Synthesis of Highly Functionalized Pyrazines by Ortho-Lithiation Reactions. Pyrazine Ladder Polymers

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Abstract: Several novel transformations on sensitive pyrazine cores are disclosed while preparing monomers for condensation polymerizations to planar polypyrazines. Two pyrazine monomers for the step growth polymerization are prepared starting from ethyl acetoacetate and proceeding via pyrazine-2,5-dicarboxylic acid as the common intermediate. The dicarboxylic acid serves as the key intermediate for the preparation of both the A and B components for the step-growth polymerization. A bis(Curtius) rearrangement followed by *tert*-butyl alcohol capture of the diisocyanate effects the high-yielding conversion of carbonyl moieties to the *tert*-butoxycarbonyl-protected aryldiamine. Since electrophilic halogenation of the pyrazine nucleus was unsuccessful due to the inherent electron deficiency of pyrazines, a directed ortho-metalation is disclosed using *tert*-butoxycarbonyl-protected amines and neopentyl glycol acetals as the metalation directing groups. Pd/Cu-catalyzed couplings of diiodopyrazines with distannylpyrazines are utilized for the polymerization schemes. This approach permits the ladder linkages of the planar polymers to (i) form in high yields upon $ZnCl_2$ activation once the polymer backbone is intact, (ii) be substituted so that the newly formed polypyrazines are soluble, unlike many other aromatic ladder polymers, and (iii) contain double-bonded ladder units to keep the consecutive aryl moieties planar which maximizes extended π-conjugation through the polymer backbones, thereby increasing the bandwidths and lowering the optical band gaps.

Introduction

Conjugated polymers are at the core of several emerging optoelectronic technologies.[1] New conjugated polymeric frameworks have been required for enhanced performance in nonlinear optics, light emitting diodes, photovoltaic devices, laser systems utilizing conductive polymer films, and optoelectronic sensors.[1,2] Modulation of the band gaps and electron densities in the polymeric materials is required to control the optical or electronic behavior in these new devices. The optoelectronic properties of conjugated polymers vary significantly based upon the degree of extended conjugation between the consecutive repeat units and the inherent electron densities in the polymer backbones.[3] By forming bridging linkages between the repeat units of conjugated polymers, the extended π-conjugation can be maximized.[4] Although we recently disclosed routes to ladder polymers based on electron-rich (thiophene) and/or electron-deficient (pyridine) heterocycles,[5] the vast majority of conjugated ladder polymers are based upon poly(*p*-phenylene) backbones.[4] Similarly, there are no reports of polymers, planar or nonplanar, based on the highly electron deficient pyrazine core as the sole backbone component.[6] This is likely due to the difficulty preparing functionalized pyrazine monomers, and we disclose here several new strategies for the preparation of highly functionalized pyrazines as well as routes to soluble polypyrazine derivatives and planar polypyrazines. These are highly

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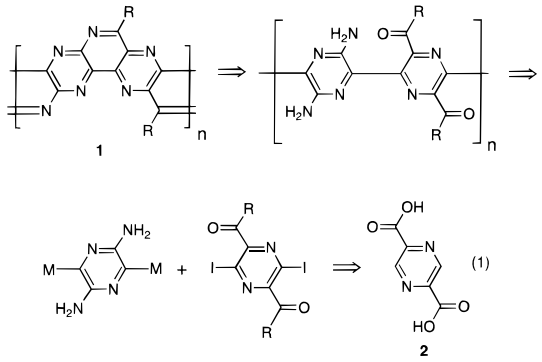
nitrogen rich polymers with a unique arrangement of the heteroaromatic cores. A convergent approach is utilized where both the A and B components for the condensation polymerizations arise from a common pyrazine intermediate. Functionalization of the monomeric heterocyclic cores is achieved by using bis(Curtius) rearrangements, and dilithiation reactions via directed di(ortho-metalation) processes. In addition to materials science, highly functionalized diazinyl heterocycles are of importance in a broad range of chemistries including odor and flavoring agents,[7] fungicides,[8] and numerous natural products such as aromatase inhibitors;[9] therefore, the new synthetic strategies described here would likely have applications far beyond the scope of this study.

Retrosynthetic Analysis

The retrosynthetic strategy for the synthesis of the planar polypyrazines (**1**) is outlined in eq 1. The planarization was

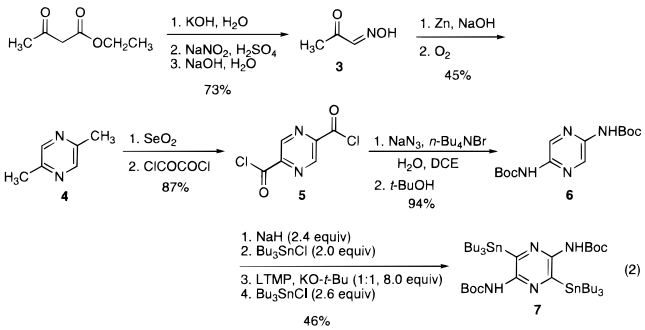


(1)

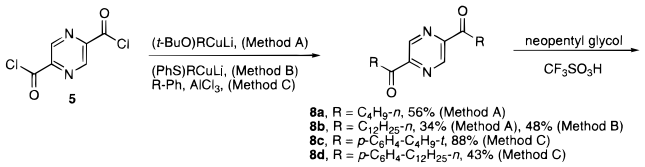
planned via Schiff base formation between alternating amine and ketone moieties. This approach permits the imine bridges to (i) form in high yields upon Lewis acid activation once the polypyrazine backbone is established, (ii) be substituted so that the newly formed polymers are soluble, and (iii) contain double-bonded ladder units to keep the consecutive aryl moieties planar which maximize extended π-conjugation through the polypyrazine backbones, thereby increasing the bandwidths and lowering the band gaps.[3] We chose to utilize dimetalodiamines and dihalodiketones as the monomer units (rather than the complementary use of dimetalodiketones and dihalodiamines) because subsequent oxidative addition reactions of the inherently electron-rich late transition metal coupling catalysts are facilitated by electron-deficient aryl halides.[2h,i,10] Finally, the two monomers can be prepared from the common pyrazinedicarboxylic acid **2**.

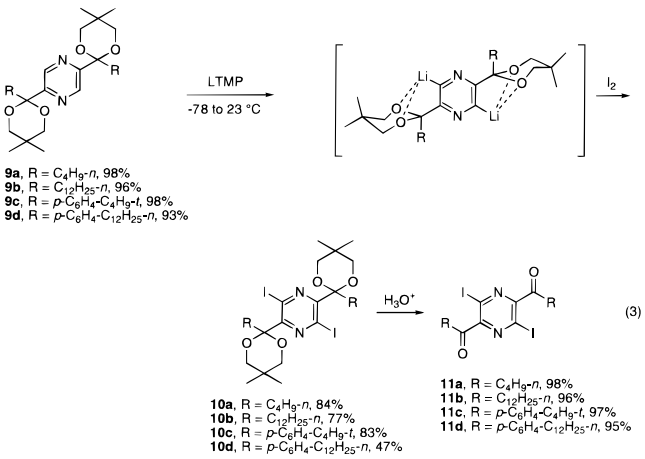
Results and Discussion

Monomer Syntheses. The pyrazine monomers were prepared as shown in eqs 2 and 3 starting from ethyl acetoacetate. Nitrosylation and decarboxylation afforded the oxime **3** which was the tautomer of the nitroso compound. Reduction and condensation yielded dihydrodimethylpyrazine that was oxidized with air to give 2,5-dimethylpyrazine (**4**).[11] Numerous attempts to dihalogenate **4**, or the bis(*n*-oxide) of **4**, with electrophilic sources were unsuccessful, a testimony of the electron deficiency



(2)





(3)

of the pyrazine nucleus. The failure to selectively halogenate **4** later necessitated the development of ortho-metalation processes on both of the monomer systems rather than using the more facile lithium−halogen exchange reactions. Di(methyl oxidation)[12] of **4** afforded the common intermediate pyrazine dicarboxylic acid **2** which, upon treatment with oxalyl chloride, gave the corresponding di(acid chloride) **5**. The di(acyl azide) derived from **5** was formed under phase transfer conditions followed by a bis(Curtius) rearrangement and *tert*-butyl alcohol capture of the isocyanates to give the di(Boc-protected) diamine **6** in high yield (eq 2).[13] **Caution!** We used dichloroethane instead of the typical dichloromethane as the organic phase solvent for the acyl azide due to some cautionary notes published regarding the dangers of azide formation in dichloromethane.[14] Moreover, the yield obtained with the safer dichloroethane solvent system was quite high. After screening numerous unsuccessful reaction conditions[15] to give the desired dimetalated species for the subsequent polymerization, we discovered that removal of the carbamate protons with NaH, addition of chlorotri-*n*-butylstan-

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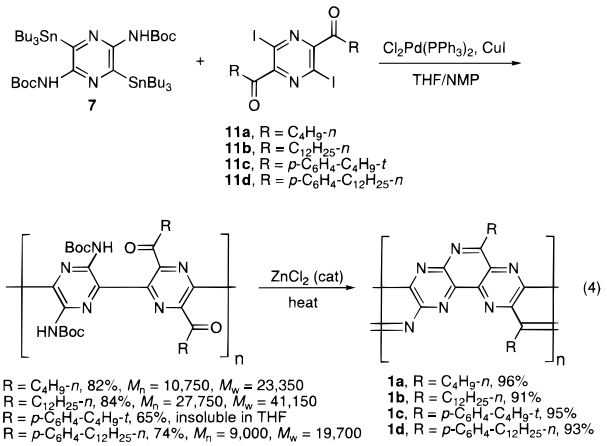
nane (though unverified, it presumably stannylates at the carbamate anions), then lithiation with the extremely basic dual Li−K system,[16] and finally quenching with the chlorostannane afforded the desired Boc-protected diaminodistannylpyrazine monomer **7** (eq 2). Deletion of potassium *tert*-butoxide from the reaction sequence resulted solely in the recovery of starting material. Substitution of lithium 2,2,6,6-tetramethylpiperidide (LTMP)[15] with LDA resulted in decomposition of the pyrazine core, presumably from base addition to the pyrazine ring system.[17]

The electrophilic component for the cross-coupling also utilized the di(acid chloride) intermediate **5**. Mild and hindered heterocuprates[18] permitted delivery of the alkyl moieties selectively to the acyl halides to afford **8a** and **8b** while Friedel−Crafts acylation afforded the di(aryl ketone)s **8c** and **8d**. Use of RCu(I), $R_2Cu(I)Li$, R_2Zn, RZnCl/Pd(0), R_2Cd, or RCdCl for the formation of the alkyl-bearing ketones resulted in additions α to the pyrazine nitrogen atoms, these positions being further activated by the conjugated carbonyl moieties and therefore having even lower LUMO energies than an unsubstituted pyrazine. Di(neopentyl glycol) acetal formation was attainable even on the diaryl ketones using CF_3SO_3H promotion (oxalic acid, TsOH, and H_2SO_4 were employed unsuccessfully) and taking advantage of the convenient Thorpe−Ingold (*gem*-dimethyl) effect for the formation of the cyclic acetals. Use of LTMP afforded the dilithio intermediate that was probably acetal stabilized as shown in eq 3. When the ethylene glycol acetals were used, lithiation conditions resulted in complete decomposition of the pyrazine ring system. Iodine quenching of the dilithiodi(neopentyl glycol acetal) followed by hydrolysis afforded the desired diiododiketopyrazines **11a**−**d** (eq 3). The yield of **10d** was depressed relative to **10a**−**c** because some benzylic lithiation and iodination occurred on the dodecyl side chains.

Polymerization Reactions. The polymerization reactions between **7** and **11a**−**d** are shown in eq 4. The optimal catalyst



(4)

system for the polymerization of the pyrazine monomers was $Cl_2Pd(PPh_3)_2$/CuI in mixed solvents of THF/NMP.[2h,i,5] A slight excess of the stannane was used to achieve the reduction of the Pd(II) to the active Pd(0). Surprisingly, lower molecular weight polymers were obtained when the PPh_3 supporting ligand was substituted with $AsPh_3$, or when the starting catalyst was Pd(dba)$_2$/PPh_3/CuI. The NMP cosolvent aided in stabilizing the Pd catalyst; in THF solvent only, the Pd(0) often precipitated from the solution. We have found that the optimal catalyst for these types of polymerizations is very difficult to predict; subtle changes in monomer structure lead to vast changes being required in catalyst formulations.[5]

Table 1. Optical Data for the Polypyrazines

	λ_{abs} (nm)		λ_{emis} (nm)[f]	
compd	THF[a]	CH_2Cl_2/TFA (2/1)[a]	THF	CH_2Cl_2/TFA (2/1)
12a	*365*, 450 (sh)[b]	—[c]	NE[b]	—[c]
12b	448	—[c]	NE	—[c]
12c	*362*, 468, 510 (sh)[b]	—[c]	NE	—[c]
12d	456	—[c]	575 (weak)	—[c]
1a	—[d]	*326*, 525 (sh)[b]	—[b]	NE
1b	—[d]	*454*, 575 (sh)[e]	—[b]	NE
1c	—[d]	*363*, 525, 625 (sh)	—[b]	NE
1d	*379*, 520 (sh)[b]	*375*, 545 (sh)	NE	NE
13	378	—[c]	520 (weak)	—[c]
14	*363*	—[c]	587 (strong)	—[c]

[a] No absorptions <310 nm are listed here. The italicized values are the more intense of the values listed. [b] The polymer was only partially soluble. [c] Addition of TFA would result in loss of the Boc group. [d] The polymer was insoluble in this solvent. [e] Recorded in CH_2Cl_2/CF_3SO_3H (10:1). [f] NE = no emission.

Planarization Reactions. The most efficacious method found for completion of Boc-removal and Schiff base formation in the conversion **12a**−**d** to **1a**−**d**, respectively, utilized $ZnCl_2$ (2 mol %) in THF at 105−115 °C in a screw cap tube. CF_3SO_3H/CH_2Cl_2, TFA/CH_2Cl_2, or $TiCl_4/CH_2Cl_2$ afforded products with inferior spectroscopic features. For example, with the $ZnCl_2$ method, there were only small amounts of carbonyl moieties (likely from end-groups), and no Boc absorptions, in the FTIR spectra of **1a**−**d**. As with other ladder polymers that we have prepared, the planar polypyrazines **1a**−**c** were soluble in acidic media only; however, **1d** was also partially soluble in THF.[4h,5] Thus the imine formation strategy provided an efficient method for planarization because all the requisite atoms are present in the monomers; we avoided the difficult problem of introducing new atoms along a rigid rod backbone from exogenous reagents. Intermolecular Schiff bases unlikely remain in the final polymers since that would have resulted in a cross-linked insoluble network; the more stable 6-membered imine ring is thermodynamically preferred.

Polymer Analyses. All the polymers were analyzed prior to complete planarization by size exclusion chromatography (SEC) in THF relative to polystyrene (PS) standards, and the data are listed in eq 4. Since SEC is a measure of the hydrodynamic volume rather than the molecular weight, significant yet consistent errors in M_n and M_w usually result when comparing rigid rod polymers to the flexible coils of PS standards. The M_n data in this range are generally larger than the actual molecular weights by a factor of 1.5−2.[19]

The optical spectral bands (Table 1) were recorded to study the effects of planarization on optical band gap levels. Bathochromic shifts in the planarized (**1a**−**d**) versus the nonplanarized forms (**12a**−**d**) were recorded, although the differences are minimized since **12a**−**d** are already in the partially planarized forms (vide infra). Furthermore, a direct comparison of spectra recorded in the neutral (THF) forms for **12a**−**d**, and protonated (CH_2Cl_2/TFA) forms for **1a**−**d**, is difficult due the perturbations

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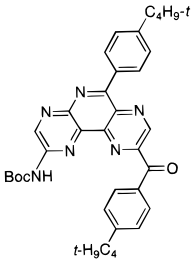
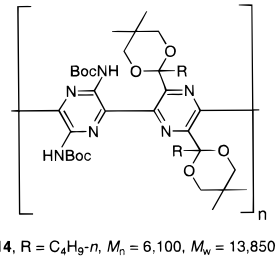
in intramolecular charge transfer upon protonation.[5] An informative case is for **12d** and **1d** where a common solvent, THF, could be used for both the planar and nonplanar forms. The 65 nm bathochromic shift on the conversion of **12d** to **1d** is indeed indicative of the optical band gap decrease upon further planarization. However, in every case, the extended heating (75−80 °C) in the nucleophilic solvent NMP caused partial Boc loss and cyclization of the polymers. This was apparent by the depressed intensity of the carbonyl bands in the FTIR spectral band of **12a**−**d**, the bathochromic bands in the absorbance spectra, and the quenching of the optical emission signals (Table 1). The FTIR and absorbance changes are obvious indicators of partial cyclization while our extensive experience with related imine planar polymers indicates that exciton quenching occurs in the planar units and not in the nonplanar units.[5] Additionally, Boc loss and premature cyclization in the presence of polar aprotic solvents has been previously observed with Boc-protected aromatic amines.[5]

Due to the partial Boc loss and premature cyclizations, two other systems were prepared to aid in our understanding of the optical properties. First, for a spectral comparison, a model dimer **13** was prepared by Pd-catalyzed cross coupling of a monoiodide and monostannane, both starting materials being obtained during yield optimization studies on the formation of **7** and **11c**. The dimer **13** showed no long wavelength absorption band (Table



13



14, R = C_4H_9-*n*, M_n = 6,100, M_w = 13,850

1) indicating that the polymers have significantly longer extended π-conjugation. Second, a complementary polymerization method was utilized by coupling the diacetal **10a** with **7** using the same Pd/Cu catalyst system to afford **14** in 72% yield. The lower molecular weight of **14** relative to **12a** is likely attributable to the slower oxidative addition on **10a** due to both steric and electronic (more electron rich in **10a**) reasons. After spectral analysis, treatment of **14** with acid effected acetal removal and Schiff base formation to yield **1a**. The optical spectrum of **14** was then compared to those of **1a**−**d**. No long wavelength absorption band was observed from **14** and there was >150 nm bathochromic shift difference in **1a**−**d** compared to **14**. Hence there were profound increases on the extended π-conjugation with commensurate declines in the optical band gaps upon planarization. In concert with these findings, **14** afforded an intense emission signal (Table 1). In accord with our previous studies on other conjugated polymers and their corresponding imine-bridges ladder forms,[5] the nonplanar forms were generally strongly emissive while the planar forms were categorically nonemissive. We attributed this, in part, to the possibility of exciton−exciton quenching from the highly conjugated backbones of the planarized systems. Therefore, the dimer **13**, and to a larger extent the nonplanar polymer **14**, permitted quantitative comparisons of the effects of planarization on these very electron deficient conjugated polymers.

Conclusion

In summary, due to the difficulty preparing functionalized pyrazine monomers, we developed several new strategies for the preparation of highly functionalized pyrazines by using bis-(Curtius) rearrangements and dilithiation reactions via directed di(ortho-metalation) processes. Additionally, heretofore there were no reports, to our knowledge, of polymers, planar or nonplanar, based on the highly electron deficient pyrazine core as the sole backbone component.[6] We described here a convergent approach to pyrazine polymers where both the A and B components for a condensation polymerization arose from a common pyrazine intermediate to afford the desired highly electron deficient systems. As expected, the planarization induced optical band gap decreases in the highly conjugated systems.

Experimental Section

General. Unless otherwise noted, all operations were carried out under a dry, oxygen-free nitrogen atmosphere. Molecular weight analyses were performed using two 30 × 75 cm Burdick and Jackson GPC columns (10^5 Å 10 μm and 500 Å 5 μm) eluted with THF at 60 °C (flow rate 1.0 mL/min). Molecular weight results were based on five polystyrene standards (M_w = 435500, 96000, 22000, 5050, and 580 with a correlation coefficient >0.9998) purchased from Polymer Laboratories Ltd. Combustion analyses were obtained from Atlantic Microlab, Inc., P.O. Box 2288, Norcross, GA 30091. Capillary GC analyses were obtained using an Alltech model 932525 (25 m × 0.25 mm, 0.2 μm film of AT-1 stationary phase) capillary GC column. Alkyllithium reagents were obtained from FMC. Reagent grade diethyl ether and tetrahydrofuran (THF) were distilled under nitrogen from sodium benzophenone ketyl. Reagent grade benzene and dichloromethane were distilled over calcium hydride. Bulk grade hexane was distilled prior to use. References to chromatography refer to flash chromatography. Silica gel, 230−400 mesh, was obtained from EM Science. Thin-layer chromatography was performed using glass plates precoated with silica gel 60 F_{254} with a layer thickness of 0.25 mm purchased from EM Science. Unless otherwise noted, all monomers for the polymerizations were >99.5% pure, and all other nonpolymeric materials were >96% pure as judged by NMR, GC, or combustion analyses. The absorption and emission spectral data are listed in Table 1 while the molecular weight data are listed in the equations.

2,5-Dimethylpyrazine (4).[11] The procedure by Beech was modified as follows.[11] To a cold solution of potassium hydroxide (6.50 g, 115.84 mmol) in water (65 mL) was added ethyl acetoacetate (13.02 g, 100.00 mmol) at 0 °C. The mixture was stirred at room temperature for 24 h. To the solution was added sodium nitrite (8.05 g, 116.67 mmol) followed by 50% sulfuric acid (12 mL) under ice-cooling. The solution was stirred for 2 h at room temperature, then made alkaline with 35% sodium hydroxide and shaken with benzene (10 mL). The aqueous layer was separated and made just acidic to Congo-red (pH 5−6) by the addition of 50% sulfuric acid. The mixture was extracted with ether (50 mL, 2×), the combined organic extracts were dried over magnesium sulfate and filtered. The solvent was removed in vacuo to afford 6.36 g of hydroxyiminoacetone (**3**), which was then dissolved in 5 N aqueous sodium hydroxide (75 mL) and stirred with zinc (granular, 10.00 g, 152.98 mmol) at room temperature for 17 h. The suspension was diluted with cold water (100 mL) and filtered. The product was extracted with hot chloroform and air was bubbled through the combined extracts for 10 h. The extracts were dried over magnesium sulfate and the solvent was removed in vacuo to afford 1.76 g (33% based on ethyl acetoacetate) of the titled compound. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (s, 2 H), 2.50 (s, 6 H).

2,5-Pyrazinedicarboxylic Acid (2). The procedure by Weygand[12] was modified as follows. To a solution of selenium dioxide (49.50 g, 446.10 mmol) in pyridine and water (10:1, 200 mL) was added 2,5-dimethylpyrazine (**4**) (9.90 g, 91.70 mmol) and the mixture was heated to reflux at 100−110 °C for 12 h. The boiling solution became a brown-red color after about 15 min while the selenium gradually precipitated as a greenish solid. The reaction mixture was allowed to cool to room temperature then filtered. The precipitate was stirred with 2 N ammonium hydroxide (30 mL, 2×) and then filtered. The combined filtrates were evaporated to dryness in vacuo, the crude brownish solid

was dissolved in warm 2 N ammonium hydroxide (500 mL), and this mixture was passed through a column of decolorizing neutral Norit A. The eluant was evaporated to a small volume in vacuo. To the concentrated eluant (60 mL) was added concentrated hydrochloric acid (20 mL) and the mixture was filtered. The white precipitate was collected and washed with 2 N hydrochloric acid (5 mL, 2×), then ice-cold water (5 mL, 2×). After drying in vacuo, 13.49 g (88%) of the titled compound was obtained. Mp 262−264 °C (lit.[12] mp 255−260 °C). FTIR (KBr) 3300−2200 (br), 1720.8, 1501.2, 1400.7, 1333.3, 1262.2, 1171.0, 1044.0, 919.9, 756.7 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) δ 9.26 (s, 2 H).

2,5-Pyrazinedicarboxylic Acid Chloride (5). A flask equipped with a reflux condenser and a drying tube was charged with 2,5-pyrazinedicarboxylic acid (**2**) (58.00 g, 345.00 mmol), 4 Å molecular sieves (ca. 20 g), and benzene (2.1 L), and the mixture was stirred at room temperature for 14 h. To the mixture was added a few drops of *N,N*-dimethylformamide, and oxalyl chloride (142.96 g, 1.1 mol) in four portions. The reaction mixture was heated to reflux at 80−85 °C for 30 h, and then allowed to cool to room temperature and stirred with calcium hydride overnight. The mixture was filtered and the solvent was removed in vacuo to afford 69.94 g (99%) of the titled compound. FTIR (KBr) 3080.5, 1738.2, 1327.5, 1239.6, 1024.7, 867.6, 678.0 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 9.43 (s, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.0, 146.8, 145.0. LRMS Calcd for $C_6H_2Cl_2N_2O_2$: 204. Found: 204. No HRMS signal could be obtained.

***N,N′*-Di(*tert*-butoxycarbonyl)-2,5-diaminopyrazine (6)**. To a solution of **5** (6.15 g, 30.00 mmol) and tetra-*n*-butylammonium bromide (20 mg, 0.06 mmol) in 1,2-dichloroethane (700 mL)[14] was added sodium azide (5.75 g, 84.00 mmol) in water (15 mL) at 0 °C and the mixture was stirred at 0 °C for 12 h. The organic phase was separated and washed with ice-cold water (50 mL, 2×), then ice-cold brine (50 mL, 2×). The organic layer was dried over magnesium sulfate and filtered. The solvent was partially removed in vacuo and the diazide was kept in 1,2-dichloroethane (approximately 170 mL) at 0 °C. To the suspension was added *tert*-butyl alcohol (130 mL) and the mixture was heated to reflux at 80−85 °C for 15 h. Upon cooling to room temperature, the product crystallized as off-white crystals was collected by filtration. After drying in vacuo, 8.78 g (94% from **5**) of the titled compound was obtained. FTIR (KBr) 3224.6, 3090.2, 2980.1, 1728.5, 1537.4, 1474.7, 1369.6, 1274.0, 1241.2, 1152.5, 1066.3, 1020.4, 893.4, 824.3, 770.5, 729.6 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.88 (s, 2 H), 7.45 (br s, 2 H), 1.52 (s, 18 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.1, 143.9, 132.2, 81.5, 28.2. HRMS Calcd for $C_{14}H_{22}N_4O_4$: 310.1641. Found: 310.1636.

***N,N′*-Di(*tert*-butoxycarbonyl)-2,5-bis(tri-*n*-butylstannyl)-3,6-diaminopyrazine (7)**. To a slurry of potassium *tert*-butoxide (2.06 g, 16.0 mmol) in ether (20 mL) was added 2,2,6,6-tetramethylpiperidine (2.76 mL, 16.0 mmol) followed by the addition of *n*-butyllithium (10.1 mL, 16.0 mmol, 1.58 M in hexanes) at −78 °C, and the mixture was stirred at −78 °C for 30 min to form the LTMP−*t*-BuOK solution. To a flask charged with **6** (0.62 g, 2.0 mmol) and sodium hydride (0.12 g, 4.8 mmol) was added THF (20 mL) at room temperature and the mixture was stirred at room temperature for 1 h. To the resulting slurry was introduced chlorotri-*n*-butylstannane (1.1 mL, 4.0 mmol) at room temperature, and the mixture was stirred at room temperature for 15 min. The THF was removed in vacuo, ether was introduced to the residue, and the mixture was then slowly added to the homogeneous solution of LTMP−*t*-BuOK in ether at −78 °C. The resulting mixture was stirred at 0 °C for 1 h, warmed to room temperature for 3 h, and cooled back to 0 °C. Chlorotri-*n*-butylstannane (1.5 mL, 5.30 mmol) was added at 0 °C, and the mixture was allowed to warm to room temperature overnight, then hydrolyzed with aqueous sodium bicarbonate at 0 °C. The organic phase was separated, washed with brine, dried over sodium sulfate, and filtered through a pad of Celite. The solvent was removed in vacuo, and the crude product was dissolved in a mixture of hexanes/dichloromethane and treated with triethylamine (5.0 mL). The resulting mixture was stirred at room temperature for 2 h, then the solvents were removed in vacuo. The product was purified by chromatography on silica gel (hexanes/ether, 10:1) followed by recrystallization from pentane at 0 °C to afford 0.82 g (46%) of the titled compound as slightly yellow crystals (creamy solid before recrystallization). FTIR (KBr) 3371.0, 2956.8, 1726.4, 1503.1, 1374.2, 1310.6, 1230.0, 1154.3, 1059.7, 668.5 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 6.92 (s, 2 H), 1.50 (p, J = 8.15 Hz, 12 H), 1.47 (s, 18 H), 1.29 (sext, J = 7.32 Hz, 12 H), 1.06 (t, J = 8.24 Hz, 12 H), 0.87 (t, J = 7.29 Hz, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 153.9, 149.8, 80.8, 29.1, 28.3, 27.4, 13.7, 11.5. HRMS Calcd for $C_{38}H_{74}N_4O_4{}^{120}Sn_2$: 833.3050. Found: 833.3045. Anal. Calcd for $C_{38}H_{74}N_4O_4Sn_2$: C, 51.38; H, 8.40; N, 6.31. Found: C, 51.56; H, 8.22; N, 6.25.

General Procedure for the Synthesis of Pyrazine Dialkyl Ketones. Thiophenol method: To a solution of thiophenol (25.0 mmol) in THF (10 mL) was added *n*-butyllithium (25.0 mmol) at 0 °C and the mixture was stirred at 0 °C for 10 min. The resulting lithium thiophenoxide was transferred via syringe to a suspension of CuI (25.0 mmol) in THF (65 mL) at 0 °C and the mixture was stirred at 0 °C for 15 min after the addition. The mixture was cooled to −78 °C and pre-prepared *n*-dodecyllithium (25 mmol) or commercial *n*-butyllithium (25.0 mmol) was added dropwise. The mixture was stirred at −78 °C for 15 min, then transferred via cannula to a pre-cooled (−78 °C) solution of **5** (5.0 mmol) in THF (30 mL). The resulting mixture was stirred at −78 °C for 15 min before quenching at −78 °C with a 1:1 mixture of methanol−aqueous ammonium chloride. The cooling bath was removed and the reaction mixture was allowed to warm to room temperature and filtered through a pad of Celite. The organic phase was separated, and the aqueous phase was extracted with dichloromethane. The combined organic layers were washed with aqueous sodium bicarbonate and brine, dried over magnesium sulfate, and filtered. The solvent was removed in vacuo and the crude product was purified as described below. ***tert*-Butyl alcohol method:** The procedure was the same as for the thiophenol method except thiophenol was substituted by *tert*-butyl alcohol and the precooled (−78 °C) solution of **5** (5.0 mmol) in THF (30 mL) was rapidly added to the mixed cuprate (12.0 mmol). The reaction time was 1−5 min before quenching with a 1:1 mixture of methanol−aqueous ammonium chloride.

2,5-Di(1′-oxo-*n*-pentyl)pyrazine (8a). **Following the *tert*-butyl alcohol method:** Lithium *tert*-butoxide (43.8 mL, 48.0 mmol, 1.1 M in THF−hexanes), *n*-butyllithium (31.7 mL, 46.0 mmol, 1.45 M in hexanes), CuI (9.15 g, 48.0 mmol) in THF (100 mL), and **5** (20.0 mmol, 4.10 g) in THF (120 mL) were used. Reaction of the mixed cuprate with **5** for 1 min before quenching, followed by column chromatography on silica gel (hexanes/ether, 5:1) and recrystallization from hexanes/dichloromethane, afforded 2.77 g (56%) of the titled compound as bright yellow crystals. FTIR (KBr) 2957.5, 2872.6, 1695.0, 1466.9, 1384.4, 1271.6, 1117.2, 1022.1, 977.9, 772.4 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 9.21 (s, 2 H), 3.18 (t, J = 7.4 Hz, 4 H), 1.70 (p, J = 7.4 Hz, 4 H), 1.40 (sext, J = 7.4 Hz, 4 H), 0.94 (t, J = 7.3 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.1, 149.0, 142.3, 37.9, 25.8, 22.4, 13.9. HRMS Calcd for $C_{14}H_{20}N_2O_2$: 248.1525. Found: 248.1513.

2,5-Bis(1′-oxo-*n*-tridecyl)pyrazine (8b). **Following the thiophenol method:** Lithium thiophenoxide (26.6 mL, 25.0 mmol, 0.94 M in THF−hexanes) was formed by reaction of *n*-butyllithium (16.6 mL, 25.0 mmol, 1.5 M in hexanes) and thiophenol (2.65 mL, 25.0 mmol) in THF (10 mL) at 0 °C. The *n*-dodecyllithium (58.0 mL, 25.0 mmol, 0.43 M in pentane−ether) was prepared by addition of 1-bromododecane (6.2 mL, 25.0 mmol) to a solution of *tert*-butyllithium (33.65 mL, 52.5 mmol, 1.56 M in pentane) in ether (25 mL) at −78 °C. After the mixture was stirred at −78 °C for 15 min, the cooling bath was removed and the mixture was allowed to warm to room temperature. The other reagents used were CuI (4.76 g, 25 mmol) in THF (65 mL) and **5** (1.03 g, 5.0 mmol) in THF (30 mL). Purification by chromatography on silica gel (hexanes/dichloromethane/ethyl acetate, 8:2:1) followed by recrystallization from hexanes/dichloromethane afforded 1.13 g (48%) of the titled compound as pale yellow solid. **Following the *tert*-butyl alcohol method:** Lithium *tert*-butoxide (13.1 mL, 12.0 mmol, 0.92 M in THF−hexanes), which was formed analogously to the lithium thiophenoxide above, *n*-dodecyllithium (26.1 mL, 12.0 mmol, 0.46 M in pentane−ether), CuI (2.29 g, 12.0 mmol) in THF (25 mL), and **13** (1.03 g, 5.0 mmol) in THF (30 mL) were used. The reaction time was 5 min before quenching. Purification as above gave 0.79 g (34%) of the titled compound. FTIR (KBr) 2921.2, 2852.0, 1694.9, 1616.8, 1466.6, 1384.5, 1264.7, 1178.8, 1028.2, 969.0, 782.4, 721.7 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 9.20 (s, 2 H), 3.17 (t, J = 7.30 Hz, 4 H), 1.71 (p, J = 7.28

Hz, 4 H), 1.23 (m, 36 H), 0.85 (t, J = 6.90 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.15, 149.03, 142.36, 38.18, 31.92, 29.66, 29.64, 29.62, 29.49, 29.43, 29.35, 29.25, 23.71, 22.69, 14.12. HRMS Calcd for $C_{30}H_{52}N_2O_2$: 472.4029. Found: 472.4018.

2,5-Di(*p*-*tert*-butylbenzoyl)pyrazine (8c). To a slurry of **5** (4.10 g, 20.0 mmol) and anhydrous aluminum chloride (13.64 g, 100.00 mmol) in dichloromethane (200 mL) at 0 °C was added dropwise *tert*-butylbenzene (13.56 g, 100.00 mmol, neat) and the mixture was allowed to warm to room temperature overnight. The reaction was quenched with aqueous ammonium chloride at 0 °C and the mixture was filtered through a pad of Celite. The organic phase was separated, and the aqueous phase was extracted with dichloromethane. The combined organic layers were washed with aqueous sodium bicarbonate and brine, dried over magnesium sulfate, and filtered. The solvent was removed in vacuo and the crude product was purified by flash chromatography on silica gel (hexanes/dichloromethane/ethyl acetate, 3:2:1) followed by recrystallization from hexanes/dichloromethane to afford 7.02 g (88%) of the titled compound as yellow crystals. FTIR (KBr) 2958.3, 1657.8, 1607.1, 1468.3, 1405.5, 1352.0, 1267.8, 1176.0, 1106.9, 1029.3, 953.1, 922.3, 843.9, 762.9, 705.5 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (s, 2 H), 8.06 (d, J = 8.59 Hz, 4 H), 7.54 (d, J = 8.58 Hz, 4 H), 1.35 (s, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 157.9, 151.2, 143.9, 132.6, 131.0, 125.6, 35.3, 31.0. HRMS Calcd for $C_{26}H_{28}N_2O_2$: 400.2151. Found: 400.2143.

2,5-Di(*p*-*n*-dodecylbenzoyl)pyrazine (8d). See the procedure for **8c**. **5** (2.05 g, 10.00 mmol), anhydrous aluminum chloride (6.82 g, 50.00 mmol), dichloromethane (100 mL), and 1-phenyldodecane (12.70 g, 50.00 mmol, neat) were used with purification by chromatography on silica gel (hexanes/dichloromethane/ethyl acetate, 8:2:1) followed by recrystallization from hexanes/dichloromethane to afford 2.68 g (43%) of the titled compound as a yellow solid. FTIR (KBr) 2919.6, 2851.0, 1667.5, 1605.8, 1467.9, 1413.7, 1348.8, 1267.5, 1167.6, 1033.9, 941.1, 911.9, 849.3, 759.1, 710.6 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 (s, 2 H), 8.04 (d, J = 8.15 Hz, 4 H), 7.31 (d, J = 8.15 Hz, 4 H), 2.68 (t, J = 7.59 Hz, 4 H), 1.64 (p, J = 7.35 Hz, 4 H), 1.24 (m, 36 H), 0.86 (t, J = 6.42 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.2, 151.2, 150.0, 143.9, 132.8, 131.2, 128.6, 36.1, 31.9, 31.0, 29.7, 29.6, 29.5, 29.4, 29.3, 29.1, 28.8, 22.7, 14.1. HRMS Calcd for $C_{42}H_{60}N_2O_2$: 624.4655. Found: 624.4641.

Diacetal 9a. To **8a** (0.98 g, 4.0 mmol) and neopentyl glycol (4.30 g, 40.0 mmol) in benzene (40 mL) and acetonitrile (20 mL) was added trifluoromethanesulfonic acid (0.1 mL) and the mixture was heated to reflux at 105−115 °C for 16 h.[20] The reaction mixture was allowed to cool to room temperature and poured into ice-cooled aqueous potassium carbonate, and the resulting mixture was stirred while warming to room temperature for 1 h. The organic phase was separated and the aqueous phase was extracted with dichloromethane. The combined organic layers were washed with brine, dried over magnesium sulfate, and filtered through a pad of Celite. The solvent was removed in vacuo and the crude product was purified by flash chromatography on silica gel (hexanes/ether, 5:1) to afford 1.65 g (98%) of the titled compound as a white solid. FTIR (KBr) 2952.9, 2865.8, 1467.2, 1364.2, 1242.9, 1176.3, 1113.2, 1079.2, 1016.9, 965.1, 926.0, 888.5. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.73 (s, 2 H), 3.50 (d, J = 11.36 Hz, 4 H), 3.35 (d, J = 11.15 Hz, 4 H), 1.79 (t, J = 7.67 Hz, 4 H), 1.34 (m, 4 H), 1.19 (s, 6 H), 1.18 (m, 4 H), 0.77 (t, J = 7.20 Hz, 6 H), 0.61 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.9, 143.7, 100.5, 72.1, 41.7, 30.1, 24.8, 22.9, 22.7, 22.1, 14.0. HRMS Calcd for $C_{24}H_{40}N_2O_4$: 420.2988. Found: 420.2979.

Diacetal 9b. See the procedure for **9a**. **8b** (1.89 g, 4.0 mmol), neopentyl glycol (4.30 g, 40.0 mmol), benzene (40 mL), acetonitrile (20 mL), and trifluoromethanesulfonic acid (0.1 mL) were used with purification by chromatography on silica gel (hexanes/dichloromethane/ethyl acetate, 8:2:1) to afford 2.48 g (96%) of the titled compound as white crystals. FTIR (KBr) 2925.9, 2856.1, 1465.7, 1395.9, 1363.9, 1313.2, 1174.6, 1086.9, 1022.3, 977.3, 920.0. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s 2 H), 3.45 (d, J = 11.04 Hz, 4 H), 3.32 (d, J = 11.15 Hz, 4 H), 1.74 (t, J = 7.49 Hz, 4 H), 1.29 (m, 4 H), 1.13−1.09 (br m, 42 H), 0.74 (t, J = 6.06 Hz, 6 H), 0.56 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.80, 143.55, 100.38, 72.01, 41.86, 31.80, 29.94, 29.52, 29.42, 29.39, 29.24, 29.02, 28.15, 22.76, 22.57, 22.49, 21.99, 14.01. HRMS Calcd for $C_{40}H_{72}N_2O_4$: 644.5492. Found: 644.5479.

Diacetal 9c. See the procedure for **9a**. **8c** (2.00 g, 5.0 mmol), neopentyl glycol (3.22 g, 30.0 mmol), benzene (40 mL), acetonitrile (20 mL), and trifluoromethanesulfonic acid (40 mL) were used with purification by chromatography on silica gel (hexanes/dichloromethane/ethyl acetate, 3:2:1) to afford 2.82 g (98%) of the titled compound as white crystals. FTIR (KBr) 2961.8, 2865.3, 1666.3, 1606.8, 1463.5, 1395.4, 1362.0, 1270.3, 1215.3, 1189.2, 1106.4, 1022.1, 982.3, 906.2, 830.0, 734.7, 671.5 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 2 H), 7.47 (d, J = 8.34 Hz, 4 H), 7.32 (d, J = 8.30 Hz, 4 H), 3.66 (d, J = 11.07 Hz, 4 H), 3.56 (d, J = 11.01 Hz, 4 H), 1.26 (s, 18 H), 1.06 (s, 6 H), 0.80 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 151.1, 141.8, 135.8, 126.8, 125.5, 99.7, 72.0, 34.5, 31.3, 30.2, 22.7, 22.2. HRMS Calcd for $C_{36}H_{48}N_2O_4$: 572.3614. Found: 572.3623.

Diacetal 9d. See the procedure for **9a**. **8d** (1.10 g, 1.76 mmol), neopentyl glycol (1.13 g, 10.56 mmol), benzene (16 mL), acetonitrile (8 mL), and trifluoromethanesulfonic acid (50 μL) were used with purification by chromatography on silica gel (hexanes/dichloromethane/ethyl acetate, 8:2:1) to afford 1.31 g (93%) of the titled compound as a white solid. FTIR (KBr) 2919.1, 2851.2, 1468.1, 1395.4, 1272.3, 1214.5, 1109.0, 1024.2, 980.1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 2 H), 7.46 (d, J = 8.14 Hz, 4 H), 7.13 (d, J = 8.11 Hz, 4 H), 3.66 (d, J = 11.14 Hz, 4 H), 3.56 (d, J = 11.10 Hz, 4 H), 2.54 (t, J = 7.63 Hz, 4 H), 1.55 (p, J = 7.56 Hz, 4 H), 1.24 (m, 36 H), 1.07 (s, 6 H), 0.86 (t, J = 6.64 Hz, 6 H), 0.79 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.72, 143.10, 141.68, 135.98, 128.63, 127.11, 99.76, 72.0, 35.70, 31.94, 31.32, 30.24, 29.69, 29.66, 29.59, 29.52, 29.45, 29.38, 29.33, 22.72, 22.24, 22.09, 14.15. HRMS Calcd for $C_{52}H_{80}N_2O_4$: 796.6118. Found: 796.6127.

Diiododiacetal 10a. To *n*-butyllithium (27.8 mL, 42.0 mmol, 1.51 M in hexanes) was slowly added 2,2,6,6-tetramethylpiperidine (7.2 mL, 42.0 mmol) at 0 °C and the mixture was stirred at 0 °C for 30 min, then cooled to −78 °C to form the LTMP solution. To the LTMP in hexanes was added dropwise a solution of **9a** (1.47 g, 3.50 mmol) in ether/THF (5:1, 24.0 mL) at −78 °C. After being stirred at −78 °C for 15 min under argon, the mixture was warmed and stirred at −25 °C for 4 h. Iodine (11.2 g, 44.0 mmol) in THF (50 mL) was added at −25 °C over 2 h via a syringe pump and the mixture was stirred at −25 °C for an additional 2 h. The reaction was quenched with aqueous sodium thiosulfate at −23 °C and allowed to warm to room temperature. The organic phase was separated and the aqueous phase was extracted with dichloromethane. The combined organic layers were washed with brine, dried over magnesium sulfate, and filtered. The solvent was removed in vacuo and the crude product was purified by chromatography on silica gel (hexanes/ether, 5:1) followed by recrystallization from pentane at −10 to 0 °C to afford 1.97 g (84%) of the titled compound as white crystals. FTIR (KBr) 2959.2, 2865.5, 1470.0, 1396.3, 1268.2, 1179.9, 1117.1, 1082.7, 1061.5, 1037.3, 1009.4, 952.3, 921.9, 888.2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.49 (d, J = 11.60 Hz, 4 H), 3.29 (d, J = 11.23 Hz, 4 H), 1.95 (t, J = 7.61 Hz, 4 H), 1.51 (p, J = 7.60 Hz, 4 H), 1.28 (sext, J = 7.37 Hz, 4 H), 1.25 (s, 6 H), 0.86 (t, J = 7.24 Hz, 6 H), 0.62 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7, 112.1, 100.3, 72.2, 40.0, 29.8, 24.5, 23.0, 22.7, 22.1, 14.1. HRMS Calcd for $C_{24}H_{38}I_2N_2O_4$: 672.0921. Found: 672.0925. Anal. Calcd for $C_{24}H_{38}I_2N_2O_4$: C, 42.87; H, 5.70; N, 4.17. Found: C, 43.12; H, 5.75; N, 4.10.

Diiododiacetal 10b. See the procedure for **10a**. 2,2,6,6-Tetramethylpiperidine (5.1 mL, 30.0 mmol), *n*-butyllithium (20.7 mL, 30.0 mmol, 1.45 M in hexanes), **9b** (0.97 g, 1.50 mmol) in ether/THF (2:1, 15 mL), and iodine (8.0 g, 31.5 mmol) in THF (40 mL) were used with chromatography on silica gel (hexanes/dichloromethane/ethyl acetate, 8:2:1) followed by recrystallization from pentane at −10 to 0 °C to afford 1.02 g (77%) of the titled compound. FTIR (KBr) 2923.0, 2854.0, 1465.5, 1266.4, 1178.9, 1084.9, 958.8. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.48 (d, J = 11.48 Hz, 4 H), 3.28 (d, J = 11.29 Hz, 4 H), 1.94 (t, J = 7.62 Hz, 4 H), 1.50 (m, 4 H), 1.25−1.21 (br m, 42 H), 0.85 (t, J = 6.47 Hz, 6 H), 0.62 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.76, 112.10, 100.30, 72.16, 40.24, 31.93, 29.81, 29.66, 29.60, 29.59, 29.55,

(20) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; Wiley: New York, 1991.

29.36, 22.99, 22.70, 22.38, 22.08, 14.14. HRMS Calcd for $C_{40}H_{70}I_2N_2O_4$: 896.3425. Found: 896.3414.

Diiodiodiacetal 10c. See the procedure for **10a**. 2,2,6,6-Tetramethylpiperidine (0.9 mL, 5.3 mmol), *n*-butyllithium (3.3 mL, 5.1 mmol, 1.54 M in hexanes), **9c** (0.16 g, 0.28 mmol) in THF (8.0 mL), and iodine (1.34 g, 5.3 mmol) in THF (6 mL) were used with chromatography on silica gel (hexanes/dichloromethane/ethyl acetate, 3:2:1) followed by recrystallization from pentane at −10 to 0 °C to afford 0.19 g (83%) of the titled compound as a pale yellow solid. FTIR (KBr) 2959.3, 2867.7, 1611.7, 1509.5, 1465.8, 1398.2, 1363.8, 1265.2, 1193.2, 1107.5, 1068.7, 971.3, 915.2, 833.4, 731.8, 687.2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, $J = 8.41$ Hz, 4 H), 7.35 (d, $J = 8.44$ Hz, 4 H), 3.64 (d, $J = 11.43$ Hz, 4 H), 3.50 (d, $J = 11.39$ Hz, 4 H), 1.29 (s, 18 H), 1.18 (s, 6 H), 0.77 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 151.5, 136.6, 126.5, 125.0, 111.5, 99.1, 72.4, 34.6, 31.3, 29.9, 23.0, 22.4. HRMS Calcd for $C_{36}H_{46}I_2N_2O_4$: 824.1547. Found: 824.1591.

Diiodiodiacetal 10d. See the procedure for **10a**. 2,2,6,6-Tetramethylpiperidine (7.2 mL, 42.0 mmol), *n*-butyllithium (29.0 mL, 42.0 mmol, 1.45 M in hexanes), **9d** (1.39 g, 1.75 mmol) in THF (24.0 mL), and iodine (10.9 g, 42.8 mmol) in THF (40 mL) were used with chromatography on silica gel (hexanes/dichloromethane/ethyl acetate, 8:2:1) followed by recrystallization from pentane at −10 to 0 °C to afford 0.85 g (47%) of **10d**. FTIR (KBr) 2921.9, 2852.7, 1466.0, 1397.7, 1265.1, 1102.4, 1071.6, 1039.1, 969.3, 920.4, 833.8. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, $J = 8.22$ Hz, 4 H), 7.16 (d, $J = 8.23$ Hz, 4 H), 3.65 (d, $J = 11.46$ Hz, 4 H), 3.52 (d, $J = 11.42$ Hz, 4 H), 2.57 (t, $J = 7.62$ Hz, 4 H), 1.59 (p, $J = 7.47$ Hz, 4 H), 1.26 (m, 36 H), 1.19 (s, 6 H), 0.89 (t, $J = 0.77$ Hz, 6 H), 0.79 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 143.5, 136.8, 128.1, 126.7, 111.6, 99.1, 72.4, 35.74, 31.94, 31.34, 29.94, 29.69, 29.66, 29.61, 29.53, 29.41, 29.38, 22.97, 22.71, 22.39, 14.15. HRMS Calcd for $C_{52}H_{78}I_2N_2O_4$: 1048.4051. Found: 1048.4033.

2,5-Diiodo-3,6-bis(1′-oxo-*n*-pentyl)pyrazine (11a). To **10a** (0.672 g, 1.0 mmol) in dichloromethane (20 mL), acetonitrile (40 mL), and water (20 mL) was added trifluoromethanesulfonic acid (2.5 mL) and the mixture was heated to 65 °C for 10 h. The mixture was cooled to room temperature, poured into aqueous sodium bicarbonate at 0 °C, and extracted with dichloromethane. The combined organic layers were washed with brine, dried over magnesium sulfate, and filtered. The solvent was removed in vacuo and the crude product was purified by chromatography on silica gel (hexanes/ether, 5:1) followed by recrystallization from pentane at −10 to 0 °C to afford 0.488 g (98%) of the titled compound as bright yellow crystals. FTIR (KBr) 2955, 2932, 2868, 1706, 1465, 1386, 1282, 1170, 1122, 1086, 1023, 960, 770. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.04 (t, $J = 7.22$ Hz, 4 H), 1.69 (p, $J = 7.26$ Hz, 4 H), 1.36 (sext, $J = 7.37$ Hz, 4 H), 0.92 (t, $J = 7.31$ Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.0, 152.4, 109.1, 39.5, 25.6, 22.2, 13.9. HRMS Calcd for $C_{14}H_{18}I_2N_2O_2$: 499.9458. Found: 499.9457. Anal. Calcd for $C_{14}H_{18}I_2N_2O_2$: C, 33.62; H, 3.63; N, 5.60. Found: C, 33.88; H, 3.67; N, 5.56.

2,5-Diiodo-3,6-bis(1′-oxo-*n*-tridecyl)pyrazine (11b). See the procedure for **11a**. **10b** (0.49 g, 0.5 mmol), dichloromethane (10 mL), acetonitrile (20 mL), water (10 mL), and trifluoromethanesulfonic acid (1.0 mL) were used followed by chromatography on silica gel (hexanes/dichloromethane/ethyl acetate, 8:2:1) and recrystallization from pentane at −10 to 0 °C to afford 0.346 g (96%) of the titled compound as bright yellow crystals. FTIR (KBr) 2917.8, 2850.5, 1706.7, 1466.4, 1399.7, 1283.8, 1103.1, 957.0, 781.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.04 (t, $J = 7.25$ Hz, 4 H), 1.69 (p, $J = 7.15$ Hz, 4 H), 1.24 (m, 36 H), 0.86 (t, $J = 6.96$ Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.08, 152.47, 109.05, 39.81, 31.93, 29.67, 29.65, 29.62, 29.47, 29.40, 29.37, 29.07, 23.54, 22.71, 14.15. HRMS Calcd for $C_{30}H_{50}I_2N_2O_2$: 724.1962. Found: 724.1971. Anal. Calcd for $C_{30}H_{50}I_2N_2O_2$: C, 49.73; H, 6.96; N, 3.87. Found: C, 50.53; H, 7.05; N, 3.74.

2,5-Diiodo-3,6-di(*p*-*tert*-butylbenzoyl)pyrazine (11c). See the procedure for **11a**. **10c** (0.148 g, 0.18 mmol) dichloromethane (5 mL), acetonitrile (10 mL), water (5 mL), and trifluoromethanesulfonic acid (0.5 mL) were used followed by chromatography on silica gel (hexanes/dichloromethane/ethyl acetate, 3:2:1) and recrystallization from pentane at −10 to 0 °C to afford 0.113 g (97%) of the titled compound as white crystals. FTIR (KBr) 2961.7, 1672.9, 1602.6, 1462.4, 1410.9, 1268.3, 1226.6, 1187.2, 1109.2, 1081.3, 926.8, 847.3, 735.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, $J = 8.61$ Hz, 4 H), 7.54 (d, $J = 8.60$ Hz, 4 H), 1.36 (s, 18 H). ^{13}C NMR (100 Hz, $CDCl_3$) δ 190.7, 159.2, 157.4, 131.2, 130.6, 126.2, 111.1, 35.5, 31.0. HRMS Calcd for $C_{26}H_{26}I_2N_2O_2$: 652.0084. Found: 652.0083.

2,5-Diiodo-3,6-di(*p*-*n*-dodecylbenzoyl)pyrazine (11d). See the procedure for **11a**. **10d** (0.21 g, 0.20 mmol), dichloromethane (5 mL), acetonitrile (10 mL), water (5 mL), and trifluoromethanesulfonic acid (0.5 mL) were used followed by chromatography on silica gel (hexanes/dichloromethane/ethyl acetate, 8:2:1) and recrystallization from pentane at −10 to 0 °C to afford 0.166 g (95%) of the titled compound as white crystals. FTIR (KBr) 2918.5, 2849.7, 1671.2, 1604.0, 1469.7, 1420.2, 1227.0, 1179.5, 1081.1, 927.6. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, $J = 8.26$ Hz, 4 H), 7.33 (d, $J = 8.26$ Hz, 4 H), 2.69 (t, $J = 7.59$ Hz, 4 H), 1.64 (p, $J = 7.62$ Hz, 4 H), 1.24 (m, 36 H), 0.86 (t, $J = 6.61$ Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.7, 157.5, 151.4, 131.5, 130.8, 129.2, 111.3, 36.3, 31.9, 31.0, 29.68, 29.66, 29.6, 29.5, 29.4, 29.3, 22.7, 14.2. HRMS Calcd for $C_{42}H_{58}I_2N_2O_2$: 876.2588. Found: 876.2578. Anal. Calcd for $C_{42}H_{58}I_2N_2O_2$: C, 57.54; H, 6.67; N, 3.20. Found: C, 57.56; H, 6.65; N, 3.20.

General Procedure for the Polymerization Reactions. To a screw-cap tube containing **7** (0.204 mmol), **11a**−**d**, or **10a** (0.200 mmol), bis(triphenylphosphine)palladium(II) chloride (0.004 mmol, 2.8 mg), and copper(I) iodide (0.004 mmol, 0.8 mg) was introduced *N*-methyl-2-pyrrolidinone (1 mL) and THF (9 mL) in a glovebox. The reaction tube was capped and heated in the dark for 1−7 days. After being cooled to room temperature, the crude reaction mixture was dissolved in warm dichloromethane and filtered through a pad of Celite. The solvent was removed in vacuo to give the crude material that was purified as described below.

Polymer 12a. Following the general procedure, **7** (0.3623 g, 0.408 mmol), **11a** (0.2000 g, 0.400 mmol), bis(triphenylphosphine)palladium(II) chloride (5.6 mg, 0.008 mmol), copper(I) iodide (1.5 mg, 0.008 mmol), *N*-methyl-2-pyrrolidinone (2.0 mL), and THF (18.0 mL) were used. The reaction time was 40 h at 70−75 °C. After removing the solvents, the crude material was dissolved in dichloromethane and the titled compound was fractionally precipitated as a black solid by the addition of methanol. The yield was 0.182 g (82%). FTIR (KBr) 2958.2, 2927.5, 2871.2, 1706.3, 1461.6, 1235.4, 1146.3, 877.4, 687.5. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.7−7.4 (br, 2 H), 3.4−3.2 (br t, $J = 7$ Hz, 4 H), 2.40−2.25 (br pent, $J = 7$ Hz, 4 H), 1.97−1.23 (br m, 18 H), 0.92−0.87 (br t, $J = 7$ Hz, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.01, 132.06, 131.98, 128.53, 128.43, 67.92, 49.39, 32.53, 30.64−25.56 (m), 22.38, 17.62, 15.22, 14.08, 13.71−13.45 (m). Anal. Calcd for $(C_{28}H_{38}N_6O_6)_n$: C, 60.64; H, 6.91; N, 15.15. Found: C, 61.44; H, 7.02; N, 13.42. Partial Boc loss and cyclization was evident in this compound.

Polymer 12b. Following the general procedure, **7** (0.1812 g, 0.204 mmol), **11b** (0.1448 g, 0.200 mmol), bis(triphenylphosphine)palladium(II) chloride (2.8 mg, 0.004 mmol), copper(I) iodide (0.8 mg, 0.004 mmol), *N*-methyl-2-pyrrolidinone (1.0 mL), and THF (9.0 mL) were used. The reaction time was 20 h at 70 °C, then 6 h at 80 °C. After the solvents were removed, the crude material was dissolved in dichloromethane and the titled compound was fractionally precipitated as a black solid by the addition of methanol. The yield was 0.1311 g (84%). FTIR (KBr) 3261.5, 2923.8, 2852.7, 1720.4, 1584.8, 1461.7, 1143.5. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.0−3.3 (m, 4 H), 1.80−1.05 (m, 54 H), 0.86 (br s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.2, 175.1, 151.7, 150.4, 150.2, 141.5, 134.0, 81.6, 81.3, 50.8, 49.4, 40.8, 34.6, 31.9, 31.6, 30.7, 30.0, 29.9, 29.7, 29.6, 29.5, 29.4, 28.4, 28.21, 28.15, 25.3, 23.5, 22.7, 22.6, 17.6, 14.1. Anal. Calcd for $(C_{44}H_{70}N_6O_6)_n$: C, 67.83; H, 9.05; N, 10.79. Found: C, 69.88; H, 9.10; N, 11.39. Partial Boc loss and cyclization was evident in this compound.

Polymer 12c. This compound was synthesized according to the general procedure except that the workup was different. The compounds used were **7** (0.2265 g, 0.255 mmol), **11c** (0.1630 g, 0.250 mmol), bis(triphenylphosphine)palladium(II) chloride (3.5 mg, 0.005 mmol), copper(I) iodide (1.0 mg, 0.005 mmol), *N*-methyl-2-pyrrolidinone (1.2 mL), and THF (11.0 mL). After being stirred at 75−80 °C for 7 days, the reaction mixture was cooled to room temperature and the resulting polymer was collected by filtration and washed with water, methanol, ether, and dichloromethane. The titled polymer was obtained as a black

solid that was only slightly soluble in organic solvents at room temperature, hence proper purification and analysis could not be performed. The yield was 0.114 g (65%). FTIR (KBr) 2960.4, 2868.8, 1735.4, 1673.5, 1604.9, 1571.6, 1456.9, 1369.1, 1268.8, 1225.5, 1190.1, 1156.4, 1106.1, 1019.0, 948.8, 847.9. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.65−1.3 (br). ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.9, 130.7, 125.7, 49.3, 45.2, 31.2, 31.0, 30.6, 29.5. Anal. Calcd for $(C_{40}H_{46}N_6O_6)_n$: C, 67.97; H, 6.56; N, 11.89. Found: C, 68.17; H, 5.62; N, 15.54. Partial Boc loss and cyclization was evident in this compound.

Polymer 12d. Following the general procedure, **7** (0.1812 g, 0.204 mmol), **11d** (0.1753 g, 0.200 mmol), bis(triphenylphosphine)palladium-(II) chloride (2.8 mg, 0.004 mmol), copper(I) iodide (0.8 mg, 0.004 mmol), *N*-methyl-2-pyrrolidinone (1.0 mL), and THF (9.0 mL) were used. The reaction time was 1 day at 50 °C, then 4 days at 60−70 °C. After the solvents were removed, the crude material was dissolved in dichloromethane and the titled compound was fractionally precipitated as a black solid by the addition of methanol. The yield was 0.137 g (74%). FTIR (KBr) 3415.8, 2924.8, 2853.6, 1736.0, 1676.8, 1606.2, 1571.1, 1463.1, 1368.7, 1146.2, 929.1. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (br s, 1 H), 8.02 (br s, 1 H), 7.80 (br s, 4 H), 7.41 (br s, 4 H), 2.63 (br s, 4 H), 1.63−1.11 (m, 58 H), 0.86 (br s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.1, 165.2, 149.5, 146.7, 141.5, 135.9, 133.1, 132.0, 130.8, 128.7, 124.8, 80.9, 36.3, 34.5, 32.9, 31.2, 29.7, 29.4, 27.8, 26.9, 26.3, 22.7, 14.1, 13.5. Anal. Calcd for $(C_{56}H_{78}N_6O_6)_n$: C, 72.22; H, 8.44; N, 9.03. Found: C, 71.55; H, 8.10; N, 9.52. Partial Boc loss and cyclization was evident in this compound.

Polymer 14. Following the general procedure, **7** (0.1812 g, 0.204 mmol), **10a** (0.1344 g, 0.200 mmol), bis(triphenylphosphine)palladium-(II) chloride (2.8 mg, 0.004 mmol), copper(I) iodide (0.8 mg, 0.004 mmol), *N*-methyl-2-pyrrolidinone (1.0 mL), and THF (9.0 mL) were used. The reaction time was 3 days at 75−80 °C. The crude material was dissolved in dichloromethane (50 mL) and washed with aqueous potassium carbonate and brine, dried over magnesium sulfate, and filtered. The solvent was removed in vacuo and the residue was applied to a plug of silica gel and washed with hexanes/ether (4:1). The silica gel plug with adsorbed polymer was scraped into an Erlenmeyer flask and stirred with dichloromethane/ethyl acetate (2:1) for 0.5 h and filtered through a pad of Celite. The solvent was removed in vacuo to afford 0.104 g (72%) of the titled polymer as a fluorescent red gel. FTIR (film) 3266.0, 2955.0, 2869.5, 1748.5, 1503.0, 1468.4, 1392.6, 1366.7, 1229.5, 1141.5, 1088.2, 1018.8. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.7−7.4 (br, 2 H), 3.7−3.2 (br m, 8H), 2.9−2.6 (br, 4 H), 1.8−1.0 (br m, 30 H), 0.91−0.87 (br t, J = 7.26 Hz, 6 H), 0.65−0.45 (br m, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.8, 182.0, 175.2, 173.5, 167.7, 153.7−125.3 (m), 113.0, 101.5, 101.2, 100.8, 81.9, 80.8, 80.4, 79.9, 72.4, 72.8, 68.1, 67.9, 66.8, 49.0, 42.2−40.7 (m), 38.7, 37.7, 37.1, 34.0−21.4 (m), 18.9, 17.6, 17.5, 16.4, 16.2, 14.5−13.6 (m), 11.9, 10.9. Anal. Calcd for $(C_{38}H_{56}N_6O_8)_n$: C, 62.95; H, 7.73; N, 11.59. Found: C, 59.32; H, 8.09; N, 9.26.[21]

General Procedure for the Preparation of Planar Polymers 1a−d. To a screw-cap tube containing the nonplanar polymers **12a−d** and THF was added anhydrous zinc chloride. The reaction tube was sealed and the mixture was heated at 130−145 °C for 2 days. The cyclized polymer precipitated from the reaction mixture and was collected by filtration upon cooling to room temperature. The solid was washed with water, methanol, acetone, and dichloromethane and dried in an oven at 120 °C for 10 h then in vacuo overnight at room temperature to give the planar polymers **1a−d** as black solids.

Polymer 1a. This material was prepared both from **12a** according to the general procedure and from the acetal polymer **14**. **From 12a and the general procedure: 12a** (0.077 g, 0.139 mmol), anhydrous zinc chloride (0.7 mg, 0.005 mmol), and THF (30 mL) were used. The reaction temperature was 140−145 °C and the yield was 0.0428 g (96%). FTIR (KBr) 2956.7, 2927.5, 2866.4, 1627.8, 1458.7, 1401.3, 1254.2, 1161.3, 1031.8, 875.2, 610.3. Anal. Calcd for $(C_{18}H_{18}N_6)_n$: C, 67.90; H, 5.70; N, 26.40. Found: C, 61.03; H, 5.44; N, 20.74.[21] Insolubility prevented further analysis. **From 14:** To a screw-cap tube containing a solution of **14** (0.0768 g, 0.106 mmol) in toluene (15 mL) was added one drop of trifluoromethanesulfonic acid at 0 °C followed by addition of water (1.0 mL). The reaction tube was sealed and heated at 100−120 °C for 18 h and the resulting planar polymer precipitated from the solution. The reaction mixture was cooled to room temperature and the planar polymer was collected by filtration. The solid was washed with water, methanol, acetone, and dichloromethane and dried at oven temperature 125 °C for 8 h, then in vacuo overnight at room temperature to give 0.0287 g (85%) of **1a** as a black solid. Anal. Calcd for $(C_{18}H_{18}N_6)_n$: C, 67.90; H, 5.70; N, 26.40. Found: C, 59.68; H, 5.46; N, 23.29.[21]

Polymer 1b. This material was prepared according to the general procedure. **12b** (0.048 g, 0.062 mmol), anhydrous zinc chloride (0.4 mg, 0.003 mmol), and THF (12 mL) were used. The reaction temperature was 130−135 °C and the yield was 0.0306 g (91%). The polymer was only slightly soluble in chloroform/trifluoroacetic acid (1:1). FTIR (KBr) 2925.1, 2858.4, 1584.2, 1457.5, 1170.2, 1036.7, 608.5. ^{1}H NMR (300 MHz, $CDCl_3$/TFA-*d* (1:1)) δ 2.18−2.05 (br t, J = 7 Hz, 4 H), 1.85−1.60 (br m, 4 H), 1.55−1.20 (br m, 32 H), 1.0−0.85 (br m, 10 H). ^{13}C NMR (125 MHz, $CDCl_3$/TFA-*d* (1:1)) δ 125.3, 34.3, 30.0, 29.7, 29.3, 28.5, 27.1, 26.4, 24.9, 22.9, 18.1, 13.7, 12.8. Anal. Calcd for $(C_{34}H_{50}N_6)_n$: C, 75.23; H, 9.28; N, 15.48. Found: C, 70.81; H, 8.42; N, 13.74.[21]

Polymer 1c. This material was prepared according to the general procedure. **12c** (0.078 g, 0.11 mmol), anhydrous zinc chloride (0.6 mg, 0.0044 mmol), and THF (25 mL) were used. The reaction temperature was 140−145 °C and the yield was 0.049 g (95%). FTIR (KBr) 2960.5, 1604.7, 1568.6, 1453.8, 1372.4, 1269.0, 1192.1, 1160.3, 1105.8, 949.6, 846.9, 688.1. ^{1}H NMR (300 MHz, $CDCl_3$/TFA-*d* (1:1)) δ 8.0−7.6 (br), 1.8−1.2 (br). ^{13}C NMR (125 MHz, $CDCl_3$/TFA-*d* (1:1)) δ 133.0, 127.2, 35.8, 30.6, 27.6, 18.1, 13.2. Anal. Calcd for $(C_{30}H_{26}N_6)_n$: C, 76.57; H, 5.56; N, 17.86. Found: C, 65.02; H, 5.28; N, 16.35.[21]

Polymer 1d. This material was prepared according to the general procedure. **12d** (0.076 g, 0.082 mmol), anhydrous zinc chloride (0.5 mg, 0.0033 mmol), and THF (15 mL) were used. The reaction temperature was 130−135 °C and the yield was 0.053 g (93%). FTIR (KBr) 2959.9, 1645.8, 1441.4, 1365.5, 1161.2, 1111.9, 1055.9, 882.5, 670.4. ^{1}H NMR (300 MHz, $CDCl_3$/TFA-*d* (1:1)) δ 8.65−8.25 (br), 2.85−2.60 (br), 2.2−0.7 (br m). ^{13}C NMR (100 MHz, $CDCl_3$/TFA-*d* (1:1)) δ 130.4, 129.1, 36.4 (br m), 32.03−29.8 (br m), 27.7, 25.5, 22.8 (br), 14.3 (br). Anal. Calcd for $(C_{46}H_{58}N_6)_n$: C, 79.50; H, 8.41; N, 12.09. Found: C, 73.77; H, 8.17; N, 10.71.[21]

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(21) It is common to obtain low carbon values in combustion analyses of highly unsaturated polymers based on arene structures. This is due to incomplete combustion with remaining carbon residues. See ref 4h and 5 and the following: (a) Chimil, K.; Scherf, U. *Makromol. Chem., Rapid Commun*. **1993**, *14*, 217. (b) Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 7411. (c) Stephens, E. B.; Tour, J. M. *Macromolecules* **1993**, *26*, 2420.