SUPPORTING INFORMATION

Bis(pyrrol-2-yl)arylenes from the Tandem Bi-directional Addition of Vinyl Grignard Reagent to Aryldiesters

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General Experimental Methods

For reactions performed under anhydrous conditions, glassware was either oven- or flame-dried and the reaction was run under a positive pressure of argon. Anhydrous solvents (THF, CH₃CN, toluene) were obtained by passage through solvent filtration systems. Analytical thin-layer chromatography was conducted with aluminium backed silica gel F₂₅₄ plates. Preparative thin-layer chromatography was conducted with glass backed silica gel F₂₅₄ plates (60 Å, 1000 µm thickness). Visualization of the developed chromatogram was performed by UV absorbance, ethanolic phosphomolybdic acid, ninhydrin, or aqueous potassium permanganate. Flash chromatography was performed using silica gel (230-400 mesh). Chemical shifts for ¹H and ¹³C NMR spectra were recorded in parts per million with the solvent resonance as the internal standard. Palladium(II) chloride (99.9 %), copper(I) chloride (99+ %), copper(I) cyanide (99 %) magnesium (99.98 %), vinyl bromide (98 %) and dimethylterephthalate (99+ %) were purchased and used as received. Dimethyl-thiophene-2,5-dicarboxylate **2c** was prepared from thiophene-2,5-dicarboxylic acid under standard conditions (H₂SO₄/MeOH, reflux). Vinylmagnesium bromide was freshly prepared according to standard procedures¹ and titrated against menthol with 2,2'-dipyridyl as indicator.² Eluants used in TLC analysis: 20:80 Et₂O/hexane (eluant 1); 5:95 EtOAc/CHCl₃ (eluant 2); 2:98 Et₂O/toluene (eluant 3); 60:40 EtOAc/hexane (eluant 4); 10:90 MeOH/CHCl₃ (eluant 5); 30:70 Et₂O/CHCl₃ (eluant 6); 30:70 acetone/CHCl₃ (eluant 7); 5:95 acetone/CHCl₃ (eluant 8); toluene (eluant 9); 10:90 acetone/CHCl₃ (eluant 10). Spectroscopic measurements were done in 10 mm cuvettes using deaerated and anhydrous acetonitrile. The quantum yields were

General Experimental Methods (cont.)

determined relative to naphthalene in acetonitrile using matched absorbances (within 2 %) at the excitation wavelength. Cyclic voltammetry measurements were done in deareated anhydrous acetonitrile with 0.1 M Bu₄NPF₆ using a saturated Ag/AgCl reference electrode, silver working and platinum auxiliary electrodes. Typical sweep rates were either 500 mV/sec or 1000 mV/sec. All the oxidation potentials are referenced to **1a** for easy comparison and normalized³ against ferrocene (395 mV vs. SCE) under the same experimental conditions. The absolute value measured for **1a** was 598 mV vs. SCE and 644 mV vs Ag⁺/AgCl. Polymerizations were achieved by repeated oxidation/reductions cycles. Polymer deposition on the electrode was also accomplished by continuous oxidation at a potential slightly more positive than the first oxidation peak. After polymerization on the electrode, the monomer-electrolyte solution was exchanged for an electrolyte-only solution in acetonitrile. Typical oxidation hold times of 5 minutes were sufficient for polymer film deposition.

Pyridine-2,5-dicarboxylic acid dimethyl ester (2b)

Pyridine-2,5-dicarboxylic acid (9.63 g, 57.6 mmol) was esterified according to the literature⁴ procedure using concentrated sulfuric acid in MeOH. The crude product thus obtained (8.65 g) was recrystallized from MeOH to give **2b** as colorless needles (7.2 g, 64 %), mp. 163–166 °C (lit.⁴ 162–163 °C).

General Procedure A: Preparation of Homoallylic Ketones (3).

A magnetic stirrer bar and CuCN (0.6 eq) were placed in a 2-neck round bottom flask. The flask and contents were briefly flame dried under a stream of argon and then allowed to cool to rt. The flask was briefly opened and diester **2** (1.0 eq) was added. The reaction mixture was diluted with a quantity of THF, cooled to –78 °C, and treated with a solution of freshly prepared vinyl magnesium bromide in THF (6.0 eq) over 15 min, giving a final concentration of *ca.* 0.15 *M* in diester **2**. After rapid stirring for 1h at –78 °C, the cooling bath was replaced with an ice bath and stirring was continued for 1h. The resultant dark solution was re-cooled to –78 °C, treated with the specified volume of MeOH, stirred for 5 min, and the dark slurry was poured onto a rapidly stirred biphasic solution of ice-chilled 2 *M* NaH₂PO₄ and Et₂O. After *ca.* 1h, the color disappeared, a white precipitate formed, and the mixture was treated with 3 *M* HCl solution. The phases were separated and the aqueous phase was extracted with EtOAc. The pooled extracts were washed with brine, dried (MgSO₄), filtered and evaporated to give a crude residue. The crude residue was suspended in Et₂O/CH₂Cl₂ (1:1) and filtered through a plug of celite to remove insoluble salts. The filtrate was evaporated and the crude product purified by chromatography over silica gel.

General Procedure B: Preparation of Dialdehydes (4)

A solution of **3** (1 eq) in the specified MeOH/CH₂Cl₂ 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 NaHCO₃ (8 equiv) and dimethylsulfide (10 equiv). Stirring was continued overnight, after which time the bath temperature had warmed to rt. The solvent was removed by rotary evaporation and the residue was partitioned between CH₂Cl₂ and H₂O. The phases were separated and the aqueous phase was extracted with CH₂Cl₂. The pooled extracts were dried (Na₂SO₄), filtered and evaporated. Dialdehydes **4** were used without further purification, and stored under argon at 0 °C for >6 months without decomposition.

General Procedure C: Preparation of 1,4-diketones (5)

A two necked flask fitted with a septum and three-way stopcock was connected to an oxygen filled balloon, charged with PdCl₂ (0.2 equiv) and CuCl (2 equiv), followed by a 4:1 THF/H₂O solution (~ 15 mL per 1 mmol **3**). The reaction flask was evacuated and flushed with oxygen three times. After stirring at room temperature for 1 h, the mixture was treated via syringe with a solution of **3** (1 equiv) in THF/H₂O (4:1, ~ 5 mL per 1 mmol **3**) and the reaction flask was immersed in an ultrasound bath. After sonication for 90 min the reaction mixture was treated with PdCl₂ (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% NH₄OH/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 (MgSO₄), filtered and evaporated to yield the corresponding 1,4-diketone. ¹H NMR analysis revealed the diketone **5** to be *ca.* 95% pure. The remaining *ca.* 5% comprised the corresponding bis-aldehyde, as identified by comparison of ¹H NMR data for bis-aldehyde **4**. The material was used without further purification.

General Procedure D: Preparation of Pyrroles (1a, 1e)

A stock solution was prepared containing KOAc (~ 0.7 g, ~ 7 mmol) and HOAc (~ 0.5 mL, ~ 8 mmol) in CH₃CN (0.5 mL) and H₂O (0.5 mL). In a round bottom flask a mixture of 1,4-dione (100 mol%) and ammonium formate (1000 mol %) was suspended in the stock solution (~ 10 mL per 1 mmol dialdehyde **4**). The reaction flask was evacuated and flushed with argon three times. The resultant mixture was heated at 60-70 °C with stirring until complete consumption of starting material was observed by TLC. After cooling to rt, the reaction mixture was partitioned between NaHCO₃ solution (saturated, aqueous) and CHCl₃ (in the case of **1e**) or EtOAc (in the case of **1a**). The phases were separated, and the organic phase was washed with NaHCO₃ solution (saturated, aqueous). The aqueous wash was extracted with CHCl₃ (**1e**) or EtOAc (**1a**) and the pooled extracts were washed with brine, dried (Na₂SO₄), filtered and evaporated to afford the crude product.

General Procedure E: Preparation of Pyrroles (1c, 1d, 1f)

A mixture of 1,4-dione (100 mol%), *n*-butyl amine (400 mol %) and NaOAc/HOAc (prepared by mixing equimolar quantities of NaOAc and HOAc; 1 eq w/w) in toluene (~ 10 mL solvent per 1 mmol 1,4-dione) was heated at 60-70 °C with stirring until complete consumption of starting material was observed by TLC. After cooling to rt, the reaction

mixture was partitioned between Et₂O/CH₂Cl₂ (2:1) and aqueous HCl solution (1 *M*). The phases were separated and the aqueous phase was extracted with Et₂O/CH₂Cl₂ (2:1). The pooled extracts were washed with pH 6.8 phosphate buffer, dried (MgSO₄), filtered and evaporated to afford the crude product.

General Procedure F: Preparation of Pyrroles (**1b**, **1g**, **1h**)⁵

A mixture of 1,4-dione (100 mol%) and ammonium formate (1000 mol%) was suspended in a solution of 28% NH₄OH/EtOH (1:25, *ca.* 30 mL per 1 mmol 1,4-dione). The reaction flask was evacuated and flushed with argon three times. The resultant mixture was heated at 60–70 °C with stirring until complete consumption of starting material was observed by TLC. After cooling to rt, 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 (Na₂SO₄), filtered and evaporated to afford the crude product.

1-(4-Pent-4-enoyl-phenyl)-pent-4-en-1-one (**3a**)

Prepared by the addition of vinyl magnesium bromide in THF

(1 *M*, 93 mL, 93 mmol) to a THF (7 mL) suspension of CuCN

(830 mg, 9.27 mmol) and dimethylterephthalate **2a** (3.0 g, 15 mmol), followed by quenching with MeOH (10 mL), pouring onto a solution containing NaH₂PO₄ (48 g), ice (100 g), H₂O (100 mL) and Et₂O (100 mL) and finally addition of 3 *M* HCl (50 mL) according to general procedure A to give a residue (4.38 g) which yielded the crude product (3.74 g) after removal of salts. Purification by chromatography over silica gel (eluant: toluene) gave **3a** as an off-white solid (2.2 g, 59 %). An analytical sample was

obtained by recrystallization from isooctane to give colorless pearley leaflets, mp. 84-85 °C (lit.⁶ 77 °C). R_f 0.38 (eluant 1). 1H NMR (400 MHz, $CDCl_3$) δ 2.46 (q, J = 7.0 Hz, 4H), 3.06 (t, J = 7.3 Hz, 4H), 4.95-5.01 (m, 2H), 5.01-5.09 (m, 2H), 5.86 (ddt, J = 16.8, 10.2, 6.5 Hz, 2H), 7.99 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.9, 38.0, 115.4, 128.1, 136.9, 139.9, 198.7. HRMS (ESI) calcd for $C_{16}H_{18}O_2$ $[M+H^+]$ 243.1380, found 243.1381.

1-(6-Pent-4-enoyl-pyridin-3-yl)-pent-4-en-1-one (3b)

Prepared by the addition of vinyl magnesium bromide in THF (1.39 M, 57 mL, 79.2 mmol) to a THF (30 mL) suspension of (1.39 M, 57 mL, 79.2 mmol) to a THF (30 mL) suspension of CuCN (710 mg, 7.92 mmol) and 2,5-dimethoxycarbonylpyridine **2b** (2.58 g, 13.2 mmol), followed by quenching with MeOH (30 mL), and pouring onto a solution containing NaH_2PO_4 (38 g), ice (80 g), H_2O (80 mL) and Et_2O (80 mL) according to general procedure A (exception: 3 M HCl was not added during workup) to give the crude product as a brown oil (3.74 g). Chromatography over silica gel (eluant: 1:99-3:97 Et_2O /toluene over 1 % increments) gave **3b** as an low-melting orange solid (2.17 g, 68 %). R_f 0.54 (eluant 2). 1H 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.

1-(5-Pent-4-enoyl-thiophen-2-yl)-pent-4-en-1-one (3c)

Prepared by the addition of vinyl magnesium bromide in THF (1 M, 12 mL, 12.0 mmol) to a THF (3 mL) suspension of CuCN (107 mg, 1.2 mmol) and thiophene-2,5-dicarboxylic acid dimethyl ester **2c** (400 mg, 2.0 mmol), followed by quenching with MeOH (3 mL), pouring onto a solution containing NaH₂PO₄ (7.2 g), ice (15 g), H₂O (15 mL) and Et₂O (15 mL) and finally addition of 3 M HCl (8 mL) according to general procedure A to give a residue (621 mg) which yielded the crude product (445 mg) after removal of salts. Chromatography over silica gel (eluant: toluene) gave **3c** (293 mg, 59 %) as an off-white solid. An analytical sample was obtained by recrystallization from isooctane to give white pearley leaflets, mp. 113-114 °C. R_f 0.35 (eluant 3). ¹H NMR (400 MHz, CDCl₃) δ 2.47 (dd, *J* = 14.4, 6.8 Hz, 4H), 2.99 (t, *J* = 7.4 Hz, 4H), 4.97-5.02 (m, 2H), 5.03-5.09 (m, 2H), 5.84 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 2H), 7.66 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 28.0, 38.7, 115.7, 131.4, 136.5, 148.6, 192.5. HRMS (ESI) calcd for C₁₄H₁₆O₂S [M+H⁺] 249.0944, found 249.0944.

4-Oxo-4-[4-(4-oxo-butyl)-phenyl]-butyraldehyde (4a)⁵

Prepared from **3a** (1.02 g, 4.13 mmol) in MeOH/CH₂Cl₂ (1:1, 100 mL) according to general procedure B to give crude **4a** (1.0 g, 96 %) as a cream-colored solid after trituration with Et₂O and collection by filtration, mp. 85-87 °C. R_f 0.35 (eluant 4). ¹H NMR (400 MHz, CDCl₃) δ 2.90 (t, *J* = 6.2 Hz, 4H), 3.28 (t, *J* = 6.2 Hz, 4H), 7.99 (s, 4H), 9.83 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 31.2, 37.3, 128.2, 139.5, 197.2, 200.3.

4-Oxo-4-[6-(4-oxo-buteryl)-pyridin-3-yl]-butyraldehyde (4b)

Prepared from **3b** (500 mg, 2.06 mmol) in MeOH/CH₂Cl₂ (1:3, 40 mL) according to general procedure B to give crude **4b** (416 mg, 82%) as a brown solid. *R*_f 0.55 (eluant 5). ¹H NMR (400

MHz, CDCl₃) 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). ¹³C NMR (100 MHz, CDCl₃) 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 C₁₃H₁₃NO₄ [M+H⁺] 248.0917, found 248.0918.

4-Oxo-4-[5-(4-oxo-buteryl)-thiophen-2-yl]-butyraldehyde (4c)⁵

Prepared from **3c** (48.4 mg, 0.19 mmol) in MeOH/CH₂Cl₂ (1:3, 8 mL) according to general procedure B to give crude **4c**

(40 mg, 81 %) as a white powder after lyophilization from acetonitrile/H₂O. *R*_f 0.21 (eluant 4). ¹H NMR (400 MHz, CDCl₃) δ 2.94 (t, *J* = 6.2 Hz, 4H), 3.25 (t, *J* = 6.2 Hz, 4H), 7.73 (s, 2H), 9.86 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 31.6, 37.3, 131.7, 148.1, 191.0, 199.9.

1-[4-(4-Oxo-pentanoyl)-phenyl]-pentane-1,4-dione (5a)

Prepared from **3a** (300 mg, 12.4 mmol) according to general procedure C to give **5a** (251 mg, 74%) as a yellow powder.

An analytical sample was obtained by chromatography over silica gel (eluant: CHCl₃): mp. 152-153 °C (lit.⁷ 150 °C). *R*_f 0.24 (eluant 6). ¹H NMR (400 MHz, CDCl₃) 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 $\text{C}_{16}\text{H}_{18}\text{O}_4$ $[\text{M}+\text{H}^+]$ 275.1278, found 275.1279.

1-[5-(4-Oxo-pentanoyl)-thiophen-2-yl]-pentane-1,4-dione (5c)

Prepared from **3c** (60 mg, 0.24 mmol) according to general procedure C to give crude **5c** (68 mg) as a pale orange powder.

R_f 0.17 (eluant 6). ^1H NMR (400 MHz, CDCl_3) δ 2.22 (s, 6H), 2.87 (t, $J = 6.2$ Hz, 4H), 3.19 (t, $J = 6.2$ Hz, 4H), 7.71 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 29.9, 33.1, 36.9, 131.6, 148.2, 191.7, 206.7. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{16}\text{O}_4\text{S}$ $[\text{M}+\text{H}^+]$ 281.0842, found 281.0843.

2-[4-(1H-Pyrrol-2-yl)phenyl]-1H-pyrrole (1a)

Prepared from **4a** (21.7 mg, 0.088 mmol) according to general procedure D to give a crude product (23 mg) which was filtered

through a short plug of Florisil (eluant: 100/0 to 95:5 CHCl_3 /acetone over 1 % increments) and evaporated to a residue that was triturated with Et_2O /pentane (1:1). The organic phase was decanted and the residue was dried under vacuum to provide the title compound (11.1 mg, 61 %) as pale green pearly leaflets: mp. > 400 °C (lit.⁵ 298–307 °C). R_f 0.71 (eluant 7). ^1H NMR (400 MHz, d_6 -acetone) δ 6.14–6.19 (m, 2H), 6.50–6.54 (m, 2H), 6.83–6.88 (m, 2H), 7.61 (s, 4H), 10.46 (br s, 2H). ^{13}C NMR (100 MHz, d_6 -acetone) δ 106.1, 110.1, 119.7, 124.6, 131.5, 132.4. HRMS (ESI) m/z 209.1079 $[\text{M}+\text{H}^+]$; calcd for $[\text{C}_{14}\text{H}_{13}\text{N}_2]^+$: 209.1073].

2-Methyl-5-[4-(5-methyl-1H-pyrrol-2-yl)phenyl]-1H-pyrrole (1b)

Prepared from **5a** (50 mg, 0.18 mmol) according to general procedure F to give a crude product (37 mg) which was triturated

with MeOH/pentane (1:1). The organic phase was decanted and the residue dried under vacuum to give the title compound (25.5 mg, 59 %) as tan colored leaflets: mp > 350 °C. R_f 0.57 (eluant 8). ^1H NMR (400 MHz, d_6 -DMSO) δ 2.24 (s, 6H), 5.76-5.80 (br m, 2H), 6.33 (t, J = 2.8 Hz, 2H), 7.51 (s, 4H), 10.89 (br s, 2H). ^{13}C NMR (100 MHz, d_6 -DMSO) δ 12.9, 105.1, 107.1, 123.0, 128.6, 129.81, 129.83. HRMS (ESI) m/z 237.1389 $[\text{M}+\text{H}^+]$; calcd for $[\text{C}_{16}\text{H}_{17}\text{N}_2]^+$: 237.1386].

1-Butyl-2-[4-(1-butyl-1H-pyrrol-2-yl)phenyl]-1H-pyrrole (1c)

Prepared from **4a** (34.7 mg, 0.14 mmol) according to general procedure E to give the title compound (28.2 mg, 63 %) as a brown solid after purification by chromatography over silica gel (eluant: toluene): mp.

72–74 °C. R_f 0.75 (eluant 9). ^1H 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) m/z 321.2327 $[\text{M}+\text{H}^+]$; calcd for $[\text{C}_{22}\text{H}_{29}\text{N}_2]^+$: 321.2325].

1-Butyl-2-[4-(1-butyl-5-methyl-1H-pyrrol-2-yl)phenyl]-5-methyl-1H-pyrrole (1d)

Prepared from **4a** (30 mg, 0.11 mmol) according to general procedure E to give

the title compound (24.6 mg, 65 %) as a tan colored solid after purification by chromatography over silica gel (eluant: toluene):

mp. 91–93 °C. R_f 0.75 (eluant 9). ^1H NMR (400 MHz, d_6 -acetone)

δ 0.78 (t, J = 7.4 Hz, 6H), 1.12–1.24 (m, 4H), 1.47–1.57 (m, 4H), 2.29 (s, 6H), 3.93–4.00 (m, 4H), 5.84–5.87 (m, 2H), 6.02 (d, J = 3.4 Hz, 2H), 7.40 (s, 4H). ^{13}C NMR (100 MHz, d_6 -acetone) δ 12.8, 13.8, 20.3, 33.8, 44.3, 107.7, 108.6, 129.3, 130.4, 133.6, 134.0. HRMS (ESI) m/z 349.2637 [$\text{M}+\text{H}^+$; calcd for $[\text{C}_{24}\text{H}_{33}\text{N}_2]^+$: 349.2638].

2,5-Bis-(1H-pyrrol-2-yl)-pyridine (1e)

Prepared from **4b** (49.0 mg, 0.19 mmol) according to general procedure

D to give a crude product (55.6 mg) which was filtered through a short plug of Florisil (eluant: CHCl_3) and evaporated to a residue that was triturated with Et_2O /pentane (1:1). The organic phase was decanted and the residue dried under vacuum to provide the title compound (34.3 mg, 83 %) as pale green pearly leaflets: mp. 281–286 °C (dec.). R_f 0.23 (eluant 10). ^1H 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, 2H). ^{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) m/z 210.1031 [$\text{M}+\text{H}^+$; calcd for $[\text{C}_{13}\text{H}_{12}\text{N}_3]^+$: 210.1026].

2,5-Bis-(1-butyl-1H-pyrrol-2-yl)-pyridine (1f)

Prepared from **4b** (50 mg, 0.20 mmol) according to general procedure

E to give the title compound (44.0 mg, 68 %) as a green oil after

chromatography over silica gel (eluant: toluene). R_f 0.46 (eluant 9). ^1H NMR (400 MHz, CDCl_3) δ 0.86 (t, $J = 7.3$ Hz, 3H), 0.89 (t, $J = 7.3$ Hz, 3H), 1.28 (m, total width between outside lines 59 Hz, 4H), 1.62-1.76 (m, 4H), 3.95 (t, $J = 7.4$ Hz, 2H), 4.51 (t, $J = 7.3$ Hz, 2H), 6.19 (dd, $J = 3.6, 2.7$ Hz, 1H), 6.24-6.28 (m, 2H), 6.60 (dd, $J = 3.7, 1.8$ Hz, 1H), 6.80 (t, $J \sim 2$ Hz, 1H), 6.82 (t, $J \sim 2$ Hz, 1H), 7.56 (d, $J = 8.3$ Hz, 1H), 7.64 (dd, $J = 8.3, 2.3$ Hz, 1H), 8.59 (br d, $J \sim 2$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.6, 13.7, 19.7, 19.8, 33.6, 33.8, 47.0, 48.6, 107.6, 108.1, 109.3, 111.0, 120.8, 122.8, 125.5, 125.8, 130.8, 131.2, 136.0, 148.1, 150.9. HRMS (ESI) m/z 322.2280 $[\text{M}+\text{H}]^+$; calcd for $[\text{C}_{21}\text{H}_{28}\text{N}_3]^+$: 322.2278].

2,5-Bis-(1H-pyrrol-2-yl)-thiophene (**1g**)

Prepared from **4c** (40 mg, 0.16 mmol) according to general procedure F to give a crude product (46 mg) which was purified by preparative TLC

(eluant: 60:40 petroleum ether/ Et_2O), evaporated to a residue, and triturated with Et_2O /pentane (1:1). The organic phase was decanted and the residue was dried under vacuum to give the title compound (17.3 mg, 51 %) as a green powder: mp 197–207 °C (dec.) (lit.⁵ 206–208 °C). R_f 0.50 (eluant 10). ^1H 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) m/z 215.0632 $[\text{M}+\text{H}]^+$; calcd for $[\text{C}_{12}\text{H}_{11}\text{N}_2\text{S}]^+$: 215.0637].

2-Methyl-5-[5-(5-methyl-1*H*-pyrrol-2-yl)thien-2-yl]-1*H*-pyrrole (1h)

Prepared from **5c** (18.8 mg, 0.067 mmol) according to general procedure F to give a crude product (27.6 mg) which was purified by preparative TLC (eluant: 30:70 Et₂O/CHCl₃), evaporated to a residue, and triturated with Et₂O/pentane (1:1). The organic phase was decanted and the residue was dried under vacuum to give the title compound (4.7 mg, 29 %) as a brown powder: mp. 243–247 °C (dec.). R_f 0.58 (eluant 6). ¹H NMR (400 MHz, *d*₆-acetone) δ 2.23 (s, 6H), 5.76–5.80 (br m, 2H), 6.14 (t, *J* = 2.8 Hz, 2H), 6.93 (s, 2H), 10.10 (br s, 2H). ¹³C NMR (100 MHz, *d*₆-acetone) δ 12.9, 106.7, 108.0, 120.5, 126.1, 129.5, 134.0. HRMS (ESI) *m/z* 243.0951 [M+H⁺; calcd for [C₁₄H₁₅N₂S]⁺: 242.0950].

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Figure 1a: ¹H NMR Spectrum of **3a** (400 MHz, CDCl₃)

Figure 1b: ^{13}C NMR Spectrum of **3a** (100 MHz, CDCl_3)

Figure 2a: ¹H NMR Spectrum of **3b** (400 MHz, CDCl₃)

Figure 2b: ¹³C NMR Spectrum of **3b** (100 MHz, cdcl₃)

Figure 3a: ¹H NMR Spectrum of **3c** (400 MHz, CDCl₃)

Figure 3b: ^{13}C NMR Spectrum of **3c** (100 MHz, CDCl_3)

Figure 4a: ¹H NMR Spectrum of Crude **4a** (400 MHz, CDCl₃)

Figure 4b: ^{13}C NMR Spectrum of Crude **4a** (100 MHz, CDCl_3)

Figure 5a: ¹H NMR Spectrum of Crude **4b** (400 MHz, CDCl₃)

Figure 5b: ^{13}C NMR Spectrum of Crude **4b** (100 MHz, CDCl_3)

Figure 6a: ¹H NMR Spectrum of Crude **4c** (400 MHz, CDCl₃)

Figure 6b: ^{13}C NMR Spectrum of Crude **4c** (100 MHz, CDCl_3)

Figure 7a: ¹H NMR Spectrum of **5a** (400 MHz, CDCl₃)

Figure 7b: ^{13}C NMR Spectrum of **5a** (100 MHz, CDCl_3)

Figure 8a: ^1H NMR Spectrum of **5c** (400 MHz, CDCl_3)

Figure 8b: ^{13}C NMR Spectrum of **5c** (100 MHz, CDCl_3)

Figure 9a: ¹H NMR Spectrum of **1a** (400 MHz, d₆-acetone)

Figure 9b: ^{13}C NMR Spectrum of **1a** (100 MHz, d_6 -acetone)

Figure 10a: ¹H NMR Spectrum of **1b** (400 MHz, d₆-DMSO)

Figure 10b: ^{13}C NMR Spectrum of **1b** (100 MHz, $\text{d}_6\text{-DMSO}$)

Figure 11a: ¹H NMR Spectrum of **1c** (400 MHz, d₆-acetone)

Figure 11b: ^{13}C NMR Spectrum of **1c** (100 MHz, d_6 -acetone)

Figure 12a: ¹H NMR Spectrum of **1d** (400 MHz, d₆-acetone)

Figure 12b: ^{13}C NMR Spectrum of **1d** (100 MHz, d_6 -acetone)

Figure 13a: ^1H NMR Spectrum of **1e** (400 MHz, d_6 -acetone)

Figure 13b: ^{13}C NMR Spectrum of **1e** (100 MHz, d_6 -acetone)

Figure 14a: ¹H NMR Spectrum of **1f** (400 MHz, CDCl₃)

Figure 14b: ¹³C NMR Spectrum of **1f** (100 MHz, CDCl₃)

Figure 15a: ^1H NMR Spectrum of **1g** (400 MHz, $\text{d}_4\text{-MeOH}$)

Figure 15b: ^{13}C NMR Spectrum of **1g** (100 MHz, $\text{d}_4\text{-MeOH}$)

Figure 16a: ^1H NMR Spectrum of **1h** (100 MHz, d_6 -acetone)

Figure 16b: ^{13}C NMR Spectrum of **1h** (100 MHz, d_6 -acetone)

Figure 17: Normalized absorption (closed squares) and fluorescence (open squares) λ_{ex} =320 nm of **1a** recorded in degassed acetonitrile.

Figure 18: Normalized absorption (closed squares) and fluorescence (open squares) λ_{ex} =316 nm of **1b** recorded in degassed and anhydrous acetonitrile.

Figure 19: Normalized absorption (closed squares) and fluorescence (open squares) λ_{ex} =331 nm of **1c** recorded in degassed and anhydrous acetonitrile.

Figure 20: Normalized absorption (closed squares) and fluorescence (open squares) λ_{ex} =327 nm of **1d** recorded in degassed and anhydrous acetonitrile.

Figure 21: Normalized absorption (closed squares) and fluorescence (open squares) $\lambda_{\text{ex}}=305$ nm of **1e** recorded in degassed and anhydrous acetonitrile.

Figure 22: Normalized absorption (closed squares) and fluorescence (open squares) $\lambda_{\text{ex}}=319$ nm of **1f** recorded in degassed and anhydrous acetonitrile.

Figure 23: Normalized absorption (closed squares) and fluorescence (open squares) $\lambda_{\text{ex}}=329$ nm of **1g** recorded in degassed and anhydrous acetonitrile.

Figure 24: Normalized absorption (closed squares) and fluorescence (open squares) $\lambda_{\text{ex}}=336$ nm of **1h** recorded in degassed and anhydrous acetonitrile.

Figure 25: Cyclic voltammogram of **1a**.

Figure 26: Cyclic voltammogram of polymer from **1a** with supporting electrolyte only in the absence of any monomer. The polymer was obtained by oxidizing the corresponding monomer at 650 mV for 5 minutes.

Figure 27: Cyclic voltammogram of **1b**.

Figure 28: Cyclic voltammogram of **1c**.

Figure 29: Cyclic voltammogram of polymer from **1c** with supporting electrolyte only in the absence of any monomer. The polymer was obtained by oxidizing the corresponding monomer at 760 mV for 5 minutes.

Figure 30: Cyclic voltammogram of **1d**.

Figure 31: Cyclic voltammogram of **1e**.

Figure 32: Cyclic voltammogram of polymer from **1e** with supporting electrolyte only in the absence of any monomer. The polymer was obtained by oxidizing the corresponding monomer at 1030 mV for 5 minutes.

Figure 33: Cyclic voltammogram of **1f**.

Figure 34: Cyclic voltammogram of polymer from **1f** with supporting electrolyte only in the absence of any monomer. The polymer was obtained by oxidizing the corresponding monomer at 1690 mV for 5 minutes.

Figure 35: Cyclic voltammogram of **1g**.

Figure 36: Repeated cyclic voltammogram leading to the polymer **1g** and cyclic voltammogram of the resulting polymer.

Figure 37: Cyclic voltammogram of **1h**.