Photocurrent increase by doping a liquid crystal host with a functionalized fullerene

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Doping a photoconductive mesogenic material with a small amount of functionalized fullerene significantly increases the photocurrent. LESR studies show the appearance of a long-lived charge-separated state under light illumination, with a negative charge on the fullerene moiety. This confirms that in the system studied the fullerene unit acts as an electron trap. In the lamellar structure of the liquid crystalline phase the fullerene units and mesogenic cores are separated, which ensures better space separation between negative and positive charges. As a result the charge recombination is slowed and the photocurrent is amplified.

1. Introduction

The fullerene (C_{60}) unit is an excellent electron acceptor, able to accept up to six electrons into a single molecule [1]. This property provides the possibility of using C_{60} derivatives in optoelectronic devices such as solar cells [2] or organic light emitting diodes (OLEDs) [3]. C_{60} materials mixed with π-conjugated polymers have been extensively applied in prototype photovoltaic (PV) cells [4], however even the best optimized devices suffer from rather low performance. Unlike in inorganic semiconductors in which the photon absorption creates directly free charges, in organic materials bonded electron–hole excitons are formed initially. The dissociation of excitons into free charges is still not a fully understood process. In polymer organic blends it is believed to take place at the interface of two materials of sufficiently differing electron affinity [5], while in some other amorphous materials exciton dissociation on the electrodes is the dominating process [6]. In both cases, one of the major problems limiting the photon–electricity conversion efficiency is the small exciton diffusion length, which allows only a few of them to reach the dissociation region.

Fast electronic conduction has also been reported recently for liquid crystalline (LC) materials [7]. In such systems, apart from hole migration, which is typical for molecular crystals and polymers, electrons also contribute significantly to the photocurrent [8]. In LC materials the charge generation is probably a complex process, as indicated by the non-linear dependence of the photocarrier generation on the light intensity [9]. It could be expected that a combination of the electron-accepting properties of fullerenes with the high charge carrier mobility in the LC state may lead to optimized PV materials. In the case of fullerene-based mesogenic materials, in which the fullerene unit is covalently attached by a flexible alkyl chain to the mesogenic electron-donating unit, the electron-acceptor and electron-donor layers are formed naturally due to the self-assembling process. This ensures a huge interface between the electron-donor and electron acceptor areas, and furthermore, the distance between the electron-donating and electron-accepting layers may be easily manipulated by changing the molecular structure. To date, only a few fullerene-based liquid crystals have been reported [10] and these exhibit weakly organized phases (nematic and smectic A phases), which are unfavourable for fast electronic conductivity. They are also extremely viscous, which makes them hard to process into devices. Recently it was recognized that liquid crystalline materials doped by a small amount of fullerenes might also show increased photocurrents [11].

Here we report photocurrent and ESR measurements of a binary liquid crystalline system. A naphthalene derivative was chosen as the host material (see figure 1), since compounds with π-conjugated bonds are known for their photoconductive properties [12]. (The synthesis and LC properties of this derivative will be reported elsewhere). A fullerene derivative was used as the

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Material **I** : Cr 159.8 Sm 223.8 I
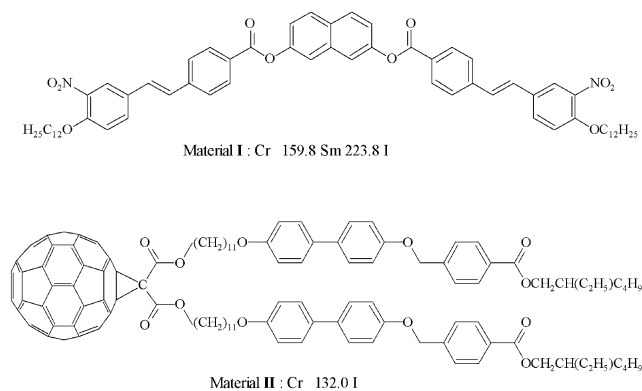
Material **II** : Cr   132.0 I

Figure 1.   Molecular structure and phase transition temperatures (in °C) of host and fullerene dopant materials.

dopant (figure 1). In this material, the fullerene was functionalized by attaching elongated rigid units through the malonate group. This molecular structure ensured good miscibility of the dopant with the host material, and moreover it might be expected that the interaction between the mesogenic cores of the host molecules and the elongated units of the dopant molecules may lead to a microseparation between the fullerene and naphthalene–mesogenic-core sublayers.

2.   Experimental

2.1.   *Characterization*

Photoconductivity measurements were carried out using glass cells with indium tin oxide (ITO) electrodes and a polyimide coating. The cell gap was fixed using Mylar spacers of 5 μm thickness. The cells were filled in the isotropic phase by the capillary method. The light source used for the studies was an intensity-stabilized halogen lamp. The emission spectrum of the lamp was recorded using a Nikon G-70 monochromator and silicon BPW-34 photodiode. An IR filter was inserted in the beam path just before the sample to reduce heating effects. The relative power of the radiation at the sample was monitored using a photodiode placed close to the sample. The photocurrent was measured by controlling the voltage at the 1 MΩ resistance, which was connected in series with the sample, using an Agilent 34401A multimeter. As a bias voltage source, an SRS DS345 generator was used. Absorption spectra of the materials studied (dissolved in methylene chloride, concentration $\sim 1.5 \times 10^{-5}$ M) were recorded using a Shimadzu UV-3101PC spectrometer.

The ESR studies were performed with a Bruker ELEXYS 500 system equipped with a liquid nitrogen cooler. The DMO 108 resonator with a side opening was mounted in the spectrometer to allow light illumination of the samples. The microwave power was adjusted to ensure a linear ESR region. The light source with broad emission spectrum from green to near-ultraviolet was used, as well as a He–Ne laser. The ESR spectra were collected in the temperature range from room temperature to 120 K. The spectra were fitted to the sum of three Gaussian signals to obtain accurate *g* values.

The molecular structures of the compounds synthesized were confirmed by elemental analysis, mass spectroscopy and NMR methods. ^{13}C NMR spectra were recorded on a Varian Unity Plus spectrometer operating at 200 MHz, while ^{1}H NMR spectra were recorded at 200 or 500 MHz when high signal separation was necessary. Tetramethylsilane was used as an internal standard. Chemical shifts are reported in ppm, *J* values in Hz.

2.2.   *Synthesis*

The synthetic procedure for obtaining the malonate derivative of fullerene is sketched in scheme 1.
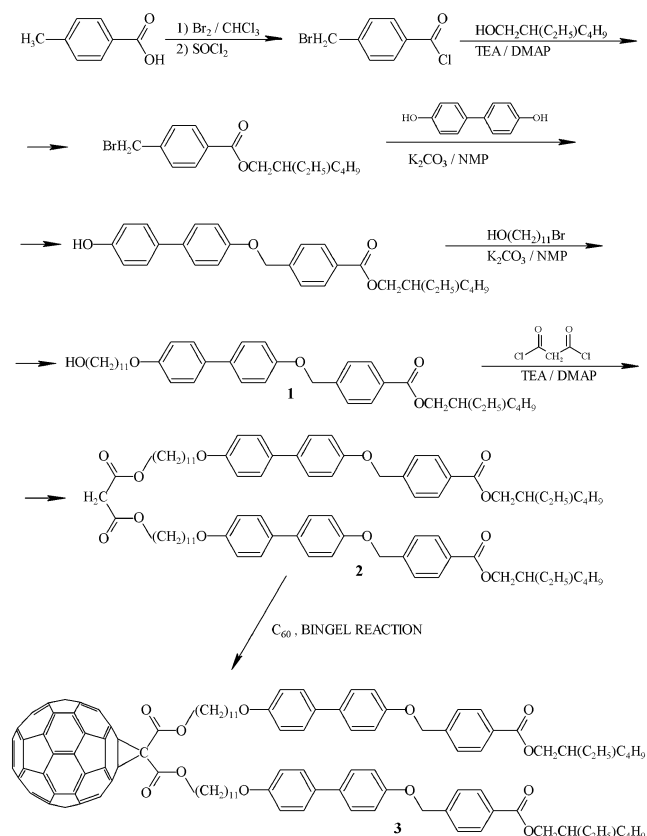
Scheme 1.   Synthetic procedure for the malonate derivative of fullerene (material II).

2.2.1. Malonate diester 2. To a mixture of alcohol **1** (1.8 g, 3 mmol) and dry triethylamine (1 cm^3) dissolved in methylene chloride (100 cm^3), malonyl dichloride (0.21 g, 1.5 mmol) was added with stirring. The reaction mixture was held at room temperature for 15 h; it was then evaporated to dryness and the crude product chromatographed on silica gel with toluene as eluant. Malonate diester **2** was obtained in 64% yield (1.21 g). Elemental analysis for C$_{81}$H$_{108}$O$_{12}$: calc. C 76.41, H 8.49; found C 76.22, H 8.58%. ^{1}H NMR (δ, CHCl$_3$, 200 MHz): 8,061 (d, 4H, $J=8.4$), 7.516 (d, 4H, $J=8.4$), 7.456 (d d, 8H, $J_1=3.2$, $J_2=8.8$), 6.997 (d, 4H, $J=8.4$), 6.933 (d, 4H, $J=8.6$), 5.146 (s, 4H), 4.244 (d, 4H, $J=5.0$) 4.134 (t, 4H), 3.969 (t, 4H), 1.83–1.55 (m, 12H), 1.52–1.22 (m,32H), 0.945 (t,12H). ^{13}C NMR (δ, CDCl$_3$, 200 MHz): 166.673, 166.418, 142.119, 133.997, 132.999, 130.042, 129.802, 127.711, 127.638, 126. 917, 115.030, 114.687, 69.352, 69.352, 67.997, 67.305, 65.630, 41.658, 38.868, 30.543, 29.508, 29.457, 29.363, 29.268, 29.173, 28.947, 28.423, 26.027, 25.750, 23.951, 22.945, 14.030, 11.073.

2.2.2. Fullerene adduct 3. To a mixture of fullerene C$_{60}$ (0.48 g, 0.66 mmol), malonate diester **2** (0.6 g, 0.47 mmol) and DBU (0.15 g, 0.98 mmol) in toluene (100 cm^3), iodine (0.12 g, 0.47 mmol) was added with stirring. After 2 h the toluene was evaporated and the product purified by column chromatography on silica gel with toluene as eluant. The fullerene adduct **3** was obtained in 54% yield. LR ESI MS: $m/z=1991.4$ [m+H]$^+$. ^{1}H NMR (δ, CHCl$_3$, 200 MHz) : 8.058 (d, 4H, $J=8.2$), 5.511 (d, 4H, $J=8.2$), 7.448 456 (d d, 8H, $J_1=4.0$, $J_2=8.0$), 6.993 (d, 4H, $J=8.4$), 6.922 (d, 4H, $J=8.6$), 5.146 (s, 4H), 4.489 (t, 4H), 4.243 (d, 4H, $J=5.4$), 3.960 (t,4H), 1.92–1.6 (m,12H), 1.59–1.20 (m, 32H), 0.945 (t, 12H). ^{13}C NMR (δ, CDCl$_3$, 200 MHz): 116.634, 163.873, 158.505, 157.711, 145.554, 145.408, 145.335, 145.015, 144.767, 144.024, 143,164, 142.349, 142.072, 141.110, 139.166, 134.234, 133.244, 130.279, 130.039, 127.948, 127.890, 127.154, 115.274, 114.946, 69.596, 68.219, 67.542, 39.105, 30.780, 29.804, 29.738, 29.622, 29.520, 29.423, 29.185, 28.798, 26.198, 24. 195, 23.183, 14.274, 11.317.

3. Results and discussion

In order to study the enhancement of the photocurrent by doping the liquid crystalline host with fullerene molecules, a binary mixtures of material I (figure 1) with fullerene derivative II was prepared with the concentration of component II up to 7 wt%. Compound I incorporates the naphthalene moiety as a central unit. Some LC naphthalene derivatives are known to exhibit weak photovoltaic properties. For pure material I we

expect bipolar carrier transport, as this seems to be a general feature of photoconducting smectic phases [13]. The chosen material belongs to a new class of liquid crystals, so called 'bent-shaped' mesogens [14]. It forms lamellar phases (layer spacing $d \approx 41$ Å) but, compared with the low organized smectic A and C phases formed by rod-like molecules the rotation of bent-shaped molecules inside the smectic plane is strongly hindered.

Microscopic observations along with DSC and X-ray studies showed that the phase transition temperatures and structure of the host material are only weakly affected by the dopant. The light absorption spectra of material II shows typical feature of fullerene mono-adducts; a shift of the colouring band to $\lambda=425$ nm and a weak signal at 690 nm are observed, the absorption of material I is mainly in the UV range (figure 2). Comparing the light absorption spectra for the naphthalene and fullerene materials and their 1:1 mixture, it was confirmed that there are no ground state electronic interactions between molecules I and II in the mixture; the absorption of the mixture is a simple sum of the absorption of the mixture components.

For pure material I in the LC state under the best experimental conditions, the relative increase of current flow through the sample under light illumination (I_{light}/I_{dark}) was less than 10. For the same experimental conditions, the mixture with ~5% of fullerene derivative II gave an increase of current by a factor of 40. It should be stressed that the strongest photocurrent was detected in the liquid crystalline state; in the isotropic and crystal phases the I_{light}/I_{dark} ratio was considerably smaller (figure 3). The observed steady-state photocurrent value is proportional to the square of light intensity (see inset in figure 3), suggesting that charge generation cannot be
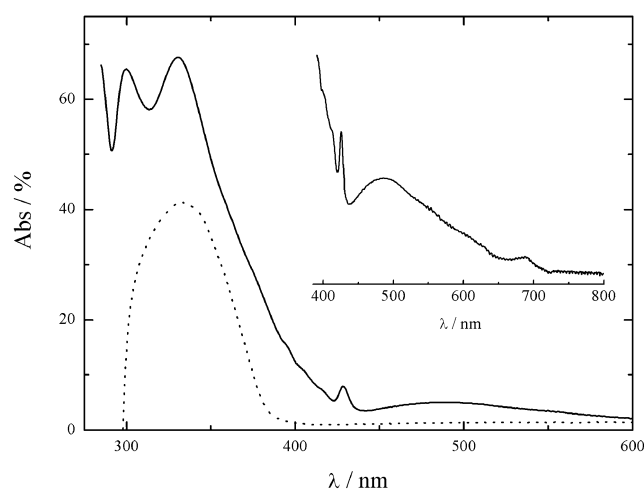

Figure 2. Absorption spectra of materials I (dotted line) and II (solid line) for the ~1.5×10^{-5} M CH$_2$Cl$_2$ solution. The inset is an enlarged visible range absorption of material II.
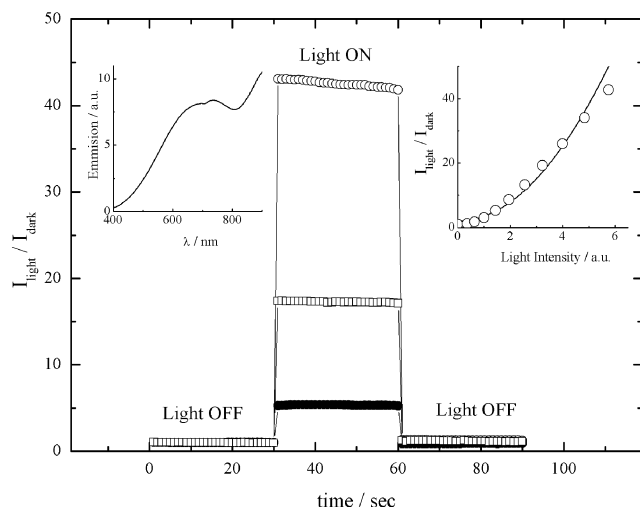
Figure 3.   Ratio of steady-state current between dark and light-on states for the mixture of material I with 5 wt%. of fullerene dopant II in the smectic (open circles), isotropic (solid circles) and crystalline (open squares) states. The right inset shows the current–light intensity dependence in the smectic phase with the fit to the square relationship. The left inset shows the emission spectrum of the halogen lamp used for photocurrent measurements, recorded with a silicon photo-diode. The linear increase of background emission is due to the increase of photodiode sensitivity.

described by the usual linear relationship of the Onsager model [15], but probably involves two-molecule exci-ton–exciton interactions [9]. As expected, in cells with two ITO electrodes the current–voltage characteristic was symmetric with almost linear current–voltage dependence for dark as well as illuminated state.

In contrast to the naphthalene system, when other LC hosts, such as, terephthal-bis(p-butylaniline) (TBBA) or malonate diester (compound **2** in scheme 1) (which do not possess, or have very weak, photoconducting properties) are doped with the fullerene derivative II, only minimal photocurrent was observed. This indicates that for small concentrations of dopant II the charge hopping between fullerene sites is a negligible process.

To understand the origin of the photocurrent increase in the fullerene-doped naphthalene LC composites, light-induced electron spin resonance (LESR) studies were performed. The LESR method enables unambig-uous detection of long-lived charged separated states. When measured at room temperature no signals are present in the mixture of materials I and II, not even under illumination, see figure 4 (*a*). At 130 K under UV-VIS illumination, three signals were obtained, fig-ure 4 (*b*). The lower field signal at $g=2.0025$, as well as two poorly resolved higher field signals at $g=2.0004$ and 1.9995, were found in the ESR spectrum. The intensity of the lowest field signal $g=2.0025$ is only
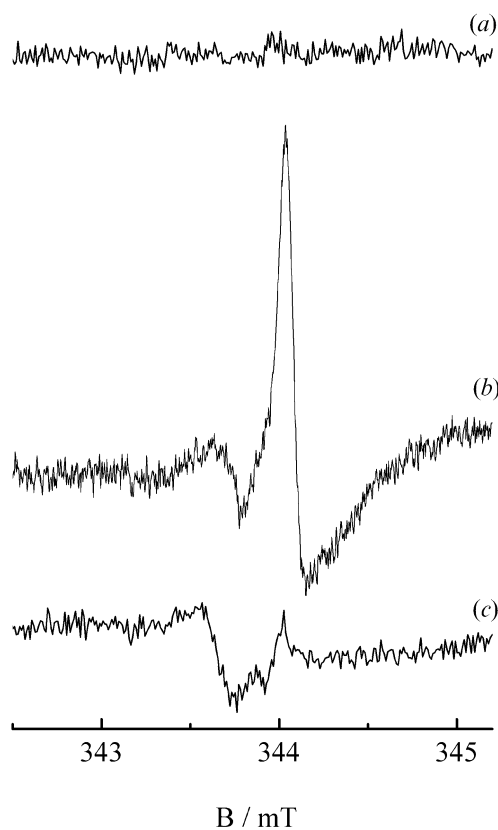

Figure 4.   LESR spectra for the mixture of material I with fullerene dopant II: (*a*) degassed sample at room temperature in light-on state; (*b*) at 130 K in the light-on state, (*c*) at room temperature in the light-off state, after heating the sample previously illuminated at low temperature.

weakly light-dependent and the signal nearly disappears in the degassed sample. The intensity of two higher field signals, $g=2.0004$ and 1.9995, increases significantly in the light-on state. In the literature, the $g=2.0025$ signal was usually assigned to a fullerene triplet state (g value in the range from 2.0012 to 2.00135) [16] or to a positively charged fullerene radical $C_{60}^{\bullet+}$ for which g in the range 2.0024–2.0030 was quoted [17]. But since in the materials studied the signal disappears in degassed samples, the triplet state may be excluded as a source of the signal.

It is known that the triplet state is strongly quenched in the presence of oxygen [18], thus for the air-degassed samples this signal intensity should increase. In the system studied, the $g=2.0025$ signal was assigned to the $C_{60}^{\bullet+}$ radical, although the origin of this radical is not understood at present. Two poorly resolved higher field signals, for which the intensity is light-dependent, were ascribed to photogenerated polarons trapped in the frozen matrix; the $g=1.9995$ signal is assigned to an electron located at the fullerene, while the signal

$g=2.0004$ arises from the hole. The $g=1.9995$ value is in a good agreement with those quoted in the literature for the fullerene anion [19]. At 130 K, polaron signals show very slow decay, remaining even several minutes after the light is turned off. However, if a sample illuminated at 130 K is heated, the intensity of the signals related to the charge-separated state are strongly reduced, and only remnants of the signals are observed at room temperature, see figure 4(*c*). This suggests that a low temperature is critical for the detection of a long-lived separation of holes and electrons, as this slows down charge recombination.

The charge-separated state for compound II was also detected by the LESR method in other mixtures, with toluene or methylene chloride as solvent. The light dependence and kinetics of the ESR spectra are very similar to that observed for the mixture with the naphthalene material I, however in these composites the signals related to charge separation are of lower intensity. This suggests that for the system studied the charge separation is enhanced by the presence of the solvent with π-conjugated bonds.

In summary, doping the mesogenic naphthalene derivative with a small amount of functionalized fullerene significantly increases the photocurrent. LESR studies showed the appearance of a long-lived charge-separated state under light illumination, with the negative charge located on the fullerene moiety. Although broadening of the light absorption range in the mixture (due to the broader light absorption range of the fullerene derivative) might play some role in the increase of the photocurrent, other mechanisms could also be important. In the pure host material both holes and electrons are conducted in the smectic sublayer consisting of mesogenic cores. The small distance between negative and positive charges in this sublayer leads to their frequent recombination. This is probably one of the main factors limiting the photocurrent in lamellar LC materials. In the fullerene-doped mixtures, the electrons are withdrawn from the mesogenic cores sublayer, as the negatively charged fullerene units are placed mainly in the alkyl chains sublayer. For the concentration of fullerene dopant studied, the negative charges are too far from each other for efficient hopping transport and thus the current is mainly due to the charges hopping between the mesogenic cores. The space separation of electrons and holes effectively prevents charge recombination, and the amplification of photocurrent is observed. Thus one may conclude that, contrary to previous findings [11], the fullerene unit acts not only as a photosensitizer, but mainly as an electron trap.

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