

A solvent additive to enhance the efficiency and the thermal stability of polymer : fullerene photovoltaic solar cells

L. Derue,^a C. Lecourtier,^{a,b} T. Gorisse,^a L. Hirsch,^a O. Dautel,^c G. Wantz,^a

^a Univ. Bordeaux, IMS, UMR 5218, F-33400 Talence, France.

^b Solvay-RHODIA, LOF, UMR 5258, F-33600 Pessac, France.

^c ICGM, AM2N, UMR 5253, F-34296 Montpellier, France.

Supporting Information

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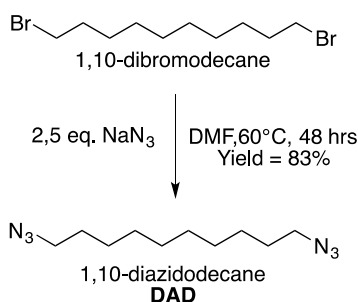
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Synthesis of 1,10-diazidodecane (DAD) :



The synthesis of 1,10-diazidodecane (**DAD**) was realized following the method described by Thomas *et al*¹. 4.87 grams of sodium azide (75 mmoles, 2,5 eq) and 30 grams of 1,10-dibromodecane (30 mmoles, 1 eq.) were stirred at 60°C in 50 mL of DMF under room atmosphere. The completion of the reaction monitored by TLC (eluent: pentane, revelator: KMnO₄, R_f = 0.3) was effective after 48 hours at 60°C. After cooling down to room temperature, the mixture was diluted by 500 mL of water and extracted twice by 200 mL of diethyl ether. The organic phase was washed twice by water, dried over magnesium sulfate and concentrated to furnish 7 grams of a colorless liquid. 5.6 grams (yield 83%) of pure 1,10-diazidodecane as a liquid were isolated by column chromatography on silica gel using pentane as eluent and KMnO₄ as revelator. Analytical data were in good accordance with the literature²³ (see supporting information). ¹H NMR (400 MHz, CDCl₃) δ ppm: 3.25 (t, J = 6.7, 4H), 1.52-1.63 (m, 4H), 1.29-1.38 (m, 12H). ¹³C (100 MHz, CDCl₃) δ ppm: 51.4 (2C), 29.3 (2C), 29.1 (2C), 28.8 (2C), 26.6 (2C); FTIR (ATR) ν cm⁻¹: 2929 ν_{asym}CH₂, 2855 ν_{sym}CH₂, 2085 νN₃.

Devices fabrication and characterization:

UV-visible spectroscopy was recorded on a SAFAS UV mc² spectrometer. The spectra were recorded between 300 and 800 nm with a resolution of 1 nm.

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 N.m⁻¹ and a resonance frequency of approximately 160 kHz. (512x512 data points were acquired.)

OPV Devices fabrication and characterizations. Inverted solar cells have been fabricated with the following structure : Glass/ITO/TiO_x/BHJ/MoO₃/Ag. The Indium tin oxide (ITO)-coated glass substrate, purchased from Kintec, with a surface resistance of ~ 10 Ω. square⁻¹ are successively cleaned in acetone, ethanol and isopropanol in an ultrasonic bath and exposed to UV-ozone for 15 min. 15 nm-thick titanium oxide is prepared as previously described by Chambon *et al*². P3HT:PC₆₁BM solutions were prepared in *o*-dichlorobenzene for P3HT:PC₆₁BM with a concentration of 40 mg.mL⁻¹ (1:1 ratio). Solutions were first stirred at 90°C for 10 min and, subsequently, at 50°C for 24 hours. 1,10-diazidodecane was introduced in the solution at room temperature. BHJ layers were spin-coated in a glove box at 1000rpm during 70s with a resulting P3HT:PC₆₁BM thickness of 228±9 nm. Thermal ageing was performed on a temperature-controlled hot plate in the glove-box. This thermal treatment is mostly performed before top electrode deposition to avoid thermal diffusion of atoms such as Mo or Ag in the active layer as we already reported in ref³. MoO₃ (10nm) and Ag (60nm) were successively thermally-evaporated at deposition rates of 0.1 nm.s⁻¹ and 0.2-0.4 nm.s⁻¹ respectively under secondary vacuum (10⁻⁶ mbar). The size of solar cells active area is 10 mm². The devices were characterized using a *K.H.S. SolarCelltest-575* solar simulator with AM1.5G filters set at 100 mW.cm⁻² with a calibrated radiometer (IL 1400BL). Labview controlled *Keithley 2400* SMU enabled the current density-voltage (J-V) curves measurements.

Materials. Regio-regular poly(3-hexylthiophene) (P3HT) was provided by Solaris Chem Inc (M_w = 40 kg.mol⁻¹; regio-regularity = 95%). 1-(3-Methoxycarbonyl)propyl-1-phenyl [6,6]C₆₁-(PCBM) was provided by Solaris Chem Inc. (purity: 99.5%).

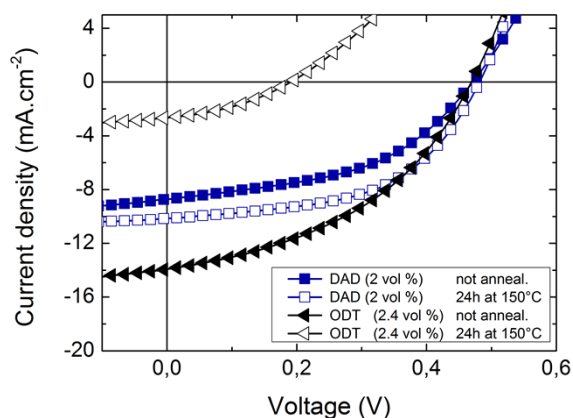


Figure S1 – J-V characteristics of P3HT:PC₆₁BM solar cells with 2 vol. % of DAD before (solid square) and after 24 hours at 150°C (open square). J-V curves of P3HT:PC₆₁BM solar cells processed with 1,8-octanedithiol before (solid triangle) and after 24 hours at 150°C (open triangle).

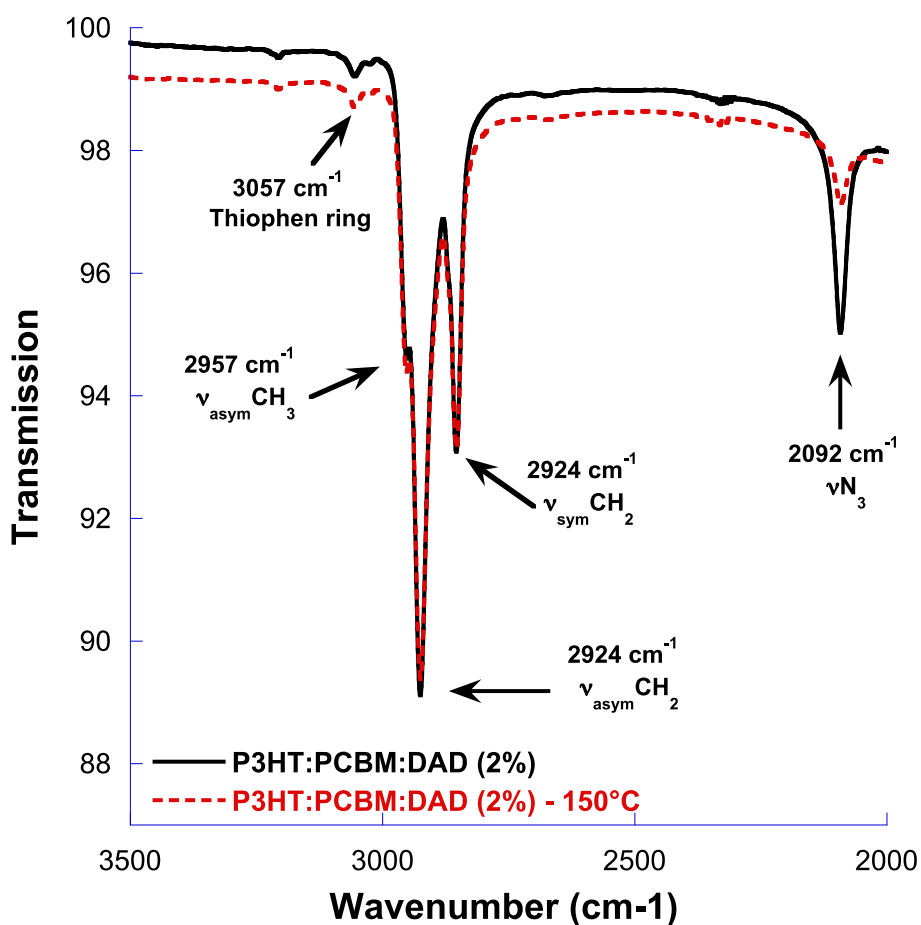


Figure S2 - Infrared spectra in transmission mode of a P3HT:PC₆₁BM composite layer processed with 2 vol. % of 1,10-diazidodecane on sapphire before and after cross-linking activation (10 min at 150°C).

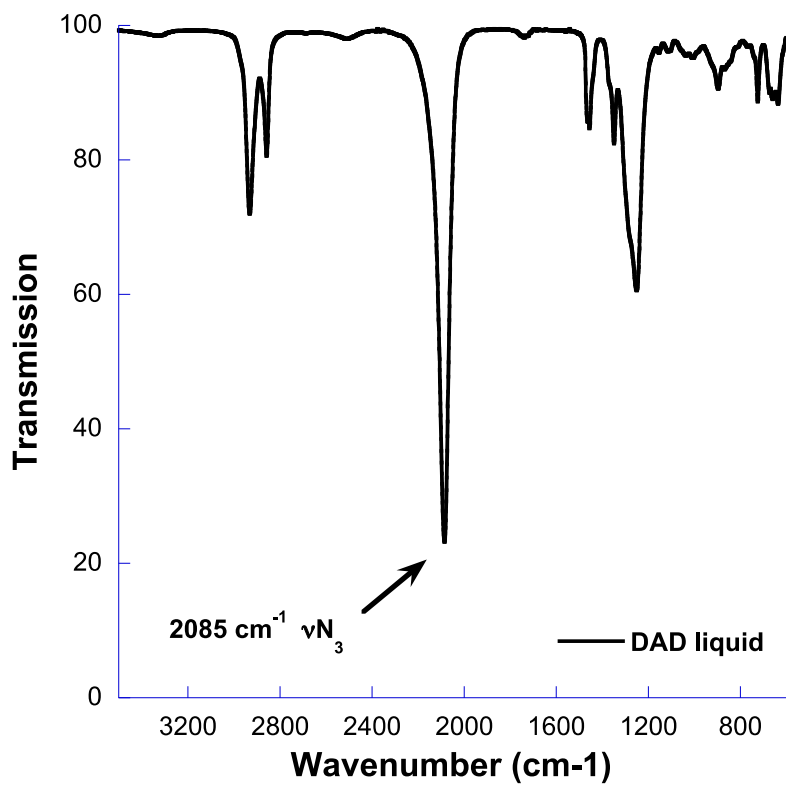


Figure S3. Infrared spectrum of 1,10-diazidodecane (DAD) recorded on Perkin Elmer spectrum 100 in ATR mode.

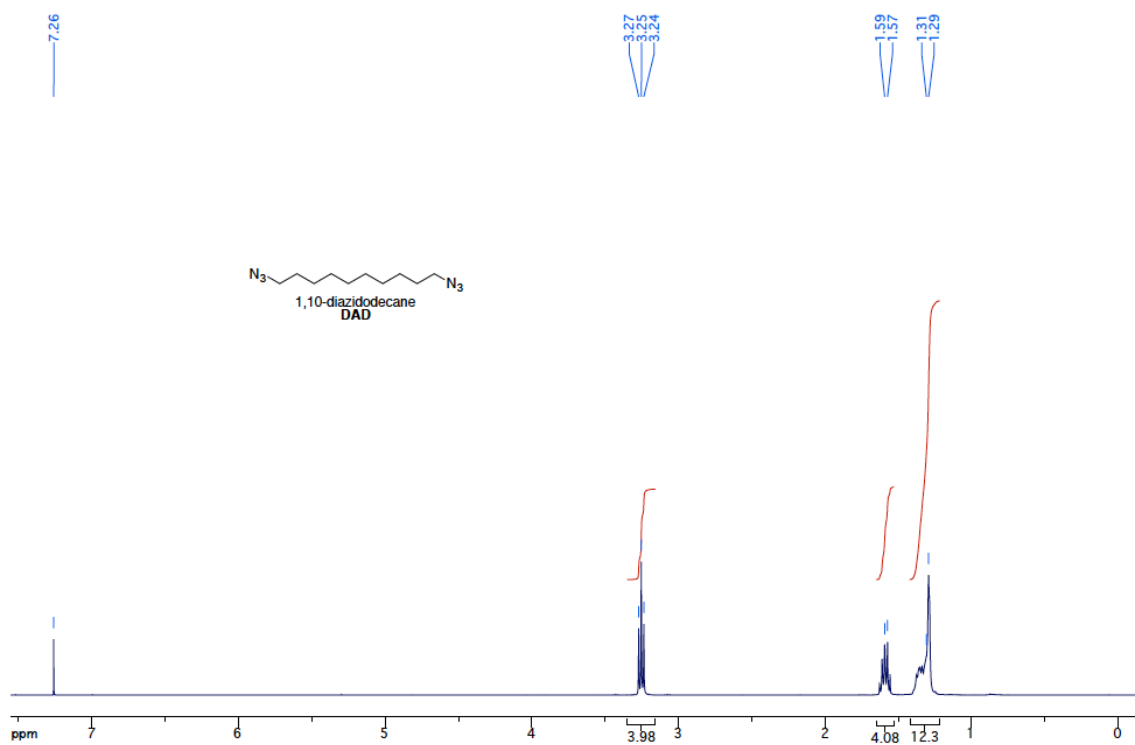


Figure S4. ¹H NMR spectrum of 1,10-diazidodecane (DAD) recorded on a Bruker Ultra Shield 400 Plus spectrometer in CDCl₃.

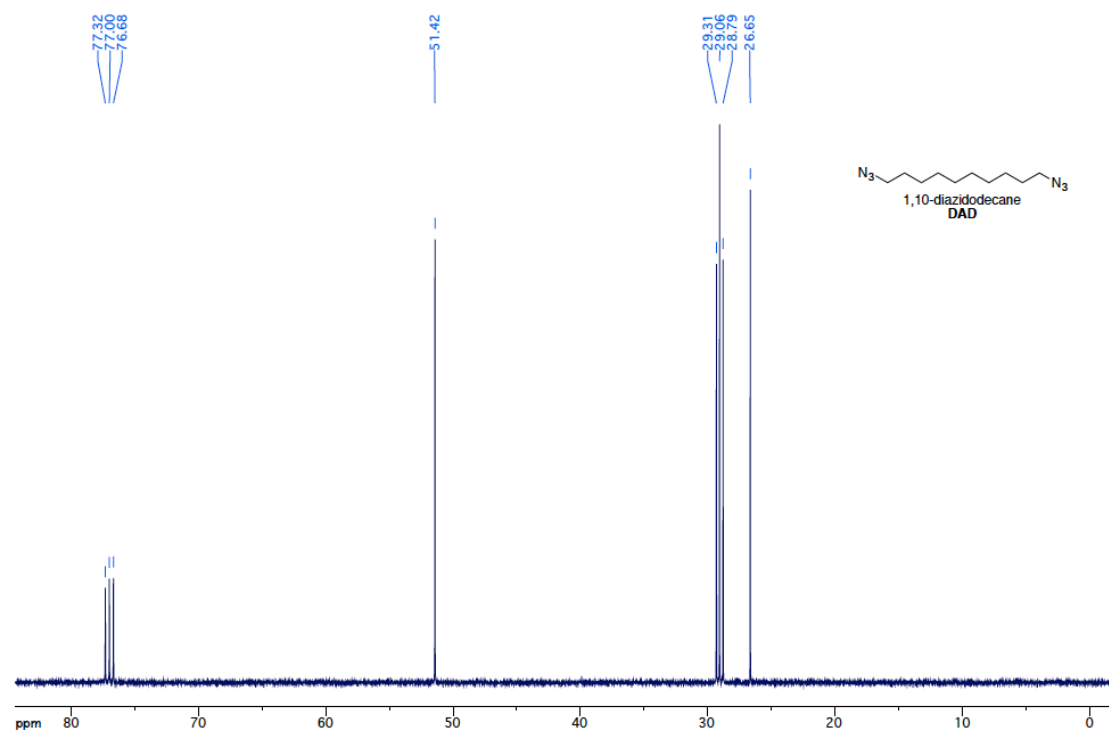


Figure S5. ^{13}C NMR spectrum of 1,10-diazidodecane (**DAD**) recorded on a Bruker Ultra Shield 400 Plus in CDCl_3 .

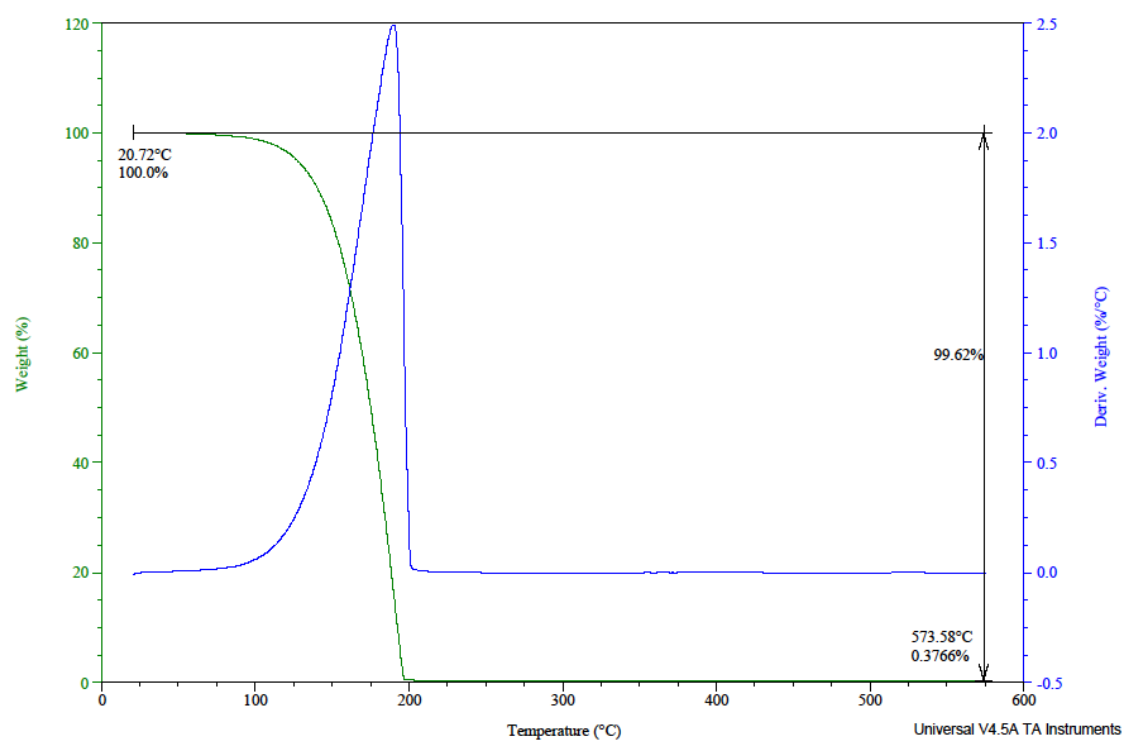


Figure S6. Thermal gravimetric analysis of 1,10-diazidodecane (**DAD**) recorded on a Texas Instrument TGA Q50 apparatus under nitrogen at the heating rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ from room temperature up to $580\text{ }^\circ\text{C}$.

¹ J.R. Thomas, X. Liu and P.J. Hergenrother, *Journal of the American Chemical Society*, 2005, **127**, 12434-12435.

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

³ S. Chambon, L. Derue, M. Lahaye, B. Pavageau, L. Hirsch and G. Wantz, *Materials*, 2012, **5**, 2521-2536.