Articles

Probing Delocalization across Alkyne-Containing Linkages: Synthesis and Cyclic Voltammetry of Bridged Phenylenediamines

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This paper presents the synthesis of *N,N,N′,N′*-tetraethyl-1,4-phenylenediamines bridged by ethynylphenyl-ethynyl and diethynyl linkages. These compounds are of interest to determine if the *N,N,N′,N′*-tetraethyl-1,4-phenylenediamines exhibit delocalized mixed oxidation states when oxidized electrochemically. 1-Butoxy-2,5-bis(*N,N*-diethylamino)-4-ethynylbenzene was a key intermediate, and nucleophilic addition of lithium (trimethylsilyl)acetylide to 2,5-bis(*N,N*-diethylamino)-1,4-benzoquinone provided an efficient synthesis of this compound. This intermediate was then assembled into the redox assemblies of interest in high yield by use of palladium-catalyzed cross-coupling and copper-catalyzed oxidative homo-coupling protocols. Cyclic voltammetry of these compounds indicate that the *N,N,N′,N′*-tetraethyl-1,4-phenylenediamine redox units behave independently and that the interactions are principally electrostatic. As a result, we conclude that the electrochemically generated radical cations and dications are highly localized.

Introduction

Alkyne linkages have demonstrated exceptional utility in the formation of large macrocycles,[1] monodisperse molecular wires,[2] porphyrin arrays,[3] rigid rod polymers,[4] sensory materials,[5] and liquid crystals.[6] The versatility of this group stems from their structural rigidity and ability to promote electronic communication, as well as the ease of synthesis by highly efficient procedures.

We are interested in expanding the potential of poly(arylene ethynylenes) and related alkyne-containing materials as electronic conductors. Electronic delocalization is generally thought to be critical for a conjugated polymer to display high conductivity. Aside from making good intuitive sense, this assertion has foundations in solid state physics which teaches that a high degree of delocalization produces broad energy bands and greater carrier mobilities.[7] Qualitatively, a conjugated polymer's band gap and band width are related to the degree of bond length alternation in the backbone with greater alternation leading to larger band gaps and smaller band widths.[8] As such for polymers with arylene-containing backbones, ethynylene linkages create a greater bond length alternation than vinylene linkages. In the absence of steric factors, poly(arylene ethynylenes) have larger band gaps and narrower band widths than the analogous poly(arylene vinylenes).[8b] As a result, poly(arylene vinylenes) have been studied extensively whereas poly(arylene ethynylenes) have generally been considered to be less effective conductors and have drawn less attention. Nevertheless, it was recently determined that poly(phenylene ethynylenes) can display relatively high conductivities when oxidized (doped).[4a] Key to this demonstrated conductivity was use of exotic conditions (electrochemical doping in SO_2 solution, −70 °C) to prevent polymer degradation in its oxidized state.

To develop useful poly(arylene ethynylene) conductors, doped compositions which are stable to ambient conditions must be constructed. One approach to more stable materials is to produce a polymer in which ethynylene linkages connect localized redox centers. We considered this a reasonable approach since localizing the charge on a redox center should decrease the charge on the ethynylenes and thereby lower the reactivity of these groups in the doped state. Such an approach can also be used to probe if high conductivity can exist in a material with minimal delocalization, an issue key to the future design of novel conductors. In the extreme case in which redox sites behave as purely localized entities, a material will behave as a pure redox conductor[9] in which self-exchange reactions are mediated by the con-

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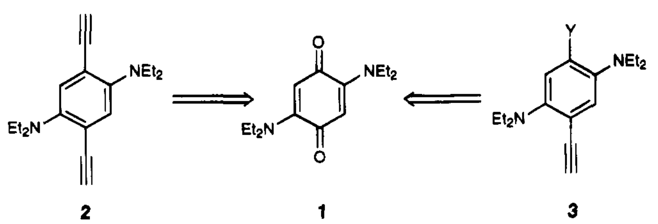
Scheme 1



jugated bridges. To determine the degree of interaction of redox groups connected by ethynyl-based bridges, we have conducted initial investigations on model systems. In the current study we have employed *N,N,N′,N′*-tetraethyl-1,4-phenylenediamine as the localized redox center and have investigated the cyclic voltammetry of this group when bridged by diethynylene and ethynyl-phenyl-ethynyl linkages. We note that Staley and co-workers have recently reported the synthesis of similarly bridged cyclooctatetraenes.[10]

Results and Discussion

Synthesis of Bridged Redox Assemblies. Palladium-catalyzed cross-coupling reactions have become the method of choice for the construction of alkynyl groups. These procedures can be conducted under mild conditions and proceed in high yield. However, the cross-coupling approach is problematic due to the difficulty in preparing diiodophenylenediamines[11] and the sluggish oxidative addition of Pd^0 species to highly electron rich aromatic halides. Hence, we have approached the synthesis of the target bridged redox systems by a more classical methodology which involves the nucleophilic addition of lithium (trimethysilyl)acetylide to the carbonyl group of 2,5-bis(*N,N*-diethylamino)benzoquinone, **1** (Scheme 1). Similar approaches have proved to be very effective for the preparation of 9,10-bis(phenylethynyl)-anthracenes,[12] thereby suggesting a route to **2**, a key difunctional compound from which polymers may be produced. We also considered that a more controlled addition of lithium (trimethysilyl)acetylide should lead to **3**, a phenylene diamine substituted with a single acetylene, which will serve as a building block for the preparation of different acetylene bridged redox systems.

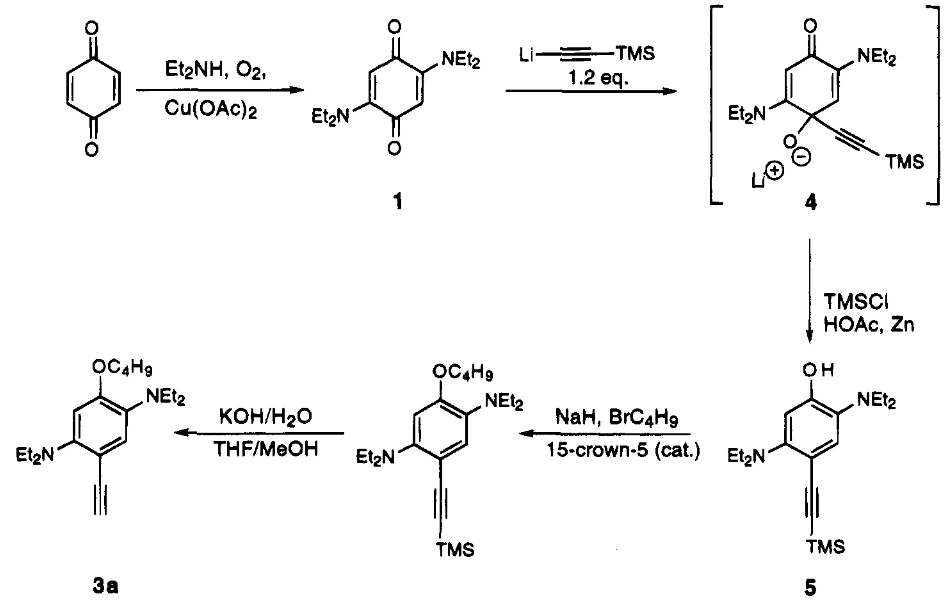
Compound **3a** (Y = OC_4H_9) was synthesized as shown in Scheme 2. The oxidative-amination of 1,4-benzoquinone to produce **1** was performed in the presence of finely-powdered $Cu(OAc)_2$ to assist O_2 oxidation.[13] Contrary to what has been observed for the addition to anthraquinones,[12] we find that **1** does not react selectively with 2 equiv lithium (trimethylsilyl)acetylide. The lower reactivity is undoubtedly related to the electron donation of the diethylamine groups, and with 1.2 equiv of lithium (trimethylsilyl)acetylide the monoaddition product is obtained in 76%. More forcing conditions with 2 equiv or more of lithium (trimethylsilyl)acetylide or prolonged reaction times gave complex mixtures. The resulting monoaddition product **4** is not isolated but is reduced *in situ* with Zn/HOAc to produce **5** as an air sensitive solid. Simple alkylation of **5** and desilylation produces **3a**.

The redox compounds studied are then prepared from **3a** by conventional coupling methods shown in Scheme 3. Palladium-catalyzed cross-coupling of **3a** with 1,4-diiodobenzene produces **6**, chemoselective cross-coupling of **3a** with 1-bromo-4-iodobenzene produces **7**, and copper-catalyzed oxidative homo-coupling of **3a** gives **8**. Although the reactions in Scheme 3 proceed in high yields, the isolation of pure compounds is problematic due the tendency of these materials to oxidize. Silica chromatography must be performed in a dark environment, and degassed solvents must be used for all chromatography and recrystallizations. Once isolated, the compounds were stored in a glove-box.

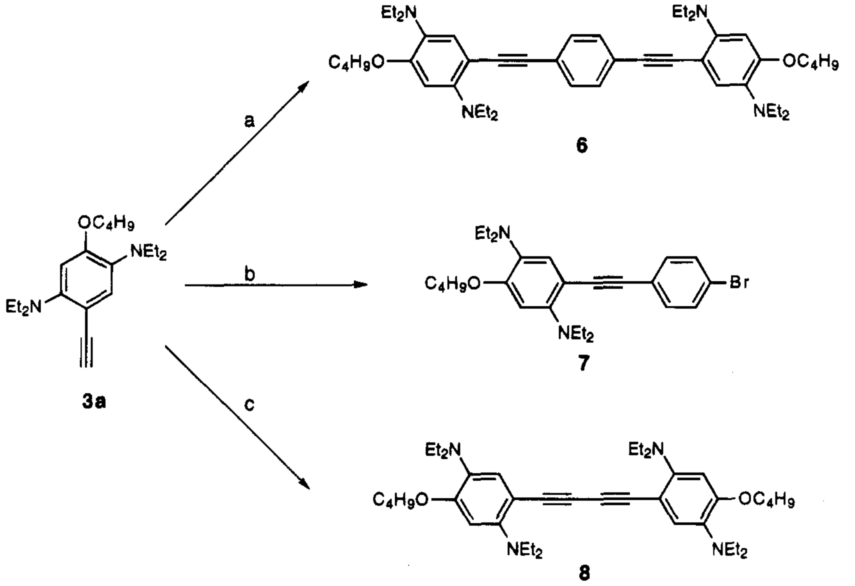
Electrochemistry. The cyclic voltammetry of the model compounds **6**–**8** was performed in CH_2Cl_2 (1.0×10^{-3} M) with the aid of a glove-box, Pt working and counter electrodes, and Bu_4NPF_6 (0.1 M) supporting electrolyte. The cyclic voltammograms (CV) of these compounds are shown in Figure 1.

As can be seen from Figure 1, compounds **6**–**8** display reversible redox events in the regions of 0.2–0.3 V and 0.7–0.8 V vs an oxidized Ag wire quasireference electrode. A summary of all the half wave potentials ($E_{1/2}$) of **6**–**8** along with ferrocene as a reference potential are given in Table 1. The two regions of electrochemical

Scheme 2



Scheme 3[a]



[a] (a) Pd(PPh$_3$)$_4$ (5%), CuI (5%), 0.5 equiv of p-I$_2$C$_6$H$_4$, (iPr)$_2$NH, rt; (b) Pd(PPh$_3$)$_4$ (5%), CuI (5%), 1.0 equiv of p-BrC$_6$H$_4$I, (iPr)$_2$NH, rt; (c) CuCl (10%), 2-methoxyethanol, TMEDA, O$_2$.

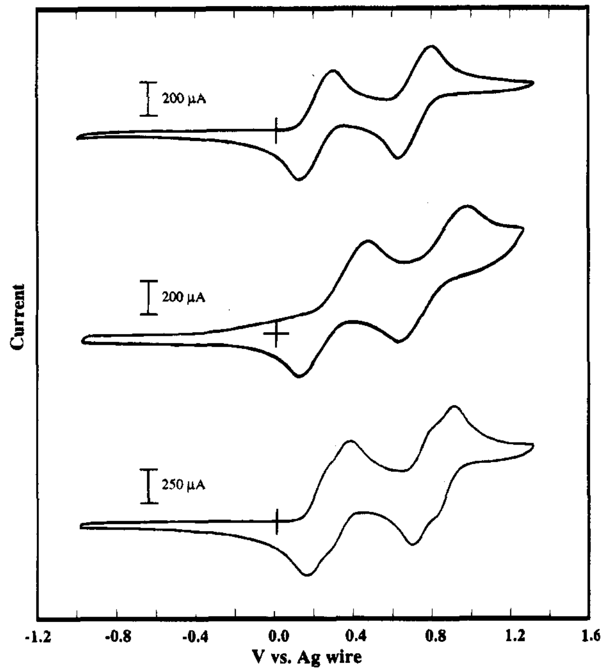


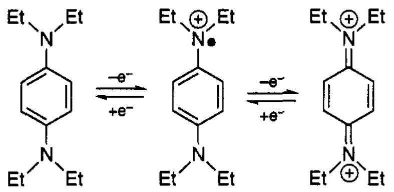
Figure 1. Cyclic voltammograms of **6–8**. Working electrode: Pt 0.275 cm^2. Scan rate = 40 mV/s. Anodic currents plotted upward.

Table 1. Measured Half Wave Potentials, $E_{1/2}$, and Potential Difference betwen the Anodic and Cathodic Peak Potentials, ΔE_p. Conditions Same as in Figure 1

compound	$E_{1/2}{}^1$ (V)	$E_{1/2}{}^2$ (V)	ΔE_p (V)[a]
6	0.198	0.704	0.17
7	0.291	0.811	0.34
8[c]	0.216, 0.305	0.690, 0.824	0.14
ferrocene[b]	0.406		

[a] The ΔE_ps were approximately the same for all of the waves of a given compound. [b] Reference potential. [c] Determined from the unresolved cyclic voltammogram (±0.02 V).

activity displayed by **6–8** are the first and second monoelectronic processes for each of 1,4-phenylenediamine units.[14] This well known behavior is shown for *N,N,N′,N′*-tetraethyl-1,4-phenylenediamine in eq 1.



(eq 1)

Compound **7** which has a single redox center displays two monoelectronic processes as indicted in eq 1. Compound **6** contains two redox centers which are very similar to that of **7** with the difference being that they are separated by an ethynyl-phenyl-ethynyl bridge. In this case the redox centers appear to be totally isolated, and both redox centers are observed to undergo oxidation at the same potential. Consistent with two-electron processes, the ΔE_p of **6** is about half as large is observed for **7**.[15] In the case of compound **8**, the redox centers are separated only by a diacetylene linkage, and we observe 4 distinguishable redox waves. The electrochemical behavior of **8**, whereby each single electron redox event occurs at a different thermodynamic potential (i.e., $\mathbf{8}^0 \rightleftharpoons \mathbf{8}^{\bullet+} \rightleftharpoons \mathbf{8}^{2(\bullet+)} \rightleftharpoons \mathbf{8}^{2+(\bullet+)} \rightleftharpoons \mathbf{8}^{2(2+)}$), indicates that the redox centers interact. However, electronic delocalization of the radical cation or dication species over both redox centers should lead to larger splittings of the redox waves than is observed.[16] As a result, the origin of the differences

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[15] For a perfectly reversible electrode reaction the potential difference between the peak anodic and cathodic currents, ΔE_p, are equal to 0.059/*n*, where *n* is the number of electrons in the reaction. Kissinger, P. T.; Heineman, W. R. *J. Chem. Edu.* **1983**, *60*, 702.

[16] Diiron complexes based upon acetylide-phenyl-acetylide bridges (i.e. similar to those of **6**) have been characterized as "slightly delocalized." In these systems the mixed valence state (Fe^{II}/Fe^{III}) is more stable by 0.2 V (CH$_2$Cl$_2$) over the Fe^{II}/Fe^{II} state. Field L. D.; George, A. V.; Laschi, F.; Malouf, E. Y.; Zanello, P. *J. Organomet. Chem.* **1992**, *435*, 347.

in the redox potentials is principally electrostatic.[17] The lower ΔE_p for **8** relative to the monoelectronic processes displayed by **7** indicates that the former compound exhibits faster electron-transfer kinetics.

Conclusions

We have synthesized alkynyl-substituted phenylenediamine redox systems and have examined the cyclic voltammetry of compounds in which the redox units are separated by alkynyl-based bridges. Our results indicate that these systems display virtually no delocalization of the radical cation or dication species. As a result, conducting polymers based upon these structural units may be considered to be purely localized redox conductors. We are continuing with our studies and plan to determine if polymeric materials based upon similar structures can display high conductivity.

Experimental Section.

Materials. All chemicals were of reagent grade. Diisopropylamine was predried over NaOH and vacuum distilled. Toluene and THF were vacuum distilled from sodium benzophenone ketyl and stored in Teflon sealed flasks under argon. All other solvents were used without further purification. TMEDA represents *N,N,N',N'*-tetramethylethylenediamine.

Equipment. NMR spectra were recorded on 100 or 250 MHz spectrometers in $CDCl_3$. Mass spectroscopy was performed using $CHCl_3$ as solvent, and FAB spectra were obtained using a 3-nitrobenzyl alcohol matrix. Chromatography was performed on 40 μm silica gel (Baker). Cyclic voltammetry was performed using an isolated silver wire quasireference electrode, and ferrocene was used as an additional reference.

2,5-Bis(*N,N*-diethylamino)benzoquinone (1). This compound was prepared by an adaptation of the procedure of Crosby and Lutz.[12] A mixture of finely-powdered cupric acetate monohydrate (20 g, 0.1 mol), diethylamine (43.9 g, 0.6 mol), and methanol (200 mL) were stirred with warming to give a homogeneous solution. After flushing with O_2, benzoquinone (10.8 g, 0.1 mol) in 200 mL of methanol was added slowly while keeping the temperature at 20−30 °C with an ice bath. After 1 h, O_2 *consumption had ceased and the* reaction mixture was dried *in vacuo*. The residue was then subjected to a soxhlet extraction with isooctane. The isooctane solution was evaporated *in vacuo*, and the residue was recrystallized twice from ethanol to yield deep red crystals (15 g, 60%): mp 111−113 °C (lit. 112−114 °C)[12]; ^{1}H NMR (250 MHz, $CDCl_3$) 1.14 (t, J = 7.0 Hz, 12H), 3.46 (q, J = 7.0 Hz, 8H), 5.30 (s, 2H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) 12.48, 46.62, 100.94, 150.31, 181.28 ppm; MS *m/z* (rel intensity) 251 ($M^+ + H$, 100), 221 (78), 207 (56), 178 (32), 164 (6), 150 (7). Anal. Calcd for $C_{14}H_{22}O_2N_2$: C, 67.15; H, 8.86; N, 11.20. Found: C, 67.13; H, 8.86; N, 11.15.

2,5-Bis(*N,N*-diethylamino)-4-[(trimethylsilyl)ethynyl]phenol (5). Lithium (trimethylsilyl)acetylide was prepared at −35 °C by adding *n*-butyllithium (7.14 mL, 0.012 mol) dropwise to (trimethylsilyl)acetylene (1.7 mL, 0.012 mol) in THF (30 mL) under N_2. This solution was slowly warmed up to 0 °C over 1 h and then transferred by cannula to a −40 °C THF (20 mL) solution of **1** (2.5 g, 0.010 mol) in a Schlenk flask. The reaction mixture was slowly warmed to 0 °C while the color changed from deep red to light yellow and then trimethylsilyl chloride (1.52 mL, 0.012 mol) was added. After 20 min, zinc dust (2 g) and HOAc (7 mL) were added and the reaction mixture was stirred for an additional 2 h. The reaction mixture was then decanted and subjected to a H_2O/CH_2Cl_2 workup. The combined organic phases were washed with H_2O, saturated $NaHCO_3$, and brine and dried over $MgSO_4$. The organic solvent was removed *in vacuo* to afford **5** as light yellow needle crystals (2.51 g, 76%): mp 53.5−55.0 °C; ^{1}H NMR (250 MHz, $CDCl_3$) 0.22 (s, 9H), 0.90 (t, J = 7.5 Hz, 6H), 1.09 (t, J = 7.5 Hz, 6H), 2.86 (q, J = 7.5 Hz, 4H), 3.31 (q, J = 7.5 Hz, 4H), 6.45 (s, 1H), 7.16 (s, 1H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) 0.10, 12.63, 12.95, 45.24, 50.42, 95.85, 103.46, 105.30, 106.52, 128.15, 129.63, 152.57, 155.40 ppm; MS *m/z* (rel intensity) 333 ($M^+ + H$, 100), 317 (59), 289 (22), 245 (12), 215 (9), 149 (7); HRMS calcd for $C_{19}H_{32}ON_2Si$ (M^+) 332.2362, found 332.2363.

2,5-Bis(*N,N*-diethylamino)-4-[(trimethylsilyl)ethynyl]-1-butyloxybenzene. To a mixture of **5** (2.39 g, 7.20 mmol), NaH (0.207 g, 8.64 mmol), and 15-crown-5 (0.1 mL) in THF (50 mL) was added *n*-butyl bromide (1.55 mL, 14.4 mmol) dropwise by syringe under N_2. The reaction mixture was refluxed for 3 days and then stopped by addition of a few drops of MeOH to quench the excess NaH. The solvent was removed *in vacuo*, and the residue was subjected to a H_2O/CH_2Cl_2 workup. The organic phases were washed with HCl (5%), H_2O, and brine, dried over $MgSO_4$, and then concentrated under vacuum. Column chromatography (hex:CH_2Cl_2 = 1:2) of the residue gave a yellow oil (1.82 g, 65%): ^{1}H NMR (250 MHz, $CDCl_3$) 0.212 (s, 9H), 0.85−1.1 (m, 15H), 1.4−1.55 (m, 2H), 1.68−1.1.88 (m, 2H), 3.03 (q, J = 7.5 Hz, 4H), 3.24 (q, J = 7.5 Hz, 4H), 3.93 (t, J = 5.9 Hz, 2H), 6.36 (s, 1H), 6.95 (s, 1H) ppm.

2,5-Bis(*N,N*-diethylamino)-4-ethynyl-1-(butyloxy)benzene (3a). To a solution of 2,5-bis(*N,N*-diethylamino)-4-[(trimethylsilyl)ethynyl]-1-(butyloxy)benzene in degassed THF (30 mL) and MeOH (20 mL) was added KOH (2 pellets in 1 mL of H_2O). The mixture was stirred at rt overnight and then acidified with HCl (10%). The solvent was removed *in vacuo*, and the residue was subjected to a H_2O/CH_2Cl_2 workup. The organic phases were washed with H_2O and brine, dried over $MgSO_4$, and then concentrated under vacuum. Column chromatography (CH_2Cl_2:THF = 100:1) of the residue gave a light yellow oil (1.33 g, 90%): ^{1}H NMR (250 MHz, $CDCl_3$) 0.92−1.05 (m, 15H), 1.38−1.54 (m, 2H), 1.68−1.84 (m, 2H), 3.06 (q, J = 7.6 Hz, 4H), 3.21 (q, J = 7.6Hz, 4H), 3.23 (s, 1H), 3.96 (t, J = 6.0 Hz, 2H), 6.44 (s, 1H), 6.98 (s, 1H) ppm; ^{13}C NMR (25 MHz, $CDCl_3$) 12.61, 12.69, 13.78, 19.39, 31.49, 46.33, 46.88, 68.20, 79.34, 83.85, 106.52, 108.67, 128.63, 133.99, 149.36, 154.93 ppm; MS *m/z* (rel intensity) 316 (M^+, 100), 301 (28), 288 (43), 259 (18), 215 (21), 178 (10), 143 (7).

Model Compound 6. A mixture of **3a** (0.2 g, 0.63 mmol), 1,4-diiodobenzene (0.104 g, 0.32 mmol), $Pd(PPh_3)_4$ (25 mg, 0.02 mmol), and CuI (6 mg, 0.03 mmol) in diisopropylamine (15 mL) was stirred at rt under N_2 overnight. The solvent was removed under vacuum, and the residue was subjected to a H_2O/CH_2Cl_2 workup. The combined organic phases were washed with HCl (5%), H_2O, and brine, dried over $MgSO_4$, and then concentrated *in vacuo*. Column chromatography (CH_2Cl_2:THF = 40:1) with degassed solvents in the dark followed by recrystallization from THF/MeOH (under N_2) afforded yellow crystals (0.126 g, 57%): mp 131−132 °C; ^{1}H NMR (250 MHz, degassed $CDCl_3$) 0.93−1.15 (m, 30H), 1.42−1.57 (m, 4H), 1.72−1.89 (m, 4H), 3.07 (q, J = 7.5 Hz, 8H), 3.29 (q, J = 7.5 Hz, 8H), 3.98 (t, J = 6.0 Hz, 4H), 6.44 (s, 2H), 7.02 (s, 2H), 7.43 (s, 4H) ppm; ^{13}C NMR (25 MHz, degassed $CDCl_3$) 12.70, 12.99, 13.83, 19.43, 31.54, 46.48, 46.55, 68.23, 91.58, 92.09, 106.46, 108.87, 123.63, 128.40, 130.98, 133.73, 149.15, 154.98 ppm; MS *m/z* (rel intensity) 708 ($M^+ + H$, 100), 692 (23), 663 (12), 605 (8). UV (CH_2Cl_2) λ_{max} (log ϵ) 232 (4.56), 292 (4.66), 322 (4.50), 386 (4.48).

Model Compound 7. This compound was prepared following the same procedure as given for **6** with the exception that the coupling reaction was done with **3a** and 1-bromo-4-iodobenzene. Column chromatography was carried out with CH_2Cl_2 under similar conditions afforded a yellow oil (80%): ^{1}H NMR (250 MHz, degassed $CDCl_3$) 0.9−1.13 (m, 15H), 1.46 (m, 2H), 1.74 (m, 2H), 3.09 (q, J = 7.0 Hz, 4H), 3.12 (q, J = 7.0 Hz, 4H), 3.98 (t, J = 6.6 Hz, 2H), 6.44 (s, 1H), 7.01 (s, 1H), 7.36 (d, J = 8.7 Hz, 2H), 7.41 (d, J = 8.7 Hz, 2H) ppm; ^{13}C NMR (62.5 MHz, degassed $CDCl_3$) 12.43, 12.81, 13.89, 19.39,

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(17) For discussions regarding electrostatic interactions see: (a) Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 3125. (b) Salaymeh, F.; Berhane, S.; Yusof, R.; de la Rosa, R.; Fung, E. Y.; Matamoros, R.; Lau, K. W.; Zheng, Q.; Kober, E. M.; Curtis, J. C. *Inorg. Chem.* **1993**, *32*, 3895.

31.33, 46.24, 46.33, 67.91, 85.29, 91.01, 105.47, 107.96, 121.40, 123.47, 127.89, 128.19, 131.43, 132.54, 149.12, 154.69 ppm; MS *m/z* (rel intensity) 472 (M^++ H, 100), 457 (35), 392 (62), 335 (13), 291 (11); HRMS calcd for $C_{26}H_{35}ON_2Br$ (M^+) 470.1932 found 470.1953; UV (CH_2Cl_2) λ_{max} (log ϵ) 232 (4.42), 280 (4.65), 306 (4.40), 356 (4.20).

Model Compound 8. A mixture of **3a** (0.2 g, 0.63 mmol) and CuCl (4.0 mg, 0.041 mmol) in 2-methoxyethanol (10 mL) was stirred at rt under a flow of O_2. TMEDA (0.6 mL) was added dropwise, and the solution turned green immediately. After the reaction mixture had turned deep brown, HCl (10%, 20 mL) was added. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (10 mL × 2). The combined organic phases were washed with H_2O, $NaHCO_3$, and brine followed by drying over $MgSO_4$. The solvent was removed *in vacuo*, and column chromatography (petroleum ether:THF = 15:1, degassed solvents, excluding light) of the residue give yellow crystals (0.17 g, 85%): mp 66–68 °C; ^1H NMR (250 MHz, degassed $CDCl_3$) 0.95 (m, 24H), 1.09 (t, J = 6.9 Hz, 6H), 1.45 (m, 4H), 1.75 (m, 4H), 3.03 (q, J = 7.0 Hz, 8H), 3.25 (q, J = 7.0 Hz, 8H), 3.95 (t, J = 6.5 Hz, 4H), 6.38 (s, 2H), 6.99 (s, 2H) ppm; ^{13}C NMR (62.5 MHz, degassed $CDCl_3$) 12.31, 12.74, 13.89, 19.37, 31.28, 46.19, 46.59, 67.86, 82.14, 104.82, 106.94, 128.48, 132.82, 150.23, 154.90 ppm; MS *m/z* (rel intensity) 631 (M^+ + H, 87), 616 (100), 588 (14), 529 (7), 372 (6), 288 (9), 183 (8), 105 (11); UV (CH_2Cl_2) λ_{max} (log ϵ) 240 (4.64), 266 (4.67), 320 (4.21), 380 (4.32).

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Supporting Information Available: Proton NMR spectra of key compounds (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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