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Optical and electrochemical properties of novel fused tricyclic thiophene–15-crown-5 systems and their complexes with Mg and Ba ions

Sergey D. Tokarev,*[a] Anatoly Botezatu,[a,b] Andrey V. Khoroshutin,[b] Yury V. Fedorov[a] and Olga A. Fedorova[a]

[a] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 9280; e-mail: tokarev@ineos.ac.ru*
[b] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. Fax: +7 495 932 8568; e-mail: tokarev@ineos.ac.ru*

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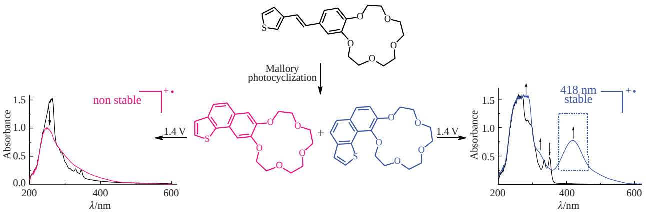
New polycyclic aromatic derivatives annulated both with thiophene and with 15-crown-5 ether moieties, crown naphthothiophenes, were synthesized *via* the Mallory photocyclization with the use of iodine as the mild oxidizer, while two isomeric products were readily separated by column chromatography. Their complexation with Ba^{2+} and Mg^{2+} cations was examined by both optical and electrochemical methods. Spectroelectrochemical studies indicate that the obtained compounds, depending on their structure, can be chemically stable in the oxidized state.



Keywords: naphthothiophenes, crown ethers, complex formation, redox properties, absorption, fluorescence, barium complexes, magnesium complexes, spectroelectrochemistry.

Crown ethers have been extensively studied since the first publication by J. Pedersen.[1] Their ability to host a variety of guests, including cations, anions and neutral molecules, laid the foundation for supramolecular chemistry[2] and made them useful in virtually all branches of chemistry. Crown-containing compounds were used as sensors and probes,[3] drug-delivery systems,[4] extractants of radioactive metals,[5] supramolecular catalysts,[6] as well as components of complex optical[7] and electrochemical[8] sensing systems.

A sensory organic system should contain both a receptor fragment and a fragment that provides an electrochemical or optical response of the system when bound with an analyte. Typically, π-extended heterocyclic moieties are used to provide an electrochemical or optical response, since they are capable of absorbing near UV and visible light and exhibiting redox transformations in the available potential range. Polyconjugated thiophenes are excellent candidates for this because of their high charge mobility and planar structure, leading to their widespread use as semiconductor materials with outstanding charge-carrier ability.[9] As a rule, the synthesis of polycyclic heteroatomic compounds involves many laborious steps.[10] Recently, our group began studying the Mallory's photocyclization of readily accessible 1-thienyl-2-(oxyphenyl)ethenes (styrylthiophenes). This reaction is a convenient one step way to obtain thiophene-annulated polyaromatics with different substituents, including (poly)alkyloxy ones. The latter series of substances exhibit promising optical and electrochemical properties.[11]

In this work, we report on the synthesis of new naphthothiophenes annulated with 15-crown-5 ether from the corresponding 2- and 3-substituted styrylthiophenes *via* the Mallory's photocyclization reaction (Scheme 1). For the synthesized derivatives, the optical and electrochemical properties, as well as the stability of the radical cations formed during oxidation, have been studied. We also report on the study of the sensory properties of polycyclic photocyclization products to Ba^{2+} and Mg^{2+} cations by optical and electrochemical methods.

The starting stilbene derivatives were synthesized by the Wittig–Horner–Emmons reaction from 3-thienyl- (**1a**) and 2-thienylphosphonates (**1b**) and 3-formylbenzo-15-crown-5 (**2**). Photocyclization of stilbenes **3a**,**b** under the Katz conditions[12] at 45 °C led to the formation of two isomers **4a**, **4′a** or **4b**, **4′b** from each stilbene as a result of free rotation around the single bond between the benzene ring and the carbon atom at the double bond.[13] The pairs of isomers were separated by column chromatography on silica gel (for synthetic details, see Online Supplementary Materials).

Both stilbenes **3a**,**b** and photocyclization products **4a**,**b** and **4′a**,**b** absorb in the near UV range (Figure 1). Absorption of naphthothiophenes **4a**,**b** and **4′a**,**b** is hypsochromically shifted

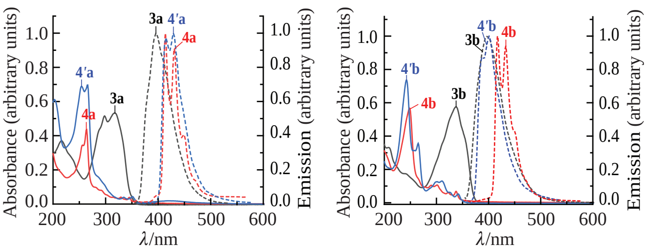
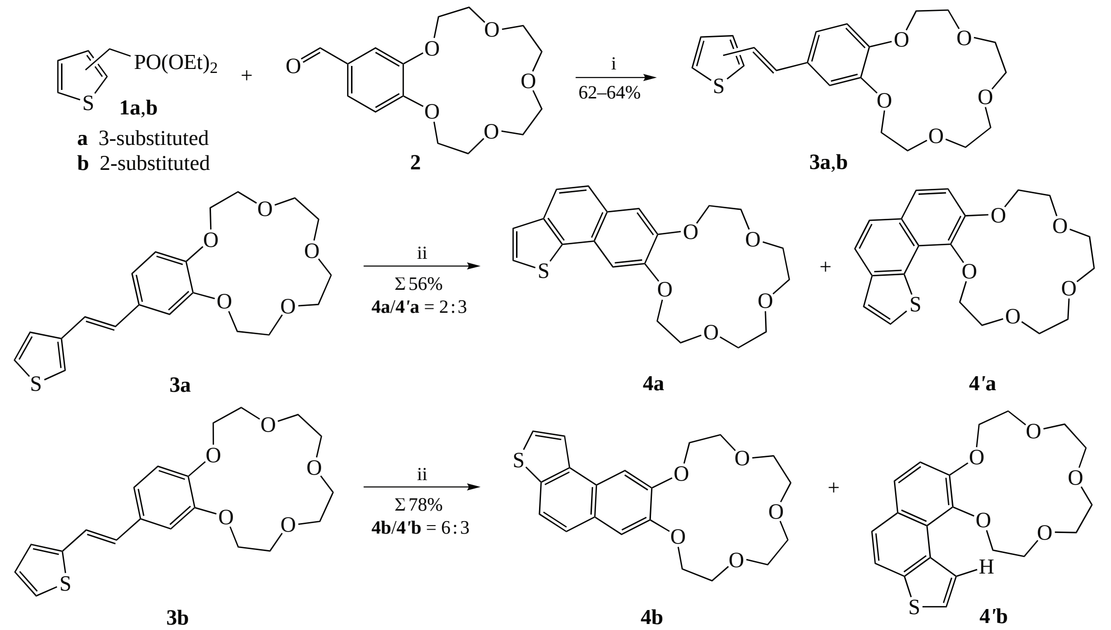


Figure 1 Absorption (solid lines) and emission (dotted lines) spectra of (*a*) **3a** – black, **4a** – red, **4′a** – blue and (*b*) **3b** – black, **4b** – red, **4′b** – blue. $C = 2\times10^{-5}$ M, MeCN, λ_{ex} = 330 nm. Quantum yields (%): for **3a** – 8.1, **3b** – 8.7, **4a** – 3.8, **4′a** – 2.8, **4b** – 7.3, **4′b** – 5.1.



Scheme 1 *Reagents and conditions*: i, NaH, DME, 40 °C, 4 h; ii, *hν*, I_2 (1 equiv.), propylene oxide (1000 equiv.), Ar, C_6H_6, 45 °C, 2 h.

with respect to the initial stilbenes **3a**,**b** perhaps due to less contribution of charge transfer to the excited state. All of the studied compounds show fluorescence in the 350–500 nm region with low (2.8–8.1%) fluorescence quantum yields. The fluorescence quantum yields of styryl compounds are significantly reduced due to the competing *cis–trans* photoisomerization process. The photocyclization products lack a non-aromatic double bond, but their fluorescence quantum yields are even lower than those of the starting compounds. This may be the result of easy formation of the triplet state, since thiophene derivatives tend to undergo intersystem crossing.[14]

Addition of Mg^{2+} or Ba^{2+} perchlorates to solutions of ligands **3**, **4a**,**b** and **4′a**,**b** leads to small changes in the absorption and fluorescence spectra as a result of metal cation coordination with crown-ether fragment and redistribution of electron density in conjugated system of ligand (for details, see Online Supplementary Materials). The ionic diameter of Mg^{2+} (1.56 Å) fits well with the internal cavity of the 15-crown-5 ether fragment, so the cation can be inserted into the cavity forming the complexes of 1 : 1 composition. On the contrary, the radius of Ba^{2+} ion is much larger than the cavity of the crown ether; therefore, it predominantly forms sandwich complexes of the 2 : 1 ligand/metal composition.[15] We calculated the stability constants of these complexes based on changes in the absorption spectra during spectrophotometric titration using the SpecFit32 program[16] according to the following complexation scheme:

$$2\mathrm{L} + \mathrm{M}^{2+} \xrightleftharpoons{K_{21}} (\mathrm{L})_2\mathrm{M}^{2+},$$

$$\mathrm{L} + \mathrm{M}^{2+} \xrightleftharpoons{K_{11}} \mathrm{LM}^{2+},$$

$$K_{11} = \frac{[\mathrm{LM}^{2+}]}{[\mathrm{L}][\mathrm{M}^{2+}]},$$

$$K_{21} = \frac{[(\mathrm{L})_2(\mathrm{M}^{2+})]}{[\mathrm{L}][\mathrm{M}^{2+}]}.$$

The calculated values of the stability constants of the complexes are given in Table 1. In all cases, stable complexes are formed. Also as expected, the barium cation forms both complexes 1 : 1 and 2 : 1 whereas magnesium cation forms only 1 : 1 complexes. Crown ether fragments of **4′a** and **4′b** suffer from steric congestion with thiophene rings, which leads to a twisted ‘swirling’ conformation resulting in less stable complexes.[11(a)] Further, less difference between **4a** and **4′a** binding constants to Ba^{2+} *vs.* those of **4b** and **4′b** may indicate that sulfur atom exerts less hindrance to the crown ether than the CH group (see Scheme 1)

Table 1 Stability constants of Ba^{2+}, Mg^{2+} complexes with **3**, **4a**,**b** and **4′a**,**b**.[a]

Ligand, metal	log(K_{21})	log(K_{11})	$\Delta\lambda$/nm	ΔE/eV
3a, Ba^{2+}	10.9 ± 0.3	5.6 ± 0.3	8	–
3b, Ba^{2+}	14.6 ± 0.8	7.6 ± 0.6	7	–
4a, Ba^{2+}	10.1 ± 0.3	–	2	0.607
4′a, Ba^{2+}	9.5 ± 0.2	5.5 ± 0.2	6	0.410
4b, Ba^{2+}	12.2 ± 0.6	6.3 ± 0.3	2	–
4′b, Ba^{2+}	10.1 ± 0.5	5.6 ± 0.2	4	–
3a, Mg^{2+}	-	5.5 ± 0.1	11	–
4a, Mg^{2+}	-	6.4 ± 0.4	3	0.326
4′a, Mg^{2+}	-	4.9 ± 0.2	2	0.235

[a] $\Delta\lambda$ – difference in absorption maxima of free ligand and fully complexed, ΔE – difference in oxidation potential between free ligand and 1 : 1 complex.

The formation of the only 1 : 1 complex in case of magnesium cation is confirmed by NMR spectroscopy. NMR spectra of **4a** upon the addition of 0.5 and 2 equiv. of Mg^{2+} demonstrate the same set of signals (see Online Supplementary Materials, Figure S19). The addition of metal perchlorate causes a downfield shift of the signals, in both the crown ether and aromatic parts, as a result of electron density transfer from the oxygen atoms of the crown ether fragment to the cation on the complexation. On gradual addition of barium perchlorate to ligands, it is possible to record the spectra of two complexes with ligand/metal composition of 2 : 1 and 1 : 1.

Complexes of 2 : 1 composition can exist in *syn-* and *anti*-conformation. To establish the preferred structure, quantum-chemical calculations were carried out for ligands **4a** and **4′a** in the MOPAC program by the PM7 method. The obtained values of the energy of formation demonstrate a large energy gain in the formation of the *syn*-conformer (ΔE = 8.77 kcal mol^{-1} for ligand **4′a**). This is probably due to π–π stacking effect, since both ligands in *syn*-complexes were calculated to be coplanar. A similar result was obtained for the $(\mathbf{4a})_2$Ba complex.

Voltammograms of both styrylthiophene **3a** and its photocyclization product **4a** possess one irreversible reduction

Table 2 First oxidation and reduction potentials (*vs*. Fc/Fc$^+$) and calculated energies for frontier orbitals of **3a**, **4a** and **4′a**.

Compound	E_{ox}/V	E_{red}/V	HOMO/eV	LUMO/eV	Gap/eV
3a	0.69	–2.83	–5.5	–2.0	3.5
4a	0.74	–3.06	–5.5	–1.7	3.8
4′a	0.81	–3.06	–5.6	–1.7	3.9

and three irreversible oxidations each. In the case of compound **4′a**, the oxidation processes are pseudo-reversible, which indicates a higher chemical stability of the radical cations in comparison with the oxidation product of another photocyclization product **4a** (for the pictures of voltammograms, see Online Supplementary Materials). Table 2 contains potentials of the first oxidation and reduction processes given relative to the $E_{1/2}$ of ferrocene/ferrocenium redox pair (0.414 V relative to the reference electrode used). Energies of the frontier molecular orbitals were calculated based on first redox potentials as follows: HOMO, eV = $-E_{ox}$, V – 4.8; LUMO, eV = $-E_{red}$, V – 4.8, since $E_{1/2}$ of the ferrocene/ferrocenium transition is 4.8 eV relative to vacuum.[17]

To evaluate prospects of **4a** and **4′a** as electrochemical sensors, formation of **4a** and **4′a** complexes with Ba^{2+} and Mg^{2+} have been studied by CVA (Figures S32–S35). Complex formation of **4′a** with Ba^{2+} causes an anodic potential shift, since the addition of a positively charged cation to the system makes it more difficult to detach an electron. Voltammograms show the sequential formation of the 2 : 1 ligand/metal complex with a simultaneous decrease in the concentration of the free ligand. Then, upon further addition of Ba^{2+}, the transition of the 2 : 1 complex to the 1 : 1 one is observed. Upon complexation with the magnesium cation, the accumulation of only one complex is manifested. Ligand **4a** demonstrates similar changes in the voltammograms upon interaction with magnesium and barium cations. Changes in voltammograms during complexation are much more noticeable than changes in absorption spectra (see Table 1); therefore, the studied compounds are more promising as electrochemical sensors than optical ones.

According to electrochemical data, the initial styryl derivative **3a** has the smallest band gap. Although the double bond provides conjugation and longer wavelength absorption than cyclization products and reduces the applicability of the stilbene in organic electronic devices, *cis*–*trans* isomerization becomes a competitor for any photo- and electro-induced intramolecular processes. In addition, the molecule capability of *trans*–*cis* isomerization makes it difficult to form regular films. Nevertheless, molecules with a double bond can be promising dopants in conducting polymer films due to their ability to increase the charge mobility in films.[18]

Due to high planarity and conjugation of compounds **4a** and **4′a**, their ability to form large crystals and stable films increases, since a π–π stacking can stabilize the macroscopic structure. Additionally, studied compounds possess suitable HOMO energy levels to increase the hole mobility in polymer layers of polyfluorenes. HOMOs of **4a** and **4′a** are higher in energy than the valence band of conducting polyfluorenes (–5.7 to –5.8 eV). As a result, dyes, when introduced into the polymer layer, will not capture holes and can themselves donate electrons, increasing the conductivity.[19]

To evaluate the possible application of the obtained derivatives as electron-donor components of devices, it is necessary to explore their stability in the oxidized state. Spectroelectrochemical studies of the stability of radical cations formed during the oxidation of compound **4′a** have been carried out. When a potential of 1.4 V is applied to a solution of compound **4′a**, the formation of a long-wavelength absorption band at 418 nm is detected, which indicates the generation of a radical cation [Figure 2(*a*)]. The same changes under oxidation were observed for another ‘swirling’ product **4′b** [Figure 2(*b*)].

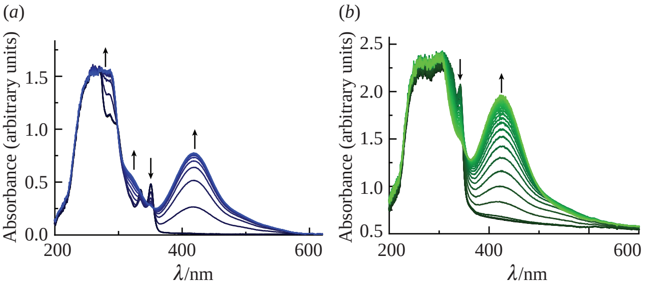


Figure 2 Changes in absorption spectra while applying potential of 1.4 V (*a*) for **4′a**, (*b*) for **4′b**.

The spectrum remains stable and resolved while maintaining the oxidizing potential. After returning to open circuit potential, the spectrum regains its original form, which may reveal the reversibility of the oxidation process or fast diffusion. In case of compounds **4a** and **4b**, the application of 1.4 V potential does not cause the formation of a band, and the spectra lose their resolution, which indicates a rapid chemical transformation of the oxidation product of **4a** and **4b** (see Online Supplementary Materials). To further address the difference in the spectroelectrochemical behavior, we performed open shell optimizations of the corresponding radical cations for **4a** and **4′a**. The analyses of single-occupied and highest-occupied MOs show that in the sterically crowded **4′a** atom orbitals of aromatic fragments (see Figure 3 and Online Supplementary Materials) do take part in the delocalization of an unpaired electron, whereas in **4a** they do not. Such difference may result in substantially different rates of the ion radical quenching either by the solvent or by the same adjacent molecule making the radical cation lifetime of **4a** short so that it does not accumulate in detectable amounts.

In summary, new tricyclic polyconjugated thiophene derivatives annulated with crown ether fragments were obtained by the Mallory photocyclization. The resulting compounds exhibit suitable HOMO levels for modifying polyfluorene conductive films in layered organic devices. Compounds **4′a** and **4′b** demonstrate reversible oxidation and the formation of a stable radical cation, which additionally indicates their prospects as electron donor modifiers. The synthesized compounds exhibit optical and noticeable electrochemical responses upon complexation with alkaline earth metals. Thus, using a convenient one-stage photoreaction, polycyclic annulated aromatic compounds with an ionophore fragment were obtained that can act as electrochemical sensors for alkaline-earths or as donor components of organic electronics.

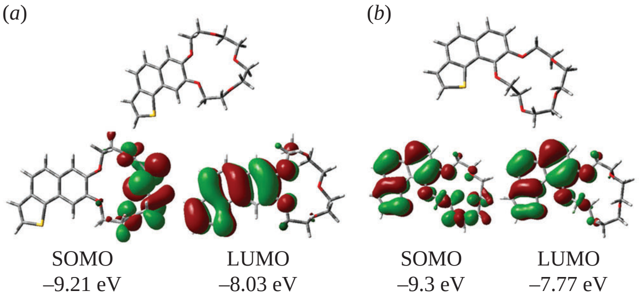


Figure 3 Frontier orbitals and their energies (eV) for the radicals cations of (*a*) compound **4a** and (*b*) compound **4′a** as the results of UB3LYP/6-31+g(d) structure optimization.

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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.2022.05.025.

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