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Multiparameter molecular sensor based on a compound containing tetrathiafulvalenium, thiophene and pyridine fragments

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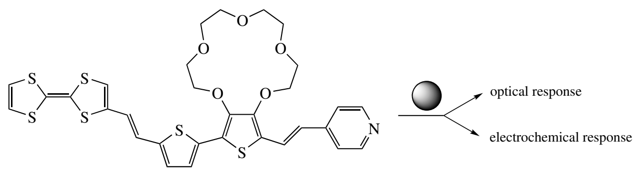
The optical and electrochemical properties of a dithiophene crown ether derivative containing vinylpyridine and vinyltetrathiafulvalene fragments have been examined. The combination of an extended chromophoric system and tetrathiafulvalene in a sensor molecule provides both optical and electrochemical responses upon complex formation.



Spectroelectrochemical analysis, in which optical and electrochemical methods are integrated, is used for food testing and the monitoring of metal cations in aqueous solutions. Multiparameter molecular sensors, which change both optical and electrochemical properties during metal cations coordination, are necessary for spectroelectrochemical analysis.[1] Several thiophene derivatives are known to demonstrate cation-induced changes in optical and electrochemical properties.[2]

We studied compound **1**, which is an extended chromophore with a tetrathiafulvalene residue. Crown ethers annulated with thiophene and pyridine act as coordination centers, whose conjugation with the chromophore system leads to a significant effect of complex formation on the optical properties of **1**. We supposed that the presence of thiophene and tetrathiafulvalene residues would result in considerable changes in electrochemical properties due to complex formation. The synthesis of compound **1** was described earlier.[3]

The complexation[†] of compound **1** can proceed with the formation of the complexes with ligand : metal cation ratios of 2 : 1 (K_{21}), 1 : 1 (K_{11}) and 1 : 2 (K_{12}). We studied the complex

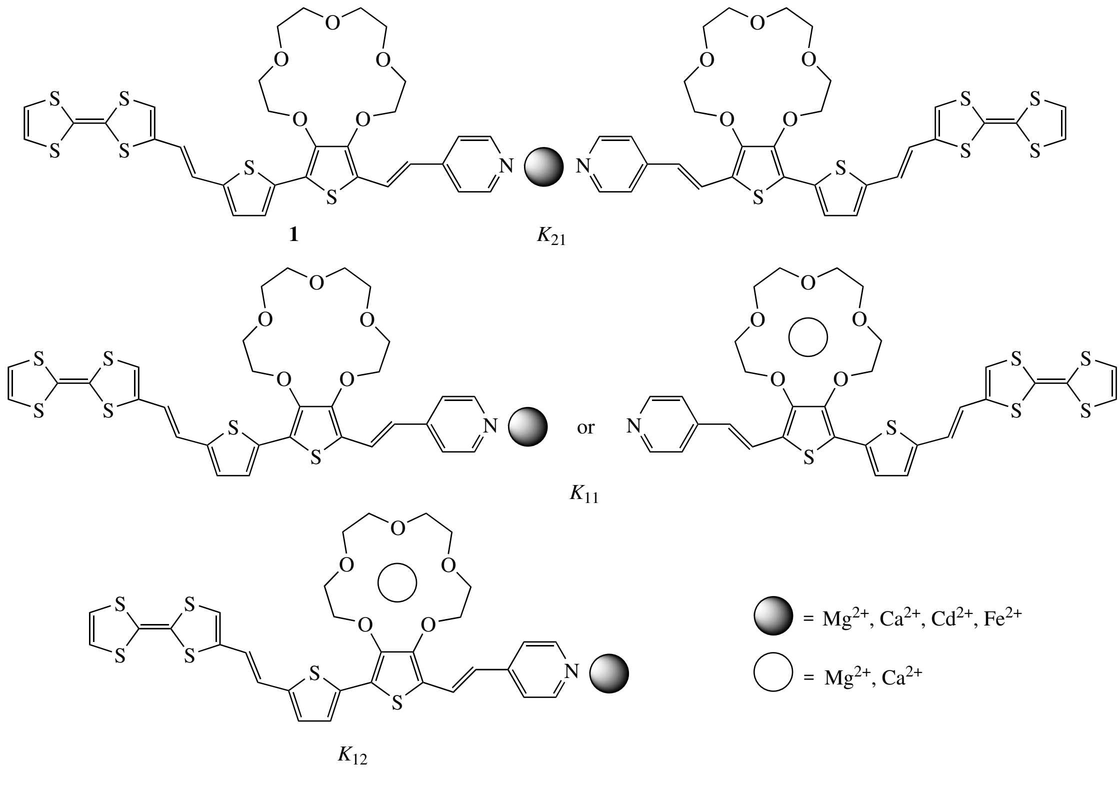


Table 1 Stability constants (lg*K*), absorption maxima of ligand **1** and its complexes with Ca^{2+}, Mg^{2+}, Fe^{2+} and Cd^{2+} perchlorates (MeCN, $T = 20\pm1$ °C), and electrochemical potentials [Ag/AgCl/KCl (sat.)] of the test compounds in MeCN–CH_2Cl_2 (3:1) in the presence of Bu_4NBF_4 on a platinum electrode (potential scanning rate, 200 mV s^{-1}).

Compound	$\lg K_{21}$	$\lg K_{11}$	$\lg K_{111}$[a]	$\lg K_{121}$[a]	λ_{max}^{abs}/nm ($\Delta\lambda$/nm)	E_{pc}/V	E_{pa}/V
1					430	–1.66 –1.80	0.40/0.32 0.82/0.73 1.19
1 + Mg^{2+}	9.52±0.15	3.88±0.09		5.32±0.09	480 (50) [$\mathbf{1}_2\cdot(Mg^{2+})$]		
1 + Ca^{2+}						–0.96 –1.60	
1 + Cd^{2+}	10.77±0.29	5.25±0.16	7.64±0.21		463 (33) ($\mathbf{1}\cdot Cd^{2+}$) 437 (7) [$\mathbf{1}_2\cdot(Cd^{2+})$]	–0.611 –1.12 –1.64 –1.80	
1 + Fe^{2+}	8.45±0.13	3.79±0.07			479 (49) ($\mathbf{1}\cdot Fe^{2+}$) 485 (55) [$\mathbf{1}_2\cdot(Fe^{2+})$]	–1.50 –1.65	
($\mathbf{1}\cdot H^+$)					487		
($\mathbf{1}\cdot H^+$) + Mg^{2+}		1.51±0.18			477 (–10) ($\mathbf{1}\cdot H^+\cdot Mg^{2+}$)		
($\mathbf{1}\cdot H^+$) + Ca^{2+}		2.06±0.03			453 (–34) ($\mathbf{1}\cdot H^+\cdot Ca^{2+}$)		

[a] Complex formation occurs with the participation of perchlorate anion.

formation of ligand **1** with Mg^{2+}, Ca^{2+}, Cd^{2+} and Fe^{2+} perchlorates. Calcium and magnesium cations can form complexes with crown ether and pyridine fragments of the molecule of **1**, and iron and cadmium cations can be coordinated to only the pyridine fragment. Changes in the absorption spectra of ligand **1** after the addition of Cd^{2+} and Mg^{2+} perchlorates are presented in Figure 1. Spectral changes after the addition of Ca^{2+} were complicated for analysis; data on the spectrophotometric titration of **1** by Fe^{2+} cations are given in Online Supplementary Materials (Figure S1).

The addition of Cd^{2+} or Fe^{2+} cations leads to a bathochromic shift in the absorption spectra of dye **1** [Figures 1(*a*) and S1]. The observed spectral changes are typical of the case of cation coordination to the pyridine residue.[1(*b*)] The results of titration processed with the SpecFit32 software[4] allowed us to propose a complex formation scheme in which the Cd^{2+} or Fe^{2+} cation coordinates one or two ligand molecules. Table 1 summarizes the stability constants and spectroscopic characteristics of the complexes. The formation of complexes in accordance with Scheme 1 was taken into account in calculations.

$$\mathrm{L + M} \xrightleftharpoons{K_{11}} [\mathrm{LM}],$$

$$\mathrm{L + 2M} \xrightleftharpoons{K_{12}} [\mathrm{LM_2}],$$

$$\mathrm{2L + M} \xrightleftharpoons{K_{21}} [\mathrm{L_2M}],$$

$$\mathrm{L + M + L^*} \xrightleftharpoons{K_{111}} [\mathrm{LML^*}],$$

$$\mathrm{L + 2M + L^*} \xrightleftharpoons{K_{121}} [\mathrm{LM_2L^*}].$$

L = ligand **1**
M = Me^{2+}
$L^* = ClO_4^-$

Scheme 1

A bathochromic shift of the absorption spectra maxima was observed at low concentrations of magnesium cations, which confirmed complex formation with the pyridine moiety of the molecule. The absorption maximum shifted to the short-wave region with a further increase in the magnesium perchlorate concentration due to interaction between magnesium cations and crown-ether moieties. The titration of the protonated form of ligand **1** by solutions of calcium and magnesium perchlorates was performed to validate the participation of the crown ether moiety of the molecule of **1** in the formation of complexes with alkaline

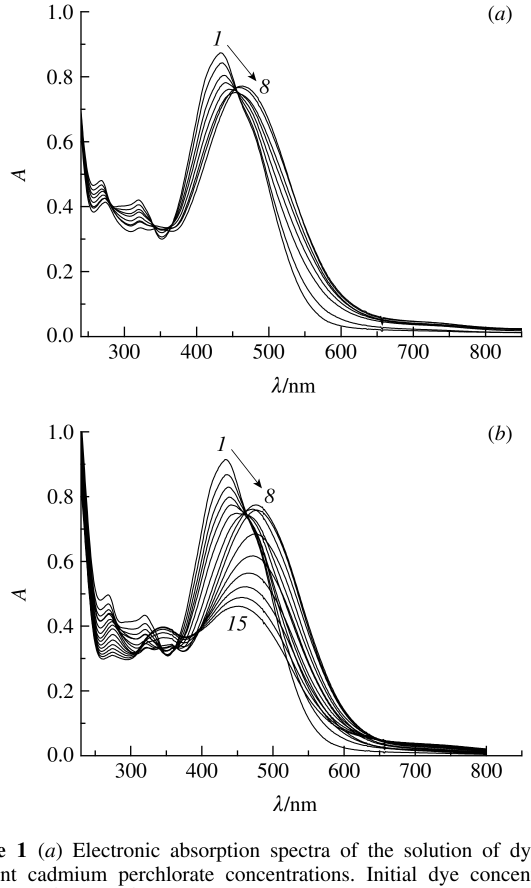


Figure 1 (*a*) Electronic absorption spectra of the solution of dye **1** at different cadmium perchlorate concentrations. Initial dye concentration $C_1 = 2.5\times10^{-5}$ mol dm^{-3}; cadmium perchlorate concentrations, 0–0.05 mol dm^{-3} (*1*)–(*8*). (*b*) Electronic absorption spectra of solution of dye **1** at different magnesium perchlorate concentrations (spectrophotometric titration). Initial dye concentration $C_1 = 2.5\times10^{-5}$ mol dm^{-3}; magnesium perchlorate concentrations, 0–0.25 mol dm^{-3} (*1*)–(*15*).

[†] The UV-VIS absorption spectra were recorded on a Varian Cary 50 spectrophotometer. Spectrophotometric titration at 20±1 °C with variation of concentration of the corresponding perchlorate at a constant ligand concentration was used to vary stability constants of the metal–ligand complexes. Cyclic voltammetric measurements were performed on a PI-50-1.1 potentiostat with a PR-8 programmer. A three-electrode electrochemical cell with a glassy carbon working electrode (disc, $d = 2$ mm), an Ag/AgCl/KCl (sat.) reference electrode and a platinum auxiliary electrode was used. A 0.1 M solution of tetrabutylammonium perchlorate (TBAP) (Fluka) in anhydrous acetonitrile was used as a supporting electrolyte. A 1 mM solution of ferrocene with a 0.1 M solution of TBAP in a corresponding solvent were used in the calibration process. Cyclic voltammograms were recorded after argon bubbling through the experimental solution. All measurements were performed at 20±1 °C. Scanning rate was 200 mV s^{-1}.

earth metal cations. Absorption spectra obtained during dye **1**·H$^+$ titration by magnesium and calcium perchlorates are presented in Figure S2 (Online Supplementary Materials).

Three peaks were observed in the anode region of the cyclic voltammogram (CVA) of ligand **1** (Table 1, Figure S3). The first two peaks are single-electron and reversible. They correspond to the step-by-step oxidation of the tetrathiafulvalene molecular fragment of **1**. The third oxidation peak is due to the oxidation of a thiophene fragment, hypothetically, a crown-containing one. Two multi-electron peaks with poor resolution were detected in the cathode region (Table 1, Figure S4). Three redox-active centers in the cathode region are the pyridine fragment and two thiophene fragments of the ligand. According to published data,[5] all these fragments can be reduced simultaneously in this region of potentials.

The two new peaks appeared in the cathode region at potentials of –0.611 and –1.12 V after the addition of cadmium perchlorates to ligand **1** in solution (Table 1, Figure S5). The first reduction peak (–0.611 V) is attributed to the two-electron reduction of Cd^{2+} to Cd^0, and the second one – to the (Cd^{2+}/Cd^0) reduction[6] in the complex composition. The third and fourth reduction potentials correspond to the reduction of ligand **1** as far as complex **1**·Cd^{2+} reduction occurs irreversibly with the complete destruction of the complex and release of the initial ligand.

Only the shift of reduction potentials in the cathode region of CVA was detected after the addition of iron perchlorate to ligand **1** solution (Table 1, Figure S6). The reduced complex destruction with the initial ligand release was observed as in the case of complex formation with Cd^{2+}, which is confirmed by the similar oxidation-reduction potentials of initial compound **1** and corresponding potentials of solution obtained after complex destruction.

Deeper changes in electrochemical properties were revealed after the addition of calcium perchlorate to ligand **1** solution in the cathode region (Table 1, Figure S7). The peak at –0.96 V corresponds to the reduction of complex **1** with Ca^{2+}. Such a significant shift of potentials to the anode region can be caused by the fact that Ca^{2+} ion also interacts with the pyridine fragment of ligand **1** along with its involvement in the traditional crown ether complex formation.

Thus, a suitable combination of fragments, which give optical and electrochemical properties to the molecule, makes it possible to obtain a miltiparameter molecular sensor that demonstrates significant changes both in absorption spectra (shift up to 50 nm) and in electrochemical characteristics (shift up to 700 mV).

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.04.007.

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