Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting Information for

Direct Potentiometric Bicarbonate/Carbon Dioxide Sensing Based on Polymeric Membranes Doped with Selective meso-Bisubstituted Calix[4]pyrroles Ionophores

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COMPUTATIONAL DETAILS

Full geometry optimizations in aqueous solution were performed to locate all the stationary points, using the B3LYP method,[1] with the 6-31+G(d,p) basis set for all the atoms,[2-3] namely B3LYP/6-31+G(d,p). Dispersion corrections were computed with Grimme's D3(BJ)[4] method in optimization. The intrinsic reaction coordinate path was traced to check the energy profiles connecting each transition state to two associated minima of the proposed mechanism.[5] All geometry calculations were run with the Gaussian 09 program.[6] ESP analysis[7] was performed on the molecular van der Waals surface.

Ionophore 1: ^{1}H NMR (500 MHz, CD_3CN): δ [ppm] 8.00 (s, 4H), 7.93 (s, 2H), 5.90 (m, 4H), 5.81 (m, 4H), 4.16 (q, *J* = 7.0 Hz, 4H), 2.69 (q, *J* = 7.5 Hz, 4H), 1.85 (s, 6H), 1.65 (s, 6H), 1.62 (s, 6H), 1.51 (s, 6H), 1.23 (t, *J* = 7.0 Hz, 6H), 1.07 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (125 MHz, CD_3CN): δ[ppm] 161.51 140.30, 138.60, 135.61, 135.25, 116.86, 115.80, 106.06, 104.05, 60.27, 41.61, 35.69, 30.41, 27.40, 25.45, 18.67, 15.38, 14.65, 9.44.

Ionophore 2: ^{1}H NMR (300 MHz, CD_3CN): δ [ppm] 11.80 (s, 2H), 9.68 (s, 4H), 7.51 (t, J = 6.63 Hz, 2H), 7.41 (d, J = 6.58 Hz, 4H), 7.12 (m, 4H), 5.75 (t, J = 2.90 Hz, 4H), 5.66 (t, J = 2.00 Hz, 4H), 2.04 (s, 6H), 1.61 (s, 6H), 1.52 (s, 6H). ^{13}C NMR (100 MHz, CD_3CN): δ[ppm] 160.18, 140.84, 136.08, 123.99, 119.12, 105.99, 104.72, 42.34, 36.36, 29.68, 25.59.

Ionophore 3: ^{1}H NMR (300 MHz, CD_3CN): δ [ppm] 10.41 (s, 4H), 7.60 (m, 4H), 7.56 (m, 4H), 6.03 (m, 4H), 5.89 (m, 4H), 3.42 (s, 12H), 2.23 (s, 6H), 1.78 (s, 6H), 1.61 (s, 6H). ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ [ppm] 156.74, 142.42, 134.41, 133.18, 128.90 114.55, 107.56, 107.20, 42.99, 37.28, 33.60, 32.99, 23.57.

EXPERIMENTAL SECTION

The ion chromatography experiments were performed on an ICS-5000 system (Thermo Scientific Dionex, Sunnyvale, CA, USA) equipped with two pumps. IC separation was performed using a capillary column (Optimix C18/SCX, 2.1 mm×30 mm×3 um, Agela Technologies) and conductivity detection; the flow rate of MSA eluent was 0.2 mL/min at 30°C; the injection volume was 50 μL[8].

The three mineral water samples are obtained from our lab, Coke and Sprite samples are bought from a local supermarket. After sampled, the detection was conducted in a sealed cup within 3 minutes to decrease the influence from the air.

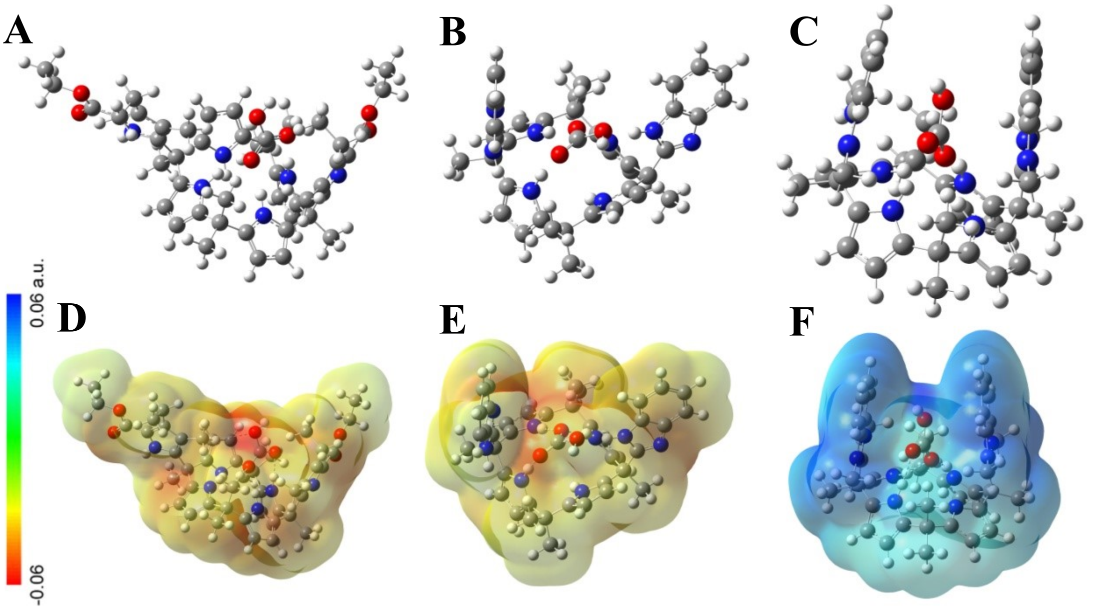

Figure S1. The geometries (A ionophore 1-HCO_3^-, B ionophore 2-HCO_3^-, C ionophore 3-HCO_3^-) and ESP (D ionophore 1-HCO_3^-, E ionophore 2-HCO_3^-, F ionophore 3-HCO_3^-) of ionophores-HCO_3^- complexes. The white, gray, red and blue balls denote H, C, O and N atoms.

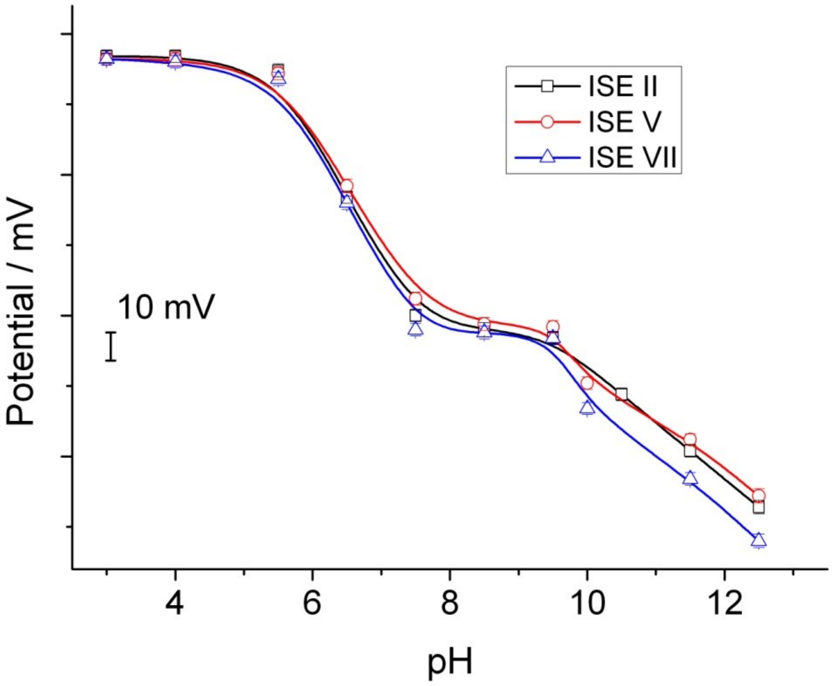

Figure S2. Effects of pH on the potential responses of the proposed ISEs in 1 mM HCO_3^- aqueous solutions.

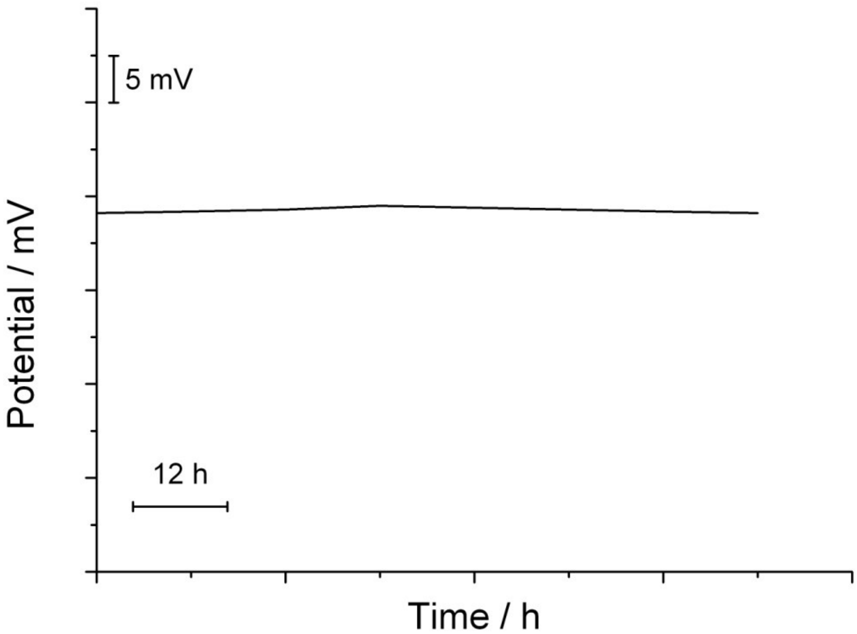

Figure S3 Potential trace of the proposed ISE VII in a period of 72 h.

Table S1. Data (ISE VII) for the slopes, detection limits (DL) and selectivity coefficients in a period of 3 months.

ISEs	Day	Slope mV/decade	DL (M)	LogK^{pot}, bicarbonate X-					
				Sal^-	SCN^-	NO_3^-	Br^-	Cl^-	$H_2PO_4^-$
XVII	1	59.2	5×10^{-7}	3.5	-1.0	-1.5	-3.1	-2.8	-4.0
	20	59.0	5×10^{-7}	3.5	-1.0	-1.5	-3.1	-2.8	-4.0
	50	59.0	5×10^{-7}	3.5	-1.0	-1.5	-3.0	-2.8	-4.0
	70	58.5	5×10^{-7}	3.5	-1.0	-1.5	-3.0	-2.8	-3.9
	90	58.0	5×10^{-7}	3.5	-1.0	-1.5	-3.0	-2.8	-3.9

Table S2 Statistical analysis of the results from our sensors and Chromatography

Samples	Levene's Test for Equality of Variances	t-test for Equality of Means	/
Mineral water 1	0.609	0.138	No significant difference
Mineral water 2	0.422	0.055	No significant difference
Mineral water 3	0.192	0.057	No significant difference
Coke	0.751	0.188	No significant difference
Sprite	0.770	0.109	No significant difference

References

1. Adamo, C.; Barone, V. Toward Reliable Density Functional Methods without Adjustable Parameters: The PBE0 Model. *J. Chem. Phys.* **1999**, 110, 6158−6170.

2. Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. Selfconsistent Molecular Orbital Methods. XX. A Basis Set for Correlated Wave Functions. *J. Chem. Phys.* **1980**, 72, 650−654.

3. Xu S., He T., Li J., Huang Z., & Hu C., Enantioselective synthesis of D-lactic acid via chemocatalysis using MgO: Experimental and molecular-based rationalization of the triose's reactivity and preliminary insights with raw biomass. *Appl. Catal. B: Environ.* **2021**, 292:120145.

4. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H., A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, 132 (15), 154104.

5. Gonzalez, C.; Schlegel, H. B. An improved algorithm for reaction path following. *J. Chem. Phys.* **1989**, 90, 2154−2161.

6. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Taroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision D.01; Gaussian Inc.: Wallingford, CT, 2013.

7. Murray, J. S.; Politzer, P., The electrostatic potential: an overview. *WIRS Comput. Mol.*

Sci. **2011**, 1 (2), 153-163.

8. A. Xu, X. Wang, Y. Fa, Y. Liu, F. Li, H. Huang, Z. Wang, Determination of bicarbonate in fermentation of cyanobacterial by non-suppress ion chromatography. Adv. J. Food Sci. Technol. 13 (2017) 7-10.