

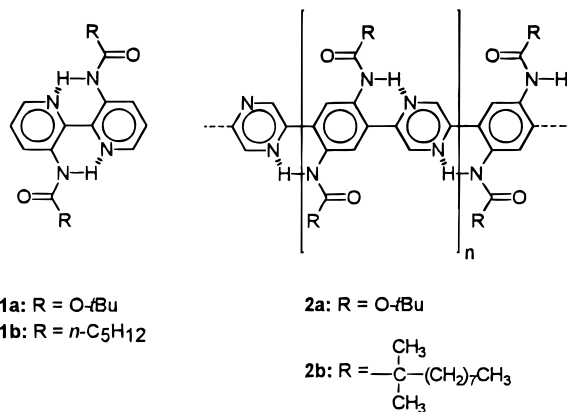
π -Conjugated Oligomers and Polymers with a Self-Assembled Ladder-like Structure

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Polyarylenes bear great promise as materials for applications in electronic devices.¹ Unsubstituted polyarylenes are insoluble and difficult to process, while substitution of the polymers with solubilizing side chains forces consecutive aromatic units away from coplanarity.² In order to solve this dilemma, substituted ladder polymers have been prepared, being both soluble and planar.^{3–6} Ladder polymers are defined as uninterrupted sequences of fused rings. In the soluble π -conjugated ladder structures described so far, covalent bonds are used to join the sequence of rings.⁷ Following the increasing interest in the use of secondary interactions in supramolecular chemistry, we like to present soluble π -conjugated oligo- and polyarylenes which self-assemble into ladders due to strong intramolecular hydrogen bonding between neighboring rings. Our concept of self-assembled π -conjugated ladder oligomers and polymers is based on the recent finding that strong intramolecular N \cdots H–N hydrogen bonding planarizes the bipyridyl derivative **1**.⁸ From the several options available to incorporate the principle of hydrogen bonding in a six-membered ring in self-assembled ladder-type structures, we selected polymer **2** and oligomers thereof, guided by the synthetic feasibility of this option.



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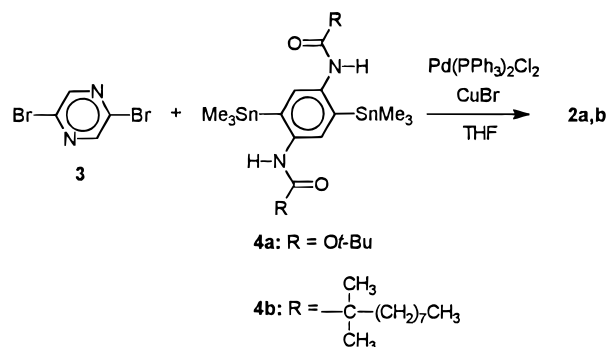
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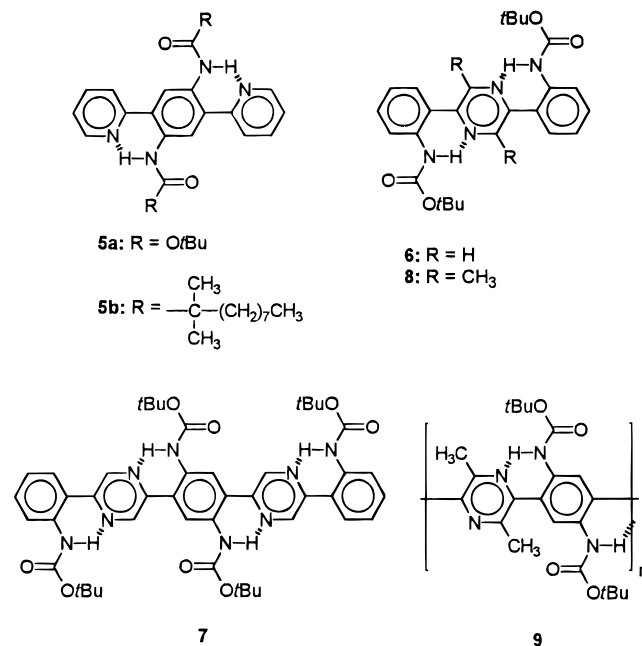
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Scheme 1



The synthetic scheme for the synthesis of oligomers and polymers is depicted in Scheme 1. Crucial steps in the synthesis of both **2a** and the more soluble **2b** are the Stille coupling of 2,5-dibromopyrazine **3** with distannyl compounds **4a** and **4b**, respectively (Scheme 1), and the preparation of the latter reactants. The synthesis of **4a,b** is based on the *ortho*-lithiation of a protected 1,4-phenylenediamine moiety as described by Tour *et al.*^{6h,9} The Stille coupling,¹⁰ as optimized on oligomers, is performed in THF in the presence of Pd(PPh₃)₂Cl₂ in combination with 5 mol % of CuBr.¹¹ The addition of CuBr is essential to guarantee high yields (over 95%) and high selectivities of the coupling.¹² Under the same conditions, monomers **3** and **4a,b** were cross-coupled with corresponding monofunctional building blocks to furnish oligomers **5a,b**, **6**, and **7** (Table 1) in reasonable to good yields.¹³



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(9) The 2,2-dimethyldecanoyl group in **4b** is used as a stable, solubilizing group which is compatible with *ortho*-metallation due to the absence of protons α to the carbonyl group.

Table 1. Spectroscopic Data of Model Compounds and Polymers

compd	¹ H-NMR		UV	IR		CV
	δ _{N-H^a} (ppm)	δ _{H-3/H-3'^a} (ppm)	λ ^a (nm)	ν _{N-H^a} (cm ⁻¹)	ν _{N-H^b} (cm ⁻¹)	E ^{0 c} (V)
2a	10.7	8.7	440	3281	3285	-1.37
2b	11.7	9.26	446	3291	3288	-1.32
5a	11.22	8.73	362	3247	3307	-1.94
5b	12.56	9.24	362	3239	3263	n.d. ^d
6	10.52	8.36	360	3290	3266	-1.73
7	10.59/ 10.55	8.85/ 8.37	399	3287	3246	-1.41/ 1.60
8	8.73	7.34	332	3438	3419	n.d.
9	8.6	7.8	367	3329/ 3427	3340	n.d.

^a In CDCl₃, ^b In KBr. ^c In THF; E⁰ vs standard calomel electrode. ^d Not determined.

From GPC analysis¹⁴ (PLgel 5 μm/500A, CHCl₃, calibrated with oligomers **5a**, **b**, **6**, and **7**) molecular weights of **2a** and **2b** were determined to be $M_n = 2 \times 10^3$ (approximately 9 aryl units) and $M_n = 5.1 \times 10^3$ (approximately 18 aryl units), respectively. Furthermore, it was found that only odd-numbered oligomers were formed during polymerization. This result is consistent with the finding that **3** is preferably coupled twice

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(12) A typical polymerization procedure is given: monomer **3** (0.080 g, 0.339 mmol) and monomer **4b** (0.277 g, 0.346 mmol) were dissolved in freshly distilled THF (5 mL), together with Cu₂Br₂ (0.0047 g, 0.0164 mmol) and potassium carbonate (0.048 g, 0.347 mmol). The solution was frozen using a liquid nitrogen bath and degassed at a pressure of 0.1 mbar. The solution was thawed again and flushed with dry argon. This cycle was repeated once before Pd(PPh₃)₂Cl₂ (0.0128 g, 0.0182 mmol) was added. The freeze-thaw cycles were repeated five times and the solution was heated under reflux for 24 h. Then **4b** (0.0104 g, 1.30 × 10⁻² mmol) was added and the mixture was heated under reflux for an additional 24 h. THF was evaporated, the residue dissolved in chloroform, and the organic phase washed successively with an aqueous 5% ethylenediamine solution (1×), water (3×), and brine (1×). After drying over magnesium sulfate and evaporation of the solvent, the crude product was purified by soxhlet extraction with methanol for 60 h, followed by chloroform extraction for 24 h. Evaporation of the chloroform fraction gave 0.138 g (62%) of an orange solid. ¹H-NMR (CDCl₃, 400 MHz): δ 11.7 (s, 2H); 9.30 (s, 2H); 9.26 (s, 2H); 1.70 (s, 4H); 1.35 (s, 12H); 1.20 (m, 24H); 0.82 (t, 6H) ppm. ¹³C-NMR (CDCl₃, 100 MHz): δ 177.6; 150.8; 141.5; 134.1; 124.6; 122.4; 43.6, 41.7, 31.8, 30.8, 30.2, 29.2, 25.6, 25.2, 22.6, 14.0; -8.6. IR: 3288.5 (NH); 1676.2 (CO) cm⁻¹. Fluorescence (CHCl₃): λ_{max} = 508 nm.

(13) Compound **6**: ¹H-NMR (CDCl₃, 400 MHz): δ 10.52 (s, 2H); 9.03 (s, 2H); 8.36 (d, *J* = 8.3 Hz, 2H); 7.75 (dd, *J* = 7.9 and 1.4 Hz, 2H); 7.48 (dt, *J* = 8.6 and 1.4 Hz, 2H); 7.18 (dt, *J* = 7.9 and 1.1 Hz, 2H); 1.54 (s, 18H); ¹³C-NMR (CDCl₃, 100 MHz): δ 153.1; 150.8; 141.4; 138.6; 130.9; 128.7; 122.6; 122.2; 120.9; 80.3; 28.3. Calcd elemental analysis: C, 67.50; H, 6.54; N, 12.12. Found: C, 67.95; H, 6.13; N, 12.02. IR: 3266.1 (NH); 1738.5 (CO) cm⁻¹. Compound **7**: ¹H-NMR (CDCl₃, 400 MHz): δ 10.59 (s, 2H); 10.55 (s, 2H); 9.22 (s, 2H); 9.03 (s, 2H); 8.85 (s, 2H); 8.37 (d, *J* = 8.2 Hz, 2H); 7.73 (dd, *J* = 7.9 and 1.4 Hz, 2H); 7.47 (dt, *J* = 8.5 and 1.4 Hz, 2H); 7.17 (dt, *J* = 8.0 and 1.1 Hz, 2H). ¹³C-NMR (CDCl₃, 100 MHz) δ 153.4; 153.2; 151.4; 150.0; 141.7; 140.9; 138.8; 133.5; 131.1; 128.8; 124.2; 122.6; 122.2; 121.1; 120.8; 80.4; 30.9; 28.4.

(14) GPC data of the polymers: **2a**: $M_n = 2 \times 10^3$; $M_w = 2.4 \times 10^3$; PDI = 1.3. **2b**: $M_n = 5.1 \times 10^3$; $M_w = 6.4 \times 10^3$; PDI = 1.27. **9**: $M_n = 2.8 \times 10^3$; $M_w = 3.3 \times 10^3$; PDI = 1.2.

in a Stille reaction. Finally, oligomer **8** and the corresponding polymer **9**, both with two methyl substituents at the pyrazine moiety, were synthesized to reveal the influence of increased steric hindrance. From GPC analysis of **9**, a molecular weight $M_n = 2.8 \times 10^3$ was determined.

Important physical properties of oligomers and polymers discussed are given in Table 1. ¹H-NMR spectroscopy in CDCl₃ showed resonances at low field for the carbamate N-H protons of **2a**, **5a**, **6**, and **7** at δ 10.5-11.3 ppm and for the amide N-H protons of **2b** and **5b** at δ 11.7-12.6 ppm. These data are indicative of strong hydrogen bonding and in correspondence with the donor-acceptor strength of the different units. The carbamate N-H protons at δ 8.7 and 8.6 ppm for the methyl-substituted pyrazines **8** and **9** point to a much weaker hydrogen bond due to severe steric hindrance. The strength of the hydrogen bonds in **2** is established from NMR experiments at higher temperatures (a Δδ/*T* of 6.5 × 10⁻³ K⁻¹ is measured for **6**) and in the presence of acetic acid. However, in the presence of TFA, **2b** is protonated and the hydrogen bonds are broken, accompanied by a shift of λ_{max} of the long-wavelength absorption band from 446 to 369 nm.¹⁵ The downfield anisotropic effect of the carbonyl group is proposed to be due to the coplanar orientation of the amide or carbamate functionality which points to H-3/3'. IR data recorded in chloroform and in the solid state are in agreement with the presence of intramolecular hydrogen bonds.

A gradual red shift of the long-wavelength absorption band in the UV-vis spectra upon increasing the number of repeating units is observed, while the extinction coefficients of oligomers and polymers are comparable. These transitions are explained by the alternating push-pull character of the π-conjugated system. Furthermore, the large difference in UV between **2a** and **9** is in agreement with the ¹H-NMR and IR data. We also examined the electrochemical properties of oligomers and polymers (Table 1). A reversible reduction potential is found for oligomers and polymers, presumably due to the electron-poor pyrazine rings in the systems under investigation. In contrast to this, we did not observe any reversible oxidations at approximately +1.7 V for **2a** or **2b** where they were expected on the basis of the band-gap. However, the reduction data clearly demonstrate the extended π-conjugation of the self-assembled ladder systems.

In conclusion, we have presented the use of intramolecular hydrogen bonds in polyarylenes to obtain self-assembled ladder structures. In sharp contrast to the general observation that side groups give rise to steric hindrance and deviation from planarity in polyarylenes, we have used hydrogen bonded acylated amines to turn a repulsive van der Waals interaction between *ortho* substituents into an attractive hydrogen bond interaction to extend π-delocalization. Due to the versatility of the new approach and the tunability of the structures, we are currently investigating the ultimate optical and electrical properties of this type of structure.

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(15) In oligomer **5b** this band moves from 362 nm to a position which is obscured by a strong absorption at 300 nm.