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New non-covalent charge–transfer complex of calix[4]pyrrole–chloranil: as a potential colorimetric anion sensor

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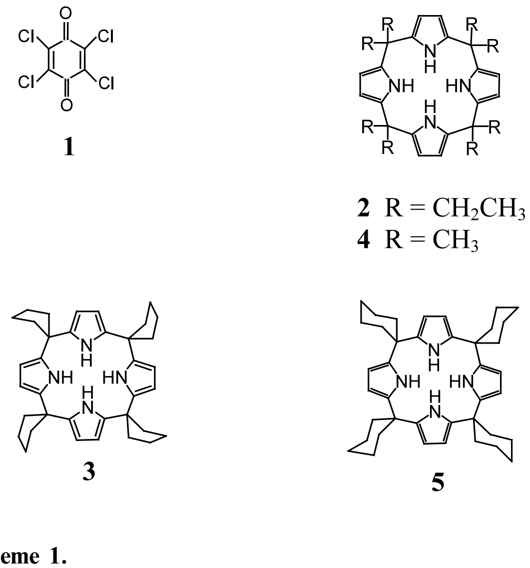
Abstract—Non-covalent calix[4]pyrrole–chloranil complex, a new class of supramolecular assembly, is reported. The formation of the complex is mainly attributed to the charge–transfer interactions between calix[4]pyrrole with electron-rich pyrrole rings and the electron-deficient chloranil subunit. As potential colorimetric anion sensors, the charge–transfer aggregation may be used for effective and selective detection of F^- and $H_2PO_4^-$ by means of dramatic visual color changes. © 2003 Elsevier Science Ltd. All rights reserved.

Molecular recognition chemistry associated with the calixpyrroles, an easy-to-make class of neutral macrocycles, has attracted intensive interest in recent years. Sessler and co-workers, in a pioneering report, stated that calixpyrroles are effective and selective receptors for anions and neutral substrates.[1] One of the more attractive developments involves the construction of calix[4]pyrrole-based anion sensors in both the optical[2] and electrochemical realms,[3] which are of particular interest in the field of the recognition and sensing of anionic analytes.[4] As major binding contributions, multiple hydrogen bonding interactions between calixpyrrole and substrate have been identified.[1] Furthermore, in some calix[4]pyrrole-based complex systems, a subsidiary interaction mode of using the periphery of calixpyrrole as an electron-rich site for binding either metals or neutral molecule species through metal–π, π–π stacking, or π–H interactions, which helps to stabilize the complex, has also been described.[5] However, no reports on the calix[4]pyrrole-based supramolecular assembly which formed mainly by π stacking and/or charge–transfer type interaction appeared until now. In our present work, we have been exploring latent possibilities that the calix[4]pyrrole with independent and conformationally flexible pyrrole rings acts as a electron-rich receptor to form molecular complex with electron-deficient species. Herein, we wish to first report the formation of a new class of non-covalent calix[4]pyrrole–chloranil charge–transfer complex, and show that the colored aggregation can be used as a powerful naked-eye sensor for selective detection of F^- and $H_2PO_4^-$ in solution. This novel colorimetric anion sensor could provide a simple, inexpensive and more general method for the rapid detection and identification of anions.

Upon addition of colorless calix[4]pyrroles (Scheme 1), which were easily prepared in high yield by modified condensation[6] of pyrrole with the relevant ketone, to the $CHCl_3$ solution of chloranil (**1**), naked eye-detectable characteristic color changes could be observed. The colorimetric properties of the complexes



Scheme 1.

Keywords: calixpyrrole; charge–transfer; chloranil; sensor; supramolecular chemistry.

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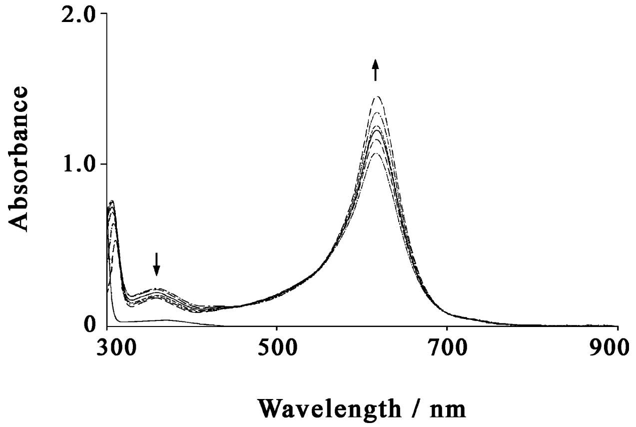

Figure 1. Absorption spectra of chloranil **1** (1.0×10^{-4} M) upon addition of 0, 40, 60, 80, 100, 150 and 200 equiv. of calixpyrrole **2** in $CHCl_3$ at 21°C, after equilibrating for 24 h. The curve with the lowest absorptivity was obtained with **1** alone.

were revealed by UV–vis spectroscopic techniques. Figure 1 shows the changes in the absorption spectrum of **1** (1.0×10^{-4} M) in chloroform observed upon the addition of *meso*-octaethylcalix[4]pyrrole **2**. Chloranil itself displays an absorption maximum at 370 nm in chloroform. In the presence of calix[4]pyrrole **2**, the peak at 370 nm undergoes obvious increasing along with a slight blue shift while a new absorption band elicits in long-wave region of the spectrum ($\lambda_{max} = 622$ nm). The color of the mixed system changed from pale yellow to blue. The observation of clear isosbestic points indicated that chloranil forms a 1:1 molecular complex with calix[4]pyrrole in $CHCl_3$, which was also confirmed by Job plot analysis. The binding constant of complex **1·2** was estimated at $K_a = 5.8\times10^2$ M^{-1} by the Benesi–Hildebrand analysis[7] of the absorbance changes at the new band maximum. Similarly, the addition of *meso*-tetracyclopentylcalix[4]pyrrole (**3**) to the solution of chloranil could induced color change from pale yellow to purple ($\lambda_{max} = 550$ nm), as shown in Figure 2. However, under the same conditions, less dramatic changes were observed upon addition of *meso*-octamethylcalix[4]pyrrole (**4**) or *meso*-tetracyclohexylcalix[4]pyrrole (**5**) to the solution of **1**. In these cases, the colors of the solutions very slowly changed from pale yellow to greenish yellow and from pale yellow to dark blue (near-complete color conversion), respectively, and the corresponding new absorption peak appeared at 470 and 615 nm, respectively.

These results displayed in the electronic absorption spectra, as well as the corresponding visual color changes, indicate the formation of the charge–transfer complex of calix[4]pyrrole with chloranil subunit in $CHCl_3$ solution. The *meso*-alkyl groups of the calix[4]pyrrole have considerable effects on the formation of charge–transfer complex with chloranil, presumably due to a combination of electronic effects and steric interactions. On the other hand, it was found that no color-based responses significant of the formation of the charge–transfer complex were observed when more polar solvents, namely MeCN and DMSO, were used.

Analyses of the solution-phase interactions between calix[4]pyrrole and chloranil were further made using ^{1}H NMR spectroscopy. The addition of 2.5 equiv. of **1** (up to solubility limit) to the 10 mM $CDCl_3$ solutions of **2**, **3**, **4** and **5** resulted in the formation of corresponding colored complex solution; however, it was found that the ^{1}H NMR spectra of these complexes showed negligible changes in the chemical shifts relative to those of uncomplexed **2**, **3**, **4** and **5**. It seems likely that no obvious hydrogen-bonding interaction between NH groups of calix[4]pyrrole and the carbonyl groups of chloranil is occurring in the $CDCl_3$ solution upon the calix[4]pyrrole–chloranil molecular complex formation. These findings suggest that the charge–transfer interaction is essential for the calix[4]pyrrole–chloranil com-

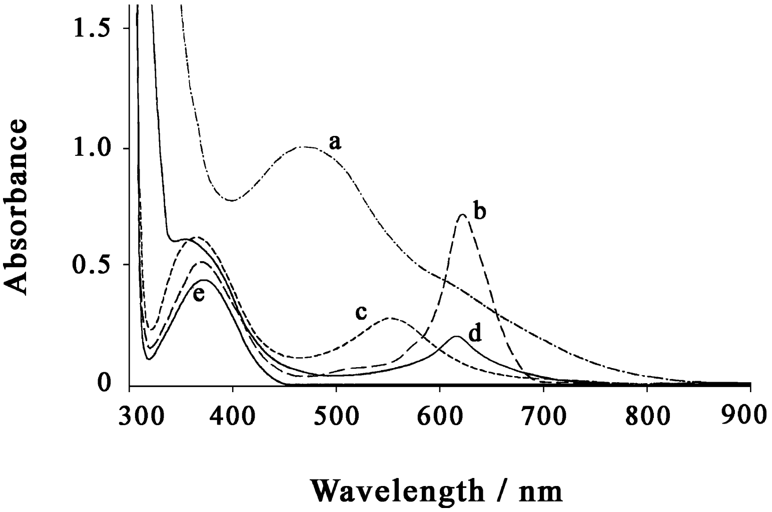

Figure 2. Absorption spectra of chloranil **1** (2.0×10^{-3} M) in $CHCl_3$ at 21°C in the absence (e) and in the presence of 2.0×10^{-2} M: (a) *meso*-octamethylcalix[4]pyrrole **4**, after 16 h; (b) *meso*-octaethylcalix[4]pyrrole **2**, after 35 min; (c) *meso*-tetracyclopentyl calix[4]pyrrole **3**, after 35 min; and (d) *meso*-tetracyclohexylcalix[4]pyrrole **5**, after 16 h.

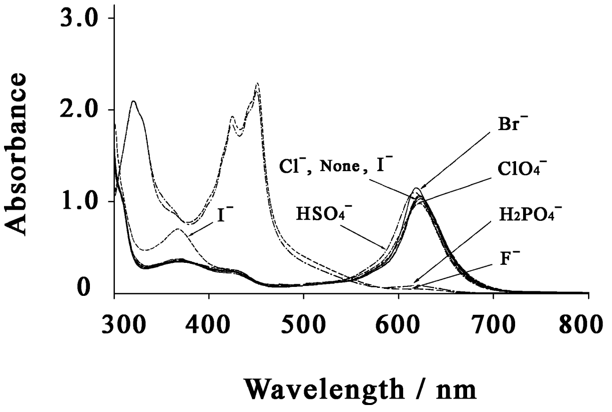

Figure 3. Absorption spectra of a stock solution containing both **1** (2.0×10^{-4} M) and **2** (2.0×10^{-3} M) in $CHCl_3$ upon addition of representative anions (2.0×10^{-2} M).

plex. Presently, further work on the structure of calix[4]pyrrole–chloranil adducts and the modes of charge–transfer interaction between calixpyrrole and chloranil or other quinone derivatives are in progress.

Our current experiments indicated that the charge–transfer interaction between calix[4]pyrrole and chloranil could be perturbed in the presence of some anions. In a general way, the addition of either tetrabutylammonium fluoride or tetrabutylammonium dihydrogenphosphate to the $CHCl_3$ solution of calix[4]pyrrole–chloranil complex could cause dramatic visual color changes. On the other hand, no distinct color changes were observed when the complex solutions was exposed to tetrabutylammonium salts of Cl^-, Br^-, I^-, HSO_4^-, and ClO_4^- ions under the same conditions (even at much higher anions concentration).

The qualitative changes are reflected in more quantitative terms in the UV–vis absorption spectra. In a typical experiment (see Fig. 3), upon addition of F^- and $H_2PO_4^-$ ions (2.0×10^{-2} M) to the stock solutions of **1** (2.0×10^{-4} M) and **2** (2.0×10^{-3} M), the charge–transfer absorption band ($\lambda_{max}=622$ nm) of the complex **1·2** nearly vanished while a new absorption band appeared in the region of 400–500 nm ($\lambda_{max}=426$ and 450 nm), and the color of the ensemble solution changes instantly from blue to orange–yellow. Interestingly, the F^- and $H_2PO_4^-$ anion-induced color changes can be reversed upon addition of water for extracting F^- or $H_2PO_4^-$ from the mixed solution, which can be due to the renewal of the charge–transfer interaction between calix[4]pyrrole and chloranil. The reversible changes in color could be more easily observed under a condign complex solution concentration (e.g. a stock solution containing 2.0×10^{-3} M **1** and 2.0×10^{-2} M **2**). However, as shown in spectra, the complex **1·2** exhibits negligible perturbation in the presence of Cl^-, Br^-, I^-, HSO_4^-, and ClO_4^- ions. Similar results could also be obtained upon addition of the representative anions to the purple solution of the complex **1·3** and the blue solution of the complex **1·5**. These results indicate that the colored calix[4]pyrrole–chloranil charge–transfer complex may be used as a colorimetric sensor for effective and selective detection of F^- and $H_2PO_4^-$ anions.

Competition experiments with F^-, Cl^- and $H_2PO_4^-$ anions were conducted by ^1H NMR spectra. Upon addition of 5.0 equiv. of F^- and $H_2PO_4^-$ to a $CDCl_3$ solution of the complex **1·2** (10 mM), corresponding changes in color were observed. The ^1H NMR spectra showed downfield shifts of the calix[4]pyrrole NH proton from its complex **1·2** value of δ 7.02 to 7.21 for F^-, and to 7.05 for $H_2PO_4^-$, due to the involvement of the calix[4]pyrrole NH protons in hydrogen bonding interactions with the anions. Moreover, a downfield shift of the pyrrole NH proton from δ 7.02 to 7.13 was observed upon addition of 5.0 equiv. of Cl^-, indicating the formation of a calix[4]pyrrole–chloride complex. However, no color changes for the break-up of the calix[4]pyrrole–chloranil complex were observed in the presence of chloride, although the affinity of chloride for calix[4]pyrrole is usually higher than that of dihydrogenphosphate.[1,2c] Different from reported calix[4]pyrrole-based colorimetric displacement assays,[2b] the perturbation of the charge–transfer complex of calix[4]pyrrole–chloranil in the presence of anion is ascribed not only to the competitive binding of anion to calix[4]pyrrole subunit but also mostly to the interactions between anion (viz. F^- or $H_2PO_4^-$) and chloranil subunit. Control experiments[8] indicated that the appearance of F^- or $H_2PO_4^-$ anion-induced strong absorption band (λ_{max} at 426 and 450 nm), as shown in Figure 3, resulted from the intermolecular interactions between F^- or $H_2PO_4^-$ anion and the chloranil moiety in the presence of calix[4]pyrrole.

In conclusion, a new class of calixpyrrole-based supramolecular assembly that may provide a significant example of the charge–transfer type interaction between calixpyrrole receptor and substrate has been developed. The non-covalent calix[4]pyrrole–chloranil aggregation has shown powerful as a simple, unexplored class of colorimetric anion sensors for the facile identification of F^- and $H_2PO_4^-$ ions in chloroform. The specific phosphate/chloride selectivity is potentially advantageous in biological sensing applications where a high concentration of Cl^- pertains. In addition, the charge–transfer complex could stand in $CHCl_3/EtOH/H_2O$ mixture, thereby, the utility of this system may be extended for the colorimetric analysis of many other analytes, particularly such as nucleotide molecules,[9] normally exist in aqueous phase. We are currently exploring this approach, and the results of this work will be reported in due course.

Acknowledgements

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8. Upon addition of 100 equiv. of F^- or $H_2PO_4^-$ to the $CHCl_3$ solution of chloranil (2.0×10^{-4} M), an undramatic color change from pale yellow to pale orange–yellow could be observed. The absorption band (λ_{max} at 370 nm) of chloranil undergoes obvious red shift along with a modest increase in absorption intensity, and the new absorption peaks at 426 and 450 nm, albeit very weak (as compared with the case of calix[4]pyrrole–chloranil complex), could be observed. Furthermore, the addition of I^- could cause obvious increase in the intensity of the chloranil absorption band at 370 nm, and the mixed solution turns yellow. But even so, the charge–transfer interaction between calix[4]pyrrole and chloranil could not be perturbed in the presence of I^-, maybe due to the lower affinities of iodide for chloranil and calix[4]pyrrole. On the other hand, no any changes in color and spectra were observed upon addition of Cl^-, Br^-, HSO_4^-, and ClO_4^- ions to the solution of chloranil under the same conditions.
9. Preliminary experiments indicate that the addition of 5′-monophosphate disodium salt of inosine, uridine or guanosine aqueous solution (3.0×10^{-4} M) to the stock solution of calix[4]pyrrole–chloranil complex **1·2** in 10% $CHCl_3$–70% EtOH–20% H_2O (v/v/v) mixture could cause instantly visual color changes from pale blue to pale yellow. The stock solution was prepared by addition of 7-fold EtOH and 2-fold H_2O to the blue complex solution containing **1** (4.0×10^{-4} M) and **2** (4.0×10^{-3} M) in $CHCl_3$.