Electronic Supplementary Material (ESI) for Chemical Communications

Benzobisoxazole fluorophore vicariously senses amines, ureas, and anions

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Supporting Information

General Methods

Amines, ureas, and tetrabutylammonium salts were purchased from commercial suppliers and used without further purification, with the exception of tetrabutylammonium benzoate, which was prepared according to literature procedure.[S1] Reagent-grade solvents were used as received. Cruciform **1** was prepared according to literature procedure.[S2]

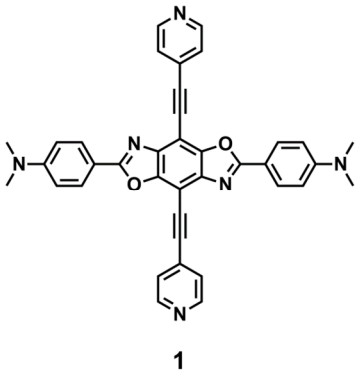

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Figure S1. Cruciform **1**.

Photographs of emission colors were taken using a FujiFilm FinePix S9000 digital camera, with a shutter speed of 0.5 s. A handheld UVLS-28 EL series UV lamp ($\lambda_{excitation}$ = 365 nm) was used as the light source. All photographs were taken in a dark windowless room, with a 45 cm (18 in) distance between the sample cuvettes and the camera lens. A photograph and the schematics of the photography setup are shown in Figure S2.[S3]

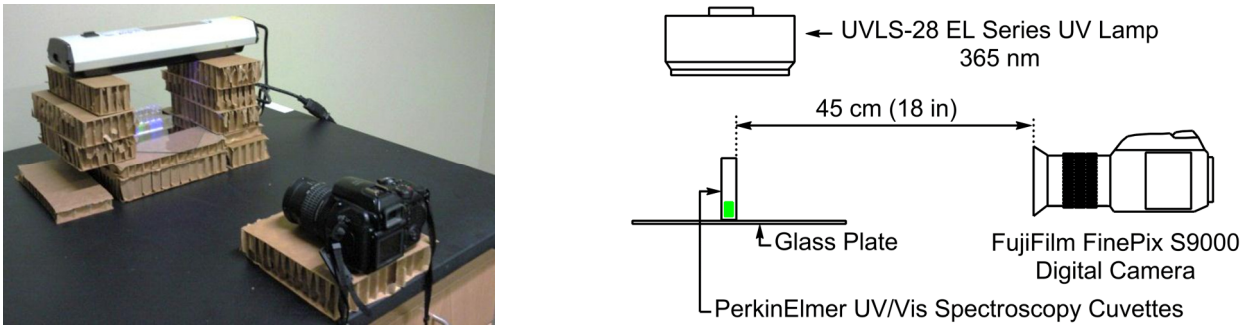

Figure S2. Darkroom setup for taking emission color photographs.

Experiments are presented in the order that follows the discussion of the manuscript.

Compound numbers are identical to those in the main text of the manuscript.

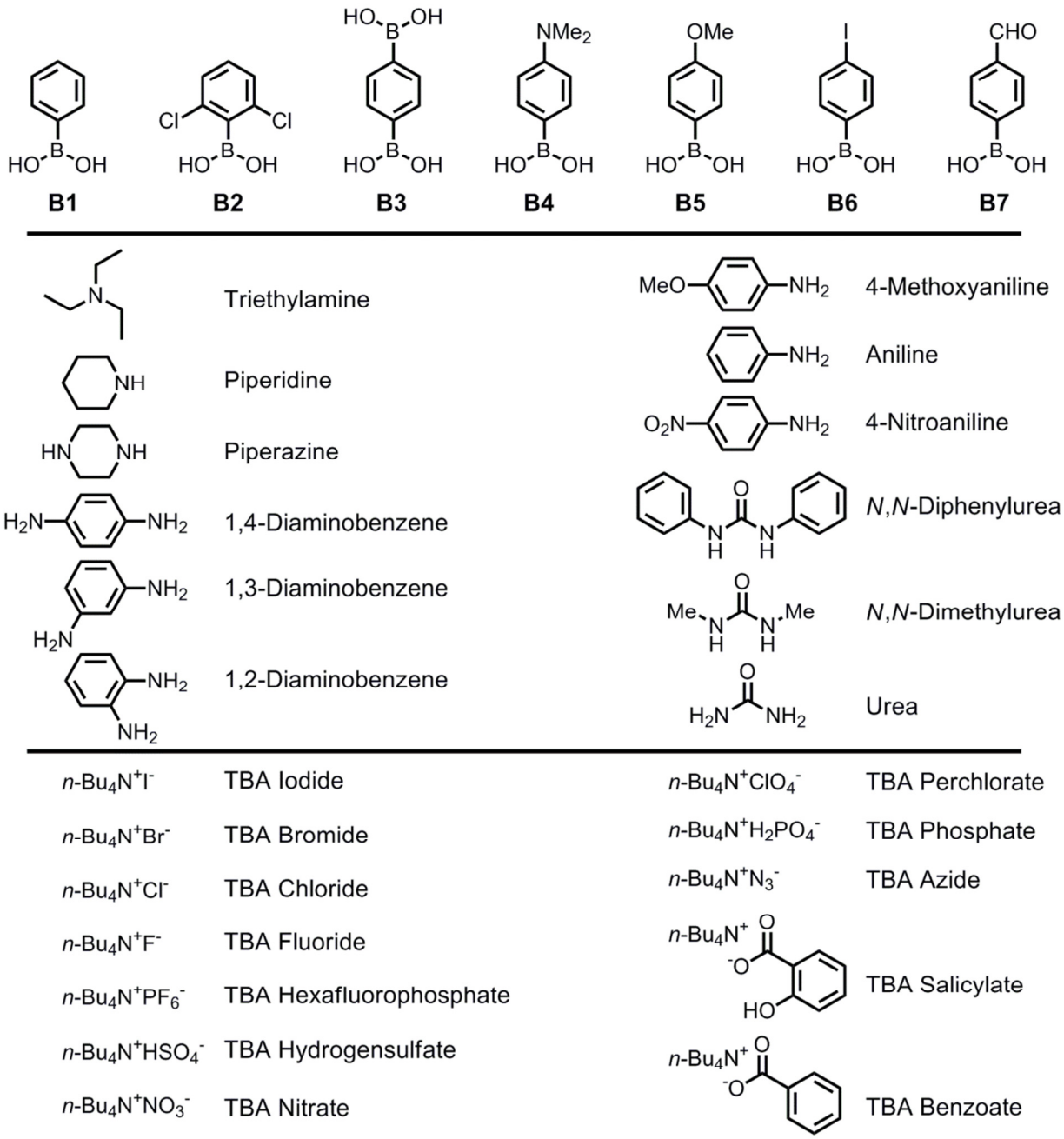

Figure S3. Cruciform **1** was used in combination with boronic acids **B1**–**B7** (top), to identify twelve organic nitrogen compounds (middle) and twelve tetrabutylammonium salts of small organic and inorganic anions (bottom).

Discrimination of Amines and Ureas Using Cruciform 1 and Boronic Acid Additives: Boronic Acid Variation

Seven solutions of cruciform **1**/boronic acids **B1**–**B7** were prepared by dissolving phenylboronic acid (**B1**, 145 mg, 1.2 mmol), 2,6-dichlorophenylboronic acid (**B2**, 229 mg, 1.2 mmol), 1,4-benzenediboronic acid (**B3**, 199 mg, 1.2 mmol), 4-(*N*,*N*-dimethylamino)phenylboronic acid (**B4**, 198 mg, 1.2 mmol), 4-methoxyphenylboronic acid (**B5**, 182 mg, 1.2 mmol), 4-iodophenylboronic acid (**B6**, 297 mg, 1.2 mmol) or 4-formylbenzeneboronic acid (**B7**, 180 mg, 1.2 mmol) in 60 mL aliquots of 1.0×10^{-6} M solution of cruciform **1** in 1,2,4-trichlorobenzene (TCB).

Each of the cruciform/boronic acid solutions was used immediately after the preparation to dissolve seven samples of 40 mg each of amines and ureas (Figure S3, middle). For each analyte, aliquots of the seven prepared analyte/boronic acid/**1** solutions were transferred to a set of seven quartz cuvettes. These seven cuvettes were placed on a glass plate, irradiated at 365 nm by a

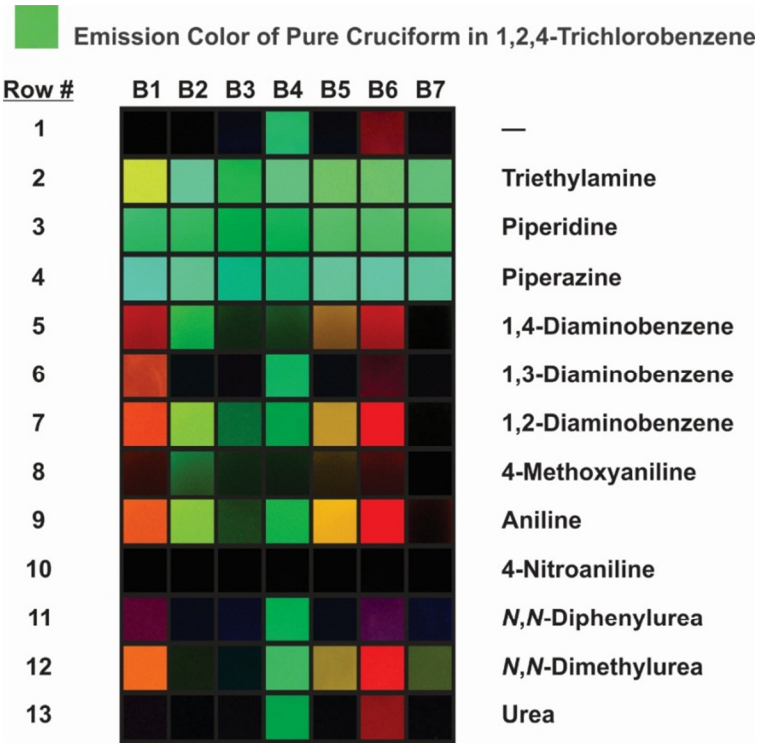

Figure S4. Panels with the photographs of the emission colors observed when the solutions of cruciform **1** with boronic acids **B1**–**B7** in TCB were exposed to amines and ureas.

handheld UV lamp, and immediately photographed (Figure S4).

Discrimination of Amines and Ureas Using Cruciform 1 and Boronic Acid Additives: Solvent Variation

Each of the examined amines and ureas was treated with ten separate sensing solutions.

First five solutions were prepared by dissolving phenylboronic acid (**B1**, 97.6 mg, 0.80 mmol) in 40 mL of 1.0×10^{-6} M solutions of cruciform **1** in acetonitrile (AN), 1,2,4-trichlorobenzene (TCB), cyclohexane (CH), dichloromethane (DCM) and chloroform (CF). Second five solutions were prepared by dissolving 2,6-dichlorophenylboronic acid (**B2**, 152.6 mg, 0.80 mmol) in 40 mL of 1.0×10^{-6} M solutions of cruciform **1** in AN, TCB, CH, DCM and CF. In each of these ten sensor solutions, the molar ratio between the boronic acid and cruciform **1** was 20,000 : 1.

Immediately after the preparation, 2 mL of each of the sensing solutions was used to dissolve

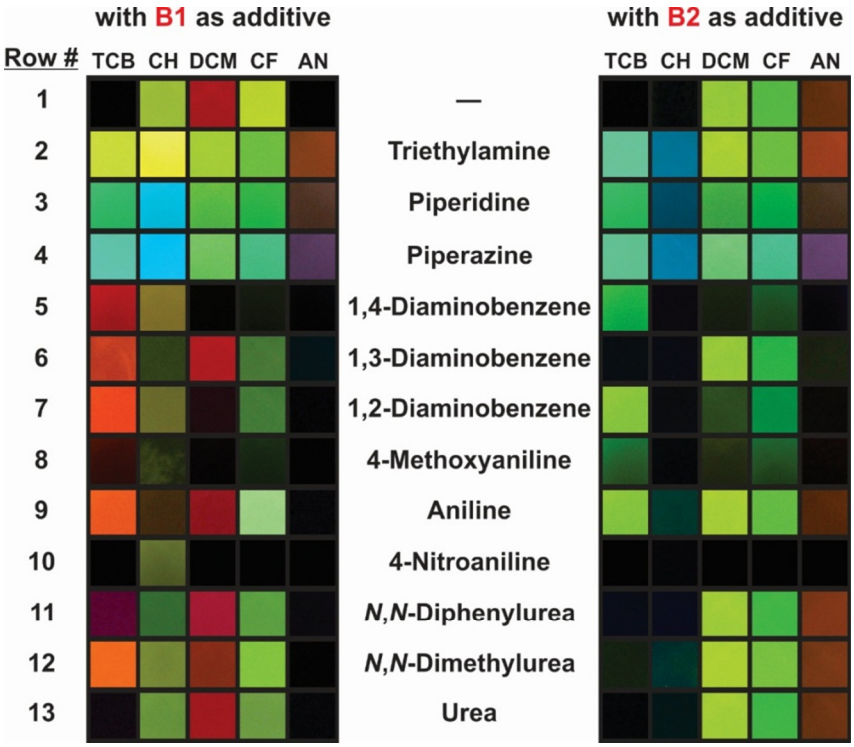

Figure S5. Panels with the photographs of the emission colors observed when the solutions of cruciform **1** in combination with **B1** (left) and **B2** (right) were exposed to amines and ureas, and irradiated at 365 nm.

ten samples of 40 mg each of amines and ureas shown in Figure S3, middle. The final molar ratios of amine (or urea) : boronic acid : **1** varied between ~333,000 : 20,000 : 1 and ~94,000 : 20,000 : 1.

For each analyte, aliquots of the ten prepared analyte/boronic acid/**1** solutions were transferred to separate quartz cuvettes. These two five-cuvette sets (one for **1**/**B1**, one for **1**/**B2**) were placed on a glass plate, irradiated at 365 nm by a handheld UV lamp, and immediately photographed (Figure S5).

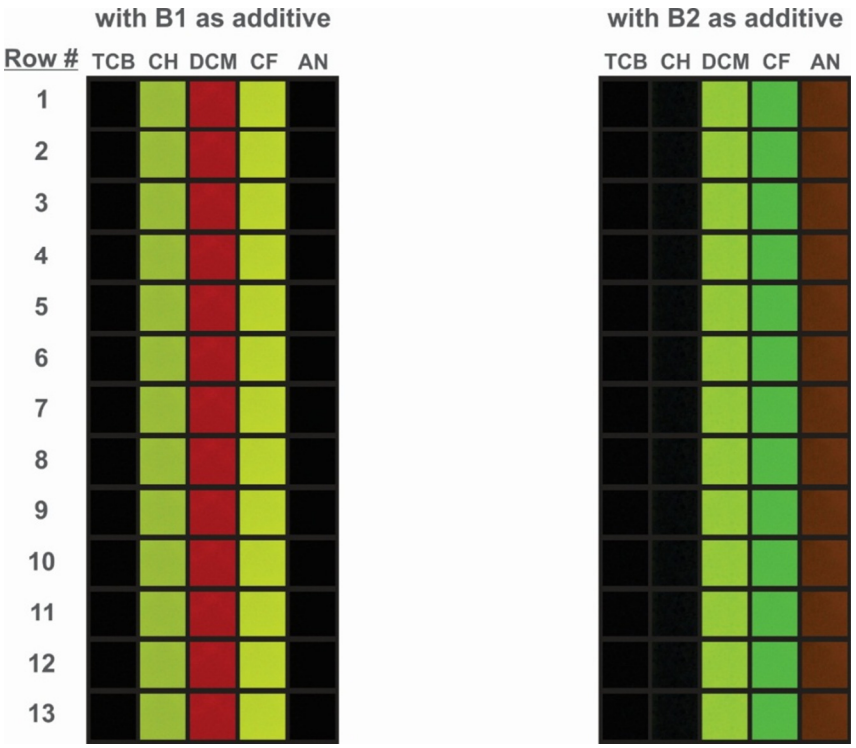

Figure S6. Mask image for both Figure S5 and Figure S11 in which each row has only emission colors of the solutions of cruciform **1** with boronic acids **B1** (left) and **B2** (right).

Calculation of RGB Changes

Numeric values for R(ed), G(reen), and B(lue) colors were extracted from the emission color panels using freely downloadable program Colour Contrast Analyzer.[S4] These values were extracted for each analyte in each solvent, and were then statistically treated and compared to other analytes and the blank solutions of **1**/**B1** or **1**/**B2** using Microsoft Excel.

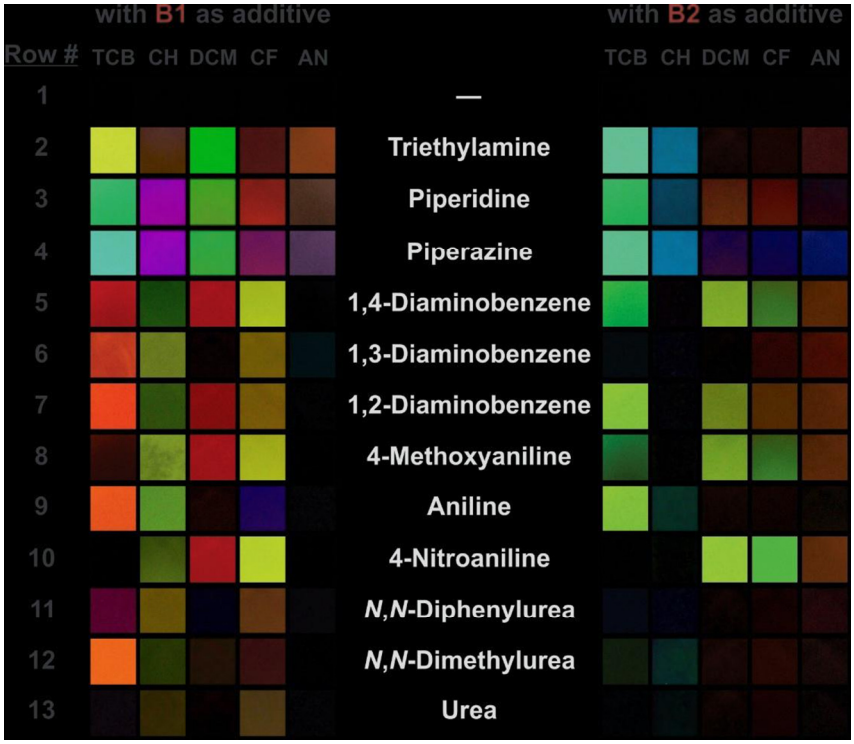

Figure S7. The difference image between Figure S5 and Figure S6, generated using image manipulation program *ImageJ*.[S5] Command: *Process* > *Image Calculator* > *Difference*.

To evaluate the correlation between the R/G/B values of different analytes within the same compound class, we also calculated relative standard deviations σ. For arbitrary compounds **X** and **Y**, this $\sigma_{\mathbf{X@Y}}$ was defined as:

$$\sigma'_{X@Y} = \sqrt{\frac{\sum_{solvent}^{i}(R_X - R_Y)^2 + (G_X - G_Y)^2 + (B_X - B_Y)^2}{3 * i}}.$$

Importantly, these relative standard deviations are not solvent-specific, as they statistically treat R/G/B differences across all examined solvents. Thus, a single number—plotted in the graphs in Figure S8 (for amine and urea analytes) and Figure S13 (for anionic analytes)—describes a difference between the two analytes.

Discrimination of Anions Using Cruciform 1 and Boronic Acid Additives: Boronic Acid Variation

Seven solutions of cruciform **1**/boronic acids **B1**–**B7** were prepared by dissolving phenylboronic acid (**B1**, 145 mg, 1.2 mmol), 2,6-dichlorophenylboronic acid (**B2**, 229 mg, 1.2

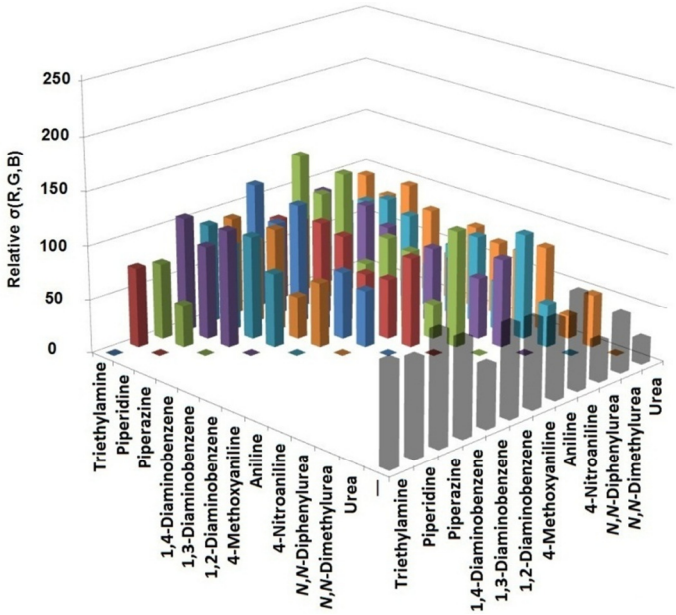

Figure S8. Standard deviations (σ) of *R*/*G*/*B* values (summed over five solvents) for amines and ureas, relative to other analytes. The semitransparent bars marked with "—" indicate standard deviations relative to the blank. Maximum possible value of σ is 255.

mmol), 1,4-benzenediboronic acid (**B3**, 199 mg, 1.2 mmol), 4-(*N*,*N*-dimethylamino) phenylboronic acid (**B4**, 198 mg, 1.2 mmol), 4-methoxyphenylboronic acid (**B5**, 182 mg, 1.2 mmol), 4-iodophenylboronic acid (**B6**, 297 mg, 1.2 mmol) or 4-formylbenzeneboronic acid (**B7**, 180 mg, 1.2 mmol) in 60 mL of 1.0×10^{-6} M solutions of cruciform **1** in 1,2,4-trichlorobenzene (TCB).

Each of the cruciform/boronic acid solutions was used immediately after the preparation to dissolve seven samples of 40 mg each of anions shown in Figure S3, bottom. For each analyte, aliquots of the seven prepared analyte/boronic acid/**1** solutions were transferred to a set of seven quartz cuvettes. These seven cuvettes were placed on a glass plate, irradiated at 365 nm by a handheld UV lamp, and immediately photographed (Figure S10).

Discrimination of Anions Using Cruciform 1 and Boronic Acid Additives: Solvent Variation

Each of the examined anions was treated with ten separate sensing solutions.

First five solutions were prepared by dissolving phenylboronic acid (**B1**, 97.6 mg, 0.80 mmol) in 40 mL of 1.0×10^{-6} M solutions of cruciform **1** in AN, TCB, CH, DCM and CF. Second five

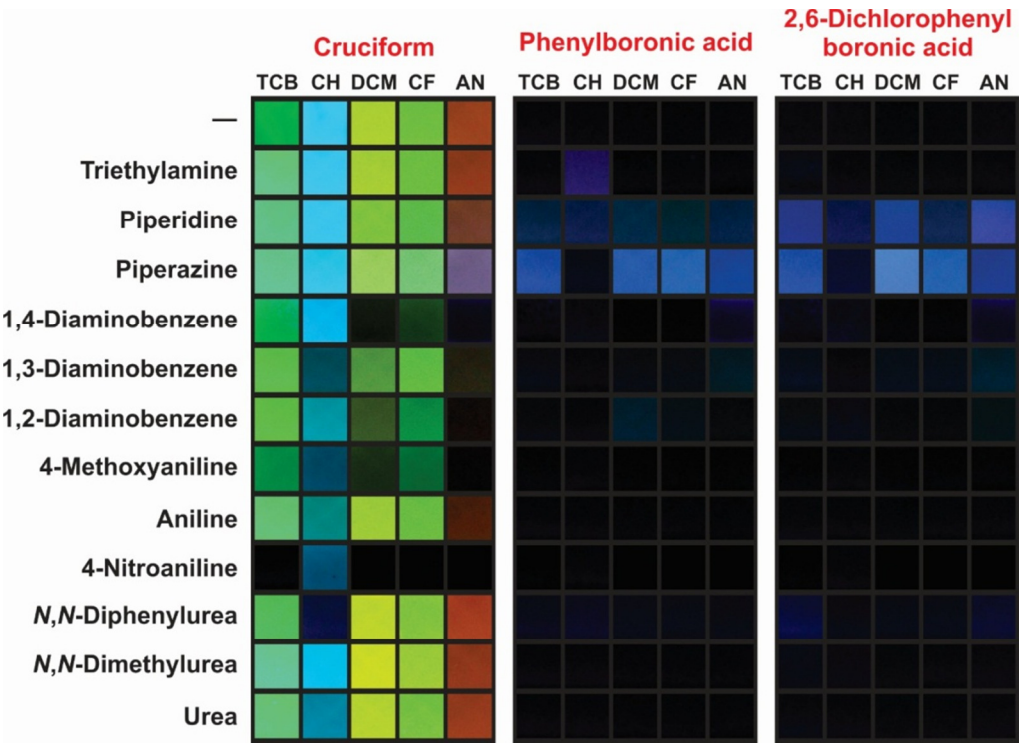

Figure S9. In three control experiments, amine and urea analytes were exposed to the solutions of only cruciform **1** (no boronic acids, left), only **B1** (no cruciform, middle) or only **B2** (no cruciform, right). The photographic workup was the same as in the above described experiments.

solutions were prepared by dissolving 2,6-dichlorophenylboronic acid (**B2**, 152.6 mg, 0.80 mmol) in 40 mL of 1.0×10^{-6} M solutions of cruciform **1** in AN, TCB, CH, DCM and CF. In each of these ten solutions, the molar ratio between the boronic acid and cruciform **1** was 20,000 : 1.

Immediately after the preparation, 2 mL of each of the sensing solutions was used to dissolve ten samples of 40 mg each of anions shown in Figure S3, bottom. The final molar ratios of amine/urea : boronic acid : **1** varied between ~76,500 : 20,000 : 1 and ~51,600 : 20,000 : 1.

For each analyte, aliquots of the ten prepared analyte/boronic acid/**1** solutions were transferred to separate quartz cuvettes. These two five-cuvette sets (one for **1**/**B1**, one for **1**/**B2**) were placed on a glass plate, irradiated at 365 nm by a handheld UV lamp, and immediately photographed (Figure S11).

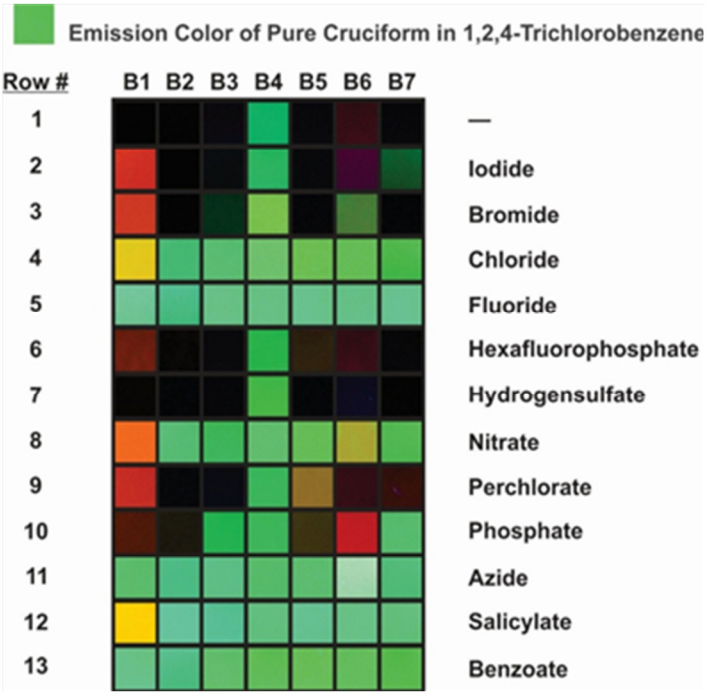

Figure S10. Panels with the photographs of the emission colors observed when the solutions of cruciform **1** with boronic acids **B1**–**B7** in TCB were exposed to anions, and irradiated at 365 nm.

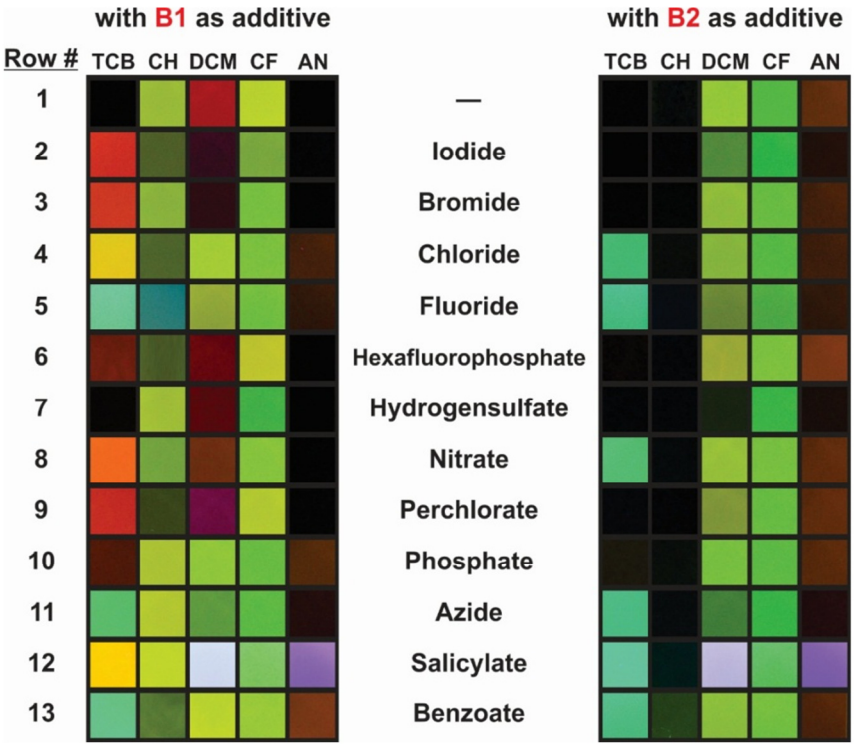

Figure S11. Panels with the photographs of the emission colors observed when the solutions of cruciform **1** and boronic acids **B1** (left) and **B2** (right) were exposed to the TBA salts of the corresponding anions, and irradiated at 365 nm.

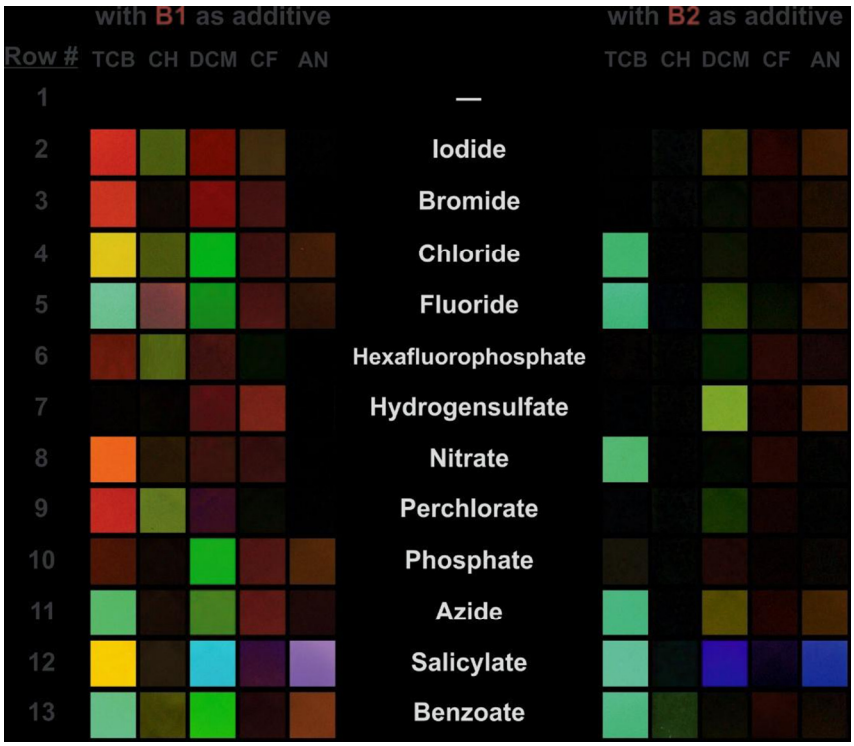

Figure S12. The difference image between Figure S11 and Figure S6, generated using image manipulation program *ImageJ*.[S5] Command: *Process* > *Image Calculator* > *Difference*.

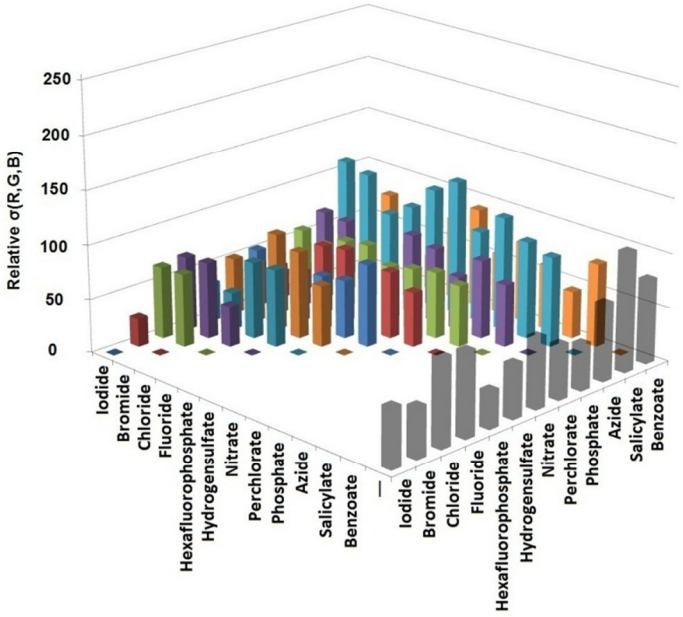

Figure S13. Standard deviations (σ) of *R*/*G*/*B* values for anions (summed over five solvents), relative to other analytes. The semitransparent bars marked with "—" indicate standard deviations relative to the blank. Maximum possible value of σ is 255.

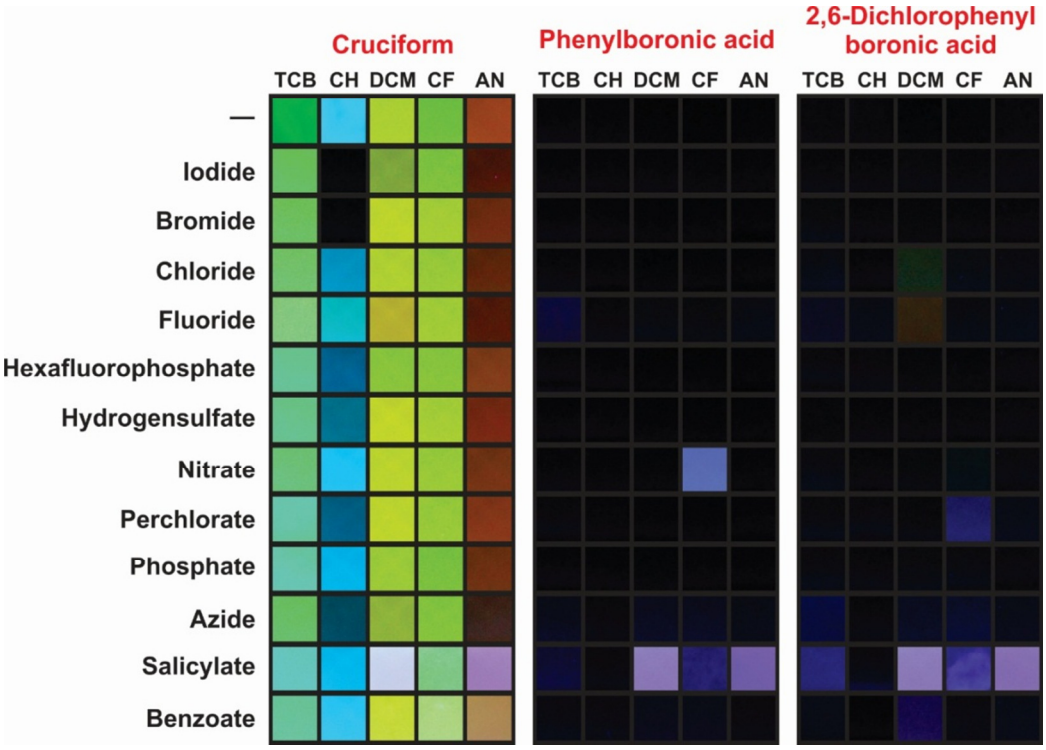

Figure S14. In three control experiments, anionic analytes were exposed to the solutions of only cruciform **1** (no boronic acids, left), only **B1** (no cruciform, middle) or only **B2** (no cruciform, right). The photographic workup was the same as in the above described experiments.

Fluorescence Titration of a Mixture of 1 and B1 with TBACl

A Perkin-Elmer Fluorescence Spectrometer LS-55 was used for the fluorescence titration of a solution of **1** and **B1** with TBACl. The concentration of cruciform **1** in the titrated solution was about 1.0×10^{-7} M, and the ratio of **1** : **B1** was 20,000 : 1.

To prepare 0.01 M stock solution of TBACl in TCB, TBACl (278 mg, 1.00 mmol) was added to TCB (30 mL) in 100 mL volumetric flask, and then the flask was filled with additional TCB to the graduation. Ten-, hundred-, and thousand-fold diluted solutions of the stock solution, 1.0×10^{-3} M, 1.0×10^{-4} M, and 1.0×10^{-5} M, were also prepared.

A quartz cuvette with the maximum volume of 4 mL was filled with 3 mL of 1.0×10^{-7} M solution of **1** in TCB to select the excitation and emission slit widths, and to see the emission intensity. After taking the emission spectrum of the solution of cruciform **1**, the cuvette was filled with 3 mL of **1**/**B1** solution, and then treated with volumes of TBACl solutions shown in Figure

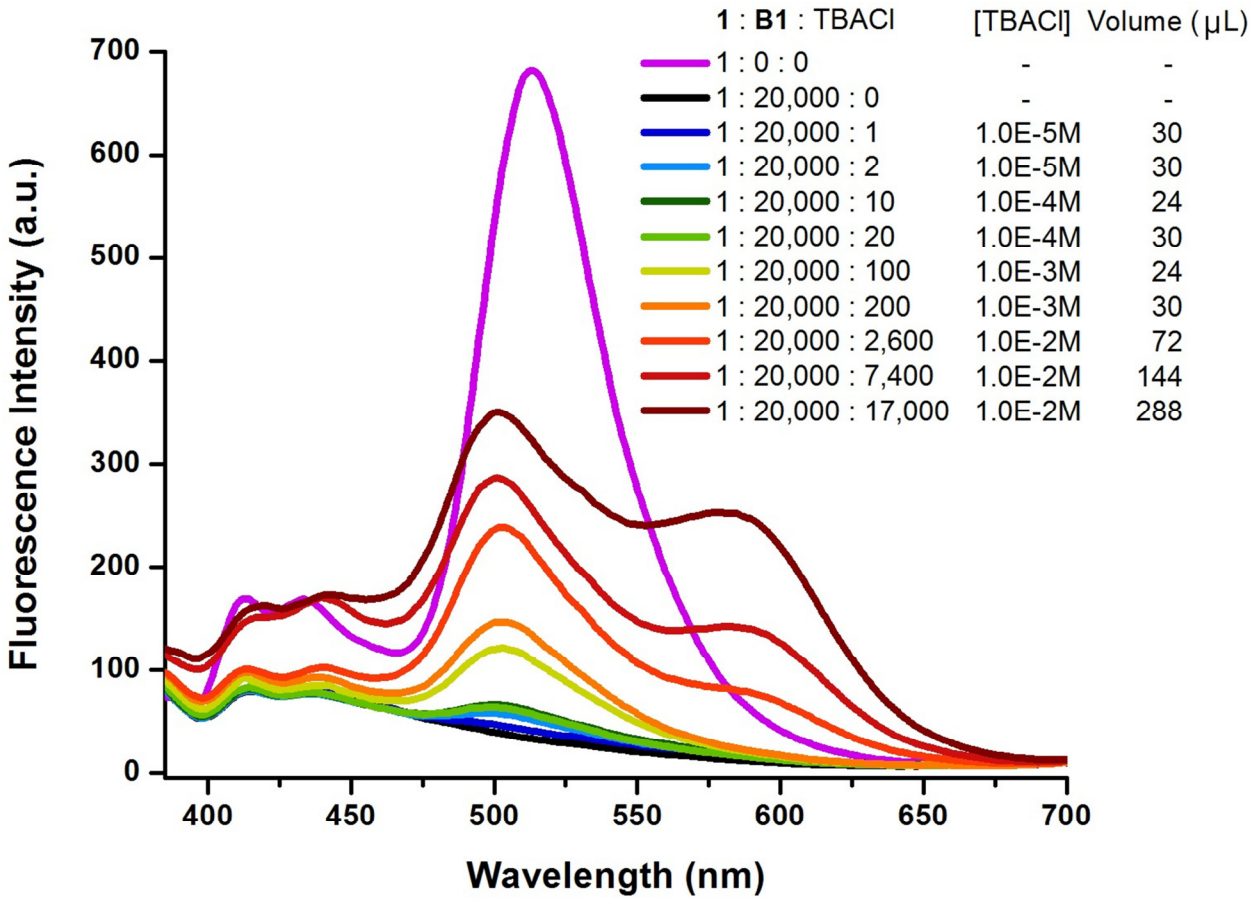

Figure S15. Fluorescence emission spectra for the titration of solution of **1**/**B1** in TCB with a concentrated solution of TBACl. Excitation wavelength is 365 nm, excitation slit width is 10 nm, and emission slit width is 10 nm.

S15 with a micro syringe. Because the ratio of added TBACl ranged from 1 to 17,000 equivalents (relative to **1**), four different stock solutions of TBACl, with progressively higher concentrations had to be used. These concentrations and volumes are indicated in the legend to Figure S15.

References

(S1) T. Wang, H.-F. Wang and X.-P. Yan, *CrystEngComm*, 2010, **12**, 3177–3182.

(S2) J. Lim, T. A. Albright, B. R. Martin and O. Š. Miljanić, *J. Org. Chem.*, 2011, **76**, 10207–10219.

(S3) A detailed description of our photographic workup and the analysis of R/G/B values can

be found in: (*a*) J. Lim, D. Nam and O. Š. Miljanić, *Chem. Sci.*, 2012, **3**, 559–563, and its Supporting Information. See also: (*b*) E. A. Davey, A. J. Zucchero, O. Trapp and U. H. F. Bunz, *J. Am. Chem. Soc.*, 2011, **133**, 7716–7718.

(S4) Colour Contrast Analyzer can be freely downloaded from: http://www.visionaustralia.org.au/info.aspx?page=628.

(S5) ImageJ can be freely downloaded from: http://rsbweb.nih.gov/ij/download.html.