Electronic Supplementary Material (ESI) for Chemical Communications

Outer-sphere anion recognition by a cyclen-based octadenate europium (III) complex: pH dependent recognition of *ortho*-phthalic acid.

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Supporting information.

Table S1. Hydration states and excited state lifetimes for $[Eu(CyD3MA)(H_2O)]^{3+}$ in H_2O and D_2O.

pH	k_{H_2O}	$\tau_{H_2O/ms}$	k_{D_2O}	$\tau_{D_2O/ms}$	q^*
		$\lambda_{em} = 580$ nm, $\lambda_{ex} = 240$ nm			
4.38	2.374	0.4212	0.556	1.799	**0.93**
4.80	2.331	0.4290	0.559	1.789	**0.88**
8.28	2.453	0.4077	0.987	1.013	**0.54**
8.65	2.392	0.4181	0.924	1.082	**0.54**
		$\lambda_{em} = 593$ nm, $\lambda_{ex} = 240$ nm			
4.38	2.305	0.4348	0.558	1.792	**0.85**
4.80	2.308	0.4333	0.565	1.770	**0.84**
8.28	2.350	0.4255	0.956	1.040	**0.46**
8.65	2.378	0.4205	0.883	1.133	**0.57**

$$^{*}q = A[\tau^{-1}_{H_2O} - \tau^{-1}_{D_2O} - k_{XH}]$$
$$\text{where } k_{XH} = \alpha + \beta n_{OH} + \gamma n_{NH} + \delta n_{O=CNH}$$
$$\beta = 0.44\ ms^{-1};\ \delta = 0.075\ ms^{-1}$$
$$\alpha = 0.31;\ n_{OH} = 1;\ n_{NH} = 0;\ n_{O=CNH} = 3$$

Table S2. Selected bond lengths for $[Eu(CyD3MA)(CF_3SO_3)](CF_3SO_3)_2(CH_3CN)_2$.

Bond	**Donor type**	**Bond length (Å)**
Eu(1) – O(1)	Hydroxycyclohexyl	2.4078(15)
Eu(1) – O(2)	Amidic	2.3633(15)
Eu(1) – O(3)	Amidic	2.3803(14)
Eu(1) – O(4)	Amidic	2.3726(14)
Eu(1) – O(5)	Triflato	2.4432(15)
Eu(1) – N(1)	Macrocyclic ammine	2.6573(17)
Eu(1) – N(2)	Macrocyclic ammine	2.6768(17)
Eu(1) – N(3)	Macrocyclic ammine	2.6728(18)
Eu(1) – N(4)	Macrocyclic ammine	2.6582(16)

Table S3. Hydration states and excited state lifetimes of $[Eu(CyD3MA)]^{3+}$ in a multicomponent buffer solution (KHP, MOPS, MES and TRIS).

pH	k_{H_2O}	$\tau_{H_2O/ms}$	k_{D_2O}	$\tau_{D_2O/ms}$	q^{a*}	q^{b*}
			$\lambda_{em} = 580$ nm, $\lambda_{ex} = 280$ nm			
4.71	3.149	0.3176	0.569	1.757	1.8	**2.2**
5.32	3.120	0.3205	0.568	1.761	1.7	**2.2**
7.42	2.849	0.3510	0.601	1.664	1.4	**1.9**
8.17	2.592	0.3858	0.637	1.570	1.1	**1.6**
8.71	2.799	0.3573	0.808	1.238	**1.1**	1.6
9.48	2.727	0.3667	1.115	0.900	**0.7**	1.2
			$\lambda_{em} = 593$ nm, $\lambda_{ex} = 280$ nm			
4.71	3.460	0.2890	0.545	1.835	2.1	**2.6**
5.32	3.301	0.3029	0.565	1.770	1.9	**2.4**
7.42	2.661	0.3758	0.613	1.631	1.2	**1.7**
8.17	2.367	0.4225	0.637	1.570	0.8	**1.3**
8.71	2.579	0.3877	0.826	1.211	**0.9**	1.3
9.48	2.497	0.4005	1.104	0.906	**0.5**	0.9

$$^{*}q = A[\tau^{-1}_{H_2O} - \tau^{-1}_{D_2O} - k_{XH}]$$

$$\text{where } k_{XH} = \alpha + \beta n_{OH} + \gamma n_{NH} + \delta n_{O=CNH}$$

$$\beta = 0.44\ ms^{-1};\ \delta = 0.075\ ms^{-1}$$

$$^{a}\ \alpha = 0.31;\ n_{OH} = 1;\ n_{NH} = 0;\ n_{O=CNH} = 3$$

$$^{b}\ \alpha = 0.31;\ n_{OH} = 0;\ n_{NH} = 0;\ n_{O=CNH} = 3$$

NB:

q values in **bold** indicate hydration states that more accurately reflect the binding mode of the pendent hydroxycyclohexyl moiety.

Table S4. Crystal Data CyD3MA.H_2O.

Empirical formula	C_{23} $H_{45.56}$ N_7 $O_{4.28}$	
Formula weight	488.16	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 9.6189(2) Å	α= 90°.
	b = 32.1984(7) Å	β= 99.5380(10)°.
	c = 8.6632(2) Å	γ = 90°.
Volume	2646.02(10) Å^3	
Z	4	
Density (calculated)	1.225 Mg/m^3	
Absorption coefficient	0.086 mm^{-1}	
F(000)	1067	
Crystal size	0.40 x 0.37 x 0.25 mm^3	
Theta range for data collection	2.15 to 26.00°.	
Index ranges	$-11 \leq h \leq 11$, $-39 \leq k \leq 33$, $-10 \leq l \leq 10$	
Reflections collected	15521	
Independent reflections	5204 [R(int) = 0.0288]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5204 / 1248 / 628	
Goodness-of-fit on F^2	1.143	
Final R indices [I>2sigma(I)]	R1 = 0.0763, wR2 = 0.1749	
R indices (all data)	R1 = 0.0936, wR2 = 0.1817	
Largest diff. peak and hole	0.472 and -0.380 e.Å^{-3}	

Table S5. Crystal Data of [Eu(CyD3MA)(CF_3SO_3)](CF_3SO_3)$_2$.(CH_3CN)$_{1.5}$.

Empirical formula	C_{29} $H_{49.50}$ Eu F_9 $N_{8.5}$ O_{13} S_3	
Formula weight	1144.41	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.8523(2) Å	α= 70.5800(10)°.
	b = 13.4938(2) Å	β= 70.7790(10)°.
	c = 15.4748(3) Å	γ = 81.9570(10)°.
Volume	2202.72(7) Å^3	
Z	2	
Density (calculated)	1.725 Mg/m^3	
Absorption coefficient	1.672 mm^{-1}	
F(000)	1158	
Crystal size	0.47 x 0.28 x 0.15 mm^3	
Theta range for data collection	1.60 to 28.00°.	
Index ranges	$-15 \le h \le 15$, $-17 \le k \le 17$, $-20 \le l \le 20$	
Reflections collected	30492	
Independent reflections	10631 [R(int) = 0.0338]	
Completeness to theta = 28.00°	100.0 %	
Absorption correction	Integration	
Max. and min. transmission	0.7876 and 0.5071	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10631 / 0 / 595	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0234, wR2 = 0.0626	
R indices (all data)	R1 = 0.0257, wR2 = 0.0637	
Largest diff. peak and hole	0.689 and -0.645 e.Å^{-3}	

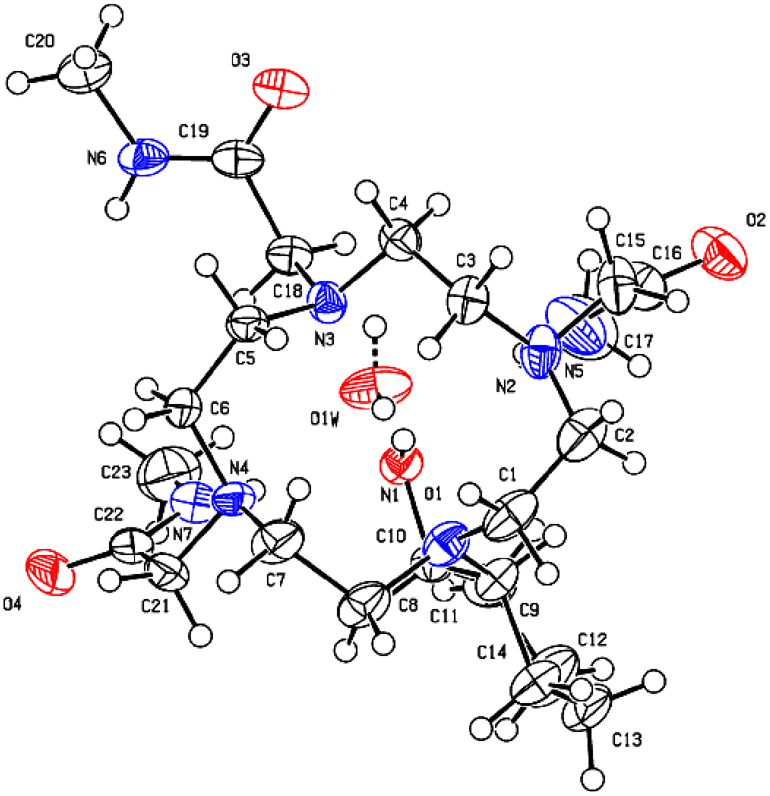


Figure S1. ORTEP diagram of octadentate 1,4,7-tris[(N-methylcarbamoyl)methyl]-10-(2-hydroxycyclohexyl)-1,4,7,10-tetraazadodecane (CyD3MA.H_2O). Thermal ellipsoids (site occupancy 0.612) are shown at 50% probability level.

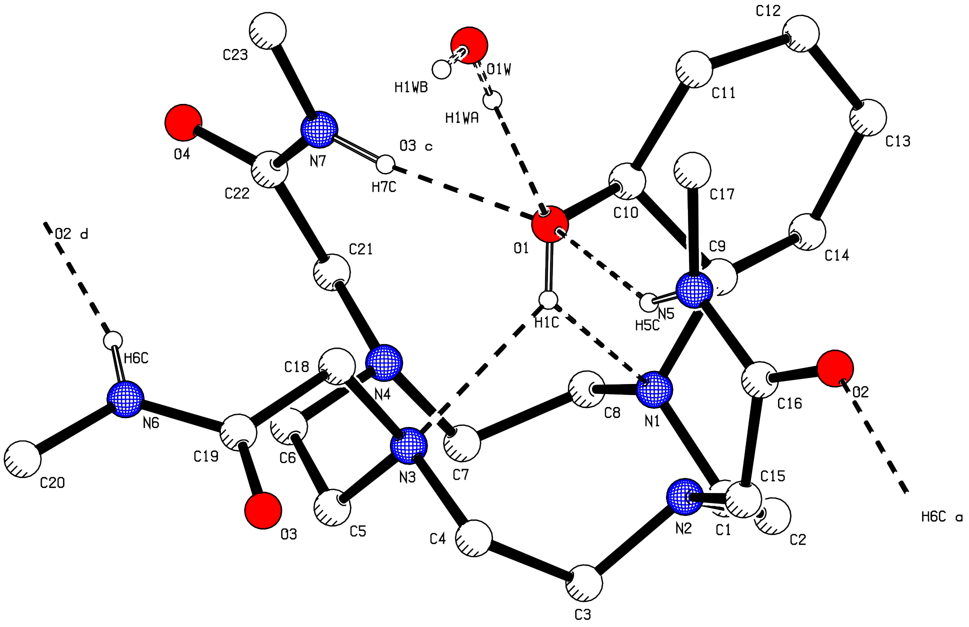


Figure S2. Ball-and-Stick diagram of *S,S*-1,4,7-tris[(N-methylcarbamoyl)methyl]-10-(2-hydroxycyclohexyl)-1,4,7,10-tetraazadodecane showing pendent N-H…O and O-H…O hydrogen bonding interactions.

In the solid state endo conformations of trans methylethanamide pendents accommodate N-H…O hydrogen-bonding interactions to the hydroxycycloalkyl oxygen, resembling endo conformations observed above the macrocyclic plane in the structure of DTMA.[17] *The endo hydroxycyclohexyl conformation directs the* O_1-H_{1C} *vector at the macrocyclic cavity placing the hydroxycyclohexyl oxygen* O_1 *2.22(1) Å above the macrocyclic* N_4 *centroid. Oxygen* O_{1W} *of the lattice water molecule, hydrogen bonded to the hydroxycyclohexyl oxygen (*O_1*), is separated from the macrocyclic* N_4 *centroid by 4.45(1) Å. Outer-sphere water molecules, at comparable distances from the metal centre in cyclen-based europium (III) complexes, marginally quench (approximately 8% efficiency) lanthanide emission.*[18] *Consequently, the* O_{1W}-H_{1WA}…O_1 *hydrogen bond involving the hydroxycyclohexyl pendent and the proximal water molecule in the solid state Cy3DMA structure, potentially resembles O-H…O interactions of this pendent arm in aqueous solution.*

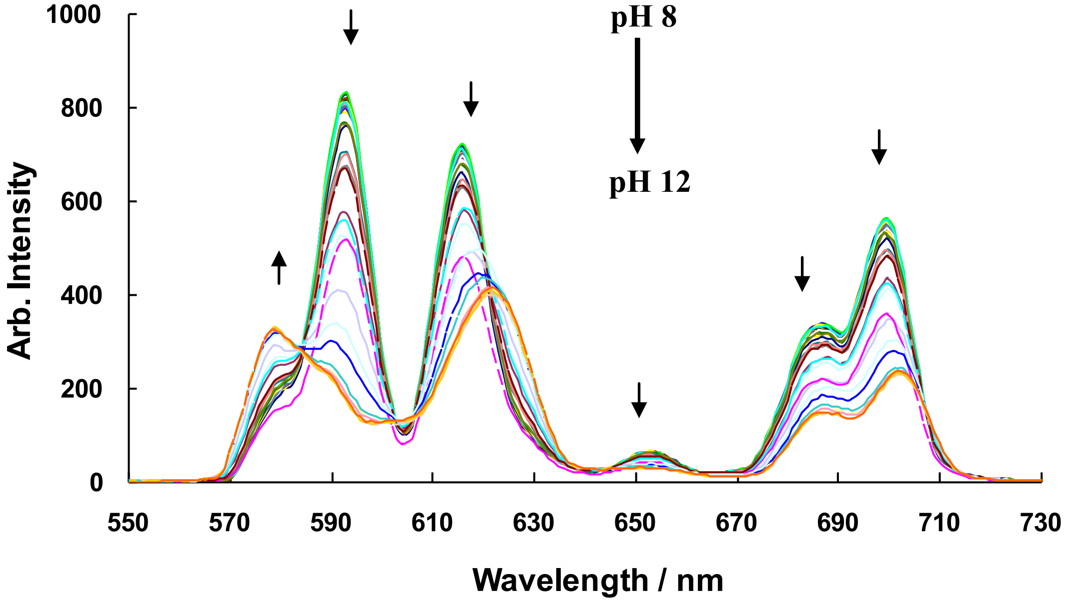


Figure S3. pH dependent emission spectra of Europium-1,4,7-tris[(*N*-methylcarbamylmethyl)-10-(2-hydroxycyclohexyl)]-1,4,7,10- tetraazacyclododecane ([Eu(CyD3MA)(H_2O)]$^{3+}$) at room temperature in aqueous solution.

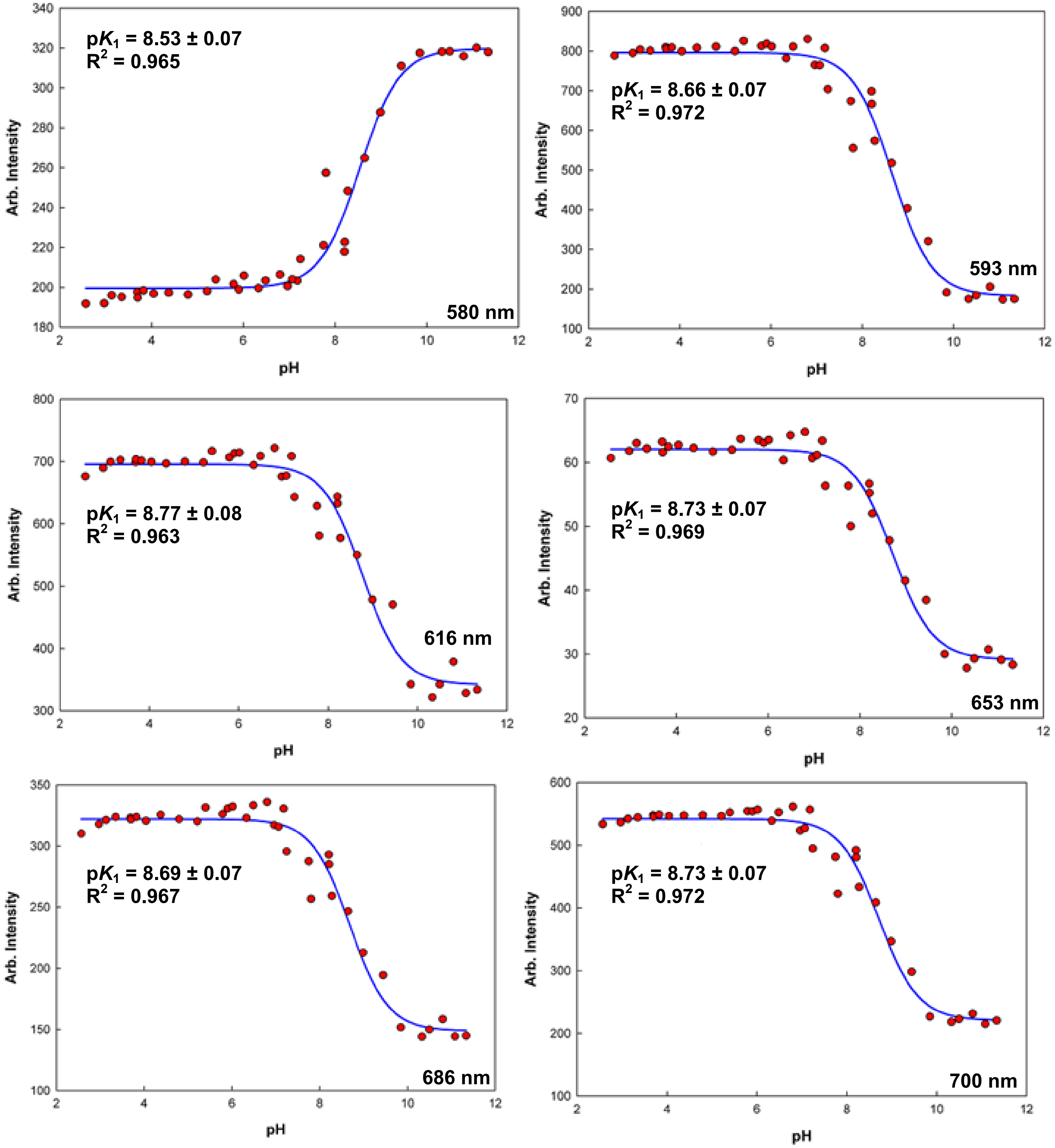


Figure S4. Regression analysis of $[Eu(CyD3MA)(H_2O)]^{3+}$ emission bands in aqueous solution with weighted pK_a average values.

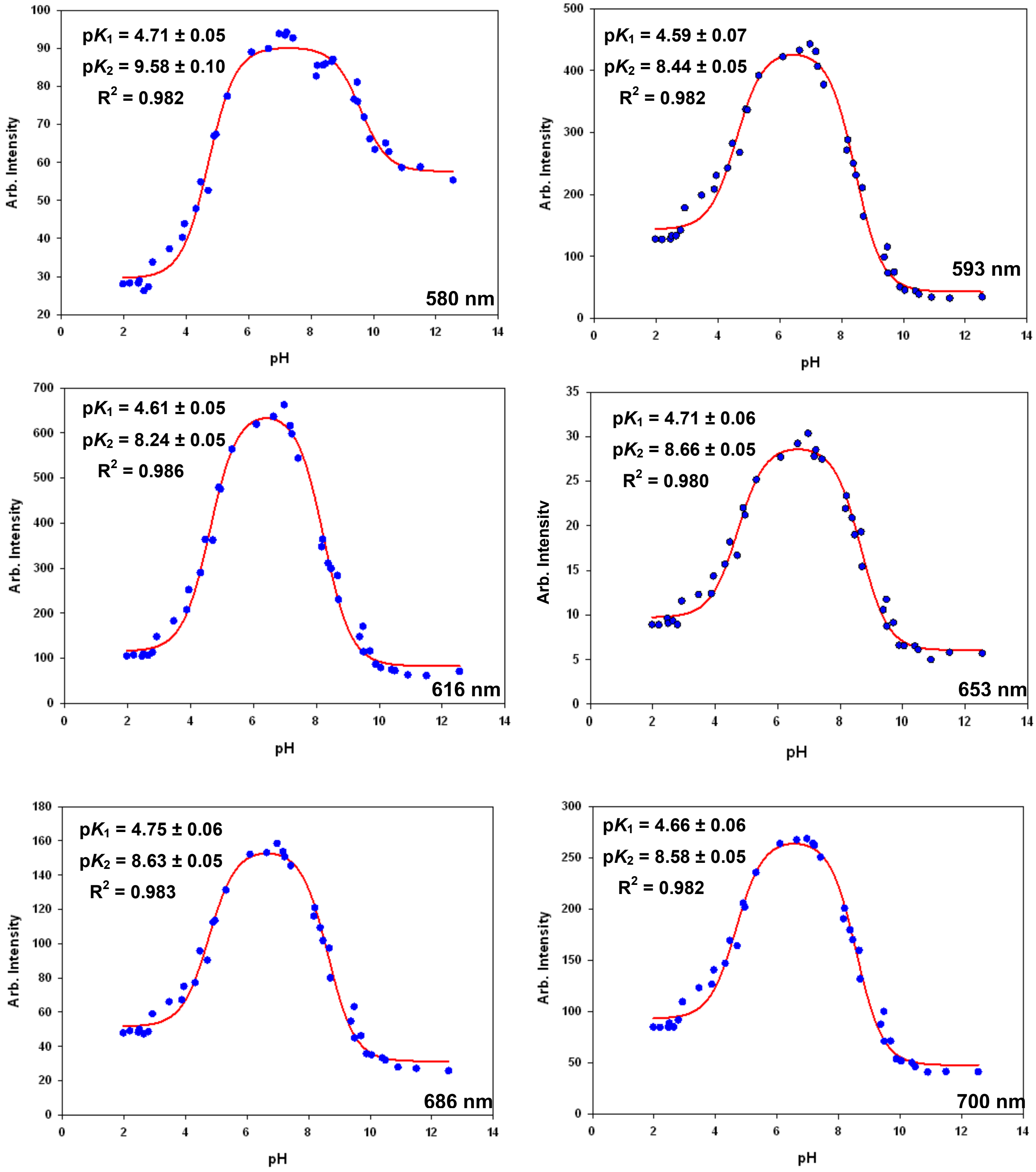


Figure S5. Regression analysis of $[Eu(CyD3MA)(H_2O)]^{3+}$ emission bands in buffered solution (KHP, MOPS, MES and TRIS) with weighted pK_a average values.

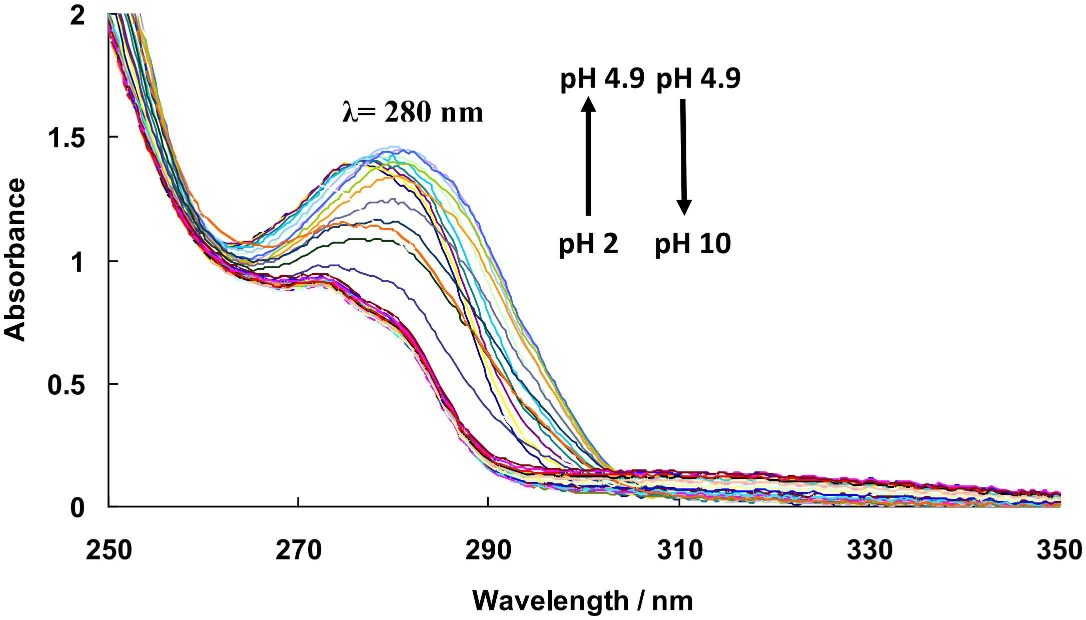


Figure S6. pH dependent UV-vis spectra of Europium-1,4,7-tris[(*N*-methylcarbamylmethyl)-10-(2-hydroxycyclohexyl)]-1,4,7,10- tetraazacyclododecane ($[Eu(CyD3MA)]^{3+}$) in a buffered solution (KHP, MOPS, MES and TRIS) at room temperature; pH 2 to pH 11.

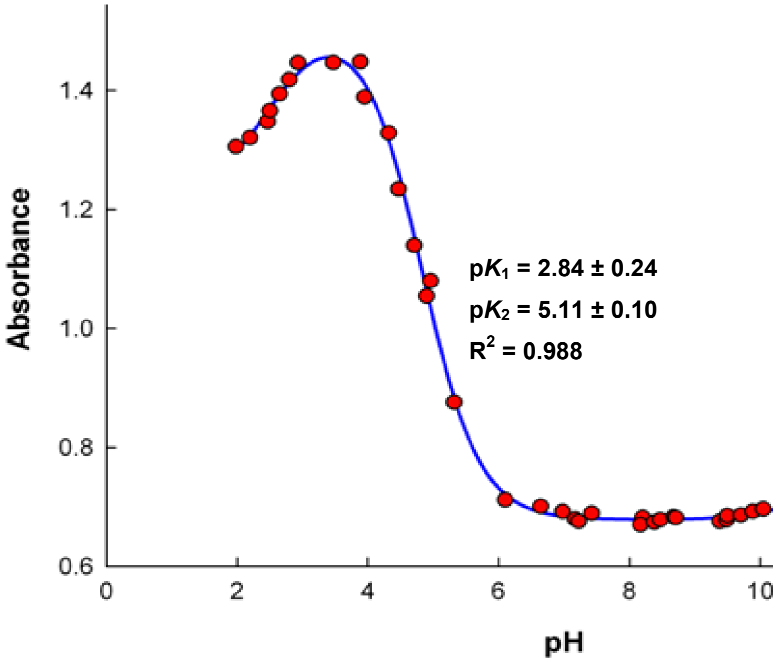


Figure S7. Non-linear regression analysis of electronic absorption data (Abs_{280} Phthalate π-π^* transition) for $[Eu(CyD3MA)]^{3+}$ in a buffered solution (KHP, MOPS, MES and TRIS); pH 2 to pH 11.

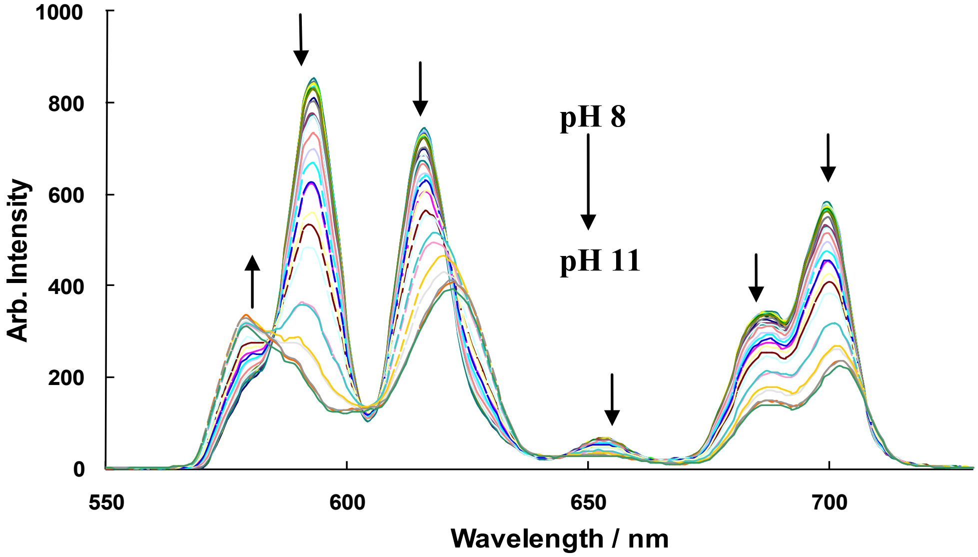


Figure S8. pH dependent emission spectra of Europium-1,4,7-tris[(*N*-methylcarbamylmethyl)-10-(2-hydroxycyclohexyl)]-1,4,7,10- tetraazacyclododecane ($[Eu(CyD3MA)(H_2O)]^{3+}$) in a buffered solution (MOPS, MES and TRIS) excluding KHP at room temperature.

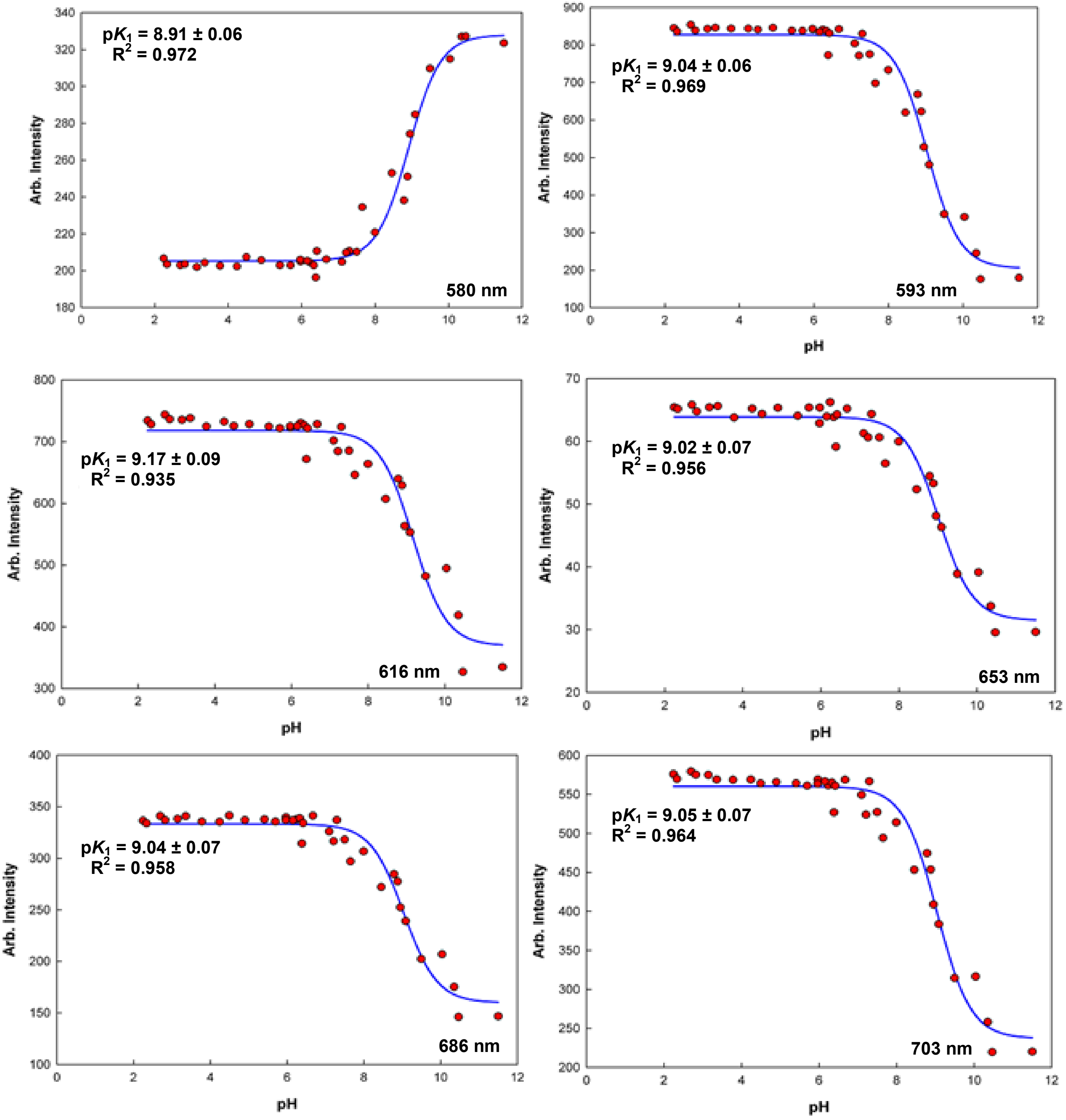
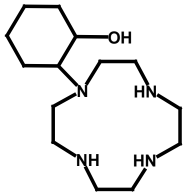


Figure S9. Regression analysis of pH dependent $[Eu(CyD3MA)(H_2O)]^{3+}$ emission bands in buffered solution (MOPS, MES and TRIS) excluding KHP from pH 2 to pH 11.

Experimental

Synthesis

1) Preparation of (2-Hydoxycyclohexyl)-1,4,7,10-tetraazacyclodecane (Cycyclen).

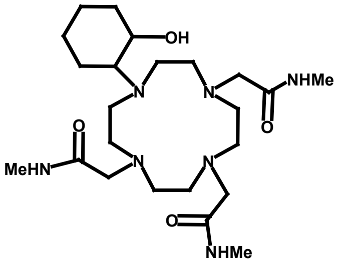


(Cycyclen)

Reference:

A. S. de Sousa*, D. Sannasy, M. A. Fernandes, H. M. Marques *"Helical self-assembly of 2-(1, 4, 7, 10-tetraazacyclododecan-1-yl)cyclohexan-1-ol (cycyclen)",* Acta Cryst. C68, o383 – o386, 2012

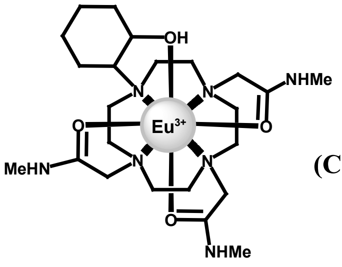
2) Preparation of 1,4,7-tris[*N*-methylcarbomylmethyl]-10-2(hydroxycyclohexyl)-1,4,7,10-tetraazacyclododecane (CyD3MA)



CyD3MA

A solution of 1-(2-Hydoxycyclohexyl)-1,4,7,10-tetraazacyclodecane or Cy-cyclen (0.3032 g , 1.12×10^{-3} mol), *N*-methyl chloroacetamide (0.4025 g, 3.76×10^{-3} mol), KI (0.6646 g, 4.01×10^{-3} mol) and $CsCO_3$ (1.8185 g, 5.58×10^{-3} mol) was refluxed in dry CH_3CN (50 ml) for 24 hrs. The reaction mixture is filtered to remove metal salts upon cooling. The solvent is removed under reduced pressure and the residue washed with diethyl ether. The off-white solid is precipitated from CH_3CN with dry diethyl ether to afford the product a white powder (49 % yield).

3) Preparation of $[Eu(CyD3MA)](CF_3SO_3)_3$



$(CF_3SO_3)_3$

Europium triflate (0.4141 g, 6.90×10^{-4} mol) was dissolved in dry acetonitrile to give a 0.02 M solution. CyD3MA (0.300 g, 6.21×10^{-4} mol) was dissolved in dry acetonitrile to give a 0.03 M solution. This was added to the triflate solution via a dropping funnel under argon. The mixture was refluxed at 90 °C for 90 hrs under a $CaCl_2$ drying tube. Upon cooling, the solvent was removed to dryness under reduced pressure. The crude product was redissolved in a minimal amount of dry acetonitrile to which diethyl ether was added dropwise until the solution became turbid. Refrigeration overnight afforded Europium-1,4,7-tris[*N*-methylcarbamylmethyl]-10-(2-hydroxycyclohexyl)-1,4,7,10-tetraazacyclododecane (0.6284 g, 5.81×10^{-4} mol) and was isolated in 94 % yield as a triflate salt.