Supplementary Information

A fluorescent turn-on probe for bisulfite based on hydrogen bond-inhibited C=N isomerization mechanism

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Experimental Section

General information and methods. All reagents and solvents were purchased from commercial sources and were of the highest grade. Solvents were dried according to standard procedures. All reactions were magnetically stirred and monitored by thin-layer chromatography (TLC). Flash chromatography (FC) was performed using silica gel 60 (200–300 mesh). Absorption spectra were taken on an Agilent 8453 spectrophotometer. Fluorescence spectra were taken on HITACHI F-2500 fluorescence spectrometer. The $^1$H NMR and $^{13}$C NMR spectra were recorded at 300 and 75MHz, respectively. The following abbreviations were used to explain the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad. High resolution mass spectra were obtained on a Varian QFT-ESI mass spectrometer.

Procedures for bisulfite sensing

The solutions of anions were prepared in deionized water. A stock solution of 1 (5 mM) was prepared in DMSO. The stock solution of 1 was then diluted to the corresponding concentration (2 µM) with the solution of DMSO–acetate buffer (0.1 M, pH = 5.0, 1:1, v/v). Spectra data were recorded in an indicated time after the addition of anions.

Determination of quantum yields

Quantum yields were measured on optically dilute samples in DMSO (absorbance < 0.05). N-butyl-4-amino-1,8-naphthalimide in absolute ethanol ($\Phi_F = 0.640)^{S1}$ was used as quantum yield standards. The fluorescence quantum yields of 1 and the adduct 1-bisulfite were determined to be 0.016 and 0.374 respectively.
Synthesis

Probe 1 was synthesized according to the procedures reported in the literature.\textsuperscript{52} \textsuperscript{1}H NMR (DMSO-\textit{d}6, 300 MHz): \(\delta\) 9.59 (d, \(J = 7.8\) Hz, 1H), 8.66 (d, \(J = 7.8\) Hz, 1H), 8.44 (d, \(J = 6.3\) Hz, 1H), 8.35 (d, \(J = 11.1\) Hz, 1H), 7.83 (s, 1H), 7.78 (d, \(J = 7.8\) Hz, 2H), 7.72 (d, \(J = 8.4\) Hz, 1H), 3.97 (t, \(J = 7.2\) Hz, 2H), 1.55 (q, \(J = 7.2\) Hz, 2H), 1.31 (q, \(J = 7.5\) Hz, 2H), 0.89 (t, \(J = 7.5\) Hz, 3H); \textsuperscript{13}C NMR (DMSO-\textit{d}6, 150 MHz): \(\delta\) 189.4, 161.7, 161.2, 142.2, 139.0, 130.8, 129.3, 127.0, 126.2, 124.3, 120.5, 117.9, 113.0, 107.7, 28.0, 18.2, 12.1 (17 carbon peaks); HRMS: calcd for (M-H)\textsuperscript{-} 322.1191, found 322.1195.
Fig. S1 ESI-MS of 1-bisulfite.

Fig. S2 The absorption intensities ratios at 535 nm for prove 1 (2 μM) in the absence or presence of bisulfite (30 equiv) at varied pH values.
Fig. S3 Time-dependent fluorescence intensity of 1 upon adding bisulfite in DMSO–acetate buffer solution (100 mM, pH = 5.0, 1:1, v/v). Each spectrum was recorded after 20 s.

Fig. S4 Fluorescence response at 535 nm of 1 to bisulfite (0–40 μM).
Table S1 Determination of bisulfite in granulated sugar.\(^a\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Added bisulfite (mg/kg)</th>
<th>Determined bisulfite (mg/kg)*</th>
<th>Recovery%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugar</td>
<td>0</td>
<td>10.72 ± 0.44(^b)</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>22.05 ± 0.37(^c)</td>
<td>106.4</td>
</tr>
</tbody>
</table>

*Mean ± standard deviation. Relative standard deviations were calculated on the basis of three measurements.

\(^a\) Bisulfite concentrations were determined using a standard addition method\(^{S3,S4}\) by measuring the increase of the intensity of the band of 1 at 535 nm. The standard curve in Fig S4 was used to extrapolate the unknown amount of bisulfite. \(^b\) A sample solution of granulated sugar was prepared by dissolving 5.0 g of sugar in water and diluting to 10 mL. \(^{S5}\) Aliquots of the sugar solution were added directly to the DMSO–acetate buffer (0.1 M, pH = 5.0, 1:1, v/v) containing probe 1 (2 µM), and the emission intensity at 535 nm was recorded, whereby the unknown concentrations of bisulfite in sugar samples were determined to be 10.27 mg/kg. \(^c\) For recovery studies, known concentrations of bisulfite were added to sugar samples and the total bisulfite concentration was determined following the method outlined above.

References


