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Synthesis and electrochemical investigations of crown-ether-functionalised bipyrroles

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The synthesis of crown-ether-functionalised 2,2′-bipyrroles leads to a new class of electrochemically polymerisable monomers. The monomers and corresponding polymers were characterised by spectroscopy and cyclic voltammetry. In the presence of alkali metal ions the oxidation potentials of the polymers are altered and according to cyclic voltammetry, the observed shifts are at least partially reversible.

Introduction

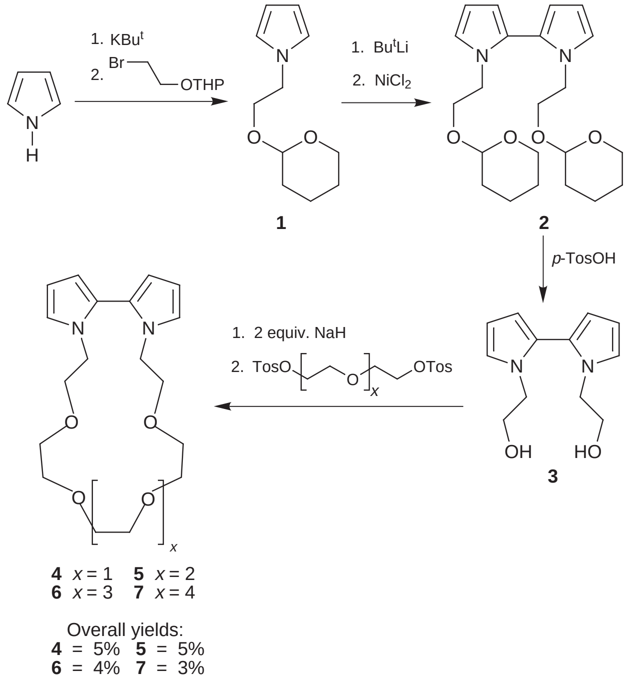
Functionalised electrically conductive polymers have received much attention and have been proposed as a source of new intelligent materials.[1,2] One method to obtain functionalised conducting polymers is *via* the polymerisation of monomers that already contain functional groups. Conjugated conducting polymers substituted with crown ether units have recently been suggested as sensor materials for alkali metal ions.

Poly(pyrrole)s substituted in the 3-position by azacrown ethers were the first conducting polymers to display an ion-specific voltammetric response towards alkali metal ions.[3] For derivatised poly(thiophene)s with remotely attached crown ether functionalities complexation of ions causes an increase in the oxidation potential of the polymer.[4] This effect was obtained even though the crown ether and the polymer backbone were electronically decoupled. Crown-ether-functionalised poly(bithiophene)s with a poly(oxyethylene) bridge connecting the 3- and 3′-positions were synthesised to induce twisting of the polymer backbone upon ion complexation.[5] These polymers show ionochromic responses towards alkali metal ions.

Here we report the synthesis and investigations of a new monomeric system consisting of crown-ether-substituted 2,2′-bipyrrole units. The use of bipyrroles permits the establishment of the crown ether functionality *via* the 1- and 1′-positions. In contrast to systems based on pyrroles or thiophenes, the electrochemical polymerisation of these monomers can be examined under mild conditions at low oxidation potentials leading to polymers with intact functionalities and uniform and regular structure. The resulting polymers combine a conductive backbone with the complexing properties of crown ether functionalities.[6] This procedure can lead to new sensory materials.[3–7]

Results and discussion

A four-step procedure was adopted in the synthesis of the new crown-ether-substituted 2,2′-bipyrrole monomers (Scheme 1). The first step involves the alkylation at the 1-position by deprotonation with KBu^t followed by reaction with 1-bromo(2-tetrahydropyran-2-yl)ethane yielding **1**, a derivative of (pyrrol-2-yl)ethanol with a protected hydroxy group, the THP ether function acting as the protecting functionality. The dimer **2** was obtained by the oxidative coupling of the carbanions upon addition of $NiCl_2$ after the deprotonation of **1** at the 2-position with Bu^tLi.[8] The cleavage of the protecting group is achieved in polar solvents under acidic conditions.[9] The presence of *p*-toluenesulfonic acid in a methanolic solution of **2** leads to the fast and quantitative formation of **3**. The final step is the establishment of the crown ether functionality *via* a dialkylation reaction of **3** with a derivative of oligo(ethylene glycol)-di-*p*-tosylate. The corresponding sodium dialcoholate is generated by deprotonation of **3** with 2 equiv. of NaH. A nucleophilic substitution reaction of the sodium dialcoholate with oligo(ethylene glycol)-di-*p*-tosylate results in the formation of the crown ether ring. The size of the ring depends on the number of ethylene glycol units in the oligo(ethylene glycol)-di-*p*-tosylate. In this manner we successfully synthesised the new compounds **4**, **5**, **6** and **7** containing four, five, six or seven oxygen atoms, respectively, in the crown ether functionality.



Scheme 1 Synthetic route to crown-ether-functionalised bipyrroles.

All monomers were characterised by cyclic voltammetry and show irreversible behaviour (Fig. 1), leading to the formation of polymers. For **4** the first oxidation potential E_{pa}^1 is at 0.37 V (Table 1). The value of E_{pa}^1 decreases as the number of oligo(ethylene glycol) units increases reaching a minimum of 0.33 V for compounds **6** and **7**, respectively. This effect can be attributed to the torsion angle between the two pyrrole rings, which is expected to be slightly reduced as the size of the crown ether ring is extended, leading to a higher degree of flexibility and a lower E_{pa}^1. In contrast to this, the absorption

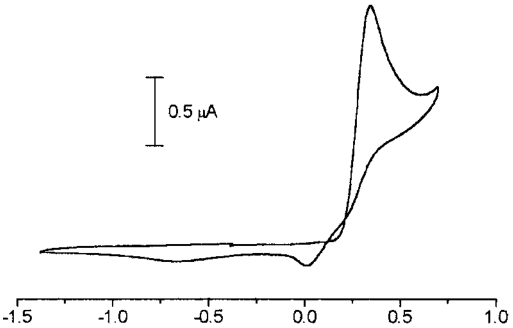


Fig. 1 Typical cyclic voltammogram of crown-ether-functionalised bipyrrole **5** in CH_2Cl_2–0.1 M $TBAPF_6$ (T = 20 °C; v = 100 mV s^{-1}).

Table 1 Peak potentials *vs.* Fc/Fc^+ and absorption maxima for the crown-ether functionalised bipyrroles and corresponding polymers

Compound	x	$E_{pa}{}^1$/V	λ_{max}/ nm	Polymer E_{pa}/V	Polymer λ_{max}/nm
4	1	0.37	252	0.24	298
5	2	0.36	253	0.19	300
6	3	0.33	253	0.16	300
7	4	0.33	253	0.14	300

maximum in the UV–VIS spectra is almost the same for all monomers. The trace crossing of the first cycle in the voltammograms is typical for compounds forming conducting polymers and is viewed as proof of initiation of electropolymerisation.[10,11] In multisweep cyclic voltammograms polymerisation is indicated by the new oxidation peak in the second scan in front of the $E_{pa}{}^1$ signal (Fig. 2). The strongly drifting cathodic peaks from −1.0 to −1.26 V are due to protons eliminated during the process of rearomatisation of the polymer.

Corresponding polymers can be deposited potentiostatically at 0.45 V *vs.* Fc/Fc^+ in CH_2Cl_2 or MeCN, with NBu_4PF_6 as electrolyte on a platinum disc electrode. CV measurements of the polymers show a sharp oxidation and reduction peak indicating a uniform and regular structure (Fig. 3). For the polymer **P4** the E_{pa} is 0.24 V (Table 1) and decreases as the number of oligo(ethylene glycol) units increases reaching a minimum of 0.14 V for the polymer **P7**, analogous to the monomers. With extension of the crown ether unit, the torsion angle between the two pyrrole rings should be reduced. In addition, larger crown ether units will lead to a higher degree of flexibility in the polymer leading to lower oxidation potentials. In front of the oxidation peak there is a shoulder at 0.00 V. The appearance of this pre-peak was also observed in cyclic voltammograms of poly(1-methylpyrrole) and poly[1,1′-dimethyl-2,2′-bipyrrole] and is traced back to structure relaxation effects.[12,13] For practical applications measurements in aqueous media are necessary. The stability of the polymer films is demonstrated by the fact that these polymers can be cycled in water (Fig. 4). There is only a small loss of charge capacity during the first scans and in further scans no decomposition of the polymer is observed.

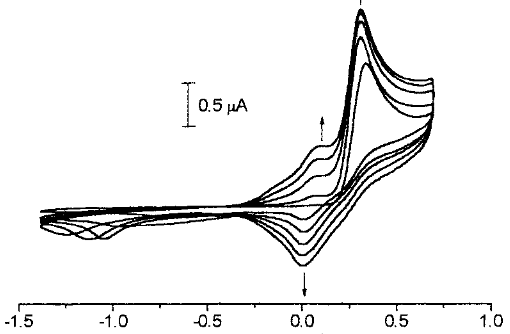


Fig. 2 Multisweep cyclic voltammogram of crown-ether-functionalised bipyrrole **5** in CH_2Cl_2–0.1 M $TBAPF_6$ (T = 20 °C; v = 100 mV s^{-1}).

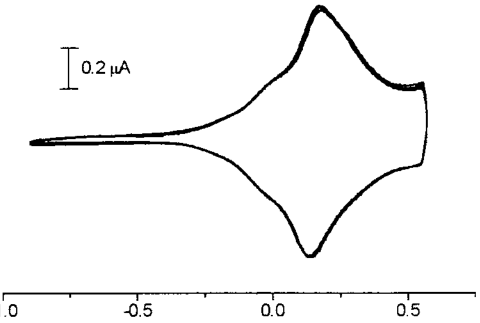


Fig. 3 Cyclic voltammogram of polymer **P5** in MeCN–0.1 M $TBAPF_6$ (T = 20 °C; v = 100 mV s^{-1}).

In bulk electrolysis experiments free-standing films can be deposited potentiostatically in MeCN–NBu_4PF_6 on platinum electrodes. These films show electrochromic behaviour being blue–violet in the oxidised state and yellow in the neutral state. The conductivity data show no significant trends and all investigated polymers reveal conductivities in the range of 10^{-4} S cm^{-1}, values typical for 1-substituted poly(pyrrole)s.[12] FTIR spectra of the polymers show that there is no loss of functionalisation, over-oxidation or branching, indicating a uniform and regular structure. The UV–VIS spectra of all of the investigated polymers show an absorption maximum at 300 nm (298 nm for the polymer **P4**). For comparison, studies on oligo(1-methylpyrrole)s show only a small shift of the absorption maximum with longer chain length and beyond the pentamer there is only an infinitesimal bathochromic shift of the π–π^* transition.[12,14] Extrapolation of the dependence observed for the oligomers to an infinite degree of polymerisation gives an expected absorption maximum of *ca.* 290 nm for the ideal neutral polymer.[12] The higher values of 300 nm that we achieved for the crown ether functionalised poly(2,2′-bipyrrole)s seem to be due to at least partial planarisation of the main chain in the solid state. This effect is very important for the structure of the polymers. Such planarisation is a requirement for a good transmission of a sensor signal and one reason why we investigated these materials as sensory materials for alkali metal ions.

The presence of alkali metal ions causes a change in the cyclic voltammogramms of the corresponding polymers of crown-ether-functionalised bipyrroles (Table 2).

For polymer **P4** (Fig. 5) the presence of alkali metal ions results in a decrease of E_{pa}. Similar effects were observed for

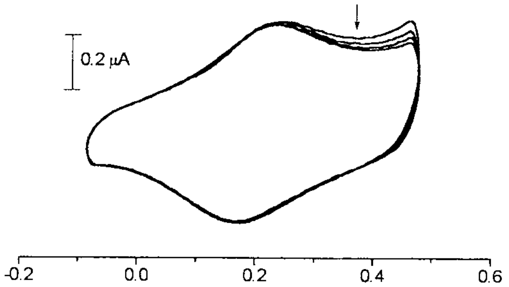


Fig. 4 Cyclic voltammogram of polymer **P6** in H_2O–0.1 M $LiClO_4$ (T = 20 °C; v = 100 mV s^{-1}).

Table 2 Electrochemical response of the polymers towards the presence of alkali metal ions

		ΔE/mV		
Polymer	E_{pa}/V	Li^+	Na^+	K^+
P4	0.24	−10	−13	−12
P5	0.19	26	36	31
P6	0.16	28	43	18
P7	0.14	11	31	28

polymers with sterically very demanding complexing groups.[15,16] The E_{pa} of polymer **P4** is higher and the λ_{max} lower than those of the other investigated polymers indicating that the compound with the smallest crown ether unit is the sterically most demanding system. Thus complexation of alkali metal ions by polymer **P4** seems to cause a decrease of the torsion angle between the pyrrole rings resulting in a higher effective conjugation and in a lower oxidation potential of the polymer. The size of Li^+ should be ideal for complexation by crown ethers with four oxygen atoms yet it causes the smallest shift of the oxidation potential (10 mV). The presence of Na^+ or K^+ results in shifts of 13 and 12 mV, respectively. The reason for the small shifts may be that for polymer **P4** two effects are directed against each other. Complexation should cause an increased π-overlap in the conductive polymer backbone, resulting in a decrease of the oxidation potential. However, complexation of cations leads to the formation of a Coulomb barrier because of the concentration of positive charges close to the conductive backbone which would lead to an increase of the oxidation potential. The measured shifts of the oxidation potential are therefore the result of two competing effects and this explains why they are of small magnitude.

For the other investigated polymers the presence of alkali metal ions causes a shift of the oxidation potentials towards higher values (Table 2, Fig. 6). It seems that complexation causes an increase of the torsion angle between the pyrrole rings so that the effective conjugation length is decreased. Moreover the Coulomb barrier tends to cause an increase in the oxidation potential. The presence of Na^+ causes the largest shift of the oxidation potential of all the polymers examined. Because of its large ionic radius, the diffusion of K^+ into the polymer, and its mobility inside the polymer, in comparison to Na^+, should be more difficult resulting in a smaller shift of E_{pa}.

The reason for absence of selectivity could be the structure of the polymer film with its lack of flexibility allowing only partial complexation by the crown ether units. The planarisation of the conductive polymer backbone seems to dominate the polymer structure leading to a lack of flexibility. As a result the inner-sphere oxygens close to the polymer backbone would be less accessible for complexation. With the formation of, for example, sandwich complexes it would mainly be the outer-sphere oxygens that would take part in complexation so that different cation and crown ether sizes would have similar small effects on the conductive polymer backbone. Crystallographic studies of the monomer ligands and their complexes should provide clues as to complexation behaviour: such studies are in progress and will be published elsewhere.

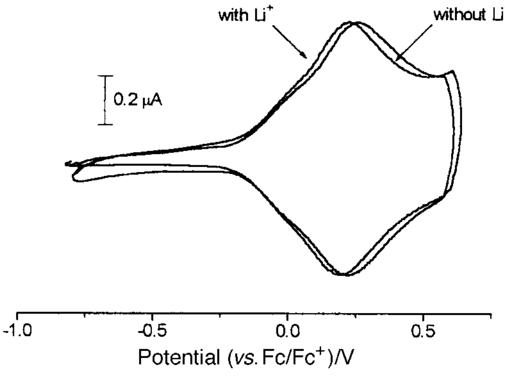


Fig. 5 Cyclic voltammogram of polymer **P4** in the absence and presence of Li^+, MeCN–0.1 M $TBAPF_6$ ($T = 20\,°C$, $v = 100\ mV\ s^{-1}$).

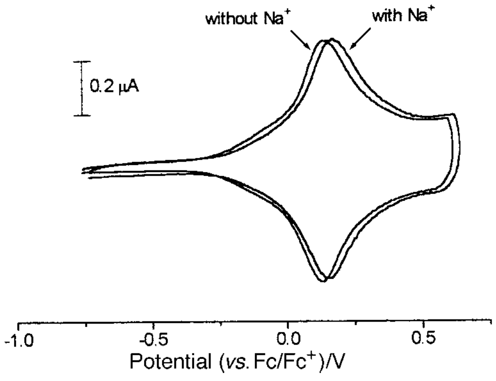


Fig. 6 Cyclic voltammogram of polymer **P6** in the absence and presence of Na^+, MeCN–0.1 M $TBAPF_6$ ($T = 20\,°C$, $v = 100\ mV\ s^{-1}$).

In further cyclic voltammetric experiments we investigated the degree of reversibility of complexation. After a polymer film was subjected to cyclic voltammetry in the presence of alkali ions the film was washed, dried and transferred into a cell in the absence of akali metal ions and the oxidation potential was remeasured. For Li^+, for all investigated polymers a complete return of the oxidation potential to its original value measured in the absence of Li^+ was observed. For Na^+ and K^+, however, degrees of reversibility of 92 and 79%, respectively, were obtained. The lower degree of reversibility for Na^+ and K^+ in comparison to Li^+ can be explained in terms of ionic radii since for larger ions (especially K^+) diffusion into and out of the polymer is hindered. Since the shifts of the oxidation potential in response to the presence, and the return of the shift in the absence of ions, are of small magnitude the values of reversibilities are subject to a loss of accuracy. To obtain a more exact impression on the nature and effects of complexation by the polymers, additional investigations such as spectroelectrochemical or XPS measurements are necessary, and these will be published elsewhere.

It can be concluded for crown-ether-functionalised bipyrroles that a new class of electrochemically polymerisable monomers can be synthesised. Electrochemical polymerisation leads to conductive polymers of regular structure, intact functionality and high stability towards aqueous media. In CV measurements the oxidation potential of the polymers shift in the presence of alkali metal ions. For Li^+ this shift is completely reversible, whereas for Na^+ and K^+ it is only partially reversible.

Further investigations will focus on why the magnitudes of the shifts of the oxidation potential are low in the presence of metal ions. For example we hope to obtain information about the distribution of ions in the polymer and the ion : ligand ratio by XPS measurement.

Experimental

Melting points are uncorrected. IR spectra were taken on a Bruker Equinox 55 FTIR spectrometer. NMR spectra were recorded in $CDCl_3$ on a Bruker AM 400 (400 MHz). Chemical shifts are reported in parts per million (δ) using tetramethylsilane as internal standard. Mass spectra were recorded on a Finnegan MAT 312 spectrometer. UV–VIS spectroscopy was performed in MeCN using a Perkin-Elmer model Lamda 5 instrument. Cyclic voltammetry measurements were performed in a Kiesele-type cell equipped with an integrated drying tube for the electrolyte (0.1 mol L^{-1} NBu_4PF_6 in superdry CH_2Cl_2 or MeCN or in ultrapure H_2O, $c_{monomer} = 1 \times 10^{-3}$ mol L^{-1}). In investigations of the electrochemical response towards the presence of alkali ions [$c_{alkali} = 0.1$ mol L^{-1} ($LiClO_4$, $NaClO_4$ or KBF_4)], the working electrode was a platinum disk, the counter electrode a platinum wire and the reference electrode an AgCl-covered silver wire. All potentials measured in CH_2Cl_2 and MeCN were calibrated against ferrocene [$E^0(Fc/Fc^+) =$ 0.35 V *vs.* Ag/AgCl]. Cyclic voltammograms were recorded using a computer-linked Heka PG 285 potentiostat with the LabVIEW-Software package from National Instruments.

Bulk electrolysis experiments were performed in an one-compartment cell employing an AgCl-covered silver wire as reference electrode and platinum foils ($A = 2.25$ cm^{-2}) as working and counter electrodes. The electrolyte consisted of 5×10^{-2} mol L^{-1} NBu_4PF_6 in purified MeCN and the concentration of the given oligomer was 2.5×10^{-2} mol L^{-1}. Purification of CH_2Cl_2 and MeCN was performed according to the literature.[17] Conductivities were measured by a standard four-probe method at room temperature on films, using osmium contacts.

1-(2-Tetrahydropyran-2-yloxyethyl)pyrrole 1

A solution of 4.03 g freshly distilled pyrrole (4.17 mL, 60 mmol) in 100 mL dry toluene was cooled to 0 °C under argon. A mixture of 6.95 g (62 mmol) $KOBu^t$ and 0.4 g (1 mmol) dibenzo-18-crown-6 in 100 mL dry toluene was added and the resulting mixture was refluxed for 1 h. After cooling to 0 °C a solution of 12.54 g (60 mmol) of 2-bromo(-tetrahydropyran-2-yl)ethane in 80 mL dry THF was added under vigorous stirring and the mixture was refluxed for 12 h. The crude reaction mixture was diluted with diethyl ether and the organic phases were washed with water (3 × 150 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the resulting dark liquid was purified by column chromatography [SiO_2, light petroleum–diethyl ether (10 : 1), $R_f = 0.27$]. Compound **1** was obtained as a yellow oil (7.61 g, 39 mmol, 65%). **1**: ^1H NMR ($CDCl_3$): δ 6.69 (t, 2H), 6.12 (t, 2H), 4.50 (t, 1H), 3.98 (m, 4H), 3.62 (m, 2H), 1.47–1.78 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 120.86, 107.89, 98.45, 67.07, 61.66, 49.44, 30.34, 25.24, 29.98. IR (KBr film, cm^{-1}) 2943, 1500, 1441, 1352, 1286, 1200, 1124, 1074, 1036, 980, 923, 871, 815, 724. MS: *m*/*z* 195 (M^+), 139, 122, 110, 95, 85, 80, 78, 67. HR-MS: *m*/*z* calc. 195.125929, found 195.126583.

1,1′-Bis(2-tetrahydropyran-2-yloxyethyl)-2,2′-bipyrrole 2

tert-Butyllithium (33 mL, 1.5 M solution in pentane) was added to a vigorously stirred solution of **1** (9.75 g, 50 mmol) in 100 mL degassed dry THF at −80 °C. The reaction mixture was stirred for 30 min maintaining the temperature at −80 °C and then allowed to reach room temperature. The resulting solution, containing carbanions of **1** was added, using a double-ended needle, to a suspension of $NiCl_2$ (9.72 g, 75 mmol) in 50 mL degassed dry THF at −80 °C. The reaction mixture was allowed to reach room temperature during which it changed from yellow to black caused by the formation of colloidal nickel. Stirring at room temperature for 12 h was followed by removal of the nickel powder by filtration and extraction with diethyl ether (3 × 100 mL). The combined organic phases were washed with water (2 × 200 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the resulting dark-brown liquid was purified by column chromatography (SiO_2, light petroleum–diethyl ether (10 : 1), $R_f = 0.06$). Compound **2** was obtained as a bright yellow oil which slowly crystallised at −40 °C (2.14 g, 5.52 mmol, 22%). **2**: ^1H NMR ($CDCl_3$): δ 6.95 (t, 2H), 6.24 (dd, 4H), 4.55 (t, 2H), 4.05 (t, 2H), 3.85 (m, 2H), 3.30–3.70 (m, 8H), 1.50–1.90 (m, 12H). ^{13}C NMR ($CDCl_3$): δ 124.11, 122.07, 111.13, 107.38, 98.47, 66.97, 61.74, 46.45, 30.36, 25.29, 19.09. IR (KBr film, cm^{-1}): 2942, 2871, 2360, 2341, 1454, 1441, 1352, 1314, 1281, 1201, 1136, 1123, 1078, 1036, 981, 871, 814, 718. MS: *m*/*z* 388 (M^+), 288, 287, 204, 203, 187, 173, 159, 144, 132, 106, 85, 67; HRMS: *m*/*z* calc. 388.236208, found: 388.235870. UV–VIS (MeCN): $\lambda_{max} = 256$ nm.

1,1′-Bis(2-hydroxyethyl)-2,2′-bipyrrole 3

p-Toluenesulfonic acid (0.1 g) was added to a solution of **2** (1.94 g, 5 mmol) in 250 mL dry methanol and stirred at room temperature for 3 h, the mixture changing from colourless to dark red. The solution was slowly saturated with KOH, washed with water (3 × 100 mL) and dried over Na_2SO_4. Removal of the solvent under reduced pressure and purification of the dark red oil by column chromatography (SiO_2, diethyl ether, $R_f = 0.18$) afforded colourless crystals of **3** (0.96 g, 4.36 mmol, 87%). **3**: ^1H NMR ($CDCl_3$): δ 6.94 (t, 2H), 6.34 (t, 2H), 6.30 (dd, 2H), 4.04 (t, 4H), 3.74 (t, 4H), 2.79 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 124.32, 121.90, 111.98, 107.70, 62.24, 48.96; IR (KBr, cm^{-1}): 3166, 2928.6, 2721, 2300, 2251, 1719, 1645, 1485, 1430, 1388, 1359, 1318, 1281, 1260, 1233, 1217, 1172, 1086, 1047, 1016, 990, 959, 782, 730. MS: *m*/*z* 220 (M^+), 201, 189, 176, 171, 157, 145, 132, 117, 104, 80. HRMS: *m*/*z* calc. 220.121178, found 220.120911. UV–VIS (MeCN): $\lambda_{max} = 253$ nm, mp 72 °C.

General procedure for the synthesis of crown-ether-containing bipyrroles

A solution of **3** (0.5 g, 2.27 mmol) in 100 mL dry THF was added to NaH (104 mg, 5.54 mmol of a dispersion in mineral oil) previously activated by washing with dry diethyl ether (2 × 25 mL) and dry THF (1 × 25 mL). The resulting mixture was refluxed under argon for 1 h and cooled to 0 °C prior to the addition of the oligo(ethylene glycol)-di-*p*-tosylate (2.27 mmol) in 100 mL dry THF and further refluxed for 14 h. The mixture was poured into diethyl ether/water (200 mL/200 mL) washed with water (2 × 200 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the resulting brown oil was purified by column chromatography.

1,1′-(3,6,9,12-Tetraoxatetradecane-1,14-diyl)-2,2′-bipyrrole 4. Compound 4 (SiO_2, ethyl acetate, $R_f = 0.46$) was obtained as a pale yellow oil (0.37 g, 1.1 mmol, 49%). ^1H NMR ($CDCl_3$): δ 6.80 (dd, 2H), 6.14 (m, 4H), 4.12 (m, 4H), 3.52–3.87 (m, 16H). ^{13}C NMR ($CDCl_3$): δ 124.33, 121.58, 110.83, 107.49, 70.75, 70.67, 70.61, 70.57, 46.64; IR (KBr film, cm^{-1}): 3100, 2869, 1956, 1735, 1639, 1514, 1451, 1355, 1313, 1281, 1238, 1192, 1121, 994, 938, 890, 843, 790, 719, 617. MS: *m*/*z* 334 (M^+), 290, 203, 185, 173, 157, 146, 132, 117, 104, 93, 79. HRMS: *m*/*z* calc. 334.189258, found 334.188171. UV–VIS (MeCN): $\lambda_{max} = 252$ nm; $E_{pa}{}^1 = 0.37$ V *vs.* Fc/Fc^+.

1,1′-(3,6,9,12,15-Pentaoxaheptadecane-1,17-diyl)-2,2′-bipyrrole 5. Compound **5** [SiO_2, ethyl acetate–triethylamine (20 : 1), $R_f = 0.38$] was obtained as a pale yellow oil (0.49 g, 1.30 mmol, 57%). ^1H NMR ($CDCl_3$): δ 6.87 (dd, 2H), 6.21 (t, 2H), 6.17 (dd, 2H), 4.09 (m, 2H), 3.86 (m, 2H), 3.48–3.70 (m, 20H); ^{13}C NMR ($CDCl_3$): δ 124.36, 121.60, 111.00, 107.47, 70.79, 70.75, 70.70, 70.62, 70.51, 46.58; IR (KBr film, cm^{-1}): 3101, 2868, 1736, 1598, 1515, 1451, 1354, 1281, 1177, 1120, 926, 818, 720, 664, 616. MS: *m*/*z* 378 (M^+), 348, 335, 304, 275, 247, 231, 203, 189, 173, 159, 146, 132, 117, 104, 93, 79. HRMS: *m*/*z* calc. 378.215472, found 378.214661. UV–VIS (MeCN): $\lambda_{max} = 253$ nm. $E_{pa}{}^1 = 0.36$ V *vs.* Fc/Fc^+.

1,1′-(3,6,9,12,15,18-Hexaoxaeicosane-1,20-diyl)-2,2′-bipyrrole 6. Compound **6** (SiO_2, ethyl acetate, $R_f = 0.15$) was obtained as a pale yellow oil (0.42 g, 1.0 mmol, 44%). ^1H NMR ($CDCl_3$): δ 6.87 (dd, 2H), 6.18 (dd, 2H), 6.15 (dd, 2H), 3.97 (m, 4H), 3.51–3.69 (m, 24H). ^{13}C NMR ($CDCl_3$): δ 124.18, 121.82, 110.90, 107.36, 70.71, 70.64, 70.61, 70.56, 70.50, 70.46, 46.47; IR (KBr film, cm^{-1}): 3100, 2868, 2362, 1736, 1514, 1450, 1352, 1313, 1281, 1248, 1191, 1121, 940, 847, 790, 720, 616. MS: *m*/*z* 422 (M^+), 392, 247, 203, 185, 173, 157, 146, 132, 117, 104, 93. HRMS: *m*/*z* calc. 422.241687, found 422.242798. UV–VIS (MeCN): $\lambda_{max} = 253$ nm. $E_{pa}{}^1 = 0.33$ V *vs.* Fc/Fc^+.

1,1′-(3,6,9,12,15,18,21-Heptaoxatricosane-1,23-diyl)-2,2′-bipyrrole 7. Compound **7** [SiO_2, ethyl acetate–triethylamine (20:1), $R_f = 0.34$] was obtained as a colourless oil (0.33 g, 0.71 mmol, 31%). ^1H NMR ($CDCl_3$): δ 6.86 (dd, 2H), 6.17 (dd, 2H), 6.14 (dd, 2H), 3.89 (m, 4H), 3.48–3.73 (m, 28H). ^{13}C NMR ($CDCl_3$): δ 124.22, 121.87, 110.97, 107.47, 70.84, 70.71, 70.68, 70.66, 70.54, 70.51, 70.47, 46.45; IR (KBr film, cm^{-1}): 3101, 2870, 2360, 2341, 1943, 1648, 1597, 1514, 1451, 1400, 1355, 1281, 1248, 1189, 1177, 1117, 1019, 925, 818, 779, 721, 666. MS: *m*/*z* 466 (M^+), 437, 423, 247, 203, 185, 173, 157, 146, 117, 132, 93. HRMS: *m*/*z* calc. 466.267902, found 466.268341. UV–VIS (MeCN): $\lambda_{max} = 253$ nm. $E_{pa}{}^1 = 0.33$ V *vs.* Fc/Fc^+.

Acknowledgements

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