

Supplementary data

Recognition and sensing of AcO^- and F^- using a calix[4]pyrrole-derived hydrazone: a potential molecular keypad lock

Qian Li, Zhenzhong Wang, Jian Xu, Ying Yue, Shijun Shao

Key Laboratory of Chemistry of Northwestern Plant Resources and Key Laboratory for Natural Medicine of Gansu Province, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China

1. Experimental

1.1. Materials

In the titration experiments, all the anions were added in the form of tetrabutylammonium (TBA) salts, which were purchased from Sigma-Aldrich Chemical, stored in avacuum desiccator. All the other common chemicals were of analytical grade, and Pyrrole was distilled prior to use.

1.2. Apparatus

^1H NMR and ^{13}C NMR spectra were obtained on a Varian UNITYPlus-400MHz Spectrometer. ESI-MS was performed with a MARINER apparatus. UV-vis spectra were recorded on a Perkin Elmer Lambda 35 UV/VIS Spectrophotometer with quartz cuvette (pathlength=1cm).

1.3. Synthesis

1.3.1. Synthesis of formyl-OMCP

Both the sensors utilize octamethylcalix[4]pyrrole (OMCP) as the starting material, and OMCP is easily synthesized by acid-catalyzed condensation of pyrrole and acetone. Formyl-OMCP was obtained by the treatment of OMCP with Vilsmeier reagent.

1.3.2. Synthesis of receptor **1**

Formyl-OMCP and 4-nitrophenylhydrazine was dissolved in ethanol and 3 drops of CH_3COOH was added to the system. And which was heated to reflux for 4h. After cooling to

room temperature, the mixture was poured into ice–water and the precipitate was collected and dried. The product was further purified by recrystalling from EtOH/H₂O. Yield 80%.

MS (ESI): M/Z 592 (M+H⁺);

¹H NMR (400Hz, DMSO-*d*₆), δ : 10.89 (s, 1H), 9.60-9.69 (d, 2H), 8.97 (s, 1H), 8.67 (s, 1H), 8.46 (s, 1H), 8.06-8.08 (m, 2H), 6.98 (s, 2H), 6.23 (s, 1H), 6.23 (d, 2H), 5.84-5.87 (dd, 2H), 5.66-5.68 (s, 4H), 3.34 (s, 1H), 1.50-1.73 (m, 24H);

¹³C NMR (400Hz, DMSO-*d*₆), δ : 150.845, 140.858, 139.304, 138.892, 138.812, 138.674, 138.484, 138.347, 137.734, 137.429, 136.861, 126.341, 113.669, 110.236, 102.615, 102.539, 102.013, 101.846, 101.625, 101.408, 36.901, 34.779, 34.402, 34.192, 30.058, 29.334, 28.622, 28.302.

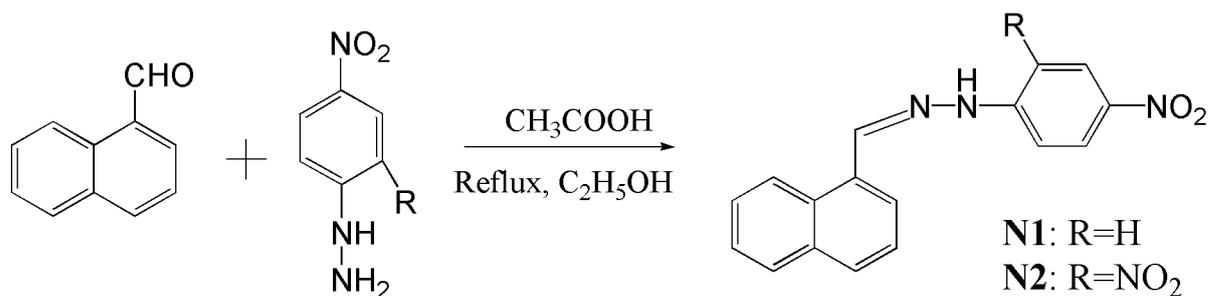
1.3.3. Synthesis of receptor 2

Formyl-OMCP and 2,4-dinitrophenylhydrazine was dissolved in ethanol and 3 drops of CH₃COOH was added to the system. And which was heated to reflux for 4h. After cooling to room temperature, the mixture was poured into ice–water and the precipitate was collected and dried. The product was further purified by recrystalling from EtOH/H₂O. Yield 85%.

MS (ESI): M/Z 637 (M+H⁺)

¹H NMR (400Hz, DMSO-*d*₆), δ : 11.68 (s, 1H), 9.70-9.72 (d, 2H), 9.06 (s, 2H), 8.80-8.86 (d, 2H), 8.31-8.34 (d, 1H), 7.97-8.00 (d, 1H), 6.32 (s, 1H), 5.85-5.90 (d, 2H), 5.66-5.69 (s, 4H), 1.53-2.09 (m, 24H);

¹³C NMR (400Hz, DMSO-*d*₆), δ : 147.572, 144.265, 142.157, 139.132, 138.972, 138.725, 138.564, 138.302, 137.505, 137.166, 135.680, 129.553, 128.182, 123.278, 116.622, 113.196, 102.852, 102.692, 102.132, 101.873, 101.754, 101.587, 36.924, 34.798, 34.592, 34.406, 34.196, 30.725, 30.108, 29.373, 28.645, 28.313.



Scheme s1. Synthesis of compounds N1 and N2

1.3.4. Synthesis of **N1**(Scheme 1)

1-Naphthaldehyde and 4-Nitrophenylhydrazine was dissolved in ethanol and 3 drops of CH₃COOH was added to the system, which was heated to reflux for 4h. After cooling to room temperature, the mixture was poured into ice-water and the precipitate was collected and dried. Recrystallization from ethanol afforded **1** as red solid. Yield 80%.

MS (ESI): M/Z 290.3 (M-H⁺)

¹H NMR (400Hz, DMSO-d₆), δ: 11.47 (s, 1H), 8.73-8.76 (d, 2H), 8.19-8.21 (d, 2H), 7.98-8.03 (m, 3H), 7.68-7.72 (t, 1H), 7.59-7.63 (m, 2H), 7.23-7.25 (d, 2H)

¹³C NMR (400Hz, DMSO-d₆), δ : 151.124, 142.219, 134.184, 130.453, 129.492, 128.004, 127.363, 126.997, 126.356, 124.456, 112.034.

1.3.5. Synthesis of receptor **N2**(Scheme 1)

1-Naphthaldehyde and 2, 4-dinitrophenylhydrazine was dissolved in ethanol and 3 drops of CH₃COOH was added to the system, which was heated to reflux for 4h, an orange precipitate formed. After cooling to room temperature, the precipitate was filtered, washed with ethanol twice and obtained in 85% yield.

MS (ESI): M/Z 337 (M+H⁺)

¹H NMR (400Hz, DMSO-d₆), δ: 11.83 (s, 1H), 9.54 (s, 1H), 8.85 (s, 1H), 8.64-8.66 (d, 1H), 8.38-8.40 (d, 1H), 8.02-8.15 (m, 4H), 7.60-7.72 (m, 3H). Anal. Calcd. for C₁₇H₁₂N₄O₄: C, 60.71; H, 3.60; N, 16.66. Found: C, 60.26; H, 3.57; N, 16.59.

2. Determination of detection limit

The detection limit DL of receptor **2** was determined from the following equation[3-4]:

$$DL = 3S/K \quad (2)$$

Where S is the standard deviation of the blank solution; K is the slope of the calibration curve.

Fig.S1 Shows the plot of absorbance versus the fluoride anions concentration in DMSO-H₂O solution.

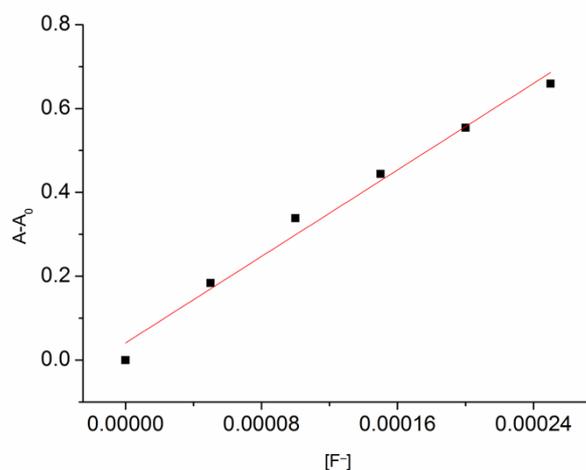


Fig. S1 The plot of absorption of receptor **1** at 510 nm *versus* fluoride anions concentration

3. Determination of the binding constant and stoichiometry

The binding stoichiometry of receptor **1** with fluoride anions was calculated through the Benesi-Hildebrand equation [1-2].

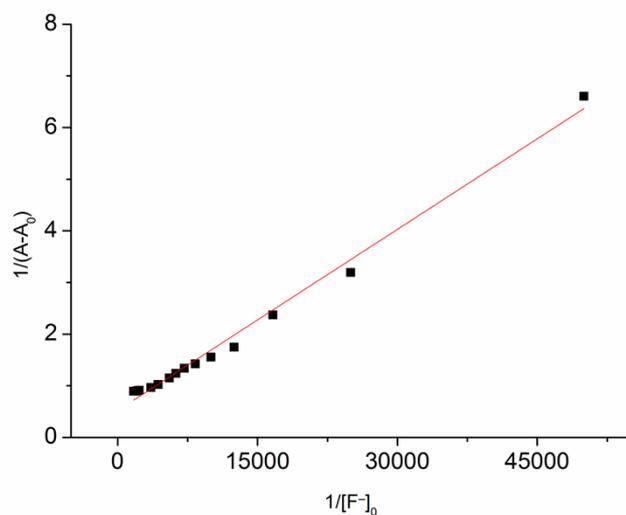


Fig. S2. Benesi-Hildebrand plot assuming 1:1 stoichiometry for association between receptor **1** and F⁻ in DMSO solvent.

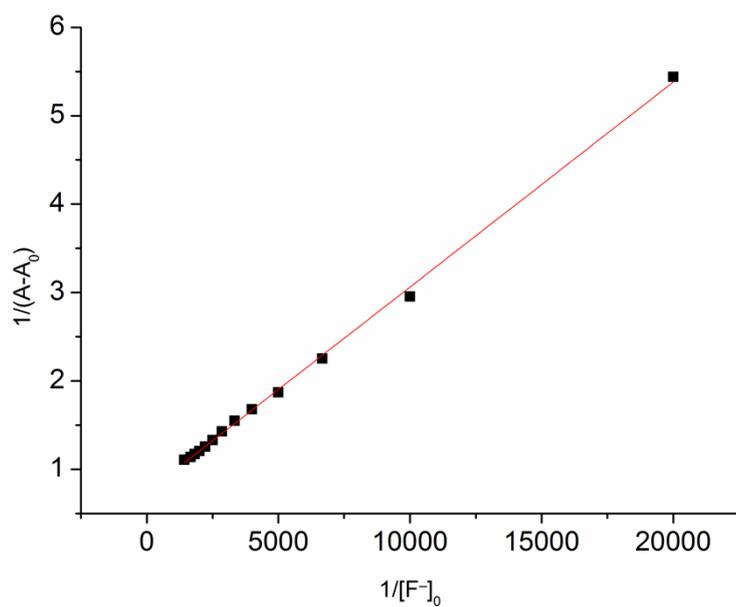


Fig. S3 Benesi-Hildebrand plot assuming 1:1 stoichiometry for association between receptor 2 and F^- in DMSO- H_2O medium.

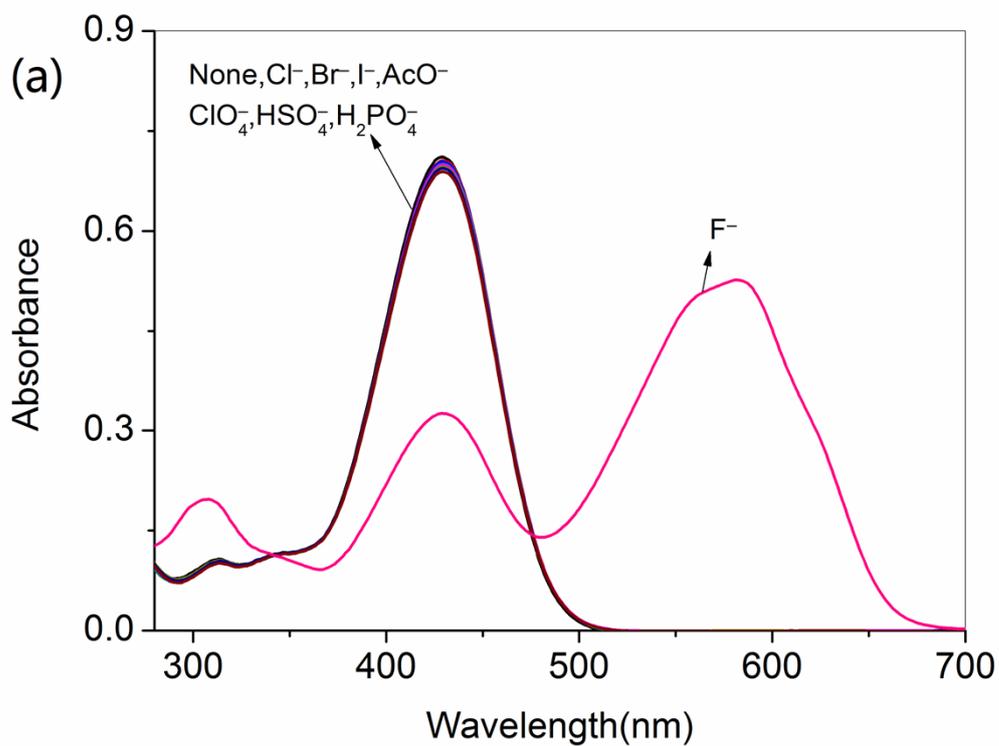


Fig. s4. Changes in the UV/vis absorption spectrum of N1 upon addition of anions in TBA salts

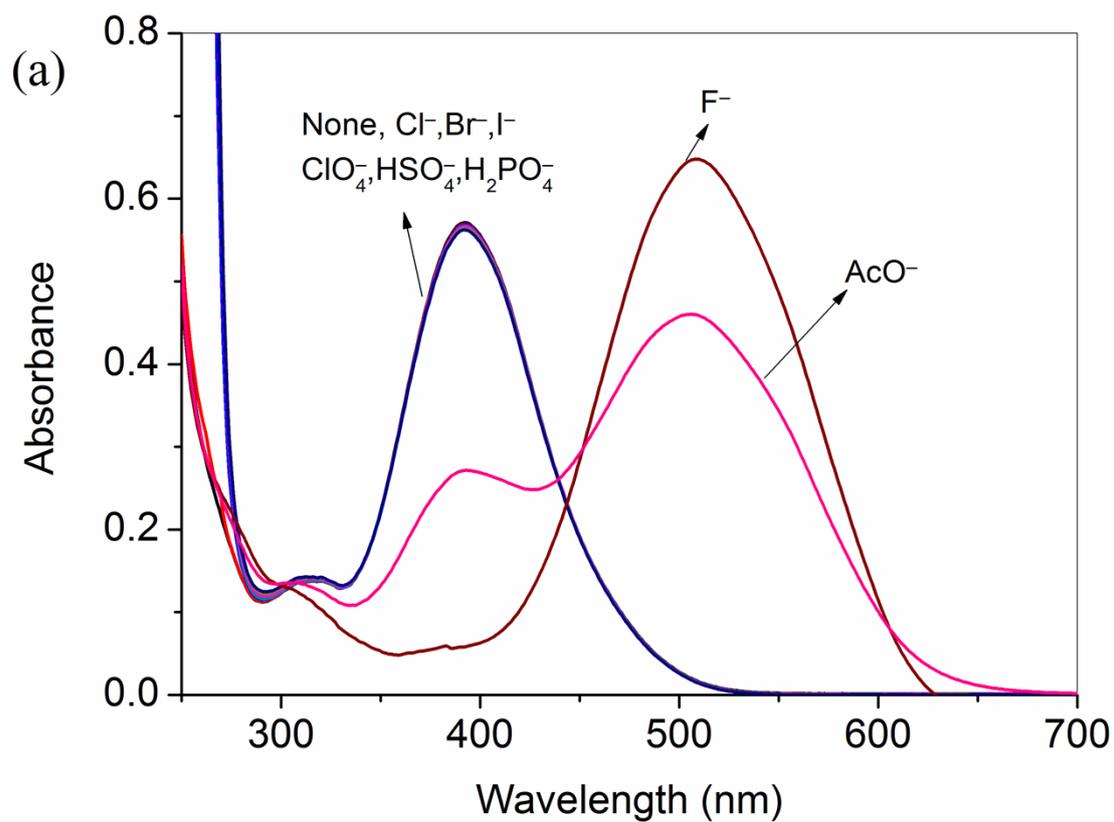


Fig. s5. Changes in the UV/vis absorption spectrum of N2 upon addition of anions in TBA salts

References:

- [1] H. A. Benesi, J. H. Hildebrand, A Spectrophotometric Investigation of the Interaction of Iodine with Aromatic Hydrocarbons, *J. Am. Chem. Soc.* 71 (1949) 2703–2707.
- [2] Y. Shiraishi, H. Maehara, T. Hirai, Indole-azadiene conjugate as a colorimetric and fluorometric probe for selective fluoride ion sensing, *Org. Biomol. Chem.* 7 (2009) 2072–2076.