Supporting Information
for DOI: 10.1055/s-0036-1591871
© Georg Thieme Verlag KG Stuttgart · New York 2018
Supporting Information

Second Generation Azafullerene Monoadducts as Electron Acceptors in Bulk Heterojunction Solar Cells

Michael Bothe\textsuperscript{a}, María Pilar Montero-Rama\textsuperscript{b}, Aurélien Viterisi\textsuperscript{b}, Werther Cambarau\textsuperscript{c}, Caterina Stenta\textsuperscript{b}, Emilio Palomares\textsuperscript{c}, Lluis F. Marsal\textsuperscript{b,\ast}, Max von Delius\textsuperscript{b,\ast}

\textsuperscript{a} Institute of Organic Chemistry and Advanced Materials, University of Ulm, Albert-Einstein-Allee 11, 89081 Ulm, Germany

\textsuperscript{b} Department d’Enginyeria Electrònica, Elèctrica i Automàtica, Universitat Rovira i Virgili, Avda. Països Catalans 16, 43007 Tarragona, Spain

\textsuperscript{c} Institute of Chemical Research of Catalonia (ICIQ), Avda. Països Catalans 26, 43007 Tarragona, Spain

max.vondelius@uni-ulm.de

lluis.marsal@urv.cat

Contents

1. General .................................................................................................................................................. S2

2. NMR spectra .......................................................................................................................................... S3

3. UV-Vis spectra ....................................................................................................................................... S14

4. HPLC chromatograms ......................................................................................................................... S16

5. Cyclic voltammetry .............................................................................................................................. S17

6. Solar cell device fabrication and characterization ................................................................................. S20
1. General

Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. C₆₀ and PCBM were purchased from IoLiTec Liquids Technologies GmbH. HPLC grade solvents were used for reactions with fullerenes.

¹H and ¹³C spectra were recorded on Bruker Avance 300 (¹H: 300 MHz, ¹³C: 75 MHz), Bruker Avance 400 (¹H: 400 MHz, ¹³C: 100 MHz) and Jeol EX400 (¹H: 400 MHz, ¹³C: 100 MHz) instruments at room temperature. Chemical shifts are given in parts per million and referenced to residual solvent (¹H: CDCl₃, 7.24 ppm; ¹³C: CDCl₃: 77 ppm). Coupling constants (J) are denoted in Hertz (Hz). Abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, b = broad. NMR spectra of azafullerenes were measured in solvent mixtures of CDCl₃ and CS₂ (v/v: 2/1).

Qualitative UV-Vis measurements were carried out on a Varian Cary 5000 UV-Vis-NIR spectrophotometer in dichloromethane at room temperature. Mass spectra were obtained on Bruker Maxis 4G (HRMS-APPI, toluene) and Thermo Scientific ISQ LT (EI) instruments. Cyclic voltammograms were recorded under nitrogen or argon atmosphere using a BAS CV-50W potentiostat and a three electrode setup (working electrode: Pt-disk, auxiliary electrode: Pt-wire, reference electrode: Ag/AgNO₃ or silver wire, supporting electrolyte: tetrabutylammonium hexafluorophosphate (0.1 mol/L), solvent: o-dichlorobenzene (ODCB), scan rate: 50 mV/sec). Potentials are referenced to the ferrocene/ferricenium couple as internal standard (Fc/Fc⁺). Estimated LUMO energy levels vs. vacuum were calculated according to \( E_{\text{LUMO}} = - (4.8 + E_{1/2}^{\text{red1}}) \) eV with \( E_{1/2}^{\text{red1}} = (E_{\text{p,c}} + E_{\text{p,a}}) / 2 \). TLC analyses were carried out on TLC plates from Macherey-Nagel (Alugram® SIL G/UV254) and visualized via UV-light (254/365 nm) or standard stains. Column chromatography was performed using Silica Gel 60M (Merck). Analytical HPLC was conducted on a Shimadzu instrument (COSMOSIL BUCKYPREP, toluene, 1.0 mL/min). Crude azafullerenes were purified by means of preparative HPLC using a Shimadzu instrument (COSMOSIL BUCKYPREP, toluene, flow rate: 18 mL/min).
2. NMR spectra

$^1$H-NMR spectrum (400 MHz, 298 K, CDCl$_3$) of n-dodecylphenylsulfide, 3.

$^{13}$C-NMR spectrum (100 MHz, 298 K, CDCl$_3$) of n-dodecylphenylsulfide 3.
$^1$H-NMR spectrum (400 MHz, 298 K, CDCl$_3$) of 7-(bromomethyl)-pentadecane S1.

$^{13}$C-NMR spectrum (100 MHz, 298 K, CDCl$_3$) of 7-(bromomethyl)-pentadecane S1.
$^1$H-NMR spectrum (400 MHz, 298 K, CDCl$_3$) of (2-hexyldecyl)oxybenzene 4.

$^{13}$C-NMR spectrum (100 MHz, 298 K, CDCl$_3$) of (2-hexyldecyl)oxybenzene 4.
\[\text{H-NMR spectrum (400 MHz, 298 K, CDCl}_3\text{)}\] of 1,2-dibutoxybenzene 5.

\[\text{\textsuperscript{13}C-NMR spectrum (100 MHz, 298 K, CDCl}_3\text{)}\] of 1,2-dibutoxybenzene 5.
$^1$H-NMR spectrum (400 MHz, 298 K, CDCl$_3$) of 1,2-dihexyloxybenzene 6.

$^{13}$C-NMR spectrum (100 MHz, 298 K, CDCl$_3$) of 1,2-dihexyloxybenzene 6.
1H-NMR spectrum (400 MHz, 298 K, CDCl₃) of 2-methoxy-ethoxy-methyl azide 1.

13C-NMR spectrum (100 MHz, 298 K, CDCl₃) of 2-methoxy-ethoxy-methyl azide 1.
$^1$H-NMR spectrum (400 MHz, 298 K, CDCl$_3$/CS$_2$ 2:1) of C$_{60}$-N-MEM-ketolactam 2.

$^{13}$C-NMR spectrum (400 MHz, 298 K, CDCl$_3$/CS$_2$ 2:1) of C$_{60}$-N-MEM-ketolactam 2.
\[ ^1H\text{-NMR spectrum (400 MHz, 298 K, CDCl}_3\text{)}\] of C_{59}NPhSC_{12}H_{25}, \text{DPS-C}_{59}\text{N.}

\[ ^{13}\text{C-NMR spectrum (100 MHz, 298 K, CDCl}_3/\text{CS}_2\text{ 2:1)}\] of C_{59}NPhSC_{12}H_{25}, \text{DPS-C}_{59}\text{N.}
$^1$H-NMR spectrum (400 MHz, 298 K, CDCl$_3$/CS$_2$ 2:1) of C$_{60}$NPhCH$_2$CH(C$_6$H$_{13}$)(C$_8$H$_{17}$), HDP-C$_{60}$N.

$^{13}$C-NMR spectrum (100 MHz, 298 K, CDCl$_3$/CS$_2$ 2:1) of C$_{60}$NPhCH$_2$CH(C$_6$H$_{13}$)(C$_8$H$_{17}$), HDP-C$_{60}$N.
$^1$H-NMR spectrum (400 MHz, 298 K, CDCl$_3$/CS$_2$ 2:1) of C$_{59}$NPh(OC$_4$H$_9$)$_2$, DBOP-C$_{59}$N.

$^{13}$C-NMR spectrum (100 MHz, 298 K, CDCl$_3$/CS$_2$ 2:1) of C$_{59}$NPh(OC$_4$H$_9$)$_2$, DBOP-C$_{59}$N.
$^{1}$H-NMR spectrum (400 MHz, 298 K, CDCl$_3$/CS$_2$ 2:1) of C$_{60}$NPh(OC$_6$H$_{13}$)$_2$, DHOP-C$_{60}$N.

$^{13}$C-NMR spectrum (100 MHz, 298 K, CDCl$_3$/CS$_2$ 2:1) of C$_{60}$NPh(OC$_6$H$_{13}$)$_2$, DHOP-C$_{60}$N.
3. UV-Vis spectra

UV-Vis spectrum (CH$_2$Cl$_2$) of C$_{59}$NPhSC$_{12}$H$_{25}$, DPS-C$_{59}$N.

UV/Vis spectrum (CH$_2$Cl$_2$) of C$_{59}$NPhCH$_2$CH(C$_6$H$_{13}$)(C$_8$H$_{17}$), HDP-C$_{59}$N.
UV-Vis spectrum (CH$_2$Cl$_2$) of C$_{60}$NPh(OCH$_3$)$_2$, DBOP-C$_{60}$N.

UV-Vis spectrum (CH$_2$Cl$_2$) of C$_{60}$NPh(OCH$_3$)$_2$, DHOP-C$_{60}$N.
4. HPLC chromatograms

HPLC chromatogram of pristine **DPS-C$_{60}$N** (COSMOSIL BUCKYPREP, toluene, 1 mL/min, Rt = 4.5 min).

HPLC chromatogram of pristine **HDP-C$_{60}$N** (COSMOSIL BUCKYPREP, toluene, 1 mL/min, Rt = 4.1 min).

HPLC chromatogram of pristine **DBOP-C$_{60}$N** (COSMOSIL BUCKYPREP, toluene, 1 mL/min, Rt = 4.3 min).

HPLC chromatogram of pristine **DHOP-C$_{60}$N** (COSMOSIL BUCKYPREP, toluene, 1 mL/min, Rt = 4.1 min).
5. Cyclic voltammetry

Cyclic voltammogram of **PCBM** (10^{-3} mol/L) in ODCB with Fc/Fc^+ as internal standard; scan rate: 50 mV/s; supporting electrolyte: 0.1 M (Bu)_4N·PF_6; working electrode: Pt; counter electrode: Pt wire; reference electrode: Ag/AgNO_3.

Cyclic voltammogram of **DPS-C_{59}N** (10^{-3} mol/L) in ODCB with Fc/Fc^+ as internal standard; scan rate: 50 mV/s; supporting electrolyte: 0.1 M (Bu)_4N·PF_6; working electrode: Pt; counter electrode: Pt wire; reference electrode: Ag/AgNO_3.
Cyclic voltammogram of HDP-C$_{59}$N (10$^{-3}$ mol/L) in ODCB with Fc/Fc$^+$ as internal standard; scan rate: 50 mV/s; supporting electrolyte: 0.1 M (Bu)$_4$NPF$_6$; working electrode: Pt; counter electrode: Pt wire; reference electrode: Ag/AgNO$_3$.

Cyclic voltammogram DBOP-C$_{59}$N (10$^{-3}$ mol/L) in ODCB without Fc/Fc$^+$ as internal standard (referenced to the spectrum below); scan rate: 50 mV/s; supporting electrolyte: 0.1 M (Bu)$_4$NPF$_6$; working electrode: Pt; counter electrode: Pt wire; reference electrode: Ag/AgNO$_3$. 

S18
Cyclic voltammogram **DBOP-C$_9$N $3$** ($10^{-3}$ mol/L) in ODCB with Fc/Fc$^+$ as internal standard; scan rate: 50 mV/s; supporting electrolyte: 0.1 M (Bu)$_4$N·PF$_6$; working electrode: Pt; counter electrode: Pt wire; reference electrode: Ag/AgNO$_3$. **Note:** irregular shape in the reductive regime likely due to contaminated Pt electrode.

Cyclic voltammogram of **DHOP-C$_9$N** ($10^{-3}$ mol/L) in ODCB with Fc/Fc$^+$ as internal standard; scan rate: 50 mV/s; supporting electrolyte: 0.1 M (Bu)$_4$N·PF$_6$; working electrode: Pt; counter electrode: Pt wire; reference electrode: Ag/AgNO$_3$. 

S19
6. Solar cell device fabrication and characterization

General:

PTB7 was purchased from One Materials (One Materials, inc. Canada) and was used without further purification. High purity (<10 ppm evaporation residue) and low water content (<10 ppm H$_2$O) CHCl$_3$ was used for the active layer deposition. Silver (99.999%) was purchased from Kurt J. Lesker and Calcium (99.5%) was purchased from Sigma-Aldrich.

Device Fabrication:

Prepatterned 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 × 10 min), methanol (1 × 10 min) and isopropanol (1 × 10 min), and finally dried under a flow of Nitrogen. The ITO substrates were ozone-treated in a UV-ozone cleaner for 30 mins in ambient atmosphere, and subsequently coated in air with a layer of filtered (0.45 nm, cellulose acetate) solution of Poly(3,4-ethylenedioxythiophene) : poly(styrenesulfonate) (PEDOT:PSS, HC Starck Baytron P) (4500 rpm 30 sec followed by 3500 rpm 30 sec). The PEDOT:PSS film was dried at 120 ºC under inert atmosphere for 15 min. Active layers were spin-coated (1000, 1300 or 1600 rpm) in air over the PEDOT:PSS layer from a 10 mg/mL (total concentration) solution of PTB7 and the different azafullerenes (1:1 or 2:3 w/w ratio). The cathode layer was deposited by thermal evaporation in an ultra-high vacuum chamber (1 x 10$^{-6}$ mbar). Metals were evaporated through a shadow mask leading to devices with an area of 9 mm$^2$. Calcium (25 nm) and Silver (100 nm) were deposited at a rate of 0.3-0.5 Å/s and 0.5-1 Å/s respectively. Following fabrication, the films 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 PerkinElmer UV-Visible-NIR spectrophotometer (lambda 950). 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$^2$ 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 via AFM, from a scratch made in the middle of the film.

Atomic Force Microscopy (AFM) of the samples was performed in tapping mode on a Molecular Imaging model Pico SPM II (pico+). Images were collected in air using silicon probes with a typical spring constant of 1–5 nN/m and at resonant frequency of 75 kHz.

**Hole and electron mobility:**

Mobility measurements were performed using electron only devices which had an ITO/ZnO/PTB7:Azafullerene/Al structure (Figure X). Thicker metal cathodes (150nm) were used to aid in cooling to prevent damage associated with device heating when measuring at high voltages. Mobility values were obtained by fitting the obtained J-V plots in the SCLC region to a Mott-Gurney as in equation (1) with the static permittivity of the active layer (ε) fixed to 3, μ0 being the zero-field mobility.

\[ J = \frac{9}{8} \left( \frac{\varepsilon \mu_0}{L^3} \right) \times V^2 \]  

(1)

Mobility measurements were repeated at least three times (using different devices) to confirm the reproducibility of the results. High electron mobility Zinc Oxide was deposited via a sol-gel.

---

![Diagram of device architecture and J-V characteristics](image)

**Device architecture used for the electron-only devices and J-V characteristics of electron-only devices made from DHOP-C_{59}N, DBOP-C_{59}N and DPS-C_{59}N.**
AFM Images

3 x 3 μm topography and phase images of active layers made from PTB7 and the corresponding azafullerene: a/a') DHOP-C_{59}N; b/b') DBOP-C_{59}N; c/c') DPS-C_{59}N; d/d') HDP-C_{59}N. Scale bar: 600 nm.

Thickness measurements

AFM images and profiles of scratches applied on active layers deposited in identical conditions as in optimum solar cell devices on top of PEDOT-PSS. The thickness of the active layer was calculated by subtracting the thickness of the PEDOT-PSS layer to the total thickness.