Supporting Information

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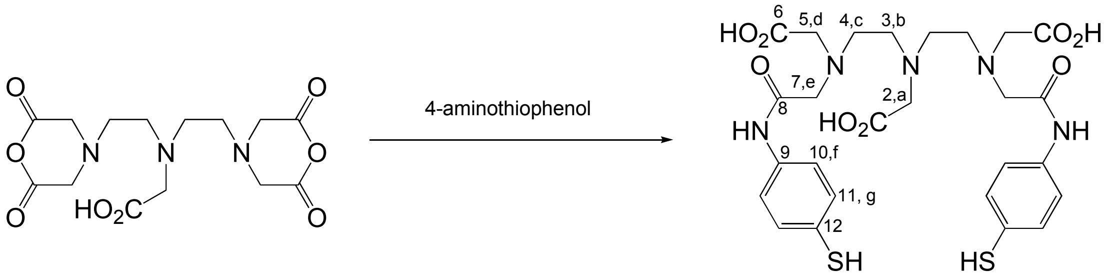
S1.0 Experimental

S1.1. 1, 11-(bis(4-amidothiophenol)-1, 11-dioxo-3, 6, 9-triaza-3,6,9-triscarboxymethyl)undecane: H$_3$L



H$_3$L was prepared by adding 4-aminothiophenol (2.0 g, 16.0 mmol) to a stirring suspension of ca.DTPA (1.02 g, 2.8 mmol) in pyridine (10 ml) following the procedure of Konings et al (*Inorg. Chem.*, 1990, **29**, 1488) and affording **H$_3$L** as a white powder (0.67 g, 40 %). ^{1}H NMR (300 MHz, d_4-MeOH), δ ppm: 7.4 (4H, d, ^3J = 8.6 Hz, ArH$_g$); 7.1 (4H, d, ^3J = 8.6 Hz, ArH$_f$); 4.12 (2H, s, H$_a$); 3.62 (4H, s, H$_d$); 3.59 (4H, s, H$_e$); 3.49 (4H, t, ^3J = 5.2 Hz, H$_c$); 3.22 (4H, t, ^3J = 5.2 Hz, H$_b$). ^{13}C PENDANT {^{1}H} NMR (75 MHz, d_4-MeOH), δ ppm: 173, 170, 168 ($\underline{C}O_2H$, $C_{1,6}$; $\underline{C}ONH$, C_8); 135 (Ar$\underline{C}$NHCO, C_9); 130 (Ar$\underline{C}$H, C_{10}); 126 (Ar$\underline{C}$SH, C_{12}); 121 (Ar$\underline{C}$H, C_{11}); 59.2 ($\underline{C}H_2$, C_5), 56.3 ($\underline{C}H_2$, C_7), 55.5 ($\underline{C}H_2$, C_2), 55.0 ($\underline{C}H_2$, C_4), 51.2 ($\underline{C}H_2$, C_3). MS (ES$^+$) m/z: 608 $\{M+H\}^+$. Anal. calc. for $C_{26}H_{41}N_5O_{12}S_2Cl_3(NH_4Cl)_{0.5}$: C, 32.6; H, 4.5; N, 8.1. Found: C, 32.3; H, 4.2; N, 8.0. UV-Vis (MeOH) λ_{max} in nm (log ε) 265 (4.5).

S1.2. Preparation of EuL *via* K$_3$L

H$_3$L (0.20 g, 0.33 mmol) was dissolved in degassed methanol (5 ml). To the stirred solution, KOH (0.055 g, 0.99 mmol) was added as a methanolic solution (5 ml) and the mixture stirred for 10 minutes. The methanol was then completely evaporated to yield the tripotassium salt, **K$_3$L** in the reaction vessel, which was redissolved in degassed deionised water (5 ml). To the aqueous solution, $EuCl_3 \cdot 6H_2O$ (0.12 g, 0.33 mmol) was added which caused an immediate precipitation of a white solid, which was isolated by suction filtration and washed with acetone (2 × 10 ml) and diethyl ether (5 ml), and dried under vacuum to yield the complex, **EuL** (0.21 g, 86 %). MS (ES$^+$): m/z 758 $\{M+H\}^+$. HRMS calc. for $EuC_{26}H_{31}N_5O_8S_2$: 758.0826. Found: 758.0833. UV-Vis (MeOH): λ_{max} in nm (log ε) 266 (4.4).

S1.3. Preparation of Gold Colloids

Gold colloids were prepared as per Grabar *et. al (Anal. Chem.*, 1995, **67**, 735).

S.1.4. Calculation of Nanoparticle Concentration

It was possible to estimate the concentration of CNPs from TEM experiments. It can be assumed (R. L. Johnston, 'Atomic and Molecular Clusters', Taylor & Francis, **2002**) for large "spherical" metal clusters such as a gold nanoparticle that:

$$V_{cluster} = NV_{atom} \qquad \textbf{(eq. 1)}$$

$$4/3\ \pi\ (R_{cluster})^3 = N\ 4/3\ \pi\ (R_{atom})^3 \qquad \textbf{(eq. 2)}$$

Where V is the cluster or atom volume, R is the cluster or atomic radius and N is the total number of atoms within the cluster. Rearranging, we obtain:

$$R_{cluster} = N^{1/3}\ R_{atom} \qquad \textbf{(eq. 3)}$$

Knowing the cluster radius we may also calculate the surface (S) area of a nanoparticle with the following equation:

$S_{cluster} = 4\ \pi\ (R_{cluster})^2$ **(eq. 4)**

For larger clusters, we may also calculate the number of surface atoms, N_s, directly by dividing the surface area of the cluster by the cross section of an individual cluster atom, and then simplifying using the relationship in **(eq. 3)**:

$N_s = (4\ \pi\ (R_{cluster})^2) / (\pi\ (R_{atom})^2) = 4\ N^{2/3}$ **(eq. 5)**

From the TEM result we know that $R_{cluster} \approx 6.5$ nm, and $R_{atom} = 0.137$ nm. The number of gold atoms per nanoparticle was estimated using **(eq. 3)**:

$N = (R_{cluster} / R_{atom})^3 = ((6.5 \times 10^{-9}) / (137 \times 10^{-9}))^3$

$N = \underline{\ 106\ 801\ }$ *gold atoms per nanoparticle*

The number of surface atoms, N_s, on a single gold nanoparticle was also estimated using **(eq. 5)**:

$N_s = 4\ N^{2/3} = 4 \times (106,\ 801)^{2/3}$

$N_s = \underline{\ 9004\ }$ *gold surface atoms per nanoparticle*

From the calculation of N, the molecular weight (M_w) of a single nanoparticle was calculated using the relative molecular mass of a single gold atom (M_{gold}):

$M_w = M_{gold} \times N$

$M_w = 196.97 \times 106\,801$

$M_w = \underline{21\,036 \text{ kDa}}$

Calculation of the amount of nanoparticles formed (N_{NP}) when 1 dm^3 of 1 mM $HAuCl_4$ is reduced by citrate was then calculated:

Moles of $HAuCl_4 = 1 \times 1 \times 10^{-3} = 1 \times 10^{-3}$ mol

No. of gold atoms, $N_{atom} = 1 \times 10^{-3} \times N_A = 1 \times 10^{-3} \times 6.022 \times 10^{23}$

$= 6.022 \times 10^{20}$

$N_{NP} = N_{atom} / N$

$N_{NP} = (6.022 \times 10^{20}) / (106\,801)$

$N_{NP} = \underline{5.639 \times 10^{15}}$ *Nanoparticles formed per 1×10^{-3} mol $HAuCl_4$*

Hence the final concentration of the gold colloid, C_{NP}, was estimated by dividing N_{NP} by Avagadro's number (N_A):

$C_{NP} = N_{NP} / N_A$

$C_{NP} = (5.639 \times 10^{15}) / (6.022 \times 10^{23})$

$C_{NP} = \underline{9.363 \times 10^{-9} \text{ mol dm}^{-3}}$

S2.0 Additional Spectra

Figure S2.1.: 300 MHz ^{1}H NMR spectrum of $\mathbf{H_3}^{\mathbf{1}}$ (d_4-MeOH)

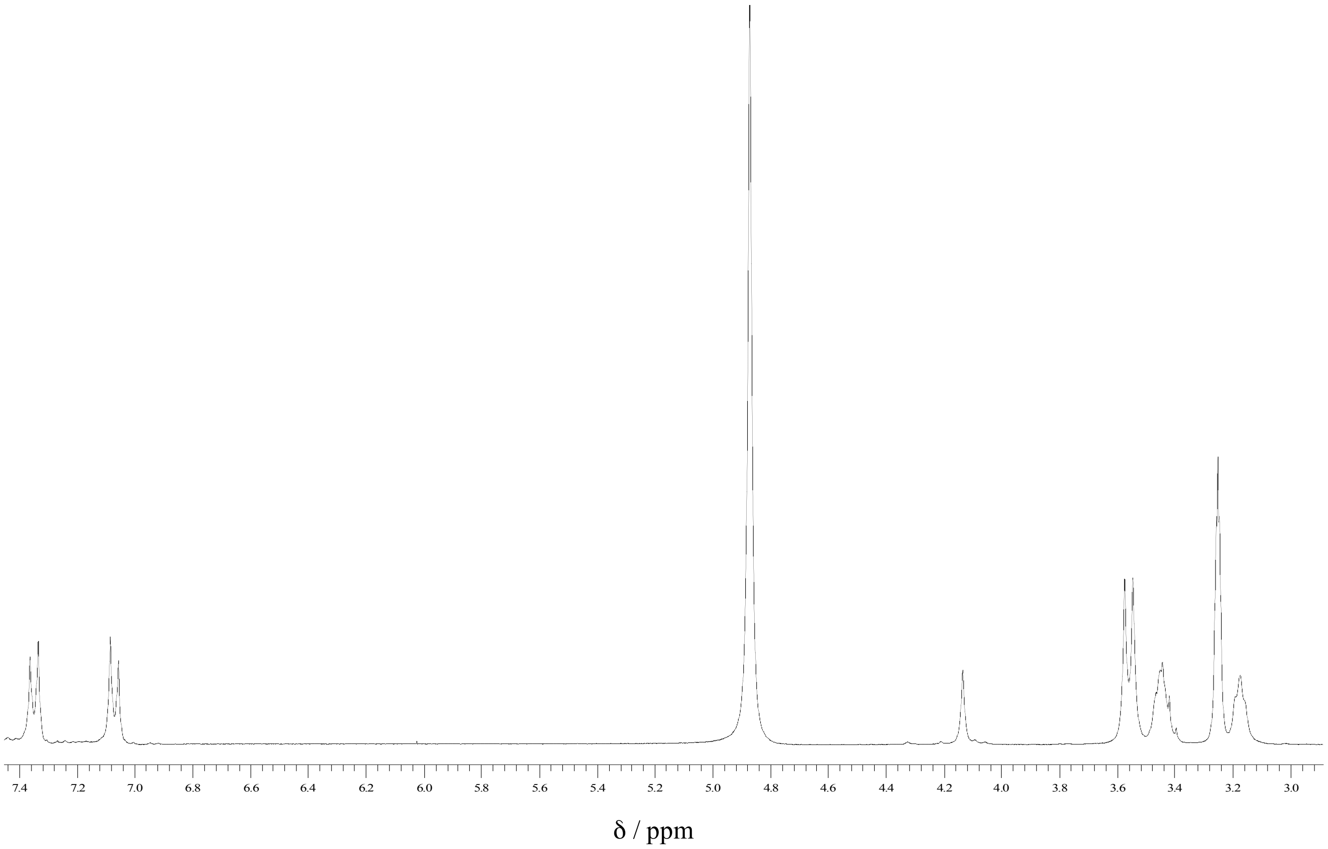


Figure S2.2. : 75 MHz ^{13}C {^{1}H} PENDANT NMR spectrum of $\mathbf{H_3L}$ (d_4-MeOH)

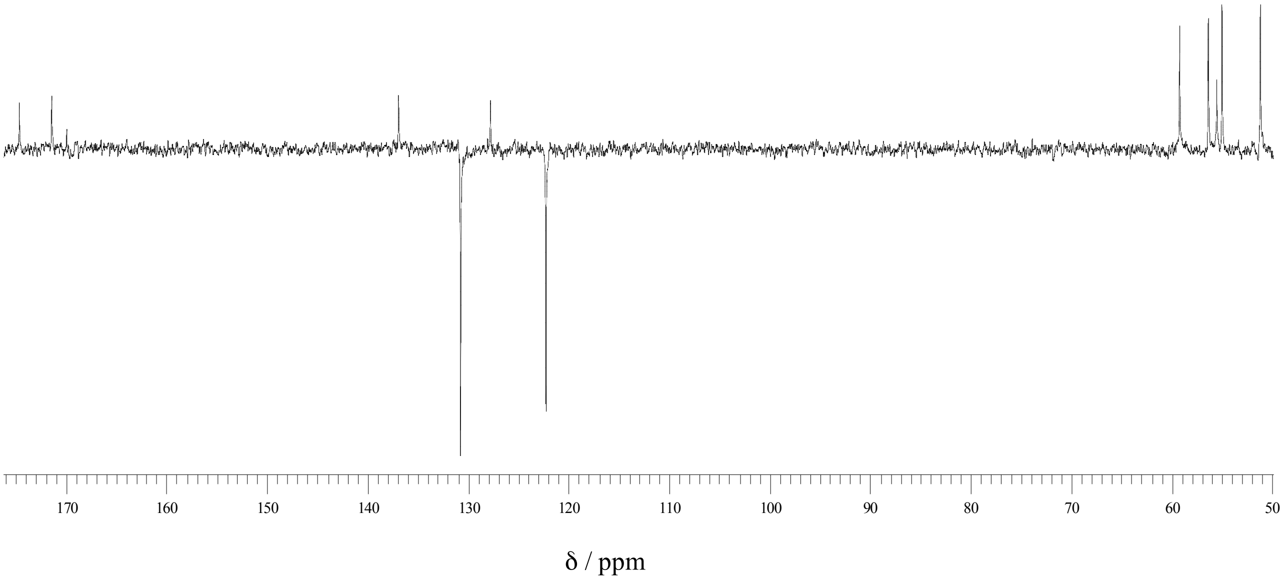
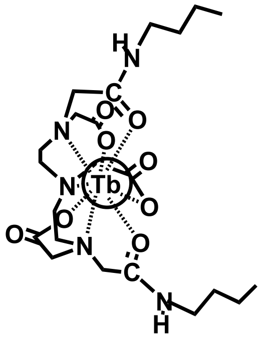


Figure S2.3. : UV-vis absorption spectrum of 0.2 nM aqueous citrate-stabilised Au colloid (solid curve), and after addition of 125 nmol of **TbX** (dashed curve).

where TbX =



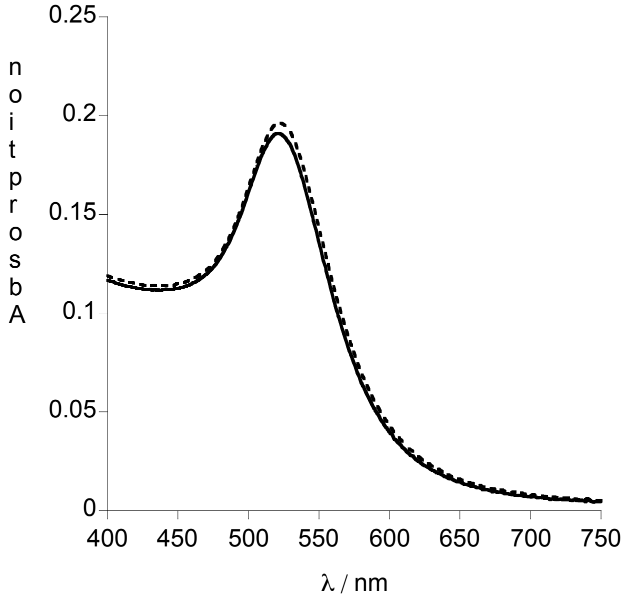


Figure S2.4. : UV-vis absorption spectrum of 0.2 nM citrate stabilised gold colloid (2.5 ml) (solid line with cross) , after addition of 175 μl methanol (solid line).

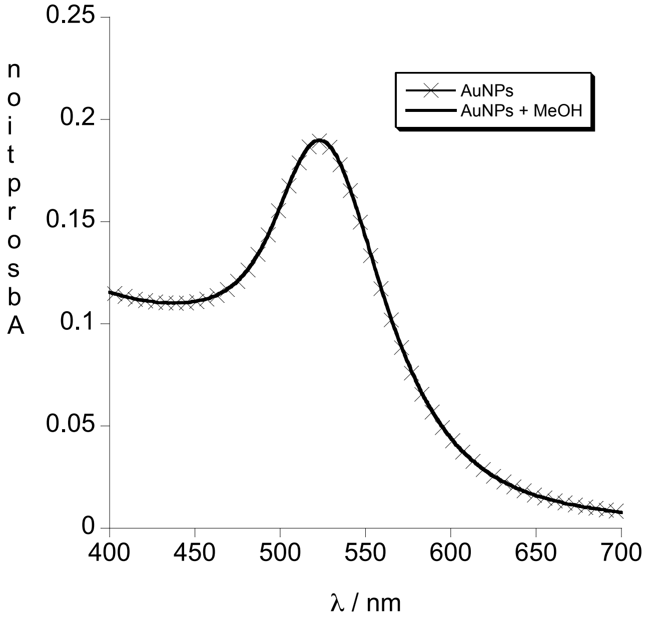


Figure S2.5. : UV-vis spectrum of nanoparticles functionalised with **EuL** after gel filtration chromatography on Sephadex G-15.