Discotic materials for organic solar cells: Effects of chemical structure on assembly and performance

Holger Christian Hesse^a, Jonas Weickert^a, Mahmoud Al-Hussein^b, Lukas Dössel^c, Xinliang Feng^c, Klaus Müllen^c, Lukas Schmidt-Mende^{a,*}

^a Ludwig-Maximilians-University Munich, Department of Physics and Center for NanoScience (CeNS), Amalienstr. 54, 80799 Munich, Germany

^b Department of Physics, University of Jordan, Amman 11942, Jordan

^c Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

A B S T R A C T

Discotic materials have attracted remarkable interest for application in organic solar cells. We analyze a series of phenyl substituted hexa peri hexabenzocoronenes (HBCs) with residue modifications blended with perylenediimide (PDI) as donor material. The effect of differing alkyl chain lengths of 6, 8, 12 and 16 carbon atoms, introduction of a triple bond linker between HBC core and residual phenyl group and a swallow tailed dialkylphenyl chain on the device performance is investigated. Detailed insight to device physics and morphology is gained by analysis of photoluminescence quenching, transient photovoltage and photocurrent decay experiments and atomic force microscopy. Complementary the investigations explain why using short alkyl side chains higher currents and consequently increased device performance can be achieved. We report an external quantum efficiency of over 27% for devices based on discotic molecules. In this work the molecular assembly and its impact on performance in photovoltaic devices is studied. The study also reveals pathways to further increase the quantum yield of small molecule organic solar cells.

Keywords:

Organic photovoltaics

Discotic materials

Inverted solar cell

Self-assembly

Transient decay measurements

1. Introduction

Fabrication of photovoltaic devices using solution processable materials is a field of intense scientific interest. The potentially low production costs and variability in device design such as flexible substrates and color of devices are clear advantages of this emerging technology to standard silicon solar cells. Great progress on device performance could be achieved for organic photovoltaics in the last decade mainly due to the introduction of the bulk heterojunction concept yielding power conversion efficiencies of up to 6% only recently [1,2]. However, superior performance is commonly only reported for devices based on polymers blended with fullerene derivatives. A photovoltaic system based on small molecules appears appealing as materials can be evaporated and materials are mono disperse leading to far enhanced reproducibility of different batches [3,4].

In many recent publications positive effect of thermal or solvent annealing, addition of additives or application of external fields on device performance is observed and mainly attributed to

morphological changes in the photoactive layer [5–7]. However, for a given donor acceptor couple the influence on morphology by such post production treatments is only limited and there is still lack in understanding the relationship between the nano morphology of the active layer and device performance [8]. For the design of novel materials for solar applications more knowledge to the influence of molecular structure on the assembly of materials and device performance is highly desired.

In this study the assembly of six residue modified donor molecules blended with a commonly used perylene dye as electron acceptor is analyzed. Changes in intermolecular packing and blend morphology by variation of side chain length and structure on the periphery of the donor molecule and their impact on solar cell performance are studied. The materials chosen, hexa peri hexabenzocoronene (HBC) as donor and perylenediimide (PDI) as acceptor, have proven to show potential for efficient photovoltaics [9–12]. HBCs have the potential to self assemble in a columnar fashion resulting in high charge carrier mobility and PDI as electron conducting acceptor is known for its strong absorbance and its organization into supramolecular architectures [12–14].

For the solar cell production an inverted structure with electron collecting TiO₂ bottom and Ag top electrode was chosen. This allows fabrication of devices with highly improved air stability without further device protection such as encapsulation. The measurements of device physics can thus be performed at

* Corresponding author. Tel.: +49 89 2180 3443; fax: +49 89 2180 3441.

E-mail addresses: Holger.hesse@physik.uni-muenchen.de (H.C. Hesse), Jonas.Weickert@physik.uni-muenchen.de (J. Weickert), m.alhussein@ju.edu.jo (M. Al-Hussein), doessel@mpip-mainz.mpg.de (L. Dössel), feng@mpip-mainz.mpg.de (X. Feng), muellen@mpip-mainz.mpg.de (K. Müllen), L.Schmidt-Mende@physik.uni-muenchen.de (L. Schmidt-Mende).

ambient conditions. Additionally, when top contacts are applied by printing techniques, this device design enables vacuum free fabrication, which is an important step towards up scaling and roll to roll processing of devices [15–17]. Details on device fabrication and stability will be shown in a separate publication [18].

2. Experiments details

2.1. Material synthesis

All materials used in this study are summarized in Scheme 1 and concise abbreviations are given. Synthesis of the hexaphenyl substituted HBCs (Fig. 1, HBC-6, HBC-8 and HBC-12) with different alkyl chain lengths in the periphery was accomplished using a synthesis procedure reported elsewhere [19]. Due to the high sterical demand of the hexadecyl alkyl chain and its limited reactivity a more complex synthetic route was necessary to obtain the HBC-16 (see Supporting information).

To introduce an additional triple bond between the HBC core and the periphery substituents, for compounds HBC≡12 and HBC≡(12,12) another synthetic route was used based on a

Scheme 1. Chemical structure of organic materials used in solar cells. 1–6: electron acceptor hexa-*peri*-hexabenzocoronene (HBC) with different residues at the periphery. 7: electron donor perylenediimide (PDI)

Fig. 1. HBC derivative absorption measured on thin films with comparable thickness of about 100 nm. The HBC peak height is correlated to the number of chromophore molecules. A bathochromic shift is observed for the molecules with a triple bond linker unit.

six fold *Sonogashira Hagihara* coupling reaction in the last synthetic step.

After synthesis, all compounds were purified by repetitive reprecipitation and silica column chromatography to remove metal ions and impurities that would affect electronic properties and morphology. All synthetic details can be found in the Supporting information.

Perylene tetracarboxydiimide (PDI) was bought from Sensient technologies and used without further purification.

2.2. Device fabrication

Devices were fabricated on ITO coated glass substrates. The ITO substrates were cleaned by ultrasonication in acetone and isopropyl alcohol bath followed by a 7 min O_2 plasma (Diener Femto) cleaning. About 150 nm of TiO_2 were deposited onto the cleaned ITO substrates by spray pyrolysis at 450 °C using a diisopropoxytitanium bis(acetylacetonate) precursor solution. A second plasma cleaning step was carried out for best wetting with the organic material prior to spin coating. HBC and PDI molecules were dissolved in chloroform at a concentration of 15 mg/ml and mixed at different ratios. Blend solution was stirred for 48 h and filtered (PTFE, 45 μm pore) immediately before use. The organic layers were deposited by spin coating (2000 rpm), resulting in an average film thickness of ~ 120 nm. PEDOT/PSS was ordered from Sigma Aldrich and applied onto the organic layers by spin coating (30 s, 6000 rpm) without subsequent annealing. Top contacts were applied through a shadow mask by sputter coating or evaporation. The cell area was about 0.125 cm^2 ; exact values were determined by microscopy. The devices were annealed for 1 or 14 h at 120 °C at ambient atmosphere prior to testing.

2.3. Absorption and photoluminescence measurements

Absorption of thin organic layers was measured on Suprasil grade 1 quartz glass with an Agilent Technologies 8453 UV visible spectroscopy system. PL measurements have been conducted on the same samples with a Horiba Yvon Fluorolog PL spectrometer equipped with a 500 W halogen lamp.

2.4. Solar cell characterization

EQE and IV curves were recorded with a Keithley 2400 Source Meter using a self made LabView based computer program. For calibration a reference silicon diode certified by the Fraunhofer Institute equipped with a KG5 filter was used. For EQE measurements a 150 W Xenon lamp was focused onto an Omni150 (LOT Oriel) monochromator ($P_{\text{incident}}=0.3 \text{ mW/cm}^2$ at 490 nm). A solar simulator equipped with AM 1.5 g filters with about 100 mW/cm² power was used for measurements.

2.5. Transient decay experiments

Photovoltage decay data were recorded under open circuit conditions. White light bias was achieved by a Xenon lamp with a light intensity of about 0.38 mW/cm². For both transient measurements pulsed laser light (532 nm, pulse frequency 10 Hz, pulse energy about 10 μJ , pulse duration $\sim 4 \text{ ns}$) was used to generate small perturbations in the device. The changes in the potential between top and bottom contact of the photovoltaic devices caused by the additional laser pulses were monitored using a digital oscilloscope (Tekscope DPO 7254) with a termination resistance of 1 M Ω .

For the photocurrent decay measurements, blend material of solar cells was excited by pulsed laser irradiation and the time dependent current characteristics recorded via potential drop over the 50 Ω termination of the oscilloscope yielding quasi short circuit conditions. Data were gathered as an average over 100 transient decay events.

2.6. Surface morphology

Surface morphology was analysed with a Veeco Dimension 3100 scanning probe microscope. Tap300Al tips with resonance frequency of 300 kHz and force constant of 40 N/m were used. Measurements were conducted on the typical annealed devices (glass/ITO/TiO₂/blend/Ag) after removal of the top contacts.

3. Results and discussion

3.1. Material analysis

The thermotropic properties of the synthesized components were analysed using differential scanning calorimetry (DSC) and 2D powder X ray diffraction analysis. All HBC compounds show a liquid crystalline phase with at least one accessible phase transition (see Supporting information).

Fig. 1 shows absorption spectra of thin films of the analyzed HBC spun from chloroform solution with equal film thickness of about 100 nm. All HBC derivatives show pronounced absorption in the range of 350–430 nm. PDI, however, absorbs mostly in the range of 430–650 nm [12]. At constant film thickness strongest absorption of the HBC derivatives is seen for short alkyl side chains. This is attributed to the increased number of chromophores per volume for small molecular weight HBCs. Both materials with triple bond linker unit, **HBC-12** and **HBC-(12,12)**, show bathochromically shifted absorption peaks when compared to the single bond HBCs. Fitting the absorption data to the Urbach model, we could derive a shift in E_g of the single bonded to the triple bonded HBC from about 3.1 to about 2.9 eV [20].

3.2. Solar cell performance

In order to compare the potential of the different HBC derivatives as donor materials in solar applications, bulk hetero

junction solar cells were fabricated, using blends of the HBCs and the acceptor PDI. Solar cells were assembled in an inverted design composed of ITO/TiO₂/blend/PEDOT/Ag. With this design strongly improved air stability was achieved compared to the standard ITO/PEDOT/blend/Al layer structure [18,21].

Subsequently devices were annealed at 120 °C for an extended period of 14 h. Even though this long term annealing treatment results in a slightly decreased absorption for all blend materials (data not shown), drastically improved solar cell performance was recorded showing both improved open circuit voltages and higher short circuit currents. We attribute this to both a favorable realignment of HBC and PDI molecules and the formation of a better contact of the blend with the Ag electrode as further explained later in connection with AFM measurements.

When illuminated at 1 sun (AM 1.5 global, 100 mW/cm²) all blend cells show photovoltaic behaviour. The effect of donor to acceptor blending ratio on solar cell performance was screened for all derivatives. A mixing ratio of 30:70 wt% was found to perform best for **HBC-(12,12):PDI**. For short side chain HBCs instead rather equal weight ratio of donor and acceptor yields best results (e.g. **HBC-6:PDI** with best blend ratio around 50:50 wt%). To summarize, for best performance the content of HBC core molecules must be decreased significantly when increasing the alkyl chain length or introducing a branched tail. We attribute this to differences in packing and morphology of the different blends. Bulky substituents on the periphery of HBC might hamper intermixing with PDI, as will be further explained later in connection with transient decay measurements and atomic force microscopy. Therefore, higher PDI content is needed to allow for sufficient interfacial area of donor and acceptor yielding maximum performance.

To compare the potential of the different HBCs among themselves, all HBC derivatives were blended with PDI at a constant mixing ratio of 40:60 wt%. Typical IV Curves at solar illumination (AM 1.5 g, 100 mW/cm²) are shown in Fig. 2 and mean values of the solar cell characteristics including standard deviation are summarized in Table 1. Additionally, external quantum efficiency (EQE) measurements have been carried out on all devices. At balanced blend ratio the spectral response mainly follows the absorption of the thin films (exemplary shown for **HBC-8:PDI**, 40:60 wt%, inset Fig.2). An EQE of over 27% was recorded at 390 and 500 nm, which is close to the peak absorption of HBC and PDI, respectively. For this blend composition the EQE remains above 20% ranging from 360 to 550 nm.

Best efficiencies of our solar cells are around $\eta=0.24\%$ upon solar illumination at 100 mW/cm² in ambient atmosphere and found to be almost similar for all blends containing HBCs with short side chains (**HBC-6**, **HBC-8** and **HBC-12**). Upon irradiation with monochromatic light at low intensity about eight times higher efficiencies have been previously reported [12] and were also reproduced with the devices presented here. However, upon increasing light intensity the performance drops significantly. The sub linear increase of currents with illumination intensity is attributed to space charge effects and drastically limits the device performance at solar illumination [22]. The open circuit voltage ranges from 540 to 700 mV and is highest for the HBC derivatives with single bond linked phenyl groups. Within this series of HBCs, the V_{OC} increases from **HBC-6** to **HBC-12**. This can be explained by shielding effects of the alkylic chains decreasing the HOMO level with increasing side chain length as reported elsewhere [23]. Accordingly, the effective bandgap of donor and acceptor ($E_{HOMO}^D - E_{LUMO}^A$) is increased, shifting also the open circuit voltage (V_{OC}) to higher values [24]. As a different synthetic approach was used and purification appeared more challenging for **HBC-16**, the low V_{OC} in this blend may be attributed to a higher content of impurities. However, also different molecular arrangement might be favored

Fig. 2. Typical IV characteristics of different HBC derivatives blended with PDI perylene (40:60 wt%). Solar cells are measured on air under 1 sun AM1.5 g, 100 mW/cm² illumination after thermal annealing. The inset shows absorption data (solid line) and EQE action spectrum (scattered) of a **HBC-8:PDI** blend at a mixing ratio of (60:40 wt%).

Table 1

Characteristics of HBC:PDI solar cells. Mean values and standard deviations are given for a set of six cells for each donor–acceptor blend.

Cell type	I_{SC} [mA/cm ²]	V_{OC} [V]	FF [%]	IPCE [%]	R_S [Ω cm ²]	R_{Sh} [Ω cm ²]
HBC-6:PDI	-1.035 ± 0.042	0.643 ± 0.023	33.4 ± 0.2	0.22 ± 0.02	61 ± 9	820 ± 13
HBC-8:PDI	-1.065 ± 0.035	0.665 ± 0.026	34.3 ± 0.6	0.24 ± 0.02	78 ± 6	906 ± 28
HBC-12:PDI	-0.815 ± 0.050	0.690 ± 0.017	39.3 ± 0.7	0.22 ± 0.02	57 ± 12	1608 ± 127
HBC≡12:PDI	-0.580 ± 0.030	0.542 ± 0.065	38.8 ± 1.4	0.12 ± 0.01	138 ± 69	1997 ± 215
HBC-16:PDI	-0.340 ± 0.027	0.593 ± 0.065	39.2 ± 3.1	0.08 ± 0.02	76 ± 35	3729 ± 324
HBC≡(12,12):PDI	-0.306 ± 0.037	0.549 ± 0.041	44.5 ± 2.9	0.07 ± 0.02	321 ± 195	5091 ± 390

for this molecule due to the long side chains which could lead to reduced V_{OC} [25].

For both HBCs with a triple bond linker unit about 200 mV lower open circuit voltages are recorded. This can be attributed to altered energy levels for these HBCs. As already mentioned, E_g of both **HBC≡12** and **HBC≡(12,12)** is shifted by about 0.2 eV to lower values. Electrons can be partially delocalized to the triple bond unit reducing the HOMO level of these molecules. The LUMO level instead is not expected to be influenced by the introduction of the triple bond – electrons remain confined to the unmodified HBC core unit [26].

A closer look to the short circuit current (I_{SC}) indicates differences in the exciton separation and charge carrier collection yield among the different blend materials. Short alkyl chains allow for highest currents and I_{SC} decreases with increasing side chain length of the HBC molecules. Differences in donor–acceptor molecular spacing are found to be the main reason as supported by PL measurements and transient photovoltage and photocurrent decay studies.

The fill factor (FF) of the devices ranges from 33.5% for **HBC-6:PDI** to 42.9 % for **HBC≡(12,12):PDI** blends. In a separate experiment I_{SC} of all cells was regulated to an arbitrary but fixed value by adaption of solar illumination intensity. The FF does not considerably differ from that reported in Table 1, showing that FF and values for equivalent resistors strongly depend on material specific properties and are not governed by contact limitations.

Both shunt and series resistances for an equivalent diode model are calculated from the IV curves (Table 1). The shunt

resistance (R_{Sh}) ranges from 10^3 to $10^4 \Omega$ cm², which is comparable to values reported in solar cells based on other organic materials [27]. However, especially for the devices with short alkyl chain HBCs increasing the shunt resistance is of key importance for further device improvement. Instead, high series resistance (R_S) of about 60–320 Ω cm² was recorded for the cells which is at least one order of magnitude larger than common values reported for morphologically optimized polymer fullerene solar cells [1,27]. High R_S values cause major limitations to both the FF and I_{SC} of our devices, especially for cells containing **HBC≡12** and particularly **HBC≡(12,12)**. Higher mobility in the blend material is needed for improve short circuit currents and FF as will be further motivated later in connection with transient decay measurements. In highly aligned material record mobility of up to $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ has been achieved in HBC and PDI thin films along the π – π axis [13,28,29]. However, in solar cells homeotropic alignment and crystal growth are necessary to yield a high mobility and allow for efficient percolation pathways. This favorable alignment and morphology is most likely not achieved in the devices studied. As already mentioned significant space charge effects are observed under normal working conditions indicating only insufficient mobility in at least one of the organic materials used. Furthermore, the IV curve analysis also indicates that optimum alignment is not achieved in our devices yet: in fact, it appears that lateral charge carrier hopping between adjacent HBC cores is necessary for current generation. This hopping process should be most probable for the hexagonally and closely packed HBCs with short side chains and might be hindered

for **HBC**≡**12** and **HBC**≡(**12,12**) with their more space demanding cubic and herringbone packing (see Table S1 in Supporting information) giving rise to increased series resistance in these devices.

3.3. Photoluminescence analysis

Photoluminescence (PL) measurements have been carried out on thin films of both pure PDI and HBC derivative films as well as on the blended compounds and their quenching analyzed. For the blends, measurements were conducted on the fully assembled solar cell devices after annealing in reflection geometry. Thus direct insight to the spectral properties of the materials used in the solar cells presented in Table 1 was gained. Excitation was set to 375 and 490 nm, where prominent absorption takes place in the HBC and PDI molecules, respectively. PL signals were spectrally resolved as exemplary shown for excitation at 375 nm in Fig. 3.

When blend material is excited at 375 nm broad features are visible at 525 and 610 nm matching well the emission of excited pure HBC and PDI films, respectively. Both HBC and predominantly PDI emission are visible for all blends indicating efficient energy transfer from the HBC to PDI. Interestingly, the feature at around 750 nm is not visible for thin films prepared of either pure HBC or PDI. We attribute this signal to a photo induced charge transfer state (CTS) [30]. In our experiments the feature could only be resolved for blends containing the HBCs with single bond linker unit. For both triple bond materials the altered energy gap is likely to induce a red shift for the CTS, which could not be resolved with our experimental setup [30].

Upon excitation of PDI (490 nm) all emission curves of the blend materials look very similar in shape varying only in the overall height with stronger quenching for short alkyl chains (data not shown). Typical PDI related emission features are visible but no signal from HBC emission could be recognized. The CTS signal at around 725 nm is still present for this excitation but decreased in intensity. Furthermore, photoluminescence excitation measurements have shown that the spectral contribution to the CTS mainly follows the absorption with higher yield upon HBC excitations.

Fig. 3. Emission photoluminescence spectrum of devices comprised of different blend materials. Samples were excited at 375 nm in reflection geometry. Detector counts are normalized to the sample absorption.

Results of the PL measurements can be explained when looking at the energy levels of donor and acceptor molecules. As known from literature, the HOMO levels of HBC and PDI are very similar at around 5.3 eV [12]. When blend material is excited at 375 nm the offset in LUMO levels of about 0.65 eV leads to both separation of excitons at the interface and energy transfer to the PDI. Upon excitation at 490 nm instead most emission occurs directly from the PDI. Despite the low driving force due to the small offset in HOMO levels a significant number of excitons is separated at the interface resulting in a spectral contribution of the EQE at wavelengths above 450 nm. In addition, some radiative loss of CTS excitons can be detected upon PDI excitation.

The overall radiative loss in the different blends can be derived from the absorption normalized area under the curve of the PL signals (Fig. 3). At both excitation wavelengths probed, best quenching is observed for HBCs with short alkyl chains, which is attributed to morphological differences in the thin films. The distance between PDI molecules and the HBC cores is likely to depend on the residue variations of the HBC molecules similar to the inter core distances measured for pure HBCs (Table S1 in Supporting information). Furthermore, better intermixing of donor and acceptor for short side chain HBCs is supported by AFM data. Intimate contact of HBC cores and the PDI is needed to efficiently separate excitons also allowing for higher photocurrents (as reported in Table 1 and Fig. 2). For long and especially swallow tailed alkyl side chains, relaxation of excited molecules by charge separation becomes less probable. Instead, charge carriers recombine and emit their energy in terms of photoluminescence giving rise to lower currents as observed in the IV curves. Generally the triple bond linker unit present in **HBC**≡**12** and **HBC**≡(**12,12**) appears to widen the radiative loss channel of the blends. The overall higher sterical demand of these HBCs is likely to be the reason: The phenyl group is located further away from the HBC core unit resulting in a less compact packing in **HBC**≡**12** (cubic lattice) and **HBC**≡(**12,12**) (tilted herringbone structure) (see Table S1 in Supporting information).

3.4. Transient decay measurements

Two types of transient decay measurements were performed on the solar cell devices in order to gain insight to charge carrier recombination and extraction.

Fig. 4 shows a typical photovoltage decay (PVD) transient monitored with a digital high resolution oscilloscope. In addition to the potential generated by white light illumination, supplementary charge carriers are created by short laser pulses (532 nm) raising also the open circuit potential of the cell temporarily. The voltage drops to the former level due to recombination of the additional charge carriers. The decay process can be described by a bi exponential function,

$$V_{Bias} = A_{fast}e^{-k_{fast}t} + A_{slow}e^{-k_{slow}t} \quad (1)$$

with decay rates k_{fast} and k_{slow} differing by about one order of magnitude and respective constants A_{fast} and A_{slow} . Investigations at different laser pulse intensities have shown that k_{fast} strongly depends on the perturbing light intensity and does not reveal blend specific properties [31]. The slow decay rate instead gives insight to the material specific recombination of the solar cells: for cells under working conditions an e^{-1} lifetime of charges can be estimated from the decay rate as

$$\tau_{1/e} = k_{slow}^{-1} \quad (2)$$

Annealed devices with blends of HBC:PDI (40:60 wt%) were analyzed and transients show lifetimes in the range of a few tens of microseconds, which is comparable to common values found

Fig. 4. Photovoltage and photocurrent decay experiments. Inset cartoon depicts the setup geometry. Exemplary curve shows photovoltage decay of a **HBC-6:PDI** cell (scattered) and the according bi-exponential fit (red line). The inset table summarizes decay rates k_{slow} and k_{fast} for photovoltage (PVD) and photocurrent (PCD) decay, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

for other organic photovoltaic systems (inset table, Fig. 4) [32]. Charge recombination occurs faster in blends containing short side chain HBCs, which further explains the differences observed in R_{sh} and FF for reported in Table 1: both FF and R_{sh} are found to decrease gradually from long to short residues at the periphery of the HBCs, implying more pronounced recombination and increased leakage currents. Even though charge separation is not favored in the **HBC≡(12,12)** containing blends manifested by the low I_{SC} and high PL loss, once excitons are separated in this blend, generated charges can efficiently be extracted and recombination is only a minor loss mechanism. For the cells containing **HBC-6** instead, considerably more free carriers are produced yielding a higher short circuit current. However, devices suffer strong recombination resulting in the low FF of these devices.

To further analyze the charge carrier generation and extraction, photocurrent decay measurements (PCD) were also carried out on the solar cell devices. Contrary to the PVD experiments, measurements were conducted under short circuit conditions with no white light bias. Transients recorded are also subject to a bi exponential decay and can be fitted with Eq. (1). For PCD measurements, slow decay rates are strongly influenced by trap states and only the short lived state incorporates blend specific information [33]. An e^{-1} lifetime is extracted from the fast decay rates (Fig.4, inset table). Reported charge extraction rates are two orders of magnitude faster than respective recombination rates determined by the PVD measurements a prerequisite for efficient charge carrier extraction in the solar cell devices: separated charges will rather exit the device via the external TiO_2 and Ag contacts than become annihilated within the active material.

All materials show a peak current response to the laser pulse of similar magnitude. However, the decay from this peak value occurs faster in the blends with long or branched side chain HBCs. The total amount of charge (Q) generated by one laser pulse on a specific cell is equal to the area under the decay curve (I vs. t). Q increases from **HBC≡(12,12)** to **HBC-6**, which is consistent with the differences in short circuit currents of the IV measurements presented (Fig. 2). Upon laser irradiation at 532 nm, only PDI molecules become excited which can either contribute to charge carrier generation, or unwanted relaxation occurs. In the blends containing long residue HBCs prominent non radiative and radiative relaxation of the excited PDI molecules are indicated by fast decay rates. For HBCs with short chain residues instead, intimate contact of the HBC core to the excited PDI is provided, recombination is suppressed and charges are generated over a

longer period of time. This results in the slow decay rates recorded and is also in accordance with the PL signals quantifying the radiative recombination loss channel. It appears that the capability to extract more charges from the excited PDI outweighs the faster recombination for blends containing short alkyl chain HBCs as shown with PVD measurements and explains the significantly higher short circuit currents of these materials [34].

The PCD decay rates reported for the HBC:PDI devices are comparable to those found in literature for high efficient polymer fullerene devices[34]. However, peak current offset after perturbation and thus the overall extracted charge is found significantly lower for the small molecule devices presented here. Optimization of alignment in the discotic blend material will lead to improved mobility and allow for faster charge carrier extraction making these small molecule solar cells competitive with morphology optimized polymer fullerene devices.

3.5. Surface morphology analysis

Tapping mode atomic force microscopy (AFM) has been carried out on the different organic blend layers studied. Images were taken on the identical samples which yielded the above shown IV characteristics after careful removal of the Ag top contact. Thus surface morphology of the different blends could be analyzed exactly where the material was previously confined between bottom and top electrode.

In open films, PDI forms long crystalline grains. Pure HBC films exhibit rather smooth and almost featureless surface structures instead [12]. Throughout the annealing treatment at 120 °C PDI is in isotropic phase and also side chains of the liquid crystalline HBCs are mobile (Table S1 in Supporting information). As the blend material was kept in confinement sandwiched between the TiO_2 and Ag electrode the formation of PDI needles could be effectively suppressed yielding RMS roughness values of only 4.7 nm for the different HBC:PDI blends studied. The confined annealing treatment leads to an improved morphology and is favorable for device performance. In non confined geometry instead, PDI needles are likely to penetrate through the entire active layer establishing direct contact between both electrodes [12,35]. Increase leakage currents and reduced shunt resistance are observed.

Furthermore, during thermal annealing also the nano morphology of the blend material changes: realignment of the discotic molecules leads to increased ordering [36,37]. An altered

Fig. 5. AFM tapping mode scans of annealed (14 h, 120 °C) HBC:PDI 40:60 wt% samples. Scale bar is 500 nm for both phase (large image) and height scans (insets). Images were taken after top contact removal and give insight to the blend morphology present in solar cell devices. Crystalline structures are observed mainly for short alkyl side chains at the periphery of HBC.

morphology showing larger grains can be visualized with AFM scans. The observed increase of device performance as already reported along with the *IV* curves is attributed to better percolation pathways. However, when annealed for over 24 h decrease of short circuit currents was observed. We attribute this to well advanced de mixing and consequently reduced interfacial area of HBC with PDI [38].

After annealing in confined geometry the blend materials studied also show differences in surface topology as summarized in Fig. 5. Flake like structures are visible for all derivatives, whereas the grain size decreases from about 500 nm (for **HBC-6** and **HBC-8**) to 100 nm (for **HBC-16** and **HBC $\equiv$ (12,12)**) in diameter. For longer side chain HBCs, the domains are interrupted by less ordered areas. This may also lead to a lower charge carrier mobility and could thus cause the lower currents observed for these materials. In contrast, the larger grains for the short side chain HBCs rather consist of better aligned material. Initial X ray experiments show, that most likely a mixed phase of HBC and PDI is present in this grains. The increased crystallite size allows for better percolation pathways towards the contacts. Intermixing of HBC and PDI is necessary for efficient exciton separation upon illumination. These findings are consistent with both PL data and the PCD measurements indicating that the charge carrier generation yield is higher when incorporating short side chain molecules.

The surface morphology of the active material indicates differences in crystallinity and quality of crystal growth. These parameters play an important role for the solar cell performance consisting of discotic molecules. For efficient devices large and ordered domains incorporating intermixed donor and acceptor material are necessary.

4. Conclusion

We have studied the influence of alkyl side chain modifications of discotic liquid crystalline donor molecules for solar cell applications. Short alkyl tails allow for a more intimate contact of the HBC cores to a PDI acceptor molecule. PCD and PL measurements indicate that radiative and non radiative loss mechanisms of excited molecules can be efficiently suppressed when using HBC with shorter side chains, where consequently best exciton separation and highest power conversion efficiencies are found. AFM measurements explain the significance of

annealing in confinement and reveal differences in cristallinity of the different blends investigated. The findings also support the formation of an intermixed donor acceptor phase for short chain HBCs. Thus large interfacial area between donor and acceptor and at the same time high mobility in the respective materials can be achieved. With this donor acceptor couple external quantum efficiency of over 27% was achieved.

Additionally, our studies reveal pathways to further increase the device performance. First of all, a more adequate matching of HOMO and LUMO levels is necessary to increase charge transfer and suppress energy transfer and radiative recombination as observed in our devices. Currently, charge carrier generation is limited by high radiative loss as indicated by PL data. Furthermore PL measurements point out that the phenyl groups should remain in close contact to the HBC core since a new radiative loss channel is introduced by a larger spacing due to a triple bond linker unit. Also higher mobility within the blend material is needed to allow for faster charge carrier extraction and accordingly lower recombination as motivated by our findings based on PVD data.

Most important will be a good homeotropic alignment of the HBC molecules in the active film. Face on aligned molecules will facilitate faster charge transport towards the electrodes leading to improved charge extraction [39]. In conjunction with molecules having long alkyl chains and consequently a lower charge carrier recombination as supported by our transient decay measurements improved external quantum efficiency and higher fill factor are expected. Thus, our results suggest that the full potential of discotic molecules can only be accessed when material is fully homeotropically aligned and recombination is suppressed by an appropriate intermolecular distance.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.solmat.2009.11.024.

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