Supporting Information for "Mechanisms of luminescence in lanthanide complexes: crucial role of metal-ligand covalency"

Liviu Ungur,*,† Bernat Szabo,‡ Zeid A. AlOthman,¶ Abdullah A. S. Al-Kahtani,¶ and Liviu F. Chibotaru*,‡,¶

†*Department of Chemistry, National University of Singapore, Block S8 Level 3, 3 Science Drive 3, 117543, Singapore*

‡*Theory of Nanomaterials Group, KU Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium*

¶*Chemistry Department, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia*

E-mail: chmlu@nus.edu.sg; Liviu.Chibotaru@kuleuven.be

Ab initio calculation of luminescence

The calculations have been done with the OpenMOLCAS package,[1] as in the previous investigation of multiplet structure of Er-trensal complex.[2].

The calculation of the rate of spontaneous emission from the electronic state n (a component of the CF multiplet) of the emitting $^4S_{3/2}$ to the electronic state m of the ground manifold $^4I_{15/2}$ is done with the formula

$$\Gamma_{nm} = \frac{\omega^3 \mathrm{n} |\mu_{nm}|^2}{3\pi\varepsilon_0 \hbar c^3}, \tag{1}$$

where ω is the frequency of the emitted radiation, $\omega = (E_n - E_n)/\hbar$, n is the refraction index at this frequency, c is the velocity of light in vacuum, and μ_{nm} is the modulus of the electric-dipole matrix element between the states n and m averaged over polarizations,

$$|\mu_{nm}|^2 = \frac{1}{3}\big(|\langle\Psi_n|\hat{D}_x|\Psi_m\rangle|^2 + |\langle\Psi_n|\hat{D}_y|\Psi_m\rangle|^2 + |\langle\Psi_n|\hat{D}_z|\Psi_m\rangle|^2\big), \tag{2}$$

where $\hat{D}_\alpha$, $\alpha = x, y, z$ are the operators of Cartesian projections of the electronic electric dipole operator and Ψ_n, Ψ_m are the wave functions of the involved multiplet components. Since the main goal is the estimation of the relative contributions to luminescence and because the frequencies of individual transitions within the ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ emission band are relatively close, we suppose n to be frequency independent and further take n=1.

Because the intensities of the emission line depend on the square of the electric-dipole matrix elements, they are expected to be sensitive to the quality of the basis of atomic orbitals. To check the effect of this sensitivity on the calculated luminescence, we have performed the calculations for two basis sets, one including basis functions of double zeta and polarization quality (ANO-RCC-VDZP) and the other of triple zeta and polarization quality (ANO-RCC-VTZP). All calculations have done at a CASSCF level of theory for an active space (11,7). Usually the CASSCF approximation is not sufficient for an accurate evaluation of CF multiplets of the complex, which requires the inclusion of the CASPT2 step allowing to account the effect of dynamical correlation in the lowest (second) order of the perturbation theory.[1] One should note, however, that the missed CASPT2 step in the calculation of the wave functions used for the evaluation of electric-dipole matrix elements in (2) is not essential for the calculation of the integral intensity of optical transition. The reason is that at the current level of CASPT2 calculations the resulting wave functions represent slightly remixed CASSCF solutions.[1]

In the first series of calculations (Table 1), the quench of metal-ligand covalency resulted in different energy separation between the states of excited ${}^4S_{3/2}$ and ground ${}^4I_{15/2}$ multiplets.

This difference being pure artefactual can strongly affect the integral intensity due to the third power dependence on *omega* of the emission rate, eq. 1. To cure this drawback, all results listed in Table 1 have been rescaled with the coefficient

$$\eta = \frac{\Delta E_0^3}{\Delta E^3}. \tag{3}$$

Here ΔE is the energy separation between the centres of gravity of the group of CF multiplets belonging to $^4S_{3/2}$ and those belonging to $^4I_{15/2}$. It is calculated as arithmetic mean of the energies of corresponding transitions ΔE_{nm}. ΔE_0 is the same quantity as ΔE but corresponding to full *ab initio* calculation.

Electric dipolar matrix element in terms of atomic orbitals

For the purpose of further analysis of mechanisms of luminescence, it is convenient to represent the active molecular orbitals of 4f (Ln) type as combinations of atomic 4f orbitals with *directly* admixed orbitals of other origin. The latter would correspond to molecular orbitals of the complex derived under quenched 4f-L hybridization. Denoting these orbitals with tilde, we can conventionally write

$$\psi_{4\mathrm{f}} \;=\; c_{4\mathrm{f}}\varphi_{4\mathrm{f}} + c_{\tilde{5\mathrm{d}}}\tilde{\varphi}_{\tilde{5\mathrm{d}}} + c_{\tilde{6\mathrm{p}}}\tilde{\varphi}_{\tilde{6\mathrm{p}}} + c_{\tilde{L}}\tilde{\varphi}_{\tilde{L}} \tag{4}$$

where $\varphi_{4\mathrm{f}}$ is a normalized combination of seven atomic 4f (Ln) orbitals appropriate for a given ligand environment, $\tilde{\varphi}_{5\mathrm{d}}$ and $\tilde{\varphi}_{6\mathrm{p}}$ are orbitals originating from even (e.g., 5d) and odd (e.g. 6p) empty Ln orbitals, and $\tilde{\varphi}_L$ denotes ligand type orbitals. Note that double occupied Ln atomic orbitals also enter the decomposition of $\psi_{4\mathrm{f}}$, however, their electric-dipole matrix elements with 4f and empty Ln orbitals is much smaller. Due to a weak hybridization of 4f (Ln) and ligands' orbitals, the admixing coefficients are small, $c_{\tilde{5\mathrm{d}}}, c_{\tilde{6\mathrm{p}}}, c_{\tilde{L}} \ll 1$ (accordingly, $c_{4\mathrm{f}} \approx 1$). On the same reason, the tilded orbitals are very close to corresponding real

molecular orbitals. In the r.h.s. of eq. 4 we only kept one representative orbital from each group, the full expression implying the summation over all admixed orbitals (i.e., over the indices $\tilde{5\mathrm{d}}$, $\tilde{6\mathrm{p}}$ and $\tilde{L}$).

These orbitals are further expanded as

$$\begin{aligned}
\tilde{\varphi}_{\tilde{5\mathrm{d}}} &= \alpha_{\tilde{5\mathrm{d}}5\mathrm{d}}\varphi_{5\mathrm{d}} + \alpha_{\tilde{5\mathrm{d}}L}\varphi_L + \alpha_{\tilde{5\mathrm{d}}6p}\varphi_{6\mathrm{p}}, \\
\tilde{\varphi}_{\tilde{6\mathrm{p}}} &= \alpha_{\tilde{6\mathrm{p}}6\mathrm{p}}\varphi_{6\mathrm{p}} + \alpha_{\tilde{6\mathrm{p}}L}\varphi_L + \alpha_{\tilde{6\mathrm{p}}5d}\varphi_{5\mathrm{d}}, \\
\tilde{\varphi}_{\tilde{L}} &= \alpha_{\tilde{L}L}\varphi_L + \alpha_{\tilde{L}5\mathrm{d}}\varphi_{5\mathrm{d}} + \alpha_{\tilde{L}6\mathrm{p}}\varphi_{6\mathrm{p}},
\end{aligned} \tag{5}$$

where $\varphi_{5\mathrm{d}}$ and $\varphi_{6\mathrm{p}}$ represent the group of excited (empty) atomic Ln orbitals of even and odd parity, respectively, whereas φ_L denotes net ligands' orbitals. The latter are conceived as solutions of a constrained HF calculation with completely quenched Ln-L covalency as in a FAIMP treatment.[3] On the contrary, the orbitals defined in eq. 5 are obtained through a full SCF calculation (within, e.g. CASSCF approximation) in which only the (weak) admixture of Ln 4f orbitals was quenched. Given a strong covalency between excited Ln orbitals with the ligands, the mixing coefficients in eq. 5 are of comparable magnitude and cannot be treated perturbatively as in eq. 4. Similarly to eq. 4, a summation over double repeating indices (5d, 6p and L) is implied. This covers the entire multitude of molecular orbitals of Ln empty and ligand type, which we divide again in three groups. However the indices of resulting orbitals ($\tilde{5\mathrm{d}}$, $\tilde{6\mathrm{p}}$ and $\tilde{L}$) have now only a genealogic meaning because these orbitals generally lack any symmetry, in particular, they possess no parity.

Note that we are not applying the FAIMP approach directly in the current quantum chemistry calculations except for the cases when the conventional ECP is simulated (Table 1). Also the tilted orbitals (eq. 5) are not employed in these calculations. The two-step decomposition of molecular orbitals of 4f type, first, in tilted orbitals (eq. 4) and then in Ln atomic and net ligand molecular orbitals (eq. 5), is done for sole meaning of emphasizing

the hierarchy of orbital interactions.

In terms of directly admixed tilted orbitals, the electric dipolar matrix element between two molecular orbitals of 4f type is given by the expression (we drop the symbol φ in the r.h.s. matrix elements):

$$\begin{aligned}\langle\psi_{4\mathrm{f}}|\mathbf{D}|\psi_{4\mathrm{f}'}\rangle = \quad & \Big(c_{4\mathrm{f}}\langle 4\mathrm{f}|\mathbf{D}|\tilde{5\mathrm{d}}\rangle c'_{\tilde{5\mathrm{d}}} + c_{\tilde{5\mathrm{d}}}\langle\tilde{5\mathrm{d}}|\mathbf{D}|4\mathrm{f}'\rangle c_{4\mathrm{f}'}\Big) + \Big(c_{4\mathrm{f}}\langle 4\mathrm{f}|\mathbf{D}|\tilde{6\mathrm{p}}\rangle c'_{\tilde{6\mathrm{p}}} + c_{\tilde{6\mathrm{p}}}\langle\tilde{6\mathrm{p}}|\mathbf{D}|4\mathrm{f}'\rangle c_{4\mathrm{f}'}\Big) + \\ & \Big(c_{4\mathrm{f}}\langle 4\mathrm{f}|\mathbf{D}|\tilde{L}\rangle c'_{\tilde{L}} + c_{\tilde{L}}\langle\tilde{L}|\mathbf{D}|4\mathrm{f}'\rangle c_{4\mathrm{f}'}\Big) + c_{\tilde{5\mathrm{d}}}\langle\tilde{5\mathrm{d}}|\mathbf{D}|\tilde{5\mathrm{d}}'\rangle c'_{\tilde{5\mathrm{d}}'} + \\ & \Big(c_{\tilde{5\mathrm{d}}}\langle\tilde{5\mathrm{d}}|\mathbf{D}|\tilde{6\mathrm{p}}\rangle c'_{\tilde{6\mathrm{p}}} + c_{\tilde{6\mathrm{p}}}\langle\tilde{6\mathrm{p}}|\mathbf{D}|\tilde{5\mathrm{d}}\rangle c'_{\tilde{5\mathrm{d}}}\Big) + \Big(c_{\tilde{5\mathrm{d}}}\langle\tilde{5\mathrm{d}}|\mathbf{D}|\tilde{L}\rangle c'_{\tilde{L}} + c_{\tilde{L}}\langle\tilde{L}|\mathbf{D}|\tilde{5\mathrm{d}}\rangle c'_{\tilde{5\mathrm{d}}}\Big) + \\ & c_{\tilde{6\mathrm{p}}}\langle\tilde{6\mathrm{p}}|\mathbf{D}|\tilde{6\mathrm{p}}'\rangle c'_{\tilde{6\mathrm{p}}'} + \Big(c_{\tilde{6\mathrm{p}}}\langle\tilde{6\mathrm{p}}|\mathbf{D}|\tilde{L}\rangle c'_{\tilde{L}} + c_{\tilde{L}}\langle\tilde{L}|\mathbf{D}|\tilde{6\mathrm{p}}\rangle c'_{\tilde{6\mathrm{p}}}\Big) + \\ & c_{\tilde{L}}\langle\tilde{L}|\mathbf{D}|\tilde{L}'\rangle c'_{\tilde{L}'}, \end{aligned} \tag{6}$$

where it is taken into account that the orbitals (and the expansion coefficients) are real. Note that contributions come from all pairs of orbitals (except for diagonal after 4f) because the tilted orbitals lack parity due strong admixture of the ligand's orbitals. In eq. 6, the prime symbol is used (besides 4f′) for two different purposes. First, it is used in the admixture coefficients of tilded orbitals in the expansion of eq. 4 to indicate that they correspond to the molecular orbital $\psi_{4\mathrm{f}'}$ (not the 4f one). Second, it distinguishes tilded orbitals of the same type in the terms diagonal after these orbitals (e.g., $\tilde{5\mathrm{d}}$ and $\tilde{5\mathrm{d}}'$) in order to keep independent summation after their indices.

The number of different contributions reduces to six when we further expand the orbitals in the electric dipolar matrix elements in eq. 6 into Ln atomic and net ligands' orbitals using eq. 5. Denoting these contributions by $\mathbf{D}^{(i)}$, i = a-f, we have

$$\langle\psi_{4\mathrm{f}}|\mathbf{D}|\psi'_{4\mathrm{f}}\rangle = \mathbf{D}^{(a)} + \mathbf{D}^{(b)} + \mathbf{D}^{(c)} + \mathbf{D}^{(d)} + \mathbf{D}^{(e)} + \mathbf{D}^{(f)}, \tag{7}$$

where the first two contributions are obtained in the form

$$
\begin{aligned}
\mathbf{D}^{(a)} = \quad & c_{4\mathrm{f}}\langle 4\mathrm{f}|\mathbf{D}|5\mathrm{d}\rangle\big(\alpha_{\tilde{5\mathrm{d}}5\mathrm{d}}c'_{\tilde{5\mathrm{d}}}+\alpha_{\tilde{6\mathrm{p}}5\mathrm{d}}c'_{\tilde{6\mathrm{p}}}+\alpha_{\tilde{L}5\mathrm{d}}c'_{\tilde{L}}\big)+\\
& \big(c_{\tilde{5\mathrm{d}}}\alpha_{\tilde{5\mathrm{d}}5\mathrm{d}}+c_{\tilde{6\mathrm{p}}}\alpha_{\tilde{6\mathrm{p}}5\mathrm{d}}+c_{\tilde{L}}\alpha_{\tilde{L}5\mathrm{d}}\big)\langle 5\mathrm{d}|\mathbf{D}|4\mathrm{f}'\rangle c_{4\mathrm{f}'},\\
\mathbf{D}^{(b)} = \quad & c_{4\mathrm{f}}\langle 4\mathrm{f}|\mathbf{D}|L\rangle\big(\alpha_{\tilde{5\mathrm{d}}L}c'_{\tilde{5\mathrm{d}}}+\alpha_{\tilde{6\mathrm{p}}L}c'_{\tilde{6\mathrm{p}}}+\alpha_{\tilde{L}L}c'_{\tilde{L}}\big)+\\
& \big(c_{\tilde{5\mathrm{d}}}\alpha_{\tilde{5\mathrm{d}}L}+c_{\tilde{6\mathrm{p}}}\alpha_{\tilde{6\mathrm{p}}L}+c_{\tilde{L}}\alpha_{\tilde{L}L}\big)\langle L|\mathbf{D}|4\mathrm{f}'\rangle c_{4\mathrm{f}'}. \qquad (8)
\end{aligned}
$$

The other four contributions are more involved and can be structured in the form:

$$
\begin{aligned}
\mathbf{D}^{(c)} = \quad & \big(c_{\tilde{5\mathrm{d}}}\alpha_{\tilde{5\mathrm{d}}5\mathrm{d}}+c_{\tilde{6\mathrm{p}}}\alpha_{\tilde{6\mathrm{p}}5\mathrm{d}}+c_{\tilde{L}}\alpha_{\tilde{L}5\mathrm{d}}\big)\langle 5\mathrm{d}|\mathbf{D}|L\rangle\big(c'_{\tilde{5\mathrm{d}}'}\alpha_{\tilde{5\mathrm{d}}'L}+c'_{\tilde{6\mathrm{p}}'}\alpha_{\tilde{6\mathrm{p}}'L}+c'_{\tilde{L}'}\alpha_{\tilde{L}'L}\big)+\\
& \big(c_{\tilde{5\mathrm{d}}'}\alpha_{\tilde{5\mathrm{d}}'L}+c_{\tilde{6\mathrm{p}}'}\alpha_{\tilde{6\mathrm{p}}'L}+c_{\tilde{L}'}\alpha_{\tilde{L}'L}\big)\langle L|\mathbf{D}|5\mathrm{d}\rangle\big(c'_{\tilde{5\mathrm{d}}}\alpha_{\tilde{5\mathrm{d}}5\mathrm{d}}+c'_{\tilde{6\mathrm{p}}}\alpha_{\tilde{6\mathrm{p}}5\mathrm{d}}+c'_{\tilde{L}}\alpha_{\tilde{L}5\mathrm{d}}\big),\\
\mathbf{D}^{(d)} = \quad & \big(c_{\tilde{5\mathrm{d}}}\alpha_{\tilde{5\mathrm{d}}5\mathrm{d}}+c_{\tilde{6\mathrm{p}}}\alpha_{\tilde{6\mathrm{p}}5\mathrm{d}}+c_{\tilde{L}}\alpha_{\tilde{L}5\mathrm{d}}\big)\langle 5\mathrm{d}|\mathbf{D}|6\mathrm{p}\rangle\big(c'_{\tilde{5\mathrm{d}}'}\alpha_{\tilde{5\mathrm{d}}'6\mathrm{p}}+c'_{\tilde{6\mathrm{p}}'}\alpha_{\tilde{6\mathrm{p}}'6\mathrm{p}}+c'_{\tilde{L}'}\alpha_{\tilde{L}'6\mathrm{p}}\big)+\\
& \big(c_{\tilde{5\mathrm{d}}'}\alpha_{\tilde{5\mathrm{d}}'6\mathrm{p}}+c_{\tilde{6\mathrm{p}}'}\alpha_{\tilde{6\mathrm{p}}'6\mathrm{p}}+c_{\tilde{L}'}\alpha_{\tilde{L}'6\mathrm{p}}\big)\langle 6\mathrm{p}|\mathbf{D}|5\mathrm{d}\rangle\big(c'_{\tilde{5\mathrm{d}}}\alpha_{\tilde{5\mathrm{d}}5\mathrm{d}}+c'_{\tilde{6\mathrm{p}}}\alpha_{\tilde{6\mathrm{p}}5\mathrm{d}}+c'_{\tilde{L}}\alpha_{\tilde{L}5\mathrm{d}}\big),\\
\mathbf{D}^{(e)} = \quad & \big(c_{\tilde{5\mathrm{d}}}\alpha_{\tilde{5\mathrm{d}}L}+c_{\tilde{6\mathrm{p}}}\alpha_{\tilde{6\mathrm{p}}L}+c_{\tilde{L}}\alpha_{\tilde{L}L}\big)\langle L|\mathbf{D}|L'\rangle\big(c'_{\tilde{5\mathrm{d}}'}\alpha_{\tilde{5\mathrm{d}}'L'}+c'_{\tilde{6\mathrm{p}}'}\alpha_{\tilde{6\mathrm{p}}'L'}+c'_{\tilde{L}'}\alpha_{\tilde{L}'L'}\big),\\
\mathbf{D}^{(f)} = \quad & \big(c_{\tilde{5\mathrm{d}}}\alpha_{\tilde{5\mathrm{d}}6\mathrm{p}}+c_{\tilde{6\mathrm{p}}}\alpha_{\tilde{6\mathrm{p}}6\mathrm{p}}+c_{\tilde{L}}\alpha_{\tilde{L}6\mathrm{p}}\big)\langle 6\mathrm{p}|\mathbf{D}|L\rangle\big(c'_{\tilde{5\mathrm{d}}'}\alpha_{\tilde{5\mathrm{d}}'L}+c'_{\tilde{6\mathrm{p}}'}\alpha_{\tilde{6\mathrm{p}}'L}+c'_{\tilde{L}'}\alpha_{\tilde{L}'L}\big)+\\
& \big(c_{\tilde{5\mathrm{d}}'}\alpha_{\tilde{5\mathrm{d}}'L}+c_{\tilde{6\mathrm{p}}'}\alpha_{\tilde{6\mathrm{p}}'L}+c_{\tilde{L}'}\alpha_{\tilde{L}'L}\big)\langle L|\mathbf{D}|6\mathrm{p}\rangle\big(c'_{\tilde{5\mathrm{d}}}\alpha_{\tilde{5\mathrm{d}}6\mathrm{p}}+c'_{\tilde{6\mathrm{p}}}\alpha_{\tilde{6\mathrm{p}}6\mathrm{p}}+c'_{\tilde{L}}\alpha_{\tilde{L}6\mathrm{p}}\big). \qquad (9)
\end{aligned}
$$

Here, the prime symbol is used also for indices denoting atomic orbitals (not tilded indices) to distinguish independent summations running over pairs of such indices in the l.h.s and r.h.s. Note that over tilded and not tilded indices independent summation is performed.

Mechanisms of electric dipolar transition

The six contributions in eqs. 8 and 9 correspond to the six mechanisms depicted in Figure 2 in the article according to the involved electric dipolar matrix element (red arrows in the figure). This is easily seen when we write down the expressions for the coefficients of

admixture of tilded orbitals:

$$\begin{aligned} c_{\tilde{5\mathrm{d}}} &= \frac{\langle \tilde{5\mathrm{d}}|H_{\mathrm{CF}}|4f\rangle}{\epsilon_{\tilde{5\mathrm{d}}} - \epsilon_{4f}}, \\ c_{\tilde{6\mathrm{p}}} &= \frac{\langle \tilde{6\mathrm{p}}|H_{\mathrm{CF}}|4f\rangle}{\epsilon_{\tilde{6\mathrm{p}}} - \epsilon_{4f}}, \\ c_{\tilde{L}} &= \frac{\langle \tilde{L}|H_{\mathrm{CF}}|4f\rangle}{\epsilon_{\tilde{L}} - \epsilon_{4f}}, \end{aligned} \tag{10}$$

where the first-order perturbation theory with respect to 4f-L orbital interactions has been applied, which is always justified in the case of lanthanides. H_{CF} is the effective one-electron operator (analog of HF operator in the case of single-determinant treatment), corresponding to a CASSCF/CASPT2 calculation within a state-averaged approximation (when the active and other molecular orbitals are chosen to be common for the entire set of electronic configurations of a given spin used in the CI mixing). As discussed in the previous section, the tilded and 4f orbitals entering in eq. 10 are eigen solution of H_{CF} in which the block mixing 4f with all other orbitals was eliminated. On the contrary, in the matrix elements in eq. 10 only this eliminated block of H_{CF} is operative. Quantities in the denominators of the above expressions are energies of the corresponding orbitals.

Substituting eq. 10 into 8, one can see that the contributions $\mathbf{D}^{(a)}$ and $\mathbf{D}^{(b)}$ involve only products of two matrix elements in all their terms, one corresponding to the electric dipolar interaction and the other describing the admixing of tilded molecular orbitals of the complex to the 4f (Ln) orbitals. For instance,

$$\begin{aligned} \mathbf{D}^{(a)} = \quad & c_{4\mathrm{f}}\langle 4\mathrm{f}|\mathbf{D}|5\mathrm{d}\rangle\Big(\alpha_{\tilde{5\mathrm{d}}5\mathrm{d}}\frac{\langle \tilde{5\mathrm{d}}|H_{\mathrm{CF}}|4f'\rangle}{\epsilon_{\tilde{5\mathrm{d}}} - \epsilon_{4f'}} + \alpha_{\tilde{6\mathrm{p}}5\mathrm{d}}\frac{\langle \tilde{6\mathrm{p}}|H_{\mathrm{CF}}|4f'\rangle}{\epsilon_{\tilde{6\mathrm{p}}} - \epsilon_{4f'}} + \alpha_{\tilde{L}5\mathrm{d}}\frac{\langle \tilde{L}|H_{\mathrm{CF}}|4f'\rangle}{\epsilon_{\tilde{L}} - \epsilon_{4f'}}\Big) + \\ & \Big(\frac{\langle \tilde{5\mathrm{d}}|H_{\mathrm{CF}}|4f\rangle}{\epsilon_{\tilde{5\mathrm{d}}} - \epsilon_{4f}}\alpha_{\tilde{5\mathrm{d}}5\mathrm{d}} + \frac{\langle \tilde{6\mathrm{p}}|H_{\mathrm{CF}}|4f\rangle}{\epsilon_{\tilde{6\mathrm{p}}} - \epsilon_{4f}}\alpha_{\tilde{6\mathrm{p}}5\mathrm{d}} + \frac{\langle \tilde{L}|H_{\mathrm{CF}}|4f\rangle}{\epsilon_{\tilde{L}} - \epsilon_{4f}}\alpha_{\tilde{L}5\mathrm{d}}\Big)\langle 5\mathrm{d}|\mathbf{D}|4\mathrm{f}'\rangle c_{4\mathrm{f}'}. \end{aligned} \tag{11}$$

The expressions in the brackets represent the admixture of the AO $\varphi_{5\mathrm{d}}$ which is distributed

over the tilded MO of the complex with the α coefficients. The latter obey usual relations for the LCAO coefficients Then the summation over tilded MO give an overall amplitude of admixture of $\varphi_{5\mathrm{d}}$ to $\varphi_{4\mathrm{f}}$ and $\varphi_{4\mathrm{f}'}$, respectively, and eq. 11 can be rewritten in the form:

$$\mathbf{D}^{(a)} = \quad c_{4\mathrm{f}} \frac{\langle 4\mathrm{f}|\mathbf{D}|5\mathrm{d}\rangle \overline{\langle 5\mathrm{d}|H_{\mathrm{CF}}|4f'\rangle}}{\overline{\epsilon_{5\mathrm{d}}} - \epsilon_{4f'}} + \frac{\overline{\langle 4f|H_{\mathrm{CF}}|5\mathrm{d}\rangle} \langle 5\mathrm{d}|\mathbf{D}|4\mathrm{f}'\rangle}{\overline{\epsilon_{5\mathrm{d}}} - \epsilon_{4f}} c_{4\mathrm{f}'}, \tag{12}$$

where the line over the matrix elements and energy denote effective admixture of the AO $\varphi_{5\mathrm{d}}$ to $\varphi_{4\mathrm{f}}$ and $\varphi_{4\mathrm{f}'}$ and its effective orbital energy, respectively. We can see that this contribution involves two matrix elements and corresponds to a two-steps mechanism of electric dipolar transition of Judd-Ofelt (JO) type (Fig. 2a). The first term in Eq. 12 (and 11) corresponds exactly to the diagram in Fig. 2a (the initial state (4f') in the right, the final state (4f) in the left). The second term corresponds to a changed order of processes: first, electric dipolar transition 4f'$\rightarrow$5d and the admixture (transition under H_{CF}) of the later to the 4f atomic orbital. This process corresponds to a second diagram of JO type, in which the colour of arrows in Fig 2a is interchanged. The contribution $\mathbf{D}^{(b)}$ is of a similar structure, one should merely replace "5d" with "L" in eqs. 11 and 12. Again, one term of this contribution corresponds precisely to the diagram in Fig. 2b, and the other to the interchanged colours of the two arrows. We stress that each process within both mechanisms involves virtual transitions to all excited MO (cf brackets in eq. 11), which is a consequence of strong covalency of the latter with the ligands.

The other four contributions to the electric dipolar transition, eq. 9 are described by three-step mechanisms (Fig. 2c-f, correspondingly). Again, substituting eq. 10 for c and c' into eq. 9, we obtain that all terms in these contributions contain products of three matrix elements, one of electric dipolar type and two describing the admixture of tilded MO to the initial (4f') and the final (4f) orbitals. With the same reasoning which led us to eq. 12, we can show that the expression for each contribution contains two terms, each involving two effective matrix elements of the admixture of excited atomic (Ln) and net ligand's orbital

to the 4f' and 4f Ln atomic orbitals (and two corresponding energy denominators). The first term in such expressions will correspond to diagrams c-f in Figure 2 and the second one to a changed order of matrix elements describing the admixture. For instance, for the contribution $\mathbf{D}^{(c)}$ the second term will correspond to a diagram in Fig. 2c in which the first green arrow connect 4f with L, the red one L with 5d and the second green arrow 5d with 4f. In other words, to describe the second term of this contribution, one should revert the direction of the red arrow and reconnect the green arrows in such a way as to provide a continuous transition from the initial (4f') to the final (4f) atomic Ln orbital. This rule holds also for the remaining three contributions.

The above description applies directly to Ln complexes with a single electron [e.g., Ce(III)] and a single hole [e.g., Yb(III)] in the 4f shell. In all other cases the multiplets of 4f (Ln) type are described by multiconfigurational wave functions in which, for a sufficiently low symmetry, all seven 4f orbitals will enter both the initial (emitting) and the final multiplet. This means that we should take into account electric dipolar transitions for each pairs of 4f orbitals in both directions, i.e., besides 4f'$\rightarrow$4f transitions described above (half of which are depicted in Figure 2) we should consider the transitions in the opposite direction, 4f'$\leftarrow$4f. In other word, we have to take into account four diagrams for each of the six mechanisms: besides two described diagrams for each of them there are another two corresponding to reversed directions of all arrows. This is particularly the case of the Er(III) complex investigated in the article.

All said above is true for a full *ab initio* calculation, when all orbital interactions are taken into account. In the case of quenched basis set of Ln atomic orbitals and/or quenched electric-dipole transitions the number of relevant mechanisms and terms in their expressions (eqs. 8 and 9) is reduced. For example, in the case of conventional ECF (completely quenched Ln-L covalency) the net ligand orbital is not involved in the expansion of the first two tilded orbitals in eq. 5, while the tilded orbital of ligand type is not relevant anymore. As a result only the the mechanism (a) and (d) are operative in this case.