Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

A highly selective colorimetric chemosensor for detection of iodide ions in aqueous solution

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1. General Methods

1.1. Materials and physical methods

All reagents for synthesis were of analytical grade and were used without further purification. All the anions were added in the form of tetrabutylammonium (TBA), which were purchased from Sigma-Aldrich Chemicals, and stored in a vacuum desiccator. UV/Vis spectra were recorded on a Shimadzu UV-2550 spectrometer at room temperature. Electrospray ionization mass spectra (ESI-MS) were measured on an Agilent 1100 LC-MSD-Trap-VL system. ^{1}H NMR spectra were recorded on aVarian Mercury Plus-400 MHz spectrometer with DMSO-d6 as the solvent and TMS as an internal reference. The infrared spectra were recorded on a Digilab FTS-3000 FT-IR spectrophotometer.

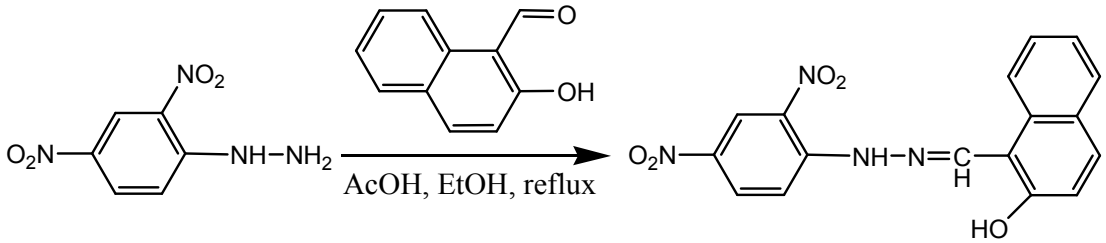
1.2. General procedure for UV–vis experiments

Stock solutions of 1.0×10^{-2} mol L^{-1} tetrabutylammonium or sodium salts of the respective anions (F^{-}, Cl^{-}, Br^{-}, I^{-}, HSO_4^{-}, CH_3COO^{-}, $H_2PO_4^{-}$,SCN^{-}, CN^{-}, ClO_4^{-} and S^{2-}) were prepared in water. A stock solution of **CS** (2.0×10^{-4}mol L^{-1}) was prepared in DMSO. The solution of **CS** was then diluted to 2.0×10^{-5} mol L^{-1} with DMSO－H_2O (v/v = 9 : 1) In titration experiments, a 2.5 mL solution of sensor **CS** (2.0×10^{-5} mol L^{-1}) was filled in a quartz optical cell of 1 cm optical path length, and the stock solution of ions was added into the quartz optical cell gradually by using a micropipette. Spectral data were recorded at 10 min after addition of the ions at room temperature.

1.3. General procedure for ^{1}H NMR experiments

For ^{1}H NMR titration, sensor **CS** was prepared in DMSO-*d6*, and Tetrabutylammonium iodide was prepared in DMSO-*d6*. First of all, only **CS** in DMSO-d6 was added into the NMR tube, and then 0.25, 0.5, 1.0, 1.5 and 2.0 equiv. of I^{-} ions were added sequentially. All solutions were mixed directly in the NMR tube.

2. Synthesis and characterization of sensors CS



Scheme 1 Structure and synthesis of the sensor **CS**

The structure and synthesis of sensor **CS** is shown in Scheme 1. 2,4-dinitrophenylhydrazine (0.40 g, 2mmol) and 2-hydroxy-1-naphthaldehyde (0.35 g, 2 mmol) in dry ethanol (30 mL) was stirred under reflux conditions for 4 h, and a red product (0.56 g, 80% yield) was obtained after recrystallization from H_2O-DMSO. m. p.＞300. IR (KBr, cm^{-1}): n = 3444(OH), 3267(N-H), 1619(-HC=N), 1595(C=N), 1328 (Ar-O). ^1H NMR (600 MHz, DMSO-d_6) δ 11.80 (s, 1H, –OH), 11.10 (s, 1H, N-H), 9.59 (s, 1H, H–C=N), 8.91 (d, J = 2.5 Hz, 1H, Ar–H), 8.81 (d, J = 8.5 Hz, 1H, Ar–H), 8.47 (d, J = 9.5 Hz, 1H, Ar–H), 8.04 – 7.78 (m, 3H, Ar–H), 7.64 (t, J = 7.9 Hz, 1H, Ar–H), 7.44 (d, J = 7.1 Hz, 1H, Ar–H), 7.27 (d, J = 9.0 Hz, 1H, Ar–H).ESI-MS calcd for $C_{17}H_{12}N_4O_5$ 352.08, found: 351.1250

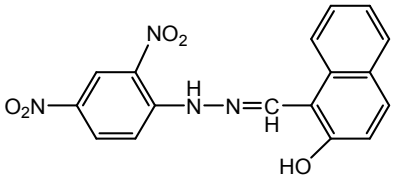
3. Determination of association constant

The association constants (K) were calculated based on the colorimetric titration curve of the probes with ions. Association constants were determined by a nonlinear least squares fit of the data with the following equation as referenced elsewhere. I_{max} and I_{min} are the corresponding maximum and minimum, respectively.

$$\log\frac{I - I_{min}}{I_{max} - I} = \log K + \log[I^-]$$

$K = 1.53\times10^6\ M^{-1}$

4. ESI-MS spectrum of CS



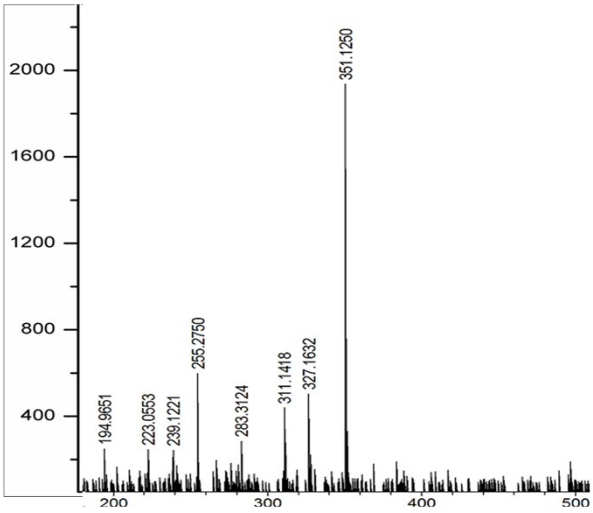


Fig. S1 ESI-MS spectra of sensor CS

5. ESI-MS spectrum of CS-I^-

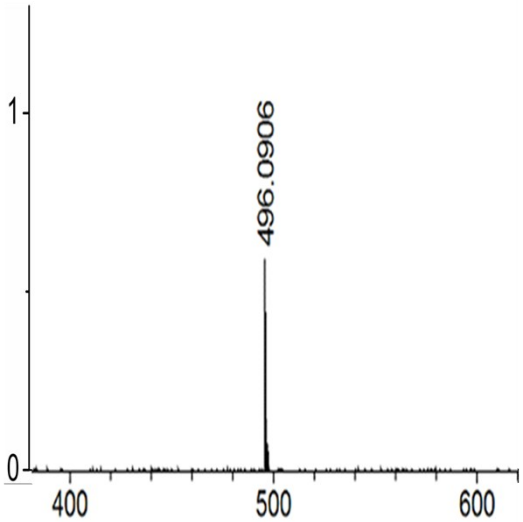


Fig. S2 ESI-MS spectra of **CS**-I^-

6. Determination of detection limit of I^-

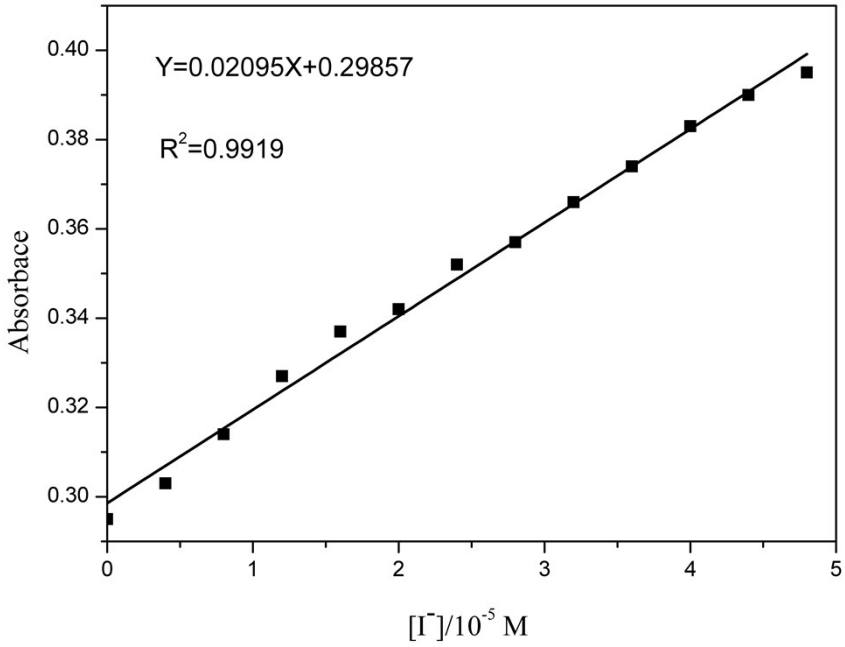


Fig. S3 Plot of the intensity at 424 nm for a mixture of CS (2×10^{-5} M) in DMSO/H_2O (9:1, v/v,) and I^- in H_2O

Linear Equation: Y=0.02095X+0.29857 R^2 =0.9919

S =2.095×10^3

$$\delta = \sqrt{\frac{\sum (F_0 - \bar{F}_0)^2}{N - 1}} = 7.7\times10^{-4}$$（N=20） K = 3

LOD = K × δ / S = $3\times7.7\times10^{-4}/2.095\times10^3=1.1\times10^{-6}$ M