

Polaron Delocalization in Ladder Macromolecular Systems

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Abstract: Organic macromolecules with conjugated building blocks have been the focus of extensive research that is motivated, in part, by the potential to create optical and electronic devices. We have shown that palladium-catalyzed amination can assemble triarylamine ladder materials with extended structures. Two ladder macromolecules have been prepared in high yields by a series of twelve or sixteen C–N coupling reactions. Studies of the electronic and optical properties of neutral and oxidized forms of the ladder structures were conducted. The optical and electronic properties of the ladder systems are compared to those of the linear tetra-phenyl-*p*-phenylenediamine as well as the tetra-*p*-anisyl-*p*-tetraazacyclophane. The electrochemistry of the ladder systems consists of a multiwave voltammogram with a relatively low first oxidation potential. Electron paramagnetic resonance spectroscopy of the ladder systems suggests the presence of a large density of delocalized polarons. Linear absorption measurements of the chemically oxidized ladders revealed both polaron and intervalence absorption bands. Steady-state and time-resolved fluorescence measurements were also carried out to characterize the dynamics in these novel systems.

Introduction

Organic macromolecules containing triarylamine building blocks have been extensively investigated due to their interesting electronic^{1–8} and magnetic^{9–12} properties. A common hurdle confronting the synthesis of macromolecular and polycyclic arylamines has been the low yields that result from multiple aminations of aryl halides, historically conducted by copper-mediated chemistry. Improved methods to prepare arylamines would, therefore, allow one to prepare new architectures with increasing complexity.

Polymeric arylamines are promising candidates for the generation of polaronic ferromagnets.^{9–12} Polaronic states of macromolecules result from charge separation after excitation and are stabilized by deformation of the molecular conformation.⁵⁴ There is a significant interaction between the polarons and phonons. While polaronic ferromagnets have attracted attention over the last two decades,^{10c,13,14} the majority of such materials are spinless bipolarons (quinonoid-type dication), or π -dimers with low spin concentrations in doped conjugated polymers. This lack of spin has limited the applications of these structures as magnetic materials.¹⁵ A notable exception is the emeraldine salt of polyaniline. In this material, polarons are favored over bipolarons, and the presence of polarons in polyaniline leads to a significant spin concentration.^{16,17} Because *n*-doped polymeric arylamines are similar to the aryl-substituted leucomeraldine form of polyaniline, interesting magnetic properties have also been observed from *n*-doping of polymeric arylamines.¹⁰

Cyclophanes have been the subject of recent interest in materials science because of their defined three-dimensional structure.^{11,18,19} To exploit the favorable electronic and magnetic

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properties of arylamine materials in combination with a defined architecture, we and others have studied cyclophane structures composed of triarylamine units. Cyclophanes that contain alternating *p*-phenylene and *m*-phenylene or related aromatic units have been prepared as means to place stable radicals in a configuration that could impart ferromagnetic interactions between spins.^{20–22} Extension of the cyclophane structure to oligomeric ladder molecules built of cyclophane units would place a series of alternating *m*- and *p*-phenylenediamines in an equally defined geometry in larger structures.²³

Polycyclic arylamines, such as ladders built from cyclophane units, could possess energy traps and electron traps at the junctions between individual macrocycles.¹¹ These electron traps could increase the density of polarons and enhance spin–spin interaction between polaronic segments in certain arylamine systems.¹¹ The large number of redox sites on macromolecular arylamines with stable polarons may also be used in the development of charge-capture and storage applications.^{1–3} Thus, the preparation of such ladder structures has been discussed as a target for materials synthesis.^{11a,b}

Although polymeric and oligomeric arylamines might possess useful electronic and magnetic properties, the fundamental optical and electronic properties of these materials are not well understood. Further investigations of the polaronic behavior of arylamines should improve the electronic and magnetic performances of new materials and should elucidate the fundamental physical chemistry of these materials. We report in this manuscript the synthesis of unusual triarylamine ladder structures by a series of palladium-catalyzed C–N coupling reactions and the use of these materials as a platform to study the fundamental electronic, magnetic, and photophysical properties of triarylamine materials of defined architectures.

Experimental Section

All palladium-catalyzed amination reactions were assembled in sealed reaction vessels in a drybox and were run either at room temperature or heated to 110 °C in an oil bath. ¹H NMR spectra were acquired at 400 or 500 MHz, and proton-decoupled ¹³C NMR spectra were obtained at 100 or 125 MHz. Mass spectrometry analyses were performed by the Mass Spectrometry Facility at the University of Illinois at Urbana-Champaign. Elemental analytical data were obtained from either Robertson Microlit Laboratories, Inc or Atlantic Microlab Inc. Toluene solvent was distilled from sodium/benzophenone ketyl. Dichloromethane was distilled from calcium hydride under a nitrogen atmosphere. Palladium bis(dibenzylideneacetone) (Pd(dba)₂) was prepared according to literature procedures.²⁴ Other chemicals were used as received from commercial suppliers.

Preparation of Intermediates and the Ladder Compounds. The synthesis routes are shown in Schemes 1–3. The square molecule, tetraazacyclophane (**1**) has been reported previously.^{11a} The protocols for these preparations are described below.

***N,N,N',N'*-Tetrakis(3-chlorophenyl)-1,4-benzenediamine (4).** In a drybox, 1,4-phenylenediamine (541 mg, 5.00 mmol, 1.00 equiv) was combined with 1,3-bromochlorobenzene (4.02 g, 21.0 mmol, 4.20 equiv), sodium *tert*-butoxide (2.40 g, 25.0 mmol, 5.00 equiv), Pd(dba)₂,

(144 mg, 0.251 mmol, 0.050 equiv), and tri-*tert* butylphosphine (40 mg, 0.20 mmol, 0.04 equiv) in 30 mL of toluene to give a purple slurry. The mixture was removed from the box and stirred at room temperature. After 17 h, the thick brown mixture was poured into a saturated aqueous solution of ammonium chloride and extracted two times with toluene. The combined organics were washed with brine, dried over magnesium sulfate, and concentrated under vacuum to give an oil. The crude material was crystallized from toluene–ethanol to give 2.45 g (89%) of **4** as a tan solid. ¹H NMR (500 MHz, C₆D₆) δ 6.65–6.69 (m, 12 H), 6.78–6.81 (m, 4 H), 7.09–7.10 (m, 4 H). ¹³C NMR (125 MHz, C₆D₆) δ 122.16, 123.49, 124.10, 125.95, 130.68, 135.44, 142.75, 148.74. Anal. Calcd for C₃₀H₂₀N₂Cl₄: C, 65.48; H, 3.66; N, 5.09. Found: C, 65.77; H, 3.64; N, 4.86.

***N,N,N',N'*-Tetrakis(3-(4-hexyloxyanilino))-1,4-benzenediamine (5).** In a drybox, **4** (275 mg, 0.500 mmol, 1.00 equiv) was combined with 4-hexyloxyaniline (502 mg, 2.60 mmol), sodium *tert*-butoxide (260 mg, 2.71 mmol), Pd(dba)₂ (14 mg, 0.025 mmol, 0.050 equiv), and tri-*tert* butylphosphine (4 mg, 0.02 mmol, 0.04 equiv) in 6 mL of toluene. The reaction was heated at 110 °C. After 40 h, the crude mixture was adsorbed onto a silica gel plug (5 g) and vacuum-filtered using toluene/hexanes (4/1) to give 538 mg (91%) of **5** as tan solid. ¹H NMR (500 MHz, C₆D₆) δ 0.86 (t, *J* = 7.0 Hz, 12 H), 1.19–1.38 (m, 16 H), 1.59–1.66 (m, 8 H), 0.3.68 (t, *J* = 6.5 Hz, 8 H), 4.82 (s, 4 H), 6.62 (dd, *J* = 8.0, 1.5 Hz, 4 H), 6.72–6.84 (m, 16 H), 6.91 (d, *J* = 6.8 Hz, 8 H), 7.04 (t, *J* = 8.0 Hz, 4 H), 7.17 (s, 4 H). ¹³C NMR (125 MHz, C₆D₆) δ 14.60, 23.34, 26.49, 30.08, 32.30, 68.64, 109.99, 112.52, 115.87, 116.01, 122.70, 126.59, 136.26, 143.93, 146.90, 150.06, 155.63. MALDI-TOF *m/z* 1176.47, requires 1177.60. Anal. Calcd for C₇₈H₉₂N₆O₄: C, 79.55; H, 7.87; N, 7.14. Found: C, 79.68; H, 7.92; N 7.15.

4-Hexyloxy-bis-tetraazacyclophane (2). In a drybox, **5** (150 mg, 0.13 mmol) was combined with 1,4-dibromobenzene (63 mg, 0.27 mmol), sodium *tert*-butoxide (62 mg, 0.65 mmol), Pd(dba)₂ (3.8 mg, 0.0065 mmol), and tri-*tert* butylphosphine (1.1 mg, 0.0052 mmol) in 15 mL of toluene. The sealed flask was removed from the drybox, and the reaction was stirred at room temperature. After 42 h, the crude mixture was concentrated, redissolved in CH₂Cl₂ (1 mL), applied onto a silica gel plug (5 g), and filtered using EtOAc/hexanes (1/20) to give 148 mg (88%) of **2** (>95% ¹H NMR pure). Crystallization from EtOAc/hexanes gave tan solid. ¹H NMR (500 MHz, C₆D₆) δ 0.89 (t, *J* = 7.2 Hz, 12 H), 1.13–1.40 (m, 16 H), 1.58–1.70 (m, 8 H), 3.65 (t, *J* = 6.3 Hz, 8 H), 6.68–6.80 (m, 24 H), 6.82 (s, 4 H), 7.02 (t, *J* = 8.1 Hz, 4 H), 7.22 (d, *J* = 8.5 Hz, 8 H), 7.31 (dd, *J* = 7.8, 1.6 Hz, 4 H). ¹³C NMR (100 MHz, C₆D₆) δ 14.61, 23.34, 26.46, 29.99, 32.24, 68.44, 114.22, 115.73, 116.02, 117.44, 125.80, 127.64, 129.42, 130.12, 140.73, 142.68, 144.36, 148.27, 150.75, 155.56. MALDI-TOF *m/z* 1325.48, requires 1325.76. Anal. Calcd for C₉₀H₉₆N₆O₄: C, 81.54; H, 7.30; N, 6.34. Found: C, 81.15; H, 7.36; N, 6.25.

***N,N'*-Bis(3-chlorophenyl)-1,4-benzenediamine (6).** In a drybox, 3-chloroaniline (3.83 g, 30.0 mmol, 3.00 equiv) was combined with 1,4-dibromobenzene (2.36 g, 10.0 mmol, 1.00 equiv), sodium *tert*-butoxide (2.88 g, 30.0 mmol, 3.00 equiv), Pd(dba)₂ (288 mg, 0.502 mmol, 0.050 equiv) and tri-*tert* butyl phosphine (81 mg, 0.40 mmol, 0.040 equiv) in 100 mL of toluene. The sealed flask was removed from the drybox, and the reaction was stirred at room temperature. After 45 h, the crude mixture was concentrated, applied onto a silica gel plug (5 g) and vacuum-filtered using EtOAc/hexanes (1/10) to give 1.96 g (60%) of **6** as a yellow solid. ¹H NMR (400 MHz, C₆D₆) δ 4.80 (s, 2 H), 6.48–6.55 (m, 2 H), 6.70 (s, 4 H), 6.75–6.82 (m, 6 H). ¹³C NMR (100 MHz, C₆D₆) δ 114.51, 116.53, 120.27, 122.08, 130.91, 135.79, 137.27, 146.53. Anal. Calcd for C₁₈H₁₄Cl₂N₂: C, 65.67; H, 4.29; N, 8.51. Found: C, 66.05; H, 4.35; N 8.40.

3-Chlorophenyl-tetraazacyclophane (7). In a drybox, **6** (400 mg, 1.22 mmol, 1.00 equiv) was combined with 1,3-dibromobenzene (287 mg, 1.22 mmol, 1.00 equiv), sodium *tert*-butoxide (352 g, 3.66 mmol, 3.00 equiv), Pd(dba)₂ (35 mg, 0.061 mmol, 0.051 equiv), and tri-*tert*

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butylphosphine (10 mg, 0.40 mmol, 0.040 equiv) in 85 mL of toluene. The reaction was stirred at room temperature. After 50 h, the crude mixture was concentrated, applied onto a silica gel plug (5 g), and vacuum-filtered using toluene/hexanes (1/5) to give 215 mg (44%) of **7** as a white solid. ^1H NMR (500 MHz, C_6D_6) δ 6.30(d, J = 3.0 Hz, 2 H), 6.60 (s, 4 H), 6.60–6.65 (m, 8 H), 6.70–6.80 (m, 6 H), 6.83 (d, J = 7.8 Hz, 4 H), 6.91 (d, J = 8.1 Hz, 4 H), 7.35 (d, J = 2.0 Hz, 4 H). ^{13}C NMR (125 MHz, C_6D_6) δ 117.20, 118.60, 122.81, 123.49, 124.61, 130.63, 130.99, 135.70, 143.36, 148.94, 149.14. MALDI-TOF m/z 805.55, requires (M^+ –1) 805.61. Anal. Calcd for $\text{C}_{48}\text{H}_{32}\text{Cl}_4\text{N}_4$: C, 71.47; H, 4.00; N, 6.95. Found: C, 70.82; H, 4.26; N, 6.65.

3-(4-Hexyloxyanilino)-tetraazacyclophane (8). In a drybox, **7** (240 mg, 0.300 mmol, 1.00 equiv) was combined with 4-hexyloxyaniline (259 mg, 1.34 mmol, 4.50 equiv), sodium *tert*-butoxide (159 mg, 1.65 mmol, 5.50 equiv), $\text{Pd}(\text{dba})_2$ (8.6 mg, 0.015 mmol, 0.050 equiv), and tri-*tert* butylphosphine (2.5 mg, 0.012 mmol, 0.040 equiv) in 15 mL of toluene. The sealed flask was heated at 110 °C. After 44 h, the crude product was vacuum-filtered through a silica pad (5 g) using toluene to give 361 mg (85%) of **8** as a yellow solid. ^1H NMR (500 MHz, C_6D_6) δ 0.88 (t, J = 7.0 Hz, 12 H), 1.11–1.29 (m, 24 H), 1.62 (t, J = 8.0 Hz, 8 H), 3.68 (t, J = 6.5 Hz, 8 H) (m, 6 H), 4.81 (s, 4 H), 6.60–7.10 (m, 48 H). ^{13}C NMR (125 MHz, C_6D_6) δ 14.63, 23.36, 26.50, 29.24, 30.06, 32.29, 68.59, 110.22, 113.11, 115.82, 116.53, 116.80, 118.00, 122.92, 126.69, 130.12, 130.67, 136.12, 147.05, 149.18, 150.06, 155.71.

4-Hexyloxy-tris-tetraazacyclophane (3). In a drybox, **8** (320 mg, 0.220 mmol, 1.00 equiv) was combined with 1,4-dibromobenzene (105 mg, 0.441 mmol, 2.00 equiv), sodium *tert*-butoxide (106 mg, 1.10 mmol, 5.00 equiv), $\text{Pd}(\text{dba})_2$ (6.3 mg, 0.011 mmol, 0.050 equiv), and tri-*tert* butylphosphine (1.8 mg, 0.0089 mmol, 0.040 equiv) in 100 mL of toluene. The reaction was stirred at room temperature. After 41 h, the crude mixture was concentrated, applied onto a silica gel plug (5 g) and vacuum-filtered using EtOAc/hexanes (1/6) to give 290 mg (82%) of **3** as a tan solid. Analytically pure sample was obtained by recrystallization from tetrahydrofuran (as a **3**·THF adduct). ^1H NMR (400 MHz, C_6D_6) δ 0.88 (t, J = 6.8 Hz, 12 H), 1.11–1.40 (m, 24 H), 1.59 (t, J = 6.8 Hz, 8 H), 3.60 (m, 8 H), 6.40–7.42 (m, 56 H). ^{13}C NMR (100 MHz, C_6D_6) δ 14.60, 23.33, 26.46, 29.98, 32.24, 68.43, 114.00, 115.37, 115.41, 116.01, 116.50, 119.75, 125.56, 125.81, 126.20, 129.83, 130.19, 140.67, 143.57, 144.29, 148.13, 148.72, 150.69, 156.63. MALDI-TOF m/z 1581.96, requires 1582.06. Anal. Calcd for $\text{C}_{108}\text{H}_{108}\text{N}_8\text{O}_4\cdot\text{C}_4\text{H}_8\text{O}$: C, 81.32; H, 7.07; N, 6.77. Found: C, 81.41; H, 6.79; N 6.87.

Preparation of Oxidized Materials. A 0.050 mM solution of the ladder molecule in CH_2Cl_2 was sequentially treated with portions of a 0.010 M solution of bis(trifluoroacetoxy)iodobenzene (PIFA) under nitrogen atmosphere. To avoid background fluorescence from PIFA, lead acetate ($\text{Pb}(\text{OAc})_4$) replaced PIFA as the oxidant for the preparation of the samples for emission measurements. A concentration of 10 mM of tetra-*n*-butylammonium tetrafluoroborate (Bu_4NBF_4) and a small amount of trifluoroacetic anhydride ($(\text{CF}_3\text{CO})_2\text{O}$) were also added to stabilize the polyradicals.^{9a–b} Increments of between 1 and 20 μL of a 0.010 M fresh solution of $\text{Pb}(\text{OAc})_4$ (10 mM) in CH_2Cl_2 were added to the portions of 1 mL of an 0.1 mM solution of the ladders in CH_2Cl_2 with the ammonium salt and $(\text{CF}_3\text{CO})_2\text{O}$. Clear solutions with a light green to blue color were obtained upon oxidation.

Electrochemistry Measurements. Electrochemical studies of the arylamine ladder macromolecules were conducted in anhydrous dichloromethane, with 0.1 M Bu_4NBF_4 as the supporting electrolyte using a BAS Model 100A electrochemical workstation at a scan rate of 100 mV/s. Solution concentrations in the range of 0.1 and 0.6 mM of the square and the ladder systems were used. A glassy carbon electrode was used as the working electrode, which was polished with an alumina paste before analysis. Counter and reference electrodes were composed of platinum wire and Ag/AgCl, respectively. The ferrocenium/ferrocene couple occurred at $E^\circ = +0.58$ V vs Ag/AgCl (satd).²⁵

Steady-State Absorption and Emission. UV–visible absorption spectra were recorded with a Hewlett-Packard 8452A diode array spectrophotometer. The fluorescence spectra were measured with a Shimadzu RF-1501 spectrofluorometer. The concentrations of the square and the ladder CH_2Cl_2 solutions were 0.1 mM. For UV–vis absorption measurements, a 1 mm quartz cell was used. The oxidized solutions (~0.3 mL) described above were transferred to the cell by a syringe under nitrogen flow. For the emission measurements, the oxidized samples were prepared in the 1 cm quartz cuvette using 0.1 mM CH_2Cl_2 solutions under a nitrogen atmosphere. To obtain the UV–vis–NIR spectra 0.05 mM ladder solutions and 1 cm quartz cuvette were used.

EPR Measurements. The X-band EPR spectra were recorded on a Bruker EMX spectrometer, equipped with a variable temperature accessory (an ER4131VT system) and an ER041XG Microwave bridge. 0.2 to 0.3 mL 0.1 mM ladder solutions oxidized by $\text{Pb}(\text{OAc})_4$ were cooled to ~120 K in a sealed 4 mm diameter quartz EPR tube under a nitrogen atmosphere. The g -values were calculated based on the peak positions of DPPH solid ($g = 2.0036$). Spin concentrations were estimated by a reported method,¹⁷ which was based on the intensity of known concentrations of aqueous solutions of 2,2,6,6-tetramethyl-1-piperidinyloxy, TEMPO. Appropriate conditions, including data resolution, sweep time, and modulation amplitude, were ascertained for all EPR measurements.

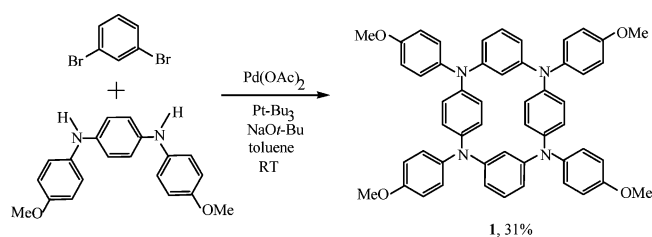
Time-Resolved Fluorescence Decay. Time-resolved polarized fluorescence was studied by femtosecond upconversion spectroscopy. The upconversion system used in our experiments has been previously described.²⁶ Briefly, the sample solution was excited with frequency-doubled light from a mode-locked Ti-sapphire laser pulse that has a pulse width of ~55 fs at a wavelength of 820 nm (Tsunami, Spectra Physics). The polarization of the excitation beam for the anisotropy measurements was controlled with a Berek compensator. The sample cell was 1 mm thick and was held in a rotating holder to avoid possible photodegradation and other accumulative effects. The fluorescence emitted from the sample was collected with achromatic lens and directed to a nonlinear crystal of β -barium borate. The rest of the fundamental light first passed through a motorized optical delay and was then mixed with the sample emission in another nonlinear crystal to generate sum frequency. This sum frequency light, i.e., the upconversion signal, was dispersed using a monochromator and detected by a photomultiplier tube (Hamamatsu R1527P).

Results and Discussion

A. Synthesis. 1. Overall Synthetic Strategy. Our synthetic approach to the ladder structures based on tetraazacyclophanes relies on recent developments in the palladium-catalyzed amination of aryl halides to form triarylamines.^{27–33} We have

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Scheme 1



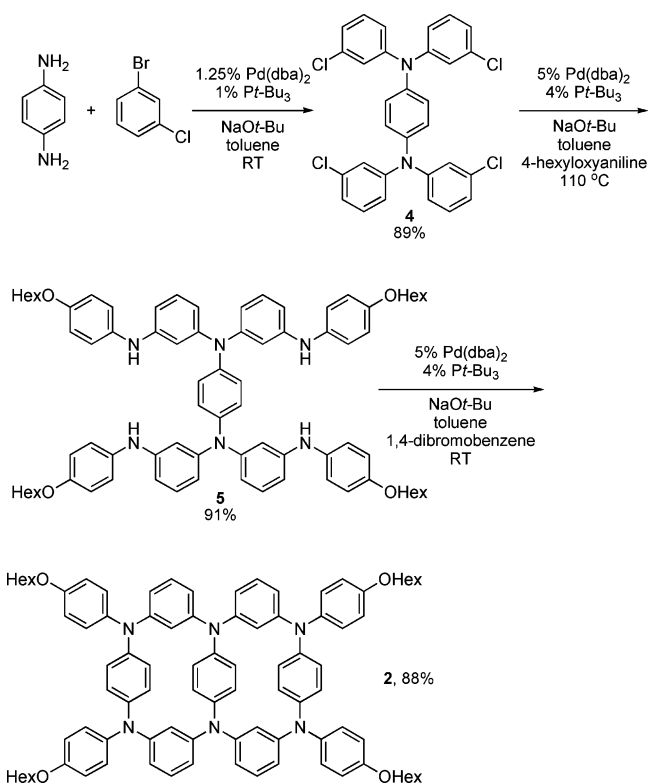
shown that catalysts generated from a 1:0.8 ratio of $\text{Pd}(\text{dba})_2$ and $\text{P}(t\text{-Bu})_3$ ^{34,35} are highly efficient for the amination of aryl bromides and chlorides. This catalyst couples bromo and chloroarenes with diarylamines under mild conditions in high yields.

In addition, we devised a synthetic route to the cyclophanes that avoids the use of any protective groups. This route would avoid protective groups by taking advantage of the selectivity of the catalyst for reactions of aryl bromides over aryl chlorides. Our strategy assembles the diarylamine precursors to the cyclophanes by coupling of a primary arylamine with the aryl bromide portion of a bromochloroarene. Although the palladium catalysts used in this study containing $\text{P}(t\text{-Bu})_3$ as ligand react with aryl chlorides, high selectivity for reaction of aryl bromides over chlorides has been observed previously with palladium catalysts containing this ligand.³⁶ Coupling of amines, either intermolecularly or intramolecularly with the remaining chloroarene function, then generates the macrocycle structures.

2. Synthesis of Tetraazacyclophane Rectangles. The synthesis of tetraazacyclophanes with identical *N*-aryl groups at each position of the periphery and with two different *N*-aryl groups at the periphery have been reported previously.^{11a} In brief, reaction 1,4-dibromobenzene with anisidine in the presence of $\text{Pd}(\text{dba})_2$ and $\text{P}(t\text{-Bu})_3$ as catalyst generated an *N,N'*-anisyl-substituted phenylenediamine, and reaction of this material with 1,3-dibromobenzene generated the tetraazacyclophane **1** in 31% yield (Scheme 1). This last step forms four C–N bonds and closes the 18-membered cyclophane ring in yields high enough to isolate substantial quantities of material.

3. Synthesis of Three-Runged Ladder 2. Ladder **2** was prepared by the three synthetic steps consisting of palladium-catalyzed amination (Scheme 2). Phenylenediamine **4** served as the center rung. Reaction of 1,4-phenylenediamine with 4.2 equiv of 1,3-bromochlorobenzene in the presence of 5 mol % $\text{Pd}(\text{dba})_2$ and $\text{P}(t\text{-Bu})_3$ per amine NH bond generated the four new C–N bonds of diamine **4**. As anticipated, the palladium catalyst showed complete selectivity for reaction with the aromatic carbon–bromine bonds and therefore generated little if any polymer. Reaction of benzenediamine **4** with 4-hexyloxyaniline in the presence of 5% $\text{Pd}(\text{dba})_2$ and 4% $\text{P}(t\text{-Bu})_3$ (1.25% versus each bromide) in toluene at 110 °C afforded hexamine **5** in 91% yield. The hexyloxy groups on the aniline were used to ensure high solubility of the ladder materials. Hexamine **5** was then treated with 1,4-dibromobenzene in the presence of the palladium catalyst in toluene at room temperature to close the two rings and provide a three-runged ladder **2**. This reaction generates four C–N bonds and closes two macrocycles

Scheme 2



in a high overall yield of 89%. The reaction was run at a low 9 mM concentration to favor the two cyclizations over polymerization.

Isolation and characterization of ladder **2** proved to be straightforward. Compound **2** was the fastest eluting reaction component on silica gel. Therefore, we isolated the desired product by simple vacuum filtration of the crude reaction mixture through a silica plug, eluting with 5% EtOAc in hexanes. The resulting product was analytically pure. The ¹³C NMR spectrum of this material was fully resolved, and the MALDI mass spectrum contained the appropriate molecular ion.

The hexyloxy side chains were required for formation of the ladder material. Precursors analogous to **5** that contained peripheral methyl, methoxy, or ethoxy groups all failed to produce the ladder materials in good yield when treated with 1,4-dibromobenzene. Because each of these derivatives is electronically and sterically similar to **5**, we presume that either partially coupled intermediates with the methyl, methoxy, or ethoxy substituents on the periphery are too insoluble to allow complete reaction in toluene or the final product was too insoluble to allow extraction from the solid salt byproducts.

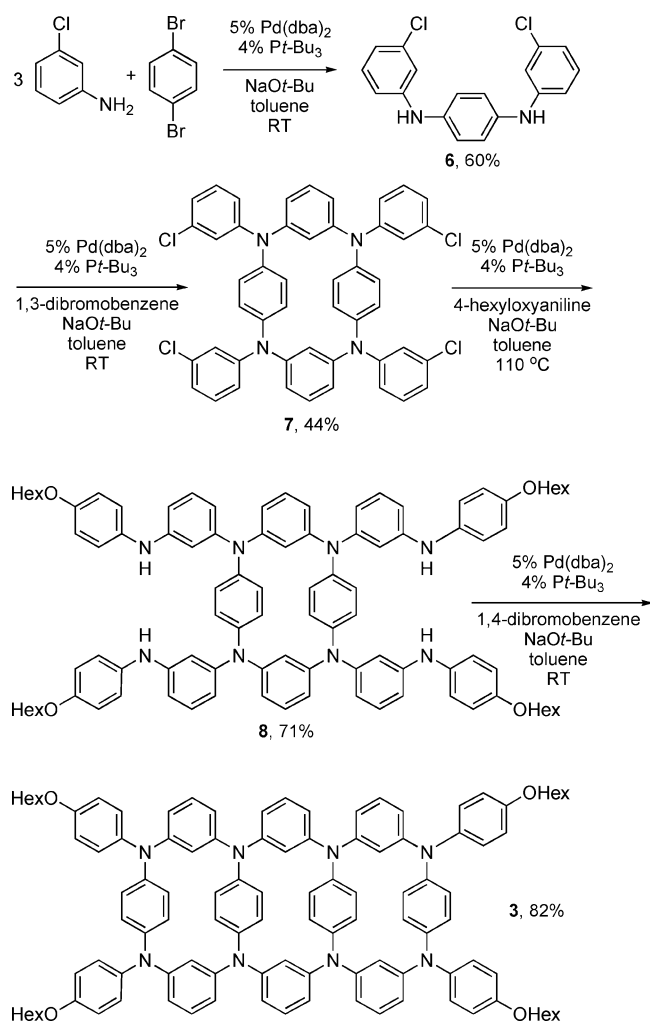
4. Synthesis of Four-Runged Ladder 3. Ladder **3** was prepared by the four coupling reactions in Scheme 3 with tetraazacyclophanes serving as the center two rungs. The precursor to the tetraazacyclophane, diamine **6**, was generated from dibromobenzene and 3-chloroaniline in acceptable yield with 5 mol % palladium, with respect to the dibromoarene. The core cyclophane **7** was then prepared in 44% yield from dichlorodiamine **7** and 1,3-dibromobenzene, by a reaction analogous to those used to prepare related tetraazacyclophanes bearing methyl, methoxy, and *tert*-butyl ester groups on the peripheral aryl rings.^{11a} The two outer rings containing the first and fourth rung of the ladder were assembled by the strategy

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Scheme 3



used to prepare bicyclic **2**. The tetrachloro tetraazacyclophane **7** was treated with 4-hexyloxyaniline under the palladium-catalyzed conditions. In the absence of any aryl bromide units, the aryl chlorides reacted in high yield to form octamine **8** in 71% yield, again by the construction of four new C–N bonds.

Octamine **8** was then treated with 1,4-dibromobenzene to generate ladder **3** in 82% yield by formation of four new C–N bonds and closure of the two outer rings to install the first and fourth rungs. Again, ladder **3** was the fastest eluting material on silica gel and was isolated by filtration of the crude reaction through a silica plug. This material was then crystallized to generate analytically pure ladder. The ^{13}C NMR spectrum of **3** was fully resolved, and the MALDI mass spectrum contained the appropriate molecular ion.

5. Structure of Ladder 2. A single crystal of the three-runged ladder **2** was obtained by slow evaporation of a benzene solution, and the structure was determined by X-ray crystallography (Figure 1). The molecule possesses a crystallographic mirror plane. The six nitrogens lie in a plane, and the three 1,4-phenylenediamine units are canted out of this plane. Each nitrogen shows the propeller arrangement of the three aryl groups of a conventional triarylamine. The distances between proximal nitrogens of a single cyclophane unit are 4.84 Å for the meta linkages and 5.65 Å for the para linkages. The distance between the two nitrogens at the ends of the support piece of

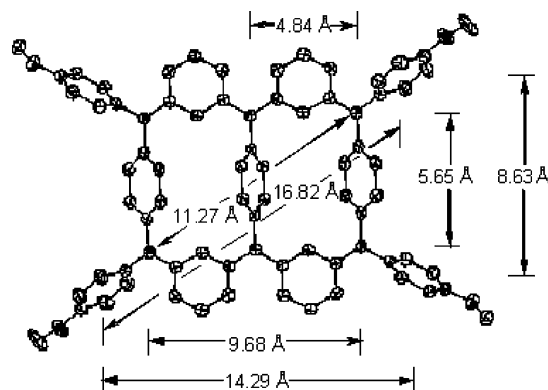


Figure 1. ORTEP drawing of the core of ladder **2**. Only one carbon of the hexyl side chains is shown.

Table 1. Formal Oxidation Potentials (E° in Volts)^a

	E°_1	E°_2 ^b	E°_3	E°_4	E°_5
TPPD	0.66	—	1.16		
1	0.52	0.76	1.09	1.23	
2	0.49	0.60	0.97	1.06	1.38

^a [**1**] = 0.6 mM, [**2**] = 0.5 mM, and [**3**] = 0.1 mM; the ferrocenium/ferrocene (Fc^+/Fc) couple occurs at $E^{\circ} = +0.58$ V vs Ag/AgCl (satd).²⁵

^b The second oxidation of TPPD is listed as E°_3 instead of E°_2 because this oxidation is analogous to the E°_3 and E°_4 waves of the ladder materials.

the ladder is 9.68 Å. The distance between the two nitrogens across a single cyclophane is 7.49 Å and between two nitrogens across the two cyclophanes is 11.27 Å. The two distances from the center of one external aromatic ring to the center of another are 8.63 Å and 14.29 Å along the sides of the rectangle and 16.82 Å across the diagonal of the full structure.

B. Electrochemical Investigations. Electrochemical measurements have been carried out on materials **1**–**3**. Listed in Table 1 are oxidation potentials for the systems investigated and oxidation potentials for a model compound (tetraphenyl-*p*-phenylenediamine, TPPD), which contains a single phenylenediamine unit. Two formal oxidation waves were observed for TPPD, one at $E^{\circ} = 0.660$ V and another at $E^{\circ} = 1.162$ V. The first wave corresponds to a one-electron oxidation process and yields a stable and delocalized *p*-phenylenediamine radical cation.^{10c} The second wave corresponds to the generation of a quinonoid dication.^{10c} The electrochemical results obtained with TPPD are similar to those reported for the analogous tetra-*p*-anisyl-*p*-phenylenediamine (TAPD).^{1–3} However, significantly lower oxidation potentials ($E^{\circ} = 0.46$ and 0.92 V) were observed for oxidation of the more electron-rich TAPD.^{1–3}

Figure 2 shows the cyclic voltammograms of **1** and the two different ladder (**2** and **3**) molecules. The cyclic voltammogram of **1** consisted of four reversible waves with potentials at $E^{\circ} = 0.516$, 0.757, 1.087, and 1.238 V. This multiwave electrochemical behavior has been reported for other similar organic macrocycles.¹¹ The first two oxidation processes are a result of the removal of an electron from each of the two *p*-phenylenediamine units. Because these *p*-phenylenediamine units may be oxidized twice, the third and fourth oxidation potentials (1.087 and 1.238 V), most likely, correspond to the second oxidation of each the two *p*-phenylenediamine units.

The cyclic voltammogram of the three-step ladder **2** consisted of a number of oxidation waves with potentials given in Table 1. The potentials resulting from the first two oxidations of the

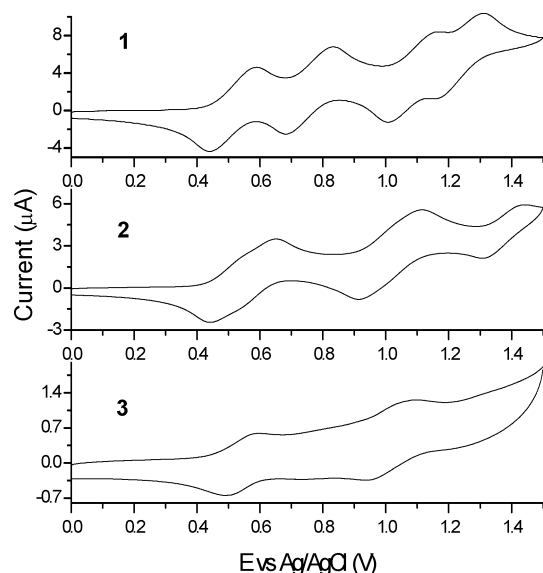


Figure 2. Cyclic voltammograms of **1–3** molecules. ($[1] = 0.6$ mM, $[2] = 0.5$ mM, and $[3] = 0.1$ mM; the ferrocenium/ferrocene (Fc^+/Fc) couple occurs at $E^0 = +0.58$ V vs Ag/AgCl (satd)).²⁵

phenylenediamine units are close to each other, and correspond to one pair of one-electron oxidations. Similarly, the two potentials for the second two oxidations (between 0.9 and 1.2 V) are close to each other, and correspond to a second pair of one-electron oxidations. A third irreversible oxidation at even higher potential is also observed. It is difficult to provide a detailed assignment of these oxidation waves, but it appears that two of the three rungs of the ladder, perhaps the outer rungs, are participating in the two pairs of redox processes that occur at potentials close to those of **1**. The first oxidation process ($E^0 = 0.49$ and 0.6 V) would then correspond to loss of an electron from each of the two phenylenediamine units that comprise the first and third rungs of the ladder. The next highest oxidation potential of **2** would then generate quinonoid structures from the phenylenediamines oxidized at the lower potential. Alternatively, E^0_5 could correspond to the loss of an electron from the center phenylenediamine unit of **2** with a potential that is higher than the potential required to oxidize the two outer phenylenediamine rings.

In either case, the potentials for oxidation of the first two phenylenediamine units are lower than the potential to oxidize the third unit, and this difference in potential could result from at least two effects. First, the oxidation of the center phenylenediamine unit would create charges on three contiguous rungs of the ladder. Second, the geometry required for generation of three contiguous phenylenediamine units would create significant steric interactions from the generation of three coplanar aryl groups in the three rungs of the ladder. Consistent with this assertion, X-ray crystallography (vide infra) showed that the central phenylene unit of the neutral ladder **2** is significantly more canted from the plane of the six nitrogens than are the outer phenylene.

The cyclic voltammogram of the four-step ladder **3**, contained two oxidation waves. Again, the first oxidation most likely results from loss of electrons from the exterior *p*-phenylenediamine units. The second wave would then correspond to oxidations of the same phenylenediamines to generate quinonoid structures, or, less likely, to oxidation of a contiguous phen-

ylenediamine unit. With **3**, oxidation of three phenylenediamine units would again require that two contiguous phenylenediamine units be oxidized, and the coplanarity of the phenylenediamine units of these two would then lead to a steric interaction that would be similar to that encountered in oxidized **2**. Because of the requirement of contiguous charges and the steric constraint, oxidation of a third phenylenediamine unit in **3** would be expected to be less favorable than oxidation of the second unit in **3**, regardless of the assignment of the oxidation wave.

C. Absorption Measurements. Absorption measurements of the neutral and oxidized forms of **1–3** were conducted. Figure 3a shows the UV–vis spectra of the neutral samples. The general characteristics of the spectra of the neutral forms of **1–3** were similar. Two major absorption peaks, one near ~ 220 nm and the other at ~ 320 nm, were observed for all of the neutral samples. A similar absorption spectrum was also obtained for the model compound TPPD (also shown in Figure 3a). The lower energy absorptions of **2** and **3** were red-shifted by about 10 nm from the absorption maximum of TPPD. The red shift is likely to correlate with the extent of conjugation in the ladder molecules.

The absorption spectra of **1**, **2**, and **3** in the presence of Bu_4NBF_4 and $(\text{CF}_3\text{CO})_2\text{O}$ are shown in Figure 3B. The combination of Bu_4NBF_4 and $(\text{CF}_3\text{CO})_2\text{O}$ has been used previously to oxidize molecules containing phenylenediamine units and to facilitate oxidation with lead acetate.^{9a–b} An immediate change in color of the solution from clear to green was observed after the addition of the salt and the anhydride. This change of color suggests that the combination of salt and anhydride functions as a weak oxidant of ladders **2** and **3**. The absorptions of the four different systems at the lower wavelengths, illustrated in Figure 3B, were unchanged by addition of the salt and anhydride. However, absorptions at higher wavelengths near 430 and 580 nm were observed in the spectra of **1**, **2**, and **3** after treatment of the amines with the additives. Addition of the salt and anhydride to the model compound TPPD generated only a single low energy band at ~ 420 nm.

The absorption spectra of the samples oxidized with $\text{Pb}(\text{OAc})_4$ in the presence of Bu_4NBF_4 and $(\text{CF}_3\text{CO})_2\text{O}$ are shown in Figure 4A. The addition of the lead oxidant, in addition to the salt and anhydride, resulted in a decrease in the absorption band at 320 nm and an increase in the intensity of the absorption bands in the visible spectral wavelengths near 430 and 580 nm. In addition to these bands, an additional absorption band in the near-IR with a maximum greater than 800 nm was generated by addition of the oxidant.

The intense green color of the solution from the oxidized **2** and **3** persisted when the solutions were kept under a nitrogen atmosphere at room temperature. When the oxidized form of **2** was incorporated into the polymer matrix poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) (PVB), the green color persisted for more than eight months. Absorption measurements of the thin film after eight months (Figure 4B) indicated that the oxidized form of **2** was still present.

D. Characterization of Polarons. We have characterized the ladder and monocyclic systems by absorption and EPR spectroscopy. As referred to above, a polaron band in polyaniline has been measured at 440 nm by linear absorption.³⁷ Likewise,

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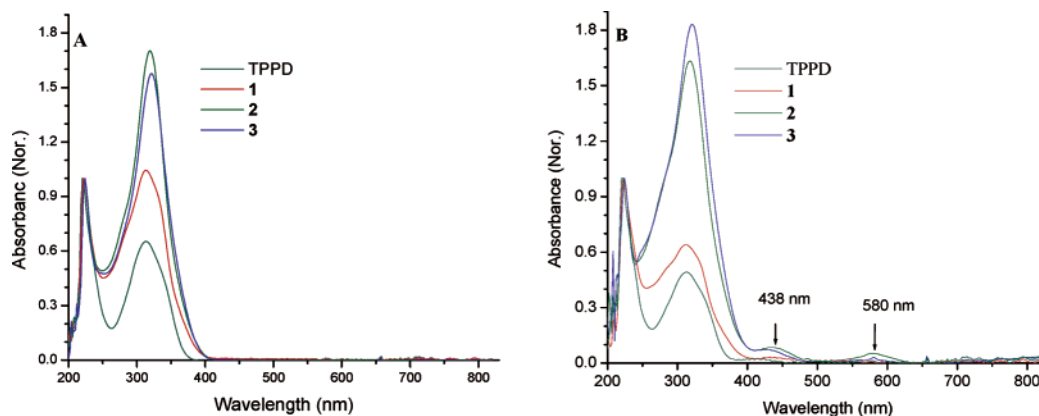


Figure 3. Absorption spectra of **1–3** and TPPD in the absence (A) and in the presence of Bu_4NBF_4 and $(\text{CF}_3\text{CO})_2\text{O}$ (B).

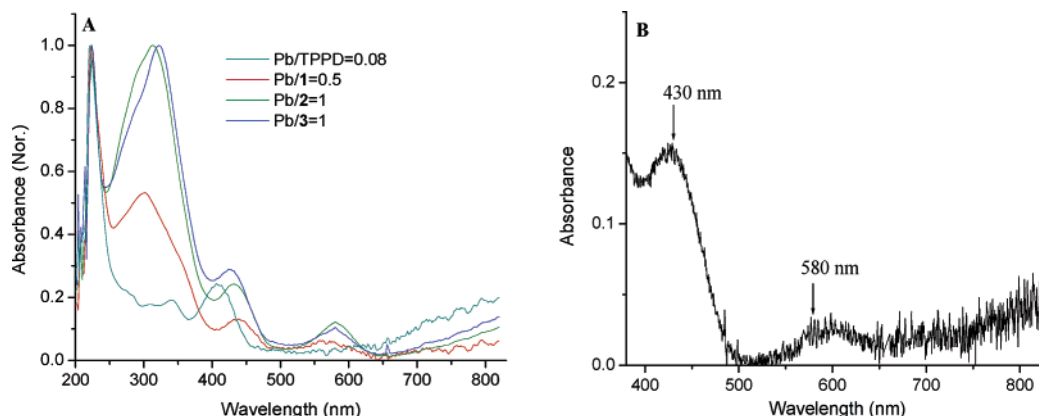


Figure 4. Absorption of oxidized forms of **1–3**. (A) The absorption spectra of **1–3** in the presence of the $\text{Pb}(\text{OAc})_4$. (B) The absorption spectrum of the oxidized **2** incorporated in a PVB film, obtained after 8 months.

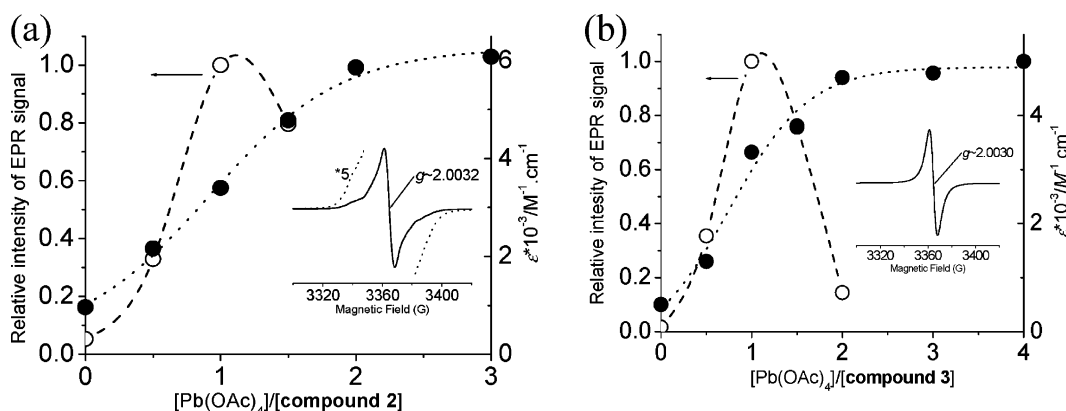


Figure 5. Relative intensities of the EPR signals (left y-axis) and the molar extinction coefficient of the polaron band at ~ 430 nm (right y-axis) as a function of the concentration of oxidant $\text{Pb}(\text{OAc})_4$ in solutions of **2** and **3** with the presence of Bu_4NBF_4 and $(\text{CF}_3\text{CO})_2\text{O}$. (a) **2**; (b) **3**; Insert: EPR spectra near $g \sim 2$ at the molar ratio $\text{Pb}(\text{OAc})_4/\text{ladder}$ of 1.

we observed a band near 430 nm in the absorption spectra of both ladder compounds **2** and **3**. The molar extinction coefficient of this polaronic band was found to be $\sim 10^3 \text{ M}^{-1}\cdot\text{cm}^{-1}$ (right y-axes of Figures 5a and 5b). The amplitude of this band depended on the concentration of oxidant added to the ladder and monocyclic compounds. As shown in Figure 5b, the absorption of the four-step ladder system increased with increasing amounts of added oxidant until it reached a maximum value at a molar ratio of $\text{Pb}(\text{OAc})_4/\textbf{3}$ of 2 and levels off afterward.

Oxidation of **2** and **3** by PIFA (Figure 6) generated an absorption band at ~ 1050 nm. This absorption at long wavelengths originates from an intervalence (IV) transition.³⁸ This IV transition of the monocationic and dicationic forms of **1** generated in CH_2Cl_2 with PIFA as oxidant had an absorption

(38) (a) Nelsen, S. F.; Ismagilov, R. F.; Trieber, D. A., *Science* **1997**, 278 (5339), 846. (b) Coropceanu, V.; Lambert, C.; Noll, G.; Bredas, J. L. *Chem. Phys. Lett.* **2003**, 373, 153. (c) Coropceanu, V.; Malagoli, M.; Andre, J. M.; Bredas, J. L. *J. Am. Chem. Soc.* **2002**, 124, 10519. (d) Lambert, C.; Noll, G. *Angew. Chem., Int. Ed.* **1998**, 37, 2107. (e) Lambert, C.; Nöll, G. *J. Am. Chem. Soc.* **1999**, 121, 8434.

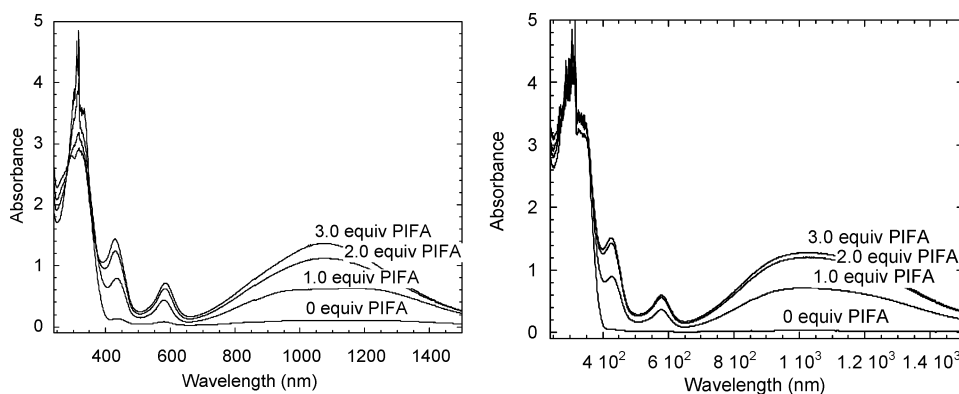
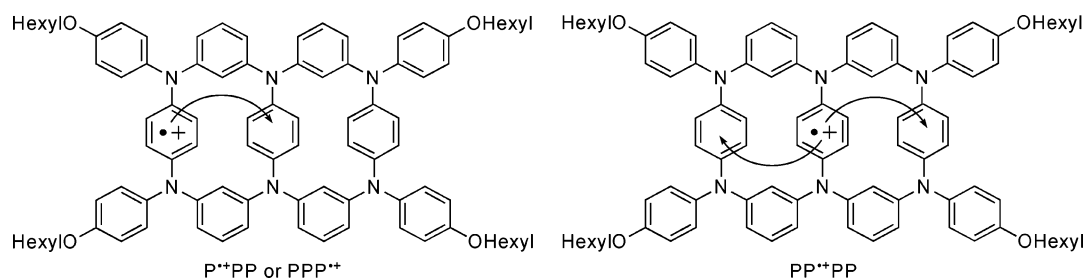
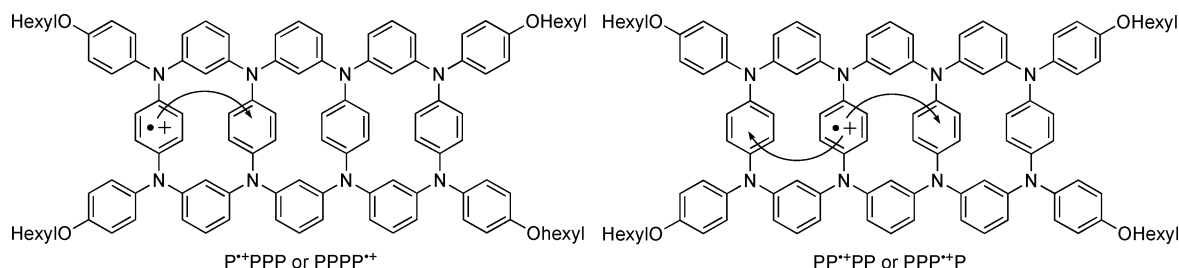


Figure 6. UV-vis-NIR spectra of neutral and oxidized **2** (left) and **3** (right) using 0.010 M PIFA in CH_2Cl_2 .

Scheme 4



Scheme 5



maximum near 900 nm.^{11a} A similar absorption at long wavelengths was also observed in a triarylamine based polymer.³⁹ The observation of IV bands may be understood by considering the interactions between polarons and redox centers. In this context, the IV band may be attributed to coupling between delocalized polarons (*p*-phenylenediamine cations) and redox centers (neutral *p*-phenylenediamines) (Schemes 4 and 5).

The linking of phenylenediamine units in the ladder systems at mutually *meta* positions on an aromatic unit apparently allows the charge of the oxidized ladder system to transfer between the phenylenediamine steps of the ladder structure that are separated by 4.84 Å. The intensity of the IV band of the monocations of the ladders results from a mixture of the two different intervalence transitions, $\text{P}^{+\bullet}\text{PP}$ (or $\text{PPP}^{+\bullet}$) \rightarrow $\text{PP}^{+\bullet}\text{P}$ and $\text{PP}^{+\bullet}\text{P} \rightarrow \text{P}^{+\bullet}\text{PP}$ (or $\text{PPP}^{+\bullet}$) for **2**⁺ as outlined in Scheme 4, and $\text{P}^{+\bullet}\text{PPP}$ (or $\text{PPPP}^{+\bullet}$) \rightarrow $\text{PP}^{+\bullet}\text{PP}$ (or $\text{PPP}^{+\bullet}\text{P}$) and $\text{PP}^{+\bullet}\text{PP}$ (or $\text{PPP}^{+\bullet}\text{P}$) \rightarrow $\text{P}^{+\bullet}\text{PPP}$ (or $\text{PPPP}^{+\bullet}$) + $\text{PPP}^{+\bullet}\text{P}$ (or $\text{PP}^{+\bullet}\text{PP}$) for **3**⁺, as illustrated in Scheme 5. Although both of these types of transitions may occur, only one relatively broad absorption band at ~1050 nm was observed. The difference in energy between these transitions is apparently too small to distinguish by the steady-state absorption measurements.

To analyze the effective electronic coupling between the redox sites in the radical cations one may apply Hush theory.⁴⁰ The coupling parameter (*V*) can be estimated by the expression:⁴⁰

$$V = \frac{0.0206}{d} (\epsilon_{\text{max}} \nu_{\text{max}} \Delta \nu_{1/2})^{1/2}$$

in which *V* is in units of cm^{-1} , *d* is the site-to-site separation of the redox positions in angstroms, ϵ_{max} is the maximum extinction coefficient, ν_{max} (in cm^{-1}) is the transition energy, and $\Delta \nu_{1/2}$ is the full width at half-maximum (fwhm, in cm^{-1}) of the IV band.⁴⁰ The absorption maximum of the IV band was found to be at ~9547 cm^{-1} (1.19 eV) and ~9872 cm^{-1} (1.23 eV) for **2** and **3**, respectively. The fwhm of the IV band of both ladder systems was ~4700 cm^{-1} . From these values, the coupling parameter between the delocalized phenylenediamine cations and the neutral phenylenediamines in both ladder systems was estimated to be in the range of 2250–2450 cm^{-1} (0.28–0.30 eV). The adiabatic charge-transfer energy [ΔG^* , $\Delta G^* = (\lambda/4 - V) + V^2/\lambda$] was estimated to be ~0.08 eV for the IV charge transfer in both ladder systems. It is interesting to note that the through-bond distance is 10.49 Å, and for this distance a

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(40) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391.

coupling constant in the range of 1060–1146 cm⁻¹ (0.13–0.14 eV) results. This coupling constant leads to a diabatic charge-transfer energy of 0.18 eV. Thus both charge-transfer energy calculations (through space and through bond) lead to an energy which is comparable in magnitude to the values obtained for weak polaron bands (~0.1 eV) in conjugated polymers.⁴¹ The transition energy at the maximum absorption of the IV band of the monocationic form of the ladders is less than 14 kcal/mol. This energy is lower than the transition energy (34.7 kcal/mol) of the TPPD monocation radical.⁴² Thus, the polaronic coupling in these macrocyclic ladder arylamines appears to be larger than that in the linear, tetraarylphenylenediamine component of the ladders, TPPD. This larger coupling may suggest that the polarons of the cyclophanes in this study are more delocalized than the polarons of the single phenylenediamines.^{4,5,38,42}

EPR measurements provided further information about the degree of delocalization of the polarons in the ladder systems. EPR signals of oxidized **2** and **3** were observed to have a Lorentzian line shape and a *g* value of 2.003. This *g* value is similar to those of organic radicals and highly electronically delocalized polarons in polyaniline.¹⁷ The magnitude of the maximum slope line widths (ΔH_{msl}) of the signals for **2** and **3**, 11–12 G at a sweep width of 4500 G, were also similar to each other. The line shape and the *g* value for these single-peak EPR spectra reflected the delocalized character of the polarons generated in these ladder systems in comparison to the EPR spectra of the polarons in polyaniline.^{17,43}

Addition of Pb(OAc)₄ as oxidant generated intense signals from the oxidized ladders. The intensity of the EPR signal increased with an increase in the molar ratio of oxidant to **2** or **3** (Figure 5). The largest intensity was observed at a molar ratio of approximately 1:1. EPR signals of samples containing a ratio of oxidant to ladder greater than 1:1 were less intense than those of samples with a 1:1 ratio of oxidant to ladder. Using a known method to calculate the spin concentration from EPR data,¹⁷ we found the spin concentration of both oxidized ladders to be ~1 spin/molecule when the molar ratio of oxidant to **2** or **3** was 1:1. The maximum spin concentration was observed when the ladders had undergone a single oxidation because the dications of the ladders are singlet ground states (vide infra). The decrease in spin concentration when the ratio of oxidant to ladder is greater than 1:1 indicates that bipolarons are generated.^{10c}

EPR measurements of the oxidized ladders were also performed at low temperature (120 K) to determine the ground spin state of the dications. The ladders **2** and **3** were oxidized by Pb(OAc)₄ with molar ratios of Pb(OAc)₄ to ladders ranging from 0.5 to 3. A forbidden transition near *g* = 4 at $\Delta m = \pm 2$, which would indicate population of a triplet spin state was not observed. Thus, the ground state of the dications is most likely a singlet in the ladder systems. In contrast, a forbidden transition due to a triplet state was observed in the low-temperature spectrum of **1** oxidized with two equiv of PIFA. This difference in ground-state further suggests that the polarons in the ladder systems are more delocalized than in the square system **1**.^{11a}

E. Steady-State Emission Spectra. The emission spectra of TPPD, cyclophane **1**, and ladders **2** and **3** were obtained with an excitation wavelength of 410 nm under a variety of experimental conditions. These spectra are shown in Figure 7. A clear emission band at 440 nm for the neutral forms of TPPD, **1**, **2**, and **3** was observed. This emission originates from a $\pi^* \rightarrow \pi$ transition. The emission spectra of all the neutral molecules in pure CH₂Cl₂ (Figure 7 marked by arrows) also contained a shoulder at 466 nm. The emission spectra of these materials in a mixture of Bu₄NBF₄ and (CF₃CO)₂O exhibited two maxima at 440 and 466 nm, and the emission spectra obtained after addition of the oxidant Pb(OAc)₄ were similar to those obtained after addition of only Bu₄NBF₄ and (CF₃CO)₂O. This similarity between the emission spectra with and without the oxidant in the presence of Bu₄NBF₄ and (CF₃CO)₂O is consistent with partial oxidation of the ladders by these additives in CH₂Cl₂ solutions. The oxidation may be due to small amounts of trifluoroacetic acid in the anhydride.

The emission spectra in Figure 7 also reveal different quenching behavior for each of the square and ladder molecules in the presence of Bu₄NBF₄ and (CF₃CO)₂O. In the presence of Bu₄NBF₄ and (CF₃CO)₂O, quenching of the emission at 440 nm was approximately 20% for TPPD, 35% for **1**, 50% for **3**, and over 60% for **2**. This high degree of quenching for **2** may result from strong ion (dynamic) quenching that can occur with charged materials.⁴⁴ The quenching of the emission of **1** at 466 nm in the presence of these additives was weaker than that of **2** and **3** (Figure 7a,b). The observation that TPPD has the lowest degree of quenching was surprising because this molecule has the smallest diameter and the highest diffusion controlled collisional frequency.⁴⁵

Upon addition of the Pb(OAc)₄ oxidant to the solutions containing Bu₄NBF₄ and (CF₃CO)₂O, the ladder systems exhibited both dynamic and static quenching. This combination of quenching mechanisms was revealed by the parabolic shape of the Stern–Volmer plots of the quenching of **2** and **3** (Figure 8).⁴⁵ Thus, it appears that the ladder systems, which have a higher density of polarons, exhibit emission quenching behavior that is different from that of **1** and TPPD. The oxidation of ladders **2** and **3** gives rise to a broad vibronic (IV) transition in the near-IR, which is related to the delocalization of polarons (Section C). The polaron delocalization and polaron-phonon interactions help to dissipate the energy of the emission and thereby accelerate the relaxation of the excited states through nonradiative pathways.^{46,47} This pathway for relaxation of the excited states may explain why a strong static quenching is observed for both oxidized ladder systems in the presence of Bu₄NBF₄ and (CF₃CO)₂O.

F. Time-Resolved Fluorescence Measurements. The fluorescence decays of **1–3** in CH₂Cl₂ measured by fluorescence upconversion are shown in Figure 9. A fast component, followed by a slower component, was observed in the fluorescence decay of the square and ladder materials. The decay time of the fast process was comparable to the duration of the fwhm of our instrument response function (IRF, ~200 fs). Thus, the decay

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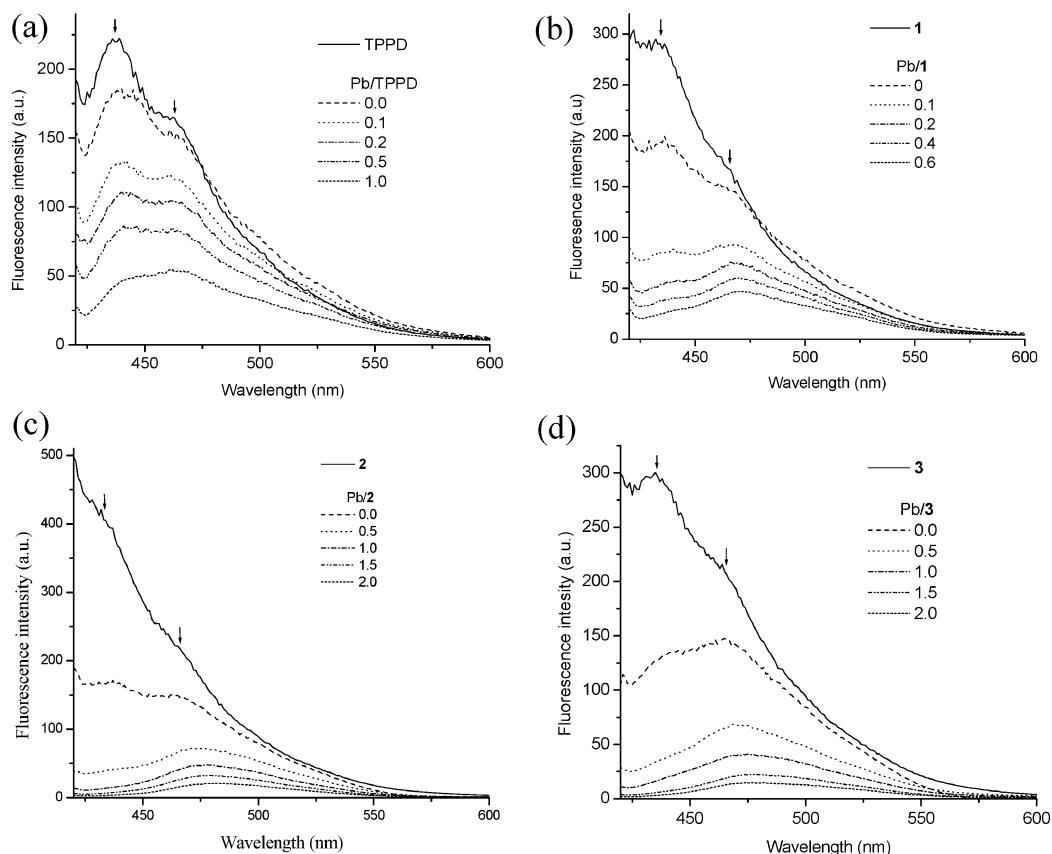


Figure 7. Emission spectra of 0.1 mM CH_2Cl_2 solutions of neutral and oxidized TPPD, **1**–**3** with an excitation of 410 nm. The oxidation level is indicated by the molar ratio of $\text{Pb}(\text{OAc})_4/\text{neutral-molecule}$ ($\text{Pb}/\text{neutral}$), and the arrows indicated the emission bands in the neutral systems.

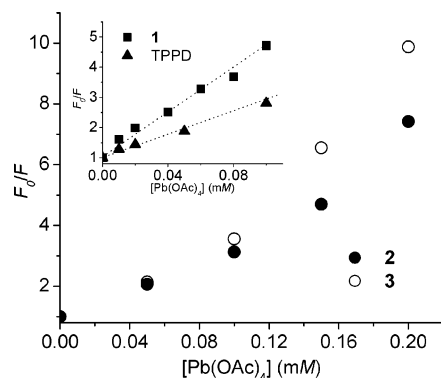


Figure 8. The Stern–Volmer plots for the ladder samples at the emission of 466 nm in the presence of $\text{Bu}_4\text{NBF}_4/(\text{CF}_3\text{CO})_2\text{O}$ (10 mM/1 mM).

time of the fast component of the fluorescence quenching of the square and ladder systems was estimated to be less than ~ 100 fs with an amplitude of ~ 0.78 for the ladders and ~ 0.82 for **1**, while the decay time of the slower decay component was found to be about ~ 6 ps with an amplitude of 0.22 for the ladders and 0.18 for **1**.

Although the fluorescence decays were similar for the ladder and square molecules, the rates of depolarization were significantly different (Figure 10). The decay of fluorescence of the linear molecule TPPD did not contain an obvious initial fast anisotropic decay component. However, the fluorescence of the square and the ladder molecules did occur with an ultrafast anisotropic decay process with a time constant of ~ 70 fs. The residual value of the decay of the fluorescence anisotropy of **1** was 0.23, while the analogous value of **3** was 0.05. A systemic

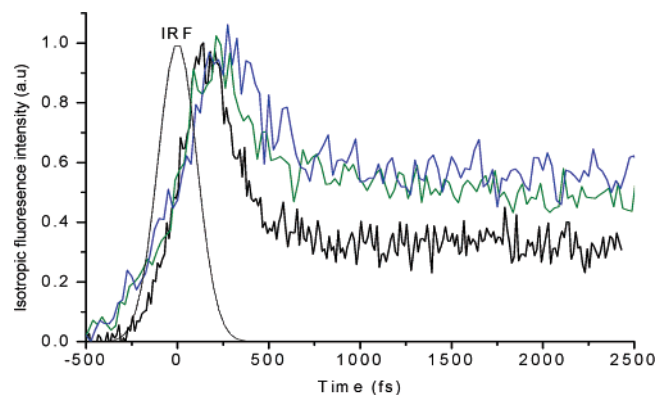


Figure 9. Fluorescence decay of the emission at 480 nm in 0.1 mM CH_2Cl_2 solutions of **1**–**3** with an excitation at 410 nm (black, **1**; green, **2**; blue, **3**).

decrease in the residual value with the increasing number of *p*-phenylenediamine units in **1**–**3** was observed.

Figure 11 shows the fluorescence dynamics of solutions of the square and ladder systems containing Bu_4NBF_4 and $(\text{CF}_3\text{CO})_2\text{O}$. As described in section C, a polaron absorption band was observed upon addition of Bu_4NBF_4 and $(\text{CF}_3\text{CO})_2\text{O}$ to a solution of the ladders in CH_2Cl_2 . In general, the fluorescence decay of square **1** in the presence of Bu_4NBF_4 and $(\text{CF}_3\text{CO})_2\text{O}$ was similar to the decay in the absence of these additives. This similarity agrees with the similar steady-state emission of **1** at 466 nm in the presence and absence of the same additives (Figure 7). The fluorescence decay curves obtained after addition of $\text{Pb}(\text{AcO})_4$ to solutions of **1**–**3** in CH_2Cl_2 containing Bu_4NBF_4 and $(\text{CF}_3\text{CO})_2\text{O}$ contained only a small amplitude from

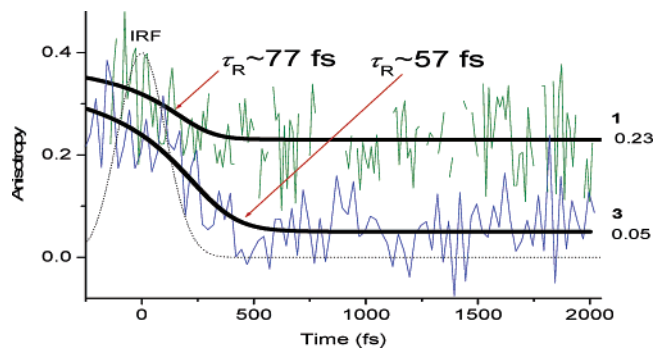


Figure 10. Fluorescence anisotropy decay of the emission at 480 nm for 0.1 mM CH_2Cl_2 solutions of **1** and **3** with an excitation at 410 nm.

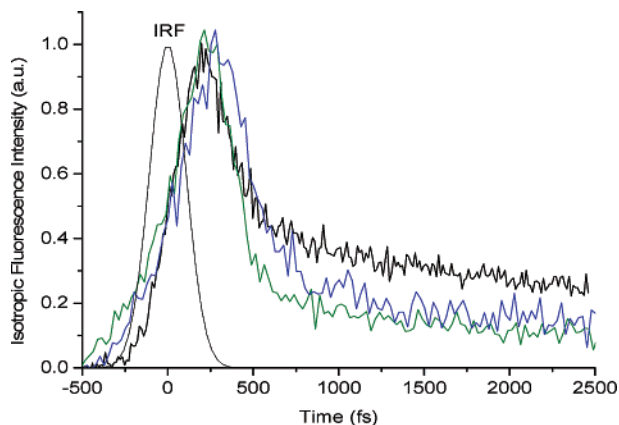


Figure 11. Fluorescence decay of the emission of 0.1 mM CH_2Cl_2 solutions of **1–3** with the presence of $\text{Bu}_4\text{NBF}_4/(\text{CF}_3\text{CO})_2\text{O}$ (10 mM/1 mM) (black, **1**; green, **2**; blue, **3**; excitation at 410 nm; emission at 480 nm).

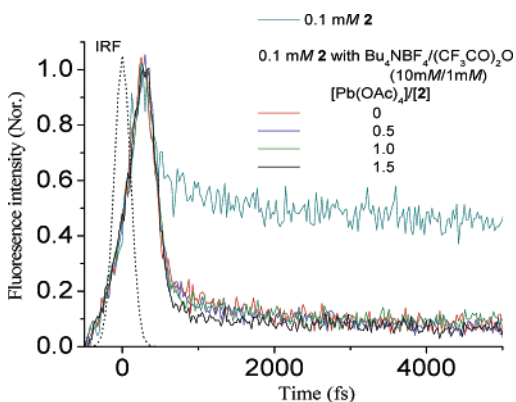


Figure 12. Fluorescence decay of the emission of 0.1 mM oxidized CH_2Cl_2 solutions of **1–3** with the presence of $\text{Bu}_4\text{NBF}_4/(\text{CF}_3\text{CO})_2\text{O}$ (10 mM/1 mM) (excitation at 410 nm; emission at 480 nm).

the slower decay component. Over 90% of the intensity of the total emission could be attributed to the fast component (Figure 12).

The mechanism of the fast fluorescence decay may be connected to polaronic–exciton delocalization and polaron–polaron interactions.^{46,48} Because the oxidation potential of the triarylamine units is low, a polaronic exciton (quasiparticle

which is induced by self-trapping of photogenerated carriers) may be generated around the nitrogen center by photoexcitation of the neutral phenylenediamine units.^{6,49–51} The overlap of the emission and the absorption spectra suggest that the electron–exciton coherence induces exciton delocalization around the frame of the tetraazacyclophane ring.²⁵ This exciton delocalization was suggested by the fast depolarization of the fluorescence anisotropy. For the oxidized ladder structures, a polaron transfer rate $\sim 10^{10}$ – 10^{12} s^{-1} (1–100 ps) was obtained. The pinning frequency of a polaron is 9×10^{12} or 3.6×10^{13} Hz.^{52,53} This thermal electron (hole) transfer process is much slower than the delocalization of the photoexcited polarons, as shown by the ultrafast decay of the fluorescence dynamics within the first ~ 100 fs. This observation agrees with the fast dephasing time observed in polyaniline, which is connected with the delocalization of photoexcited polarons.⁴⁶

Conclusions

In summary, we have shown that palladium-catalyzed amination can assemble triarylamine materials with a complex, but well-defined, architecture. In each operation, four C–N bonds are formed, and in the final two steps of each synthesis two rings are closed in yields between 71 and 89%. During the preparation of **2**, twelve C–N bonds are constructed in three synthetic operations, with an overall yield that corresponds to over 97% for each C–N coupling. During the preparation of **3**, sixteen C–N bonds are formed in four operations, with a yield that corresponds to over 89% for each coupling. A crystal structure analysis of one ladder reveals that the aryl groups that serve as the ladder rungs are canted from the plane containing the nitrogens and *m*-phenylene units that link the nitrogens on the ladder sidepieces.

We have utilized electrochemical and EPR measurements, as well as steady-state and time-resolved spectroscopy, to probe the properties of these materials. Both ladder systems demonstrated significant polaronic behavior. A multiwave oxidation process for both ladder systems was observed and was concluded to result from consecutive oxidation processes. Absorption measurements of oxidized forms of the ladder systems revealed polaron and intervalence bands at long wavelengths. An electronic coupling parameter for the coupling between the phenylenediamine cation radicals and the neutral phenylenediamine units of ~ 0.1 eV was deduced for the ladder systems. The spin concentration obtained by EPR measurements increased with the amount of oxidant added, and the *g* values and line shape of the EPR signals suggested that the polarons have a delocalized character. The quenching of the steady-state emission of the ladder systems depended on the amount of oxidant added. Also, an ultrafast decay of the fluorescence anisotropy for the square and the ladder molecules was observed and may be connected with the interactions of polarons. These results provide a direct comparison of the electronic and optical properties of the macromolecular ladder architecture with the

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properties of the related linear system containing the same building blocks. This comparison draws analogies to previous reports that compare branched dendritic structures with linear chromophores that are the building blocks of the macromolecule.

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Supporting Information Available: Experimental procedures, metrical parameters, and .cif files for the structure of **2** determined by X-ray diffraction. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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