Journal of Visualized Experiments

Indacenodithienothiophene-Based Ternary Organic Solar Cells: Concept, Devices and optoelectronic analysis

--Manuscript Draft--

Manuscript Number:	JoVE54007R6
Full Title:	Indacenodithienothiophene-Based Ternary Organic Solar Cells: Concept, Devices and optoelectronic analysis
Article Type:	Methods Article - JoVE Produced Video
Keywords:	Ternary Organic Solar Cells; Indacenodithienothiophene; Photo-CELIV; Transient Photovoltage; Charge Extraction; Photo-induced Absorption Spectroscopy
Manuscript Classifications:	93.33.75: solar cells (electrical design); 94.44.18: solar cells (energy conversion)
Corresponding Author:	Nicola Gasparini Friedrich-Alexander-Universitat Erlangen-Nurnberg Erlangen, Bayern GERMANY
Corresponding Author Secondary Information:	
Corresponding Author E-Mail:	nicola.gasparini@fau.de
Corresponding Author's Institution:	Friedrich-Alexander-Universitat Erlangen-Nurnberg
Corresponding Author's Secondary Institution:	
First Author:	Nicola Gasparini
First Author Secondary Information:	
Other Authors:	Amaranda García-Rodríguez
	Athanasios Katsouras
	Apostolos Avgeropoulos
	Georgia Pagona
	Vasilis G. Gregoriou
	Christos L. Chochos
	Sybille Allard
	Ulrich Scherf
	Christoph J. Brabec
	Tayebeh Ameri
Order of Authors Secondary Information:	
Abstract:	We report on a novel ternary bulk-heterojunction solar cell by implementing a novel conjugated polymer (ADV-2) containing alternating pyridyl[2,1,3]thiadiazole (PT) between two different donor fragments, dithienosilole (DTS) and indacenodithienothiophene (IDTT), into a host system of indacenodithieno[3,2-b]thiophene,2,3-bis(3-(octyloxy)phenyl)quinoxaline (PIDTTQ) and [6,6]-phenyl C71 butyric acid methyl ester (PC71BM). A clear absorption contribution in the near infrared (NIR) region leads to a power conversion efficiency (PCE) exceeding 4.6% in ternary device processed by doctor blading in air, fully avoiding any thermal treatment. Current-voltage (J-V) characteristics, external quantum efficiency (EQE) spectrum ,

	charge extraction (CE) as well as photo-induced absorption (PIA) spectroscopy reveal the higher charge carrier generation in the ternary devices compared to the reference binary cells. Despite an enhancement of about 20% in the short circuit current density (Jsc), the lower fill factor (FF) achieved in PIDTTQ:ADV-2:PC71BM ternary system limits the solar cell performance. With the complementary use of photoinduced charge carrier extraction by linearly increasing voltage (photo-CELIV) and transient photovoltage (TPV) measurements we found that the ternary cells suffer from a lower mobility-lifetime () product, adversely impacting the FF. However, the significant improvement of light harvesting in the NIR region, compensating the transport losses, results in an overall power conversion efficiency enhancement of ~7% for ternary blends as compared to the PIDTTQ: PC71BM devices.
Author Comments:	
Additional Information:	
Question	**Response**
If this article needs to be "in-press" by a certain date to satisfy grant requirements, please indicate the date below and explain in your cover letter.	

TITLE:
Indacenodithienothiophene-Based Ternary Organic Solar Cells: Concept, Devices and Optoelectronic Analysis

AUTHOR:
Nicola Gasparini
Institute of Materials for Electronics and Energy Technology (I-MEET)
Friedrich-Alexander-University Erlangen-Nuremberg
Martensstraße 7, Erlangen, Germany
nicola.gasparini@fau.de

Amaranda García-Rodríguez
Macromolecular Chemistry Group (buwmakro) and Institute for Polymer Technology
Bergische Universität Wuppertal
Gaußstraße 20, Wuppertal, Germany
amaranda.garcia@yahoo.de

Athanasios Katsouras
Department of Materials Science Engineering
University of Ioannina
Ioannina, Greece
athanasioskatsouras@gmail.com

Apostolos Avgeropoulos
Department of Materials Science Engineering
University of Ioannina
Ioannina, Greece
aavger@cc.uoi.gr

Georgia Pagona
Advent Technologies SA
Patras Science Park
Patra, Greece
and
National Hellenic Research Foundation (NHRF)
Athens, Greece
gpagona@eie.gr

Vasilis G. Gregoriou
Advent Technologies SA
Patras Science Park
Patra, Greece
and
National Hellenic Research Foundation (NHRF)

Athens, Greece
vgregoriou@advent-energy.com

Christos L. Chochos
Department of Materials Science Engineering
University of Ioannina
Ioannina, Greece
and
Advent Technologies SA
Patras Science Park
Patra, Greece
cchochos@advent-energy.com

Sybille Allard
Macromolecular Chemistry Group (buwmakro)
Institute for Polymer Technology
Bergische Universität Wuppertal
Gaußstraße 20, Wuppertal, Germany
sallard@uni-wuppertal.de

Ulrich Scherf
Macromolecular Chemistry Group (buwmakro)
Institute for Polymer Technology
Bergische Universität Wuppertal
Gaußstraße 20, Wuppertal, Germany
scherf@uni-wuppertal.de

Christoph J. Brabec
Institute of Materials for Electronics and Energy Technology (I-MEET)
Friedrich-Alexander-University Erlangen-Nuremberg
Martensstraße 7, Erlangen, Germany

Bavarian Center for Applied Energy Research (ZAE Bayern)
Haberstrasse 2a, Erlangen, Germany
christoph.brabec@fau.de

Tayebeh Ameri
Institute of Materials for Electronics and Energy Technology (I-MEET)
Friedrich-Alexander-University Erlangen-Nuremberg
Martensstraße 7, Erlangen, Germany
tayebeh.ameri@fau.de

CORRESPONDING AUTHOR:
Nicola Gasparini

+49 (0)9131 85-27730

Dr. Tayebeh Ameri
+49-(0)9131/85-27722

KEYWORDS:
ternary organic solar cells, indacenodithienothiophene, photo-CELIV, Transient Photovoltage, Charge extraction, Photo-induced absorption spectroscopy

SHORT ABSTRACT:
In this study, in addition to the synthesis of a novel polymer, we fully characterize a ternary bulk-heterojunction solar cell, with a power conversion efficiency exceeding 4.6%, with the complementary use of optical and electrical techniques.

LONG ABSTRACT:
We report on a novel ternary bulk-heterojunction solar cell by implementing a novel conjugated polymer (ADV-2) containing alternating pyridyl[2,1,3]thiadiazole (PT) between two different donor fragments, dithienosilole (DTS) and indacenodithienothiophene (IDTT), into a host system of indacenodithieno[3,2-*b*]thiophene,2,3-bis(3-(octyloxy)phenyl)quinoxaline (PIDTTQ) and [6,6]-phenyl C71 butyric acid methyl ester ($PC_{71}BM$). A clear absorption contribution in the near infrared (NIR) region leads to a power conversion efficiency (PCE) exceeding 4.6% in ternary device processed by doctor blading in air, fully avoiding any thermal treatment. Current-voltage (J-V) characteristics, external quantum efficiency (EQE) spectrum, charge extraction (CE) as well as photo-induced absorption (PIA) spectroscopy reveal the higher charge carrier generation in the ternary devices compared to the reference binary cells. Despite an enhancement of about 20% in the short circuit current density (J_{sc}), the lower fill factor (*FF*) achieved in PIDTTQ:ADV-2:$PC_{71}BM$ ternary system limits the solar cell performance. With the complementary use of photoinduced charge carrier extraction by linearly increasing voltage (photo-CELIV) and transient photovoltage (TPV) measurements, we found that the ternary cells suffer from a lower mobility-lifetime ($\mu\tau$) product, adversely impacting the *FF*. However, the significant improvement of light harvesting in the NIR region, compensating the transport losses, results in an overall power conversion efficiency enhancement of ~7% for ternary blends as compared to the PIDTTQ: $PC_{71}BM$ devices.

INTRODUCTION:
During the last decades, the power conversion efficiency (PCE) of organic bulk-hetorojunction (BHJ) solar cells based on donor/acceptor blends surpassed the 10% threshold, mainly due to the discovery of novel materials as well as device structure engineering.[1–6] Nowadays, one of the main challenges in order to further boost the PCE of organic solar cells is to achieve better absorption match to the solar irradiance spectrum, by extending the narrow absorption window of organic polymers. In this regards, two main concepts have been developed: tandem and ternary organic solar cells.[7–17] The former are based on a complex multi-layer stack with the main challenge of designing a robust solution-processed intermediate layer.[18] The latter, made of two donors and one acceptor, mixed together in a unique solution, overcomes the

complexities of the tandem device architecture, maintaining the easy processability of a single junction organic BHJ solar cell.[19–25] To date, polymers,[20] small molecules,[21] dyes,[26] quantum dots[27] and fullerene derivates,[23] have been adopted as “guest” in the polymer-fullerene “host” system.

In addition to the need for donor materials with the complementary absorption, one of the key points to surpass the performance of binary cells in ternary devices is to find donor materials with compatible physical and chemical natures.[20] This can prevent the formation of recombination centers, or morphological traps, that deteriorate the photovoltaic properties.[28,29]

Here, we report a ternary organic solar cell system processed in air that shows a pronounced sensitization effect, resulting in a power conversion efficiency of more than 4.6%. As a sensitizer, we incorporate the near infrared (NIR) polymer ADV-2 that contains alternating pyridyl[2,1,3]thiadiazole (PT) between two different donor fragments, dithienosilole (DTS) and indacenodithienothiophene (IDTT), into a host system of indacenodithieno[3,2-b]thiophene,2,3-bis(3-(octyloxy)phenyl)quinoxaline (PIDTTQ)[30] blended with [6,6]-phenyl C71 butyric acid methyl ester ($PC_{71}BM$). In fact, in order to have components with a similar chemical nature in the ternary blend system, we used two polymers with the same backbone unit of indacenodithienothiophene for the host and the guest donors. We studied the aforementioned ternary system by employing various optoelectronic techniques such as current-voltage (J-V) characteristics, external quantum efficiency (EQE), photoinduced charge carrier extraction by linearly increasing voltage (photo-CELIV), charge extraction (CE), transient photovoltage (TPV) measurements and photo-induced absorption (PIA) spectroscopy.

PROTOCOL:

1. Planning of experiment

1.1 Identify two donor copolymers with complementary absorption in the visible-NIR range and with suitable energy levels in comparison with the fullerene derivative acceptor ($PC_{71}BM$).

2. Synthesis of M1

2.1 Add a 10 mL freshly distilled toluene solution containing 5,5’-bis(trimethylstannyl)-3,3’-di-2-ethylhexylsilylene-2,2’-bithiophene (0.372 g, 0.5 mmol, the quantity as well as the representative mmol corresponds to 5,5’-bis(trimethylstannyl)-3,3’-di-2-ethylhexylsilylene-2,2’-bithiophene), 4,7-dibromo-[1,2,5]thiadiazolo[3,4-*c*]pyridine (0.295 g, 1 mmol) and $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol) into a microwave tube under the protection of nitrogen.

2.2 Perform the Stille coupling with the following procedure: 120 ^oC for 10 min, 140 ^oC for 10 min, 160 ^oC for 10 min and 170 ^oC for 40 min (microwave step-wise).

2.3 Cool down the reaction to room temperature, and extract with chloroform (100 mL × 3) in a separatory funnel. Wash with deionized water (100 mL × 3) and dry with anhydrous magnesium sulfate.

2.4. Using a rotary evaporator, remove the solvent under reduced pressure. Separate the mixture by adding the solute directly to a silica column (25 mm inner diameter x 300 mm length) with hexane/chloroform (from 100/0 to 0/100 in v/v) to give 0.49 g of dark-purple solid (92% yield).

3. Synthesis of ADV-2:

3.1 Dissolve dibromo monomer M1 (180 mg, 1 equiv) and distannyl monomer M2 (286 mg, 1 equiv) in 1 mL toluene in a microwave vial. Fix the volume of the solvent and the quantity of the monomers to 0.025 M in concentration for each polymerization procedure.

3.2 Add $Pd_2dba_3 \cdot CHCl_3$ (4.4 mg, 0.02 equiv) and tri(*o*-tolyl)phosphine ($P(o\text{-tol})_3$) (2.6 mg, 0.04 equiv) in the reaction mixture and stir at 120 °C under argon atmosphere for 48 h.

3.3 Purify the polymer by precipitation in methanol in a beaker, and then filter through a thimble and Soxhlet extract with methanol, acetone, ethyl acetate, chloroform and dichlorobenzene (DCB) in sequential order. Use 20% in excess of the volume of the polymeric solution.

3.4 Collect the DCB fraction with a rotary evaporator and remove the solvents under reduced pressure.

3.5 Isolate the polymer by precipitation into methanol in a beaker. Use 20% excess in volume. Filter and finally dry under high vacuum to give ADV-2 as a blue solid in 79% yield (142.2 mg).

4. Preparation of material solution

4.1 Prepare 10 mg/mL solution of indacenodithieno[3,2-b]thiophene,2,3-bis(3-(octyloxy)phenyl)quinoxaline in 1,2 dichlorobenzene (DCB).

4.2 Prepare 10 mg/mL solution of ADV-2 in DCB.

4.3 Prepare 40 mg/mL solution of [6,6]-phenyl C70 butyric acid methyl ester ($PC_{71}BM$) in DCB.

4.4 Stir all the solutions overnight on hot plate at 80 °C.

5. Preparation of bulk-heterojunction(BHJ) solar cells

5.1 Mix the solutions with different composition ratios (Table 1), keeping the total solution concentration at 20 mg/mL; add 3% v/v 1-Chloronaphtalene (CN). Stir the ternary as well as binary solutions 1 hour at 80 °C.

5.2 Clean the pre-structured indium tin oxide (ITO) substrates in acetone and isopropyl alcohol in an ultrasonic bath for 10 minutes each.

5.3 After drying, coat the substrates with 40 nm of zinc oxide (ZnO) with a doctor-blade.[30]

5.3.1 Coat the aforementioned (Table 1) active layer materials with a doctor-blade. Set the temperature of doctor blade at 80 °C, the gap between the blade and the substrate at 400 µm, use 60 µL of solution and adjust the coating speed (10 mm/s) in order to have approximately 100 nm active layer thickness.

5.4 To complete the fabrication of the devices, transfer the substrate in glove-box filled with nitrogen.

5.5 In an ultra-vacuum chamber, thermally evaporate 10 nm of MoOx and 100 nm of Ag through a mask with a 10.4 mm^2 active area opening and under a vacuum of 2×10^{-6} mbar.

6. Electrical and optical characterization of solar cells

6.1 J-V characteristics:

6.1.1 Measure the J-V characteristics of the BHJ devices between -2 V to 2 V under darkness using a source measurements unit according to manufacturer's protocol. Scan the voltages between -2 V and 2 V with steps of 20 mV to record the corresponding current (I). Calculate the current density (J) by the equation J=I/A, where A is the area of the solar cells (here, 10.4 mm^2).

6.1.2 Provide illumination with a solar simulator with AM1.5G spectrum at 100 mW cm^{-2}. Measure the J-V characteristics of the BHJ devices between -2 V to 2 V under light conditions in ambient air using a source measurements unit according to manufacturer's protocol.

6.1.2.1. Scan the voltages between -2 V and 2 V with steps of 20 mV to record the corresponding current (I). Calculate the current density (J) by the equation J=I/A, where A is the area of the solar cells (here, 10.4 mm^2).

6.2 Absorption spectra and External Quantum Efficiency (EQE) measurements:

6.2.1 Measure the absorption spectra of the solar cells on film with a UV-VIS spectrometer according to manufacturer's protocol.

6.2.2 Calibrate the EQE setup with a silicon diode reference cells between 350 and 900 nm.

6.2.3 Measure solar cells EQEs using an integrated system between 350 and 900 nm. [30]

6.3 Photoinduced charge carrier extraction by linearly increasing voltage (photo-CELIV): [30]

6.3.1 Illuminate the devices with a 405 nm laser diode.

6.3.2 Connect the solar cells with the oscilloscope with BNC cable. Record the current transient across an internal 50 Ω resistor of an oscilloscope[30].

6.3.3 After a variable delay time (delay time reflects the time passing from the laser pulse to the start of the voltage ramp, can vary between 1υs to 1-10 ms), apply a linear extraction ramp via a function generator. Set the ramp, which is 60 µs long and 2 V in amplitude, to start with an offset matching the V_{oc} of the cell for each delay time.

6.4 Transient Photo-Voltage (TPV): [31]

6.4.1 Use two lasers at 405 nm, one as background illumination and the other one for creating voltage perturbation.

6.4.2 Connect the solar cell to an oscilloscope with BNC cable and adjust the intensity of the background illumination to reach the open circuit condition.

6.4.3 Adjust the laser intensity pulse to keep the voltage perturbation below 10 mV, typically at 5 mV. After the pulse, the voltage decays back to its steady state value in a single exponential decay.

6.4.4 Change intensity of background illumination in a range of 0.1 to 4 suns.

6.4.5 Record the transient with the oscilloscope.

6.5 Charge extraction (CE): [31]

6.5.1 Use a 405 nm laser diode for background illumination.

6.5.2 Connect the solar cell to an oscilloscope with BNC cable and adjust the intensity of the background illumination to reach the open circuit condition.

6.5.3 Turn off the laser and trigger the bilateral switch in order to switch the solar cell from open-circuit to short-circuit (50 Ω) conditions within less than 50 ns.

6.5.4 Record the transient with the oscilloscope.

6.6 Photo-induced spectroscopy (PIA):

6.6.1 Place the solar cell in a cryostat in order to reach a temperature of 10 K and a pressure of 5×10^{-7} mbar.

6.6.2 Check the optical alignments for a 532 nm Nd:YAG laser (as pump) and a UV-VIS lamp light (as probe), focused on the same position on the sample.

6.6.3 Turn off the laser and measure the sample transmittance by a standard lock-in technique under the UV-VIS lamp light which is modulated by a mechanical chopper.

Note: In this method the excitation (laser PUMP) is done by using a green laser (λ=532 nm), which is modulated by a mechanical chopper. The sample is additionally illuminated by a monochromated light beam (“probe”) of a white light source. First the sample’s transmittance and the sample’s photoluminescence is measured. The measured signal is analyzed with a lock-in amplifier using the chopper frequency as the reference signal, allowing a very precise quantification of the change in absorption induced by the pump-light. Using various detectors (Si, Ge) a broad wavelength region ranging from 400 nm up to 1800 nm can be analyzed. Varying the material composition, material dependent effects can be characterized.

6.6.4 Turn off the lamp and turn on the laser beam, modulated by a mechanical chopper.

6.6.5 Measure the photoluminescence of the solar cells through the standard lock-in technique.

6.6.6 Turn on the lamp and then measure the PIA spectrum by a standard lock-in technique under modulated laser pulse.

REPRESENTATIVE RESULTS:

Figure 1 shows 1H and 13C NMR spectra of M1 (a-b, respectively) and ADV-2 (c-d, respectively) with their respectively list of peaks. **Figure 2** shows the synthetic route for the low band gap donor-acceptor copolymer ADV-2. **Figure 3** shows the absorption spectrum of ADV-2 in DCB solution and as solid. The copolymer for both cases shows a single band in the high energy region which is assigned to a localized π−π* transition and another absorption band in the low energy region (up to 1000 nm) which is assigned to an intramolecular charge transfer transition. The maximum of the near infrared absorption band of ADV-2 in the solid state is bathochromic shifted (738 nm) in comparison to the corresponding UV-Vis solution (695 nm). The optical band gap energy estimated from the absorption edge of film spectrum was estimated to be 1.87. Based on the onsets of the oxidation and reduction peaks in cyclic voltammetry measurements, the electrochemical HOMO and LUMO energies were estimated to be −5.34 and −3.71 eV, respectively, corresponding to an electrochemical band gap energy of 1.63 eV.

Figure 4a shows the device architecture used in this work, based on ITO/ZnO/active layer/MoO_x/Ag. PIDTTQ has been previously presented in the literature.[30] All the solution processed layers are doctor-bladed in air. **Figure 4b** and **4c** depict the energy levels of the polymers and the fullerene derivate, measured by cyclic-voltammetry (CV) and the chemical structure of the materials used, respectively.

Figure 5a shows the current-voltage characteristics of the binary PIDTTQ:$PC_{71}BM$ (1:2 wt/wt) as well as ternary PIDTTQ:ADV-2:$PC_{71}BM$ (different composition) under 1 sun illumination (100 mW cm^{-2}). In agreement with previous reports binary cells delivered a PCE of 4.35% with an open circuit voltage (V_{oc}) of 0.84V, a short circuit current (J_{sc}) of 8.62 mA cm^{-2} and a fill factor (*FF*) of 60%. Adding 15 wt% of the NIR sensitizer, the ternary device delivered the highest performance with a J_{sc} of 10.60 mA cm^{-2}, V_{oc} of 0.84 V and *FF* of 52%, resulting the overall power conversion efficiencies of 4.6%. As shown in **Table 1**, the J_{sc} increased monotonically by increasing the of ADV-2 content up to 15 wt%, due to the better photon harvesting of the ternary system in the NIR region. For PIDTTQ:ADV-2:$PC_{71}BM$ (0.85:0.15:2) ternary blend a J_{sc} improvement of ~20% was achieved as compared to PIDTTQ:$PC_{71}BM$ binary system. Notably, the V_{oc} obtained in the ternary cells are identical to the binary PIDTTQ:$PC_{71}BM$, reflecting a cascade alignment between the HOMO and LUMO energy levels of the three components (**Figure 4b**).[25] However, we observed a continuously decrease in *FF* by introducing higher amount of ADV-2, which can be attributed to the undesired morphology of the ternary blends. We further measured external quantum efficiency (EQE) spectra of OPV devices made from PIDTTQ:ADV-2:$PC_{71}BM$, PIDTTQ:$PC_{71}BM$ and ADV-2:$PC_{71}BM$ (**Figure 5b**). Increasing the ADV-2 content, the EQE showed improved photoresponse at 700-800 nm region, which is the origin of the enhanced J_{sc}. We note that the integrated EQE for these devices matches the measured short circuit current within a margin of 5%.

In order to understand the lower *FF* obtained in the ternary BHJ solar cells we first studied the charge transport properties by employing the technique of photoinduced charge carrier extraction by linearly increasing voltage (photo-CELIV).[32–34] From the measured photocurrent transients, the charge carrier mobility (μ) was calculated using the following equation:

$$\mu = \frac{2d^2}{3At_{max}^2\left[1+0.36\frac{\Delta j}{j(0)}\right]} \; if \; \Delta j \leq j0, \tag{1}$$

where d is the active layer thickness, A is the voltage rise speed A=dU/dt, U is the applied voltage, t_{max} is the time corresponding to the maximum of the extraction peak, and j(0) is the displacement current.[32] **Figure 6a** shows the transient recorded by applying a 2V/60 μs linearly increasing reverse bias and a delay time (t_d) of 10 μs. From analysis of the photo-CELIV traces the charge carrier mobility values of 1.13×10^{-4} $cm^2V^{-1}s^{-1}$, 8.54×10^{-5} $cm^2V^{-1}s^{-1}$, 7.53×10^{-5} $cm^2V^{-1}s^{-1}$ and 7.42×10^{-5} $cm^2V^{-1}s^{-1}$ were calculated for PIDTTQ:$PC_{71}BM$ (1:2), PIDTTQ:ADV-2:$PC_{71}BM$ (0.90:0.10:2), PIDTTQ:ADV-2:$PC_{71}BM$ (0.85:0.15:2), PIDTTQ:ADV-2:$PC_{71}BM$ (0.80:0.20:2) devices, respectively. The lower charge carrier mobilities measured with Photo-CELIV technique are in agreement with the lower *FFs* obtained for the ternary cells. We then analyzed the lifetime of charge carriers by employing transient photovoltage technique (TPV).[35,36] The samples were connected to the terminal of an oscilloscope with the input impedance of 1 MΩ and illuminated with a continuous background laser to keep the samples at V_{oc} condition. A small voltage perturbation was applied using a blue laser (λ=405 nm). The pulse intensity was adjusted to keep the height of the photovoltage transient smaller than 10 mV resulting in a voltage transient with amplitude $\Delta V \ll V_{oc}$. The measured transient decays show the form of single exponentials, as expected for the pseudo-first order kinetic.[35]

$$\frac{d\Delta V}{dt} \propto \frac{d\Delta n}{dt} = -k_{eff} = -\frac{\Delta n}{\tau_{\Delta n}} \tag{2}$$

V is the photovoltage, t is the time, Δn is change in the density of photogenerated carriers due to the perturbation pulse, k_{eff} is the pseudo-first order rate constant and $\tau_{\Delta n}$ is the carrier lifetime. **Figure 6b** depicts normalized photovoltage decays as a function of time for the binary and ternary devices. As reported in **Table 2**, quite similar charge carriers lifetime of 6.72 µs, 7.35 µs and 7.23 µs were achieved for PIDTTQ:$PC_{71}BM$ (1:2), PIDTTQ:ADV-2:$PC_{71}BM$ (0.90:0.10:2), PIDTTQ:ADV-2:$PC_{71}BM$ (0.85:0.15:2), respectively, suggesting that these ternary blends are not limited by the short lifetime of charge carriers.[37] Otherwise, a reduce τ of 4.72 μs is observed for the PIDTTQ:ADV-2:$PC_{71}BM$ (0.80:0.20:2) based ternary system. Combining the results of Photo-CELIV and TPV measurements we were able to calculate the mobility-lifetime product *($\mu\tau$)*. As presented in **Table 2**, $\mu\tau$ decrease from 7.59×10^{-10} for PIDTTQ:$PC_{71}BM$ (1:2) to 6.72×10^{-10}, 5.44×10^{-10} and 3.50×10^{-10} cm^2 V^{-1} for, PIDTTQ:ADV-2:$PC_{71}BM$ (0.90:0.10:2), PIDTTQ:ADV-2:$PC_{71}BM$ (0.85:0.15:2) and PIDTTQ:ADV-2:$PC_{71}BM$ (0.80:0.20:2), respectively, owing to the poorer transport properties of the ternary systems compared to the binary reference device.

To have a better insight into the charge photogeneration in the ternary blends, we employed the charge extraction (CE) and photoinduced absorption (PIA) spectroscopy. In CE measurements the samples were illuminated under a continuous background laser to keep it at V_{oc} condition. A nanosecond switch was used to sweep the photocurrent from open circuit to short circuit condition. The charge carrier density (n) was calculated based on the transient decay (**Figure 7a**).[31] In agreement with the J_{sc} values obtained, we calculated n as 2.97×10^{16}, 3.02×10^{16}, 3.66×10^{16} and 1.15×10^{16} cm^{-3} for PIDTTQ:$PC_{71}BM$ (1:2), PIDTTQ:ADV-2:$PC_{71}BM$ (0.90:0.10:2), PIDTTQ:ADV-2:$PC_{71}BM$ (0.85:0.15:2) and PIDTTQ:ADV-2:$PC_{71}BM$ (0.80:0.20:2) devices, respectively (**Table 2**). Furthermore, the charge generation mechanism in the BHJ solar cells was studied with PIA spectroscopy.[38,39] We utilized a 532 nm laser for pump and a UV-VIS lamp for probing. **Figure 7b** depicts the PIA spectra of binary and ternary devices measured under 60 mW cm^{-2} pump intensity at 10 K. All spectra showed a pronounced transmission minimum (bleach) around 1.81 eV and a photoinduced absorption feature around 1.24 eV. The ternary blends showed a novel bleaching feature around 1.55 eV. We ascribe the two transmission maxima at 1.81 eV and 1.55 eV to the photobleaching of the electronic ground states of PIDTTQ and ADV-2, respectively. As shown in Figure 6b, a higher polaron signal was observed for the PIDTTQ:ADV-2:$PC_{71}BM$ (0.90:0.10:2), PIDTTQ:ADV-2:$PC_{71}BM$ (0.85:0.15:2) ternary devices compared to the binary cell, confirming the higher charge photogeneration by adding 10-15% of ADV-2 into the PIDTTQ:$PC_{71}BM$ host system.

Figure 1 NMR of the NIR polymer. 1H and 13C NMR spectra of M1 (a-b, respectively) and ADV-2 (c-d, respectively).

Synthesis of M1:

^{1}H-NMR (600 MHz, $CDCl_3$), δ (ppm): 8.75 (t, 2H, J = 8.76 Hz), 8.63 (s, 2H), 1.55 (q, J = 1.53, 2H), 1.38-1.09 (m, 20H), 0.84-0.81 (m, 12H).

^{13}C-NMR (151 MHz, $CDCl_3$), δ (ppm): 156.52 (C), 154.12 (C), 148.12 (C), 147.85 (C), 147.60 (C), 146.16 (CH), 144.10, 136.18 (CH), 107.77, 36.22 (CH), 35.97(CH_2), 29.17 (CH_2), 29.13 (CH_2), 23.15 (CH_2), 17.86 (CH_2), 14.31 (CH_3), 10.98 (CH_3).

MALDI-TOF: m/z: 847.2 (M^+, 100).

Synthesis of ADV-2:

^{1}H-NMR (600 MHz, $CDCl_3$), δ (ppm): 8.80-8.76 (m), 8.04-8.00 (m), 7.36 (dd, J = 7.4 Hz), 7.02 (dd, J = 7 Hz), 2.73 (s), 2.62 (s), 1.74-1.61 (m), 1.39-1.22 (m), 0.89-0.85 (m). ^{13}C-NMR (151 MHz, $CDCl_3$), δ (ppm): 154.73, 153.71, 153.59, 148.07, 147.45, 146.14, 144.84, 143.76, 143.62, 142.71, 140.85, 136.68, 136.22, 135.28, 130.97, 130.57, 129.54, 129.35, 128.75, 128.21, 125.68, 119.52, 36.13, 35.87, 31.92, 30.81, 30.73, 29.68, 29.60, 29.48, 29.35, 29.28, 29.06, 29.04, 23.07, 22.68, 17.80, 14.22, 14.09, 10.87. GPC (TCB): Mn = 36800 g/mol; Mw = 120600 g/mol; PDI 3.3.

Figure 2: Synthetic route for ADV-2.

Figure 3: Optical properties of the NIR polymer. Absorption spectra of ADV-2 in solution (DCB)

and as thin film.

Figure 4: Device representation, electrical and chemical structures of ternary blends. a) Schematic representation of the BHJ solar cells with the layout ITO/ZnO/Active layer/MoOx/Ag. b) Energy levels and c) Chemical structure of the materials used in this work.

Figure 5: Photovoltaic properties of ternary devices. a) Current density-Voltage characteristics and b) External quantum efficiency curves of PIDTTQ:ADV-2:$PC_{71}BM$ and PIDTTQ:$PC_{71}BM$ solar cells under solar simulator illumination (100 mW cm-2).

Figure 6: Transport characterizations of ternary blends. a) Time-dependent photo-CELIV traces and b) transient photovoltage (TPV) plots of PIDTTQ:ADV-2:$PC_{71}BM$ and PIDTTQ:$PC_{71}BM$ solar cells.

Figure 7: Charge generation ability of ternary devices. a) Charge extraction (CE) traces and b) PIA spectra of PIDTTQ:ADV-2:$PC_{71}BM$ and PIDTTQ:$PC_{71}BM$ solar cells recorded under 60 mW cm^{-2} blue light intensity (λ=405 nm) at 10K.

Table 1: Photovoltaic parameters of PIDTTQ:ADV-2:$PC_{71}BM$ and PIDTTQ:$PC_{71}BM$ inverted solar cells under 1 sun illumination (100 mW cm^{-2}). The values are averaged on 12 devices. Composition considered by weight.

Table 2: Summary of calculated charge generation and charge transport parameters of PIDTTQ:ADV-2:$PC_{71}BM$ and PIDTTQ:$PC_{71}BM$ devices: charge carrier (μ), charge carrier density (n), charge carrier lifetime (τ) and mobility-lifetime product ($\mu\tau$).

DISCUSSION

We reported a novel ternary system with a clear contribution in the incident photon-to-current efficiency in the near IR region. A J_{sc} improvement of around 20% was obtained for PIDTTQ:ADV-2:$PC_{71}BM$ (0.85:0.15:2) ternary devices compared to PIDTTQ:$PC_{71}BM$ binary cells. However, the low *FF* limited the performances of the ternary BHJ solar cells.

We found that by adding ADV-2 into the host system of PIDTTQ:$PC_{71}BM$ the $\mu\tau$ product is reduced, explaining the lower *FFs*. Despite the poorer transport properties, the complementary results of CE and PIA spectroscopy showed an improved charge generation in PIDTTQ:ADV-2:$PC_{71}BM$ (0.85:0.15:2) ternary solar cells, leading to a PCE of more than 4.6%. We studied the photogeneration ability of the ternary solar cells using these two complementary techniques that require the whole device architecture and just the active layer in CE and PIA measurements, respectively, allowing us to have a better insight into the process, by combining the two methods.

We use common state-of-the-art techniques to fully characterize organic ternary solar cells. In particular we study the transport mechanism of the organic solar cells by employing photo-CELIV and TPV techniques directly on the devices, without the fabrication of any “ad hoc” devices used for instance in space-charge limited current measurements.[40] Moreover, in order to calculate reliable mobility values, we recorded more than 10 curves with different delay time and voltage ramp. Concerning the lifetime calculation, we used TPV as small perturbation method, allowing us to evaluate τ at the real operating condition of the solar cells (1 sun condition). With our experimental procedure not only organic solar cells can be characterized but our method can be easily used for inorganic and hybrid solar cells as well.

In conclusion, the combination of the aforementioned techniques allowed us to study the limitation mechanisms of ternary devices compared to the binary solar cells. Overcoming the losses will be a future challenge for the fabrication of high efficiency ternary organic solar cells.

Overall, we reported a combination of standard characterizations, i.e. J-V measurements, with powerful tools such as PIA spectroscopy. The main problem that can arise during the characterization is the device degradation. Therefore, encapsulation as well as characterization in inert condition might preserve the stability of those devices. Having the aforementioned techniques in N_2 or Ar atmosphere, i.e. glove-boxes, will increase the reliability of the device behavior.

ACKNOWLEDGMENTS:
This project has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under the Grant Agreement n° 607585 project OSNIRO. In addition, this project has received funding from the European Community's Seventh Framework Programme (FP7/2007–2013) under the Grant Agreement no. 331389. C. L. C. acknowledges the financial support of a Marie Curie Intra European Fellowship (FP7-PEOPLE-2012-IEF) project ECOCHEM. G. P. would like to thank the Ministry of Education and Religious Affairs in Greece for the financial support of this work provided under the co-operational program "AdvePol: E850". The authors gratefully acknowledge the support of the Cluster of Excellence ''Engineering of Advanced Materials'' at the University of Erlangen-Nuremberg, which is funded by the German Research Foundation (DFG) within the framework of its ''Excellence Initiative'', Synthetic Carbon Allotropes (SFB953) and Solar Technologies go Hybrid (SolTech).

DISCLOSURES:
The authors have nothing to disclose.

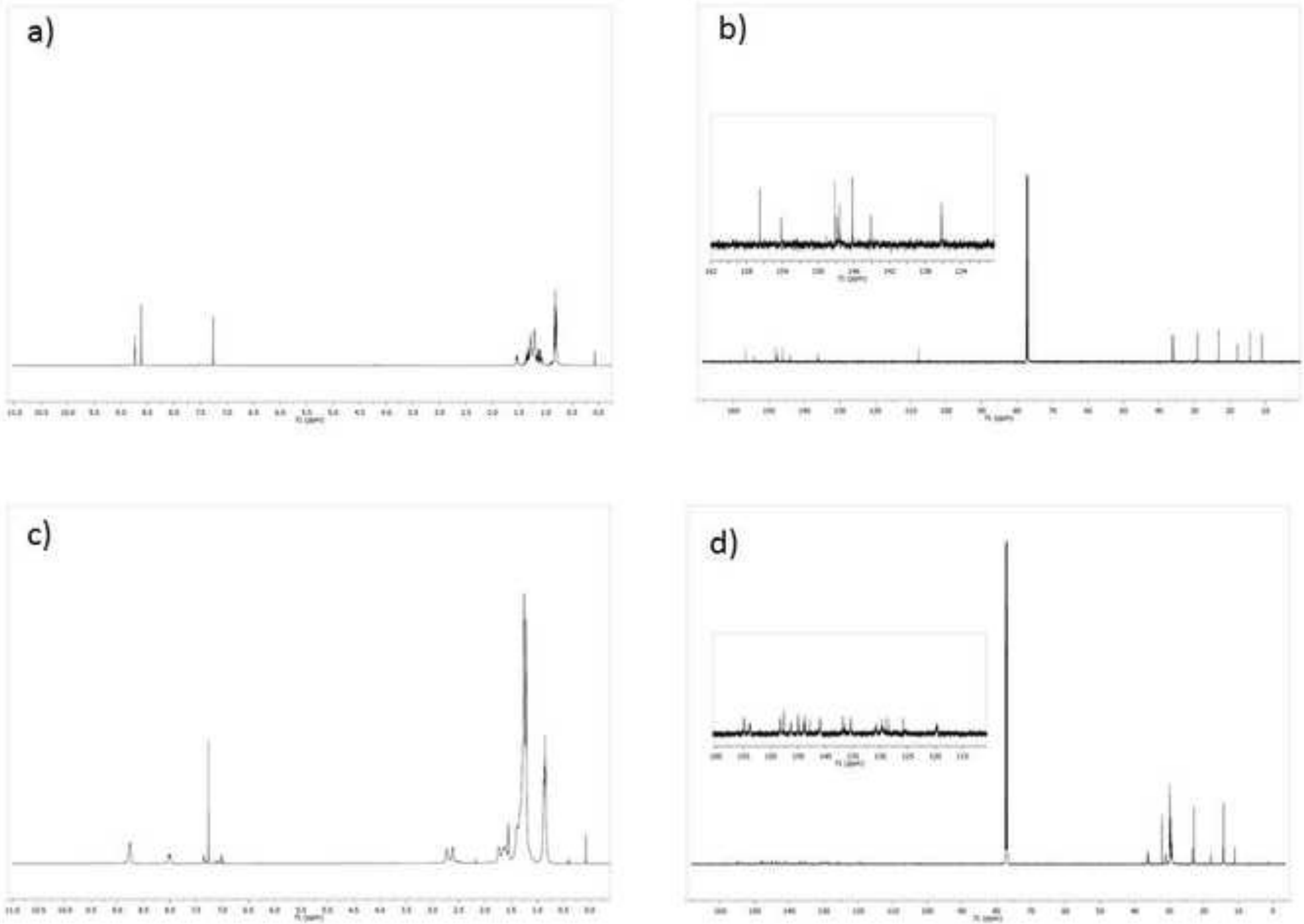
REFERENCES
1. Brabec, C. J., Sariciftci, N. S. & Hummelen, J. C. Plastic Solar Cells. *Adv. Funct. Mater.* **11** (1), 15–26, doi:10.1002/1616-3028(200102)11:1<15::aid-adfm15>3.0.co;2-a (2001).
2. Vohra, V., *et al.* Efficient inverted polymer solar cells employing favourable molecular orientation. *Nat. Photon.* **9**, 403–408, doi:10.1038/nphoton.2015.84 (2015).
3. He, Z., *et al.* Single-junction polymer solar cells with high efficiency and photovoltage. *Nat. Photon.* **9** (3), 174–179, doi:10.1038/nphoton.2015.6 (2015).
4. Chen, J.-D., *et al.* Single-Junction Polymer Solar Cells Exceeding 10% Power Conversion Efficiency. *Adv. Mater.* **27** (6), 1035–1041, doi:10.1002/adma.201404535 (2014).

5. Liu, Y., *et al.* Aggregation and morphology control enables multiple cases of high-efficiency polymer solar cells. *Nat. Commun.* **5** (9), 5293, doi:10.1038/ncomms6293 (2014).
6. Po, R., Carbonera, C., Bernardi, A. & Camaioni, N. The role of buffer layers in polymer solar cells. *Energy Environ. Sci.* **4** (2), 285, doi:10.1039/c0ee00273a (2011).
7. Ameri, T., Dennler, G., Lungenschmied, C. & Brabec, C. J. Organic tandem solar cells: A review. *Energy Environ. Sci.* **2** (4), 347, doi:10.1039/b817952b (2009).
8. Ameri, T., Li, N. & Brabec, C. J. Highly efficient organic tandem solar cells: a follow up review. *Energy Environ. Sci.* **6** (8), 2390–2413, doi:10.1039/c3ee40388b (2013).
9. You, J., *et al.* A polymer tandem solar cell with 10.6% power conversion efficiency. *Nat. Commun.* **4**, 1446, doi:10.1038/ncomms2411 (2013).
10. Guo, F., *et al.* Solution-Processed Parallel Tandem Polymer Solar Cells Using Silver Nanowires as Intermediate Electrode. *ACS Nano* **8** (12), 12632–12640, doi:10.1021/nn505559w (2014).
11. Chen, C.-C., *et al.* An Efficient Triple-Junction Polymer Solar Cell Having a Power Conversion Efficiency Exceeding 11%. *Adv. Mater.* **26** (32), 5670–5677, doi:10.1002/adma.201402072 (2014).
12. Ameri, T., Khoram, P., Min, J. & Brabec, C. J. Organic ternary solar cells: A review. *Adv. Mater.* **25**, 4245–4266, doi:10.1002/adma.201300623 (2013).
13. Koppe, M., *et al.* Near IR Sensitization of Organic Bulk Heterojunction Solar Cells: Towards Optimization of the Spectral Response of Organic Solar Cells. *Adv. Funct. Mater.* **20** (2), 338–346, doi:10.1002/adfm.200901473 (2010).
14. Ameri, T., *et al.* Performance enhancement of the p3ht/pcbm solar cells through nir sensitization using a small-bandgap polymer. *Adv. Energy Mater.* **2**, 1198–1202, doi:10.1002/aenm.201200219 (2012).
15. Guo, F., *et al.* A generic concept to overcome bandgap limitations for designing highly efficient multi-junction photovoltaic cells. *Nat. Commun.* **6**, 7730, doi:10.1038/ncomms8730 (2015).
16. Gasparini, N., *et al.* An Alternative Strategy to Adjust the Recombination Mechanism of Organic Photovoltaics by Implementing Ternary Compounds. *Adv. Energy Mater.*, n/a–n/a, doi:10.1002/aenm.201501527 (2015).
17. Spyropoulos, G. D., *et al.* Flexible organic tandem solar modules with 6% efficiency: combining roll-to-roll compatible processing with high geometric fill factors. *Energy Environ. Sci.* **7** (10), 3284–3290, doi:10.1039/C4EE02003K (2014).
18. Li, N., *et al.* Towards 15% energy conversion efficiency: a systematic study of the solution-processed organic tandem solar cells based on commercially available materials. *Energy Environ. Sci.* **6** (12), 3407–3413, doi:10.1039/c3ee42307g (2013).
19. Lu, L., Chen, W., Xu, T. & Yu, L. High-performance ternary blend polymer solar cells involving both energy transfer and hole relay processes. *Nat. Commun.* **6**, 7327, doi:10.1038/ncomms8327 (2015).
20. Yang, Y. M., *et al.* High-performance multiple-donor bulk heterojunction solar cells. *Nat. Photon.* **9** (3), 190–198, doi:10.1038/nphoton.2015.9 (2015).
21. Zhang, Y., *et al.* Synergistic Effect of Polymer and Small Molecules for High-Performance Ternary Organic Solar Cells. *Adv. Mater.* **27** (6), 1071–1076, doi:10.1002/adma.201404902 (2015).

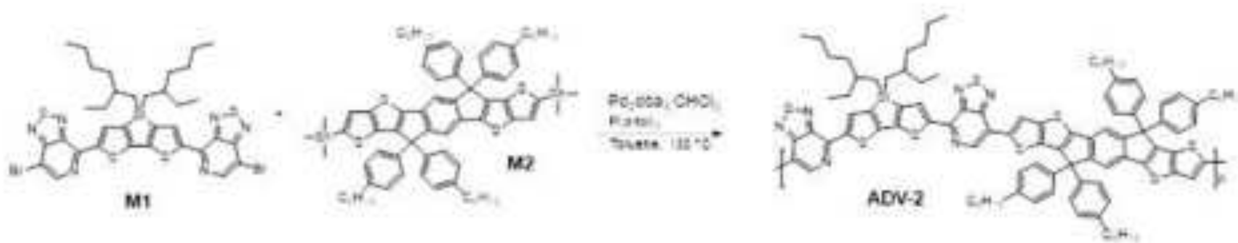
22. Ameri, T., *et al.* Morphology analysis of the near IR sensitized polymer / fullerene organic solar cells by implementing low bandgap polymer analogous of C-/Si-PCPDTBT. *J. Mater. Chem. A* **2**, 19461–19472, doi:10.1039/c4ta04070h (2014).
23. Cheng, P., Li, Y. & Zhan, X. Efficient ternary blend polymer solar cells with indene-C60 bisadduct as an electron-cascade acceptor. *Energy Environ. Sci.* **7** (6), 2005, doi:10.1039/c3ee44202k (2014).
24. Khlyabich, P. P., Rudenko, A. E., Street, R. A. & Thompson, B. C. Influence of Polymer Compatibility on the Open-Circuit Voltage in Ternary Blend Bulk Heterojunction Solar Cells. *ACS Appl. Mater. Interfaces* **6** (13), 9913–9919, doi:10.1021/am502122a (2014).
25. Lu, L., Xu, T., Chen, W., Landry, E. S. & Yu, L. Ternary blend polymer solar cells with enhanced power conversion efficiency. *Nat. Photon.* **8** (9), 716–722, doi:10.1038/nphoton.2014.172 (2014).
26. Lim, B., Bloking, J. T., Ponec, A., Mcgehee, M. D. & Sellinger, A. Ternary Bulk Heterojunction Solar Cells: Addition of Soluble NIR Dyes for Photocurrent Generation beyond 800 nmDyes for Photocurrent Generation beyond 800 nm. *ACS Appl. Mater. Interfaces* **6**, 6905, doi:dx.doi.org/10.1021/am5007172 (2014).
27. Itskos, G., *et al.* Optical properties of organic semiconductor blends with near-infrared quantum-dot sensitizers for light harvesting applications. *Adv. Energy Mater.* **1** (5), 802–812, doi:10.1002/aenm.201100182 (2011).
28. Mulherin, R. C., *et al.* Ternary photovoltaic blends incorporating an all-conjugated donor-acceptor diblock copolymer. *Nano Lett.* **11** (11), 4846–4851, doi:10.1021/nl202691n (2011).
29. Savoie, B. M., Dunaisky, S., Marks, T. J. & Ratner, M. a. The Scope and Limitations of Ternary Blend Organic Photovoltaics. *Adv. Energy Mater.* **5** (3), 1400891, doi:10.1002/aenm.201400891 (2015).
30. Gasparini, N., *et al.* Photophysics of Molecular-Weight-Induced Losses in Indacenodithienothiophene-Based Solar Cells. *Adv. Funct. Mater.* **25** (30), 4898–4907, doi:10.1002/adfm.201501062 (2015).
31. Heumueller, T., *et al.* Disorder-Induced Open-Circuit Voltage Losses in Organic Solar Cells During Photoinduced Burn-In. *Adv. Energy Mater.*, doi:10.1002/aenm.201500111 (2015).
32. A. Pivrikas, N. S. Sariciftci, G. J. and R. O. A Review of Charge Transport and Recombination in Polymer / Fullerene. *Progr. Photovoltaics: Res. Appl* **15**, 677–696, doi:10.1002/pip (2007).
33. Clarke, T. M., Lungenschmied, C., Peet, J., Drolet, N. & Mozer, A. J. A Comparison of Five Experimental Techniques to Measure Charge Carrier Lifetime in Polymer/Fullerene Solar Cells. *Adv. Energy Mater.* **5** (4), doi:10.1002/aenm.201401345 (2014).
34. Min, J., *et al.* Effects of Alkyl Terminal Chains on Morphology, Charge Generation, Transport, and Recombination Mechanisms in Solution-Processed Small Molecule Bulk Heterojunction Solar Cells. *Adv. Energy Mater.* **5** (17), doi:10.1002/aenm.201500386 (2015).
35. Shuttle, C. G., *et al.* Experimental determination of the rate law for charge carrier decay in a polythiophene: Fullerene solar cell. *Appl. Phys. Lett.* **92** (2008), 90–93, doi:10.1063/1.2891871 (2008).
36. Street, R. a., Krakaris, A. & Cowan, S. R. Recombination through different types of localized

states in organic solar cells. *Adv. Funct. Mater.* **22**, 4608–4619, doi:10.1002/adfm.201200031 (2012).

37. Azimi, H., Senes, A., Scharber, M. C., Hingerl, K. & Brabec, C. J. Charge Transport and Recombination in Low-Bandgap Bulk Heterojunction Solar Cell using Bis-adduct Fullerene. *Adv. Energy Mater.* **1** (6), 1162–1168, doi:10.1002/aenm.201100331 (2011).
38. Salvador, M., *et al.* Electron accumulation on metal nanoparticles in plasmon-enhanced organic solar cells. *ACS Nano* **6** (11), 10024–10032, doi:10.1021/nn303725v (2012).
39. Noone, K. M., *et al.* Photoinduced charge transfer and polaron dynamics in polymer and hybrid photovoltaic thin films: Organic vs inorganic acceptors. *J. Phys. Chem. C* **115** (49), 24403–24410, doi:10.1021/jp207514v (2011).
40. Gasparini, N., *et al.* Neat C70 -Based Bulk-Heterojunction Polymer Solar Cells with Excellent Acceptor Dispersion. *Appl. Mater. Interfaces* **6**, 21416–21425 doi: 10.1021/am506394m (2014).

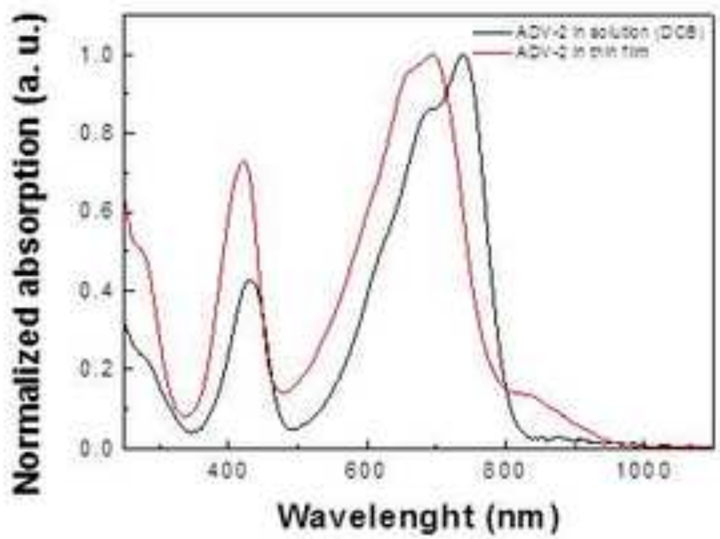

a)
b)
c)
d)

Figure



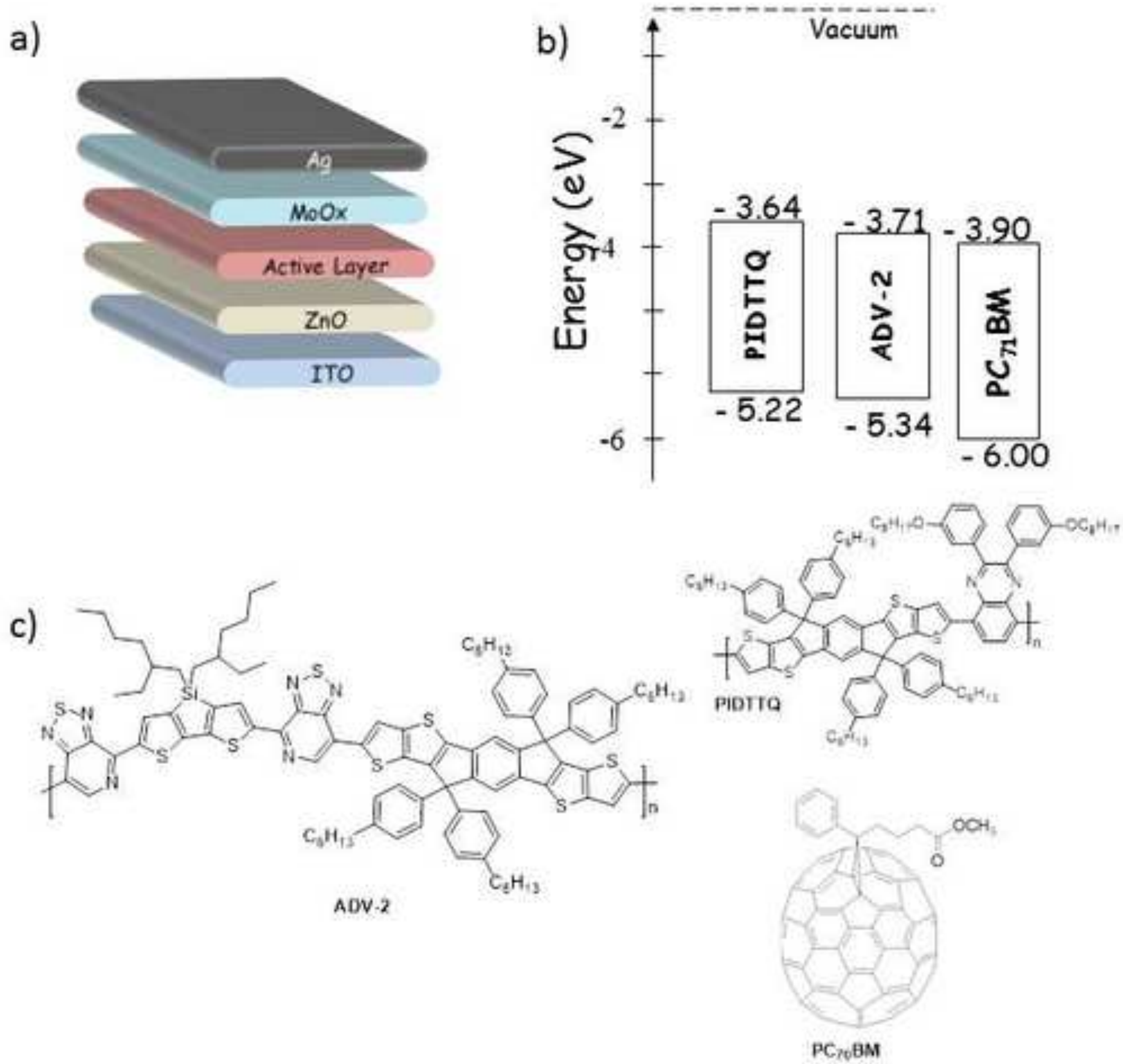
Figure

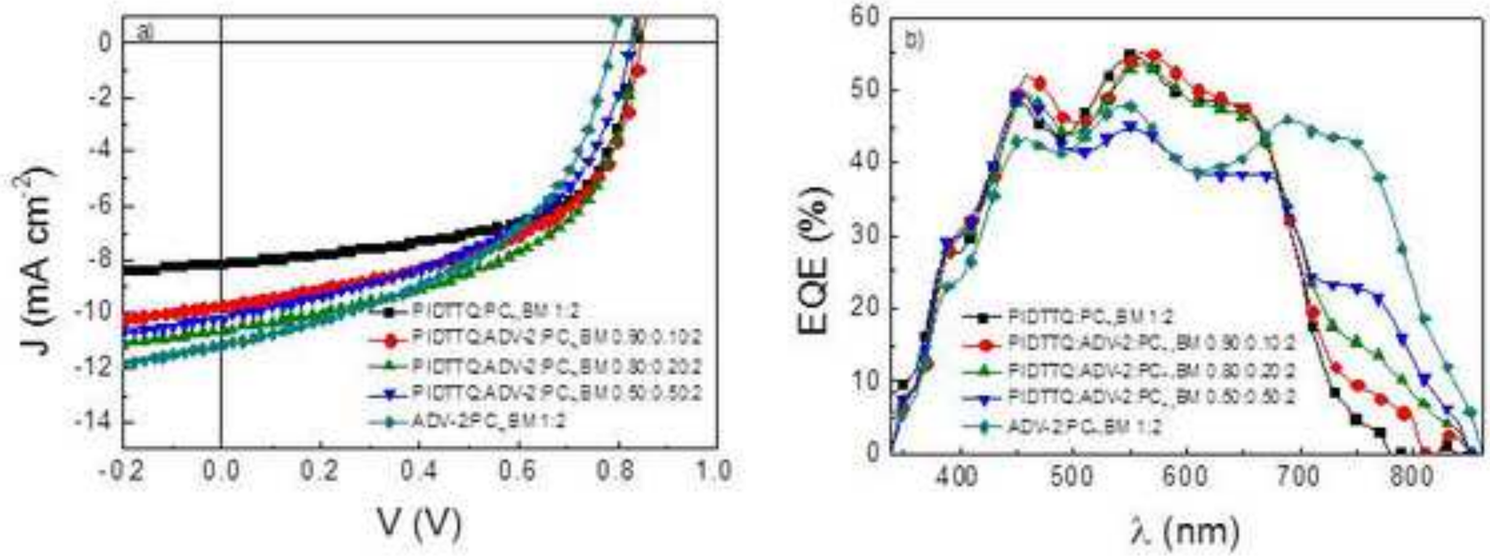
Click here to download Figure Figure 3.JPG

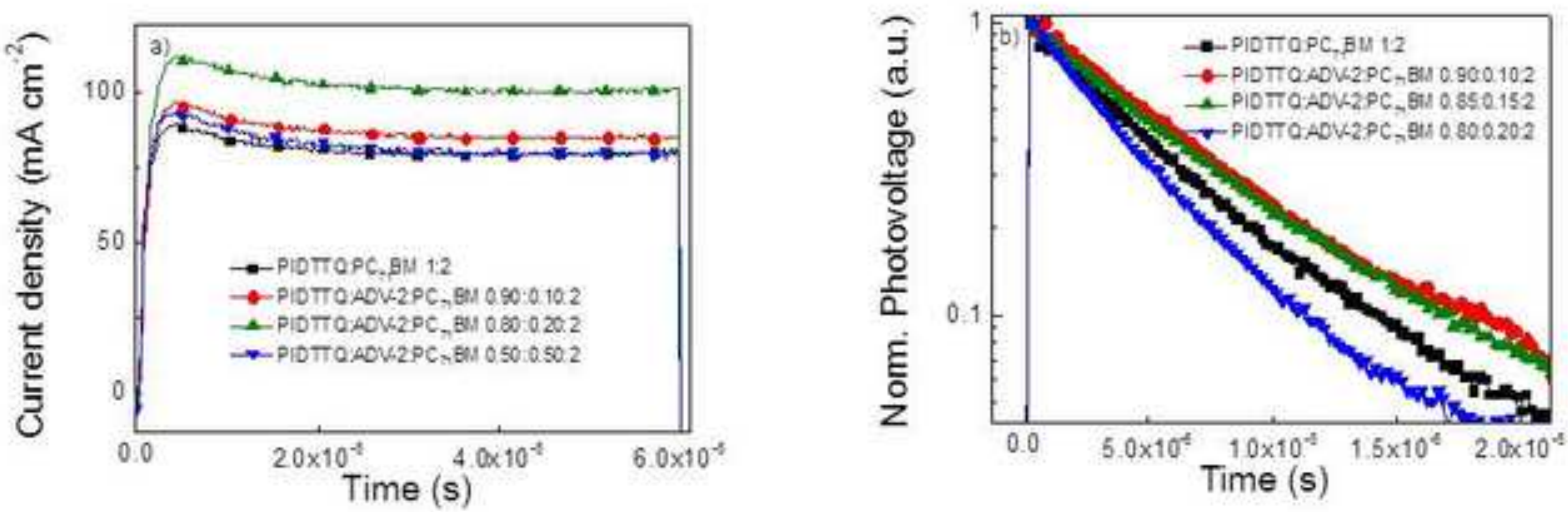


Figure

Click here to download Figure Figure 4.JPG




a)
J (mA cm^{-2})
V (V)
0
-2
-4
-6
-8
-10
-12
-14
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
PIDTTQ:PC BM 1:2
PIDTTQ:ADV-2:PC BM 0.90:0.10:2
PIDTTQ:ADV-2:PC BM 0.80:0.20:2
PIDTTQ:ADV-2:PC BM 0.50:0.50:2
ADV-2:PC BM 1:2
b)
EQE (%)
λ (nm)
60
50
40
30
20
10
0
400
500
600
700
800
PIDTTQ:PC BM 1:2
PIDTTQ:ADV-2:PC BM 0.90:0.10:2
PIDTTQ:ADV-2:PC BM 0.80:0.20:2
PIDTTQ:ADV-2:PC BM 0.50:0.50:2
ADV-2:PC BM 1:2


a)
Current density (mA cm^{-2})
Time (s)
PIDTTQ:PC71BM 1:2
PIDTTQ:ADV-2:PC71BM 0.90:0.10:2
PIDTTQ:ADV-2:PC71BM 0.80:0.20:2
PIDTTQ:ADV-2:PC71BM 0.50:0.50:2
b)
Nom. Photovoltage (a.u.)
Time (s)
PIDTTQ:PC71BM 1:2
PIDTTQ:ADV-2:PC71BM 0.90:0.10:2
PIDTTQ:ADV-2:PC71BM 0.85:0.15:2
PIDTTQ:ADV-2:PC71BM 0.80:0.20:2

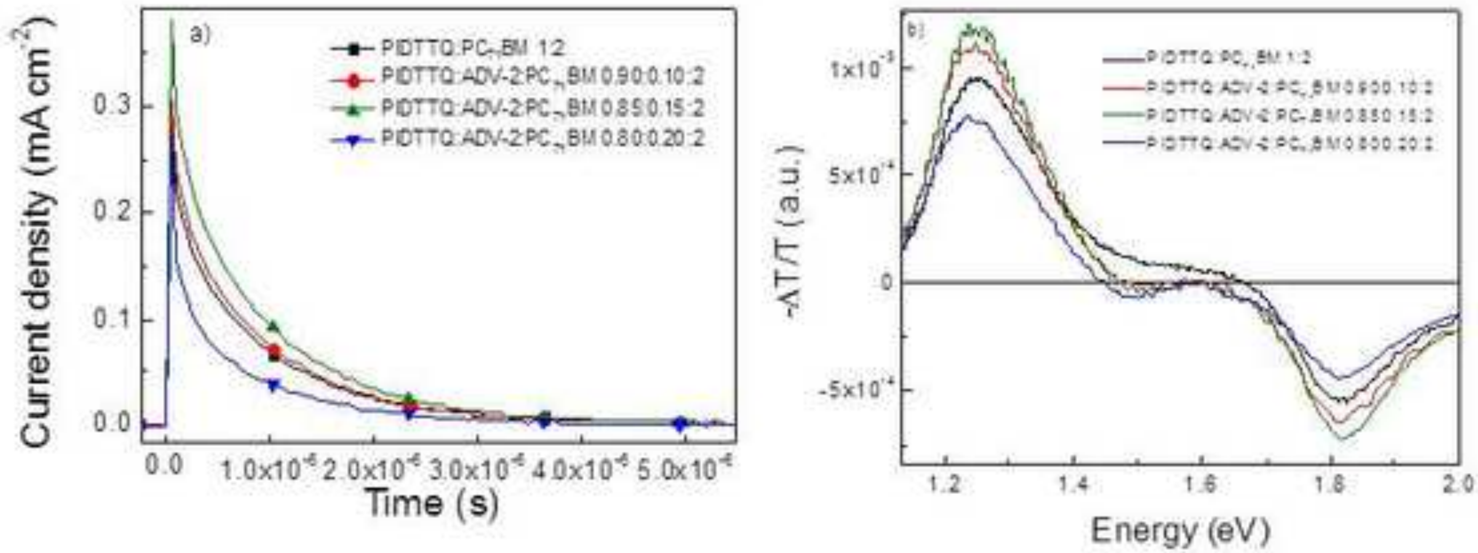

a)
Current density (mA cm^{-2})
0.0
0.1
0.2
0.3
Time (s)
0.0
1.0x10^{-6}
2.0x10^{-6}
3.0x10^{-6}
4.0x10^{-6}
5.0x10^{-6}
b)
-ΔT/T (a.u.)
1x10^{-3}
5x10^{-4}
0
-5x10^{-4}
Energy (eV)
1.2
1.4
1.6
1.8
2.0

Table 1 Click here to download Table Table 1.xlsx

PIDTTQ:ADV-2:$PC_{71}BM$	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	η (%)
1:00:02	0.84 (0.84±0.00)	8.62 (8.49±0.23)	60.33 (59.72±0.65)	4.35 (4.24±0.10)
0.90:0.10:2	0.84 (0.84±0.01)	9.69 (9.50±0.18)	53.14 (52.48±0.55)	4.29 (4.20±0.10)
0.85:0.15:2	0.84 (0.84±0.01)	10.60 (10.43±0.22)	51.87 (50.64±1.17)	4.63 (4.45±0.19)
0.80:0.20:2	0.84 (0.84±0.01)	10.14 (9.64±0.44)	48.86 (48.64±0.20)	4.04 (3.86±0.17)
0:01:02	0.81 (0.81±0.00)	10.87 (10.37±0.41)	46.61 (45.57±0.69)	3.95 (3.79±0.10)

PIDTTQ:ADV-2:$PC_{71}BM$	μ [$cm^2V^{-1}s^{-1}$]	τ [s]	$\mu\tau$ [cm^2V^{-1}]	n [cm^{-3}]
1:00:02	1.13×10^{-4}	6.72×10^{-6}	7.59×10^{-10}	2.97×10^{16}
0.90:0.10:2	8.54×10^{-5}	7.35×10^{-6}	6.72×10^{-10}	3.02×10^{16}
0.85:0.15:2	7.53×10^{-5}	7.23×10^{-6}	5.44×10^{-10}	3.66×10^{16}
0.80:0.20:2	7.42×10^{-5}	4.72×10^{-6}	3.50×10^{-10}	1.15×10^{16}

Name of Reagent/ Equipment
1,2-Dichlorobenzene
1-Chloronaphtalene
chloroform
PC71BM
Toluene
Chloroform-d
trichlorobenzene
5,5'-bis(trimethylstannyl)-3,3'-di-2-ethylhexylsilylene-2,2'-bithiophene
$Pd(PPh_3)_4$
source measurements unit
Solar simulator Oriel Sol 1A
Spectrometer Lambda 950
EQE setup
oscilloscope DSO-X 2024A
NMR setup
GPC setup
Doctor blade
evaporator
glove boxes
Laser 405 nm
funtion generator

Company	Catalog Number	Comments/Description
Aldrich	606078	solvent
Aldrich	970836	solvent
Aldrich	1731042	solvent
Solenne	07099	BHJ material
Aldrich	2036259	solvent
Aldrich	1697633	solvent
Aldrich	956819	solvent
Aldrich	143367-56-0	starting material
Aldrich	14221-01-3	catalyst
BoTEst		
Newport		
Perkin Elmer		
Enlitech		
Agilent Technologies		
Bruker AVANCE III 600		
Alliance 2000		
Zehntner ZAA 2300		
mbraun		
mbraun		
THORLABS		
Agilent Technologies 33500B series		

1 Alewife Center #200
Cambridge, MA 02140
tel. 617.945.9051
www.jove.com

ARTICLE AND VIDEO LICENSE AGREEMENT

Title of Article: Indacenodithienothiophene-based ternary organic solar cells; concept, devi and optoelec characterizati

Author(s): Nicola Gasparini, ..., Tayebeh Ameri

Item 1 (check one box): The Author elects to have the Materials be made available (as described at http://www.jove.com/publish) via: [X] Standard Access [ ] Open Access

Item 2 (check one box):

[X] The Author is NOT a United States government employee.

[ ] The Author is a United States government employee and the Materials were prepared in the course of his or her duties as a United States government employee.

[ ] The Author is a United States government employee but the Materials were NOT prepared in the course of his or her duties as a United States government employee.

ARTICLE AND VIDEO LICENSE AGREEMENT

1. Defined Terms. As used in this Article and Video License Agreement, the following terms shall have the following meanings: "**Agreement**" means this Article and Video License Agreement; "**Article**" means the article specified on the last page of this Agreement, including any associated materials such as texts, figures, tables, artwork, abstracts, or summaries contained therein; "**Author**" means the author who is a signatory to this Agreement; "**Collective Work**" means a work, such as a periodical issue, anthology or encyclopedia, in which the Materials in their entirety in unmodified form, along with a number of other contributions, constituting separate and independent works in themselves, are assembled into a collective whole; "**CRC License**" means the Creative Commons Attribution-Non Commercial-No Derivs 3.0 Unported Agreement, the terms and conditions of which can be found at: http://creativecommons.org/licenses/by-nc-nd/3.0/legalcode; "**Derivative Work**" means a work based upon the Materials or upon the Materials and other pre-existing works, such as a translation, musical arrangement, dramatization, fictionalization, motion picture version, sound recording, art reproduction, abridgment, condensation, or any other form in which the Materials may be recast, transformed, or adapted; "**Institution**" means the institution, listed on the last page of this Agreement, by which the Author was employed at the time of the creation of the Materials; "**JoVE**" means MyJove Corporation, a Massachusetts corporation and the publisher of *The Journal of Visualized Experiments;* "**Materials**" means the Article and / or the Video; "**Parties**" means the Author and JoVE; "**Video**" means any video(s) made by the Author, alone or in conjunction with any other parties, or by JoVE or its affiliates or agents, individually or in collaboration with the Author or any other parties, incorporating all or any portion of the Article, and in which the Author may or may not appear.

2. Background. The Author, who is the author of the Article, in order to ensure the dissemination and protection of the Article, desires to have the JoVE publish the Article and create and transmit videos based on the Article. In furtherance of such goals, the Parties desire to memorialize in this Agreement the respective rights of each Party in and to the Article and the Video.

3. Grant of Rights in Article. In consideration of JoVE agreeing to publish the Article, the Author hereby grants to JoVE, subject to **Sections 4** and **7** below, the exclusive, royalty-free, perpetual (for the full term of copyright in the Article, including any extensions thereto) license (a) to publish, reproduce, distribute, display and store the Article in all forms, formats and media whether now known or hereafter developed (including without limitation in print, digital and electronic form) throughout the world, (b) to translate the Article into other languages, create adaptations, summaries or extracts of the Article or other Derivative Works (including, without limitation, the Video) or Collective Works based on all or any portion of the Article and exercise all of the rights set forth in (a) above in such translations, adaptations, summaries, extracts, Derivative Works or Collective Works and (c) to license others to do any or all of the above. The foregoing rights may be exercised in all media and formats, whether now known or hereafter devised, and include the right to make such modifications as are technically necessary to exercise the rights in other media and formats. If the "Open Access" box has been checked in **Item 1** above, JoVE and the Author hereby grant to the public all such rights in the Article as provided in, but subject to all limitations and requirements set forth in, the CRC License.

4. Retention of Rights in Article. Notwithstanding the exclusive license granted to JoVE in **Section 3** above, the Author shall, with respect to the Article, retain the non-exclusive right to use all or part of the Article for the non-commercial purpose of giving lectures, presentations or teaching classes, and to post a copy of the Article on the Institution's website or the Author's personal website, in each case provided that a link to the Article on the JoVE website is provided and notice of JoVE's copyright in the Article is included. All non-copyright intellectual property rights in and to the Article, such as patent rights, shall remain with the Author.

5. Grant of Rights in Video – Standard Access. This **Section 5** applies if the "Standard Access" box has been checked in **Item 1** above or if no box has been checked in **Item 1** above. In consideration of JoVE agreeing to produce, display or otherwise assist with the Video, the Author hereby acknowledges and agrees that, Subject to **Section 7** below, JoVE is and shall be the sole and exclusive owner of all rights of any nature, including, without limitation, all copyrights, in and to the Video. To the extent that, by law, the Author is deemed, now or at any time in the future, to have any rights of any nature in or to the Video, the Author hereby disclaims all such rights and transfers all such rights to JoVE.

6. Grant of Rights in Video – Open Access. This **Section 6** applies only if the "Open Access" box has been checked in **Item 1** above. In consideration of JoVE agreeing to produce, display or otherwise assist with the Video, the Author hereby grants to JoVE, subject to **Section 7** below, the exclusive, royalty-free, perpetual (for the full term of copyright in the Article, including any extensions thereto) license (a) to publish, reproduce, distribute, display and store the Video in all forms, formats and media whether now known or hereafter developed (including without limitation in print, digital and electronic form) throughout the world, (b) to translate the Video into other languages, create adaptations, summaries or extracts of the Video or other Derivative Works or Collective Works based on all or any portion of the Video and exercise all of the rights set forth in (a) above in such translations, adaptations, summaries, extracts, Derivative Works or Collective Works and (c) to license others to do any or all of the above. The foregoing rights may be exercised in all media and formats, whether now known or hereafter devised, and include the right to make such modifications as are technically necessary to exercise the rights in other media and formats. For any Video to which this Section 6 is applicable, JoVE and the Author hereby grant to the public all such rights in the Video as provided in, but subject to all limitations and requirements set forth in, the CRC License.

7. Government Employees. If the Author is a United States government employee and the Article was prepared in the course of his or her duties as a United States government employee, as indicated in **Item 2** above, and any of the licenses or grants granted by the Author hereunder exceed the scope of the 17 U.S.C. 403, then the rights granted hereunder shall be limited to the maximum rights permitted under such statute. In such case, all provisions contained herein that are not in conflict with such statute shall remain in full force and effect, and all provisions contained herein that do so conflict shall be deemed to be amended so as to provide to JoVE the maximum rights permissible within such statute.

8. Likeness, Privacy, Personality. The Author hereby grants JoVE the right to use the Author's name, voice, likeness, picture, photograph, image, biography and performance in any way, commercial or otherwise, in connection with the Materials and the sale, promotion and distribution thereof. The Author hereby waives any and all rights he or she may have, relating to his or her appearance in the Video or otherwise relating to the Materials, under all applicable privacy, likeness, personality or similar laws.

9. Author Warranties. The Author represents and warrants that the Article is original, that it has not been published, that the copyright interest is owned by the Author (or, if more than one author is listed at the beginning of this Agreement, by such authors collectively) and has not been assigned, licensed, or otherwise transferred to any other party. The Author represents and warrants that the author(s) listed at the top of this Agreement are the only authors of the Materials. If more than one author is listed at the top of this Agreement and if any such author has not entered into a separate Article and Video License Agreement with JoVE relating to the Materials, the Author represents and warrants that the Author has been authorized by each of the other such authors to execute this Agreement on his or her behalf and to bind him or her with respect to the terms of this Agreement as if each of them had been a party hereto as an Author. The Author warrants that the use, reproduction, distribution, public or private performance or display, and/or modification of all or any portion of the Materials does not and will not violate, infringe and/or misappropriate the patent, trademark, intellectual property or other rights of any third party. The Author represents and warrants that it has and will continue to comply with all government, institutional and other regulations, including, without limitation all institutional, laboratory, hospital, ethical, human and animal treatment, privacy, and all other rules, regulations, laws, procedures or guidelines, applicable to the Materials, and that all research involving human and animal subjects has been approved by the Author's relevant institutional review board.

10. JoVE Discretion. If the Author requests the assistance of JoVE in producing the Video in the Author's facility, the Author shall ensure that the presence of JoVE employees, agents or independent contractors is in accordance with the relevant regulations of the Author's institution. If more than one author is listed at the beginning of this Agreement, JoVE may, in its sole discretion, elect not take any action with respect to the Article until such time as it has received complete, executed Article and Video License Agreements from each such author. JoVE reserves the right, in its absolute and sole discretion and without giving any reason therefore, to accept or decline any work submitted to JoVE. JoVE and its employees, agents and independent contractors shall have

ARTICLE AND VIDEO LICENSE AGREEMENT

full, unfettered access to the facilities of the Author or of the Author's institution as necessary to make the Video, whether actually published or not. JoVE has sole discretion as to the method of making and publishing the Materials, including, without limitation, to all decisions regarding editing, lighting, filming, timing of publication, if any, length, quality, content and the like.

11. Indemnification. The Author agrees to indemnify JoVE and/or its successors and assigns from and against any and all claims, costs, and expenses, including attorney's fees, arising out of any breach of any warranty or other representations contained herein. The Author further agrees to indemnify and hold harmless JoVE from and against any and all claims, costs, and expenses, including attorney's fees, resulting from the breach by the Author of any representation or warranty contained herein or from allegations or instances of violation of intellectual property rights, damage to the Author's or the Author's institution's facilities, fraud, libel, defamation, research, equipment, experiments, property damage, personal injury, violations of institutional, laboratory, hospital, ethical, human and animal treatment, privacy or other rules, regulations, laws, procedures or guidelines, liabilities and other losses or damages related in any way to the submission of work to JoVE, making of videos by JoVE, or publication in *JoVE* or elsewhere by JoVE. The Author shall be responsible for, and shall hold JoVE harmless from, damages caused by lack of sterilization, lack of cleanliness or by contamination due to the making of a video by JoVE its employees, agents or independent contractors. All sterilization, cleanliness or decontamination procedures shall be solely the responsibility of the Author and shall be undertaken at the Author's expense. All indemnifications provided herein shall include JoVE's attorney's fees and costs related to said losses or damages. Such indemnification and holding harmless shall include such losses or damages incurred by, or in connection with, acts or omissions of JoVE, its employees, agents or independent contractors.

12. Fees. To cover the cost incurred for publication, JoVE must receive payment before production and publication the Materials. Payment is due in 21 days of invoice. Should the Materials not be published due to an editorial or production decision, these funds will be returned to the Author. Withdrawal by the Author of any submitted Materials after final peer review approval will result in a US$1,200 fee to cover pre-production expenses incurred by JoVE. If payment is not received by the completion of filming, production and publication of the Materials will be suspended until payment is received.

13. Transfer, Governing Law. This Agreement may be assigned by JoVE and shall inure to the benefits of any of JoVE's successors and assignees. This Agreement shall be governed and construed by the internal laws of the Commonwealth of Massachusetts without giving effect to any conflict of law provision thereunder. This Agreement may be executed in counterparts, each of which shall be deemed an original, but all of which together shall be deemed to me one and the same agreement. A signed copy of this Agreement delivered by facsimile, e-mail or other means of electronic transmission shall be deemed to have the same legal effect as delivery of an original signed copy of this Agreement.

A signed copy of this document must be sent with all new submissions. Only one Agreement required per submission.

CORRESPONDING AUTHOR:

Name: Tayebeh Ameri
Department: Materials Science and Engineering
Institution: Materials for Electronics and Energy Technology (iMEET)
Article Title: Indacenodithienothiophene-based ternary organic solar cells; concep, device and optoelectrical characterization
Signature: Tayebeh Ameri
Date: 31.07.2015

Please submit a signed and dated copy of this license by one of the following three methods:

1) Upload a scanned copy of the document as a pfd on the JoVE submission site;
2) Fax the document to +1.866.381.2236;
3) Mail the document to JoVE / Attn: JoVE Editorial / 1 Alewife Center #200 / Cambridge, MA 02139

For questions, please email submissions@jove.com or call +1.617.945.9051

Dr. Nam Nguyen
Editorial Board of Journal of Visualized Experiments

Re: Revised submission of manuscript titled "Indacenodithienothiophene-Based Ternary Organic Solar Cells: Concept, Devices and optoelectronic analysis." by the authors Nicola Gasparini, Amaranda García-Rodríguez, Athanasios Katsouras, Apostolos Avgeropoulos, Georgia Pagona, Vasilis G. Gregoriou, Christos L. Chochos, Sybille Allard, Ulrich Scherf, Christoph J. Brabec and Tayebeh Ameri

January, 21st 2016

Dear Dr. Nam Nguyen,

Thank you very much for your letter from January 12th, 2016 and for your comments on our paper entitled "Indacenodithienothiophene-Based Ternary Organic Solar Cells: Concept, Devices and optoelectronic analysis." by the authors Nicola Gasparini, Amaranda García-Rodríguez, Athanasios Katsouras, Apostolos Avgeropoulos, Georgia Pagona, Vasilis G. Gregoriou, Christos L. Chochos, Sybille Allard, Ulrich Scherf, Christoph J. Brabec and Tayebeh Ameri. We have carefully read the reports and agree with most of the issues raised, whom we thank for your valuable comments. Following closely their advice, we have revised the manuscript accordingly. We hope you will find the manuscript in suitable form for publication in Journal of Visualized Experiments. Thank you for your consideration.

Yours Sincerely,

Nicola Gasparini

What is the size of the column in step 2.4?
The size of the column is I.D. × L 25 mm × 300 mm.
As currently written, step 6 cannot be filmed.

In step 6.1.1/6.1.3, what is used to measure the J-V characteristics? How was the measurement done and what are the parameters? Again, you cannot reference the specifics of the procedural detail. How many measurements are taken? For how long? etc.
In order to make clear how the JV characteristics are taken, we reported a schematic of the setup (Fig 1).

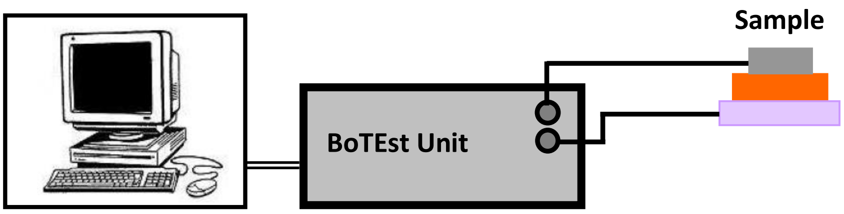


Fig. 1: Schematic experimental setup to measure J-V characteristics of the devices under ambient condition.

Specifically, we scan the voltages between -2V and 2V with a ΔV=20mV and point by point we obtained the corresponding current (I). The current density (J) is then calculated by the equation J=I/A, where A is the area of the solar cells (10.4 mm^2 in our case).

In step 6.2.1, how much was used to measure UV-Vis spectrum? Was there a dilution?
The UV-VIS spectra are taken directly on film, not in solution, therefore no dilution are needed.

For step 6.3.2, please specify that the BNC cables are used to connect the oscillator. Can a supplemental figure be provided for scripting?

Done.

For step 6.3.3, please explain the variable time delay briefly in the protocol. This is necessary if you want this step filmed.

Done.

For step 6.5.3, where did the analog switch come from? A supplemental figure is necessary here.

The analog switch, also called the bilateral switch, is an electronic component that behaves in a similar way to a relay, but has no moving parts. I cannot take a picture because is an homemade system. During the filming on the oscilloscope will be clear the function of the analog switch.

How is the lock in technique performed? Please explicitly detail how this standard technique is performed, especially if this is to be filmed.

How is the mechanical chopper used? What is done?
In order to make clear how the PIA spectroscopy is working, we reported a schematic of the setup (Fig 2).

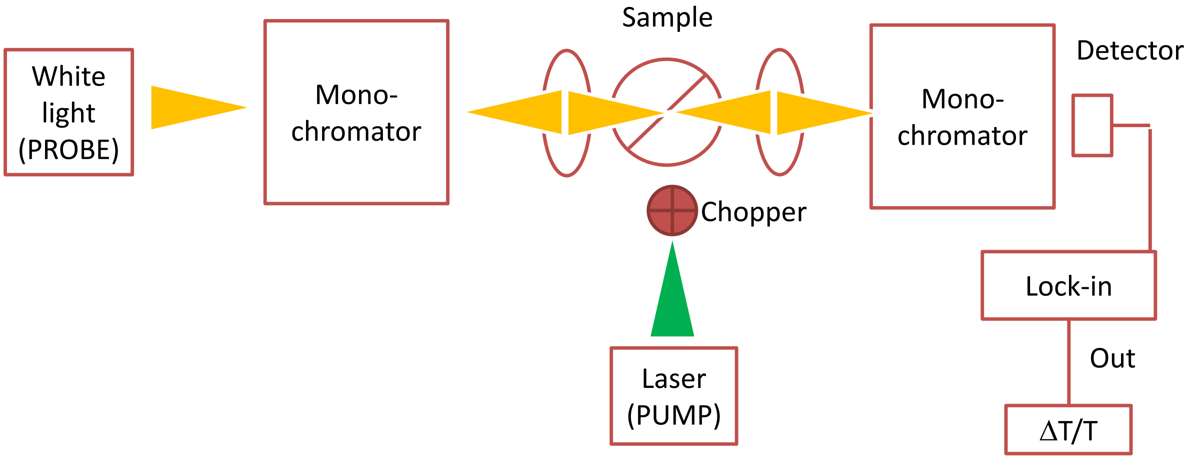


Fig. 1: Schematic experimental setup to measure J-V characteristics of the devices under ambient condition.

In this method the excitation (laser PUMP) is done by using a green laser (λ=532 nm), which is modulated by a mechanical chopper. The sample is additionally illuminated by a monochromated light beam ("probe") of a white light source. First the sample's transmittance and the sample's photoluminescence is measured. The measured signal is analysed with a lock-in amplifier using the chopper frequency as the reference signal, allowing a very precise quantification of the change in absorption induced by the pump-light. Using various detectors (Si, Ge) a broad wavelength region ranging from 400nm up to 1800nm can be analysed. Varying the material composition, material dependent effects can be characterized.

2. Please discuss the significance of the technique with respect to other methods, the critical steps of the protocol, and any modifications/troubleshooting that can be performed. This must be explicit.

Done.