A Highly Selective Calix[4]arene-Based Chromoionophore for Ni^{2+}

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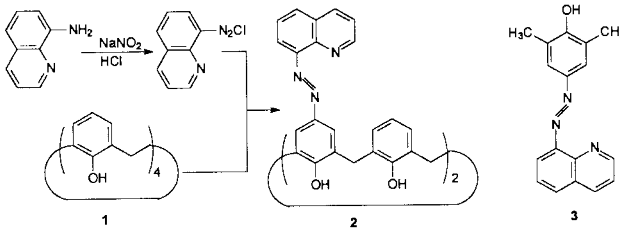
A novel chromoionophore 5,17-bis(quinolyl-8-azo)-25,26,27,28-tetrahydroxycalix[4]arene has been synthesized as a highly selective reagent for Ni^{2+} in the presence of excess alkali, alkaline earth and other transition metal ions.

Molecular design of chromogenic calixarenes has attracted much attention for their potential applications in optical sensors.[1] In the past years, a lot of chromogenic calix[n]arene derivatives have been synthesized to achieve highly selective ligands for alkali[2–5] and alkaline earth[6–8] metal ions, but relatively less attention was paid to transition metals.[9] Furthermore, many of the transition metal ions (Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+}) have a similar reaction properties with commonly used chromogenic reagents such as diphenylthiocarbazone and 1-(2-pyridylazo)-2-naphthol,[10] and interferences often occur when an individual analyte is determined. Therefore, the development of new chromoionophores is of significant importance for selective species detection in various systems. Calixarenes as a platform have been utilized in the design of optical sensors for Ag^+, Co^{2+}, Cu^{2+}, Mn^{2+}, Fe^{3+} and Zn^{2+}.[11] However, to the best of our knowledge, only one calixarene-based optical sensor for Ni^{2+} (fluorescence quenching) was reported.[12] Herein, a new chromoionophore deriving from calix[4]arene was designed for Ni^{2+}-selectivity. Since the quinolylazo group has a high selectivity for Ni^{2+},[13] 8-aminoquinoline was chosen as an optical moiety. The diazo-coupling reaction was employed to couple with calix[4]arene. The resulting azo group together with the nitrogen atom in the quinoline ring was expected to serve as the chromogenic and coordination group. We now report the results of these studies.



Scheme 1.

The chromoionophore 5,17-bis(quinolyl-8-azo)-25,26,27,28-tetrahydroxycalix[4]arene **2** was synthesized by diazotizing 8-aminoquinoline and then coupling with calix[4]arene **1** in DMF–pyridine–H_2O (v/v/v 10:2:7) media (Scheme 1). The structure of **2** was characterized by ^1H NMR, mass spectroscopy and elemental analysis.[14] Although some of the diazo coupling reactions on calix[4]arene take place in an autoaccelerative manner due to the specific hydrogen-bonding effect among the calix[4]arene OH groups,[5] leading to the formation of a tetrasubstituted calix[4]arene as a main product, the present observation is not such a case. Namely, even though an excess of the diazonium salt was used for the coupling, two phenolic units remained unsubstituted, and it was a bis(arylazo) compound instead of the corresponding tetrasubstituted calix[4]arene as main product that was isolated after chromatography ($CHCl_3$/methanol, v/v 10/1). This presumably results from the steric hindrance of quinoline ring, similar to the literature reports that incompletely *p*-position-substituted derivatives can be formed.[4,8] The ^1H NMR spectral patterns of methylene hydrogens of the bis(arylazo) compound isolated above displayed one pair of doublets but appeared as two broad signals at room temperature (25 °C), suggesting that the bis(arylazo) compound was a symmetrical one, that is, 1,3-bis(arylazo) derivative, and existed in the cone conformation.[15] Combined with the data of mass spectrometry and elemental analysis, the bis(arylazo) compound was identified as the chromoionophore **2**.

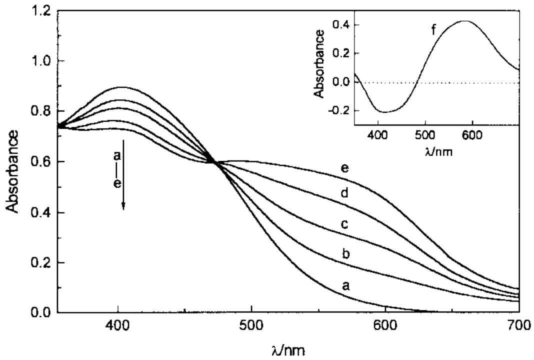


Figure 1. Absorption spectra of **2** (2.0×10^{-5} mol dm^{-3}) in buffer solution (pH=10.7) containing 1% (v/v) DMF in the presence of Ni^{2+}: (a) 0, (b) 0.8×10^{-6}, (c) 1.6×10^{-6}, (d) 2.4×10^{-6}, (e) 3.2×10^{-6} mol dm^{-3}. Spectra (a-e) against water blank. The inset (f) shows the spectrum (e) but against the corresponding reagent blank.

Figure 1 shows the absorption spectra of **2**, whose absorption maximum is located at 400 nm. Addition of Ni^{2+} to such a solution of **2** caused a large bathochromic shift (wavelength change of 180 nm) with an increase in absorbance, indicating that the formation of the **2**–Ni^{2+} complex increases the rigidity and conjugation of the chromoionophore. A new band at 580 nm of the **2**–Ni^{2+} complex [see the inset (f) in Figure 1] and an isosbestic point at 478 nm can be clearly observed. The optimal pH range for the complex formation was found to be pH = 10.5–11.2 in this system (Na_2HPO_4–NaOH buffer). With a 2.0×10^{-5} mol dm^{-3} concentration of **2**, the absorbance was directly proportional to the concentration of Ni^{2+} in the range 1.6×10^{-7}–4.8×10^{-6} mol dm^{-3}, and the apparent molar absorptivity (ε) is 1.28×10^5 dm^3 mol^{-1} cm^{-1}. Use of the continuous variation method revealed that the stoichiometric ratio of **2** to Ni^{2+} in the complex is 1:1, and the stability constant is 2.9×10^6 dm^3 mol^{-1}. Similarly, the complex stability constants of **2** with Co^{2+}

Table 1. The approximate selectivity coefficients for Ni^{2+} to other cations

M^{n+}	Cu^{2+}	Co^{2+}	Ag^{+}	Cd^{2+}	Zn^{2+}	Fe^{3+}	Hg^{2+}	Mn^{2+}	Pb^{2+}	Cr^{3+}	Ca^{2+}	Mg^{2+}	K^{+}
$K_{Ni^{2+},M^{n+}}$	15	25	50	50	110	280	300	>1000	>1000	>1000	>5000	>5000	>5000

and Cu^{2+} (two often coexistent ions of Ni^{2+}) are 1.12×10^6 and 0.96×10^6 dm^3 mol^{-1}, respectively, showing that **2** has the highest affinity for Ni^{2+}.

In contrast, addition of other transition metal ions caused only minor changes in the absorption spectra, and no change was observed after adding alkali metal, alkaline earth metal and some of the transition metal ions, also indicating that **2** is highly selective for Ni^{2+}. To further verify the little interference of other metal ions on the **2**–Ni^{2+} complex, the color reaction contrast $\Delta\lambda$ [λ_{max}(complex) – λ_{max}(ligand)] was measured in the presence of different metal ions (Figure 2). From these data, the approximate selectivity coefficients for Ni^{2+} to other cations can be calculated as $K_{Ni^{2+},M^{n+}} = C_{M^{n+}}/C_{Ni^{2+}}$ using the salt concentrations required to give an absorbance value of 0.22 at 580 nm,[3,4,8] and the results were summarized in Table 1. It can be seen that the chromoionophore **2** exhibits excellent selectivity for Ni^{2+} over a wide range of transition, alkali and alkaline earth metal cations.

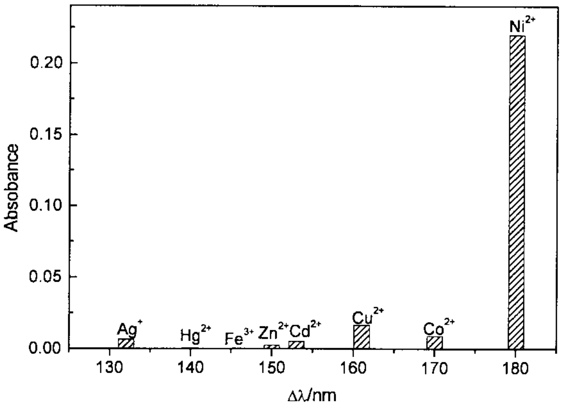


Figure 2. The color reaction contrast $\Delta\lambda$ [λmax (complex) – λmax (ligand)] of **2** (2.0×10^{-5}mol dm^{-3}) in the presence of different metal ions in buffer solution (pH=10.7) containing 1% (v/v) DMF. Ni^{2+} and other metal ions: 1.6×10^{-6} mol dm^{-3}. Pb^{2+}, Mn^{2+}, Cr^{3+}, Ca^{2+}, Mg^{2+} and K^{+} are not included in the figure because no change of absorption spectra of **2** was caused by them.

On the other hand, 8-(3,5-dimethyl-4-hydroxyphenylazo)-quinoline **3** (Scheme 1),[14] which is a monomer-type of **2**, gave an absorption peak at 470 nm. A shorter bathochromic shift ($\Delta\lambda$ = 96 nm) and a smaller increase in absorbance was induced by Ni^{2+}, and a similar change was caused by other transition metal cations. The superior analytical features of **2** to **3** might result from the cooperating coordination of the two quinolylazo groups of **2** with Ni^{2+}, and such a coordination would raise conjugation and provide some rigidification for the whole molecule, causing a large bathochromic shift. Also, the calix[4]arene skeleton of **2** might serve as a shielding unit, which prevents close approach of other metal ions to the quinolylazo coordination group, thus making a part contribution to the high Ni^{2+}-selectivity of **2**.

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14 **2:** Yield: 24%, mp > 300 °C; IR (KBr): 3400 (OH), 1450 (N=N) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, 298 K): δ 10.18 (s, 4H, ArOH), 8.62 (d, 2H, ArH in the quinoline moiety), 6.90–7.78 (m, 18H, ArH in the phenol and quinoline moieties), 6.60–6.52 (m, 2H, ArH in the quinoline moiety), 4.32 (s, 4H, $ArCH_2Ar$), 3.68 (s, 4H, $ArCH_2Ar$). FAB-MS: *m/z* 734 (M^+). Anal. Calcd for $C_{46}H_{34}O_4N_6\cdot0.5CHCl_3$: C, 70.30; H, 4.38; N, 10.58%. Found: C, 69.90; H, 4.40; N, 10.21%.
3: Yield: 62% (from ethanol), FAB-MS: *m/z* 277 (M^+). Anal. Calcd for $C_{17}H_{15}ON_3\cdot0.5C_2H_5OH$: C, 71.98; H, 6.04; N, 13.99%. Found: C, 71.87; H, 5.96; N, 13.16%.

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