

Supplementary Information

Diketopyrrolopyrrole-based oligomer modified TiO₂ nanorods for air-stable and all solution processed poly(3-hexylthiophene):TiO₂ bulk heterojunction inverted solar cell

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Synthesis procedure of oligomer PZFDPP

¹⁵ The synthesis procedure of PZFDPP oligomer is shown in **Fig. S1**. All chemicals were used as purchased without further purification. To sum up, 2-iodo-biphenyl and 1,10-phenanthroline were purchased from Alfa Aesar; potassium permanganate, potassium hydroxide, acetic acid (glacial, 99%) magnesium (turnings), sec-butyllithium (1.4M) and tetrakis(triphenylphosphine)palladium(0) were purchased from Sigma-Aldrich; iron (III) chloride, bromine and triphenylphosphine were purchased from Acros. The accepters, 3,6-bis(5-bromothiophen-2-yl)-2,5-dioctylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DPP) was purchased from Luminescence Technology Corp.
²⁰ (Taiwan) with purity of 97%.

The 4,5-diaza-9,9'-spirobifluorene was first synthesized and the details can be found elsewhere¹. For the synthesis of 4,5-diaza-2',7'-dibromo-9,9'-spirobifluorene, 3g of as synthesized 4,5-diaza-9,9'-spirobifluorene and 1g of AlCl₃ were first dissolved in 50mL of CH₂Cl₂, followed by adding 3.5g of N-bromosuccinimide (NBS) and stirred at room temperature for 24hrs. Afterward, the solution was quenched by water and extracted by CH₂Cl₂. The concentrated organic extracts was purified with column chromatography on silica gel
²⁵ (eluent: hexane/ ethyl acetate=1:1). The chemical yield was 75% and ¹H-NMR (CDCl₃, 400MHz) δ 8.78(dd, 2H), 7.70(d, 2H), 7.54(dd, 2H), 7.19-7.12(m, 4H) 6.85(d, 2H).

For obtaining 4,5-diaza-2',7'-bis(trimethyltin)-9,9'-spirobifluorene, the 4.76g (10mmol) of 4,5-diaza-2',7'-dibromo-9,9'-spirobifluorene was added into a three-necked round flask under argon atmosphere followed by adding 500ml of dry tetrahydrofuran (THF) and cooling to -78°C. Afterward, the sec-butyllithium (1.4M in cyclohexane, 15ml, 2.1eq) was added dropwise. After stirred at -
³⁰ 78°C for 1hr, 4.18g (2.1eq) of trimethyltin chloride was added portionwise and stirred for another 1hr. Then the cooling bath was removed and the reaction was warmed up to room temperature under stirred overnight. The work-up was conducted by pouring the above solution into water and extracting by dichloromethane twice then removing the dichloromethane by rotor-evaporator. The crude product was obtained as sticky dark brown oil (5g, 77.6%) and vacuumed dried for 24hrs under 2x10⁻² torr. The obtained compound was used for polymerization without further purification.

³⁵ The PZFDPP oligomer was obtained by Stille coupling of corresponding monomers. Briefly, 1mmol of 4,5-diaza-2',7'-bis(trimethyltin)-9,9'-spirobifluorene was first added into a three-necked flask under argon purging followed by adding 1.05mmol of 3,6-bis(5-bromothiophen-2-yl)-2,5-dioctylpyrrolo [3,4-c] pyrrole-1,4(2H,5H)-dione (DPP) dissolved in degassed toluene. The solution was flushed with argon for 10mins, and 10mol% of Pd(PPh₃)₄ was added. The reaction was heated and refluxed for 72 hours. The work-up of polymers was first precipitated by adding 200mL of methanol, filtered through Soxhlet thimble, and subjected to Soxhlet extraction with
⁴⁰ methanol, hexane and chloroform. Finally, the polymer was recovered as solid by rotary evaporation. The yield of PZFDPP was 50%.

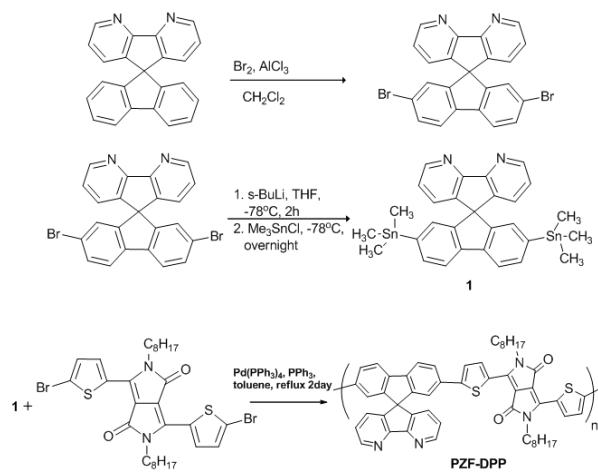
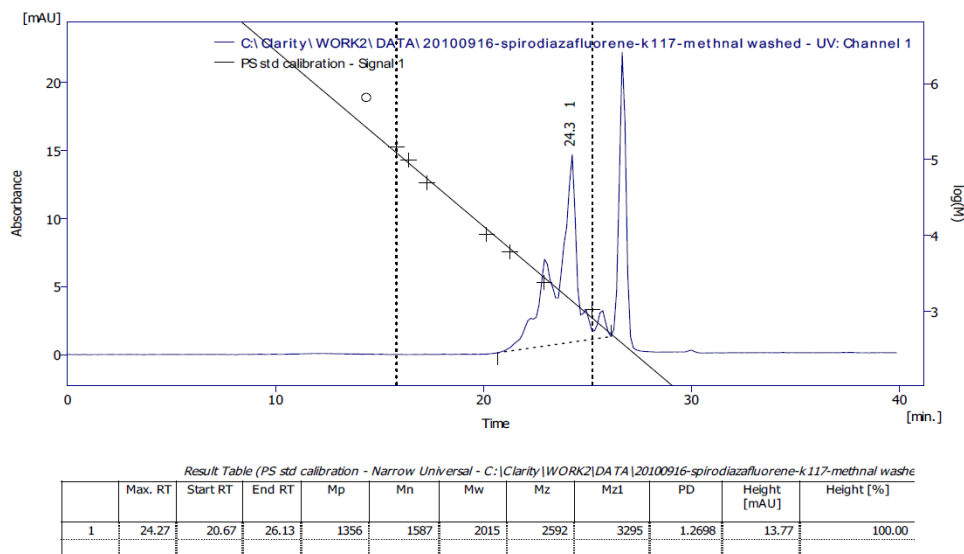


Fig. S1. Reaction scheme of oligomer PZF-DPP.

Characterization of oligomer PZFDPP

The number average molecular weight ($M_n=1587$), weight average molecular weight ($M_w=2015$) and polydispersity index ($PDI=1.27$) were obtained by gel permeation chromatography (GPC, Breeze system) (**Fig. S2**). The system was equipped with two Waters Styragel columns (HR3 and HR4E), a refractive index detector (Waters 2414), and a dual-wavelength absorbance detector (Waters 2487). The molecular weights and molecular weight distributions were estimated by reference to the polystyrene standard and tetrahydrofuran was used as a mobile phase (1 mL/min). The $^1\text{H-NMR}$ spectrum (Bruker Avance 400 MHz) is shown in **Fig. S3** and the main characteristic peaks of functional group are marked on the spectrum. The energy level of the surface modifier PZFDPP was determined by cyclic voltammeter (CH Instrument 611B potentiostat/galvanostat system). The oligomers were dissolved in a 0.05 M solution of tetra-*n*-butyl-ammonium hexafluorophosphate (Bu₄NPF₆, Aldrich, 98%) in anhydrate dichloromethane. Ferrocene/ferrocinium (Fc/Fc⁺) couple (Acros, 98%) was used as the internal reference, and all potentials were calibrated with Fc/Fc⁺. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular level (LUMO) are -5.0 eV and -3.5 eV respectively. Hence it can form a cascade energy alignment between P3HT, PZFDPP and TiO₂ nanorods which can improved the carrier dissociation at the organic/inorganic interfaces.



15 **Fig. S2** GPC spectra of oligomer PZFDPP.

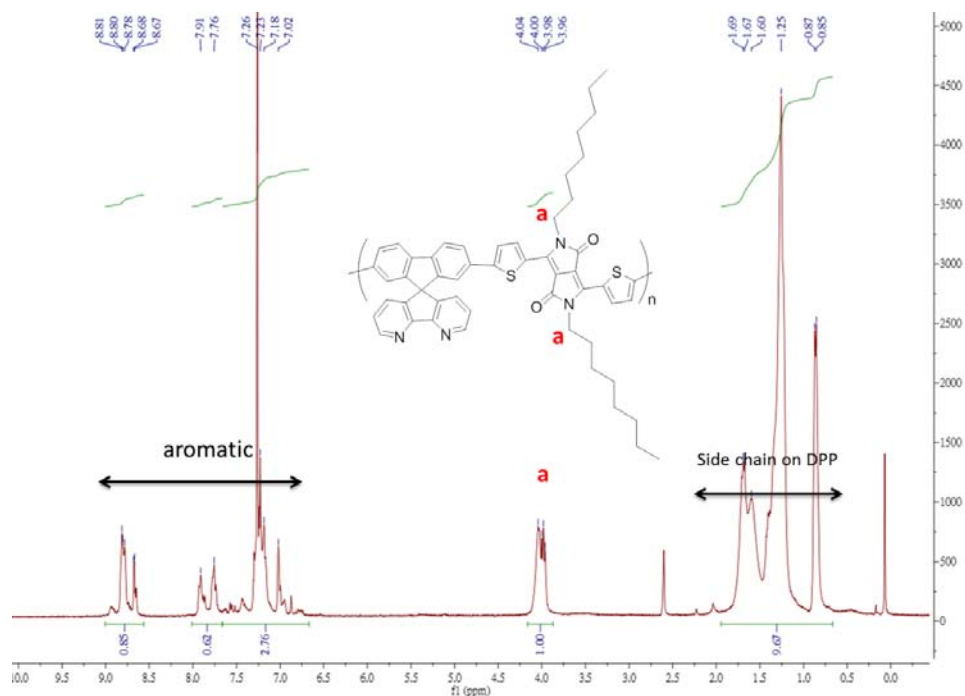


Fig. S3. The $^1\text{H-NMR}$ spectrum of PZFDPP.

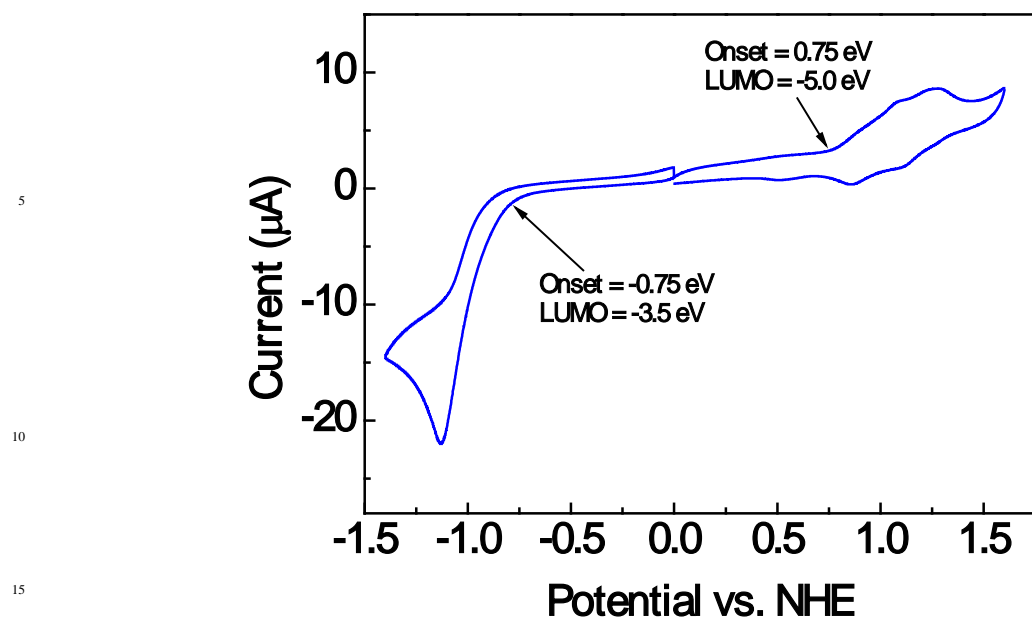


Fig. S3. The $^1\text{H-NMR}$ spectrum of PZFDPP.

Reference:

20 1 C. C. Chi, C. L. Chiang, S. W. Liu, H. Yueh, C. T. Chen and C. T. Chen, *J. Mater. Chem.*, 2009, **19**, 5561.