

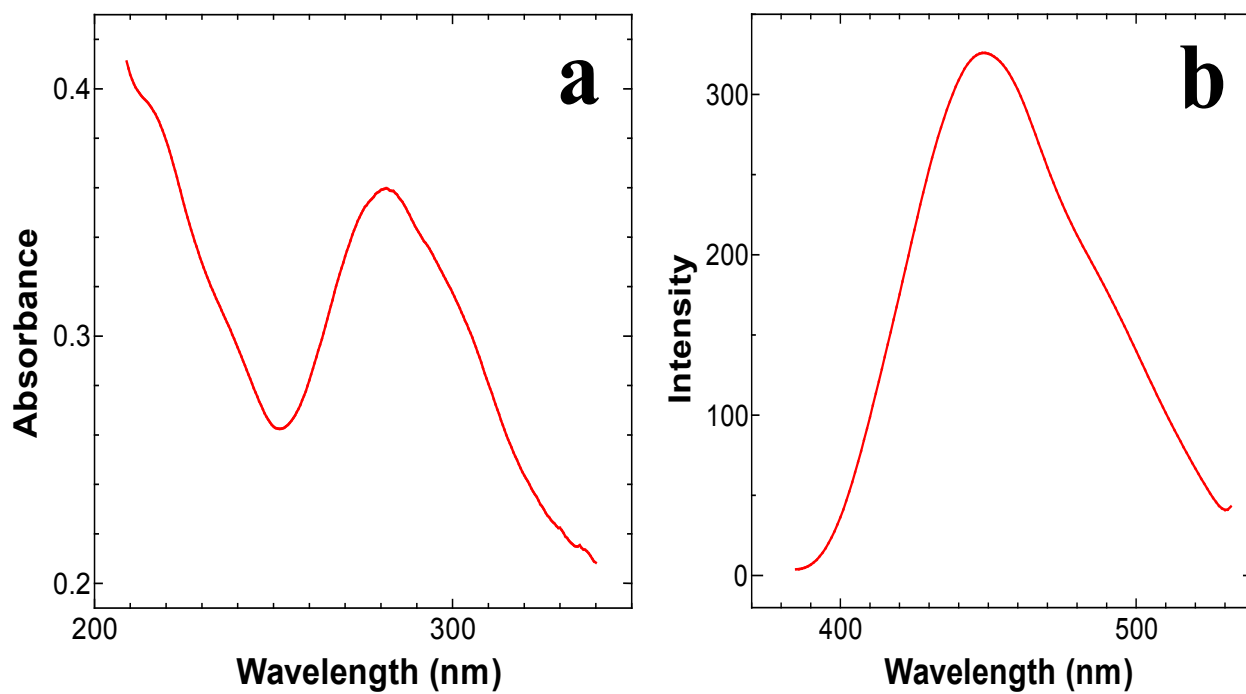
# **Aggregation and de-aggregation of gold nanoparticles induced by polyionic drugs: Spectrofluorimetric determination of picogram protamine and heparin drugs in the presence of 1000-fold major interferences**

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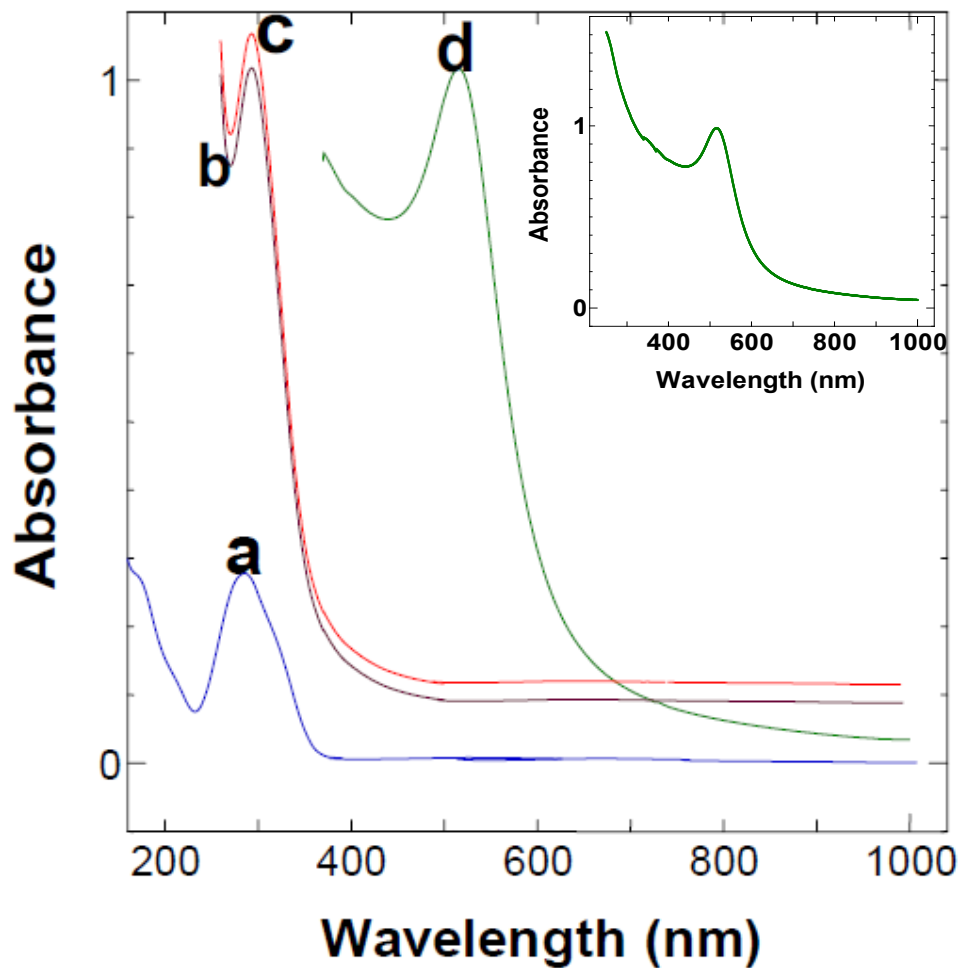
**Fig.S1:**

UV-visible (a) and emission (b) spectra of folic acid ( $\lambda_{\text{ex}}$ : 285 nm;  $\lambda_{\text{em}}$ : 447 nm).



**Fig.S2:**

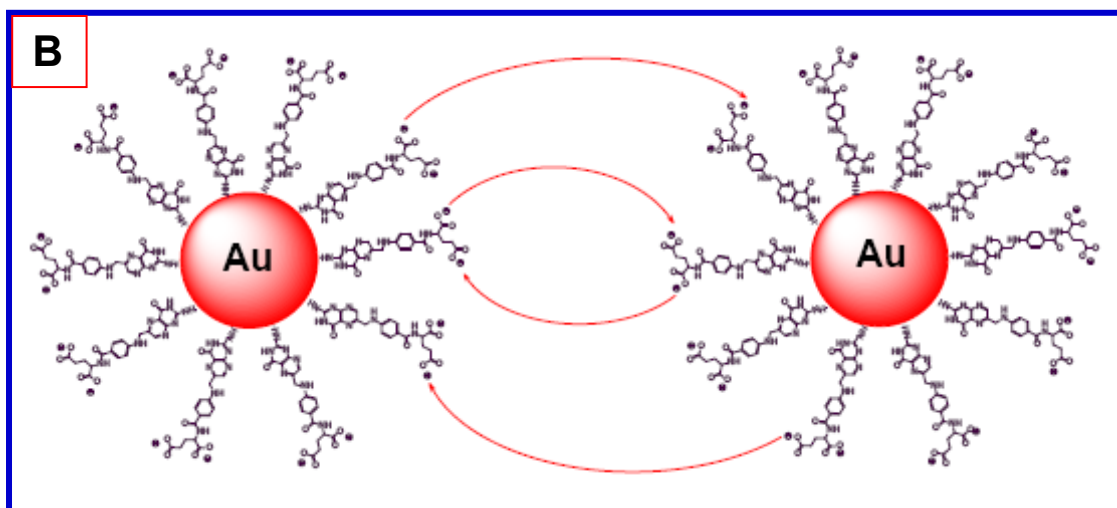
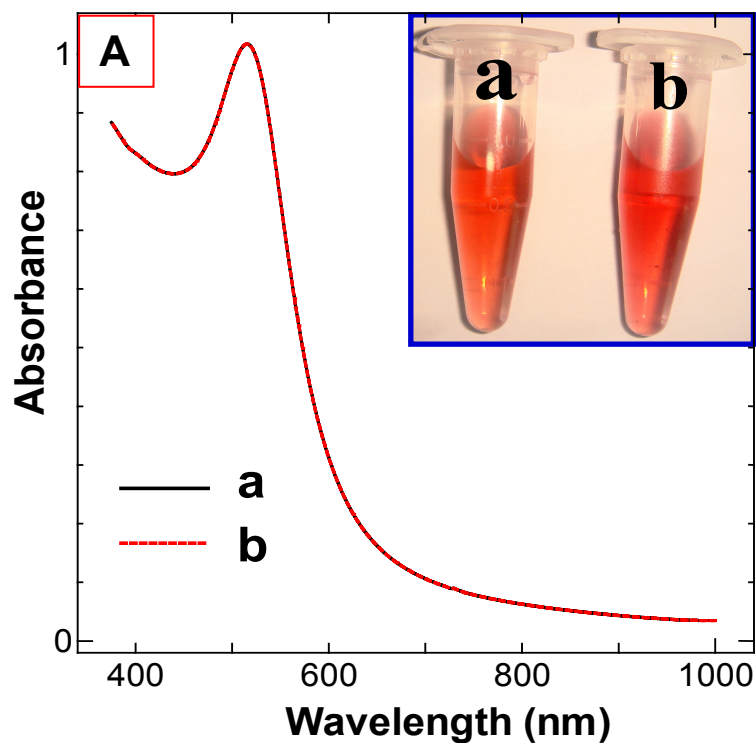
(A) UV-visible spectra of (a) folic acid, (b)  $\text{HAuCl}_4$  and (c) after the addition of  $\text{HAuCl}_4$  to folic acid and (d)  $\text{NaBH}_4$  to a mixture of  $\text{HAuCl}_4$  and folic acid. **Inset:** UV-visible spectrum of FA-AuNPs.



**Fig. S3:**

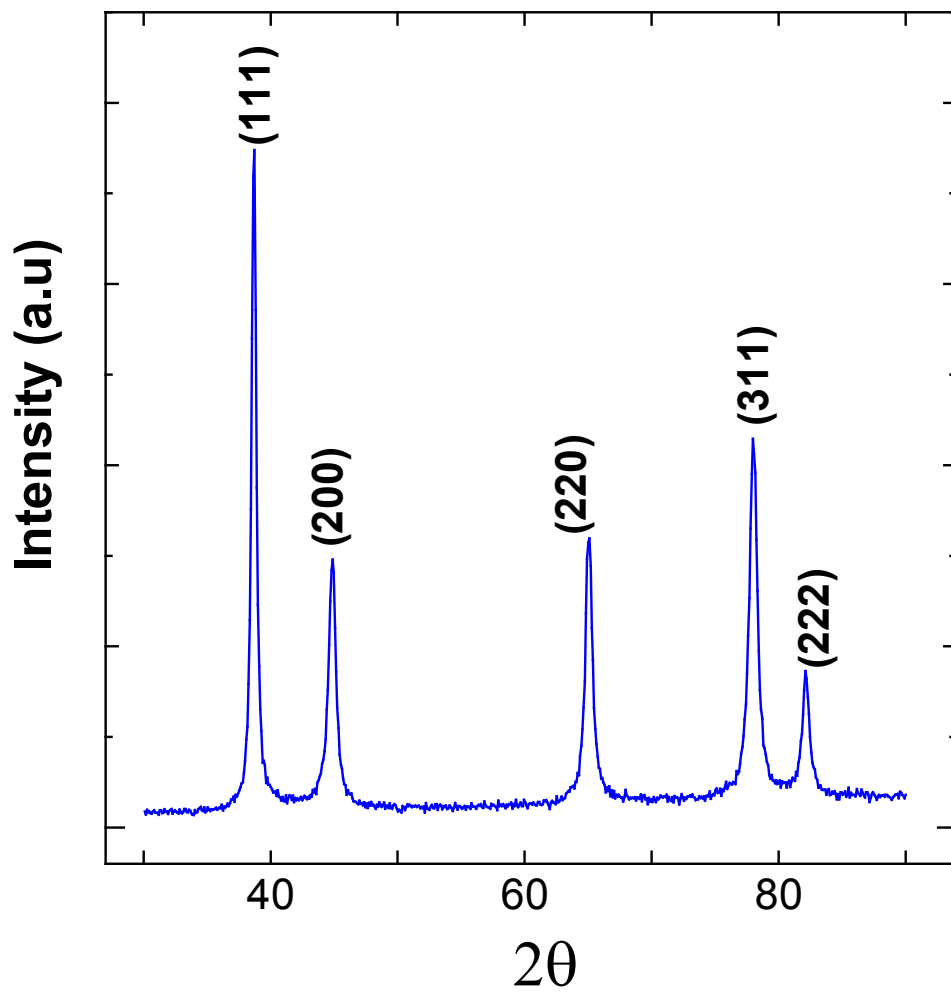
(A) UV-visible spectra obtained for FA-AuNPs (a) freshly prepared and (b) after 6 months.

**Inset:** Photographs (a) freshly prepared and (b) 6 months aged FA-AuNPs. (B) Schematic representation of stability of FA-AuNPs.



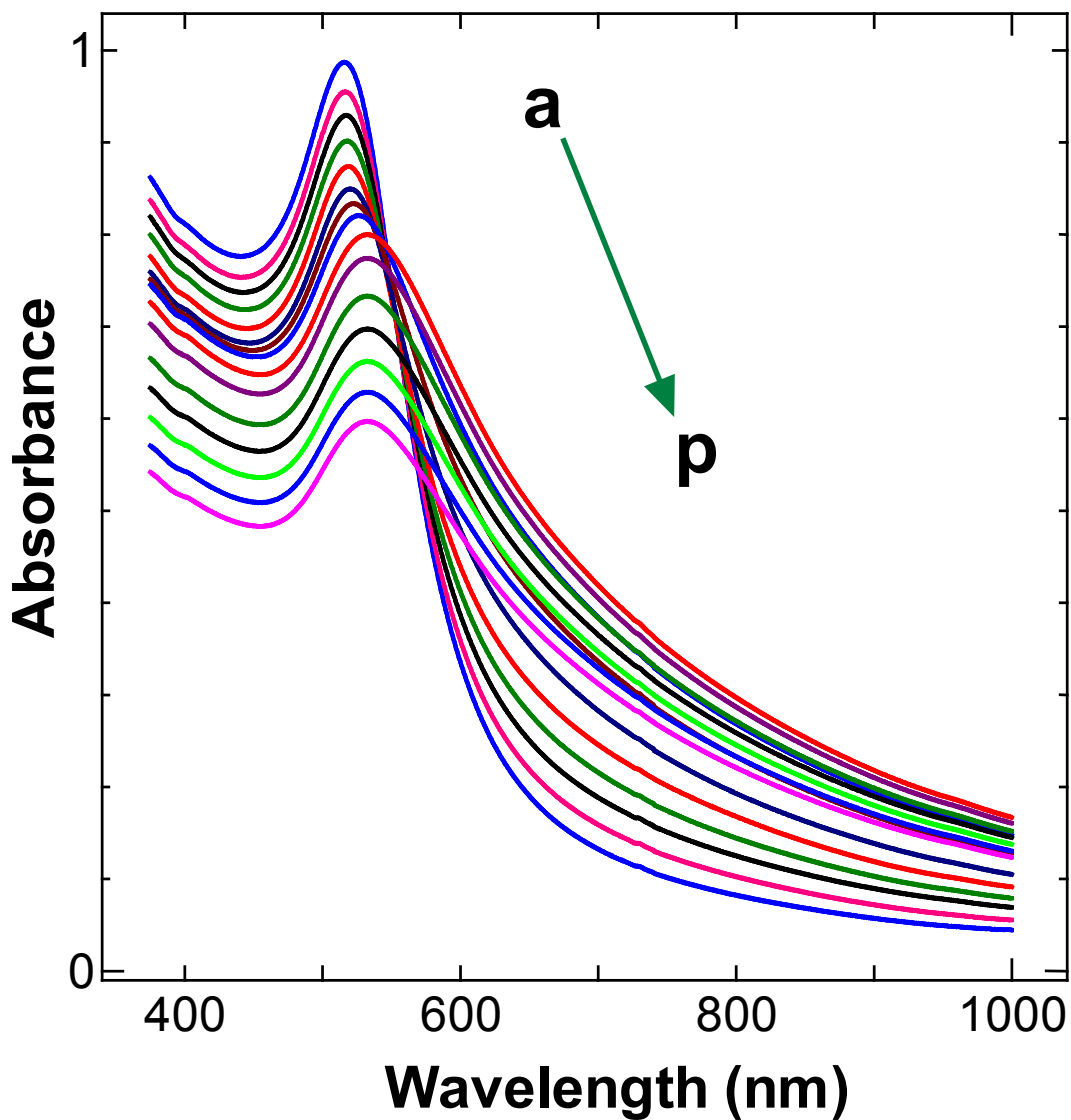
**Fig. S4.**

X-ray diffraction pattern of FA-AuNPs.



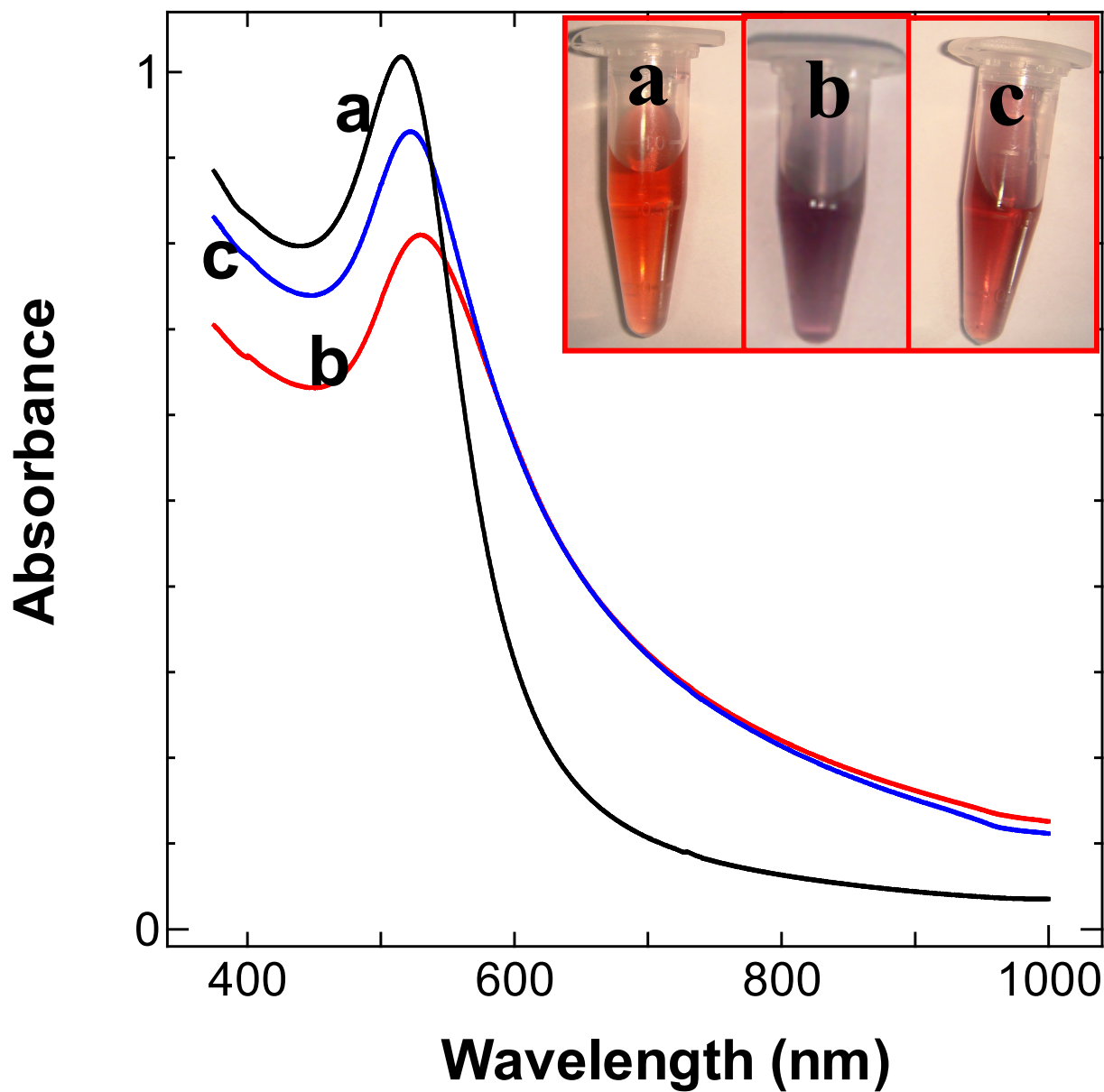
**Fig. S5.**

UV-visible spectra of FA-AuNPs in the presence of different concentrations of protamine: (a) 0, (b) 0.05, (c) 0.1, (d) 0.15, (e) 0.2, (f) 0.25, (g) 0.3, (h) 0.35, (i) 0.4, (j) 0.45, (k) 0.5, (l) 0.55, (m) 0.6, (n) 0.65, (o) 0.7 and (p)  $0.75 \times 10^{-6}$  g/L.



**Fig. S6.**

UV-visible spectra of (a) FA-AuNPs alone, (b) after the addition of  $0.45 \times 10^{-6}$  g/L protamine and (c) followed by the addition of  $4.5 \times 10^{-6}$  g/L heparin. **Insets:** The corresponding photographs of curves a, b and c.



**Fig. S7.**

UV-visible spectra of FA-AuNPs in the presence of  $0.45 \times 10^{-6}$  g/L protamine (a) before and (b) after one week. **Inset:** Corresponding Photographs of curves a and b.

