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*′-diallyliminochlorofluorene 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]

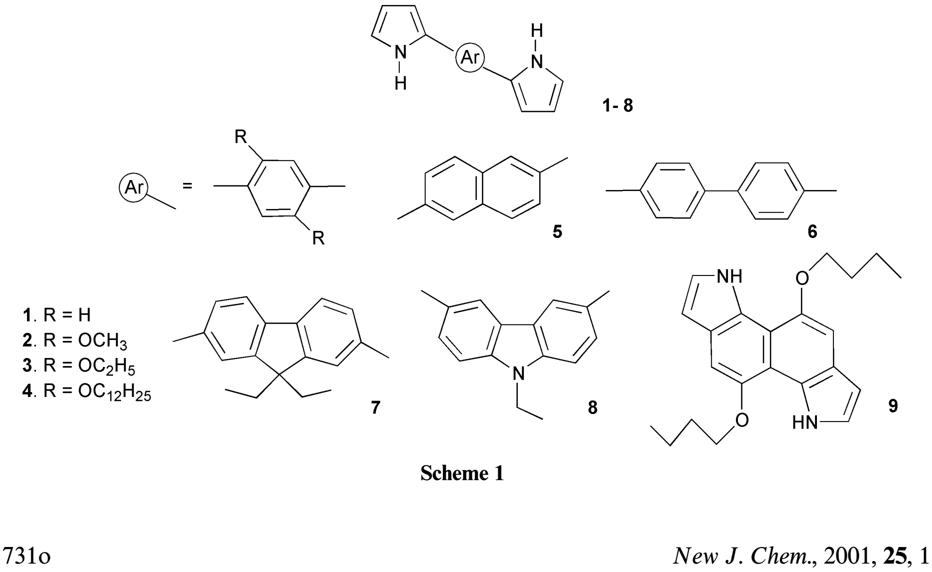
Preliminary molecular modeling studies were also performed to assess the usefulness of the synthesized moieties for polymerization. Structures, ionization energies, and electronic charge distribution are correlated with the available experimental data.

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 fluorene[6] (**10**) with Bu^{n}Li, 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 dinitriles[7] 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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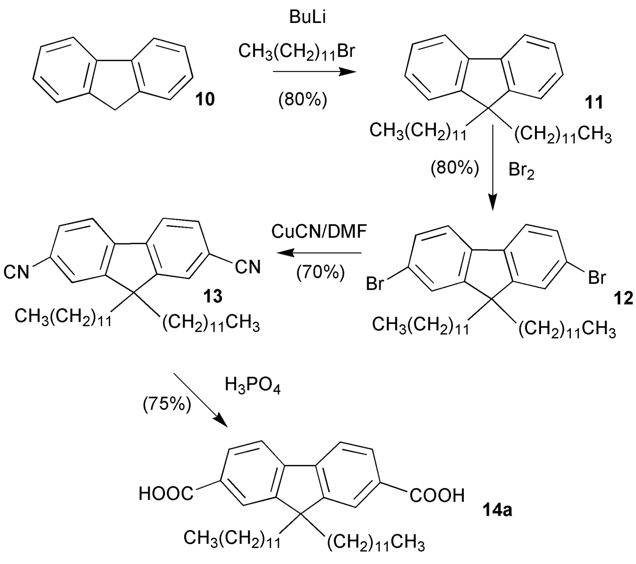
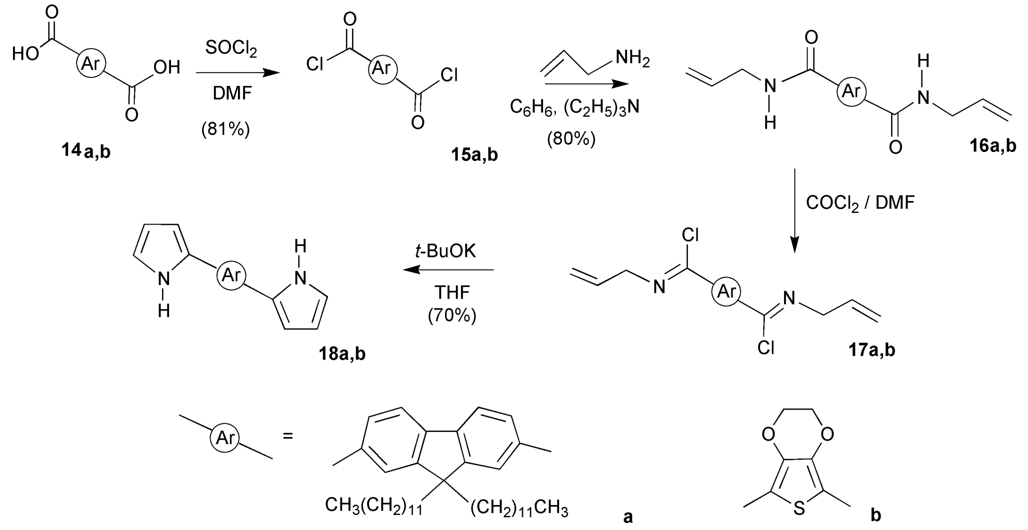


Scheme 2

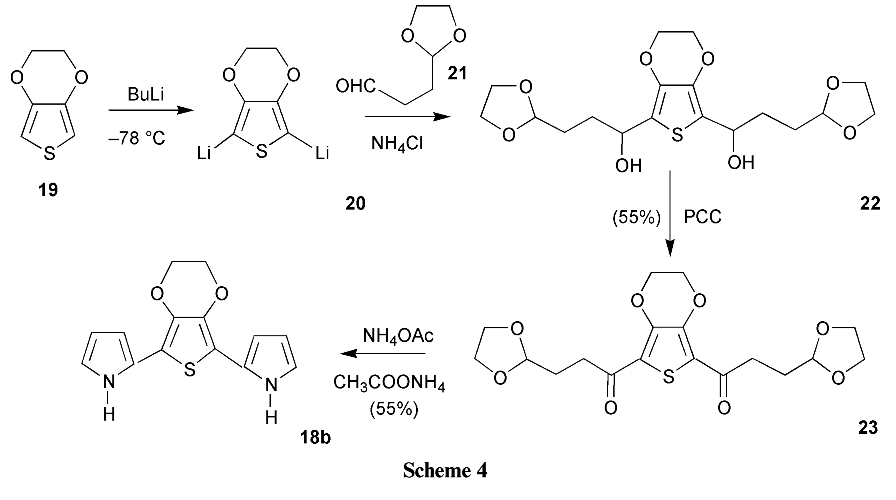
allylchloroimino) fluorene. Compound **17a** was cyclized without isolation by potassium *tert*-butoxide[4] in THF into 9,9-didodecyl-2,7-bis(pyrrol-2-yl)fluorene (**18a**), which was isolated after column chromatography in 70% yield.

In this paper we also report a synthetic study of 2,5-bis(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 bandgap[11] 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-2,5-dicarboxylic acid (**14b**).[13] With this route we obtained **18b** in a seven-step procedure in an overall yield of 28% based on 3,4-dihydroxythiophenedicarboxylic acid **14b**. The very useful methodology of Route 2 (Scheme 4) was modeled after work done by Lucchesini.[14] Commercially available 2,3-dihydrothieno[3,4-*b*][1,4]dioxane (**19**) was metallated with Bu^{n}Li 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 3



Scheme 4

large-scale preparation. Novel compounds were characterized by ^{1}H NMR and ^{13}C 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 μm wide and spaced, and 50 nm thick) photolithographically fixed on SiO_2 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, $K = k_a/k_d$. 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.

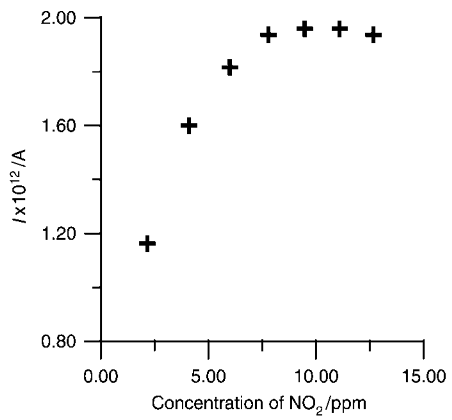
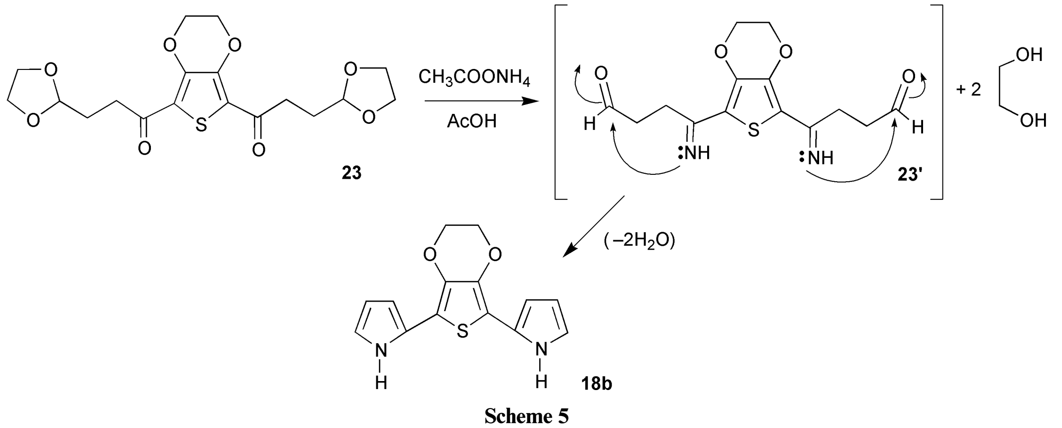
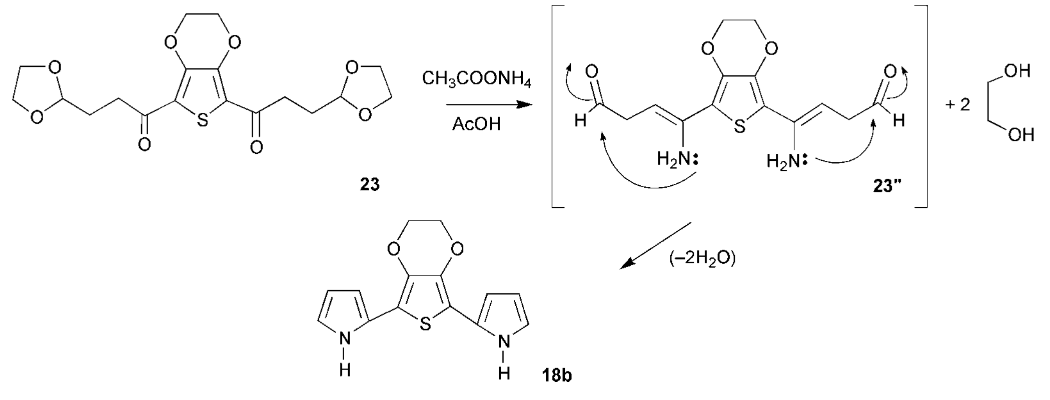


Fig. 1 Conductivity response of a 5-layer LB film of DDF–TCNQ to NO_2.

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-



Scheme 5



Scheme 6

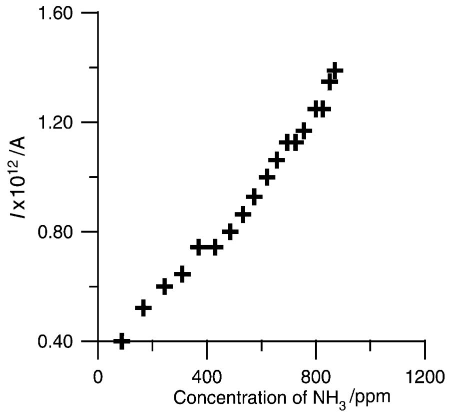


Fig. 2 Conductivity response of a 5-layer LB film of DDF–TCNQ to ammonia; first cycle of measurements.

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

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 ($E_{\mathrm{p,\,m}}$) of the studied monomers

		Calc. vertical ionization energy/eV		
Monomer	φ/°	HF	B3LYP	$E_{\mathrm{p,\,m}}$/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

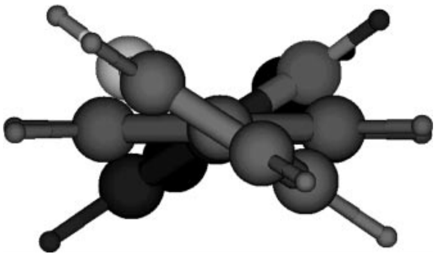


Fig. 3 The optimized structure of 1,4-bis(pyrrol-2-yl)benzene (**1**). The view is along the longest axis of the molecule.

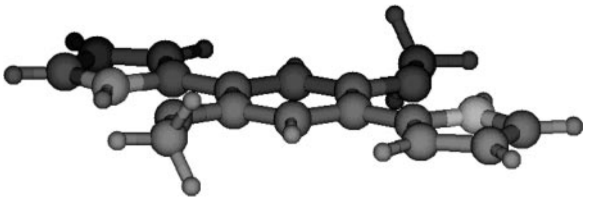


Fig. 4 The calculated geometry of 1,4-bis(pyrrol-2-yl)-2,5-dimethoxybenzene (**2**).

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.

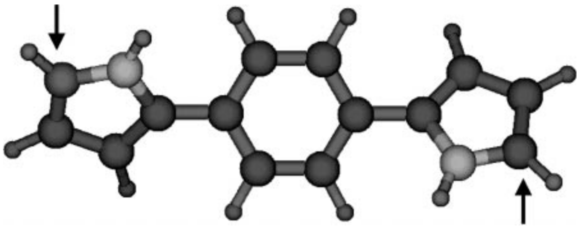


Fig. 5 Arrows indicate atoms with the largest change due to the ionization in 1,4-bis(pyrrol-2-yl)benzene (**1**).

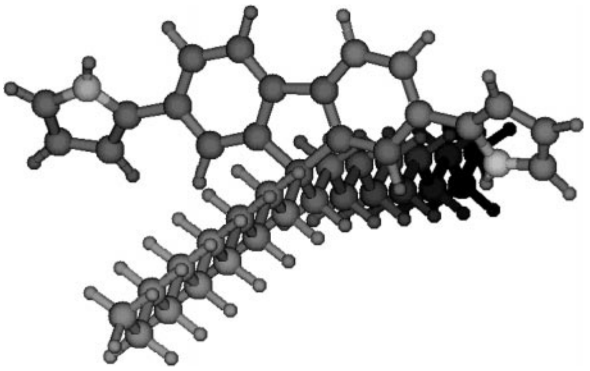


Fig. 6 The optimized structure of 9,9-didodecyl-2,7-bis(pyrrol-2-yl)-fluorene (**18a**).

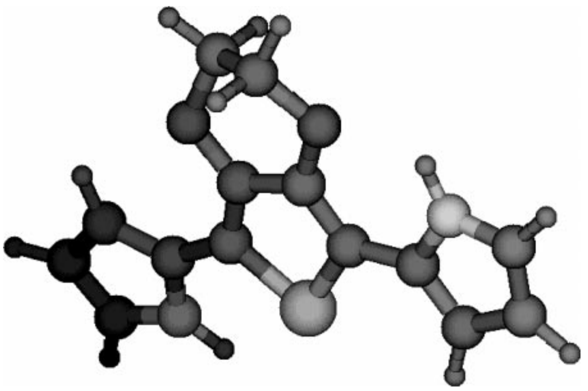


Fig. 7 The optimized structure of 2,5-bis(pyrrol-2-yl)-1,4-dioxane-[3,4-*b*]thiophene (**18b**).

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 (^{1}H) and 75 (^{13}C) MHz in $CDCl_3$ 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). Bu^{n}Li (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%. ^{1}H NMR δ ($CDCl_3$): 0.71–0.82 (m, 4H, CH_2), 0.97 (t, J = 6.99 Hz, 6H, CH_3), 1.92–2.06 (m, 4H, CH_2), 1.32–1.62 (m, 36H, CH_2), 7.37–7.48 (m, 6H arom. H), 7.78–7.80 (m, 2H, arom. H). ^{13}C NMR δ ($CDCl_3$): 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 $C_{37}H_{58}$: 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 $NaHSO_3$ (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 $MgSO_4$. The volatiles were removed under reduced pressure and the crude product was recrystallized from hexane. Yield 80%, mp 45 °C. ^{1}H NMR δ ($CDCl_3$): 0.70–0.80 (m, 4H, CH_2), 0.96 (t, J = 6.98 Hz, 6H, CH_3), 1.32–1.36 (m, 36 H, CH_2), 1.92–2.06 (m, 4H, CH_2), 7.4–7.54 (m, 6H, arom. H). ^{13}C NMR δ ($CDCl_3$): 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. ^{1}H NMR δ ($CDCl_3$): 0.73–0.81 (m, 4H, CH_2), 0.97 (t, J = 7.0 Hz, 6H, CH_3), 1.13–1.26 (m, 36H, CH_2), 1.92–2.0 (m, 4H, CH_2), 7.60 (d, J = 8.3 Hz, 4H, arom. H), 7.82 (s, 2H, arom. H). ^{13}C NMR δ ($CDCl_3$): 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 $C_{39}H_{56}N_2$: 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. ^{1}H NMR δ (DMSO): 0.8 (s, 4H, CH_2), 0.97 (t, J = 6.87 Hz, 6H, CH_3), 1.13–1.62 (m, 36 H, CH_2), 1.92–2.07 (m, 4H, CH_2), 2.52 (s, 2H, OH), 7.78–7.82 (m, 6H, arom. H). ^{13}C NMR δ ($CDCl_3$): 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 $C_{39}H_{58}O_4$; 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. ^{1}H NMR δ ($CDCl_3$): 0.72 (s, 4H, CH_2), 0.96 (t, J = 6.54 Hz, 6H, CH_3), 0.94–1.3 (m, 36 H, CH_2), 1.92–2.06 (m, 4H, CH_2), 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). ^{13}C NMR δ ($CDCl_3$): 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 $C_{39}H_{56}Cl_2O_2$: 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. ^{1}H NMR δ ($CDCl_3$): 0.70 (s, 4H, CH_2), 0.95 (t, J = 6.6 Hz, 6H, CH_3), 0.94–2.1 (m, 36 H, CH_2), 1.92–2.1 (m, 4H, CH_2), 4.13 (t, J = 7.2 Hz, 4H, $NHCH_2$), 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, $CHCH_2$), 7.31–7.45 (m, 4H, arom. H), 7.8 (br s, 2H, arom. H). ^{13}C NMR δ ($CDCl_3$): 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 $MgSO_4$, 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 ($CDCl_3$): 0.70 (s, 4H, CH_2), 0.96 (t, $J = 6.72$ Hz, 6H, CH_3), 1.13–1.36 (m, 36H, CH_2), 2.02–2.1 (m, 4H, CH_2), 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). ^{13}C NMR δ ($CDCl_3$): 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 $C_{45}H_{64}N_2$: 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 ($CDCl_3$): 4.49 (4H, s, CH_2). ^{13}C NMR δ ($CDCl_3$): 65.0, 119.5, 146.6, 156.8. Anal. calc. for $C_8H_4\ Cl_2\ O_4S$: 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 ($CDCl_3$): 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). ^{13}C NMR δ ($CDCl_3$): 41.8, 65.0, 116.5, 117.6, 134.1, 139.2, 160.3. Anal. calc. for $C_{14}H_{16}N_2O_4S$: 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 $MgSO_4$, evaporated to dryness and the residue was purified by column chromatography (dichloroethane–hexane 2 : 1). Yield 56%, mp. 182 °C. ^1H NMR δ ($CDCl_3$): 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). ^{13}C NMR δ ($CDCl_3$): 67.0, 104.5, 106.6, 109.1, 117.8, 122.2, 125.3, 130.2, 132. Anal. calc. for $C_{14}H_{12}N_2O_2S$: 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 ($MgSO_4$) 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 CO_2 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 ($CDCl_3$): 2.17 (m, 4H, CH_2), 3.15 (t, $J = 7.2$ Hz, 4H, CH_2), 3.87 (m, 8H, CH_2), 4.5 (s, 4H, CH_2), 5.03 (t, $J = 4.4$ Hz, 2H, –CH–). ^{13}C NMR δ ($CDCl_3$): 27.8, 32.9, 65.0, 103.5, 119.5, 146.6, 190.6. Anal. calc. for $C_{18}H_{22}O_8S$: 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 $MgSO_4$ 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 ($CDCl_3$): 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). ^{13}C NMR δ ($CDCl_3$): 67.0, 104.5, 106.6, 109.1, 117.8, 122.2, 125.3, 130.2. Anal. calc. for $C_{14}H_{12}N_2O_2S$: 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 functional[18] and the 6-31G* basis set.[19] The results reported here were obtained by utilizing the GAUSSIAN 98 code.[20]

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References

1 J. Grimshaw and S. D. Petera, *J. Electroanal. Chem.*, 1989, 335.

2 G. A. Sotzing, J. R. Reynolds, A R Katritzky, J. Sołoducho, S. Belyakov and R. Musgrave, *Macromolecules*, 1996, **29**, 1679.

3 G. A. Sotzing, J. L. Reddinger, A. R. Katritzky, J. Sołoducho, R. Musgrave, J. R. Reynolds and P. J. Steel, *Chem. Mater.*, 1997, **9**, 1578.

4 B. Tsuie, J. L. Reddinger, G. A. Sotzing, J. Sołoducho, A. R. Katritzky and J. R. Reynolds, *J. Mater. Chem.*, 1999, **9**, 2189.

5 J. Sołoducho, *Tetrahedron Lett.*, 1999, **40**, 2429.

6 R. G. Harvey, P. P. Fu and P. W. Rabideau, *J. Org. Chem.*, 1976, **41**, 2706.

7 M. Rehahn, A. D. Schluter and W. J. Feast, *Synthesis*, 1988, 386.

8 M. Dotrong and R. C. Evers, *J. Polym. Sci., Part A: Polym. Chem.*, 1990, **28**, 3241.

9 H. Ringsdorf and P. Tschirner, *Macromol. Chem. Phys.*, 1986, **188**, 1431.

10 J. R. Reynolds, *Adv. Mater.*, 2000, **12**, 481.

11 S. Akoudad and J. Roncali, *Chem. Commun.*, 1998, 2081.

12 S. Akoudad, P. Frere, N. Mercier and J. Roncali, *J. Org. Chem.*, 1999, **64**, 4267.

13 V. N. Gogte, L. G. Shah and B. D. Tilak, *Tetrahedron*, 1967, **23**, 2437.

14 F. Lucchesini, *Tetrahedron*, 1992, **48**, 995.

15 A. Chyla, J. Sołoducho and K. Kowalska, in preparation.

16 R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724.

17 W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986.

18 A. D. Becke, *J. Chem. Phys.*, 1996, **104**, 1040.

19 M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. De Frees and J. A. Pople, *J. Chem. Phys.*, 1982, **77**, 3654.

20 M. J. Frisch, G. W. Truck, H. B. Schleger, G. E. Scuseria, M. A. Robb, J. R. Cheesman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Milam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomeli, C. Adamo, S. Clifford, J. Ochterski, G. A. Peterson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaroni, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzales, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, GAUSSIAN 98, rev. A.7, Gaussian, Inc., Pittsburgh, PA, 1998.