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### Supporting Information

### Structural Influence of the Proquinoidal Acceptor Moiety on Transistor Performance and Doping Capability for Diketopyrrolopyrrole-based Dual-Acceptor Conjugated Polymers

Ying-Sheng Wu,<sup>a</sup> Jian-Sian Li,<sup>a,b</sup> Chih-Yuan Chang,<sup>a</sup> Waner He,<sup>c</sup> Tsuyoshi Michinobu,<sup>c</sup> Yan-Cheng Lin,<sup>d\*</sup> Wen-

Chang Chen,<sup>*a,b*\*</sup> and Chu-Chen Chueh<sup>*a,b*\*</sup>

<sup>a</sup> Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan

<sup>b</sup> Advanced Research Center for Green Materials Science and Technology, National Taiwan University, Taipei 10617, Taiwan

<sup>c</sup> Department of Materials Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama,

Meguro-ku, Tokyo 152-8552, Japan

<sup>d</sup> Department of Chemical Engineering, National Cheng Kung University, Tainan 70101, Taiwan

\*Corresponding authors: cchueh@ntu.edu.tw; chenwc@ntu.edu.tw; ycl@gs.ncku.edu.tw

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#### Characterizations

<sup>1</sup>H NMR spectra were recorded using Bruker DPX400 MHz and deuterated chloroform (CDCl<sub>3</sub>) was used as the solvent for the synthesized monomers and polymers. Microwave polymerization was executed in a 5 mL vessel using a Biotage microwave reactor. The weight-/number-average molecular weight ( $M_w/M_n$ ) values of the synthesized polymers were determined using a size exclusion chromatograph (SEC) in Enshine SUPER CO-150 with polystyrene gel columns (Stryagel HR2 and styragle 4) eluted with dichlorobenzene at 1.0 mL/min calibrated by standard polystyrene. The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were conducted at a heating rate of 10 °C/min using TA instrument TGA55 and DSC25. The EPR spectra were recorded at room temperature using Bruker ELEXSYS E-580. The ultraviolet–visible (UV–vis) absorption spectrum was recorded using a Hitachi U-4100 spectrophotometer. Cyclic voltammetry (CV) was measured using a CHI 6273E electrochemical analyzer with a three-electrode method, wherein the indium tin oxide (ITO) substrate coated with polymers, the platinum wire, and Ag/AgCl, KCl (*sat.*) served as the working electrode, auxiliary electrode, and reference electrode, respectively. The electrolyte was made of 0.1 M tetrabutylammonium perchlorate (TBAP) in freshly distilled acetonitrile. Surface morphology of the polymer film was characterized using a Bruker Innova atomic force microscopy (Bruker Nano Surfaces) under a tapping mode at room temperature. Grazing incidence X-ray diffraction (GIXD) analysis of the polymer film was carried out on beamline 23A1 in National Synchrotron Radiation Research Center (NSRRC), Taiwan with an X-ray wavelength of 1.240 Å and an incident angle at 0.12°.

#### **Material Synthesis and Characterization**

#### Synthesis of 2,5-bis(9-methyl-9-octylheptadecyl)-3,6-bis(5-(trimethylstannyl)thiophen-2-yl)-2,5-

#### dihydropyrrolo[3,4-c]pyrrole-1,4-dione (DPP-2T)

2,5-bis(9-methyl-9-octylheptadecyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c] pyrrole-1,4-dione was added into THF under argon atmosphere. The solution was cooled to -78 °C, and *n*-butyllithium (2.2 equivalent molar ratio) was added dropwise to the solution and stirred for 30 min (at -78 °C). Afterwards, trimethyltin chloride (2.4 equivalent molar ratio) was syringed into the solution, and the temperature of the solution gradually rose to room temperature and stirred overnight. Then, t solution was quenched with DI water. The mixture was extracted with water and brine. The organic phase was collected and dried with magnesium sulfate, followed by filtration and the solvent was removed under vacuum. The final product was

obtained and the <sup>1</sup>H NMR spectrum (Figure S1) matched exactly with the spectrum reported in the literature.<sup>[22]</sup>

#### Synthesis of 4,8-bis(5-bromothiophen-2-yl)-benzo[1,2-c:4,5-c']bis([1,2,5]thiadiazole) (M1)

4,8-dibromo-benzo[1,2-c:4,5-c']bis([1,2,5]thiadiazole), tributyl(thiophen-2-yl)stannane, and Pd(PPh<sub>3</sub>)<sub>4</sub> were added into toluene under argon atmosphere. The solution was heated to 120 °C and stirred for 12 hours. After cooling back to room temperature, the solvent was then removed under vacuum. 4,8-di(thiophen-2-yl)benzo[1,2-c:4,5-c']bis([1,2,5]thiadiazole) was obtained with column chromatography on silica gel using DCM as the eluent. The compound and *n*-bromosuccinimide was added to CF, and the flask was covered by aluminum coil and stirred under room temperature overnight. The solvent was then removed under vacuum. **M1** was obtained by washing the residue with methanol, hexane, and acetone. Due to solubility issue, <sup>1</sup>H NMR cannot be implemented. Elemental analysis is thus conducted to prove its successful synthesis. Anal. Calcd. for [C<sub>14</sub>H<sub>6</sub>Br<sub>2</sub>N<sub>4</sub>S<sub>4</sub>]: C, 32.4; H, 1.2; N, 10.8; S, 19.2. Found: C, 33.5; H, 0.8; S, 20.1.

# Synthesis of 4,8-bis(5-bromothiophen-2-yl)-6-(2-ethylhexyl)-[1,2,3]triazolo[4',5':4,5]benzo[1,2-c][1,2,5] thiadiazole (M2)

4,8-dibromo-6-(2-ethylhexyl)-[1,2,3]triazolo[4',5':4,5]benzo[1,2-c][1,2,5]thiadiazole, tributyl(thiophen-2-yl)stannane, and Pd(PPh<sub>3</sub>)<sub>4</sub> were added to toluene under argon atmosphere. The solution was heated to 120 °C and stirred for 12 hours. After cooling back to room temperature, the solvent was removed under vacuum. 6-(2-ethylhexyl)-4,8-di(thiophen-2-yl)-[1,2,3]triazolo[4',5':4,5]benzo[1,2-c][1,2,5]thiadiazole was obtained with column chromatography on silica gel using hexanes/DCM (1:3) as the eluent. The compound and *n*- bromosuccinimide were added to CF, and the flask was covered by aluminum coil and stirred under room temperature overnight. The solvent was then removed under vacuum. The product was finally purified with column chromatography on silica gel using hexanes/DCM (1:1) as the eluent to obtain the pure compounds and the <sup>1</sup>H NMR (**Figure S2**) matched exactly with the spectrum reported in the literature.<sup>[31]</sup>

## Synthesis of 4,8-bis(5-bromothiophen-2-yl)-2,6-bis(2-ethylhexyl)-benzo[1,2-d:4,5-d']bis([1,2,3] triazole) (M3)

4,8-dibromo-2,6-bis(2-ethylhexyl)-benzo[1,2-d:4,5-d']bis([1,2,3]triazole), tributyl (thiophen-2yl)stannane, and Pd(PPh<sub>3</sub>)<sub>4</sub> were added to toluene under argon atmosphere. The solution was heated to 120 °C and stirred for 12 hours. After cooling back to room temperature, the solvent was removed under vacuum. 2,6-bis(2-ethylhexyl)-4,8-di(thiophen-2-yl)-benzo[1,2-d:4,5-d']bis([1,2,3]triazole) was obtained with column chromatography on silica gel using hexanes/DCM (1:1) as the eluent. The compound and *n*-bromosuccinimide were added to CF, and the flask was covered by aluminum coil and stirred under room temperature overnight. The solvent was then removed under vacuum. The product was finally purified with column chromatography on silica gel using hexanes/DCM (2:1) as the eluent to obtain the pure compounds and the <sup>1</sup>H NMR (**Figure S3**) matched exactly with the spectrum reported in the literature.<sup>[29]</sup>



Figure S1. <sup>1</sup>H-NMR of DPP-2T in CDCl<sub>3</sub>.









Figure S4. <sup>1</sup>H-NMR of DPP-SS in CDCl<sub>3</sub>.



Figure S5. <sup>1</sup>H-NMR of DPP-NS in CDCl<sub>3</sub>.



<sup>5.0</sup> f1 (ppm) 10.0 9.5 7.0 6.0 2.5 2.0 0.0 9.0 8.5 8.0 7.5 6.5 5.5 4.5 3.5 3.0 1.5 1.0 0.5

Figure S6. <sup>1</sup>H-NMR of DPP-NN in CDCl<sub>3</sub>.



Figure S7. TGA curves of the synthesized polymers.



Figure S8. DSC curves of the synthesized polymers.



Figure S9. CV curves of the synthesized polymers.



**Figure S10**. DFT calculation of electron cloud distribution of (a) **DPP-NN**, (b) **DPP-NS**, and (c) **DPP-SS**.



Figure S11. Bond length plots for DPP-NN/NS/SS obtained from DFT calculation.



**Figure S12**. Transfer curves of the FET devices based on the as-cast films of (a) **DPP-NN**, (b) **DPP-NS**, and (c) **DPP-SS**.