Electronic supplementary information (ESI) for:

Diketopyrrolopyrrole as p-channel organic semiconductor for high performance OTFTs

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1. General methods

The starting compound 2,5-di(2-ethylhexyl)-3,6-bis(5-cyano-thiophen-2-yl)pyrrolo[3,4-c]-pyrrole-1,4-dione **2** was prepared according to the literature.[1] All other reagents and solvents were obtained from commercial suppliers and purified and dried according to standard procedures.[2] Column chromatography was performed on silica gel (Merck Silica 60, particle size 0.040-0.063 mm). Solvents for spectroscopic studies were of spectroscopic grade and used as received.

Elemental analysis was performed on a CHNS 932 analyzer (Leco Instruments GmbH, Mönchengladbach, Germany). ^{1}H and ^{13}C spectra were recorded in CD_2Cl_2 on a Bruker Avance 400 spectrometer. Residual undeuterated solvent was used as internal standard (5.32 ppm for ^{1}H, 53.84 ppm for ^{13}C). High-resolution ESI-TOF mass spectrometry was carried out on a microTOF focus instrument (Bruker Daltronik GmbH). UV-vis measurements were performed in CH_2Cl_2 (10^{-5} M) in a conventional quartz cell (light pass 10 mm) on a Perkin-Elmer Lambda 950 spectrometer. For cyclic voltammetry, a standard commercial electrochemical analyzer (EC epsilon; BAS Instruments, UK) with a three electrode single-compartment cell was used. Dichloromethane (HPLC grade) was dried over calcium hydride under argon and degassed before using. The supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAHFP) was prepared according to the literature,[3] and recrystallized from ethanol/water. The measurements were carried out in dichloromethane at a concentration of about 10^{-4} M with ferrocene (Fc) as an internal standard for the calibration of the potential. Ag/AgCl reference electrode was used. A Pt disc and a Pt wire were used as working and auxiliary electrodes, respectively.

2. Experimental procedures, analytical and spectroscopic data

2,5-Di(2-ethylhexyl)-3,6-bis(5-cyano-thiophen-2-yl)pyrrolo[3,4-c]-pyrrole-1,4-dione (1)

A mixture of compound **2** (249 mg, 0.365 mmol) and copper(I)cyanide (1.50 g, 16.7 mmol) in dry DMF (8 mL) was heated under argon for 8 h at 130 °C. The reaction mixture was allowed to cool down to room temperature and a saturated solution of sodium cyanide in water was added. The aqueous phase was extracted with dichloromethane. The solvent was removed under reduced pressure and the residue was purified by column chromatography (dichloromethane) affording 48.8 mg (31%) of a dark violet solid.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.82 (d, ^3J = 4.2 Hz, 2H), 7.76 (d, ^3J = 4.2 Hz, 2H), 4.03-3.91 (m, 4H), 1.84-1.72 (m, 2H), 1.40-1.18 (m, 16H), 0.91-0.82 (m, 12H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 161.5, 139.8, 138.3, 135.7, 134.8, 113.9, 113.7, 110.9, 46.4, 39.7, 30.5, 28.7, 23.9, 23,4, 14.2, 10.5. HRMS (ESI, acetonitrile/$CHCl_3$ 1:1, pos. mode): *m/z* 575.2510 $[M+H]^+$ (calcd. for $C_{32}H_{39}N_4O_2S_2$ 575.2510). Elemental Anal. Calcd. for $C_{32}H_{38}N_4O_2S_2$: C, 66.87; H, 6.66; N, 9.75; S, 11.16; O, 3.94. Found: C, 66.60; H, 6.62; N, 9.77; S, 11.09. CV (CH_2Cl_2, 0.1 M TBAHFP, vs. Fc/Fc$^+$): $E_{1/2}^{red}$ (X^-/X^{2-}) = -1.77 V, $E_{1/2}^{red}$ (X/X^-) = -1.24 V, $E_{1/2}^{ox}$ (X/X^+) = 0.86 V. UV-vis (CH_2Cl_2): λ_{max} (ε) = 586 (28500), 546 nm (26500 M^{-1} cm^{-1}).

3. ^{1}H NMR, ^{13}C NMR spectra and ESI-HRMS of DPP 1

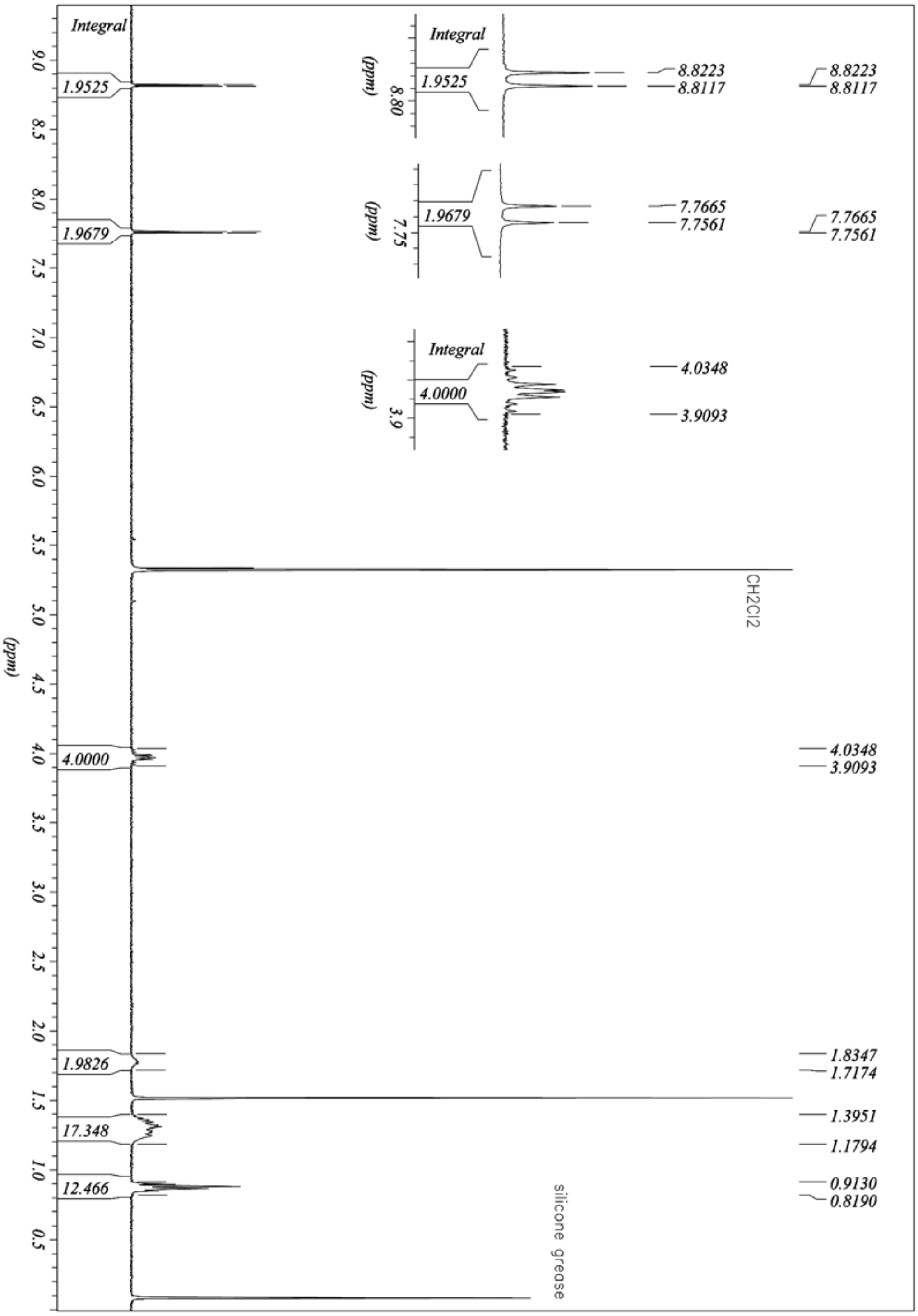

Fig. S1 ^{1}H NMR spectrum (400 MHz) of DPP **1** in CD_2Cl_2.

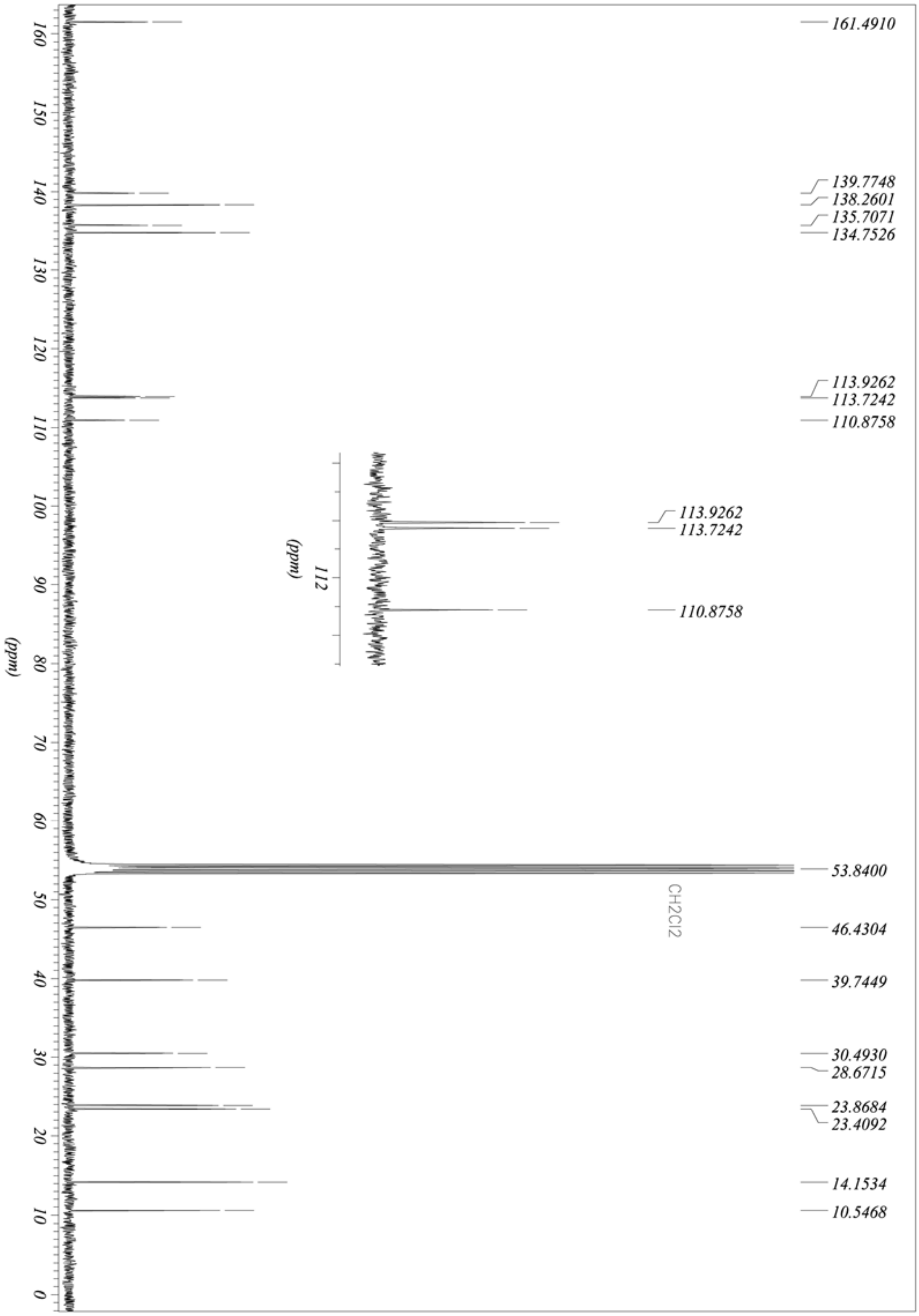

Fig. S2 ^{13}C NMR spectrum (101 MHz) of DPP **1** in CD_2Cl_2.

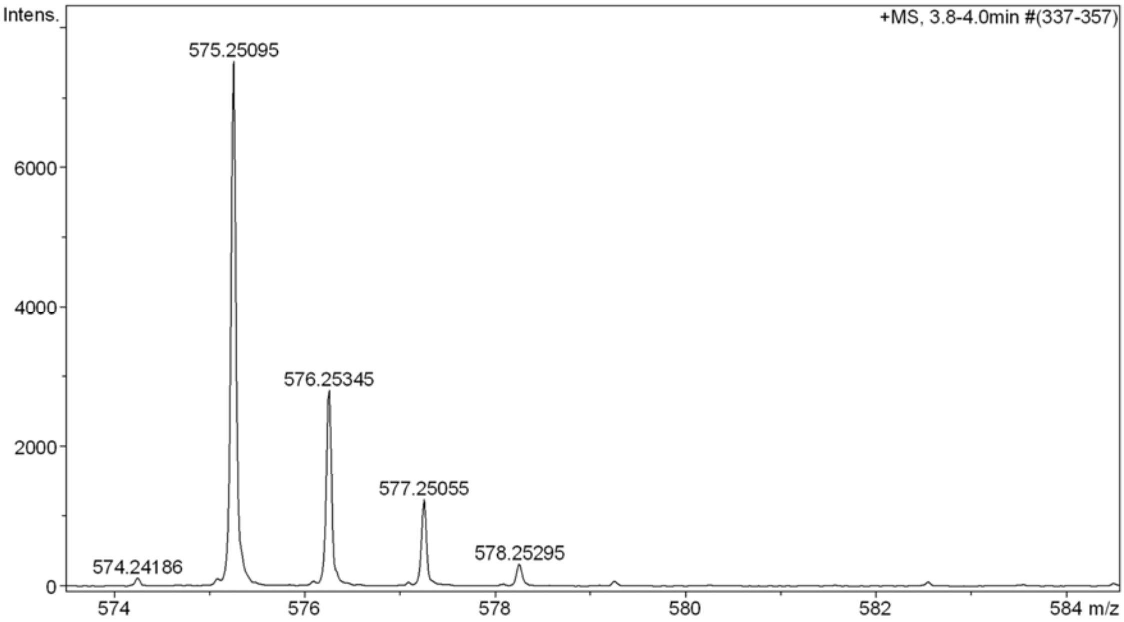

Fig. S3 High-resolution ESI-TOF mass spectrum of DPP **1** in acetonitrile/chloroform 1:1.

4. Cyclic voltammogram and UV-vis spectrum

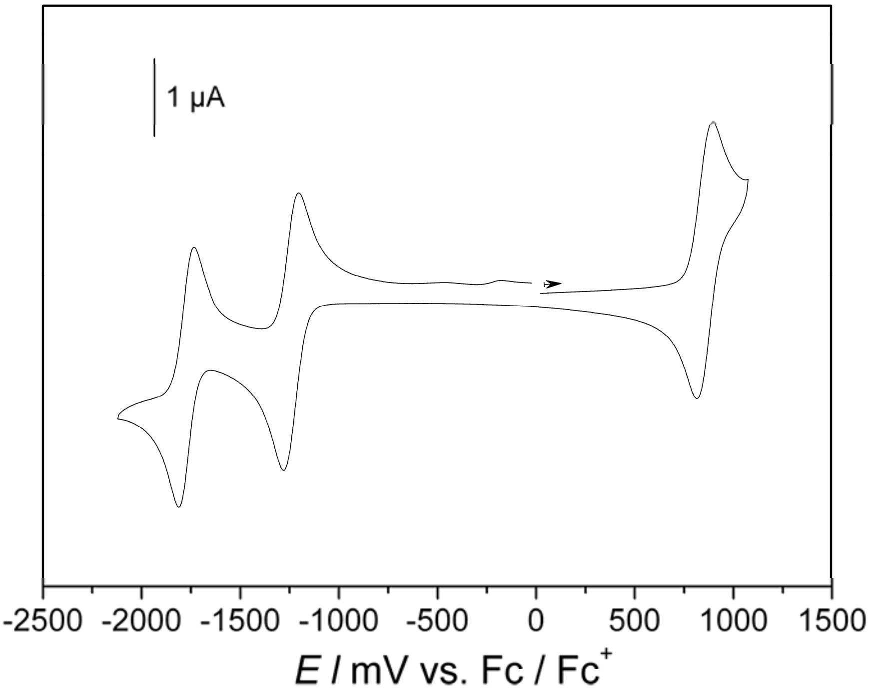

Fig. S4 Cyclic voltammogram of **1** in dichloromethane using ferrocene as an internal standard.

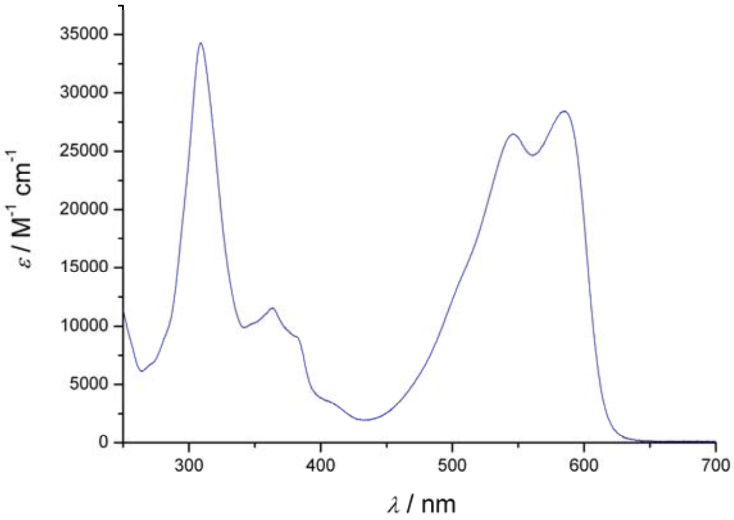

Fig. S5 Absorption spectrum of **1** in dichloromethane.

5. Fabrication and characterization of organic TFTs

Organic TFTs were fabricated on heavily doped silicon substrates, which also served as a common gate electrode of the transistors. The gate dielectric consists of a 100 nm thick layer of SiO_2, plus an 8 nm thick layer of AlO_x, plus a 2.1 nm thick self-assembled monolayer of pentadecylfluoro-octadecylphosphonic acid. The SiO_2 layer was obtained by thermal oxidation of the Si substrate, the AlO_x was deposited by atomic layer deposition, and the SAM was obtained by immersing the substrate in a 2-propanol solution of the phosphonic acid molecules. (In principle, phosphonic acid SAMs can also be obtained on SiO_2, but we have found that AlO_x is a more suitable surface for high-quality phosphonic acid SAMs). A 30 nm thick layer of the organic semiconductor DPP **1** was then deposited onto the SiO_2/AlO_x/SAM gate dielectric by thermal sublimation in a vacuum evaporator. TFTs were completed by evaporating 30 nm thick gold source and drain contacts through a polyimide shadow mask, defining a channel length of 100 µm and a channel width of 1000 µm. The current-voltage characteristics were measured using an Agilent 4156C Semiconductor Parameter Analyzer in ambient conditions. The sample of DPP **1** was measured again after six months storage under ambient conditions, showing a significantly reduced performance of 10^{-5} cm^2 V^{-1} s^{-1}.

The AFM images were processed with WSXM, a freeware scanning probe microscopy software.[4]

6. References

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