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EDGE ARTICLE

Identification of carboxylic and organoboronic acids and phenols with a single benzobisoxazole fluorophore†

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The fluorescence of a single donor–acceptor benzobisoxazole-based cruciform, dissolved in five different solvents, dramatically changes upon exposure to Brønsted and Lewis acids. The changes in emission colors strongly depend on the analyte's structure, and this cruciform can discern among structurally closely related carboxylic (twelve examples) and organoboronic acids (nine examples). In combination with two commercially available phenylboronic acids, this cruciform sensor also distinguishes among substituted phenols (twelve examples).

Direct identification of acidic organic compounds—carboxylic and organoboronic acids, as well as phenols—is a significant analytical challenge. Their high polarity, low volatility, and tendency towards dehydration generally necessitate derivatization prior to chromatographic or distillative analysis.[1] At the same time, the ubiquity of these three classes of analytes requires reliable methods for their qualitative and quantitative analysis. Qualitative identification of compounds with closely related structures[2] is of tremendous importance in the identification of counterfeited, decomposed, or otherwise compromised pharmaceuticals, food additives, and alcoholic beverages. Carboxylic acids and phenols, as well as their derivatives, are commonly found in all of these consumer products. A 2010 US compilation lists 23 carboxylic acids and 33 phenols among the top-200 brand-name drugs—including six among the top-ten prescribed drugs![3] Carboxylic acids and their esters are also trace ingredients in foods and alcoholic beverages,[4] while phenols play hugely important roles in the industrial syntheses of dyes, pesticides, disinfectants, flavors, fragrances, and explosives.[5] First organoboronic acids are being commercialized as drugs[6]—including Bortezomib, a chemotherapy agent—again raising potential counterfeiting concerns. The use of boronic acids in numerous coupling reactions also requires analytical methods adapted to follow their consumption, especially since their thin-layer chromatography is challenging. Barder and Buchwald recently reported a fluorescence-based method for following the consumption of boronic acids during coupling reactions.[7] Organoboronic acids are additionally important as sensors for sugars[8] and other analytes,[9] and precursors to porous covalent-organic frameworks (COFs).[10]

An ability to distinguish multiple analytes using a single sensor is an optimal union of chemical synthesis and analysis, as important information can be obtained without a large expense of time and material associated with the preparation of multiple sensors. A promising class of general sensors is based on the cruciform-shaped conjugated molecules which localize their highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO) on different portions of the molecule. Analyte binding to such systems invariably alters the HOMO–LUMO gap and leads to a change in their optical properties. This phenomenon had been extensively studied by Bunz[11] and Haley,[12] who demonstrated that both protons and transition metal ions cause measurable changes in the fluorescence of these cruciforms. Very recently, Bunz has shown that the fluorescent response of distyrylbis(arylethynyl)benzene cruciforms to protonation strongly depends on the nature of the carboxylic acid.[11a] A battery of three closely related sensors (in six different solvents) was sufficient to unambiguously identify ten carboxylic acids with similar pK_a values and closely related structures.

Recently, our group[13] developed benzobisoxazole cruciforms such as **1** (Fig. 1) as a new class of compounds with spatially separated frontier molecular orbitals. In **1**, the HOMO is positioned along the donor-substituted horizontal axis, while the LUMO resides along the electron-poor vertical axis. In this Edge Article, we show that cruciform fluorophore **1** represents a remarkably versatile sensor which can distinguish among twelve carboxylic acids **C1–C12** (Fig. 2, top left) and among nine organoboronic acids **B1–B9** (Fig. 3, top left). We also demonstrate that a hybrid fluorescent sensor system—constructed by combining **1** with simple phenylboronic acids **B1** and **B5**—can discriminate among weakly acidic phenols **P1–P12** (Fig. 6, center).

Rapid identification of the desired analytes was achieved using digital photography of emission colors, rather than exhaustive fluorescence spectroscopy. In our first series of experiments,

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† Electronic supplementary information (ESI) available: statistical analysis (Excel spreadsheet) of the observed R/G/B values for all analytes; a detailed description of data collection and analysis, including images of emission colors for all reported analytes and several additional acids. See DOI: 10.1039/c1sc00610j

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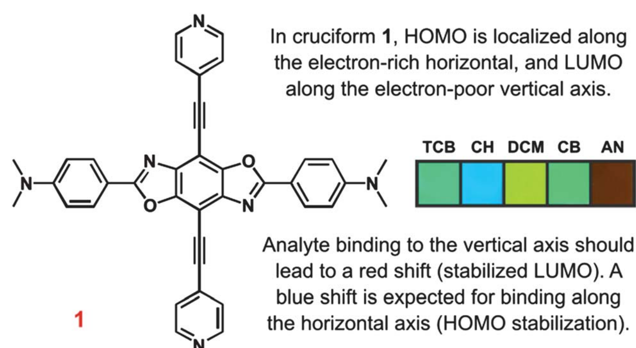
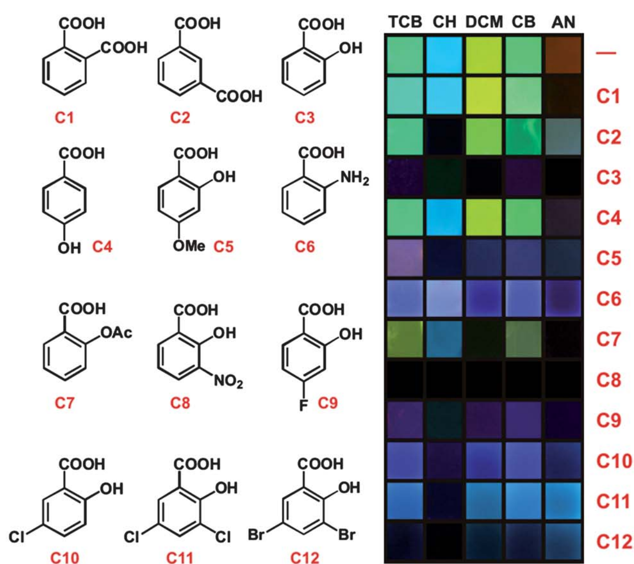


Fig. 1 Cruciform **1** is the fluorescent sensor used in this study. The panel on the right shows emission colors of **1** in various solvents (see text for solvent abbreviations; $\lambda_{excitation}$ = 365 nm; shutter speed 0.5 s).



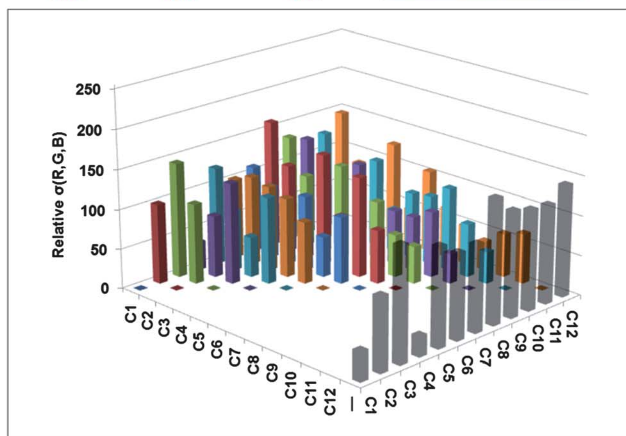
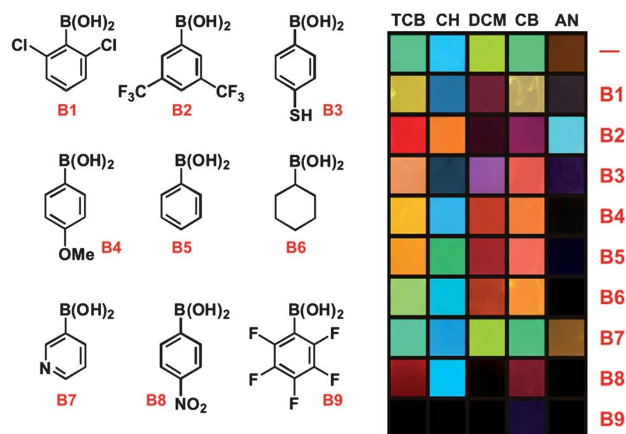


Fig. 2 Identification of substituted benzoic acids **C1–C12** (top left) using cruciform **1**. Emission colors of **1** upon exposure to excess analytes are shown in the top right panel ($\lambda_{excitation}$ = 365 nm; shutter speed 0.5 s). On the bottom, the correlation diagram shows standard deviations of *R*/*G*/*B* values for **C1–C12** (summed over five solvents), relative to all other analytes. The semi-transparent bars in the row marked with "—" indicate standard deviations relative to the blank solution of **1**, summed over all five solvents.



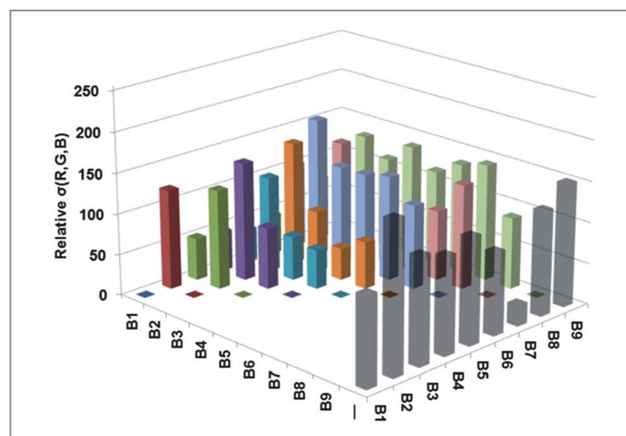


Fig. 3 Identification of boronic acids **B1–B9** (top left) using cruciform **1**. Emission colors of **1** upon exposure to excess analytes are shown in the top right panel ($\lambda_{excitation}$ = 365 nm; shutter speed 0.5 s). On the bottom, the correlation diagram shows standard deviations of *R*/*G*/*B* values for analytes **B1–B9** (summed over five solvents), relative to all other analytes. The semi-transparent bars in the row marked with "—" indicate standard deviations relative to the blank solution of **1**, summed over all five solvents.

substituted benzoic acids **C1–C12** were examined using the methodology developed by Bunz.[11a] Each of the analytes was dissolved in five solvents: 1,2,4-trichlorobenzene (TCB), cyclohexane (CH), dichloromethane (DCM), chlorobenzene (CB), and acetonitrile (AN), at concentrations of ~17 g L^{-1}. To 1.8 mL of each such solution, 20 μL of a dilute stock solution of **1** (1.0 × 10^{-4} M in DCM) was added, resulting in a very large molar excess of the analyte relative to **1**. In a darkened room, the mixture was illuminated by a handheld UV lamp (365 nm) in a 10 × 10 mm quartz cuvette, and a photo was taken using FujiFilm FinePix S9000 digital camera (shutter speed: 0.5 s). From each photo, square segments representative of emission colors were cut out using Adobe PhotoShop, and the squares were arranged into the panels shown in Fig. 2 (top right).

Even a cursory examination of the panel of emission colors in Fig. 2 shows dramatic differences among the studied analytes, as no two compounds have the same emission color in all five examined solvents. In general, exposure of **1** to carboxylic acids **C1–C12** resulted in blue shifts in its emission. In light of our previous work on **1**, this observation suggests that the initial protonation occurs at pyridine (red shift), but that excess acid ultimately also protonates the dimethylamino group, leading to

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a more pronounced blue shift. Analytes **C3** and **C8** lead to almost complete quenching of fluorescence of **1** in all solvents. Quenching of fluorescence by salicylic acid (**C3**) had been precedented;[14] in the case of electron-poor nitrosalicylic acid **C8**, we ascribe the quenching to the electron-transfer from the charge-separated excited state of **1** onto **C8** as a good acceptor.[15]

Next, we put these "obvious" distinctions on quantitative footing. Emission colors were converted into numerical values using Colour Contrast Analyzer[16] software, which extracted *R*(ed), *G*(reen), and *B*(lue) values for each individual acid in each of the five solvents. Thus, every analyte was initially assigned 15 numbers: *R*, *G*, and *B* values for each of the 5 solvents. For each compound–solvent combination, we obtained a standard deviation (σ)[17] of that compound's *R*/*G*/*B* values from the corresponding values for the blank solution of **1**. For example, $\sigma_{\mathbf{C1}@\mathrm{AN}}$—which characterizes acid **C1** in AN, is derived as:

$$\sigma_{C1@AN} = \sqrt{\frac{(R_{C1}^{AN} - R_1^{AN})^2 + (G_{C1}^{AN} - G_1^{AN})^2 + (B_{C1}^{AN} - B_1^{AN})^2}{3}} \quad (1)$$

where $R_{\mathrm{C1}}^{\mathrm{AN}}$and R_1^{AN}represent *R*-values for **1** + **C1** and **1** in AN, respectively (and analogously for *G* and *B* values).

We observed no statistically significant correlation between the pK_a values[18] of **C1–C12** and their σ values in any of the five examined solvents. Interestingly, such a correlation was also absent within the subset of substituted salicylic acids **C3**, **C5**, and **C8–C12**, even though σ values for this subset were clustered away from all other examined acids in both DCM (145.44–171.59) and CH (154.43–184.17).

Judicious statistical evaluation of differences in emission colors among individual acids was performed, with the aim of establishing whether this method can be used to distinguish them. Thus, for each combination of two carboxylic acids, we calculated relative standard deviations σ' defined as, for the example of **C1** *vs.* **C2**:

$$\sigma'_{C1@C2} = \sqrt{\frac{\sum_{solv}^{i}(R_{C1} - R_{C2})^2 + (G_{C1} - G_{C2})^2 + (B_{C1} - B_{C2})^2}{3*i}} \quad (2)$$

Each such number defines the relationship between two acids across all examined solvents. These relative standard deviations are plotted in the bottom part of Fig. 2. To highlight the distinction between individual analytes and the blank sample of **1**, we also plotted those standard deviations in the row of semi-transparent value bars marked with "—". This graph suggests that all the investigated analytes can be distinguished from each other and from the blank solution of **1**, as the correlation value drops to zero only for the auto-correlation data points.

Organoboronic acids **B1–B9** (Fig. 3, top left) were examined next, using the same methodology as for the carboxylic acids. Again, very dramatic changes in fluorescence emission colors were observed (Fig. 3, top right). In the majority of cases, emission colors were red-shifted, suggesting dominant stabilization of the LUMO through a stronger pyridine–boron interaction. ^{1}H NMR spectroscopic titration of **1** with **B5** confirmed this hypothesis, as dramatic shifts in the pyridine signals of **1** occurred first, and were followed by shifts in the signals of the 4-(dimethylamino)phenyl group at significantly higher concentrations of **B5**. While all nine boronic acids can be distinguished from each other, emission of the **1**/**B7** combination is not sufficiently different from the emission of pure **1**—presumably because the pyridine moiety of **B7** (which is in excess) replaces the pyridine of **1** in binding to boron. Pentafluorophenylboronic acid (**B9**) causes unselective quenching of fluorescence of **1** in all solvents (much like carboxylic acids **C3** and **C8** described above), which can be explained by electron-transfer from the excited state of **1** onto acceptor **B9**.[15]

Having demonstrated the fluorescent response of **1** to both carboxylic and boronic acids, we turned our attention to establishing detection limits for this method. Fig. 4 shows the dependence of emission color responses on the concentrations of cruciform **1** and two representative analytes, **C6** and **B5**. Concentration of the analytes was varied first (rows 2–5), from 0.0017 g L^{-1} to 17 g L^{-1}—when analytes started precipitating. While the response of **1** to **B5** was almost indistinguishable from the emission colors of pure **1** until the concentration of **B5** reached 1.7 g L^{-1}, carboxylic acid **C6** induced changes at much lower levels (0.017 g L^{-1}). Next, concentration of **1** was varied from approx. 1.1 × 10^{-9} M to 1.1 × 10^{-4} M (rows 6–11), while the analyte concentration was kept constant at 17 g L^{-1}. Poor solubility of cruciform **1** prevented us from examining higher concentrations than 1.1 × 10^{-4} M. At low concentrations of **1**, excess of analytes is more than sufficient to fully bind to **1**, but **1**'s fluorescence is so weak that these changes are barely observable (rows 6–8 for **C6** and 6–7 for **B5**). In the region we deemed analytically useful (row 9 for **C6** and rows 8 and 9 for **B5**), dramatic emission color changes are observed. Finally, as the concentration of cruciform **1** is increased further (rows 10 and 11), emission colors in the case of **C6** revert almost fully to those of pure **1**. This observation suggests that the excess of weak acid **C6** is now insufficient to fully protonate **1**. On the other hand, emission colors of **1** + **B5** are still clearly distinct from those of pure **1**, but not so from each other. In addition, **1** + **B5** may be exhibiting concentration-induced quenching at these high concentrations since its emission appears qualitatively dimmer than that at lower concentrations of **1**. At the highest concentration

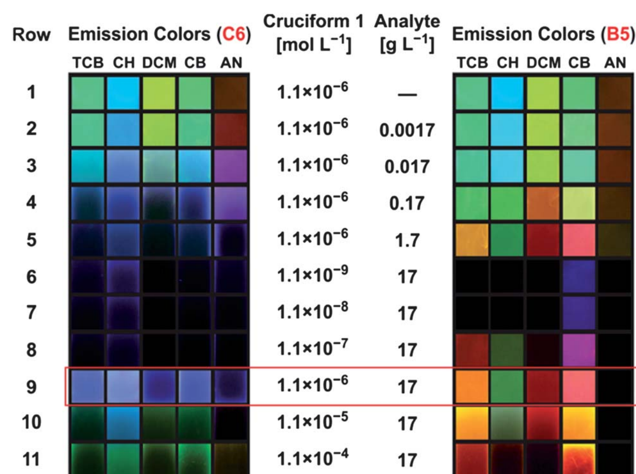

Fig. 4 Investigation of the dependence of fluorescence emission colors of **1** ($\lambda_{\mathrm{excitation}}$ = 365 nm; shutter speed 0.5 s) on the concentrations of **1** and representative analytes **C6** and **B5**. The conditions used in qualitative discrimination experiments shown in Fig. 2 and Fig. 3 are highlighted in the red frame.

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(row 11), observation is further complicated by partial precipitation of **1** and both examined analytes. Overall, our final choice of concentrations for **1** (1.1×10^{-6} M) and analytes (17 g L^{-1}) is among the optimal ones for standardized analyses of both compound classes; some other ratios would also perform well for carboxylic or boronic acids taken separately. Lower detection limits for both carboxylic and boronic acids are estimated at 0.017 g L^{-1} and 1.7 g L^{-1}, respectively, while the upper limit is determined chiefly by solubilities of **1** and corresponding analytes.

Notably, preliminary results suggest that this methodology holds some potential for the identification of mixtures of carboxylic acids. Three distinct mixtures of four carboxylic acids each show significantly different emission responses (Fig. 5, rows 1–3). From these emission colors, the composition of individual mixtures cannot be elucidated. Nevertheless, these differences can still be relevant to quality control applications, as they could be used to “fingerprint” individual standard mixtures, and thus detect an alteration in the composition of a well-defined mixture.[11a] Similar distinction among three mixtures of boronic acids (Fig. 5, rows 4–6) is much less pronounced.

Since fluorescent boronic acids have been used as sensors for sugars and other compounds of a general R–OH structure,[8,9] we were curious to examine the effects that substituent exchange on the boron[19] would exert over the emission colors of complexes of **1** and boronic acids. The mechanism of this optical response involves exchange of the –OH groups on the boronic acid for one or two –OR functionalities, which alter the electron density on boron and change the associated fluorescence. We speculated that an inexpensive non-fluorescent boronic acid could be used to bind to a phenol, and that the associated change in electron density on the boron could be sensed by cruciform **1** as the fluorescent responder. To evaluate this hypothesis, we prepared 0.02 M solutions of non-fluorescent boronic acids **B1** and **B5** in TCB, CH, DCM, chloroform (CF), and AN. Each solution was treated with a small amount of cruciform **1**, to set the final $ArB(OH)_2$: **1** molar ratio to 20,000 : 1. These solutions[20] were then exposed to an approximately fivefold molar excess of phenols **P1–P12** (Fig. 6, top center). Fluorescence emission photographs were recorded, and a numerical analysis analogous to the one performed for carboxylic and organoboronic acids was conducted. The results, summarized in Fig. 6, clearly show that all twelve phenols can be discerned from each other and from the blank solution of **1** + **B1**/**B5**. Remarkably, even subtle structural differences—such as those among the three positional isomers of methoxyphenol—are identifiable. The presence of boronic acid additives is indispensable in eliciting changes in the fluorescence of **1** in response to phenolic analytes. With pK_a values above 8.00, electron-rich and electron-neutral phenols are insufficiently acidic to protonate **1** and thus cause negligible shifts in emission colors. On the other hand, electron-poor nitrophenols, while sufficiently acidic, completely and unselectively quench the fluorescence of **1** (see Supporting Information†).[15,19]

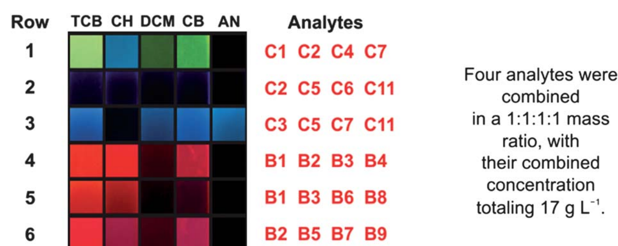

Fig. 5 Preliminary analysis of mixtures of carboxylic (rows 1–3) and boronic (rows 4–6) acids using cruciform **1** ($\lambda_{excitation}$ = 365 nm; shutter speed 0.5 s). Differences in emission colors, particularly pronounced for carboxylic acid mixtures, could be used to qualitatively indicate alteration of a well-defined composition.

Conclusions

Our results show that effective discrimination of twelve carboxylic and nine boronic acids from each other can be achieved using differences in the fluorescence response of cruciform **1** to these species. Furthermore, using two-component sensors composed of **1** and simple boronic acids, we have demonstrated that structurally related phenols can be distinguished as well—which is a potentially

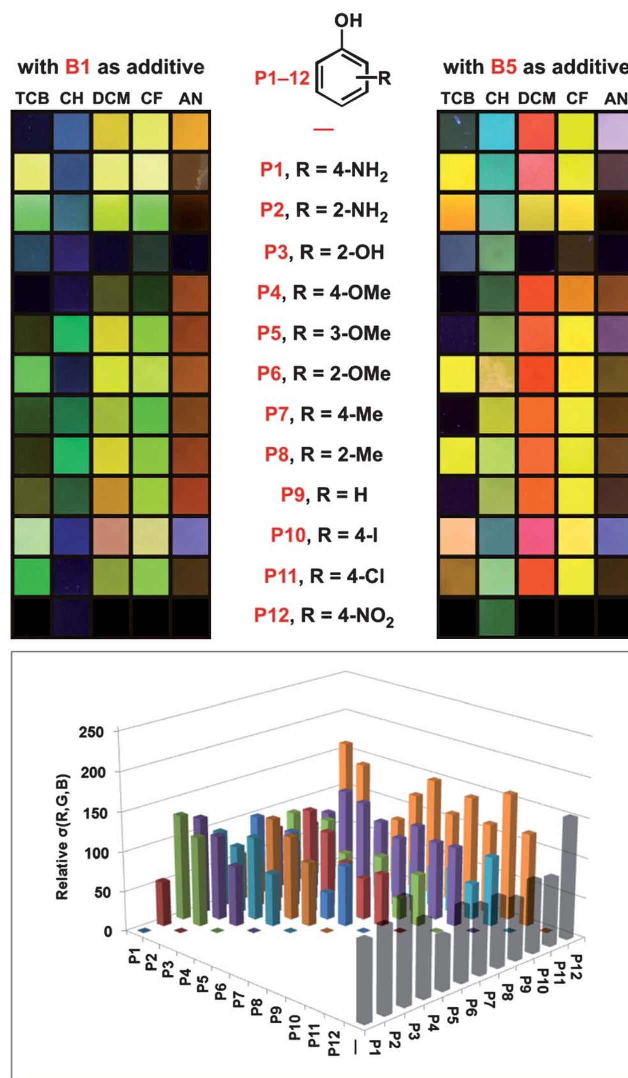

Fig. 6 Identification of phenols **P1–P12** (top center) using a combination of cruciform **1** and boronic acids **B1** (top left) and **B5** (top right). On the bottom, the correlation diagram shows standard deviations of the sum of *R*/*G*/*B* values for analytes **P1–P12**, relative to all other analytes. The semi-transparent bars in the row marked with “—” indicate standard deviations relative to the blank solution of **1** + **B1**/**B5**, summed over all five solvents.

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broadly applicable result. Other classes of hydroxy compounds—including sugars—should be susceptible to a similar method of analysis, provided that their solubility could be matched to that of **1** (or its analog). Future work will focus on the exploration of these new classes of analytes, as well as on rationalizing the observed dramatic differences in emission properties upon exposure to structurally similar analytes. Specifically, we will attempt to co-crystallize **1** with the analytes studied here, and analyze these assemblies by crystallography and solid-state IR spectroscopy. The results of these studies will be reported in due course.

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