Synthetic routes to bis(pyrrolyl)arylenes. Experimental and molecular modeling studies

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The synthesis and characterization of compounds derived from 9,9-dialkylfluorene and 1,4-dioxane[3,4-b]thiophene are described. The key step involves a modified Steglich reaction between 9,9-dialkyl-2,7-N,N'-diallyliminochloro-fluorene or 2,5-N,N'-diallyliminochloroethylenedioxythiophene and *tert*-BuOK (Route 1). Route 2 for bis(pyrrol-2-yl)dioxanethiophene, involving the reaction between 1,4-dioxane[2,3-c]thiophene and a dioxolanepropanol, is also a useful and general strategy. Molecular modeling studies indicate relationships between the molecular parameters (structure, ionization potential, atomic charges) of the synthesized moieties and their polymerization properties.

In recent years, polypyrrole and its derivatives have been widely investigated because of their easy electrosynthesis, good stability and excellent conductivity in the oxidized state.¹ A few years ago, we reported a unique synthesis of 1,4-bis(pyrrol-2-yl)arylenes **1–8** (Scheme 1), their electropolymerization and properties of the electroactive and electrically conducting polymers obtained.^{2–4} This new synthetic route opens up a number of opportunities for the synthesis of derivatized, potentially soluble and processable, pyrrole-containing polymers. Using a different method, we also synthesized the indolo[7,6-g]indole system starting from 1,5-dihydroxynaphthalene.⁵

Preliminary molecular modeling studies were also performed to assess the usefulness of the synthesized moieties for polymerization. Structures, ionization energies, and electronic charge distribution are correlated with the available experimental data.

Results and discussion

Synthesis of the bis(pyrrole)arylenes

Herein we present our synthesis of 9,9-didodecyl-2,7-

bis(pyrrol-2-yl)fluorene. We hoped that this compound would be as good a candidate for polymerization as the 9,9-diethyl-2,7-bis(pyrrol-2-yl)fluorene analog.⁴ The synthesis was carried out as outlined in Scheme 2. Double deprotonation of fluorene⁶ (10) with BuⁿLi, followed by addition of 3 equiv. of 1-bromododecane afforded 9,9-didodecylfluorene (11). Using the procedure developed for bromination of the aromatic moiety of alkylbenzenes, 11 was converted into 2,7-dibromo-9,9-didodecylfluorene (12) in 80% yield. Copper(I) cyanide, previously used for preparing aromatic dinitriles⁷ from haloaromatics, converted 12 into 9,9-didodecyl-2,7-dicyanofluorene (13). 9,9-Didodecylfluorene-2,7-dicarboxylic acid (14a) was obtained by heating the dinitrile 13 with phosphoric acid (100%) according to a general literature procedure.⁸

The diacid was reacted with excess thionyl chloride at room temperature, similarly to a general method,⁹ to give 9,9-didodecylfluorene-2,7-dicarboxylic acid dichloride (15a) (Scheme 3). 9,9-Didodecylfluorene-2,7-dicarboxylic acid diallylamide (16a) was obtained in 80% yield by reaction of the crude dichloride 15a with allylamine in the presence of triethylamine in benzene.³ Treatment of compound 16a with 6 equiv. of phosgene afforded the 9,9-didodecyl-2,7-bis(N,N'-



Scheme 1

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allylchloroimino) fluorene. Compound **17a** was cyclized without isolation by potassium *tert*-butoxide⁴ in THF into 9,9-didodecyl-2,7-bis(pyrrol-2-yl)fluorene (**18a**), which was isolated after column chromatography in 70% yield.

In this paper we also report a synthetic study of 2,5bis(pyrrol-2-yl)-1,4-dioxane[2,3-c]thiophene (**18b**, BPDT). This study has been inspired by a literature review concerning conjugated oligomers based on various combinations of thiophene and 3,4-ethylenedioxythiophene (**19**, EDOT). As exemplified in several works, the use of EDOT as a building block allows for the development of interesting new conjugated systems, such as polymers with improved electrochromic properties, precursors of electrogenerated functional conjugated polymers with a better aptitude for electropolymerization,¹⁰ polymers with a small intrinsic bandgap¹¹ and extended tetrathiafulvalene analogs with enhanced π -donor ability.¹² Despite a rich literature on diverse derivatives of 3,4-ethylenedioxythiophene, the synthesis of BPDT has not been carried out previously. Two different and independent routes were used to prepare the bis(pyrrole)dioxanethiophene 18b. In Route 1 the compounds 14b-18b were synthesized as for bis(pyrrole)arylenes in accordance with the general pathway shown in Scheme 3. In this case we started from 1,4-dioxane[2,3-c]thiophene-2,5dicarboxylic acid (14b).¹³ With this route we obtained 18b in a seven-step procedure in an overall yield of 28% based on 3,4dihydroxythiophenedicarboxylic acid 14b. The very useful methodology of Route 2 (Scheme 4) was modeled after work done by Lucchesini.¹⁴ Commercially available 2,3dihydrothieno[3,4-b][1,4]dioxane (19) was metallated with BuⁿLi to give dilithiodioxanethiophene (20), which was immediately reacted with 2 equiv. of 1,3-dioxolane-2-propanal (21) to give the dioxolanol derivative 22, used without purification in the next step.

Reaction of compound 22 with pyridinium chlorochromate (PCC) and sodium acetate yielded the oxidized product 2,5-bis[3-(1,3-dioxolan-2-yl)propanoyl]-3,4-ethylenedioxythiophene (23), which was refluxed in acetic acid with ammonium acetate for 15 h to afford 18b in 55% yield. The overall yield for compound 18b in Route 2 was 30% from a commercially available compound (in a three-step procedure). Therefore, we chose to use a variation of the Lucchesini approach for a



Scheme 4

large-scale preparation. Novel compounds were characterized by ¹H NMR and ¹³C NMR.

According to the classical Paul-Knorr pyrrole synthesis, there are two possible alternative mechanisms for the cyclization of diketone 23 to 18b: the first proceeding via an imine intermediate 23' (Scheme 5) and the other via the tautomeric form of the imine—the enamine 23": (Scheme 6). These intermediates subsequently cyclicize by intramolecular attack on the aldehyde groups to form 18b, eliminating H_2O in the process.

CT complexes of fluorene derivatives with TCNQ

An investigation of the electrical conductivity of films consisting of several monolayers of the CT complexes of 9,9-didodecylfluorene (11, DDF) with tetracyanoquinodimethane (TCNQ) exposed to various concentrations of nitrogen dioxide and ammonia was carried out. The DDF–TCNQ films were deposited onto a set of interdigital Au electrodes (230 μ m wide and spaced, and 50 nm thick) photolithographically fixed on SiO₂ coated silicon substrates, using the Langmuir–Blodgett technique.

In the case of nitrogen dioxide the first admission of the gas leads to a linear dependence of conductivity on gas concentration, with saturation occuring at higher NO_2 concentrations (Fig. 1). After a complete series of measurements, the measurement compartment was opened to air and the recovery of conductivity was observed for half an hour. If one assumes that the conductivity is directly related to the number of molecules of the active gas adsorbed on the sample surface, then under a constant voltage, the current as a function of the partial gas pressure can be described by the Langmuir isotherm, characteristic of pure chemisorption:

$$S(p) = \frac{Kp}{1 + Kp} \tag{1}$$

where K is an experimental parameter, understood as a ratio of, respectively, the absorption and desorption rate constants,



Fig. 1 Conductivity response of a 5-layer LB film of DDF–TCNQ to $\ensuremath{\mathsf{NO}_2}$.

 $K = k_a/k_d$. The observed linear pressure dependence of the conductivity at low concentrations of nitrogen oxide and its saturation at higher concentrations confirms that the process of adsorption may be approximated by the Langmuir isotherm. Moreover, the Langmuir isotherm predicts that a straight line should be obtained when p/S(p) is plotted against p.

Similar measurements were also performed for ammonia. However, in this case almost a linear proportionality of electrical conductivity to gas concentration was observed during the first treatment of the sample with gas (Fig. 2). During the second admission of ammonia the conductivity increased by more than three orders of magnitude. Although hysteresis of conductance was observed during partial aeration of the measuring enclosure, which might suggest some kind of capillary condensation at the surface, a slight tendency to overlinearity, observed at higher concentrations of ammonia, did not allow us to apply the BET adsorption isotherm. The high volatility of ammonia allows, however, for its complete desorption from the surface during the regeneration process. Reasonable repro-





Fig. 2 Conductivity response of a 5-layer LB film of DDF-TCNQ to ammonia; first cycle of measurements.

ducibility and fair sensitivity at room temperature make this CT complex a prospective material for gas sensors. The CT mechanism of sensing is to be presented in a forthcoming paper.¹⁵

Molecular modeling results

It is reasonable to assume that the properties of polymers are closely related to the properties of the monomers and one should seek such correlations. The main difference between the structures of the monomers in the present work is the value of the dihedral angle between the pyrrole and benzene rings. The pyrrole rings in the studied molecules (Table 1) follow two different patterns. Planar structures were obtained for the compounds containing –OR substitutes on the aryl ring. Examples of planar and nonplanar structures are presented in Fig. 3–7. The presence of the oxygen atom interacting with the closest hydrogen of the pyrrole ring stabilizes the global planar skeleton of the complexes (Fig. 4, 7). In com-

Table 1 The dihedral angle (φ) between the benzene and pyrrole rings, vertical ionization energy calculated by the HF and B3LYP methods and experimental oxidation potential maximum $(E_{p,m})$ of the studied monomers

Monomer	$arphi/^\circ$	Calc. vertical ionization energy/eV		
		HF	B3LYP	 E _{p, m} /V
1	33	6.03	6.50	0.35
2	0.2	5.39	5.98	0.15
3	4.7	5.35	5.93	
4	3.1	5.27	5.85	0.17
5	34.8	6.00	6.38	0.35
6	32.3	6.32	6.38	0.45
7	36.1	5.45	6.05	0.30
8	32.8	5.77	6.20	0.15
9	0.0	5.34	5.68	_
18a	33.4	5.85	6.16	0.30
18b	12.0	5.09	5.97	0.15



Fig. 3 The optimized structure of 1,4-bis(pyrrol-2-yl)benzene (1). The view is along the longest axis of the molecule.



Fig. 4 The calculated geometry of 1,4-bis(pyrrol-2-yl)-2,5-dimethoxy-benzene (2).

pounds without oxygen the dihedral angle amounts to about 35°, indicating weak coupling between the rings (Fig. 5).

The calculations indicate that vertical ionization energy values (Table 1) are the lowest in compounds containing oxygen atoms. For compounds where experimental data are available, the ionization potentials correlate well with the measured oxidation potentials. The calculations indicate that ionization leads to the largest change of atomic charges on the carbon atoms that are the centers for polymerization. These carbon atoms are neighbors of the nitrogen atoms in the pyrrole rings, as indicated in Fig. 5.



Fig. 5 Arrows indicate atoms with the largest change due to the ionization in 1,4-bis(pyrrol-2-yl)benzene (1).



Fig. 6 The optimized structure of 9,9-didodecyl-2,7-bis(pyrrol-2-yl)-fluorene (18a).



Fig. 7 The optimized structure of 2,5-bis(pyrrol-2-yl)-1,4-dioxane-[3,4-b]thiophene (18b).

Conclusions

The results reported herein offer simple methods for the preparation of compounds belonging to the class of bis-(pyrrolyl)arylenes. Bis(pyrrolyl)dioxanethiophene was obtained in moderate yield by using two different routes. The modified Lucchesini procedure can be easily adapted for the short synthesis of 2,5-bis(pyrrol-2-yl)-1,4-dioxane[2,3-c]thiophene starting from commercially available 2,3-dihydrothieno[3,4-b][1,4] dioxin.

The structures and properties of synthesized molecules were also modeled theoretically with the aim of determining the relation of their properties to their polymerization potentials. The correlation between experimentally determined oxidation potentials and theoretically established structures (the dihedral angle φ) and ionization potentials indicates the important role of the -OR substituent. The oxygen atom present in the substituent interacts with the pyrrole ring, stabilizing the planar structure. Planar molecules possess lower ionization potentials compared to values found for nonplanar moieties. The calculated ionization potentials correlate well with the oxidation potentials. The newly synthesized molecules (nonplanar 18a and planar 18b) fit well with these trends. The charge distribution change due to the ionization correlates well with the expected sites of polymerization.

Experimental

General

Melting points are uncorrected. All NMR spectra were acquired using a Brucker VXR-300 at 300 (¹H) and 75 (¹³C) MHz in CDCl₃ using TMS as internal standard. Column chromatography was carried out on Merck Kiesel silica gel 60. Dry THF was used immediately after distilling from a solution containing benzophenone–sodium. Other starting materials, reagents and solvents were used as received from suppliers.

Syntheses

9,9-Didodecylfluorene (11). BunLi (1.6 M solution in hexane, 1.8 mmol) was added to a solution of fluorene (1.00 g, 6 mmol) in THF (50 mL) at -60 °C over a period of 5 min. The resulting solution was stirred at -60 °C for 1.5 h. A solution of 1-bromododecane (2.99 g, 1.2 mmol) in THF (10 mL) was added dropwise and stirring continued at -60 °C for 30 min. Ammonium chloride (5 g in 30 mL of water) was added, then the organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the crude oily product was purified by column chromatography, eluent: (1) hexane, (2) hexane-ethyl acetate (2:1). Yield 80%. ¹H NMR δ (CDCl₃): 0.71–0.82 (m, 4H, CH₂), 0.97 (t, J = 6.99 Hz, 6H, CH₃), 1.92–2.06 (m, 4H, CH₂), 1.32-1.62 (m, 36H, CH₂), 7.37-7.48 (m, 6H arom. H), 7.78-7.80 (m, 2H, arom. H). ¹³C NMR δ (CDCl₃): 14.1, 22.6, 22.7, 23.7, 29.2, 29.6, 30.0, 31.9, 40.3, 54.9, 119.6, 122.8, 126.9, 130.6, 141.1, 150.6. Anal. calc. for C37H58: C, 83.37; H, 11.62; found C, 83.2; H, 11.35%.

9,9-Didodecyl-2,7-dibromofluorene (12). Bromine (0.15 mL, 3.0 mmol) in CH_2Cl_2 was added quickly to a stirred solution of compound **11** (2.01 g, 4.0 mmol) and I_2 (1.0 mg, 0.4 mmol) in CH_2Cl_2 (20 mL) at room temperature. The reaction mixture was stirred at room temperature for 20 h. An aqueous solution of NaHSO₃ (15 mL, 15%) was added and the resulting two phases were stirred until the color disappeared (30 min). The organic layer was separated, washed with water and dried over MgSO₄. The volatiles were removed under reduced pressure and the crude product was recrystallized

from hexane. Yield 80%, mp 45 °C. ¹H NMR δ (CDCl₃): 0.70–0.80 (m, 4H, CH₂), 0.96 (t, J = 6.98 Hz, 6H, CH₃), 1.32–1.36 (m, 36 H, CH₂), 1.92–2.06 (m, 4H, CH₂), 7.4–7.54 (m, 6H, arom. H). ¹³C NMR δ (CDCl₃): 14.1, 22.6, 22.7, 23.7, 29.2, 29.6, 30.0, 31.9, 40.3, 54.8, 119.6, 122.9, 126.9, 130.5 141.3, 150.6. Anal. calc. for C $_{37}H_{56}Br_2$: C, 67.26; H, 8.54; found C, 67.05; H, 8.40%.

9,9-Didodecyl-2,7-dicyanofluorene (13). A mixture of copper(I) cyanide (0.4 g, 4.5 mmol) and compound **12** (1.0 g, 1.5 mmol) in DMF (30 mL) was refluxed for 24 h. The mixture was poured into a solution of ammonia (20 mL, 15%) to form a precipitate. The solid was collected by filtration and washed with an ammonia solution, followed by water. The solid was recrystallized from acetone to give yellow crystals. Yield 70%, mp 156–157 °C. ¹H NMR δ (CDCl₃): 0.73–0.81 (m, 4H, CH₂), 0.97 (t, J = 7.0 Hz, 6H, CH₃), 1.13–1.26 (m, 36H, CH₂), 1.92–2.0 (m, 4H, CH₂), 7.60 (d, J = 8.3 Hz, 4H, arom. H), 7.82 (s, 2H, arom. H). ¹³C NMR δ (CDCl₃): 14.1, 22.6, 22.8, 29.2, 29.5, 29,6, 30.0, 31.91, 40.4, 54.8, 119.6, 122.8, 126.1, 126.8, 130.5, 142.2, 151.4. Anal. calc. for C₃₉H₅₆N₂: C, 84.72; H, 10.21; N, 5.06; found C, 84.55; H, 10.0; N, 4.90%.

9,9-Didodecylfluorene-2,7-dicarboxylic acid (14a). A mixture of compound 13 (1.0 g. 1.8 mmol) and phosphoric acid (17.2 mL) in water (2.55 mL) was stirred under nitrogen at 170 °C for 24 h. The mixture was poured into hot water to precipitate the diacid 14a, which was isolated by filtration and washed repeatedly with water. The crude product was recrystallized from methanol to give white crystals. Yield 75%, mp 305 °C. ¹H NMR δ (DMSO): 0.8 (s, 4H, CH₂), 0.97 (t, J = 6.87 Hz, 6H, CH₃), 1.13–1.62 (m, 36 H, CH₂), 1.92–2.07 (m, 4H, CH₂), 2.52 (s, 2H, OH), 7.78–7.82 (m, 6H, arom. H). ¹³C NMR δ (CDCl₃): 14.1, 22.6, 22.8, 29.2, 29.5, 29.6, 30.1, 31.8, 40.5, 54.8, 122.8, 126.2, 126.8, 130.4, 141.5, 151.4, 167.4. Anal. calc. for C₃₉H₅₈O₄; C, 79.27; H, 9.89; found C, 79.0; H, 9.6%.

9,9-Didodecylfluorene-2,7-dicarboxylic acid dichloride (15a). A mixture of compound 14a (1.0 g, 1.8 mmol), thionyl chloride (15 mL) and 2 drops of anhydrous DMF was stirred at room temperature for 12 h and then stirred at 50 °C for 1 h. Excess thionyl chloride was removed under reduced pressure. The crude product was taken up in chloroform and treated with activated charcoal, filtered and crystallized to give yellowish-green crystals. Yield 81%, mp 134–135 °C. ¹H NMR δ (CDCl₃): 0.72 (s, 4H, CH₂), 0.96 (t, J = 6.54 Hz, 6H, CH₃), 0.94–1.3 (m, 36 H, CH₂), 1.92–2.06 (m, 4H, CH₂), 7.4 (d, J = 7.6 Hz, 2H, arom. H), 7.8 (s, 2H, arom. H), 8.0 (d, J = 7.5 Hz, 2H, arom. H). ¹³C NMR δ (CDCl₃): 14.1, 22.5, 22.8, 29.1, 29.5, 29.6, 30.2, 31.7, 40.5, 54.7, 119.6, 126.8, 130.4, 133.3, 141.4, 152.6, 168.0. Anal. calc. for C₃₉H₅₆Cl₂O₂: C, 74.61; H, 8.99; found C, 74.2; H, 8.62%.

9,9-Didodecylfluorene-2,7-dicarboxylic acid diallylamide (16a). A solution of compound 15a (1.0 g, 1.6 mmol) in dry benzene (30 mL) was added slowly with vigorous stirring to a solution of allylamine (0.2 g, 3.5 mmol) and triethylamine (0.35 g, 3.5 mmol) in dry benzene (10 mL). The mixture was stirred at room temperature for 6 h and then heated for 1 h at 50 °C. The mixture was cooled and the precipitate was collected by filtration and washed with benzene. Recrystallization from methanol afforded colorless needles. Yield 80%, mp 169-170 °C. ¹H NMR δ (CDCl₃): 0.70 (s, 4H, CH₂), 0.95 (t, J = 6.6Hz, 6H, CH₃), 0.94-2.1 (m, 36 H, CH₂), 1.92-2.1 (m, 4H, CH₂), 4.13 (t, J = 7.2 Hz, 4H, NHCH₂), 5.09 (d, J = 14 Hz, 2H, $=CH_2$), 5.30 (d, J = 9.1 Hz, 2H, $=CH_2$), 6.95–6.99 (m, 2H, CHCH₂), 7.31–7.45 (m, 4H, arom. H), 7.8 (br s, 2H, arom. H). ¹³C NMR δ (CDCl₃): 14.1, 22.5, 22.8, 29.0, 29.5, 29.6, 30.1, 31.7, 40.5, 115.3, 119.5, 122.5, 126.9, 130.6, 135.5, 143.6, 151.7, 167.3. Anal. calc. for $C_{45}H_{68}O_2N_2$: C, 80.78; H, 10.24; N, 4.18; found C, 80.51; H, 10.0; N, 3.98%.

9,9-Didodecyl-2,7-bis(pyrrol-2-yl)fluorene (18a). A mixture of compound 16a (1.0 g, 1.59 mmol), a solution of 20% phosgene in toluene (8.2 mL) and anhydrous DMF (0.1 mL) was stirred for 12 h at room temperature. The mixture was then heated to 40°C for 1 h. The solvent was removed under reduced pressure and crude 9,9-didodecyl-2,7-bis(N,N'-allylchloroimino)fluorene (17a) was used without isolation for the next step. A solution of crude compound 17a in THF (50 mL) was added dropwise to a solution of potassium tert-butoxide (0.63 g, 5.6 mmol) in dry THF (30 mL) held at a temperature between -10 and 0 °C under nitrogen. The mixture was stirred for 1 h, then the mixture was poured into ice and extracted with diethyl ether (50 mL). The organic phase was dried with MgSO₄, the volatiles were removed under reduced pressure, and the residue was purified by column chromatography. The first eluent was hexane and a second column was run with hexane-ethyl acetate (2:1) to yield 18a. Yield 70%, mp 172 °C. ¹H NMR δ (CDCl₃): 0.70 (s, 4H, CH₂), 0.96 (t, J = 6.72 Hz, 6H, CH₃), 1.13–1.36 (m, 36H, CH₂), 2.02–2.1 (m, 4H, CH₂), 6.13 (s, 2H, pyrrole H), 6.57 (s, 2H, pyrrole H), 6.8 (s, 2H, pyrrole H), 7.5-7.6 (m, 4H, arom. H), 7.7 (br s, 2H, arom. H), 8.0 (s, 2H, NH). ¹³C NMR δ (CDCl₃): 14.1, 22.5, 22.8, 29.0, 29.5, 29.6, 30.1, 31.7, 54.7, 105.3, 109.1, 110.9, 117.9, 119.5, 126.8, 130.6, 132.7, 139.5, 150.6. Anal. calc. for C45H64N2: C, 85.38; H, 10.19; N, 4.42; found: C, 85.14; H, 9.91; N, 4.18%.

1,4-Dioxane [2,3-c] thiophene-2,5-dicarboxylic acid dichloride (15b). The title compound was prepared as compound 15a above from 3,4-dihydroxythiophene-2,5-dicarboxylic acid. Yield 78%, mp 144 °C. ¹H NMR δ (CDCl₃): 4.49 (4H, s, CH₂). ¹³C NMR δ (CDCl₃): 65.0, 119.5, 146.6, 156.8. Anal. calc. for C₈H₄ Cl₂ O₄S: C, 35.98; H, 1.51; found C, 35.84; H 1.40%.

2,5-Diallylamido-1,4-dioxane[**2,3-***c*]**thiophene** (16b). The title compound was prepared as compound **16a** above from compound **15b**. Yield 64%, mp 166–167 °C. ¹H NMR δ (CDCl₃): 4.06 (t, J = 5.69 Hz, 4H, $-CH_2$ –), 4.46 (s, 4H, $-CH_2$ –), 5.17 (d, J = 10.22 Hz, 2H, $=CH_2$), 5.24 (d, J = 17.1 Hz, 2H, =CH–), 5.90 (m, 2H, -CH=), 6.83 (2H, m, NH). ¹³C NMR δ (CDCl₃): 41.8, 65.0, 116.5, 117.6, 134.1, 139.2, 160.3. Anal. calc. for C₁₄H₁₆N₂O₄S: C, 54.53; H, 5.22; N, 9.08; found C, 54.77; H, 5.27; N, 9.04%.

2,5-Bis(pyrrol-2-yl)-1,4-dioxane[2,3-c] thiophene (18b, Route 1). A mixture of 1.0 g (3.2 mmol) of 16b, a solution of 20% phosgene in toluene (19.2 mL), and two drops of dimethylformamide was stirred for 8 h at room temperature. The solution was then heated to 50 °C and the toluene was removed in vacuo simultaneously. The crude unstable product 17b was used directly in the next step without purification. Yield 74.77%. A solution of crude compound 17b (1.0 g, 3 mmol) in THF (50 mL) and 3 ml DMF was added dropwise to a solution of potassium tert-butoxide (4.15 g, 7 mmol after sublimation) in dry THF (30 mL) held at a temperature between -10 and 0 °C under nitrogen. The mixture was stirred for 1 h, then the mixture was poured into ice and extracted with diethyl ether (50 mL). The organic phase was dried with MgSO₄, evaporated to dryness and the residue was purified by column chromatography (dichloroethane-hexane 2:1). Yield 56%, mp. 182 °C. ¹H NMR δ (CDCl₃): 4.28 (s, 4H, $-CH_2$ -), 6.14 (s, 2H, pyrrole), 6.21 (s, 2H, pyrrole), 6.72 (s, 2H, pyrrole), 8.97 (s, 2H, NH). ¹³C NMR δ (CDCl₃): 67.0, 104.5, 106.6, 109.1, 117.8, 122.2, 125.3, 130.2, 132. Anal. calc. for C14H12N2O2S: C, 61.76; H, 4.44; N, 10.29; found C, 61.73; H, 4.40; N, 10.15%.

2,5-Bis [3-(1,3-dioxolan-2-yl)propanoyl]-1,4-dioxane [2,3-c]thiophene (23). n-Butyllithium (28.2 mL, 1.6 M in hexane) was added to 6.40 g (5 mmol) 3,4-ethylenedioxythiophene (19) in dry THF (70 mL). The mixture was stirred at -78 °C for 1 h. Two equivalents of 1,3-dioxolane-2-propanal [21,4 obtained from commercially available 2-(2-bromoethyl)-1,3-dioxolane] were then added dropwise and the resulting mixture was stirred for 1 h at -70 °C. The mixture was warmed to room temperature and saturated ammonium chloride (10 mL) was added. The organic layer was separated and the aqueous layer was extracted with diethyl ether (50 mL). The phases were separated, the organic layer was dried (MgSO₄) and the volatiles were removed to afford compound 22. A solution of compound 22 in anhydrous methylene chloride (10 mL) was added to a suspension of pyridinum chlorochromate (PCC, 1.95 g, 9.00 mmol) and sodium acetate (0.3 g, 4.07 mmol) in methylene chloride (6 mL). The mixture was stirred for 1.5 h at room temperature followed by further addition of PCC (0.3 g). The mixture was stirred for 1 h. Saturated sodium hydrogen carbonate (25 mL) was added to the solution until evolution of CO₂ ceased. The slurry was filtered and the residue was washed with methylene chloride (60 mL). The filtrate was concentrated under pressure and the crude compound 23 was purified by flash chromatography (silica gel: hexane-ethyl acetate 2:1). Yield 55%, mp 172 °C. ¹H NMR δ (CDCl₃): 2.17 (m, 4H, CH₂), 3.15 (t, J = 7.2 Hz, 4H, CH₂), 3.87 (m, 8H, CH₂), 4.5 (s, 4H, CH₂), 5.03 (t, J = 4.4 Hz, 2H, -CH-). ¹³C NMR δ (CDCl₃): 27.8, 32.9, 65.0, 103.5, 119.5, 146.6, 190.6. Anal. calc. for C₁₈H₂₂O₈S: C, 54.27; H, 5.56; found C, 54.1; H, 5.42%.

2,5-Bis(pyrrol-2-yl)-1,4-dioxane[2,3-c] thiophene (18b, Route 2). Compound 23 (0.50 g, 1.2 mmol) and ammonium acetate (2.2 g, 2.8 mmol) in acetic acid (10 mL) were refluxed for 18 h under nitrogen. Acetic anhydride was added until compound 23 was consumed as monitored by TLC (hexane-ethyl acetate 2:3). The mixture was poured into water (35 mL), neutralized with sodium hydrogen carbonate and extracted with methylene chloride (40 mL) The combined organic layers were dried with MgSO₄ and volatiles were removed under reduced pressure. The crude compound 18b was purified by flash chromatography (silica gel: hexane-ethyl acetate 3:2). Yield 55%, mp 182 °C. ¹H NMR δ (CDCl₃): 4.28 (s, 4H, -CH₂-), 6.14 (s, 2H, pyrrole), 6.21 (s, 2H, pyrrole), 6.72 (s, 2H, pyrrole), 8.97 (s, 2H, NH). ¹³C NMR δ (CDCl₃): 67.0, 104.5, 106.6, 109.1, 117.8, 122.2, 125.3, 130.2. Anal. calc. for C₁₄H₁₂N₂O₂S: C, 61.76; H, 4.44; N, 10.29; found C, 61.70; H, 4.30; N, 10.15%.

Molecular modeling

The molecular modeling applied in this work is based on *ab initio* calculations. Since the experimental structures of the studied moieties were not available, the structures were derived theoretically. The geometry optimization was performed applying the Hartree–Fock (HF) method utilizing the standard 6-31G* atomic basis set.¹⁶ This method has been shown to be a reasonable compromise between quality and cost of calculations for similar size molecules.¹⁷ The derived structures were used for calculations of vertical ionization potentials. These properties were calculated within the DFT approach applying the B3LYP functional¹⁸ and the 6-31G* basis set.¹⁹ The results reported here were obtained by utilizing the GAUSSIAN 98 code.²⁰

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