# **Supporting Information**

# Increased short circuit current in an azafullerene-based organic solar cell

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#### 1. General

Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. All <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker Avance 300, Bruker Avance 400 or Joel EX400 instruments, at constant temperature of 298 K. Chemical shifts are reported in parts per million and referenced to residual solvent (<sup>1</sup>H: CDCl<sub>3</sub>, 7.24 ppm; <sup>13</sup>C: CDCl<sub>3</sub>, 77.23 ppm). Coupling constants (*J*) are reported in Hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: m = multiplet, quint. = quintet, q = quartet, t = triplet, d = doublet, s = singlet, b = broad. CDCl3 (99.8%, Deutero GmbH) was stored over 4 Å molecular sieves. UV-Vis measurements were carried out on a Varian Cary 5000 UV- Vis-NIR spectrophotometer at rt. Mass spectra were obtained from a Bruker 9.4T Apex-Qe FTICR (MALDI, Matrix: DCTB), Bruker micro TOF II, and Bruker maxis 4G (APPI, ESI, in MeOH/ACN) instruments. IR spectra were recorded on a Bruker Tensor 27- IR spectrometer as solids in ATR-mode. Cyclic voltammograms were recorded under nitrogen atmosphere using a BAS CV-50W potentiostat and a three electrode setup, with Pt-disk (working), Pt-wire (auxiliary), and Ag/AgNO<sub>3</sub> electrode (reference). Potentials are referenced to the ferrocenium/ferrocene (Fc/Fc+) couple used as an internal standard. TLC analyses were carried out on TLC plates from Macherey-Nagel (ALUGRAM<sup>®</sup> SIL G/UV254) and visualized via UV-light (264/364 nm) or standard coloring reagents. Column chromatography was performed using Silica Gel 60M (Merck).

#### 2. Synthetic procedures and spectral data

 $C_{60}$ -N-MEM-Ketolactam <sup>1</sup> and (dodecyloxy)benzene<sup>2</sup> were prepared according to literature procedures.

**DPC**<sub>59</sub>**N**: In a dry 50 mL round bottom flask the C<sub>60</sub>-N-MEM-Ketolactam (60 mg, 0.070 mmol, eq. 1) was dissolved in ODCB (15 mL). To this solution dodecyloxy)benzene (0.183 g, 0.701 mmol, 10 eq.) and p-TsOH (0.133 g, 0.701 mmol, 10 eq.) were added and this solution was

stirred at 150°C on a pre-heated Heat-On block for 23 minutes. The progress of the reaction was monitored by analytical HPLC (COSMOSIL, toluene, 1.0 mL/min) or TLC (toluene/EtOAc 9:1).

After quick cooling to room temperature, the reaction mixture was directly subjected to flash column chromatography (4 x 15 cm, 40 g SiO<sub>2</sub>, toluene). For further purification the solvents were removed under reduced pressure at ambient temperature and purified by the means of preparative HPLC (COSMOSIL, toluene, 15 mL/min,  $R_t = 5.9$  min) and precipitation from *n*-pentane.



Yield: 25.7 mg, 26.2 mmol, 37%

<sup>1</sup>H NMR (400 MHz, 295 K, CDCl<sub>3</sub>): δ = 8.76 (d, J = 8.7 Hz, 1H), 7.38 (d, J = 8.8 Hz, 1H), 4.18 (t, J = 6.5 Hz, 2H), 1.98 − 1.85 (m, 2H), 1.61 − 1.52 (m, 2H), 1.32 − 1.25 (m, 16H), 0.90 − 0.86 (m, 3H).

<sup>13</sup>**C NMR (101 MHz, 295 K, CDCl<sub>3</sub>):** δ = 160.5, 154.8, 149.3, 147.9, 147.9, 147.5, 147.5, 146.9, 146.7, 146.5, 146.1, 146.1, 145.9, 145.3, 145.3, 144.6, 144.3, 143.4, 143.0, 142.3, 142.0, 141.8, 141.6, 141.2, 141.1, 140.0, 137.8, 133.5, 133.2, 128.8, 124.3, 115.9, 82.8, 68.5, 31.9, 29.7, 29.6, 29.6, 29.4, 29.3, 29.3, 26.1, 22.7, 14.1.

HRMS (APPI) for C<sub>77</sub>H<sub>29</sub>NO: calc.: 983.2249

found: 983.2244

**UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>)**:  $\lambda_{max}$  ( $\epsilon$  [M<sup>-1</sup>cm<sup>-1</sup>]) = 259 (111670), 321 (34107), 445 (6187), 498 (1494), 698 (584).

IR (ATR, rt):  $\tilde{v} = 647$ , 718, 822, 900, 966, 1175, 1248, 1423, 1507, 2849, 2918, 3035, 3068, 3121, 3245 cm<sup>-1</sup>.



Figure S1: IR spectrum of DPC<sub>59</sub>N.

# 3. Cyclic voltammetry



Figure S2: CV spectrum of DPC<sub>59</sub>N





Cyclic voltammogram of **DPC**<sub>59</sub>**N** and **PC**<sub>60</sub>**BM** (10<sup>-3</sup> mol/L) in ODCB with Fc/Fc<sup>+</sup> as internal standard and a scan rate of 150 mV/s (supporting electrolyte: 0.1 M (Bu)<sub>4</sub>N·BF<sub>4</sub>; working electrode: Pt; counter electrode: Pt wire; reference electrode: Ag/AgNO<sub>3</sub>.

# DPC59N :

The first reduction takes place at 1173 mV and the estimated value for the LUMO energy level vs. vacuum, determined by the equation LUMO energy level =  $-(4.80 + E_{1/2}^{red1})$ , is - 3.63 eV.

## PC60BM:

The first reduction takes place at 1215mV and the estimated value for the LUMO energy level vs. vacuum, determined by the equation LUMO energy level = -(4.80 +  $E_{1/2}^{red1}$ ), is - 3.59 eV.

#### 4. General procedure for determination of absorptivity coefficients (ε)

Compound **DPC**<sub>59</sub>**N** (3.60 mg) was dissolved in  $CH_2Cl_2$  and treated with ultrasound for 45 minutes. This stock solution was further diluted to concentrations between 7.311 x  $10^{-6}$  mol/L and 9.15 x  $10^{-7}$  mol/L in order that all measurements obey the Beer-Lambert law.

The absorptivity coefficient was determined by plotting the absorbance *vs.* the concentration. According to the Beer-Lambert law the slope of the linear regression correlates with the absorptivity coefficient.



Figure S4: Representative dilution series for obtaining absorptivity coefficients (ε)

The absorptivity coefficients of other wavelengths were determined in the same manner.







Figure S6: UV-Vis spectrum of PCBM

# 5. HPLC chromatogram of pristine DPC<sub>59</sub>N

(COSMOSIL BUCKYPREP, toluene, 1 mL/min, Rt = 4.5 min)



Figure S7: HPLC chomatomagramm of pristine DPC<sub>59</sub>N.

6. NMR spectra of DPC<sub>59</sub>N



Figure S9: <sup>13</sup>C NMR of compound DPC<sub>59</sub>N (101 MHz, CDCl<sub>3</sub>, 295 K)

## 7. Solar cell devices fabrication and characterization

#### General:

P3HT was purchased from the American dye source (American dye source, Inc., Canada) and was used without further purification. PC<sub>60</sub>BM was purchased from Solenne (Solenne BV, the Netherlands). High purity solvents (>99%) were used for the active layer deposition. Aluminium (99.999%) and LiF (99.995%) were purchased from Sigma-Aldrich.

# **Device Fabrication:**

Pre-patterned Indium Tin Oxide (ITO) 5 Ohm/square (PSiOTec, Ltd., UK) sodalime glass substrates were first rinsed with acetone to remove the residual photoresist layer. The substrates were then placed in a teflon holder and sequentially sonicated in acetone (1 x 10 min) and isopropanol (2 x 10 min), and finally dried under a flow of Nitrogen. The ITO substrates where ozone-treated in a UV-ozone cleaner for 30 mins in ambient atmosphere, and subsequently coated in air with a filtered (0.45 cellulose layer of um. acetate) solution of Polv(3.4ethylenedioxythiophene) : poly(styrenesulfonate) (PEDOT:PSS, HC Starck Baytron P) (4500 rpm 30 seconds followed by 3500 rpm 30 seconds). The PEDOT:PSS film was dried at 120 °C under inert atmosphere for 15 min. Active layers were spincoated (1200 rpm 60 seconds for a 80 nm thin film) in a Nitrogen atmosphere glove box ( $O_2 < 0.1$  ppm;  $H_2O < 0.1$  ppm) over the PEDOT:PSS layer from a 20 mg/ml (total concentration) solution of P3HT and fullerene. The cathode layer was deposited by thermal evaporation in an ultra high vacuum chamber (1x10<sup>-6</sup> mbar). Metals were evaporated through a shadow mask leading to devices with an area of 9 mm<sup>2</sup>. LiF (0.8 nm) and AI (80 nm) were deposited at a rate of 0.1 Å/s and 0.5-1 Å/s respectively. Devices were subsequently thermally annealed at a temperature ranging from 80 to 140°C. Following fabrication, the devices were maintained under a Nitrogen atmosphere and stored in the dark until used.

#### Device Characterization:

The UV-Vis absorption of films was measured using a Shimadzu UV-1700 spectrophotometer. The *J*-*V* characteristics of the devices were measured using a Sun 2000 Solar Simulator (150 W, ABET Technologies). The illumination intensity was measured to be 100 mW/cm<sup>2</sup> with a calibrated silicon photodiode (NREL). The appropriate filters were utilised to faithfully simulate the AM 1.5G spectrum. The applied potential and cell current were measured with a Keithley 2400 digital source meter. The current to voltage (*J*–*V* curve) was plotted automatically with a home-built Labview© software. The IPCE (Incident Photon to Current conversion Efficiency) was measured using a home made set up consisting of a 150 W Oriel Xenon lamp, a motorized monochromator and a Keithley 2400 digital source meter. The photocurrent and irradiated light intensity were measured simultaneously and processed with a home-built Labview© software.

The thickness of the films was measured with a stylus profilometer Ambios Tech. XP-1, from a scratch made in the middle of the film.

# Device active layer thickness, annealing temperature and processing solvent optimization:

The optimization of the active layer blend of P3HT:DPC<sub>59</sub>N was carried out by adjusting the ratio between polymer and fullerene as well as the thickness of the film. The effect of thermal annealing on device performance was also investigated, with temperatures ranging from 80°C to 140 °C. Results are summarised in tables S1 to S5, where the best efficiencies are reported.

Several combinations of solvents were assessed: pristine chlorobenzene (CB) and binary mixtures of CB with1,2-dichlorobenzene (ODCB) or carbon disulfide (CS<sub>2</sub>). The use of 1,8-diiodooctane (DIO) as a solvent additive was also investigated. The different blends were kept stirring continuously at 50 °C from one day to a week, prior to active layer deposition, after which time an evident evolution in device performance was observed (Table S4, Figure S12 and Figure S14).

The analysis of the P3HT:DPC<sub>59</sub>N active layer films by optical microscopy revealed that aggregates, attributed to DPC<sub>59</sub>N, were present in the films. The amount of

aggregates was seen to decrease gradually with stirring time, however some aggregates were still detected even after one week of continuous stirring (see pictures in Figure S10 and S11). The use of  $CS_2$  in the binary mixture  $CB:CS_2$  produced fewer aggregates compared to the other solvent systems, leading to higher FF with respect to devices processed from pristine CB, although the  $J_{SC}$ , and thus the efficiency, remained lower.

D:A (wt:wt)	Jsc (mA/cm²)	Voc (V)	FF (%)	PCE (%)
1:0.4	5.55	0.524	40.55	1.18
1:0.6	6.50	0.553	32.93	1.18
1:0.8	6.46	0.556	43.10	1.55
1:1	6.83	0.552	44.99	1.70

Table S1: D:A ratio optimization.

Annealing temperature: 110 °C ; Active layer thickness: 80 nm ; Solvent: CB.

Solvent	Annealing temperature	Jsc (mA/cm²)	Voc (V)	FF (%)	PCE (%)
CB + DIO*	0°C	5.29	0.486	40.06	1.03
CB + DIO*	80 °C	6.59	0.499	45.99	1.51
CB + DIO*	110 °C	7.64	0.519	49.19	1.95
CB + DIO*	140 °C	3.78	0.502	36.13	0.69
СВ	110 °C	7.19	0.560	51.36	2.07

Table S2: annealing temperature optimization.

D:A ratio 1:1 ; Active layer thickness: 80 nm.

\* 3% vol.

Jsc (mA/cm²)	Voc (V)	FF (%)	PCE (%)
5.33	0.517	47.88	1.32
6.82	0.514	49.16	1.72
7.64	0.519	49.19	1.95
	Jsc (mA/cm²) 5.33 6.82 7.64	Jsc (mA/cm²)Voc (V)5.330.5176.820.5147.640.519	Jsc (mA/cm²)Voc (V)FF (%)5.330.51747.886.820.51449.167.640.51949.19

Table S3: active layer thickness optimization.

D:A ratio 1:1 ; Annealing temperature: 110 °C ; Solvent: CB + DIO (3% vol.).

Table S4: blend stirring time optimization.

Blend stirring time	Jsc (mA/cm²)	Voc (V)	FF (%)	PCE (%)
1 day	6.83	0.552	44.99	1.70
2 days	7.19	0.560	51.36	2.07
6 days	8.27	0.560	50.21	2.33
8 days	8.39	0.578	49.92	2.42

D:A ratio 1:1 ; Annealing temperature: 110 °C ; Active layer thickness: 80 nm ; Solvent: CB.

# Table S5: solvent optimization.

Solvent	Jsc (mA/cm²)	Voc (V)	FF (%)	PCE (%)
СВ	8.39	0.578	49.92	2.42
CB + DIO*	7.64	0.519	49.19	1.95
CB : CS <sub>2</sub> **	7.28	0.574	53.43	2.23
CB : ODCB**	1.72	0.531	21.46	0.20

D:A ratio 1:1 ; Annealing temperature: 110 °C ; Thickness: 80 nm. \* (3% vol.) ; \*\* (50:50 v/v).



**Figure S10:** Optical micrographs of the active layers processed from pristine CB after (a) 1 day, (b) 2 days and (c) 6 days of continuous stirring before deposition.



**Figure S11:** Optical micrographs of the active layers processed from (a) pristine CB, (b) CB:CS<sub>2</sub> (50:50 v/v) and (c) CB:ODCB (50:50 v/v) after several days of continuous stirring before deposition.



Figure S12: J-V characteristics of devices reported in Table S4.



Figure S13: J-V characteristics of devices reported in Table S5.



**Figure S14:** Evolution of the main parameters in P3HT:DPC<sub>59</sub>N based solar cells with blend stirring time (ref. Table S4).

**Table S6** *J-V* parameters of best-performing devices. Shockley parameters derived from the electrical characteristics in the dark: reverse saturation current density  $J_0$ , series resistance R<sub>S</sub>A, and shunt resistance R<sub>P</sub>A.

Acceptor	J <sub>sc</sub> (mA/cm²)	V <sub>oc</sub> (V)	FF (%)	PCE (%)	Device area A (cm <sup>2</sup> )	J <sub>0</sub> (nA/cm²)	R <sub>s</sub> A (Ω cm²)	R⊧A (MΩ cm²)
DPC <sub>59</sub> N	8.39	0.578	50	2.42	0.09	3	5.3	6.4
PC <sub>60</sub> BM	7.54	0.616	58	2.70	0.09	12	1.6	1.8

Donor/acceptor ratio: 1:1. Solvent: chlorobenzene. Active layer thickness: 80 nm.

## 8. References

<sup>&</sup>lt;sup>1</sup> J.C.Hummelen, B. Knight, J. Pavlovich, R.Gonzales, F.Wudl Science, **1995**, 269, 1553.

<sup>&</sup>lt;sup>2</sup> Fuji PhotoFilm Co LTD Patent US 2006/68997