ELECTRONIC SUPPORTING INFORMATION

Bifunctional heterobimetallic 3d-4f [Co(II)-RE, RE = Dy, Eu, Y] ionic complexes: modulation of the magnetic-luminescent behaviour

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Table S1. Selected bond lengths (Å) and angles (°) in **Eu-Co** and **Y-Co**.

M (Eu in **Eu-Co** and Y in **Y-Co)**		**Co**	
	Eu-Co / Y-Co		**Eu-Co / Y-Co**
M1-O1D	2.392(2) / 2.345(2)	Co1-O1A	2.058(2) / 2.058(2)
M1-O2D	2.378(2) / 2.333(2)	Co1-O2A	2.059(2) / 2.058(2)
M1-O1E	2.376(2) / 2.328(2)	Co1-O1B	2.060(2) / 2.060(3)
M1-O2E	2.423(2) / 2.375(2)	Co1-O2B	2.059(2) / 2.063(2)
M1-O3	2.524(2) / 2.492(3)	Co1-O1C	2.074(2) / 2.070(2)
M1-O4	2.473(2) / 2.428(2)	Co1-O2C	2.076(2) / 2.071(3)
M1-O5	2.487(2) / 2.450(2)		
M1-O6	2.438(2) / 2.390(2)		
M1-O7	2.512(2) / 2.475(2)		
	Eu-Co / Y-Co		**Eu-Co / Y-Co**
O1D-M1-O2D	70.77(7) / 71.70(8)	O1A-Co-O2A	88.71(8) / 88.6(1)
O1D-M1-O1E	140.47(7) / 139.59(8)	O1A-Co1-O1B	88.68(8) / 88.6(1)
O1D-M1-O2E	134.92(7) / 134.69(8)	O1A-Co1-O2B	176.64(8) / 176.5(1)
O1D-M1-O3	75.368(7) / 75.66(8)	O1A-Co1-O1C	86.75(8) / 86.7(1)
O1D-M1-O4	71.89(7) / 72.12(8)	O1A-Co1-O2C	92.82(8) / 93.3(1)
O1D-M1-O5	67.69(7) / 67.68(8)	O2A-Co1-O1B	91.76(8) / 91.7(1)
O1D-M1-O6	86.45(7) / 86.26(8)	O2A-Co1-O2B	93.46(8) / 93.63(9)
O1D-M1-O7	135.85(7) / 136.72(8)	O2A-Co1-O1C	173.02(8) / 172.8(1)
O2D-M1-O1E	111.01(7) / 110.60(8)	O2A-Co1-O2C	87.72(8) / 87.5(1)
O2D-M1-O2E	140.78(7) / 139.60(8)	O1B-Co1-O2B	88.69(8) / 88.65(9)
O2D-M1-O3	72.55(7) / 71.75(8)	O1B-Co1-O1C	93.43(8) / 93.64(9)
O2D-M1-O4	129.68(7) / 130.31(8)	O1B-Co1-O2C	178.40(8) / 178.0(1)
O2D-M1-O5	125.85(6) / 126.35(8)	O2B-Co1-O1C	91.33(8) / 91.36(9)
O2D-M1-O6	78.60(6) / 77.51(8)	O2B-Co1-O2C	89.84(8) / 89.55(9)
O2D-M1-O7	70.39(6) / 69.78(8)	O1C-Co1-O2C	87.22(8) / 87.28(9)
O1E-M1-O2E	69.60(7) / 70.62(8)		
O1E-M1-O3	68.08(7) / 67.74(8)		
O1E-M1-O4	79.43(6) / 78.24(8)		
O1E-M1-O5	123.14(7) / 123.05(8)		

O1E-M1-O6	133.08(7) / 134.13(8)		
O1E-M1-O7	74.30(7) / 73.91(8)		
O2E-M1-O3	134.21(7) / 135.56(8)		
O2E-M1-O4	89.49(6) / 90.02(8)		
O2E-M1-O5	67.23(6) / 67.01(8)		
O2E-M1-O6	75.26(6) / 75.39(8)		
O2E-M1-O7	72.46(6) / 72.26(8)		
O3-M1-O4	66.40(6) / 67.14(8)		
O3-M1-O5	125.90(6) / 126.82(8)		
O3-M1-O6	149.72(6) / 147.90(8)		
O3-M1-O7	111.17(6) / 109.41(8)		
O4-M1-O5	65.18(6) / 65.75(8)		
O4-M1-O6	130.85(6) / 132.03(8)		
O4-M1-O7	151.98(6) / 150.66(8)		
O5-M1-O6	65.83(6) / 66.48(8)		
O5-M1-O7	122.89(6) / 123.74(8)		
O6-M1-O7	66.01(6) / 66.91(8)		

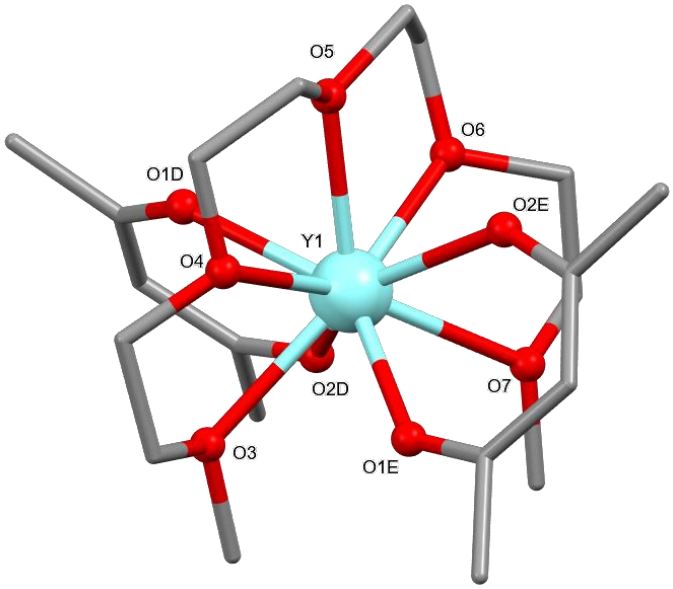

Fig. S1. Ball and stick view of the structure of $[Y(hfa)_2 \cdot tetraglyme]^+$ cation in **Y-Co**; hydrogen and fluorine atoms have been omitted for sake of clarity.

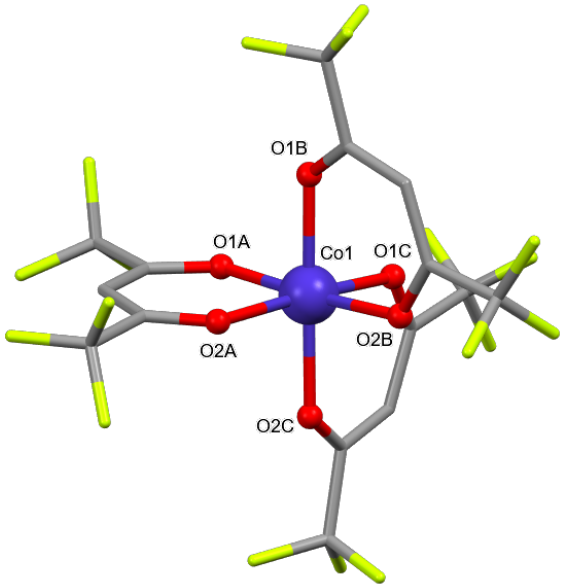

Fig.S2. Ball and stick view of the structure of $Co(hfa)_3^-$ anion of **Y-Co,** hydrogen atoms have been omitted for sake of clarity.

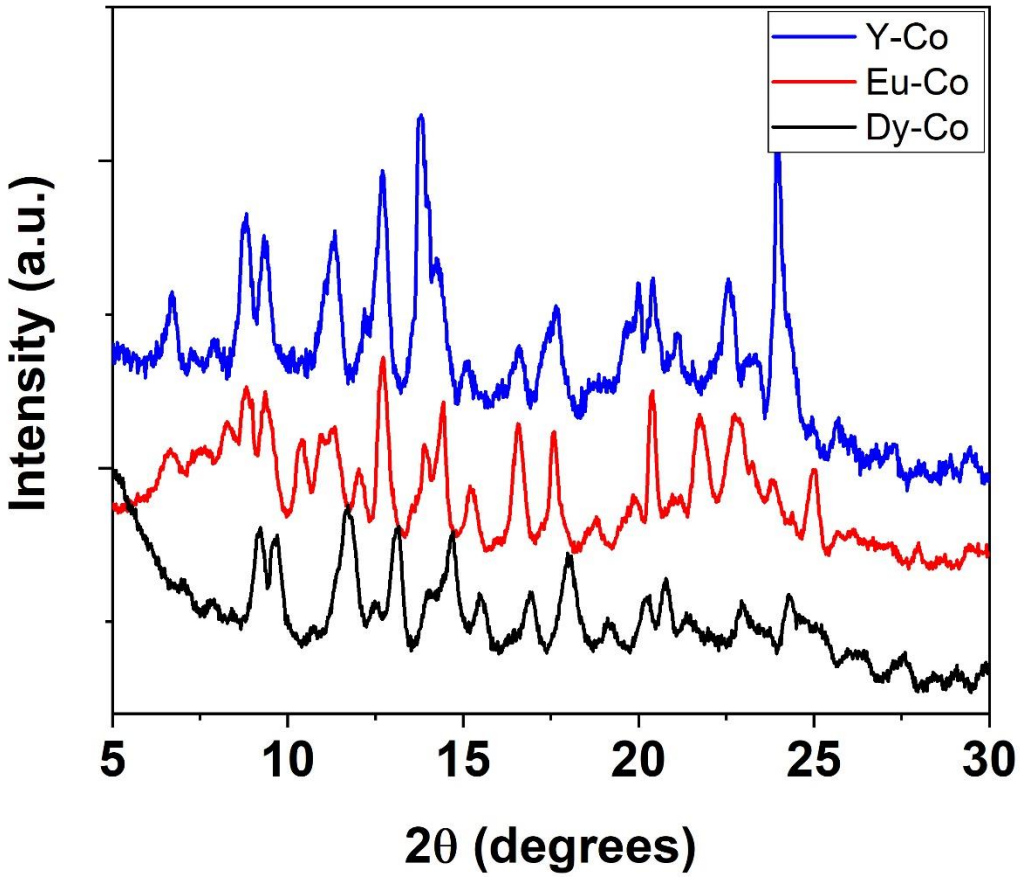

Fig. S3. PXRD patterns of **Dy-Co** (black, experimental), **Eu-Co** (red, experimental) and **Y-Co** (blue, experimental).

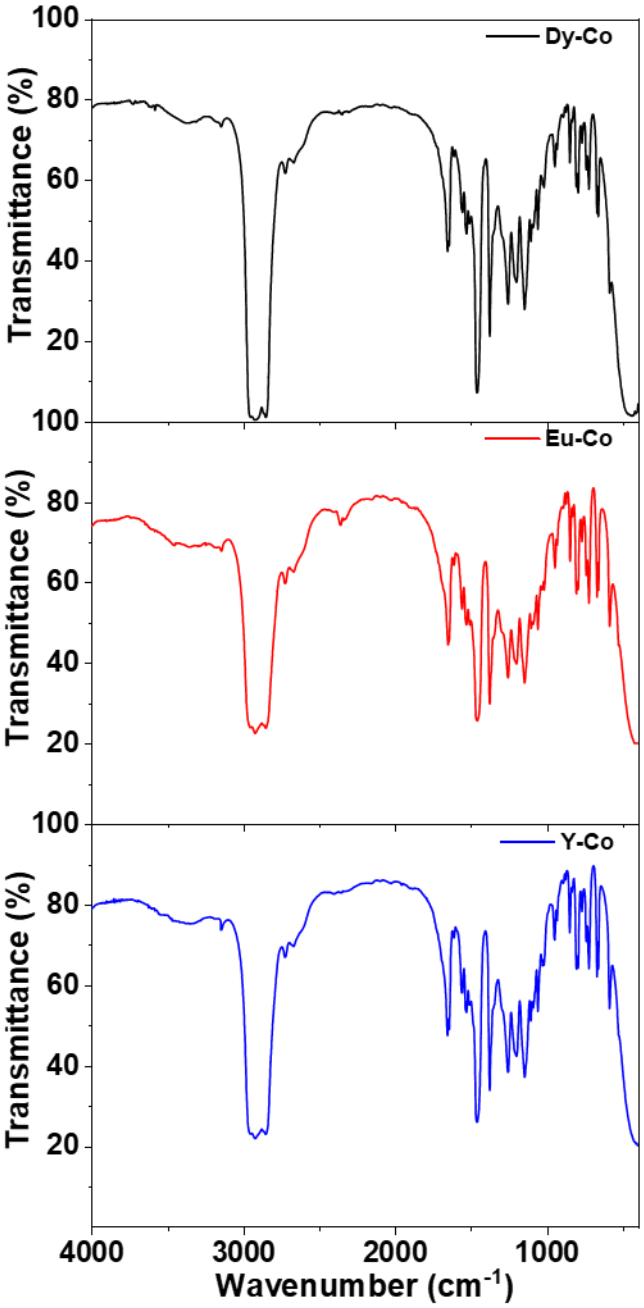

Fig.S4. FT-IR spectra of the **Y-Co, Dy-Co** and **Eu-Co** complexes.

	HP-6 Hexagon (D_{6h})	PPY-6 Pentagonal pyramid C_{5v}	**OC-6** **Octahedron** **O_h**	TPR-6 Trigonal prism D_{3h}	JPPY-6 Johnson pentagonal pyramid J2 C_{5v}
$Et_4N[Co^{II}(hfa)_3]$	32.862	27.854	**0.181**	14.538	31.583
Y-Co	32.878	27.371	**0.169**	14.129	31.090

Table S2 SHAPE parameters for the coordination sphere of Cobalt(II) in Y-Co and $(NEt_4)Co(hfa)_3$ (ref. 1).

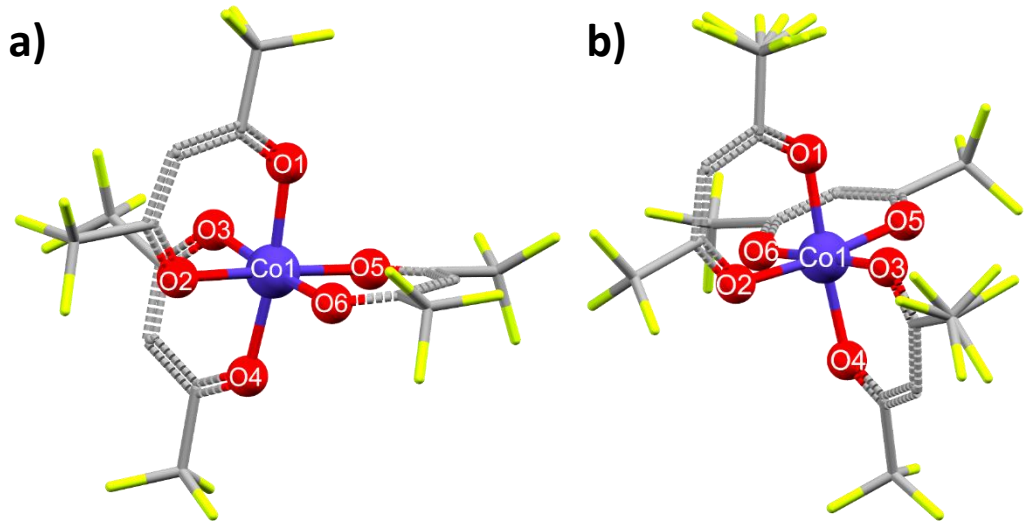

Fig. S5. Coordination environment of the Co(II) centre in the two complexes: **a**) $Et_4N[Co^{II}(hfa)_3]$; **b**) **Y-Co.**

Bond distances (Å)			
$Et_4N[Co^{II}(hfa)_3]$		**YCo**	
Co1 – O1	2.077(2)	Co1 – O1	2.058(2)
Co1 – O2	2.078(2)	Co1 – O2	2.058(2)
Co1 – O3	2.053(1)	Co1 – O3	2.060(2)
Co1 – O4	2.084(2)	Co1 – O4	2.063(2)
Co1 – O5	2.077(2)	Co1 – O5	2.071(2)
Co1 – O6	2.047(1)	Co1 – O6	2.070(2)

Table S3 Co-O bond distances in the Co(II) coordination environment for the two complexes.

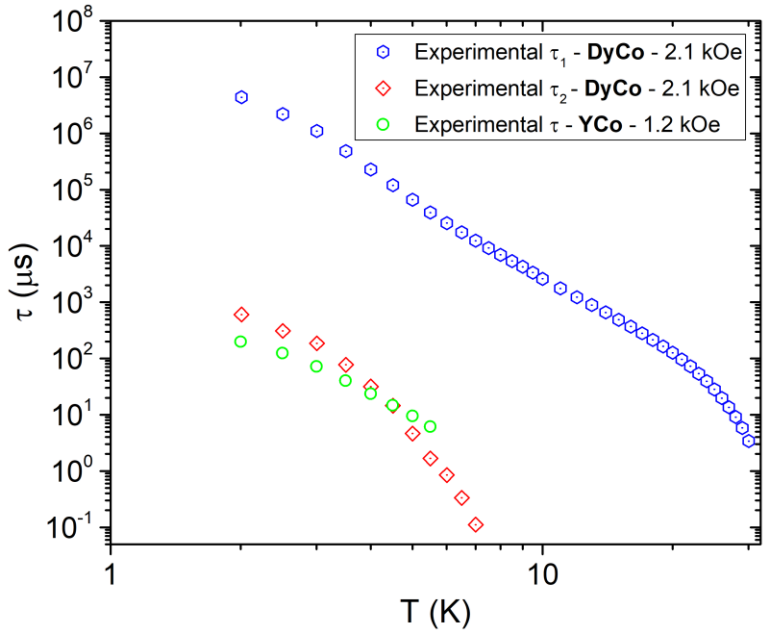

Fig. S6. Comparison of the relaxation rate observed for **Y-Co** under an external applied field of 1.2 kOe and for **Dy-Co** in an applied field of 2.1 kOe.

Supplementary Note S1. Fitting procedure of experimental DC magnetometry data and g factors.

The fitting procedure was conducted with a custom-written MATLAB script based on the toolkit EASYSPIN and the *fminuit* minimization routine. The goodness of fit between the experimental data and the simulated ones was evaluated as the coefficient of determination R^2 (worst value = $-\infty$, best value = +1) (ref. 2).

$$R^2 = 1 - \frac{\sum_{i=1}^{m}(Y_i - \bar{Y})^2}{\sum_{i=1}^{m}(Y_i - X_i)^2}$$

In this equation Y_i, $\bar{Y}$ and X_i represent the experimental data set, the averaged value of the experimental data set and the simulated dataset.

Since *fminuit* is a minimization routine (i.e., it minimizes a scalar value by adjusting free parameters), the code was designed to minimize the quantity $1 - R^2$ (worst value = $+\infty$, best value = 0). The expression for it is given by:

$$1 - R^2 = \frac{\sum_{i=1}^{m}(Y_i - \bar{Y})^2}{\sum_{i=1}^{m}(Y_i - X_i)^2}$$

In this specific case, the goodness of fit was evaluated as $1 - R^2 = 0.0407$, corresponding to $R^2 = 0.9593$.

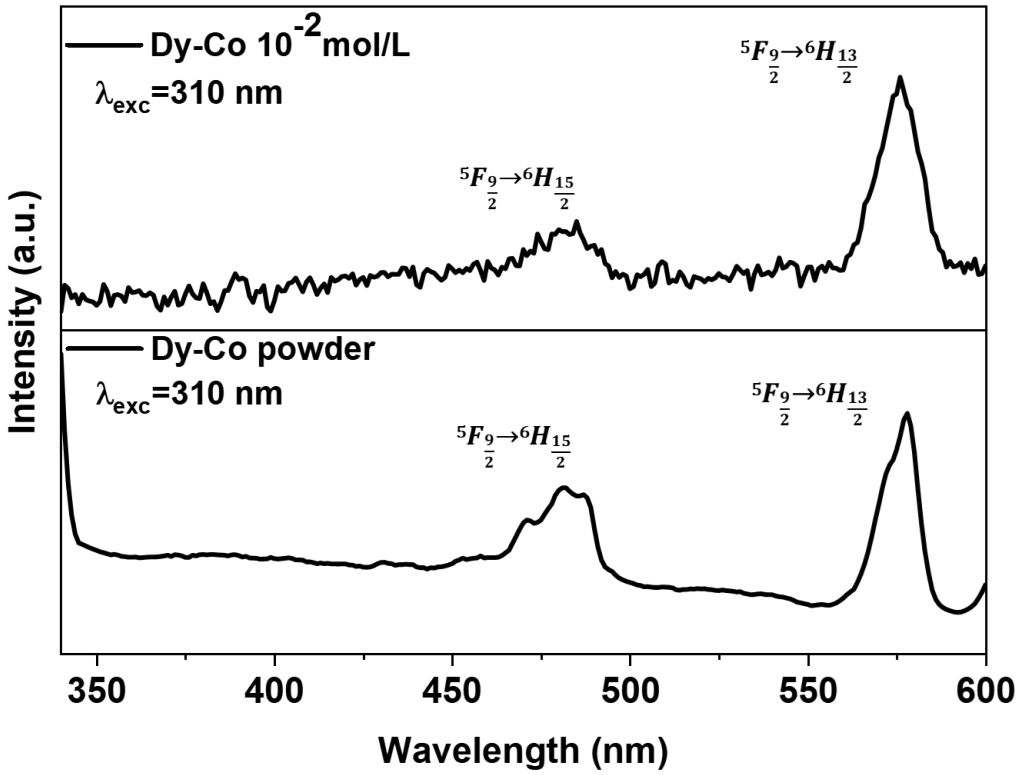

Fig. S7. Emission spectra, recorded at room temperature, with an excitation wavelength of 310 nm for the Dy-Co solution (CH_2Cl_2) and Dy-Co powder film obtained through drop-casting on quartz.

References

1. A. V. Palii, D. V. Korchagin, E. A. Yureva, A. V. Akimov, E. Ya. Misochko, G. V. Shilov, A. D. Talantsev, R. B. Morgunov, S. M. Aldoshin and B. S. Tsukerblat, *Inorg. Chem.*, 2016, **55**, 9696–9706.
2. D. Chicco D, M. J. Warrens, G. Jurman, The coefficient of determination R-squared is more informative than SMAPE, MAE, MAPE, MSE and RMSE in regression analysis evaluation. *PeerJ Computer Science,* 2021, 7:e623.