Supporting Information Available

Label-free non-invasive fluorescent pattern discrimination of thiols and chiral recognition of cysteine enantiomers in biofluids using bioinspired copolymers-Cu²⁺ hybrid sensor array regulated by pH

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Figure S1. Fluorescence response of PDA/PEI₄₈ in acetate acid, phosphoric acid and citric acid at pH=4.



Figure S2. The optimization of concentration for Cu^{2+} in the system of PDA/PEI₄₈- Cu^{2+} -GSH in acetate buffer (pH=4).



Figure S3. The optimization of reaction time between PDA/PEI₄₈-Cu²⁺ and GSH in acetate buffer (pH=4).



Figure S4. (a) Pattern responses to the mixtures comprising of GSH and L-Cys in aqueous solution. (b) Heat map derived from the fluorescence intensity of PDA/PEI₄₈-Cu²⁺ sensors towards different mixtures of GSH and L-Cys. (c) Canonical score plots for the fluorescence response patterns obtained with PDA/PEI₄₈-Cu²⁺ sensors different mixtures of GSH and L-Cys. (d) Plot of PC1 vs the mixtures of GSH and L-Cys with different molar ratios indicated.



Figure S5. Pattern responses of PDA/PEI₄₈- Cu^{2+} sensors towards amino acids and metal ions.

| а | | | | _ | b | 0.6 | | | | |
|--------------|--|--------|--------|-------------------------|----------------|---|---------------|-------|------|--------|
| PC2 (0.612%) | 0.4- 0.2- 0.0- -0.2- (GSH, μM) | | | | PC2 (17.083%) | $ \begin{array}{c} 0.0 \\ 0.4 \\ 5:35 \\ 0.2 \\ 0.2 \\ 0.0 \\ -2 \\ \hline (\mu M) \\ 0:40 \\ \hline (\mu M)$ | | | | |
| | -2 | | | -2 0 2 PC1 (82 540%) | | | | | | |
| | | | | | | | | | | , |
| | | GSI | Н / µМ | | | | | | | |
| | | | Entry | Actual | DNTB method | | Our method | | | |
| | | | Α | 5 | 4.8 | | 0-10 | | | |
| | В | | | 15 14 | | .91 | 10-20 | | | |
| | | | с | 25 | | 5.42 2 | | 0-30 | | |
| d | GSH / μM | | | | | L-Cy | | | s/μM | |
| | Entry | Actual | DNTB | 0 | Dur | Ac | tual | DN | ITB | Our |
| | | | method | me | thod | | me | | hod | method |
| | D | 10 | 10.43 | 5 | -15 | 30 | | 30.89 | | 25-35 |
| | E | 20 | 19.28 | 15 | 5-25 | 20 | | 19 | .12 | 15-25 |
| | F | 30 | 29.86 | 9.86 2 | | 10 | | 9.65 | | 5-15 |

Figure S6. (a) Pattern response to the different spiked concentrations of GSH in saliva samples. (b) Pattern response to the mixtures comprising of GSH and L-Cys in saliva samples. Tables show the analytical performances of PDA/PEI₄₈-Cu²⁺ sensors toward (c) various concentrations of GSH and (d) mixtures of GSH and L-Cys compared with that to DTNB methods.



Figure S7. (a) (c) UV spectra of the DTNB method toward the detection of GSH and L-Cys; (b) (d) Plots of absorbance at 412 nm toward increasing concentration of GSH and L-Cys.