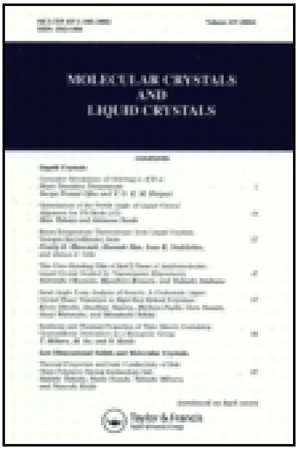

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ORGANIC HETEROJUNCTION PHOTOVOLTAIC CELLS MADE OF DISCOTIC, MESOGENIC MATERIALS

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We made photovoltaic cells containing two organic layers. The hole-conducting layer consists of a hexa-peri-hexabenzocoronene (HBC) derivative. The electron-conducting component is an alkylester of perylene tetracarboxylic acid. Both compounds form columnar mesophases which can provide 1D pathways for transport. The current/voltage-characteristics of the two-layer devices indicate a photovoltaic effect with an open circuit voltage of $V_{oc} \approx 0.8\,V$*, a short circuit current of* $I_{sc} \approx 3.9\,\mu A/cm^2$*, and a filling factor of* $FF \leq 31\%$*. The spectral distribution of the photocurrent of different samples indicates that excitations of the perylene derivative or of the HBC derivative both can lead to a photovoltaic effect.*

Keywords: columnar liquid crystals; discotic; photovoltaic cells

INTRODUCTION

Some liquid crystals have semiconducting properties and exhibit a high charge carrier mobility [1]. In particular, columnar liquid crystals have been demonstrated to be efficient hole conducting materials, while materials made of rod-like molecules containing heterocycles like an oxadiazole- or

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thiadiazole- unit are efficient electron conducting materials [2,3]. Consequently, a variety of effects known from organic semiconductors have been studied in liquid crystals. For example, the photoconducting properties of triphenylene compounds were extensively investigated. Liquid crystalline polymers, as well as low molar mass columnar liquid crystals and calamitic liquid crystals show electroluminescence [4–6] and may be useful to make organic light emitting diodes (OLED). The alignment of polymers and calamitic liquid crystals can be applied in order to generate linearly polarized light [4,6,7].

Photovoltaic effects in liquid crystals are known for a long time [8,9]. However, organic heterojunction solar cells containing mesogenic compounds were reported only recently [10]. In general, several types of organic solar cells are currently under development. Very well studied are the dye-sensitized solar cells containing colloidal TiO_2 particles in a conducting matrix. The first devices of this type contained an aqueous electrolyte solution [11] which was later substituted by solid organic conductors [12]. Of a different type are the organic thin film photovoltaic elements which consist of a very thin ($<100\,nm$) organic multilayer structure sandwiched between two different electrode materials. The photovoltaic effect may be due to charge transfer at the interface between two organic compounds (heterojunction) or due to charge transfer at the organic-metal interface. Very efficient examples of heterojunction solar cells are the combination of phthalocyanine and perylene compounds [13], or of poly phenylene vinylene (PPV) derivatives with fullerene compounds [14]. Besides the planar layers of an electron donating and an electron accepting compound, interpenetrating networks of such compounds turned out to be very efficient because of the large contact area [15,16]. These bulk heterojunction solar cells reach an integrated quantum efficiency of up to 3.5% under solar illumination conditions (AM 1.5) [17]. Based on doped pentacene single crystals, Schottky-type photovoltaic cells have been described which show an external energy conversion efficiency up to 2.4% [18].

Recently, Schmidt-Mende *et al.* [19] reported a photovoltaic cell of the bulk heterojunction type, which contained one columnar liquid crystalline hexa-*peri*-hexabenzocoronene (HBC) compound and a crystalline perylene derivative. In the present paper, we report the combination of an electron conducting columnar perylene derivative with hole conducting HBC derivatives in order to make use of their good charge transporting properties in an all-columnar photovoltaic cell.

EXPERIMENT

The layer-structure of the fabricated devices is shown in Figure 1. A glass substrate coated with indium tin oxide (ITO) serves as a transparent

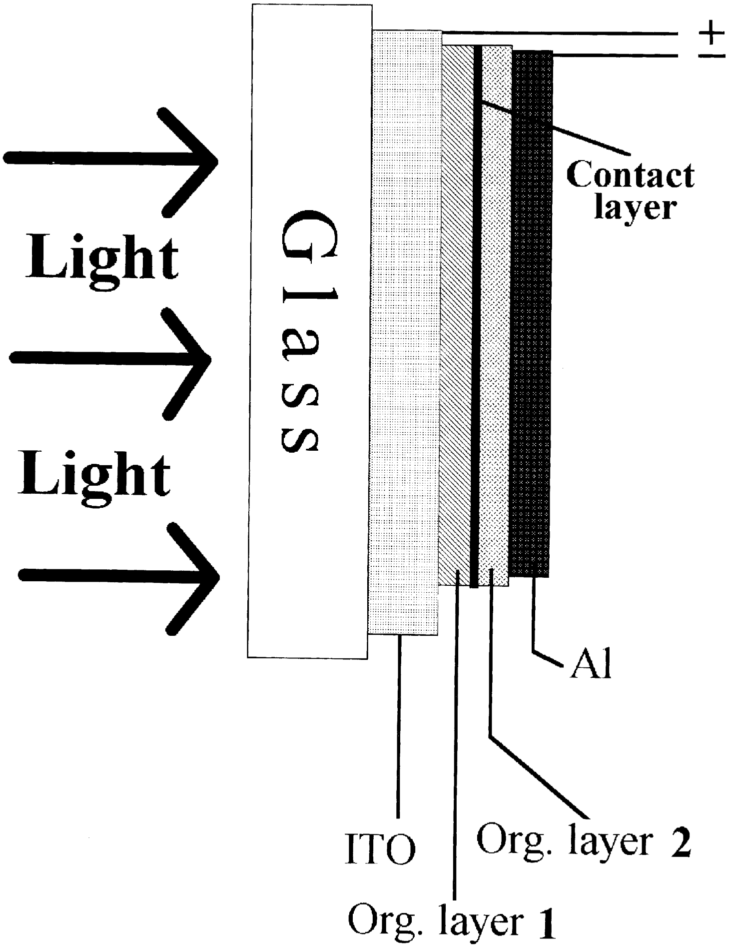
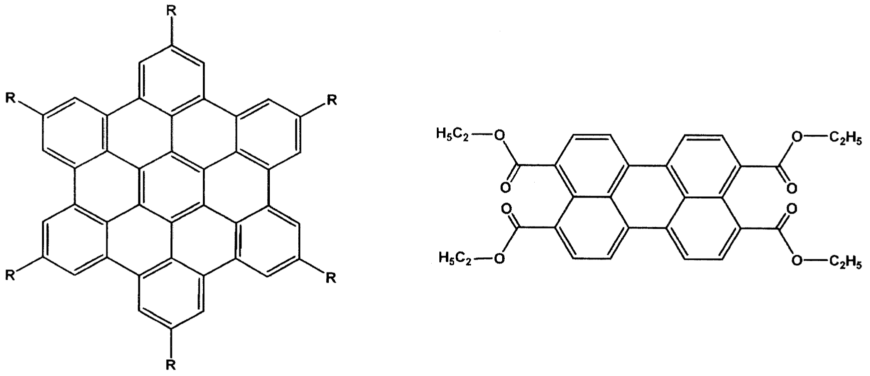


FIGURE 1 Schematic structure of an organic heterojunction solar cell.

electrode. On this substrate, two organic layers are deposited which consist of an electron donor and an electron acceptor, respectively. An Al-layer represents the counter-electrode. We expect that the separation of positive and negative charge carriers starts essentially at the interface between the two organic layers. This heterojunction is composed of either a hexaphenyl- or a hexaalkyl-substituted hexabenzocoronene (HBC-Ph-C_{12} or HBC-$C_{8,2}$), and a perylene tetraethylester (Perylene-C_2), as shown in Figure 2. At elevated temperatures, both HBC derivatives form columnar mesophases where the columns are hexagonally packed and the disc cores are perpendicular to the columnar axes. At room temperature the cores of



HBC-PhC$_{12}$: R = Ph-$C_{12}H_{25}$
HBC-C$_{8,2}$: R = 3,7-dimethyloctyl

Perylene-C$_2$

FIGURE 2 Chemical structures of the discotic, liquid crystalline compounds.

HBC-C$_{8,2}$ "crystallize" and tilt relative to the columnar axis [20], while crystallization is precluded in the case of the HBC-Ph-C$_{12}$ [21]. The perylene compound (Perylene-C$_2$) forms a columnar phase between 244°C and 313°C and is crystalline at room temperature [22].

The compounds were deposited on the substrate either by thermal evaporation in high vacuum or by spin coating. The compounds HBC-C$_{8,2}$ and perylene-C$_2$ were evaporated at a pressure of $1\cdot10^{-4}$ mbar and temperatures of about 500°C and 200°C, respectively. We checked the molecular structures of the deposited HBC compound by mass spectroscopy (MALDI-TOF). The results indicate that some thermal cleavage of alkyl side chains occurs, but the HBC cores remain unaffected. The compound HBC-Ph-C$_{12}$ can not be deposited by thermal evaporation. It was spin-cast from a 0.5% $CHCl_3$ solution. As a final step, aluminium was thermally evaporated to give a thin (100 nm) electrode layer.

From the HOMO- and LUMO-levels of the compounds, we expect two possible mechanisms of the charge-carrier transport within the device. The perylene compound and the HBC derivatives absorb light strongly, although in different wavelength regions. Obviously, both compounds are capable of generating excitons (electron-hole pairs). Close to the interface between the two compounds, two types of charge transfers are possible. Either the electron of an excited HBC molecule is transferred from the HBC-LUMO to the LUMO of a perylene acceptor molecule (Fig. 3a), or an electron from the HOMO of an HBC molecule is transferred to the HOMO of an excited perylene molecule (Fig. 3b). In both cases, the migration of the separated charge carriers to the electrodes is energetically favourable.

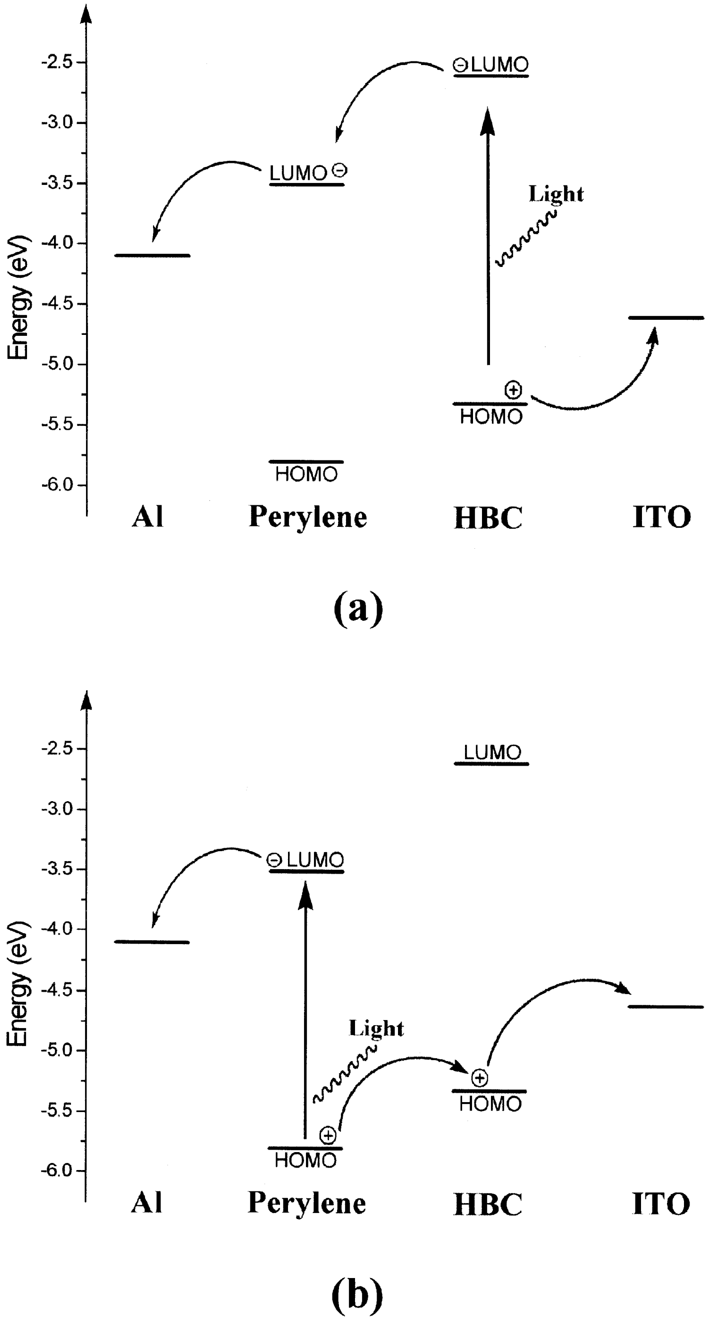


FIGURE 3 Two possible mechanisms of charge-carrier transport within the photovoltaic cell with the layer structure ITO/HBC-Ph-C_{12}/Perylene-C_2/Al.

In order to characterize the photovoltaic properties, we measured the current/voltage-characteristics of the devices in the dark and under illumination. The typical behaviour under illumination is shown in Figure 4. Without an external bias voltage, the samples show a short circuit current of about −1 μA. Under illumination, the samples show a negative current even when a moderate positive bias voltage is applied. When the external bias voltage compensates the open circuit voltage of the solar cell, the current becomes zero. For the sample corresponding to Figure 4, the open circuit voltage V_{oc} is about 825 mV. Not surprisingly, we noticed a rather strong dependence of the open circuit voltage on the preparation conditions (Table 1). In some cases it can be higher than the difference of the work functions of ITO and aluminium. This behaviour is also known from other heterojunction photovoltaic cells.

In order to explore the maximum power output of the respective devices, we determined a polynomial fitting to the I(V) curve. From this polynomial, the maximum of the product P_{max} of voltage and current was calculated. We obtained the fill factor which is defined as $FF = P_{max}/(V_{oc}\ I_{sc})$. In order to make simultaneous use of a high voltage and high current, the fill factor should be as high as possible. It is essentially limited by a high serial

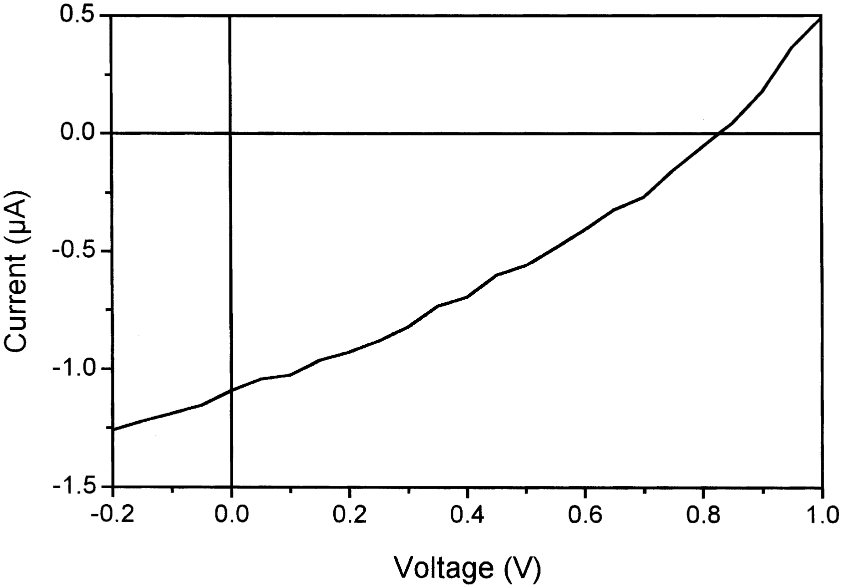


FIGURE 4 Current/voltage-characteristics of a photovoltaic device, consisting of the layers ITO/HBC-$C_{8,2}$/Perylene-C_2/Al. Solid line: illuminated.

TABLE 1 Photovoltaic Characteristics of the Investigated Sample Structures (V_{OC} = Open Circuit Voltage, I_{SC} = Short Circuit Current, V_{OP} = Operation Voltage for Maximum Power, I_{OP} = Operation Current for Maximum Power, P = Power Density, FF = Fill Factor). The Electrode Area was 0.28 cm^2

Device structure	V_{oc}[mV]	I_{sc}[μA]	V_{op}[mV]	I_{op}[μA]	P[mW/m^2]	FF[%]
ITO/HBC-PhC$_{12}$/Perylene-C$_2$/Al	1100	0.49	510	0.22	4.0	20.8
ITO/HBC-C$_{8,2}$/Perylene-C$_2$/Al	825	1.1	459	0.61	10.0	30.9
ITO/Perylene-C$_2$/HBC-C$_{8,2}$/Al	350	0.10	150	0.06	0.3	25.7

resistance or a low shunt resistance of the sample. In our case, we found values up to 30.9% for the fill factor. This indicates that the diode behaviour still has to be improved. (See Table 1 for a comparison of the photovoltaic parameters of the investigated solar cells.)

In a different experimental setup, we measured the power conversion efficiency. For this purpose, a sample with the layer structure ITO/HBC-C$_{8,2}$/Perylene-C$_2$/Al was illuminated with a xenon high-pressure arc lamp. The irradiance was 200 mW/m^2. A power conversion efficiency of about $2 \cdot 10^{-4}$% was calculated.

Illuminating with monochromatic light, the spectral response of the photocurrent can be obtained (by means of a fluorescence spectrometer and a lock-in amplifier). Figure 5 shows the absorption spectra of the organic layers and the spectral distribution of the external quantum efficiency (EQE) for a sample consisting of ITO/HBC-Ph-C$_{12}$/Perylene-C$_2$/Al. The EQE indicates the ratio between the rate of incident photons per area and the generated electrons per area (incident photon to current efficiency [23]). For samples containing the spin coated compound HBC-Ph-C$_{12}$ it is of the order 0.1% in the visible wavelength range. However, for samples containing the evaporated HBC-C$_{8,2}$ derivative, it is one order of magnitude lower.

In spite of its lower quantum efficiency, the compound HBC-C$_{8,2}$ has the advantage that it can be deposited by evaporation. This allows us to vary the thickness of the organic layers conveniently, and even to change the sequence of deposition of the organic layers. The influence of this sequence is shown in Figure 6. If the perylene compound is located directly at the transparent substrate, the highest photocurrent appears in the spectral range of HBC absorption (Fig. 6a). However, if the HBC compound is close to the glass substrate, the maximum photocurrent appears when the sample is illuminated with green light (Fig. 6b). Obviously, in the latter case the main part of the photocurrent results from the excitation of the perylene molecules.

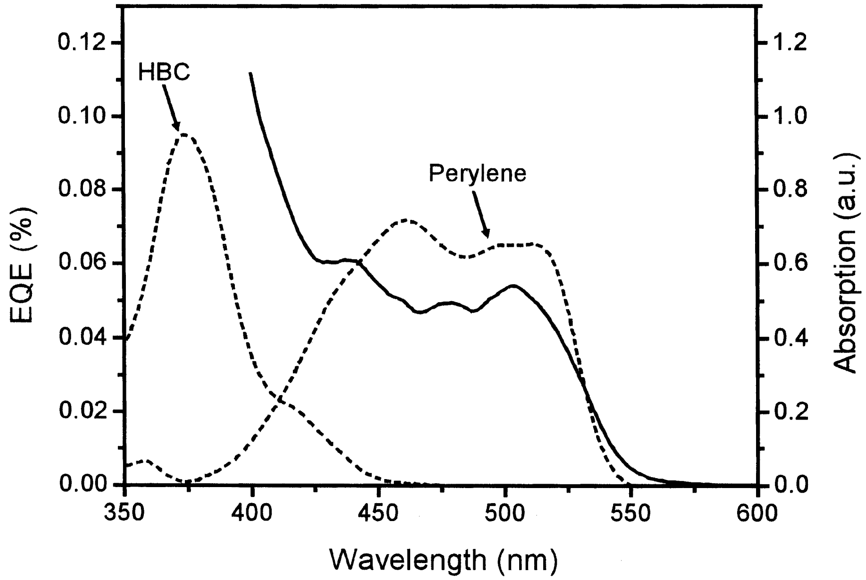


FIGURE 5 Solid line: incident photon to current efficiency of a solar cell with the layer-structure: ITO/HBC-Ph-C_{12} (40 nm)/Perylene-C_2 (16 nm)/Al. Dashed lines: absorption spectra of the organic compounds (HBC-Ph-C_{12}: maximum at ≈375 nm; Perylene-C2: maximum at ≈465 nm).

These differences of the spectral response can be understood by regarding the microstructure of the heterojunction. It consists of two organic bulk-layers whereas only a very thin contact area is responsible for the charge-carrier separation. The light, which reaches this contact area has already passed through one of the bulk-layers. Since the light of the appropriate wavelength is extensively absorbed in this layer, the light intensity available for excitation is considerably lower. We conclude that the efficiency can be enhanced by adjusting the thickness of the first organic layer appropriately. For this purpose, the thickness of the HBC-$C_{8,2}$ layer in the configuration ITO/HBC-$C_{8,2}$/Perylene-C_2/Al was varied systematically between 10 nm and 50 nm (Fig. 7). The layer thickness of Perylene-C_2 is 25 nm for all samples displayed in Figure 7. The results indicate a maximum photocurrent for the HBC-$C_{8,2}$ layer thickness of 10 nm. For this small thickness, we have almost equal contributions from the absorptions of the two organic compounds to the photocurrent. However, in agreement with the data shown in Figure 6, samples with a large HBC-$C_{8,2}$ layer thickness show a lower contribution to the photocurrent in the blue wavelength range than in the green wavelength range.

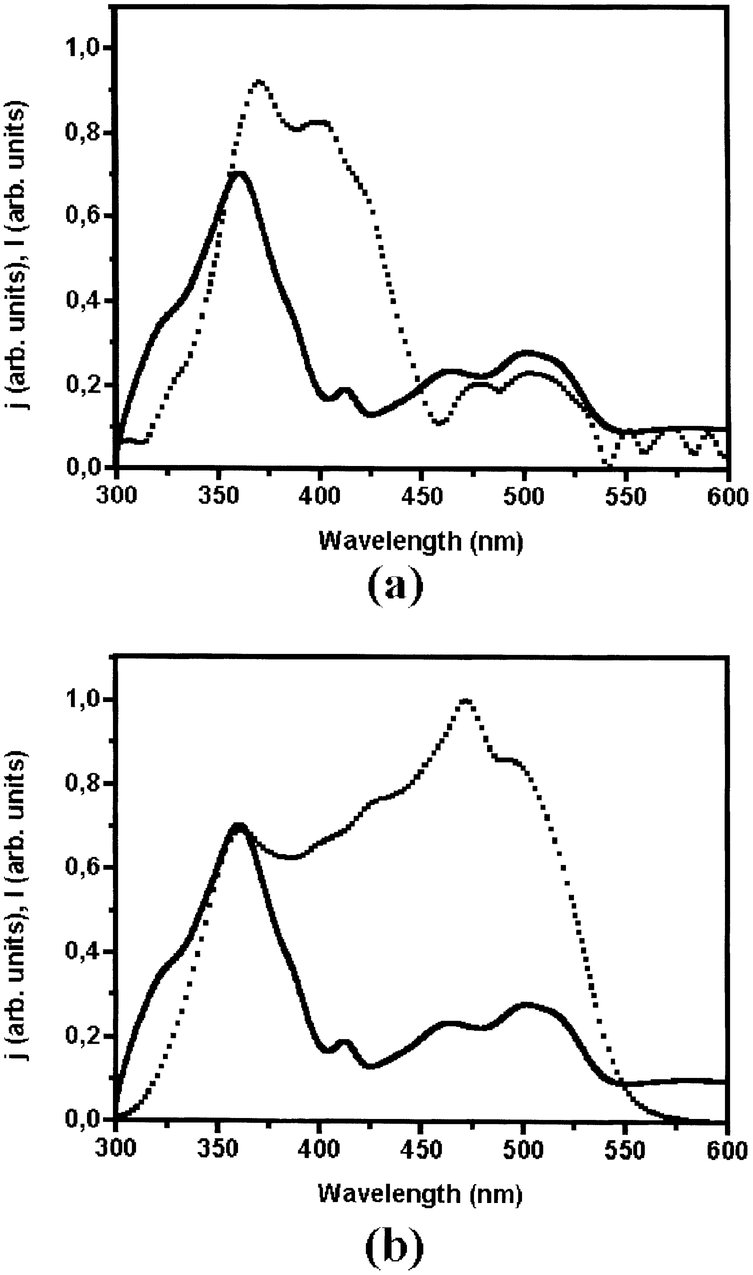


FIGURE 6 Dashed lines: spectral photocurrent response of a solar cell with the following layer-structures: (a) ITO/Perylene-C_2 (28 nm)/HBC-$C_{8,2}$ (45 nm)/Al. (b) ITO/HBC-$C_{8,2}$ (40 nm)/Perylene-C_2 (30 nm)/Al. Solid lines: absorption spectrum of the organic double layers.

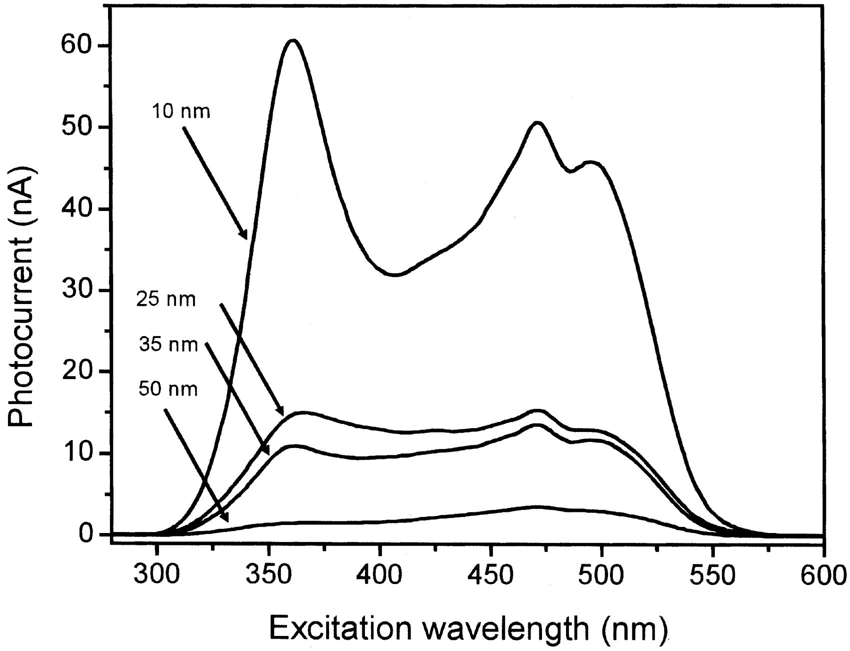


FIGURE 7 Spectral photocurrent response of a solar cell with the layer-structure ITO/HBC-$C_{8,2}$/Perylene-C_2/Al. The layer thickness of HBC-$C_{8,2}$ is varied between 10 nm and 50 nm. The Perylene-C_2 layer thickness is 25 nm in all cells.

CONCLUSION

It is demonstrated that two columnar compounds can be combined to give photovoltaic heterojunction cells with considerable open circuit voltages. The spectral response is favourable because both the hole conducting layer and the electron conducting layer can be excited to induce a photocurrent. The absorption spectra of the perylene and the hexa-*peri*-hexabenzocoronene are very well matched to cover the visible spectral range efficiently. However, the typical current density obtained in our samples is rather low. Schmidt-Mende *et al.* [19] observed much higher external quantum efficiencies for a bulk heterojunction solar cell made of a non-mesogenic perylene compound and a HBC derivative. The latter result is in agreement with the finding [15,16] that the morphology of the interpenetrating network of a bulk heterojunction cell is very favourable in comparison with planar layers. Yet, we have not controlled the orientation of the columnar phases. The perylene compounds used in this work are known to crystallise in a columnar arrangement similar to the columnar mesophase.

This behaviour supports a self-organizing process due to the occurrence of the liquid crystalline state. On the other hand, the columnar phase of hexa-*peri*-hexabenzocoronene derivatives tends to align with the columns in plane which is desirable for the application in organic field effect transistors, but not for a heterojunction solar cell composed of flat layers. We conclude that careful control of the alignment and making use of the annealing behaviour can further improve the performance of our cells.

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