

A Selective Colorimetric Anion Sensor Based on Di(hydroxymethyl) Di-(2-pyrrolyl)methane -TCBQ System

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Abstract: A new class of non-covalent charge-transfer complex for anion sensing, consisting of di(hydroxymethyl) di-(2-pyrrolyl) methane and chloranil (TCBQ) is characterized. The new colorimetric anion sensors can generate visual color change against PO_4^{3-} and HPO_4^{2-} anions in EtOH/H₂O (1:1 v/v) mixture solution. The dipyrromethane-quinone aggregations may be used for higher selective detection of PO_4^{3-} than other inorganic anions in water solution.

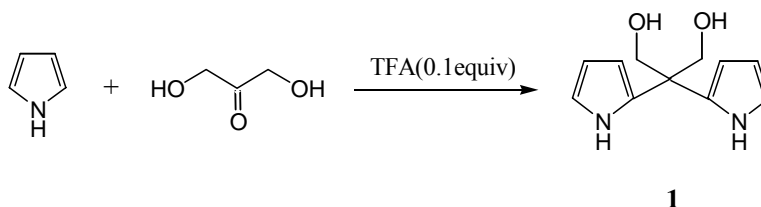
Keywords: Dipyrromethane, charge-transfer complex, anion detection, sensor.

The development of new selective chemosensors for anion sensing based on a supra molecular concepts is a field of current interest¹. A significant amount of work in this field has been devoted to obtain colorimetric anion sensors that allow naked-eye detection without the use of any spectroscopic instrumentation. However, a number of colorimetric anion sensors have been devised to use organic solvents as the detection medium because these sensors rely on hydrogen bonding for the recognition of analytes². In our present work, we use the water soluble di(hydroxymethyl) di-(2-pyrrolyl)methane **1** with chloranil (TCBQ)**2** to form charge-transfer complex colorimetric sensor for selective detection of PO_4^{3-} and HPO_4^{2-} in C₂H₅OH/H₂O mixture solution. We report herein a colorimetric sensor that can selectively detect PO_4^{3-} anions in water solution.

The water-soluble di(hydroxymethyl) di-(2-pyrrolyl) methane **1** was prepared in 90% yield by condensation of dihydroxyacetone with excessive pyrrole in the presence of a catalytic amount of trifluoroacetic acid (**Scheme 1**), and purified by crystallization³. In assembling the sensor, we took advantage of the charge-transfer interactions by formation of **1** with **2**. The charge-transfer complex was readily obtained by dissolving quinone **2** and dipyrromethane **1** in C₂H₅OH. The complexes are blue and can be mixed with water, which are features desirable for using the complexes as a sensing probe for the inorganic anions. UV-Vis spectroscopy was employed to determine the association constant of complex **1**·**2** ($K_a=3.7\times 10^2 \text{ L mol}^{-1}$) in the EtOH/H₂O = 1:1 (v/v) solvent system, using the Benesi-Hildebrandt analysis⁴ of the absorbance changes at the new band maximum.

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Scheme 1



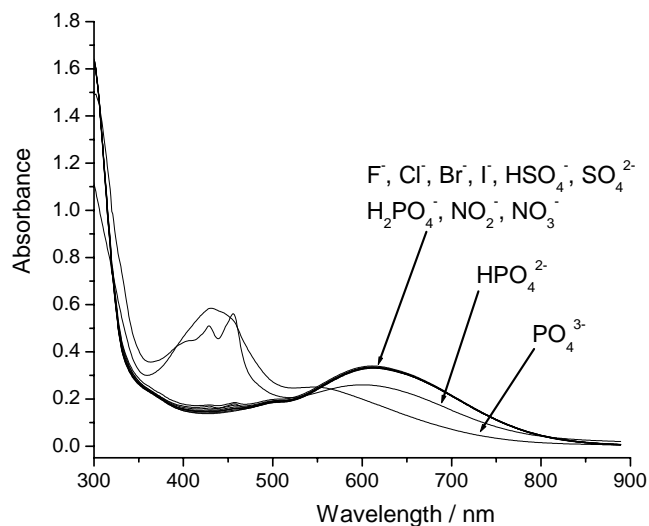
However, under the same conditions a control experiment indicated that addition of different inorganic anions to the EtOH/H₂O = 1:1 (v/v) solution of **1** (1.0×10^{-4} mol/L) or **2** (1.0×10^{-4} mol/L) could not cause notable color change.

The dipyrromethanes were regarded as an important precursor for the synthesis of various *meso*-substituted calixpyrroles⁵, expanded calixpyrroles, and calixpyrrole analogues⁶. However, it was hardly reported as a chemosensor for inorganic anions sensing in the supra-molecular system. Changes in color were studied by addition of 20 equiv. (relative to quinone) of the corresponding anion (F⁻, Cl⁻, Br⁻, I⁻, HSO₄⁻, SO₄²⁻, PO₄³⁻, HPO₄²⁻, H₂PO₄⁻, NO₃⁻ and NO₂⁻ added as their inorganic sodium salts.) to C₂H₅OH/H₂O = 1:1 (v/v) mixtures solution of complex (1.0×10^{-3} mol/L **1**, 1.0×10^{-4} mol/L **2**). The most remarkable effect was the selective detectable color change with naked eye in the presence of PO₄³⁻ or HPO₄²⁻ anions. Specifically, it was found that the ensemble solution from blue to orange-yellow for PO₄³⁻, from blue to yellow-green for HPO₄²⁻. **Figure 1** shows the changes in the absorption spectrum of the complex **1·2**, containing 1.0×10^{-3} mol/L **1** and 1.0×10^{-4} mol/L **2**, in the presence of various anions (2.0×10^{-3} mol/L).

The spectrum of the free complex **1·2** in EtOH/H₂O (1:1, v/v) mixture was characterized by the presence of peak at $\lambda_{\max} = 611$ nm. Upon addition of inorganic anions, HPO₄²⁻ and PO₄³⁻ to the blue complex solution, the charge-transfer absorption band ($\lambda_{\max} = 611$ nm) of the complex **1·2** obvious decreased while a new absorption band appeared in the region of 400-500 nm ($\lambda_{\max} = 427$ and 453 nm), ascribed to the intermolecular interactions between anions and the chloranil moiety with help of dipyrromethane. On the other hand, no any noticeable changes in color and UV-Vis absorption spectra were observed for F⁻, Cl⁻, Br⁻, I⁻, HSO₄⁻, SO₄²⁻, H₂PO₄⁻, NO₃⁻, and NO₂⁻ under the same conditions (even at much higher anion concentration), which means the complex **1·2** exhibits negligible perturbation in the presence of these anions. Moreover, the high selectivity for phosphate is very advantageous in biological sensing applications, meaning it would allow the sensing ensemble to quantities phosphate ion in the presence of high concentration of Cl⁻.

In summary, the new water soluble di(hydroxymethyl) di-(2-pyrrolyl)methane was synthesized. The blue charge-transfer complex consisting of dipyrromethane **1** and TCNQ has been designed to selectively distinguish the phosphate ions through the change of color in water/organic solvent mixtures. We believe that the dipyrromethanes/quinone complex must play a significant role in the development of a new generation of colorimetric probe for the selective recognition of amino acids, dipeptides, and nucleotide molecules.

Figure 1 Absorption spectra of the complex **1·2** ($[1]=1.0\times 10^{-3}$ mol/L, $[2]=1.0\times 10^{-4}$ mol/L) in EtOH/H₂O (1:1, v/v) upon additions of various inorganic anions (2.0×10^{-3} mol/L).



Acknowledgment

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References and Notes

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- ¹H-NMR (400 MHz, CDCl₃, ppm) of compound **1**: 8.74(s, 2H, NH), 6.73(m, 2H, pyrrole-H_α), 6.23(m, 2H, pyrrole-H_β), 6.14(m, 2H, pyrrole-H_β), 4.08(s, 4H, CH₂), 1.94(s, 2H, OH). MS (EI⁺) *m/z* 206(M⁺, 65%), 175(100). Anal, calcd. for C₁₁H₁₄O₂N₂: C 64.06; H 6.84; N 13.59; Found: C 64.21; H 6.71; N 13.68.
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