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Quinones based molecular receptors for recognition of anions and metal ions

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1. Introduction

The sensing of a target analyte (anion/metal ion) in the environment or in biological samples using abiotic receptors is one of the major thrust areas at the boundaries of organic, inorganic, analytical, environmental, and medicinal chemistry. Molecular recognition is the genesis of these sensing protocols and involves the design of receptors possessing steric and electronic features in complementary to the target analytes.^{1–11} A receptor mainly contains a binding site and a signaling subunit and these two parts are linked through a covalent bond in the receptor. The interaction of the target analyte with the binding sites changes the electronic properties of the signaling subunit resulting in the sensing of the target anion or metal ion via color or emission modulation.¹² The choice of a signaling subunit,^{13–18} which is capable of giving information about the binding event; i.e., change in the absorbance or the fluorescence emission behavior or electrochemical shift of the redox potential in redox-active molecules, is very important in the development of a receptor. The quinones such as anthraquinones, naphthoquinones, and benzoquinones are highly colored compounds and also good fluorophores showing excitation in the range of 350–500 nm with wide emission bands centered between 500 and 600 nm.¹⁹

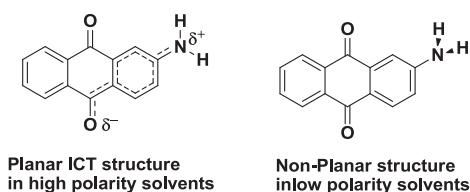
In 2001, Sessler et al.²⁰ in their article ‘off-the shelf colorimetric anion sensors’ for the first time systematically showed that substituted quinones can be used to signal the qualitative or quantitative presence of anions. Before that there was only a single report by Yamamura et al. where cerium(III)–alizarin complex was used for the colorimetric sensing of fluoride ions in water.²¹ Since then, quinones appended with variety of functional moieties have been used for the recognition of both anions and metal ions and only a brief review on chemistry of constrained crown ring systems including some examples of anthraquinone derivatives as metal ion receptors has appeared in the literature.²² In the present review, the applications of such functionalized quinones in recognition of anions and metal ions using absorbance or fluorescence as signaling channel have been discussed. However, for the benefit of the reader, the electrochemical behavior of quinones based receptors toward metal ions has been discussed. For the simplicity, the recognition of anions and metal ions has been presented in two separate sections and electrochemical behavior in a separate section.

2. Quinones based receptors for anions

In this section, various receptors for the recognition of anions based on anthraquinone, naphthoquinone, benzoquinone, and pentaquinone derivatives have been discussed. These receptors are sub-divided according to the binding groups present on the molecules for the recognition of an anion viz.

2.1. Amino and hydroxyl substituted quinones as anion receptors

The photophysical properties of anthraquinones have been extensively investigated in literature. Amino and hydroxyl anthraquinones are capable of forming intramolecular hydrogen bonds. These molecules possess non-planar structure in non-polar solvents, however, in polar solvents internal charge-transfer (ICT) coupled with stronger intramolecular hydrogen-bonding forces a planar ICT structure (Scheme 1). Owing to this difference in nature, the photophysical characteristics of anthraquinones are unusually different in solvents of moderate to higher polarities compared to those in non-polar solvents. In non-polar solvents, as the amino lone pair will have a largely reduced resonance with the anthraquinone π -cloud, the absorption and fluorescent maxima are largely blue-shifted and fluorescence quantum yields and

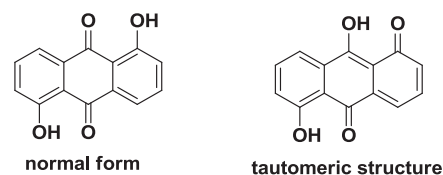


Scheme 1. Effect of solvent polarity on ICT behavior of aminoanthraquinone.

fluorescence life times are unusually higher in comparison to those in higher polarity solvents.^{23–26}

The excited states of aminoanthraquinones bear large electron density on the carbonyl oxygen and promote strong intermolecular hydrogen-bonding interaction with protic solvents like alcohols and water. This results in their radiationless deactivation to the ground state as the electronic excited energy is dissipated through the hydrogen bond as vibrational energy.^{27–33}

In case of α -hydroxy anthraquinone, in non-polar solvents, the excited state proton-transfer reaction (Scheme 2)^{34,35} participates significantly in the de-excitation of 1-hydroxy- and 1,5-dihydroxyanthraquinones. For example in case of 1,5-dihydroxyanthraquinone, highly structured fluorescence at short wavelength between 485 and 540 nm is due to normal form and the unstructured emission at wavelengths longer than 550 nm is approximately ten-fold stronger, and is assigned to arise from tautomeric structure achieved through ESIPT phenomenon. Other α -hydroxyanthraquinones also behave similarly. However, 1,4-dihydroxyanthraquinones do not show excited-state proton-transfer.^{36–41}



Scheme 2. ESIPT in hydroxyanthraquinones.

These amino and hydroxyanthraquinones undergo hydrogen-bonding or deprotonation at NH or OH moieties with anions, though in most of the cases, it is difficult to differentiate between hydrogen-bonding and deprotonation processes. This enhances the internal charge-transfer in the receptor and as a result leads to the red-shift of the absorption maxima.

Sessler et al.²⁰ studied the changes in the absorption spectra of anthraquinones, 1,2- (3), 1,4- (4), 1,5- (5), 1,8- (6), and 2,6-diaminoanthraquinones (7) as well as 1- (1) and 2-aminoanthraquinone (2) induced upon the addition of various anions like F^- , Cl^- , Br^- , I^- , AcO^- , CN^- , NO_3^- , $H_2PO_4^-$, HSO_4^- , etc. in dichloromethane. Amongst these, significant bathochromic shifts in the absorption spectra were observed for 3 and 6 in dichloromethane in the presence of Cl^- , Br^- , and $H_2PO_4^-$ ions. These spectral changes were particularly dramatic in the case of 1,2-diaminoanthraquinone (3). The solution of 3, initially yellow in color (λ_{max} 478 nm) became dark purple (λ_{max} 555 nm), red (λ_{max} 519 nm), reddish orange (λ_{max} 513 nm), orange (λ_{max} 499 nm), purple (λ_{max} 548 nm), and orange (λ_{max} 493 nm) when exposed to F^- , Cl^- , Br^- , I^- , $H_2PO_4^-$, and SO_4^{2-} ions, respectively. These color changes could be attributed to the increased ICT in the anthraquinone moiety on hydrogen-bonding with the anions. The solutions of 6 in dichloromethane also underwent change in color when exposed to these anions albeit to a lesser extent due to decreased cooperation of two NH_2 moieties in binding with anions. The solutions of aminoanthraquinones 1, 2, 4, 5, and 7 possessing isolated NH_2 moieties did not show any significant color changes when exposed to these anions.

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