

Patterned Redox Arrays of Polyarylamines I. Synthesis and Electrochemistry of a *p*-Phenylenediamine and Arylamino-Appended *p*-Phenylenediamine Arrays

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The synthesis of tetra-*p*-anisyl-*p*-phenylenediamine (TAPD, **1**) and its derivatives containing appended diarylamino (AA) redox groups (2AA/PD, **2** and 4AA/1PD, **3**) is presented. Such mixed redox arrays are of interest in a materials context for their projected directional electron transport properties and potential charge-trapping properties. Redox array **3** has a shell/core structure in which the four AA groups of higher oxidation potential surround a central *p*-phenylenediamine (PD) group of lower oxidation potential. Electrochemical characterization of these substrates is reported, and the redox gradients in arrays **2** and **3** are estimated to be ~ 0.2 V. The meta-linked AA and PD groups of **2** and **3** are observed to be weakly electronically coupled. EPR and electrochemical data show **2**^{•+} and **3**^{•+} to be PD-localized radical cations (i.e., 2AA/PD^{•+} and 4AA/PD^{•+}, respectively). Despite AA shielding of the core PD group in **3**, its solution-phase cyclic voltammogram appears to be normal, indicating relatively facile heterogeneous electron transfer at the electrode surface/solution interface under ambient conditions. The radical cations of **1–3** are prepared as robust, isolable salts. Finally, evidence for intervalent charge transfer is found in the near-IR spectra of **2**^{•+} and **3**^{•+}.

Introduction

Arylamines have found widespread use as hole transport agents in advanced materials.^{1,2} The stable cationic and neutral oxidation states of these structures and their ability to form glassy amorphous phases^{3,4,5,6} contribute to such materials applications. By adjoining N-based redox functions of differing oxidation potential, we seek to create redox arrays designed for directional hole transport and charge capture and trapping. Here, we report the synthesis and electrochemical behavior of some prototype oligomeric arylamines with mixed redox groups of varied oxidation potential. Structures under study include tetra-*p*-anisyl-*p*-phenylenediamine (TAPD, **1**) and two oligomeric derivatives thereof, structures **2** and **3**. The latter two structures are composed of arylamino (AA) groups attached to a *p*-phenylenediamine (PD) group via C–N bond formation at the meta position of the PD N-aryl substituent(s). In this contribution, we present the molecular synthesis and redox characterization of **1–3** and their corresponding radical cations. In an accompanying paper, we report on film properties of these compounds, including a study of film morphology and electrochemistry as a function of oligomer structure.

The present work seeks to contribute new knowledge useful for the design and control of electron transport within redox arrays on the nanoscale. Designed redox arrays may ultimately serve as active components in future information storage media or other electronic devices built to perform molecular scale operations. Some current work in the area of molecular systems for charge trapping and/or directional charge transport includes that of Gorman⁷ et al. on iron–sulfur cluster core dendrimers, Roffia and Balzani⁸ et al. on patterned organometal dendrimers, and our own work⁹ and that by Walder¹⁰ et al. on redox-gradient dendrimers. The general field of redox active arrays, and redox active dendrimers in particular, has been active in recent years, and some excellent reviews of this subject are available.¹¹

Results and Discussion

Substrates **1–3** were prepared in good yield by Cu- and Pd-mediated N-arylation sequences as shown in Schemes 1 and 2. In the synthesis of **2** and **3**, advantage

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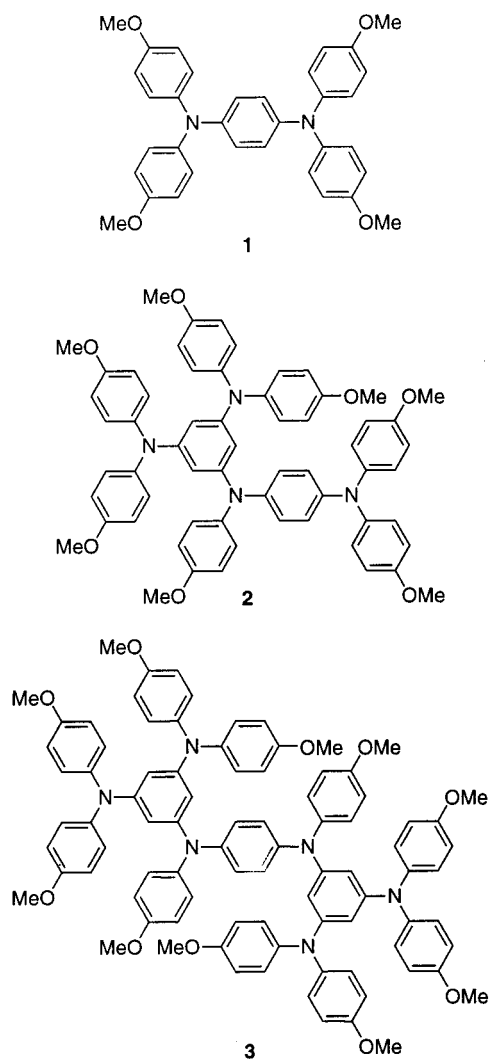
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is taken of the Ullmann reaction selectivity for reaction of aryl iodides over aryl chlorides, which are completely unreactive. The Hartwig¹²/Buchwald¹³ Pd-based method is employed to aminate the exceptionally deactivated (electron rich) aryl chloride **7** in impressive yield.

Electrochemical analysis of **1–3** by cyclic voltammetry (CV) in CH₂Cl₂ has been performed. Multiple chemically reversible oxidations are observed for all substrates (Figures 1). The derived formal oxidation potentials (E° values) for **1–3** are summarized in Table 1.

Assignment of the E° oxidation events is as follows. For **1**, the two oxidations observed correspond to successive one electron removal from the *p*-phenylene-

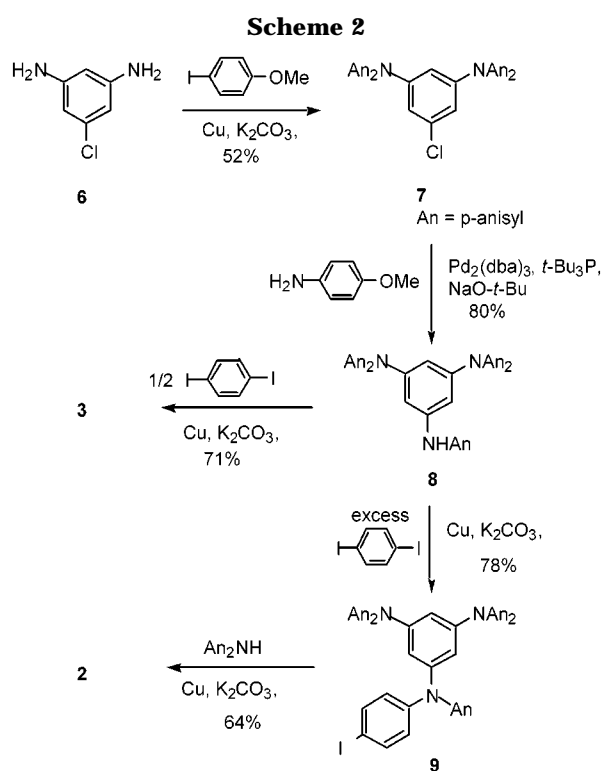
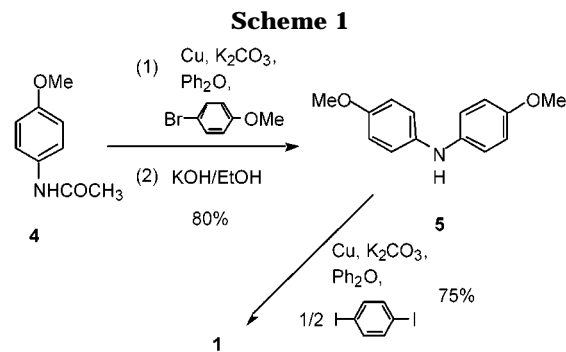


Table 1. Oxidation Potentials for *p*-Phenylenediamine Substrates 1–3

substrate	$E^{\circ}(1)^a$	$E^{\circ}(2)^a$	$E^{\circ}(3)^a$	$E^{\circ}(4)^a$
TAPD (1)	0.46	0.92		
2AA/PD (2)	0.48	0.87	0.98	
4AA/PD (3)	0.49	0.87	0.87	1.05

^a V vs SCE, in CH₂Cl₂ (0.1 M Bu₄NBF₄).

diamine (pPD) functionality of **1** to yield, first, a stable, delocalized pPD radical cation **1^{•+}** and, second, a quinonoid-type dication **1²⁺** (eq 1). Both oxidized forms of **1** can be prepared independently as isolably stable salts by chemical oxidation methods. The mixed trimer array 2AA/PD (**2**) shows a first oxidation at 0.48 V which is assigned to electron loss from the pPD unit. The next two oxidation waves (0.87 and 0.98 V) appear to involve one electron loss from the AA group(s) and a second oxidation of the PD moiety, respectively, to yield a 2AA/**PD²⁺** trication. These potentials are similar to those associated with monocation formation from TAPD (**1**) and dication formation from the previously reported tris(AA) compound **10**.¹⁴ There appears to be a fourth

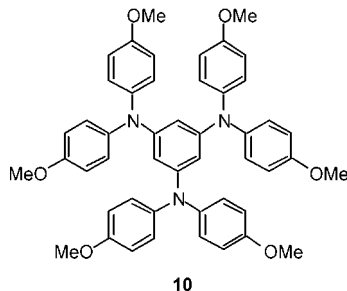
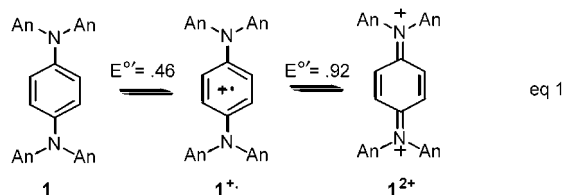
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reversible oxidation wave for **2**. Its E° value is difficult to extract accurately from the voltammogram and has therefore not been included in Table 1. This fourth oxidation to yield 2^{4+} presumably involves, in total, double oxidation of the pPD unit and single oxidation of each of the AA units.



$E^{\circ}(1) = 0.67$ V vs SCE
 $E^{\circ}(2) = 0.87$
 $E^{\circ}(3) = 0.98$

The shell/core array 4AA/PD (**3**) shows a first oxidation ($E^{\circ}(1) = 0.49$ V) which is assigned as electron loss from the pPD group and is followed by a two-electron oxidation event ($E^{\circ}(2) = E^{\circ}(3) = 0.87$ V) assigned as simultaneous electron loss from individual remote 2AA groups to give a $2AA^+/PD^+/2AA^+$ trication. The remote nature of the two 2AA moieties in **3** is consistent with their oxidation occurring at a single potential. Electrochemical equivalence is typically observed for multiple redox-active surface groups on dendrimers.¹⁵ The fourth oxidation ($E^{\circ}(4) = 1.05$ V) for **3** is assigned to pPD dication formation. Using the first oxidation potential of **10** as a model for shell oxidation in **3**, we can estimate the shell/core redox potential gradient in **3** (and the linear gradient in **2**) to be ~ 0.2 V.

The ESR spectra of $1^+\cdot PF_6^-$ and of $3^+\cdot ClO_4^-$ in $(CH_3)_2CO$ and $2^+\cdot PF_6^-$ in CH_2Cl_2 are shown in Figures 2 and 3. Spectra of both $1^+\cdot$ and $3^+\cdot$ radicals display a dominant $a(2N) = 5.75$ G feature, indicating the presence of an oxidized pPD unit, as also expected from their similar $E^{\circ}(1)$ values. These ESR data support the assignment of a localized pPD core radical cation in $3^+\cdot$. Small splittings used in the simulation of the $1^+\cdot$ ESR spectrum were determined independently by ENDOR analysis. A broad 5-line ESR signal is observed for $2^+\cdot$. The splitting here is also ~ 5.7 G, suggesting that this species too is a pPD radical cation having two N-atoms with (nearly) equal spin density.

The optical spectra of $1^+\cdot PF_6^-$, $2^+\cdot PF_6^-$, and $3^+\cdot PF_6^-$ have been measured in $CHCl_3$ (Figure 4). These structures all exhibit a strong absorption near 1000 nm in

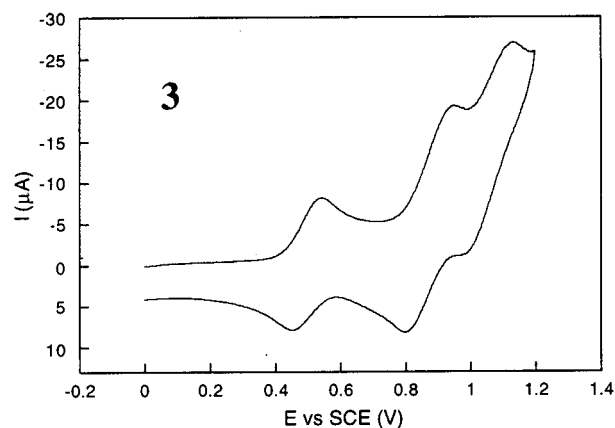
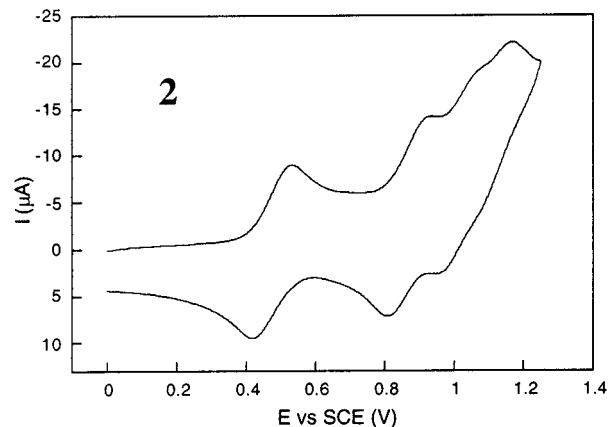
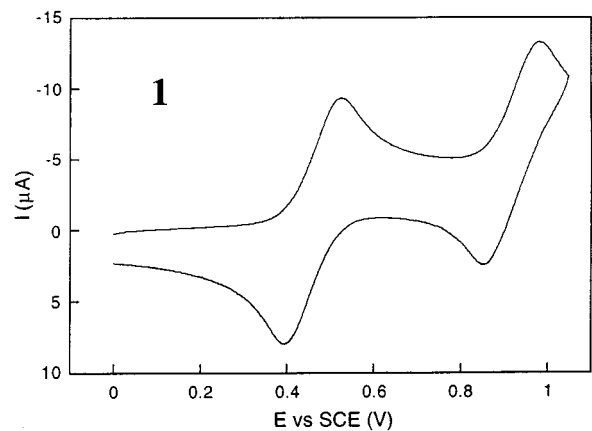


Figure 1. Cyclic voltammograms of 1.0 mM substrate in CH_2Cl_2 (0.1 M Bu_4NBF_4) at 200 $mV\ s^{-1}$ scan rate.

the near-IR which is assigned to a pPD^+ transition.¹⁶ The long wavelength shoulders observed on these bands for $2^+\cdot PF_6^-$ and $3^+\cdot PF_6^-$ are tentatively assigned as internal charge-transfer excitations involving promotion of an electron from the AA groups to the pPD^+ group within these compounds. This assignment is consistent with a Koopmans' theorem¹⁷ approximation of the electronic transition as calculated by AM1 (using the neutral in cation geometry (ncg) method).¹⁸

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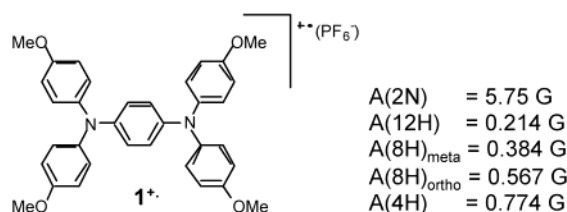
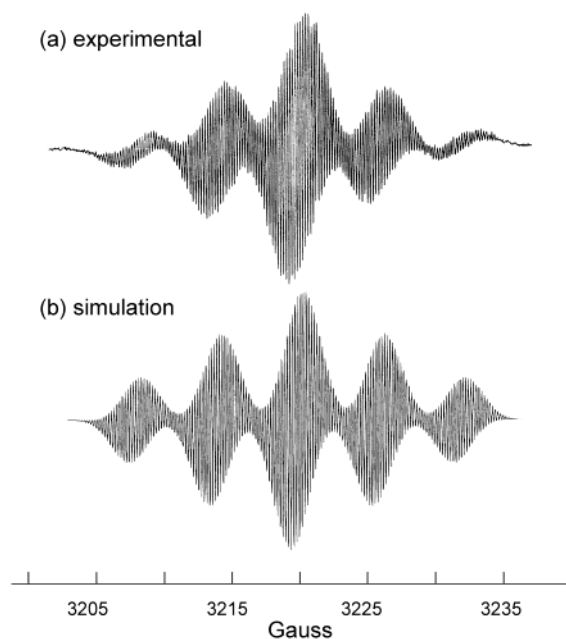


Figure 2. ESR spectrum of 0.5 mM 1^+PF_6^- in $(\text{CH}_3)_2\text{CO}$ at 298 K (top) and simulation (bottom).

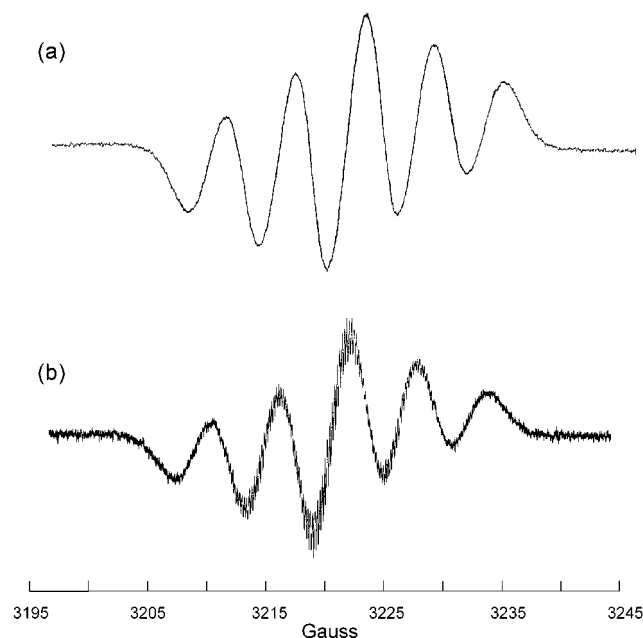


Figure 3. ESR spectra at 298 K of (a) 0.5 mM 2^+PF_6^- in CH_2Cl_2 and (b) 0.5 mM 3^+ClO_4^- in $(\text{CH}_3)_2\text{CO}$.

Conclusions

The synthesis of a shell/core redox array **3** allows investigation of the redox and charge-trapping character of this novel redox oligomer which contains, nominally, a radial redox gradient. The core-only analogue, **1**, and a linear redox gradient fragment, **2**, are prepared for comparative study. It is found that meta-connection of

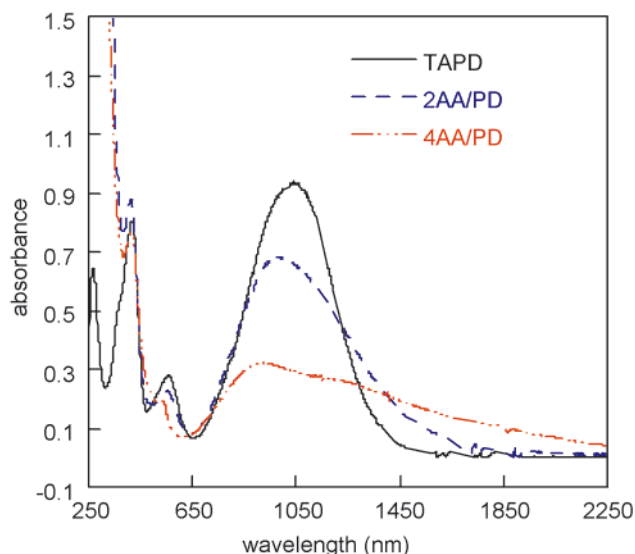


Figure 4. Optical absorption spectra for 1^+PF_6^- (line), 2^+PF_6^- (dash), and 3^+PF_6^- (dot/dash) in CHCl_3 .

the AA and pPD redox groups produces weak electronic exchange between the groups whose oxidation potentials are relatively unaffected by adjoining functionality at a given charge state. The monocations of this series are isolably stable salts of high thermal stability and possess localized pPD⁺ cationic structures. Electrochemical studies suggests that the effective 2AA/PD potential gradient in **2** and in **3** is $\sim 0.2 \text{ V}$. This is an estimate of the charge-trapping ability of the array within **3**, i.e., the approximate adiabatic energy difference between the core-charged ($2\text{AA}/\text{PD}^+/2\text{AA}$) and shell-charged ($2\text{AA}^+/\text{PD}/2\text{AA}$) states of 3^+ . Evidence for shell-to-core photo charge transfer is observed in the NIR spectrum of 3^+ . The stabilities and novel electronic structures of compounds such as **2** and **3** make them ideal molecular components for detailed evaluation and elaboration as active ingredients of designed nanoscale electronic materials.

Experimental Section

Materials and Equipment. Starting materials were purchased from Aldrich Chemical Co., Frinton Laboratories, or Fisher Scientific. All reactions were performed under a nitrogen or argon atmosphere. For Pd-catalyzed reactions, reactants were weighed out in a drybox. Cu powder (for organic synthesis) from Aldrich (29,258-3) was used for best results in the Cu-catalyzed reactions. Thin-layer chromatography was performed on Selecto Scientific precoated silica gel F-254 (200 μm) or basic alumina F-254 (200 μm) plates. Column chromatography was performed on silica gel (J. T. Baker, 40 μm flash) or basic alumina (Aldrich, activated Brockmann I, ~ 150 mesh).

IR spectra were recorded on a Nicolet 360 FT-IR. NMR spectra were recorded on a Bruker AM360 spectrometer. Chemical shifts are reported (δ) relative to TMS for ^1H spectra and relative to the solvent signal for ^{13}C spectra. Microanalyses were performed by Atlantic Microlab Inc., Norcross, GA. Melting points are uncorrected.

***N,N,N,N*-Tetrakis(4-methoxyphenyl)-1,4-benzene-diamine (1).** **5** (2.00 g, 8.72 mmol), *p*-diiodobenzene (1.30 g, 3.93 mmol), K_2CO_3 (1.21 g, 8.72 mmol), Cu powder (0.56 g, 8.7 mmol), and diphenyl ether (5 mL) were heated together at 190 $^\circ\text{C}$ for 48 h with stirring. The mixture was allowed to cool, taken up in benzene, and passed through a column of basic alumina. Elution with benzene gave **1** as colorless crystals (1.57 g, 75%): mp 160 $^\circ\text{C}$. ^1H NMR (360 MHz, CDCl_3): δ 7.02

(d, $J = 9$ Hz, 8H), 6.84 (s, 4H), 6.80 (d, $J = 9$ Hz, 8H), 3.78 (s, 12 H); ^{13}C NMR (90 MHz, CDCl_3): δ 155.13, 142.60, 141.59, 125.38, 123.08, 114.51, 55.46. Anal. Calcd for $\text{C}_{34}\text{H}_{32}\text{N}_2\text{O}_4$: C, 76.67; H, 6.06; N, 5.26. Found: C, 76.67; H, 6.14; N, 5.21.

***N,N,N,N,N'*-pentakis(4-methoxyphenyl)-1,3,5-benzenetriamine (2)**. **5** (0.32 g, 1.4 mmol), **9** (1.20 g, 1.40 mmol), anhydrous K_2CO_3 (0.19 g, 1.4 mmol), Cu powder (0.090 g, 1.4 mmol), and diphenyl ether (1 mL) were heated together at 190 °C for 48 h with stirring. The reaction mixture was allowed to cool, taken up in benzene, filtered, and passed through a column of silica gel. Elution with Et_2O /hexane (1:1) gave **2** (0.851 g, 64%): mp 118–119 °C. ^1H NMR (360 MHz, CDCl_3): δ 7.00–6.93 (m, 14H), 6.82–6.69 (m, 18H), 6.09 (d, $J = 2.1$ Hz, 2H), 6.03 (t, $J = 2.1$ Hz, 1H), 3.79 (s, 6H), 3.75 (s, 3H), 3.74 (s, 12H); ^{13}C NMR (90 MHz, benzene- d_6): δ 156.32, 156.06, 155.97, 150.49, 150.30, 144.12, 142.21, 142.07, 141.39, 141.00, 127.22, 126.98, 126.65, 126.01, 125.46, 123.44, 115.09, 114.93, 114.84, 108.17, 108.11, 55.02, 54.89, 54.83. IR (KBr cm^{-1}) 3037 (w), 2996 (w), 2950 (w), 2833 (w), 1587 (s), 1576 (s), 1504 (s), 1463 (s), 1240 (s), 1180 (m), 1036 (s), 826 (s). Anal. Calcd for $\text{C}_{61}\text{H}_{56}\text{N}_4\text{O}_7$: C, 76.55; H, 5.90; N, 5.85. Found: C, 76.43; H, 5.92; N, 5.75.

***N,N,N,N,N'*-pentakis(4-methoxyphenyl)-1,3,5-benzenetriamine (3)**. **8** (2.62 g, 4.00 mmol), *p*-diiodobenzene (0.66 g, 2.0 mmol), anhydrous K_2CO_3 (1.10 g, 7.96 mmol), Cu powder (0.50 g, 7.9 mmol), and diphenyl ether (5 mL) were heated together at 190 °C for 48 h with stirring. The reaction mixture was allowed to cool, taken up in benzene, filtered, and passed through a column of basic alumina. Elution with Et_2O gave **3** (1.96 g, 71%): mp 272 °C. ^1H NMR (360 MHz, CDCl_3): δ 6.93 (d, $J = 8.9$ Hz, 16H), 6.89 (d, $J = 9.5$ Hz, 4H), 6.75 (s, 4H), 6.73–6.68 (m, 20H), 6.07 (d, $J = 1.7$ Hz, 4H), 6.04 (t, $J = 1.7$ Hz, 2H), 3.77 (s, 6H), 3.71 (s, 24H); ^{13}C NMR (90 MHz, benzene- d_6): δ 156.59, 156.48, 150.90, 150.57, 143.44, 141.75, 141.46, 127.11, 127.02, 125.57, 115.36, 115.25, 109.24, 108.76, 55.28, 55.25. IR (KBr, cm^{-1}) 3035 (w), 2995 (w), 2954 (w), 2930 (w), 2834 (w), 1589 (s), 1575 (s), 1505 (s), 1456 (s), 1440 (s), 1281 (s), 1240 (s), 1180 (m), 1037 (s), 825 (s). Anal. Calcd for $\text{C}_{88}\text{H}_{80}\text{N}_6\text{O}_{10}$: C, 76.50; H, 5.84; N, 6.08. Found: C, 76.42; H, 5.89; N, 6.02.

***N,N*-Bis(4-methoxyphenyl)amine (5)**.¹⁹ **4** (99 g, 0.60 mol), *p*-bromoanisole (140 g, 0.750 mol), K_2CO_3 (87 g, 0.63 mol), and Cu powder (6.4 g, 0.10 mol) were heated together at 190 °C for 48 h under nitrogen with vigorous stirring. The mixture was poured into a continuous extractor and extracted for 7 days using hexane. Removal of the solvent followed by recrystallization with Et_2O gave the diarylamide (132 g, 81%). This amide (95 g, 0.35 mol) and KOH (44.9 g, 0.800 mol) were dissolved in EtOH (400 mL) and refluxed for 10 h. The solution was then cooled to –20 °C and **5** crystallized (79 g, 99%): ^1H NMR (360 MHz, CDCl_3): δ 6.93 (d, $J = 8.5$ Hz, 2H), 6.82 (d, $J = 8.5$ Hz, 2H), 5.28 (br s, 1H), 3.77 (s, 6H).

1-Chloro-*N,N,N,N*-tetrakis(4-methoxyphenyl)-3,5-benzenediamine (7). **6** (5.00 g, 35.1 mmol), 4-iodoanisole (32.8 g, 0.140 mol), copper powder (8.90 g, 0.140 mol), K_2CO_3 (19.3 g, 0.140 mol), and diphenyl ether (20 mL) were heated together at 190 °C for 36 h with stirring. The cooled mixture was taken up in ethyl acetate, filtered, preabsorbed onto basic alumina (~10 g), and loaded onto a column of basic alumina. Elution with ethyl acetate/hexanes (1:5) gave **7** as a white crystalline solid (10.4 g, 52%). ^1H NMR (360 MHz, CDCl_3): δ 6.98 (d, $J = 8.9$ Hz, 8H), 6.78 (d, $J = 8.9$ Hz, 8H), 6.32 (t, $J = 1.9$ Hz, 1H), 6.30 (d, $J = 1.9$ Hz, 2H), 3.77 (s, 12H); ^{13}C NMR (90 MHz, CDCl_3): δ 156.00, 150.05, 140.18, 134.81, 126.67, 114.61, 111.98, 110.15, 55.41; IR (KBr, cm^{-1}) 2955 (w), 2832 (w), 1590 (m), 1564 (m), 1505 (s), 1451 (m), 1241 (s), 1038 (m), 827 (m). Anal. Calcd for $\text{C}_{34}\text{H}_{31}\text{ClN}_2\text{O}_4$: C, 72.01; H, 5.51; N, 4.94. Found: C, 72.23; H, 5.25; N, 5.17.

***N,N,N,N,N'*-Pentakis(4-methoxyphenyl)-1,3,5-benzenetriamine (8)**. **7** (5.00 g, 8.79 mmol), *p*-anisidine (1.08 g, 8.79 mmol), $\text{Pd}_2(\text{dba})_3$ (0.24 g, 0.26 mmol), tri-*tert*-butylphosphine (42.1 mg, 0.208 mmol), sodium-*t*-butoxide (1.27 g, 13.2 mmol), and toluene (30 mL) were weighed out and mixed together in

a drybox. The mixture was heated at 70 °C for 24 h under an argon atmosphere with stirring. The mixture was filtered through Celite, and the solvent was removed in vacuo. Column chromatography (basic alumina; benzene) gave **8** (4.59 g, 80%): mp 182 °C. ^1H NMR (360 MHz, CDCl_3): δ 7.00 (d, $J = 9$ Hz, 8H), 6.86 (d, $J = 9$ Hz, 2H), 6.75 (d, $J = 9$ Hz, 8H), 6.70 (d, $J = 9$ Hz, 2H), 6.05 (t, $J = 2$ Hz, 1H), 6.01 (d, $J = 2$ Hz, 2H), 5.28 (broad s, 1H), 3.76 (s, 12H), 3.73 (s, 3H); ^{13}C NMR (90 MHz, benzene- d_6): δ 156.11, 155.28, 150.92, 146.58, 141.10, 136.03, 126.69, 121.61, 114.89, 114.68, 107.49, 102.71, 54.93, 54.87. IR (KBr, cm^{-1}) 3392 (m), 2996 (w), 2950 (w), 2827 (w), 1592 (s), 1578 (m), 1505 (s), 1466 (m), 1241 (s), 1036 (m), 827 (m). Anal. Calcd for $\text{C}_{41}\text{H}_{38}\text{N}_3\text{O}_5$: C, 75.32; H, 6.01; N, 6.42. Found: C, 75.41; H, 6.11; N, 6.36.

***N*-(4-Iodophenyl)-*N,N,N,N,N'*-pentakis(4-methoxyphenyl)-1,3,5-benzenetriamine (9)**.²⁰ **8** (7.90 g, 0.0121 mol), *p*-diiodobenzene (17.88 g, 0.05420 mol), anhydrous K_2CO_3 (4.99 g, 0.0361 mol), Cu powder (2.30 g, 0.0361 mol), and diphenyl ether (10 mL) were heated together at 190 °C for 24 h with stirring. At this time, the excess diiodobenzene and diphenyl ether were removed by vacuum distillation. The resulting solid residue was taken up in benzene, filtered, and chromatographed on a column of basic alumina. Elution with benzene gave **9** (7.56 g, 73%): mp 182–183 °C. ^1H NMR (360 MHz, CDCl_3): δ 7.36 (d, $J = 9$ Hz, 2H), 6.96 (d, $J = 9$ Hz, 2H), 6.93 (d, $J = 9$ Hz, 8H), 6.76 (d, $J = 9$ Hz, 2H), 6.70 (d, $J = 9$ Hz, 8H), 6.67 (d, $J = 9$ Hz, 2H), 6.13 (t, $J = 2$ Hz, 1H), 6.10 (d, $J = 2$ Hz, 2H), 3.77 (s, 3H), 3.75 (s, 12H); ^{13}C NMR (90 MHz, benzene- d_6): δ 157.30, 155.67, 151.14, 149.55, 148.67, 141.45, 140.48, 138.38, 127.11, 126.98, 124.40, 115.47, 115.32, 109.96, 109.26, 83.79, 55.29, 55.24. IR (KBr, cm^{-1}) 2991 (w), 2950 (w), 2899 (w), 2833 (w), 1589 (m), 1572 (m), 1505 (s), 1483 (m), 1463 (m), 1441 (m), 1283 (m), 1240 (s), 1035 (m), 824 (m). Anal. Calcd for $\text{C}_{47}\text{H}_{42}\text{N}_3\text{O}_5\text{I}$: C, 65.97; H, 4.93; N, 4.91. Found: C, 66.10; H, 4.97; N, 4.91.

Preparation of Isolated Radical Cation Salts. $1^{+\bullet}(\text{PF}_6^-)$.²⁰ In a 50 mL round-bottomed flask was placed **1** (76.1 mg, 0.143 mmol) and 20 mL of dry CH_2Cl_2 . The mixture was placed under N_2 atmosphere and cooled to –78 °C and solid nitrosonium hexafluorophosphate (25.0 mg, 0.143 mmol), preweighed in a drybox, was added quickly with stirring. After 30 min of stirring at –78 °C, the radical cation salt was precipitated by trituration with ethyl ether and the solid was collected by suction filtration and dried under vacuum (0.5 mmHg). Anal. Calcd for $\text{C}_{34}\text{H}_{32}\text{N}_2\text{O}_4\text{PF}_6$: C, 60.27; H, 4.76; N, 4.13. Found: C, 60.55; H, 4.88; N, 4.47.

$2^{+\bullet}(\text{PF}_6^-)$. Prepared as described above for $1^{+\bullet}(\text{PF}_6^-)$. Anal. Calcd for $\text{C}_{61}\text{H}_{56}\text{N}_4\text{O}_7\text{PF}_6$: C, 66.48; H, 5.12; N, 5.08. Found: C, 66.16; H, 5.24; N, 5.25.

$3^{+\bullet}(\text{PF}_6^-)$. Prepared as described above for $1^{+\bullet}(\text{PF}_6^-)$. Anal. Calcd for $\text{C}_{88}\text{H}_{80}\text{N}_6\text{O}_{10}\text{PF}_6$: C, 69.24; H, 5.28; N, 5.51. Found: C, 69.34; H, 5.30; N, 5.37.

Cyclic Voltammetry. Cyclic voltammetry (CV) was performed on a PAR 273 electrochemical potentiostat (EG&G Instruments). A four-necked CV cell (10 mL) equipped with a Pt disk (1.6 mm diameter) working electrode, a Pt wire counter electrode, and a saturated calomel electrode (SCE) reference was used for routine CV measurements which were carried out under an inert atmosphere. Tetrabutylammonium tetrafluoroborate (0.1 M) was used as supporting electrolyte for electrochemical experiments. A capacitor (0.1 μF), connected between the reference electrode and counter electrode, was used to reduce background noise.

ESR Spectroscopy. X-band ESR spectra were recorded on a Varian E-3 spectrometer. All glassware was flame dried prior to use and allowed to cool under a dry nitrogen atmosphere. Solvents used in ESR measurements were purified by standard methods²¹ and deaerated with nitrogen or freeze–pump–thaw degassed. ESR samples of the radical cations were prepared

(19) **4**, 4'-Dimethoxydiphenylamine (**5**) is also commercially available from Lancaster and TCI.

(20) A preliminary report of this salt has appeared (ref 9).

(21) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Pergamon Press: New York, 1996.

by mixing neutral **1**, **2**, or **3** with stoichiometric amounts of thianthrenium perchlorate²² in CH₂Cl₂ to achieve monocation formation in situ or by dissolution of isolated cation hexafluorophosphate salts prepared as described above.

UV/Vis/NIR Spectrophotometry. Spectra were recorded on a CARY 5G UV/vis/NIR spectrophotometer. Isolated radical cation salt was dissolved in chloroform, and the spectrum was

(22) **Caution!** Thianthrenium perchlorate (TH⁺ClO₄⁻) is a shock sensitive explosive solid and should be handled with due care. For preparation and properties, see: Murata, Y.; Shine, H. J. *J. Org. Chem.* **1969**, *34*, 3368.

taken in a quartz cell. Chloroform was washed with water, then dried for 5 h over anhydrous CaCl₂, and fractionally distilled.²¹ Samples of isolated radical cations were prepared as described above.

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