Supporting Information
Functionalized Guanidinium Chloride Based Colourimetric Sensors for Fluoride and Acetate: Single Crystal X-ray Structural Evidence of -NH Deprotonation and Complexation

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\[
y = 0.00373x + 0.05527
\]

\[
R^2 = 0.9867
\]

\[
\log K = 2.42
\]
**Figure S35.** a) UV-Vis absorption changes of the titration of a $1.0 \times 10^{-5}$ M solution of S2 in MeCN/DMF (9.6:0.4)(v/v) with a standard solution of 0.01(M) [Bu4N]F in MeCN. b) Absorbance changes for S2 at 514 nm on addition of various concentration of [Bu4N]F. c) Benesi–Hildebrand plot.

$$y = 0.02021x - 13.49295$$

$$R^2 = 0.98671$$

$$\log K = 1.69$$
Figure S36. a) UV-Vis absorption changes of the titration of a 1.0×10⁻⁵ M solution of S2 in MeCN/DMF(9.6:0.4)(v/v) with a standard solution of 0.01(M) [Bu₄N]AcO in MeCN. b) Absorbance changes for S2 at 428 nm on addition of various concentration of [Bu₄N]AcO. c) Benesi–Hildebrand plot.
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Mathematical expressions:

\[ y = 0.00601x - 0.41421 \]

\[ R^2 = 0.98876 \]

\[ \log K = 2.22 \]
Figure S38. a) UV-Vis absorption changes of the titration of a 1.0×10⁻⁵ M solution of S3 in MeCN/DMF(9.6:0.4)(v/v) with a standard solution of 0.01(M) [Bu₄N]F in MeCN. b) Absorbance changes for S3 at 600 nm on addition of various concentration of [Bu₄N]F in MeCN. c) Benesi–Hildebrand plot.

$$y = 0.000622x + 0.54754$$

$$R^2 = 0.98231$$

$$\log K = 3.20$$
**Figure S39.** a) UV-Vis absorption changes of the titration of a 1.0×10^{-5} M solution of S3 in MeCN/DMF (9.6:0.4)(v/v) with a standard solution of 0.01(M) [Bu₄N]AcO in MeCN. b) Absorbance changes for S3 at 478 nm on addition of various concentration of [Bu₄N]AcO. c) Benesi–Hildebrand plot.

\[ y = 0.000823x + 0.80247 \]

\[ R^2 = 0.99494 \]

\[ \log K = 3.08 \]
Figure S40. a) UV-Vis absorption changes of the titration of a 1.0×10^{-5} M solution of S3 in MeCN/DMF(9.6:0.4)(v/v) with a standard solution of 0.01(M) [Bu4N]H2PO4 in MeCN. b) Absorbance changes for S3 at 503 nm on addition of various concentration of [Bu4N]H2PO4. c) Benesi–Hildebrand plot.
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$A = \frac{(A_{\text{max}} - A_{\text{min}})}{(A - A_{\text{min}})}$

$R^2 = 0.98488$

$logK = 2.51$
Figure S42. a) UV-Vis absorption changes of the titration of a 1.0×10⁻⁵ M solution of S⁴ in MeCN/DMF (9.6:0.4)(v/v) with a standard solution of 0.01 (M) [Bu₄N]AcO in MeCN. b) Absorbance changes for S⁴ at 473 nm on addition of various concentration of [Bu₄N]AcO. c) Benesi–Hildebrand plot.
Figure S43. a) UV-Vis absorption changes of the titration of a 1.0×10^{-5} M solution of S6 in MeCN/DMF (9.6:0.4)(v/v) with a standard solution of 0.01 (M) [Bu_4N]F in MeCN. b) Absorbance changes for S6 at 468 nm on addition of various concentration of [Bu_4N]F. c) Benesi–Hildebrand plot.

\[ y = 0.000278x + 0.05107 \]
\[ R^2 = 0.98385 \]
\[ \log K = 4.55 \]
**Figure S44.** a) UV-Vis absorption changes of the titration of a 1.0×10^{-5} M solution of S6 in MeCN/DMF(9.6:0.4)(v/v) with a standard solution of 0.01(M) [Bu4N]AcO in MeCN. b) Absorbance changes for S6 at 468 nm on addition of various concentration of [Bu4N]AcO. c) Benesi–Hildebrand plot.

\[ y = 0.000728x + 0.54123 \]

\[ R^2 = 0.99515 \]

\[ \log K = 3.13 \]
Figure S45. a) UV-Vis absorption changes of the titration of a 1.0×10⁻⁵ M solution of S7 in MeCN/DMF(9.6:0.4)(v/v) with a standard solution of 0.01 (M) [Bu₄N]F in MeCN. b) Absorbance changes for S7 at 586 nm on addition of various concentration of [Bu₄N]F. c) Benesi–Hildebrand plot.
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$y = 0.00858x + 0.89378$

$R^2 = 0.99688$

$logK = 2.1$
Figure S47. a) UV-Vis absorption changes of the titration of a 1.0×10⁻⁵ M solution of S9 in MeCN/DMF (9.6:0.4)(v/v) with a standard solution of 0.01 (M) [Bu₄N]F in MeCN. b) Absorbance changes for S9 at 642 nm on addition of various concentration of [Bu₄N]F. c) Benesi–Hildebrand plot.

\[ y = 0.0000681x + 0.81418 \]
\[ R^2 = 0.98945 \]
\[ \log K = 4.17 \]
Figure S48. a) UV-Vis absorption changes of the titration of a 1.0×10^{-5} M solution of S9 in MeCN/DMF(9.6:0.4)(v/v) with a standard solution of 0.01 (M) [Bu4N]AcO in MeCN. b) Absorbance changes for S9 at 642 nm on addition of various concentration of [Bu4N]AcO. c) Benesi–Hildebrand plot.
Figure S49. a) UV-Vis absorption changes of the titration of a $1.0 \times 10^{-5}$ M solution of S9 in MeCN/DMF(9.6:0.4)(v/v) with a standard solution of 0.01 (M) [Bu4N]H2PO4 in MeCN. b) Absorbance changes for S9 at 441 nm on addition of various concentration of [Bu4N]H2PO4. c) Benesi–Hildebrand plot.
Figure S50. a) UV-Vis absorption changes of the titration of a $1.0 \times 10^{-5}$ M solution of S10 in MeCN/DMF(9.6:0.4)(v/v) with a standard solution of 0.01(M) $[\text{Bu}_4\text{N}]\text{F}$ in MeCN. b) Absorbance changes for S10 at 354 nm on addition of various concentration of $[\text{Bu}_4\text{N}]\text{F}$. c) Benesi–Hildebrand plot.
Table S1. Table of Crystallographic parameters

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<tr>
<th>Parameters</th>
<th>1</th>
<th>Complex 2</th>
<th>Complex 3</th>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>( \text{C}_{16} \text{H}<em>9 \text{F}</em>{10} \text{N}_5 \text{O} )</td>
<td>( \text{C}<em>{36} \text{H}</em>{22} \text{F}_{10} \text{N}_5 \text{O}_6 )</td>
<td>( \text{C}<em>{37} \text{H}</em>{31} \text{N}_5 \text{O}_4 )</td>
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<tr>
<td>Formula weight</td>
<td>477.28</td>
<td>810.59</td>
<td>609.67</td>
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<td>crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
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<tr>
<td>Space group</td>
<td>( \text{P}_2(1)/\text{n} )</td>
<td>( \text{P}_2(1)/\text{m} )</td>
<td>( \text{P}_{\text{bca}} )</td>
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<tr>
<td>( a ) (Å)</td>
<td>16.012(10)</td>
<td>6.8654(13)</td>
<td>14.5032(10)</td>
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<tr>
<td>( b ) (Å)</td>
<td>11.932(7)</td>
<td>34.567(6)</td>
<td>9.6882(7)</td>
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<td>( c ) (Å)</td>
<td>19.682(12)</td>
<td>7.1380(14)</td>
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<td>( \gamma ) (deg)</td>
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<td>( V ) (Å³)</td>
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<td>1675.1(5)</td>
<td>6255.7 (8)</td>
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<td>( Z )</td>
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<td>2</td>
<td>8</td>
</tr>
<tr>
<td>( d_{\text{calc}} ) (g/cm³)</td>
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<td>1.607</td>
<td>1.295</td>
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<td>Crystal size (mm³)</td>
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<td>0.15 x 0.09 x 0.08</td>
<td>0.18 x 0.03 x 0.02</td>
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<td>Diffractometer</td>
<td>Smart CCD</td>
<td>Smart CCD</td>
<td>Smart CCD</td>
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<tr>
<td>( F(000) )</td>
<td>1904</td>
<td>822</td>
<td>2560</td>
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<tr>
<td>( \mu ) (MoKα mm⁻¹)</td>
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<td>100 (2)</td>
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<td>( R_1; \text{WR}_2 )</td>
<td>0.0499 ; 0.1123</td>
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<td>GOF (( F^2 ))</td>
<td>1.022</td>
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Table S2. Hydrogen bonding interactions in 1.

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<th>D-H•••A</th>
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<th>D•••A(Å)</th>
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<tr>
<td>N9-H9···O42</td>
<td>0.843</td>
<td>1.944</td>
<td>2.766(5)</td>
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<tr>
<td>O44-H44···N12</td>
<td>0.800</td>
<td>2.042</td>
<td>2.807(6)</td>
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<tr>
<td>N29-H29···O44</td>
<td>0.895</td>
<td>1.914</td>
<td>2.790(6)</td>
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<tr>
<td>O42-H42···N32</td>
<td>0.850</td>
<td>1.982</td>
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Table S3. Hydrogen bonding interactions in Complex 2.

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<tbody>
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<td>N11-H11···O25</td>
<td>0.860</td>
<td>2.070</td>
<td>2.8623(18)</td>
<td>152.3</td>
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<tr>
<td>N9-H9···O17</td>
<td>0.860</td>
<td>1.930</td>
<td>2.7916(14)</td>
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<tr>
<td>O26-H26···O17</td>
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<td>1.810</td>
<td>2.6179(11)</td>
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Table S4. Hydrogen bonding interactions in Complex 3.

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<td>O3-H3X···O2</td>
<td>0.820</td>
<td>1.770</td>
<td>2.593(4)</td>
<td>175.40</td>
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<td>N2-H2A···O1</td>
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<td>1.930</td>
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<td>N3-H3A···O1</td>
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<td>2.240</td>
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<td>N3-H3B···O4</td>
<td>0.860</td>
<td>2.180</td>
<td>2.899(4)</td>
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<td>N4-H4A···O2</td>
<td>0.860</td>
<td>1.920</td>
<td>2.741(4)</td>
<td>158.90</td>
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</table>
Methods.

The binding constant values of anions with S1-S10 have been determined from the absorption data following the modified Benesi–Hildebrand equation.

\[
\frac{1}{\Delta A} = \frac{1}{\Delta A_{\text{max}}} + \left(\frac{1}{K[\text{Anion}]}\right)\left(\frac{1}{\Delta A_{\text{max}}}\right).
\]

Here, \(\Delta A = A - A_{\text{min}}\), \(\Delta A_{\text{max}} = A_{\text{max}} - A_{\text{min}}\).

Where, \(A_{\text{min}}, A, A_{\text{max}}\) are the absorption of S1-S10 considered in the absence of anions, at an intermediate, and at a concentration of complete concentration.

\(K\) is Binding constant, \([\text{Anion}]\) is concentration of anion.

From the Plot of \((A_{\text{max}} - A_{\text{min}})/(A - A_{\text{min}})\) against \([\text{Anion}]\) for S1-S10, the value of \(K (\pm 10\%)\) extracted from the slope.

References


(5) Mercury 2.2 supplied with Cambridge Structural Database, CCDC, Cambridge, UK.