



## Effect of the chromophoric unit on the complex formation properties in the crown ether containing styryl dyes



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### ABSTRACT

The benzo- and thieno-crown ethers containing styryl dyes have been designed and synthesized. The two series of the compounds were based on different combinations of the oxa- and azaoxa-crown ether fragments together with 2-benzovinyl- and thienylvinyl-benzothiazolium units. Their complexing, optical and electrochemical behaviors were characterized, while one and two dimensional NMR was employed to evaluate the structures of free and complexed ligands. The results of these studies showed that thienylvinyl derivatives display the poor ability for binding with metal ions through the crown ether moiety. The phenomenon was explained by the particular charge distribution in thienylvinyl derivatives preventing the interaction of chromophoric crown ethers with metal ions.

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### 1. Introduction

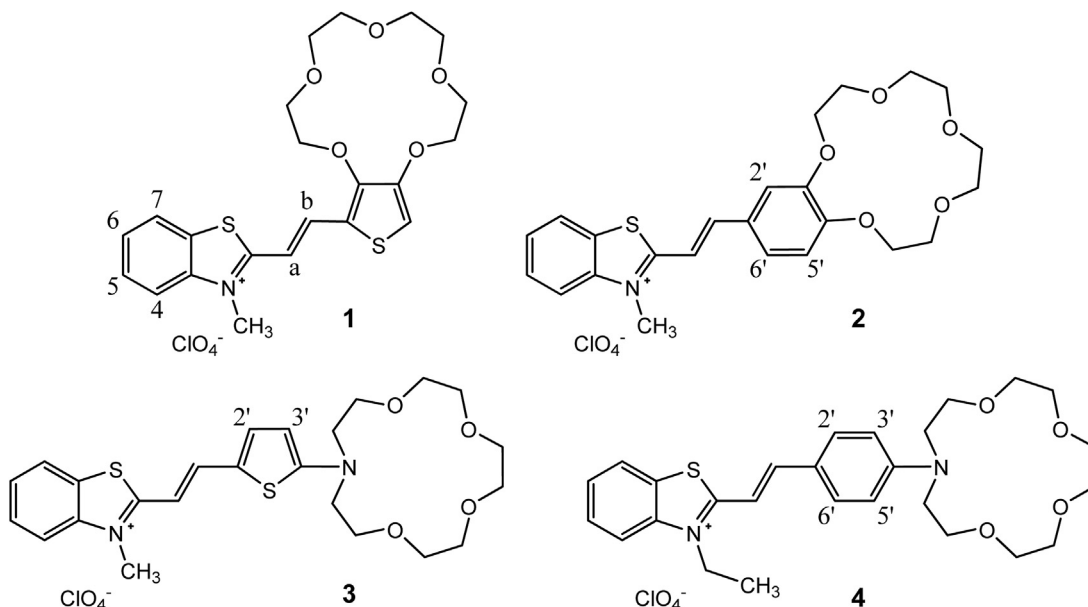
Styryl dye molecules showing  $\pi$ -extended conjugation, exhibit in general high thermal stability and can present electroconductive, magnetic and optical properties [1,2]. Several potential applications such as artificial photosynthesis [3], photocatalysis [4], molecular photovoltaic cells [5], molecular informatics [6], and optoelectronic devices [7,8] are beginning to emerge from this new field of research. Many styryl or stilbene dyes [9,10] were employed in optical molecular systems which contain an ion-sensitive receptor as an integral part of their signal generating chromophore. The systems are of particular interest in optical analysis. These so-called intrinsic chromophoric ionophores usually combine an electron rich donor (D) as the ion-sensitive receptor and an electron acceptor unit (A) in a  $\pi$ -conjugated D–A arrangement. The spectroscopic behavior of such dyes is usually governed by an intramolecular charge transfer (ICT) process which leads to broad, structureless, and significantly Stokes-shifted absorption and emission bands. Upon cation binding to the receptor (= donor part), strong hypsochromic shifts in absorption and fluorescence are found.

The effect of heteroatoms on the photochemical behavior of stilbene like molecules has been investigated in depth in the last decade [9–15]. As indicated by previous photophysical and photochemical investigations on these compounds, the presence of heteroaromatic groups can markedly affect the relaxation properties of the excited states of the corresponding hydrocarbons favoring either the radiative or the reactive (or none of them) deactivation pathways, depending on the type of substitution at the central ring (n) and the nature and position of the heteroatom. In particular, replacement of benzene with thiophene rings induces the S1  $\rightarrow$  T1 intersystem crossing (ISC) that favors photoisomerization in the triplet manifold [16].

Ionically controlling molecular systems which contain an ion-sensitive receptor as an integral part of thiophene molecules have not been the subject of detailed studies up to now. There are a few examples of thiophene-containing cationic sensors [17] without deep analysis of the structure – sensor properties correlation. Such type of sensor systems is of particular interest in fluorometric analysis as well as in electrochemical ion detection. The aim of the present work is to study the oxa- and azaoxa-15-crown-5 ether 3-methyl-2-thienylvinylbenzothiazolium perchlorates (compounds **1** and **3**, Scheme 1) and to compare their optical and complex formation properties with those of 2-styrylbenzothiazoles, where a benzene ring replaces the central thiophene ring unit (compounds **2** and **4**, Scheme 1).

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Scheme 1. Structures of the dyes 1–4 and numbering of protons in NMR spectra.

A comparison of complex formation ability has been made between the closely related styryl families aimed to reveal to what extent the chromophoric unit of the ligand can influence on the ability of the ionophoric moiety to coordinate with metal ions. This is very important point which should be considered while choosing the appropriate design for optical receptors.

## 2. Experimental

### 2.1. Materials

Anhydrous MeCN,  $\text{Mg}(\text{ClO}_4)_2$  (Aldrich) were used as received.

### 2.2. Synthesis

2,3-Dimethyl-1,3-benzothiazol-3 perchlorate was prepared as described [18].

Compounds 2 and 4 have been prepared early [19,20].

#### 2.2.1. 2,3,5,6,8,9,11,12-octahydrothieno[3,4-b][1,4,7,10,13]pentaoxacyclopentadecine-14-carbaldehyd (5)

$\text{POCl}_3$  (94.4 mg, 0.62 mmol) was added to solution of DMF (44.9 mg, 0.62 mmol) and crown-ether 7 (150 mg, 0.55 mmol) in  $\text{CH}_2\text{Cl}_2$  under stirring at  $0^\circ\text{C}$ , than the solution was warmed to room temperature. The reaction mixture was refluxed for 5 h and cooled.  $\text{NaOAc}$  (2.5 ml) was added to the bulb and stirred for 6 h. After addition of water to reaction mixture, the water layer was extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic layer was washed with water and dried over  $\text{Na}_2\text{SO}_4$ . After evaporation, the solid residue was recrystallized from *n*-hexane yielding yellow crystals of compound 5 (44.9 mg, 27%).  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 3.68 (m, 6H), 3.74 (m, 2H), 3.85 (m, 2H), 4.14 (m, 2H) ( $\text{CH}_2\text{O}$ ), 3.93 (t, 2H,  $^3J = 5.5$  Hz), 4.48 (t, 2H,  $^3J = 5.5$  Hz) ( $\text{CH}_2\text{OTh}$ ), 6.64 (s, 1H, H(Th)), 9.97 (s, 1H) (CHO).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CHCl}_3$ ) (APT):  $\delta$  68.97, 69.97, 70.07, 70.19, 70.45, 71.01, 71.14, 73.47 ( $\text{CH}_2\text{O}$ ), 107.70 (CH(Th)), 181.66 (CHO), 124.53, 149.10, 153.60 ( $\text{C}_{\text{quat}}$ ). Found (%): C, 51.54, H, 6.01. Calc. for  $\text{C}_{13}\text{H}_{18}\text{O}_6\text{S}$  (%): C, 51.64, H, 6.00.

#### 2.2.2. 3-Methyl-2-[(E)-2-(2,3,5,6,8,9,11,12-octahydrothieno[3,4-b][1,4,7,10,13]pentaoxacyclopenta-decine-14-yl)vinyl]-1,3-benzothiazol-3 perchlorate (1)

A solution of pyridine (0.07 ml) in ethanol (2 ml) was added to a mixture of perchlorate 8 (41.0 mg, 0.16 mmol) and aldehyde 5 (47.0 mg, 0.16 mmol). The reaction mixture was stirred for 30 h under reflux. After evaporation, the solid residue was recrystallized from methanol and filtrated yielding brown compound 1 (47.1 mg, 55%), mp:  $60\text{--}63^\circ\text{C}$ .  $\delta_{\text{H}}$  ( $\text{CD}_3\text{CN}$ ) 3.61(m, 6H), 3.68 (m, 2H), 3.79 (m, 2H), 4.18 (m, 2H) ( $\text{CH}_2\text{O}$ ), 3.93 (t, 2H,  $^3J = 5.3$  Hz), 4.49 (t, 2H,  $^3J = 5.5$  Hz) H(2,12), 4.14 (s, 3H,  $\text{N}^+\text{CH}_3$ ), 6.91 (s, 1H, H(Th)), 7.34 (d, 1H,  $^3J = 15.5$  Hz,  $\text{CH}=\text{CH}$ ), 7.74 (m, 1H), 7.83 (m, 1H) H(5',6'), 7.97 (d, 1H,  $^3J = 8.4$  Hz), 8.16 (d, 1H,  $^3J = 8.0$  Hz) H(4',7'), 8.04 (d, 1H,  $^3J = 15.5$  Hz,  $\text{CH}=\text{CH}$ ).  $\delta_{\text{C}}$  ( $\text{CD}_3\text{CN}$ ) (APT) 36.48 ( $\text{CH}_3$ ), 68.76, 69.85, 70.18, 70.60, 71.05, 73.91 ( $\text{CH}_2\text{O}$ ), 107.56, 109.47, 116.76, 124.21, 129.06, 130.17, 139.37 (CH), 95.14, 128.17, 138.19, 141.52, 169.52, 173.62 ( $\text{C}_{\text{quat}}$ ). Found (%): C 48.13, H 4.80, N 2.63. Calc. for  $\text{C}_{22}\text{H}_{26}\text{ClNO}_9\text{S}_2$  (%): C 48.22, H 4.75, N 2.56. ESI-Macc,  $m/z$  ( $I_{\text{rel}}$ , (%)): 448  $[\text{M}]^+$  (100).

#### 2.2.3. 5-(1,4,7,10-Tetraoxa-13-azacyclopentadecan-13-yl)thiophene-2-carbaldehyde (6)

$\text{TsOH}$  (25 mg) was added to the mixture of 5-bromthiophene-2-carbaldehyde 9 (0.728 g, 3.8 mmol) and 1,4,7,10-tetraoxa-13-azacyclopentadecan (10) (1.647 g, 7.6 mmol). The reaction mixture was fused in argon atmosphere for 28 h and cooled to room temperature. After addition of water to reaction mixture, the water layer was extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic layer was washed with water and dried over  $\text{Na}_2\text{SO}_4$ . After evaporation, column chromatography of the residue ( $\text{Al}_2\text{O}_3$  neutral, hexane: ethyl acetate 1:1) yielded 6 (0.88 g, 71%).  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 3.62 (m, 7H), 3.65 (m, 9H) ( $\text{CH}_2\text{O}$ ), 3.80 (t, 4H,  $^3J = 6.0$  Hz,  $\text{CH}_2\text{N}$ ), 5.98 (d, 1H,  $^3J = 4.5$  Hz, H(Th)), 7.45 (d, 1H,  $^3J = 4.5$  Hz, H(Th)), 9.48 (s, 1H, CHO).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) (APT):  $\delta$  55.77 ( $\text{CH}_2\text{N}$ ), 67.61, 69.96, 70.35, 71.14 ( $\text{CH}_2\text{O}$ ), 179.99 (CHO), 103.18, 126.11 (CH), 140.38, 166.54 ( $\text{C}_{\text{quat}}$ ). Found (%): C 54.72, H 7.01, N 4.26, S 9.57. Calc. for  $\text{C}_{15}\text{H}_{23}\text{NO}_5\text{S}$  (%): C 54.69, H 7.04, N 4.25, S 9.73.

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