

Electronic Supplementary Information for

Speciation of organic-soluble Lanthanide α -1-Wells-Dawson complexes

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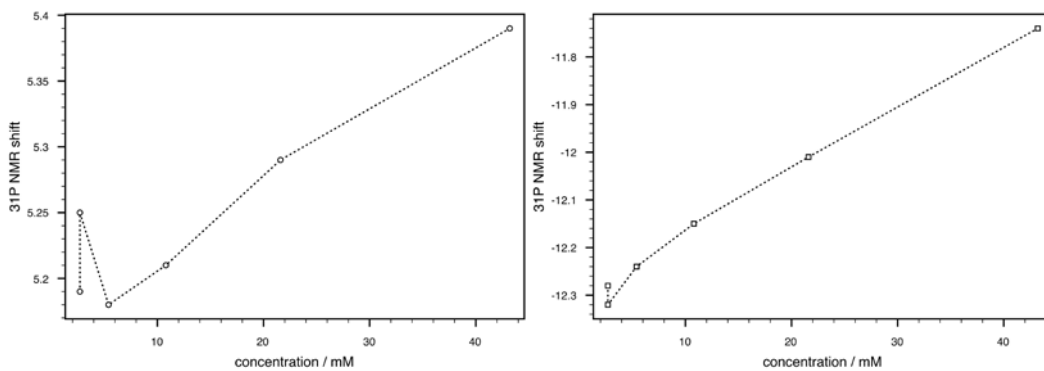


Figure S1. ^{31}P NMR chemical shift variation of $\text{TBA}^+\text{-Eu-}\alpha\text{-1}$ in d^3 acetonitrile containing 10% D_2O at various concentrations. Left graph shows the variation in the P1 resonance (close to the europium(III) ion, right graph shows the chemical shift variation of the remote P2 resonance.

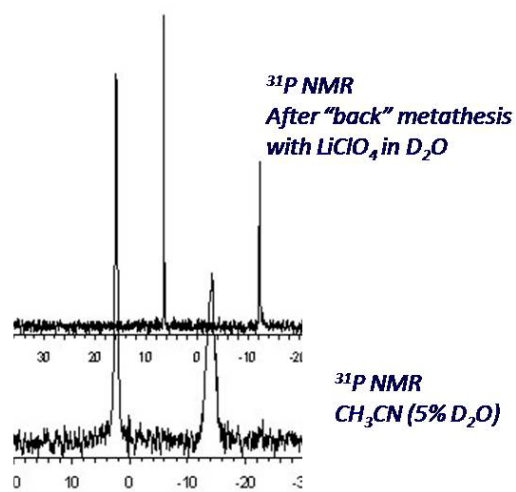
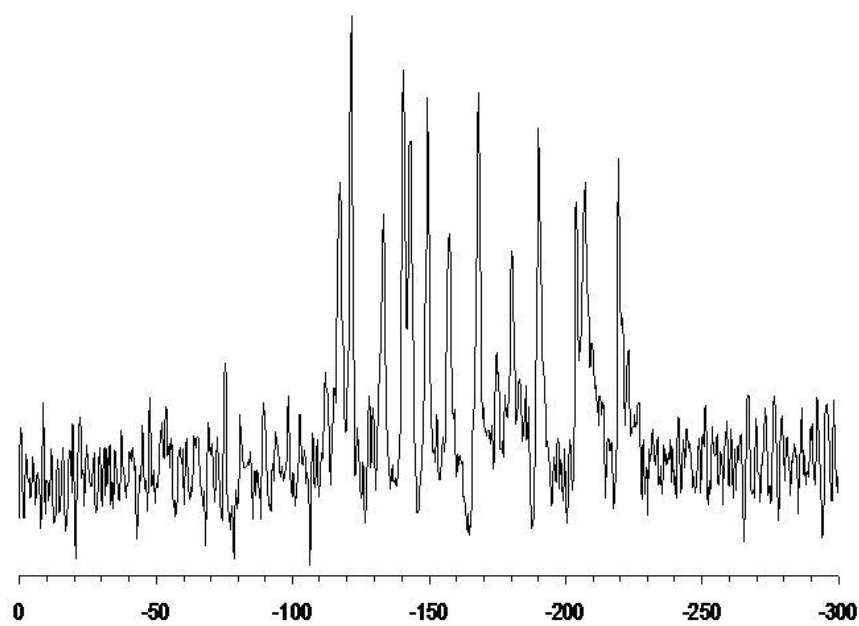


Figure S2. Top: ^{183}W NMR of $\text{TBA}^+\text{-Eu-}\alpha\text{-1}$ in d^3 acetonitrile containing 10% D_2O . 14 resonances are visible which are approaching 17 expected for $\text{TBA}^+\text{-Eu-}\alpha\text{-1}$. Bottom: lower spectrum: ^{31}P NMR taken of $\text{TBA}^+\text{-Eu-}\alpha\text{-1}$ in d^3 acetonitrile containing 5% D_2O . Upper spectrum: ^{31}P NMR of $\text{TBA}^+\text{-Eu-}\alpha\text{-1}$ taken in water after “back” metathesis to Li^+ salt. The resonances match those of a genuine sample of the K^+ or $\text{Li}^+\text{-Eu-}\alpha\text{-1}$ salt. This experiment confirms that the $\text{TBA}^+\text{-Eu-}\alpha\text{-1}$ possesses the same structure as the K^+ or $\text{Li}^+\text{-Eu-}\alpha\text{-1}$ salt.

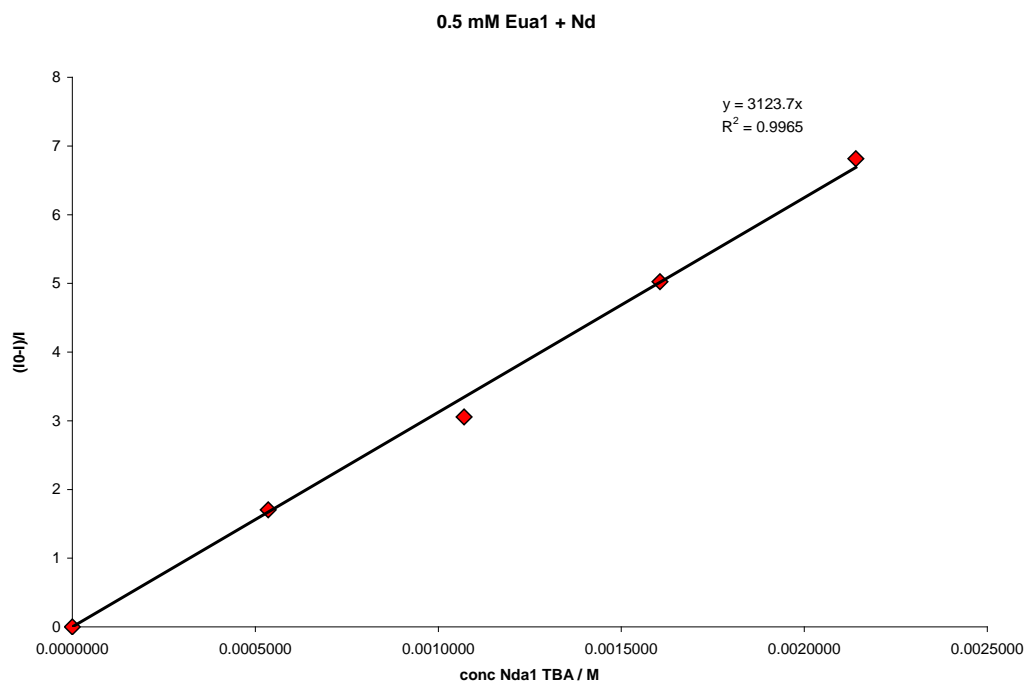


Figure S3. Luminescence intensity of TBA⁺-Eu- α -1 as a function of TBA⁺-Nd- α -1 in dry acetonitrile.

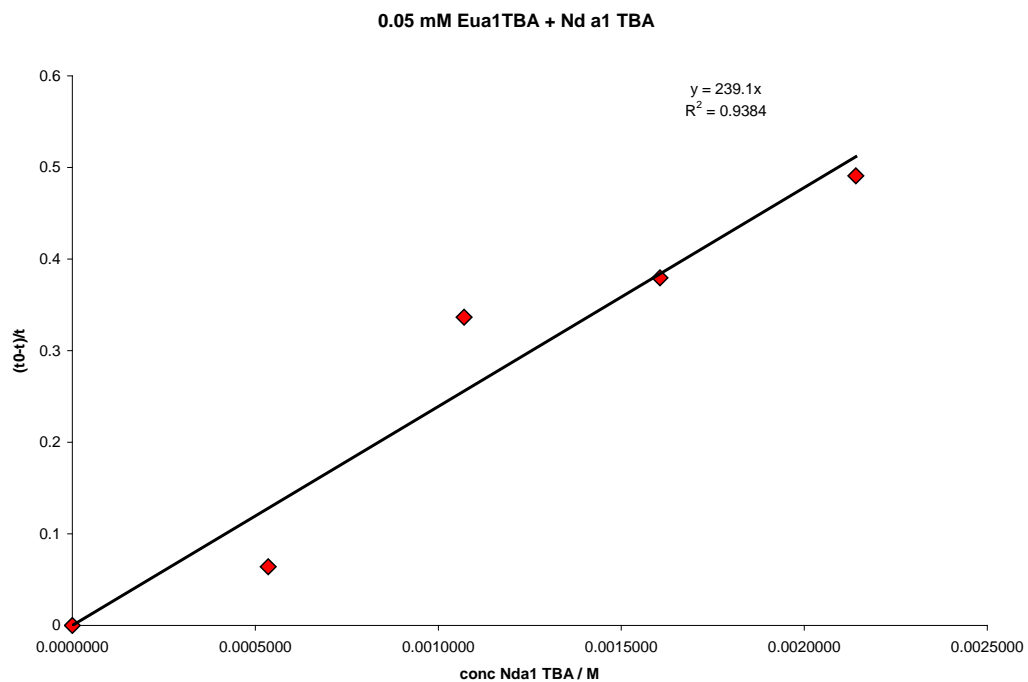


Figure S4. Luminescence lifetime of TBA⁺-Eu- α -1 as a function of TBA⁺-Nd- α -1 in dry acetonitrile.

Details of Stern Volmer Quenching Experiment:

The efficiency of lifetime quenching is, at a maximum, 36 %, which is rather low for the formation of dimeric species in solution. The low lifetime quenching efficiency observed in this experiment is atypical for most dimer/aggregations of Eu(III)/Nd(III) species. The lifetime quenching efficiency can be related to the distance between the two lanthanide centers. For distances ~ 7 Å the efficiency of such a process is usually in excess of 89 %^{1,2}. According to available crystallographic data of Wells-Dawson lanthanide complexes the lanthanide centers in dimeric (2:2) species should be c.a. 6.8 Å apart^{3,4}, which should allow for very efficient quenching if the dimer consists of 1 molecule of TBA⁺-Eu- α -1 and 1 molecule of TBA⁺-Nd- α -1. From our experimental observations this does not seem to be the case and could be the cause of an average amount of quenching from closely diffusing combinations of TBA⁺-Eu- α -1 and TBA⁺-Nd- α -1. Close proximations of TBA⁺-Eu- α -1 and TBA⁺-Nd- α -1 are unlikely to occur at distances less than 10 Å in the solution state due to electrostatic repulsions, and pursuit of the lowest energy conformation. This would mean that, in this case, the quenching efficiency would be approximately 3 times lower than that of known examples where the Ln³⁺ centers are on the order of 6-7 Å apart (~ 29 -30%) as we observe. The observed efficiency for quenching the emission intensity is consistent with that expected for weak association of the complexes⁵. The addition of TBA⁺-Nd- α -1 quenches the intensity initially by 63 % all the way down to 87 %, which is due to static and dynamic quenching (i.e. associated TBA⁺-Eu- α -1 and TBA⁺-Nd- α -1 (static) and collisional (dynamic) quenching). Eu(III) species are generally quenched by Nd(III) as it's energy levels are appropriately lower in energy in order for phonon transfer from the Eu(III) emissive ⁵D₀ level to occur, and do not necessarily have to be in close proximity to quench the emission intensity.

The observation of the quenching phenomenon and the indication of lower than expected lifetime quenching efficiency lead us to probe the inter-molecular distances between donor and quencher, namely the lanthanide ions Nd(III) and Eu(III). Assuming the quenching is facilitated through a dipole-dipole exchange mechanism the efficiency

of energy transfer (E) is proportional to the distance between the donor and acceptor (r) (given the critical distance for 50% energy transfer (R_0)) by:

$$E = \left[1 + \left(\frac{r}{R_0} \right)^6 \right]^{-1} \quad (5)$$

R_0 can be calculated from equation 6, where k^2 is the statistical orientation factor ($2/3$ for isotropic media), Q is the quantum yield of the donor, n^4 is the refractive index of the solvent (1.343 for MeCN) and J is the spectral overlap in $M^{-1}cm^3$

$$R_0^6 = 8.78 \times 10^{-25} k^2 Q_D n^4 J \quad (6)$$

The spectral overlap is calculated from equation 7:

$$J = \frac{\int F(\nu)\epsilon(\nu)\nu^{-4}d\nu}{\int F(\nu)d\nu} \quad (7)$$

$F(\nu)$ is the normalised emission intensity at wavenumber ν , $\epsilon(\nu)$ is the molar absorptivity of the acceptor at wavenumber ν . The complexes were mixed at a concentration that mimicked the most concentrated sample used for the steady state measurements; the $TBA^+-Nd-\alpha-1$ was 0.2 mM and the $TBA^+-Eu-\alpha-1$ was 0.002 mM to statistically ensure the formation of Nd:Eu dimers. From our experimental data the distance between donor and acceptor (r) is equal to 67 Å, which is extensive given the size of the polyoxometalate (10-17 Å). This shows that even though it appears that static quenching is occurring in solution, the $TBA^+-Nd/Eu-\alpha-1$ POM units are not approaching each other to a considerable degree in dry acetonitrile. As mentioned above, given the size of the spectral overlap of the neodymium and the europium emission (**Figure 7**), the europium emission can be quenched effectively by the neodymium without the two molecules having to approach each other significantly. This explains why we observe such a large decrease in emission intensity and such a small influence on the emission lifetime.

References

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Figure S5. Normalized excitation spectra of 0.02 μM TBA⁺-Eu- α -1 in dry acetonitrile (solid circles) and upon the addition of 200 μM TBA⁺-Nd- α -1 in dry acetonitrile (open circles). $\lambda_{\text{em}} = 614$ nm.

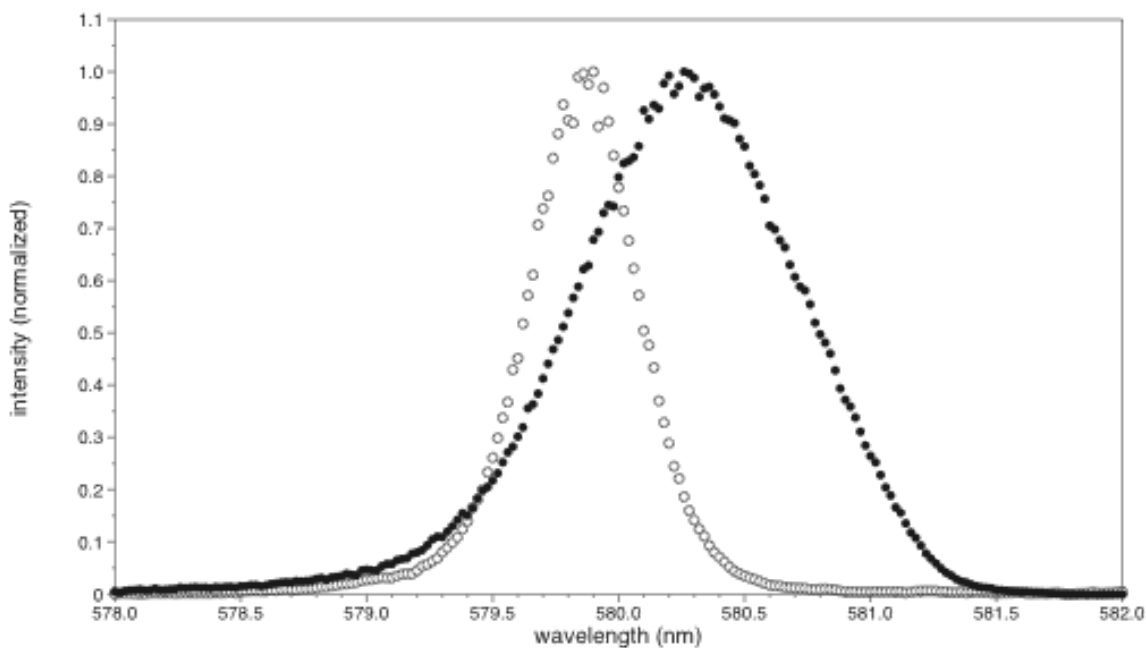


Figure S6. Luminescence enhancement graph of the sensitization of Eu(III) luminescence from 0.4 μM TBA⁺-Eu- α -1 in dry acetonitrile upon the addition of 1,10-phenanthroline; $\lambda_{\text{ex}} = 325 \text{ nm}$, $t_{\text{g}} = 10 \mu\text{s}$. The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ emission band was monitored at 618 nm.

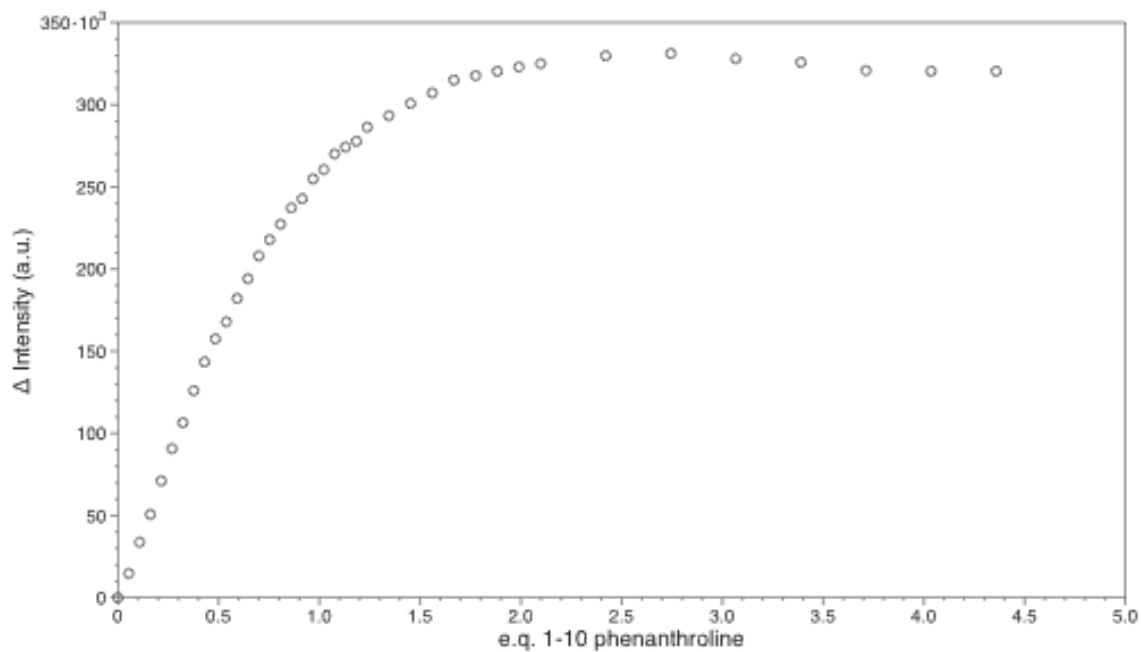


Figure S7. Job plots of TBA-Eu- α 1 in dry acetonitrile (0.4 μ M (left) and 40 μ M (right)) monitoring the $^5D_0 \rightarrow ^7F_2$ emission band at 618 nm as a function of added 1,10-phenanthroline. $\lambda_{ex} = 325$ nm.

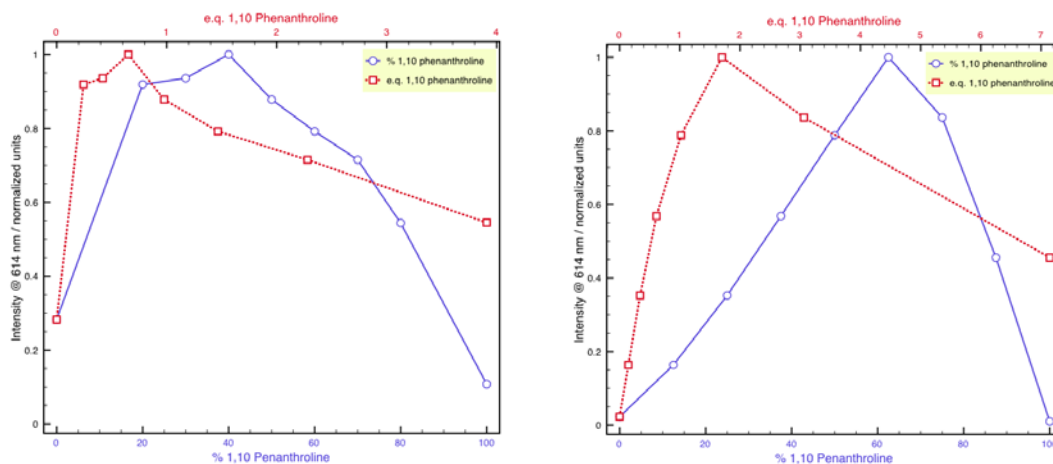


Figure S8. Luminescence enhancement graph of the sensitization of Eu(III) luminescence from 40 μ M TBA⁺-Eu- α -1 in dry acetonitrile upon the addition of 1,10-phenanthroline; $\lambda_{ex} = 325$ nm, $t_g = 10$ μ s. The $^5D_0 \rightarrow ^7F_2$ emission band was monitored at 618 nm.

