# JOC Article

Bis(pyrrol-2-yl)arylenes from the Tandem Bidirectional Addition of Vinyl Grignard Reagent to Aryl Diesters

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i. ⟋⟍MgBr, CuCN; ii. O₃, Me₂S or O₂, PdCl₂, CuCl; iii. RNH₂
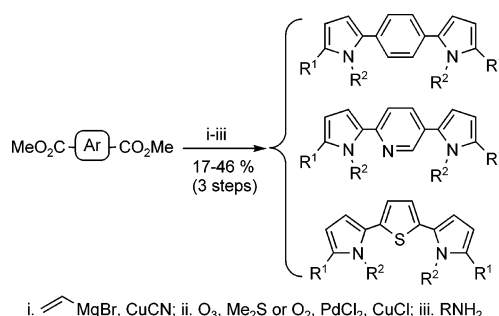
A practical three-step synthesis of bis(pyrrol-2-yl)arylenes has been accomplished, featuring a copper-catalyzed tandem bidirectional addition of vinylmagnesium bromide to aryldicarboxylates. Spectroscopic and cyclic voltammetric analyses revealed the influence of the central aromatic core and pyrrole substitution pattern on the electrochemical properties of these comonomers.

Introduction

The synthesis of π-conjugated polymers is an intensive area of research, owing to their unique properties and commercial potential in a vast array of mechanical, electrical, electrochemical, and optical applications.[1] π-Conjugated polymers are typically prepared from the electropolymerization of heterocyclic monomers; however, polymer defects often arise from competing side reactions such as overoxidation, β-coupling, and cross-linking, as well as homopolymer formation due to mismatching of monomer redox potentials. Monomers containing the elements of the copolymer structure, so-called comonomers, have been employed to minimize such defects leading to insoluble and infusible products and to provide materials for accurate structure−property correlations. Comonomers[2] incorporating a central aromatic core (acceptor) sandwiched between electron-rich heterocycles (donors) display high reactivity at the terminal positions, have lower oxidation potentials relative to the parent monomer, and lead to more highly ordered polymers with higher electrical conductivities in their doped form relative to their unsymmetrically substituted analogues. Pyrrole-donor comonomers such as 1,4-bis(pyrrol-2-yl)-benzene (1a) are particularly attractive because they are more readily oxidized[3] than their furan-donor and thiophene-donor counterparts, providing electroactive poly[1,4-bis(pyrrol-2-yl)arylene] polymers[4] with polypyrrole-like electrochromic properties that are useful for biomedical applications.[5]

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SCHEME 1. Synthesis of Bis(pyrrol-2-yl)arylenes 1a–h[a]

1	R^1	R^2
a	H	H
b	Me	H
c	H	*n*-Bu
d	Me	*n*-Bu
e	H	H
f	H	*n*-Bu
g	H	H
h	Me	H
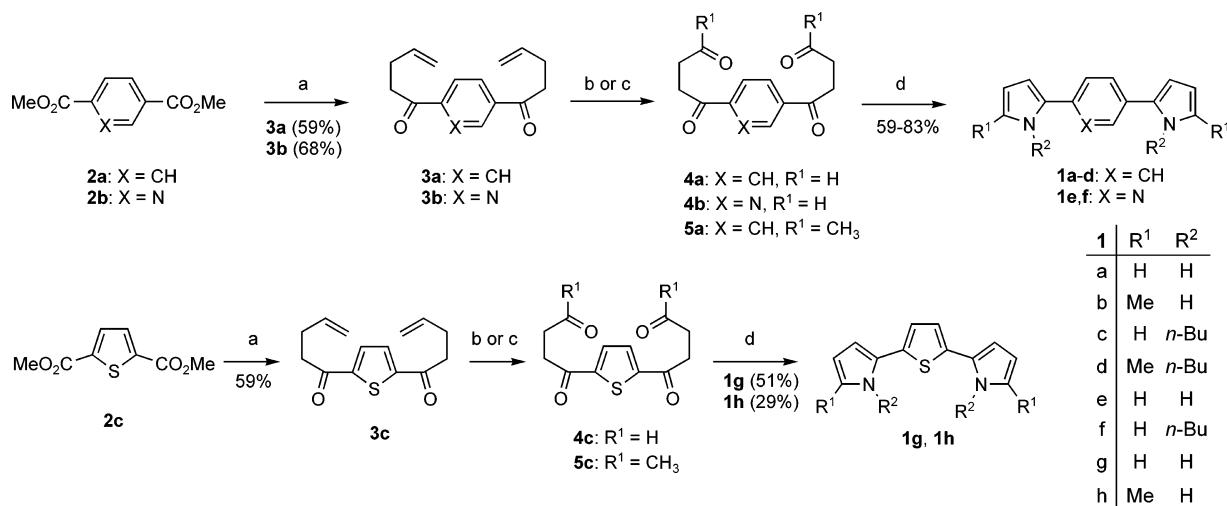
[a] Conditions: (a) vinylmagnesium bromide (6 equiv), CuCN (0.6 equiv), −78 to 0 °C; (b) (i) O$_3$, CH$_2$Cl$_2$/MeOH, −78 °C, (ii) NaHCO$_3$, Me$_2$S; (c) PdCl$_2$, CuCl, O$_2$, THF/H$_2$O, ultrasound; (d) NH$_4$CO$_2$H or *n*-BuNH$_2$, for conditions, see Experimental Section.

Practical synthetic strategies[6] are desired which allow for the ready incorporation of a variety of substituted donor and acceptor subunits within the comonomer to enable fine-tuning of the polymer band gap for optimal conduction.[7] Three strategies have been typically used to construct bis(pyrrol-2-yl)arylenes **1**: (a) construction of the aromatic core from a flanked bispyrrole system,[5a,8] (b) transition-metal-catalyzed attachment of preformed pyrrole analogues to a suitably derivatized aromatic core,[2f,4b] and (c) tandem pyrrole synthesis on the aromatic core from linear precursors.[2a–c,4d,e,9,10] Multiple steps, relatively harsh conditions, and low yields have typically limited bis(pyrrol-2-yl)arylene diversity with these approaches.

Recently, we described a practical protocol for synthesizing homoallylic ketones by copper-catalyzed cascade addition of vinyl Grignard reagent to carboxylic esters[11a] and demonstrated its utility in a three-step synthesis of substituted pyrroles.[11b] By applying this methodology in a tandem fashion on aromatic diesters, we have now developed a relatively concise synthesis of bis(pyrrol-2-yl)arylenes (**1**). The influence of pyrrole regioalkylation and the central aryl core on the spectroscopic and electronic properties of **1a–h** was determined using UV–visible and fluorescence spectroscopy and cyclic voltammetry.

Results and Discussion

Bis(pyrrol-2-yl)arylenes **1a–h** were prepared in three steps from the corresponding aryldicarboxylates **2** by a route featuring vinyl Grignard reagent addition, olefin oxidation, and Paal–Knorr[12] condensation (Scheme 1). Aryldicarboxylates **2a–c** were treated with freshly prepared vinylmagnesium bromide (600 mol %) in the presence of CuCN (60 mol %) at −78 °C, warmed to 0 °C for 1 h, quenched at −78 °C with MeOH, and poured onto a rapidly stirred biphasic mixture of aqueous NaH$_2$PO$_4$ and Et$_2$O. After isolation and chromatography over silica gel, bis-homoallylic ketones **3a–c** were isolated in yields of 59, 68, and 59%, respectively (Scheme 1). Bis-1,4-keto aldehydes **4** were prepared by ozonolysis of **3** in CH$_2$Cl$_2$/MeOH at −78 °C, followed by treatment with excess dimethyl sulfide in the presence of NaHCO$_3$.[13] After extractive workup, bis-1,4-keto aldehydes **4** were used without further purification and stored for >6 months under argon at 0 °C without decomposition. Bis-1,4-diketones **5** were best obtained using a modification[14] of the Tsuji–Wacker[15] protocol employing PdCl$_2$ (0.4 equiv) and CuCl (2 equiv) in THF/H$_2$O (4:1) under an atmosphere of oxygen with ultrasound agitation (Scheme 1). After aqueous workup, the crude ketones were sufficiently pure for subsequent use.[16] Bis-homoallylic ketone **3b** failed to react under similar conditions,[17a] presumably due to complexation with palladium, while attempts using its trifluoroacetate led to decomposition.[17b]

Bis(pyrrol-2-yl)arylenes **1** were prepared by tandem ring closure on 1,4-dicarbonyl compounds **4** and **5** using different Paal–Knorr[12] reaction conditions contingent

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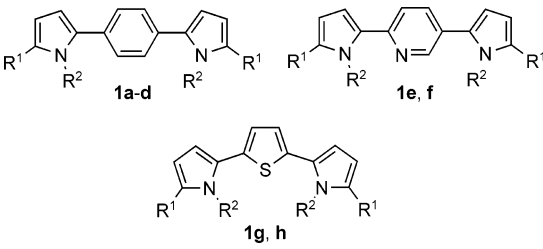
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(16) Crude products contained ca. 5% of the corresponding bis-1,4-keto aldehyde by ^{1}H NMR analysis.

(17) (a) PdCl$_2$ (0.2 equiv), 1,4-benzoquinone (0.9 equiv), THF/H$_2$O (4:1), ultrasound, 90 min. (b) PdCl$_2$ (0.4 equiv), CuCl (1 equiv), TFA (1 equiv), O$_2$, DMF/H$_2$O (7:1), 72 h.

TABLE 1. Cyclic Voltammetry Results of 1a–h[a]

sample	yield (%)[b]	R[1]	R[2]	comonomer[c] $E_{p,a}^1$ (mV)	$E_{p,a}^2$ (mV)	ΔE^1 (mV)	polymer[c,d] $E_{p,a}^1$ (mV)
1a	61 (36)	H	H	0 (644)	576 (1228)	576	−75 (569)
1b	59 (35)	Me	H	−118 (496)	292 (771)	410	
1c	63 (36)	H	n-Bu	264 (851)	737 (1317)	473	146 (660)
1d	65 (38)	Me	n-Bu	88 (692)	377 (1082)	289	
1e	83 (46)	H	H	189 (792)	657 (1256)	468	378 (1022)
1f	68 (38)	H	n-Bu	288 (875)	734 (1298)	446	1034 (1678)
1g	51 (24)	H	H	−99 (316)	599 (813)	698	176 (820)
1h	29 (17)	Me	H	−172 (386)	25 (632)	197	

[a] Conditions: in deaerated anhydrous acetonitrile with 0.1 M Bu_4NPF_6 measured against a saturated Ag/AgCl reference electrode, silver working and platinum auxiliary electrodes, sweep rate 500 mV/s. The first and second anodic potentials are given. [b] Isolated yield from 1,4-dicarbonyl precursor (yield over three steps from starting diester in parentheses). [c] The oxidation potentials are referenced to 1a, taken as 598 mV vs SCE by referencing to ferrocene.[21b] Values in parentheses are relative to Ag/AgCl. [d] Polymerization was achieved by repeated oxidation/reduction cycles or continuous oxidation (ca. 5 min) at a potential slightly more positive than the first oxidation peak (see the Supporting Information).

TABLE 2. Spectroscopic Results of Bis(pyrrol-2-yl)arylenes 1a–h

sample	λ_{abs} (nm)[a]	λ_{fl} (nm)[b]	Φ[c]	ϵ_{max} (cm^{-1} M^{-1})	τ (ns)	$\Delta\lambda_{HOMO-LUMO}$[d] (eV/kcal mol^{-1})	E_g^e (eV/kcal mol^{-1})
1a	330	378	0.74	26 440	1.9	3.5/80.4	3.1/71.5
1b	317	394	0.59	32 800	2.0	3.4/77.8	3.3/75.2
1c	293	440	0.64	48 230	1.9	3.7/84.3	3.4/78.9
1d	315	418	0.43	25 780	2.0	3.5/80.5	3.3/76.9
1e	344	397	0.56	25 590	2.6	3.3/76.5	3.2/73.9
1f	330	391	0.27	23 310	1.2	3.4/78.5	3.3/76.2
1g	352	422	0.78	18 880	2.8	3.2/73.7	2.9/68.7
1h	367	438	0.84	12 490	2.9	3.1/71.1	2.9/66.3

[a] Absorption. [b] Fluorescence. [c] Quantum yield relative to bis-(thiophene).[21c] [d] Absorption−emission intercept. [e] Spectroscopic band gap.

their parent counterparts **1a,e**, respectively, demonstrated that pyrrole N-alkylation increased the oxidation potential, making oxidative polymerization more difficult. The smaller oxidation potential of analogue **1d**, however, indicated that the effect of N-alkylation was counterbalanced by C-5 alkylation. In all cases, smaller ΔE values were observed relative to benchmark **1a**, indicating that N-alkylation decreased the overall stability of the system[20,21a] (Table 1).

The comonomer oxidation potential was also influenced by the nature of the π-acceptor core. The electron-deficient pyridine core destabilized the radical cation product derived from comonomer **1e**, as shown by the increased anodic potential, making oxidation more difficult (Table 1). In contrast, incorporation of the electron-rich thiophene moiety (analogue **1g**) promoted both monomer and polymer oxidation via a relatively more stable radical cation intermediate, suggesting that this analogue may be suitable for practical applications.

In the UV−visible spectra, **1a−h** were observed to undergo direct $S_0 \rightarrow S_1$ absorption transitions (Table 2). Both the absorption and fluorescence spectra of **1a−h** revealed structureless ground- and excited-state geometries, suggesting free aryl−aryl bond rotation was the major pathway for excited-state deactivation. This was supported by the observed monoexponential fluorescence decays. The quantum yields (Φ) exhibited by **1a−h** were found to be higher than most other related[22] electronically active compounds, indicating a limited number of available quenching pathways for excited deactivation (Table 2). The LUMO lowering influence of the pyridyl and thiophenyl cores was reflected in the bathochromic shifts displayed by **1e,g** in their UV−visible spectra, respectively, consistent with an enhanced degree of ground-state stabilization.

In summary, a series of bis-(pyrrol-2-yl)arylene comonomers was prepared by a practical three-step synthesis featuring treatment of aromatic diesters with excess vinylmagnesium bromide in the presence of CuCN in THF. The spectroscopic and redox properties of this comonomer series were examined by UV−visible and

upon the substitution pattern (Scheme 1, Table 1). For example, N-butylpyrroles **1c,d,f** were readily prepared by condensation of the appropriate 1,4-dicarbonyl compound with n-butylamine in the presence of a 1:1 mixture of NaOAc/HOAc (1 equiv w/w) in toluene at 60−70 °C.[18a] On the other hand, attempts to prepare **1a,e** using NH_4CO_2H and similar conditions led to significant polymerization. In this case, best results were obtained by treating bis-1,4-keto aldehydes **4a,b** with NH_4CO_2H and KOAc in a $HOAc/CH_3CN/H_2O$ mixture (1:1:1) at 60−70 °C under argon.[18b] For the formation of bis-pyrroles **1b,g,h**, improved yields were obtained by treatment[10] of the respective 1,4-dicarbonyl compounds with NH_4CO_2H in NH_4OH/EtOH at 60−70 °C under argon.[18c]

The cyclic voltammograms of **1a−h** exhibited two sequential one-electron oxidations corresponding to a radical cation followed by cation formation. The oxidative process was irreversible even at fast sweep rates, indicating the formation of highly reactive intermediates.[2a,4a,b,e,19] A comparison of the comonomer oxidation potentials of **1a,b** revealed that alkylation at the 5-position facilitated oxidation but inhibited both 4,4′- and 5,5′-electropolymerization, even at prolonged oxidation times, due to stable radical cation formation[20] (Table 1). To improve solubility properties in acetonitrile, we examined the N-alkylated analogues **1c,d,f**. A comparison of analogues **1c,f** versus

(18) (a) Purified by chromatography over silica gel. (b) Purified by chromatography over Florisil. (c) Purified by trituration (**1b**) or preparative TLC over silica gel (**1g,h**).

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fluorescence spectroscopy and cyclic voltammetry to determine the influences of pyrrole alkylation and modification of the central aromatic core. Oxidation potentials were lowered by C-5-alkylation and raised by N-alkylation. The thiophene core unit had the most desired effect by lowering both monomer and polymer oxidation potentials. This methodology should thus be of general use for synthesizing a variety of substituted donor—acceptor comonomers for the preparation of π-conjugated polymers.

Experimental Section

General Procedure for the Preparation of Bis-Homoallylic Ketones (3). A teflon coated magnetic stirrer bar and CuCN (0.6 equiv) were placed in a two-neck round-bottom flask fitted with a septum and gas inlet. The flask and contents were briefly flame-dried under a stream of argon and then cooled to room temperature. The flask was briefly opened, and diester **2** (1.0 equiv) was added. The reaction mixture was diluted with a quantity of THF, cooled to −78 °C, and treated with a solution of freshly prepared vinylmagnesium bromide in THF (6.0 equiv) over 15 min, giving a final concentration of ca. 0.15 M in **2**. After rapid stirring for 1 h at −78 °C, the cooling bath was replaced with an ice bath and stirring was continued for 1 h. The resultant dark slurry was recooled to −78 °C, treated with the specified volume of MeOH, and poured onto a rapidly stirred biphasic solution of ice-chilled 2 M NaH_2PO_4 and Et_2O. After ca. 1 h, the color disappeared, a white precipitate formed, and the mixture was treated with the specified volume of 3 M HCl solution. The phases were separated, and the aqueous phase was extracted with EtOAc. The pooled extracts were washed with brine, dried, filtered, and evaporated to give the corresponding bis-homoallylic ketone **3**, which was purified by flash chromatography over silica gel (eluant: toluene or toluene/Et_2O).

1-(6-Pent-4-enoyl-pyridin-3-yl)pent-4-en-1-one (3b): yield 68% from **2b**; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.43−2.55 (m, 4H), 3.10 (t, J = 7.3 Hz, 2H), 3.33 (t, J = 7.3 Hz, 2H), 4.95−5.04 (m, total width between outside lines 26.8 Hz, 2H) partly overlapped with 5.04−5.12 (m, total width between outside lines 23.4 Hz, 2H), 5.81−5.94 (m, 2H), 8.09 (d, J = 8.2 Hz, 1H), 8.31 (dd, J = 8.2, 2.1 Hz, 1H), 9.17 (br d, J ≈ 2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 27.7, 27.8, 37.1, 38.4, 115.2, 115.8, 121.6, 134.1, 136.3, 136.5, 137.1, 148.8, 155.5, 197.7, 200.5; HRMS (ESI) calcd for $C_{15}H_{17}NO_2$ [M + H$^+$] 244.1332, found 244.1339.

General Procedure for the Preparation of Bis-1,4-keto Aldehydes (4). A solution of **3** (1 equiv) in the specified MeOH/CH_2Cl_2 mixture was treated with ozone at −78 °C until a blue color persisted. The −78 °C reaction mixture was purged with a stream of argon to remove excess ozone and then treated successively with solid NaHCO$_3$ (8 equiv) and dimethyl sulfide (10 equiv). Stirring was continued overnight, after which time the bath temperature had warmed to room temperature. The solvent was removed by rotary evaporation, and the residue was partitioned between CH_2Cl_2 and H_2O. The phases were separated, and the aqueous phase was extracted with CH_2Cl_2. The pooled extracts were dried, filtered, and evaporated to yield **4**, which was used without further purification and stored under argon at 0 °C for >6 months without decomposition.

4-Oxo-4-[6-(4-oxobutyryl)-pyridin-3-yl]butyraldehyde (4b): prepared from **3b** in MeOH/CH_2Cl_2 (1:3); crude yield 82% from **3b**; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.91 (t, J = 6.3 Hz, 2H), 2.97 (t, J = 6.1 Hz, 2H), 3.31 (t, J = 6.1 Hz, 2H), 3.54 (t, J = 6.3 Hz, 2H), 8.08 (d, J = 8.1 Hz, 1H), 8.33 (dd, J = 8.1, 2.1 Hz, 1H), 9.20 (br d, J ≈ 2 Hz, 1H), 9.85, 9.86 (two partly overlapped s, total area 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 30.7, 31.4, 37.3, 37.6, 121.6, 133.9, 136.4, 148.8, 155.2, 196.3, 198.9, 199.8, 200.4; HRMS (ESI) calcd for $C_{13}H_{13}NO_4$ [M + H$^+$] 248.0917, found 248.0918.

General Procedure for the Preparation of Bis-1,4-diketones (5). A two-necked flask was fitted with a septum and a three-way stopcock connected to an oxygen-filled balloon. The flask was charged with PdCl$_2$ (0.2 equiv) and CuCl (2 equiv), diluted with THF/H_2O (4:1; 15 mL per 1 mmol of **3**), evacuated and flushed with oxygen three times. After it was stirred at room temperature for 1 h, the mixture was treated via syringe with a solution of **3** (1 equiv) in THF/H_2O (4:1; 5 mL per 1 mmol of **3**) and the reaction flask was then immersed in an ultrasound bath. After sonication for 90 min the reaction mixture was treated with PdCl$_2$ (0.2 equiv) and sonication was continued for 90 min. The resultant mixture was diluted with a small quantity of EtOAc, transferred to a separatory funnel, and agitated with a solution of 28% NH$_4$-OH/brine (10:90). The phases were separated, and the aqueous phase was extracted with EtOAc. The pooled extracts were washed with a solution of pH 6.7 sodium phosphate buffer/brine (1:1), dried, filtered, and evaporated to yield **5**, which was used without further purification.

1-[4-(4-Oxopentanoyl)phenyl]pentane-1,4-dione (5a): crude yield 74% from **3a**; mp 152−153 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.23 (s, 6H), 2.88 (t, J = 6.2 Hz, 4H), 3.25 (t, J = 6.2 Hz, 4H), 8.01 (s, 4H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 30.0, 32.7, 36.9, 128.2, 139.7, 198.0, 207.0; HRMS (ESI) calcd for $C_{16}H_{18}O_4$ [M + H$^+$] 275.1278, found 275.1279.

General Procedure for the Preparation of Pyrroles (1a,e). A stock solution was prepared containing KOAc (∼0.7 g, ∼7 mmol) and HOAc (∼0.5 mL, ∼8 mmol) in CH$_3$CN (0.5 mL) and H$_2$O (0.5 mL). In a round-bottom flask a mixture of bis-1,4-keto aldehyde **4a** or **4b** (100 mol %) and ammonium formate (1000 mol %) was suspended in a quantity of the stock solution (10 mL per 1 mmol of **4**). The reaction flask was evacuated and flushed with argon three times, and the contents were heated to 60−70 °C with stirring. After it was cooled to room temperature, the reaction mixture was partitioned between saturated NaHCO$_3$ solution and EtOAc. The phases were separated, and the aqueous phase was extracted with EtOAc. The pooled extracts were washed with brine, dried, filtered, and evaporated to afford the corresponding pyrrole. The resulting pyrroles were purified by a successive sequence of chromatography over Florisil (eluant: CHCl$_3$ or CHCl$_3$/acetone) and trituration (1:1 Et$_2$O/pentane).

2,5-Bis(1*H*-pyrrol-2-yl)pyridine (1e): yield 83% from **4b**; mp 281−286 °C dec; ^{1}H NMR (400 MHz, d_6-acetone) δ 6.21 (dt, J = 5.9, 2.6 Hz, 2H), 6.92−6.96 (m, 2H), 6.73−6.76 (m, 1H), 6.60−6.63 (m, 1H), 7.65 (dd, J = 8.4, 0.6 Hz, 1H), 7.93 (dd, J = 8.4, 2.4 Hz, 1H), 8.78 (m, 1H), 10.52−10.84 (br s, 3H); ^{13}C NMR (100 MHz, d_6-acetone) δ 106.9, 107.8, 110.3, 110.4, 118.5, 120.5, 120.9, 126.7, 129.6, 131.9, 132.4, 145.0, 149.1; HRMS (ESI) calcd for $C_{13}H_{12}N_3$ [M + H$^+$] 210.1026, found 210.1031.

General Procedure for the Preparation of Pyrroles (1c,d,f). A mixture of 1,4-dione **4a** or **5a** (100 mol %), *n*-butylamine (400 mol %), and NaOAc/HOAc (prepared by mixing equimolar quantities of NaOAc and HOAc; 1 equiv w/w) in toluene (10 mL per 1 mmol of 1,4-dione) was heated to 60−70 °C with stirring. After it was cooled to room temperature, the reaction mixture was partitioned between Et$_2$O/CH_2Cl_2 (2:1) and aqueous HCl solution (1 M). The phases were separated, and the aqueous phase was extracted with Et$_2$O/CH_2Cl_2 (2:1). The pooled extracts were washed with pH 6.8 phosphate buffer, dried, filtered, and evaporated to afford the corresponding pyrrole. The resulting pyrroles were purified by chromatography over silica gel (eluant: toluene).

1-Butyl-2-[4-(1-butyl-1*H*-pyrrol-2-yl)phenyl]-1*H*-pyrrole (1c): yield 63% from **4a**; mp 72−74 °C; ^{1}H NMR (400 MHz, d_6-acetone) δ 0.80 (t, J = 7.4 Hz, 6H), 1.14−1.25 (m, 4H), 1.57−1.66 (m, 4H), 4.04 (t, J = 7.3 Hz, 4H), 6.11 (t, J = 3.1 Hz, 2H), 6.15 (dd, J = 3.5, 1.8 Hz, 2H), 6.85 (t, J = 2.4 Hz, 2H), 7.44 (s, 4H); ^{13}C NMR (100 MHz, d_6-acetone) δ 13.8, 20.3, 34.2, 47.5, 108.5, 109.5, 123.4, 129.3, 133.1, 134.3; HRMS (ESI) calcd for $C_{22}H_{29}N_2$ [M + H$^+$] 321.2325, found 321.2327.

General Procedure for the Preparation of Pyrroles (1b,g,h). A mixture of 1,4-dione **4c**, **5a**, or **5c** (100 mol %) and ammonium formate (1000 mol %) was suspended in a solution of 28% NH_4OH/EtOH (1:25; 30 mL per 1 mmol of 1,4-dione). The reaction flask was evacuated and flushed with argon three times, and the contents were heated to 60−70 °C with stirring. After it was cooled to room temperature, the reaction mixture was partitioned between EtOAc and brine. The phases were separated, and the aqueous phase was extracted with EtOAc. The pooled extracts were dried, filtered, and evaporated to afford the corresponding pyrrole. Pyrrole **1b** was purified by trituration (1:1 MeOH/pentane). Pyrroles **1g,h** were purified by a successive sequence of preparative TLC (eluant: 60:40 petroleum ether/Et_2O or 30:70 Et_2O/$CHCl_3$, respectively) followed by trituration (1:1 Et_2O/pentane).

2,5-Bis(1*H*-pyrrol-2-yl)thiophene (1g): yield 51% from **4c**; mp 197−207 °C dec; [^1]H NMR (400 MHz, d_4-MeOH) δ 6.13 (dd, J = 3.3, 2.9 Hz, 2H), 6.28 (dd, J = 3.4, 1.4 Hz, 2H), 6.77 (dd, J = 2.6, 1.4 Hz, 2H), 6.98 (s, 2H); [^13]C NMR (100 MHz, d_4-MeOH) δ 106.6, 109.9, 119.5, 121.5, 127.8, 134.8; HRMS (ESI) calcd for $C_{12}H_{11}N_2S$ [M + H[^+]] 215.0637, found 215.0632.

Supporting Information Available: Text giving detailed experimental procedures and figures giving [^1]H and [^13]C NMR spectra of all compounds, absorption and fluorescence spectra of **1a−h**, and cyclic voltammograms of **1a−h** and of the corresponding polymers derived from **1a,c,e−g**. This material is available free of charge via the Internet at http://pubs.acs.org.

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