epsilon$  =  $1.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ] as would be expected in a tris complex. At the same time the intensity of the visible band in the complexes [ $\epsilon$  =  $(5.5–6.5) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ] is less than threefold higher than the neutral ligand [ $\epsilon$  =  $2.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ]. The ligand-centred visible absorption band gains intensity moving from lighter to heavier lanthanides and is redshifted probably due to the increased Lewis acidity of the metal ion, while no significant changes occur in the UV band.

The ligand HL and its La<sup>III</sup> and Gd<sup>III</sup> complexes do not display any emission in dmso solution at room temperature. No emission could be detected from the Gd<sup>III</sup> complex in dmso glass at 77 K either, but weak emission is seen in the solid state at 77 K. It consists of two very broad bands centred at 526 and 723 nm, which are tentatively assigned to the fluorescence and phosphorescence of the coordinated ligand L<sup>−</sup>, respectively (Figure S4) (the first excited state of Gd<sup>III</sup> is located above  $32000 \text{ cm}^{-1}$ <sup>[33]</sup> and thus cannot accept energy from the ligand; as a result, Gd<sup>III</sup> chelates generally display ligand-centred photophysical processes only).

Attempts to enforce a time delay (10  $\mu$ s) in the luminescence measurements resulted in the complete disappearance of both bands. Attempts to measure the lifetime of the emission band at 723 nm failed due to weak intensity and an apparent poly-exponential decay profile; however, the long timescale of the decay up to a microsecond range is consistent with a phosphorescence process. The energy of the 0–0 transition of the triplet state of ligand L<sup>-</sup>, estimated to be around 16500 cm<sup>-1</sup> from the onset of the phosphorescence band, indicates that this ligand is potentially suitable for the sensitization of infrared emission of lanthanide ions.

Indeed, [LnL<sub>3</sub>phen] complexes (Ln = Nd, Er, and Yb) display a characteristic line-like infrared emission due to f–f transitions upon excitation in ligand absorption bands, both in the solid state and in solutions in dmsO (Figure 4). Luminescence spectra of the lanthanide complexes are red-shifted by 3–11 nm in solution compared to the solid state (Figure 4, Figures S5, S6), a fact we trace back to the dissociation of the ancillary phen ligand in solution (see discussion of <sup>1</sup>H NMR spectra above). Energies of the bands in the excitation spectra of the Nd<sup>III</sup> and Yb<sup>III</sup> complexes (Figures S7, S8) match those of the absorption spectra, thus confirming that the ligand sensitizes lanthanide luminescence. We note, however, that the band intensity in absorption and excitation spectra is similar for the Nd<sup>III</sup> complex (Figure S7) but is different in the case of Yb<sup>III</sup>: excitation of Yb<sup>III</sup> within the visible absorption band is less efficient compared to the UV band (Figure S8). The reason for this difference between Nd<sup>III</sup> and Yb<sup>III</sup> is not clear, but it may be traced back to the fact that excitation of Yb<sup>III</sup> ion in its complexes may occur through a double electron transfer<sup>[34]</sup> in addition to a common phonon-assisted transfer mechanism.<sup>[35,36]</sup> The excitation spectrum of Er<sup>III</sup> could not be recorded due to weak emission intensity.

The luminescence decays of the [LnL<sub>3</sub>phen] complexes are in all cases single exponential functions, indicating the presence of either only one emitting centre (in solution or solid state) or rapid equilibrium between different species in solution. The luminescence lifetimes ( $\tau$ , Table 1) in solution are about 1.5-fold longer than in the solid state which might indicate the presence of intermolecular quenching

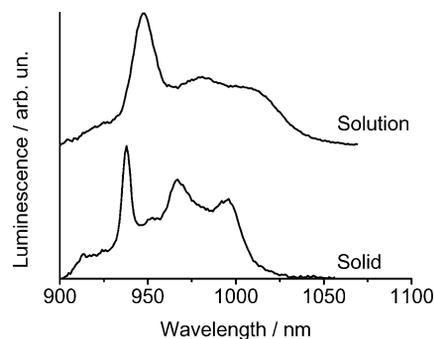


Figure 4. Corrected and normalized luminescence spectra of [YbL<sub>3</sub>phen] in dmsO solution ( $1.8 \times 10^{-6}$  M) and in the solid state at room temperature under excitation at 430 nm.

processes in the solid state. The complexes are photo-stable in dmsO solution but undergo some photochemical decomposition in the solid state during photophysical experiments, as evidenced by gradual reduction of the absolute quantum yield in a series of consecutive experiments. At the same time, the luminescence decays of the solid-state sample are still single exponential functions, and the associated lifetimes do not vary in consecutive experiments, indicating that the products of photo-decomposition do not contribute to the observed emission.

Absolute quantum yields of the metal-centred luminescence upon ligand excitation ( $Q^{Ln}_L$ ) of the new complexes in solution turned out to be an order of magnitude lower than those of other lanthanide complexes with 1,3-diketones. For example, the emission quantum yield for the model compound [Yb(dbm)<sub>3</sub>phen] was reported to be  $5.9 \times 10^{-3}$  in toluene solution,<sup>[37]</sup> whereas for the new [YbL<sub>3</sub>phen] complex it only amounts to  $4.0 \times 10^{-4}$  in dmsO. The  $Q^{Ln}_L$  in a simplified form can be expressed as  $Q^{Ln}_L = \eta \times Q^{Ln}_{Ln}$ , where  $\eta$  is a ligand-to-metal energy transfer (sensitization) efficiency and  $Q^{Ln}_{Ln}$  is an intrinsic quantum yield of a lanthanide ion. A rough estimate of the intrinsic quantum yield  $Q^{Ln}_{Ln} = \tau_{obs}/\tau_{rad}$ , taking accepted literature values<sup>[2]</sup> for the radiative lifetimes (0.42 ms for Nd<sup>III</sup> and 2 ms for Yb<sup>III</sup>), gives  $Q^{Nd}_{Nd} = 2.9 \times 10^{-3}$  and  $Q^{Yb}_{Yb} = 6 \times 10^{-3}$ , leading to very low ligand-sensitization efficiencies

Table 1. Spectroscopic properties of ligand HL, its lanthanide complexes, and related 1,3-diketones at room temperature.

Compound	Absorption (dmsO) <sup>[a]</sup> $\lambda_{max}/nm$ (log $\epsilon$ )	$\lambda_{max}/nm$ (dmsO, solid)	Luminescence <sup>[b]</sup>	
			$\tau/\mu s$ , $Q^{Ln}_L$ (dmsO)	$\tau/\mu s$ (solid) <sup>[c]</sup>
HL	442 (4.38), 339 (4.26)	[d]		
[LaL <sub>3</sub> phen]	424 (4.75), 342 (4.74)	[d]		
[NdL <sub>3</sub> phen]	424 (4.75), 341 (4.74)	1062, 1059	1.2, $7.8 \times 10^{-5}$	0.71
[GdL <sub>3</sub> phen]	423 (4.74), 340 (4.75)	[d]		
[ErL <sub>3</sub> phen]	426 (4.77), 341 (4.73)	1520, 1509	1.9 <sup>[e]</sup>	1.4
[YbL <sub>3</sub> phen]	428 (4.81), 343 (4.72)	948, 938	12, $4.0 \times 10^{-4}$	8.6
HL-NMe <sub>2</sub>	436 (4.76), 352 (1.26)			
dbm	352 (4.34)			

[a] Spectra were recorded in the spectral range 300–800 nm. Estimated errors are  $\pm 1$  nm for  $\lambda_{max}$  and  $\pm 5\%$  for  $\epsilon$ . The concentration of the samples was in the range  $(8\text{--}27) \times 10^{-5}$  M. The complexes were present in dmsO solution in the form of solvates [LnL<sub>3</sub>(dmsO)<sub>n</sub>]. [b] At room temp. with  $\lambda_{exc} = 355$  ( $\tau$ ) and 430 nm ( $Q^{Ln}_L$ ). Estimated error on  $Q^{Ln}_L$  is  $\pm 15\%$ . The concentration of the complexes was  $(0.2\text{--}13) \times 10^{-5}$  M. The complexes were present in dmsO solution in the form of solvates [LnL<sub>3</sub>(dmsO)<sub>n</sub>]. [c] Photochemical degradation of the sample (see text); the lower-limit estimation for  $Q^{Yb}_L$  in solid state is 0.20%. [d] The compounds did not display emission under stated conditions. [e] Luminescence quantum yield could not be determined as a result of a low emission intensity.

of 2.7 and 6.7%, respectively. In the case of [Yb(dbm)<sub>3</sub>phen] ( $\tau = 10.3 \mu\text{s}$ ) similar calculations give  $Q_{\text{Yb}}^{\text{Yb}} = 5 \times 10^{-3}$  and a ligand-sensitization efficiency of 87%. Therefore, the observed difference between [YbL<sub>3</sub>phen] and [Yb(dbm)<sub>3</sub>phen] complexes lies in a less efficient ligand-to-metal energy transfer in the case of ligand L<sup>-</sup>, probably as a result of fast electronic energy loss within the ligand which competes with the energy-transfer step. The energy transfer is, however, significantly improved in the solid-state sample of [YbL<sub>3</sub>phen] which displays a quantum yield equal to  $2.0 \times 10^{-3}$  (a lower limit estimate due to a photochemical decomposition). The corresponding lifetime is 8.6  $\mu\text{s}$  which results in  $Q_{\text{Yb}}^{\text{Yb}} = 4.3 \times 10^{-3}$  and a ligand-sensitization efficiency of 47% (again, a lower limit estimate). This difference may indicate that in dmsO solution the average metal–ligand bonds are longer than in the solid state probably due to a partial dissociation of the 1,3-diketonato ligand<sup>[38]</sup> which leads to a diminished energy-transfer efficiency.

## Conclusion

We have demonstrated that 1,3-diketonato ligands containing push-pull chromophores are suitable for visible-light excitation of NIR-emitting lanthanide ions. The main advantage of the ligand L<sup>-</sup> is its lowest-energy absorption transition which extends into the visible range and allows excitation of lanthanide luminescence with wavelengths up to 550 nm. For instance, the overall luminescence efficiency of the Yb<sup>III</sup> complex,  $\epsilon \times Q_{\text{L}}^{\text{Ln}}$ , is  $26 \text{ M}^{-1} \text{ cm}^{-1}$  at 428 nm (absorption maximum in the visible range),  $5.2 \text{ M}^{-1} \text{ cm}^{-1}$  at 500 nm, and ca.  $0.4 \text{ M}^{-1} \text{ cm}^{-1}$  at 550 nm. However, further improvement of the ligand design ought to be implemented to increase the energy-transfer efficiency and photostability. If successful, these ligands might be used in the design of lanthanide complexes with NIR emission and, possibly, metal complexes with non-linear optical properties. This aspect is being presently investigated in our laboratory.

## Experimental Section

**Chemicals and General Procedures:** Chemicals obtained from commercial suppliers were used without further purification. Elemental analyses were performed by Dr. E. Solari, Service for Elemental Analysis, Institute of Chemistry and Chemical Engineering Sciences (EPFL). Absorption spectra were measured with a Perkin–Elmer Lambda 900 UV/Vis/NIR spectrometer. <sup>1</sup>H NMR spectra (presented as  $\delta$  in ppm and  $J$  in Hz) were recorded with a Bruker Avance DRX 400 MHz spectrometer. Luminescence emission and excitation spectra were measured with a Fluorolog FL 3-22 spectrometer from Horiba-Jobin Yvon-Spex equipped for both Vis and NIR measurements. Quantum-yield data for solid samples and for solutions were determined with the same instrument, through an absolute method using a home-modified integrating sphere.<sup>[39]</sup> Luminescence lifetimes were measured with a previously described instrumental setup.<sup>[16]</sup> All luminescence spectra were corrected for the instrumental function. Spectroscopic studies in solutions were conducted in dmsO (Fluka, >99.9%, A.C.S. spectrophotometric grade) using optical cells of either 2 or 10 mm path length and quartz capillaries with i.d. of 2 mm. The concentration of the sam-

ples for absorption studies was in the range  $(8\text{--}27) \times 10^{-5} \text{ M}$  and for luminescence studies in the range  $(0.2\text{--}13) \times 10^{-5} \text{ M}$ .

**1,3-Diketone HL:** The reaction was performed under nitrogen using degassed and dry solvents. NaH (Fluka; 55–65% suspension in mineral oil) (110 mg, containing at least 60.5 mg, 2.52 mmol of NaH) was washed with hexane under nitrogen and was suspended in dry THF (4 mL) at room temp. 4-(Dimethylamino)acetophenone (TCI Europe; 250 mg, 1.53 mmol) was added, and the mixture was stirred or sonicated at room temp. for 10 min. The reaction mixture was then cooled to 0 °C. This was followed by addition of methyl 4-nitrobenzoate (Aldrich; 300 mg, 1.66 mmol, small excess) in small portions over 5 min. The colour of the reaction mixture changed instantly from colourless to orange upon addition of the ester. The reaction mixture was stirred at 0 °C for 30 min, warmed to room temp. and stirred with occasional sonication at room temp. for further 2 or 3 hrs. The reaction had an initiation time and was sluggish for the first 1 hr, the colour of the reaction mixture at that stage was dark orange, and both of the starting materials were observed by TLC. The reaction rapidly self-accelerated after about 1 hr and evolved heat while the colour of the mixture changed to dark brownish-red, almost black. At that point both starting materials were completely consumed. The “rapid” stage of the reaction took about 5–10 min to complete, and one should be careful of that when planning a synthesis on a larger scale. The mixture was quenched with methanol, concentrated to dryness and suspended in water. Acetic acid was added to the water, the product was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the organic layer was separated and dried (MgSO<sub>4</sub>). Purification by column chromatography (17 g of silica, eluting with CH<sub>2</sub>Cl<sub>2</sub>) provided a crude product, containing at least three by-products, which was dissolved in CH<sub>2</sub>Cl<sub>2</sub>; ethanol (10 mL) was added, and the CH<sub>2</sub>Cl<sub>2</sub> was evaporated to leave a suspension of pure crystalline product in ethanol. The product was filtered and washed with ethanol (5 mL) and diethyl ether (5 mL). The compound can be re-crystallized in the same manner, if required; the loss of product is minimal due to its very low solubility in ethanol. The compound was soluble in CH<sub>2</sub>Cl<sub>2</sub> up to 3 mg in 1 mL. Bright red solid, yield 157 mg (0.50 mmol, 33%). C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub> (312.32): calcd. C 65.38, H 5.16, N 8.97; found C 65.05, H 4.98, N 9.11. In dmsO, the compound was present as a mixture of 95% enol and 5% ketone. <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]dmsO): enol signals:  $\delta = 8.35$  (s, 4 H), 8.07 (d,  $J = 8.8$  Hz, 2 H), 7.31 (s, 1 H, methine CH), 6.80 (d,  $J = 8.8$  Hz, 2 H), 3.07 (s, 6 H) ppm; some of the ketone signals:  $\delta = 8.18$  (d,  $J = 8.8$  Hz, 2 H), 7.82 (d,  $J = 8.8$  Hz, 2 H), 6.74 (d,  $J = 9.2$  Hz, 2 H), 4.80 (s, 2 H, methylene CH<sub>2</sub>), 3.04 (s, 6 H) ppm.

**Lanthanide Complexes [LnL<sub>3</sub>phen] (Ln = La, Nd, Gd, Er, Yb):** The reaction was performed under air. Ligand HL (50 mg, 0.16 mmol), 1,10-phenanthroline (9.6 mg, 0.053 mmol) and NaOH (6.4 mg, 0.16 mmol, dissolved in 1 mL of water) were suspended in a mixture of boiling ethanol (7 mL) and CH<sub>3</sub>CN (10 mL) and were stirred until the suspension had dissolved to give a red solution. The latter was stirred for additional 5 min, followed by dropwise addition of the appropriate lanthanide chloride hydrate (Aldrich; 0.053 mmol) dissolved in 2 mL of ethanol. This resulted in the formation of a dark red precipitate which was stirred at reflux for 15 min. The suspension was filtered while hot, and the resulting solid was washed with CH<sub>3</sub>CN, a 1:1 mixture of ethanol/water, ethanol, and finally diethyl ether. The complexes were obtained as deep-red solids and were soluble in CH<sub>2</sub>Cl<sub>2</sub> and dmsO (upon slight warming) with the solubility significantly decreasing for heavier lanthanides. [LaL<sub>3</sub>phen]·H<sub>2</sub>O: Yield 47 mg (0.037 mmol, 70%). C<sub>63</sub>H<sub>53</sub>LaN<sub>8</sub>O<sub>12</sub>·H<sub>2</sub>O (1271.06): calcd. C 59.53, H 4.36, N 8.82; found C 59.82, H 4.33, N 8.85. <sup>1</sup>H NMR spectrum of the complex in dmsO shows clearly the resolved signals of phen which coincides

with those of “free” phen. This indicates that in dmsO, phen is not coordinated to the lanthanide ion and the complex is present as a solvate  $[\text{LaL}_3(\text{dmsO})_n]$ . The  $^1\text{H}$  NMR spectra of the complex in dmsO at room temp. in the range of the signals of the 1,3-diketone ligand are independent of the concentration in the range  $7.3 \times 10^{-4}$  to  $2.5 \times 10^{-3}$  M and show the presence of a major and a minor species (possibly isomers) in the ratio  $> 10:1$ . The signals of the major and minor species coalesce at higher temperatures in the range 320–340 K. Integration of signal intensities confirms the 1:3 ratio of phen/1,3-diketone in the complex.  $^1\text{H}$  NMR (400 MHz,  $[\text{D}_6]\text{dmsO}$ ): at r.t.: major species:  $\delta = 9.12$  (br. s, 2 H, phen), 8.50 (d,  $J = 7.2$  Hz, 2 H, phen), 8.10–8.25 (m, 12 H), 8.00 (s, 2 H, phen), 7.94 (d,  $J = 8.4$  Hz, 6 H), 7.78 (dd,  $J = 8.0$ ,  $J = 4.4$  Hz, 2 H, phen), 6.72 (s, 3 H, methine CH), 6.64 (d,  $J = 8.8$  Hz, 6 H), 2.98 [s, 18 H,  $\text{N}(\text{CH}_3)_2$ ] ppm; some signals of minor species:  $\delta = 8.3$ –8.4 (br.), 8.3–8.10 (d, br.), 6.78 (s, br.), 6.55–6.65 (d, br.) ppm; at 340 K:  $\delta = 9.11$  (dd, 2 H, phen), 8.48 (dd,  $J = 8.0$ ,  $J = 1.6$  Hz, 2 H, phen), 8.05–8.25 (m, 12 H), 7.98 (s, 2 H, phen), 7.93 (d,  $J = 8.4$  Hz, 6 H), 7.76 (dd,  $J = 8.0$ ,  $J = 4.4$  Hz), 6.55–6.75 (m, 9 H), 2.98 [s, 18 H,  $\text{N}(\text{CH}_3)_2$ ] ppm.  $^1\text{H}$  NMR spectra of the complex in  $\text{CDCl}_3$  are complicated and concentration-dependent due to the partial dissociation of the phen ligand.  $[\text{NdL}_3\text{phen}]\cdot\text{H}_2\text{O}$ : Yield 53 mg (0.042 mmol, 78%).  $[\text{C}_{63}\text{H}_{53}\text{N}_8\text{NdO}_{12}]\cdot\text{H}_2\text{O}$  (1276.40): calcd. C 59.28, H 4.34, N 8.78; found C 59.32, H 4.15, N 8.85. No water molecules coordinated to  $\text{Nd}^{\text{III}}$  were observed in the X-ray structure of the complex.  $[\text{GdL}_3\text{phen}]$ : Yield 57 mg (0.045 mmol, 85%).  $\text{C}_{63}\text{H}_{53}\text{GdN}_8\text{O}_{12}$  (1271.39): calcd. C 59.52, H 4.20, N 8.81; found C 59.03, H 4.29, N 8.55.  $[\text{ErL}_3\text{phen}]$ : Yield 58 mg (0.045 mmol, 85%).  $\text{C}_{63}\text{H}_{53}\text{ErN}_8\text{O}_{12}$  (1281.40): calcd. C 59.05, H 4.17, N 8.74; found C 58.53, H 3.87, N 8.49.  $[\text{YbL}_3\text{phen}]$ : Yield 56 mg (0.044 mmol, 82%).  $\text{C}_{63}\text{H}_{53}\text{N}_8\text{O}_{12}\text{Yb}$  (1287.18): calcd. C 58.79, H 4.15, N 8.71; found C 58.26, H 4.04, N 8.66.

**Synthesis of 1,3-Diketone HL-NMe<sub>2</sub>:** The reaction was performed under nitrogen using degassed and dry solvents. NaH (Fluka; 55–65% suspension in mineral oil) (110 mg, contains at least 60.5 mg, 2.52 mmol of NaH, excess) was washed with hexane and suspended in dry THF (4 mL) at room temp. 4-(Dimethylamino)acetophenone (TCI Europe; 250 mg, 1.53 mmol) was added, and the mixture was stirred or sonicated at room temp. for 10 min. This was followed by addition of ethyl 4-(dimethylamino)benzoate (Acros; 340 mg, 1.76 mmol, small excess). The reaction mixture was refluxed for 7 h to give a viscous yellow suspension. It was quenched by successive addition of methanol (3 mL), acetic acid (3 mL) and water (50 mL). The product was extracted from the resulting bright greenish-yellow suspension with  $\text{CH}_2\text{Cl}_2$ . Purification by column chromatography (18 g of silica, eluting first with  $\text{CH}_2\text{Cl}_2$  to remove impurities and then with 0.2%  $\text{CH}_3\text{OH}$  in  $\text{CH}_2\text{Cl}_2$  to recover the product) provided a crude product. It was dissolved in  $\text{CH}_2\text{Cl}_2$ , ethanol (10 mL) was added and the  $\text{CH}_2\text{Cl}_2$  was evaporated to leave a suspension of pure product in ethanol which was filtered and washed with cold ethanol (5 mL) and cold diethyl ether (5 mL). The compound has a reasonable solubility in ethanol, and recrystallization results in a diminished yield. Yield 332 mg (1.07 mmol, 70%); bright yellow solid.  $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2$  (310.39): calcd. C 73.52, H 7.14, N 9.03; found C 73.58, H 7.15, N 9.05. In dmsO, the compound is present as a mixture of 81% enol and 19% ketone.  $^1\text{H}$  NMR (400 MHz,  $[\text{D}_6]\text{dmsO}$ ): enol signals:  $\delta = 7.96$  (d,  $J = 9.2$  Hz, 4 H), 6.95 (s, 1 H, methine CH), 6.76 (d,  $J = 8.8$  Hz, 4 H), 3.04 (s, 12 H) ppm; ketone signals:  $\delta = 7.80$  (d,  $J = 9.2$  Hz, 4 H), 6.72 (d,  $J = 8.8$  Hz, 4 H), 4.46 (s, 2 H, methylene  $\text{CH}_2$ ), 3.02 (s, 12 H) ppm.

**X-ray Structural Studies:** Single crystals for X-ray analysis were obtained by slow concentration of solutions of HL or  $[\text{NdL}_3\text{phen}]$  in  $\text{CH}_2\text{Cl}_2$ /heptane or  $\text{CH}_2\text{Cl}_2$ /hexane. Data were collected at low

temperature using Mo- $K_\alpha$  radiation. The used equipment was an Oxford Diffraction Sapphire/KM4 CCD for  $[\text{NdL}_3\text{phen}]$  and a Bruker APEX II CCD for HL having both kappa geometry goniometers. Data were reduced by CrysAlis PRO<sup>[40]</sup> in the case of  $[\text{NdL}_3\text{phen}]$  and EvalCCD<sup>[41]</sup> in the case of HL. Semiempirical absorption correction<sup>[42]</sup> was applied to the data sets. Structure solutions and refinements were carried out by SHELXTL.<sup>[43]</sup> Crystal structures were refined using full-matrix least squares on  $F^2$  with all non-hydrogen atoms anisotropically refined. Hydrogen atoms were placed in calculated positions by means of the “riding” model. Disorder problems dealing with the solvent were found for compound  $[\text{NdL}_3\text{phen}]$ , and these were treated by applying some restraints and constraints. Additional crystal data and structure-refinement parameters are provided in Tables S1 and S2. CCDC-666466 and CCDC-666467 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Supporting Information** (see footnote on the first page of this article): Description of an attempted synthesis of  $[\text{La}(\text{L-NMe}_2)_3\text{phen}]$ , crystallographic tables (Tables S1, S2), crystal packing of  $[\text{NdL}_3\text{phen}]$  (Figure S1), additional absorption spectra (Figures S2, S3), luminescence spectra (Figures S4–S6) and luminescence excitation spectra (Figures S7, S8).

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