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Eu(III)-cyclen-*phen* conjugate as a luminescent copper sensor: the formation of mixed polymetallic macrocyclic complexes in water

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Electronic supplemental Information

Synthesis

2-chloro-*N*-[1,10]phenanthrolin-5-yl-acetamide (2)

5-Amino - [1,10] – Phenanthroline (0.3 g; 1.54mmol) was placed in a round bottomed flask under argon. THF (dry 55 mL) and triethylamine (0.156 g; 1.58 mmol; 0.22 mL) were added and the suspension was stirred for thirty minutes. The mixture was cooled to 0 ^{o}C before chloroacetyl chloride (0.213 g; 1.89 mmol; 0.22 mL; 1.2 equivalents) in THF (5 mL) was added dropwise. The mixture was left stirring overnight at room temperature. The solution was washed with 5% $NaHCO_3$. The organic layer was collected, evaporated and the residue washed with water and ether to yield a brown solid 0.241 g; 0.88 mmol; 59% yield. Calculated for $C_{14}H_{10}N_3OCl$: C, 61.89; H, 3.71; N, 15.47. Found: C, 60.84; H, 3.71; N, 14.84. δ_H(400 MHz, $CDCl_3$) 9.27 (d, 1H, *J* = 4.0 Hz, H2), 9.18 (d, 1H, *J* = 4.0 Hz, H9), 8.91 (s broad, 1H, NH), 8.39 (s, 1H, H6), 8.33 (d, 1H, *J* = 8.52 Hz, H4), 8.27 (d, 1H, *J* = 8.04 Hz, H7), 7.74 (dd, 1H, *J* = 4.02 Hz, *J* = 8.03 Hz, H3), 7.67 (dd, 1H, *J* = 4.02 Hz, *J* = 7.78 Hz, H8), 4.43 (s, 2H, CH_2). δ_c (100 MHz, $CDCl_3$) 164.2, 150, 149.8, 146.1, 144.2, 138.9, 137.2, 135.6, 128.5, 127.6, 123.2, 122.6, 119.2, 26.5. Calculated for $C_{14}H_{11}N_3OCl$: *m/z* = 272.0579. Found: *m/z* = 272.0591. [M+H] I.R (υ_{max}/cm^{-1}) 1687, 1541, 1422, 1318, 1250, 1153, 1130, 896, 804, 739, 653.

N-[1,10]Phenanthrolin-5-yl-2-(4,7,10-tris-dimethylcarbamoylmethyl-1,4,7,10teraaza-cyclododec-1-yl)-acetamide. (2)

2-(4,7-Bis-dimethylcabamoylmethyl-1,4,7,10tetraazacyclododec-1-yl)-*N,N*-dimethyl-acetamide (0.228 g; 0.534 mmol), 2-chloro-*N*-[1,10]phenanthrolin-5-yl-acetamide (0.174 g; 0.64 mmol) and Cs_2CO_3 (0.21 g; 0.641 mmol) were dissolved in DMF (10 mL) and refluxed overnight under argon. The mixture was allowed cool and then filtered. The solvent was then evaporated under reduced pressure and the resulting brown oil purified by alumina column chromatography using gradiant elution of CH_2Cl_2: MeOH (0 to 5%). Yielding a pale brown solid 0.135 g; 0.02 mmol, (38%). δ_H (400 MHz, $CDCl_3$) 11.12 (s, NH), 9.05 (m, phen), 8.19 (m, phen), 7.52 (m, phen), 3.87 (broad s, CH_2), 2.94 (bs, CH_2), 2.85 (s, CH_3), 2.84 (s, CH_3), 2.54 (broad s, CH_2). δ_c (100 MHz, $CDCl_3$) 172, 170, 149, 148, 135, 133, 132, 127, 125, 122, 121, 119.3, 65, 56, 54, 35.5.Calculated for $C_{34}H_{51}N_{10}O_4$: *m/z* = 663.4069. Found: *m/z* = 663.4095. I.R (υ_{max}/cm^{-1}) 3467, 3207, 2941, 2827, 1450, 1114, 1047, 1012, 679.

1.Eu

1 (16 mg; 24.1 μmol) and $Eu(CF_3SO_3)_3$ (Europium triflate) (15.9 mg; 26.5 μmol) were dissolved in acetonitrile (5 mL). The solution was freeze-thawed twice in order to remove any gasses. The reaction was refluxed under argon overnight. The complex was precipitated from ether and then from DCM before being collected by filtration and dried under vacuum. Yield 27.6 mg; 21.87 μmol,(90%). δ_H(400 MHz, D_2O) 28.3, 9.1, 8.1, 7.6, 3.21, 2.8, 1.0, 0.2, -3, -8, -12, -15. Calculated for $C_{35}H_{51}N_{10}O_7F_3SEu$: *m/z* = 965.2876. Found: *m/z* = 965.2827. [M+1Trif]. I.R (υ_{max}/cm^{-1}) 3362, 2945, 2833, 1656, 1449, 1414, 1278, 1257, 1114, 1028

Figure 1. Eu(III) emission spectra upon titration form pH 5.5→ 1.3

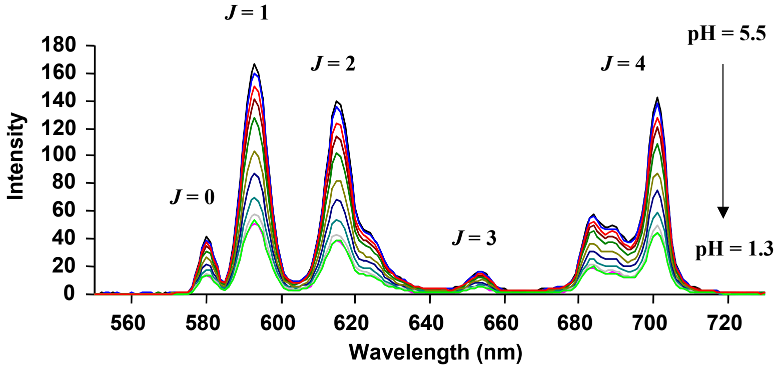
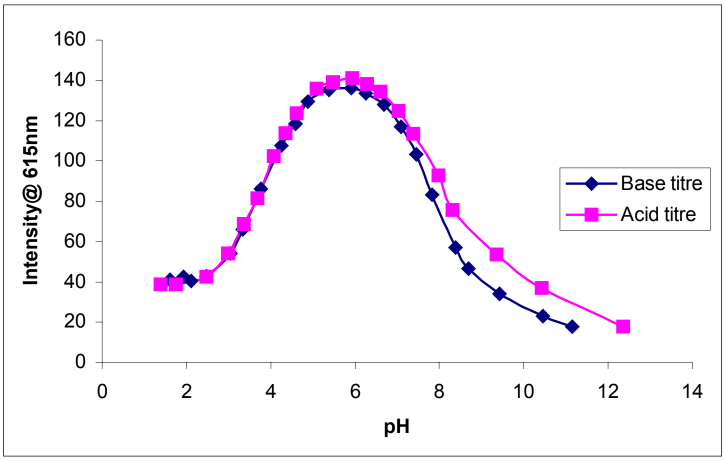


Figure 2. Changes in the Eu(III) emission at different $^5D_0 \rightarrow {}^7F_J$ for 1.Eu



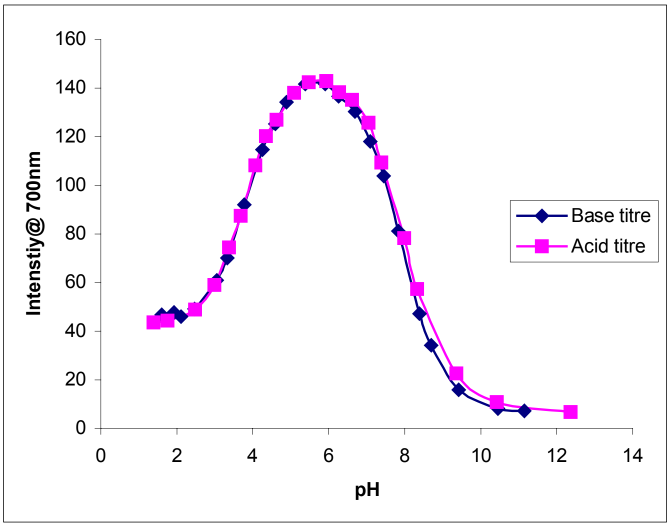


Table 1. The hydration state (±0.5) of 1.Eu at different pH

pH	$1/\tau_{H2O}$ (ms^{-1})	$1/\tau_{D2O}$ (ms^{-1})	q
1.39	2.320	1.270	0.96
3.0	2.443	1.133	1.27
4.02	2.643	1.554	1.01
5.3	2.559	1.160	1.38
7.1	3.050	1.892	1.09
7.9	3.359	1.930	1.41
10.08	3.709	2.695	0.92

Figure 3. Changes in the absorption spectra of 1.Eu upon Cu(II) titration.

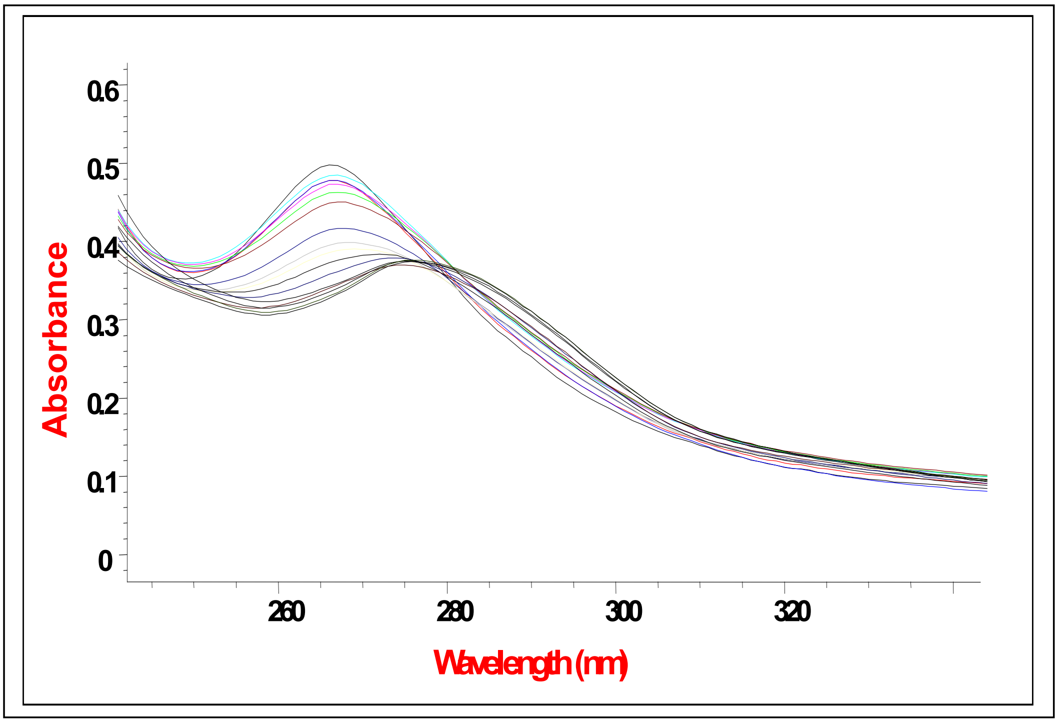


Figure 4. Changes in the fluorescence emission spectra of 1.Eu upon Cu(II) titration.

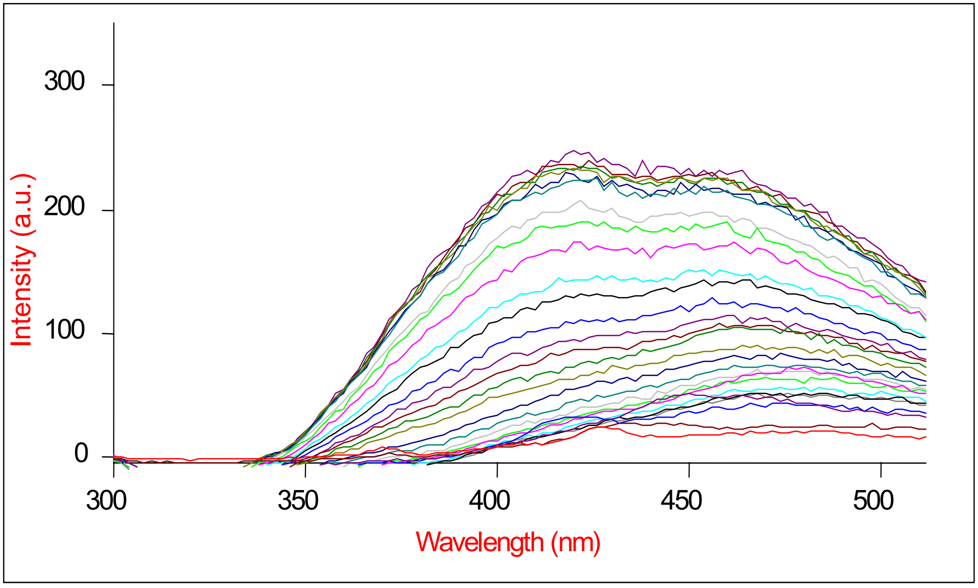


Figure 5. Changes in the fluorescence emission spectra of 1.Eu upon Cu(II) titration.

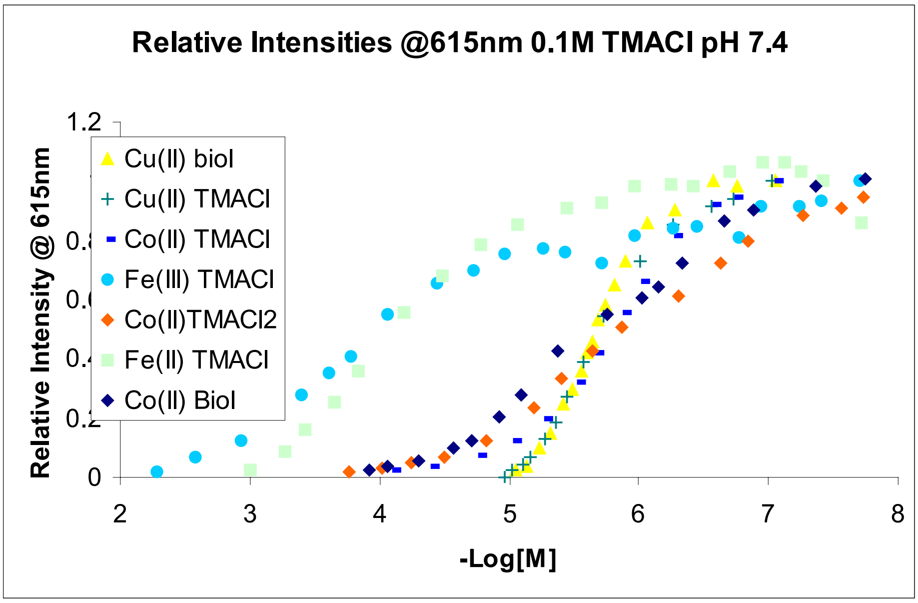


Figure 6. Ratio plot for the titration of 1.Eu with Cu(II).