

Supporting Information for

Potentiometric Sensing of Aqueous Phosphate by Competition Assays Using Ion-Exchanger Doped-Polymeric Membrane Electrodes as Transducers

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Reagents and Materials. Tridodecylmethylammonium chloride (TDMA⁺Cl⁻), tetrabutyl ammonium chloride (TBuA⁺Cl⁻), tetradodecylammonium chloride (TDDA⁺Cl⁻), *o*-nitrophenyl octylether (*o*-NPOE), di-*n*-octyl phthalate (DOP), bis(*o*-ethylhexyl) sebacate (DOS) and poly(vinyl chloride) (PVC) were purchased from Sigma-Aldrich. Catechol, 4-bromine catechol, 4-*tert*-butyl catechol, *o*-mercaptophenol, benzenedithiol, 3-methyl benzenedithiol and horseradish peroxidase (HRP) were obtained from J&K Scientific Ltd. Hydrogen peroxide was purchased from Sinopharm Group Co. Ltd. All other reagents were obtained from Aladdin Industrial Inc.

Electrode Preparation and Electromotive Force Measurements. Polymeric liquid membranes containing PVC, different kinds of plasticizers (1:1) and 1% (weight percentage) the receptor salt were prepared by the solvent-casting technique with tetrahydrofuran as the casting solvent. After transferring the cocktail into a glass ring fixed on a glass plate and letting tetrahydrofuran evaporate overnight, a uniform membrane of 200 μm thickness was obtained. Disks of 5-mm diameter were punched

from the parent membrane and glued to plasticized PVC tubes (i.d. 3 mm, o.d. 5 mm) to fabricate the polymeric membrane electrodes. The inner filling medium of the electrode was 20 mM HEPES buffer (pH=7.0) contacting 10 mM NaCl. All electrodes were conditioned in 20 mM HEPES buffer (pH=7.0) containing 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/20 mM HEPES, 10 mM NaCl/AgCl, Ag.

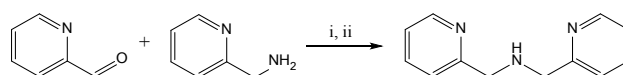
Real Sample Detection Mineral waters were purchased from local supermarket, human urine sample were from healthy volunteers, and saliva samples were obtained after cleaning the mouth with water. After diluting the samples with 20 mM HEPES buffer (with dilution factors of 2, 1000 and 500 for mineral waters, human urine and saliva, respectively), the concentrations of phosphate in these samples were determined using the proposed sensor.

Synthesis of bis(2-pyridylmethyl)amine¹ 4.75 mL pyridine-2-carboxaldehyde was dissolved in 40 mL of ethanol. 5.15 mL 2-pyridylmethylamine was added dropwise while stirring followed by 2.2 g (60 mmol) sodium tetrahydridoborate in small portions. The stirring was continued for 2.5 hours at room temperature. Then the filtered, ice-cooled solution was acidified (pH=4) with hydrochloric acid (6 M). To the ice-cooled filtrate was added hydrochloric acid (6 M) to strong acid reaction, ethanol and ether. The solid was filtered and washed with ethanol. The crude product was dissolved in hydrochloric acid and reprecipitated with ethanol. 2.3 g products were observed with yield 70%.

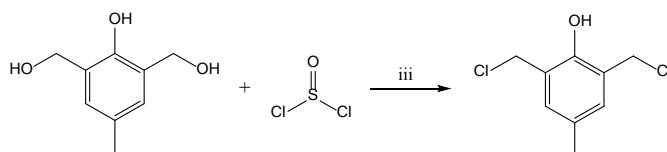
Synthesis of 2,6-bis(chloromethyl)-4-methylphenol² 2,6 -Bis(hydroxymethyl)-4-methylphenol (5.0 g, 30 mmol) in 5 mL of methylene chloride was added to a solution of 14 g (120 mmol) of thionyl chloride in 50 mL of methylene chloride. After stirring for 24 h, the mixture was poured over 50 mL of ice and made neutral (pH 7) with aqueous NaOH. The aqueous solution was extracted with three 50-mL portions of methylene chloride, washed with brine, and dried over anhydrous Na₂SO₄. The dried solution was evaporated to dryness at reduced pressure, and 5.0 g (81%) of the product was obtained as a pale-yellow solid, which was used without further purification.

Synthesis of H-BPMP³ Under a dinitrogen atmosphere, a mixture of bis(2-pyridylmethyl)amine (2.90 g, 14.6 mmol) and triethylamine (3.03 g, 30 mmol) in 7 mL of dry THF was added dropwise to a stirred solution of 2,6-bis(chloromethyl)-4-methylphenol (1.5 g, 7.31 mmol) in 15 mL of dry THF at 0 °C. When the addition was completed, the resulting mixture was allowed to warm to room temperature. After 3 days, the resulting mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was dissolved in 100 mL of methylene chloride,

washed with brine, and dried over anhydrous Na_2SO_4 . The solution was evaporated to dryness at reduced pressure, and a crude product was obtained as a sticky solid. Recrystallization from hexane/ether (1/1) afforded 2.9 g (76%) of H-BPMP as a whitish solid.

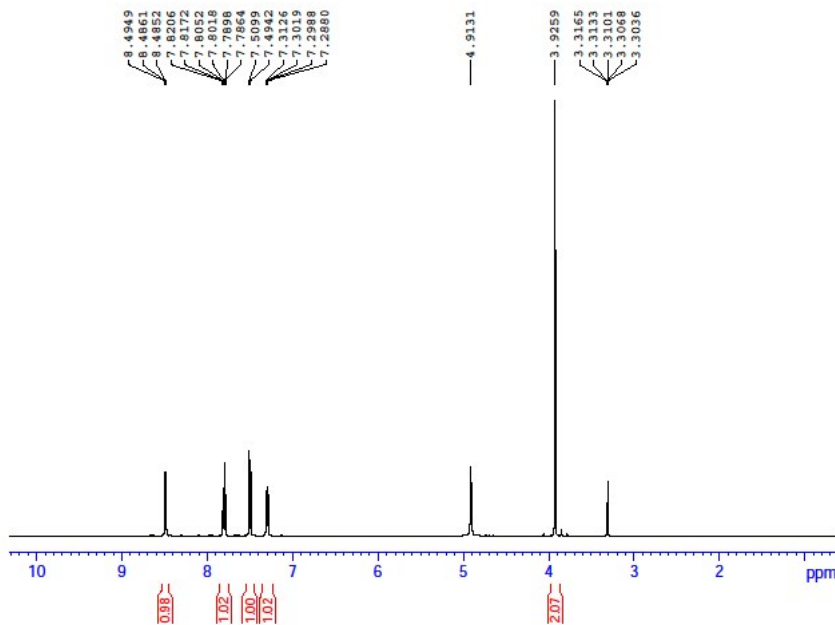


Scheme S1 Synthesis path of bis(2-pyridylmethyl)amine. Reagents and conditions: (i) Ethanol; (ii) NaBH_4 .



Scheme S2 Synthesis path of 2,6-bis(chloromethyl)-4-methylphenol. Reagents and conditions: (iii) CH_2Cl_2 .

(a)¹



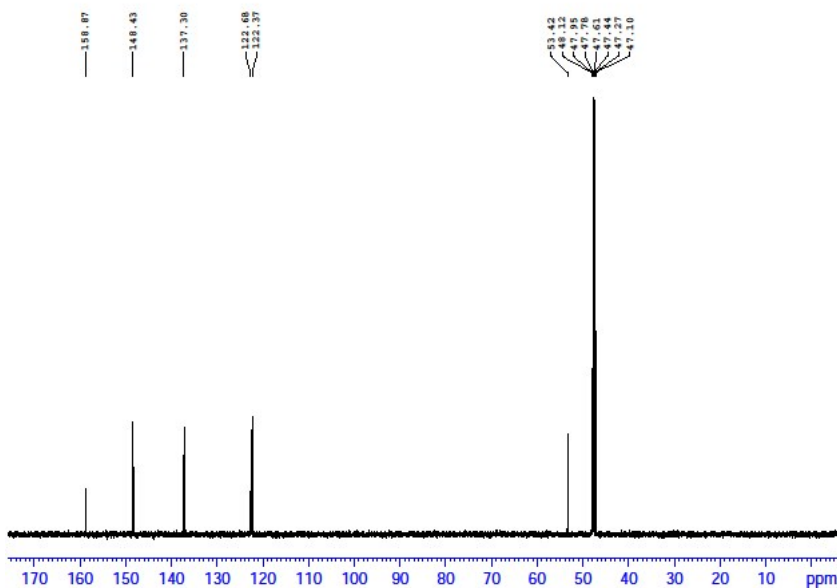
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TE       293.1 K
D1       1.00000000 sec
TDO      1

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SFO1     500.1330885 MHz

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(b)



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PLM12    0.31130999 W
PLM13    0.19924000 W
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Fig. S1 (a) ^1H -NMR (CD_3OD , 500MHz) and ^{13}C -NMR (CD_3OD , 100MHz) of bis(2-pyridylmethyl)amine.

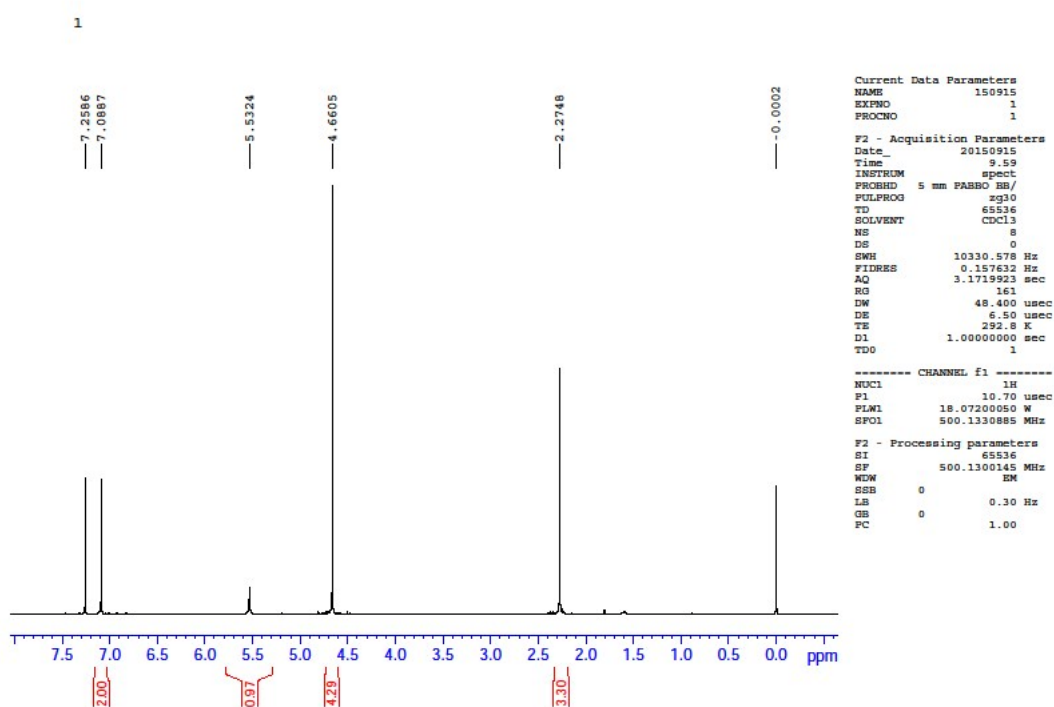


Fig. S2 ^1H -NMR (CDCl_3 , 500MHz) of 2,6-bis(chloromethyl)-4-methylphenol.

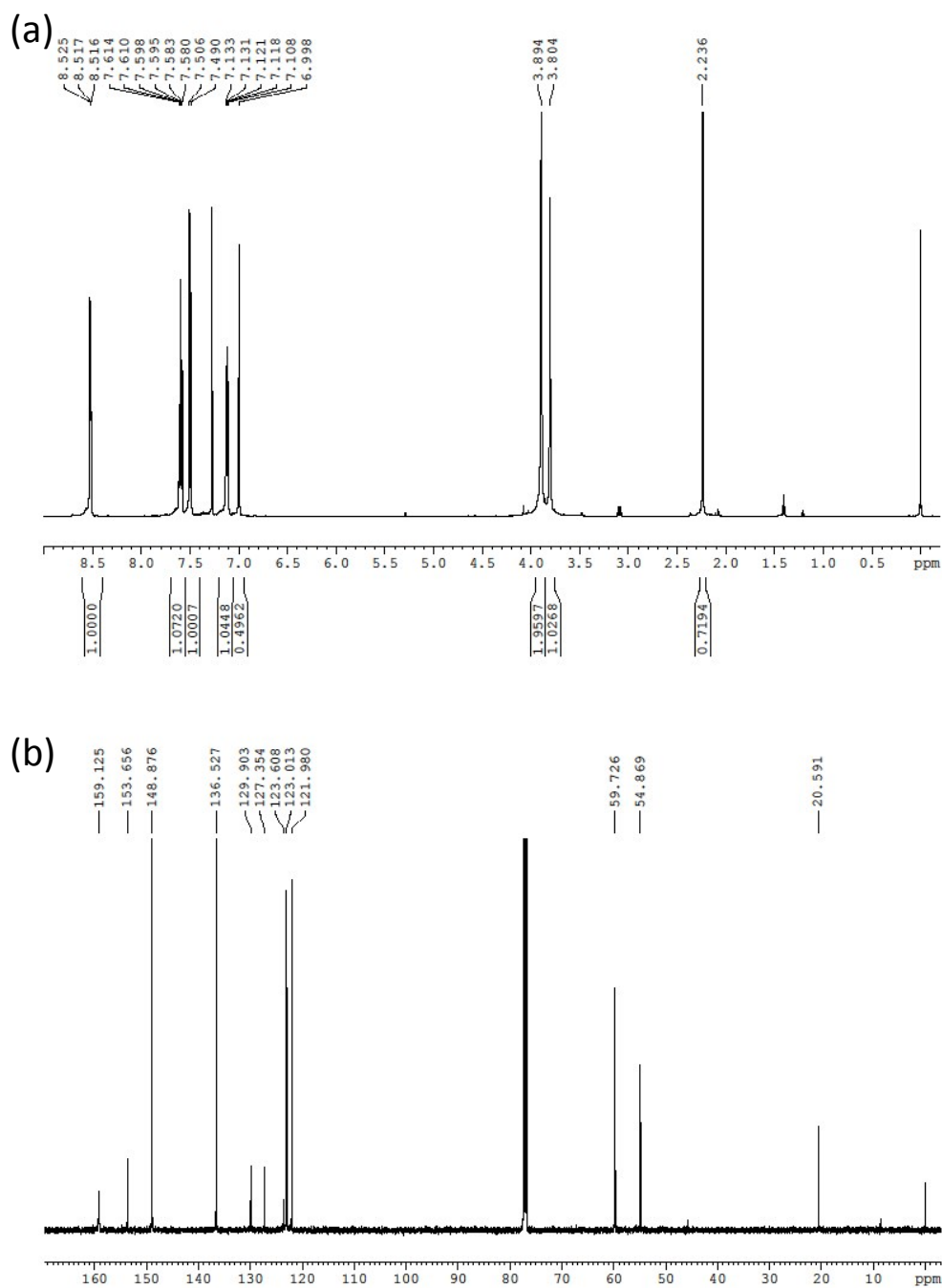


Fig. S3 (a) ^1H -NMR (CDCl_3 , 500MHz) and ^{13}C -NMR (CDCl_3 , 100MHz) of H-BPMP.

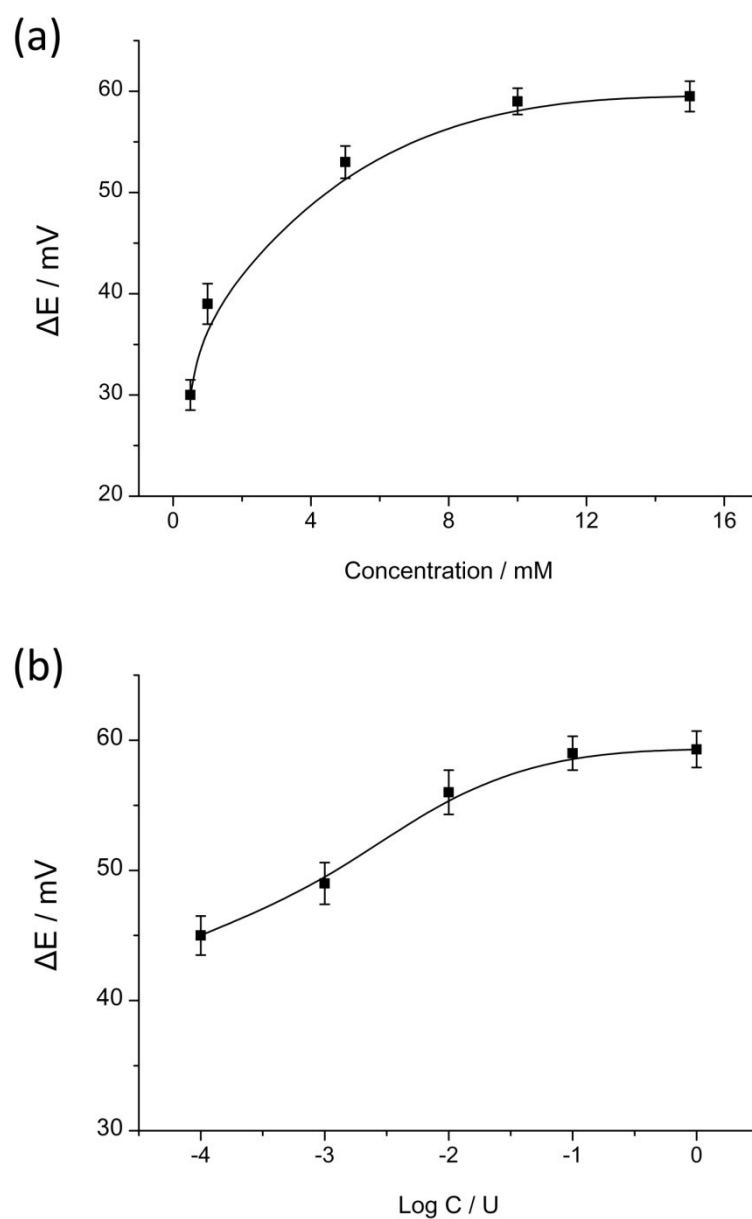


Fig. S4 Potential changes of the TDMACl-doped polymeric membrane electrodes to 50 μM o-mercaptophenol in the presence of (a) H_2O_2 at different concentrations (0.1 U HRP) and (b) HRP at different concentrations (10 mM H_2O_2). Each error bar represents one standard deviation of 3 replications. The sample medium was 20 mM HEPES buffer (pH = 7.0).

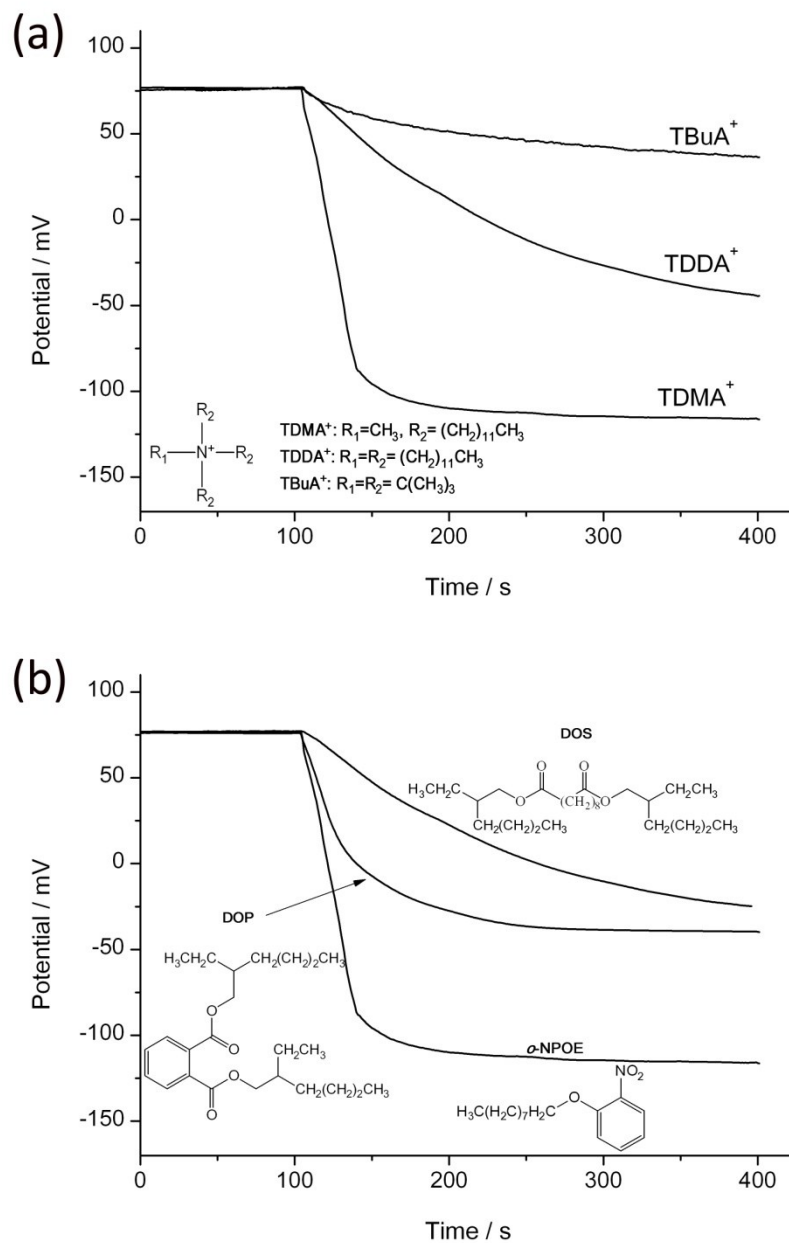


Fig. S5 Potential responses of (a) NPOE plasticized polymeric membrane electrodes containing different recognition elements and (b) TDMACl-doped polymeric membrane electrodes plasticized with different plasticizers to indicator 4. The sample medium was 20 mM HEPES buffer (pH = 7.0).

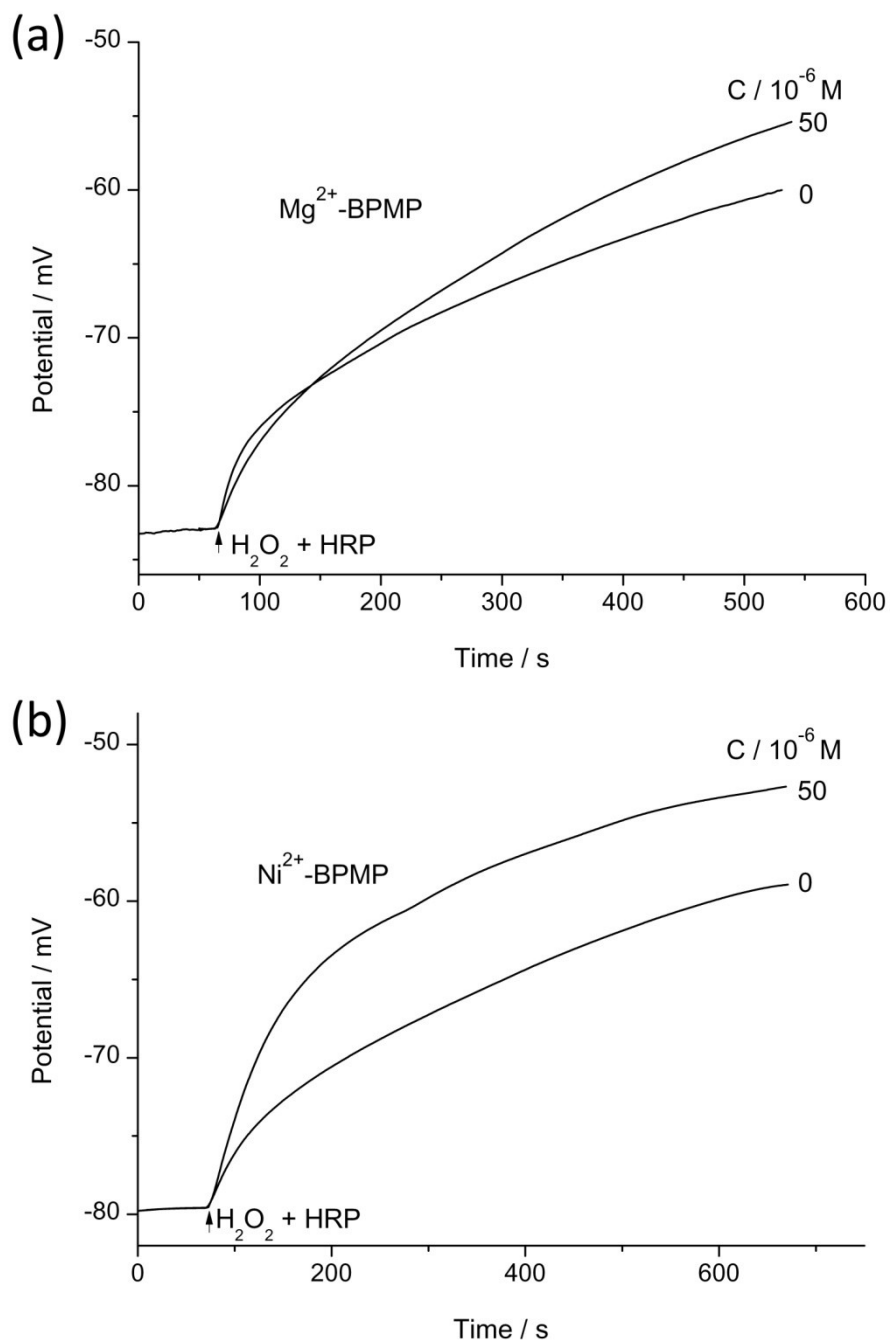


Fig. S6 Potential responses of the TDMACl-doped polymeric membrane electrodes to the oxidation of indicator 4 displaced from (a) Mg^{2+} -BPMP and (b) Ni^{2+} -BPMP by phosphate at different concentrations. The concentration of H_2O_2 and HRP is 10 mM and 0.1 U, respectively. The sample medium was 20 mM HEPES buffer (pH = 7.0).

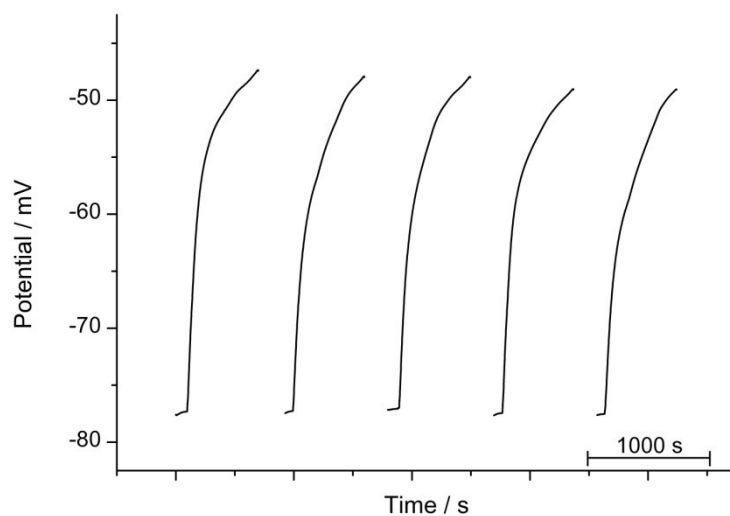


Fig. S7 Potential detection of 50 μM phosphate using the Zn-based sensor (five times).
The sample medium was 20 mM HEPES buffer (pH = 7.0).

Notes and references

- 1 C. Li, C. Ma, P. Xu, Y. Gao, J. Zhang, R. Qiao and Y. Zhao, *J. Phys. Chem. B*, 2013, **117**, 7857-7867.
- 2 A. S. Borovik, V. Papaefthymiou, L. F. Taylor, O. P. Anderson and L. Que, *J. Am. Chem. Soc.*, 1989, **111**, 6183-6195.
- 3 S. Torelli, C. Belle, I. Gautier-Luneau, J. L. Pierre, E. Saint-Aman, J. M. Latour, L. Le Pape and D. Luneau, *Inorg. Chem.*, 2000, **39**, 3526-3536.