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Supporting information

Small molecular push-pull donors for organic photovoltaics: effect of the heterocyclic π-spacer

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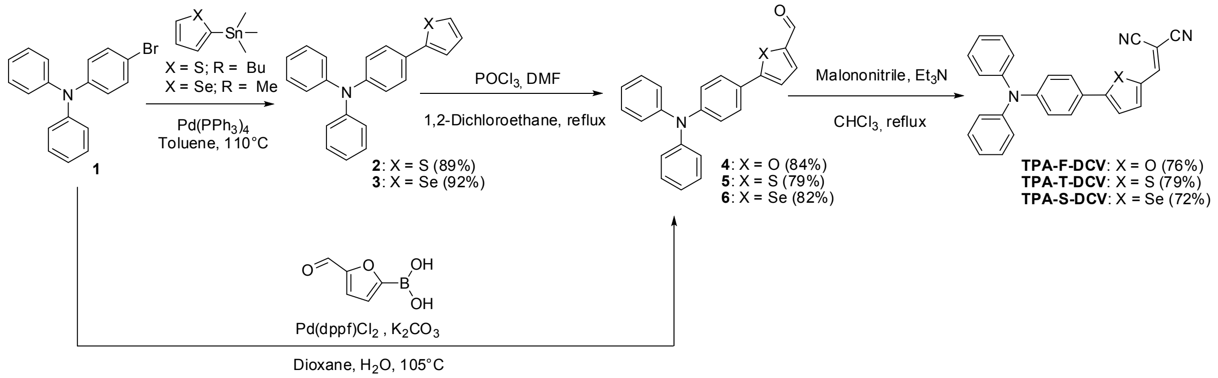
All reagents and chemicals from commercial sources were used without further purification. Reactions were carried out under nitrogen atmosphere unless otherwise stated. Solvents were dried and purified using standard techniques.

1. Measurements and characterization

Flash chromatography was performed with analytical-grade solvents using Aldrich silica gel (technical grade, pore size 60 Å, 230-400 mesh particle size). Flexible plates ALUGRAM® Xtra SIL G UV_{254} from MACHEREY-NAGEL were used for TLC. Compounds were detected by UV irradiation (Bioblock Scientific) or staining with I_2, unless stated otherwise. NMR spectra were recorded with a Bruker AVANCE III 300 (^{1}H, 300 MHz and ^{13}C, 75 MHz). Chemical shifts are given in ppm relative to TMS and coupling constants *J* in Hz. IR spectra were recorded on a Bruker spectrometer Vertex 70 and UV-Vis spectra with a Perkin Elmer 950 spectrometer. Matrix Assisted Laser Desorption/Ionization was performed on MALDI-TOF MS BIFLEX III Bruker Daltonics spectrometer using dithranol as matrix. Cyclic voltammetry was performed in 0.10 M Bu_4NPF_6/CH_2Cl_2 (HPLC grade). Solutions were degassed by nitrogen bubbling prior to each experiment. Experiments were carried out in a one-compartment cell equipped with platinum electrodes and a saturated calomel reference electrode (SCE) using a Biologic SP-150 potentiostat with positive feedback compensation. Thermogravimetric analysis (TGA) were performed with TA Instruments Q500 under nitrogen at a heating rate of 5°C/ min.

2. Synthetic procedures



*Scheme 1. Synthetic route to **TPA-F-DCV**, **TPA-T-DCV** and **TPA-S-DCV***

Trimethyl(thiophen-2-yl)stannane,[1] trimethyl(selenophen-2-yl)stannane,[2] *N*,*N*-diphenyl-4-(thiophen-2-yl)aniline **2**,[3] 5-(4-(diphenylamino)phenyl)furan-2-carbaldehyde **4**[4] and 5-(4-(diphenylamino)phenyl)thiophene-2-carbaldehyde **5**[3] were synthesized according to previously reported methods.

N,*N*-diphenyl-4-(selenophen-2-yl)aniline 3

4-Bromo-*N*,*N*-diphenylaniline **1** (2 g, 6.18 mmol), trimethyl(selenophen-2-yl)stannane (1.85 g, 6.25 mmol), $Pd(PPh_3)_4$ (169 mg, 0.14 mmol) were combined in a dry Schlenk flask and purged several time by argon-vacuum cycles. Then, 20 mL of freshly degased toluene were added and the reaction mixture was stirred at 110°C for 18 hours. After evaporation of the solvent, the residue was dissolved in dichloromethane (50 mL), washed with water (3 x 100 mL), dried over magnesium sulfate and concentrated under vacuum. The crude was finally purified on silica gel (eluent: CH_2Cl_2/hexane: 1/9) yielding 2.12 g of pure *N*,*N*-diphenyl-4-(selenophen-2-yl)aniline **3** (92 %) as yellow powder. ^1H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.89 (d, J = 4.2 Hz, 1 H); 7.45 (d, J = 8.8 Hz, 2 H); 7.38-7.37 (m, 1 H); 7.31-7.25 (m, 5 H); 7.14-7.02 (m, 8 H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ: 150.6; 147.5; 147.3; 130.6; 130.5; 129.3; 129.0; 127.1; 124.5; 124.2; 123.6; 123.1. LRMS MALDI-TOF: calculated for $C_{22}H_{17}Se$, 375.3 found 375.2.

5-(4-(Diphenylamino)phenyl)selenophene-2-carbaldehyde 6

Phosphoryl trichloride (310 µL, 3.24 mmol) was added to a solution of *N*,*N*-diphenyl-4-(selenophen-2-yl)aniline **3** (1.15 g, 3.07 mmol) and anhydrous dimethylformamide (326 µL, 3.31 mmol) in 1,2-dichloroethane (70 mL). The mixture was then refluxed under inert atmosphere for 15 hours. Once cooled to room temperature, 20 mL of dichloromethane and 40 mL of saturated aqueous solution of sodium acetate were added to the mixture and the later was stirred for further 6 hours. After extraction with dichloromethane (3 x 75 mL), the combined organic phases were washed with brine, dried over magnesium sulfate and concentrated under vacuum. The crude was finally purified by column chromatography on silica gel (eluent: CH_2Cl_2) affording the desired compound **6** (1.0 g, 82 %) as an orange powder. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 9.73 (s, 1 H); 7.95 (d, J = 4.2 Hz, 1 H); 7.48-7.45 (m, 3 H); 7.32-7.26 (m, 4 H); 7.15-7.02 (m, 8 H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ: 183.9; 161.4;149.2; 146.9; 140.9; 129.5; 128.4; 127.6; 125.2; 124.8; 123.9; 122.32. LRMS MALDI-TOF: calculated for $C_{23}H_{17}OSe$, 403.3 found 403.2.

General procedure for the Knoevenagel condensation reaction:

To a solution of 5-(4-(diphenylamino)phenyl)chalcogenophene-2-carbaldehyde **4**, **5** or **6** (0.56 mmol) and malononitrile (74 mg, 1.12 mmol) in chloroform (15 mL) were added two drops of triethylamine. After being refluxed overnight, the reaction mixture was washed with water (3 x 50 mL), dried over magnesium sulfate and concentrated under vacuum. The crude was then purified by column chromatography (eluent: chloroform) followed by a recrystallization from ethanol.

2-((5-(4-(Diphenylamino)phenyl)furan-2-yl)methylene)malononitrile (TPA-F-DCV): red crystalline powder (165 mg, 76% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.74 (s, 1 H), 7.68 (d, J = 4.10 Hz, 1 H), 7.54 (d, J = 8.8 Hz, 2 H); 7.34-7.29 (m, 5 H); 7.16-7.09 (m, 6 H); 7.06 (d, J = 8.8 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ: 162.1; 150.1; 146.7; 146.5; 129.6; 126.9; 125.6; 124.4; 121.2; 120.4; 114.9; 113.9; 108.3; 73.1. ESI HRMS: calculated for $C_{26}H_{17}N_3O$ 387.1372, found 387.1369. IR (neat): $\nu = 2218$ cm^{-1} (C≡N).

2-((5-(4-(Diphenylamino)phenyl)thiophen-2-yl)methylene)malononitrile (TPA-T-DCV) : dark red crystalline powder (178 mg, 79% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.75 (s, 1H); 7.69 (d, J = 8.9 Hz, 1H); 7.54 (d, J = 8.9 Hz, 2H); 7.36-7.27 (m, 5 H); 7.18-7.09 (m, 6 H), 7.05 (d, J = 8.8 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ: 157.5; 150.7; 150.3; 147.0;

133.5; 129.9; 127.9; 125.9; 124.7; 123.6; 122.1; 114.9; 114.1; 75.4. ESI HRMS: calculated for $C_{26}H_{17}N_3S$ 403.1143, found 403.1148. IR (neat): $\nu = 2220$ cm^{-1} (C≡N).

2-((5-(4-(Diphenylamino)phenyl)selenophen-2-yl)methylene)malononitrile (TPA-S-DCV): red-brown crystalline powder (181 mg, 72% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ: 7.81-7.79 (m, 2 H), 7.49-7.44 (m, 3 H); 7.34-7.29 (m, 4 H); 7.16-7.10 (m, 6 H); 7.03 (d, J = 8.77 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ:165.4; 153.6; 150.5; 146.9; 145.1; 137.6; 130.0; 128.2; 127.6; 125.9; 124.8; 122.0; 114.9; 114.4; 75.3. ESI HRMS: calculated for $C_{26}H_{17}N_3Se$ 451.0588, found 451.0573. IR (neat): $\nu = 2214$ cm^{-1} (C≡N).

3. Device fabrication

3.1 Solar cells

Indium-tin oxide coated glass slides of 24×25×1.1 mm with a sheet resistance of RS = 7 Ω/□ were purchased from Praezisions Glas & Optik GmbH. The ITO layer was patterned *via* a 37% hydrochloric acid solution and zinc powder etching. The substrates were then washed with a diluted Deconex® 12 PA-x solution (2% in water) and scrubbed using dishwashing soap before being cleaned by a series of ultrasonic treatments for 15 min in distilled water (15.3 MΩ cm^{-1}), acetone and isopropanol. Once dried under a steam of nitrogen, a UV-ozone plasma treatment (UV/Ozone ProCleaner Plus, Bioforce Nanosciences) was performed for 15 min. A filtered aqueous solution of poly(3,4-ethylenedioxy-thiophene)-poly(styrenesulfonate) (PEDOT:PSS; Clevios P VP. AI 4083) through a 0.45 µm PTFE membrane (Millex®) was spun-cast onto the patterned ITO surface at 5000 rpm for 40 s before beeing baked at 140°C for 30 min. The best devices were obtained with films spun-cast from chloroform solutions at 1200 rpm for **TPA-F-DCV** and 1300 rpm for **TPA-T-DCV** and **TPA-S-DCV** containing 10 mg/mL of donor and acceptor in a 1:2 weight to weight ratio. Finally, OSCs were completed by the successive thermal deposition of lithium fluoride (1 nm) and aluminum (120 nm) at a pressure of 1.5 x 10^{-5} Torr through a shadow mask defining six cells of 27 mm^2 each (13.5 mm x 2 mm). *J vs V* curves were recorded in the dark and under illumination using a Keithley 236 source-measure unit and a home-made acquisition program. The light source is an AM1.5 Solar Constant 575 PV simulator (Steuernagel Lichttecknik, equipped with a metal halogen lamp). The light intensity was measured by a broad-band power meter

(13PEM001, Melles Griot). EQE was recorded under ambient atmosphere using a halogen lamp (Osram) with an Action Spectra Pro 150 monochromator, a lock-in amplifier (Perkin-Elmer 7225) and a S2281 photodiode (Hamamatsu).

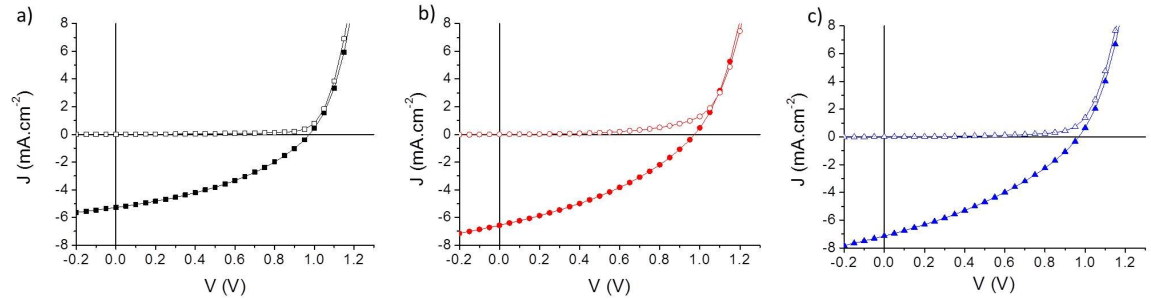


*Figure 1. J –V characteristics of **TPA-F-DCV**(black squares) **TPA-T-DCV** (red circles) and **TPA-S-DCV** (bleu triangles) based OSCs in the dark (opened) and under illumination (filled).*

3.2 Space charge limited current (SCLC) measurments

A solution of neat molecular donor **TPA-F-DCV**, **TPA-T-DCV** or **TPA-S-DCV** (20 mg/mL) in chloroform was spun cast at 1000 rpm on the above described PEDOT: PSS substrates to provide organic layers of *ca* 110 nm. Gold cathodes (150 nm) were thermally evaporated under a vacuum of 1.5 x 10^{-5} Torr, through a shadow mask defining actives area of 12.60 mm², 3.10 mm² and 0.78 mm² per substrates. Hole mobilities μ_h were evaluated using the Mott-Gurney law, *ie*, $J_{SCLC} = (9/8)\varepsilon_0\varepsilon_r\mu_h(V^2/d^3)$ where ε_r is the static dielectric constant of the medium ($\varepsilon_r = 3$) and d, the thickness of the active layer.[5]

4. References

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