

SUPPORTING INFORMATION for

**Cross-Linkable Azido C₆₀-Fullerene Derivatives for Efficient Thermal Stabilization
of Polymer Bulk-Heterojunction Solar Cells**

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I. Experimental procedures and spectroscopic data:

General procedures: All starting materials were obtained from commercial suppliers and were used without any purification (C_{60} : 99+% MER Corporation). Dichloromethane (HPLC quality and stabilized on amylene) was used as received. Analytical thin layer chromatography was performed on pre-coated silica gel 60-F254 plates. Purifications on column chromatography were carried out on silica gel (60 Å, 230-400 mesh). 1H and ^{13}C NMR spectra (1H : 300 MHz and ^{13}C : 75 MHz) were recorded on a Bruker Avance III 300 spectrometer. Chemical shifts are reported as δ values in parts per million (ppm) relative to the peak of residual $CHCl_3$ as the internal standard. Matrix-assisted laser desorption-ionization (time-of-flight) mass spectrometry (MALDI-TOF) was performed on a Bruker Biflex III MALDI-TOF spectrometer operating in the positive reflection mode and dithranol used as the matrix.

Compound [60]PCB-C₃-N₃ :

To a degassed suspension of [60]PCBA (275 mg, 0.31 mmol) in CH_2Cl_2 (40 mL) were added successively 1-hydroxybenzotriazole (HOBt) (45 mg, 0.33 mmol), N-(3-dimethylaminopropyl) N'-carbodiimide (EDC) (162 μ L, 0.92 mmol), 4-N,N-dimethylaminopyridine (38 mg, 0.31 mmol) then a solution of 3-azidopropan-1-ol (116 mg, 0.93 mmol) in 10 mL of CH_2Cl_2 . The solution was stirred for 2-3 days under argon atmosphere. The solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel using CH_2Cl_2 / Pentane (4/1) as the mixture of eluents. The solvents were concentrated without heating, and compound [60]PCB-C₃-N₃ was isolated as a black powder (240 mg, 80% yield) and kept in 1,2-dichlorobenzene solution at the desired concentration (40 mg/mL).

1H NMR ($CDCl_3$, 300 MHz): δ = 7.94 (d, J = 6.0 Hz, 2H), 7.53 (m, 3H), 4.17 (t, J = 6.3 Hz, 2H), 3.36 (t, J = 6.6 Hz, 2H, CH_2N_3), 2.91 (m, 2H), 2.53 (t, J = 7.2 Hz, 2H), 2.18 (m, 2H), 1.9 (m, 2H).

^{13}C NMR ($CDCl_3$, 75 MHz): 172.9, 148.7, 147.7, 145.8, 145.2, 145.0, 144.8, 144.6, 144.5, 144.4, 144.0, 143.7, 143.0, 142.99, 142.91, 142.2, 142.16, 142.12, 140.9, 140.7, 138.0, 137.5, 136.7, 132.1, 128.4, 128.3, 79.8, 61.5, 51.8, 48.2, 33.9, 33.6, 28.1, 22.3.

MS (MALDI-TOF, pos. mode, dithranol): m/z: 979.13, calcd for: $C_{77}H_{17}N_3O_2$; found: 980.2 [M]⁺.

Compound [60]PCB-C₆-N₃ :

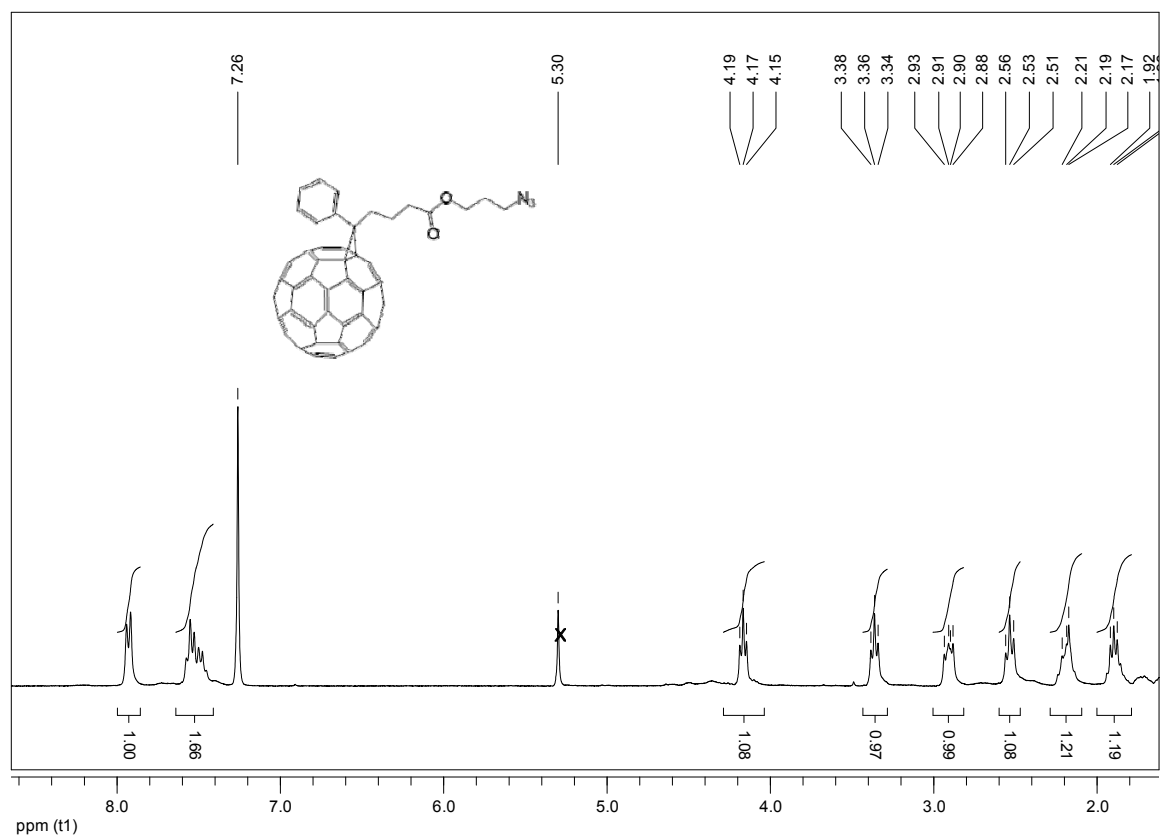
To a degassed suspension of [60]PCBA (275 mg, 0.31 mmol) in CH_2Cl_2 (40 mL) were added successively 1-hydroxybenzotriazole (HOBt) (45 mg, 0.33 mmol), N-(3-dimethylaminopropyl) N'-carbodiimide (EDC) (162 μ L, 0.92 mmol), 4-N,N-dimethylaminopyridine (38 mg, 0.31 mmol) then a solution of 6-azidohexan-1-ol (220 mg, 1.53 mmol) in 10 mL of CH_2Cl_2 . The solution was stirred for 2-3 days under argon atmosphere. The solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel using CH_2Cl_2 / Hexane (7/3) as the mixture of eluents. The solvents were concentrated without heating, and compound [60]PCB-C₆-N₃ was isolated as a black powder (254 mg, 81% yield) and kept in a 1,2-dichlorobenzene solution at the desired concentration (40 mg/mL).

1H NMR ($CDCl_3$, 300 MHz): δ = 7.94 (d, J = 6.9 Hz, 2H), 7.52 (m, 3H), 4.07 (t, J = 6.6 Hz, 2H), 3.26 (t, J = 6.6 Hz, 2H, CH_2N_3), 2.91 (m, 2H), 2.53 (t, J = 7.5 Hz, 2H), 2.23-2.15 (m, 2H), 1.63 (m, 4H), 1.4-1.33 (m, 4H).

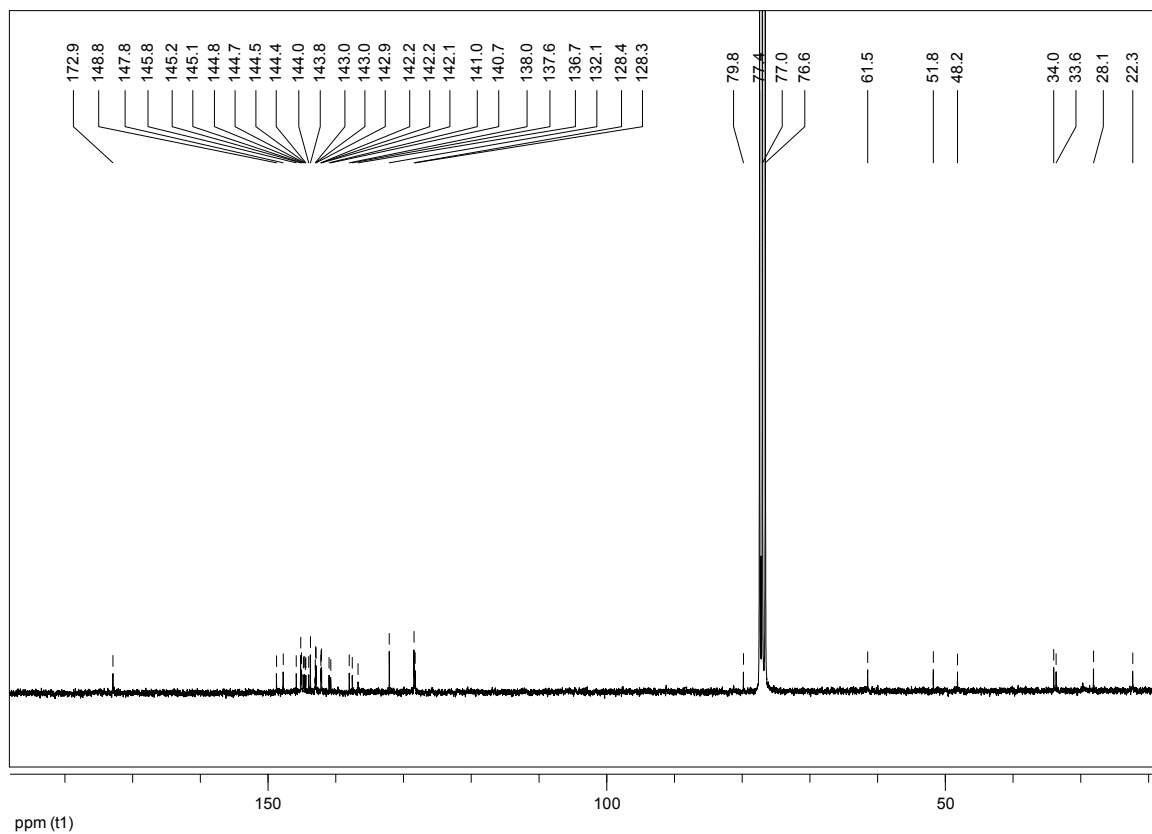
^{13}C NMR ($CDCl_3$, 75 MHz): 173.1, 148.8, 148.0, 145.9, 145.8, 145.3, 145.2, 145.2, 145.1, 145.0, 145.0, 144.8, 144.7, 144.7, 144.6, 144.5, 144.4, 144.0, 143.7, 143.1, 143.02, 142.97, 142.92, 142.90, 142.2, 142.2, 142.1, 142.0, 141.0, 140.7, 138.0, 137.5, 136.7, 132.1, 128.4, 128.2, 79.9, 64.5, 51.8, 51.3, 34.1, 33.6, 28.7, 28.5, 28.4, 26.4, 25.5, 22.4

MS (MALDI-TOF, pos. mode, dithranol): m/z: 1021.18, calcd for: $C_{77}H_{23}N_3O_2$; found: 1022.19 [M]⁺.

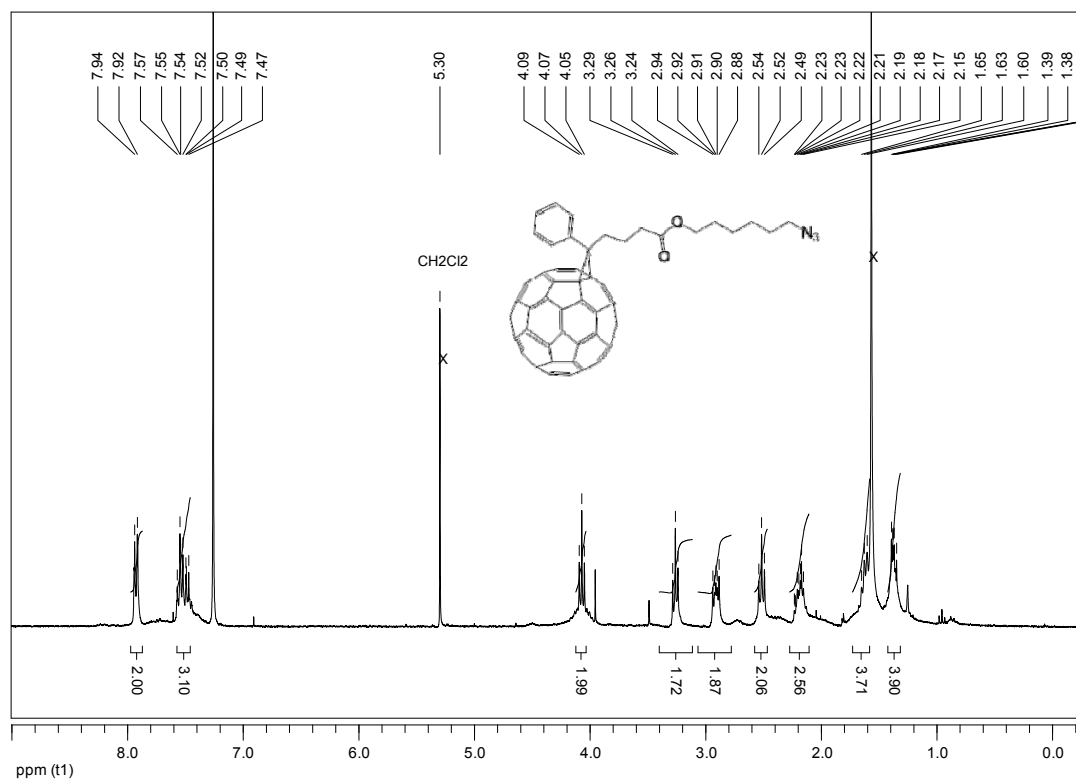
^1H NMR spectrum of [60]PCB-C₃-N₃ (CDCl₃, 300 MHz):



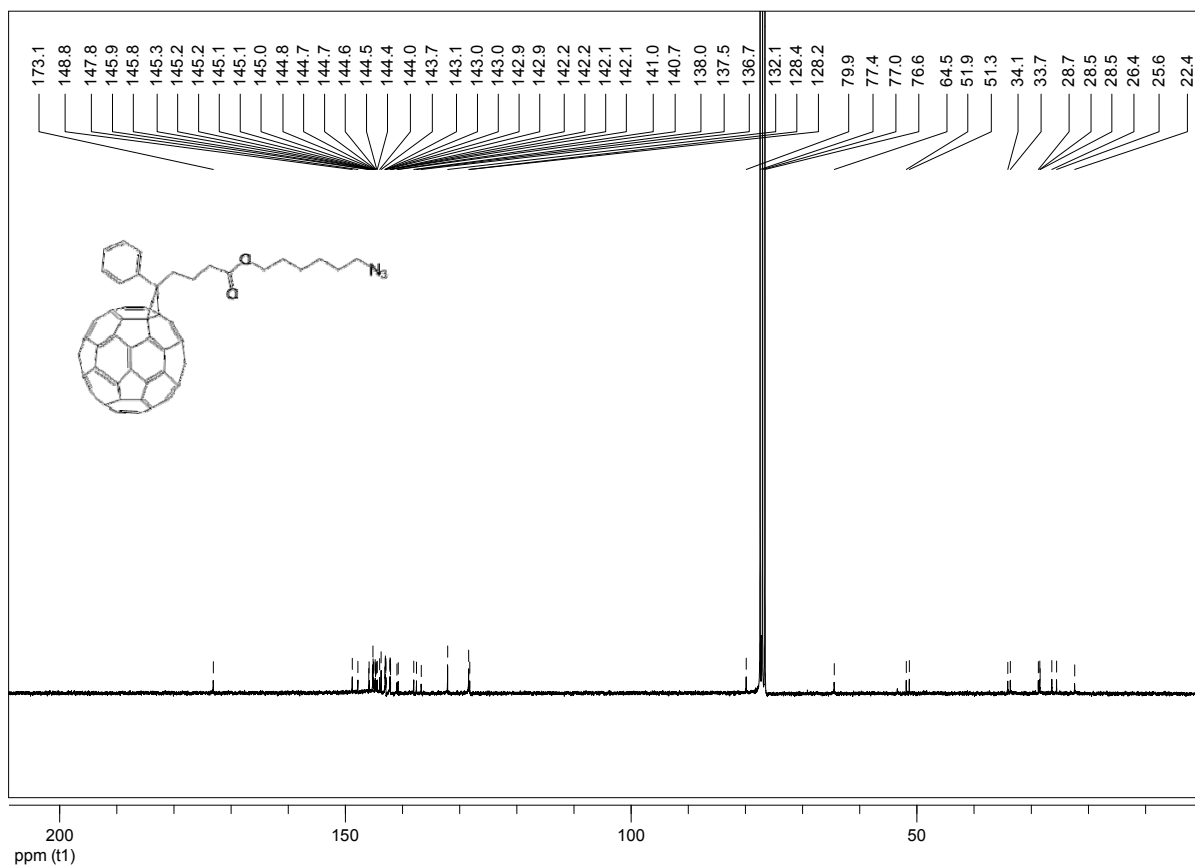
^{13}C NMR spectrum of [60]PCB-C₃-N₃ (CDCl₃, 75 MHz):



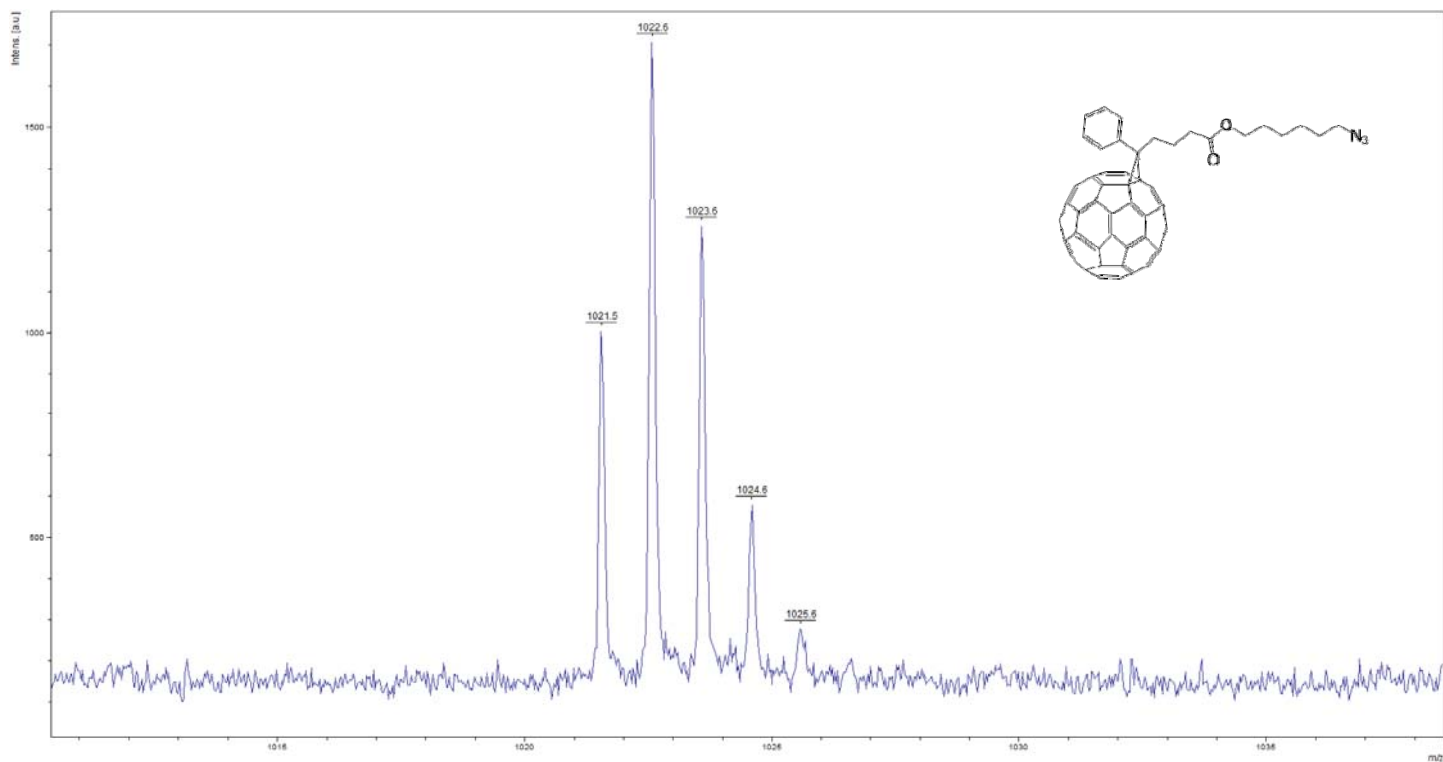
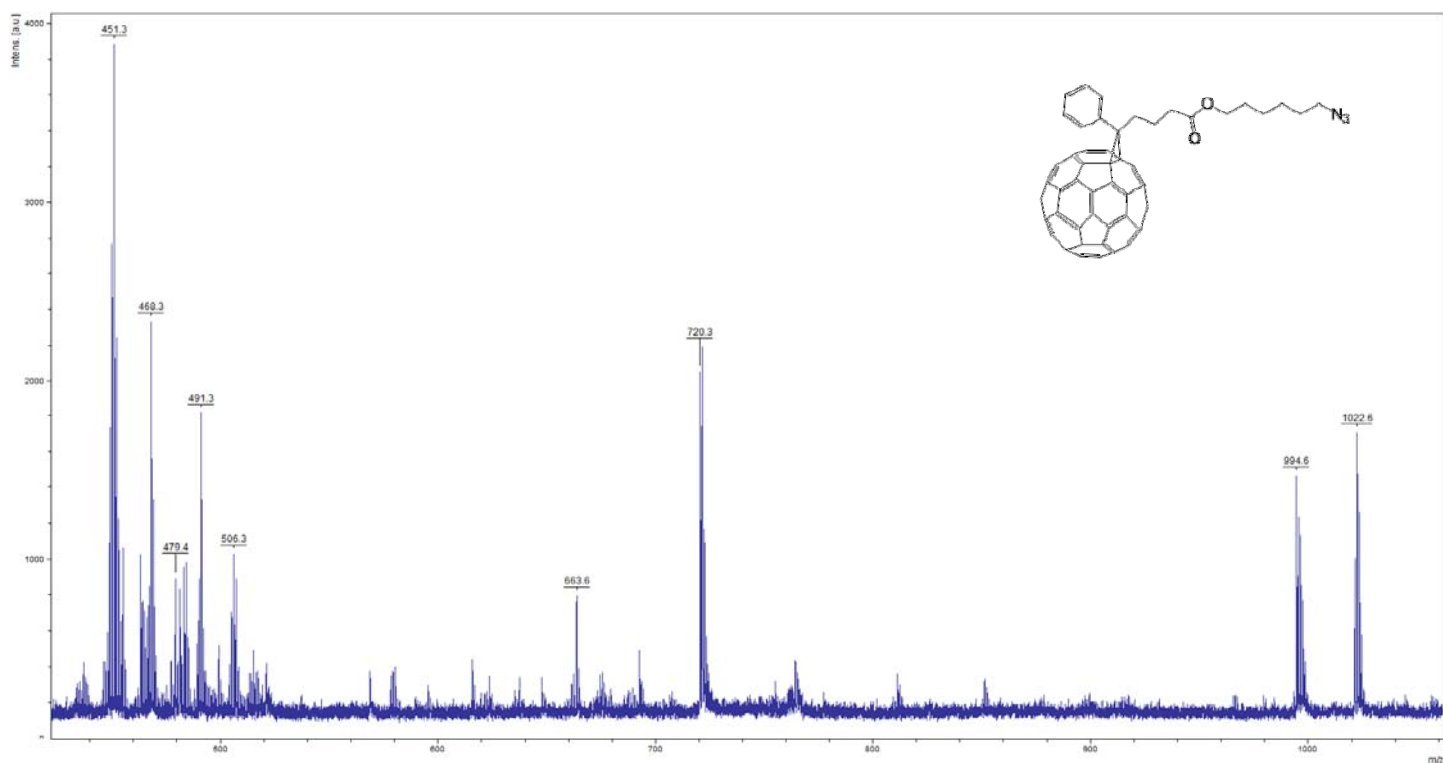
^1H NMR spectrum of [60]PCB-C₆-N₃ (CDCl₃, 300 MHz):



^{13}C NMR spectrum of [60]PCB-C₆-N₃ (CDCl₃, 75 MHz):



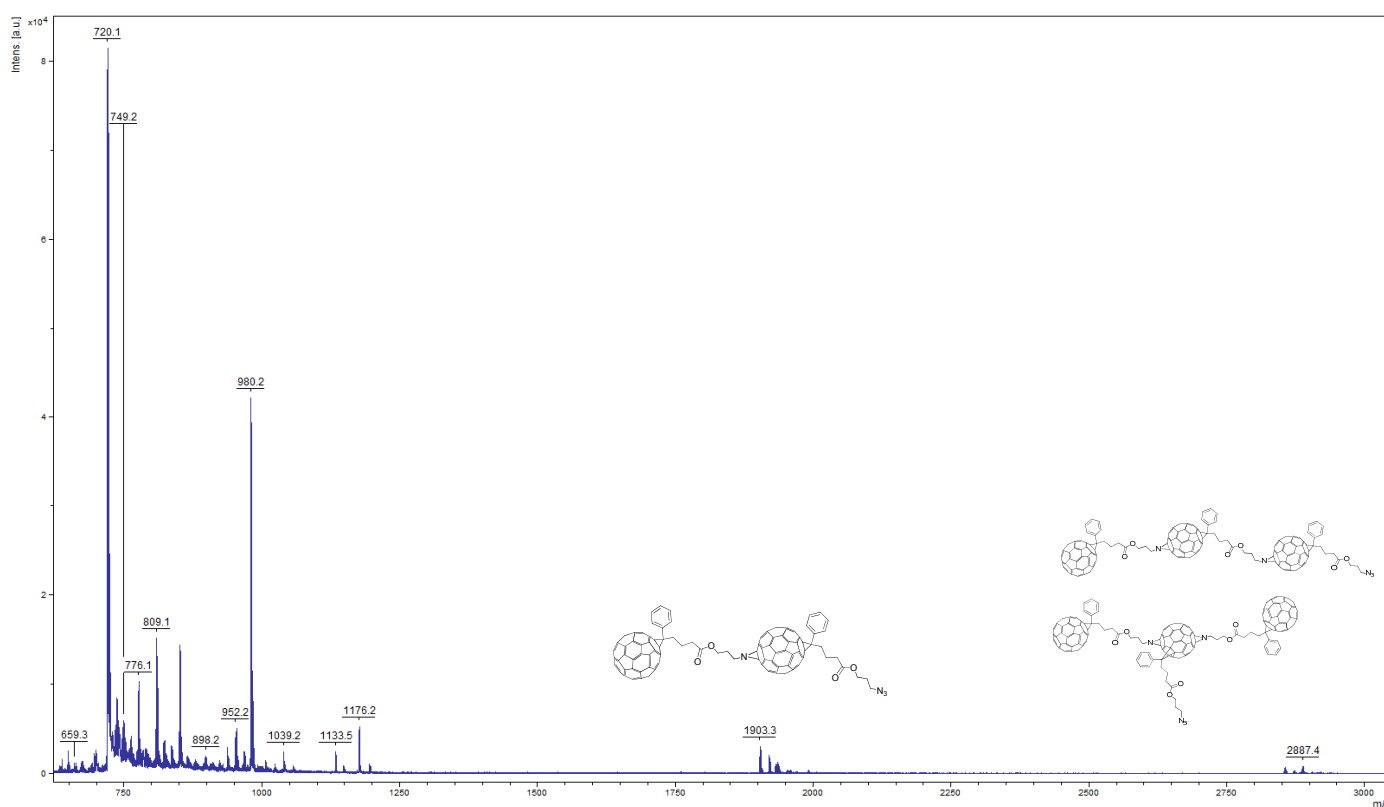
MALDI-TOF spectrum of [60]PCB-C₆-N₃ (matrix = dithranol):



MALDI-TOF spectrum of [60]PCB-C₃-N₃ (matrix = dithranol) after heating in 1,2-dichlorobenzene solution at 150°C:

A solution of PCB-C₃-N₃ was heated at 150°C in 1,2-dichlorobenzene and the resulting material was further analyzed by MALDI-TOF mass spectrometry. Some dimer and trimer structures containing aziridine heterocycles were clearly evidenced resulting from the 1,3-dipolar cycloaddition of the azido group onto the C₆₀ core followed by loss of N₂ from the triazolone intermediate.

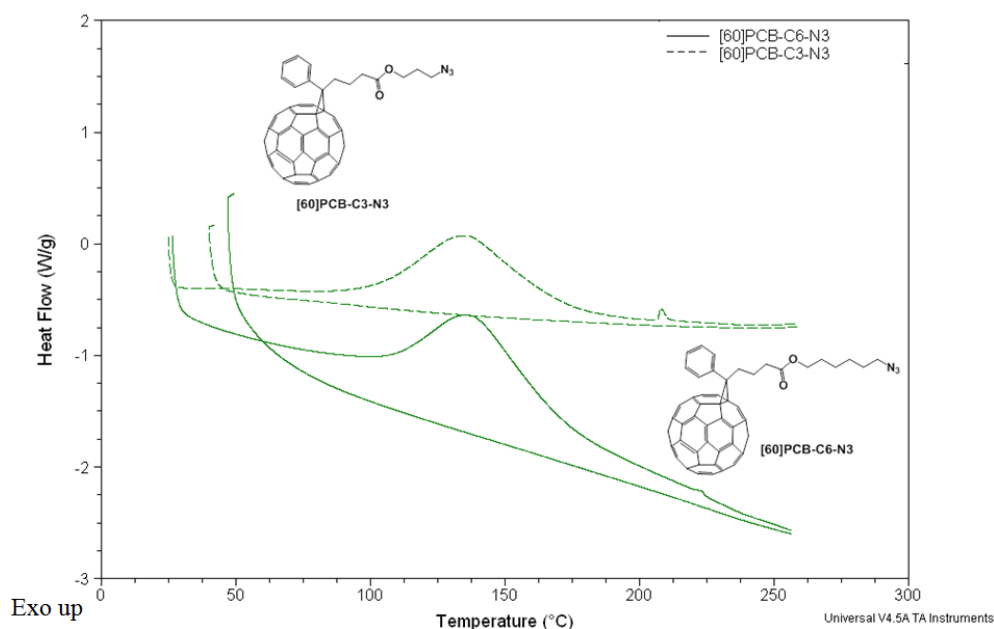
Some structures could be proposed resulting from thermal treatment of [60]PCB-C₃-N₃. No regioselectivity can be announced for this second or third substitution onto C₆₀.



II. DSC (differential scanning calorimetry) spectra

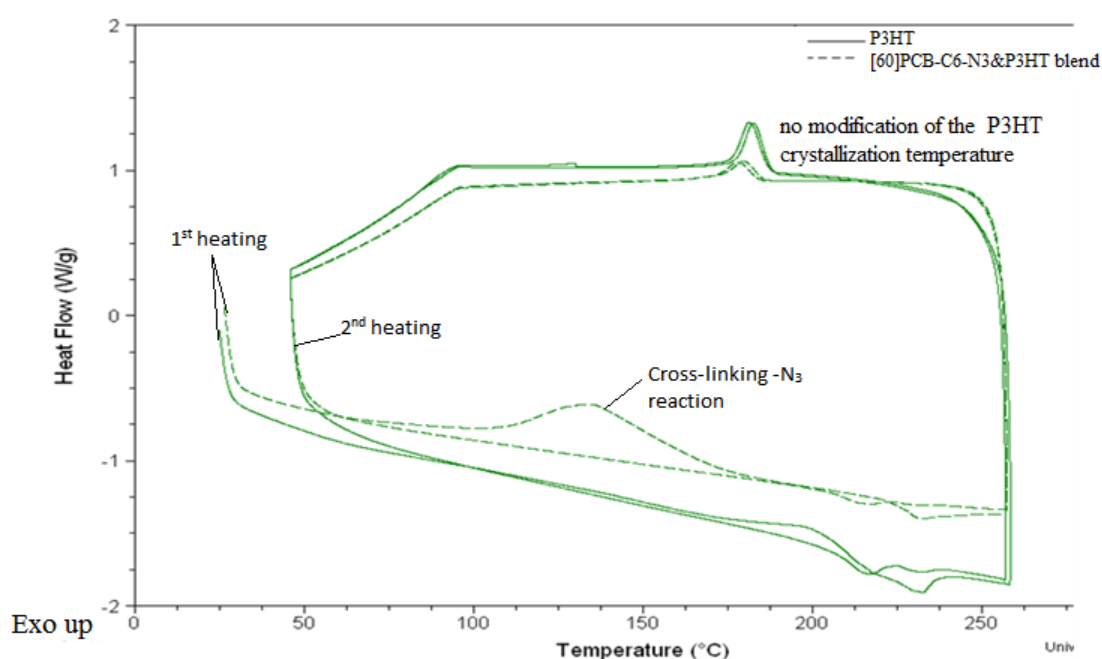
Differential scanning calorimetry (DSC) was conducted using a DSC Q20 (TA Instruments) equipment at heating rate of 10°C/min, using usually 2 cycles of heating and cooling.

DSC spectra of [60]PCB-C₃-N₃ and [60]PCB-C₆-N₃ :



DSC spectra of a mixture P3HT : [60]PCB-C₆-N₃ in a 1:1 weight ratio :

The DSC experiment was designed to prove the selectivity of the azido temperature triggered reaction towards other C₆₀ derivatives. These DSC studies clearly indicated that no reaction occurred between [60]PCB-C₆-N₃ and P3HT polymer. The reaction between the [60]PCB-C₆-N₃ and P3HT would lead to a modification of the physical properties of the polymer (melting/crystallization temperature) as it was reported by Miyanishi *et al.* who described the DSC spectra showing the effect of the cross-linkability on P3HT polymer.¹



¹ S. Miyanishi, K. Tajima and K. Hashimoto, *Macromolecules*, 2009, **42**, 1610.

III. Detailed devices fabrication and characterization

Devices fabrication and characterization: $15 \times 15 \text{ mm}^2$ ITO-coated glass substrates (10 Ohm square, *Kintec*) were successively cleaned by sonication in acetone, ethanol and isopropanol and exposed to UV-ozone for 20 minutes. A thin layer of titanium oxide (15 nm) is prepared as previously described by Chambon *et al.*² and spin-coated on top of ITO-coated glass substrates at 1000 RPM during 60 sec. Samples are after baked at 150°C during 10 minutes under nitrogen.

Three separate solutions of **P3HT** (*Plexcore OS2100, Plextronics*), **[60]PCBM** (99.5%, *Solaris-Chem Inc*) and **[60]PCB-C₆-N₃** at 40 mg/mL each were prepared in 1,2-dichlorobenzene solvent. These concentrations were chosen relative to that of [60]PCB-C₃-N₃ or [60]PCB-C₆-N₃ solutions synthesized. P3HT:[60]PCBM solutions were first stirred at 90°C during 10 minutes and, subsequently, at 50°C during 24 hours. [60]PCB-C₃-N₃ or [60]PCB-C₆-N₃ solutions were finally added in the P3HT:[60]PCBM solution at room temperature (above 25°C) and stirred at least 10 min. As an example, for the mixture corresponding to the 1 : 0.8 : 0.2 weight ratio, 100 μL P3HT + 80 μL [60]PCBM + 20 μL [60]PCB-C₆-N₃ of each solution were mixed. This quantity of [60]PCB-C₆-N₃ corresponds to a fifth of the overall fullerene quantity.

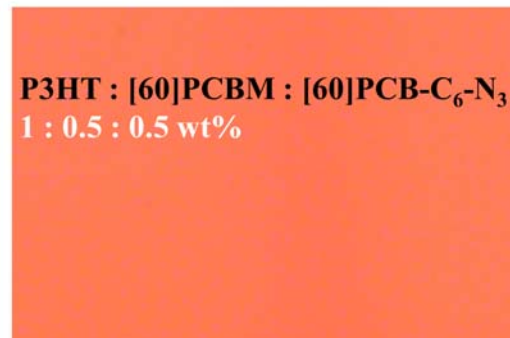
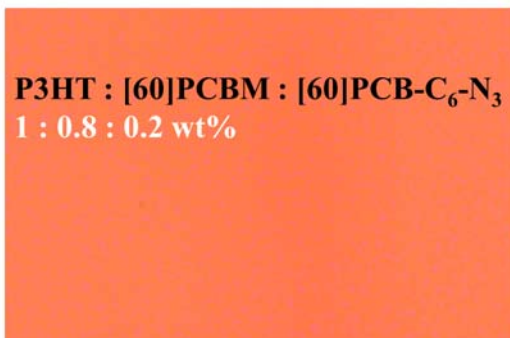
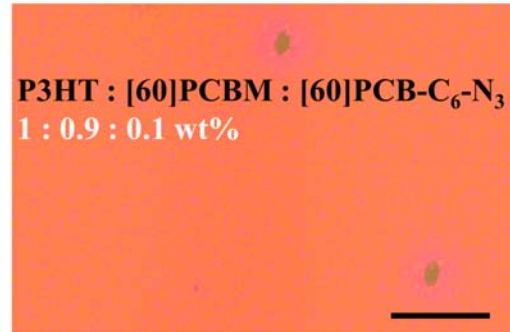
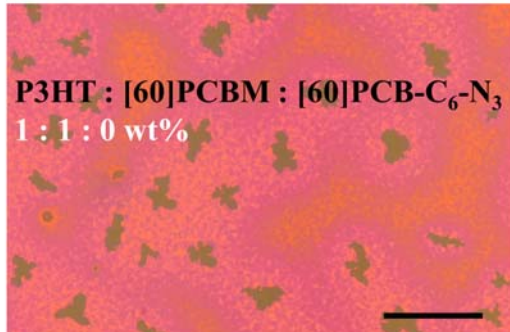
Bulk-heterojunctions were spin-coated in a glove-box at 1000 RPM during 45 sec. Solvent annealing in closed Petri dishes was used to achieve optimized phase segregation between the polymer and the fullerene derivative. The resulting active layer thickness was $175 \pm 8 \text{ nm}$. Thermal ageing was performed on a temperature-controlled hot plate under nitrogen atmosphere in the dark before top electrode deposition to avoid thermal diffusion of atoms such as Mo or Ag in the active layer. At the final stage, the substrates were pumped down to high vacuum ($<4 \times 10^{-6} \text{ Torr}$). A 10 nm-thick MoO₃ (*Serac*) followed by 60 nm-thick silver electrodes were thermally evaporated at deposition rates of $0.1 \text{ nm}\cdot\text{s}^{-1}$ and $0.2\text{-}0.4 \text{ nm}\cdot\text{s}^{-1}$ respectively.

The devices were characterized using a K.H.S SolarCelltest-575 solar simulator with AM 1.5G filters set at $100 \text{ mW}/\text{cm}^2$ with a calibrated radiometer (IL 1400BL). Labview controlled Keithley 2400 SMU enabled the current density-voltage (J-V) curves measurements. Devices were characterized under nitrogen in a set of glove boxes (O_2 and $\text{H}_2\text{O} < 0.1 \text{ ppm}$).

Atomic Force Microscopy. AFM imaging was carried out at room temperature using an AFM Nanoman from Bruker Instrument with Nanoscope 5 controller. Images were obtained in tapping mode using silicon tips (PointProbe® Plus AFM-probe, Nanosensors, Switzerland) with a spring constant of $50 \text{ N}\cdot\text{m}^{-1}$ and a resonance frequency of approximately 160 kHz.

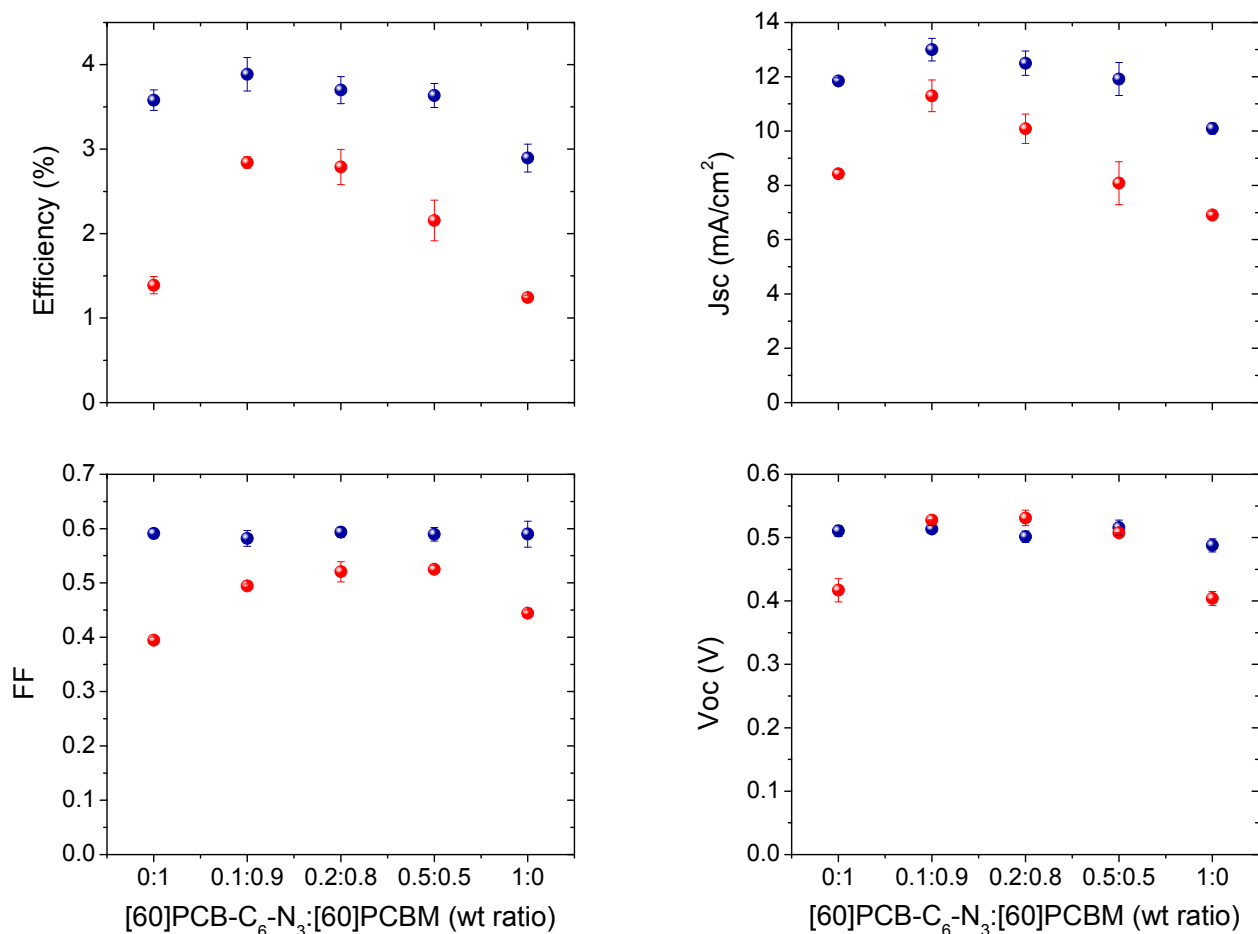
² S. Chambon, E. Destouesse, B. Pavageau, L. Hirsch and G. Wantz, , *J. Appl. Phys.*, **2012**, *112*, 094503.

Optical microscopy images before and after 24 hours at 150°C of P3HT:[60]PCBM devices as function of [60]PCB-C₆-N₃ content. We should note that a weight ratio of 0.1:0.9 of [60]PCB-C₆-N₃ vs [60]PCBM is not enough to avoid completely macro-phase segregation. Scale-bar = 100 μm.



Photovoltaic parameters (Efficiency, short-circuit current, fill factor and open-circuit voltage) of P3HT:[60]PCBM devices as function of [60]PCB-C₆-N₃ incorporated. Before annealing (blue symbols) and after 24 hours at 150°C (red symbols).

The error-bar was determined after the fabrication of 8 solar cells (four cells on two different substrates), thus indicating the good reproducibility of the results.



Thermal ageing of OPV devices :

This figure represents the evolution of the PCE as a function of time for the thermally aged cells, *i.e.* for P3HT:[60]PCBM in 1:1 weight ratio and P3HT:[60]PCBM:[60]PCB-C₆-N₃ in 1:0.8:0.2 weight ratio, respectively.

