Supporting Information of

"Benzodipyrrolidones and Their Polymers" by

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Experimental section

Materials. Toluene and DMF (*N*, *N*-dimethylformamide) were purified through a solvent purification system. Commercially available reagents were used without further purification unless otherwise stated. Compounds **2a** and **3a** were prepared following the same procedure as in literature.

General Measurements. ¹H NMR and ¹³C NMR were recorded on Varian-NMR 600 spectrometers in D6-DMSO, CDCl₃ or CD₂Cl₄ with tetramethylsilane (TMS) as interval standard. Mass spectrometry was performed by the UC Santa Barbara Mass Spectrometry Laboratory. GPC measurements were conducted on a Waters 2695 system using polystyrene as standard. Electronic absorption spectra were obtained on an Agilent Technologies G1103A UV/vis Spectrometer. Thermogravimetric analysis (TGA) was carried out on a TGA Q50 (TA Instruments) at a heating rate of 10 °C min⁻¹ at a nitrogen flow. Differential scanning calorimetry (DSC) was run on a DSC Q10 (TA Instrument) at a heating/cooling rate of 10/-10 °C min⁻¹ at a nitrogen flow. Cyclic voltammetry (CV) were performed on a Princeton Applied Research Model 263A Potentiostat/Galvanostat with a three-electrode cell in a solution 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) as supporting electrolyte dissolved in methylene chloride or o-dichlorobenzene at a scan rate of 50 mV/s. A Pt disk was used as working electrode, a Pt wire as the counter electrode and an Ag/AgCl electrode as the reference electrode. The potential was calibrated by the ferrocene/ferrocenium standard. HOMO energy levels were estimated by the equation: HOMO = $-(4.80 + \Delta E_{oxd}^{onset})$.



1,4-Bis(α -hydroxyphenylacetylamino)benzene (2a).¹⁶ A mixture of *p*-phenylenediamine (1.80 g, 16.7 mmol) and mandelic acid (7.60 g, 50.0 mmol) in chlorobenzene (30 mL) was heated at 130 °C for 18 h. On cooling to the room temperature, the precipitate was filtered, washed with ethanol and dried in vacuo to yield **1a** (80 %) as a white solid. ¹H NMR (D6-DMSO, 600 MHz) δ ppm 9.83 (s, 2H), 7.58 (s, 4H), 7.53 (d, *J*= 8.4 Hz, 4H), 7.48 (d, *J*= 7.2 Hz, 4H), 7.33 (t, *J*= 7.8 Hz, 4H), 7.26 (t, *J*= 7.2 Hz, 2H), 6.37 (d, *J*= 4.8 Hz, 2H), 5.05 (d, *J*= 4.8 Hz, 2H).



1,4-Bis(*a*-hydroxy(4-bromophenyl)acetylamino)benzene (2b). 2b was prepared following the same procedure as 2a. Yield 85%. ¹H NMR (D6-DMSO, 600 MHz) δ ppm 9.85 (s, 2H), 7.56 (s, 4H), 7.53 (d, *J*= 8.4 Hz, 4H), 7.43 (d, *J*= 8.4 Hz, 4H), 6.47 (d, *J*= 4.8 Hz, 2H), 5.06 (d, *J*= 4.8 Hz, 2H). ¹³ C NMR (D6-DMSO, 600 MHz) δ ppm 170.88, 140.71, 134.62, 131.43, 129.16, 121.19, 120.46, 73.69.



3.7-Diphenyl-2,6-dioxo-1,2,3,4,5,6,7-hexahydrobenzo[**1,2-***b***:4,5-***b***']dipyrrole** (**3a**). 1,4-Bis(α -hydroxyphenylacetylamino)benzene (**2a**) (2.50 g, 6.50 mmol) was added to sulfuric acid (25 mL). After stirred at room temperature for 20 h, the mixture was poured into ice water. The precipitate was filtered, washed with water and dried to yield **3a** (90 %) as a light red solid. ¹H NMR (D6-DMSO, 600 MHz) δ ppm 10.40 (s, 2/3H), 10.30 (s, 4/3H), 7.26-7.35 (m, 6H), 7.14-7.16 (m, 8/3H), 6.79 (s, 2/3H), 6.73-6.78 (m, 4/3H), 6.56 (s, 4/3H), 4.72-4.73 (m, 4/3H), 4.51 (s, 2/15H), 3.84 (s, 8/15H). (NMR spectrum is complicate because of the existence of different isomers)



3.7-Di(**4**-bromophenyl)-2,6-dioxo-1,2,3,4,5,6,7-hexahydrobenzo[1,2-*b*:4,5-*b*']dipyrrole (**3b**). **3b** was prepared following the same procedure as **3a**. Yield 95%. ¹H NMR (D6-DMSO, 600 MHz) δ ppm 10.43 (s, 0.4H), 10.38 (s, 0.4H), 10.36 (m, 1.2H), 7.46-7.55 (m, 2.4H), 7.45 (d, *J*= 8.4 Hz, 0.8H), 7.10-7.14 (m, 2.4H), 7.02 (d, *J*= 9.0 Hz, 0.8H), 6.79 (s, 0.8H), 6.73 (d, *J*= 8.4 Hz, 0.8H), 6.57 (s, 1.2H), 6.53 (d, J= 7.8 Hz, 0.8H), 4.78 (s. 0.4H), 4.76 (s, 0.8H), 4.55 (s, 0.4H), 3.99 (s, 0.4H). (NMR spectrum is complicate because of the existence of different isomers) TOF MS (FD+): m/z (%): 497.94 (100)[M]+.



3,7-Diphenyl-2,6-dioxo-1,2,5,6-tetrahydrobenzo[**1,2-***b***:4,5-***b***'**]**dipyrrole** (**4a**). Sodium hydroxide solution (0.75 mL, 5 N) was dropwised to a suspension of **3a** (0.700 g, 2.06 mmol) in ethanol. Then potassium persulfate (1.50 g, 5.55 mmol) in water (5 mL) was added. The resulting mixture was heated at reflux for 2 h. The precipitate in the mixture was filtered, washed with water and ethanol, dried to yield **4a** (80 %). ¹H NMR (D6-DMSO, 600 MHz) δ ppm 10.25 (s, 2H), 7.64 (d, *J*= 7.8 Hz, 4H), 7.49 (t, *J*= 7.8 Hz, 4H), 7.42 (t, *J*= 7.5 Hz, 4H), 6.36 (s, 2H).



3,7-Di(4-bromophenyl)-2,6-dioxo-1,2,5,6-tetrahydrobenzo[**1,2**-*b*:**4,5**-*b*']dipyrrole (**4b**). **4b** was prepared following the same procedure as **4a**. Yield 75 %. ¹H NMR (D6-DMSO, 600 MHz) δ ppm 10.34 (s, 2H), 7.69 (d, *J*= 7.8 Hz, 4H), 7.60 (d, *J*= 7.8 Hz, 4H), 6.34 (s, 2H). TOF MS (FD+): m/z (%): 495.94 (100)[M]+.



N,*N*'-Dimethyl-3,7-diphenyl-2,6-dioxo-1,2,5,6-tetrahydrobenzo[1,2-b:4,5-b']dipyrrole (5a-1). A mixture of 4a (0.050 g, 0.15 mmol) and *t*-BuOK (0.132 g, 1.18 mmol) in DMF (1.50

mL) was added MeI (0.168 g, 1.18 mmol). After stirred for 24 h at room temperature, the mixture was poured into water and extracted with DCM. The organic layer was washed with brine and dried over anhydrous MgSO₄. On removal of the solvent, the residue was purified by column chromatography on silica gel with DCM:EA=50:1 as eluent to yield **5a-1** (73%) as a dark brown solid. ¹H NMR (CDCl₃, 600 MHz) δ ppm 7.72 (d, *J*= 7.8 Hz, 4H), 7.50-7.53 (m, 4H), 7.44-7.46 (m, 2H), 6.37 (s, 2H).



N,N'-Di(2-ethylhexyl)-3,7-diphenyl-2,6-dioxo-1,2,5,6-tetrahydrobenzo[1,2-b:4,5-b']dipyrrole (5a-2). A mixture of 4a (0.200 g, 0.590 mmol) and *t*-BuOK (0.265 g, 2.36 mmol) in DMF (3.0 mL) was added ethylhexyl bromide (0.455 g, 2.36 mmol). After stirred for 24 h at 80 °C, the mixture was poured into water and extracted with DCM. The organic layer was washed with brine and dried over anhydrous MgSO₄. On removal of the solvent, the residue was purified by column chromatography on silica gel with Hexane: DCM=1:2 as eluent to yield 5a-2 (0.150 g, 45 %) as a dark brown solid. ¹H NMR (CDCl₃, 600 MHz) δ ppm 7.70 (d, *J*= 7.8 Hz, 4H), 7.47-7.49 (m, 4H), 7.40-7.42 (m, 2H), 6.37 (s, 2H). ¹³C NMR (CDCl₃, 600 MHz) δ ppm 169.94, 144.09, 134.39, 131.24, 129.54, 128.95, 128.74, 127.37, 97.35, 43.51, 38.42, 38.41, 30.81, 28.93, 28.92, 24.18, 23.00, 14.06, 10.70, 10.69. TOF MS (FD+): m/z (%): 562.36 (100)[M]+.



N,*N*'-Di(2-octyldodecyl)-3,7-di(4-bromophenyl)-2,6-dioxo-1,2,5,6-tetrahydrobenzo[1,2b:4,5-b']dipyrrole (5b). 5b was prepared following the same procedure as 5a-2. Yield 60%. ¹H NMR (CDCl₃, 600 MHz) δ ppm 7.60 (d, *J*= 9.0 Hz, 4H), 7.57 (d, *J*= 8.4 Hz, 4H), 6.29 (s, 2H). ¹³C NMR (CDCl₃, 600 MHz) δ ppm 169.50, 144.31, 134.46, 132.01, 130.90, 130.03, 126.24, 123.58, 97.09, 43.99, 37.10, 34.65, 34.51, 31.92, 31.89, 31.77, 31.58, 30.00, 29.67, 29.65, 29.60, 29.37, 29.35, 29.31, 29.05, 26.69, 25.26, 22.68, 22.66, 22.64, 20.65, 14.06. TOF MS (FD+): m/z (%): 1056.5 (100)[M]+.

PBDPDP-B.

A mixture of the di-bromoBDPP (0.300 g, 0.284 mmol), $Pd_2(dba)_3$ (13 mg), PPh_3 (8 mg), K_3PO_4 (0.241 g, 1.14 mmol) and Aliquat 336 (0.3 mL) was degassed and added toluene (10 mL) and H_2O (1.5 mL). The resulting mixture was heated at reflux under nitrogen for 3 days. After cooling to room temperature, the mixture was dropped to methanol to precipitate. The solid was collected by filter. After Soxhlet extraction with methanol, acetone, hexane, the solid was extracted with chloroform. On being concentrated, the chloroform solution was dropped into methanol to precipitate. Polymer **PBDPDP-B** (0.22 g, 79.4 %) was collected by filter as a dark brown solid with metallic luster. ¹H NMR (CD₂Cl₄, 600 MHz) δ ppm 7.44-7.88 (br, 12H), 6.47 (s, 2H), 3.57 (br, 4H), 1.84 (br, 2H), 1.65 (br, 8H), 1.14-1.44 (br, 56H), 0.87-0.96 (br, 12H).

PBDPDP-T.

The preparation of polymer **PBDPDP-T** (Blue purple solid, 0.21 g, 75.5 %) was followed the same procedure as that of **PBDPDP-B**. ¹H NMR (CD₂Cl₄, 600 MHz) δ ppm 7.73-7.82 (br,

8H), 7.45-7.48 (br, 2H), 6.45 (s, 2H), 3.56 (br, 4H), 1.83 (br, 2H), 1.64 (br, 8H), 1.25-1.36 (br, 56H), 0.87-0.90 (br, 12H).

Device Fabrication and Measurements

Transistors were fabricated in the bottom gate, bottom contact configuration on heavily-doped ntype Si substrates as the gate and thermally grown 200 nm silicon dioxide as the dielectric layer (Silicon Quest, dry oxide). The source and drain electrodes were patterned using standard photolithography and formed on SiO2 with e-beam evaporation of 3 nm of nickel and 47 nm of gold. Prior to casting, devices were cleaned in acetone and isopropanol and dried in an oven at 120°C for 15 min. The samples were then surface-activated with acid hydrolysis, dried and then exposed for 0.5 hrs to UV light in air. The devices were surface treated with DTS for 20 min by immersion in a 1% by volume of DTS in toluene. The devices were then cleaned by rinsing with toluene and dried under nitrogen flow followed spin-coating of the polymer. Polymer films were spin-cast at 4000-5000 RPM in a glove box from 10mg/mL solutions in chloroform. Samples were dried at 60 °C for 0.5 hrs and then annealed at the desired temperature for 10 min in a glove box. FET mobility measurements were performed in a glovebox using a Keithley 4200 Semiconductor Parametric Analyzer and a Signotone Micromanipulator S-1160 probe station. Samples measured had channel lengths of 5µm and channel widths of 1mm.



Figure S1. TGA curves of **5a-1** and **5a-2**. (10 $^{\rm o}\text{C/min},$ under N_2)



Figure S2. DSC curve of **5a-2**. (10 $^{\circ}$ C/min, under N₂, 2nd circle)



Figure S3. Cyclic voltammetry curves of **5a-1**, **5a-2**. (DCM, 50 mV/s, Fc, ferrocene/ferrocenium)



Figure S4. Mobility dependence on annealing temperature (PBDPDP-B, 10 min in glovebox).



Figure S5. Mobility dependence on annealing temperature (**PBDPDP-T**, 10 min in glovebox).