Supporting Information

Efficient sensitized emission in Yb(III) pentachlorotropolonate complexes

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Contents:

S1. Materials and general methods:

DMF-d_7 was purchased from Apollo Scientific and was of 99.5 atom% isotopic purity. MALDI mass spectra were recorded using a Bruker Daltonics Autoflex. CI mass spectra were obtained by the EPSRC National Mass Spectrometry Service Centre, Swansea using a Finnigan MAT 95XP. CHN elemental analyses were performed by MEDAC Ltd, Egham, Surrey. Single crystals for X-ray crystallography were deposited from solutions in DMF. X-Ray diffractograms were collected at 120 K using a Nonius Kappa CCD area detector mounted at the window of a molybdenum rotating anode (50 kV, 85 mA, $\lambda = 0.71069$ Å). An empirical absorption correction was applied using SADABS [G.M. Sheldrick, SADABS, version 2007/2, Bruker AXS Inc., Madison, Wisconsin, USA, 2007.].

Photoluminescence measurements were done employing a Panther OPO laser pumped by a Surelite Nd: YAG, tunable in the visible range and providing 6 ns pulses, as the excitation source. The detection system consisted of a JY Triax 550 monochromator equipped with 600 or 1200 lines/mm gratings in combination with a liquid nitrogen cooled Hamamatsu R5509-72 IR photomultiplier. Additional glass band-pass filters (Edmund Optics) guaranteed the purity of the signal and the elimination of spurious signals and harmonics. Time resolved measurements were done with a Lecroy LC372 digital oscilloscope, its time-integrated signal providing the emission or excitation spectra. Solid (powder or crystal) samples and solutions were placed in corresponding quartz-windowed holders/cuvettes. Optical absorption was done in a Varian Cary 6000i spectrophotometer.

S2. Synthetic Chemistry:

Pentachlorotropolone (2,3,4,5,6-pentachloro-7-oxocyclohepta-1,3,5-triene)

Pentachlorotropolone ($C_7Cl_5O_2H$) was prepared from hexachlorocyclopentadiene in four steps according to K. Kusuda, N. Hara and R. West, *Chem. Lett.*, 1982, 1119-1122.

[Yb(pctrop)$_3$(DMF)$_2$]

A yellow solution of pentachlorotropolone monohydrate (94.3 mg, 0.30 mmol) in acetonitrile (2 mL) was treated with a solution of Cs_2CO_3 (52.2 mg, 0.16 mmol) in water (2.5 mL), after which the solution became blood-red. Addition of $YbCl_3{\cdot}6H_2O$ (41.4 mg, 0.107 mmol) gave a yellow precipitate, which was filtered off, washed with water and dried *in vacuo*, to leave Cs[Yb(pctrop)$_4$] (96.1 mg) as a yellow solid. The salt was taken up in DMF (2 mL), filtered, and the filtrate was kept at room temperature. The orange crystals that formed were filtered off, washed with Et_2O, then pentane and dried *in vacuo* to give [Yb(pctrop)$_3$(DMF)$_2$] (58.5 mg) as orange needles, mp > 300 °C. Found: C, 27.24; H, 1.18; N, 2.43. Calcd for $C_{27}H_{14}Cl_{15}N_2O_8Yb$: C, 27.04; H, 1.18; N, 2.33. Calcd for $C_{27}H_{14}Cl_{15}YbN_2O_8{\cdot}0.5C_3H_7NO$: C, 27.70; H, 1.43; N, 2.83; ν_{max}/cm^{-1} (ATR) 2936 (C–H, DMF), 1649 (C=O, DMF), 1506 (C=O, pctrop); *m/z* (CI–) Found: 1063 (3%), 1062 (6), 1061 (9), 1060 (18), 1059 (14), 1058 (42), 1057 (28), 1056 (73), 1055 (45), 1054 (94), 1053 (58), 1052 (100), 1051 (55), 1050 (79), 1049 (53), 1048 (53), 1047 (22), 1046 (18), 1045 (8), 1044 (4). $C_{21}Cl_{15}O_6Yb$ (M^+ – 2DMF) requires 1063 (1), 1062 (6), 1061 (5), 1060 (17), 1059 (13), 1058 (37), 1057 (25), 1056 (66), 1055 (42), 1054 (92), 1053 (56), 1052 (100), 1051 (59), 1050 (81), 1049 (56), 1048 (47), 1047 (25), 1046 (18), 1045 (9), 1044 (4); *m/z* (MALDI–) Found: 1346 {11%, $[Yb(pctrop)_4]^-$}, 1089 {22%, $[YbCl(pctrop)_3]^-$}, 830 {33%, $[YbCl_2(pctrop)_2]^-$}, 574 {75%, $[YbCl_3(pctrop)]^-$}, 316 {100%, $[YbCl_4]^-$}.

[Y(pctrop)$_3$(DMF)$_2$] was prepared by analogy with $[Yb(pctrop)_3(DMF)_2]$, using $YCl_3{\cdot}6H_2O$ in place of $YbCl_3{\cdot}6H_2O$. Found: C, 29.63; H, 1.62; N, 2.78. Calcd for $C_{27}H_{14}Cl_{15}N_2O_8Y$: C, 29.08; H, 1.27; N, 2.51. Calcd for $C_{27}H_{14}Cl_{15}YN_2O_8{\cdot}0.5C_3H_7NO$: C, 30.81; H, 1.51; N, 2.99; □$_{max}$/cm^{-1} (ATR) 2934 (C–H, DMF), 1649 (C=O, DMF), 1505 (C=O, pctrop); *m/z* (CI–) Found: 979 (1%), 978 (1), 977 (5), 976 (3), 975 (13), 974 (7), 973 (36), 972 (13), 971 (64), 970 (21), 969 (92), 968 (24), 967 (100), 966 (17), 965 (65), 964 (7), 963 (32), 962 (1), 961 (4). $C_{21}Cl_{15}O_6Y$ (M^- – 2DMF) requires 979 (1%), 978 (1), 977 (5), 976 (3), 975 (9), 974 (8), 973 (37), 972 (15), 971 (59), 970 (21), 969 (97), 968 (22), 967 (100), 966 (21), 965 (71), 964 (7), 963 (31), 962 (1), 961 (7).

[Yb(pctrop)$_3$(DMF-*d*$_7$)$_2$]

This was prepared by analogy with **[Yb(pctrop)$_3$(DMF)$_2$]**, by replacing DMF with DMF-*d*$_7$. ν_{max}/cm^{-1} (ATR) 2214 (C-D, DMF), 1621 (C=O, DMF), 1506 (C=O, pctrop).

[Y$_{1\text{-}x}$Yb$_x$(pctrop)$_3$(DMF-*d*$_7$)$_2$]

This was prepared by analogy with **[Yb(pctrop)$_3$(DMF-*d*$_7$)]**, replacing corresponding amounts of $YbCl_3{\cdot}6H_2O$ by $YCl_3{\cdot}6H_2O$.

S3. Crystallographic data:

Table 1: Crystallographic data

	[Yb(pctrop)$_3$(DMF)$_2$](0.5DMF)
CCDB number	832669
Formula	$C_{27}H_{14}Cl_{15}N_2O_8Yb{\cdot}0.5C_3H_7NO$
Formula weight	1235.74
Temperature	120(2) K
Crystal system	Monoclinic
Space group	P 2_1/n
a	7.7050(2) Å
b	20.5764(7) Å
c	25.2321(8) Å
α	90°
β	96.087(2)°
γ	90°
V	3977.8(2) Å^3
Z	4
Density (calculated)	2.063 Mg/m^3
Absorption coefficient	3.412 mm^{-1}
Crystal size	0.36 × 0.05 × 0.03 mm^3
Reflections collected	44322
Independent reflections	9052 [R(int) = 0.0590]
Final R indices	R1 = 0.0591
[$I > 2\ \sigma(I)$]	wR2 = 0.1180
R Indices (all data)	R1 = 0.0861, wR2 = 0.1308

Table 2: Yb-O, Yb-N distances

Atoms	Distance (Å)
Yb-O(1)	2.36
Yb-O(2)	2.3
Yb-O(3)	2.33
Yb-O(4)	2.34
Yb-O(5)	2.29
Yb-O(6)	2.33

Yb-O(7)	2.27
Yb-O(8)	2.28
Yb-N(1)	4.35
Yb-N(2)	4.29

Table 3: Actual and average Yb-H distance to nearest H in DMF.

Yb - closest H in DMF(1)	3.46 Å
Average Yb - closest H in DMF(2)*	3.6 Å

* note the occupancy of each of the two closest possible positions is ~ 0.5

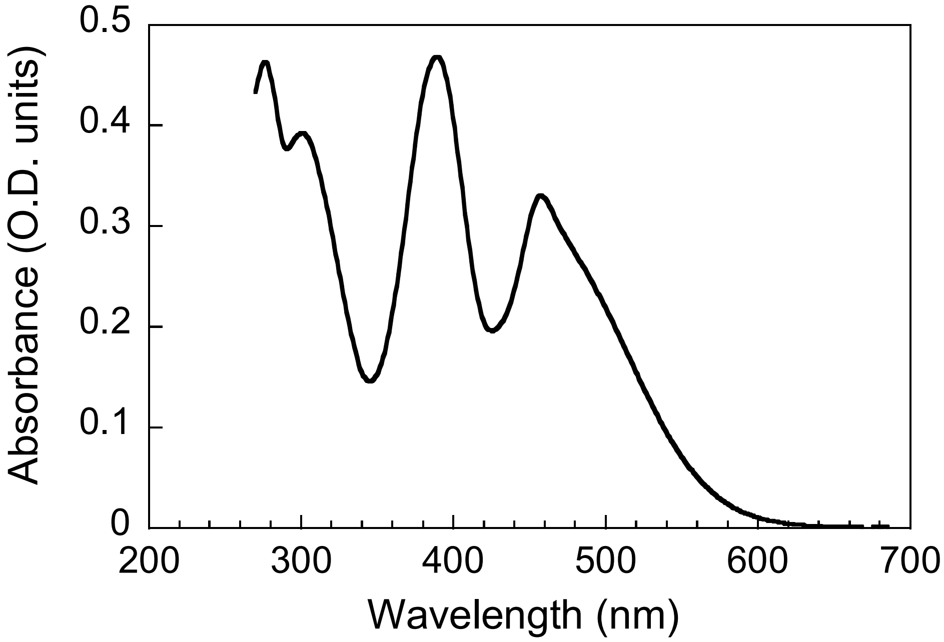
Table 4: Selected O-Yb-O angles

Atoms	Angle (degrees)
O(1)–Yb–O(2)	64.8
O(3)– Yb –O(4)	64.9
O(5)– Yb –O(6)	66.3
O(7)– Yb –O(8)	147.9
O(3)– Yb –O(5)	83.5
O(3)– Yb –O(7)	76.9
O(5)– Yb –O(7)	81.3
O(2)– Yb –O(6)	73.3
O(2)– Yb –O(8)	77.4
O(6)– Yb –O(8)	75.0

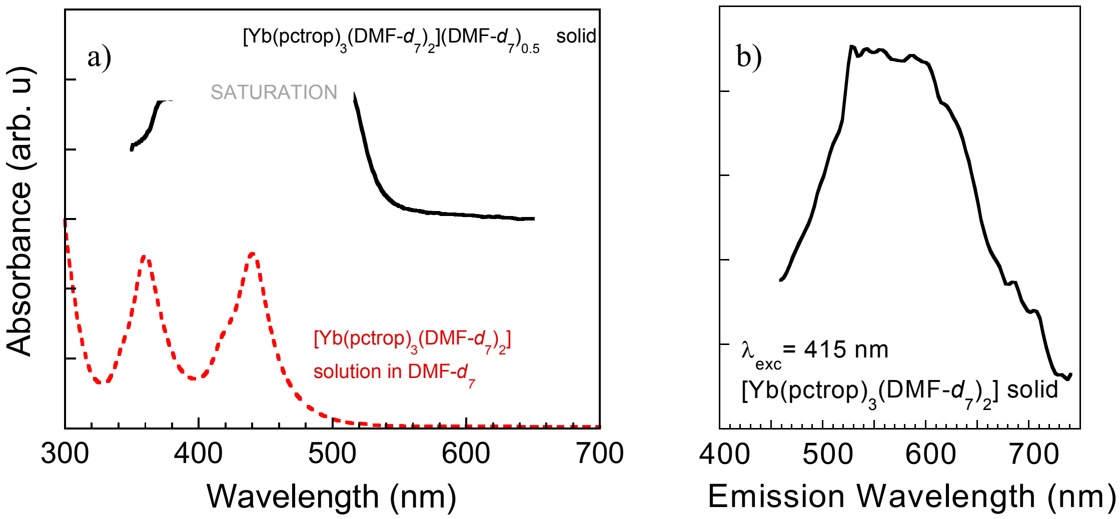
There is disorder associated with both coordinated and non-coordinated DMF molecules. One DMF ligand was modelled for disorder, using SHELX^{x} program facilities. L-N(2) is rotationally disordered about the O–N axis, component site occupancies refining to 0.4778, 0.4925 and 0.4842 and their complement for [Yb(pctrop)$_3$(DMF)$_2$](0.5DMF), and 0.5436, 0.5730 and 0.5498 and their complement for [Y(pctrop)$_3$(DMF)$_2$] (0.5DMF). The non-coordinated DMF molecule is disordered in a ratio of 1:1 by an inversion about atom N(3).

S4. Supplementary Spectroscopic Analysis:

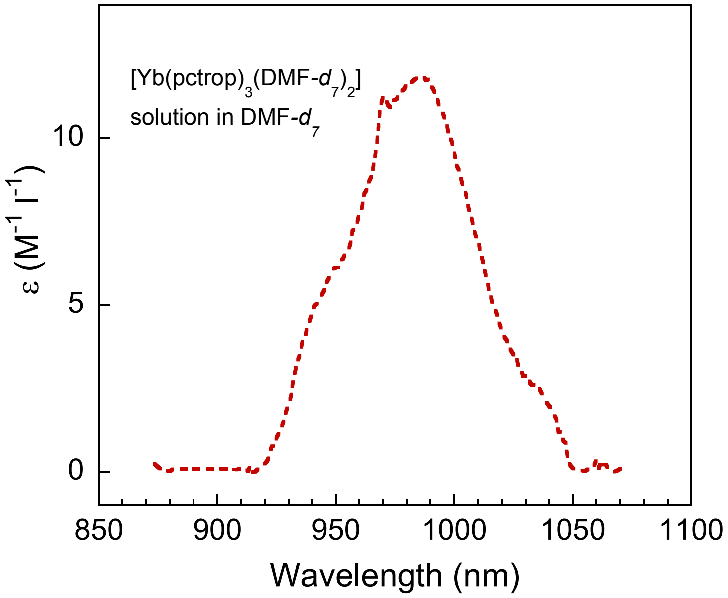
Supplementary Figure 1: Perchlotropolonate absorption spectrum, as taken from a sodium pentachlorotropolonate DMF solution ($5x10^{-5}$ M).



Supplementary Figure 2: (a) UV/Vis absorption spectrum of the Yb(pctrop)$_3$(DMF-d_7)$_2$ complex in crystal (thickness: 80 μm) and solution phases. (b) fluorescence spectrum of Yb(pctrop)$_3$(DMF-d_7)$_2$ (solid) in the visible range.



Supplementary Figure 3: NIR absorption spectrum of the Yb(pctrop)$_3$(DMF-d_7)$_2$ complex in a 0.3 mM solution in DMF-d_7.



The radiative lifetime of Yb^{3+} in the Yb(pctrop)$_3$(DMF-d_7)$_2$ complex was estimated from the infra-red absorption spectrum of the solution using the formula:

$$\tau_{\mathrm{rad}}^{-1} = 2303 \frac{8\pi c n^2 \langle \tilde{\nu} \rangle (2J+1)}{N_A (2J'+1)} \int_{band} \varepsilon(\tilde{\nu}) d\tilde{\upsilon}$$

Where c is the speed of light, n is the refractive index, N_A is Avogadro's number, J and J' are the quantum numbers for the ground and excited states, respectively, $\langle \tilde{\nu} \rangle = \frac{\int_{band} \nu \cdot \varepsilon(\tilde{\nu}) d\tilde{\upsilon}}{\int_{band} \varepsilon(\tilde{\nu}) d\tilde{\upsilon}}$ and $\varepsilon(\tilde{\nu})$ is the corresponding absorption spectrum of the f-f transition (figure 2b of this supplementary information). We took the corresponding refractive index of DMF $n_{\mathrm{DMF}} = 1.43$ and the commonly employed value $n = 1.5$ for solid coordination compounds [N.M. Shavaleev, R. Scopelliti, F. Gumy and J.-C. G. Bünzli, *Inorg. Chem.,* 2009, **48**, 7937]. We assumed the same value for the perdeuterated and non-deuterated cases.