Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.
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Electronic Supplementary Information

Three label-free thrombin aptasensors based on aptamers and $[Ru(bpy)_2(o\text{-}mopip)]^{2+}$

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Synthesis and characterization

Cis-$[Ru(bpy)_2Cl_2]\cdot 2H_2O$, cis-$[Ru(bpy)_2(py)_2]Cl_2$, Δ-$[Ru(bpy)_2(py)_2]$ [o,o′-dibenzoyl-D-tartrate]$\cdot 12H_2O$, 2-(2-methoxylphenyl)imidazo[4,5-f]-[1,10]phenanthroline (o-mopip) and Δ-$[Ru(bpy)_2(o\text{-}mopip)](PF_6)_2\cdot 2H_2O$ were prepared and characterized according to the literature.[22]

Δ-$[Ru(bpy)_2$-$(py)_2]$[o,o′-dibenzoyl-D-tartrate]$\cdot 12H_2O$ (260 mg, 0.2 mmol) and o-mopip (163 mg, 0.5 mmol) were added to 20 ml ethylene glycol–water (9:1, v/v). The mixture was refluxed for 6 h under an argon atmosphere. The cooled reaction mixture was diluted with water (40 ml) and filtered to remove solid impurities, and then ammonium hexafluorophosphate was added to the filtrate. The precipitated complex was dried, dissolved in a small amount of acetonitrile, and purified by chromatography over alumina, using MeCN–toluene (2:1, v/v) as eluent, yield: 153 mg, 72%. ^{1}H NMR [$(CD_3)_2SO$]: δ 9.33 (d (double), 1 H), 9.11 (d, 1 H), 8.87 (d, 2 H), 8.83 (d, 2 H), 8.22–8.18 (m (multiplet), 3H), 8.12 (t (triplet), 2 H), 8.08 (d, 2 H), 7.92 (t, 2 H), 7.89 (d, 2 H), 7.76–7.57 (m, 5 H), 7.37 (m 3 H) and 7.22 (t, 1 H). Calc. for $C_{40}H_{34}F_{12}N_8O_3P_2Ru$: C: 45.08; H: 3.22; N: 10.51. Found: C: 45.05; H: 3.23; N: 10.50. ESIMS (electrospray ionisation mass spectrometry): m/z 739.3 (M-2PF_6-H), 370.2 (M-2PF_6/2). UV–vis (UV–visible) (λ (nm), ε (M^{-1} cm^{-1})) (CH_3CN): 457 (18200), 286 (90550), 243 (33400). CD (circular dichroism) (λ (nm), Δε (M^{-1} cm^{-1})) (CH_3CN): 472 (2.1), 423 (2.3), 293 (26.6), 278 (10.1).

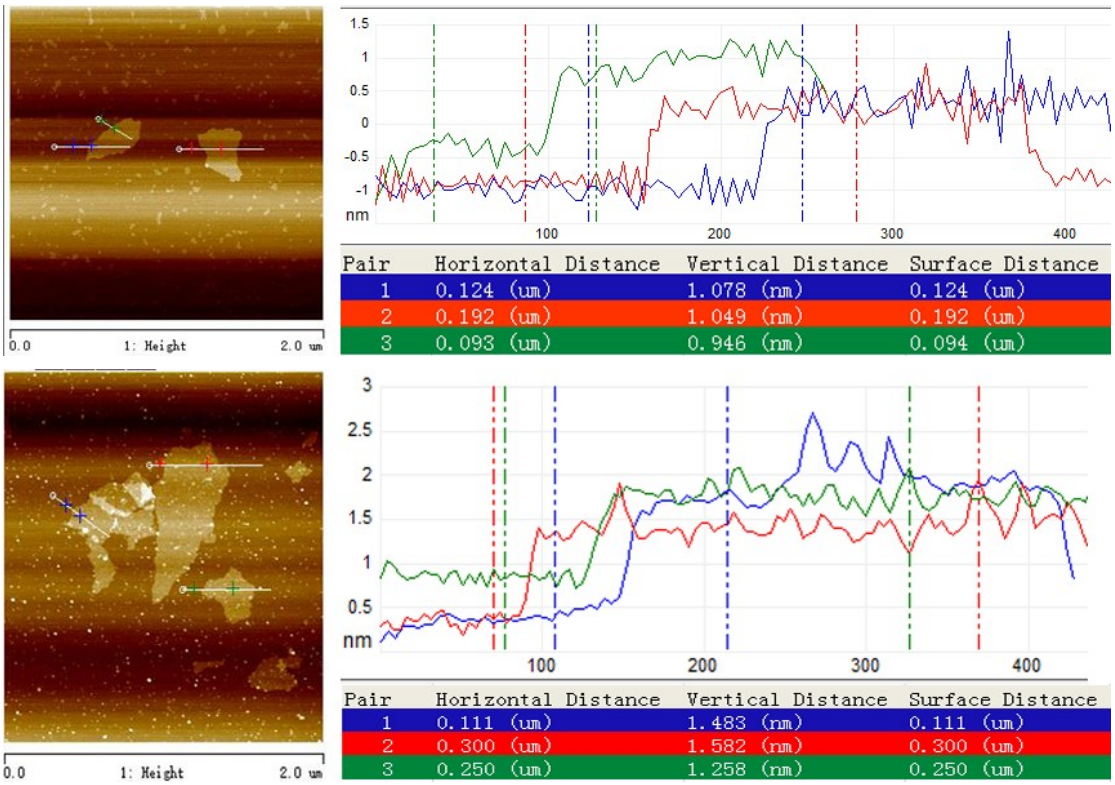

Fig. S1 The atomic force microscopic (AFM) images of GO (above) and GO-OMO hybrid (below). The average vertical distance of monolayer GO and GO-OMO were 1.02 nm and 1.44 nm, respectively.

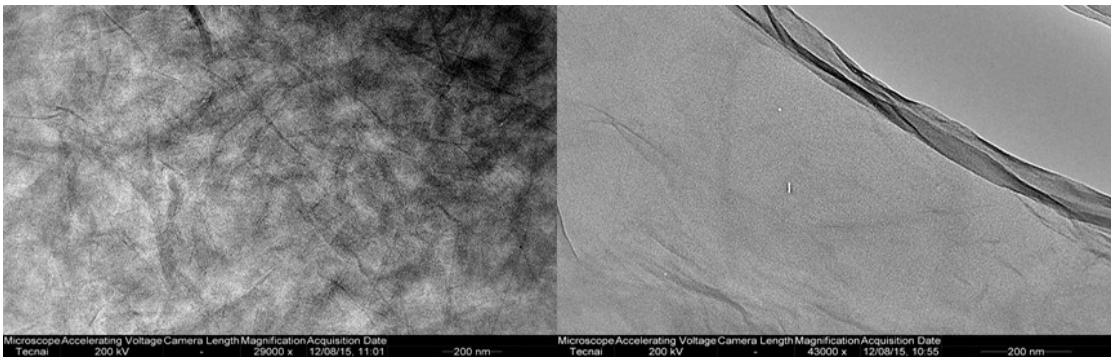

Fig. S2 TEM images of GO (left) and GO–OMO hybrid (right). The concentration of GO and OMO were 40 ug/ml and 2 uM, respectively.

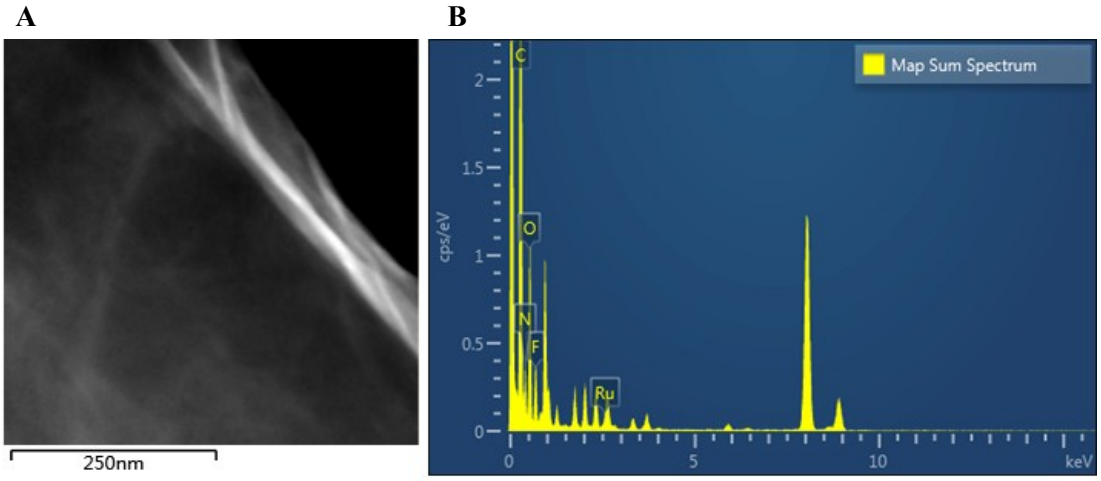

Fig. S3 Electron images of GO–OMO hybrid (A) and EDS (B).

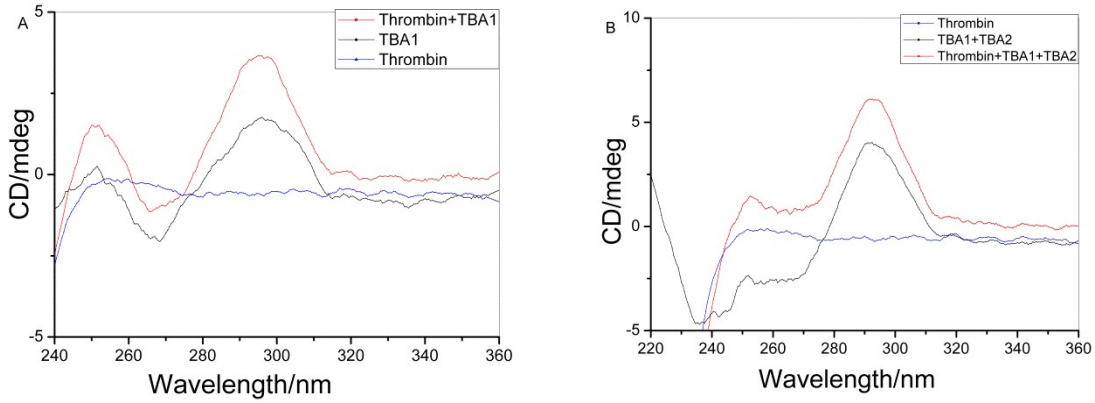

Fig. S4 CD spectra of TBA 1(2.5 μM), TBA 2 (2.5 μM) and Thrombin (63.6 nM), under different conditions in 10 mM Tris-HCl, pH = 7.0.

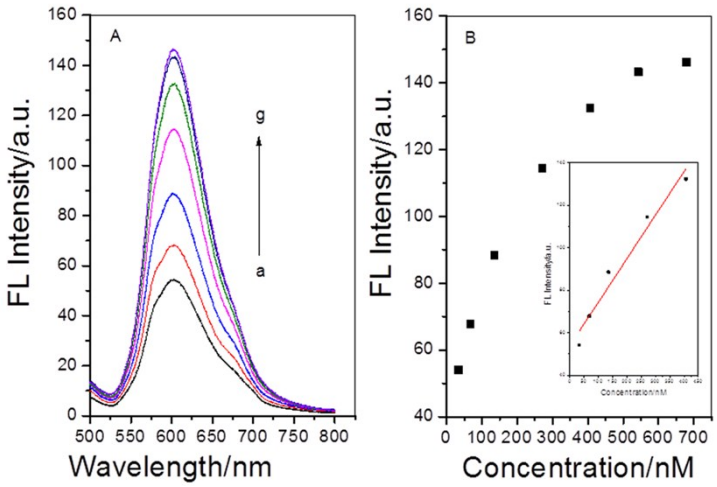

Fig. S5. The detailed information based on TBA1 to detect thrombin. (A) Fluorescence emission spectra of sensing platform in response of thrombin at 33.9, 67.8, 135.7, 271.4, 407.0, 542.7 and 678.4 nM (from a to g). (B) Calibration curve for thrombin detection.

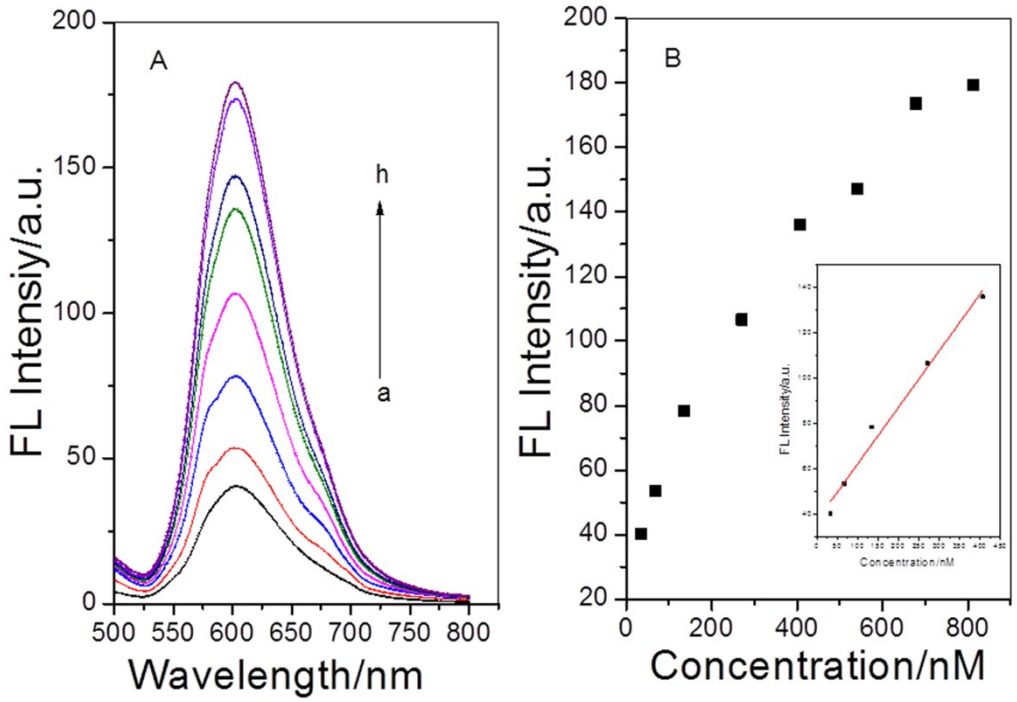

Fig. S6. The detailed information based on TBA2 to detect thrombin. (A)Fluorescence emission spectra of sensing platform in response of thrombin at 33.9, 67.8, 135.7, 271.4, 407.0, 542.7, 678.4 and 814.0 nM (from a to h). (B) Calibration curve for thrombin detection.

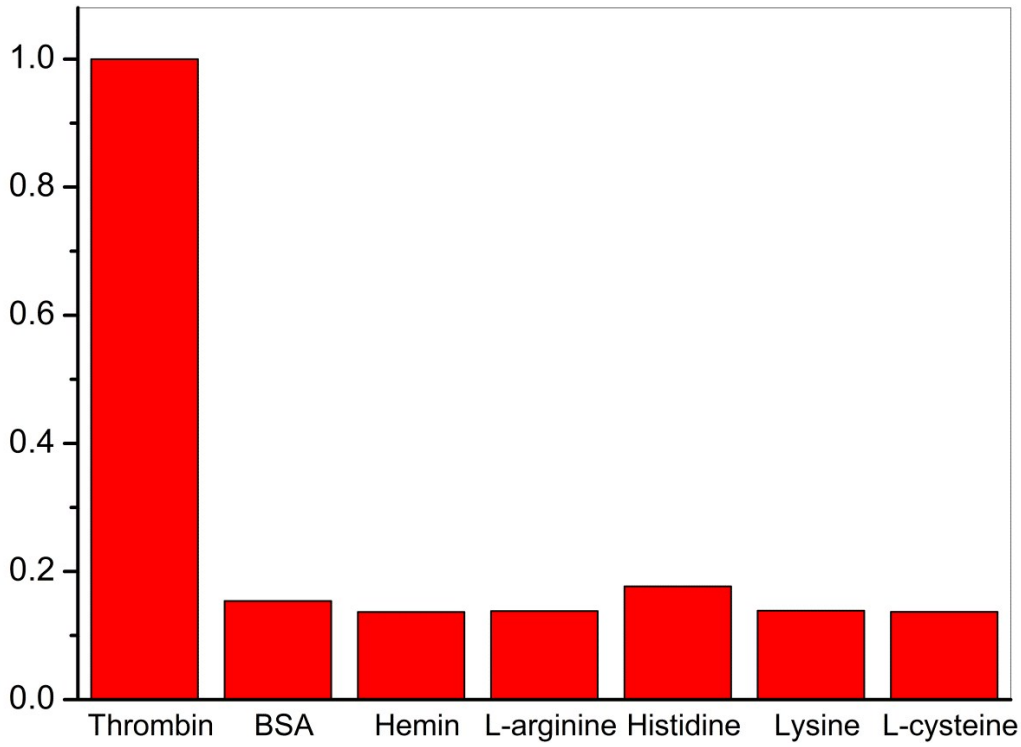

Fig. S7. The detailed information based on TBA1 to detect thrombin. Fluorescence intensity changes of the aptasensor toward thrombin and other biomoleculars under the same condition. The concentrations of thrombin, hemin, BSA , L-arginne, histidine and L-cysteine were 407 nM, respectively.

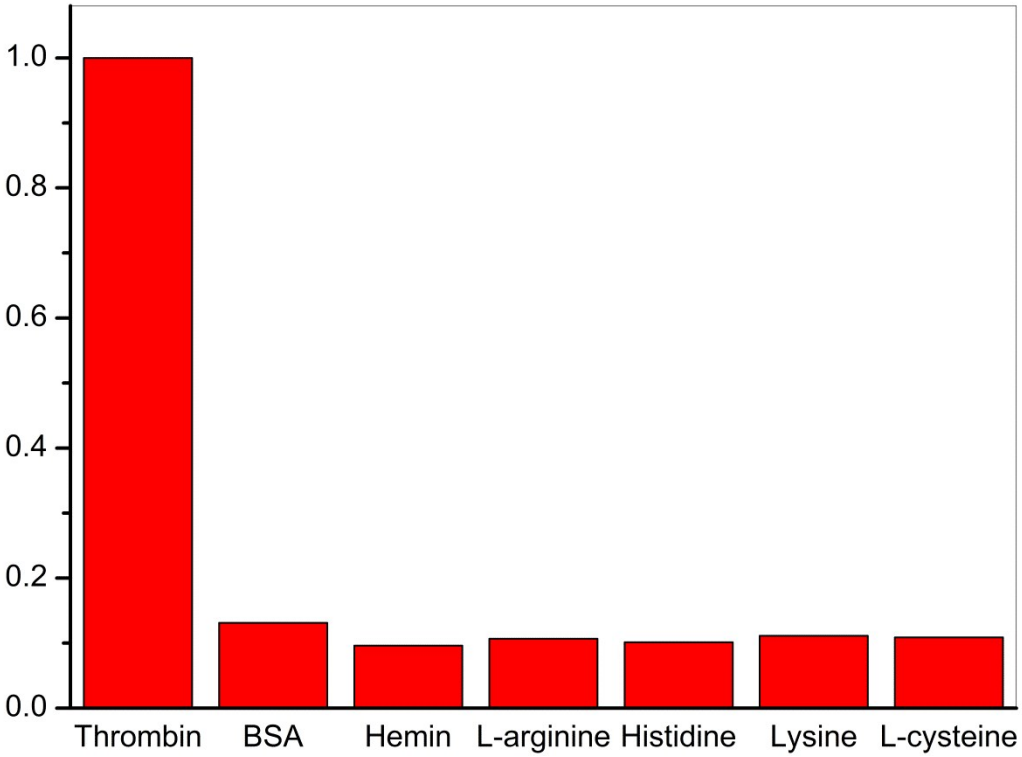

Fig. S8. The detailed information based on TBA2 to detect thrombin. Fluorescence intensity changes of the aptasensor toward thrombin and other biomoleculars under the same condition. The concentrations of thrombin, hemin, BSA, L-arginne, histidine and L-cysteine were 407 nM, respectively.

Table S1 Detection of thrombin based on TBA1 in diluted serum samples. (N=3)

Samples	Amount spiked (nM)	Amount measured(nM)	Recovery (%)	RSD (%)
1	30．8	27．9	90．6	1．5
2	246．7	291．2	118．0	0．78
3	370．0	417．2	112．7	1．25

Table S2 Detection of thrombin based on TBA2 in diluted serum samples. (N=3)

Samples	Amount spiked (nM)	Amount measured(nM)	Recovery (%)	RSD (%)
1	61．7	53．2	86．2	1．2
2	123．3	114．4	92．8	0．98
3	370．0	317．8	85．9	1．4