Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

Potential Responses to Neutral Thiophenols of Polymeric Membrane Electrodes and Their Applications in Potentiometric Biosensing

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Reagents and Materials. Tridodecylmethylammonium chloride ($TDMA^+Cl^-$), tetrabutyl ammonium chloride ($TBuA^+Cl^-$), tetradodecylammonium tetrakis(4-chlorophenyl)borate ($TDMA^+TCPB^-$), *o*-nitrophenyl octylether (*o*-NPOE) and poly(vinyl chloride) (PVC) were purchased from Sigma-Aldrich. p-nitrothiophenol, p-fluorothiophenol, p-chlorothiophenol, p-toluenethiol, p-aminothiophenol, p-methoxthiophenol and horseradish peroxidase (HRP) were obtained from J&K Scientific Ltd.. Hydrogen peroxide was purchased from Sinopharm Group Co. Ltd. Other reagents were obtained from Aladdin Industrial Inc. Tridodecylmethylammonium thiocyanate ($TDMA^+SCN^-$) was prepared by metathesis.[1] A solution of tridodecylmethylammonium chloride in benzene (1 mM, 10 mL) was mixed vigorously with an aqueous solution of sodium thiocyanate (100 mM, 10 mL). The organic phase was then washed several times with water. After evaporation of the solvent, the solid product was obtained.

Electrode Preparation and Electromotive Force Measurements. The inner filling medium of the electrode was 10 mM NaCl. All electrodes (except for the $TDMA^+SCN^-$ doped membrane) were conditioned in 10 mM NaCl overnight before use. All electromotive force (EMF) values were measured using a CHI 760D electrochemical workstation (Shanghai Chenhua Apparatus Corporation, China) in the following galvanic cell in a Faraday cage: Ag, AgCl/3 M KCl/1 M LiOAc/sample solution (well-stirred, 1500 rpm)/sensing membrane/10 mM NaCl/AgCl, Ag.

UV Titration Experiments. To determine the association constants of the complexes of TDMA$^+$Cl$^-$ and ArSHs, different equivalents of TDMA$^+$Cl$^-$ were added into 1 mM ArSH solutions in $CHCl_3$.The relationship between the absorbance and the concentration of TDMA$^+$Cl$^-$ was nonlinear least-curve fitted to a 1:1 model using Matlab 7.1.[2]

Liquid-liquid Extraction. 10 mL $CHCl_3$ with or without 10 mM TDMA$^+$Cl$^-$ was added to 10 mL aqueous solution (pH=4.0) with or without p-chlorothiophenol (1 mM). The mixture was vigorously shaken with a vortex shaker for 5 min. After phase separation, the $CHCl_3$ phase was interrogated by UV spectroscopy, while the aqueous phase was interrogated by a PXSJ-216 Leici pH meter (Shanghai, China) and a Cl$^-$ selective electrode (PCL-1-01, Shanghai, China) to measure the pH and Cl$^-$ concentration, respectively.

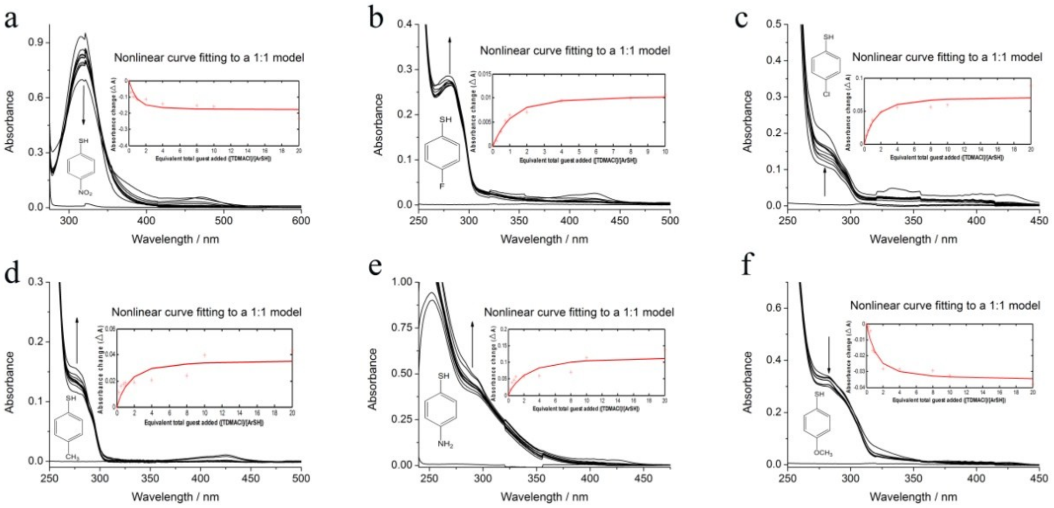


Fig. S1 UV titration of ArSHs at the concentration of 10^{-3} M with different equivalents of TDMA$^+$Cl$^-$ in chloroform. Insets: the absorbance changes of ArSHs at different wavelengths (the absorbance of TDMA$^+$Cl$^-$ has been subtracted) were nonlinear fitted to a 1:1 model using Matlab 7.1.[2] The calculated Ka values can be found in Table 1.

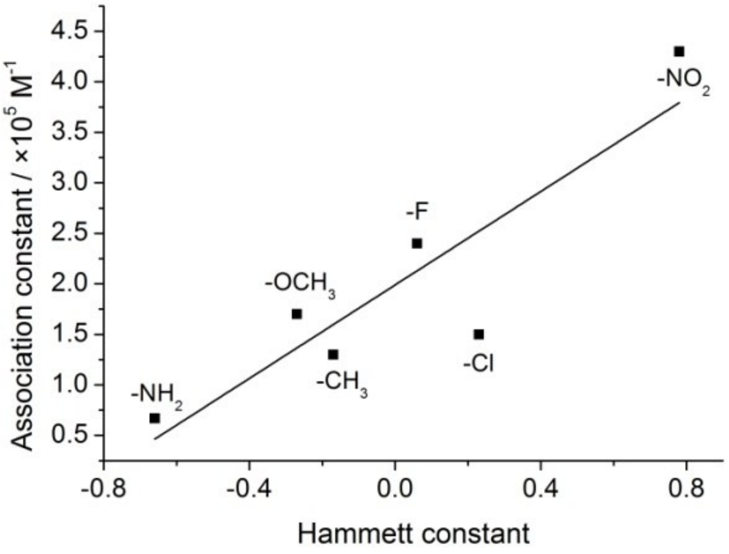


Fig. S2 Experimental association constants of the 1:1 complexes between thiophenols and TDMA$^+$Cl$^-$ correlated with the Hammett constants values for the substituents.

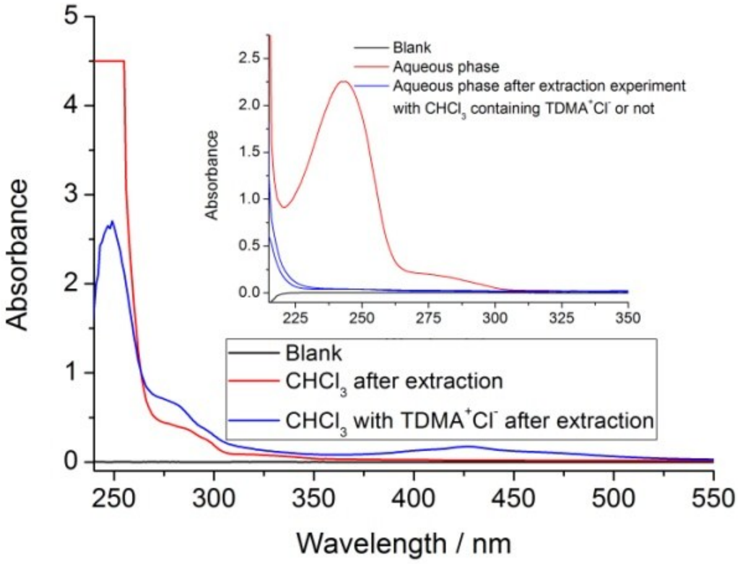


Fig. S3 UV spectra of CHCl$_3$ with and without TDMA$^+$Cl$^-$ (10 mM) after extraction of *p*-chlorothiophenol from an aqueous solution (5 mM, pH 4.0). Inset: absorbance change of aqueous phase before and after extraction experiment.

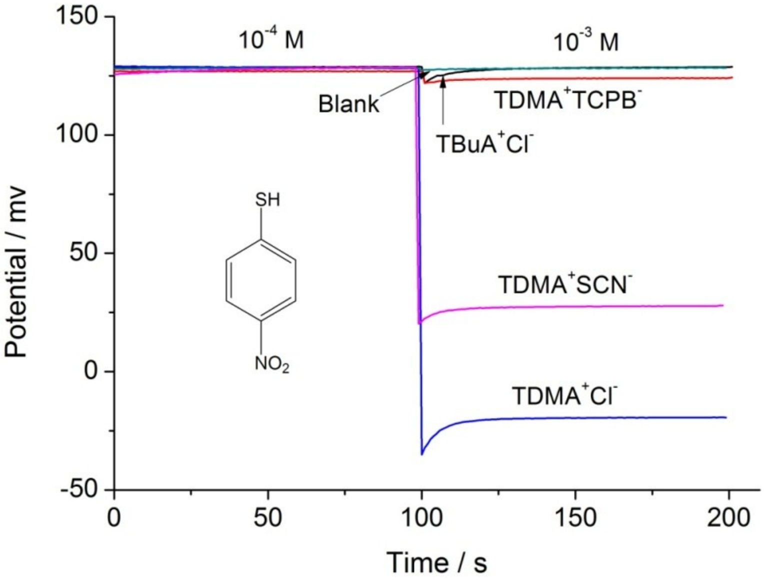


Fig. S4 Potential responses to p-nitrothiophenol in acetate buffer (pH=4.0) of an o-NPOE-PVC blank membrane and o-NPOE-PVC membranes doped with different receptors.

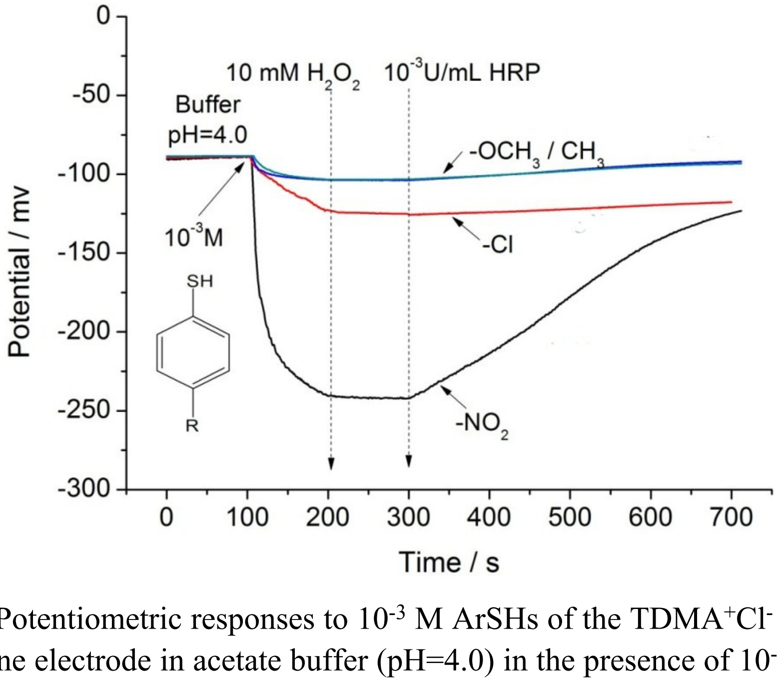
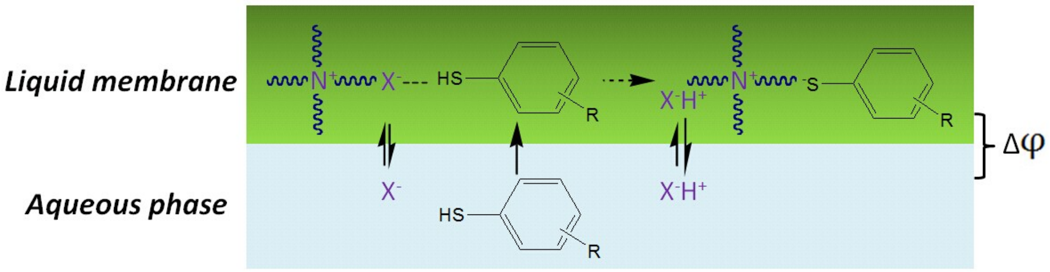


Fig. S5 Potentiometric responses to 10^{-3} M ArSHs of the TDMA$^+$Cl$^-$ doped polymeric membrane electrode in acetate buffer (pH=4.0) in the presence of 10^{-3} U/mL HRP and 10 mM H_2O_2.



Scheme S1 Response mechanism for ArSHs on a polymeric membrane

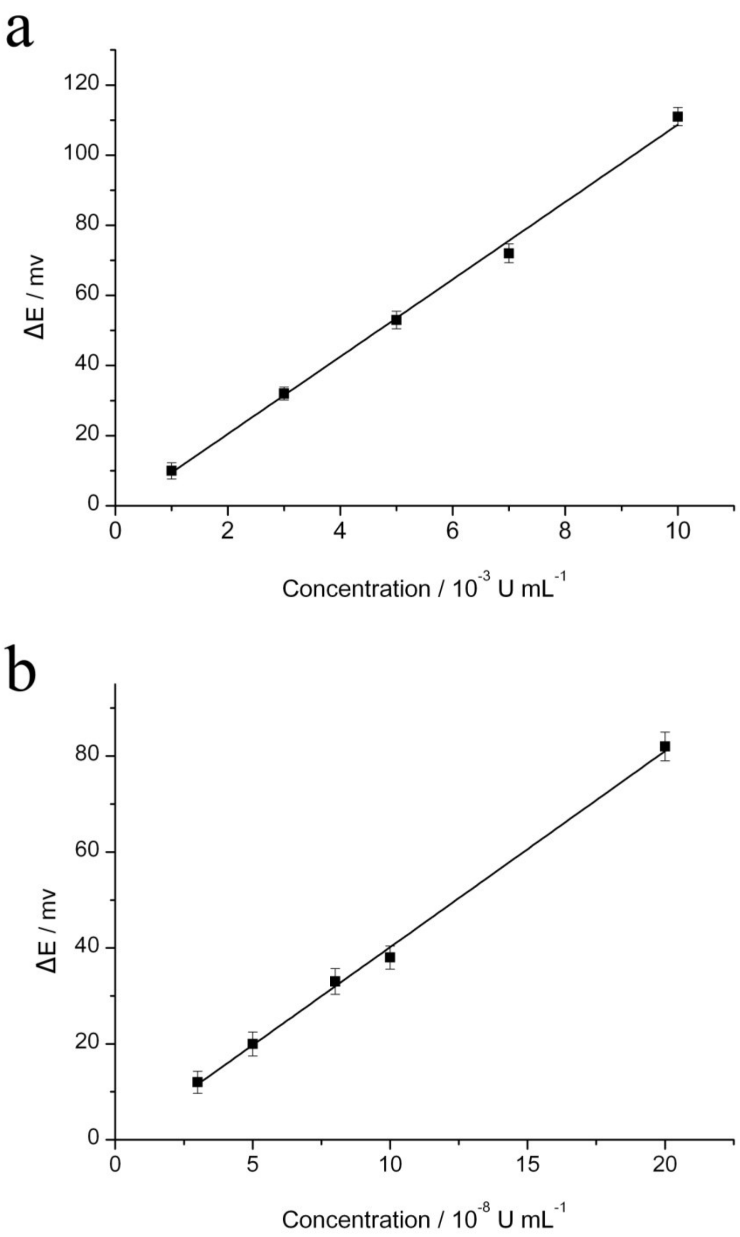


Fig. S6 Calibration curves for HRP detection in the absence (a) and presence (b) of H_2O_2.

Table S1 *p*-Chlorothiophenol extractions between the $CHCl_3$ and aqueous phases.

Organic phase	*p*-Chlorothiophenol in aqueous phase （M）	pH of aqueous phase[a]	Chloride in aqueous phase (M)[b]
Chloroform+10 mM $TDMA^+Cl^-$	1×10^{-3}	3.5	2×10^{-4}
Chloroform	1×10^{-3}	4.0	/
Chloroform+10 mM $TDMA^+Cl^-$	0	4.0	6×10^{-6}

[a] The initial pH of the aqueous phase was 4.0 prepared by sulfonic acid.

[b] The chloride concentrations in the aqueous solution were detected by a Cl^--selective electrode.

References

1 T. Ito, H. Radecka, K. Tohda, K. Odashima and Y. Umezawa, *J. Am. Chem. Soc.,* 1998, **120**, 3049-3059.
2 P. Thordarson, *Chem. Soc. Rev.,* 2011, **40**, 1305-1323.