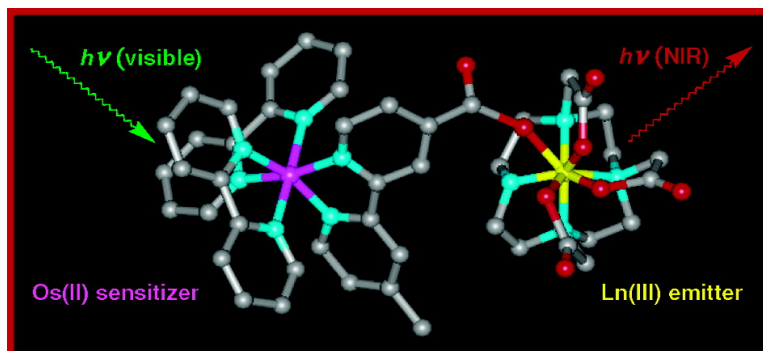


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Self-Assembly of Heterobimetallic d–f Hybrid Complexes: Sensitization of Lanthanide Luminescence by d-Block Metal-to-Ligand Charge-Transfer Excited States

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Luminescence from lanthanide (Ln) complexes has been widely exploited in bioassays.¹ The longevity of such luminescence permits the use of time-gating techniques to separate the signal from fluorescent background.^{2,3} Europium and terbium complexes, which emit visible light with millisecond-order lifetimes, have been especially well-exploited.^{4–6} However, the high-energy emissive states of such species restrict the range of sensitizing chromophores available and limit the sensitivity of assays *in vivo*.⁷

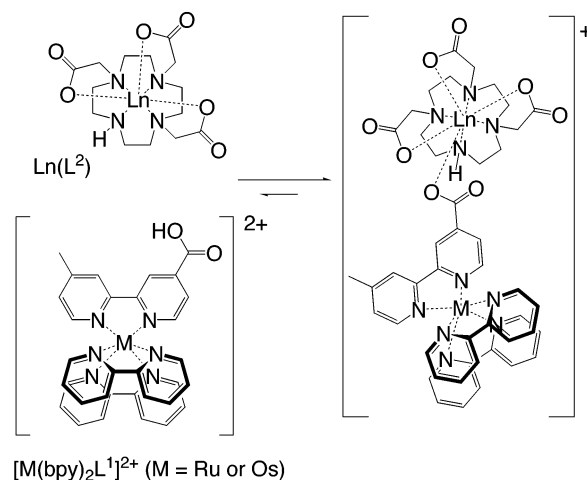
Recent developments in luminescence spectroscopy have opened the way for solution-state spectroscopy of Ln^{III} ions which emit light in the near-IR.^{8–10} When compared with Eu^{III} or Tb^{III}, such ions have lower-energy emissive states and can therefore be combined with chromophores which absorb visible light. Excitation can then be accomplished outside the range of biological absorption, offering the potential for improved detection limits in bioassays.¹¹

Attention has recently turned to the use of d-block complexes as sensitizers for near-IR-emitting lanthanides. When using an emissive sensitizer, electronic energy transfer results in the attenuation of its emission, combined with the growth of the Ln-based signal. Such an approach could be readily applied to probes, sensors, and assays. The range of chromophores described to date includes complexes of Ru^{II},¹² Cr^{III},¹³ and Pt^{II},^{14,15} as well as ferrocenyl derivatives.¹² However, the requirement for time-consuming synthetic procedures has tended to limit the variety of complexes investigated, and any photophysical complications are manifested only when the final system is studied. For example, complications can arise from reversible energy transfer from the chromophore to Ln¹⁶ or from difficulties in separating the Ln emission from the tail of the metal-to-ligand charge-transfer (MLCT) emission.¹² We have attempted to address these difficulties by using relatively simple heteronuclear complexes to test the feasibility of a given sensitizer,^{14,15} but this approach is also limited in scope, since the complexes dissociate in protic solvents.

We have previously shown that seven-coordinate Ln complexes associate with aryl carboxylates to afford ternary complexes in which the aryl group acts as a sensitizer.¹⁷ Here we report the self-assembly of heterobimetallic d–f complexes in protic media, using an approach which permits unprecedentedly rapid and effective screening of sensitizing chromophores.

Various d-block complexes can be used as potential sensitizers, and an equally wide range of Ln ions can act as potential energy acceptors. For the purposes of this study, we chose well-studied 2,2'-bipyridyl (bpy) complexes of Re^I, Ru^{II}, or Os^{II}. The complexes *fac*-Re^ICl(CO)₃L¹, [Ru^{II}(bpy)₂L]²⁺, and [Os^{II}(bpy)₂L]²⁺ (L¹ = 4'-methyl-2,2'-bipyridyl-4-carboxylic acid) are known to be luminescent^{18–20} and possess carboxyl substituents which allow coordination

Scheme 1. Ternary Complex Formation in Solution



dination to a Ln center. To our knowledge, Os^{II} chromophores have never been used previously to sensitize Ln emissions. For the Ln acceptor, we chose Yb^{III}, Nd^{III}, and Er^{III}, the emissive properties of which are well-characterized. By using complexes derived from DO3A, Ln(L²), which contain no sensitizing chromophore, it is possible to use the luminescence from the metal center to probe the Ln coordination environment by using established parameters to calculate inner sphere hydration numbers (*q*).^{21,22}

Ternary complexes were formed in methanol solutions by mixing the d-block metal-containing components with Ln(L²) in equimolar quantities (as shown for the Ru or Os complexes in Scheme 1). These complexation processes were clearly evidenced in solution by ¹H NMR: upon titrations with the Ln complexes, paramagnetic line broadening was invariably observed for the bpy resonances of the d-block complexes. In all of the cases studied, the luminescence from the MLCT state of the d-block chromophore is attenuated upon addition of the Ln complex, whilst the Ln-derived emission appears in the near-IR. The results of the whole series of experiments are shown in Table 1, together with the derived *q* values. A representative emission decay trace is shown in Figure 1.

The Er^{III} complexes proved to be somewhat problematic. Due to facile nonradiative quenching of the Er^{III}-centered emissive states by inner- and outer-sphere O–H oscillators. Thus, while Er^{III}-centered emissions can be observed in deuterated media, the signals detected in CH₃OH are too weak to permit measurement of the luminescence lifetimes. This implies that Er^{III} complexes are likely to be of limited utility in protic media until more sensitive detectors can be developed.

In the case of the Yb^{III} complexes, significant overlap is observed between the Ln^{III} emissions and those from the MLCT states. In

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Table 1. Luminescence Lifetimes and Calculated Ln Inner Sphere Hydration Numbers (q_{Ln}) for the Ternary Complexes ($\lambda_{ex} = 337$ nm)

complex ^a	λ_{em}/nm	τ_{CH_3OH}/ns	τ_{CD_3OD}/ns	q_{Ln}
Re ^I Cl(CO) ₃ (L ¹)Nd ^{III} (L ²)	1055	353	754	0
Re ^I Cl(CO) ₃ (L ¹)Er ^{III} (L ²)	1530	—	398	—
Re ^I Cl(CO) ₃ (L ¹)Yb ^{III} (L ²)	980	1850	4764	0.6
Ru ^{II} (bpy) ₂ (L ¹)Nd ^{III} (L ²) ⁺	1340	174	413	0.6
Ru ^{II} (bpy) ₂ (L ¹)Er ^{III} (L ²) ⁺	1530	—	427	—
Ru ^{II} (bpy) ₂ (L ¹)Yb ^{III} (L ²) ⁺	980	319, 1998	9602	0.7
Os ^{II} (bpy) ₂ (L ¹)Nd ^{III} (L ²) ⁺	1340	237	565	0.3
Os ^{II} (bpy) ₂ (L ¹)Er ^{III} (L ²) ⁺	1530	—	490	—
Os ^{II} (bpy) ₂ (L ¹)Yb ^{III} (L ²) ⁺	980	1.38	8192	1.1

^a No emission could be detected from the isolated Ln complexes at the concentrations used in these experiments. The observed lifetimes were unchanged when using visible excitation into the MLCT bands.

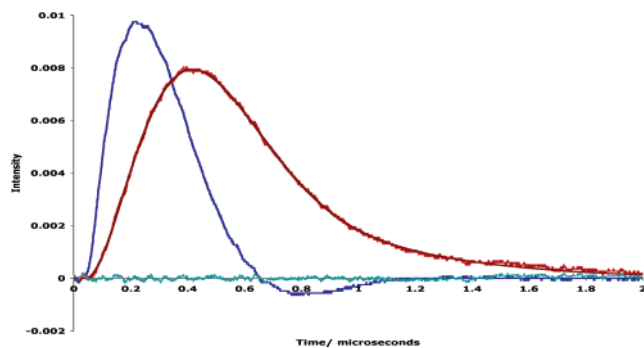


Figure 1. Typical fitted decay, showing the fitted time-resolved emission from Os^{II}(bpy)₂(L¹)Er^{III}(L²)⁺ at 1530 nm. The figure shows the observed decay and fitted decay superimposed on one another (red/brown) the detector response (blue), and the residual (pale blue).

all of the systems studied, the Yb^{III}-centered emissions have microsecond-order lifetimes in CH₃OH, and much longer lifetimes in CD₃OD. The q values of about 1 suggest monodentate binding of the carboxylate to the Ln^{III} center. The changes in lifetime also permit the contribution of the MLCT state to be determined. The emissive lifetimes of the Re^I complexes are very short and comparable to the laser pulse duration. These emissions are intimately convoluted with scattered light and can readily be removed by using time-gating.

Os^{II}-derived luminescence tends to have slightly longer lifetimes (~40 ns) than that from Re^I. In the Os^{II}-Ln^{III} assemblies, fitting requires the use of two exponentials, although the considerable difference between the lifetimes permits the use of time-gating to separate signals arising from Ln^{III} and MLCT states. In the case of the Ru^{II} complex, the MLCT emission lifetime is comparable to that of the Ln^{III} ion in methanol, necessitating signal separation by data analysis, and precluding the use of time-gating. The Nd^{III} complexes have transitions at 880 and 1055 nm, which tend to be convoluted with the MLCT emissions, and a further transition at 1340 nm, which is not convoluted with the MLCT emission to a significant degree. The q values are all well below 1. As with the Yb^{III} complexes, the Os^{II} and Re^I complexes are amenable to time-

gating. For the Ru^{II} complex, the luminescence lifetime of the Nd^{III} center is very similar to that of the Ru^{II} MLCT state; signal separation can only be achieved by studying the relatively weak emission at 1340 nm where the MLCT signal is negligible.

In summary, we have developed an approach that allows screening of large numbers of heteronuclear d-f complexes without recourse to often difficult and time-consuming syntheses. Our results suggest that difficulties with detecting the emission from Er^{III} are likely to rule out its use in protic media and that short-lived emissive MLCT states based on Re^I or Os^{II} are more suitable as donor chromophores when compared with Ru^{II} species.

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Supporting Information Available: Time-resolved emission spectra; NMR spectra illustrating ternary complex formation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Faulkner, S.; Matthews, J. L. In *Comprehensive Coordination Chemistry II*; Ward, M. D., Ed.; Elsevier: Oxford, United Kingdom, 2004; pp 913–944.
- (2) Beeby, A.; Botchway, S. W.; Clarkson, I. M.; Faulkner, S.; Parker, A. W.; Parker, D.; Williams, J. A. G. *J. Photochem. Photobiol. B: Biol.* **2000**, *57*, 83–89.
- (3) Charbonnière, L. J.; Ziessel, R.; Montalti, M.; Prodi, L.; Zaccaroni, N.; Boehme, C.; Wipff, G. *J. Am. Chem. Soc.* **2002**, *124*, 7779–7788.
- (4) Parker D.; Williams, J. A. G. *J. Chem. Soc., Dalton Trans.* **1996**, 3613–3628.
- (5) Muller, G.; Bünzli, J.-C. G.; Riehl, J. P.; Suhr, D.; von Zelewsky, A.; H. Mürner, H. *Chem. Commun.* **2002**, 1522–1523.
- (6) Werts, M. H. V.; Jukes, R. T. F.; Verhoeven, J. W. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1542–1548.
- (7) Dadabhoy, A.; Faulkner, S.; Sammes, P. G. *J. Chem. Soc., Perkin Trans. 2* **2002**, 348–357.
- (8) Beeby, A.; Faulkner, S. *Chem. Phys. Lett.* **1997**, *266*, 116–122.
- (9) Beeby, A.; Dickins, R. S.; Faulkner, S.; Parker, D.; Williams, J. A. G. *Chem. Commun.* **1997**, 1401–1402.
- (10) Werts, M. H. V.; Hofstraat, J. W.; Geurts, F. A. J.; Verhoeven, J. W. *Chem. Phys. Lett.* **1997**, *276*, 196–201.
- (11) Werts, M. H. V.; Woudenberg, R. H.; Emmerink, P. G.; van Gassel, R.; Hofstraat, J. W.; Verhoeven, J. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 4542–4544.
- (12) Klink, S. I.; Keizer, H.; Van Veggel, F. C. J. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4319–4321.
- (13) Imbert, D.; Cantuel, M.; Bünzli, J.-C. G.; Bernardinelli, G.; Piguet, C. *J. Am. Chem. Soc.* **2003**, *125*, 15699–15699.
- (14) Shavaleev, N. M.; Moorcraft, L. P.; Pope, S. J. A.; Bell, Z. R.; Faulkner, S.; Ward, M. D. *Chem. Commun.* **2003**, 1134–1135.
- (15) Shavaleev, N. M.; Moorcraft, L. P.; Pope, S. J. A.; Bell, Z. R.; Faulkner, S.; Ward, M. D. *Chem. Eur. J.* **2003**, *9*, 5283–5291.
- (16) Beeby, A.; Dickins, R. S.; FitzGerald, S.; Govenlock, L. J.; Parker, D.; Williams, J. A. G.; Maupin, C. L.; Riehl, J. P.; Siligardi, G. *Chem. Commun.* **2000**, 1183–1184.
- (17) Faulkner, S.; Burton-Pye, B. P.; Khan, T.; Martin, L. R.; Wray, S. D.; Skabara, P. J. *Chem. Commun.* **2002**, 1668–1669.
- (18) Lin, R.-J.; Chang, I.-J. *J. Chin. Chem. Soc.* **2002**, *49*, 161–164.
- (19) Lay, P. A.; Sasse, W. H. F. *Inorg. Chem.* **1984**, *23*, 4123–4125.
- (20) Striplin, D. R.; Wall, C. G.; Erickson, B. W.; Meyer, T. J. *J. Phys. Chem. B* **1998**, *102*, 2383–2390.
- (21) Beeby, A.; Clarkson, I. M.; Dickins, R. S.; Faulkner, S.; Parker, D.; Royle, L.; de Sousa, A. S.; Williams, J. A. G.; Woods, M. *J. Chem. Soc., Perkin Trans. 2* **1999**, 493–503.
- (22) Beeby, A.; Burton-Pye, B. P.; Faulkner, S.; Motson, G. R.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *Dalton Trans.* **2002**, 1923–1928.

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