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Effective Synthesis of Ladder-type Oligo(*p*-aniline)s and Poly(*p*-aniline)s via Intramolecular S_NAr Reaction

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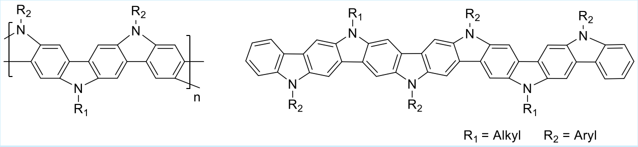

ABSTRACT: Symmetric ladder-type oligo(*p*-aniline)s and poly(*p*-aniline)s were successfully synthesized by an intramolecular ring closure in a highly efficient S_NAr reaction from oligo(*p*-phenylene)s and poly(*p*-phenylene)s with fluorine (F) and secondary amine (NH) groups. Unlike Cadogan ring closure, the newly designed cyclization reaction will not produce a mixture of symmetric and nonsymmetric structures. Moreover, the introduction of the F atom does not hinder Suzuki polymerization. The result indicates that preparing regular oligomers and polymers with a nitrogen bridge is possible.

Fully conjugated ladder-type macromolecules are of great interest as potential active materials in electronic devices.[1] The development of synthetic strategies has promoted the preparation of many unique structures and useful materials for their physical, optical, and chemical properties.[2] The fully conjugated ladder-type polymers are an important member of the conjugated polymer family. The unique multiple-stranded architecture of the conjugated ladder polymer endows material with a constrained chain conformation that results in good conjugation, carrier mobility, and luminescence intensity, so it has been widely investigated in organic light-emitting diodes and the organic field effect.[3] Despite remarkable advances in the past decade, fully conjugated ladder-type macromolecules still remain a major synthetic challenge.[4]

The first ladder-type poly(*p*-phenylene) (LPPP) reported by Scherf and Müllen in 1991 was synthesized through a popular two step approach: polymerization followed by ladderization.[5] The fused-ring backbones of LPPP and its derivatives were achieved by transition-metal-mediated polymerization, especially palladium-catalyzed Suzuki polycondensation. There have been various intramolecular ring-closure reactions for the ladder structure of the precursor polymers. In the preparation of LPPPs, Lewis-acid-mediated Friedel−Crafts ring annulations were used. Swager and coworkers reported electrophile-induced cyclization.[2c] The acetylenic functional group on the conjugated polymer could be easily cyclized in the presence of trifluoroacetic acid. Müllen and coworkers used oxidative dehydrogenation catalyzed by $FeCl_3$ to prepare 2D graphene nanoribbons.[2d] Fang et al. developed a strategy for a fully conjugated ladder-type polymer with an extremely low level of unreacted defects via the thermodynamically controlled ring-closing olefin metathesis (RCM) reaction.[6] Meanwhile, various kinds of fully conjugated ladder-type materials with heteroatom bridges such as N, S, Si, B, and O have also been reported,[7] but fully conjugated ladder polymers with heteroatom bridges are seldom.[2b,8]

Among the fully conjugated ladder-type materials, carbazole is one of the archetypical molecules and is adopted as the most promising building block in optoelectronic applications because of its good stability and high charge-carrier mobility. Scherf and Müllen et al. prepared carbazole-based ladder-type polymers with a methine bridge, ethene bridge, and ethane bridge, which were all blue-green emitters with emission at ∼470 nm.[9] Bo and coworkers synthesized a carbazole-based ladder-type polymer with an azomethine bridge by a Bischler−Napieralski reaction.[10] Fang et al. prepared carbazole-based fully ladder-type polymers with an ethene bridge via a RCM reaction.[6b] Some other carbazole-based ladder-type polymers with heteroatom bridges were also reported.[11] However, LPPPs with full nitrogen bridges, usually called ladder-type poly(*p*-aniline)s, are attractive,[12] and the desire for these polymers is still present. Inspired by the previous research and with our continuous interest in exploring the novel methods of fully ladder-type polymers, we developed a strategy for preparing LPPPs and oligo(*p*-phenylene)s with a full nitrogen bridge that is promising for application in optoelectronic devices.

In the preparation of ladder-type oligo(*p*-aniline)s and poly(*p*-aniline)s, the intramolecular C−N bond-forming reaction is the key step. The classical Ullmann reactions are popular in the C−N bond-forming reaction.[13] The palladium-catalyzed version of C−N bond formation discovered by Buchwald and Hartwig was a major breakthrough in this field.[14] Transition-metal-catalyzed reactions for C−N bond

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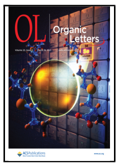

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formation usually proceed in the presence of halogen I, Br, or Cl. The existence of a halogen may bring mixed cross-coupling in the preparation of the ladder polymer precursor. Transition-metal-catalyzed intramolecular oxidation and Cadogan ring-closure reactions provide an efficient approach for C−N bond formation,[15] but the product of the isomers is an impediment to the regular ladder structure. Halogen F is usually passive in the transition-metal-catalyzed coupling reaction but is easily substituted through an intramolecular S_NAr reaction.[16] We combine the advantages of halogen F to design a synthetic route for ladder-type oligo(*p*-aniline)s **1**, **2**, and **3** and poly(*p*-aniline)s **4** shown in Figure 1.

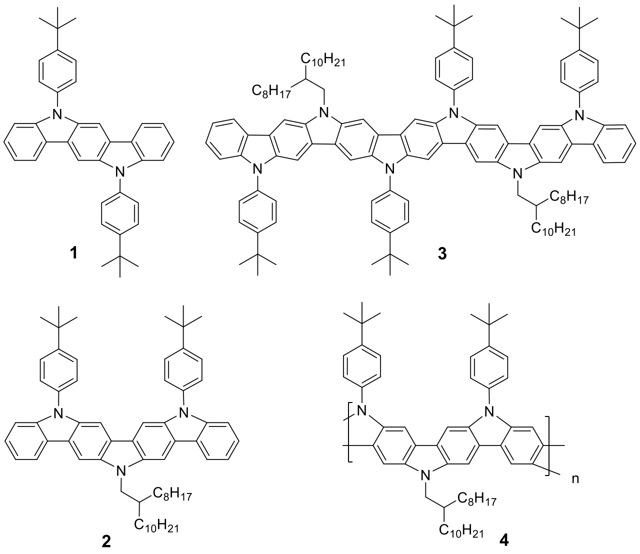
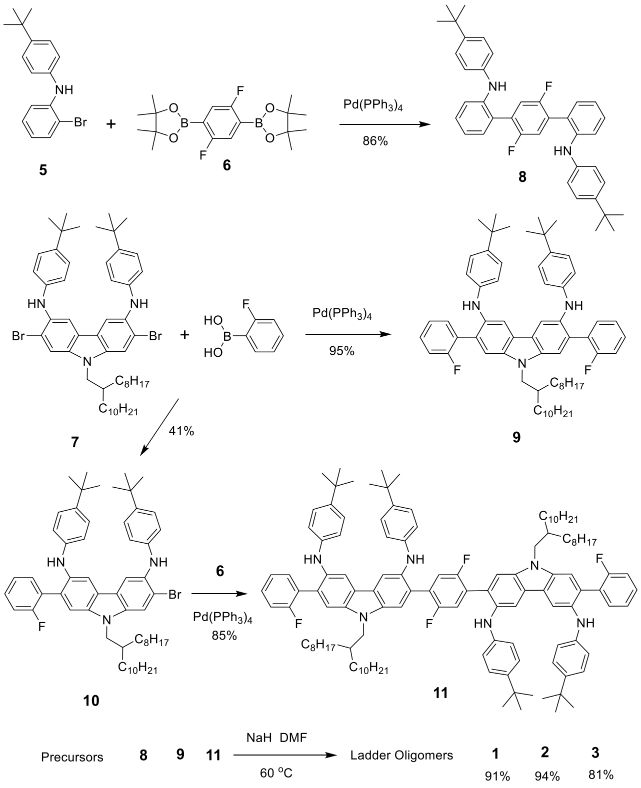


Figure 1. Structures of ladder-type oligo(*p*-aniline)s **1**, **2**, and **3** and poly(*p*-aniline)s **4**.

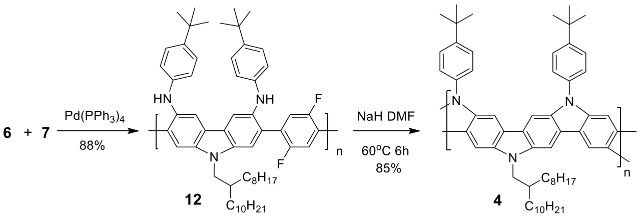
As shown in the Scheme 1, we started our synthesis by preparing compounds **6** and **7**. **6** was obtained via the reaction of 1,4-dibromo-2,5-difluorobenzene with an excess of bis(pinacolato)diboron in the presence of the $Pd(dppf)Cl_2$ catalyst in 31% yield. The key intermediate **7** was prepared by coupling 4-*tert*-butylbenzeneboronic acid and 3,6-diamino-2,7-dibomo-9-(2-octyldodecyl)-9*H*-carbazole catalyzed by copper acetate $Cu(CH_3COO)_2$ in 80% yield. Similar to **7**, compound **5** was synthesized from 2-bromoaniline and 4-*tert*-butylbenzeneboronic acid in 83% yield. A typical Suzuki−Miyaura coupling of compounds **5** and **6** afforded precursor **8** of ladder-type oligo(*p*-aniline)s in 86% yield, which could be smoothly converted to the desired ladder-type oligomer **1** in 91% yield in a mixture of NaH and dimethylformamide (DMF) at 60 °C. The coupling of 2-fluorobenzeneboronic acid and monomer **7** gave precursor **9** in 95% yield, which could be smoothly converted to ladder oligo(*p*-aniline)s **2** in 94% yield. The success of compounds **1** and **2** demonstrated that the intramolecular S_NAr reaction could easily proceed in the presence of a base. The good yields and unique structures of compounds **1** and **2** also indicated the possibility for ladder poly(*p*-aniline)s. The enlarged conjugated system **3** with six nitrogen bridges was obtained in 81% yield from the precursor **11**, which was achieved by coupling compounds **6** and **10** in 85% yield. Compound **10** could be synthesized by coupling 2-fluorobenzeneboronic acid and an excess of **7** in 41% yield. All intermediates and final products were purified and characterized with ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry (MS), or matrix-assisted laser desorption ionization−time-of-flight (MALDI-TOF) MS.

Scheme 1. Synthetic Routes to Oligo(*p*-aniline)s 1, 2, and 3



The desire for a fully ladder conjugated polymer with nitrogen bridges kept the synthetic strategy going on, and the polymerization of monomers **6** and **7** was carried out in a biphasic mixture of aqueous $NaHCO_3$ and tetrahydrofuran (THF) with $Pd(PPh_3)_4$ as the catalyst (Scheme 2). After the capping of bromo end groups with 2-fluorobenzeneboronic acid, polymer **12** was obtained in 88% yield. The infrared (IR) spectrum of polymer **12** showed an obvious absorption peak at 3411 cm^{-1} due to its secondary amine NH stretching vibrations. The characteristic signal of the secondary amine NH is shown at 5.41 ppm in the ^1H NMR spectrum (Figure 2). After treatment with NaH in DMF, the ladder-type poly(*p*-aniline)s **4** were achieved in 85% yield. The complete disappearance of the characteristic signals of the secondary amine NH in the ^1H NMR spectrum (ppm 5.41) and the IR spectrum (3411 cm^{-1}) confirmed that the intramolecular ring-closure S_NAr reaction was efficient. Further evidence of the formation of the ladder structure was the shift of the resonance

Scheme 2. Synthetic Route to Ladder-type Poly(*p*-aniline)s 4



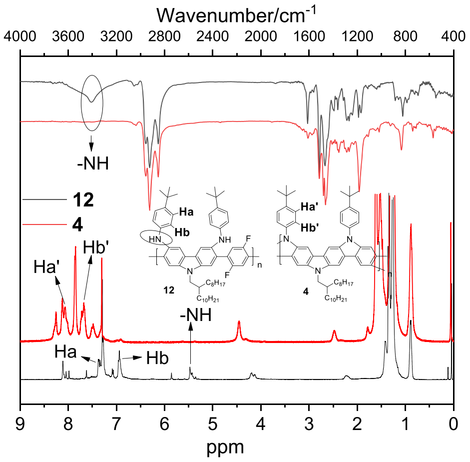


Figure 2. IR and NMR spectra of the precursor **12** and ladder-type poly(*p*-aniline)s **4**.

peaks associated with the aromatic protons on the 4-*tert*-butylbenzene groups (Hb) from 6.90 to 7.51 ppm and (Ha) from 7.37 to 8.07 ppm. A series of evidence showed that ladder-type poly(*p*-aniline)s were successfully prepared, and the polymer was easily soluble in common organic solvents such as dichloromethane and THF.

The molecular weights of polymers **12** and **4** were measured by gel permeation chromatography (GPC) against polystyrene standards with THF as an eluent. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of polymer **12** were 10.0 and 17.6 kg·mol^{-1}, respectively. After ring closure, the M_n and M_w of **4** were 10.7 and 18.4 kg·mol^{-1}, respectively. The molecular weights of the precursor polymer and the ladder polymer were nearly same. Thermal stabilities of ladder-type oligo(*p*-aniline)s **1**, **2**, and **3** and poly(*p*-aniline)s **4** were measured by thermogravimetric analysis (TGA) thermograms. **1** and **2** exhibited good thermal stability up to 250 °C. Weight loss (5%) started at nearly the same temperature, 405 °C, for **1** and **2** and at a lower temperature, 315 °C, for **3** and **4**. When the temperature increased to 800 °C, the weight loss of **1** was nearly 100%, and **3** and **4** showed nearly the same 50% weight loss. The larger conjugated structure may cause more residues of **3** and **4**. Differential scanning calorimetry (DSC) studies indicated that oligomer **2** had a melting point at 157 °C, and no melting point or phase transition was observed for oligomer **1** or **3** or polymer **4**.

The optical properties of all oligo(*p*-aniline)s **1**, **2**, and **3** and poly(*p*-aniline)s **4** were acquired in diluted dichloromethane solutions. The normalized solution ultraviolet (UV) and photoluminescence (PL) spectra are shown in Figure 3. The UV and PL spectra of the precursors **8**, **9**, **11**, and **12** (see the Supporting Information) and ladder-type compounds **1**, **2**, **3**, and **4** present significant differences that could be attributed to the changes in the conformation. With the increase in the main chain length, all of the UV absorption and PL emission peaks red-shifted. The PL quantum yields of compounds **1**−**4** were 0.93, 0.53, 0.38, and 0.45, respectively. In contrast with LPPPs, all of the ladder-type compounds did not exhibit well-resolved absorption or emission spectra, and the results are similar to some previous literature. The nontypical UV and PL spectra of ladder-type compounds could possibly be attributed to the weakness of HOMO−LUMO transitions.[6a] The differences in the UV and PL spectra of precursor polymer **12** and ladder-type polymer **4** also indicate that the ladder structure was formed in polymer **4**.

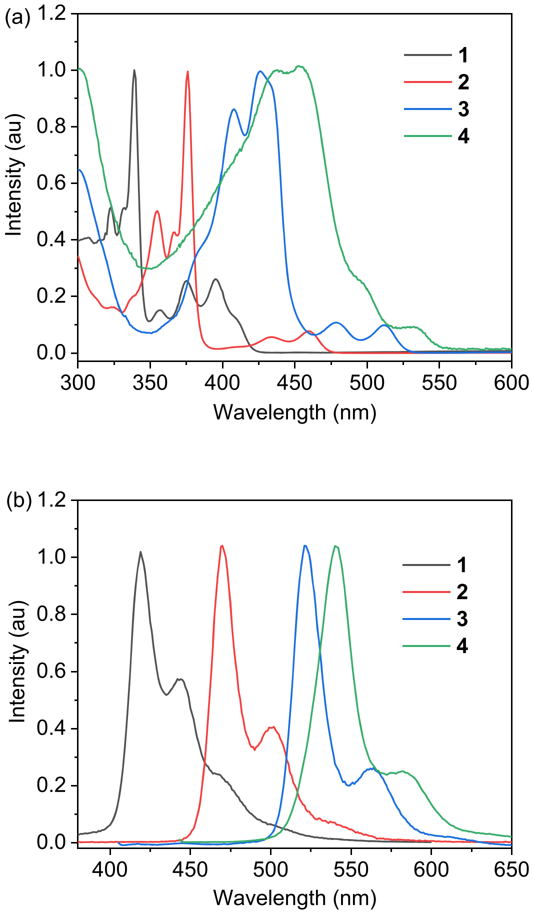


Figure 3. (a) UV and (b) PL spectra of ladder-type oligo(*p*-aniline)s **1**, **2**, and **3** and poly(*p*-aniline)s **4** in CH_2Cl_2.

The electrochemical behaviors of oligomers **1**, **2**, and **3** and polymer **4** in CH_2Cl_2 solution were investigated by cyclic voltammetry. As shown in Figure 4, no obvious cathodic wave was observed for polymer and oligomers. All of the ladder-type compounds showed reversible processes in the first redox cycle, and with increasing chain length, the oxidation peaks moved to more negative values. The band gaps were estimated

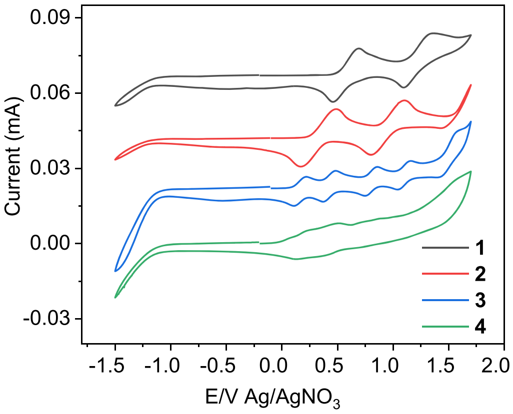


Figure 4. Cyclic voltammograms of ladder-type oligo(*p*-aniline)s **1**, **2**, and **3** and poly(*p*-aniline)s **4**.

from the onsets of the absorption spectra. The HOMO, LUMO, and band gap values are listed Table 1.

Table 1. HOMO and LUMO Energies and Band-Gap Data of Ladder-type Oligo(*p*-aniline)s 1, 2, and 3 and Poly(*p*-aniline)s 4

compounds	**1** (eV)	**2** (eV)	**3** (eV)	**4** (eV)
HOMO	−5.19	−4.97	−4.81	−4.76
LUMO	−2.24	−2.33	−2.44	−2.49
band gap	2.95	2.64	2.37	2.27

In conclusion, we have described a new approach for the synthesis of regular ladder-type oligo(*p*-aniline)s and poly(*p*-aniline)s via the intramolecular S_NAr reaction as the ring-closure reaction. In the synthesis strategy, the precursors containing F and NH groups were synthesized, and the aromatic F atom was easily substituted by nucleophiles, so the transition-metal-catalyzed ring-closure reaction was replaced by a S_NAr reaction for the formation of the C−N bond. The small steric hindrance also made Suzuki polymerization proceed smoothly. The yields of the intramolecular S_NAr reaction and the Suzuki polymerization were satisfying. The characterizations demonstrated that we had prepared ladder-type oligo(*p*-aniline)s and poly(*p*-aniline)s.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c00363.

> Experimental details, ^{1}H, ^{13}C, ^{19}F NMR, ESI-TOF, MS, and HRMS spectra, UV and PL spectra of all compounds, GPC elution curves, TGA and DSC traces, and DFT calculations (PDF)

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Notes

The authors declare no competing financial interest.

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