Palladium-Catalyzed Synthesis of Monodisperse, Controlled-Length, and Functionalized Oligoanilines

Joseph P. Sadighi, Robert A. Singer, and Stephen L. Buchwald*

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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Abstract: The palladium-catalyzed amination of aryl halides, in conjunction with an orthogonal protective group scheme, forms the basis of two routes to oligoaniline precursors. One method consists of a bidirectional chain growth from a symmetric core piece, whereas the other involves a divergent−convergent synthesis of nonsymmetric fragments, followed by coupling to a symmetric core fragment. The oligoaniline precursors are soluble in a variety of common organic solvents and are easily converted to the deprotected oligoanilines. The method allows the preparation of even or odd chain lengths and the incorporation of a variety of functional groups. The synthesis of phenyl-capped heptaaniline through decaaniline, of four end-functionalized octaaniline derivatives, and of phenyl-capped 16-mer and 24-mer is described. The effects of chain length and substitution upon oligomer behavior have been investigated by electronic absorption spectroscopy and cyclic voltammetry.

Introduction

Well over a century after the first oxidation of aniline,[1] the electrical conductivity of polyaniline was recognized.[2] Among conductive polymers, polyaniline is remarkable for its excellent environmental stability,[3] and unique in the ease with which its properties may be tuned by changes in oxidation state[4] or in degree of protonation.[5] Advances in the electropolymerization of aniline,[6] and in solution-processing of the chemically synthesized polymer,[7] have allowed the study of polyaniline in numerous practical applications, including rechargeable organic batteries,[8] electrochromic displays,[9] electromechanical actuators,[10] anticorrosion coatings for steel,[11] and electromagnetic interference shielding.[12]

Soon after polyaniline was identified as an electrical conductor, Honzl et al. prepared and investigated the first phenyl-capped oligoanilines of controlled chain length as models for the poorly defined polymer.[13] The synthetic method involved the condensation of small oligoanilines (dimer, trimer, and tetramer)[14] with diethyl succinoylsuccinate, followed by hydrolysis, decarboxylation, and aromatization. This sequence afforded phenyl-capped tetraaniline and hexaaniline; diazotization and reduction of tetraaniline gave rise to phenyl-capped trianiline. The authors apparently did not isolate phenyl-capped octaaniline from the condensation reaction when tetraaniline was used.

In 1986, Wudl and co-workers modified the Honzl condensation approach (Scheme 1) and succeeded in obtaining phenyl-capped octaaniline.[15] This compound proved identical to bulk polyaniline by ESR, UV−vis, and IR spectroscopy and displayed conductivity on the same order of magnitude as that of the bulk polymer, demonstrating that useful electrical properties may be realized even in relatively short oligoaniline systems.

More recently, other methods for the synthesis of oligoanilines have been reported. A titanium alkoxide-mediated coupling of anilines with phenols has been used to prepare phenyl-capped tetraaniline and pentaaniline.[16] An Ullmann coupling reaction between acetanilides and 4-iodonitrobenzene was used in an iterative coupling/reduction sequence, followed by deacetylation to afford trianiline and tetraaniline, the starting anilines for the Wudl−Honzl oligoaniline synthesis.[17] Finally, in a modern variant of the Wilstätter−Moore approach,[14] MacDiarmid and Epstein et al. have oxidized *N*-phenyl-1,4-phenylenediamine to tetraaniline; they report that oxidation of the latter compound affords a 16-mer.[18]

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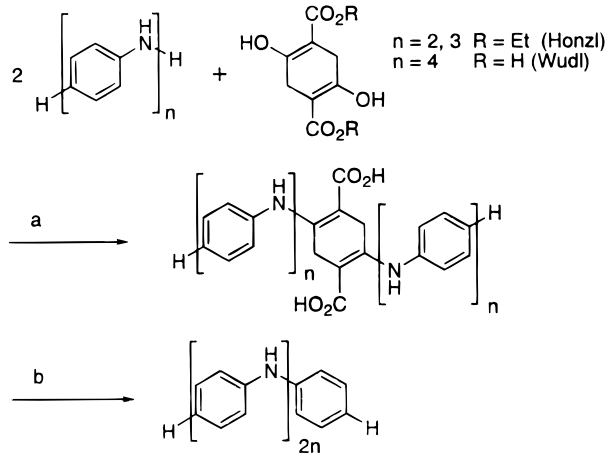
Scheme 1. Oligoaniline Synthesis of Honzl[13] and Wudl[15] [a]



[a] Key: (a) Δ, then (for R = Et) NaOH, EtOH, dioxane, Δ; (b) Δ, O_2.

The palladium-catalyzed amination of aryl halides and triflates[19] has emerged as a powerful method for the synthesis of a wide variety of arylamines. The high efficiency and broad substrate scope of the reaction make it an ideal method for the preparation of novel oligoaniline derivatives. We have developed a general route to oligoanilines, using palladium catalysis to assemble the aryl-nitrogen framework and an orthogonal protective group scheme to control the course of the reactions. The protective groups confer excellent solubility upon the products and are easily removed to form the electroactive oligomers. This method offers great synthetic flexibility: even- or odd-numbered oligomers may be prepared, and functional groups may be introduced at the ends of the chains to modify the properties of the materials without disrupting the coplanarity between rings. We have prepared and investigated phenyl-capped heptaaniline through decaaniline, a series of end-functionalized octamers, and the phenyl-capped 16-mer and 24-mer.

Results and Discussion

Oligomer Synthesis. The simplest palladium-catalyzed synthesis of polyaniline would involve the polymerization of 4-bromoaniline or the copolymerization of 1,4-phenylenediamine with 1,4-dibromobenzene. However, the coupling products would be easily oxidized, even short oligomers would present problems in solubility and purification, and precise control over chain length would be difficult.

Several strategies,[20] illustrated in Figure 1, may be envisioned for the synthesis of discrete oligoanilines by sequences of aryl amination and deprotection. The reaction of an arylamine with a protected 4-bromoaniline, followed by deprotection, would result in an increase in chain length of one unit for each iteration. The disadvantages of such a method are the relatively slow increase in chain length for a given number of steps and the increasing difficulty of separating the products from any unreacted starting material or byproducts as the chain length increases. An outward growth of the oligoaniline from a symmetric core would permit the chain to grow by two units in one iteration and result in a larger difference in size between starting material and desired product. As in the monodirectional strategy, the chain length increases by the same increment with each iteration of the sequence.

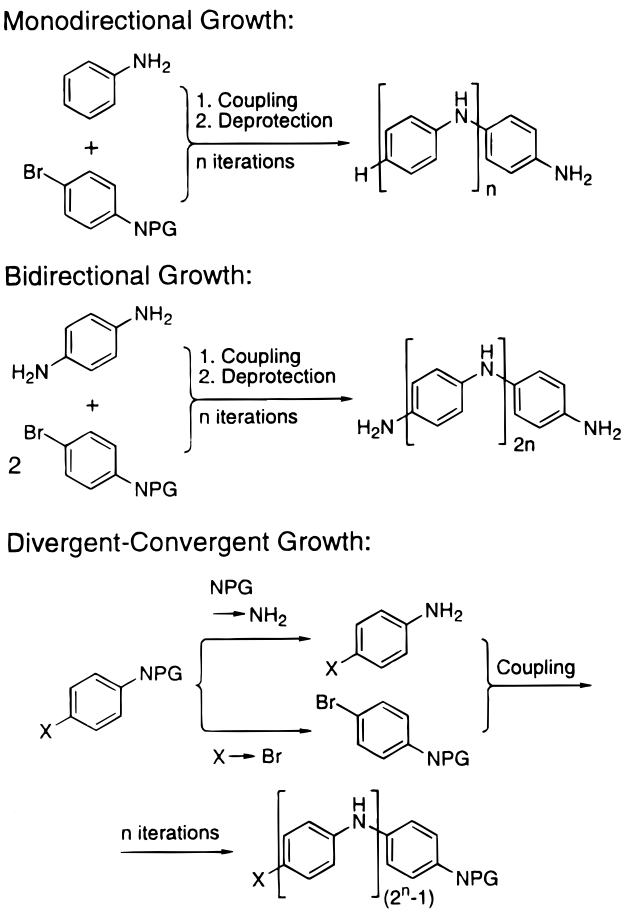


Figure 1. Possible strategies for the synthesis of oligoanilines by aryl amination.

A geometric growth in chain length is possible using a divergent−convergent approach.[21] In this strategy, a suitably protected oligomer is divided into two portions; one is converted to an arylamine, and the other to an aryl bromide. The coupling of the two produces a homologous oligomer, with a doubling in chain length.

For electrochemical studies and applications of oligoanilines, symmetric products are desirable, to avoid the complications of parallel and antiparallel orientations between chains. Our synthetic methods combine the divergent−convergent approach with a modified bidirectional approach, which links the chain fragments to form a symmetric oligomer. This strategy requires the use of suitable equivalents for the aryl bromide and arylamine functional groups, so that each may be unmasked without affecting the other.

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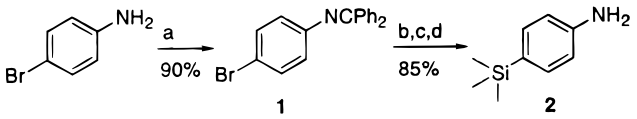
Scheme 2[a]



[a] Key: (a) Ph_2CO, 5 Å molecular sieves, $PhCH_3$, 120 °C; (b) *n*-C_4H_9Li, THF, −78 °C; (c) $(CH_3)_3SiCl$, THF, −78 °C; (d) $H_2NOH{\cdot}HCl$ (1.5 equiv), NaOAc (2 equiv), CH_3OH.

The facile electrophilic substitution of the trimethylsilyl group[22] allows it to function as a masked aryl bromide. The nitrogen protecting group was therefore required to be stable to the reaction conditions of bromodesilylation as well as to those of aryl amination, and to be removable without the use of strong acid, which would cleave the aryl−silicon bond.

After investigating a number of possibilities, we found the diphenylmethylene group to be extremely useful for several reasons. Condensation of 4-bromoaniline with benzophenone is easily carried out on large scale and in high yield. The resulting *N*-(diphenylmethylene)-4-bromoaniline (**1**) is a convenient substrate for palladium-catalyzed aryl amination; the reactions proceed rapidly and cleanly, with no detectable transamination, and the diphenylmethylene group imparts excellent crystallinity to the products. This protective group is stable to bromine under the conditions used in bromodesilylation. The free primary amine may be liberated by hydrogenolysis[23] or by treatment with hydroxylamine under weakly acidic conditions.[24] Finally, the stability of the imine to alkyllithium reagents at low-temperature allows halogen−metal exchange to be carried out on **1**, leading to a convenient preparation of 4-(trimethylsilyl)aniline (**2**).[25] The preparation of 4-bromoaniline equivalents **1** and **2** is outlined in Scheme 2.

Palladium-catalyzed coupling of **1** and **2** affords an aniline dimer with a masked bromide at one end and a protected amine at the other. Protection of the internal NH group as its *tert*-butyl carbamate (BOC) derivative forms a dimer derivative (**3**) which may be homologated by the divergent−convergent approach. The *tert*-butyl carbamate confers excellent solubility upon intermediates and products, prevents the oxidation of the phenylenediamine moieties in higher oligomers to quinonediimines, and allows bromodesilylation to occur without detectable overbromination. The divergent−convergent process is easily carried out on multigram scale; the yield for each step is high, and the intermediates are easily purified by crystallization. Scheme 3 shows the synthesis of several chain fragments (**5**, **7**, **10**) used in the preparation of symmetric oligomers.

Other nonsymmetric chain fragments may be prepared by modifications of this synthetic methodology; the synthesis of a trimer derivative (**12**) is shown in Scheme 4. The synthesis of aryl bromide **14** (Scheme 5) is noteworthy for the selective monoamination of 1,4-dibromobenzene; the highly electron-rich coupling product **13.2** reacts so slowly with the palladium catalyst that, under these conditions, the amination stops cleanly at this stage. Protection of the secondary amine as its BOC derivative results in an aryl bromide substrate (**14**) which is activated toward oxidative addition.

The synthesis of substituted octamers **18** was carried out by the bidirectional approach illustrated in Scheme 6. The symmetric N_4-diamine **15** is obtained by the reaction of 1,4-phenylenediamine with 2 equiv of monomer **1**, followed by BOC-protection and imine cleavage.[27] Iteration of the sequence using aryl bromide **5** allows more rapid growth, giving the N_8-diamine **17**. This diamine reacts with simple aryl bromides to give a variety of α,ω-disubstituted phenyl-capped octamers (**18a**−**d**) from a common precursor. Alternatively, the N_4-diamine **15** may be converted directly to a capped octamer by reaction with the appropriate N_2-aryl bromide, as in the synthesis of the bis(methoxy)-substituted octamer (**18e**).

Symmetric oligomers also result from the reaction of arylamines with symmetric dibromides, prepared as shown in Scheme 7; odd- or even-numbered oligomers may be obtained, depending on the core piece used. Regioselective *para*-bromination of diphenylamine[28] affords 4,4′-dibromodiphenylamine, which is activated toward aryl amination by conversion to its BOC derivative (**19**). Even-numbered dibromides (**20**, **21**) are prepared by the coupling of diamines with 2 equiv of 1,4-dibromobenzene (see the preparation of **14**, above), followed by BOC-protection. Scheme 8 illustrates the synthesis of phenyl-capped heptamer **22** and a series of α,ω-bis-(trimethylsilyl) phenyl-capped oligomers: nonamer **23**, decamer **24**, 16-mer **25**, and 24-mer **26**.

The protected oligomers exhibit good solubility in numerous common solvents; they are moderately soluble in tetrahydrofuran and hot alcohols, highly soluble in toluene, and extremely soluble in dichloromethane and chloroform. Removal of the *tert*-butyl carbamate groups decreases the solubility of the materials considerably; however, the deprotected oligoanilines are sufficiently soluble in polar aprotic solvents such as *N*,*N*-dimethylformamide and *N*-methylpyrrolidinone to permit their characterization by UV−vis spectroscopy and the casting of films for electrochemical studies. Deprotected oligoanilines as long as the decamer could be characterized by ^{1}H NMR. To examine the solubilizing influence of alkyl groups at the termini of oligoanilines, we prepared the bis(*tert*-butyl)- and bis(*n*-dodecyl)-substituted octaanilines **27c** and **27d**, but these exhibited the same solubility as the other oligoanilines. In any case, the facile cleavage of the BOC groups allows them to function as removable solubilizing groups.

Oligomer Deprotection. Thermolysis of the protected oligomers under an inert atmosphere results in clean and quantitative removal of the BOC group,[29] affording the oligoaniline in its lowest oxidation state as shown in Scheme 9. Infrared spectroscopy of a thin film of **18a** on a NaCl plate, heated under argon at 185 °C, showed that the complete disappearance of the carbonyl absorption required a reaction time of approximately 7 h. Likewise,^{1}H NMR spectroscopy of **18a**, heated at 185 °C in DMSO-d_6 solution, indicated a reaction time of nearly 7 h for the complete loss of the *tert*-butyl resonance. The preparation of octaanilines **27a**−**e** was accomplished by heating the powders in Schlenk tubes under argon for 9 h.

(22) For a review of electrophilic substitutions of arylsilanes, see: Bennetau, B.; Dunogues, J. *Synlett* **1993**, 171−176.

(23) Wessjohann, L.; McGaffin, G.; de Meijere, A. *Synthesis* **1989**, 359−363.

(24) Fasth, K.-J.; Antoni, G.; Långström, B. *J. Chem. Soc., Perkin Trans. 1* **1988**, 3081−3084.

(25) This compound had been obtained previously by an analogous sequence using 4-bromo-*N*,*N*-bis(trimethylsilyl)aniline: Walton, D. R. M. *J. Chem. Soc. C* **1966,** 1706−1707. We found it more convenient to use the crystalline and moisture-stable *N*-(diphenylmethylene)-4-bromoaniline.

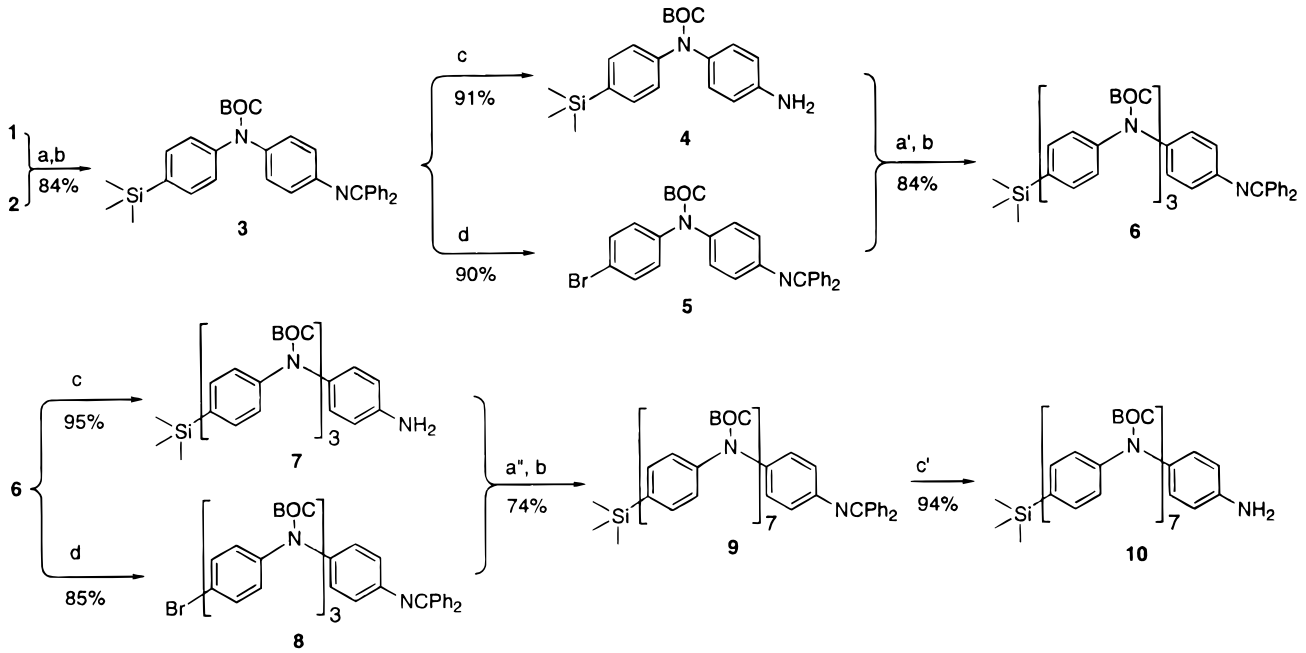
(26) For reasons of availability at the time that this work was carried out, we employed *S*-BINAP. The significantly less expensive racemic form, now available commercially from Strem Chemical Company, is an equally effective ligand in these coupling reactions, with no observable differences in yields.

(27) The corresponding N_3-diamine, a core piece for odd-numbered oligomers, has been prepared; see ref 19m.

(28) Berthelot, J.; Guette, C.; Essayegh, M.; Desbene, P. L.; Basselier, J. J. *Synth. Commun.* **1986**, *16*, 1641−1645.

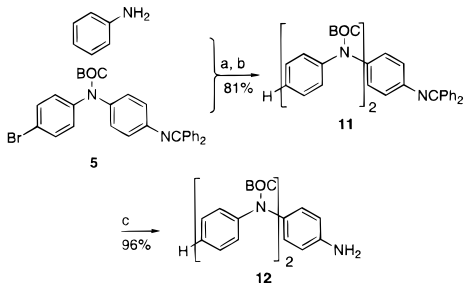
(29) Thermal deprotection of BOC-protected pyrroles and indoles has been reported to proceed more rapidly: Rawal, V. H.; Jones, R. J.; Cava, M. P. *J. Org. Chem.* **1987**, *52*, 19−28.

Scheme 3[a]



[a] Key: (a) $Pd_2(dba)_3$ (0.25 mol %), *S*-BINAP[26] (0.75 mol %), NaO*t*Bu (1.4 equiv), THF, reflux; (a′) $Pd_2(dba)_3$ (1 mol %), *S*-BINAP (2.4 mol %), NaO*t*Bu (1.4 equiv), toluene, 80 °C; (a″) $Pd_2(dba)_3$ (2 mol %), *S*-BINAP (4.8 mol %), NaO*t*Bu (1.4 equiv), toluene, 80 °C; (b) $(BOC)_2O$ (1.3 equiv), 4-DMAP (0.2 equiv), THF, reflux; (c) $NH_4^+HCO_2^-$ (12 equiv), 10% Pd/C (0.1 equiv of Pd), THF/CH_3OH, 60 °C; (c′) $NH_4^+HCO_2^-$ (>30 equiv), 20% $Pd(OH)_2$/C (0.5 equiv of Pd), *i*PrOH, 80 °C; (d) NaOAc (1 equiv), Br_2 (2 equiv), THF, −78 °C to 0 °C.

Scheme 4[a]

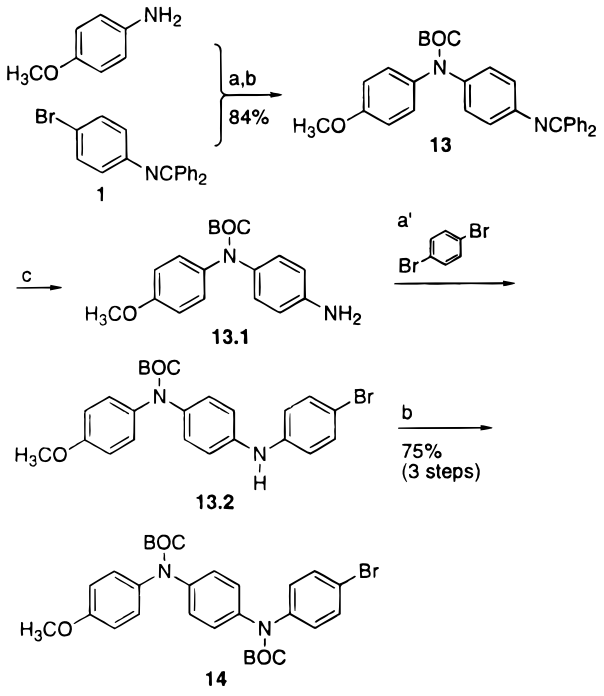


[a] Key: (a) $Pd_2(dba)_3$ (1 mol %), *S*-BINAP (2.5 mol %), NaO*t*Bu (1.4 equiv), toluene, 80 °C; (b) $(BOC)_2O$ (1.5 equiv), 4-DMAP (0.2 equiv), THF, 60 °C; (c) 5% Pd/C (0.1 equiv of Pd), $NH_4^+HCO_2^-$ (15 equiv), THF/CH_3OH, 60 °C.

Alternatively, the BOC group may be cleaved using iodotrimethylsilane. The protected oligomers react rapidly with iodotrimethylsilane to form the corresponding trimethylsilyl carbamates.[30] The trimethylsilyl carbamate group confers the same solubility as the *tert*-butyl carbamate but is extremely labile in the presence of moisture or protic solvents. For preparative purposes, a solution of the trimethylsilyl carbamate is prepared in dichloromethane; subsequent addition of excess methanol causes the deprotected oligoaniline to precipitate immediately. Phenyl-capped heptaaniline (**28**), nonaaniline (**29**), decaaniline (**30**), 16-mer (**31**), and 24-mer (**32**) were prepared by this method, as shown in Scheme 10. Note that the acid generated upon reaction of the remaining iodotrimethylsilane with methanol effects the protodesilylation of arylsilanes **23**−**26** in the same operation. Octaanilines prepared by this method were analytically and spectroscopically identical to those prepared by thermolysis. Solutions of the trimethylsilyl carbamates in dichloromethane may be cast into films, which are converted to their redox-active, deprotected forms by immersion in alcohols or in aqueous solutions. All samples used in electrochemical studies were prepared in this manner.

(30) Removal of benzyl and *tert*-butyl carbamate groups from peptides using TMSI is well-known: Lott, R. S.; Chauhan, V. S.; Stammer, C. H. *J. Chem. Soc., Chem. Commun.* **1979**, 495−496.

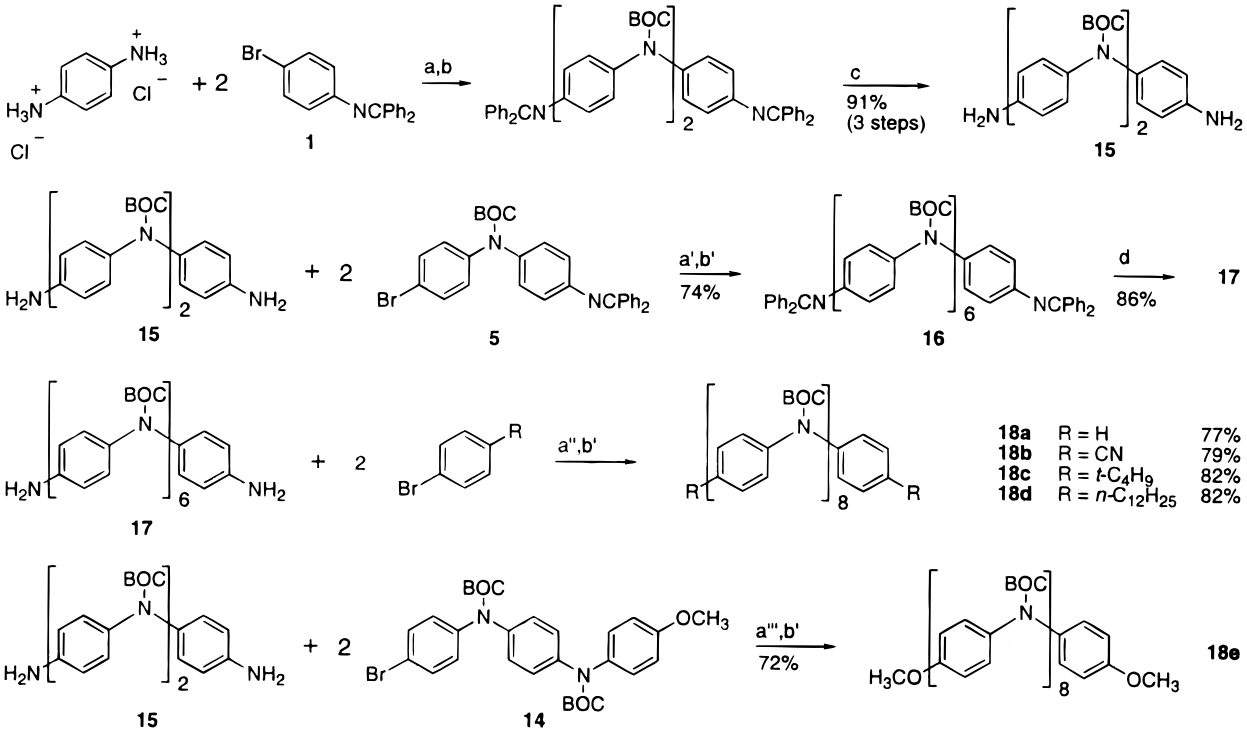
Scheme 5[a]



[a] Key: (a) $Pd_2(dba)_3$ (0.5 mol %), *S*-BINAP (1.5 mol %), NaO*t*Bu (1.4 equiv), THF, reflux; (a′) $Pd_2(dba)_3$ (1 mol %), *S*-BINAP (3 mol %), NaO*t*Bu (1.4 equiv), THF, reflux; (b) $(BOC)_2O$ (1.5 equiv), 4-DMAP (0.1 equiv), THF, reflux; (c) 20% $Pd(OH)_2$/C (0.1 equiv of Pd), $NH_4^+HCO_2^-$ (20 equiv), EtOH, 60 °C.

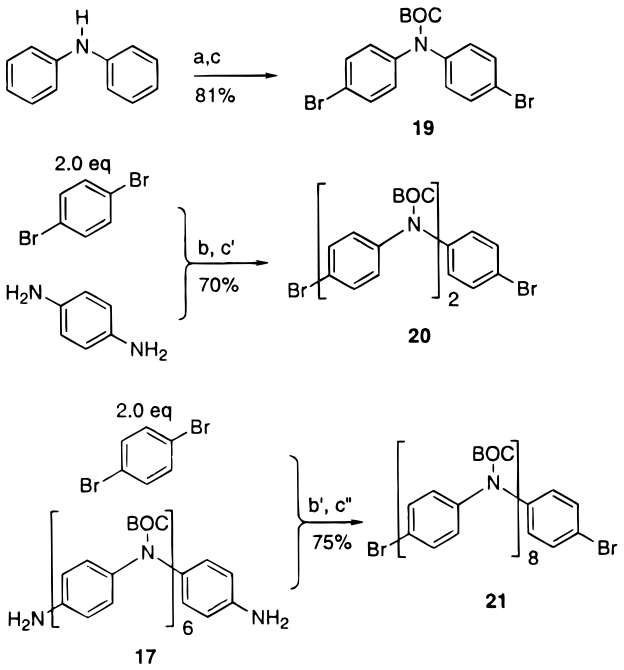
Oxidation States of Aniline Oligomers. The lowest oxidation state of polyaniline is the insulating leucoemeraldine form, in which all nitrogen atoms are neutral and sp^3-hybridized, and all aromatic rings are in the benzenoid form. Oxidation of half

Scheme 6[a]



[a] Key: (a) $Pd(OAc)_2$ (1 mol %), *S*-BINAP (1.5 mol %), NaO*t*Bu (4.5 equiv), toluene, 80 °C; (a′) $Pd_2(dba)_3$ (6 mol %), *S*-BINAP (7 mol %), NaO*t*Bu (2.8 equiv), toluene/Et_3N, 90 °C; (a″) $Pd_2(dba)_3$ (2 mol %), *S*-BINAP (6 mol %), NaO*t*Bu (2.5 equiv), THF, reflux; (a‴) $Pd_2(dba)_3$ (2 mol %), *S*-BINAP (5 mol %), NaO*t*Bu (2.5 equiv), toluene, 80 °C; (b) $(BOC)_2O$ (3 equiv), 4-DMAP (0.1 equiv), THF/toluene, reflux; (b′) $(BOC)_2O$ (3 equiv), 4-DMAP (0.1 equiv), THF, reflux; (c) $H_2NOH{\cdot}HCl$ (2.5 equiv), pyridine (4 equiv), $CHCl_3$/THF/EtOH, room temperature; (d) 20% $Pd(OH)_2/C$ (0.4 equiv of Pd), $NH_4^+HCO_2^-$ (20 equiv), THF/EtOH, 70 °C.

Scheme 7[a]



[a] Key: $(n\text{-}C_4H_9)_4N^+Br_3^-$ (2 equiv), CH_2Cl_2, room temperature, 5 min; (b) $Pd_2(dba)_3$ (1.2 mol %), *S*-BINAP (3.7 mol %), NaO*t*Bu (2.6 equiv), THF, reflux; (b′) $Pd(OAc)_2$ (4 mol %), *S*-BINAP (4.8 mol %), NaO*t*Bu (2.6 equiv), toluene/Et_3N, 90 °C; (c) $(BOC)_2O$ (1.1 equiv), 4-DMAP (0.2 equiv), THF, reflux; (c′) $(BOC)_2O$ (3.5 equiv), 4-DMAP (0.2 equiv), THF, reflux; (c″) $(BOC)_2O$ (3.5 equiv), 4-DMAP (0.1 equiv), THF/toluene/Et_3N, 67 °C.

of the phenylenediamine moieties to their quinoid forms results in the insulating emeraldine form, which becomes conductive when the imine nitrogen atoms are protonated. This form has been described as a repeating semiquinoid cation to explain its paramagnetism and electrical conductivity. Oxidation of all phenylenediamine moieties to their quinoid forms gives rise to the pernigraniline form, with significant (though not necessarily complete) deprotonation under most conditions. Even when generated by oxidation under extremely nonbasic conditions, and thus probably in its fully protonated form, pernigraniline is an insulator.[31] These oxidation states are illustrated in Figure 2.

Electrochemical studies of polyaniline show two oxidation waves of equal intensity, consistent with the transitions shown in Figure 2. In contrast, the cyclic voltammogram of phenyl-capped octaaniline, published by Wudl,[32] displays a distinct split in the second oxidation wave, suggesting an intermediate "nigraniline" form[33] in the oxidation from the emeraldine to the pernigraniline form.

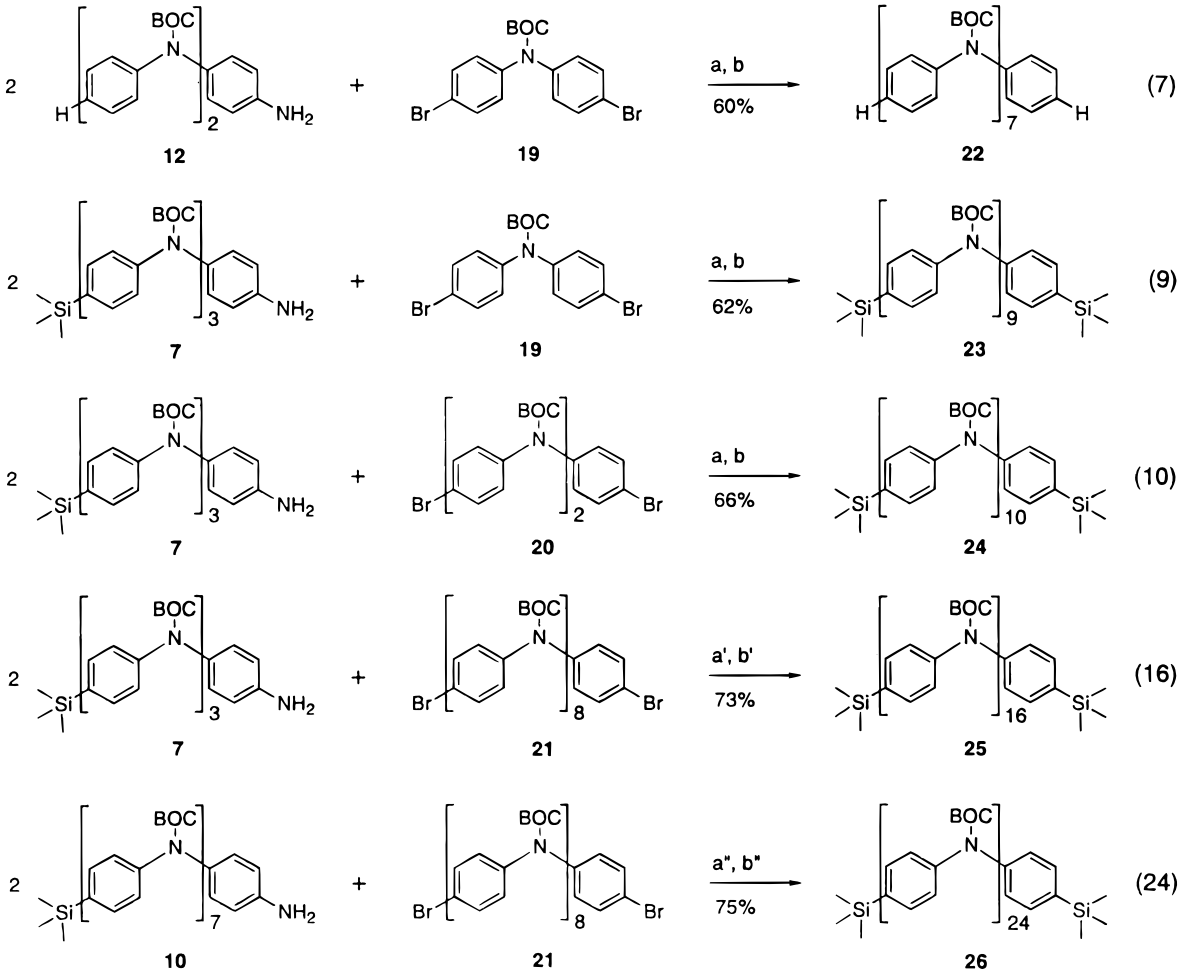
We wished to investigate effects of susbtitution in octaanilines and the effects of chain length on oligoaniline redox behavior. We have examined the oligoanilines in varying degrees of oxidation and protonation by UV−vis spectroscopy and have studied their electrochemical behavior by cyclic voltammetry.

(31) Ofer, D.; Crooks, R. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 7869−7879. For other discussions of polyaniline oxidation states, see: refs 3−5.

(32) Wudl, F.; Angus, R. O.; Lu, F. L.; Allemand, P. M.; Vachon, D. J.; Nowak, M.; Liu, Z. X.; Heeger, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 3677−3684.

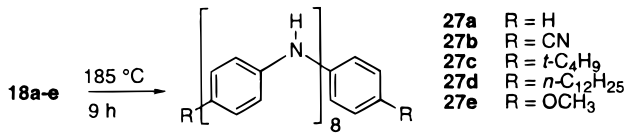
(33) Early studies described a "nigraniline" oxidation state in polyaniline. Described as an intermediate between emeraldine and pernigraniline, it may well have been a mixture of the two. This possibility was not discussed, and the evidence was inconclusive: (a) Willstätter, R.; Dorogi, S. *Chem. Ber.* **1909**, *42*, 2147−2168. (b) Willstätter, R.; Dorogi, S. *Chem. Ber.* **1909**, *42*, 4118−4135. (c) Green, A. G.; Woodhead, A. E. *J. Chem. Soc.* **1910**, *97*, 2388−2403. (d) Green, A. G.; Woodhead, A. E. *J. Chem. Soc.* **1912**, *101*, 1117−1123.

Scheme 8[a]



[a] Key: (a) $Pd_2(dba)_3$ (2 mol %), *S*-BINAP (4.8 mol %), NaO*t*Bu (2.9 equiv), toluene, 80 °C; (a′) $Pd(OAc)_2$ (4 mol %), *S*-BINAP (4.8 mol %), NaO*t*Bu (2.8 equiv), toluene/Et_3N, 90 °C; (a″) $Pd(OAc)_2$ (6 mol %), *S*-BINAP (7.2 mol %), NaO*t*Bu (3 equiv), toluene/Et_3N, 90 °C; (b) $(BOC)_2O$ (2.5 equiv), 4-DMAP (0.5 equiv), THF, 60 °C; (b′) $(BOC)_2O$ (3.5 equiv), 4-DMAP (0.1 equiv), THF/toluene/Et_3N, 67 °C; (b″) $(BOC)_2O$ (4 equiv), 4-DMAP (0.2 equiv), THF/toluene/Et_3N, 67 °C.

Scheme 9

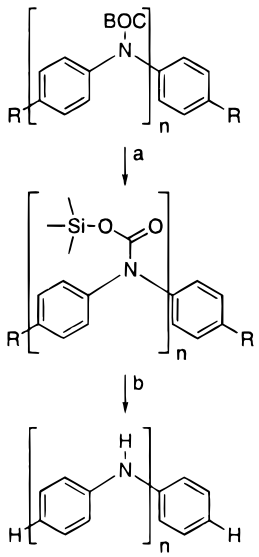


27a R = H
27b R = CN
27c R = *t*-C_4H_9
27d R = *n*-$C_{12}H_{25}$
27e R = OCH_3

Electronic Absorption Spectroscopy. Under neutral conditions, the UV−vis spectra of the oligoanilines (**27**−**32**) in a given oxidation state are essentially identical; no significant changes result from substitution or from variations in chain length. The leucoemeraldine forms exhibit a single strong absorption at 334−338 nm; lower-energy transitions are observed for the partially and fully oxidized states. Oxidation of a colorless leucoemeraldine solution in dilute DMF by silver(I) oxide results in an intense blue-purple solution of the emeraldine base, with a sharp peak at 320 nm and a broad band at 620 nm. Silver(II) oxide in DMF converts the leucoemeraldine to a red-pink pernigraniline solution, with a sharp peak at 320 nm and a broad band at 520 nm. The strong blue shift of this band, compared to that of emeraldine, reflects the decreased charge-transfer absorption in the pernigraniline state.

The addition of a drop of sulfuric acid (a large excess) to the UV−vis samples of the emeraldine and pernigraniline forms produces a green color. Protonation of the emeraldine causes the higher-energy absorption to broaden and split; the lower-energy absorption begins at ca. 540 nm and increases in intensity up to the spectrometer's limit at 1050 nm. In the case of the pernigraniline, the lower-energy absorption is broadened, and

Scheme 10[a]



n = 7, R = H: **22**
n = 9, R = $Si(CH_3)_3$: **23**
n = 10, R = $Si(CH_3)_3$: **24**
n = 16, R = $Si(CH_3)_3$: **25**
n = 24, R = $Si(CH_3)_3$: **26**

n = 7: **28**
n = 9: **29**
n = 10: **30**
n = 16: **31**
n = 24: **32**

[a] Key: (a) $(CH_3)_3SiI$ (1.2n equiv), CH_2Cl_2, room temperature; (b) CH_3OH (excess), Et_3N, CH_2Cl_2, room temperature.

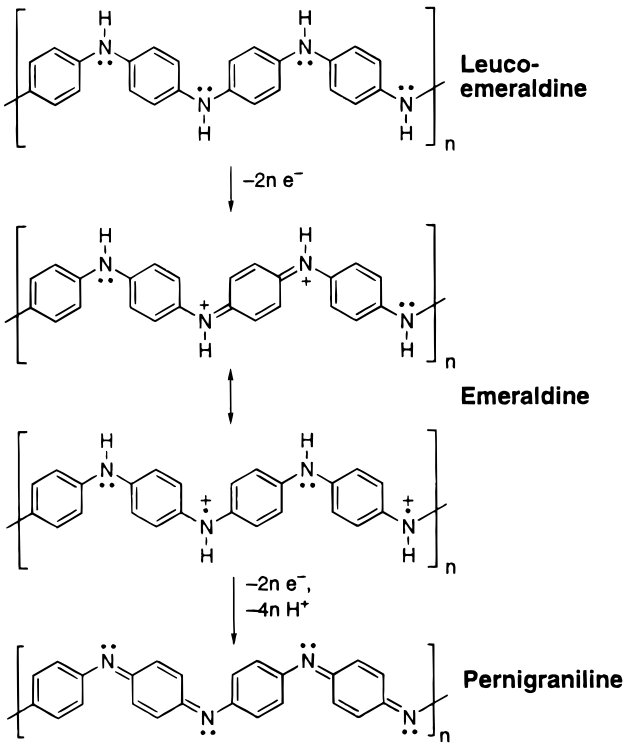


Figure 2. Principal oxidation states of polyaniline.

its maximum is red-shifted from 520 to 830 nm. The UV−vis spectra of phenyl-capped octaaniline (**27a**) are shown in Figure 3.

The spectra of the protonated emeraldine forms vary considerably with changes in electron density or in chain length, as shown in Figure 4. The absorbance in the near-IR region of **27** becomes more intense with the increase in electron density from the cyano-substituted to the methoxy-substituted octamer. The twin peaks at higher energy, of nearly equal intensity for phenyl-capped octaaniline, show complementary patterns for the cyano- and methoxy-substituted analogues. A comparison of the spectra for different chain lengths shows subtle differences between heptamer, nonamer, and decamer; the distinct curvature in the shape of the near-IR absorption contrasts with the near-linear slope observed for the octamer. In the longer oligomers (16-mer and 24-mer), this absorption shows a much more definite maximum, occurring at somewhat shorter wavelengths.

Electrochemistry. Cyclic voltammetry of the oligoanilines affords valuable insight into the electronic structures of the oxidized forms. We wished to examine, for instance, whether the presence of electron-donating or electron-withdrawing groups at the chain ends would affect the redox behavior of phenyl-capped octaaniline, or whether the electronic effects would be insignificant for the chain as a whole. The salient question with regard to chain length is the behavior of those oligoanilines that do not correspond to the tetraaniline-based model depicted in Figure 2. Phenyl-capped heptaaniline, nonaaniline, and decaaniline behave quite similarly to the octaaniline upon chemical oxidation, but the nature of the "emeraldine" and "pernigraniline" forms obtained for these chain lengths is not obvious a priori. If the oligoaniline framework were able to stabilize radical cations effectively, either by resonance or by π-stacking between chains,[34] several odd-electron states would be accessible for the heptamer and

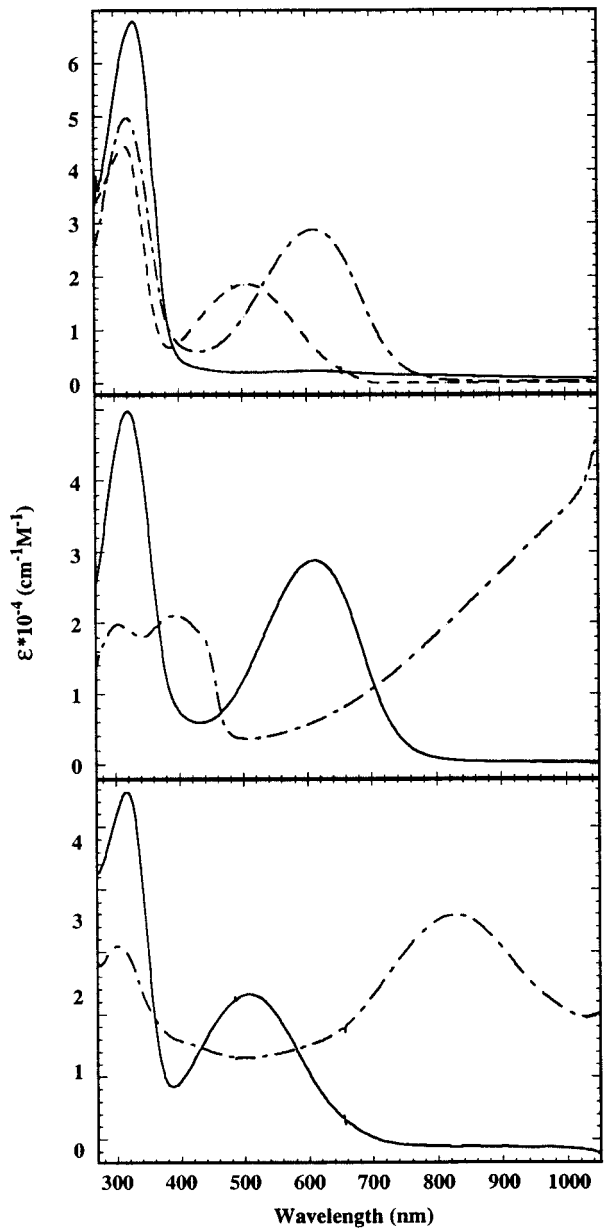


Figure 3. UV−vis spectra of phenyl-capped octaaniline (**27a**) in DMF. (top) Leucoemeraldine, ——; emeraldine, — -; pernigraniline, — —. Emeraldine (middle) and pernigraniline (bottom): in neutral solution, ——; acidified, — -.

nonamer, and the decamer emeraldine might be the five-electron oxidation product, containing five equivalent semiquinoid moieties.

The electrochemical studies discussed below employed thin films of the oligoanilines on ITO (indium−tin oxide) coated glass electrodes. The films were prepared by evaporation of a dilute solution of the trimethylsilyl carbamate in dichloromethane, followed by immersion in the electrolyte, dilute aqueous sulfuric acid.[35] The first cycle of each film indicated significant loss of material (approximately 20−30%) during the reduction,[36] but the films exhibited good stability after this break-in scan.

(34) For a review of π-dimers and π-stacks in conducting polymers, see: Miller, L. L.; Mann, K. R. *Acc. Chem. Res.* **1996**, *29*, 417−423.

(35) The indium−tin oxide coating is known to be unstable to strong acids; however, immersion of the slides in 1.0 M sulfuric acid, for the short time periods involved in these CV studies, caused no discernible degradation.

(36) The cause of this material loss is unclear. It is possible that the evolution of carbon dioxide during hydrolysis causes blistering of the films, with some initial physical instability.

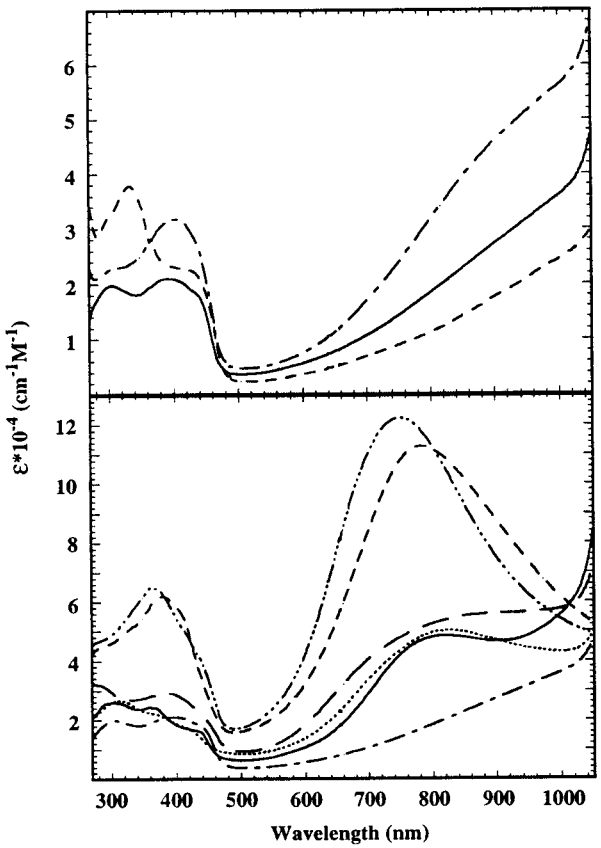


Figure 4. (top) α,ω-Substituent effects upon the protonated emeraldine form of phenyl-capped octaanilines in DMF: H (**27a**), ——; CN (**27b**), — — —; OCH_3 (**27e**), — -. (bottom) Protonated emeraldines of phenyl-capped oligoanilines in DMF: 7-mer (**28**), ——; 8-mer (**27a**), — -; 9-mer (**29**), ···; 10-mer (**30**), — — —; 16-mer (**31**), - - -; 24-mer (**32**), — - - -.

In dilute hydrochloric acid, the major peaks diminish in intensity with each scan, while a broad peak grows in at ca. 0.55 V in the oxidation wave and 0.40 V in the reduction wave. This degradation had been observed previously for both phenyl-capped octaaniline and bulk polyaniline.[32] In dilute sulfuric acid, however, this degradation occurs more slowly.

Integration of the oxidation peaks of phenyl-capped octaaniline (5.0 nanomoles) in the first scan corresponded reproducibly, within 2%, to the removal of eight electrons per molecule, but the oxidations occurred at markedly higher potentials than in subsequent scans. The reduction peaks in the first scan represent a significantly smaller area than the oxidation peaks, but subsequent scans showed good reversibility. In the discussion of oxidation states below, the total number of electrons removed from each molecule is determined by integration of the oxidation peaks in the first scan; the oxidation states of each compound are determined by comparison of the relative peak areas in the second (i.e., first stable) scan.

Phenyl-capped octaaniline (**27a**) oxidizes from the leucoemeraldine to the emeraldine form in one four-electron step. In contrast, the oxidation from emeraldine to pernigraniline shows a split, with peaks at 0.79 and at 0.90 V. This split is highly sensitive to changes in electron density at the chain termini. The methoxy groups of **27e** cause a larger split in the emeraldine-pernigraniline oxidation wave, with peaks at 0.66 and at 0.87 V, whereas the cyano groups of **27b** cause the split to disappear entirely, with a smooth four-electron oxidation centered at 0.84 V. This disparity is consistent with formation of the nigraniline form, with three quinoid moieties, by a two-electron oxidation of emeraldine. The greater partial positive charge adjacent to the chain ends, compared to the emeraldine state, would be stabilized by resonance with the methoxy group, as shown in Figure 5, and destabilized by conjugation with the cyano group.

Figure 6 shows the cyclic voltammograms obtained for **27**−**30**, with proposed oxidation mechanisms for some of the oxidation steps. The intermediates are depicted in their expected major resonance forms. For many of the intermediates the degree of protonation may vary, and several tautomers may exist in addition to those shown.

In the cyclic voltammogram of phenyl-capped heptaaniline, two reversible oxidations occur as the potential is increased from −0.3 to 0.95 V. Integration of the first scan for a known film quantity showed that only six electrons were removed per molecule of heptaaniline, reproducibly within 3%. Comparison of the areas of the two oxidation peaks showed the first to be approximately twice as large as the second,[37] suggesting that the heptaaniline undergoes a four-electron oxidation followed by a two-electron oxidation.

Similarly, oxidation of phenyl-capped nonaaniline within the same potential range results in the removal of only eight electrons per molecule. The cyclic voltammogram displays two oxidation waves, corresponding in area to two four-electron oxidations. The second of these displays a prominent shoulder at the left side. We believe that the extra nitrogen lone pair, relative to phenyl-capped octaaniline, allows oxidation to a mixture of several nonequivalent but energetically similar nigraniline-like states, beginning at relatively low potentials, en route to the formation of the eight-electron oxidation product.

Oxidation of phenyl-capped decaaniline from −0.3 to 1.0 V results in the removal of 10 electrons, consistent with the conversion of all five phenylenediamine moieties to their quinoid forms. The cyclic voltammogram displays two oxidation waves, the first of which encompasses approximately 50% more area than the second.[37] The oxidation of phenyl-capped decaaniline thus appears to proceed via a six-electron oxidation, followed by a four-electron oxidation.

The simplest electrochemical behavior is that of the 16-mer (**31**) and the 24-mer (**32**). Cyclic voltammograms of these oligomers are shown in Figure 7; due to the high molecular weight of **32**, a smaller molar quantity (2.5 nmol) was used to obtain a thin film. In contrast to phenyl-capped octaaniline, these longer tetraaniline multiples display no distinct intermediate in the oxidation of their emeraldine forms. The oxidation from the leucoemeraldine to the pernigraniline state, like that of the bulk polymer, results in two peaks of equal area.

The even-numbered oligomers investigated here are stable at potentials up to and beyond +1.0 V vs SCE, and polyaniline in nonnucleophilic solvents has been found to be stable at very high potentials.[31] In marked contrast, the odd-numbered oligomers are unstable at potentials above 0.95 V (Figure 8). At higher potentials a third oxidation peak is observed, at 1.07 V for the heptaaniline and 1.08 V for the nonaaniline, with no corresponding reduction peak. This two-electron oxidation occurs only once for each film: a second scan to 1.25 V fails to reproduce this peak, and the voltammogram resembles that of an even-numbered oligomer.

The irreversibility of the oxidation, and the fact that no corresponding peak is observed for even-numbered oligomers, is consistent with the formation of a highly unstable odd-electron

(37) Some ambiguity is involved in assigning the peak areas, but the first peak is clearly larger, in the CVs of both the heptaaniline and the decaaniline, for any reasonable choice of demarcation. The narrow peak at high potential is smaller than it appears.

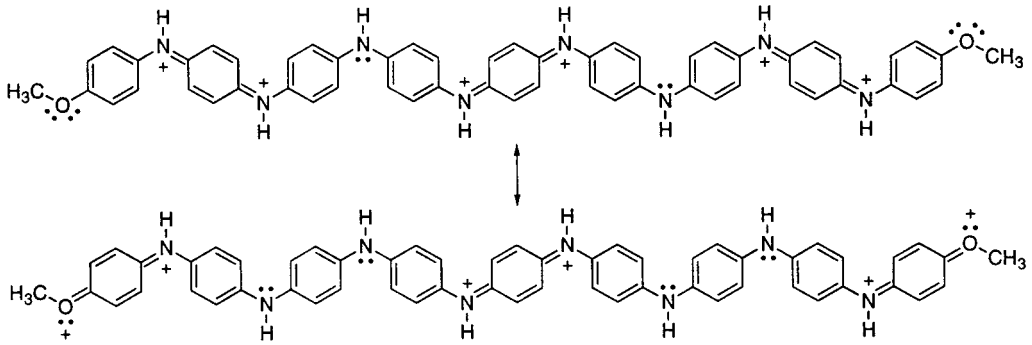


Figure 5. Stabilization of the nigraniline oxidation state by π-donating substituents.

species, followed by decomposition to a species which undergoes facile one-electron oxidation. The oxidation pattern does not rule out the tail-to-tail dimerization of the radical cation, followed by dehydrogenation, but the product of this reaction should be reduced easily to a benzidine derivative during the reduction wave. Intramolecular C−C bond formation by the odd-electron cation, followed by deprotonation and one-electron oxidation to the carbazole, represents one possible explanation for the observed behavior. Since the carbazole moiety is quite difficult to oxidize,[38] the product would contain an even number of redox-active nitrogen atoms, and the formation of additional carbazole units during a subsequent scan would not be expected. Figure 9 illustrates the proposed carbazole formation; for simplicity, only one product is shown, although the cyclization could also occur in the middle of the chain.

Concluding Remarks

Using palladium catalysis and an orthogonal protective group strategy, we have developed divergent−convergent and convergent methods for the synthesis of well-defined, air-stable oligoaniline precursors, soluble in a variety of common organic solvents. These precursors are easily deprotected to form the leucoemeraldine forms of the corresponding oligoanilines. The synthetic methods are highly versatile, allowing the synthesis of end-functionalized oligoanilines, and the preparation of even or odd chain lengths.

The presence of electron-donating or electron-withdrawing groups at the chain ends results in significant modifications of the UV−vis spectra and electrochemical behavior of phenyl-capped octaaniline. An increase in electron density results in more intense electronic absorption by the emeraldine in the low band gap region and stabilizes the electrochemically observed nigraniline state. The electrochemistry of the heptamer, nonamer, and decamer illustrates the importance of electron-pairing in the redox behavior of these compounds. Oxidation of oligoanilines occurs through even-electron transitions when possible; thus, the decamer oxidizes in unequal steps, and the odd-numbered oligomers generate radical cations only transiently and at high potential. Our observations suggest that the ability of polyaniline to stabilize an unpaired electron through resonance or π-stacking is limited.

Experimental Section

General Information. Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on Varian XL-300, UN-300, or XL-500 spectrometers and referenced with respect to residual solvent. The letter "a" before a multiplicity notation indicates an apparent multiplicity. Infrared spectroscopy was carried out on a Perkin-Elmer 1600 Series FT-IR spectrometer. UV−vis spectra were obtained using a Hewlett-Packard 8451A or 8453A spectrophotometer. FAB mass spectra were recorded on a Finnigan MAT System 8200 using a 3-nitrobenzyl alcohol matrix. Elemental analyses were carried out by E & R Microanalytical Laboratory Inc., Corona, NY. Gas chromatographic analyses were carried out on a Hewlett-Packard HP-5890 Series II gas chromatograph, fitted with an HP-1 capillary column (25 m, 0.20 mm, 0.11 μm). Thin-layer chromatography was carried out on E. Merck SIlica Gel 60 F-254 TLC plates. Melting points were obtained using a Haake Buchler melting point apparatus and are uncorrected.

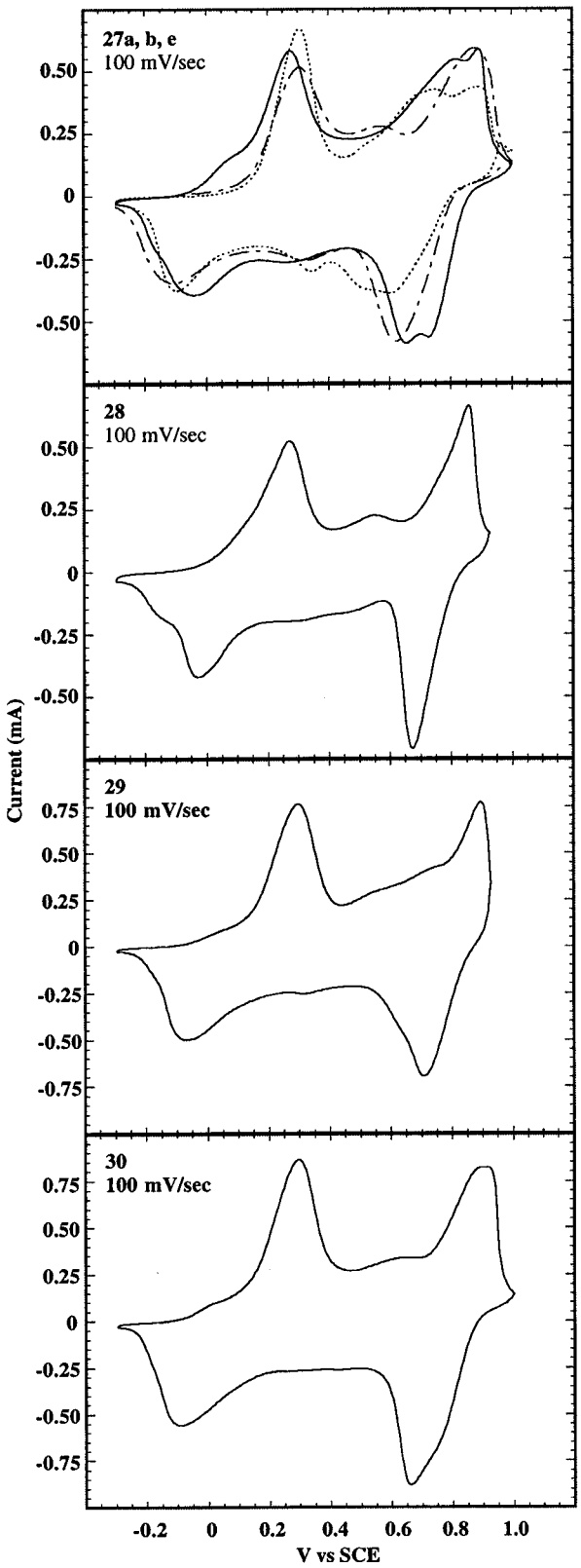
Reactions under an argon atmosphere were carried out in oven-dried glassware using standard Schlenk techniques. Tetrahydrofuran was distilled under argon from sodium benzophenone ketyl. Toluene was distilled under nitrogen from molten sodium. Dichloromethane used in oligomer deprotections was purchased in anhydrous form from Aldrich Chemical Co. and stored under nitrogen over activated 3 Å molecular sieves. Absolute ethanol was purchased from Pharmco and used as supplied. Diethyl ether, analytical reagent grade, was purchased from Mallinckrodt and used as supplied. *N*-Methylpyrrolidinone, anhydrous, and *N*,*N*-dimethylformamide, reagent grade, were purchased from Aldrich Chemical Co. and used as supplied. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as supplied. All other solvents were of liquid chromatography grade quality, purchased from EM Science and used as supplied.

Molecular sieves were purchased from Aldrich Chemical Co. and activated at 180 °C and 10^{-3} mmHg for 12 h prior to use. Sodium *tert*-butoxide was purchased from Aldrich Chemical Co. and stored in a Vacuum Atmospheres glovebox under nitrogen. Small amounts were removed from the glovebox as needed, stored in a desiccator for up to 1 week, and weighed in the air. 4-Bromoaniline, benzophenone, chlorotrimethylsilane, *p*-anisidine, di-*tert*-butyl dicarbonate solution (1.0 M in tetrahydrofuran), tetra-*n*-butylammonium tribromide, palladium hydroxide (moist, 20% on carbon), 1,4-phenylenediamine dihydrochloride, aniline, diphenylamine, 4-bromo-*tert*-butylbenzene, 4-bromobenzonitrile, ammonium formate, hydroxylamine hydrochloride, and hexamethyldisilane were purchased from Aldrich Chemical Co. and used as supplied. Di-*tert*-butyl dicarbonate and 4-(dimethylamino)-pyridine were purchased from Lancaster Synthesis Inc. and used as supplied. 4-Bromo-*n*-dodecylbenzene was purchased from TCI America and used as supplied. *S*-BINAP, a gift from Pfizer, was used as supplied. Tris(dibenzylideneacetone)dipalladium, palladium acetate, palladium on carbon, *n*-butyllithium (1.60 M in hexanes), and bromine were purchased from Strem Chemical Company and used without further purification. All other inorganic reagents were analytical reagent grades purchased from Mallinckrodt and used as supplied.

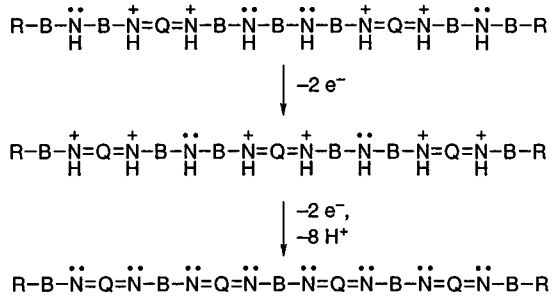
Synthesis. *N*-(Diphenylmethylene)-4-bromoaniline (1). The method of Taguchi and Westheimer[39] was modified as follows: Benzophenone (455 g, 2.50 mol) and 4-bromoaniline (473 g, 2.75 mol) were dissolved in toluene (1.2 L, distilled) under argon in a 5 L flask, containing molecular sieves (5 Å, 1.25 kg), fitted with a reflux condenser, rubber septum, and pressure outlet. The mixture was heated to gentle reflux

(38) Carbazole itself undergoes anodic oxidation at +1.16 V relative to SCE: Ambrose, J. F.; Nelson, R. F. *J. Electrochem. Soc.* **1968**, *115*, 1159−1164. Conjugation of the carbazole moiety with a protonated iminoquinone might well raise the oxidation potential beyond the range investigated here.

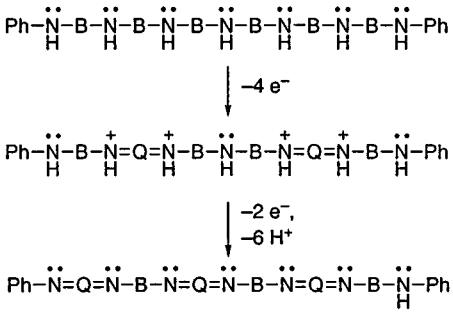
(39) Taguchi, K.; Westheimer, F. H. *J. Org. Chem.* **1971**, *36*, 1570−1572.



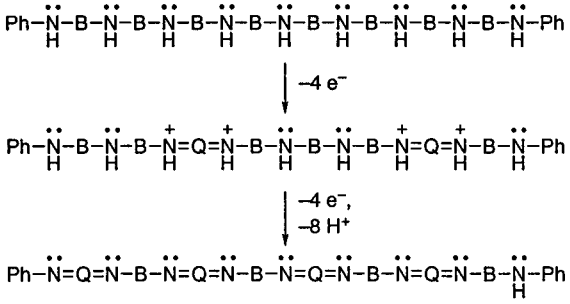
Phenyl-Capped Octaanilines:



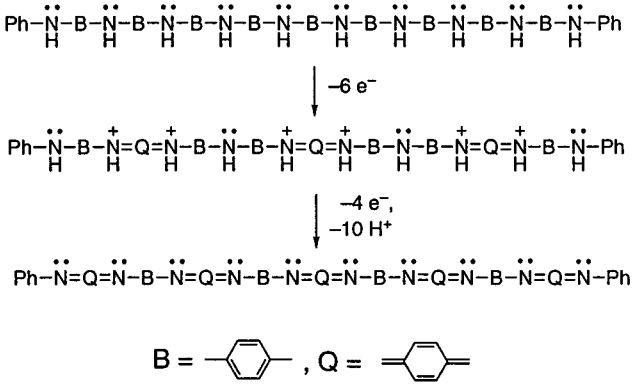
Phenyl-Capped Heptaaniline:



Phenyl-Capped Nonaaniline:



Phenyl-Capped Decaaniline:



B = , Q =

Figure 6. Cyclic voltammetry of phenyl-capped heptaaniline (**28**), octaanilines **27** (H, **27a**, ——; CN, **27b**, — -; OCH_3, **27e**, ···), nonaaniline **29**, and decaaniline **30** on ITO (working electrode) in aqueous H_2SO_4 (1.0 M). Proposed oxidation mechanisms at right.

and shaken occasionally; an intense yellow color soon developed. Analysis by GC after 18 h showed that product formation was nearly complete. The mixture was allowed to cool to room temperature, and the yellow solution was decanted from the molecular sieves, which were washed with diethyl ether until the filtrate was colorless. The organic solutions were combined and concentrated to give an orange oil, 900 mL. Methanol (ca. 80 mL) and a seed crystal of authentic product were added. The product was allowed to crystallize at 0 °C and collected by filtration. The mother liquor was further concentrated. A second crop of crystals formed and was isolated by filtration. Recrystallization of the combined product from methanol afforded the title compound as yellow crystals (760 g, 90%): mp 82−83 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (dd, J = 6.9, 1.6 Hz), 7.52−7.39 (m, 3H), 7.32−7.23 (m, 5H), 7.11 (dd, J = 8.4, 1.9 Hz, 2H), 6.61 (dt, J =

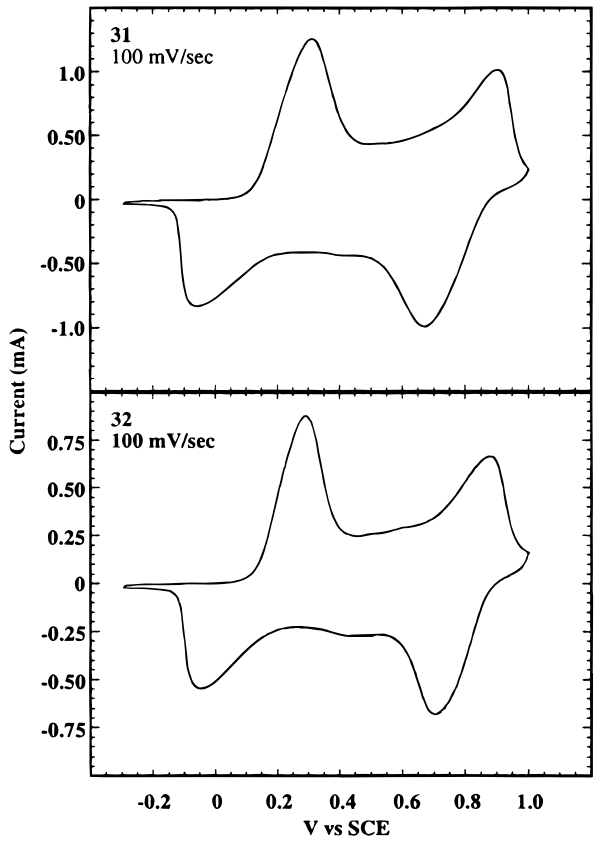


Figure 7. Cyclic voltammetry of phenyl-capped 16-mer (**31**) and phenyl-capped 24-mer (**32**), same conditions as above.

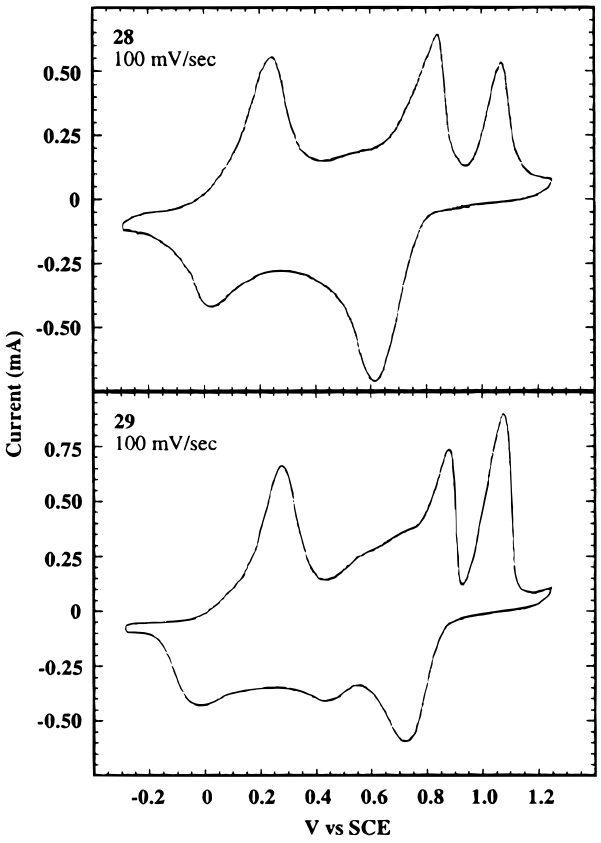


Figure 8. Irreversible oxidation of phenyl-capped heptaaniline (**28**) and nonaaniline (**29**) at high potential, same conditions as above.

8.5, 2.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.7, 150.4, 139.5, 136.1, 131.6, 131.0, 129.5, 128.8, 128.3, 128.2, 122.8, 116.3, 103.6;

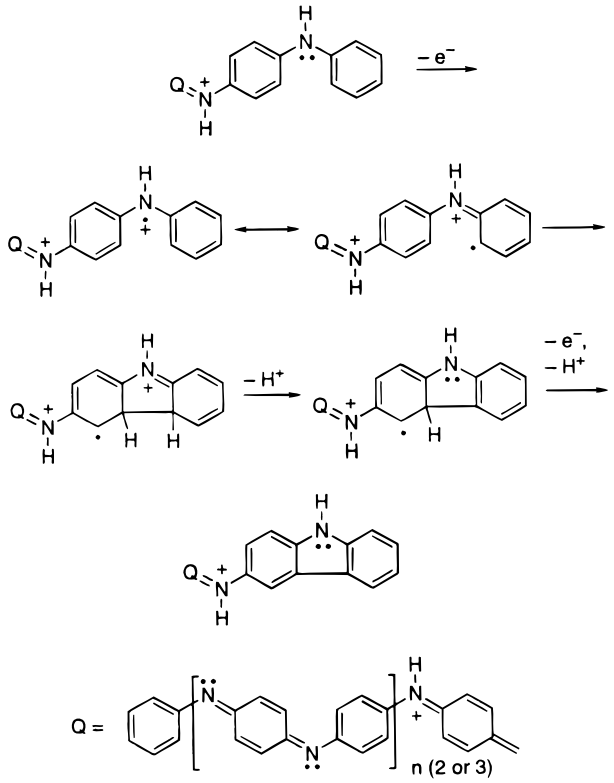


Figure 9. Proposed carbazole formation in odd-numbered oligoanilines at high potential.

IR (neat, cm^{-1}) 3058, 3024, 1615, 1478. Anal. Calcd for $C_{19}H_{14}BrN$: C, 67.87; H, 4.20. Found: C, 68.08; H, 4.28.

4-(Trimethylsilyl)aniline (2).[25] Aryl bromide **1** (16.8 g, 50.0 mmol) was dissolved in tetrahydrofuran (250 mL) in a dry Schlenk flask under argon. The resulting solution was cooled with stirring to −78 °C. A solution of *n*-butyllithium in hexanes (1.60 M, 31.5 mL, 50.4 mmol) was added dropwise via syringe, causing the yellow solution to turn a deep red color. The reaction mixture was stirred for 30 min at −78 °C. Chlorotrimethylsilane (6.5 mL, 51 mmol) was added dropwise via syringe over 5 min, causing the red solution to turn a light orange color. The reaction mixture was warmed to room temperature and stirred for 45 min. Triethylamine (10 mL) and methanol (20 mL) were added, resulting in a cloudy, pale yellow suspension. The suspensions obtained from two reactions carried out in this manner were combined and concentrated; the solid residue was taken up in diethyl ether (250 mL) and washed with brine (100 mL). The aqueous phase was extracted with two 75-mL portions of diethyl ether. The organic solutions were combined, dried over potassium carbonate, filtered, and concentrated.

The yellow crystalline product was dissolved in methanol (200 mL). Sodium acetate (16.4 g, 200 mmol) and hydroxylamine hydrochloride (10.4 g, 150 mmol) were added with rapid stirring. After 5 min, solid potassium bicarbonate (15 g, 150 mmol) was added, and the mixture was stirred for 30 min. Diethyl ether (100 mL) was added, and the mixture was filtered to remove precipitated salts. The collected solid was dissolved in water (200 mL), and the resulting solution was extracted with two 50-mL portions of diethyl ether. The combined organic solutions were dried over potassium carbonate, filtered, and concentrated. The residue was taken up in dichloromethane (20 mL), cooled to −78 °C, and filtered to remove the precipitated benzophenone oxime. The collected solid was suspended in dichloromethane to dissolve adsorbed **2**, and the mixture was cooled to −78 °C and filtered. The filtrates were combined and concentrated, and the precipitation of benzophenone oxime was repeated as described above. The crude aniline was distilled from calcium hydride under high vacuum, affording the title compound as a colorless oil (14.1 g, 85%): bp 44 °C/0.01 mmHg (lit.[25] 102 °C/6 mmHg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, J = 8.1 Hz, 2H), 6.75 (d, J = 8.1 Hz, 2H), 3.75 (s, 2H), 0.29 (s, 9H).

Dimer 3. Aryl bromide **1** (25.15 g, 74.8 mmol), arylamine **2** (13.0 g, 78.6 mmol), sodium *tert*-butoxide (10.06 g, 105 mmol), $Pd_2(dba)_3$ (0.171 g, 0.187 mmol, 0.25 mol %), and *S*-BINAP (0.349 g, 0.560 mmol, 0.75 mol %) were dissolved in tetrahydrofuran (75 mL) in a Schlenk flask under argon. The reaction mixture was heated to a gentle reflux. Analysis by TLC after 17 h showed complete consumption of aryl bromide **1**. The reaction mixture was cooled to room temperature and concentrated. The residue was taken up in dichloromethane (200 mL), washed with brine, dried over potassium carbonate, and concentrated. The crude product, 4-(dimethylamino)pyridine (1.635 g, 13.4 mmol, 20 mol %), and di-*tert*-butyl dicarbonate (21.90 g, 100 mmol) were dissolved in tetrahydrofuran (67 mL) in a Schlenk flask under argon. The resulting solution was heated to 60 °C with stirring. After 2 h the solution was cooled to room temperature and concentrated. Crystallization of the product from methanol afforded dimer **3** as pale yellow crystals (32.89 g, 84%): mp 123−124 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 7.0 Hz, 2H), 7.49−7.40 (m, 5H), 7.28 (d, J = 6.2 Hz, 3H), 7.19 (d, J = 8.2 Hz, 4H), 6.98 (d, J = 8.5 Hz, 2H), 6.69 (d, J = 8.7 Hz, 2H), 1.41 (s, 9H), 0.24 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 154.0, 149.5, 143.9, 139.8, 138.4, 137.0, 136.4, 133.8, 131.0, 129.7, 129.5, 128.8, 128.4, 128.1, 127.9, 125.3, 121.6, 81.1, 28.4, −0.9; IR (neat, cm^{-1}) 3059, 3022, 2954, 1711, 1500, 1327, 1162, 852. Anal. Calcd for $C_{33}H_{36}N_2O_2Si$: C, 76.11; H, 6.97. Found: C, 76.06; H, 7.18.

Dimer Amine 4. A Schlenk flask was charged with dimer **3** (3.64 g, 7.00 mmol), ammonium formate (5.297 g, 84.0 mmol), and palladium on carbon (10%, 0.740 g, 0.70 mmol Pd) and purged with argon. Methanol (100 mL) was added,[40] and the resulting mixture was heated with stirring to 60 °C. Analysis by TLC after 45 min showed complete consumption of imine **3**. The reaction mixture was cooled to room temperature and concentrated. The residue was taken up in dichloromethane, and the resulting solution was filtered through Celite and concentrated. The white solid residue was triturated with hexanes (20 mL), cooled to 0 °C, and filtered to afford arylamine **4** as a white solid (2.251 g, 90%): mp 108−109 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, J = 8.5 Hz, 2H), 7.20 (d, J = 8.5 Hz, 2H), 7.00 (d, J = 8.5 Hz, 2H), 6.64 (d, J = 8.5 Hz, 2H), 3.66 (s, 2H), 1.45 (s, 9H), 0.24 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.3, 144.7, 144.1, 136.7, 134.1, 133.7, 128.8, 125.2, 115.4, 80.9, 28.4, −0.9; IR (neat, cm^{-1}) 3465, 3367, 3227, 2955, 1696, 1515, 1162, 852. Anal. Calcd for $C_{20}H_{28}N_2O_2Si$: C, 67.38; H, 7.92. Found: C, 67.54; H, 7.99.

Dimer Bromide 5. Procedure A: A Schlenk flask was charged with dimer **3** (7.291 g, 14.0 mmol) and sodium acetate (1.148 g, 14.0 mmol) and purged with argon. Tetrahydrofuran (100 mL) was added, and the resulting mixture was cooled to −78 °C with stirring. Bromine (1.50 mL, 29.1 mmol) was added dropwise, causing the mixture to turn a deep green color. The mixture was stirred for 10 min at −78 °C and then warmed to 0 °C, causing the solution to turn a brown color. Analysis by TLC after 20 min indicated complete consumption of arylsilane **3**. A solution of sodium bicarbonate (0.5 M) and sodium sulfite (0.5 M) in water was added to the reaction mixture with vigorous stirring, dispelling the brown color. The mixture was transferred to a separatory funnel containing diethyl ether (50 mL). The phases were separated, and the aqueous phase extracted with two 50-mL portions of diethyl ether. The ether portions were combined, dried over potassium carbonate, filtered, and concentrated, giving a yellow oil which crystallized on standing. Recrystallization of the product from a 4:1 mixture of hexanes and ethyl acetate afforded aryl bromide **5** as pale yellow crystals (6.545 g, 89%): mp 161−162 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, J = 8.7 Hz, 2H), 7.49−7.36 (m, 5H), 7.28 (d, J = 8.8 Hz, 3H), 7.13 (dd, J = 7.8, 2.0 Hz, 2H), 7.05 (d, J = 8.7 Hz, 2H), 6.96 (d, J = 8.6 Hz, 2H), 6.70 (d, J = 8.6 Hz, 2H), 1.41 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.9, 153.6, 149.6, 142.4, 139.5, 137.8, 136.2, 131.6, 131.0, 129.6, 129.5, 128.8, 128.4, 128.0, 127.7, 127.5, 121.6, 118.3, 81.3, 28.3; IR (neat, cm^{-1}) 3058, 2977, 1711, 1489, 1325, 1161, 697. Anal. Calcd for $C_{30}H_{27}BrN_2O_2$: C, 68.31; H, 5.16. Found: C, 68.53; H, 5.35.

Procedure B: Aryl bromide **1** (14.1 g, 41.8 mmol), aniline (4.00 mL, 43.9 mmol), sodium *tert*-butoxide (5.63 g, 58.5 mmol), $Pd_2(dba)_3$ (95.7 mg, 0.105 mmol, 0.25 mol %), and *S*-BINAP (0.195 g, 0.314 mmol, 0.75 mol %) were dissolved in tetrahydrofuran (80 mL) in a Schlenk flask under argon. The reaction mixture was heated to a gentle reflux. Analysis by TLC after 24 h showed complete consumption of the starting bromide. The mixture was cooled to room temperature, taken up in ethyl acetate (80 mL), and washed with a 2.0 M aqueous sodium hydroxide solution (80 mL), followed by brine (80 mL). The organic phase was dried over sodium sulfate, filtered, and concentrated. The residue was taken up in dichloromethane (88 mL), and tetra-*n*-butylammonium tribromide (23.3 g, 48.3 mmol) was added in one portion with stirring. After 30 min, a saturated aqueous solution of sodium sulfite (80 mL) was added. The mixture was stirred for 10 min, and then 2.0 M aqueous sodium hydroxide solution (40 mL) was added. The layers were separated, and the organic phase was washed with brine (80 mL), dried over sodium sulfate, filtered, and concentrated. The residual solid, 4-(dimethylamino)pyridine (0.536 g, 4.39 mmol, 11 mol %), and di-*tert*-butyl dicarbonate (1.054 g, 4.82 mmol) were dissolved in tetrahydrofuran (50 mL). The resulting solution was heated to reflux. After 3 h at reflux the solution was cooled to room temperature and concentrated. Crystallization of the residue from methanol afforded aryl bromide **5** as pale yellow crystals (18.7 g, 81%). Spectroscopic data were identical to those reported above; mp 159−160 °C. Anal. Calcd for $C_{30}H_{27}BrN_2O_2$: C, 68.31; H, 5.16. Found: C, 68.52; H, 5.33.

Tetramer 6. Dimer amine **4** (2.353 g, 6.60 mmol), dimer bromide **5** (3.165 g, 6.00 mmol), sodium *tert*-butoxide (0.807 g, 8.40 mmol), $Pd_2(dba)_3$ (54.9 mg, 0.060 mmol, 1 mol %), and *S*-BINAP (89.7 mg, 0.144 mmol, 2.4 mol %) were dissolved in toluene (24 mL) in a Schlenk flask under argon. The reaction mixture was heated with stirring to 80 °C. Analysis by TLC after 19 h indicated complete consumption of the starting bromide. The mixture was cooled to room temperature and taken up in dichloromethane (100 mL), washed with water (50 mL), dried over potassium carbonate, filtered, and concentrated. The residual solid and 4-(dimethylamino)pyridine (0.1466 g, 1.20 mmol, 20 mol %) were dissolved in tetrahydrofuran (12 mL) in a Schlenk tube under argon. A solution of di-*tert*-butyl dicarbonate in tetrahydrofuran (1.0 M, 8.0 mL, 8.0 mmol) was added, and the resulting solution was heated with stirring to 60 °C. After 2 h the solution was cooled to room temperature and concentrated. Crystallization of the residual solid from methanol afforded tetramer **6** as pale yellow crystals (4.63 g, 85%): mp 131−133 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, J = 7.2 Hz, 2H), 7.50−7.42 (m, 5H), 7.28 (m, 3H), 7.19 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 11.7 Hz, 10H), 6.98 (d, J = 8.6 Hz, 2H), 6.69 (d, J = 8.5 Hz, 2H), 1.469 (s, 9H), 1.453 (s, 9H), 1.408 (s, 9H), 0.26 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.0, 154.1, 154.0, 149.5, 143.5, 140.8, 140.6, 140.5, 139.8, 138.3, 137.8, 136.4, 134.0, 131.1, 129.8, 129.6, 129.0, 128.5, 128.2, 127.8, 127.5, 127.3, 127.2, 126.4, 126.2, 121.7, 81.6, 81.3, 28.4, −0.9; IR (neat, cm^{-1}) 3008, 2977, 1711, 1509, 1327, 1161, 851, 756. Anal. Calcd for $C_{55}H_{62}N_4O_6Si$: C, 73.14; H, 6.92. Found: C, 72.79; H, 6.86.

Tetramer Amine 7. A Schlenk flask was charged with tetramer **6** (4.155 g, 4.6 mmol), ammonium formate (4.061 g, 64.4 mmol), and palladium on carbon (5%, 0.979 g, 0.460 mmol Pd) and purged with argon. Methanol (25 mL) and tetrahydrofuran (15 mL) were added, and the resulting mixture was heated to 50 °C with stirring. Analysis by TLC after 11 h indicated complete consumption of the starting imine. The mixture was cooled to room temperature and concentrated. The residue was taken up in dichloromethane (75 mL), and the resulting mixture was filtered through Celite and concentrated. The white solid residue was triturated with hexanes (30 mL), cooled to 0 °C, and collected by filtration to afford amine **7** as a white solid (3.243 g, 95%): mp 190−192 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, J = 5.0 Hz, 2H), 7.18−7.09 (m, 10H), 6.97 (d, J = 5.0 Hz), 6.62 (d, J = 5.0 Hz, 2H), 3.67 (s, 2H), 1.46 (s, 9H), 1.44 (s, 18H), 0.25 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.3, 153.91, 153.88, 144.8, 143.4, 141.2, 140.4, 140.4, 139.6, 137.7, 133.9, 133.9, 129.01, 128.6, 127.4, 127.2, 127.1, 126.4, 126.2, 126.0, 115.4, 81.4, 81.4, 81.0, 28.4, 28.4, 28.4, −0.9; IR (neat, cm^{-1}) 3472, 3366, 2978, 1708, 1508, 1331, 1161, 1055, 844. Anal. Calcd for $C_{42}H_{54}N_4O_6Si$: C, 68.26; H, 7.36. Found: C, 68.38; H, 7.52.

(40) This reaction is carried out under argon; we note that, under air, palladium on carbon may ignite upon contact with methanol. Once started, the imine hydrogenolysis reaction does not require rigorously air-free conditions.

Tetramer Bromide 8. A Schlenk flask was charged with tetramer **6** (2.50 g, 2.77 mmol) and sodium acetate (227 mg, 2.77 mmol) and purged with argon. Tetrahydrofuran (28 mL) was added, and the resulting mixture was cooled with stirring to 0 °C. Bromine (299 μL, 5.81 mmol) was added dropwise. The mixture was stirred for 20 min at 0 °C, and then triethylamine (1.54 mL, 11.1 mmol) and a 1.0 M aqueous solution of sodium sulfite (20 mL) were added with vigorous stirring. The mixture was stirred for 5 min, and then partitioned between ethyl acetate (60 mL) and a 2.0 M sodium hydroxide solution (50 mL). The organic layer was washed with saturated aqueous sodium chloride solution (50 mL) dried over anhydrous sodium sulfate, filtered, and concentrated. Crystallization of the solid residue from methanol afforded aryl bromide **8** as pale yellow crystals (2.13 g, 85%): mp 174−176 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (dd, J = 8.5, 1.6 Hz, 2H), 7.50−7.35 (m, 6H), 7.27 (d, J = 8.5 Hz, 2H), 7.12 (dd, J = 7.7, 1.5 Hz, 2H), 7.02 (dd, J = 9.0, 2.1 Hz, 2H), 6.94 (d, J = 8.5 Hz, 2H), 6.69 (d, J = 8.5 Hz, 2H), 1.39 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 153.5, 149.4, 142.3, 139.4, 137.8, 136.1, 131.5, 130.9, 129.5, 129.3, 128.7, 128.2, 127.9, 127.5, 127.4, 121.5, 118.1, 81.2, 28.2; IR (neat, cm^{-1}) 1710. Anal. Calcd for $C_{52}H_{53}BrN_4O_6$: C, 68.64; H, 5.87. Found: C, 68.38; H, 5.85

Octamer 9. Arylamine **7** (1.55 g, 2.10 mmol), aryl bromide **8** (1.82 g, 2.00 mmol), sodium *tert*-butoxide (0.269 g, 2.80 mmol), $Pd_2(dba)_3$ (37 mg, 0.026 mmol, 2 mol %), and *S*-BINAP (60 mg, 0.096 mmol, 4.8 mol %) were dissolved in toluene (15 mL) in a Schlenk tube under argon. The reaction mixture was heated to 65 °C. Analysis by TLC after 17 h indicated complete consumption of the starting bromide. The reaction mixture was cooled to room temperature and taken up in dichloromethane (75 mL). The resulting mixture was washed with brine (50 mL), dried over potassium carbonate, filtered, and concentrated. The residue, 4-(dimethylamino)pyridine (49 mg, 0.40 mmol, 20 mol %), and di-*tert*-butyl dicarbonate (0.576 g, 2.64 mmol) were dissolved in tetrahydrofuran (20 mL) in a Schlenk tube under argon. The resulting solution was heated to 65 °C. After 3 h the solution was cooled to room temperature and concentrated. Crystallization of the residual solid from methanol afforded octamer **9** as pale yellow crystals (2.48 g, 74%): mp 169−171 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, J = 8.4 Hz, 2H), 7.50−7.39 (m, 8H), 7.28−7.26 (m, 2H), 7.17 (d, J = 8.4 Hz, 2H), 7.16−7.13 (m, 24H), 6.97 (d, J = 8.4 Hz, 2H), 6.71 (d, J = 8.4 Hz, 2H), 1.45 (s, 9H), 1.43 (s, 45H), 1.39 (s, 9H), 0.25 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.6, 153.7, 153.7, 153.6, 149.2, 143.2, 140.5, 140.2, 140.1, 139.5, 138.0, 137.5, 136.1, 133.7, 130.8, 129.5,-129.3, 128.6, 128.2, 127.9, 127.4, 127.2, 127.0, 126.8, 126.1, 125.8, 121.3, 81.3, 81.2, 80.9, 28.2, −1.1; IR (neat, cm^{-1}) 1712. Anal. Calcd for $C_{99}H_{114}N_8O_{14}Si$: C, 71.28; H, 6.88. Found: C, 71.07; H, 7.00.

Octamer Amine 10. A Schlenk tube was charged with imine **9** (500 mg, 0.300 mmol), ammonium formate (568 mg, 9.00 mmol), and palladium hydroxide on carbon (20%, 0.105 g, 0.150 mmol Pd) and purged with argon. 2-Propanol (30 mL) was added, and the resulting mixture was heated to 80 °C with stirring, causing a visible effervescence. After ca. 15 min the effervescence slowed, and an additional portion of ammonium formate (568 mg, 9.00 mmol) was added. Small portions of ammonium formate were added at 15 min intervals until conversion to amine **10** was complete as judged by thin-layer chromatography (ca. 1 h). The reaction mixture was cooled to room temperature, taken up in dichloromethane (20 mL), and filtered through Celite. The filtrate was diluted with dichloromethane (60 mL), washed with a 2.0 M aqueous sodium hydroxide solution (50 mL), dried over anhydrous sodium sulfate, filtered, and concentrated. The white solid residue was recrystallized from a 5:1 mixture of 2-propanol and water to afford arylamine **10** as white needles (425 mg, 94%): mp 168−170 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, J = 8.4 Hz: 2H), 7.16 (d, J = 8.4 Hz, 2H), 7.14−7.12 (m, 24H), 7.02 (d, J = 8.4 Hz, 2H), 6.77 (d, J = 8.4 Hz, 2H), 3.65 (bs, 2H), 1.44 (s, 9H), 1.43 (s, 54 H), 0.24 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1, 153.6, 153.6, 144.6, 143.2, 141.0, 140.3, 140.3, 140.1, 140.1, 140.0, 139.3, 137.5, 133.7, 128.8, 128.4, 127.2, 127.0, 126.8, 126.2, 125.8, 115.1, 81.3, 81.2, 80.8, 28.1, −1.2; IR (neat, cm^{-1}) 3468, 3368, 1710. Anal. Calcd for $C_{86}N_{106}N_8O_{14}$: C, 68.68; H, 7.10. Found: C, 68.43; H, 6.86.

***N*-(Diphenylmethylene)-*N*′,*N*″-bis(*tert*-butoxycarbonyl)teraniline (11).** Dimer bromide **5** (3.06 g, 5.80 mmol), aniline (0.56 mL, 6.1 mmol), sodium *tert*-butoxide (0.8072 g, 8.40 mmol), $Pd_2(dba)_3$ (54.9 mg, 0.060 mmol, 1.0 mol %), and *S*-BINAP (89.7 mg, 2.5 mol %) were dissolved in toluene (20 mL) in a Schlenk flask under argon. The reaction mixture was heated to 80 °C with stirring. Analysis by TLC after 14 h indicated complete consumption of the starting bromide. The mixture was cooled to room temperature and taken up in diethyl ether (75 mL). The resulting mixture was washed with brine (50 mL), dried over potassium carbonate, filtered, and concentrated. The residue, di-*tert*-butyl dicarbonate (1.53 g, 7.0 mmol), and 4-(dimethylamino)-pyridine (0.131 g, 1.16 mmol, 20 mol %) were dissolved in tetrahydrofuran (15 mL) in a Schlenk flask under argon. The reaction mixture was heated with stirring to 60 °C. After 3 h the solution was cooled to room temperature and concentrated. The solid residue was crystallized from ethanol. Recrystallization of the product from ethanol afforded the title compound as pale yellow crystals (3.00 g, 81%): mp 149−151 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 8.5 Hz, 2H), 7.48−7.38 (m, 3H), 7.33−7.24 (m, 5H), 7.21−7.16 (m, 3H), 7.14−7.07 (m, 6H), 6.97 (d, J = 8.8 Hz, 2H), 6.77 (d, J = 8.8 Hz, 2H), 1.45 (s, 9H), 1.40 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.9, 154.0, 149.4, 143.0, 140.6, 140.0, 139.7, 138.2, 136.3, 131.0, 129.7, 129.5, 128.9, 128.4, 128.1, 127.7, 127.2, 127.0, 126.3, 125.9, 121.6, 81.4, 81.2, 28.4, 28.4; IR (neat, cm^{-1}) 2977, 2930, 1710, 1509, 1324, 1161, 758, 696. Anal. Calcd for $C_{41}H_{41}N_3O_4$: C, 76.97; H, 6.46. Found: C, 77.16; H, 6.70.

***N*-Phenyl-*N*′-(4-aminophenyl)-*N*,*N*′-bis(*tert*-butoxycarbonyl)-1,4-phenylenediamine (12).** A Schlenk flask was charged with imine **11** (1.245 g, 1.95 mmol), ammonium formate (1.840 g, 29.2 mmol), and palladium on carbon (5%, 0.414 g, 1.95 mmol Pd). Methanol (8 mL) and tetrahydrofuran (4 mL) were added via syringe. The resulting mixture was heated to 60 °C with stirring. Analysis by TLC after 90 min showed incomplete consumption of the starting imine. An additional portion of palladium on carbon (5%, 0.414 g, 1.95 mmol Pd) was added, and the solid ammonium formate which collected above the mixture was periodically redissolved. Analysis by TLC after 2 h showed complete consumption of the starting imine. The mixture was cooled to room temperature and concentrated. The residue was taken up in dichloromethane, and the resulting mixture was filtered through Celite and concentrated. The residual white solid was triturated in hexanes (30 mL), cooled to 0 °C, and collected by filtration, affording the title compound as a white solid (0.884 g, 96%): mp 180−182 °C with slow decomposition; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (dd, J = 8.2, 3.9 Hz, 2H), 7.21−7.10 (m, 7H), 6.98 (dd, J = 5.3, 1.2 Hz, 2H), 6.62 (dd, J = 5.3, 1.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.3, 154.0, 144.8, 143.0, 141.0, 139.8, 134.0, 129.1, 128.8, 128.7, 128.6, 127.2, 127.0, 126.4, 126.2, 125.8, 115.4, 81.3, 81.0, 28.4, 28.4; IR (neat, cm^{-1}) 3460, 3366, 3037, 2978, 2919, 1702, 1508, 1337, 1161, 1055. Anal. Calcd for $C_{28}H_{33}N_3O_4$: C, 70.71; H, 6.99. Found: C, 70.84; H, 6.78.

***N*-(Diphenylmethylene)-4-[4-methoxy-*N*-(*tert*-butoxycarbonyl)anilino]aniline (13).** Aryl bromide **1** (2.60 g, 7.74 mmol), *p*-anisidine (1.00 g, 8.13 mmol), sodium *tert*-butoxide (1.04 g, 10.8 mmol), $Pd_2(dba)_3$ (35.0 mg, 0.0387 mmol, 1.0 mol %), and *S*-BINAP (72.0 mg, 0.116 mmol, 1.5 mol %) were dissolved in tetrahydrofuran (25 mL) in a Schlenk flask under argon. The reaction mixture was heated to reflux. After 18 h, the mixture was cooled to room temperature. 4-(Dimethylamino)pyridine (47.0 mg, 0.774 mmol, 10 mol %) and a solution of di-*tert*-butyl dicarbonate in tetrahydrofuran (1.0 M, 11.6 mL, 11.6 mmol) were added, and the resulting mixture was heated to reflux. After 3 h the reaction mixture was cooled to room temperature, taken up in a 2:1 mixture of hexanes and ethyl acetate (25 mL), filtered through Celite, and concentrated. Crystallization of the residual solid from methanol afforded the title compound as yellow crystals (3.11 g, 84%): mp 148−149 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, J = 7.1 Hz, 2H), 7.50−7.36 (m, 4H), 7.25 (d, J = 6.0 Hz, 2H), 7.11 (d, J = 7.1 Hz, 2H), 7.07 (d, J = 9.1 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.80 (d, J = 9.1 Hz, 2H), 6.65 (d, J = 8.8 Hz, 2H), 3.77 (s, 3H), 1.39 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 157.0, 153.9, 148.4, 139.4, 138.5, 130.7, 129.4, 129.2, 128.5, 128.1, 127.8, 127.6, 126.8, 121.2, 113.7, 80.6, 55.4, 28.3; IR (neat, cm^{-1}) 1705, 1612. Anal. Calcd for $C_{31}H_{30}N_2O_3$: C, 77.80; H, 6.32. Found: C, 77.77; H, 6.38.

***N*-(4-Methoxyphenyl)-*N*′-(4-bromophenyl)-*N*,*N*′-bis(*tert*-butoxycarbonyl)-1,4-phenylenediamine (14).** A Schlenk flask was charged with imine **13** (1.00 g, 2.09 mmol), ammonium formate (2.64 g, 41.8 mmol), and palladium hydroxide on carbon (20%, 0.291 g, 0.209 mmol Pd). Ethanol (20 mL) was added, and the resulting mixture was heated to 60 °C. After 30 min the reaction mixture was cooled to room temperature, taken up in ethyl acetate (40 mL), and filtered through Celite. The filtrate was diluted with ethyl acetate (60 mL), washed with a 2.0 M aqueous solution of sodium hydroxide (100 mL) and with brine (50 mL), dried over anhydrous sodium sulfate, filtered, and concentrated. The residual white solid, 1,4-dibromobenzene (470 mg, 1.99 mmol), sodium *tert*-butoxide (268 mg, 2.79 mmol), $Pd_2(dba)_3$ (18.2 mg, 0.0199 mmol, 1.0 mol %), and *S*-BINAP (37.2 mg, 0.0598 mmol, 3.0 mol %) were dissolved in tetrahydrofuran (10 mL) in a Schlenk tube under argon. The reaction mixture was heated to reflux. After 24 h, the mixture was cooled to room temperature. 4-(Dimethylamino)-pyridine (24.0 mg, 0.199 mmol, 10 mol %) and a solution of di-*tert*-butyl dicarbonate in tetrahydrofuran (1.0 M, 3.0 mL, 3.0 mmol) were added, and the resulting mixture was heated to reflux. After 3 h, the reaction mixture was cooled to room temperature, taken up in a 2:1 mixture of hexanes and ethyl acetate (10 mL), filtered through Celite, and concentrated. Crystallization of the residual solid from methanol containing a small proportion of dichloromethane afforded the title compound as white crystals (0.847 g, 75%): mp 169−170 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, J = 8.7 Hz, 2H), 7.17−7.06 (m, 8H), 6.84 (d, J = 9.0 Hz, 2H), 3.80 (s, 3H), 1.44 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.7, 153.9, 153.4, 142.0, 141.0, 139.3, 135.6, 131.7, 128.5, 128.3, 127.0, 126.4, 118.9, 114.1, 81.6, 81.1, 55.4, 28.2, 28.2; IR (neat, cm^{-1}) 1709. Anal. Calcd for $C_{29}H_{33}BrN_2O_5$: C, 61.16; H, 5.84. Found: C, 61.15; H, 5.81.

Tetramer Diamine 15. 1,4-Phenylenediamine dihydrochloride (4.53 g, 25.0 mmol), aryl bromide **1** (17.0 g, 50.5 mmol), sodium *tert*-butoxide (10.8 g, 113 mmol), $Pd(OAc)_2$ (56.1 mg, 0.250 mmol, 1.0 mol %), and *S*-BINAP (234 mg, 0.375 mmol, 1.5 mol %) were dissolved in toluene (200 mL) in a Schlenk flask under argon. The reaction mixture was heated to 80 °C with stirring. After 24 h, the mixture was cooled to room temperature. 4-(Dimethylamino)pyridine (305 mg, 2.50 mmol, 10 mol %), a solution of di-*tert*-butyl dicarbonate in tetrahydrofuran (1.0 M, 87.5 mL, 87.5 mmol), and tetrahydrofuran (50 mL) were added. The resulting mixture was heated to 80 °C with stirring. After 24 h the hot reaction mixture was poured into hot ethanol (400 mL). Heating was discontinued and the mixture was allowed to stand for 6 h. The yellow powder which formed was collected by filtration. The crude product and hydroxylamine hydrochloride (4.34 g, 62.5 mmol) were suspended in pyridine (8.1 mL, 100 mmol), chloroform (400 mL), tetrahydrofuran (100 mL), and ethanol (50 mL). The suspension was stirred for 3 h and then treated with triethylamine (34.8 mL, 250 mmol). After an additional 3 h the reaction mixture was concentrated. The residual solid was heated in 2-propanol (600 mL), chloroform (120 mL), and water (60 mL) for 10 min, then allowed to cool to room temperature, and to stand for 12 h. The precipitated product was collected by filtration, washed with water followed by 2-propanol, and dried in vacuo to afford diamine **15** as a white powder (11.1 g, 91%): mp 208−211 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.06 (s, 4H), 6.81 (d, J = 8.4 Hz, 4H), 6.49 (d, J = 8.4 Hz, 4H), 5.11 (s, 4H), 1.33 (s, 18 H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 153.4, 146.9, 140.2, 131.1, 128.0, 125.9, 113.8, 79.6, 27.8; IR (neat, cm^{-1}) 3460, 3364, 1707. Anal. Calcd for $C_{28}H_{34}N_4O_4$: C, 68.55; H, 6.99. Found: C, 68.57; H, 7.05.

Octamer Bis-Imine 16. Diamine **15** (4.23 g, 8.63 mmol), dimer bromide **5** (9.56 g, 18.1 mmol), sodium *tert*-butoxide (2.32 g, 24.2 mmol), $Pd(OAc)_2$ (116 mg, 0.518 mmol, 6.0 mol %), and *S*-BINAP (376 mg, 0.604 mmol, 7.0 mol %) were dissolved in tetrahydrofuran (43 mL) and triethylamine (11 mL) in a Schlenk flask under argon. The reaction mixture was heated to 90 °C. After 48 h, the mixture was cooled to room temperature. 4-(Dimethylamino)pyridine (105 mg, 0.863 mmol, 10 mol %), tetrahydrofuran (20 mL), and a solution of di-*tert*-butyl dicarbonate in tetrahydrofuran (1.0 M, 34.5 mL, 34.5 mmol) were added. The resulting mixture was heated to 67 °C. After 24 h the mixture was cooled to room temperature. Ethyl acetate (100 mL) and a 2.0 M aqueous solution of sodium hydroxide (60 mL) were added. The mixture was stirred for 15 min and then partitioned between ethyl acetate (100 mL) and water (250 mL). The organic layer was washed with brine (200 mL), dried over anhydrous sodium sulfate, filtered, and concentrated. The residual solid was crystallized from a mixture of chloroform and 2-propanol. The mother liquor was concentrated, and the residue was taken up in 2-propanol. A second crop of crystals formed and was collected by filtration. The crops were combined and dried under vacuum to afford bis-imine **16** as yellow crystals (10.1 g, 74%): mp 154−158 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, J = 7.0 Hz, 4H), 7.48−7.381 (m, 8H), 7.27−7.23 (m, 8H), 7.11 (s, 16H), 7.08 (s, 4H), 6.95 (d, J = 8.4 Hz, 4H), 6.67 (d, J = 8.4 Hz, 4H), 1.42 (s, 36 H), 1.38 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.5, 153.6, 153.5, 149.0, 140.5, 140.1, 140.0, 140.0, 139.4, 139.4, 137.9, 136.0, 130.7, 130.7, 129.4, 129.2, 128.6, 128.1, 127.8, 127.4, 126.9, 126.8, 126.0, 121.3, 81.3, 81.3, 81.0, 28.3; IR (neat, cm^{-1}) 1711. Anal. Calcd for $C_{98}H_{102}N_8O_{12}$: C, 74.31; H, 6.49. Found: C, 74.36; H, 6.54.

Octamer Diamine 17. A Schlenk flask was charged with bis-imine **16** (3.00 g, 1.89 mmol), ammonium formate (2.39 g, 37.9 mmol), and 20% palladium hydroxide on carbon (0.758 mmol). Tetrahydrofuran (50 mL) and ethanol (25 mL) were added, and the resulting mixture was heated to 70 °C, causing an effervescence which slowed after ca. 30 min. An additional portion of ammonium formate (2.39 g, 37.9 mmol) was added. Ammonium formate was added in portions every 60 min until conversion to the diamine was complete as judged by TLC analysis. The mixture was cooled to room temperature, taken up in ethyl acetate (40 mL), and filtered through Celite. The filtrate was diluted with a 2:1 mixture of hexanes and ethyl acetate (40 mL). The resulting solution was washed with a 2.0 M aqueous solution of sodium hydroxide (40 mL) and with brine (40 mL), dried over anhydrous sodium sulfate, filtered, and concentrated. Crystallization of the residual solid from a mixture of hexanes and 2-propanol afforded diamine **17** as white crystals (2.03 g, 86%): mp 169−172 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16−7.07 (m, 20H), 6.96 (d, J = 8.4 Hz, 4H), 6.60 (d, J = 8.4 Hz, 4H), 3.65 (bs, 4H), 1.43 (s, 54 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1, 153.6, 153.6, 144.6, 141.0, 140.3, 140.1, 140.0, 139.4, 137.8, 133.7, 128.4, 126.9, 126.9, 126.8, 126.2, 115.1, 81.2, 81.2, 80.7, 28.2, 28.1; IR (neat, cm^{-1}) 3460, 3369, 1702. Anal. Calcd for $C_{72}H_{86}N_8O_{12}$: C, 68.88; H, 6.90. Found: C, 68.68; H, 6.84.

General Procedure for the Conversion of Octamer Diamine 17 to Octamers 18a−d. Diamine **17** (1.26 g, 1.00 mmol), aryl bromide (2.30 mmol), sodium *tert*-butoxide (240 mg, 2.50 mmol), $Pd_2(dba)_3$ (18.7 mg, 0.0204 mmol, 2.0 mol %), and *S*-BINAP (38.1 mg, 0.0613 mmol, 6 mol %) were dissolved in tetrahydrofuran (10 mL) in a Schlenk tube under argon. The reaction mixture was heated to reflux. After 48 h, the mixture was cooled to room temperature. 4-(Dimethylamino)-pyridine (12.0 mg, 0.100 mmol, 10 mol %) and a solution of di-*tert*-butyl dicarbonate in tetrahydrofuran (1.0 M, 3.5 mL, 3.5 mmol) were added, and the resulting mixture was heated to reflux. After 3 h, the mixture was cooled to room temperature, taken up in a 2:1 mixture of hexanes and ethyl acetate (10 mL), and filtered through Celite. The filtrate was concentrated and the residue was crystallized.

Phenyl-Capped Octamer 18a. Obtained as pale yellow crystals from a 6:1 mixture of methanol and chloroform in 77% yield: mp 171−173 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (t, J = 8.7 Hz, 2H), 7.20−7.15 (m, 4H), 7.13 (s, 32H), 1.44 (s, 18H), 1.43 (s, 54H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.7, 153.6, 153.6, 142.8, 140.5, 140.2, 140.0, 128.7, 127.0, 125.7, 81.3, 81.3, 81.2, 28.2; IR (neat, cm^{-1}) 1711; HRMS (FAB) m/z 1606.8043 (1606.8037 calcd for $C_{94}H_{110}N_8O_{16}$, M$^+$). Anal. Calcd for $C_{94}H_{110}N_8O_{16}$: C, 70.22; H, 6.90. Found: C, 70.25; H, 6.91.

α,ω-Bis(cyano)phenyl-Capped Octamer 18b. Obtained as pale yellow crystals from methanol in 79% yield: mp 163−166 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, J = 9.0 Hz, 4H), 7.31 (d, J = 9.0 Hz, 4H), 7.21 (d, J = 8.7 Hz, 2H), 7.16−7.13 (m, 24H), 7.08 (d, J = 8.7 Hz, 2H), 1.44 (s, 36H), 1.43 (s, 36H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6, 153.5, 151.6, 147.0, 140.2, 140.1, 140.1, 140.1, 136.9, 132.5, 128.2, 128.0, 127.3, 127.0, 126.7, 125.6, 82.6, 82.2, 81.3, 28.2, 27.9; IR (neat, cm^{-1}) 1713; HRMS (FAB) m/z 1656.7952 (1656.7945 calcd for $C_{96}H_{114}N_8O_{16}$, M$^+$). Anal. Calcd for $C_{96}H_{114}N_8O_{16}$: C, 69.55; H, 6.57. Found: C, 69.24; H, 6.68.

α,ω-Bis(*tert*-butyl)phenyl-Capped Octamer 18c. Obtained as pale yellow crystals from a 10:1 mixture of ethanol and chloroform in 82% yield: mp 172−176 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, J = 9.0 Hz, 4H), 7.12 (s, 28H), 7.10 (d, J = 9.0 Hz, 4H), 1.44 (s, 18H), 1.43 (s, 54H), 1.29 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.8, 153.6, 153.6, 148.6, 140.6, 140.2, 140.1, 139.9, 127.0, 126.3, 125.6, 81.3, 81.3, 81.0, 24.4, 31.3, 28.2; IR (neat, cm^{-1}) 1713; HRMS (FAB) *m*/*z* 1718.9275 (1718.9292 calcd for $C_{102}H_{126}N_8O_{16}$, M^+). Anal. Calcd for $C_{102}H_{126}N_8O_{16}$: C, 71.22; H, 7.38. Found: C, 71.02; H, 7.27.

α,ω-Bis(*n*-dodecyl)phenyl-Capped Octamer 18d. Obtained as pale yellow crystals from a 10:1 mixture of ethanol and chloroform in 82% yield: mp 172−175 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16−7.08 (m, 36H), 2.57 (t, J = 8.0 Hz, 4H), 1.65−1.53 (m, 4H), 1.43 (s, 72H), 1.32−1.20 (m, 36H), 0.88 (t, J = 7.3 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.8, 153.7, 153.6, 140.6, 140.3, 140.2, 139.8, 128.7, 127.0, 126.9, 126.8, 81.3, 81.3, 81.0, 35.4, 31.9, 31.3, 29.6, 29.6, 29.6, 29.5, 29.3, 29.3, 28.2, 27.9, 22.6, 14.1; IR (neat, cm^{-1}) 1712. Anal. Calcd for $C_{118}H_{158}N_8O_{16}$: C, 72.88; H, 8.19. Found: C, 72.71; H, 8.24.

α,ω-Bis(methoxy)phenyl-Capped Octamer 18e. Aryl bromide **14** (300 mg, 0.527 mmol), diamine **15** (123 mg, 0.251 mmol), sodium *tert*-butoxide (60 mg, 0.627 mmol), $Pd_2(dba)_3$ (4.6 mg, 0.00502 mmol), and *S*-BINAP (9.4 mg, 0.0151 mmol) were dissolved in toluene (3 mL) in a Schlenk tube under argon. The reaction mixture was heated to 80 °C. After 48 h, the mixture was cooled to room temperature. 4-(Dimethylamino)pyridine (3.1 mg, 0.0251 mmol, 10 mol %) and a solution of di-*tert*-butyl dicarbonate in tetrahydrofuran (1.0 M, 0.88 mL, 0.88 mmol) were added, and the resulting mixture was heated to reflux. After 3 h the reaction mixture was cooled to room temperature, taken up in a 2:1 mixture of hexanes and ethyl acetate (6 mL), filtered through Celite, and concentrated. Crystallization of the residual solid from a mixture of 2-propanol and water afforded **18e** as white crystals (0.301 g, 72%): mp 173−176 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (s, 28H), 7.11 (d, J = 9.0 Hz, 4H), 6.84 (d, J = 9.0 Hz, 4H), 3.79 (s, 6H), 1.43 (s, 72H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.6, 153.9, 153.6, 140.8, 140.2, 139.7, 135.8, 128.4, 127.0, 126.9, 114.1, 81.3, 81.2, 81.0, 55.4, 28.2; IR (neat, cm^{-1}) 1711; HRMS (FAB) *m*/*z* 1666.8244 (1666.8251 calcd for $C_{96}H_{114}N_8O_{18}$, M^+). Anal. Calcd for $C_{96}H_{114}N_8O_{18}$: C, 69.13; H, 6.89. Found: C, 69.28; H, 7.11.

***N*-(*tert*-Butoxycarbonyl)-4,4′-dibromodiphenylamine (19).** Diphenylamine (4.231 g, 25.0 mmol) was converted to 4,4′-dibromodiphenylamine by the method of Berthelot et al.[28] The crude product and 4-(dimethylamino)pyridine (0.611 g, 5.00 mmol, 20 mol %) were dissolved in tetrahydrofuran (20 mL) in a Schlenk flask under argon. Di-*tert*-butyl dicarbonate (neat, 6.30 mL, 27.5 mmol) was added via syringe, and the resulting solution was heated to reflux. After 1 h the mixture was cooled to room temperature and concentrated. Crystallization of the residual solid from methanol afforded the title compound as white crystals with a faint pink cast (8.65 g, 81% based on diphenylamine): mp 113−115 °C; ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.44 (d, J = 8.7 Hz, 4H), 7.08 (d, J = 8.7 Hz, 4H), 1.46 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.3, 141.9, 132.1, 128.7, 119.5, 82.2, 28.4; IR (neat, cm^{-1}) 2977, 1712, 1488, 1322, 1160, 1072, 1011, 824. Anal. Calcd for $C_{17}H_{17}Br_2NO_2$: C, 47.80; H, 4.01. Found: C, 48.02; H, 3.87.

***N*,*N*′-Bis(4-bromophenyl)-*N*,*N*′-bis(*tert*-butoxycarbonyl)-1,4-phenylenediamine (20).** 1,4-Phenylenediamine (1.00 g, 9.25 mmol) 1,4-dibromobenzene (4.58 g, 19.4 mmol), sodium *tert*-butoxide (2.31 g, 24.0 mmol), $Pd_2(dba)_3$ (0.085 g, 0.093 mmol, 1.0 mol %), and *S*-BINAP (0.173 g, 0.278 mmol, 3.0 mol %) were dissolved in tetrahydrofuran (20 mL) in a Schlenk flask under argon. The reaction mixture was heated to a gentle reflux. Analysis by TLC after 15 h indicated an incomplete reaction. Additional portions of $Pd_2(dba)_3$ (0.020 g, 0.022 mmol, 0.24 mol %) and *S*-BINAP (0.040 g, 0.064 mmol, 0.69 mol %) were added. Analysis by TLC after a further 15 h at reflux indicated a complete reaction. The mixture was cooled to room temperature. Di-*tert*-butyl dicarbonate (7.07 g, 32.4 mmol) and 4-(dimethylamino)-pyridine (0.226 g, 1.85 mmol, 20 mol %) were added. The resulting solution was heated to a gentle reflux. After 3 h the reaction mixture was cooled to room temperature and filtered through a plug of silica gel and Celite, which was then washed with a 1:1 mixture of hexanes and ethyl acetate. The filtrate was concentrated. Crystallization of the residual solid from methanol containing a small proportion of chloroform afforded the title compound as white crystals (3.98 g, 70%): mp 174−176 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, J = 8.6 Hz, 4H), 7.12 (s, 4H), 7.07 (d, J = 8.6 Hz, 4H), 1.43 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.3, 141.9, 140.1, 131.8, 128.4, 127.1, 119.1, 81.7, 28.2; IR (neat, cm^{-1}) 2976, 1711, 1510, 1488, 1322, 1159. Anal. Calcd for $C_{28}H_{30}Br_2N_2O_4$: C, 54.39; H, 4.89. Found: C, 54.15; H, 4.79.

Octamer Dibromide 21. Diamine **17** (2.03 g, 1.62 mmol), 1,4-dibromobenzene (955 mg, 4.05 mmol), sodium *tert*-butoxide (404 mg, 4.20 mmol), $Pd(OAc)_2$ (14.5 mg, 0.0648 mmol, 4.0 mol %), and BINAP (48.4 mg, 0.0778 mmol, 5 mol %) were dissolved in toluene (15 mL) and triethylamine (3 mL) in a Schlenk flask under argon. The reaction mixture was heated to 90 °C. After 48 h, the mixture was cooled to room temperature. 4-(Dimethylamino)pyridine (20.0 mg, 0.162 mmol, 10 mol %) and a solution of di-*tert*-butyl dicarbonate in tetrahydrofuran (1.0 M, 5.7 mL, 5.7 mmol) were added. The resulting mixture was heated to 67 °C. After 3 h, the mixture was cooled to room temperature and partitioned between ethyl acetate (50 mL) and a 2.0 M aqueous solution of sodium hydroxide (25 mL). The organic layer was washed with brine (30 mL), dried over sodium sulfate, filtered, and concentrated. Crystallization of the residual solid from 2-propanol afforded dibromide **21** as white crystals (2.15 g, 75%): mp 145−147 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, J = 7.8 Hz, 4H), 7.12 (s, 28H), 7.07 (d, J = 7.8 Hz, 4H), 1.43 (s, 72 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.9, 153.8, 153.6, 153.4, 145.1, 142.0, 140.6, 140.4, 140.2, 139.9, 139.7, 137.6, 133.1, 131.8, 128.4, 128.3, 127.9, 127.0, 124.1, 119.0, 81.6, 81.4, 81.2, 81.1, 28.2; IR (neat, cm^{-1}) 1712. Anal. Calcd for $C_{94}H_{108}Br_2N_8O_{16}$: C, 63.94; H, 6.16. Found: C, 63.76; H, 5.93.

Phenyl-Capped Heptamer 22. Arylamine **12** (0.799 g, 1.68 mmol), dibromide **19** (0.326 g, 0.764 mmol), sodium *tert*-butoxide (0.2153 g, 2.24 mmol), $Pd_2(dba)_3$ (14.0 mg, 0.0153 mmol, 2 mol %), and *S*-BINAP (22.8 mg, 0.0366 mmol, 4.8 mol %) were dissolved in toluene (6 mL) in a Schlenk tube under argon. The reaction mixture was heated to 80 °C with stirring. After 27 h the mixture was cooled to room temperature and taken up in dichloromethane (75 mL). The resulting mixture was washed with brine (50 mL), dried over potassium carbonate, filtered, and concentrated. The residue and 4-(dimethylamino)pyridine (46.4 mg, 0.38 mmol, 25 mol %) were dissolved in tetrahydrofuran (10 mL) in a Schlenk tube under argon. A solution of di-*tert*-butyl dicarbonate in tetrahydrofuran (1.0 M, 2.0 mL, 2.0 mmol) was added, and the resulting solution was heated to 60 °C with stirring. After 6 h the solution was cooled to room temperature and concentrated. The residual solid was crystallized from ethanol containing a small proportion of chloroform and recrystallized from a mixture of ethanol and toluene, to afford heptamer **22** as white crystals (0.647 g, 60%): mp 168−170 °C with slow decomposition; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (at, 4H), 7.21−7.16 (m, 4H), 7.14 (ad, 26H), 1.45 (s, 27H), 1.44 (s, 36H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.9, 153.9, 153.9, 143.0, 140.6, 140.4, 140.2, 128.9, 127.2, 127.2, 125.9, 81.6, 81.5, 81.4, 28.4; IR (neat, cm^{-1}) 2977, 2931, 1711, 1509, 1327, 1161, 1057, 757. Anal. Calcd for $C_{83}H_{97}N_7O_{14}$: C, 70.37; H, 6.90. Found: C, 70.15; H, 6.98.

α,ω-Bis(trimethylsilyl)phenyl-Capped Nonamer 23. Arylamine **7** (1.301 g, 1.76 mmol), dibromide **19** (0.3417 g, 0.800 mmol), sodium *tert*-butoxide (0.2153 g, 2.24 mmol), $Pd_2(dba)_3$ (14.7 mg, 0.016 mmol, 2 mol %), and *S*-BINAP (23.9 mg, 0.0384 mol, 4.8 mol %) were dissolved in toluene (7 mL) in a Schlenk tube under argon. The reaction mixture was heated to 80 °C with stirring. After 27 h the mixture was cooled to room temperature and taken up in dichloromethane (75 mL). The resulting mixture was washed with brine (50 mL), dried over potassium carbonate, filtered, and concentrated. The residue and 4-(dimethylamino)pyridine (48.9 mg, 0.40 mmol, 25 mol %) were dissolved in tetrahydrofuran (10 mL) in a Schlenk tube under argon. A solution of di-*tert*-butyl dicarbonate in tetrahydrofuran (1.0 M, 2.0 mL, 2.0 mmol) was added. The resulting solution was heated to 60 °C with stirring. After 6 h the solution was cooled to room temperature and concentrated. The residual solid was crystallized from ethanol containing a small proportion of chloroform, and recrystallized from a mixture of ethanol and toluene, to afford nonamer **23** as white crystals (0.970 g, 62%): mp 183−185 °C with slow decomposition; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, J = 8.3 Hz, 4H), 7.18 (d, J = 8.3 Hz, 4H), 7.14 (s, 32H), 1.46 (s, 18H), 1.44 (s, 63H), 0.25 (s, 18H); ^{13}C

NMR (125 MHz, $CDCl_3$) δ 153.9, 153.9, 143.4, 140.5, 140.3, 140.3, 137.7, 133.9, 127.5, 127.2, 126.1, 81.6, 81.5, 81.5, 81.4, 28.4, 28.4, −0.9; IR (neat, cm^{-1}) 2976, 2932, 1713, 1509, 1327, 1161, 1057, 851, 756. Anal. Calcd for $C_{111}H_{139}N_9O_{18}Si_2$: C, 68.60; H, 7.21. Found: C, 68.57; H, 7.13.

α,ω-Bis(trimethylsilyl)phenyl-Capped Decamer 24. Arylamine **7** (1.301 g, 1.76 mmol), dibromide **20** (0.495 g, 0.800 mmol), sodium *tert*-butoxide (0.2153 g, 2.24 mmol), $Pd_2(dba)_3$ (14.7 mg, 0.016 mmol, 2 mol %), and *S*-BINAP (23.9 mg, 0.0384 mol, 4.8 mol %) were dissolved in toluene (8 mL) in a Schlenk tube under argon. The reaction mixture was heated to 80 °C with stirring. After 27 h the mixture was cooled to room temperature and taken up in dichloromethane (75 mL). The resulting mixture was washed with brine (50 mL), dried over potassium carbonate, filtered, and concentrated. The residue and 4-(dimethylamino)pyridine (48.9 mg, 0.40 mmol, 25 mol %) were dissolved in tetrahydrofuran (10 mL) in a Schlenk tube under argon. A solution of di-*tert*-butyl dicarbonate in tetrahydrofuran (1.0 M, 2.0 mL, 2.0 mmol) was added. The resulting solution was heated to 60 °C with stirring. After 6 h the solution was cooled to room temperature and concentrated. The residual solid was crystallized from ethanol containing a small proportion of chloroform, and recrystallized from a mixture of ethanol and toluene, to afford decamer **24** as white crystals (1.128 g, 66%): mp 188−189 °C with slow decomposition; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, J = 7.3 Hz, 4H), 7.19−7.14 (m, 40H), 1.46 (s, 36H), 1.44 (s, 54H), 0.25 (s, 18H); IR (neat, cm^{-1}) 2977, 2931, 1713, 1509, 1328, 1161, 1057, 851, 756. Anal. Calcd for $C_{122}H_{152}N_{10}O_{20}Si_2$: C, 68.64; H, 7.18. Found: C, 68.84; H, 7.31.

α,ω-Bis(trimethylsilyl)phenyl-Capped 16-mer 25. Dibromide **21** (750 mg, 0.425 mmol), arylamine **7** (659 mg, 0.892 mmol), sodium *tert*-butoxide (114 mg, 1.19 mmol), $Pd(OAc)_2$ (3.8 mg, 0.0170 mmol, 4.0 mol %), and BINAP (12.7 mg, 0.0204 mmol, 4.8 mol %) were dissolved in toluene (3 mL) and triethylamine (1 mL) in a Schlenk tube under argon. The reaction mixture was heated to 90 °C with stirring. After 18 h, the solution was cooled to room temperature. 4-(Dimethylamino)pyridine (5.00 mg, 0.0425 mmol, 10 mol %) and a solution of di-*tert*-butyl dicarbonate in tetrahydrofuran (1.0 M, 1.49 mL, 1.49 mmol) were added, and the resulting mixture was heated to 67 °C. After 3 h the solution was cooled to room temperature and partitioned between ethyl acetate (30 mL) and a 2.0 M aqueous solution of sodium hydroxide (20 mL). The organic layer was washed with brine (20 mL), dried over sodium sulfate, filtered, and concentrated. Crystallization of the residual solid from a 10:1 mixture of methanol and chloroform afforded 16-mer **25** as white crystals (1.01 g, 73%): mp 182−185 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, J = 8.4 Hz, 4H), 7.16 (d, J = 8.4, 4H), 7.13 (s, 60H), 1.43 (s, 144H), 0.24 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6, 143.2, 140.4, 140.2, 137.5, 128.2, 127.0, 126.6, 125.9, 81.3, 28.2, −1.1; IR (neat, cm^{-1}) 1713. Anal. Calcd for $C_{188}H_{233}N_{16}O_{32}Si$: C, 68.80; H, 7.06. Found: C, 68.53; H, 6.85.

α,ω-Bis(trimethylsilyl)phenyl-Capped 24-mer (26). Dibromide **21** (177 mg, 0.100 mmol), arylamine **10** (316 mg, 0.210 mmol), sodium *tert*-butoxide (28.8 mg, 0.300 mmol), $Pd(OAc)_2$ (1.3 mg, 6.0 μmol, 6.0 mol %), and BINAP (4.5 mg, 7.2 μmol, 7.2 mol %) were dissolved in toluene (2 mL) and triethylamine (0.5 mL) in a Schlenk tube under argon. The reaction mixture was heated to 90 °C. After 18 h the solution was cooled to room temperature. 4-(Dimethylamino)pyridine (2.40 mg, 0.0200 mmol, 20 mol %) and a solution of di-*tert*-butyl dicarbonate in tetrahydrofuran (1.0 M, 0.40 mL, 0.40 mmol) were added, and the resulting mixture was heated to 67 °C. After 4 h the solution was cooled to room temperature and partitioned between ethyl acetate (30 mL) and a 2.0 M aqueous solution of sodium hydroxide (20 mL). The organic layer was washed with brine (20 mL), dried over sodium sulfate, filtered, and concentrated. Crystallization of the residual solid from 2-propanol afforded 24-mer **26** as white crystals (362 mg, 75%): mp 185−188 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, J = 8.4 Hz, 4H), 7.16 (d, J = 8.4, 4H), 7.13 (s, 92H), 1.44 (s, 18H), 1.43 (s, 198H), 0.24 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 143.0, 140.2, 140.0, 137.3, 133.6, 128.0, 127.2, 126.9, 125.8, 81.3, 28.3, −1.1; IR (neat, cm^{-1}) 1714. Anal. Calcd for $C_{272}H_{334}N_{24}O_{48}Si_2$: C, 68.89; H, 7.00. Found: C, 69.06; H, 6.93.

Chain-Length Confirmation for 16-mer and 24-mer by ^{1}H NMR. The oligomer and hexamethylbenzene were weighed into a vial, dissolved in CD_2Cl_2 (0.75 mL), and transferred to an NMR tube. Three samples were prepared for each oligomer. Each spectrum was recorded with 16 scans and a relaxation delay of 20 s. Relative integration of the resonances for the internal standard, the BOC groups, and the trimethylsilyl endgroups yielded the ratios of repeat units to end groups; for each oligomer, the average ratio of the three runs was taken. The spectra are available as Supporting Information.

BOC/TMS ratio calcd for 16-mer **25**: 8/1. Found: (8.6 ± 0.3)/1.

BOC/TMS ratio calcd for 24-mer **26**: 12/1. Found: (12.5 ± 0.1)/1.

Iodotrimethylsilane. Iodotrimethylsilane was prepared from iodine and hexamethyldisilane according to the procedure of Seitz and Ferreira,[41] except for the use of 1.05 equiv of hexamethyldisilane to ensure complete consumption of iodine. The product was vacuum-transferred from a trace of zinc dust and stored in a resealable Schlenk tube under argon, over copper wire. The colorless liquid was approximately 95% pure as judged by ^{1}H NMR, the remainder consisting principally of hexamethyldisilane.

General Procedure for Deprotection of Oligomers by Thermolysis. The protected oligomer was heated in a Schlenk tube under argon, for 9 h at 185 °C, and then cooled to room temperature. The deprotected oligomers were obtained as powders in quantitative yield.

Phenyl-capped octaaniline (27a): No melting observed below 360 °C. ^{1}H NMR (300 MHz, DMF-d_7) δ 7.76 (s, 2H), 7.59 (s, 2H), 7.51 (s, 2H), 7.49 (s, 2H), 7.18 (t, J = 7.4 Hz, 4H), 7.10−6.96 (m, 32H), 6.71 (t, J = 7.4 Hz, 2H); IR (neat, cm^{-1}) 3388, 1598, 1514, 1495, 1292, 1214, 814, 744, 697, 509; UV−vis (NMP) λ_{max} 337 nm (ϵ = 6.6 × 10^4). Anal. Calcd for $C_{54}H_{46}N_8$: C, 80.37; H, 5.75. Found: C, 80.24; H, 5.62.

α,ω-Bis(cyano)phenyl-capped octaaniline (27b): No melting observed below 360 °C. ^{1}H NMR (300 MHz, DMF-d_7) δ 8.60 (s, 2H), 7.79 (s, 2H), 7.58 (d, J = 8.4 Hz, 4H), 7.53 (s, 2H), 7.52 (s, 2H), 7.14−6.98 (m, 28H); IR (neat, cm^{-1}) 3385, 2213, 1602, 1498, 1293, 1237, 1172, 815, 515; UV−vis (NMP) λ_{max} 336 nm (ϵ = 7.3 × 10^4). Anal. Calcd for $C_{56}H_{44}N_{10}$: C, 78.48; H, 5.17. Found: C, 78.53; H, 4.95.

α,ω-Bis(*tert*-butyl)phenyl-capped octaaniline (27c): No melting observed below 360 °C. ^{1}H NMR (300 MHz, DMF-d_7) δ 7.60 (s, 2H), 7.48 (s, 2H), 7.43 (s, 2H), 7.41 (s, 2H), 7.16 (d, J = 8.7 Hz, 4H), 6.93 (d, J = 8.7 Hz, 4H), 6.88−6.82 (m, 28H), 1.22 (s, 18H); IR (neat, cm^{-1}) 3389, 2957, 1610, 1499, 1291, 815; UV−vis (NMP) λ_{max} 336 nm (ϵ = 7.8 × 10^4); HRMS (FAB) *m*/*z* 918.5090 (918.5097 calcd for $C_{62}H_{62}N_8$, M^+).

α,ω-Bis(*n*-dodecyl)phenyl-capped octaaniline (27d): No melting observed below 360 °C. ^{1}H NMR (300 MHz, DMF-d_7) δ 7.64 (s, 2H), 7.54 (s, 2H), 7.49 (s, 2H), 7.48 (s, 2H), 7.06−6.94 (m, 36H), 2.51 (t, J = 7.5 Hz, 4H), 1.61−1.50 (m, 4H), 1.36−1.24 (m, 36H), 0.88 (t, J = 6.2, 6H); IR (neat, cm^{-1}) 3390, 2922, 2852, 1610, 1515, 1498,-1293, 1215, 815; UV−vis (NMP) λ_{max} 336 nm (ϵ = 7.3 × 10^4). Anal. Calcd for $C_{78}H_{94}N_8$: C, 81.92; H, 8.28. Found: C, 81.74; H, 8.09.

α,ω-Bis(methoxy)phenyl-capped octaaniline (27e): No melting observed below 360 °C. ^{1}H NMR (300 MHz, DMF-d_7) δ 7.48 (s, 4H), 7.47 (s, 4H), 7.01 (d, J = 8.7 Hz, 4H), 6.99 (s, 28H), 6.84 (d, J = 8.7 Hz, 4H), 3.74 (s, 6H); IR (neat, cm^{-1}) 3389, 1514, 1498, 1292, 1237, 815, 515; UV−vis (NMP) λ_{max} 335 nm (ϵ = 5.38 × 10^4). Anal. Calcd for $C_{56}H_{50}N_8O_2$: C, 77.57; H, 5.81. Found: C, 77.37; H, 5.75.

General Procedure for Preparative Deprotection of Oligomers by Iodotrimethylsilane. The protected oligomer (0.020 mmol) was dissolved in anhydrous dichloromethane (5.0 mL) in a Schlenk tube under argon. Iodotrimethylsilane (20% excess) was added dropwise, with stirring, causing the solution to turn a pale yellow color. The solution was stirred for 15−30 min, and then degassed methanol (200 μL) was added dropwise. Within seconds, the clear solution became cloudy and deposited a pale yellow precipitate. Degassed triethylamine (200 μL) was added, and the suspension was vacuum-filtered rapidly under air. The collected product was washed with degassed methanol (5 mL) and dried in vacuo, affording a white powder.

(41) Seitz, D. E.; Ferreira, L. *Synth. Commun.* **1979**, 931−939.

Phenyl-Capped Heptaaniline (28). No melting observed below 360 °C. ^{1}H NMR (500 MHz, DMF-d_7) δ 7.79 (s, 2H), 7.62 (s, 2H), 7.54 (s, 2H), 7.52 (s, 1H), 7.18 (t, J = 7.8 Hz, 4H), 7.09−6.99 (m, 28H), 6.71 (t, J = 7.1 Hz, 2H); ^{13}C (125 MHz, DMF-d_7) δ 147.3, 141.0, 139.7, 139.2, 138.8, 138.1, 136.2, 131.5, 130.1, 122.2, 120.3, 119.6, 119.3, 119.0, 119.0, 118.2, 115.8; IR (neat, cm^{-1}) 3387, 3025, 1598, 1512, 1302, 814; UV−vis (DMF) λ_{max} 334 nm ($\epsilon = 7.9 \times 10^4$). Anal. Calcd for $C_{48}H_{41}N_7$: C, 80.53; H, 5.77. Found: C, 80.52; H, 5.54.

Phenyl-Capped Nonaaniline (29). No melting observed below 360 °C. ^{1}H NMR (500 MHz, DMF-d_7) δ 7.77 (s, 2H), 7.60 (s, 2H), 7.52 (s, 2H), 7.49 (s, 3H), 7.18 (t, J = 12.0 Hz, 4H), 7.09−7.00 (m, 36H), 6.70 (t, J = 12.5 Hz, 2H); ^{13}C NMR (125 MHz, DMF-d_7) δ 146.5, 140.3, 139.0, 138.6, 138.3, 138.2, 137.9, 137.3, 135.5, 129.4, 121.4, 119.5, 118.9, 118.7, 118.6, 118.4, 118.2, 118.2, 117.4, 115.0; IR (KBr, cm^{-1}) 3386, 3021, 1598, 1496, 1290, 814; UV−vis (DMF) λ_{max} 336 nm ($\epsilon = 8.4 \times 10^4$). Anal. Calcd for $C_{60}H_{51}N_9$: C, 80.24; H, 5.72. Found: C, 79.99; H, 5.61.

Phenyl-Capped Decaaniline (30). No melting observed below 360 °C. ^{1}H NMR (500 MHz, DMF-d_7) δ 7.77 (s, 2H), 7.60 (s, 2H), 7.52 (s, 2H), 7.49 (s, 2H), 7.48 (s, 2H), 7.18 (t, J = 13.0 Hz, 4H), 7.09−6.98 (m, 40H), 6.71 (t, J = 12.0 Hz, 2H); ^{13}C NMR (125 MHz, DMF-d_7) δ 147.3, 141.1, 139.8, 139.3, 139.2, 139.1, 138.9, 138.7, 138.1, 136.2, 134.9, 130.1, 122.2, 120.3, 119.7, 119.5, 119.4, 119.3, 119.2, 119.0, 118.9, 118.2, 115.7; IR (KBr, cm^{-1}) 3386, 3021, 1598, 1496, 1289, 815; UV−vis (DMF) λ_{max} 336 nm ($\epsilon = 1.1 \times 10^5$). Anal. Calcd for $C_{66}H_{56}N_{10}$: C, 80.13; H, 5.71. Found: C, 79.93; H, 5.64.

Phenyl-Capped 16-mer (31). No melting observed below 360 °C. IR (KBr, cm^{-1}) 3378, 3021, 1596, 1496, 1284, 814; UV−vis (DMF) λ_{max} 338 nm ($\epsilon = 1.8 \times 10^5$). Anal. Calcd for $C_{102}H_{86}N_{16}$: C, 79.77; H, 5.64; N, 14.59. Found: C, 79.59; H, 5.46; N, 14.38.

Phenyl-Capped 24-mer (32). No melting observed below 360 °C. IR (KBr, cm^{-1}) 3378, 3025, 1596, 1496, 1284, 814; UV−vis (DMF) λ_{max} 338 nm ($\epsilon = 2.2 \times 10^5$). Anal. Calcd for $C_{150}H_{126}N_{24}$: C, 79.55; H, 5.61; N, 14.84. Found: C, 79.52; H, 5.54; N, 14.66.

Preparation of Films for Electrochemistry. The protected oligomer (10.0 μmol, except 5.00 μmol in the case of **32**) was dissolved in anhydrous dichloromethane (5.0 mL) in a Schlenk tube under argon. Iodotrimethylsilane (20% excess) was added dropwise, with stirring, causing the solution to turn a pale yellow color. The solution was stirred for 15 min, then concentrated, and dried in vacuo to remove excess iodotrimethylsilane. The residual solid was dissolved in anhydrous dichloromethane (20.0 mL) to form a clear solution. An aliquot of 10.0 μL was withdrawn *via syringe* and allowed to evaporate on an ITO-coated glass slide.

Electrochemistry. Electrochemical studies were carried out using an EcoChemie Autolab potentiostat. Cyclic voltammograms were recorded at a scan rate of 100 mV/s in a three-electrode cell with a platinum foil counter electrode and a SCE reference electrode. Working electrodes were prepared by evaporation of an oligomer trimethylsilylcarbamate solution, prepared as described above, onto ITO-coated spectroelectrochemistry slides (40 Ω, coated both sides) purchased from Delta Technologies, Limited. Experiments were run under noncontrolled atmosphere using 1.0 M aqueous sulfuric acid as the electrolyte.

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Supporting Information Available: ^{1}H NMR spectra of 16-mer **25** and 24-mer **26** for chain-length confirmation (7 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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