

X-ray experimental: Data were collected at 173 K on a Siemens SMART PLATFORM equipped with A CCD area detector and a graphite monochromator utilizing MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). Cell parameters were refined using up to 8192 reflections. A full sphere of data (1850 frames) was collected using the ω -scan method (0.3° frame width). The first 50 frames were re-measured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was < 1 %). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structure was solved by the Direct Methods in *SHELXTL6*, and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. The asymmetric unit consists of two half molecules (each located on an inversion center). One of the molecules has a disorder in the C18-C19 unit and was refined in two parts (minor part is labeled C18'-C19'). Their site occupation factors were dependently refined. A total of 270 parameters were refined in the final cycle of refinement using 3205 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 3.74% and 9.23%, respectively. Refinement was done using F^2 .

SHELXTL6 (2000). Bruker-AXS, Madison, Wisconsin, USA.

Electrochemistry: Electrochemistry was performed in a three electrode cell consisting of a 0.02 cm² platinum button working electrode, a platinum flag counter electrode, and a silver wire pseudo reference electrode calibrated to the ferrocene-ferricinium redox couple after every experiment. All polymer characterization was performed in a 0.1 M TBAP/ACN solution unless noted. Polymers were deposited from a 5 mM monomer 0.1 M TBAP/DCM solution via repeated scan cyclic voltammetry at 50 mV/s for 10 cycles or galvanostatically until 37.5 mC of charge had passed. Measurements were made with an EG&G PAR model 273A potentiostat/galvanostat. Optical data was measured with a Cary 500 UV/Vis/near IR spectrophotometer.

4,7-Dibromo-2,1,3-benzothiadiazole,¹ 4,7-dibromo-5,6-dinitrobenzo[c][1,2,5]thiadiazole,² and (2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)trimethylstannane³ were made according to literature. THF was distilled from sodium/benzophenone. Glacial acetic acid was purchased from Fisher and used as received. Anhydrous pyridine was purchased from Aldrich and used as received. All reactions were performed under argon.

4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-5,6-dinitrobenzo[c][1,2,5]thiadiazole (2).

To a flame dried 100 mL 3-neck round bottom flask was added 2.59 g (0.0067 mol) of **1** and 4.29g (0.014 mol) of trimethyltinEDOT. Then 25 mL of THF was added and the solution was degassed for 30 minutes. Then 0.23 g (0.00033 mol) of Pd(II)Cl₂(PPh₃)₂ was added and the solution was refluxed for 3 hours. The solution was cooled and the solvent was removed under reduced pressure. Column chromatography (CHCl₃, SiO₂) yielded 2.30 g (68 %) of a red solid. mp 255-257 °C. ¹H NMR (300 MHz, DMSO) δ 4.17-4.23 (m, 8H), 7.15 (s, 2H); ¹³C NMR (75

MHz, DMSO) δ 64.15, 64.64, 104.02, 105.94, 119.97, 140.72, 141.67, 142.28, 152.09.

Elemental Anal. Calcd. for $C_{18}H_{10}N_4O_8S_3$: C, 42.68; H, 1.99; N, 11.06; O, 25.27; S, 18.99.

Found: C, 42.89; H, 1.88; N, 10.84. HRMS calcd. for $C_{18}H_{10}N_4O_8S_3$ (M+H) 506.97335 Found 506.97328

4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)benzo[c][1,2,5]thiadiazole-5,6-diamine (3).

To a dry 100 mL 3-neck round bottom flask equipped with a condenser was added 1.01 g (0.0020 mol) of **2** and 1.34 g (0.024 mol) of iron powder. To this was added 38 mL of degassed AcOH. The reaction was heated to 100 °C for 3 hours and then allowed to cool. A golden yellow color solid was collected by filtration and washed with water, saturated sodium bicarbonate, and water in this order. The solid was dissolved in CH_2Cl_2 , dried over anhydrous $MgSO_4$, adsorbed onto silica. Column Chromatography (7:1 CH_2Cl_2 :EtOAc, SiO_2) yielded 0.77 g (87 %) of a yellow solid. mp decomp. >260 °C. 1H NMR (300 MHz, DMSO) δ 4.22 (s, 8H), 5.70 (s, 4H), 6.73 (s, 2H); ^{13}C NMR (75 MHz, DMSO) δ 64.13, 64.32, 98.62, 99.65, 109.14, 138.96, 140.67, 141.48, 152.62. Elemental Anal. Calcd. for $C_{18}H_{14}N_4O_4S_3$: C, 48.42; H, 3.16; N, 12.55; O, 14.33; S, 21.54. Found: C, 48.52; H, 3.04; N, 12.12. HRMS calcd. for $C_{18}H_{14}N_4O_4S_3$ (M+H) 447.0255 Found 447.0252

4,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)benzo[1,2-c;4,5-c']bis[1,2,5]thiadiazole (4)

To a flame dried 25 mL 3-neck round bottom flask was added 0.55 g (0.0012 mol) of **3**, 7 mL of anhydrous pyridine, 0.36 g (0.0026 mol) of N-thionylaniline, and 0.24 g (0.0022 mol) of TMS-Cl. The solution was heated to 80 °C overnight. The reaction was allowed to cool, poured into water, and a dark purple solid was collected by filtration. Column chromatography (CH_2Cl_2 , SiO_2) yielded 0.47 g (84 %) of a dark purple solid. decomposition > 292 °C. 1H NMR (300 MHz, DMSO) δ 4.22-4.29 (m, 8H), 7.05 (s, 2H). Elemental Anal. Calcd. for $C_{18}H_{10}N_4O_4S_4$: C, 45.56; H, 2.12; N, 11.81; O, 13.49; S, 27.03. Found: C, 45.52; H, 1.96; N, 11.62. HRMS calcd. for $C_{18}H_{10}N_4O_4S_4$ (M+) 473.9585 Found 473.9604

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