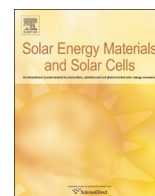




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## CuI as versatile hole-selective contact for organic solar cell based on anthracene-containing PPE–PPV

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## ABSTRACT

An important issue in construction of organic photovoltaic cells concerns the selective contacts. Here, especially the modification of the hole-extraction is challenging, as energy levels have to match the polymer's highest occupied molecular orbital (HOMO). We took the view to the mutual anode interface and we sought for a solution-based alternative for commonly used PEDOT:PSS – with an eye on improving the hole-extraction with an inorganic interlayer. We present copper iodide (CuI) as a versatile inorganic p-type semiconductor that meets the requirements for enhanced charge extraction in donor polymers. We applied two types of anthracene-containing PPE–PPV block-copolymers that recently gained attention as efficient active absorbers in bulk heterojunction photovoltaic cells. We report on the advantages using CuI as hole-selective contact and show an improvement of the power conversion efficiency in polymer-based solar cells.

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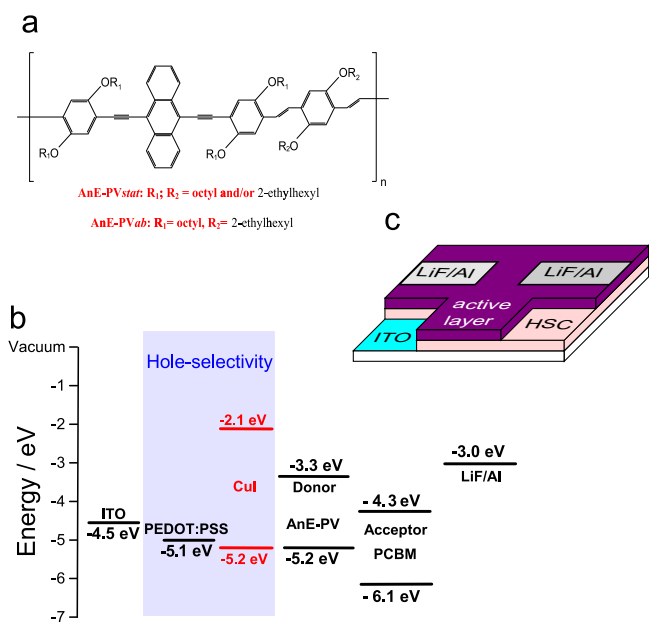
## 1. Introduction

Thin film organic photovoltaic cells (OPVs) employ various organic conductive polymers as a donor absorber-part in bulk heterojunction type solar cells. They attract attention for their solution processibility and are suggested as powerful option for the photovoltaic market due to their flexibility, lightness and moderate cost as well as low environmental impact [1–6]. One significant concern discussed in all-solution based bulk heterojunction solar cells is the contact interface [7–10]. In order to achieve efficient charge extraction, selective contacts have to be applied between the active layer and electrodes to tune the work function by preventing the exciton quenching at the electrode surface and recombination of the photogenerated carriers [11,12]. Various types of interlayer materials are available to match the corresponding active layer's energy levels, however, when strictly following a solution-based route, the portfolio of available materials becomes limited. On the electron-selective side, for instance, polyethyleneimine-based interlayers (PEI) have recently gained

attention to form excellent band-matching to the active layers [13]. Calcinated ZnO and In<sub>2</sub>S<sub>3</sub> derived from sol–gel processing shows similar results [14,15]. On the hole-selective side, solution-cast options are rare [16]. Predominantly most device structures rely on PEDOT:PSS [17,18]. Taking into consideration various reports on interface-problems related to the use of PEDOT:PSS and the necessity to find additional useful options consequently [19,10]. The variety of conjugated polymer–fullerene systems used as the active layers leads to very individual demands on the hole-contact side, which cannot be covered by PEDOT:PSS alone [20–22]. This argument applies in particular for the non-thiophene-based polymers that use p-phenylene-ethynylene and p-phenylene-vinylene (PPE–PPV) backbones as an example [23–27]. Here the interface matching with PEDOT:PSS can suffer from detrimental energy level offsets and/or degradation effects attributed to residual water, ionic species and the layer's acidity [28,10]. In order to overcome barriers and improve the mutual interface between the polymer's HOMO and the electrode, thin films of the copper (I) iodide have been applied in various photovoltaic devices earlier [29–32]. In this work, we demonstrate the capability of using solution-processed CuI as a hole selective contact (HSC) in the conjugated systems based on the non-thiophene polymer. Specifically, we use high molecular weight anthracene-containing

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**Fig. 1.** (a) Chemical structure of the donor polymers for the AnE-PVstat and AnE-PVab. The schematic energy (b) and structural diagram (c) showing the solar cell structure and highlighting the hole-selective contact side. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

poly (p-phenylene-ethynylene)-alt-poly (p-phenylene-vinylene) (PPE-PPV) with and without statistical distribution of octyloxy and 2-ethylhexyloxy side chains as active layers in combination with PCBM (see Fig. 1a) [23–27]. CuI as an interfacing layer is sandwiched between the active matrix and the final contact on the anode-side. For a complementary study of the interface, we conducted experiments with and without CuI as selective contact and discuss its role serving as a useful solution-processible alternative to PEDOT:PSS and as add-on contact layer in combination with PEDOT:PSS. Finally, we report on an increase in the power conversion efficiency by including CuI as a hole-selective contact (HSC) layer.

## 2. Experimental

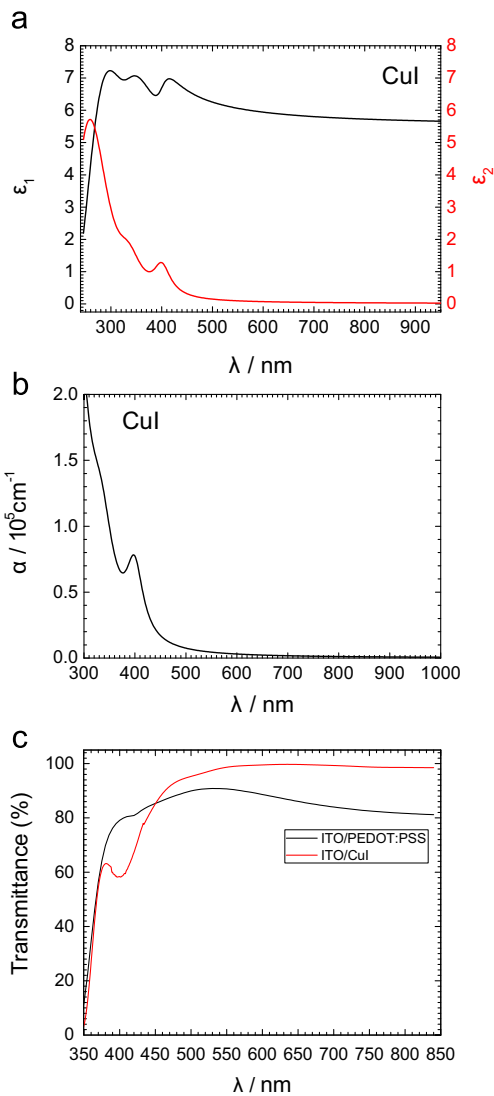
For the photovoltaic cells as an active matrix we employed anthracene-containing poly (p-phenylene-ethynylene)-alt-poly (p-phenylene-vinylene) (PPE-PPV) with and without statistical distribution of octyloxy and 2-ethylhexyloxy side chains and respectively donated AnE-PVstat and AnE-PVab for the donor part. Both polymers have the same band gap 2.1 eV but different structure as depicted in Fig. 1a. The detailed synthesis of the polymers is described elsewhere [33,34]. As an acceptor part, phenyl  $C_{61}$  butyric acid methyl ester (PC<sub>61</sub>BM, Sigma Aldrich) was used as received. Aqueous solution of poly (3,4-ethylenedioxythiophene) doped with poly(styrene-sulfonic acid) (PEDOT:PSS, Baytron/Clevios PH 500) is purchased from Heraeus and filtered (0.45 m teflon filter) prior to use. Microcrystalline CuI powder is synthesized and purified following the procedure from Mohamed et al. [35]. The CuI solution for spin-casting is prepared in an inert atmosphere by dissolving 10 mg ml<sup>-1</sup> CuI powder in dry acetonitrile under vigorous stirring (3 h). The solar cells are fabricated as followed: Patterned 2.5 cm<sup>2</sup> glass-indium tin oxide (glass-ITO, with a sheet resistance of 15 Ω/square) slides are rinsed with deionized water and cleaned in an ultrasonic bath with a detergent (Hellmanex, Hellma Inc.) followed by acetone, isopropyl alcohol, and again deionized water for 15 min each. After washing,

samples are dried. Then, the substrates are treated with oxygen plasma for 5 min right before usage. For the hole selective layer (s) 100 μl of CuI solution is spun onto the top of glass-ITO at 2000 rpm for 1 s and 4000 rpm for 45 s and annealed on a hot plate at 120 °C for 5 min. The same recipe is applied for PEDOT:PSS (Baytron). The CuI thickness on top of glass-ITO and on top of PEDOT:PSS respectively is similar and measured at 34 nm by a Dektak profilometer (Bruker). The active layer AnE-PV:PCBM (1:2 ratio, 10 mg ml<sup>-1</sup> in chlorobenzene) is spun on top at 1500 rpm for 15 s. The samples are annealed again at 120 °C for 5 min directly after the deposition and transferred to a nitrogen-filled glovebox. Finally, for the electron selective contact 0.7 nm lithium fluoride (LiF) and 100 nm aluminum are thermally evaporated under a pressure of  $2 \cdot 10^{-6}$  mbar. We used three different solar cell structures. One batch (20 devices) of reference cells applied PEDOT:PSS as HSC (black, control), one batch used CuI (red, CuI solely) and another batch a combined device structure with PEDOT:PSS and CuI on top (blue, combined). The solar cell device structure and the energy diagram of the layers are depicted in Fig. 1a and c. The photovoltaic cells are characterized in dark and under simulated AM1.5 solar irradiation using a Steuernagel 575 sun simulator with 100 mW cm<sup>-2</sup> intensity. A Keithley 236 source meter is used to record the current density–voltage  $J$ - $V$  characteristics. We add the standard deviation  $\sigma$  for all parameters per batch (20 samples). The spectral photocurrent external quantum efficiency (EQE) is measured using an optical fiber monochromatized Xenon-lamp with a typical illumination density of 5–10 W, connected to a ACTON Spectra Pro150 monochromator and EG&G 7260 DSP Lock-in amplifier to measure the photocurrent response. The short circuit current  $J_{sc}$  values are derived by integrating spectral EQEs and corrected in all  $J$ - $V$  plots and tables accordingly. For the optical characterizations transmission measurements are carried out at room temperature using a Perkin-Elmer T80 UV/VIS Spectrophotometer with wavelength range between 400 and 900 nm. A Woollam M-2000 (rotating compensator) ellipsometer covering an energy range from 1.1 to 5 eV is used for gaining the dielectric function and absorption coefficient of CuI respectively. For this thin films on glass are characterized at 6 different angles (variable angle spectroscopic ellipsometry, VASE). The optical data (real and imaginary part of the dielectric function  $\epsilon_1$ ,  $\epsilon_2$ ) are derived from an optical model fit. The morphology of the thin-films is characterized using an atomic force microscope (AFM, Digital Instruments DIMENSION 3100, and tapping mode). A Bruker Dektak profilometer was used to verify thin films thicknesses.

## 3. Results and discussion

In order to elucidate the impact of CuI as hole-selective contact (HSC), we present photovoltaic devices using both AnE-PVstat and AnE-PVab. The corresponding chemical structures of the polymers, the energy and device diagram are depicted in Fig. 1. We highlight the hole-selective part of the cell and our strategy to improve the interface between the donor polymer's HOMO and the work function of the contact electrode (in this case indium tin oxide ITO).

A major motivation in this work has been finding an alternative for PEDOT:PSS – as mentioned earlier various detrimental effects are associated with the polymer composite. Hence we pursue a device study for implementation of solution-cast CuI as a possible candidate. The first subject, we have been interested in, is the optical properties. Different to similar inorganic selective contacts as molybdenum(VI)oxide CuI's absorption (optical band gap 400 nm, peak absorption) critically overlaps with the active layer. For application in a solar cell we therefore sought for an optical



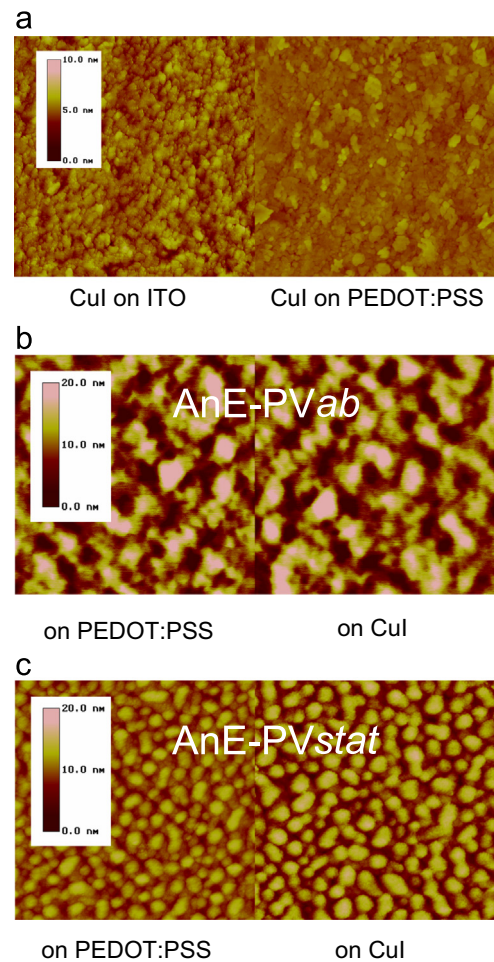
**Fig. 2.** (a) The dielectric function determined in detail by variable angle spectroscopic ellipsometry (VASE) from as-spun CuI layer on top of glass is shown for the UV-visible part of the spectrum. (b) According to the dielectric function the absorption coefficient  $\alpha$  is derived. (c) We compare the optical transmittance of 34 nm CuI and ITO/glass with a control layer of PEDOT:PSS on ITO/glass.

crosscheck. We derive the dielectric function, absorption coefficient and the transmission using variable angle spectroscopic ellipsometry (VASE) and in a separate experiment UV-VIS transmission of solution-cast thin-film CuI. We denote that earlier studies covered predominantly vacuum-deposited CuI films [36,37].

The response of a 34 nm solution-cast thin-film reflects an absorption feature at 400 nm ( $\alpha = 0.5 \text{ cm}^{-1}$ ). The optical model fitting the experimental values  $\Psi(\omega)$  and  $\Delta(\omega)$  at six incident angles yield the dielectric function ( $\epsilon_1, \epsilon_2$ ) of the material and the calculated absorption coefficient  $\alpha$  using Eq. (1)

$$\alpha = \frac{\omega \cdot \epsilon_2(\omega)}{c \cdot n_r(\omega)} \quad \text{with } n_r = \sqrt{\frac{\epsilon_1^2 + \epsilon_2^2}{2} + \epsilon_1} \quad (1)$$

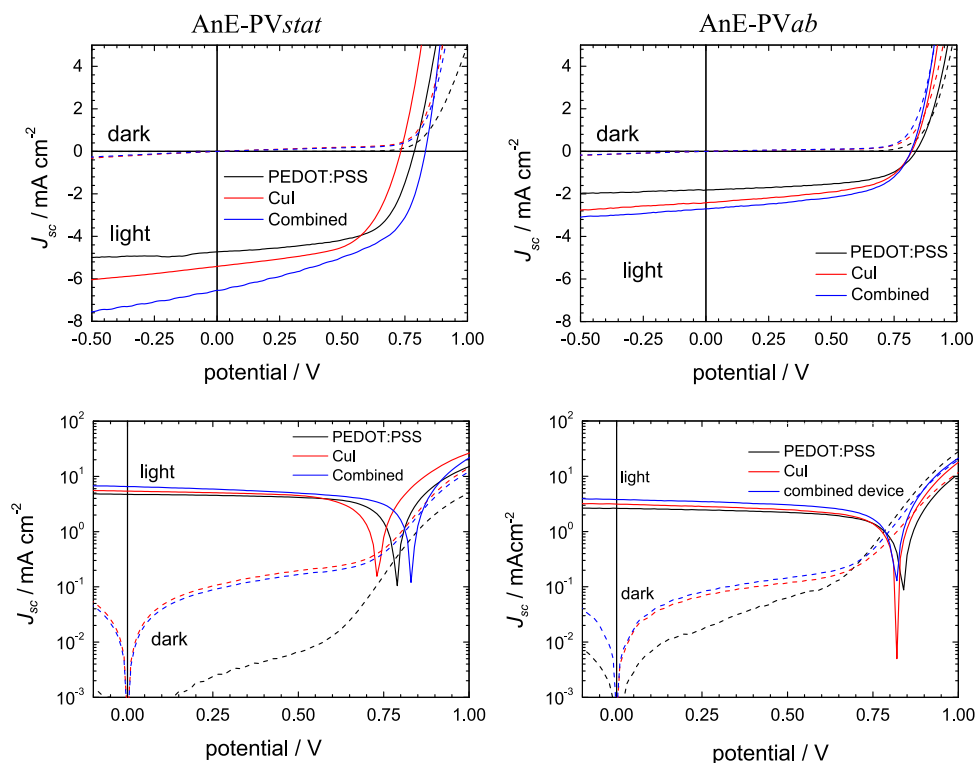
with  $c$  being the speed of light,  $\omega$  the angular frequency and  $n_r$  the refractive index. The corresponding spectra are plotted in Fig. 2a and b. For full consistency we have included the transmission of CuI and PEDOT besides. Interestingly, the results reflect a higher transmission for CuI in the visible-near infrared regime – except



**Fig. 3.** (a) AFM topographies of thin-film CuI on plane ITO and ITO-PEDOT:PSS. The values vary from nm to nm with PEDOT:PSS acting as a smoothing layer. (b, c) Impact of CuI on the nanomorphology of the bulk-heterojunction. Left-hand the control devices are shown, right-hand side topographies with CuI underneath.

for the mentioned band absorption below 500 nm (Fig. 2c). Because of the absorption band we define layers below 34 nm to suit the requirements in terms of transparency as hole-selective contact on top of glass-ITO. The next step has been now a comparison of CuI's thin film morphology on ITO (left) and on ITO/PEDOT:PSS (right) by AFM (Fig. 3a). For both cases we report on a homogeneous film formation of as-spun CuI. The root mean square roughness RMS is found slightly increased on bare ITO as compared to PEDOT:PSS coated ITO (Fig. 3a, 3.2 nm and 1.89 nm for CuI on ITO and ITO/PEDOT:PSS respectively). For a complete device study we are also interested, how the active layers are impacted by CuI. We pursue an AFM study elucidating the consecutive active layer's nanomorphology. Earlier contributions have addressed morphological aspects in the polymer-fullerene blends of AnE-PVstat and AnE-PVab and its impact on the cell performance [25]. Within one active layer system, however, we observe minor morphological changes followed by introduction of CuI (Fig. 3cb). Such consistency rules out a major contribution to nanomorphology consequently, confirm our main statement to assign CuI's role to improve on interfacial energy level alignment.

To confirm this statement further, we compare photovoltaic devices based on two similar polymers both hole-contacted either by CuI and PEDOT:PSS (control), respectively. The resulting  $J-V$  curves of the photovoltaic cells are shown in Fig. 4 including the linear and semi-logarithmic graphs for AnE-PVstat (left) and AnE-PVab (right). We present the results from sets of control devices



**Fig. 4.** The  $J$ - $V$  curves (linear, semi-logarithmic) of the glass/ITO/HSC/AnE-PVstat:PCBM/LiF/Al (left) and glass/ITO/HSC/AnE-PVab:PCBM/LiF/Al in dark and under illumination of AM 1.5G at  $100 \text{ mW cm}^{-2}$ .

**Table 1**  
Solar cell results measured under illumination.

HSC	PCE (%)	FF	$V_{OC}$ (V)	$J_{SC}$ ( $\text{mA cm}^{-2}$ )	$R_S$ ( $\Omega$ )	$R_{Sh}$ ( $\Omega$ )
<b>AnE-PVab</b>						
PEDOT:PSS	$1.0 \pm 0.05$	$57 \pm 1.7$	$0.84 \pm 0.02$	$1.81 \pm 0.07$	$33 \pm 2$	$1945 \pm 60$
CuI	$1.3 \pm 0.06$	$52 \pm 1.6$	$0.82 \pm 0.02$	$2.42 \pm 0.07$	$34 \pm 3$	$827 \pm 27$
Combined	$1.5 \pm 0.08$	$57 \pm 1.6$	$0.83 \pm 0.03$	$2.70 \pm 0.10$	$28 \pm 3$	$842 \pm 27$
<b>AnE-PVstat</b>						
PEDOT:PSS	$2.9 \pm 0.18$	$63 \pm 1.7$	$0.79 \pm 0.10$	$4.76 \pm 0.30$	$15.5 \pm 1.4$	$1524 \pm 37$
CuI	$3.2 \pm 0.19$	$63 \pm 1.8$	$0.76 \pm 0.02$	$5.45 \pm 0.17$	$12.6 \pm 1.5$	$781 \pm 27$
Combined	$3.5 \pm 0.18$	$51 \pm 1.3$	$0.84 \pm 0.02$	$6.65 \pm 0.20$	$8.7 \pm 0.9$	$788 \pm 30$

(black, PEDOT:PSS), sets of CuI-based (red) devices and, in addition, sets of combined devices (blue, double layer CuI on PEDOT:PSS). The latter combinatorial strategy (double layer) has been applied, in order to crosscheck for benefits from both HSC-types. It is exactly the most promising approach, as  $V_{OC}$  and  $J_{SC}$  values have improved significantly with respect to the single layer strategies. An overview of all corresponding PV-parameters is presented in Table 1. A detailed look to the  $J$ - $V$  curves shows the control device (black line) with PEDOT:PSS and a PCE of 1.0% and 2.9% for AnE-PVstat and AnE-PVab. By introducing CuI instead, the efficiencies are slightly increased to 1.3% and 3.2% respectively. Using CuI and PEDOT:PSS the PCEs have been improved mainly due to higher (or equal)  $V_{OC}$  and  $J_{SC}$  respectively.

Considering now all insights from optics, morphology and devices we finally evaluate the merit for using solution processed CuI thin-films. Our initial motivation has been mainly driven by the need for alternative solution-based and transparent hole-selective contact electrodes. Taking PEDOT:PSS now as a reference point our complementary study demonstrates CuI as a serious competitor – finally even beneficially improving photovoltaic performances in our photovoltaic system. The optical study

reflects the transmission profile with a feature peak at 400 nm. To meet a similar transparency like PEDOT:PSS, we suggest to limit the CuI-thickness to maximum 35 nm. We additionally view to nanomorphology, both CuI itself and its impact to the consecutive active layers. Most important, in the latter we find consistency in the nanomorphologies, which appears independent from the hole-selective contact underneath. Differently, the device performance is indeed impacted: CuI applied as a direct substitute or as add-on layer on PEDOT:PSS serves as excellent hole-selective contact at least equal to the control devices. Our choice for the polymer-fullerene system has been made with care, to work out the role in a particularly interface-sensitive PPV-system. We outline the positive effects of CuI: Although they exhibit poorer serial resistances and, in combination with PEDOT:PSS, also lower fill factors, the  $J_{SC}$ -values improved significantly. The reasons for the enhancement relate to the presence of CuI – different to PEDOT:PSS it is cast from non-aqueous solutions, it is neither acidic nor basic and it offers similar smoothness as PEDOT:PSS. Hence we assign the enhanced performance to an interfacial effect. Furthermore, the spectral EQE measurements indicate no active contribution of CuI to the charge-separation (Fig. 5) – the spectra

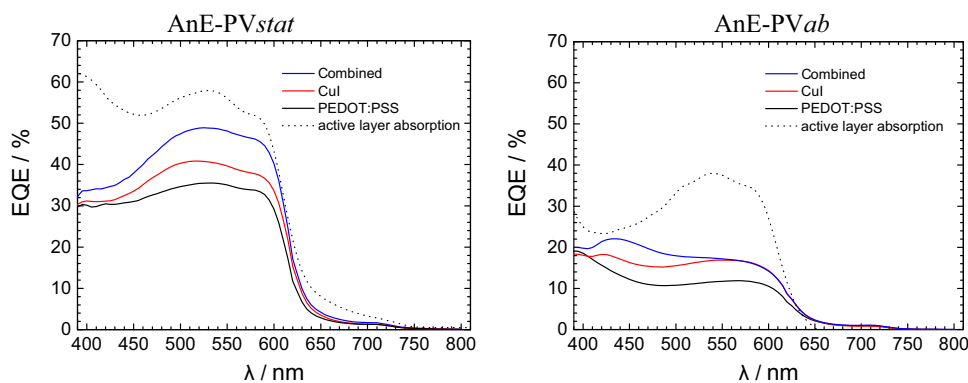


Fig. 5. EQE for both type of polymers AnE-PVstat and AnE-PVab. The dashed lines correspond to the active layer's absorption.

match the active layer's absorption shown in the dashed line in the graph. Though the absorption in the 34 nm HSC-layer can lead to reduced fill-factors and reduced serial resistances. Both subjects are reflected in our photovoltaic devices, however they can be resolved by optimizing the device design and layer-thickness in future.

#### 4. Conclusions

Alternative solution-processed hole-selective contacts in polymer solar cells are rare – we took the view on this central front in device research and introduced CuI as inorganic thin-film option. The as-spun p-type semiconductor serves as an excellent contact layer on a level with the predominantly used PEDOT:PSS. We point out the advantages of interfacing non-thiophene based polymers and show in a combinatorial strategy that CuI interlayers help improving the PCE efficiency significantly. We include a detailed characterization of the optical properties of as-spun CuI layers and work out its absorption properties, film-form properties and impact on the active layer's morphology. Its optical qualities together with its thin-film properties and, in particular, its performance in the device make CuI a versatile hole-selective alternative for organic photovoltaic applications.

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