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SUPPORTING INFORMATION

Title: 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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Attempt to prepare lanthanide complexes [La(L-NMe_2)$_3$Phen].

The reaction was performed under air. Ligand HL-NMe_2 (50 mg, 0.16 mmol), 1,10-phenanthroline (9.7 mg, 0.053 mmol) and NaOH (6.4 mg, 0.16 mmol, dissolved in 1 ml of water) were dissolved in boiling ethanol (9 ml) to give yellow solution. The solution was stirred for 5 min, followed by drop-wise addition of $LaCl_3 \cdot 7H_2O$ (Aldrich, 0.053 mmol) dissolved in 2 ml of ethanol. This resulted in the immediate formation of bright yellow precipitate. After stirring for 15 min at reflux the suspension was filtered while warm; the resulting solid was washed with ethanol, 1:1 mixture of ethanol:water, ethanol again and ether. The yield of the solid was 33 mg. It was soluble in CH_2Cl_2 and dmso. ^{1}H NMR of the solid in dmso contained signals due to 1,3-diketonate ligand and Phen. According to integration of ^{1}H NMR signals, Phen was present in the sample in approx. 1:6 molar ratio relative to 1,3-diketonate ligand, indicating that the synthesis was not successful (the expected ratio was 1:3).

Table S1. Crystal data and structure refinement for HL.

Empirical formula	$C_{17}H_{16}N_2O_4$	
Formula weight	312.32	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 6.8169(14) Å	α= 90°.
	b = 12.179(2) Å	β= 90°.
	c = 34.775(7) Å	γ = 90°.
Volume	2887.1(10) $Å^3$	
Z	8	
Density (calculated)	1.437 Mg/m^3	
Absorption coefficient	0.104 mm^{-1}	
F(000)	1312	
Crystal size	0.75 x 0.16 x 0.07 mm^3	
Theta range for data collection	3.35 to 25.02°.	
Index ranges	-6<=h<=8, -14<=k<=14, -41<=l<=41	
Reflections collected	36574	
Independent reflections	2538 [R(int) = 0.1882]	
Completeness to theta = 25.02°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.4164	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2538 / 0 / 208	
Goodness-of-fit on F^2	1.058	
Final R indices [I>2sigma(I)]	R1 = 0.1018, wR2 = 0.2258	
R indices (all data)	R1 = 0.1868, wR2 = 0.2893	
Largest diff. peak and hole	0.356 and -0.611 $e.Å^{-3}$	

Table S2. Crystal data and structure refinement for $[Nd(L)_3Phen]$.

Empirical formula	$C_{64.15}H_{55.30}Cl_{2.30}N_8NdO_{12}$	
Formula weight	1356.04	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.9664(6) Å	α= 90.803(3)°.
	b = 14.6395(6) Å	β= 94.021(4)°.
	c = 17.3452(7) Å	γ = 113.024(4)°.
Volume	3019.7(2) $Å^3$	
Z	2	
Density (calculated)	1.491 Mg/m^3	
Absorption coefficient	1.032 mm^{-1}	
F(000)	1383	
Crystal size	0.17 x 0.15 x 0.13 mm^3	
Theta range for data collection	2.74 to 25.03°.	
Index ranges	-15<=h<=15, -17<=k<=17, -20<=l<=20	
Reflections collected	23943	
Independent reflections	10612 [R(int) = 0.0814]	
Completeness to theta = 25.03°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.82447	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10612 / 21 / 817	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0770, wR2 = 0.1563	
R indices (all data)	R1 = 0.1367, wR2 = 0.1888	
Largest diff. peak and hole	1.485 and -1.145 e.$Å^{-3}$	

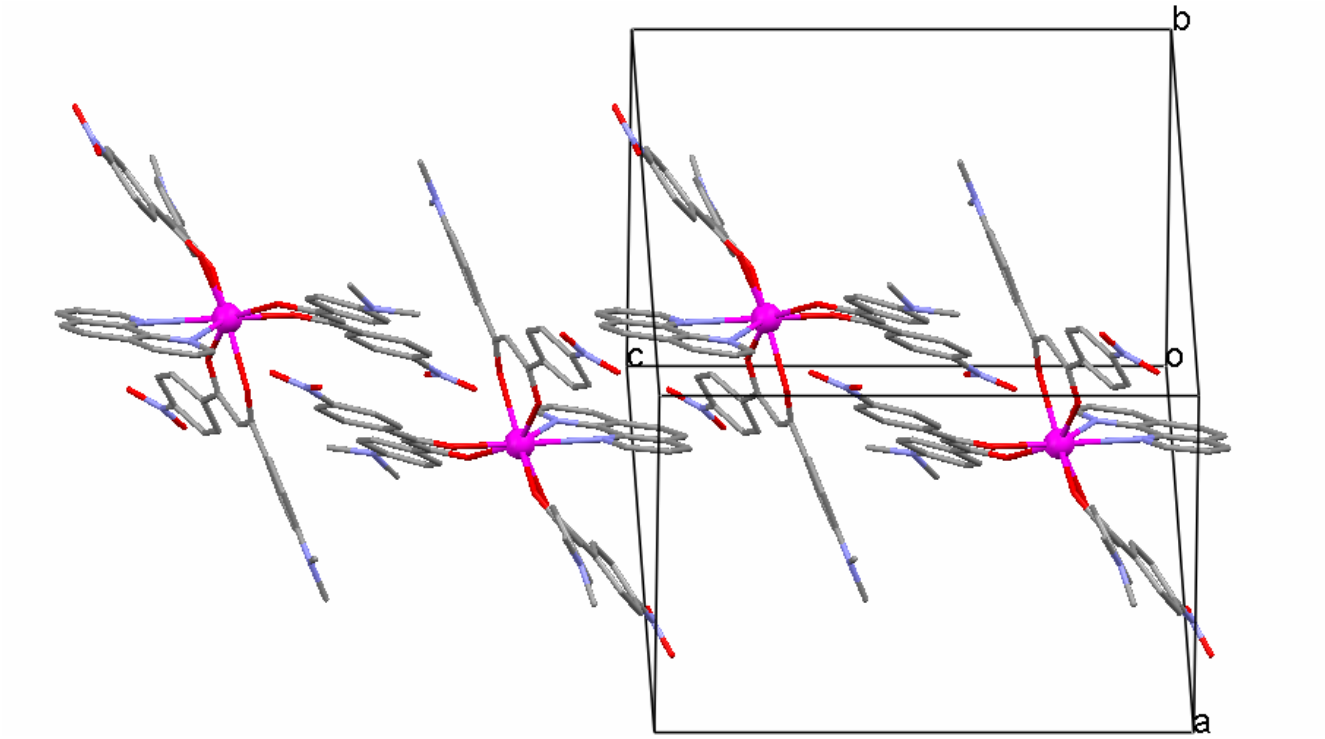

Figure S1. Packing of molecules of [NdL_3Phen] in a chain-like structure running along the crystallographic *c*-axis as a result of π-π interactions between pairs of 1,3-diketonate ligands and Phen ligands (H atoms and co-crystallized solvent molecules omitted).

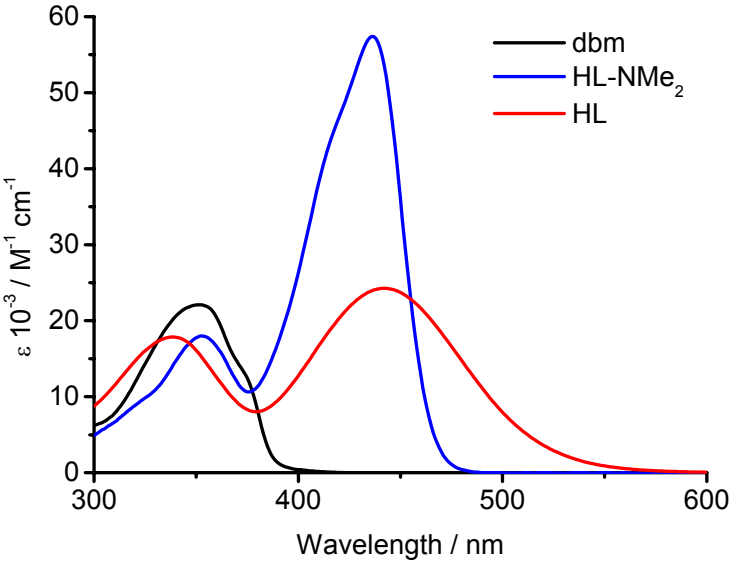

Figure S2. Comparison of the absorption spectra of dibenzoylmethane (dbm) (2.45×10^{-4} M), di-(4-dimethylaminobenzoyl)methane ($HL\text{-}NMe_2$) (9.75×10^{-5} M) and ligand HL (2.69×10^{-4} M) in dmso solution at rt.

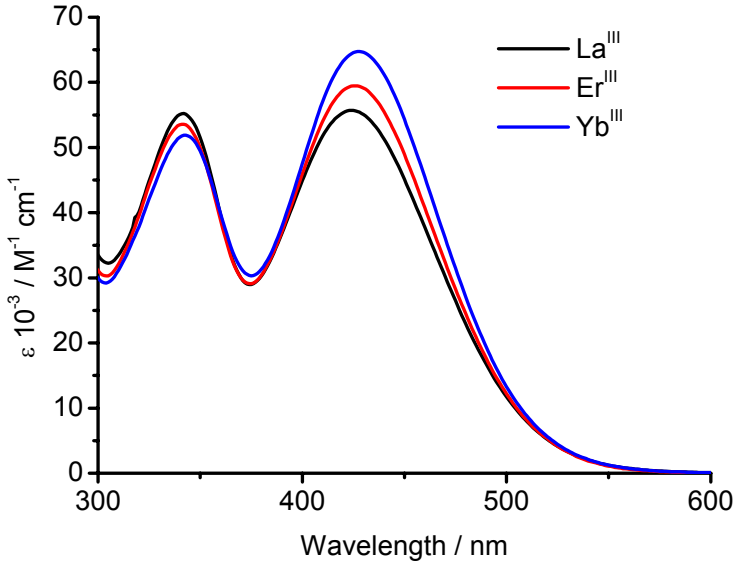

Figure S3. Comparison of the absorption spectra of the complexes [LnL_3Phen] [Ln = La^{III} (9.13×10^{-5} M), Er^{III} (8.31×10^{-5} M), and Yb^{III} (1.26×10^{-4} M)] in dmso solution. Absorption spectra of Nd^{III} (1.01×10^{-4} M) and Gd^{III} (9.16×10^{-5} M) complexes coincided with the spectrum of La^{III} and thus are not shown.

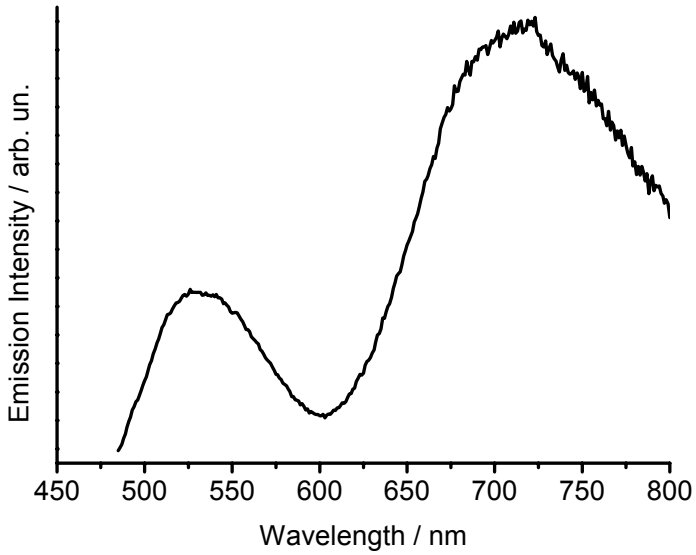

Figure S4. Corrected luminescence spectrum of [GdL_3Phen] in solid state at 77 K.

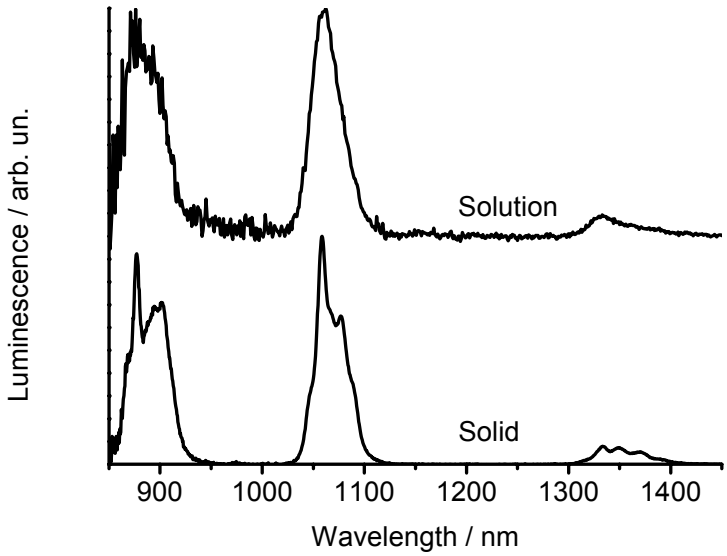

Figure S5. Corrected and normalized luminescence spectra of $[NdL_3Phen]\cdot H_2O$ in dmso solution (3.5×10^{-6} M) and in solid state at rt.

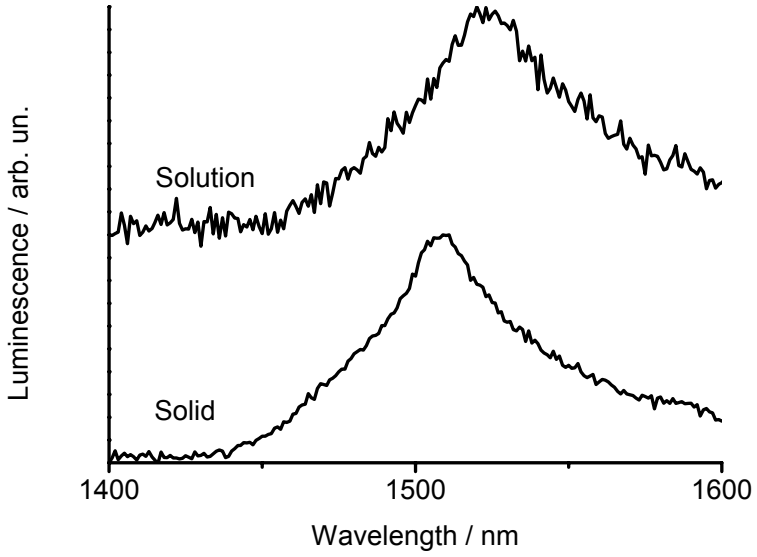

Figure S6. Corrected and normalized luminescence spectra of $[ErL_3Phen]$ in dmso solution (8.31×10^{-5} M) and in solid state at rt.

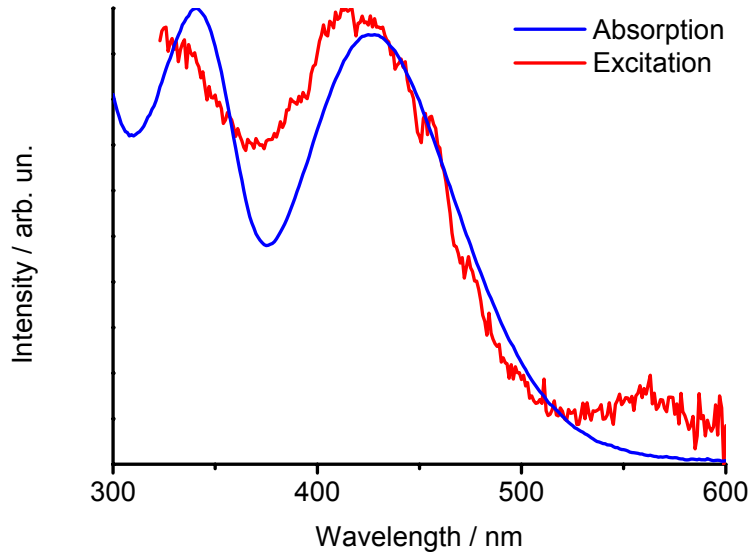

Figure S7. Comparison of the normalized absorption and excitation (corrected) spectra of [NdL_3Phen] in dmso solution rt (3.5×10^{-6} M) The luminescence was monitored at 1060 nm; excitation slit was 10 nm; optical density of the solution of the Nd^{III} complex was less than 0.2. Poor quality of excitation spectrum is a result of weak emission intensity.

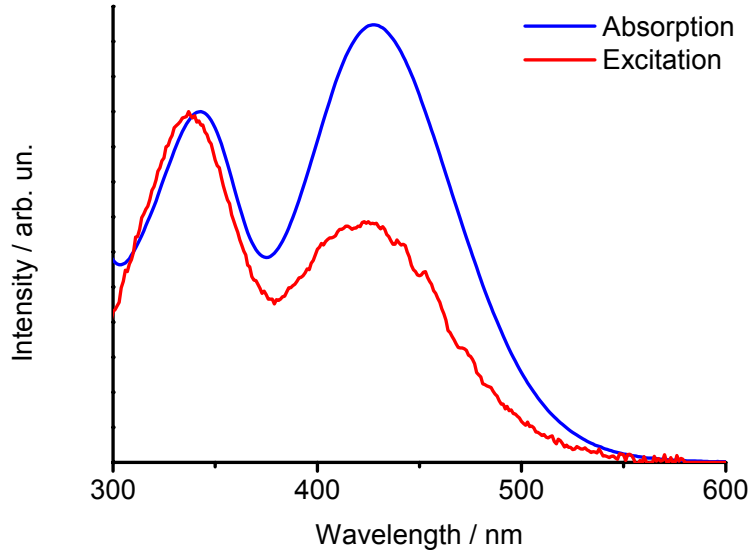

Figure S8. Comparison of the absorption and excitation (corrected) spectra of [YbL_3Phen] in dmso solution rt (1.8×10^{-6} M) The spectra were normalized with respect to the intensity of the UV band. The luminescence was monitored at 980 nm; excitation slit was 10 nm; optical density of the solution of the Yb^{III} complex was less than 0.1.