

## Supporting Information

for

### **Investigation of the Interaction Modes between Nonpolar Organic Pollutants with Ionizable Functional Groups and Natural Organic Matter via AuNPs-Based Colorimetric Assays**

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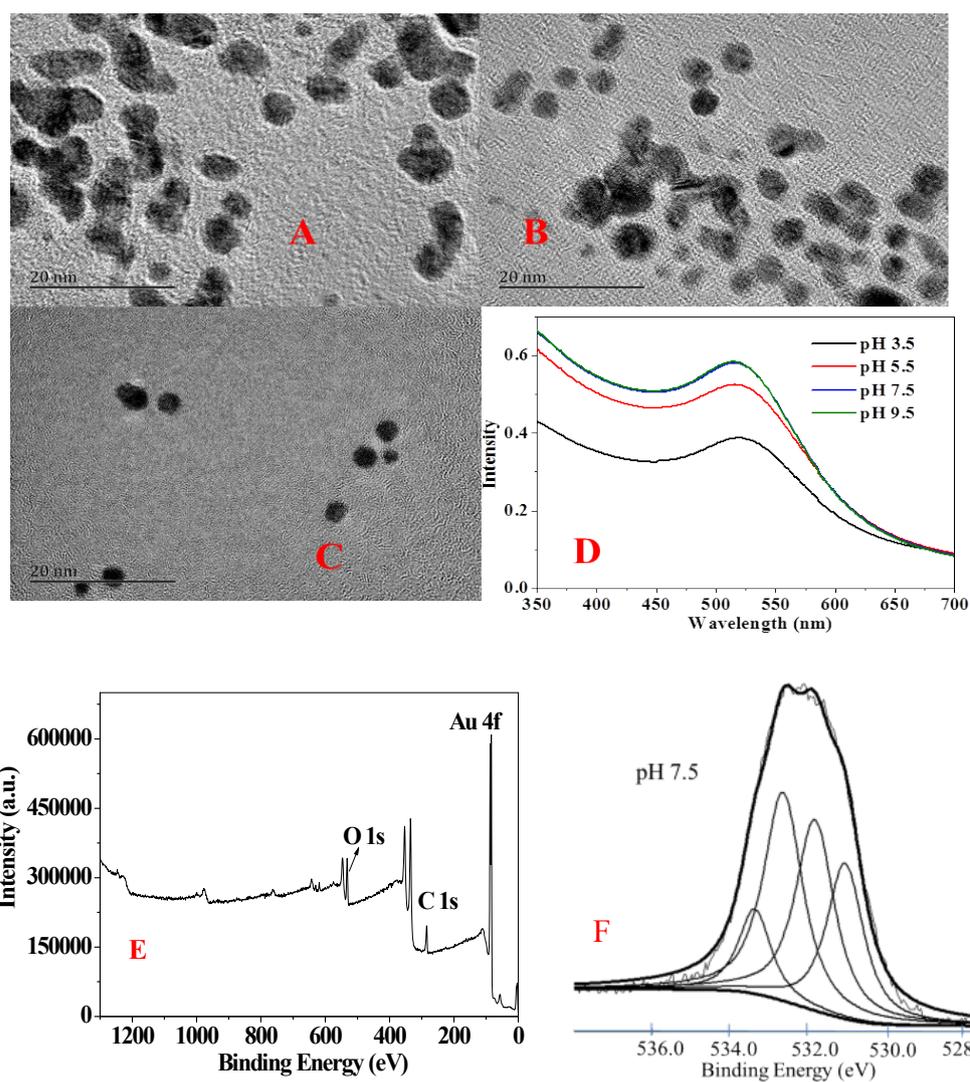
**Materials and Reagent Preparation.** Five humic substances were obtained from the International Humic Substance Society (IHSS, Colorado, U.S.A), Suwannee River humic acid (SRH), Suwannee River fulvic acid (SRF), Pahokee peat humic acid (PPH), Pahokee peat fulvic acid (PPF), and Lenoardtic humic acid (LH). Bisphenol A (BPA) was supplied by Acros Organics (Morris Plains, NJ, USA). Tetrabromobisphenol A (TBBPA), pentabromophenol (PBP), 4-bromophenol (4-BP), 2,6-dibromophenol (DBP), and 2,4,6-tribromophenol (TBP) were purchased from Sigma-Aldrich (Oakville, ON, Canada). Pentachlorophenol (PCP) and tetrachlorobisphenol A (TCBPA) were from TCI (Shanghai) Development Co. LTD (Shanghai, Beijing). Chloroauric acid tetrahydrate ( $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ ), sodium borohydride ( $\text{NaBH}_4$ ), calcium chloride, and ethanol were obtained from Sinopharm Chemical Reagent Company, Ltd. (Beijing, China). All chemicals were used as received. Ultrapure water was prepared using a Milli-Q SP reagent water system (Millipore, Bedford, MA, U.S.A.). The SRF and PPF stocks ( $1000 \text{ mg L}^{-1}$ ) were prepared from powder and dissolved in pure water. The SRH, PPH and LH stocks ( $1000 \text{ mg L}^{-1}$ ) were prepared from powder and dissolved in pure water with the addition of a few drops of 1 M NaOH to disperse aggregates. They were then shaken by hand for 1 min, and left in the dark at  $4 \text{ }^\circ\text{C}$  for at least 24 h without any further preparation. Stock solutions of each model compound ( $1000\text{-}2000 \text{ mg L}^{-1}$ ) were prepared from their powders in ethanol and stored at  $4 \text{ }^\circ\text{C}$ .

**Synthesis of HAs or FAs modified Au NPs Suspensions.** All synthesis steps were performed at ambient conditions ( $\sim 20 \text{ }^\circ\text{C}$ ). 0.6 mL of NOM solution ( $1000 \text{ mg L}^{-1}$ ) was mixed with 40 mL of 0.25 mM of  $\text{HAuCl}_4$  solution, and the final concentration of NOM in reaction solution was  $15 \text{ mg L}^{-1}$ . The mixture was allowed to stir for 0.5-1 h. After mixing, 1 mL of freshly prepared  $0.1 \text{ mol L}^{-1}$  of  $\text{NaBH}_4$  solution was added and shaken vigorously for 2–3 min. Suspensions were aged under ambient conditions for approximately 8 h and then stored in the dark at  $4 \text{ }^\circ\text{C}$ . The Au NPs were named according to the type of NOM in reaction solution (such as SRF modified AuNPs can be named as SRF-AuNPs).

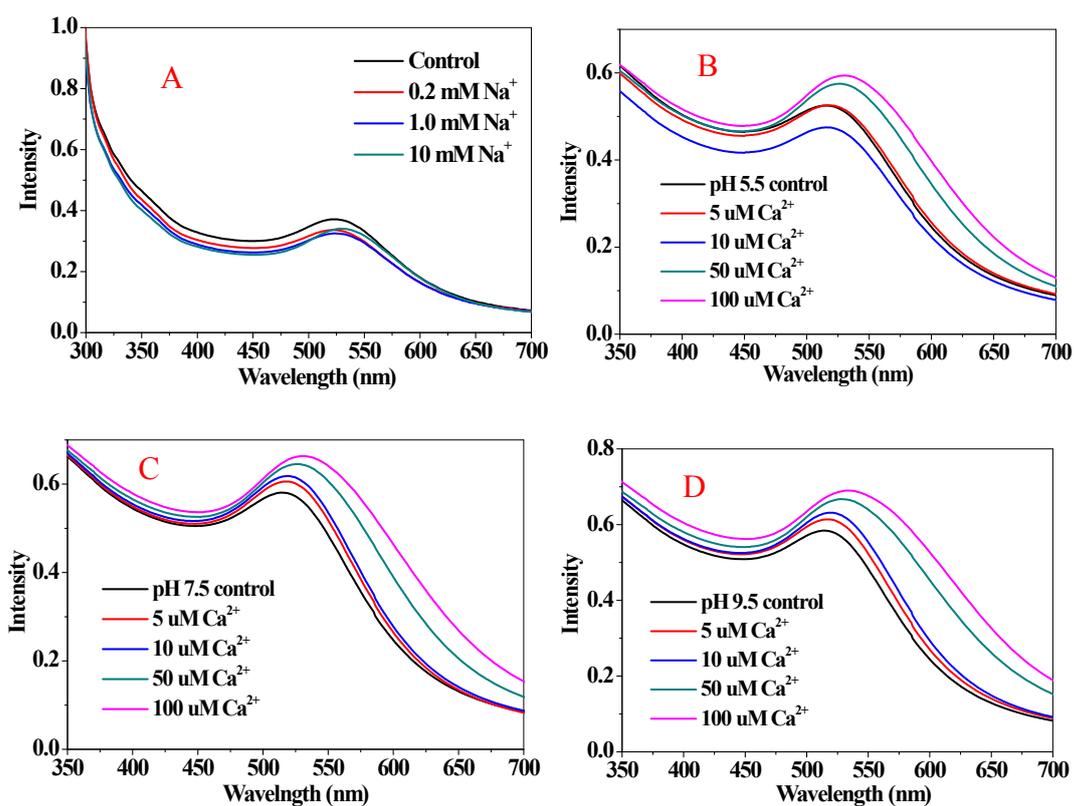
**Colorimetric Assay.** The colorimetric sensing of model compounds using the NOM

modified Au NPs probes was performed by adding 10  $\mu\text{M}$  of each target in the as-synthesized Au NPs colloids. To decrease the adsorption of hydrophobic TCBPA, TBBPA, PCP, and PBP on PP vials, 10 % of ethanol was added in reaction solutions. The residual NOM in Au NPs colloids can significantly increase the solubility of these model compounds as well. The effects of solution pH on colorimetric assays were studied by changing solution pH in the range of 3.5-9.5. The influence of cations ( $\text{Ca}^{2+}$ ,  $\text{Na}^{+}$ ) on affinity of targets to NOM was analyzed, and the concentration of  $\text{Ca}^{2+}$  and  $\text{Na}^{+}$  was 5, 10, 50 and 100  $\mu\text{M}$  and 0.2, 1.0, 10 mM respectively. Before the addition of targets, the NOM-AuNPs were incubated with monovalent or divalent cations for 2 h in advance. In all, 48 h reaction conditions were investigated. All color changes were noted and photographed. The UV-Vis spectra of suspensions were characterized by using a Varioskan Flash Spectral Scanning Multimode Reader.

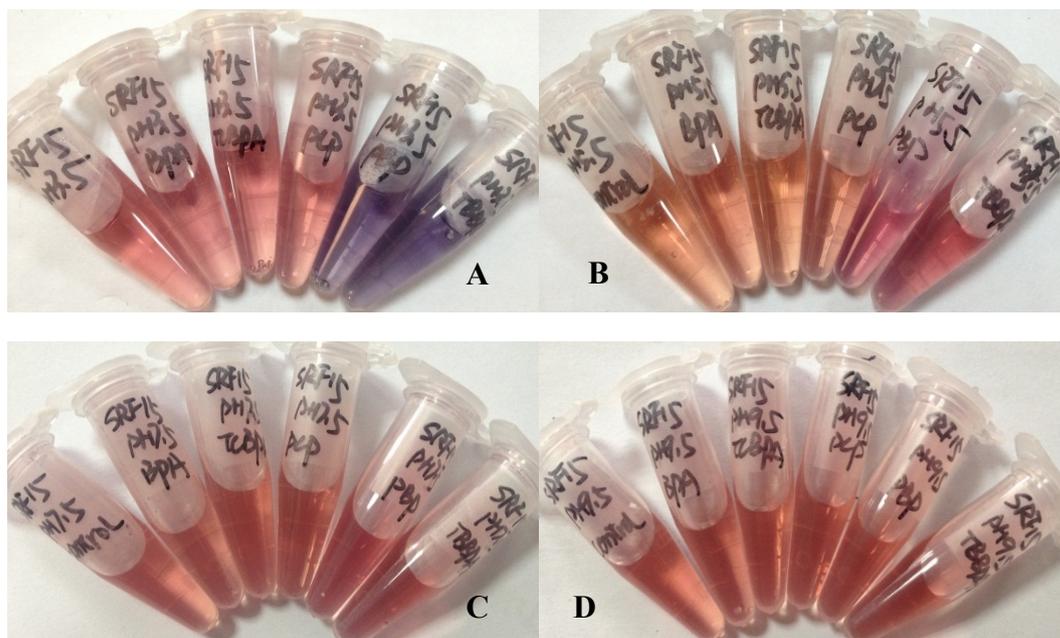
To better understand the binding mechanisms, 10  $\mu\text{M}$  of targets was added into 40 mL of SRF-AuNPs sensors solution in the presence of  $\text{Ca}^{2+}$  at pH5.5. After reaction for 48h, the aggregated sensors were collected by centrifuging sensor solution at 15000 rpm; the well-dispersed sensors were collected by removing water with a stream of  $\text{N}_2$ . The concentrated sensors were washed with deionized water three times and then dropped on the surface of silicon wafers for XPS measurements using a Thermo Scientific ESCA-Lab-200i-XL spectrometer (Waltham, MA) with monochromatic Al  $K\alpha$  radiation (1486.6 eV). The  $\zeta$ -potentials of SRF-AuNPs with and without  $\text{Ca}^{2+}$  at different pHs were measured using Zetasizer Nano series (Malvern, United Kingdom). The size and morphology of the synthesized materials were surveyed using a JEOL JEM-2010 high-resolution transmission electron microscope (HRTEM, Kyoto, Japan), and a Hitachi H-7500 transmission electron microscope (TEM, Tokyo, Japan).



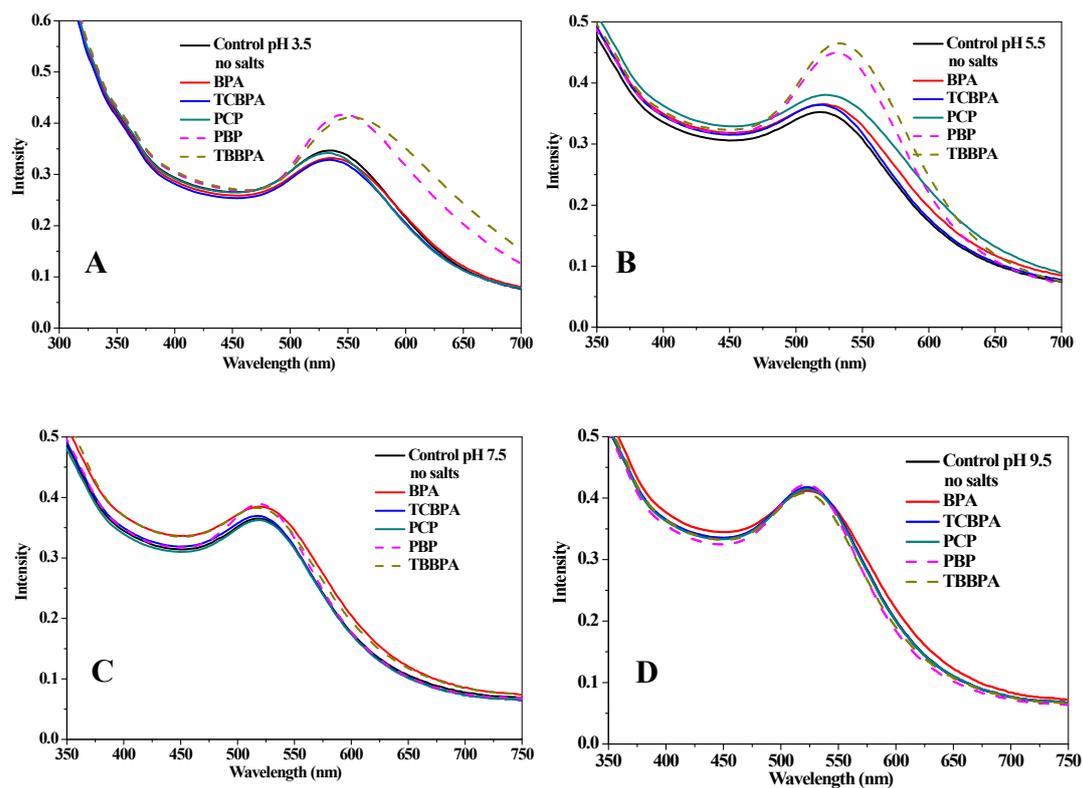
**Fig. S1** TEM images of the as-prepared SRF-AuNPs at pH 3.5 (A), pH 5.5 (B) and pH 9.5 (C), the UV-Vis spectra of sensors suspension at different solution pHs (D), XPS survey spectra of SRF-AuNPs (E), and fitted XPS O 1s spectra of SRF-AuNPs pH7.5 (F).



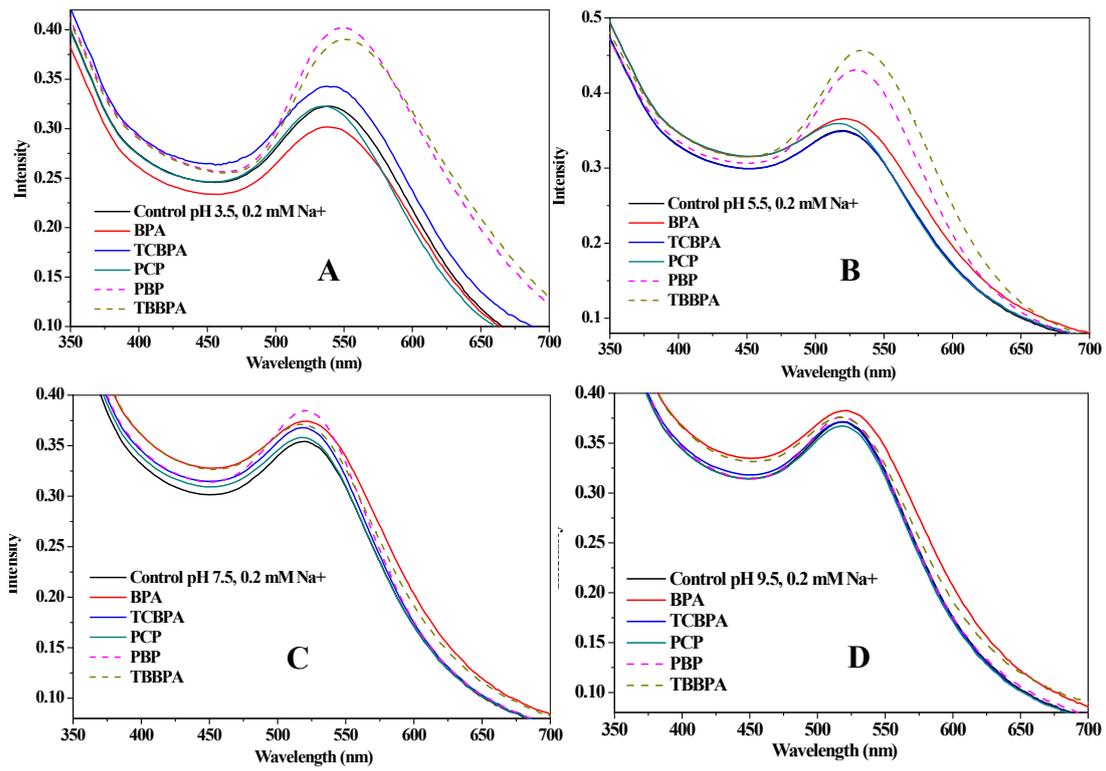
**Fig. S2** UV-Vis spectra of SRF-AuNPs sensors suspension in the presence of different concentration of  $\text{Na}^+$  at pH 7.5 (A), and  $\text{Ca}^{2+}$  cations at pH 5.5 (B), 7.5 (C) and 9.5 (D).



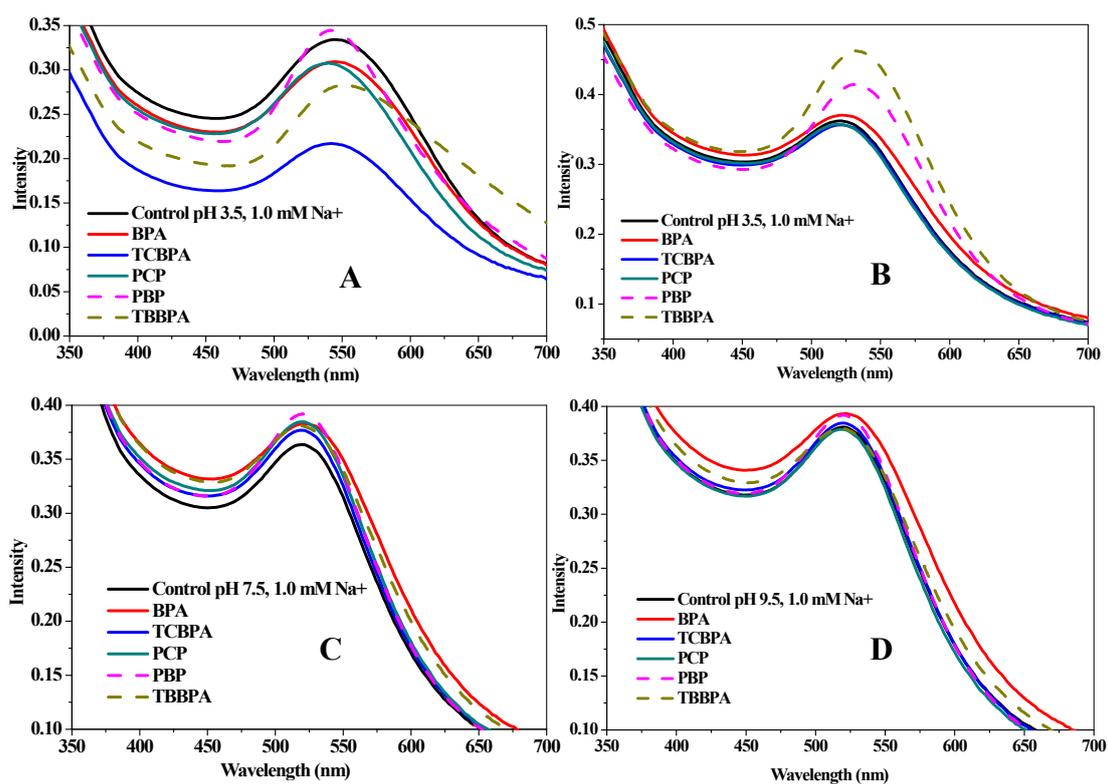
**Fig. S3** Photographs of SRF-AuNPs suspension in the presence of 10  $\mu\text{M}$  of each target at (A) pH 3.5, (B) pH 5.5, (C) pH 7.5, and (D) pH 9.5 without the addition of cations. From left to right: Control, BPA, TCBPA, PCP, PBP, and TBBPA.



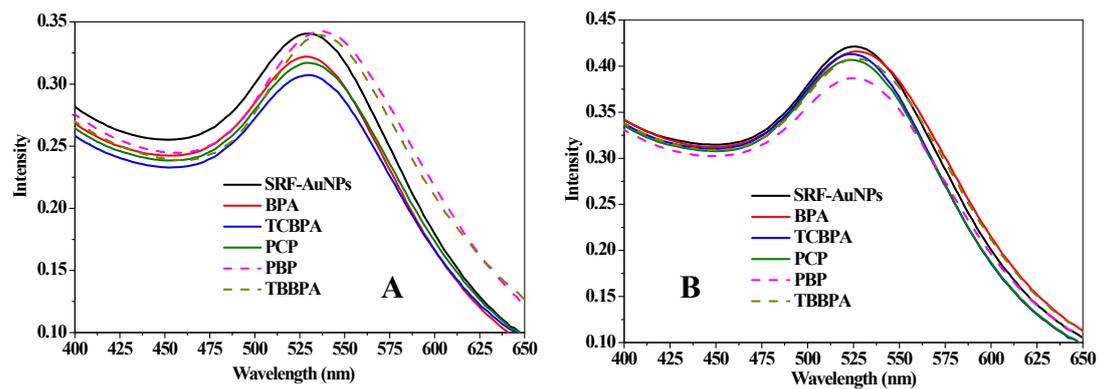
**Fig. S4** UV-Vis spectra of the SRF-AuNPs suspension in response to different targets without the addition of cations at pH 3.5 (A), pH 5.5 (B), pH 7.5 (C), and pH 9.5 (D), concentration of target 10  $\mu$ M.



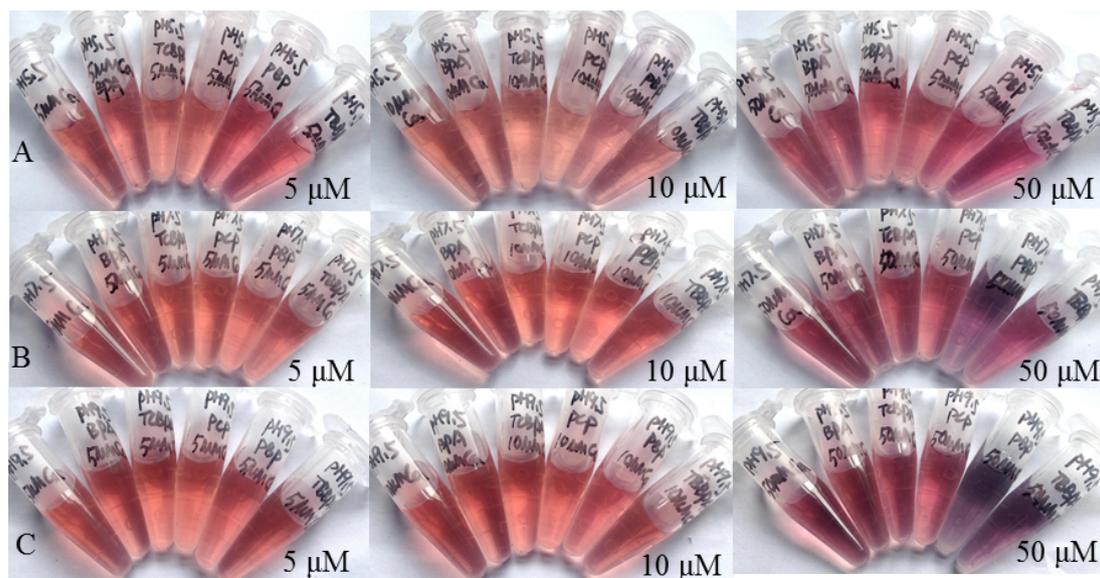
**Fig. S5** UV-Vis spectra of the SRF-AuNPs suspension in response to different targets with 0.2 mM of Na<sup>+</sup> at pH 3.5 (A), pH 5.5 (B), pH 7.5 (C), and pH 9.5 (D), concentration of target 10  $\mu$ M.



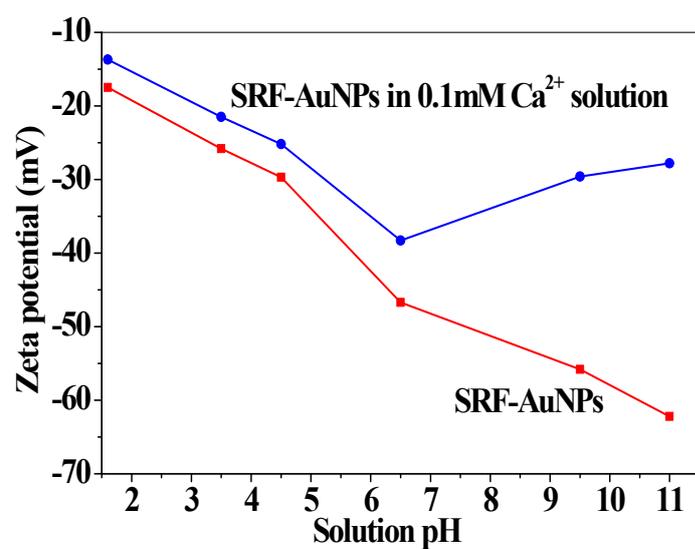
**Fig. S6** UV-Vis spectra of the SRF-AuNPs suspension in response to different targets with 1.0 mM of Na<sup>+</sup> at pH 3.5 (A), pH 5.5 (B), pH 7.5 (C), and pH 9.5 (D), concentration of target 10 μM.



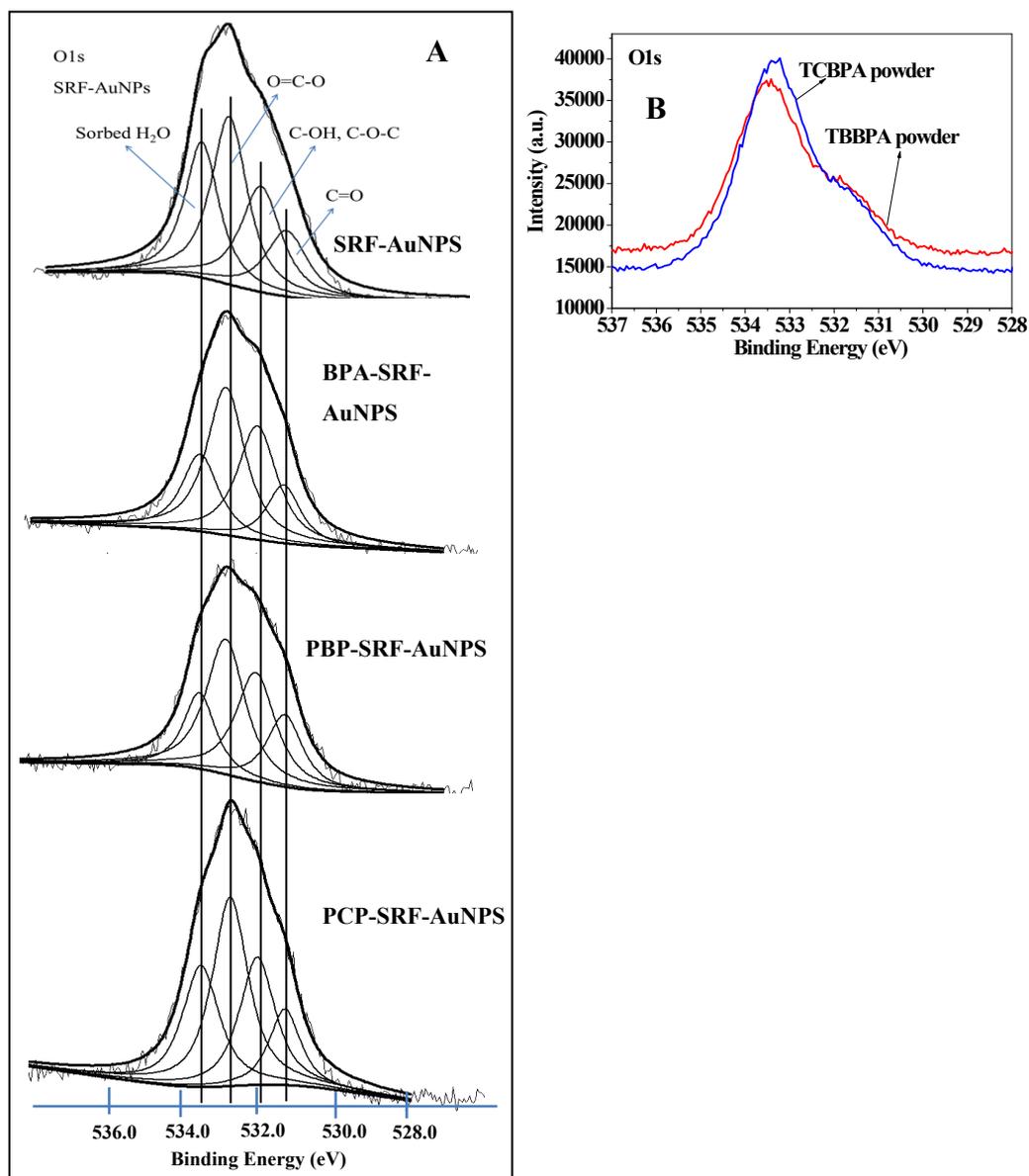
**Fig. S7** UV-Vis spectra of the SRF-AuNPs suspension in response to different targets with 10 mM of  $\text{Na}^+$  at pH 5.5 (A) and pH 9.5 (B), concentration of target 10  $\mu\text{M}$ .



**Fig. S8** Photograph of SRF-AuNPs suspension in the presence of targets with 5, 10, and 50  $\mu\text{M}$   $\text{Ca}^{2+}$  at pH 5.5 (A), pH 7.5 (B), and pH 9.5 (C), from left to right: Control, BPA, TCBPA, PCP, PBP, and TBBPA, Concentration of targets: 10  $\mu\text{M}$ .

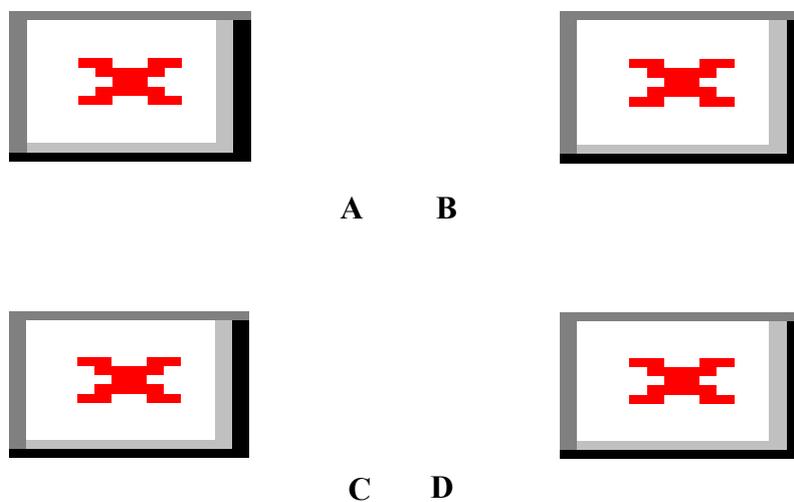


**Fig. S9**  $\zeta$ -potential of SRF-AuNPs at different solution pHs with and without the addition of 0.1 mM Ca<sup>2+</sup>.

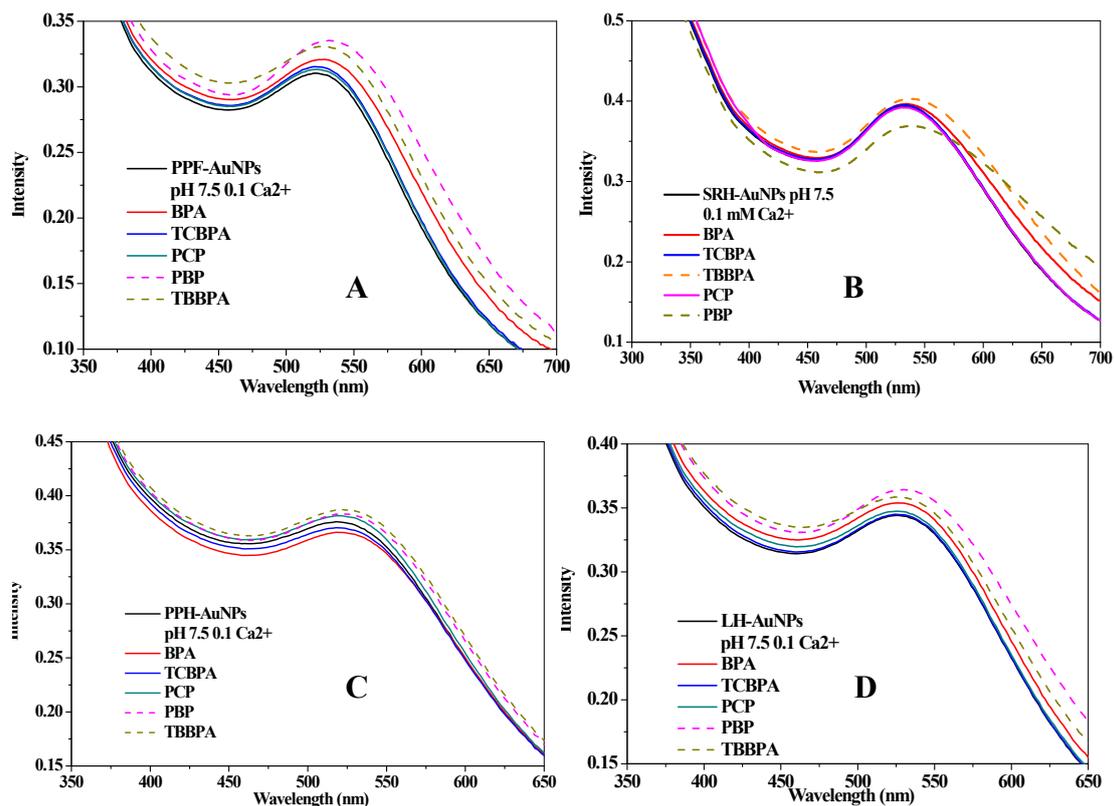


**Fig. S10** Fitted XPS O 1s spectra of the as-prepared SRF-AuNPs sensors and sensors after reaction with BPA, PBP, and PCP at pH 5.5 (A), and O 1s spectra of TCBPA and TBBPA powder (B). Concentration of targets and Ca<sup>2+</sup>: 10  $\mu$ M and 0.1 mM, respectively. For the halogenated phenols sorbed sensors, the BEs of C-OH species ( $\sim$ 531.9 eV) exhibit slight upshift, probably resulting from the higher binding energies of phenolic groups in halogenated phenols ( $\sim$ 533.5 eV). The sorption of BPA yields a small shift of O=C-O component to stronger BE, which suggests that the carboxylic groups have been occupied by a newly formed hydrogen bond.<sup>1</sup> In this case, the carboxylic groups of NOM and phenolic groups of BPA serve as electron donors and electron acceptor, respectively.

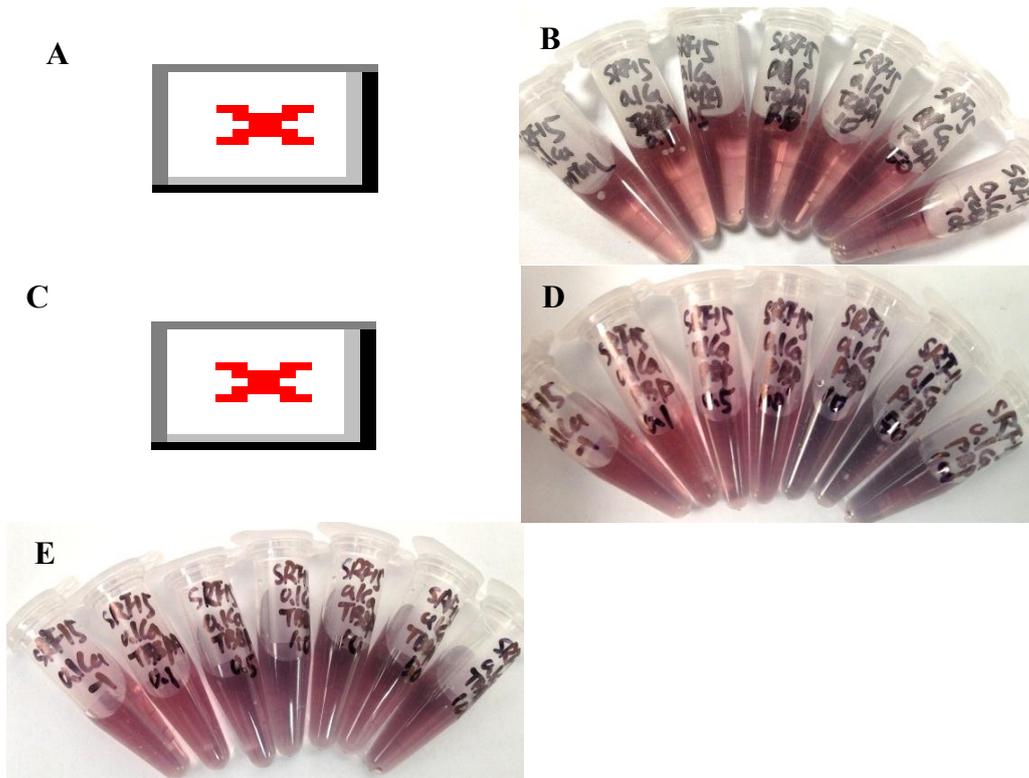
(1) Bisti, F.; Stroppa, A.; Perrozzi, F.; Donarelli, M.; Picozzi, S.; Coreno, M. *J. Chem. Phys.* **2013**, *138*(1), 014308.



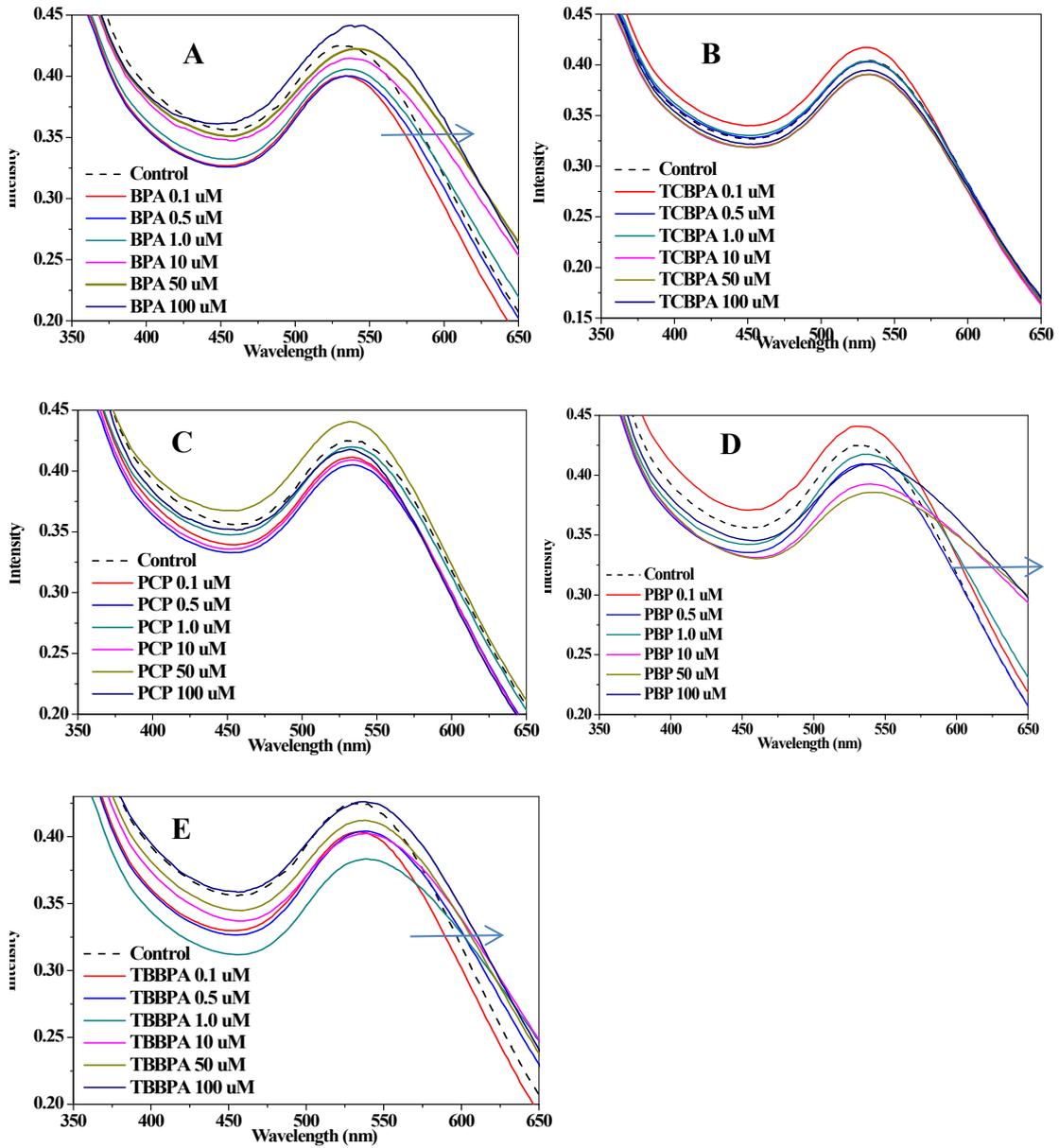
**Fig. S11** Photographs of different types of NOM modified AuNPs suspension in the presence of 10  $\mu\text{M}$  of each target, pH=7.5, 0.1 mM  $\text{Ca}^{2+}$ , (A) PPF-AuNPs, (B) SRH-AuNPs, (C) PPH-AuNPs, and (D) LH-AuNPs; from left to right: control, BPA, TCBPA, PCP, PBP, and TBBPA.



**Fig. S12** UV-Vis spectra of different types of NOM modified AuNPs suspension in the presence of 10  $\mu\text{M}$  of each target, pH=7.5, 0.1 mM  $\text{Ca}^{2+}$ , (A) PPF-AuNPs, (B) SRH-AuNPs, (C) PPH-AuNPs, and (D) LH-AuNPs.



**Fig. S13** Photographs of SRF-AuNPs suspension in the presence of different concentration of BPA (A), TCBPA (B), PCP (C), PBP (D), and TBBPA (E) in the presence 0.1 mM of  $\text{Ca}^{2+}$  at pH 7.5. The concentration of target from left to right: 0, 0.1, 0.5, 1.0, 10, 50, and 100  $\mu\text{M}$ .



**Fig. S14** UV-Vis spectra of the SRF-AuNPs suspension in the presence of different concentration of BPA (A), TCPBP (B), PCP (C), PBP (D), TBBPA (E) in the presence 0.1 mM of  $\text{Ca}^{2+}$  at pH 7.5. The direction of arrow represents red-shift of SPR peaks of suspension.