Miniaturization of molecular conjugated systems for organic solar cells: towards pigmy donors

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Supplementary information

**General**

NMR spectra were recorded with a Bruker AVANCE III 300 (1H, 300 MHz and 13C, 75 MHz) or Bruker AVANCE DRX 500 (1H, 500 MHz and 13C, 125 MHz). Chemical shifts are given in ppm relative to TMS. IR spectra were recorded on a Bruker spectrometer Vertex 70 and UV-Vis spectra with a Perkin Elmer Lambda 19 or 950 spectrometer. Melting points are uncorrected. 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 Bu₄NPF₆/CH₂Cl₂ (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. Elemental analyses were performed with a thermo-electron instrument. Column chromatography purifications were carried out on Acros silica gel Si 60 (35-70 mm). DSC and TGA were performed with TA Instruments.

**Device preparation**

Indium-tin oxide coated glass slides of 24×25 ×1.1 mm with a surface resistance of 10 Ω/□ were purchased from Kintec company. Part of the ITO layer was etched away with 37% HCl. The ITO electrodes were then cleaned in ultrasonic bath successively with Deconex (from VWR international GmbH), distilled water (15.3 MΩ cm⁻¹), acetone, ethanol and distilled water again for 10 min each and dried in an oven at 100°C. The electrodes were then modified by a spin-cast layer of PEDOT:PSS (Clevios P VP. Al 4083 (HC-Starck) filtered through a 0.45 µm membrane just prior use). Spin-casting was achieved at 5000 rpm (r = 10 s, t = 60 s), and the electrode was then dried at 130 °C for 15 min. Films of donor materials of 30-35 nm thickness were spun-cast in atmospheric conditions from choloform solutions containing 10 mg mL⁻¹. Chloroform (HPLC grade) was distilled over P₂O₅ before use. After film deposition the devices were introduced in an argon glovebox (200B, MBraun) equipped with a vacuum chamber and a 30 nm film of C₆₀ fullerene (99+% (MER Corporation) and a 100 nm thick aluminium electrode were thermally evaporated on top of the donor film under a pressure of 2×10⁻⁶ mbar through a mask defining two cells of 6.0 mm diameter (0.28 cm²) on each ITO electrode. C₇₀ (99+% was purhased from MER Corporation and used as received.
The $J$ vs $V$ curves of the devices were recorded in the dark and under illumination using a Keithley 236 source-measure unit and a home-made acquisition program. The light source was an AM1.5 Solar Constant 575 PV simulator (Steuernagel Lichttechnik, equipped with a metal halogen lamp). The light intensity was measured by a broad-band power meter (13PEM001, Melles Griot). The devices were illuminated through the ITO electrode side. The efficiency values reported here are not corrected for the possible spectral mismatch of the solar simulator. External quantum efficiency (EQE) was measured using a halogen lamp (Osram) with an Action Spectra Pro 150 monochromator, a lock-in amplifier (Perkin-Elmer 7225) and a S2281 photodiode (Hamamatsu).

**Synthesis**

![Synthesis diagram]

**Bis(4-methoxyphenyl)phenylamine**$^{1,2,3,4}$

This already known compound has been obtained here with better yields using a new method. A mixture of 4-bromobenzene (0.45 mL, 4.3 mmol), 4,4'-dimethoxydiphenylamine (0.98 g, 4.3 mmol), sodium tert-butoxide (1.8 g, 19 mmol) is dissolved in 50 mL of dry toluene under Ar. The solution is

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degassed and tris(dibenzylideneacetone)dipalladium(0) [Pd(dba)$_3$] (0.15 g, 0.17 mmol, 4%) and tri-tert-butylphosphine [P(t-Bu)$_3$] (0.26 ml, 1 mmol) are added under Ar atmosphere at room temperature. After 14 h stirring at 110 °C, the solution is cooled to r.t. ethyl acetate is added and the organic phase is washed with water and dried over MgSO$_4$. After removal of solvent the crude is chromatographed on silica gel (eluents 1:1 CH$_2$Cl$_2$/petroleum ether) to afford the target compound, which is then reprecipitated from CH$_2$Cl$_2$-pentane to give 1 g, (77%) of a white solid. M.p. 101-102 °C. $^1$H NMR (300 MHz, CDCl$_3$): 7.19-7.14 (m, 2H), 7.05 (d, 4H, J=9 Hz), 6.95 (d, 2H, J=7.5 Hz), 6.88 (t, J=7.2 Hz, 1H), 6.83 (d, 4H, J=9 Hz), 3.79 (s, 6H).

4-(bis(4-methoxyphenyl)amino)benzaldehyde 7.$^5$ POCl$_3$ (0.2 ml, 2.0 mmol) in dry DMF (0.2 ml, 2.6 mmol) is added to a cold solution of Bis(4-methoxyphenyl)phenyamine (0.3 g, 0.98 mmol) in 1,2-dichloroethane (25 ml) at 0 °C under Ar. After reflux overnight, the solution is diluted with CH$_2$Cl$_2$ and stirred with a solution of NaCO$_2$CH$_3$ 2 for 2 h. The organic layer is washed with water and brine, dried over MgSO$_4$. After removal of solvent the residue is chromatographed on silica gel (eluents CH$_2$Cl$_2$) to give 0.28 g (86%) of a yellow solid. $^1$H NMR (300 MHz, CDCl$_3$): 9.75 (s, 1H), 7.62 (d, 2H, 8.7 Hz), 7.13 (d, 4H, J=9 Hz), 6.89 (d, 4H, J=9 Hz), 6.85(d, 2H, J=8.7 Hz), 3.81 (s, 6H).

2-(4-(bis(4-methoxyphenyl)amino)benzylidene)malononitrile 2. Aldehyde 7 (0.12 g, 0.36 mmol) is dissolved in a solution of malonitrile (0.023 g, 0.35 mmol) in dry CHCl$_3$ (50 ml), three drops of triethylamine are added and the solution is refluxed overnight. The mixture is diluted with CH$_2$Cl$_2$, washed with a solution of sodium hydroxide (1M), water and brine. After removal of solvent the residue is chromatographed on silica gel (eluents CH$_2$Cl$_2$) to give 0.2 g (86%) of a yellow solid. $^1$H NMR (300 MHz, CDCl$_3$): 109.1, 55.51.$^5$

5-(bis(4-methoxyphenyl)amino)thiophene-2-carboxaldehyde 8.$^6$ A mixture of 5-bromothiophene-2-carboxaldehyde (0.27 ml, 2.28 mmol), 4,4'-dimethoxydiphenylamine (0.26 g, 1.14 mmol), sodium tert-butoxide (0.036 g, 3.8 mmol) is dissolved in 50 ml of dry toluene under Ar. The solution is degassed and tris(dibenzylideneacetone)dipalladium(0) [Pd(dba)$_3$] (0.03 g, 0.034 mmol, 4%) and tri-tert-butylphosphine [P(t-Bu)$_3$] (0.05 ml, 0.2 mmol) are added under Ar atmosphere at room temperature. After 14 h stirring at 130 °C, the solution is cooled to r.t., ethyl acetate is added and the organic phase is washed with water and dried over MgSO$_4$. After removal of solvent the crude is chromatographed on silica gel (eluents CH$_2$Cl$_2$) to afford a yellowish oil (230 mg, 60%). $^1$H NMR (300 MHz, CDCl$_3$): 9.50 (s, 1H), 7.43 (d, 1H, J=4.5 Hz), 7.24 (d, 4H, J=9 Hz), 6.90 (d, 4H, J=9 Hz), 6.19 (d, 1H, J=4.5 Hz), 3.82 (s, 6H) $^{13}$C NMR (75 MHz, CDCl$_3$): 181, 166.3, 157.9, 139, 138.9, 128.5, 127.1, 115.02, 102.1, 55.51.

2-((5-(bis(4-methoxyphenyl)amino)thiophen-2-yl)methylene)malononitrile 3. Aldehyde 6 (0.08 g, 0.24 mmol) is dissolved in a solution of malonitrile (0.023 g, 0.35 mmol) in dry CHCl$_3$ (50 ml), three drops of triethylamine are added and the solution is stirred 24 h at r.t. The reaction mixture is diluted with CH$_2$Cl$_2$, washed with a solution of sodium hydroxide, water and brine. After removal of solvent the residue is chromatographed on silica gel (eluents CH$_2$Cl$_2$) to give a red solid (68 mg, 74%). M.p. = 204-209 °C. IR (neat): $\nu$ = 2217 cm$^{-1}$ (C≡N). $^1$H NMR (300 MHz, Acetone-d$_6$): 7.45 (s, 1H), 7.65 (d, 1H, J=4.2 Hz), 7.44 (d, 4H, J=9 Hz), 7.05 (d, 4H, J=9 Hz), 6.22 (d, 1H, J=4.2 Hz), 3.84 (s, 6H). $^{13}$C NMR (75 MHz, Acetone-d$_6$): 170.4, 159.9, 150.7, 145.5, 138.9, 128.7, 122.2, 117.1, 116.4, 116.1, 110.5, 64.4, 55.9. HRMS (FAB): calculated 381.1477; found 381.1487.

4,4'-ditolylo-methinothiophene 12.$^7$ A mixture of 2-bromothiophene (0.48 ml, 4.9 mmol), p,p'-ditolylamine (1 g, 4.9 mmol), sodium tert-butoxide (1.4 g, 14.7 mmol) is dissolved in 50 ml of dry toluene under Ar. The solution is degassed during a few minutes and tris(dibenzylideneacetone)dipalladium(0) [Pd(dba)$_3$] (0.18 g, 0.19 mmol, 4%) and tri-tert-butylphosphine [P(t-Bu)$_3$] (0.30 ml, 1.2 mmol) are added under Ar atmosphere at r.t. After 14 stirring at 115 °C, the solution is cooled to r.t., washed with water and dried over MgSO$_4$. After removal of solvent the crude is chromatographed on silica gel (eluents 1:3 methylene chloride/petroleum ether) to

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give (1.25 g, 91%) of a yellow oil. \(^1\)H NMR (300 MHz, CDCl\(_3\)): 7.06 (d, 4H, J=8.7 Hz), 7.01 (d, 4H, J=8.7 Hz), 6.92 (d, 1H, J=4 Hz), 6.84 (m, 1H), 6.64 (d, 1H, J=3.6 Hz), 2.30 (s, 6H)

4,4'-ditolylnthiophene carboxaldehyde 9. POCl\(_3\) (0.09 mL, 0.96 mmol) in dry DMF (0.10 mL, 1.28 mmol), is added to a cold solution of 10 (0.18 g, 0.64 mmol) in 1,2-dichloroethane (20 mL) at 0 °C under Ar. After 2h stirring at 40 °C, the solution is diluted with CH\(_2\)Cl\(_2\) and stirred with a solution of NaCOOCH\(_3\) for 2 h. The organic layer is washed with water and brine, dried over MgSO\(_4\). After removal of solvent the residue is chromatographed on silica gel (eluent: 3:1 CH\(_2\)Cl\(_2\)/petroleum ether to give (160 mg, 82%) of a yellowish compound. \(^1\)H NMR (300 MHz, CDCl\(_3\)): 9.53 (s, 1H), 7.45 (d, 1H, J=4.5 Hz), 7.18 (s, 4H), 6.27 (d, 1H, J=4.5 Hz), 2.35 (s, 6H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): 181.2, 165.2, 143.8, 139.0, 136.7, 130.7, 129.7, 125.9, 110.8, 21.1. MS MALDI: calculated 307.1030; found 307.1021.

4,4'-ditolylnthiophene dicyanovinylene 4. Aldehyde 8 (0.16 g, 0.52 mmol) is dissolved in a solution of malonitrile (0.24 g, 3.64 mmol) in dry chloroform (40 mL), three drops of triethylamine are added and the resulting solution is stirred overnight at room temperature under inert atmosphere. The reaction mixture is diluted with CH\(_2\)Cl\(_2\), washed with a solution of sodium hydroxide (1M), and water. After removal of solvent the residue is chromatographed on silica gel (eluent: 131 CH\(_2\)Cl\(_2)/petroleum ether) to give the target compound as a pale yellow oil (1.30 g, 93%). \(^1\)H NMR (300 MHz, CDCl\(_3\)): 7.28-7.23 (m, 4), 7.13 (d, 4H, J=7.5 Hz), 7.04-6.99 (m, 3H), 6.90 (dd, 1H, J=5.7 Hz, J=3.6 Hz), 6.73 (dd, 1H, J=3.6 Hz, J=1.5 Hz)

N,N-Diphenylamino-thiophene 13. A mixture of 2-bromothiophene (0.58 mL, 5.9 mmol), diphenylamine (1 g, 5.9 mmol), sodium tert-butoxide (0.86 g, 8.85 mmol) is dissolved in 50 mL of dry toluene under Ar. The solution is degassed during a few minutes and PdOAc (54 mg, 0.24 mmol, 4%) and tri-tert-butylphosphine [P(t-Bu)\(_3\)] (0.06 mL, 0.24 mmol) are added under Ar atmosphere at r.t. After being stirred at 120 °C overnight, the solution is cooled room temperature, washed with water and dried over MgSO\(_4\). After removal of solvent the crude is chromatographed on silica gel (eluent: 2:1 CH\(_2\)Cl\(_2)/petroleum ether) to give the target compound as a pale yellow oil (1.30 g, 93%). \(^1\)H NMR (300 MHz, CDCl\(_3\)): 7.19 (m, 8H), 7.26 (m, 8H), 7.23 (m, 8H), 7.13 (d, 4H, J=7.5 Hz), 7.04-6.99 (m, 3H), 6.90 (dd, 1H, J=5.7 Hz, J=3.6 Hz), 6.73 (dd, 1H, J=3.6 Hz, J=1.5 Hz)

N,N-Diphenylamino-thiophene carboxaldehyde 10. POCl\(_3\) (0.18 mL, 1.94 mmol) in dry DMF (0.31 mL, 4 mmol) is added to a cold solution of 12 (0.5 g, 1.99 mmol) in 1,2-dichloroethane (50 mL) at 0 °C under Ar. After being stirred at 70 °C overnight, the solution is cooled room temperature, washed with water and dried over MgSO\(_4\). After removal of solvent the residue is chromatographed on silica gel (eluent: 4:1 CH\(_2\)Cl\(_2)/petroleum ether) to give an orange compound (0.48 g, 87%). \(^1\)H NMR (300 MHz, CDCl\(_3\)): 7.56 (s, 1H), 7.46 (d, 1H, J=4.5 Hz), 7.4-7.2 (m, 1H), 7.25 (m, 4H), 6.93 (d, 1H, J=4.5 Hz)

N,N-Diphenylamino-thiophene dicyanovinylene 5. Aldehyde 9 (0.20 g, 0.71 mmol) is dissolved in a solution of malonitrile (0.33 g, 5.02 mmol) in dry chloroform (40 mL) and then three drops of triethylamine are added and the resulting solution is stirred at room temperature under inert atmosphere overnight. The reaction mixture is then diluted with CH\(_2\)Cl\(_2\), washed with water and brine. After removal of solvent the residue is chromatographed on silica gel using methylene chloride as eluent to afford a brick reddish solid (190 mg, 81%). M.p.: 130-135 °C. IR (neat): ν=2211, 2203 cm\(^{-1}\) (C≡N). \(^1\)H NMR (300 MHz, CDCl\(_3\)): 7.47 (s, 1H), 7.44-7.39 (m, 5H), 7.31-7.27 (m, 6H), 6.37 (d, 1H, J=4.5 Hz). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): 166.9, 149.3, 145.0, 141.9, 130.1, 127.3, 125.7, 122.5, 116.0, 115.0, 112.2, 67. MS MALDI: calculated 326.9, HRMS FAB: calculated 327.0830; found 327.0837 (2.14 ppm)

N-Thienylcarbazole 14. 9H-Carbazole (167 mg, 1.0 mmol), Cs\(_2\)CO\(_3\) (326 mg, 1.0 mmol), bromothiophene (0.11 mL, 1.1 mmol), Cul (19.4 mg, 0.1 mmol) and DMF (2 mL) are added to a 10-mL vial. The vial is sealed with a crimp cap and placed in the microwave cavity (CEM Discover). After irradiation at 300 W, 220 °C for 75 minutes and subsequent cooling, the reaction mixture is diluted with saturated aqueous ammonium chloride and the organic layer is extracted with ethyl acetate, dried over magnesium sulfate, filtered and concentrated. The residue is chromatographed on silica gel (eluent: 1:2 CH\(_2\)Cl\(_2)/petroleum ether to give (130 mg, 52%) of a yellowish oil.\(^1\)H NMR (300 MHz,
CDCl₃: 8.12 (d, 2H, J=7.8 Hz), 7.45-7.43 (m, 4H), 7.40 (dd, 1H, J=5.4 Hz, J=1.5 Hz), 7.33-7.27 (m, 2H), 7.21-7.18 (m, 2H)

**Carboxaldehyde 11.** POCI₃ (0.05 mL, 0.53 mmol) in dry DMF (0.07 mL, 0.96 mmol), is added to a cold solution of 13 (0.12 g, 0.48 mmol) in 1,2-dichloroethane (20 mL) at 0 °C under Ar. After 24 h stirring at 70 °C another equivalent of Vilsmeier reagent is prepared using the same quantities and added to the solution of 13 at r.t. After another 36 h at 70 °C, the solution is cooled and diluted with CH₂Cl₂ and stirred with a solution of NaCOOCH₃ for 2 h. The organic layer is washed with water and brine and dried over MgSO₄. After removal of solvent the residue is chromatographed on silica gel (eluent 1:1 CH₂Cl₂/petroleum ether) to afford a yellowish oil, which solidifies in the fridge (130 mg, 97%). ¹H NMR (300 MHz, CDCl₃): 9.96 (s, 1H), 8.12 (m, 2H), 7.89 (d, 1H, J=4.2 Hz), 7.68 (d, 2H, J=8.4 Hz), 7.50-7.45 (m, 2H), 7.38-7.35 (m, 2H), 7.35 (d, 1H, J=4.2 Hz). ¹³C NMR (75 MHz, CDCl₃): 182.8, 148.5, 140.5, 139.6, 136.1, 126.6, 124.2, 123.6, 121.6, 120.4, 110.3. MS MALDI: 276.9. HRMS FAB: calculated 277.0561; found 277.0561.

**Compound 6.** Aldehyde 10 (60 mg, 0.22 mmol) is dissolved in a solution of malonitrile (21.4 mg, 0.32 mmol) in dry chloroform (10 mL) and three drops of triethylamine are added and the resulting solution is stirred 30 min at room temperature under inert atmosphere. The reaction mixture is diluted with CH₂Cl₂, washed with water and brine. After removal of solvent the residue is chromatographed on silica gel (eluent 1:1 CH₂Cl₂/petroleum ether: 1/1) to afford an orange powder (68 mg, 97%). M.p. 135-140 °C. IR (neat): ʋ=2221 cm⁻¹ (C≡N). ¹H NMR (300 MHz, CDCl₃): 8.12 (d, 2H, J=8 Hz), 7.87 (d, 1H, J=4.2 Hz), 7.85 (s, 1H), 7.73 (d, 2H, J=8 Hz), 7.53-7.47 (m, 2H), 7.41-7.36 (m, 3H). ¹³C NMR (75 MHz, CDCl₃): 150.6, 150.3, 140.0, 138.6, 130.8, 126.9, 124.6, 123.6, 122.0, 120.5, 113.9, 113.2, 110.4 MS MALDI: 324.9. HRMS FAB: calculated 325.0674; found 325.0679.

Electronic Supplementary Material (ESI) for RSC Advances
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Table S1. PV results of OSCs ITO/PEDOT:PSS/Donor/C_{60}/Al under AM 1.5 conditions, 90 mW/cm². *italics:* average values on 4-devices, *boldface:* best results. RT Initial values at room temperature, TT after 10 min annealing at 110°C.

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Fig. S1 Contours of frontier orbitals of the donors. Left: LUMO, right HOMO
TPA – OMe SHORT Derivatives

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Electronic Supplementary Material (ESI) for RSC Advances
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