Supporting information for *Chemical Communications*

**Colorimetric fluoride sensors based on deprotonation of pyrrole-hemiquinone compounds**

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Table S2. Calculated energy differences between the tautomeric isomers in various solvents

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Fig. S16. (a) $^1$H NMR spectral changes of 1 (11.5 mM) in CDCl$_3$ upon addition of DMSO-$d_6$, (b) the corresponding percentages of tautomeric isomers 1 and 1a calculated from the ratio of related peak areas in the $^1$H NMR spectra, and (c) UV-vis spectral changes of 1 (10 μM in CH$_2$Cl$_2$) upon addition of DMSO.

Fig. S17. (a) $^1$H NMR spectral changes of 2 (6.4 mM) in CDCl$_3$ (0.5 mL) upon addition of DMSO-$d_6$, (b) the corresponding percentages of tautomeric isomers 2 and 2a calculated from the ratio of related peak areas in the $^1$H NMR spectra.

Fig. S18. UV-vis spectral changes of 2 (10 μM) observed upon addition of a) 100 eq. of Cl$^-$ (TBA salt) in DMSO; b) 0-84 eq. of Cl$^-$ (TBA salt) in CH$_2$Cl$_2$.

Fig. S19. $^1$H NMR spectrum change of 2 (6.4 mM) upon addition of TBACl (1 eq) in DMSO-$d_6$. 
Experimental Section

General

Commercial available solvents and reagents were used without further purification. Deuterated solvents for NMR measurements were obtained from Aldrich. UV/Vis absorption spectra were measured using a Varian Cary 100 spectrophotometer, with a quartz cell (path length = 1 cm). 1H NMR spectra were obtained on a Bruker AVANCE spectrometer (400 or 500 MHz). Spectrophotometric titrations were performed on 1.0 × 10^{-5} M solutions of 1 and 2 in CH2Cl2 or DMSO (analytical grade). Typically, aliquots of a freshly prepared alkylammonium salt standard solution of the envisaged anion (CH3COO⁻, F⁻, Cl⁻, Br⁻, or I⁻) were added, and the UV-vis spectra were recorded. 1H NMR titrations were carried out in CDCl3 or DMSO-d6 solution.

Scheme S1 Synthesis of sensors 1 and 2.

Synthesis of i1

153 µL of TFA was added with syringe to the mixture of pyrrole (13.8 mL, 0.20 mol) and 3,5-Di-tert-butyl-4-hydroxybenzaldehyde (469 mg, 2.0 mmol). After stirred at room temperature for 30 min, saturated NaHCO3 (30 mL) was added, and then the mixture was extracted with CH2Cl2 (30 mL × 2). The combined organic phase was washed with water, dried over Na2SO4, filtered and evaporated. Pyrrole was recycled by distillation under reduced pressure and the residue was purified by a silica gel column to afford the desired product dipyrromethane i1 (479 mg, yield: 68%). 1H NMR (CDCl3, Bruker 500 MHz, 298K): δ 1.39 (s, 18H, -C(CH3)3), 5.13 (s, 1H, phenolic-OH), 5.36 (s, 1H, -CH), 5.92 (s, 2H, pyrrolic), 6.15 (d, J = 2.8 Hz, 2H, pyrrolic), 6.68 (s, 2H, pyrrolic), 7.00 (s, 2H, phenyl), 7.89 (br, 2H, -NH).

Synthesis of i2

TFA (2.2 mmol, 170 µL) was added to the mixture of 3, 5-Di-tert-butyl-4-hydroxy-benzaldehyde (22 mmol, 5.2 g) and pyrrole (100 mmol, 7.6 mL). After stirred at room temperature for 5 min under nitrogen, aqueous NaOH (0.1 M, 20 mL) was added. and then the mixture was extracted with CH2Cl2 (50 mL × 2). The combined organic phase was washed with water, dried over Na2SO4, filtered and evaporated. Pyrrole was recycled by distillation under reduced pressure. Chromatography of the resulting oil (silica gel, CH2Cl2/petroleum ether 1:4) afforded the product i2 (1.23g, 18%). 1H NMR (CDCl3, Bruker 500 MHz, 298K): δ 1.37 (m, 36H, -C(CH3)3), 5.13 (s, 1H, phenolic-OH), 5.27 (s, 2H, -CH), 5.75-5.80 (m, 2H, pyrrolic), 5.85 (d, J = 2.1 Hz, 2H, pyrrolic), 6.07-6.12 (m, 2H, pyrrolic), 6.62-6.67 (m, 2H, pyrrolic), 6.97 (s, 4H, phenyl), 7.74 (br, 1H, central NH), 7.89 (br, 2H, peripheral NH).

Synthesis of 1

DDQ (111 mg, 0.49 mmol) was added to a solution of i1 (114 mg, 0.33 mmol) in 50 mL of CH2Cl2. The mixture was stirred at room temperature for 30 min and then directly purified by silica gel column (Eluent: CH2Cl2 : MeOH) to afford the crude product 1 which was recrystallized from CH2Cl2 and n-hexane (71 mg, yield: 63%). mp. 235-236 °C. IR νmax (KBr)/cm⁻¹: 3432, 3392, 3270, 2962, 1610, 1572, 1535, 1471, 1446, 1401, 1384, 1358, 1335, 1128, 1115, 1041, 1021, 986, 630, 579, 532. 1H NMR (DMSO-d6, Bruker 500 MHz, 298K): δ 1.26 (s, 18H, -C(CH3)3), 6.33-6.42 (m, 2H, pyrrolic), 6.44-6.52 (m, 2H, pyrrolic), 7.18-7.27 (m, 2H, pyrrolic), 7.36 (s, 2H, hemiquinone), 11.47 (s, 2H, -NH). 13C NMR (DMSO-d6, Bruker 75 MHz, 298K): δ 183.76, 143.59, 139.73, 132.34, 129.82, 125.29,
HRMS (ESI): calcd for C_{23}H_{29}N_{2}O [M]^+, 349.2280; found, 349.2273.

Synthesis of 2

DDQ (108 mg, 0.48 mmol) was added to a solution of i_2 (100 mg, 0.16 mmol) in 50 mL of CH_2Cl_2. The mixture was stirred at room temperature for 30 min and then directly purified by silica gel column (Eluent: PE : CH_2Cl_2). The crude product was further purified by another silica gel column (Eluent: PE : CH_2Cl_2 = 1 : 1, 1% Et_3N), and then recrystallized from methanol and water to afford the desired product 2 (61 mg, yield: 62%). mp. > 280 °C. IR \nu_{\text{max}} (KBr)/cm^{-1}: 3424, 2954, 1610, 1572, 1539, 1484, 1447, 1397, 1386, 1359, 1334, 1295, 1255, 1232, 1197, 1091, 1045, 987, 931, 881, 836, 739, 638, 534. ^1H NMR (DMSO-d_6, Bruker 500 MHz, 298K): \delta 1.26 (s, 18H, -C(CH_3)_{3}), 1.28 (s, 18H, -C(CH_3)_{3}), 6.40-6.43 (m, 2H, pyrrolic), 6.66 (m, 2H, pyrrolic), 6.75 (d, J = 2.0 Hz, 2H, pyrrolic), 7.29 (m, 2H, pyrrolic), 7.39 (d, J = 2.3 Hz, 2H, hemiquinone), 7.52 (d, J = 2.2 Hz, 2H, hemiquinone), 11.45 (s, 2H, peripheral NH), 11.81 (s, 1H, central NH). ^13C NMR (DMSO-d_6, Bruker 75 MHz, 298K): \delta 184.71, 145.14, 144.43, 138.35, 135.71, 133.02, 132.20, 130.36, 125.83, 124.77, 120.33, 119.57, 111.62, 35.40, 35.32, 29.79, 29.65. HRMS (ESI): calcd for C_{42}H_{52}N_{3}O_{2} [M]^+, 630.4060; found, 630.4066.

DFT calculations

Density functional theory (DFT) calculations were carried out by the Gaussian03 program,\(^1\) using the hybrid B3LYP functional and 6-31G(d) basis set. The geometries of mono- and di-deprotonated species, 2b and 2c (Fig. S9), were optimized in vacuum, and subsequent single point calculations as well as time-dependent density functional theory (TDDFT) calculations were performed with the polarizable continuum model (PCM)\(^2\) to take into account the solvent effect of DMSO. The results are presented in Table S1 and Fig. S9.

To gain insights of the isomerization behaviors of compound 1 and 2, density functional theory (DFT) calculations are also carried out by the Gaussian03 program, using the hybrid B3LYP functional and 6-31G(d) basis set. The geometries of compound 1 and 2 are optimized in vacuum, and subsequent single point calculations are performed with solvent effects taken into account by the polarizable continuum model (PCM), using CHCl_3 and DMSO as solvents, respectively. The energies are compared between isomers, and the energy differences are listed in Table S2.

References


Table S1. Calculated TDDFT excitation energies (eV, nm), oscillator strengths ($f$), and composition in terms of molecular orbital contributions

<table>
<thead>
<tr>
<th>Compound</th>
<th>State</th>
<th>Composition a</th>
<th>E(eV, nm)</th>
<th>$f$</th>
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<tbody>
<tr>
<td>2b</td>
<td>$S_1$</td>
<td>H$\rightarrow$L(83%)</td>
<td>1.72, 720.4</td>
<td>0.2539</td>
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<td>$S_2$</td>
<td>H1$\rightarrow$L(70%)</td>
<td>2.25, 552.2</td>
<td>0.9865</td>
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<tr>
<td>2c</td>
<td>$S_1$</td>
<td>H$\rightarrow$L(82%)</td>
<td>1.83, 675.9</td>
<td>0.4371</td>
</tr>
<tr>
<td></td>
<td>$S_2$</td>
<td>H1$\rightarrow$L(80%)</td>
<td>1.94, 638.3</td>
<td>0.2695</td>
</tr>
</tbody>
</table>

a H = HOMO, L = LUMO, H1 = HOMO-1.

Table S2. Calculated energy differences between the tautomeric isomers in various solvents (in kJ/mol)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$E_{1a} - E_1$</th>
<th>$E_{2a} - E_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum</td>
<td>4.75</td>
<td>-9.50</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>25.15</td>
<td>10.29</td>
</tr>
<tr>
<td>DMSO</td>
<td>34.49</td>
<td>20.59</td>
</tr>
</tbody>
</table>
Fig. S1. The $^1$H NMR spectrum of 1 in DMSO-$d_6$.

Fig. S2. The $^{13}$C NMR spectrum of 1 in DMSO-$d_6$.

Fig. S3. ESI HRMS of 1 in MeOH.
Fig. S4. The $^1$H NMR spectrum of 2 in DMSO-$d_6$ (Asterisks represent the peaks of methanol).

Fig. S5. The $^{13}$C NMR spectrum of 2 in DMSO-$d_6$.

Fig. S6. ESI-HRMS of 2 in MeOH.
Fig. S7. $^1$H NMR spectra of 1 (11.5 mM) with fluoride anion (TBA salt) in DMSO-$d_6$ (0-5 eq).

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Fig. S9. Calculated HOMO and LUMO levels for mono- and di-deprotonated species of 2.

Fig. S10. UV-vis spectral changes of 2 (10 μM in DMSO) observed upon the addition of anions. a) CN\(^-\), b) CH\(_3\)COO\(^-\), and c) H\(_2\)PO\(_4\)^\(^-\) (TBA salt).
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**Fig. S15** UV-vis spectral changes of 2 (10 μM in DMSO/H$_2$O (29:1, v/v)) observed upon addition of 100 eq. of various anions (TBA salt).
**Fig. S16.** (a) $^1$H NMR spectral changes of $1$ (11.5 mM) in CDCl$_3$ upon addition of DMSO-$d_6$, (b) the corresponding percentages of tautomeric isomers $1$ and $1a$ calculated from the ratio of related peak areas in the $^1$H NMR spectra, and (c) UV-vis spectral changes of $1$ (10 μM in CH$_2$Cl$_2$) upon addition of DMSO.

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Fig. S19. ¹H NMR spectrum change of 2 (6.4 mM) upon addition of TBACl (1 eq) in DMSO-d₆.