Supplementary Information

Comparative analysis of lanthanide excited state quenching by electronic energy and electron transfer processes [1]

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Details of the experimental methods and spectroscopic instrumentation used have been reported elsewhere. [1]

Table S1 Quenching studies for [EuL^7], [EuL^8] and [EuL^9], (mean lifetime values (± 5%) were recorded in MeOH, 295 K).

	gradient [a]	τ_0 / ms	k_2 / M^{-1} s^{-1} $\times$ 10^9 (±0.05)
[EuL^7]	0.81	1.26	0.64
[EuL^8]	0.67	1.18	0.57
[EuL^9]	1.33	0.95	1.40

[a] gradient refers to the slope of the τ_0/τ vs [Q] plots (see Fig. S1)
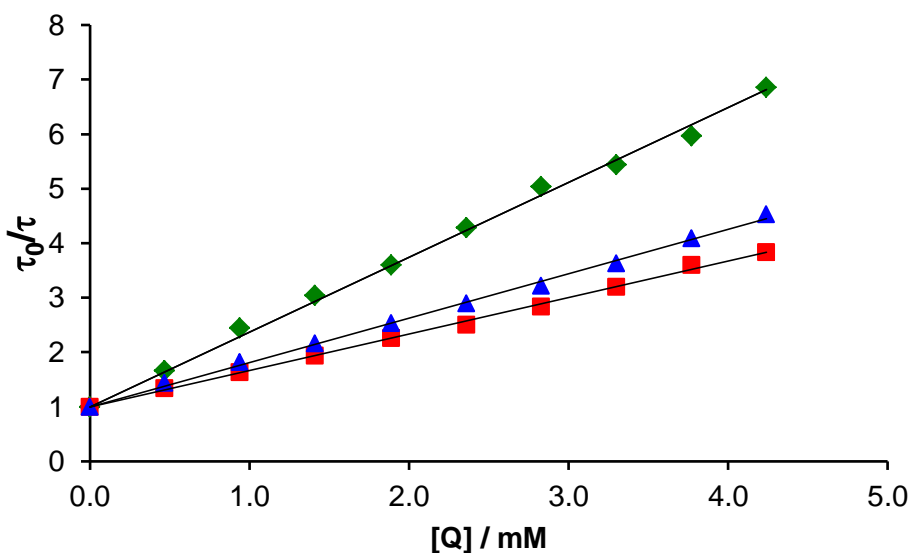
Supplementary Figures

Fig. S1 Variation of the Eu emission lifetime of [EuL^7] (*blue*), [EuL^8] (*red*), and [EuL^9] (*green*) with cyanine dye concentration (lifetime values (±5%), 295 K, MeOH).
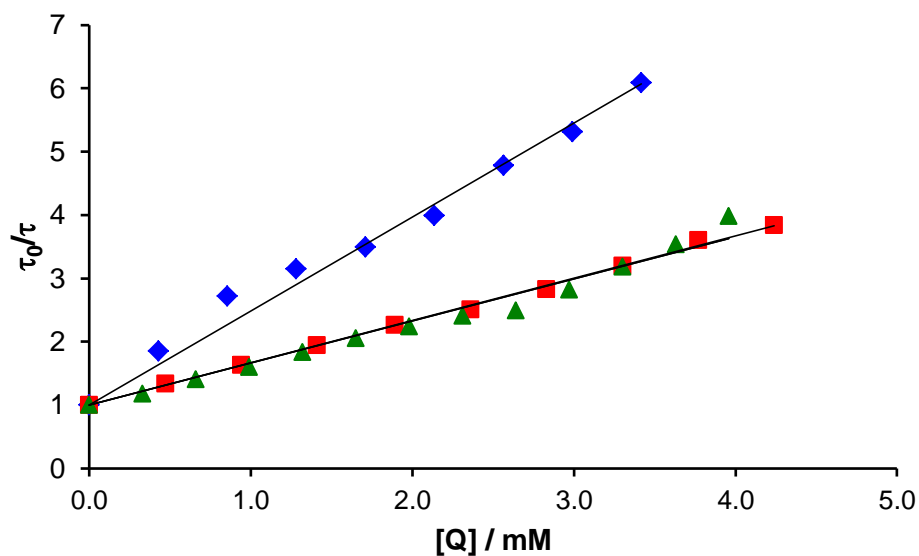
Fig. S2 Quenching behaviour of [EuL^8] in different solvents. Lifetime values were recorded at 295 K in: 100% 50 mM HEPES buffer, 50 mM NaCl, pH = 7.4 (*blue*); 50% 50 mM HEPES buffer, 50 mM NaCl and 50% MeOH (*green*); 100% MeOH (*red*). λ_{ex} = 332 nm.

In order to understand the FRET mechanism better, and in particular consider the differences in behaviour of the carboxylate and phosphinate complexes, additional structurally related complexes, [EuL^{10}-EuL^{15}], were examined in buffered aqueous solution, (Table 4, 50 mM HEPES buffer, 50 mM NaCl, pH = 7.4).[2] The quenching of these water-soluble complexes was examined in the presence of quencher concentrations that varied from 0.3 to 2.5 μM.
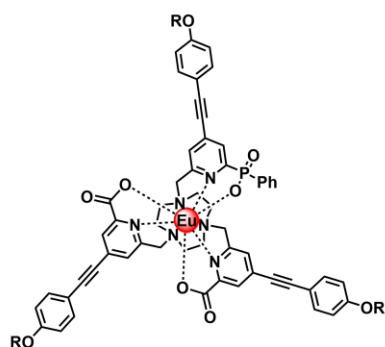
RO
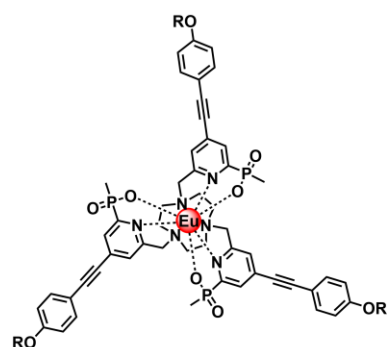
[EuL^{12}]   R = Me
[EuL^{13}]$^{3-}$ R = CH$_2$CO$_2^-$

R'O
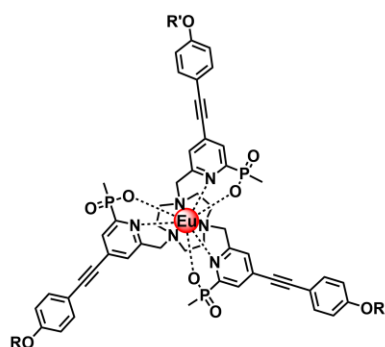
[EuL^{14}]   R = R' = (CH$_2$CH$_2$O)$_3$Me
[EuL^{15}]$^-$ R = (CH$_2$)$_3$SO$_3^-$, R' = (CH$_2$)$_3$NH$_3^+$
[EuL^{16}]$^+$ R = (CH$_2$CH$_2$O)$_3$Me, R' = (CH$_2$)$_3$NH$_3^+$
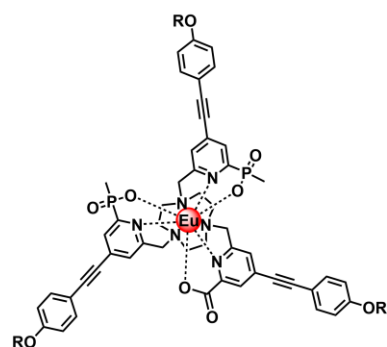
[EuL^{17}]   R = Me

[EuL^{18}]$^+$ R = (CH$_2$CH$_2$O)$_3$Me

Table S1   Quenching studies. (Values recorded (± 5%) in 50 mM HEPES buffer, 4 μM complex, 50 mM NaCl, pH = 7.4, 295 K).

		gradient	τ_0 / ms	k_2 / M^{-1} s^{-1} ×10^9
[EuL^{12}]	3P-Me (3OMe)	1.64	1.03	1.59
[EuL^{13}]$^{3-}$	3P-Me (3OCH$_2$COO$^-$)	1.84	1.04	1.77
[EuL^{14}]	3COO$^-$ (3PEG)	0.68	0.82	0.84
[EuL^{15}]$^-$	3COO$^-$ (2SO$_3^-$, 1NH$_3^+$)	1.65	0.80	2.06
[EuL^{16}]$^+$	3COO$^-$ (2PEG, 1NH$_3^+$)	1.72	0.76	2.26
[EuL^{17}]	2P-Me 1COO$^-$ (3OMe)	0.95	0.89	1.07
[EuL^{18}]$^+$	1P-Ph 2COO$^-$ (2PEG, 1NH$_3^+$)	2.06	0.84	2.45

The analysis of the rate constants calculated for these complexes (Table S2) showed little difference in the behaviour of the tris-phosphinate and the tris-carboxylate systems in water. In addition, the hybrid systems (containing both carboxylate and phosphinate) did not give rise to any particular changes with regard to rate constants. The introduction of negative charge on the periphery of the chromophore enhanced

complex water solubility (see log *P* values below), but did not change the energy transfer kinetics, as seen when comparing the behaviour of [EuL[12]] and [EuL[13]][3-].

Log *P* determination of europium(III) complexes

Experiments to quantify the relative hydrophilicity of these complexes (log *P* in water/octanol) were carried out in order to assess if there was any correlation between the rate of energy transfer to the cyanine dye and the lipophilicity of each complex. Three equimolar solutions of complex were prepared in MeOH. The solvent was removed under reduced pressure and the resulting solid was dissolved and stirred for 24 h in 0.9 mL of a mixture of water/octanol (2:1, 1:1, 1:2) giving a total concentration of approximately 2 μM for each mixture. After equilibration, an emission spectrum for each layer was recorded in MeOH (50 μL of solution in 1 mL of MeOH). For each mixture, the log *P* value was calculated, according to the following equation:

$$\mathbf{Log}P = \mathbf{Log}\left(\frac{\int_{605\,\mathbf{nm}}^{635\,\mathbf{nm}} I(\mathbf{oct})}{\int_{605\,\mathbf{nm}}^{635\,\mathbf{nm}} I(\mathbf{H_2O})}\right)$$

Final log *P* values were calculated as the average of three solvent mixtures at 295 K.

In addition to the previously reported complexes, further examples (Fig. S3) [2] were examined in order to seek a better understanding of the structural features that determine the hydrophilicity of these systems.
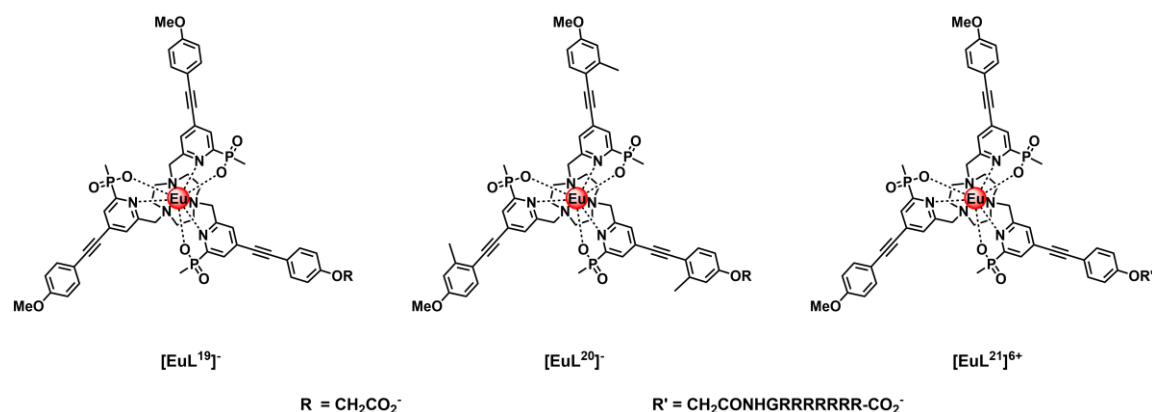

R = CH₂CO₂⁻   R' = CH₂CONHGRRRRRRR-CO₂⁻

Fig. S3 Additional Eu(III) complexes examined for log *P* comparative studies.

Table S3 Log P Values (octanol/water) for Eu(III) complexes [a] (values of k_2 for energy transfer quenching by the cyanine dye are given in parentheses, Table S2)

	Log P
[EuL[12]]	1.4 ± 0.3 (1.59)
[EuL[18]][+]	1.2 ± 0.2 (2.45)
[EuL[14]]	1.1 ± 0.2 (0.84)
[EuL[17]]	1.1 ± 0.2 (1.07)
[EuL[20]][-]	0.8 ± 0.2 (nd)
[EuL[16]][+]	0.7 ± 0.2 (2.26)
[EuL[19]][-]	0.3 ± 0.1 (nd)
[EuL[21]][6+]	0.3 ± 0.1 (nd)
[EuL[15]][-]	- 1.1 ± 0.2 (2.06)
[EuL[13]][3-]	- 2.2 ± 0.4 (1.77)

[a] Complexes [EuL[7]] and [EuL[9]] have a log$P$ value > 2; nd = not determined.

From these data (Table S3), the introduction of charged moieties close to the periphery of the chromophore (*e.g.* [EuL[4]][3-]) increased the water solubility of the system, whereas the PEG groups only showed a small effect (*i.e.* [EuL[14]] with 3 PEG groups). This data set did not reveal any significant linear correlation (Fig. S4, R^2 = 0.048) between experimental log P values and the rate of energy transfer quenching by the cyanine dye, consistent with the process occurring over long distances.
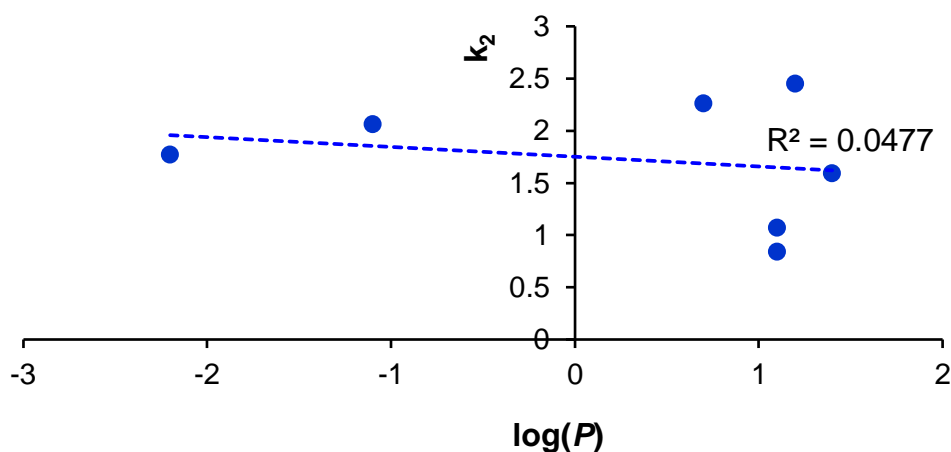

Fig. S4 Correlation of the second order rate constant , k_2, for quenching of Eu complexes by the cyanine dye (295 K), with the log P value of each complex (octanol/water).

References

1. M. Starck, J. D. Fradgley, R. Pal, J. M. Zwier, L. Lamarque and D. Parker, *Chem.-Eur. J.* 2021, **27**, 766–777.
2. L. Lamarque, D. Parker, S. J. Butler, M. Delbianco, *World patent application*, WO 2014/111661, PCT/FR20 14/0500085, published July 24, 2014, US Patent 9,920,082; granted 20 March 2018.