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Development of colorimetric receptors for selective discrimination between isomeric dicarboxylate anions

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Abstract—Three new chromogenic receptors (**1**, **2**, and **3**) containing *p*-nitrophenyl or *p*-nitronaphthyl group appended to the thiourea units or containing *p*-nitrophenyl group appended to the urea moiety were synthesized and characterized. Upon addition of a series of isomeric dicarboxylate anions to receptor **1** in DMSO/H_2O (80:20 v/v), the appearance of the solution of receptor **1** with maleate or phthalate showed color changes from blue to green or blue to dark-green, respectively, which those can be detected by naked eye at parts per million. Similar experiments were repeated using **2**, the solution showed a distinct color change from blue to pink only when **2** is formed as a complex with maleate. Whereas, the addition of the same isomeric dicarboxylate anions to receptor **3**, did not induce any color change. Thus, for unique color change, both receptors **1** and **2** can act as optical chemosensors for recognition of maleate versus fumarate. In addition, the receptor **1** can also be a colorimetric receptor for selective discrimination between aromatic isomeric dicarboxylate anions.

Construction of colorimetric chemosensors for a specific anion is a particular attractive research area. However, most of the chemosensors have been developed for the colorimetric sensing of inorganic anions[1] whereas very few have been designed for recognition of organic anions.[2] Development of chromogenic reagents for such species remains a challenge. A colorimetric sensor for anions can be built following the binding site-signaling unit approach by attaching an appropriate chromophore to a specific anion receptor.[3] Urea and thiourea subunits are currently used in the design of neutral receptors for anions, owing to their ability to act as H-bond donors,[4] and many ligands containing either one or two of these groups have been reported to be excellent sensors for dicarboxylate anions.[5] During recent years, we have been studying the synthesis of colorimetric chemosensors for dicarboxylate anions and their possible application in sensing.[6] Now we would like to report the preparation of new chromogenic receptors **1**–**3** and their utility in the selective colorimetric discrimination between certain organic isomers (*cis*/*trans* and *ortho*/*meta*/*para* dicarboxylates) (Chart 1). Differentiation of geometric isomers is, in general, a difficult task because of their rather similar chemical and physical properties. To the best of our knowledge, only few examples have been published.[7]

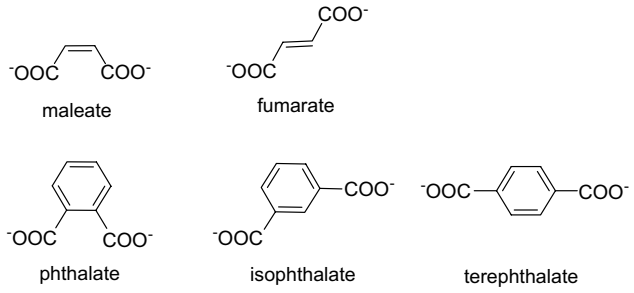

Chart 1.

The interest in selective sensors able to distinguish maleate versus fumarate is not only related to π-diastereoisomer recognition but is also due to the different biological behavior of these anions. In fact, whereas fumarate is generated in the Krebs cycle, maleate is a well known inhibitor of this cycle and its implication in different kidney diseases has been widely described.[8] Moreover, the interest to selectively discriminate between the three phthalic acid isomers (*ortho*, *meta*, and *para*) is due

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to *ortho*-phthalate being a high-production-volume synthetic chemical and also due to ubiquitous environmental contaminant. The potential health risk associated with exposure to it has been increasingly concerned.[9]

In this work, a chromogenic unit, an anthraquinone was chosen as a scaffold to link the recognition units (Scheme 1). The introduction of binding sites at 1- and 4-positions of 1,4-diaminoanthraquinone through an ethylene spacer form a convergent binding site for a feasible complexation with target species. The *p*-nitrophenyl or *p*-nitronaphthyl fragment which is linked to the thiourea moiety was chosen as chromophore to provide spectral sensing character upon complexation with anions. In spite of lacking electronic conjugation between the thiourea and anthraquionone moiety, the receptors **1**–**3** showed UV–vis spectral changes on complexation with anions.

The receptors **1**–**3** were synthesized by the reaction of *p*-nitrophenyl isothiocyanate or *p*-nitronaphthyl isothiocyanate or *p*-nitrophenyl isocyanate with 1,4-di-(2-aminoethylamino)-anthraquinone (**4**) in high yields (Scheme 1).[10] All of these compounds were characterized by ^{1}H NMR, ^{13}C NMR, IR, and HRMS.

The colorimetric selective sensing ability of the receptors **1**–**3** with maleate and fumarate anions in DMSO/H_2O (80:20 v/v) was monitored by UV–vis absorption and by 'naked eye' observation. The anions were added as tetrabutylammonium salts to the DMSO/H_2O (80:20 v/v) solutions of the receptors **1**–**3** (5×10^{-5} M). Figure 1a shows that the UV–vis absorption spectra of a mixture of receptor **1** with different concentrations of maleate in DMSO/H_2O (80:20 v/v). When the concentration of maleate was increased, a new absorption band at 480 nm was substantially enhanced, while the intensity of absorption at 362 nm decreased correspondingly. Interestingly, the color of the solution of receptor **1** was changed from blue to green (Fig. 2), which could be easily observed by the naked eyes. A clear isobestic point was observed at 393 nm. This result demonstrates that a complex formation of **1** with maleate anion takes place via hydrogen bonding electrostatic interactions.

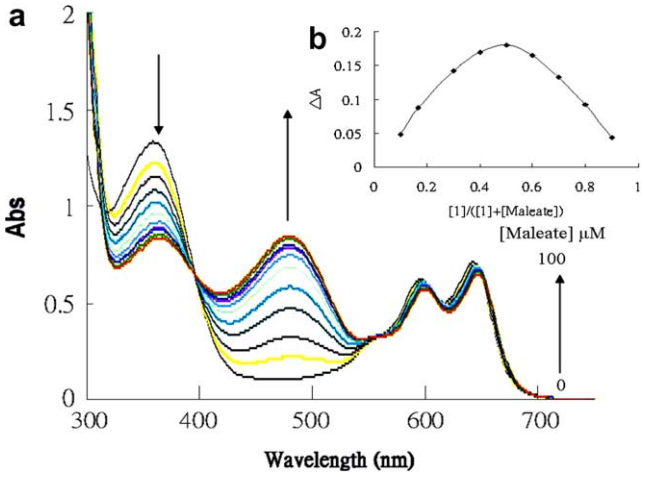
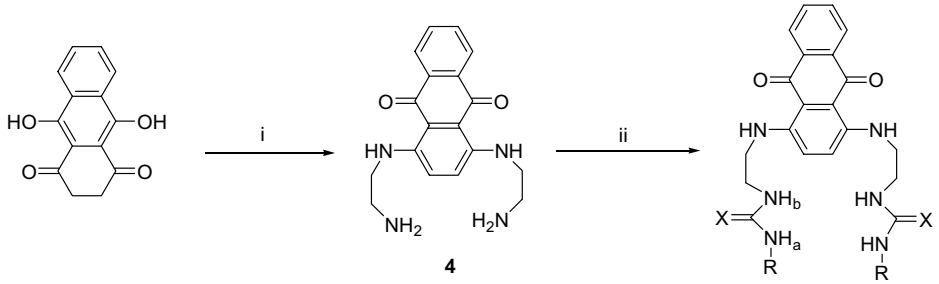


Figure 1. Family of spectra taken in the course of the titration of a 5×10^{-5} M DMSO/H_2O (80:20 v/v) solution in **1** with a standard solution of maleate at 25 °C titration profiles (insert) indicate the formation of a 1:1 complex.

Figure 2. Effect of anions (as $(C_4H_9)_4N^+$ salt) on color changes of **1** in DMSO/H_2O (80:20 v/v) (5×10^{-5} M) after the addition of 2 equiv of anion: (a) **1** only; (b) **1**+maleate; (c) **1**+fumarate; (d) **1**+phthalate; (e) **1**+isophthalate and (f) **1**+terephthalate.

The formation of these hydrogen bonds affects the electronic properties of the chromophore, resulting in a color change with a subsequent new charge transfer interaction between the electron donor nitrogen atom of thiourea unit and the electron deficient 4-nitrophenyl moiety.[11] Judging from the titrations, the strong binding of maleate allowed the Job's plot method[12] (as shown in the inset of Fig. 1) to be used in the determination



1. X = S, R = p-NO_2-phenyl (Yield : 81%)
2. X = S, R = p-NO_2-naphthyl (Yield : 91%)
3. X = O, R = p-NO_2-phenyl (Yield : 58%)

Scheme 1. Reagents and conditions: (i) ethylenediamine, 50 °C, 2 h, 37.2% and (ii) R-isothiocyanate or R-isocyanate, THF, reflux, 18 h.

of the binding stoichiometry, which was found to be a 1:1 host-to-anion complexation with an association constant $(1.09 \pm 0.78) \times 10^4\ M^{-1}$. This also showed that for receptor **1**, two thiourea functionalities simply act as cooperative binding sites. In contrast, similar experiments with corresponding fumarate salts were repeated and no significant changes in spectra were observed in the UV–vis absorption. The solution remains blue color (Fig. 2). Thus, it indicates that the receptor **1** is weakly binding or not interacting significantly with fumarate in this solvent medium. Apparently, receptor **1** has a unique color change and higher selectivity for maleate than fumarate. The different color observed with maleate and fumarate can be related to the receptor stereochemistry that gives rise to different geometries depending on the anion stereochemistry. Thus, the maleate anion with its *cis* configuration perfectly fits into the complex inducing a conformation change in the receptor. By contrast, the fumarate anion with a *trans* disposition of carboxylate moieties does not induce changes in the ligand conformation and only a small increase of the UV–vis absorption is observed. The proposed conformational structure for the complex formed between receptor **1** and the maleate anion is shown in Figure 3.

Parallel investigations were carried out with a series of other isomeric dicarboxylate anions (phthalate, isophthalate, and terephthalate). A similar phenomena of UV–vis absorptions are observed in Figure 4. Spectrum (a) was measured in the absence of anions where **1** has a UV–vis spectrum with λ_{max} at 362, 596, and 643 nm. As shown in spectra (b) and (c), **1** exhibits negligible perturbations upon addition of 2 equiv of isophthalate and terephthalate anions, respectively. By contrast, a significant change is observed in the presence of phthalate anion. As shown in spectrum (d), the CT absorption band appears at 480 nm and the solution color changes from blue to dark-green color (Fig. 2). It is apparent that **1** has a unique color change and higher selectivity for phthalate anion than other isomeric anions. The selectivity of **1** for recognition of these anions can be rationalized on the basis of the chain length and the geometry of the anionic species.

When these measurements were repeated using **2**, similar behavior was observed. Upon addition of different concentrations of maleate to receptor **2** in DMSO/H_2O (80:20 v/v), the initial absorption peak at 382 nm was gradually decreased and a new absorption band appeared with a maximum absorption at 523 nm (Fig. 5). This red-shift is ascribed to the occurrence of H-bond interactions involving the four N–H fragments of the

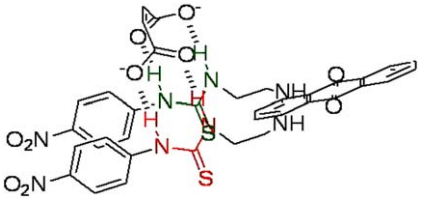


Figure 3. Possible binding model of **1** with maleate anion.

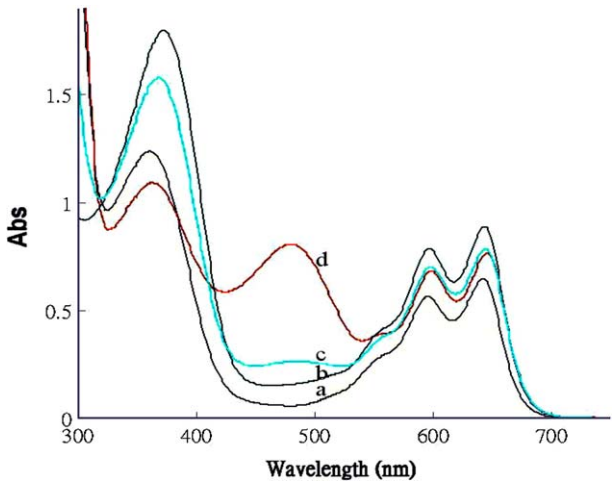


Figure 4. UV–visible changes of **1** operated in DMSO/H_2O (80:20 v/v) (5×10^{-5} M) after the addition of 2 equiv of anion: (a) **1** only; (b) **1**+isophthalate; (c) **1**+terephthalate and (d) **1**+phthalate.

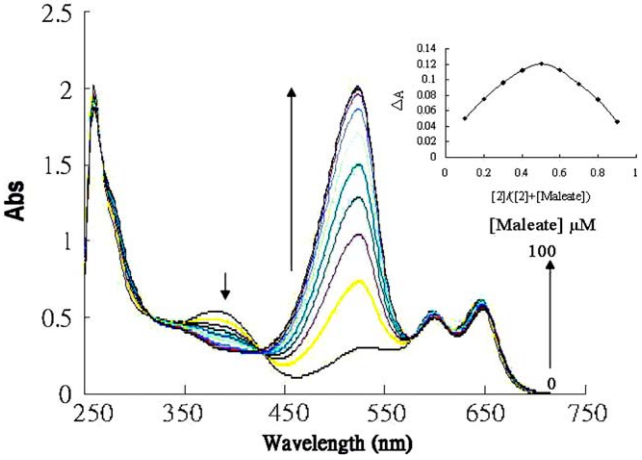


Figure 5. Family of spectra taken in the course of the titration of a 5×10^{-5} M DMSO/H_2O (80:20 v/v) solution in **2** with a standard solution of maleate at 25 °C titration profiles (insert) indicate the formation of a 1:1 complex.

two thiourea subunits and four oxygen atoms of dicarboxylate ions: in particular, electron density is transferred on the thiourea moiety, which makes the intensity of the dipole increase and shifts the charge-transfer band to longer wavelength. These changes are accompanied by a color change from a blue solution to pink color (Fig. 6), visible to the naked eye. The changes in the absorbance as a function of the concentration of maleate added can be fitted to a 1:1 binding equilibrium model, giving association constant in Table 1.[12] On the contrary, however, after addition of fumarate, no significant changes in spectra were observed in the UV–vis absorption. The solution remains blue color (Fig. 6). This result demonstrates that the receptor **2** can form a complex with maleate. Similarly, a dark-red color can be observed while adding a series of aromatic isomeric dicarboxylate anions (phthalate, isophthalate, and terephthalate) into the solution of **2** in DMSO/H_2O (8:2 v/v), but the color changes were not

Figure 6. Effect of anions (as $(C_4H_9)_4\,N^+$ salt) on color changes of **2** in DMSO/H_2O (80:20 v/v) (5×10^{-5} M) after the addition of 2 equiv of anion: (a) **2** only; (b) **2**+maleate; (c) **2**+fumarate; (d) **2**+phthalate; (e) **2**+isophthalate and (f) **2**+terephthalate.

distinct (Fig. 6). Apparently, the chromogenic reagent **2** is unable to be used for discrimination between the isomeric aromatic dicarboxylate anions.

In order to gain a clear picture of how thiourea or urea unit affects the binding property of **1**, a UV–vis study was conducted on the control compound **3**. In a manner similar to **1**, **3** showed three absorption bands at 359, 596, and 643 nm. Upon gradual increase of the concentrations of maleate or phthalate or other isomeric anions, no significant changes but only small increase of the absorptions in UV–vis spectra and no color change were observed. This weak binding could be explained by the strongly electronegative oxygen atom of the urea subunit which poorly contributes to the charge-transfer transition. Thiourea is a much stronger protonic acid than urea ($pK_a = 21.1$ and 26.9, respectively, in DMSO).[13] The Job's plots of these isomeric anions in DMSO/H_2O (80:20 v/v) showed a 1:1 binding stoichiometry, and the association constants were calculated by the Benesi–Hildebrand equation[12] and are listed in Table 1. The values of the association constant are smaller than those of receptor **1** or **2**. Based on these results, the receptors **1** and **2** can provide suitable chromophores and binding sites for maleate anions.

To investigate the interaction between receptor and *cis*/*trans* isomeric anions further, we also monitored the changes in the ^{1}H NMR spectra of **1** or **2** upon addition of maleate and fumarate anions. Addition of 1 equiv of the tetrabutylammonium salts of maleate to **1** or **2** in DMSO-d_6 caused remarkable downfield shifts of the NH resonances in the ^{1}H NMR. In the case of **1** with maleate, the proton chemical shifts of thiourea (H_a, H_b) changed from 10.26 to 10.90 ($\Delta\delta = 0.64$ ppm), 8.51 to 8.90 ($\Delta\delta = 0.39$ ppm), respectively (Fig. 7). The larger downfield shifts indicate the formation of two hydrogen bondings between H_a, H_b and maleate. These results show that receptor **1** and maleate form a 1:1 stoichiometry complex via hydrogen-bonding interaction between thiourea and carboxyl groups. In contrast, when **1** formed a complex with fumarate, the proton chemical shifts of thiourea (H_a, H_b) changed from 10.28 to 10.42 ($\Delta\delta = 0.14$ ppm), 8.52 to 8.67 ($\Delta\delta = 0.15$ ppm), respectively (Fig. 8). These smaller downfield shifts indicate the formation of two weak hydrogen bondings between H_a, H_b and fumarate.

In conclusion, the new colorimetric anion receptors **1**–**3** were synthesized in high yields. Among them, both **1** and **2** have higher selectivity for maleate than fumarate and there are distinct color changes that can be observed by the naked-eyes. Besides that, receptor **1** can also form a complex with phthalate which results in a distinct color change. Thus, both the receptors **1** and **2** can act as optical chemosensors for recognition of maleate versus fumarate. And the receptor **1** can also be a colorimetric receptor for selective discrimination between aromatic isomeric dicarboxylate anions.

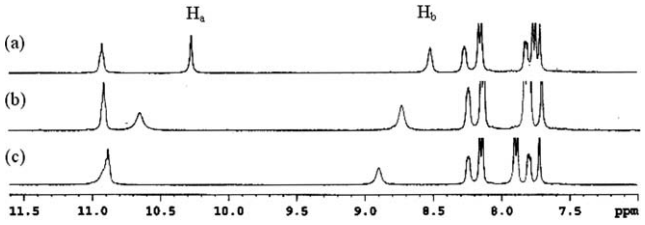


Figure 7. ^{1}H NMR (400 MHz) spectra of sensor **1** (10 mM) in DMSO-d_6: (a) Sensor **1** only; (b) **1**+0.5 equiv of tetrabutylammonium maleate and (c) **1**+1.0 equiv of tetrabutylammonium maleate.

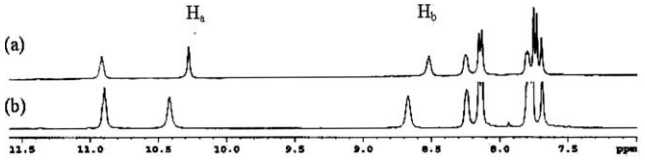


Figure 8. ^{1}H NMR (400 MHz) spectra of sensor **1** (10 mM) in DMSO-d_6: (a) Sensor **1** only (b) **1**+1.0 equiv of tetrabutylammonium fumarate.

Table 1. Association constants K_a (M^{-1}) of receptors **1**, **2** and **3** with guest anions

Anion	Receptor **1** K (M^{-1})[a]	R[b]	Receptor **2** K (M^{-1})[a]	R	Receptor **3** K (M^{-1})[a]	R
Maleate[c]	$(1.09\pm0.78)\times10^4$	0.9905	$(1.34\pm0.26)\times10^4$	0.9915	$(4.26\pm1.44)\times10^2$	0.9944
Fumarate[c]	$(6.65\pm1.22)\times10^2$	0.9926	$(6.05\pm0.37)\times10^2$	0.9912	$(1.28\pm0.61)\times10^2$	0.9964
Phthalate[d]	$(9.13\pm0.77)\times10^3$	0.99	$(1.30\pm0.68)\times10^4$	0.9909	$(5.50\pm1.24)\times10^2$	0.9933
Isopthalate[c]	$(1.58\pm0.24)\times10^3$	0.9932	$(1.07\pm0.09)\times10^4$	0.9953	$(3.34\pm0.17)\times10^2$	0.9971
Terephthalate[c]	$(3.17\pm0.16)\times10^3$	0.9923	$(1.17\pm0.02)\times10^4$	0.9923	$(4.26\pm0.36)\times10^2$	0.9912

[a] The data were calculated from UV–visible titration in DMSO/H_2O (80:20 v/v).
[b] The data values of R were obtained by the results of nonlinear curve fitting.
[c] The anions were use as their tetrabutylammonium salts.
[d] The anions were use as their sodium salts.

Acknowledgements

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10. Data for Compound **1**: Yield: 81%. Mp 213–214 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ: 3.74–3.76 (m, 8H), 7.71 (s, 2H), 7.75–7.77 (m, 4H), 7.80–7.82 (m, 2H), 8.14–8.16 (m, 4H), 8.25–8.27 (m, 2H), 8.49 (br s, 2H), 10.24 (br s, 2H), 10.90 (br s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 40.6, 44.1, 109.0, 120.9, 124.7, 125.9, 132.6, 134.0, 142.1, 146.2, 146.3, 180.7, 181.1. IR (KBr): $\nu = 3329$, 3067, 2933, 2858, 2356, 2335, 1639, 1598, 1511, 1326 cm^{-1}. UV (DMSO): 362 nm ($\varepsilon = 3504$), 596 nm ($\varepsilon = 9370$), 643 nm ($\varepsilon = 8635$). HRMS (FAB): calcd for $C_{32}H_{28}N_8O_6S_2$ [M^+] 684.1576; found 684.1584. Compound **2**: Yield: 91 %. Mp 206–207 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.72–3.75 (m, 8H), 7.67–7.69 (m, 4H), 7.76–7.83 (m, 6H), 8.10 (d, $J = 8.4$ Hz, 2H), 8.26–8.31 (m, 6H), 8.41 (d, $J = 8.4$ Hz, 2H), 10.13 (br s, 2H), 10.92 (br s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 30.9, 40.8, 44.3, 108.9, 122.4, 122.9, 123.9, 124.8, 125.6, 125.9, 127.7, 129.5, 130.0, 132.7, 134.0, 141.0, 143.4, 146.4, 181.1, 182.2. IR (KBr): $\nu = 3293$, 3068, 2930, 2853, 2330, 1639, 1568, 1506, 1311, 1265, 1168, 1045, 1025, 830. cm^{-1}. UV (DMSO): 382 nm ($\varepsilon = 2510$), 532 nm ($\varepsilon = 7493$), 597 nm ($\varepsilon = 2662$), 644 nm ($\varepsilon = 1442$). HRMS (FAB): calcd for $C_{40}H_{32}N_8O_6S_2$ [M^+] 784.1890; found 784.1891. Compound **3:** Yield 58%. Mp 210–211 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.38–3.39 (m, 4H), 3.59–3.60 (m, 4H), 6.69 (s, 2H), 7.60–7.62 (m, 4H), 7.78 (s, 2H), 8.09–8.11 (m, 4H), 8.20 (br s, 2H), 8.49 (br s, 2H), 10.24 (br s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 42.1, 108.9, 117.1, 124.7, 125.3, 125.9, 132.6, 134.0, 140.6, 147.3, 155.0, 181.0. IR (KBr): $\nu = 3313$, 3113, 3062, 2929, 2857, 2432, 1643, 1592, 1556, 1505, 1326, 1300, 1239, 1239, 1172, 1111, 1044, 1018 cm^{-1}. UV (DMSO): 359 nm ($\varepsilon = 2817$), 596 nm ($\varepsilon = 7691$), 643 nm ($\varepsilon = 6782$). HRMS (FAB): calcd for $C_{32}H_{28}N_8O_8$ [M^+] 652.2030: found 652.2025.
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