Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Proton Switching as a Driving Force for the Metal-Organic Complex - Mediated Growth of Gold Colloids

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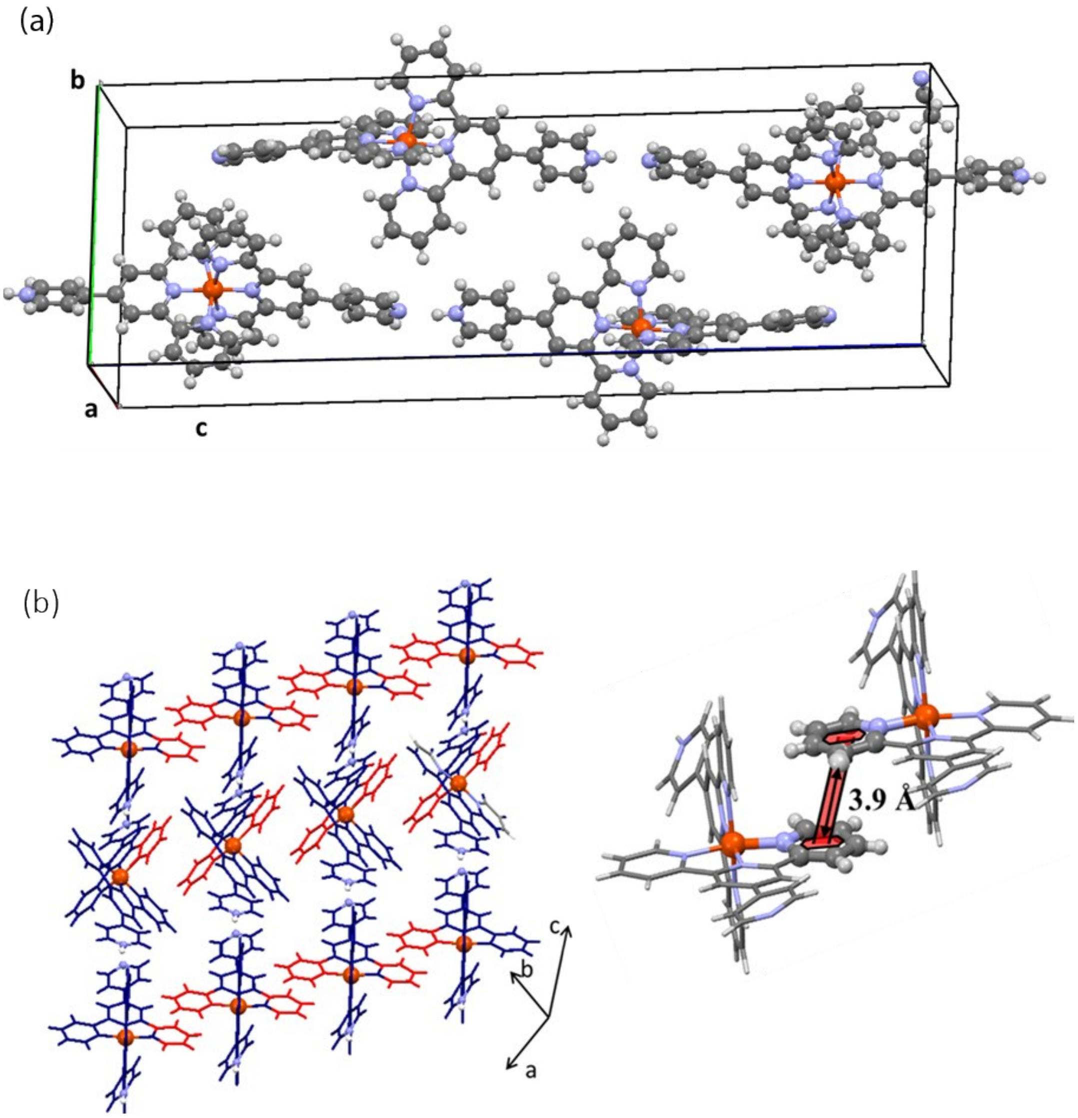

Fig. S1 (a) Unit cell crystal structure showing 4 units of $[Fe(ptpy)(Hptpy)]^{3+}$ complex . (b) Extended unit cell structure showing characteristic twisted π-stacking in the protonated complex.

Estimation of ΔG values for individual proton and electron transfer, along with the coupled process:

$$\Delta G_{P_1} = G_{[MH]^{4+}} - G_{[M]^{3+}} - G_{[H]^{+}} \qquad \text{(SE1)}$$

$$\Delta G_{P_2} = G_{[MH]^{3+}} - G_{[M]^{2+}} - G_{[H]^{+}} \qquad \text{(SE2)}$$

$$\Delta G_{red} = G_{[M]^{2+}} - G_{[M]^{3+}} \qquad \text{(SE3)}$$

$$\Delta G_{red,P} = G_{[MH]^{3+}} - G_{[MH]^{4+}} \qquad \text{(SE4)}$$

$$\Delta G = G_{[MH]^{3+}} - G_{[M]^{3+}} - G_{[H]^{+}} \qquad \text{(SE5)}$$

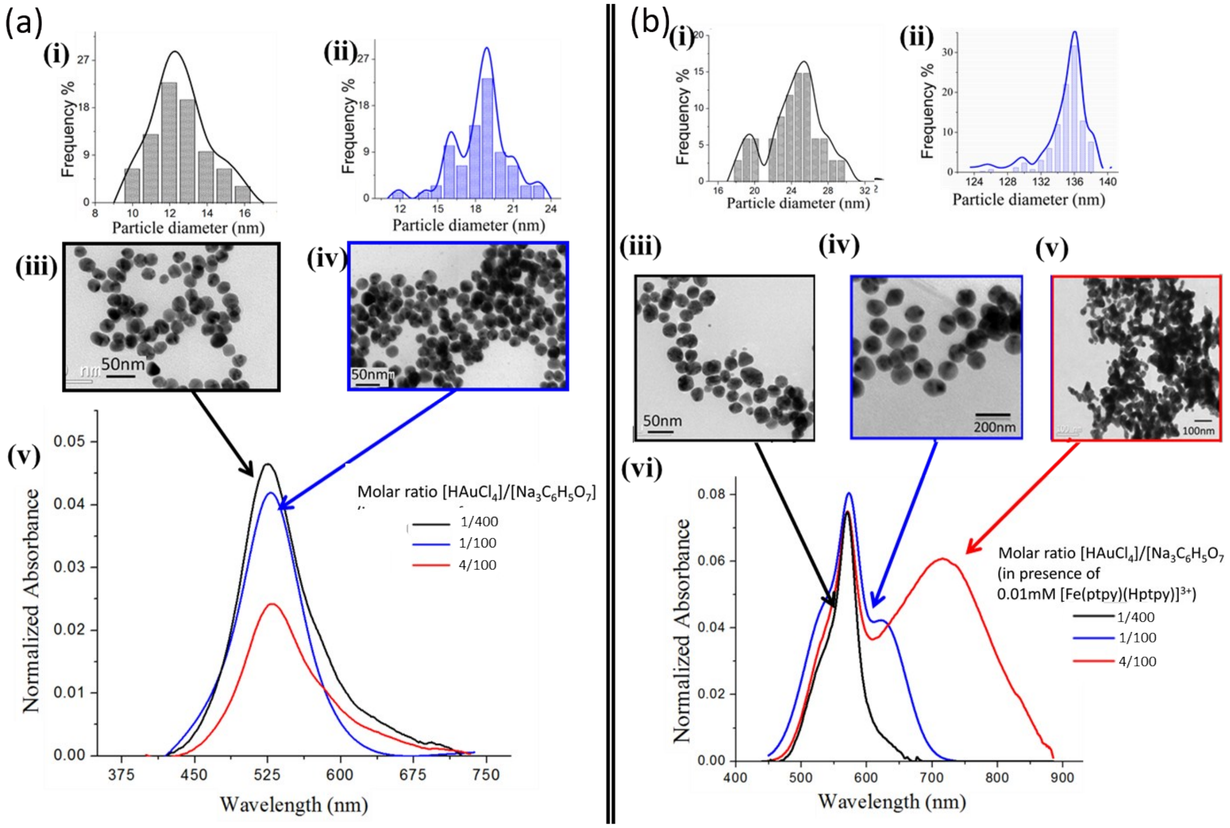

Fig. S2 Particle size distribution (a(i) and a(ii)), and TEM images (a (iii) and a(iv)) of citrate capped GN showing minimal increase in size from 13 nm to 18nm upon increasing molar ratio of HAuCl$_4$ to citrate. Similarly, particle size distribution (b(i) and b(ii)), and TEM images of 0.01mM [Fe(ptpy)(Hptpy)]$^{3+}$ linked GN with varying molar ratio of HAuCl$_4$ to citrate [(b(iii) , b(iv)] showing size enhancement from 24 to 135 nm. The 4/100 molar ratio in b (v) results in agglomeration.

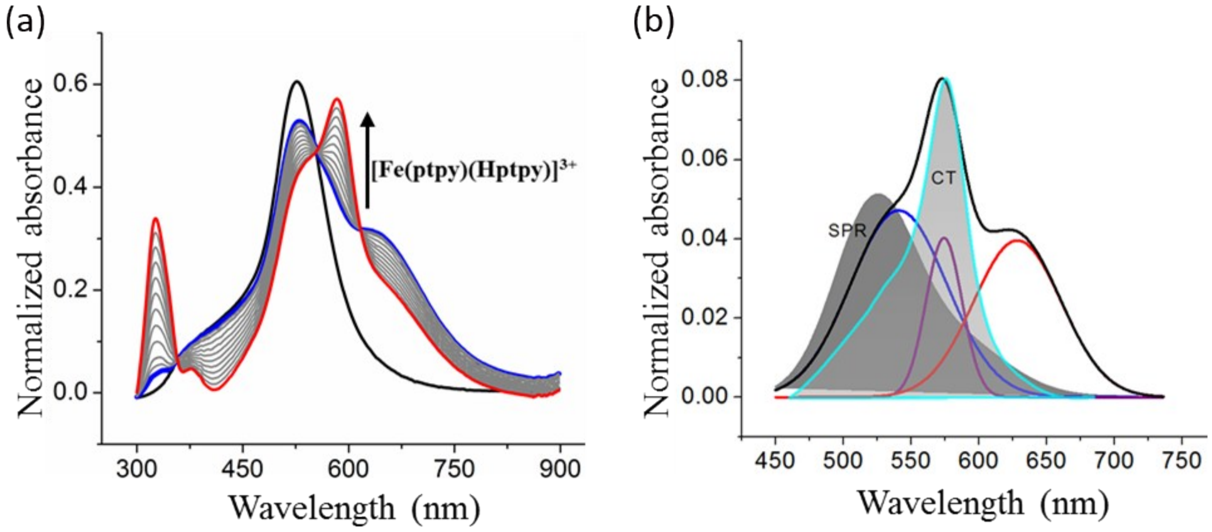

Fig. S3 (a) UV-vis photometric titration curves of $(Au)_n$ prepared from 1:100 $HAuCl_4$ (0.01mM) and citrate (1mM), obtained upon successive 200μL addition of 0.01mM $[Fe(ptpy)(Hptpy)]^{3+}$ complex showing two new rising spectral features at 569 nm (MLCT of complex) and 645 nm (secondary aggregation of nanoparticle) along with decrease in intensity and red shifting of the surface plasmon band. (b) Gaussian fitted spectra of 0.01mM $[Fe(ptpy)(Hptpy)]^{3+}$@ GN along with bare citrate capped GN and 0.01mM $[Fe(ptpy)(Hptpy)]^{3+}$ complex in water.

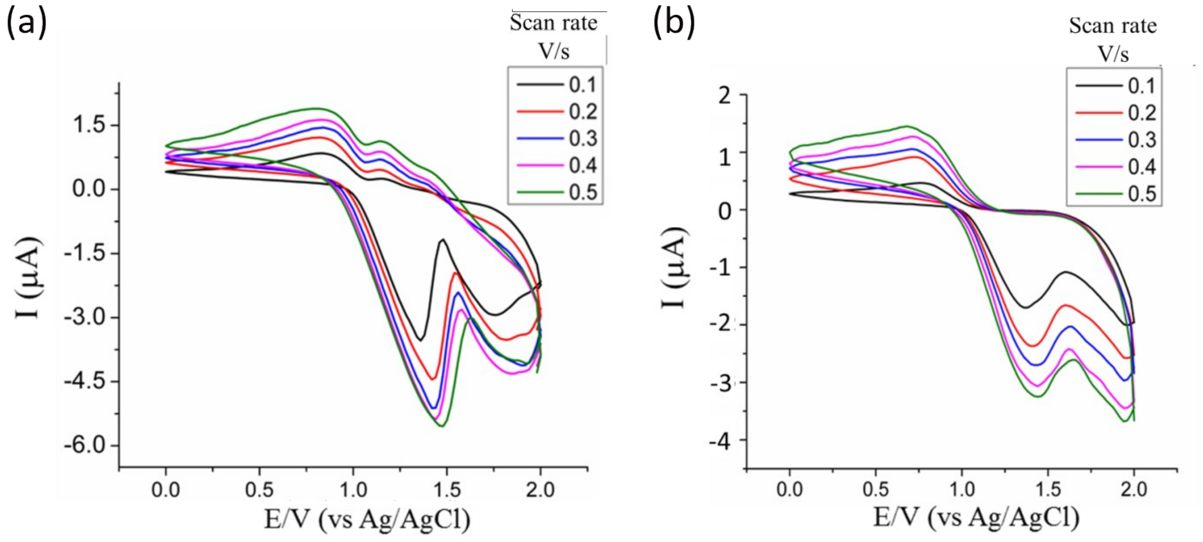

Fig. S4 Cyclic voltammograms from (a) citrate capped GN and (b) citrate capped $[Fe(ptpy)(Hptpy)]^{3+}$ linked GN complex modified ITO electrode at different scan rates (0.1 - 0.5 Vs^{-1}) in 0.1M H_2SO_4 supporting electrolyte.

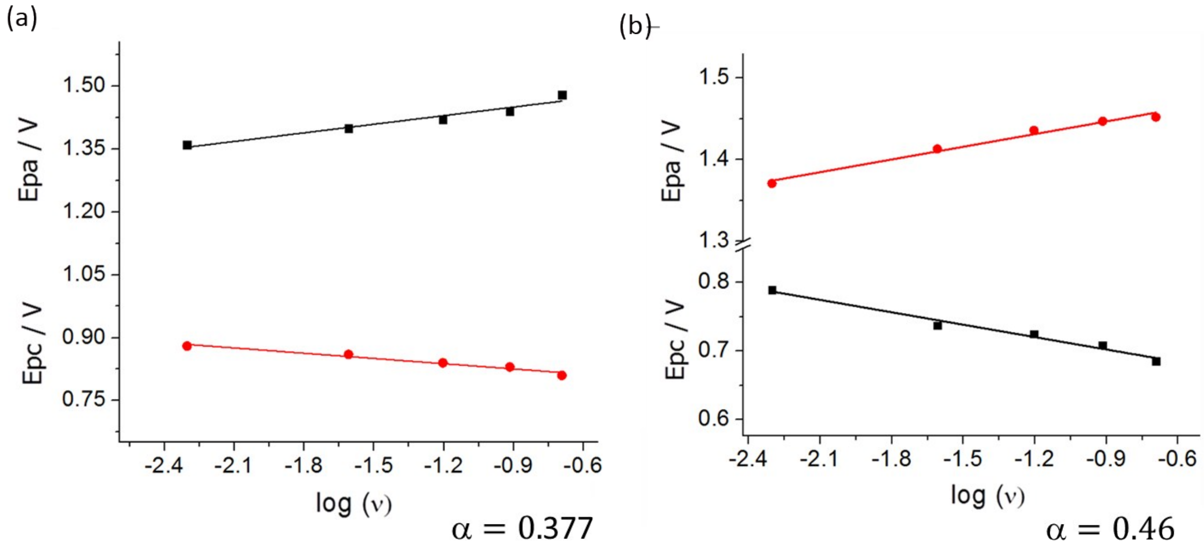

Fig. S5 (a) and (b) represent the linear variation of cathodic and anodic potentials with scan rate from the ITO modified citrate capped $Au_{(n)}$ with and without the complex $[Fe(ptpy)(Hptpy)]^{3+}$ respectively.

<u>Laviron formalism</u>:

$$\log k_s = \alpha \log(1-\alpha) + (1-\alpha)\log\alpha - \log\frac{RT}{nF\upsilon} - \frac{\alpha(1-\alpha)nF\Delta \mathrm{E}p}{2.3RT} \qquad \text{(SE6)}$$