Sensitized near infrared emission through supramolecular d→f energy transfer within an ionic Ru(II) – Er(III) pair

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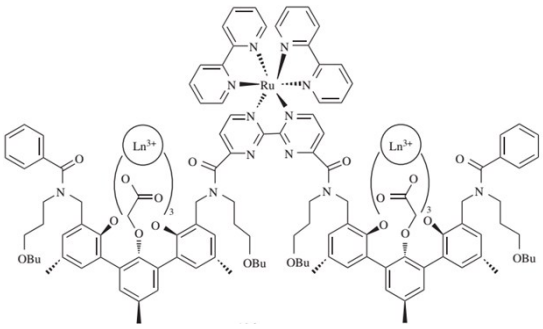
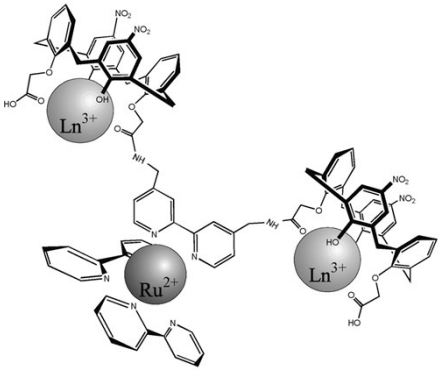
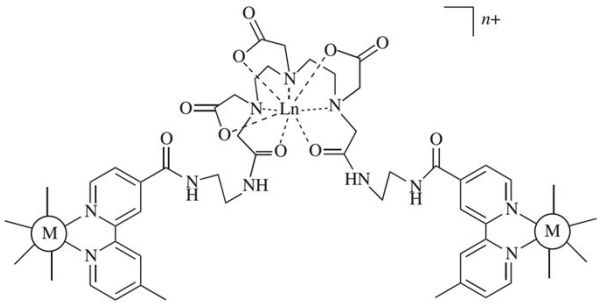
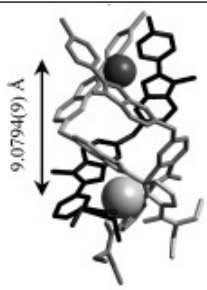
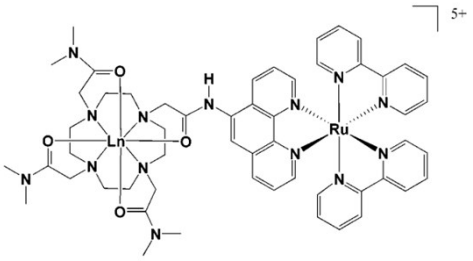
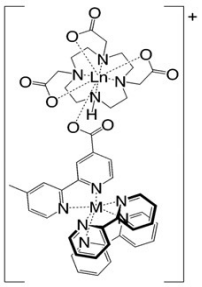
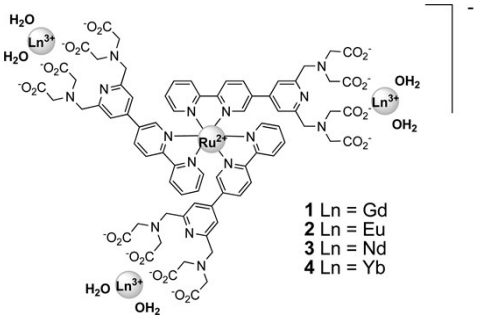
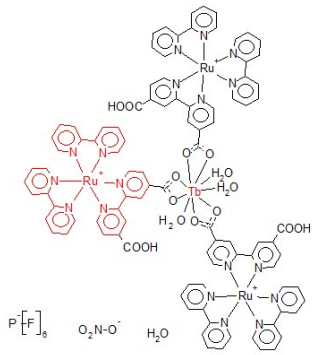
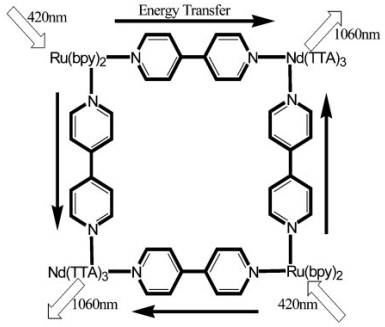
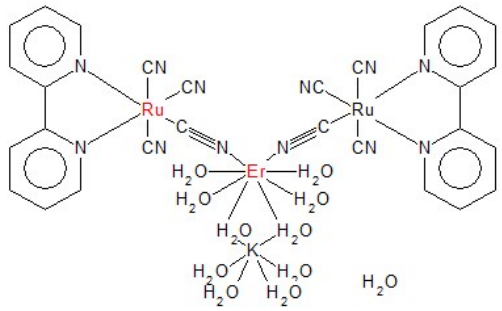
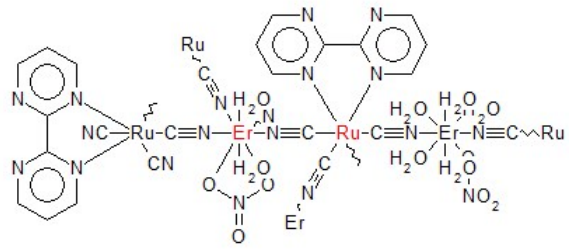
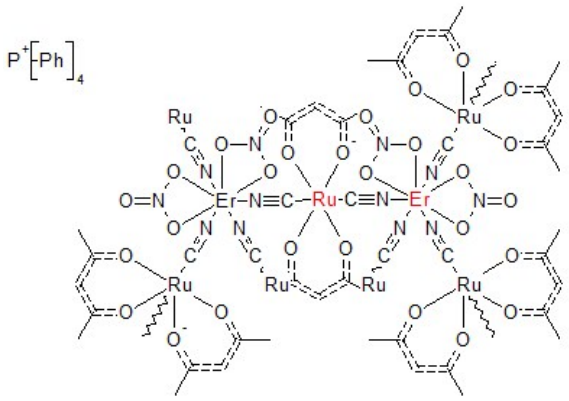
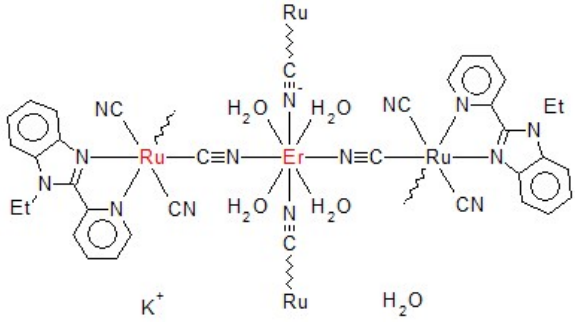
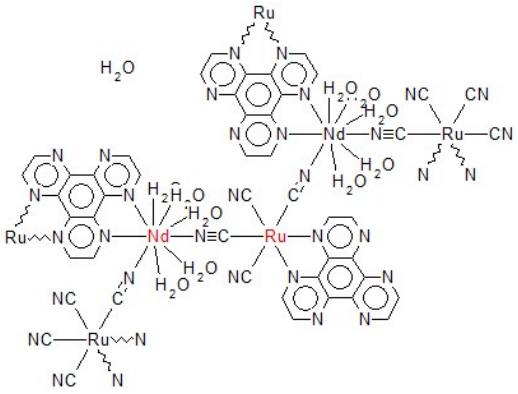
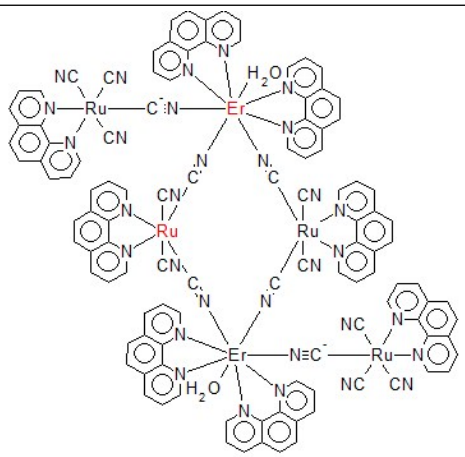
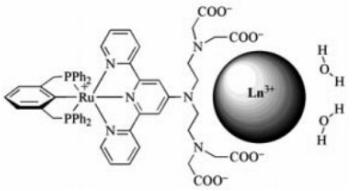
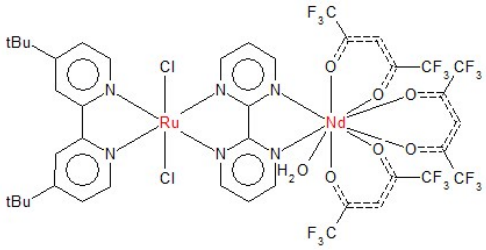
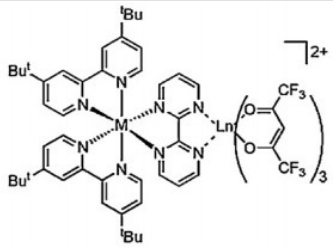
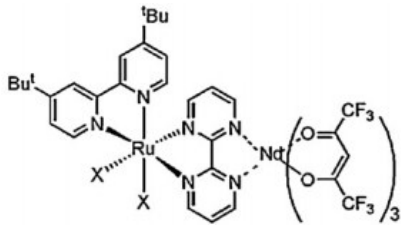
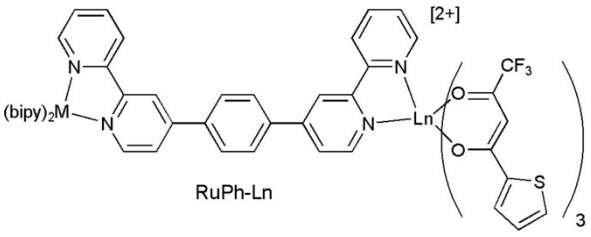
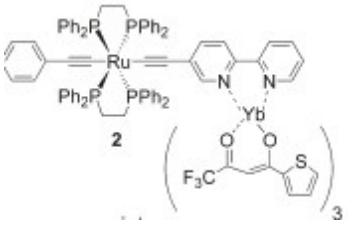
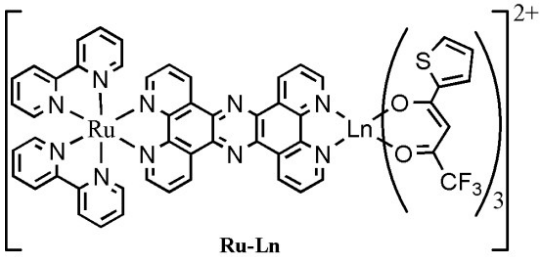
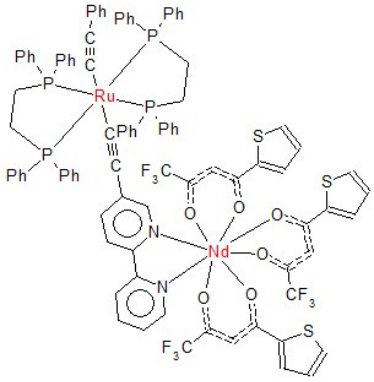
Table S1. Examples of Ru→Ln energy transfer for sensitized lanthanide emission

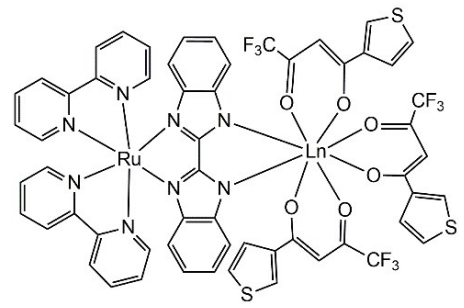
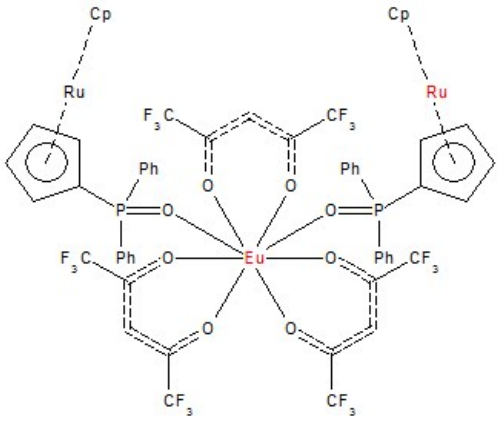
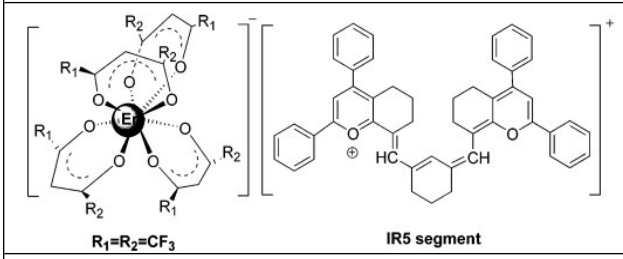
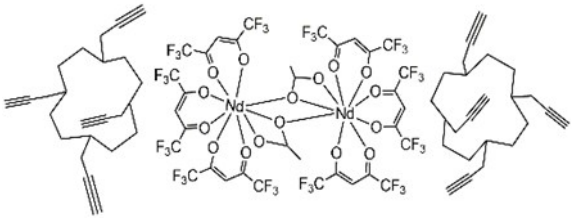
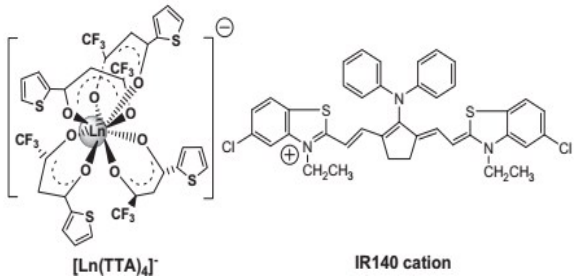
Intramolecular *d*→*f* energy transfer		
Complexes	d-f distance (Å)	Ref.
through-space multipolar energy transfer		
Category I		
	~12	*Angew. Chem. Int. Ed*. **2000**, *39*, 4319–4321
	~12	*Inorg. Chem.,* **2004***,* *43,* 3965–3975
	~15	*Dalton Trans.,* **2005***,* 1482–1490
	8.70	*Chem. Eur. J.,* **2005***,* *11,* 3228–3242

	~11	*Inorg. Chem.*, **2006**, *45,* 10040–10042
Category II		
	11.8	*J. Am. Chem. Soc.* **2004**, *126,* 9490–9491
		*Inorg. Chem.* **2015**, *54,* 1414−1425
	9.08	*New J. Chem.*, **2016**,*40,* 5379–5386
orbital overlap (double electronic exchange mechanisms)		

	~10.5	*Chem. Commun.*, **2004**, 1486–1487
	5.44	*Inorg. Chem.* **2005**, *44*, 4656–4665
	5.46	*Inorg. Chem.* **2006**, *45*, 3895–3904
	5.41	*Inorg. Chem.* **2006**, *45*, 6756–6760
	5.50	*Dalton Trans.* **2006**, 39–50

	5.63	*J. Am. Chem. Soc.*, **2007**, *129,* 11491–11504
	5.55	*Dalton Trans.* **2007**, 2419–2430
	~7.5	*Eur. J. Inorg. Chem.*, **2007**, 2853–2861
	6.22	*Dalton Trans.* **2008**,691–698
	6.21	*Dalton Trans.*, **2008**,

		
	~20	*Chem. Eur. J.*, **2008**, *14*, 9389–9399
	8.67	*J. Am. Chem. Soc.* **2011**, *133*, 6174–6176
	~12.7	*Dalton Trans*., **2012**, *41*, 11219–1225
	8.53	*Organometallics,* **2014**, *33*, 4824-4835

	~5.6	*Dalton Trans.*, **2015**,*44,* 15212–15219
	5.83	*J. Phys. Chem. A.* **2015**, *119,* 4825–4833
Intermolecular energy transfer (supramolecular sensitization)		
		*J. Phys. Chem. B.* **2004**, *108,* 8084–8088
		*Inorg. Chem. Commun.* **2007**, *10,* 1129–1131
		*Dyes and Pigments,* **2012**, *95,* 69–73

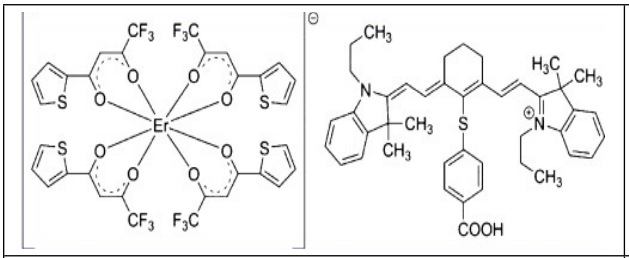
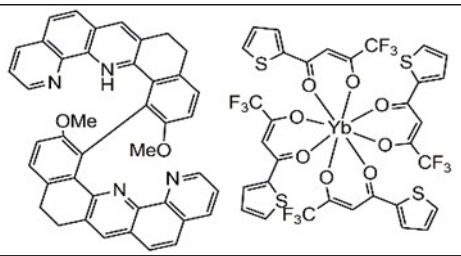
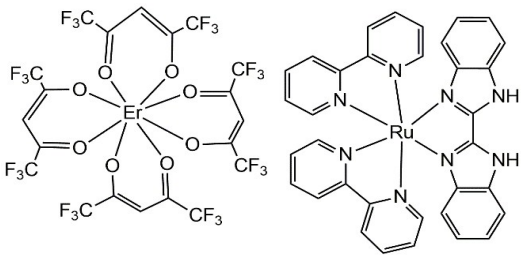
		*ACS Photonics,* **2014**, *1,* 394–397
		*Eur. J. Inorg. Chem.* **2017**, 2100
	8.6	*This work*

Table S2. Crystallographic Data of **$N(C_2H_5)_4[Eu(hfac)_4]$** and **1**.

	$N(C_2H_5)_4[Eu(hfac)_4]$	**1**
empirical formula	$C_{28}H_{24}EuF_{24}NO_8$	$C_{56}H_{30}ErF_{27}N_8O_{10}Ru$
fw	1085.91	1756.21
space group	$P\,2_1/n$	$C\,2/c$
a, Å	13.325(4)	18.085(6)
b, Å	16.993(5)	37.766(12)
c, Å	18.776(6)	11.710(4)
α, deg	90.00	90.00
β, deg	94.905(4)	112.791(6)
γ, deg	90.00	90.00
V, Å^3	4236(2)	7373(4)
Z	4	4
ρ_{calcd}, g/cm^3	1.703	1.582
μ, mm^{-1}	1.625	1.458
radiation (λ, Å)	0.71073	0.71073
temp, K	293(2)	293(2)
R_1 $(F_o)^{[a]}$	0.0886	0.0543
wR_2 $(F_o^2)^{[b]}$	0.2769	0.1575
GOF	1.025	0.941

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, [b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$

Table S3. Bond lengths (Å) and angles (°) in **1** and **$N(C_2H_5)_4[Eu(hfac)_4]$**

	1	**$N(C_2H_5)_4[Eu(hfac)_4]$**
O1–Ln	2.047(18)	2.406(4)
O2–Ln	2.187(18)	2.373(4)
O3–Ln	2.27(2)	2.406(3)
O4–Ln	2.07(4)	2.397(4)
O5–Ln		2.405(4)
O6–Ln		2.389(4)
O7–Ln		2.392(4)
O8–Ln		2.383(4)
O1–Ln–O4	85.2(14)	75.86(14)
O2–Ln–O3	76.0(10)	74.24(13)
O5–Ln–O7		76.77(14)
O6–Ln–O8		71.17(13)

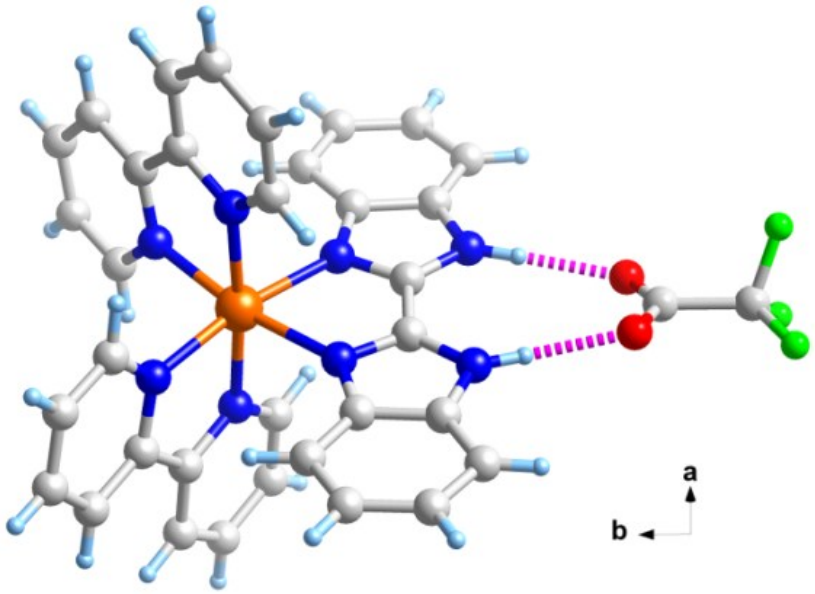


Figure S1. The H-bonds between $[Ru(bpy)_2(dbim)]^{2+}$ and $[CF_3COO]^-$ in **1**.

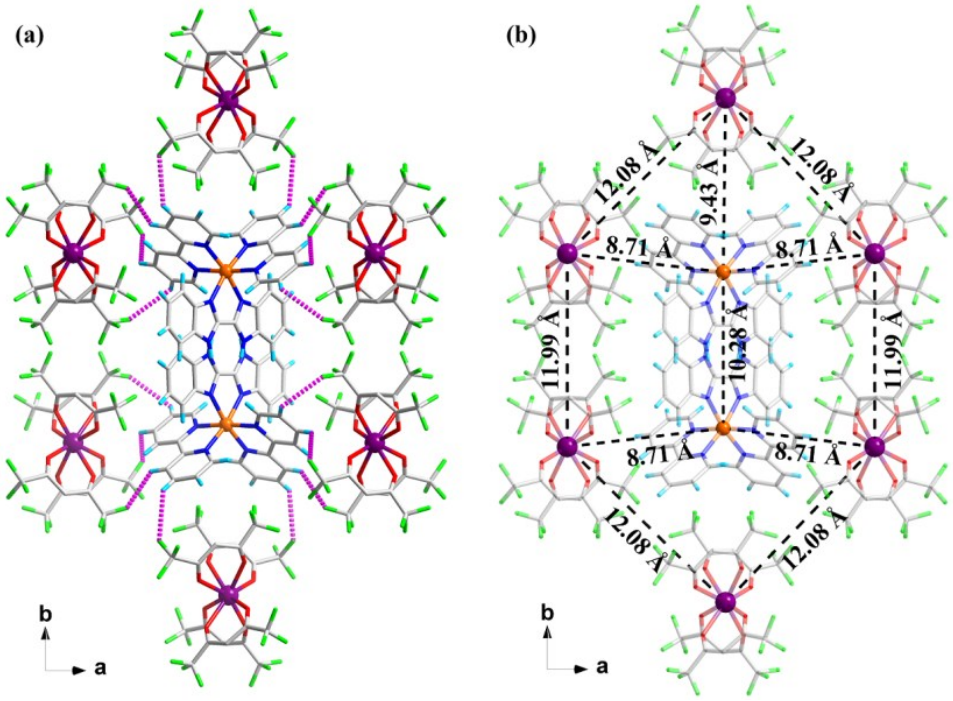


Figure S2. (a) The H-bonds between $[Er(hfac)_4]^-$ and $[Ru(bpy)_2(dbim)]^{2+}$ moieties. The purple dashed lines correspond to C-H…F interactions. (b) The distance between the metal centres of $[Er(hfac)_4]^-$ and $[Ru(bpy)_2(dbim)]^{2+}$ moieties.

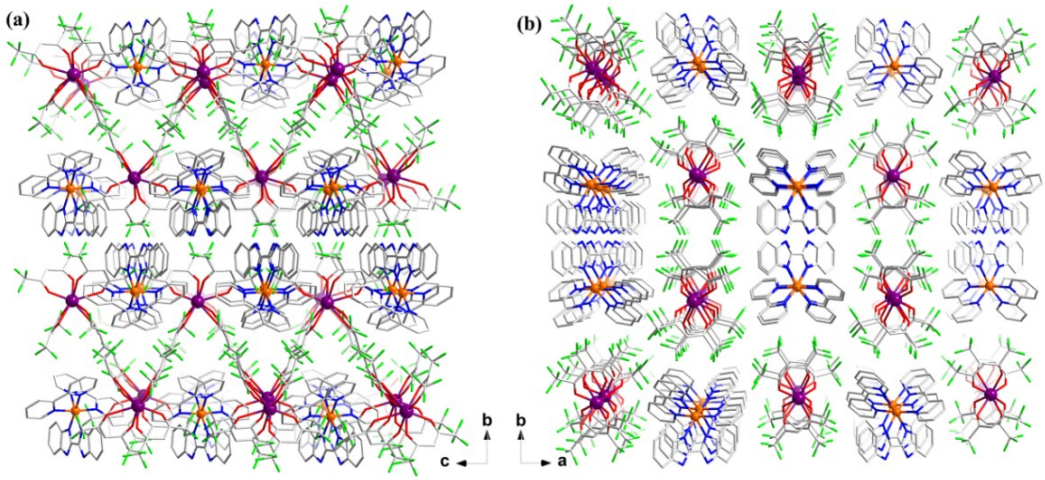


Figure S3. The crystal packing of $[Er(hfac)_4]^-$ and $[Ru(bpy)_2(dbim)]^{2+}$ moieties in **1** viewed along *a* (left) and *c* (right)-axis. For clarity, the $[CF_3COO]^-$ and hydrogen atoms are omitted.

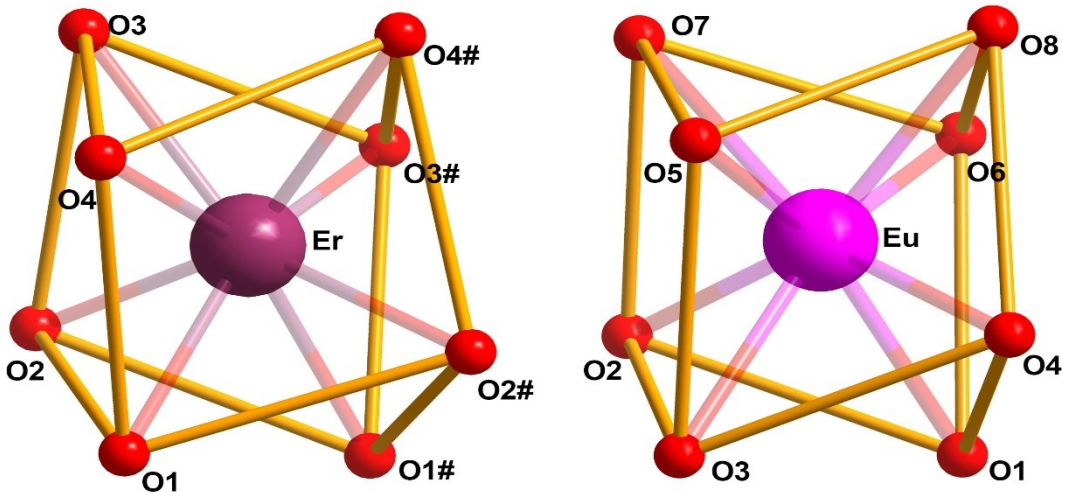


Figure S4. Coordination environment of Er^{III} and Eu^{III}.

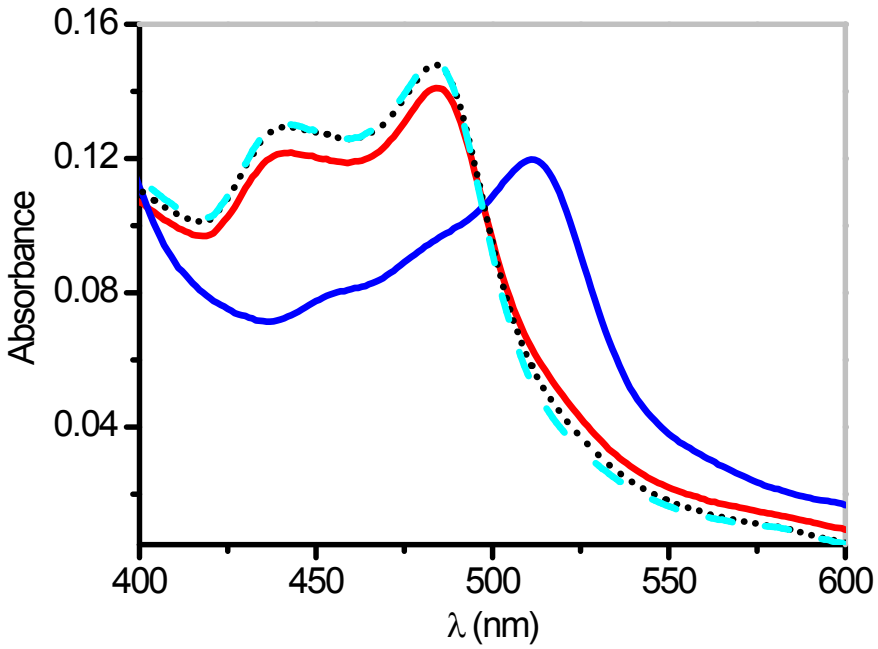


Figure S5. Titration of $Ru(bpy)_2(dbim)(PF_6)_2$ with $N(C_2H_5)_4Er(hfac)_4$ in dichloromethane solutions, showing blue-shift in electronic absorption spectra. The molar ratio between $Ru(bpy)_2(dbim)(PF_6)_2$ and $N(C_2H_5)_4Er(hfac)_4$ are 1 : 0 (blue), 1: 0.5 (red), 1 : 1 (black), and 1:1.5 (cyan), respectively.

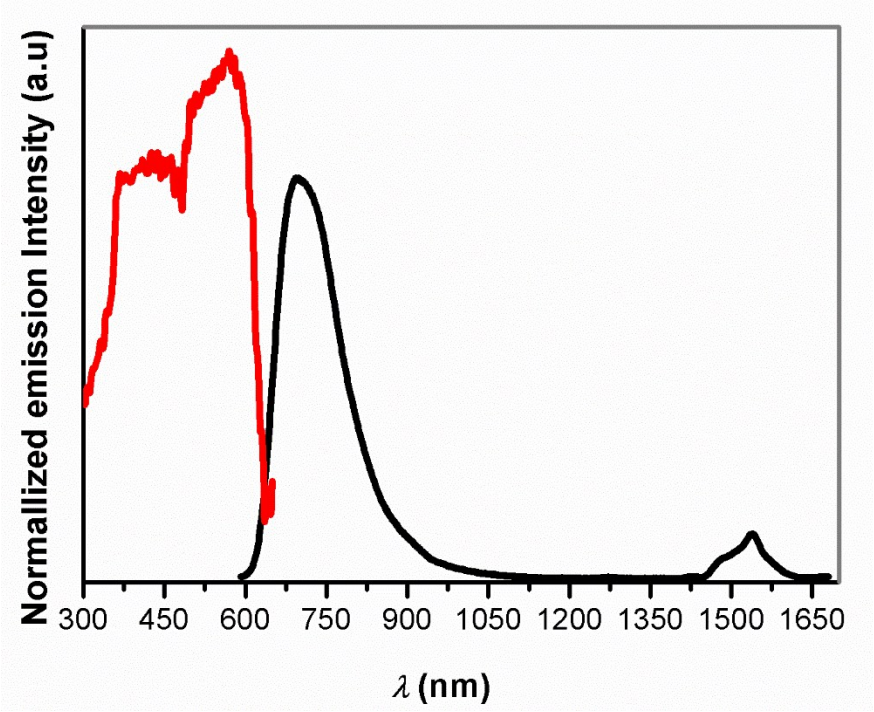


Figure S6. A full normalized excitation (λ_{em} = 1535 nm, red) and emission (λ_{em} = 420 nm, black) spectra of **1** in solid state at room temperature

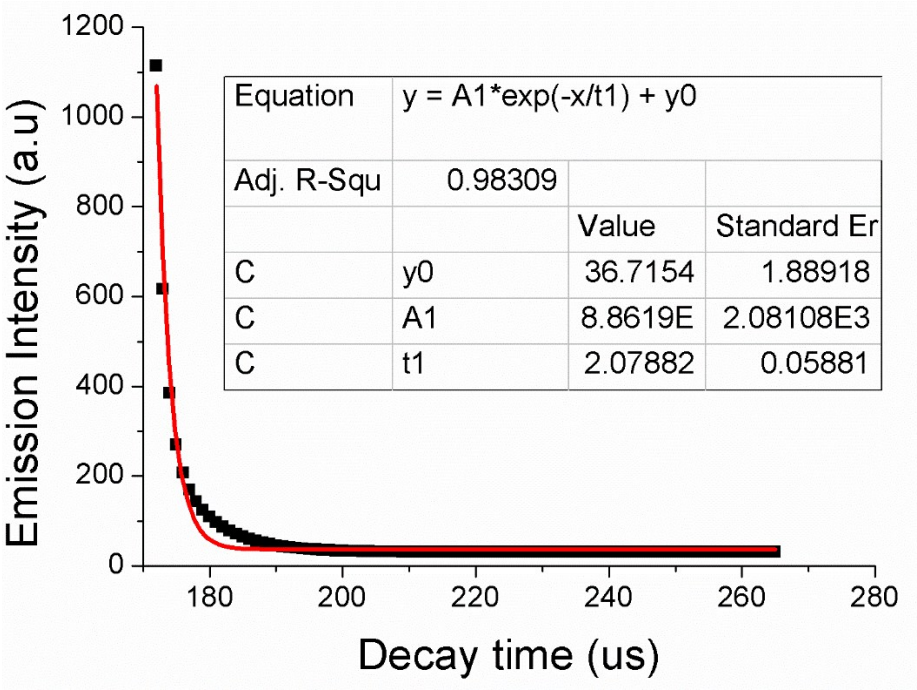


Figure S7. Lifetime decay curves of **1** in solid state after heating to remove solvent molecule in crystals.

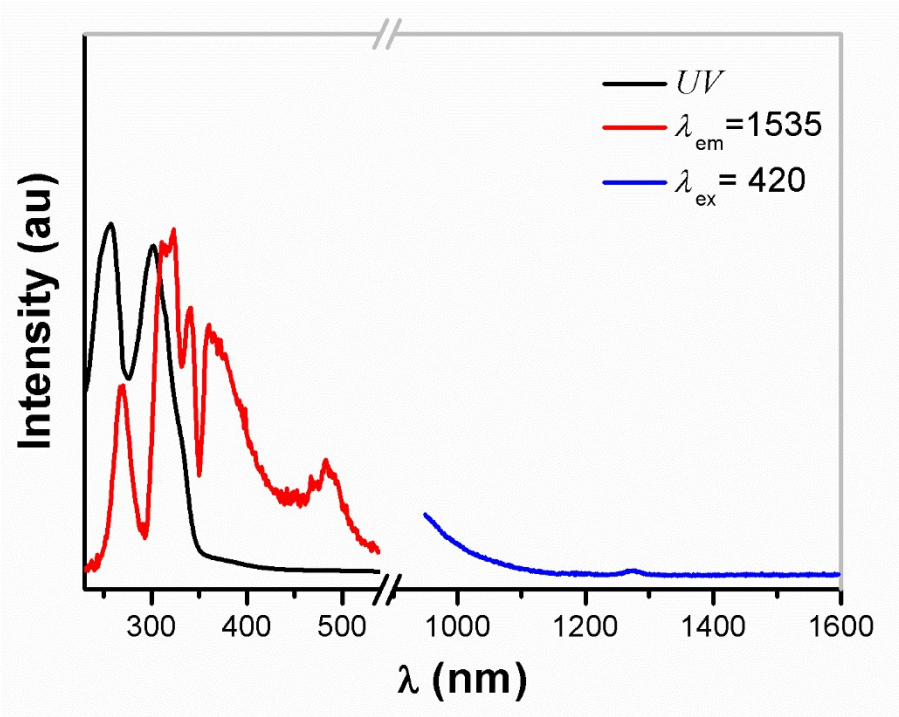


Figure S8 Excitation (λ_{em} = 1535 nm, red) and emission (λ_{ex} = 420 nm, blue) spectra of **1**, and the absorption spectra of **$N(C_2H_5)_4[Eu(hfac)_4]$** (black) in dichloromethane solutions with a concentration of 10^{-5} M.