Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting Information
for

Carbon Nanohorn-based electrolyte for Dye-Sensitized Solar Cells

By Fabian Lodermeyer, Rubén D. Costa, Rubén Casillas, Florian T. U. Kohler, Peter Wasserscheid, Maurizio Prato, and Dirk M. Guldi

Materials

All chemicals were purchased from chemical suppliers and used without further purification. $TiCl_4$ (0.09 M in HCl), guanidinium thiocyanate, 4-*tert*-butylpyridine, 1-ethyl-3-methylimidazolium iodide, 1-butyl-3-methylimidazolium tetrafluoroborate, cis-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) bis(tetrabutyl-ammonium), and H_2Cl_6Pt x H_2O were purchased from Sigma-Aldrich. TiO_2 paste (Ti-Nanoxide T/SP) and the sealing foil (Meltonix 1170-25) were purchased from Solaronix. SWCNHs were produced by Carbonium s.r.l., Padova (Italy) by direct graphite evaporation in Ar flow, according to a patented method and used without purification.[1]

Dye-sensitized solar cell fabrication and characterization

FTO substrates were sonicated for 15 min with a detergent solution, washed with deionized water, and again sonicated in isopropyl alcohol for 15 min. FTOs were immersed into a 40 mM aqueous $TiCl_4$ solution at 70 °C for 30 min and washed with water and ethanol. Treated substrates were sintered at 450 °C for 30 min. The transparent nanocrystalline TiO_2 layer were prepared on FTO glass plates by using a doctor blade technique. The TiO_2 anodes were gradually heated under air flow at 450 °C for 30 min. For alpha-step thickness measurements, we utilized a profilometer Dektak XT from Bruker. The average thickness of the films was 7 μm. Solaronix claims a pore size between 15 – 20 nm when applying the standard Ti-Nanoxide T/SP paste. The electrodes were immersed at around 80 °C in a solution of N719 (0.5 mM in ACN:EtOH 1:1 v/v) over night and rinsed with EtOH.

For preparation of the counter-electrodes two holes (0.1 mm) were drilled into FTOs *via* sandblasting prior to the cleaning procedure (*vide supra*). FTOs were coated with a thin film of chloroplatinic solution (4.88 mM) in isopropyl alcohol. Thereby, always the same amount of chloroplatinic solution (26 μL) was used to assure the same coverage of the FTO. Then, the slides were annealed to 390 °C for 15 min. For every measurement counter-electrodes were freshly prepared to assure reproducible results.

The photoanodes and the counter-electrodes were assembled into a sealed sandwich-type cell by heating at 130 °C with a controlled pressure using a hot-melt ionomer film (Surlyn). The electrolytes were introduced *via* capillary forces. Finally, the two holes were sealed using an additional Surlyn and a cover glass. For every experiment three cells were assembled to prove good reproducibility.

The photocurrent measurements and electrochemical impedance spectroscopy (EIS) were performed using a 150 W lamp (Xenon lamp, calibrated to 1000 W m^{-2} under AM 1.5 conditions with a Si-Reference cell (Oriel SRC-1000-TC-K-KG5-N). Current-voltage measurements were measured by using a potentiostat/galvanostat (PGSTAT30N, Autolab equipped with a frequency response analyzer module – FRA) in the range of -0.8 to 0.2 V. EIS measurements for ssDSSCs were performed at the respective open-circuit voltage of the different devices at 1000 W m^{-2} and AM 1.5 conditions. The AC signal amplitude was set at 10 mV, modulated in a frequency range from 0.1 to 100000 Hz. The Nova ver. 1.10 software was used to obtain the parameters from the equivalent circuit.

The linear sweep voltammetry of the electrolytes in the FTO-Pt/electrolyte/Pt-FTO configuration measurements and were performed with an Autolab potentiostat/galvanostat (PGSTAT30, Autolab equipped with a frequency response analyzer module – FRA) in the range of 0.8 to 0.2 V. Here, EIS was performed without applying a potential. The AC signal amplitude was set at 10 mV, modulated in a frequency range from 0.1 to 100000 Hz.

Transmission electron microscopy

Transmission electron microscopy (TEM) was performed with Zeiss TEM 912 Omega.

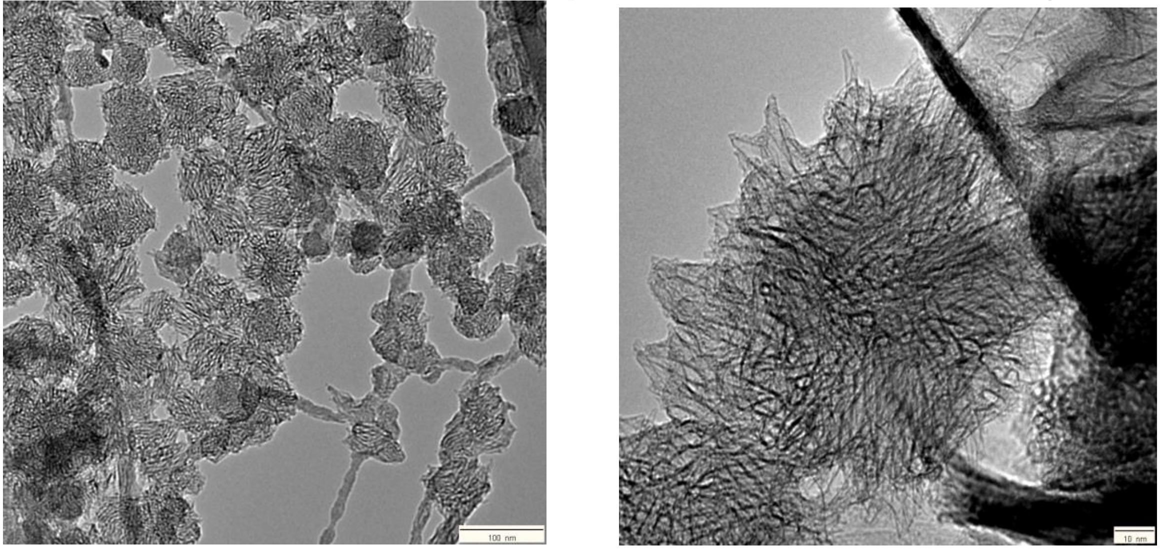

Figure S1. Transmission electron microscopy (TEM) image (left) and zoom in (right) of a drop casted dispersion of CNH in chlorobenzene onto a lacey carbon grid.

Raman experiments

Raman experiments were performed using Bruker RFS 100/3 with an excitation of 532 nm and a power of 50 mW.

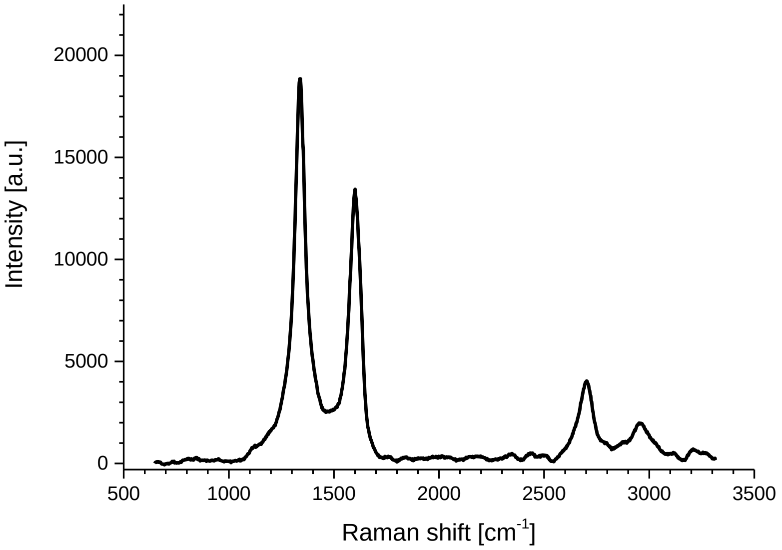

Figure S2. Raman spectrum of pristine CNHs measured in solid state at 532 nm excitation.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed with a TGA Q500 TA Instruments at 10 °C/min under nitrogen.

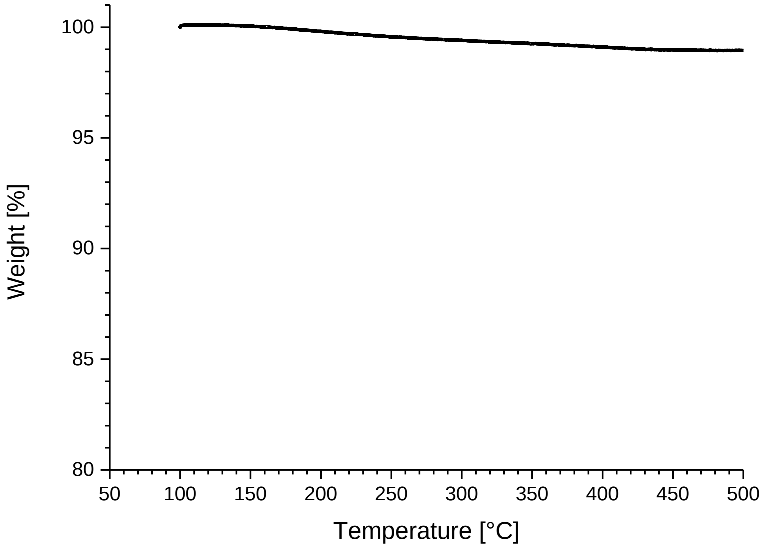

Figure S3. Thermogravimetric analysis profile of pristine CNHs measured under nitrogen conditions.

Differential scanning calorimetry measurements

Differential scanning calorimetry (DSC) was measured on a Netzsch DSC 204 with a heating rate of 5 K min^{-1} under ambient conditions.

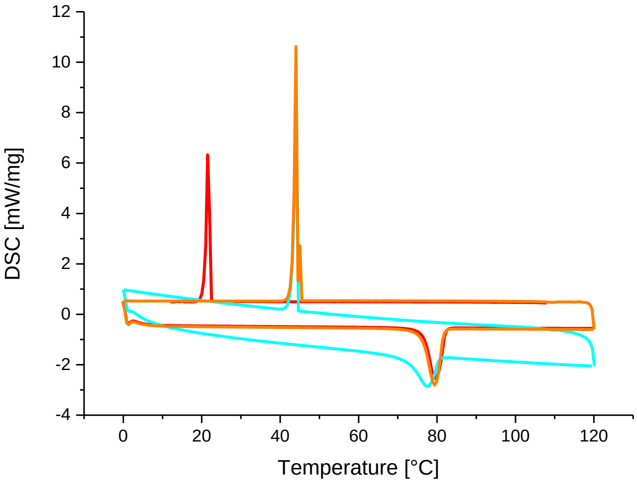

Figure S4. DSC measurements of pure [EMIM]I (red) and mixtures of [EMIM]I:CNHs weight ratios of 5:1 (cyan) and 10:1 (orange).

Scanning Electronic Microscopy

Scanning Electronic Microscopy (SEM) images were performed with Zeiss Gemini 55 Ultra under vacuum (10^{-9} mbar).

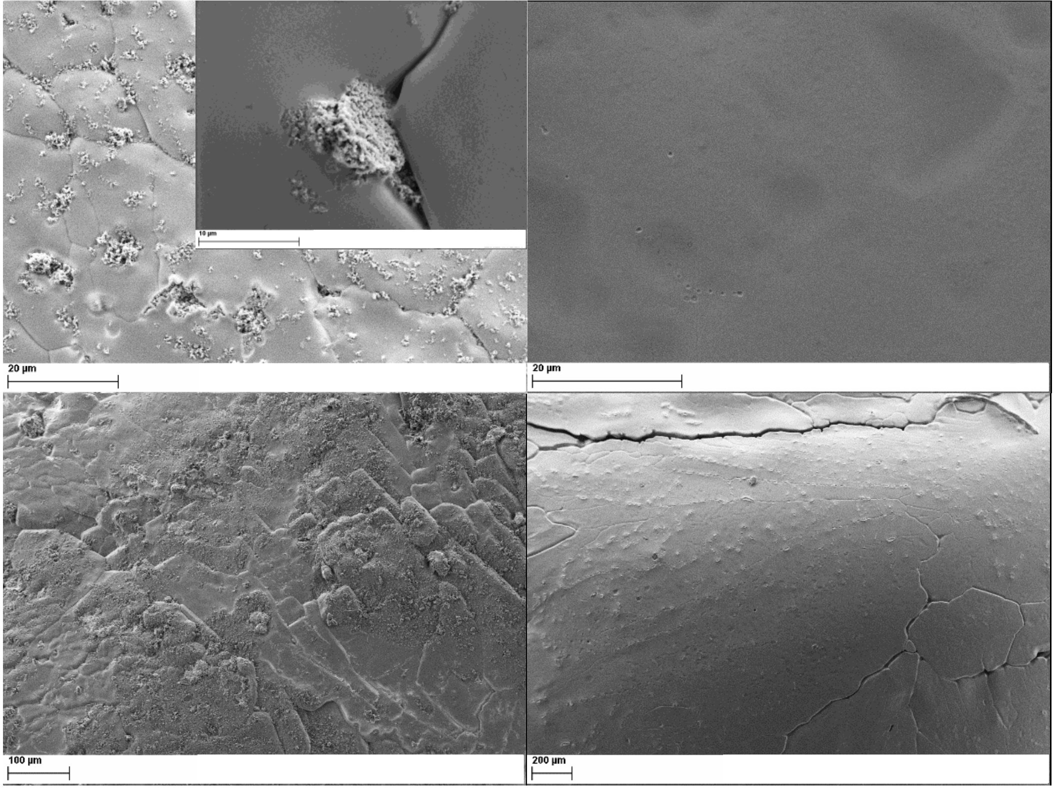

Figure S5. Upper part: SEM images of [EMIM]I:CNHs 1:1 wt% (left) and pure [EMIM]I (right). The inset displays the intercalation of CNH aggregates into the [EMIM]I matrix. Lower part: Lower magnification of the aforementioned electrolytes.

Linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS)

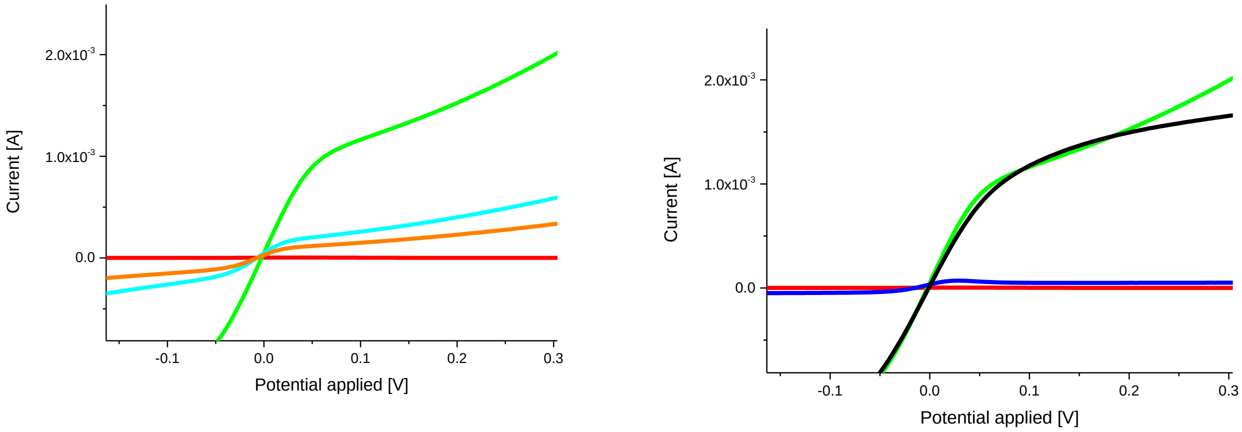

Figure S6: Left: LSV measurements of pure [EMIM]I (red) and mixtures of [EMIM]I:CNHs weight ratios of 10:1 (orange), 5:1 (cyan), and 1:1 (green). Right: LSV measurements of pure EMII (**E1,** red), [EMIM]I:CNHs 1:1 wt% (**E2**, green), [EMIM]I:[BMIM][BF$_4$]:TBP:GuSCN 1:0.25:0.83:0.17 wt% (**E3**, blue), and [EMIM]I:CNHs:[BMIM][BF$_4$]:TBP:GuSCN 1:1:0.25:0.83:0.17 wt% (**E4**, black).

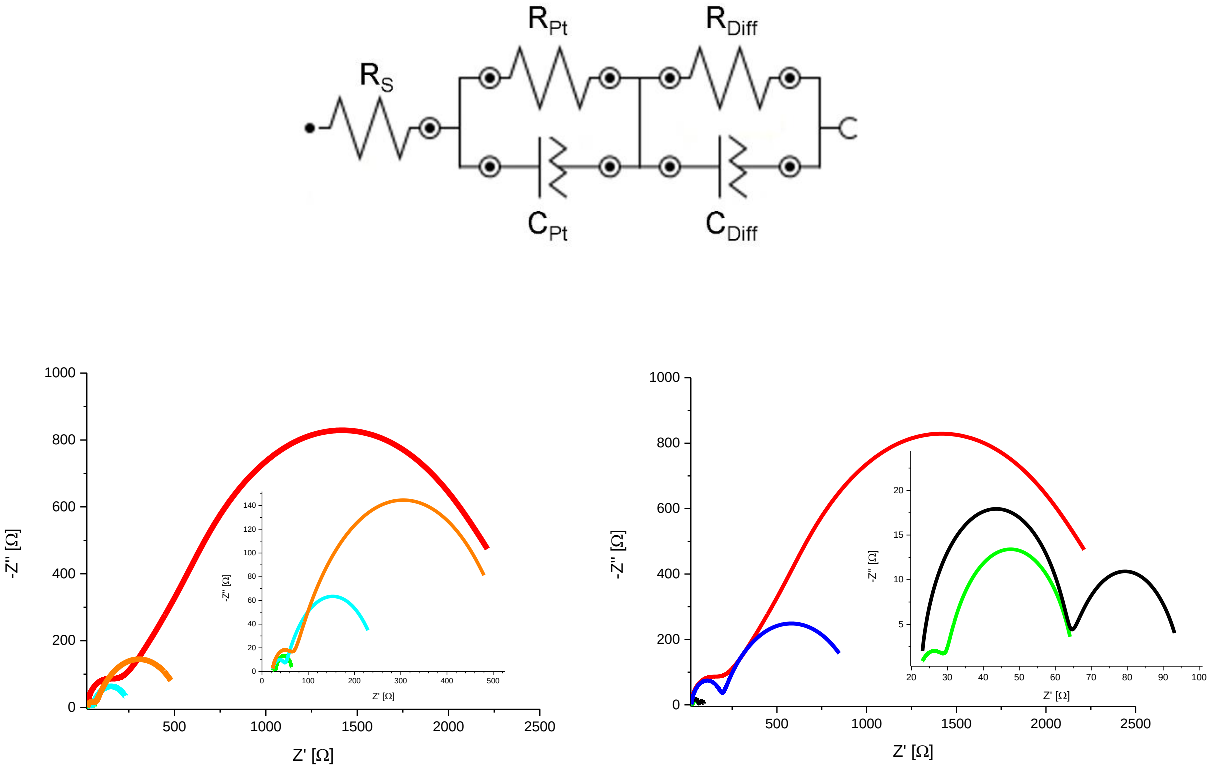

Figure S7. Upper part: The equivalent circuit is shown. Left bottom part: EIS spectra of pure [EMIM]I (red) and mixtures of [EMIM]I:CNHs weight ratios of 10:1 (orange), 5:1 (cyan), and 1:1 (green). Right bottom part: EIS spectra of pure [EMIM]I (**E1**, red), [EMIM]I:CNHs 1:1 wt% (**E2**, green), [EMIM]I:[BMIM][BF$_4$]:TBP:GuSCN 1:0.25:0.83:0.17 wt% (**E3**, blue), and [EMIM]I:CNHs:[BMIM][BF$_4$]:TBP:GuSCN 1:1:0.25:0.83:0.17 wt% (**E4**, black).

Table S1: Charge transport resistance at the Pt counter electrode (R_{Pt}), Warburg diffusion (R_{diff}), and diffusion coefficient (D_{diff}) of electrolytes obtained from EIS analysis at room temperature.

Electrolyte	R_{Pt}	R_{diff}	D_{diff}
	[Ω]	[Ω]	[x 10^{-10} m^2 s^{-1}]
[EMIM]I (**E1**)	190.47	2676.10	0.08
[EMIM]I:CNHs 10:1 wt%	44.84	477.65	0.42
[EMIM]I:CNHs 5:1 wt%	28.13	205.63	0.98
[EMIM]I:CNHs 1:1 wt% (**E2**)	7.38	35.86	5.63
E3	167.33	781.04	0.26
E4	41.21	31.39	6.44

Table S2. ssDSSC parameters measured at 70 °C for different amounts of CNHs in [EMIM]I obtained under AM1.5 conditions and 1 sun illumination.

[EMIM]I:CNH	J_{SC}	V_{OC}	FF	η	Relative improvement in η
wt%	[mA/cm^2]	[V]		[%]	
[EMIM]I (**E1**)	1.27	0.47	0.71	0.42	1.00
10:1	1.46	0.51	0.72	0.54	1.29
5:1	2.53	0.45	0.59	0.68	1.62
1:1 (**E2**)	8.29	0.45	0.56	2.09	4.98

Temperature dependence of ssDSSCs

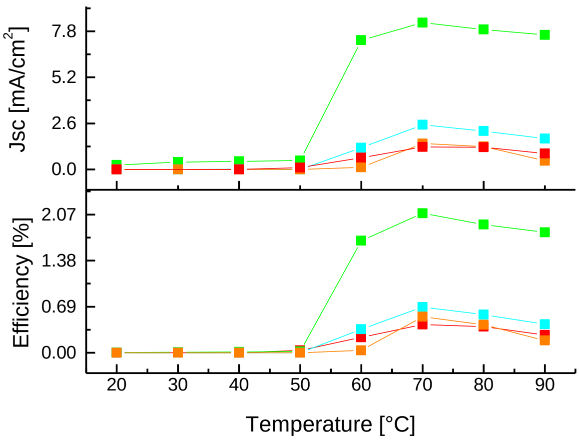

Figure S8. Solar cell parameters of ssDSSCs with different amounts of CNHs inside the [EMIM]I electrolyte. Legend: pure [EMIM]I (red) and mixtures of [EMIM]I:CNHs weight ratios of 10:1 (orange), 5:1 (cyan), 1:1 (green).

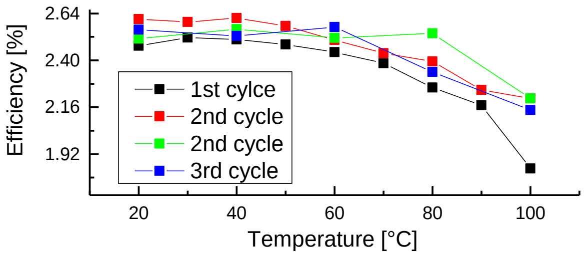

Figure S9. ssDSSC performance with several heating and cooling processes of the solar cell. The electrolyte composition was [EMIM]I:CNHs 1:1 wt%.

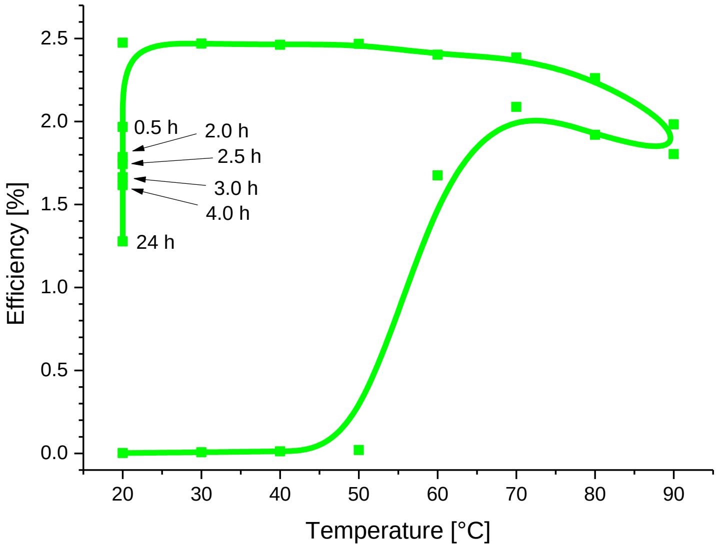

Figure S10. Efficiency of ssDSSCs with **E2** at different temperatures and measured at room temperature for different times after heating-cooling cycles.

Bode phase of ssDSSCs

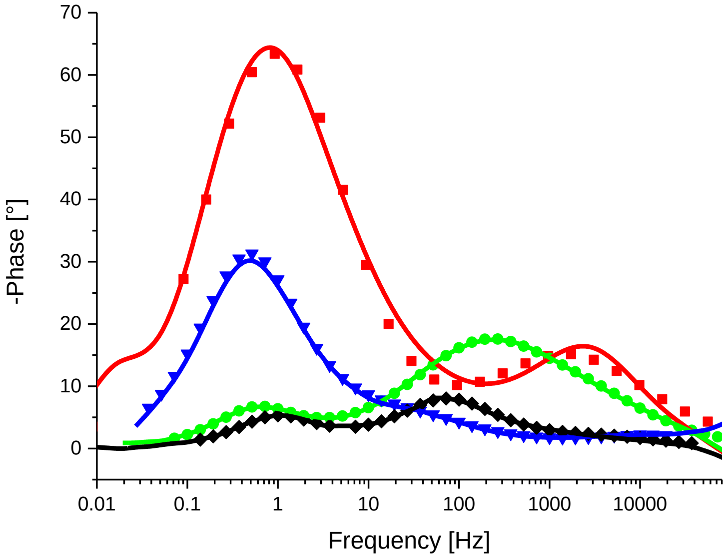

Figure S11. Bode phase of ssDSSCs with **E1** (red), **E2** (green), **E3** (blue), **E4** (black).

Short-circuit density *versus* light intensity

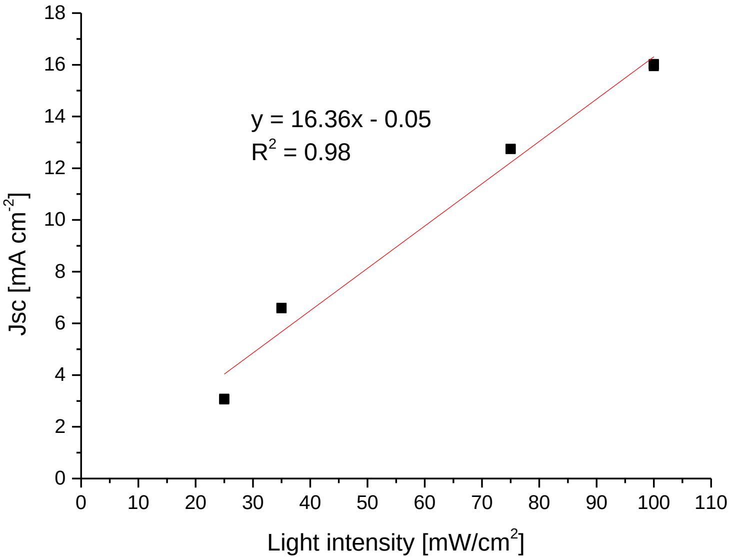

Figure S12. J_{SC} versus illumination conditions at AM 1.5 conditions of devices with **E4**.

Time dependent evolution of the D/G ratio of E4

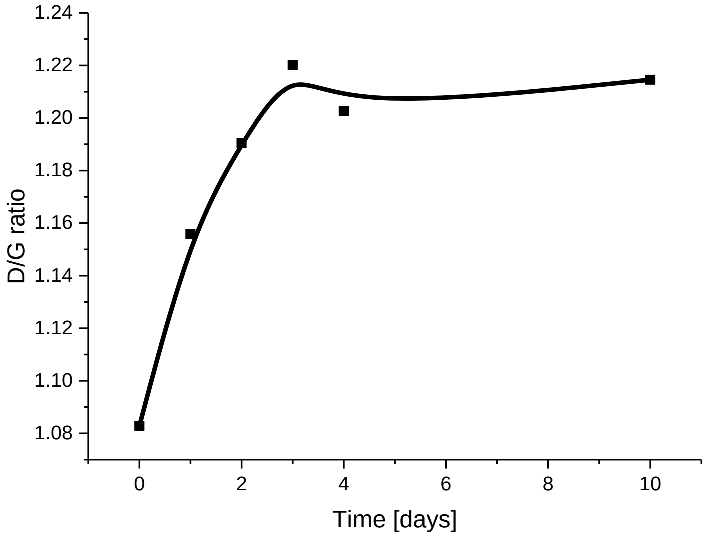

Figure S13. D/G ratio from Raman experiments of CNHs present in different ssDSSCs with **E4** over the time. The excitation wavelength was $\lambda = 532$ nm.

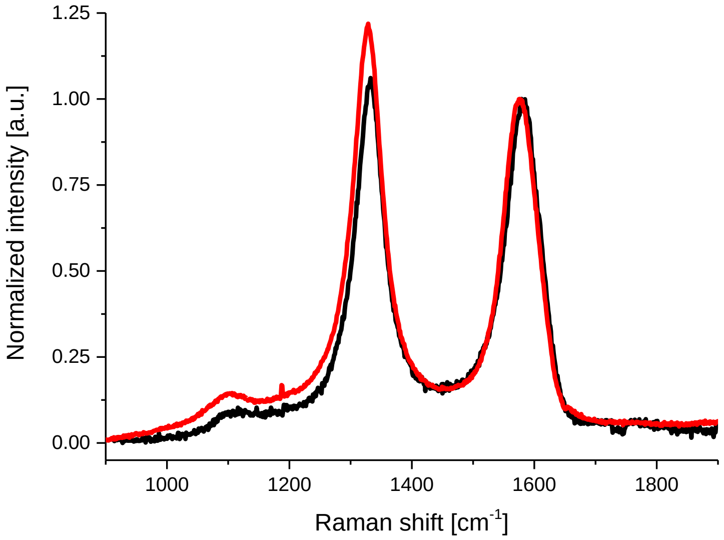

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Figure S14. Exemplary Raman experiments of CNHs present in **E4** normalized to the G band after 0 (black) and 3 (red) days.

[1] M. Schiavon, *US Pat. 7,125,525* **2006**, *2*.