anisotropic displacement parameters: 897 parameters, $wR2 = 0.1835$ for 18516 unique data ($2.69 \leq \theta \leq 26.39^{\circ}$), $R1 = 0.0666$ for 14232 data with $F_o > 4\sigma(F)$, max./min. residual electron density 0.789/ -0.549 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-148156. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Off-the-Shelf Colorimetric Anion Sensors**

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The recognition[1] and sensing[2] of anionic analytes has emerged recently as a key research theme within the generalized area of supramolecular chemistry.[3] Of particular interest in this regard are "colorimetric anion sensors", species that would allow the so-called "naked-eye" detection of anions without resort to any spectroscopic instrumentation. However, few such systems exist at present.[4–7] For instance, alizarin complexone[4a] has been used to effect the colorimetric sensing of fluoride anions in water, wet acetone, and wet acetonitrile as has 2,3-dipyrrol-2-yl-quinoxaline in dichloromethane.[6b] Thiourea has also been used to sense halide, phosphate, and carboxylate ions.[4b] Appropriately functionalized calix[4]pyrroles also show potential as naked-eye anion sensors.[7] Separately, displacement-based strategies have been used by Lavigne and Anslyn to detect citrate anions colorimetrically[5] and, more recently by Gale et al. to sense halide anions.[6a] Still, there remains a cogent need for species whose changes in color could be used to signal either qualitatively or quantitatively the presence of particular anionic analytes. Such agents would be especially valuable were they to be obtained readily without resort to dedicated synthesis. Herein we report that a wide range of commercially available entities, such as 1,2-diaminoanthraquinone, 1,8-diaminoanthraquinone, 4-nitroaniline, 4-nitro-1,2-phenylenediamine, L-leucine-4-nitroanilide, 1-(4-nitrophenyl)-2-thiourea, 4-nitrophenol, alizarin, 2,2′-bi(3-hydroxy-1,4-naphthoquinone), acid blue 45, naphthol AS, 9(10*H*)-acridone, and Direct Yellow 50 may be used as "off-the-shelf" color-based anion sensors in organic solvent. We also show that some of these agents may be used in combination with a crown ether phase-transfer catalyst to extract and detect anions colorimetrically in a two-phase organic–aqueous set-up, even in those instances where the anions being detected were originally present in the aqueous phase.

Initially, we focused on 1,8-diaminoanthraquinone as a potential off-the-shelf anion sensor. We were attracted to this system because 1) it contains two aniline-like NH_2 donor groups that appeared properly positioned to bind a chloride ion by cooperative hydrogen-bonding interactions, as judged from structural analyses of previous chloride-binding[8] and noncolorimetric sensing agents[2c] containing a similar structural motif, 2) such binding was expected to result in a bathochromic shift in the absorption bands in the visible region,[7b] and 3) various control compounds, with other modifications of the anthraquinone skeleton, would be readily available. In accord with the latter predicative thought, we studied the changes (if any) in the absorption spectra of anthraquinone, 1,2-, 1,4-, 1,5-, 1,8-,[8] and 2,6-diaminoanthraquinone, as well as 1- and 2-aminoanthraquinone, induced upon the addition of various anions, namely F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, and HSO_4^- in dichloromethane. Although, no change in the absorption spectrum of anthraquinone itself was found upon the addition of any of the analytes tested, the spectra of the other anthraquinone derivatives (those containing at least one hydrogen bond donor group) were all found to be modified in the presence of tetrabuthylammonium fluoride. On the other hand, only the spectra of 1,2- and 1,8-anthraquinone were seen to undergo a discernable change when exposed to tetrabutylammonium chloride in this same solvent. Presumably, the fluoride ion, in contrast to the chloride ion, is a strong enough hydrogen-bond acceptor that it can interact with anthraquinone derivatives that contain only a single hydrogen-bond donor group or single accessible donor group.

Significant bathochromic shifts in the absorption spectra were also observed for 1,2- and 1,8-diaminoanthraquinone in dichloromethane in the presence of chloride, bromide, and phosphate ions. These spectral changes were particularly dramatic in the case of 1,2-diaminoanthraquinone, being

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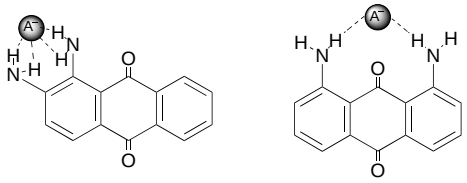
sufficiently large that this species was found to function as an effective colorimetric anion sensor. Figure 1 shows the color changes induced upon the addition of various anions (100 equiv each) to solutions of 1,2-diaminoanthraquinone in dichloromethane. Specifically, it was found that solutions,

Figure 1. Photograph showing the color of dilute solutions of 1,2-diaminoanthraquinone in dichloromethane ([quinone] = 1.0×10^{-4} M). A) Before addition of the anion. After addition of 100 equivalents of B) fluoride, C) chloride, D) bromide, E) iodide, F) phosphate, and G) sulfate ions. All anions were added in the form of their tetrabutylammonium salts.

initially yellow in color ($\lambda_{max} = 478$ nm), became dark purple ($\lambda_{max} = 555$ nm), red ($\lambda_{max} = 519$ nm), reddish orange ($\lambda_{max} = 513$ nm), orange ($\lambda_{max} = 499$ nm), purple ($\lambda_{max} = 548$ nm), and orange ($\lambda_{max} = 493$ nm) when exposed to fluoride, chloride, bromide, iodide, phosphate, and sulfate ions, respectively.[9]

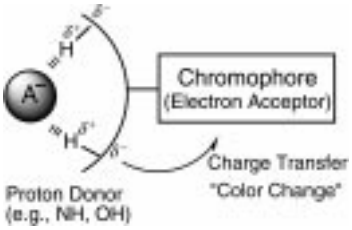
Solutions of 1,8-diaminoanthraquinone in dichloromethane were also found to change color when exposed to these anions, albeit to a lesser extent.[10] On the other hand, no significant changes in color were observed when solutions of 1,4-, 1,5-, 2,6-diaminoanthraquinone or 1- and 2-aminoanthraquinone in dichloromethane were exposed to 100 equivalents of chloride, bromide, iodide, phosphate, or sulfate ions. Such findings are consistent with the proposal that less basic anions, such as Cl^-, Br^-, I^-, $H_2PO_4^-$, and HSO_4^-, are not bound to an appreciable extent by a single NH_2 site but do interact cooperatively with two appropriately spaced NH_2 donor moieties (that is, in the 1,2 and 1,8 positions of anthraquinone). Although not studied in detail, the color change itself is ascribed to the formation of a charge-transfer complex as the result of these proposed solution-phase hydrogen-bonding interactions (Scheme 1).



Scheme 1. Proposed modes of anion binding for 1,2-diaminoanthraquinone and 1,8-diaminoanthraquinone.

Although hydrogen-bonding interactions are considered key to the success of the off-the-shelf anion sensing demonstrated by 1,2- and 1,8-diaminoanthraquinone, and while the initial choice of solvent, dichloromethane, was chosen to maximize these interactions, it was found that a discernable color-based response was observed when more polar solvents, namely CH_3CN and DMSO, were used.

The results obtained with 1,2- and 1,8-diaminoanthraquinone, led to the consideration that many species should be able to function as off-the-shelf anion sensors, provided that they possess hydrogen bond donor functionality, preferably two or more -NH_2, -C(O)NHR, or OH-derived binding sites, and a chromophore subunit whose electronic properties are modified as the result of interaction with a bound anionic substrate (through, for example, electrostatic or charge transfer effects; see Scheme 2). In accord with the above thinking,



Scheme 2. Schematic representation illustrating the origins of the generalized "off-the-shelf" approach to anion sensing being proposed here.

many commercially available compounds were screened as possible off-the-shelf anion sensors. A listing of compounds showing readily discernable changes is given as Scheme 3 while Figure 2 illustrates representative color changes observed using some of these species.

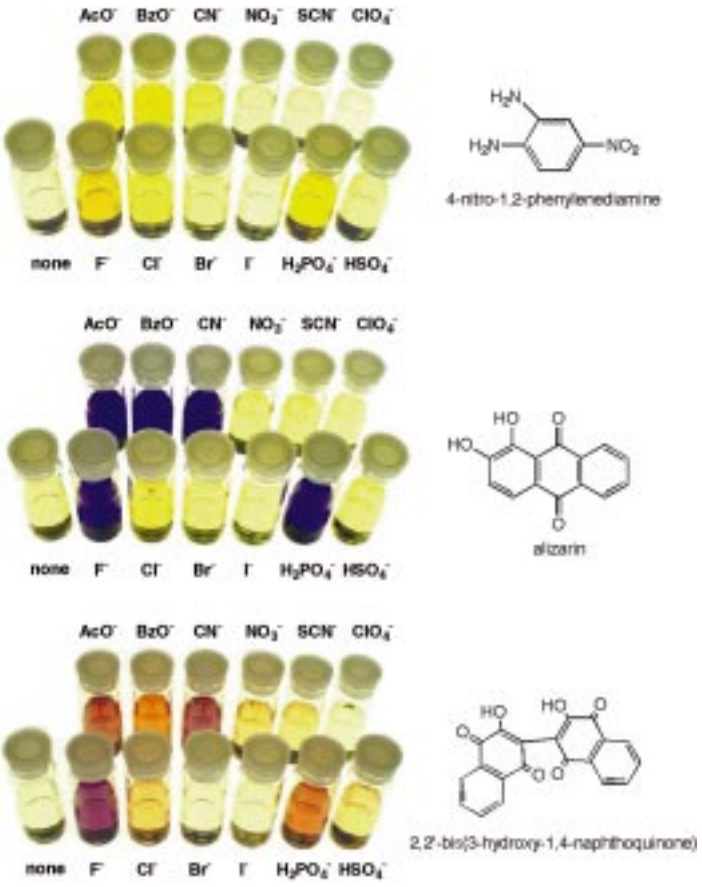


Figure 2. Color changes observed before and after dilute (1×10^{-4} M) solutions of 4-nitro-1,2-phenylenediamine, alizarin, and 2,2′-bis(3-hydroxy-1,4-naphthoquinone) in dichloromethane were treated with 100 equivalents of the indicated anionic analytes. All anions were added in the form of their tetrabutylammonium salts.

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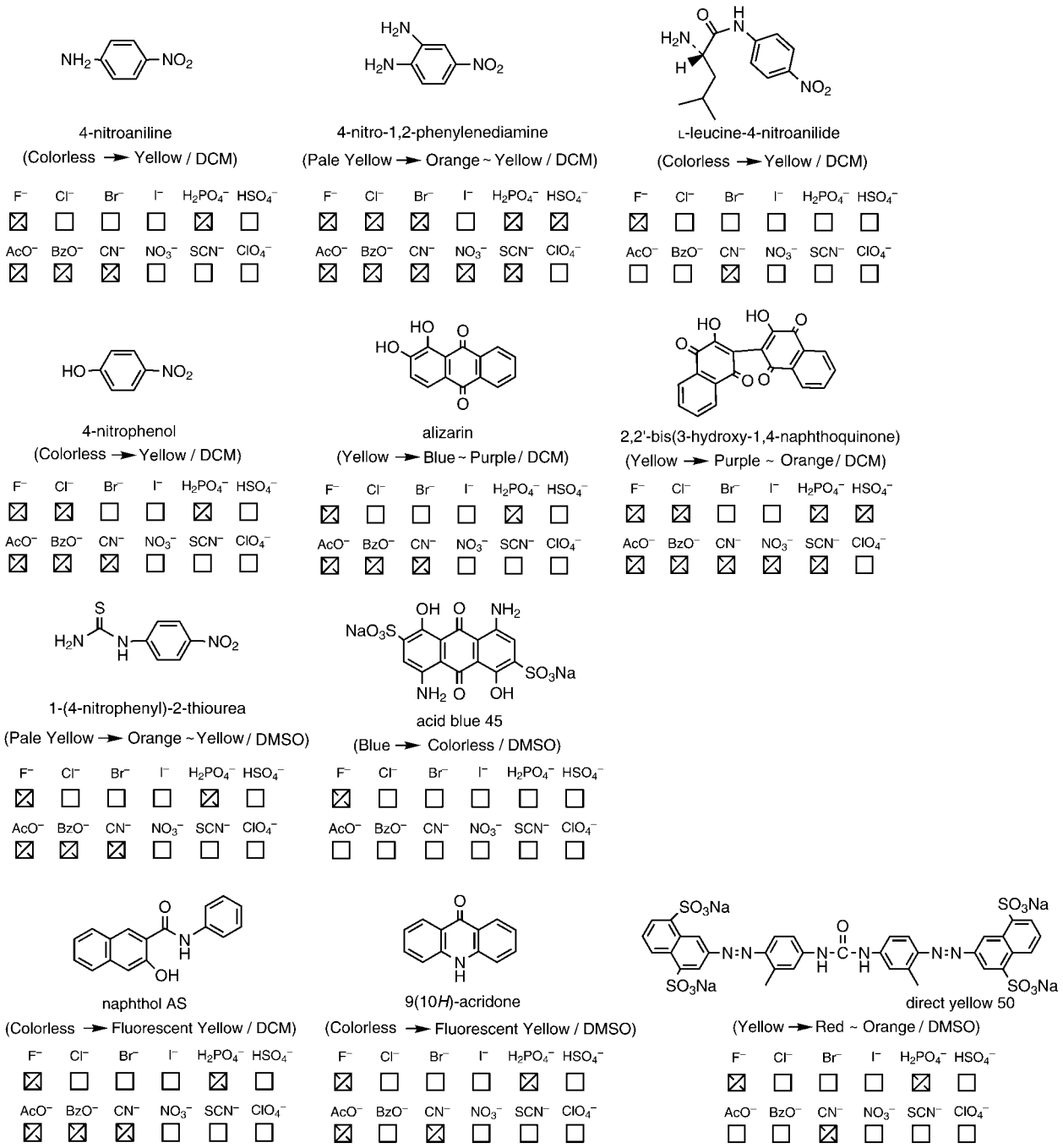

Scheme 3. Examples of commercially available colorimetric anion sensors. A checked box indicates a "naked-eye" detectable change in color is observed in the indicated solvents upon addition of 100 equivalents of the anionic analyte in question. DCM = dichloromethane; DMSO = dimethyl sulfoxide.

Based on the results summarized in Scheme 3, we believe that the use of appropriate off-the-shelf molecular entities could provide a generalized new approach to anion sensing. While lacking the specificity inherent in more sophisticated approaches to anion detection (for example, those based on specific receptor design), the fact that some inherent discrimination between anionic analytes is observed, coupled with its low cost, leads us to suggest that this new approach could find application in a variety of end-use areas, including multi-analyte array construction,[11] where ease of use and cost of goods are important considerations.

In support of the above contention, 2,2′-bis(3-hydroxy-1,4-naphthoquinone)[12] was used as a potential chloride sensor under extraction-type conditions. As illustrated in Figure 3, it was found that in a two-phase, aqueous – dichloromethane system containing [15]crown-5 as a phase-transfer catalyst present in the organic phase acts as a colorimetric indicator of chloride anions originally present in the aqueous layer.[13] This

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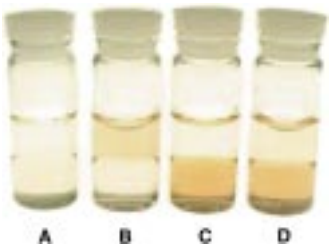

Figure 3. Color changes observed upon exposing aqueous solutions of chloride ions to dichloromethane phases containing 2,2′-bis(3-hydroxy-1,4-naphthoquinone) (1×10^{-3} M). A) Control experiment. The aqueous phase is distilled water (pH 7.41). B) The aqueous phase contains NaCl at a concentration of 1×10^{-1} M. C) The aqueous phase contains NaCl (1×10^{-1} M) and benzo[15]crown-5. D) The aqueous phase is Gulf of Mexico sea water (pH 7.34) and benzo[15]crown-5.

ability to sense qualitatively in a naked-eye-detectable fashion chloride anions is not limited to laboratory samples but was also found to work for sea water obtained from the Gulf of Mexico.[14] This observation leads us to suggest that this particular species could prove useful as a chloride anion sensor.[15]

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[10] The change in color for 1,8-diaminoanthraquinone was smaller than for 1,2-diaminoanthraquinone. For example, the color of a solution of 1,8-diaminoanthraquinone in dichloromethane (1×10^{-4} M) changed from orange ($\lambda_{max} = 487$ nm) to red ($\lambda_{max} = 503$ nm) upon the addition of 500 equivalents of fluoride ions.

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[12] As a result of a strong interaction with the crown ether and a resulting color change in the absence of anions, 1,2-diaminoanthraquinone could not be used for such extraction-type experiments.

[13] Chloride, rather than fluoride, ions were chosen for these tests since this larger anion is less basic and less prone to modulate the pH of the aqueous phase. Since changes in pH can affect the color of the indicators in this study, rigorous efforts were made to maintain the pH (through, for example, the use of dilute samples) as well as to control any differences in color that changes in pH could induce.

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Resolution and Kinetic Stability of a Chiral Supramolecular Assembly Made of Labile Components**

Andreas J. Terpin, Marco Ziegler, Darren W. Johnson, and Kenneth N. Raymond*

The importance of chirality for recognition processes in nature is impressively exemplified by the different tastes of (*R*)- and (*S*)-asparagine,[1] and the vastly different pharmacological effects of the two enantiomers of thalidomide.[2] Chirality is not the exclusive domain of organic chemistry, many metals can also serve as centers of chirality.[3] The most frequent case is an octahedral arrangment of three bidentate ligands around a metal center to form Δ or Λ absolute configurations. Chirality at metal centers has been found to play an important role in nature, for example, for the siderophore-mediated iron uptake in many organisms.[4]

Δ/Λ Isomerization of tris-bidentate complexes of the labile high-spin ferric ion or its closely related gallium(III) analogues is rapid in aqueous solution. Tris(catecholate)gallium(III) complexes, model compounds of iron siderophores, usually racemize fast. Racemization rates of 10(1) s^{-1} for a mononuclear complex[5] and 0.10(1) s^{-1} for a dinuclear helix[6] were determined by NMR studies. The isomerization was found to

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