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Synthesis and evaluation of bipendant-armed (oligo)thiophene crown ether derivatives as new chemical sensors

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ABSTRACT

Three new (oligo)thiophene bipendant-armed ligands **2a**–**c**, derived from 2-(aminomethyl)-15-crown-5, have been synthesized and characterized. Compounds **2a–c** were prepared by reductive amination of the corresponding macrocycle with formyl thiophene derivatives **1a**–**c** in the presence of $NaBH(OAc)_3$ in fair to good yields. The photophysical properties of ligands **2a**–**c** were studied and they were also evaluated as chemosensors in the presence of Na(I), Ag(I), Pd(II) and Hg(II) cations in acetonitrile solution.

Since Pederson published his discovery of crown ethers in 1967, these heterocycles have attracted much attention due to their interesting binding properties with metallic and organic cations and application in the design of chemosensors, molecular machines, and supramolecular polymers.[1]

The synthesis of functionalized (oligo)thiophene derivatives is a very challenging and interesting topic in organic synthesis due to their several optoelectronic applications such as conducting polymers, organic light emitting diodes (OLEDs), photovoltaic cells, nonlinear optical, and multiphoton absorbing materials.[2] Moreover, functionalized (oligo)thiophene systems bearing appropriate recognition units could also find application as sensors that are able to provide optical and electronic responses upon *stimuli* or in the presence of a large variety of analytes such as cations and anions, being the subject of intense research during the past decade.[3]

In recent years, we have synthesized and characterized several functionalized (oligo)thiophene derivatives, which exhibited excellent thermal stability, conducting, solvatochromic, electrochemical, fluorescence, nonlinear optical (NLO) properties,[4] and also for sensor applications.[5] We were therefore motivated to explore the potential of π-electron conjugated (oligo)thiophene moieties as pendant substituents on amine-crown ether derivatives as potential new sensors for cations.

The $NaBH(OAc)_3$ is a versatile and extraordinarily useful reagent for the N-alkylation of primary and secondary amines with aldehydes and ketones in a novel amination process.[6] The reductive amination using $NaBH(OAc)_3$ as the reductive agent has been used recently to prepare several armed azacrown ethers having aromatic and (hetero)aromatic pendants such as 3,5-difluorobenzyl, pyridinylmethyl, and quinolinylmethyl at normal pressure or under high pressure conditions (1 MPa).[7]

The tertiary amines **2a**–**c** (Scheme 1, Table 1) functionalized with a crown ether moiety and two (oligo)thiophene pendants were synthesized by reductive amination of the corresponding macrocycle, 2-(aminomethyl)-15-crown-5, with formyl thiophene derivatives **1a**–**c** in the presence of $NaBH(OAc)_3$ in 1,2-dichloroethane (DCE), at room temperature in a one-pot reaction. Ligands **2a**–**c** were obtained as oils in fair to good yields (32–64%).[8] As far as we know, this is the first time that the synthesis and characterization of tertiary amines bearing two (oligo)thienylmethyl pendants and a crown ether unit are reported.

In order to study the potential application of ligands **2a–c** as chemosensors for metal cations, the characterization by absorption and by fluorescence emission spectroscopies was carried out. Several (oligo)thiophene moieties were used in order to study the influence of the length of the π-conjugated system on the overall optical properties of compounds **2a–c**.

Absorption and emission spectra of compounds **2a**–**c** in acetonitrile were obtained and revealed that the wavelength of maximum absorption was shifted to longer wavelengths as the number of thiophene units increased, ca. 50–65 nm for each added thiophene

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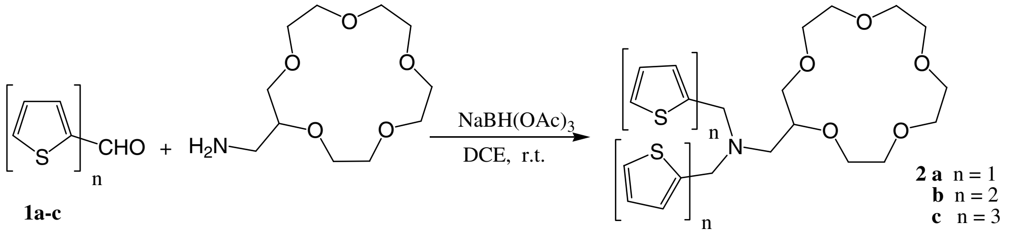

Scheme 1. Synthesis of crown ether bipendant-armed ligands **2a**–**c**.

Table 1
Yields, UV–vis absorption, and emission data for crown ether bipendant-armed ligands **2a**–**c** in acetonitrile

Compd.	Yield (%)	Absorption		Emission λ_{max} (nm)	Stokes' shift (nm)
		λ_{max} (nm)	(log ε)		
2a	45	238	(5.55)	–	–
2b	32	315	(5.74)	378	63
2c	64	365	(6.31)	437	72

(Table 1). Compound **2a**, with a thiophene unit, was not emissive, while compounds **2b** and **2c**, bearing bithiophene and terthiophene moieties, respectively, showed an emission band centered at 378 and 437 nm, respectively (Fig. 1, Table 1). As can be seen, the trend found for the absorption spectra was also observed in the emission spectra as the position of the wavelength of maximum emission was red-shifted with the increase of the number of thiophene units. The fluorescence quantum yields were determined using a 0.1 M solution of 1-naphthylamine in cyclohexane as standard ($\Phi_F = 0.46$),[9] and in both cases the values obtained were below 10^{-3}.

Compounds **2a**–**c** are provided with three different binding sites: an amine nitrogen atom, a crown ether unit, and sulfur atoms at the thiophene rings. According to the Pearson rules on hard and soft acid-base properties, metals such as Ag(I), Pd(II), and Hg(II) are considered soft and for this reason they will preferably coordinate to soft donor atoms such as sulfur.[10] Taking this into account, as well as the fact that, depending on the counter ion, 15-crown-5 moieties have a preference for Na(I) cations,[1a] modulation of the emission properties can be attained by adding protons and sodium atoms before the introduction of soft metals. Protons will bind to the lone pair of electrons present at the amine nitrogen atom, and the emission is expected to increase because the photoinduced electron transfer (PET) process from the amine to the chromophore is interrupted.[11] On the other hand, when Na(I) is added, it will occupy the crown ether unit.

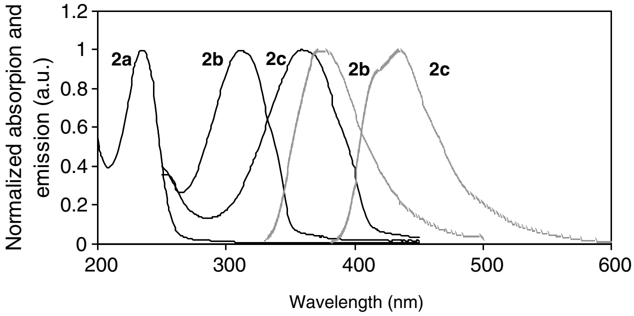

Figure 1. Normalized absorption (black line) and emission (grey line) spectra of compounds **2a**–**c** in acetonitrile solution ($T = 298$ K, $\lambda_{exc} = 315$ nm (**2b**) and 365 nm (**2c**)).

Keeping this idea in mind, we decided to perform spectrofluorimetric titrations of compounds **2b**–**c** with standard solutions of methanesulfonic acid, Na(I), Ag(I), Pd(II), and Hg(II) cations. After addition of one proton equivalent to ligands **2b**–**c**, in both cases the emission of the free ligands was increased in ca. 30%. The addition of one equivalent of Pd(II) to these solutions resulted in an increase in the emission only for compound **2b**, confirming the interaction between the metallic species and the ligand. No effect was observed, when Ag(I) and Hg(II) were added.

More information about Pd(II) complexation can be obtained by the UV–vis spectra. Upon interaction with Na(I) the absorption spectra of compound **2b** was not affected, but with the increasing addition of Pd(II) the band centered at 315 nm was red-shifted to 320 nm. This effect could be attributed to the metal ion coordination by the chromophore, which indicates that cation complexation results in the rigidification of the conjugated system.[3c,12]

In another approach, and in order to involve the crown ether in complexation before the addition of Pd(II), 1 equiv of Na(I) ions was added to acidic solutions of ligands **2b**–**c**. Again, an increase in the intensity of the emission of **2b** of ca. 10% was observed. This result was also observed when an equivalent of proton and Na(I) was added to a solution of ligand **2c**.

This observation confirmed the interaction of sodium with the crown ether unit. Addition of Pd(II) to this solution gave a similar result to the one described previously (only with the addition of acid), that is, an increase in the emission intensity of ca. 50%. Once the crown is occupied in complexation, we can suppose that Pd(II) ions interact with the sulfur atoms at the thiophene units (Fig. 2).

For compound **2c**, bearing two terthiophene pendants, no effect was observed upon Pd(II) interaction. This result could indicate that there is a relationship between the length of the (oligo)thiophene π-conjugated system and the sensing ability towards Pd(II) ions. Factors such as the different degrees of torsion between the thiophene units, in the various chains (thiophene, bithiophene, and terthiophene), could lead to variations in the effective conjugation length, affecting the planarity and the steric hindrance of the whole heteroaromatic system.[13]

Our results are significative for future applications of **2b** in sensing phenomena, for example, in organic synthesis, due to the widespread application of Pd(II) as catalyst in organic reactions. Another important fact arises from the CHEF (chelation enhancement of fluorescence) effect observed upon Pd(II) interaction with **2b**, because as Pd(II) is a d^8 element (open-shell), its presence normally produces a quenching in the fluorescence intensity.[14] Many examples are reported in the literature for Pd(II) detection based on the CHEQ (chelation enhancement of quenching) effect but less attemption has been paid to systems in which this metal produces a CHEF effect.[15]

In conclusion, we report here the synthesis of a novel family of fluorescent ligands derived from (oligo)thiophene and 2-(aminomethyl)-15-crown-5 moieties. To the best of our knowledge, this is the first time that a tertiary amine has been prepared bearing two pendant (oligo)thiophene units and a crown ether recognition unit in a one-pot reaction. Interaction with protons and cations

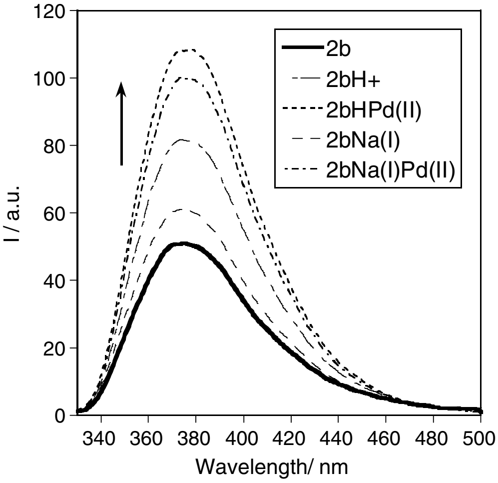

Figure 2. Fluorescence spectrum of compound **2b** in acetonitrile solution and after the addition of 1 equiv of methanesulfonic acid, methanesulfonic acid plus Pd(II), Na(I) and Na(I) plus Pd(II) ([**2b**] = 3.5E-7 M, *T* = 298 K, λ_{exc} = 315 nm).

such as Na(I), Ag(I), Pd(II), and Hg(II) has been also studied and showed that compound **2b** could have potential application as a palladium chemosensor, due to the observed increase in the fluorescence intensity upon simultaneous interaction of protons and palladium(II), or protons, sodium(I), and palladium(II). Successive additions of Na(I) and Pd(II) progressively enhanced the intensity of the emission band indicating first by a complexation of Na(I) at the crown ether binding site and secondly, the existence of interaction of Pd(II) with the sulfur atoms of the bithiophene segment, according to the Pearson rules. The existence of a PET process in compounds **2b**–**c**, after the addition of one equivalent of proton reacting with the electron lone pair of nitrogen, was observed and allowed the recovering of the fluorescence properties of the oligothiophene units.

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8. *General method for the synthesis of compounds* **2a**–**c**: the corresponding 2-formylthiophenes **1a**–**c** (2.2 mmol), 2-(aminomethyl)-15-crown-5 (1 mmol) and $NaBH(OAc)_3$ (2.2 mmol) were dissolved in 1,2-dichloroethane (5 mL), under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2–6 days. A saturated $NaHCO_3$ (30 mL) solution was added and the mixture was extracted with chloroform (3 × 30 mL). The organic phase was washed with water (30 mL) and dried with magnesium sulfate. After evaporation of the solvent, the crude residue was purified by column chromatography in silica gel with mixtures of diethyl ether and dichloromethane of increasing polarity to give the pure compounds **2a**–**c** as oils.
   N-(1,4,7,10,13-pentaoxacyclopentadecan-2-yl)-N,N-bis(thien-2-ylmethyl)methanamine **2a**: Yellow oil (62 mg, 45%). UV (acetonitrile): λ_{max} nm ($\log\varepsilon$) 238.0 (5.55). IR (cm^{-1}, KBr) υ = 3101, 3069, 2865 (br), 1447, 1349, 1292, 1250, 1120, 1036, 976, 937, 851, 830, 699. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.65 (br s, 2H, N–CH_2-cr.eth.), 3.64–3.68 (m, 17H, CH and 8 × CH_2 cr.eth.), 3.90–3.96 (m, 6H, CH_2 cr.eth. and 2 × CH_2 thiop), 6.92–6.94 (m, 4H, 2 × (H-3 and H-4)), 7.21–7.24 (m, 2H, 2 × H-5) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 52.83 (CH_2 thiop), 54.22 (N–CH_2-cr.eth.), 70.09 (CH_2 cr.eth.), 70.45 (CH_2 cr.eth.), 70.49 (CH_2 cr.eth.), 70.56 (CH_2 cr.eth.), 70.89 (CH_2 cr.eth.), 78.36 (CH cr.eth.), 124.86 (C5), 126.35 (C3 and C4), 142.36 (C2) ppm. MS (FAB) *m*/*z* (%): 442 ($[M+H]^+$, 100), 441 ($[M]^+$, 20), 440 (62), 344 (24), 222 (67). HRMS (FAB) *m*/*z* for $C_{21}H_{32}NO_5S_2$: calcd 442.1722, found 442.1720.
   N-(1,4,7,10,13-pentaoxacyclopentadecan-2-yl)-N,N-bis(bithien-5-ylmethyl)methanamine **2b**: Colorless oil (55 mg, 32%). UV (acetonitrile): λ_{max} nm ($\log\varepsilon$) 245.0 (5.36), 315.0 (5.74). IR (cm^{-1}, KBr) υ = 302, 3068, 2923, 2857, 1448, 1426, 1354, 1294, 1248, 1201, 1126, 1044, 938, 838, 800, 695. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.70 (br s, 2H, N–CH_2-cr.eth.), 3.64–3.70 (m, 17H, CH and 8 × CH_2 cr.eth.), 3.83–3.89 (m, 6H, CH_2 cr.eth. and 2 × CH_2 thiop), 6.84 (br s, 2H, 2 × H-4), 7.00–7.03 (m, 4H, 2 × (H-3 and H-4′)), 7.16 (dd, *J* = 3.6 and 0.9 Hz, 2H, 2 × H-3′), 7.20 (dd, *J* = 5.1 and 0.9 Hz, 2H, 2 × H-5′). ^{13}C NMR ($CDCl_3$): δ 53.13 (CH_2 thiop), 54.42 (N–CH_2-cr.eth.), 70.15 (CH_2 cr.eth.), 70.50 (CH_2 cr.eth.), 70.55 (CH_2 cr.eth.), 70.63 (CH_2 cr.eth.), 70.93 (CH_2 cr.eth.), 78.53 (CH cr.eth.), 123.04 (C3), 123.37 (C3′), 124.05 (C5′), 126.59 (C4), 127.69 (C4′), 136.81 (C2), 137.71 (C2′), 141.77 (C5). MS (FAB) *m*/*z* (%): 606 ($[M+H]^+$, 39), 426 (18), 179 (100), 154 (18). HRMS (FAB) *m*/*z* for $C_{29}H_{36}NO_5S_4$: calcd 606.1476, found 606.1472.
   N-(1,4,7,10,13-pentaoxacyclopentadecan-2-yl)-N,N-bis(terthien-5-ylmethyl)methanamine **2c**: Yellow oil (130 mg, 64%). UV (acetonitrile): λ_{max} nm ($\log\varepsilon$) 255.0 (5.86), 365.0 (6.31). IR (cm^{-1}, KBr) υ = 3102, 3007, 2865 (br), 1710, 1659, 1509, 1449, 1425, 1358, 1296, 1249, 1221, 1202, 1121, 1042, 939, 868, 835, 795, 696. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.71 (br s, 2H, N–CH_2-cr.eth.), 3.62–3.77 (m, 17H, CH and 8 × CH_2 cr.eth.), 3.84–3.91 (m, 6H, CH_2 cr.eth. and 2 × CH_2), 6.85 (d, *J* = 3.3 Hz, 2H, 2 × H-4), 7.01–7.09 (m, 8H, 2 × (H-3, H-3′, H-4′ and H-4″)), 7.18 (dd, *J* = 3.6 and 1.2 Hz, 2H, 2 × H-3″). 7.22 (dd, *J* = 5.1 and 1.2 Hz, 2H, 2 × H-5″). ^{13}C NMR (300 MHz, $CDCl_3$): δ 53.23 (CH_2 thiop), 54.45 (N–CH_2-cr.eth.), 70.14 (CH_2 cr.eth.), 70.49 (CH_2 cr.eth.), 70.59 (CH_2 cr.eth.), 70.89 (CH_2 cr.eth.), 70.96 (CH_2 cr.eth.), 78.53 (CH cr.eth.), 123.02 (C3), 123.58 (C3″), 123.94 (C4″), 124.26 (C3′ and C4′), 124.36 (C5″), 126.73 (C4), 135.90 (C5′), 136.54 (C2 and C2′), 137.17 (C2″), 142.00 (C5). MS (FAB) *m*/*z* (%): 770 ($[M+H]^+$, 13), 262 (21), 261 (100), 155 (11), 154 (36). HRMS (FAB) *m*/*z* for $C_{37}H_{40}NO_5S_6$: calcd 770.1231, found 770.1241.
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