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Supporting Information

An enzyme-free glucose sensor based on a difunctional diboronic acid for molecular recognition and potentiometric transduction

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Reagents and materials

Tetradodecylammonium chloride ($TDDA^+Cl^-$), *o*-nitrophenyl octylether (*o*-NPOE), high molecular weight poly(vinyl chloride) (PVC), 2-formylbenzeneboronic acid, 3,3'-diaminodiphenylmethane, glucose, fructose, galactose, sodium borohydride and tetrahydrofuran (THF) were purchased from Sigma-Aldrich. Solvents were purified before being used for synthesis. Aqueous solutions were prepared with freshly deionized water (18.2 MΩ specific resistance) obtained with a Pall Cascada laboratory water system. NMR spectra were taken on a Bruker Avance III 500 NMR spectrometer and Mass spectra were recorded with a Q-TOF Micro MS spectrometer.

Synthesis and characterization of the DBA

The DBA was synthesized as described before.[1] 2-Formylbenzeneboronic acid (300 mg, 2 mmol) was slowly added to a solution of 3,3'-diaminodiphenylmethane (198 mg, 1 mmol) in methanol (10 mL). The yellow solution was stirred at room temperature for 2 h before it was heated at 50 ℃ for 24 h. Then the mixture was cooled to 0 ℃ and sodium borohydride (380 mg, 10 mmol) was slowly added in small portions. The reaction mixture was stirred at room temperature for another 3 h before the solvent was removed under vacuum. After that, brine (30 mL) was added dropwise to the residue to obtain a white cloudy mixture. Then the pH value was adjusted to 7-8 with hydrochloric acid (10 %). The precipitated white solid was collected by filtration and washed successively with water. The solid was dried further under vacuum without further purification (242 mg, 52%). ^{1}H NMR (500 MHz, CD_3OD): δ 3.74 (s, 2H, Ph-*CH₂*-Ph), 4.29 (s, 4H, Ph-*CH₂*-NH-Ph), 6.53-6.67 (m, 6H, Ar*H*), 7.01-7.03 (t, 2H, Ar*H*), 7.16-7.42 (m, 8H, Ar*H*); ^{13}C NMR (75 MHz, CD_3OD): δ 148.86, 145.20, 143.43, 133.12,129.96, 129.80, 129.45, 128.56, 127.46, 121.55, 117.37, 114.49, 51.28, 43.07; HRMS (ESI-TOF, m/z): $[M\text{-}2H_2O\text{-}H]^-$ calcd for $C_{27}H_{24}B_2N_2O_2^-$, 429.1946; found 429.1959.

Membrane preparation and EMF measurements

Polymeric liquid membranes containing PVC and *o*-NPOE in a weight ratio of 1:1 and $TDDA^+Cl^-$ (10 mM/kg) were prepared by the solvent-casting method.[2] After transferring the mixture into a glass ring (i.d. 50 mm) fixed on a glass plate and letting THF evaporate overnight, a uniform membrane was obtained. For each membrane, a disk of 5 mm diameter was punched from the membrane and glued to a plasticized PVC tube (i.d 3 mm, o.d. 5 mm) with THF/PVC slurry. 10 mM KCl was used as the inner filling medium for the electrode.

All measurements of electromotive force (E) were carried out at 25 ± 2 ℃ using a PXSJ-216 pH meter (Shanghai, 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 KCl/AgCl, Ag.

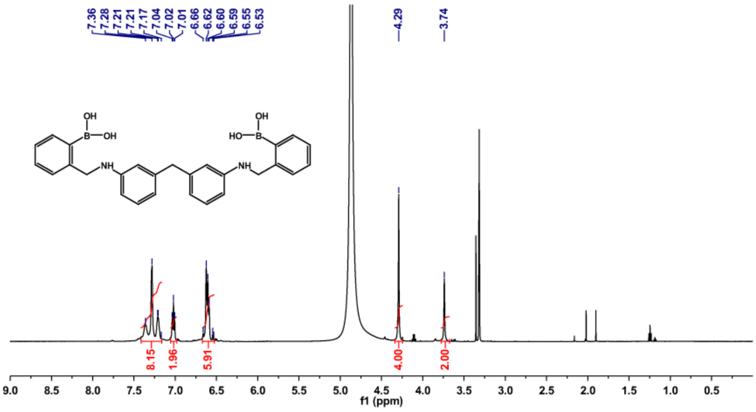

Figure S1 ^{1}H NMR spectrum of the DBA (CD_3OD, 500MHz).

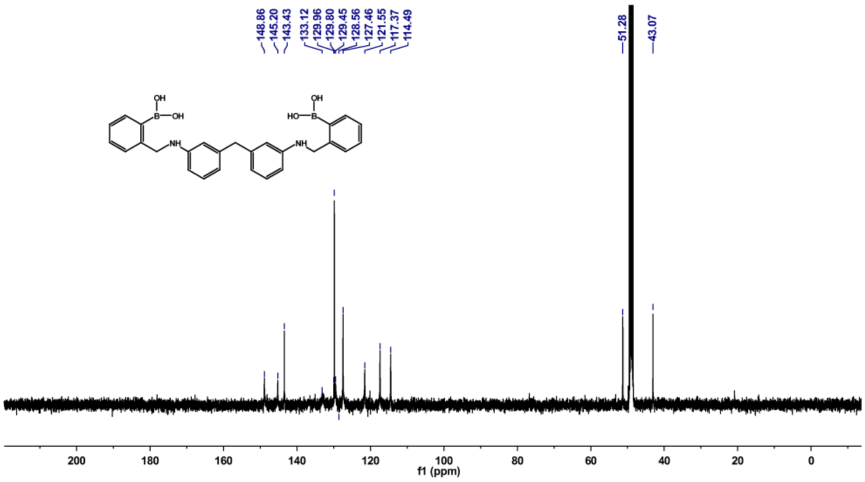

Figure S2 ^{13}C NMR spectrum of the DBA (CD_3OD, 75MHz).

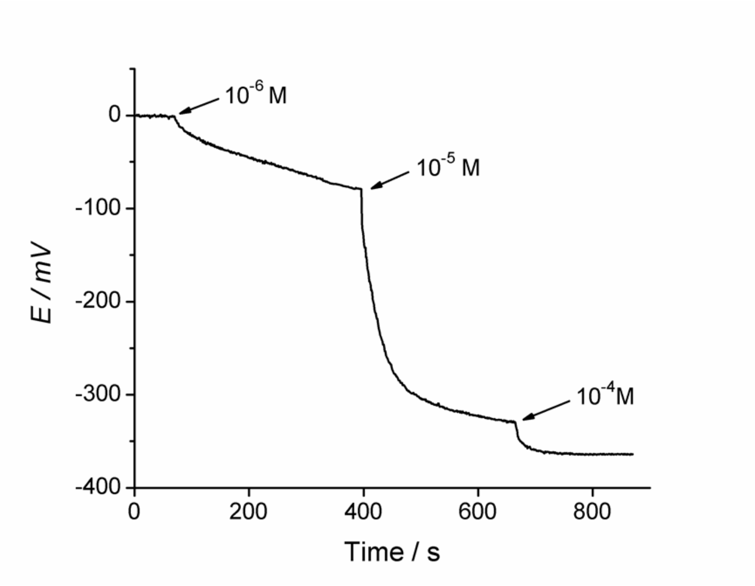

Figure S3 Potential responses to the DBA at different concentrations measured with the TDDA$^+$Cl$^-$- doped PLME in 50 mM phosphate buffer (pH 8.0).

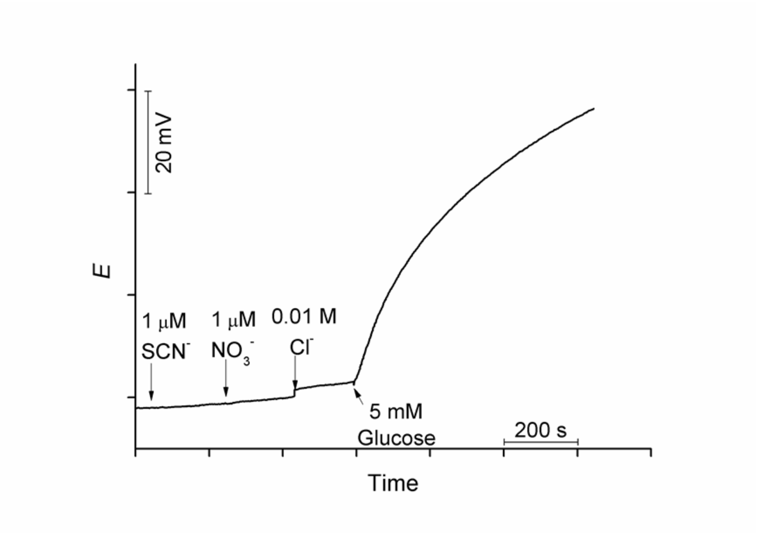

Figure S4 Potential responses to 1 μM SCN$^-$, 1 μM NO$_3^-$, 0.01 M Cl$^-$ and 5 mM glucose on the TDDA$^+$Cl$^-$-doped PLME. Conditions: 10^{-5} M DBA in 50 mM phosphate buffer (pH 8.0).

References

1. S. Arimori, L. I. Bosch, C. J. Ward and T. D. James, *Tetrahedron Lett.*, 2002, **43**, 911.
2. X. W. Wang, D. F. Yue, E. G. Lv, L. Wu and W. Qin, *Anal. Chem.*, 2014, **86**, 1927-1931.