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

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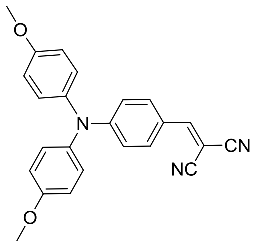
Supplementary information



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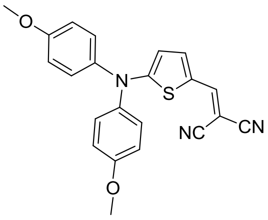

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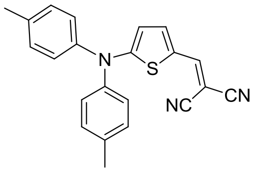

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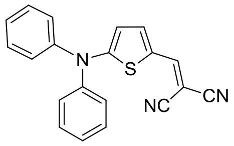

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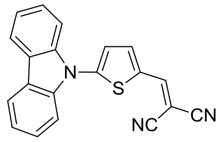

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General

NMR spectra were recorded with a Bruker AVANCE III 300 (^{1}H, 300 MHz and ^{13}C, 75 MHz) or Bruker AVANCE DRX 500 (^{1}H, 500 MHz and ^{13}C, 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.

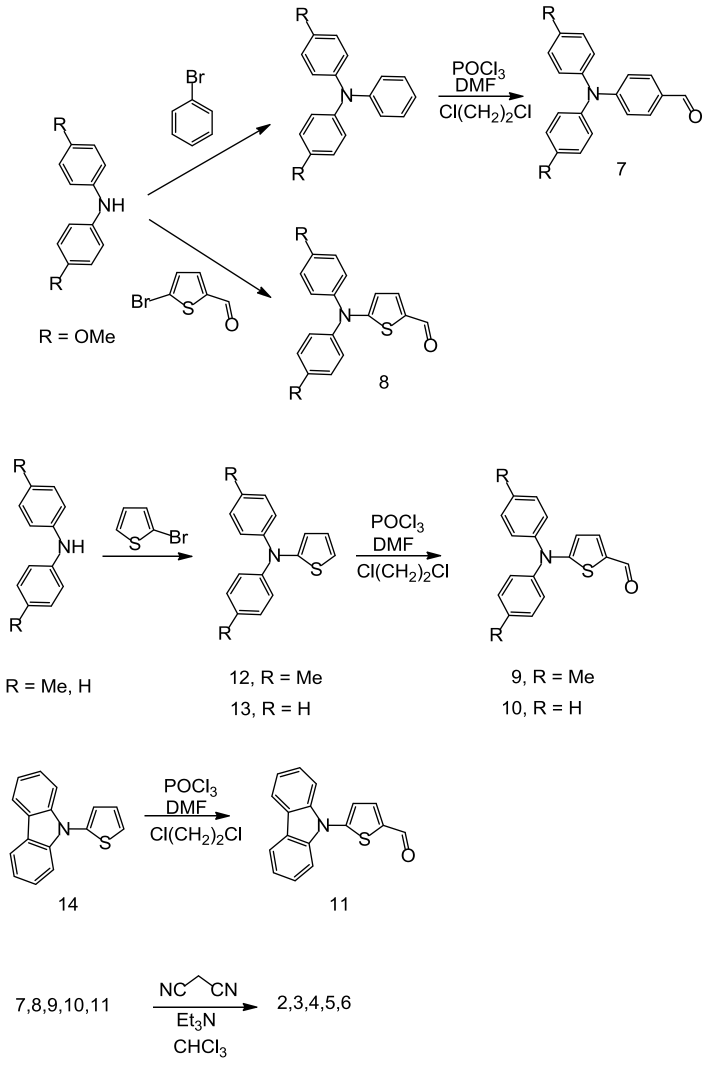
Cyclic voltammetry was performed in 0.10 M Bu_4NPF_6/CH_2Cl_2 (HPLC grade). Solutions were degassed by nitrogen bubbling prior to each experiment. Experiments were carried out in a one-compartment cell equipped with platinum electrodes and a saturated calomel reference electrode (SCE) using a Biologic SP-150 potentiostat with positive feedback compensation. 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. AI 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 P_2O_5 before use. After film deposition the devices were introduced in an argon glovebox (200B, MBraun) equiped with a vacuum chamber and a 30 nm film of C_{60} 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 cm^2) on each ITO electrode. C_{70} (99+%) was purshased 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 Lichttecknik, 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



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 ter-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) [$Pd_2(dba)_3$] (0.15 g, 0.17 mmol, 4%) and tri-ter-butylphosphine [$P(t\text{-}Bu)_3$] (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 rt, 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 (eluent 1:1 CH_2Cl_2/petroleum ether) to afford the target compound, which is then reprecipitated from CH_2Cl_2-pentane to give 1 g, (77%) of a white solid. M.p.101-102 °C. ^1H 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)phenylamine (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_2Cl_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 (eluent CH_2Cl_2) to give 0.28 g (86%) of a yellow solid. ^1H 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 (0.036 g, 0.54 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_2Cl_2, washed with a solution of sodium hydroxide (1M), water and brine. After removal of solvent the residue is chromatographed on silica gel (eluent CH_2Cl_2) to give 110 mg (80%) of a red solid. m.p. = 90-95 °C IR (neat): $\nu = 2217\ cm^{-1}$ (C≡N)**.** ^1H NMR (300 MHz, Acetone-d_6): 7.94 (s, 1H), 7.85 (d, 2H, J=9 Hz), 7.27 (d, 4H, J=9 Hz), 7.02 (d, 4H, J=9 Hz), 6, 78 (d, 2H, J=9 Hz), 3.83 (s, 6H)**.** ^{13}C NMR (75 MHz, Acetone-d_6): 159.4, 159.1, 138.7, 134.1, 129.4, 122.6, 116.7, 116.3, 116.1, 115.4, 74.1, 55.9**.** HRMS (FAB): calculated 381.1477; found 381.1487.

5-(bis(4-methoxyphenyl)amino)thiophene-2-carbaldehyde 8.[6] A mixture of 5-bromothiophene-2-carbaldehyde (0.27 mL, 2.28 mmol), 4,4'-dimethoxydiphenylamine (0.26 g, 1.14 mmol), sodium tert-butoxide (0.36 g, 3.8 mmol) is dissolved in 50 mL of dry toluene under Ar. The solution is degassed and tris(dibenzylideneacetone)dipalladium(0) [$Pd_2(dba)_3$] (0.03 g, 0.034 mmol, 4%) and tri-tert-butylphosphine [$P(t\text{-}Bu)_3$] (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 (eluent CH_2Cl_2) to afford a yellowish oil (230 mg, 60%). ^1H 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, 109.1, 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_2Cl_2, washed with a solution of sodium hydroxide, water and brine. After removal of solvent the residue is chromatographed on silica gel (eluent CH_2Cl_2) to give a red solid (68 mg, 74%). m.p. = 204-209 °C. IR (neat): $\nu = 2207\ cm^{-1}$ (C≡N). ^1H NMR (300 MHz, Acetone-d_6): 7.90 (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 387.1041; found 387.1038.

4,4'-ditolyl-aminothiophene 12[7,8] A mixture of 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) [$Pd_2(dba)_3$] (0.18 g, 0.19 mmol, 4%) and tri-tert-butylphosphine [$P(t\text{-}Bu)_3$] (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 (eluent 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'-ditolyl-aminothiophene carboxyaldehyde 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 diluted with CH_2Cl_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_2Cl_2 / petroleum ether to give (160 mg, 82%) of a yellowish compound. ^{1}H NMR (300 MHz, CD_2Cl_2): 9.53 (s, 1H), 7.45 (d, 1H, J=4.5 Hz), 7.18 (s-el, 8H), 6.27 (d, 1H, J=4.5 Hz), 2.35 (s, 6H). ^{13}C NMR (75 MHz, CD_2Cl_2): 181.2, 165.2, 143.8, 139.0, 136.7, 130.7, 129.7, 125.9, 110.8, 21.1. MS MALDI: 308.1. HRMS: calculated 307.1030; found 307.1021.

4,4'-ditolyl-aminothiophene 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_2Cl_2, washed with a solution of sodium hydroxide (1M), water and brine. After removal of solvent the residue is chromatographed on silica gel (eluent eluent CH_2Cl_2)to give a reddish solid (170 mg, 92%). M.p.: 105-108 °C. IR (neat): ν=2207 cm^{-1} (C≡N). ^{1}H NMR (500 MHz, CD_2Cl_2): 7.48 (s, 1H), 7.41 (d, 1H, J=4.5 Hz), 7.26-7.19 (m, 8H), 6.29 (d, 1H, J=4.5 Hz), 2.37 (s, 6H). ^{13}C NMR (75 MHz, CD_2Cl_2): 168.2, 149.6, 142.9, 138.1, 131.0, 126.1, 122.1, 116.7, 115.8, 111.4, 65.9, 21.2. MS MALDI: 355.1; HRMS: calculated 355.1143; found 355.1130 (3.6 ppm)

***N,N*-Diphenylamino-thiophene 13**[9,10,11]A mixture of 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 to room temperature, washed with water and dried over $MgSO_4$. After removal of solvent the crude is chromatographed on silica gel (eluent 1:3 CH_2Cl_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 carboxaldehyde 10**[12,13] $POCl_3$ (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, diluted with CH_2Cl_2 and stirred 2h with a solution of $NaCOOCH_3$. The organic layer is washed with water and brine and dried over $MgSO_4$. After removal of solvent the residue is chromatographed on silica gel using CH_2Cl_2 as eluent to give an orange compound (0.48 g, 87%). ^{1}H NMR (300 MHz, CD_2Cl_2): 9.60 (s, 1H), 7.46 (d, 1H, J=4.5 Hz), 7.4-7.2 (m, 10H), 6.39 (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_2Cl_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: 326.9. HRMS FAB: calculated 327.0830; found 327.0837 (2.14 ppm)

***N*-Thienylcarbazole 14**[14]. 9H-Carbazole (167 mg, 1.0 mmol), Cs_2CO_3 (326 mg, 1.0 mmol), bromothiophene (0.11 ml, 1.1 mmol), CuI (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_2Cl_2 /petroleum ether to give (130 mg, 52%) of a yellowish oil . ^{1}H NMR (300 MHz,

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$CDCl_3$): 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. $POCl_3$ (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 CH_2Cl_2 and stirred with a solution of $NaCOOCH_3$ for 2 h. The organic layer is washed with water and brine and dried over $MgSO_4$. After removal of solvent the residue is chromatographed on silica gel (eluent 1:1 CH_2Cl_2/petroleum ether) to afford a yellowish oil, which solidifies in the fridge (130 mg, 97%). ^{1}H NMR (300 MHz, $CDCl_3$): 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). ^{13}C NMR (75 MHz, $CDCl_3$): 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 CH_2Cl_2, washed with water and brine. After removal of solvent the residue is chromatographed on silica gel (eluent 1:1 CH_2Cl_2/petroleum ether: 1/1) to afford an orange powder (68 mg, 97%). M.p. 135-140 °C**.** IR (neat): ν=2221 cm^{-1} (C≡N)**.** ^{1}H NMR (300 MHz, $CDCl_3$): 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)**.** ^{13}C NMR (75 MHz, $CDCl_3$): 150.6, 150.3, 140.0, 138.6, 130.8, 126.9, 124.6, 123.1, 122.3, 120.5, 113.9, 113.2, 110.4
MS MALDI: 324.9. HRMS FAB: calculated 325.0674; found 325.0679.

Table S1. PV results of OSCs ITO/PEDOTPSS/Donor/C_{60}/Al under AM 1.5 conditions , 90 mW/cm^2 *italics*: average values on 4-devices, **boldface**: best results. RT Initial values at room temperature, TT after 10 min annealing at 110°C

Donor	**Voc (V)**	**Jsc (mA/cm²)**	**FF (%)**	**PCE (%)**
2 RT	*0.64*	*1.24*	*25.25*	*0.22*
	0.68	**1.28**	**25**	**0.24**
TT	*0.62*	*2.82*	*34.9*	*0.70*
	0.67	**3.04**	**37.4**	**0.85**
3 RT	*0.63*	*2.00*	*39.7*	*0.56*
	0.79	**1.89**	**40.9**	**0.68**
TT	*0.65*	*5.00*	*37.5*	*1.37*
	0.66	**5.27**	**37**	**1.43**
4 RT	*0.75*	*2.10*	*23*	*0.40*
	0.83	**2.03**	**23**	**0.43**
TT	*0.65*	*4.27*	*38.2*	*1.19*
	0.65	**4.83**	**41.1**	**1.42**
5 RT	*0.44*	*1.72*	*26*	*0.22*
	0.45	**1.93**	**28**	**0.27**
TT	*0.63*	*7.02*	*36*	*1.77*
	0.65	**6.80**	**39**	**1.92**
6 RT	**0.57**	**1.10**	**38**	**0.26**
TT	*0.55*	*0.84*	*39*	*0.19*

Fig. S1 Contours of frontier orbitals of the donors. Left : LUMO, right HOMO

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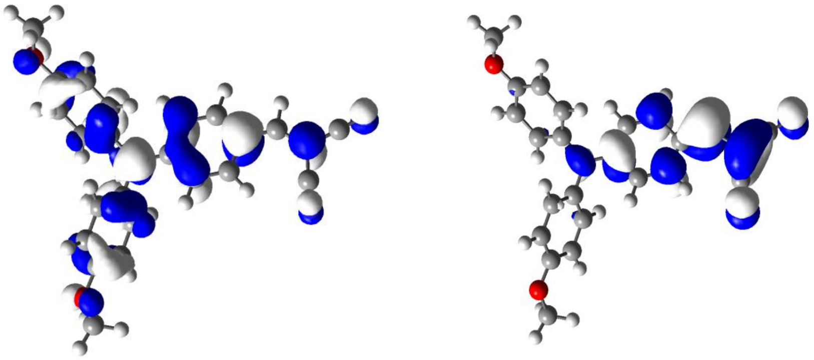

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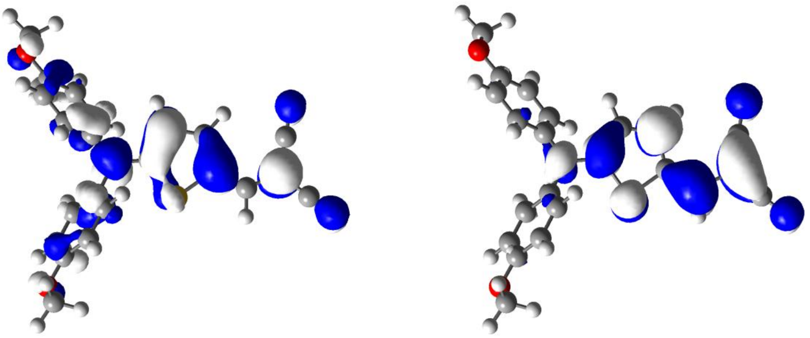

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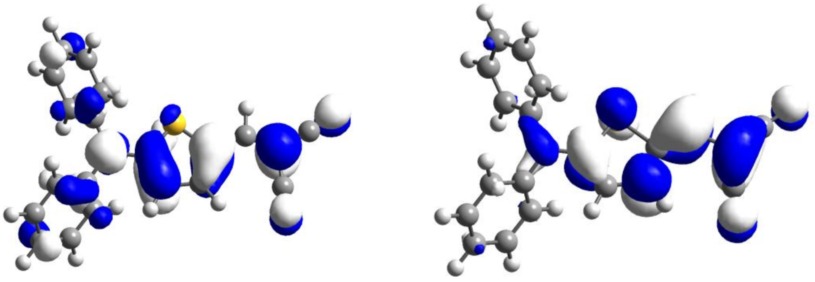

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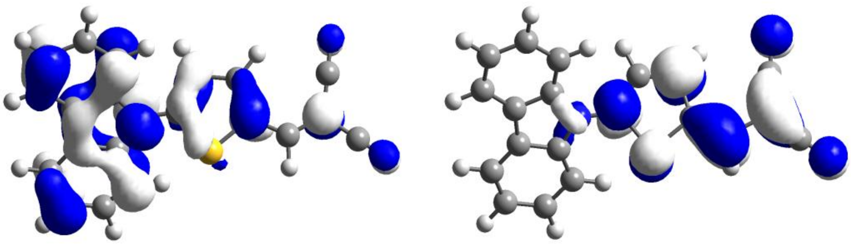
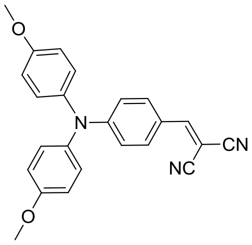


TPA – OMe SHORT Derivatives



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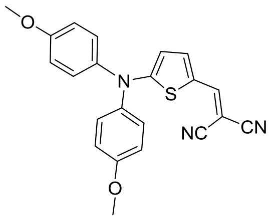

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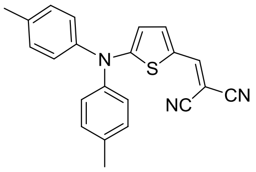

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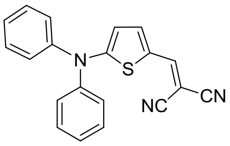

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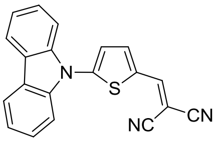
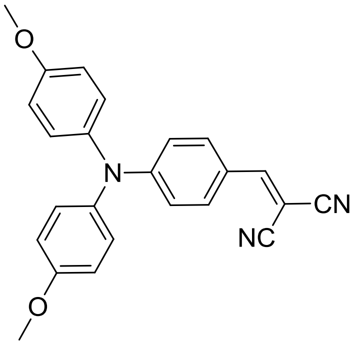
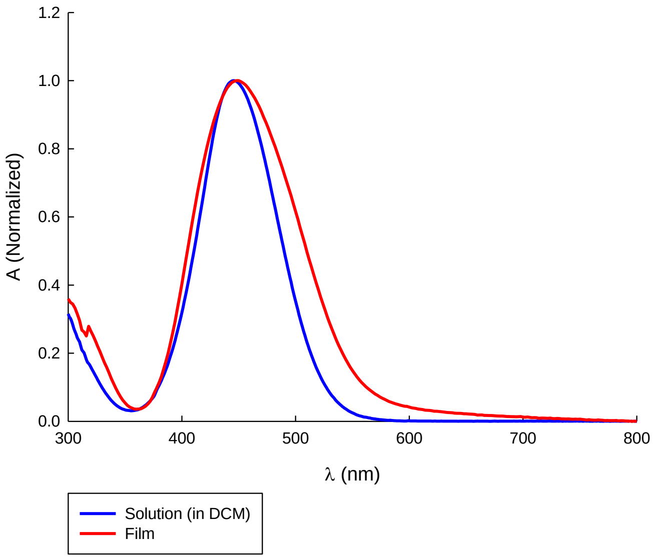
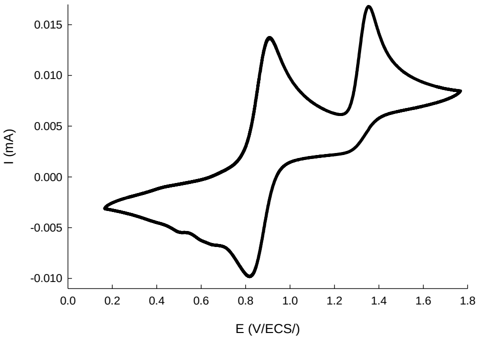


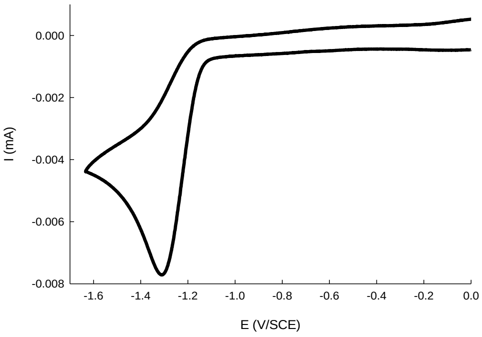
6

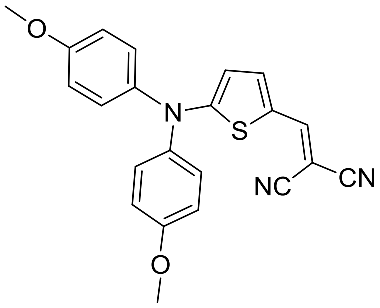

O
N
CN
NC
O

2

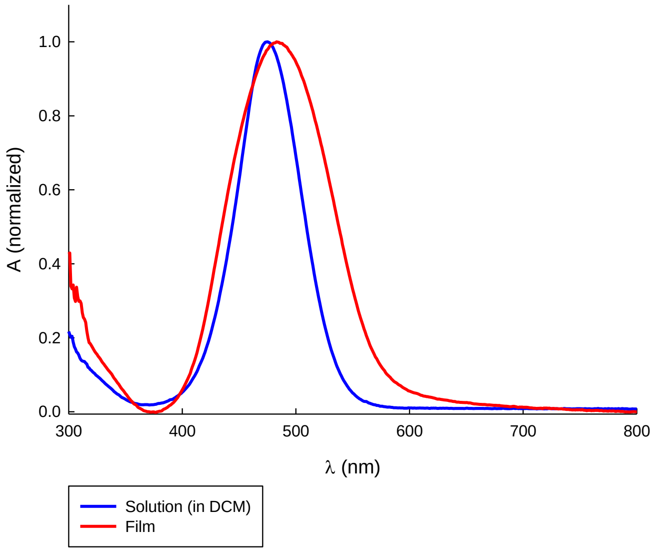

A (Normalized)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
300
400
500
600
700
800
λ (nm)
Solution (in DCM)
Film

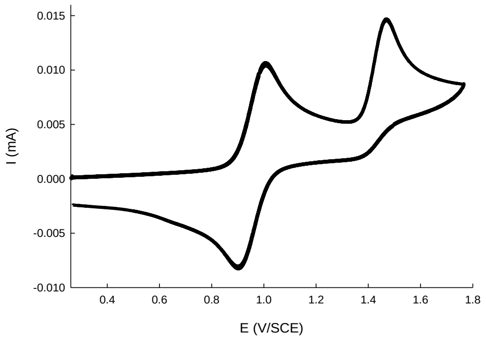

I (mA)
0.015
0.010
0.005
0.000
-0.005
-0.010
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
E (V/ECS/)

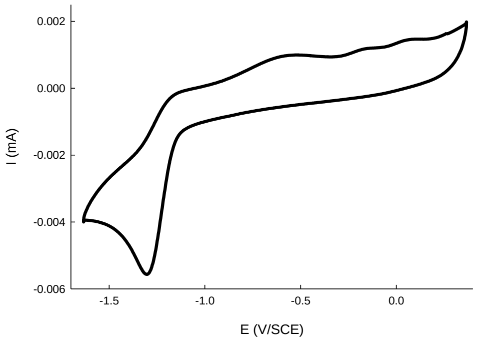

I (mA)
0.000
-0.002
-0.004
-0.006
-0.008
-1.6
-1.4
-1.2
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
E (V/SCE)

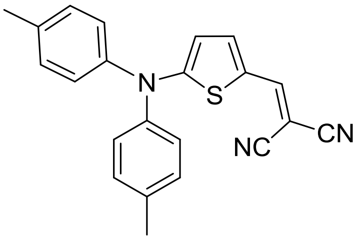

O
N
S
NC
CN
O

3

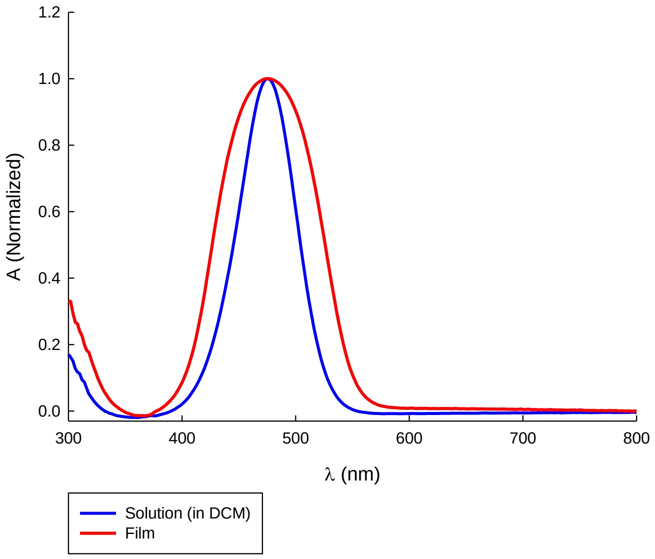

A (normalized)
1.0
0.8
0.6
0.4
0.2
0.0
300
400
500
600
700
800
λ (nm)
Solution (in DCM)
Film

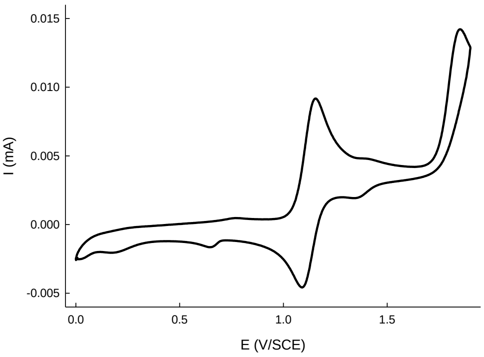

I (mA)
0.015
0.010
0.005
0.000
-0.005
-0.010
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
E (V/SCE)

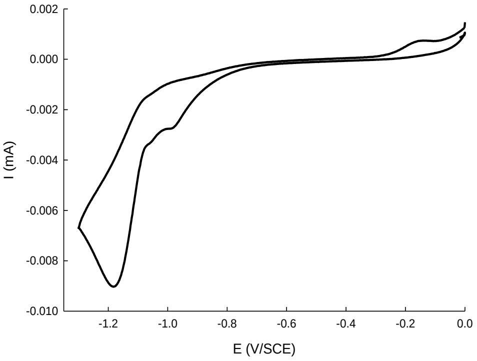

I (mA)
0.002
0.000
-0.002
-0.004
-0.006
-1.5
-1.0
-0.5
0.0
E (V/SCE)

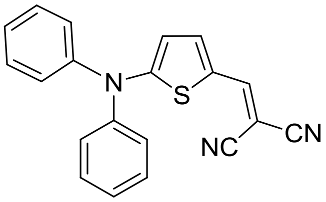

N
S
NC
CN

4

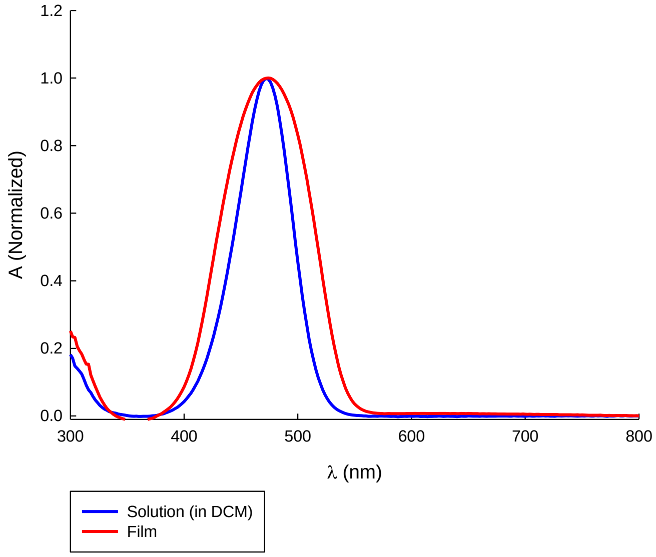

1.2
1.0
0.8
0.6
0.4
0.2
0.0
A (Normalized)
300
400
500
600
700
800
λ (nm)
Solution (in DCM)
Film

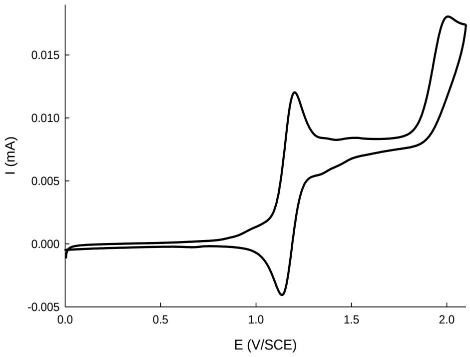

0.015
0.010
0.005
0.000
-0.005
I (mA)
0.0
0.5
1.0
1.5
E (V/SCE)

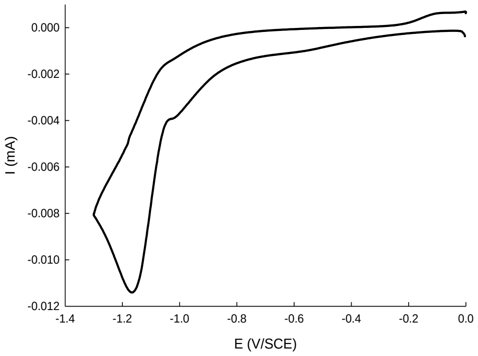

0.002
0.000
-0.002
-0.004
-0.006
-0.008
-0.010
I (mA)
-1.2
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
E (V/SCE)

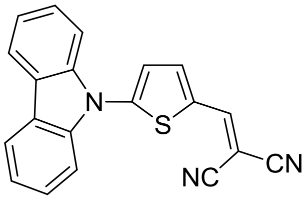

N
S
NC
CN

5

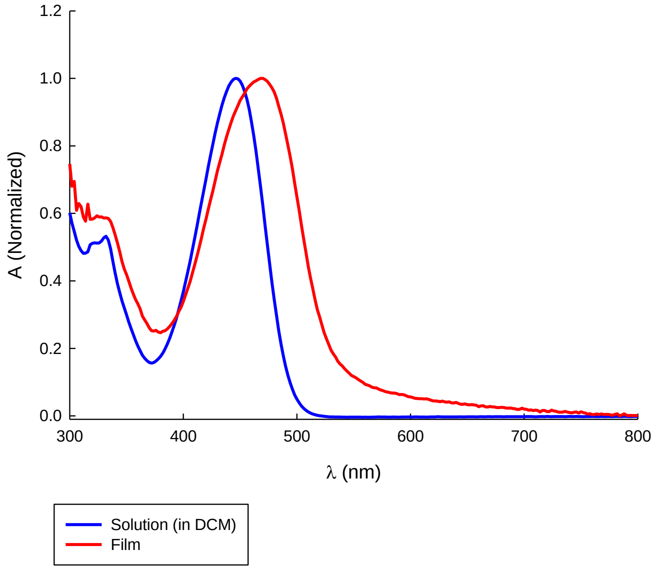

A (Normalized)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
300
400
500
600
700
800
λ (nm)
Solution (in DCM)
Film

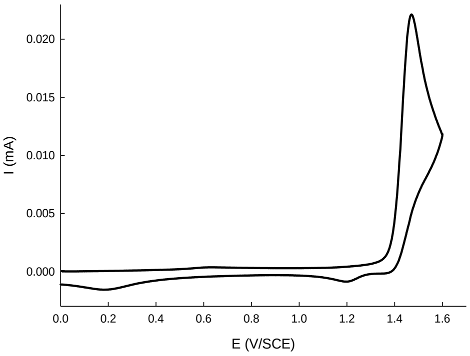

I (mA)
0.015
0.010
0.005
0.000
-0.005
0.0
0.5
1.0
1.5
2.0
E (V/SCE)

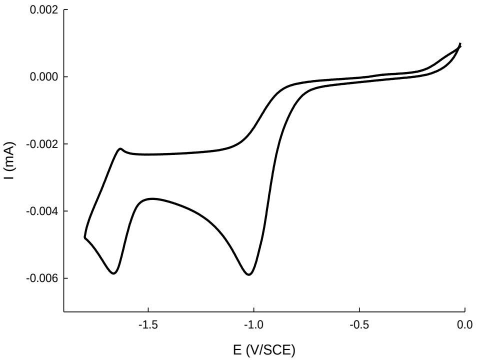

I (mA)
0.000
-0.002
-0.004
-0.006
-0.008
-0.010
-0.012
-1.4
-1.2
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
E (V/SCE)


N
S
NC
CN

6


1.2
1.0
0.8
0.6
0.4
0.2
0.0
A (Normalized)
300
400
500
600
700
800
λ (nm)
Solution (in DCM)
Film


0.020
0.015
0.010
0.005
0.000
I (mA)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
E (V/SCE)


0.002
0.000
-0.002
-0.004
-0.006
I (mA)
-1.5
-1.0
-0.5
0.0
E (V/SCE)