Supplementary Information for

Ligand-field excited states of hexacyanochromate and hexacyanocobaltate as sensitisers for near-infrared luminescence from Nd(III) and Yb(III) in cyanide-bridged d-f assemblies

Theodore Lazarides,[a] Graham M. Davies,[a] Harry Adams,[a] Cristiana Sabatini,[b] Francesco Barigelletti,[b] Andrea Barbieri,[*,b] Simon J. A. Pope,[d] Stephen Faulkner,[c] and Michael D. Ward[*,a]

Photoinduced energy transfer within $[M(CN)_4(\mu\text{-}CN)_2Ln(H_2O)_2(dmf)_4]\bullet nH_2O$ species, M = Co(III) and Cr(III), Ln =Gd(III), Nd(III), and Yb(III).

The energy transfer rate constant for the dipole-dipole (Förster) mechanism, k_{en}^{F}, can be estimated by using spectroscopic quantities and according to the following equations.[15]

$$k_{en}^{F} = \frac{8.8\times10^{-25}K^2\phi}{n^4\tau d_{MM}^{6}}J_F \qquad (1)$$

$$J_F = \frac{\int F(\bar{\upsilon})\varepsilon(\bar{\upsilon})/\bar{\upsilon}^4 d\bar{\upsilon}}{\int F(\bar{\upsilon})d\bar{\upsilon}} \qquad (2)$$

where K^2 is a geometric factor (K^2 = 2/3 for statistical reasons), ϕ and τ are the luminescence quantum yield and lifetime of the donor, respectively, n is the refractive index of the medium (taken n = 2 for our solid samples) and J_F is the Förster overlap integral between the luminescence spectrum of the donor, $F(\bar{\upsilon})$ and the absorption spectrum of the acceptor, $\varepsilon(\bar{\upsilon})$, on an energy scale ($cm^{-1}$). For the cases of **Co-Nd** and **Co-Yb**, Table SI_1 lists values for the pertinent parameters and results.

In order to estimate the exchange rate constant (Dexter),[16] k_{en}^{D}, the following equations can be employed in the presence of a weak interaction, H, between the donor and acceptor units; J_D is the Dexter integral.

$$k_{en}^{D} = \frac{4\pi^2 H^2}{h} J_D \qquad (3)$$

$$J_D = \frac{\int F(\bar{\upsilon})\varepsilon(\bar{\upsilon})d\bar{\upsilon}}{\int F(\bar{\upsilon})d\bar{\upsilon}\int \varepsilon(\bar{\upsilon})d\bar{\upsilon}} \qquad (4)$$

For the **Co-Nd** and **Co-Yb** cases, the emission of the donor unit (**Co**) is available from the **Co-Gd** spectroscopy (see main text) and the exctinction coefficient profile, $\varepsilon(\bar{\upsilon})$, of the **Nd** and **Yb** units has been evaluated based on the available absorption profiles (Figure 2), and using the measured peak values $\varepsilon_{794}^{Nd} = 12.6\ M^{-1}\ cm^{-1}$ and $\varepsilon_{975}^{Yb} = 2.1\ M^{-1}\ cm^{-1}$ for water solutions of $NdCl_3 \cdot 6H_2O$ and $Yb(NO_3)_3 \cdot 6H_2O$ as reference compounds. Computations were performed with the help of Matlab 5.2 (MatWorks).

Table SI_1: Parameters used to evaluate the energy transfer features within the **Co-Nd** and **Co-Yb** complexes

		ref
Co-Ln		
Intercenter distance	5.6 Å	
ϕ (Co)	0.1	10g
τ (Co)	630 ns	
Co-Nd		
J_F	$6.4 \times 10^{-17}\ cm^3\ M^{-1}$	
R_c	7.8 Å	
k_{en}^{F} (5.6 Å)	$1.6 \times 10^{7}\ s^{-1}$	
J_D	1.1×10^{-4} cm	
Co-Yb		
J_F	$5.2 \times 10^{-18}\ cm^3\ M^{-1}$	
R_c	5.2 Å	
k_{en}^{F} (5.6 Å)	$1.3 \times 10^{6}\ s^{-1}$	
J_D	5.4×10^{-5} cm	