A New Type of Cation Responsive Chromoionophore with Spectral Sensitivity in the Near-Infrared Spectral Range

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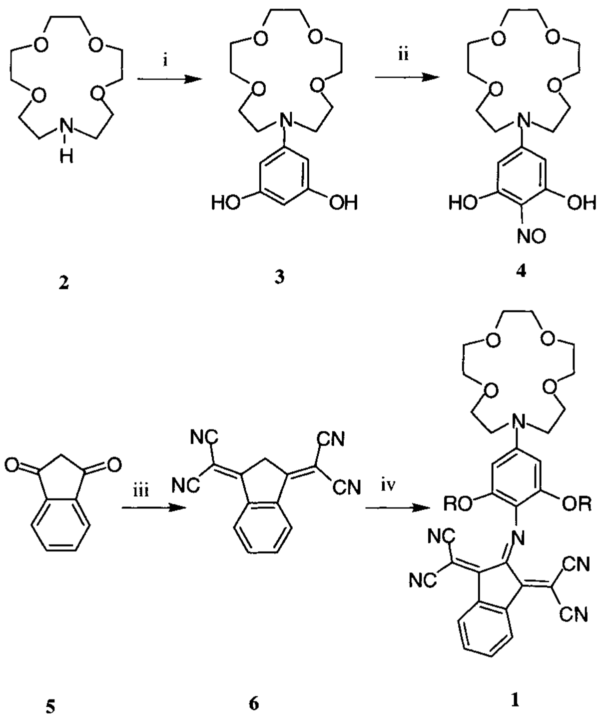
A long wavelength absorbing cation responsive chromoionophore **1** based on the strongly π-electron accepting dicyanovinylindane subunit and an electron donating *N*-phenylazacrown ether binding site was synthesized. The absorption spectra of this compound in CH_3CN show strong changes in the near-infrared (NIR) spectral range upon binding of cations in the crown-ether moiety.



Scheme 1. R=$COCH_3$; Reagents and conditions: i, phloroglucinol, toluene / *n*-BuOH 1:1, reflux (Dean–Stark), 48 h, 11%[6]; ii, $NaNO_2$, HCl / H_2O, 0 °C, 25 min, 40%; iii, malononitrile, EtOH, r. t., 15 min, then $NaOAc\cdot 3H_2O$, reflux, 5 h, 85%[7]; iv, **4**, acetic anhydride, r. t., 3 h, 16%.

The near-infrared spectral range ($\lambda > 750$ nm) is favored as the spectral working range for optical chemical sensors because of the absence of naturally occurring absorbing species and the availability of low-cost compact size solid-state devices for optical measurement systems. Operating in the deep-red region of the spectrum also eliminates the photodegradation of biological compounds often found in the case of UV irradiation. So far, several NIR absorbing and emitting ion selective chromoligands have been presented in the literature, based on the long wavelength absorbing squaraine chromophore, characterized by narrow and extremely intensive absorption bands.[1–6] Despite these useful characteristics, many of the squaraine-based sensing molecules suffer from the drawback of small ion-induced spectral effects, low solubility and dye aggregation.

Merocyanine dyes incorporating the dicyanovinylindane moiety are an example of a typical donor–acceptor chromophore with relatively long wavelength absorption bands of moderate intensity.[7] Because of their spectral characteristics and high chemical and photochemical stability, they have been used as pH-sensitive indicators for NIR optical chemical sensors.[8]

In this letter, we report on the synthesis and the spectral characteristics of a new dicyanovinylindane incorporating merocyanine-type chromoionophore **1**, designed according to the basic principles of donor–acceptor chromophores. Compound **1** is composed from an aromatic nitrogen π-electron donor as part of an azacrown ether and the strongly electron-withdrawing dicyanovinylindane acceptor,[9] connected through a nitrogen substituted methine bridge. This combination results in a cation-responsive chromoionophore with spectral sensitivity reaching into the NIR wavelength range.

In order to investigate the usefulness and the spectral characteristics of dicyanovinylindane-connected chromogenic crown ethers, a commercially available monoaza-15-crown-5-ether **2** was used as the starting material. However, any other monoazacrown ether could be used instead, making the presented synthetic pathway a general route to obtain a variety of chromoionophores. Chromoionophore **1** was synthesized according to Scheme 1. Crown ether **2** was condensed with 1,3,5-trihydroxybenzene (phloroglucinol) with azeotropic water removal, making use of the presence of a small amount of the keto tautomer of phloroglucinol.[10] In the next step, the resulting *N*-phenylazacrown compound **3** was converted into its nitroso derivative **4**, and then condensed with 1,3-bisdicyanovinylindane **6**, prepared by the reaction of malononitrile with 1,3-indandione, to yield the chromoionophore **1**[11] as a green crystalline solid. During the last reaction step, the phenolic hydroxy groups of **4**, originating from phloroglucinol, are converted into acetoxy groups due to the presence of acetic anhydride. This transformation reduces the pH cross-sensitivity of the chromoionophore and increases the degree of spectral changes during cation binding. The response mechanism is based on a photoinduced intramolecular charge transfer (ICT)[12] from the crown nitrogen center to the dicyanovinylindane acceptor. Due to its interaction with the positively charged cation bound in the crown cavity, the π-electron donating strength of the anilinic nitrogen is weakened, resulting in a hypsochromic spectral shift. The disturbance of the π-electron distribution by ion binding is rather small, especially for monovalent alkali metal cations with low charge density. Therefore, the presence of π-electron donor groups in the chromoionophore that are not involved in cation binding such as the phenolic hydroxy group, is expected to decrease the cation induced signal shifts. With the acetoxy group being a weaker π-electron donor than the hydroxy group, this undesired side-effect is reduced.

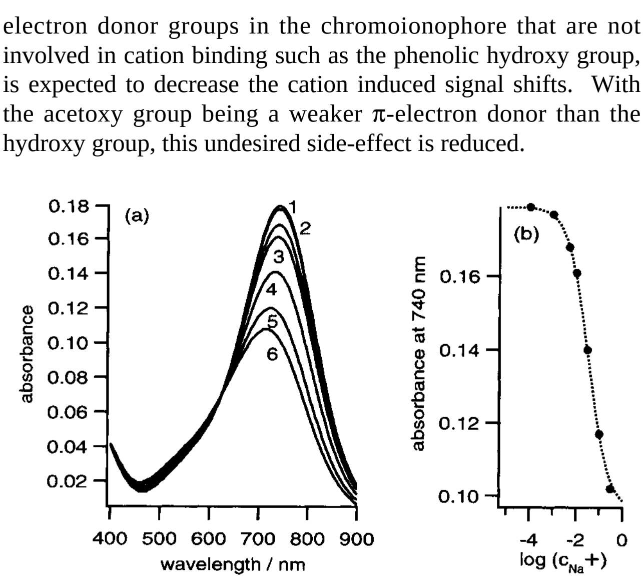


Figure 1. (a) Change in the absorption spectra of **1** upon addition of sodium perchlorate in CH_3CN (1: ion free – 1 mM; 2: 5 mM; 3: 10 mM; 4: 30 mM; 5: 0.1 M; 6: 0.3 M); $\Delta\lambda_{max}$ = 28 nm. (b) response curve for **1** (at 740 nm) in the presence of Na^+ (●); (....) theoretically calculated response ($K_a = 30\ M^{-1}$); [**1**] = 1.1×10^{-5} M.

First, the spectral characteristics of **1** were investigated. The longest wavelength absorption band was found in chloroform solution at 762 nm. In order to study the effect of the presence of metal cations, measurements were performed in acetonitrile solution. In this case, the absorption maximum was found at 741 nm wavelength. As shown in Figure 1a, the expected hypsochromic spectral shift together with a strong decrease in absorbance was observed, when increasing the sodium ion concentration in the sample. In Figure 1b, the normalized response curves for sodium cations extracted from the absorbance values at 740 nm are presented. A signal decrease is found in the concentration range of 10^{-4} M to 10^{-1} M. The association constant, K_a, was calculated as 30 M^{-1}. For lithium cations, K_a was found to be 200 M^{-1}. Even though the ionic diameter of Na^+ matches the size of the crown ether, this difference in binding strength reflects the higher charge density of the lithium ion. The rather low complex stability might be explained by the very strong π-electron accepting properties of the two dicyanovinylindane groups, reducing the electron density at the anilinic nitrogen in a similar way as described by Lapouyade and coworkers[13]. In order to confirm the role of the crown ether as a binding site, spectra of a structurally similar dye without a crown ether and acetoxy substituents were recorded (data not shown). No ion concentration dependent spectral changes were observed in this case.

In the present letter, a model compound for a new type of NIR sensitive chromoionophore has been presented. Strongly ion concentration dependent spectral changes between 700 nm and 800 nm have been observed. Due to the promising results, further examples of dicyanovinylindane chromoligands will be prepared, using modified azacrown ethers bearing bulky sidewalls[14] to obtain NIR chromoionophores with high ion selectivity. Such compounds will be useful for optical ion determination in solvent extraction experiments. Furthermore, lipophilic derivatives obtained by replacing the acetoxy group, can be incorporated into ion selective ion-exchanger optode membranes made from plasticized PVC.

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11 Spectral data of **1**: ^1H NMR ($CDCl_3$) δ 2.09 (s, 6H), 3.63–3.82 (m, 20H), 6.55 (s, 2H), 7.80–7.83 (m, 2H), 8.60–8.62 (m, 2H); ESI-MS ($[M+Na]^+$) found 687.01, calcd for $C_{35}H_{32}N_6NaO_8$ 687.22.

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