

Supporting Information

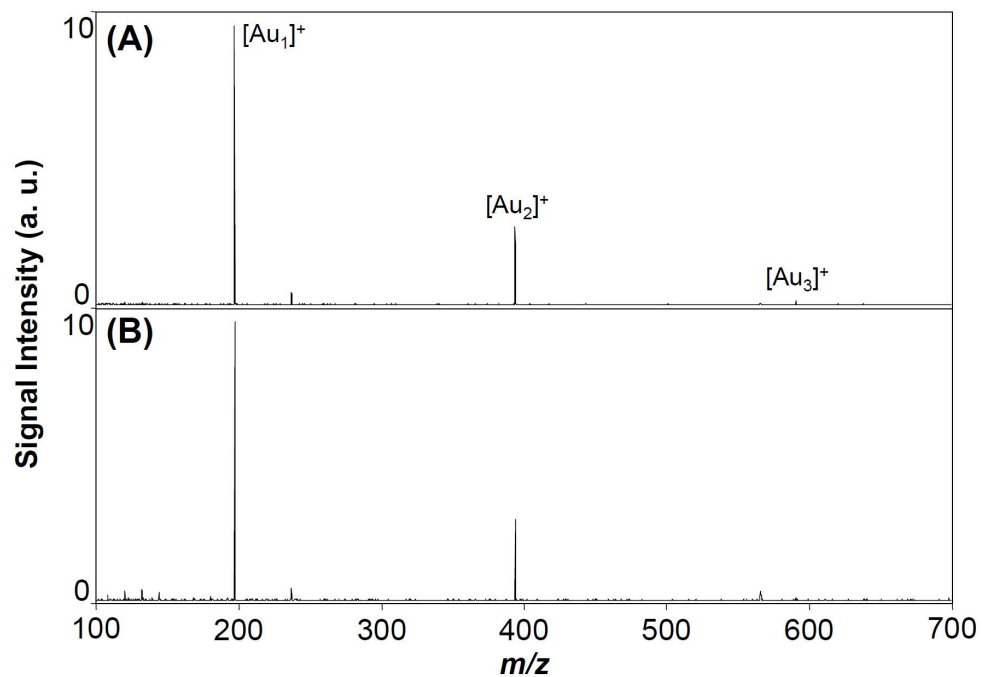
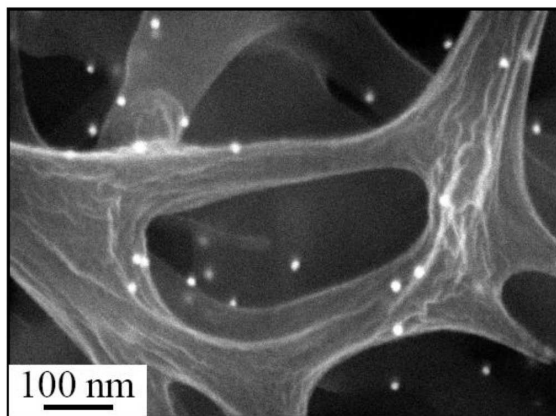


Figure S1 Mass spectra of BSA–AuNP/NCM (10 pM) or rDNA–AuNPs/NCM (10 pM) in the (A) absence and (B) presence of thrombin (100 pM). Other conditions were the same as those described in Figure 1.

(A)



(B)

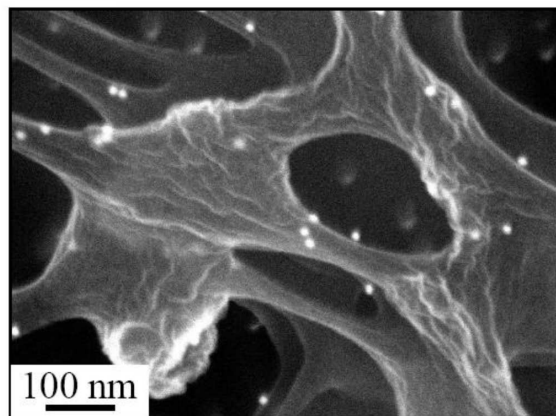


Figure S2 SEM images of TBA₂₉-AuNP/NCM in the (A) absence and (B) presence of thrombin (1.0 nM). Other conditions were the same as those described in Figure 1.

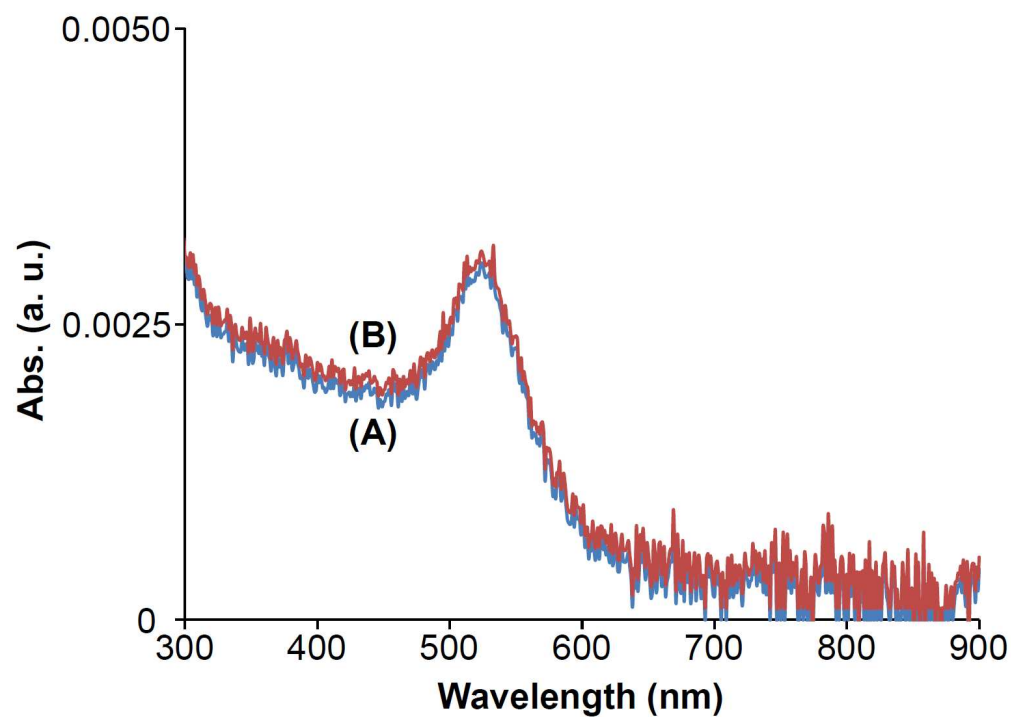


Figure S3 UV-Vis absorption spectra of a TBA₂₉-AuNP solution (10 pM) in the (A) absence and (B) presence of thrombin (100 pM) in a biological buffer containing BSA (100 μ M). Other conditions were the same as those described in Figure 1.

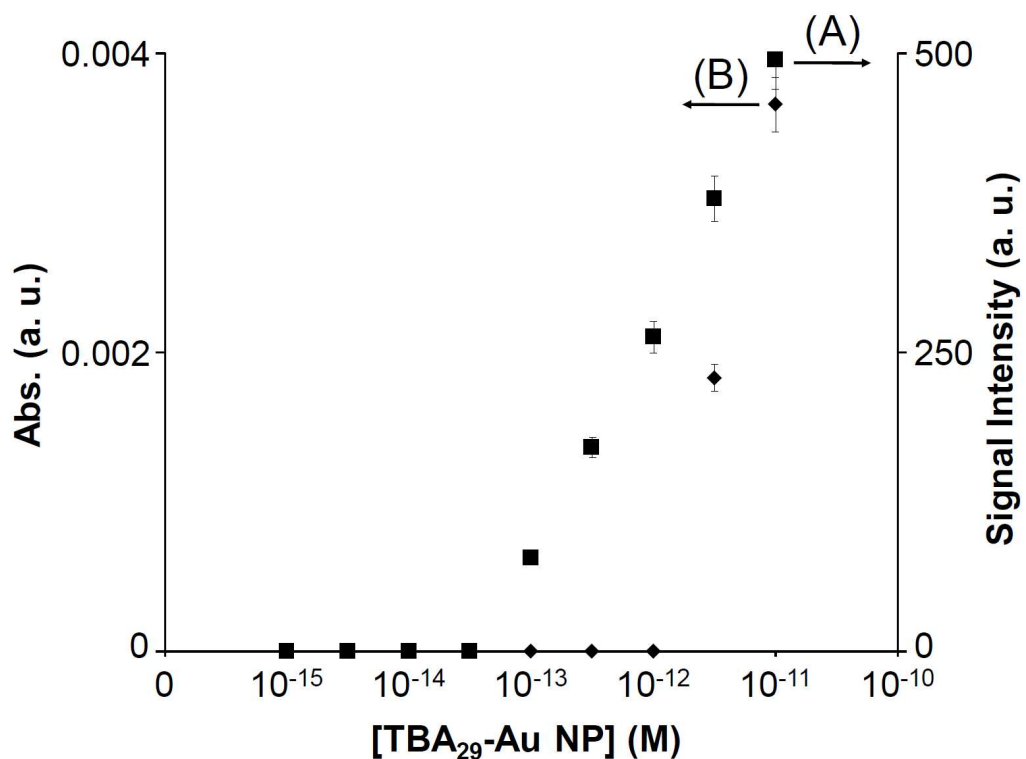


Figure S4 (A) Signal intensities of $[\text{Au}_1]^+$ ions recorded through LDI-MS from a TBA₂₉-AuNP/NCM substrate after the NCM had been immersed in TBA₂₉-AuNP solutions of various concentrations (1 fM–10 pM). (B) UV-Vis absorptions at 520 nm (SPR band) of TBA₂₉-AuNPs at concentrations from 1 fM to 10 pM.

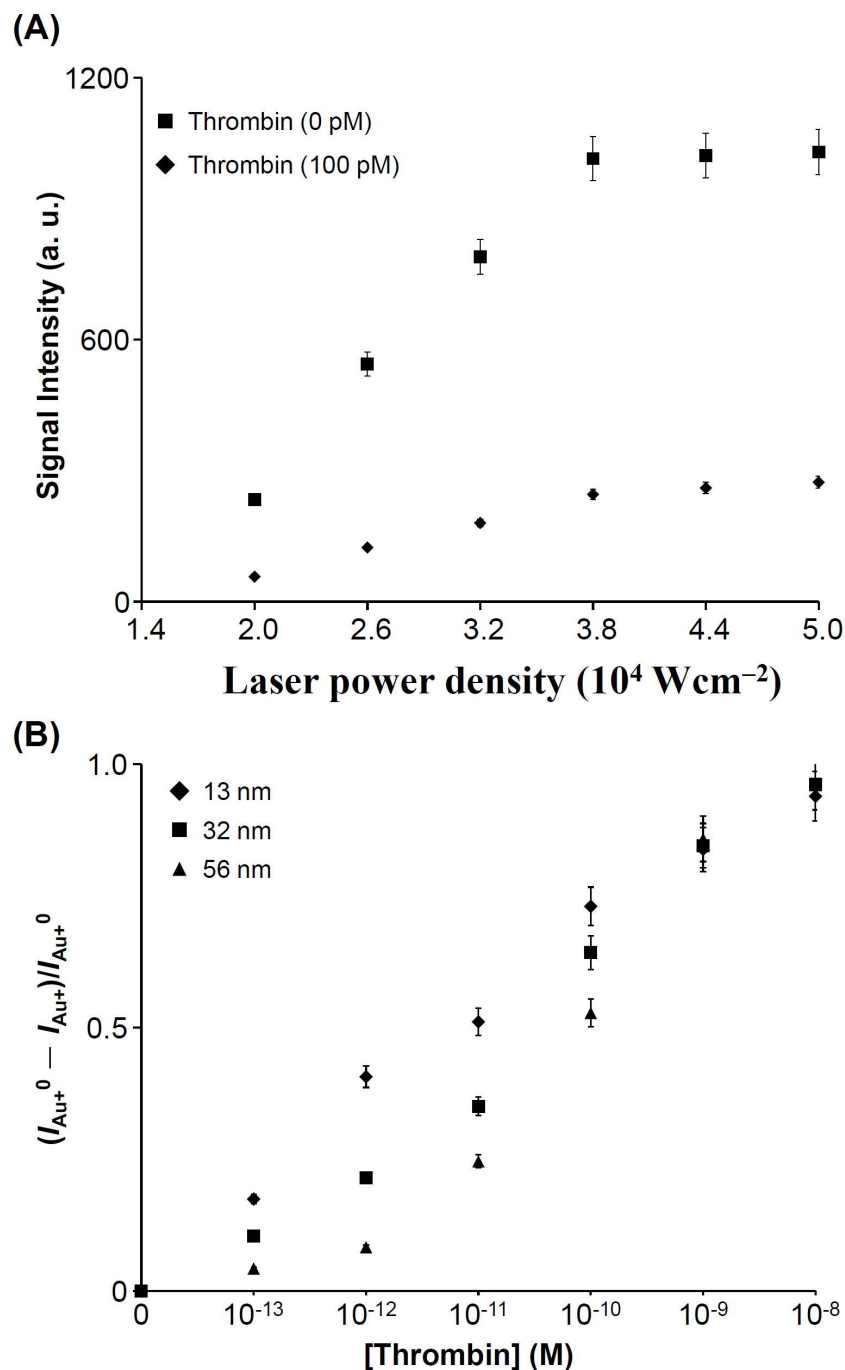


Figure S5 Effects of (A) laser fluence and (B) particle size of TBA₂₉-AuNPs on LDI-MS analysis of thrombin using the TBA₂₉-AuNP/NCM substrate as the matrix. The descriptors $I_{\text{Au}^+}^0$ and I_{Au^+} in (B) represent the intensities of the $[\text{Au}]^+$ ions from TBA₂₉-AuNP/NCM in the absence and presence of thrombin, respectively. Error bars represent standard deviations from five repeated experiments. Other conditions were the same as those described in Figure 1.

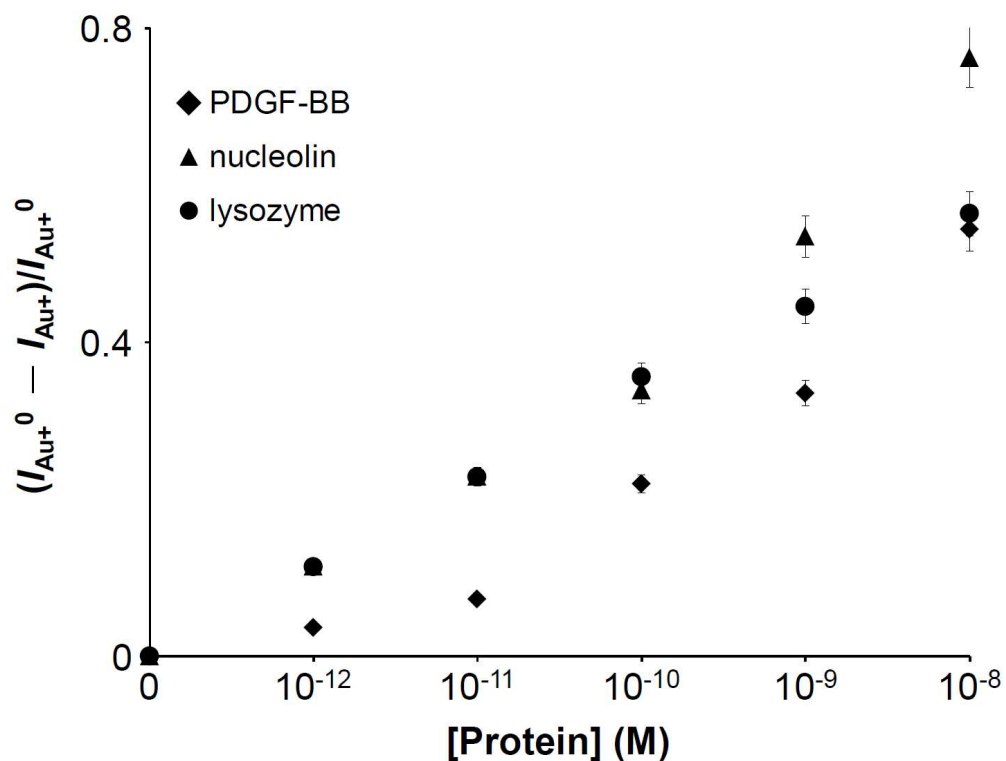


Figure S6 Relative signal intensities of $[Au_1]^+$ ions obtained from the Apt–AuNP/NCM probe in analytical solutions containing a biological buffer, BSA (100 μ M), and various concentrations of target proteins (0–10 nM). Other conditions were the same as those described in Figure 1.