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2-Dimensional Analytic Approach for Anion Differentiation with Chromofluorogenic Receptors

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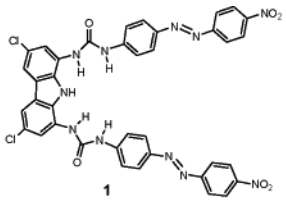

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By linking the urea moiety at the 1,8 positions of the carbazole fragment, we synthesized host systems **1**, **2**, and **3** having both chromogenic and fluorogenic signaling subunits. The spectral changes in both the signaling subunits could be easily analyzed via a simple 2-dimensional (2D) analytic approach described here, which enables us to differentiate the given set of anions. Structural studies are also reported.

The rational design and synthesis of efficient receptors to selectively recognize biologically and environmentally important anion species is an emerging field of supramolecular chemistry.[1] Both fluorogenic[2,3] and chromogenic[4] anion receptors have attracted a considerable amount of attention due to the simplicity in recording their optical responses upon forming complexes with anions. In general, chromo/fluorogenic receptors use one signaling subunit (S) as in S-L-R, R-L-S-L-R, and S-L-R-L-S models[2−4] (L means spacer/linker; R, receptor site). Meanwhile, an array of synthetic differential receptors has the capability of pattern recognition of diverse sets of analytes.[5] Further advancement in this area is the introduction of chromogenic or fluorogenic moieties to visualize the binding events and to readily diagnose patterns with the aid of spectroscopic changes.

Here, we adopted a novel S1-R-S2(R)-R-S1 model, where S1 and S2 could be both/either a fluorophore and/or a chromophore, and S1 is not equal to S2. We chose a neutral moiety such as urea[1,2,4,6] linked at the 1,8 positions of the carbazole fragment[3a] (fluorophore **F** represents S2(R)) by which the binding of anions would be facilitated via hydrogen bonding with the −NH groups of both urea and carbazole moieties. Similar to the color change previously observed in the urea derivatives upon adding fluoride/pyrophosphate,[7] the color of 1-[4-(4-nitrophenylazo)phenyl]-3-phenylurea changes from yellow (400 nm) to blue (600 nm) upon adding $[(n\text{-Bu})_4N^+]OH^-$. This is associated with the deprotonation of the more acidic urea and the subsequent charge-transfer phenomenon (Supporting Information). We utilized these fluorogenic and/or chromogenic moieties in designing hosts **1** to **3**. We demonstrate that a simple 2D analytic approach enhances the pattern-recognition capabilities of these receptors by virtue of the reflection of different optical responses from different signaling subunits upon binding with a diverse set of anions.

Reactions of 1:2 molar ratios of 1,8-diamino-3,6-dichlorocarbazole and 4-Isocyanato-4′-nitroazobenzene/naphthyl isocyanate/phenyl isocyanate in acetonitrile followed by filtration afforded novel compounds **1** (red color)/**2** (colorless)/**3** (colorless) as microcrystals (Scheme 1). All these receptors were characterized by NMR (^1H and ^{13}C), mass spectrometry and elemental analysis.

A single crystal of $\mathbf{2}\cdot CH_3COO^-$ was obtained by slow evaporation of the DMSO/CH_3CN solution mixture at 35 °C. The X-ray analysis revealed that $\mathbf{2}\cdot(CH_3COO^-)\cdot[(n\text{-Bu})_4N^+]$ adopts a craw-fish-like conformation,[8] with two naphthalene-urea groups on a plane at the opposite sides of carbazole (Figure

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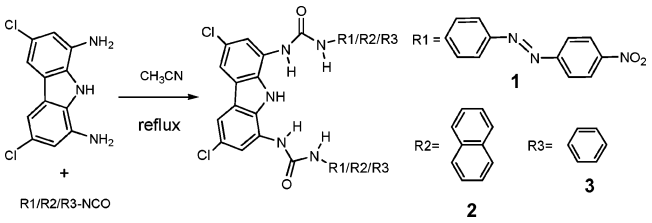
SCHEME 1. General Synthetic Scheme of Host Systems 1−3



1). The CH_3COO^- anion is located at the center of the carbazole cage, forming a 1:1 complex, where the two urea groups of the carbazole cage form hydrogen bonds with the anion. The (NH···O) distances are 1.903−2.497 Å. The carbazole moieties and CH_3COO^- in **2**·(CH_3COO^-)·[(*n*-Bu)$_4N^+$] are arranged with a wavy double layer structure in the *bc*-plane and packed along the *a*-axis with the layer distance ∼3.4 Å with the formation of extended $\pi-\pi/\pi-$H intermolecular interaction[9,10] between the receptors at the top and bottom layers (Supporting Information).

The chromogenic anion sensing capacity of **1** was studied by a visual inspection of color changes in the CH_3CN:DMSO (9:1) solution of receptor **1** (0.075 mM as the optimal concentration) in the presence of various anionic guests (100 equiv each) (Figure 2a). In the absence of anions, the spectrum of receptor **1** was characterized by two peaks at λ_{max} = 379 and 419 nm. The anions can be divided into six groups: G1−G6, depending on the bathochromic shift in the absorption spectra of the **1**−anion mixture solution with respect to that of the host solution (yellow color, λ_{max} = 419 nm) induced by anions (Figure 2b).

Group G1 comprises SCN^-, NO_3^-, ClO_4^-, I^-, and Br^- with no significant color/absorption spectral change. G2 comprises Cl^- and HSO_4^- (yellowish orange color, λ_{max} = 426−431 nm). Group G3 (BzO^-, CH_3COO^-, glutarate) showed an orange color (λ_{max} = ∼443 nm) and group G4 (adipate, $H_2PO_4^-$, and oxalate) showed a reddish orange color (λ_{max} = ∼450 nm); however, due to the similar λ_{max} values, the visual discrimination between G3 and G4 anions could not be readily made. Group G5 exhibited an orange-scarlet color (λ_{max} = ∼460, CN^- and $HP_2O_7^{3-}$), while group G6 showed dark blue (λ_{max} = 618 nm) for OH^-, green (λ_{max} = 623 nm) for F^-, dark green (λ_{max} = 627 nm) for succinate, and bluish teal (λ_{max} = 632 nm) for malonate (Figure 2a,b). The visible color changes for G2−G5/G6 anions upon complexing with **1** are associated with the charge transfer from the electron-deficient carbazole moiety to the electron-rich azo-nitro-phenyl center of **1** in neutral/deprotonated form (Supporting Information).

Fluorescent spectra of **1** (10 μM) upon the addition of tetrabutylammonium anion salts as a 1:100 equiv ratio in the CH_3CN:DMSO (9:1, v/v) mixture (Figure 2c) showed the enhanced emission due to the more planar form of **1** upon complexing with anions[11] by virtue of the nonradiative decay from the excited state less probable.[2b,12] Interestingly, due to the planarity of **1**, it could form excimer with I^- and BzO^-. Host **3** showed fluorescent quenching with most of the anions via the photoinduced electron-transfer (PET) mechanism (Figure 2c,d).[13a,14] The additional peak (445 nm) of **1** upon mixing with OH^- could be due to the charge transfer involved in the excited state from the carbazole moiety to the deprotonated urea group.

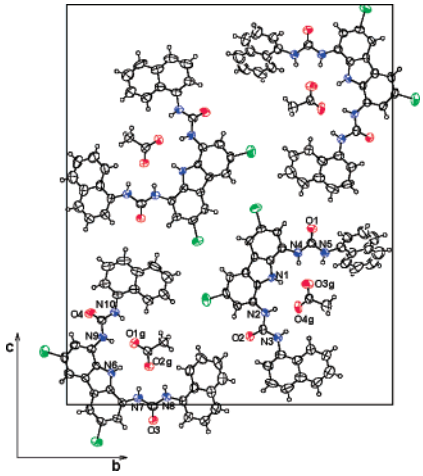


FIGURE 1. Partial cross section of **2**·CH_3COO^- in the unit cell of **2**·[(n-Bu)$_4N^+$](CH_3COO^-)], with displacement ellipsoids at 50% probability.

TABLE 1. UV-Absorption and Fluorescent Spectral Changes for 1 and 3 upon the Addition of Various Anions[a]

	1		3
anions	$\Delta\lambda$, group (419 nm)	F_i/F_o, F_{pi}	F_i/F_o, F_{pi}
SCN^-	1, G1	1.34	0.72
NO_3^-	1, G1	1.53	0.79
ClO^{4-}	1, G1	1.40	0.83
I^-	2, G1	1.34, 433	1.24
Br^-	3, G1	2.24	0.67
Cl^-	7, G2	1.59	0.87
HSO_4^-	11, G2	5.85	0.92
BzO^-	21, G3	2.49, 430	0.66
$CH_3CO_2^-$	25, G3	1.54	1.21
Glu^{2-}	26, G3	2.25	0.73
Adi^{2-}	30, G4	1.72	0.65
$H_2PO_4^-$	31, G4	6.93	0.53, 412, 435
Oxa^{2-}	32, G4	5.37, 440[b]	1.17
CN^-	38, G5	1.64	1.01
$HP_2O_7^{3-}$	41, G5	1.65	0.23, 414, 435
OH^-	199, G6	2.21, 445	1.00
F^-	204, G6	1.40	0.59, 428
Suc^{2-}	208, G6	1.59	0.77
Mal^{2-}	213, G6	1.72	0.96

[a] Host:guest equivalent ratio (1:100), absorption shift ($\Delta\lambda = \lambda - \lambda_o$ in nm) is the bathochromic shift in the absorption spectra of **1** (419 nm) upon mixing with anions. F_i values are the fluorescent intensity of the *i*th anion and F_o for **1**(**3**) is calculated as the average value within the spectral range of 376−386 nm (370−395 nm). F_{pi} is the additional peak in the fluorescent spectra of host with the *i*th anion. [b] Broad peak.

(8) Crystallographic data for **2**·(CH_3COO^-)·[(n-Bu)$_4N^+$], monoclinic, $P2_1/c$, a = 11.5481(13) Å, b = 26.263(3) Å, c = 32.445(4) Å, β = 96.146(3)°, V = 9783.8(19) Å^3, Z = 8, GOF = 1.069, $R_1(I>2\sigma(I))$= 0.13.04, wR_2 = 0.27.54. CCDC-283277 contains the supplementary crystallographic data for this paper in supporting material. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc-.cam.ac.uk/data_request/cif.

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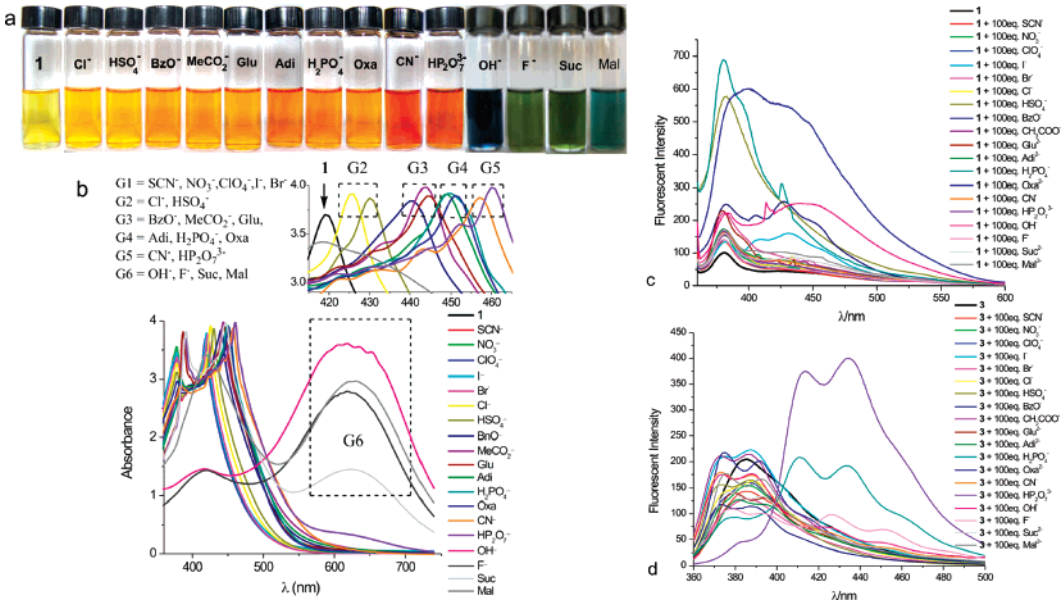

FIGURE 2. Visual features of (a) 0.075 mM **1** upon the addition of tetrabutylammonium salts of anions (7.5 mM) as a 1:100 equivalent ratio in the CH_3CN:DMSO (9:1, v/v) mixture; (b) the corresponding absorption spectra at the same condition. The color pictures of **1** with OH^-, F^-, succinate, and malonate were taken after diluting twice with solvent in order to have more clarity in color. (c and d) Fluorescence spectra of receptors **1** and **3** (10 μM), respectively, upon the addition of tetrabutylammonium salts of anions (1000 μM) as a 1:100 equivalent ratio in the CH_3CN:DMSO (9:1, v/v) mixture (slit width = 10 nm; excitation = 340 nm).

On the other hand, due to the presence of the phenyl group the distorted planarity of **3** could not form an excimer upon binding with anions (associated with the PET quenching effect). Instead, it displays intramolecular charge transfer (ICT) emission spectra with $H_2PO_4^-$ and $HP_2O_7^{3-}$, as these larger anions would start interacting with the −NH group of carbazole with the increasing concentration of anions.[14c,15] However, the ICT peak associated with F^- is red-shifted due to the deprotonation of the acidic urea group and its associated extended conjugation through the carbazole ring.[14c,15]

We performed ^{1}H NMR titration of **2** in DMSO-d_6 for a few selected anions (F^-, CH_3COO^-, $HP_2O_7^{3-}$). We could not perform ^{1}H NMR titration of **1** with anions due to the disappearance of the carbazole urea −NH proton signal after the addition of small equivalents of anion during ^{1}H NMR titration. During ^{1}H NMR titration in DMSO-d_6, addition of one equimolar amount of anions CH_3COO^- and $HP_2O_7^{3-}$ to **2** induced a downfield chemical shift of the −NH signal for the carbazole-attached urea by 0.474 and 0.459 ppm, respectively. The job plot analysis showed a maximum peak at the mole fraction of 0.5, inferring the 1:1 binding stoichiometry. The titration data were fitted to the 1:1 binding profile with the CH_3COO^- and $HP_2O_7^{3-}$ anions ($K_a > 10^5$ M^{-1}) and the 1:2 binding profile with the F^- anion (Figures S7−S9, Supporting Information) according to the method of Wilcox.[16]

The simple 2D plot for **1** (Figure 3), by combining the changes in absorption peak and fluorescent intensity, can differentiate I^- (peak at 433 nm) and Br^- (by the large change in intensity) in G1. In G2, Cl^- and HSO_4^- are differentiated due to the large difference in relative fluorescent intensity. In G3, BzO^- and CH_3COO^- (peak at 430 and 444 nm, respec-

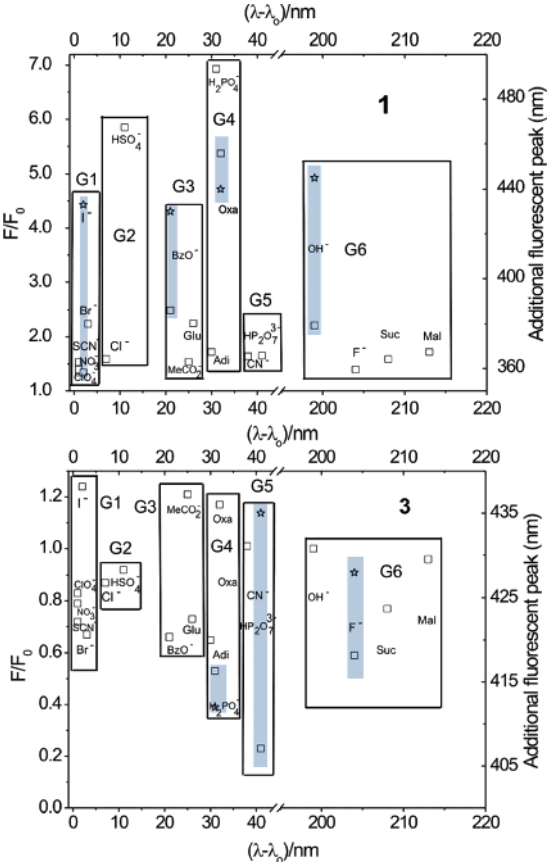

FIGURE 3. 2D plot: fluoresecence relative intensity (F/F_o) and additional fluorescent peaks (marked with a star) vs absorption shift ($\Delta\lambda = \lambda - \lambda_o$ in nm) for **1** and **3** upon adding different anions.

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tively) are distinguished from Glu^{2-}. In G6, OH^- (peak at 445 nm) is differentiated from F^-.

In the absorption spectra of **1**, two peaks (379 and 418 nm) merged into one peak at 420 nm upon the addition of malonate, and the 418 nm peak was red-shifted by ~30 nm in the case of succinate. In the 2D plot of **3**, we observed that among G1 anions, Br^- showed large quenching in the fluorescent intensity. In G3 anions, CH_3COO^- showed negligible changes in the fluorescent intensity, while BzO^- and glutarate showed the quenching effect. In G4 anions, only $H_2PO_4^-$ showed the emission peak at ~410 and 435 nm. In G5, $HP_2O_7^{3-}$ was easily differentiated from CN^- due to the appearance of a peak at 435 nm. Among the G6 anions, F^- showed a visible broad peak at 428 nm. Though ClO_4^-, NO_3^-, and SCN^- of G1 remained unresolved, **1** and **3** distinguished almost all anions.

In conclusion, we have designed and synthesized a family of easy-to-prepare novel carbazole-based receptors having both a chromophore and a fluorophore which can effectively differentiate diverse sets of anions in organic solvents. The ability to differentiate anions was enhanced as each signaling subunit showed different optical responses upon interacting with the anions. Such differentiation was easily made with simple 2D model plots based on the signal information from both signaling subunits. Further advancement in this area would lead to the design of such receptors that work in the protic media.

Experimental Section

1,8-Di(4′-nitroazobenzene)-3,6-dichlorocarbazole (1). To a solution of 1,8-diamino-3,6-dichlorocarbazole (0.5 mmol, 133 mg) in acetonitrile (25 mL) was added 4-isocyanato-4′-nitroazobenzene[17] (1 mmol, 268 mg) in acetonitrile (25 mL). The mixture was refluxed overnight. After cooling to room temperature, the precipitate was filtered off and washed with acetonitrile and dried in vacuo. Yield 85%; mp > 300 °C dec. Anal. Calcd for $C_{38}H_{25}N_{11}O_6Cl_2$: C, 56.85; H, 3.14; N, 19.19. Found: C, 56.86; H, 3.15; N, 19.20. MS (FAB) 802.34; IR (KBr) (cm^{-1}) 3451, 1649, 1560, 1522, 1342; ^1H NMR (500 MHz, $(CD_3)_2SO$, 25 °C) δ 7.53 (s, 2H,), 7.80 (d, 4H, J_{ortho} = 8.75 Hz), 7.94 (d, 4H, J_{ortho} = 8.50 Hz), 7.99 (d, 4H, J_{ortho} = 8.80 Hz), 8.10 (s, 2H), 8.29 (d, 4H, J_{ortho} = 8.70 Hz), 9.28 (s, 2H), 9.69 (s, 2H), 10.76 (s, 1H); ^{13}C NMR (125 MHz, $(CD_3)_2SO$) δ 118.5, 123.1, 124.7, 124.9, 146.8, 147.8, 152.5, 155.4.

1,8-Di(naphthylurea)-3,6-dichlorocarbazole (2). The reaction conditions are the same as above, using 1,8-diamino-3,6-dichlorocarbazole (1 mmol, 266 mg) and naphthyl isocyanate (2 mmol, 288 μL). Yield 80%; mp >300 °C dec. Anal. Calcd for $C_{34}H_{23}N_5O_2Cl_2$: C, 67.54; H, 3.84; N, 11.59. Found: C, 67.52; H, 3.81; N, 11.58. MS (*m*/*z*) 604.36; ^1H NMR (500 MHz, $(CD_3)_2SO$, 25 °C) δ 7.43−7.46 (t, 2H, J_1 = 7.45 Hz, J_2 = 7.05 Hz,), 7.55−7.62 (m, 4H), 7.65 (s, 2H), 7.69 (d, 2H, J_{ortho} = 7.10 Hz), 7.95 (d, 2H, J_{ortho} = 7.55 Hz), 8.02 (d, 2H, J_{ortho} = 7.40 Hz), 8.08 (s, 2H), 8.18 (d, 2H, J_{ortho} = 8.70 Hz), 9.05 (s, 2H), 9.34 (s, 2H), 10.66 (s, 1H); ^{13}C NMR (125 MHz, $(CD_3)_2SO$) δ 110.2, 116.2, 118.7, 119.5, 122.3, 122.5, 123.7, 124.0, 124.1, 124.5, 125.5, 126.2, 126.6, 126.7, 126.77, 126.82, 129.29, 129.34, 134.6, 135.2, 154.2, 154.3.

1,8-Di(phenylurea)-3,6-dichlorocarbazole (3). The reaction conditions are the same as above, using 1,8-diamino-3,6-dichlorocarbazole (1 mmol, 266 mg) and phenyl isocyanate (2 mmol, 217 μL). Yield 80%; mp >300 °C dec. Anal. Calcd for $C_{26}H_{19}N_5O_2Cl_2$: C, 61.92; H, 3.80; N, 13.89. Found: C, 61.89; H, 3.79; N, 13.90. MS (*m*/*z*) 504.14; ^1H NMR (500 MHz, $(CD_3)_2SO$, 25 °C) δ 6.98−7.01 (t, 2H, J_1 = 7.35 Hz, J_2 = 7.3 Hz), 7.27−7.30 (t, 2H, J_1 = 7.65 Hz, J_2 = 7.9 Hz), 7.51 (s, 2H), 7.53 (s, 2H), 7.56 (s, 2H), 8.04 (s, 2H), 8.94, 8.98 (two d, 4H), 10.61 (s, 1H); ^{13}C NMR (125 MHz, $(CD_3)_2SO$) δ 116.2, 119.11, 119.31, 119.53, 123.0, 124.4, 125.3, 126.1, 129.7, 132.2, 140.4, 153.7.

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Supporting Information Available: Product characterization of **1**, **2**, and **3** (copies of ^1H and ^{13}C NMR), design approach, experimental details, crystallographic data, and theoretical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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