Photophysical Properties and Optoelectronic Device Applications of a Novel Naphthalene−Vinylene Type Conjugated Polymer

Gerald Zerza,*,† Birgit Röthler, and N. Serdar Sariciftci

Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University Linz, Altenbergerstrasse 69, A-4040 Linz, Austria

Rafael Gómez, José L. Segura, and Nazario Martín*,‡

Departamento de Química Orgánica, Facultad de Química, Universidad Complutense, E-28040 Madrid, Spain

We report on photoinduced charge transfer and energy transfer reactions using a new cyano-substituted naphthalene−vinylene type conjugated polymer. Optical absorption and emission spectra of thin films of mixtures of this polymer with the fullerene derivative 1-(3-(methoxycarbonyl)propyl)-1-phenyl-(6,6)C$_{61}$ (PCBM) exhibit several interesting features such as luminescence quenching and polaronic photoinduced absorption (PIA) of charges indicating photoinduced charge transfer. On the other hand this new polymer exhibits energy transfer phenomena in blends with MDMO−PPV (poly((2-methoxy-5-((3,7-dimethyloctyl)oxy)-1,4-phenylene)-vinylene)). Photovoltaic devices and light emitting diode (LED) devices have been fabricated and characterized using this novel conjugated polymer in composite with fullerenes and MDMO−PPV's, respectively.

1. Introduction

In the past two decades, research on conjugated, semiconducting polymers has experienced an increasing attraction in the scientific community.[1] Especially due to their application in light-emitting diodes (LED)[2−7] which was discovered around a decade ago and is today entering large scale commercialization as well as due to their potential for cost-effective photovoltaic cells,[8−12] these materials are more and more getting to the focus of industrial optoelectronic applications. In this context of optoelectronic device applications, special attention has been drawn to photoinduced charge generation,[13−25] charge transport, and charge recombination at interfaces.[26−28] Important for understanding the involved photophysics is also the question of the nature of the primary photoexcitations in conjugated polymers.[29]

For an efficient light emission in electroluminescent devices, both electron and hole transport have to be balanced. Though most of the conventional conjugated polymers have a hole-conducting character, efficient electron-conducting polymers are rare. Cyano-substituted conjugated polymers have been widely investigated as candidates for electron conductors. The electron accepting character of the cyano side groups reduces the electron density on the polymer backbone and enhances the electron affinity of the polymer. Especially cyano-substituted phenylene−vinylene type polymers (CN−PPV) have been synthesized and utilized in LED devices.[5] In bilayer structures of CN−PPV with poly[phenylenevinylene] (PPV), injected electrons accumulate at the CN−PPV side of the interface where mobile holes injected into the PPV layer travel to and recombine at this interface with accumulated electrons giving rise to high electroluminescence quantum efficiencies. The enhanced electron affinity of these CN−PPV polymers has also been utilized in photovoltaic cells,

where they are used as electron-conducting materials together with poly[(2-methoxy-5-((2′-ethylhexyl)oxy)-1,4-phenylene)-vinylene] (MEH−PPV) in bilayers or in blend films.[9, 30] Principally, both charge transfer as well as energy transfer may be observed depending on the relative energetic positions of the donor and acceptor components prior to photoexcitation.[28] Only minor changes in the substituents on the side chain can turn the balance from one process in favor of the other one. This opens up a possibility of chemical tailoring and "engineering" of optoelectronic properties.

In this work we present studies on the electronic properties and photoactivity of a new cyano-substituted naphthalene−vinylene type conjugated polymer. Due to the cyano groups it combines the interesting properties of an electron-accepting, n-conducting cable and a strongly luminescent material. The aim was to investigate besides the photophysical properties also possible applications of this conjugated polymer in optoelectronic devices, like polymer solar cells and LEDs. The chemical structure of the polymer **1** is shown in Figure 1. The repeating unit consists of two cyano-substituted naphthalene−vinylene units terminated with a naphthalene unit (**2**). Four alkyloxy side groups provide sufficient solubility in common organic solvents. The syntheses of polymer **1** and the corresponding monomer **2** have been described elsewhere.[31]

Photoinduced energy and charge transfer was observed in the presence of fullerenes and other conjugated polymers, respectively. It is further shown that this new conjugated polymer exhibits redox properties acting both as electron donor and as electron acceptor. LED devices emitting in the blue-green spectral range with surprisingly low turn on voltages could be fabricated out of this polymer.

2. Experimental Section

Poly[(2-methoxy-5-((3,7-dimethyloctyl)oxy)-1,4-phenylene)-vinylene] (MDMO−PPV) was delivered by Covion Inc. and

† Tel: 0043-732-2468-8767. Fax: 0043-732-2468-8770. E-mail: Gerald.Zerza@jk.uni-linz.ac.at.
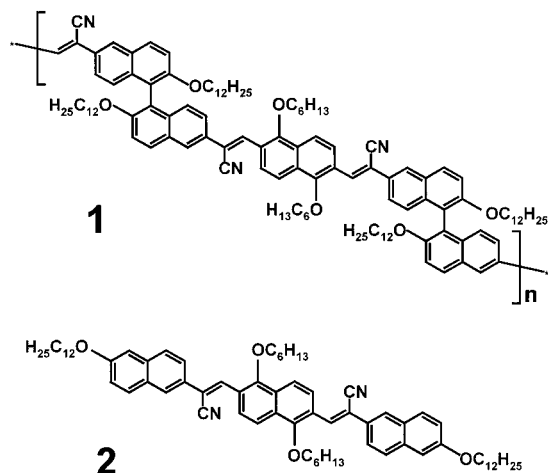‡ E-mail: nazmar@eucmax.sim.ucm.es.

Figure 1. Chemical structure of the polymer **1** and the corresponding monomer **2**.

Figure 2. UV/vis absorption spectra of thin films of (a) polymer **1** and (b) the corresponding monomer **2** shown in Figure 1.

used as received. For the photoinduced absorption (PIA) studies in the vis/NIR spectral region the samples were prepared as solution cast films on glass substrates using a concentration of 1 mg/mL polymer in toluene. PIA spectra were taken using an Ar-ion laser at 457 or 488 nm as a pump beam (typically 40 mW on a 4 mm diameter spot). The pump beam was mechanically modulated at a frequency of typically 270 Hz, and the changes in the white light (120 W tungsten−halogen lamp) probe beam transmission ($-\Delta T$) were detected after dispersion with a 0.3 m monochromator in the range from 0.55 to 2.1 eV with a Si−InGaAsSb sandwich detector. The detector signals were recorded phase sensitively with a dual-phase lock-in amplifier. The probe light transmission (T) was recorded separately using the same chopper frequency. The PIA spectra ($-\Delta T/T$) are obtained after correction for the sample luminescence and normalization on the probe light transmission. For the PIA experiments the samples were cooled to approximately 100 K in a liquid-nitrogen cryostat.

Photovoltaic devices were produced using blends of polymer **1** with 1-(3-(methoxycarbonyl)propyl)-1-phenyl-(6,6)C$_{61}$ (PCBM) or using blends of polymer **1** with MDMO−PPV. Results were compared to reference photovoltaic devices with MDMO−PPV/PCBM blends. All devices were produced on transparent indium tin oxide (ITO) coated plastic (PET) substrates with 6 cm by 4 cm by doctor blading technique. These substrates were covered by a thin film of poly(3,4-((ethylenedioxy)thiophene)−poly-(styrenesulfonate) (PEDOT) from Bayer AG by doctor blading. After drying of the PEDOT film, the photoactive polymer mixture was cast by doctor blading from a heated toluene solution. The counter electrode was in all cases thermally evaporated aluminum. One substrate carried 36 device cells with an active area of 15 mm^2 each.

For the production of LED devices the same procedure was used as for the production of photovoltaic devices. Instead of a polymer mixture the pristine polymer **1** was used. I/V curves were recorded with a Keithley SMU 2400, typically by averaging over 80 measurements for one point. Illumination for the photovoltaic devices was provided by white light from a halogen lamp with 60 mW/cm^2. The electroluminescent emission characteristics from the polymer LED devices were measured using a calibrated Si photodiode.

3. Results and Discussion

3.1. UV/Vis Absorption Spectra.

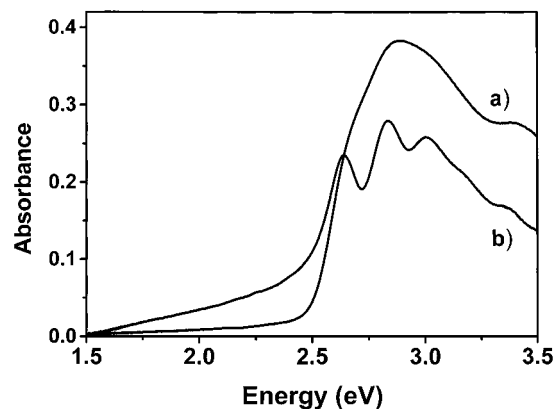Figure 2 shows the absorption spectrum of the polymer **1**.

The broad and mainly structureless absorption has an onset around 2.4 eV, a shoulder of vibronic origin around 2.66 eV, and peaks at 2.87 eV. Also shown in Figure 2 is the absorption of the corresponding monomer **2** (for structure, see Figure 1). In this case the vibronic structure is clearly resolved with 3 main peaks at 2.64, 2.84, and 3.01 eV. The steadily rising background between 1.5 and 2.5 eV is due to scattering. It is quite remarkable that for both the monomer **2** and the polymer **1** the onsets of the absorption spectra are observed at nearly the same energetic positions. Generally for π-conjugated systems a red shift of the absorption is expected with increasing chain or conjugation length, which clearly is not the case for this polymer. A reduction in the effective conjugation length may be caused by a distorted structure. Steric hindrance of the long alkyloxy side chains favors the formation of a zigzag nonplanar configuration which limits the conjugation of the π-system to nearly one monomer (see Figure 1).[31] A similar effect has been observed for binaphthyl−oligothiophene copolymers.[32,33] These materials have a well-defined conjugation length, which is independent of the chain length of the polymer due to the twisting of the adjacent naphthyl groups. The absorption and emission spectra of the repeating units have been found to be close to those of the corresponding polymers.

The observation of the optical absorption gap in Figure 2 is also in accordance with electrochemical gap calculated from the oxidation and reduction potentials of this polymer versus a calomel reference electrode ($E_{ox., peak} = 1.34$ V; $E_{red., peak} = -1.54$ V).

3.2. Photophysics.

3.2.1. Photoinduced Absorption.

Figure 3a compares the steady-state PIA spectra of the polymer **1** to that of the monomer **2**. In both cases we observe a peak centered around 1.65 eV. The PIA signal of the monomer is considerably narrower and also weaker compared to that of the polymer, which extends from 1.4 eV to well above 2 eV. The latter may be composed of several components. For the PIA spectra of both samples at 1.65 eV a linear pump intensity dependence has been observed for low excitation intensities saturating at higher laser powers, as expected for monomolecular recombination kinetics (Figure 4a). In addition to this the experimental determined modulation frequency dependence of the PIA signal may be fitted assuming a monomolecular recombination behavior of the photoexcited states,[34,35] as shown in Figure 4b. Lifetimes of the order of some 100 μs typical for triplet states of conjugated polymers can be extracted.[22] We attribute these excited-state absorption features at 1.65 eV based on their intensity and modulation frequency dependence (Figure 4) to triplet−triplet absorption of the polymer **1** and monomer
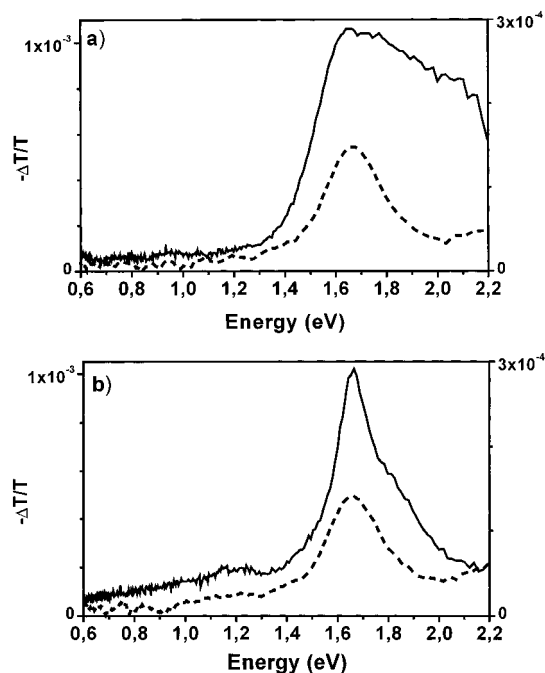
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Figure 3. Photoinduced absorption (PIA) spectra of thin films of (a) pristine monomer **2** (dashed line, right axis) and pristine polymer **1** (solid line, left axis) and (b) monomer **2** (10% C_{60}; dotted line, right axis) and polymer **1** (10% C_{60}; solid line, left axis). Excitation is at 457 nm.

2, respectively. A similar intensity dependence has been also been observed for triplet excitons of conjugated polymers formed from geminate recombination of polaron pairs, assuming a further annihilation of the latter in a bimolecular process.[36,37] The higher energetic absorption feature in the PIA spectrum of polymer **1** around 1.8 eV may be due to polaron pairs formed by interchain charge transfer.[38,39] Vardeny and co-workers observed by photoabsorption detected magnetic resonance (PADMR) spectroscopy for various conjugated polymers features in the range between 1.7 and 1.9 eV and identify these as polaron pairs.[40,41] Both triplet−triplet absorption peaks of the polymer as well as of the monomer have nearly identical energetic positions, confirming the assumption of a reduction in the effective conjugation length of the polymer stated already in the previous section. Besides the 1.8 eV absorption peak of polymer **1** mentioned above, which may be due to polaron pairs, there are no further indications, as for example polaronic absorption features in the low-energy range (<0.8 eV) of the PIA spectra, for any charged photoexcitations in the pristine polymer and/or monomer samples. Infrared activated vibrational spectra (IRAV) measurements,[42] sensitive to charged excitations, did not give any indications for photoinduced charge separation in the pristine polymer **1** and/or monomer **2** system.

Fullerenes were found to show very efficient light-induced electron transfer in combination with various conjugated polymers.[14,16] Figure 3b compares the results of PIA measurements for composite films of the polymer **1** and monomer **2** with the C_{60} molecule as electron acceptor. For the monomer **2**/fullerene composites no drastic changes are observed as compared to the results of the pristine monomer sample (compare Figure 3a,b). The two PIA spectra are nearly identical, even concerning the maximum intensity. Again the absorption at 1.65 eV is attributed to the neutral photoexcitation of a triplet state of the molecule. Slight but distinct changes can be observed in the PIA spectra for the polymer **1**/fullerene composite film in Figure 3b. The broad shoulder between 1.8 and 2.2 eV present
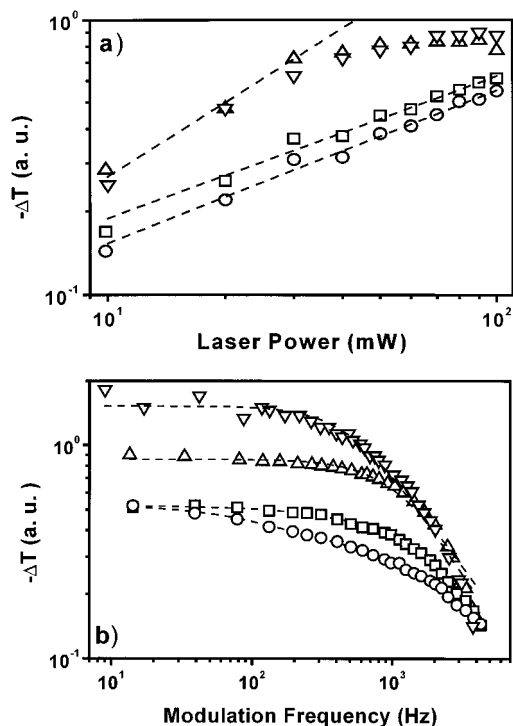

Figure 4. (a) Excitation intensity dependence and (b) modulation frequency dependence for the PIA spectrum of the polymer **1** and the monomer **2** (Figure 3), for 457 nm excitation at $T = 100$ K. Key: up triangles, pristine polymer **1** at 1.66 eV; down triangles, pristine monomer **2** at 1.66 eV (dashed lines show fits to monomolecular recombination behavior); squares, polymer **1** (10% C_{60} at 1.66 eV); circles, polymer **1** (10% C_{60} at 1.16 eV; dashed lines show fits to bimolecular recombination behavior).

in the spectrum of the pristine polymer (Figure 3a) is reduced in intensity, and a peak at 1.65 eV, the same position as that of the the triplet state of the monomer, is left over. In addition to this a broad unstructured feature between 0.8 and 1.4 eV appears peaking around 1.2 eV. The C_{60} anion is well-known to have an electronic absorption between 1.1 and 1.2 eV.[43] In addition to this a polaronic absorption feature may be hidden underneath this broad feature too, although leaving in question the second low-energy polaron peak, which should show up somewhere in the range below 0.8 eV. The pump intensity dependence for the peak at 1.65 eV as well as for the additional absorption around 1.2 eV follows clearly a square root behavior as confirmed by the fits to the experimental data shown in Figure 4a. Moreover the modulation frequency dependence of the PIA signals changes from a monomolecular type behavior to a bimolecular [34,35] type behavior in going from the pristine sample to the fullerene-doped sample (Figure 4b). As already observed for polaronic absorption peaks of different kinds of conjugated polymers, a broad distribution of lifetimes up to several milliseconds has to be assumed for best fitting of the observed relaxation kinetics.[34] Although some changes are clearly observed in the PIA spectra (Figure 3) between the pristine polymer **1** and the polymer **1**/fullerene composite, these minor changes are not comparable to other conjugated polymer/ fullerene systems where massive qualitative and quantitative changes in the PIA spectra are observed by addition of fullerene into the polymers.[17]

This polymer is also tested for its electron-accepting capability in light-induced charge transfer studies to an electron-donating polymer with lower ionization potential like for instance MDMO−PPV. Figure 5a shows the PIA spectra of the blend of MDMO−PPV with 10 mol % polymer **1** and of polymer **1**
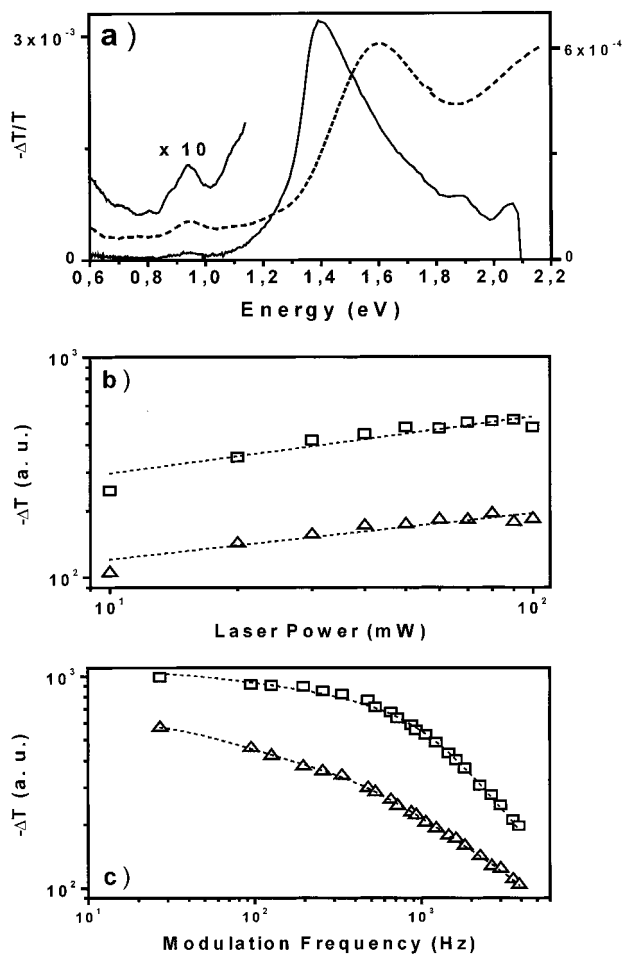
Figure 5. (a) Photoinduced absorption spectrum of thin film of MDMO−PPV with 10 mol % polymer **1**, excitation at 488 nm (solid line, left axis), and for a film of polymer **1** with 10 mol % of MDMO−PPV, excitation at 457 nm (dashed line, right axis), and (b, c) excitation intensity dependence and modulation frequency dependence of PIA signals of MDMO−PPV with 10 mol % polymer **1** at 1.24 eV (triangles) and 1.42 eV (squares). Dashed lines show fits to bimolecular recombination behavior.

with 10 mol % of MDMO−PPV. The main excited-state absorption features at 1.4 and 1.65 eV are due to the triplet states of MDMO−PPV[44] and polymer **1**, respectively. Weak PIA features around 0.95 eV are present in both spectra. They may be ascribed to the radical anion (negative polaron) on the chain of polymer **1** whereas the radical cation (positive polaron) of MDMO−PPV is well-known to be at 1.24 eV[44] and maybe hidden underneath the strong triplet absorption. In addition to this a second weak light-induced absorption feature can be observed starting below 0.7 eV, which may be indicative for the low-energy polaronic absorption of either of the two polymers. Thus the excitation is mainly on the MDMO−PPV or the polymer **1**, respectively, and the insignificant quenching of the MDMO−PPV or the polymer **1** triplet in Figure 5a indicates a negligible electron-transfer interaction between MDMO−PPV and polymer **1**. Figure 5b,c presents the excitation intensity and the modulation frequency dependence of the PIA signals in Figure 5a of the blend of MDMO−PPV with 10 mol % polymer **1**. The pump intensity dependence for the peak at 1.42 eV as well as at 1.24 eV, where we assume the PIA signal of the MDMO−PPV polaron, follows clearly a power law with exponents smaller than 0.3. The modulation frequency behavior in Figure 5c can be fitted assuming a bimolecular recombination kinetics,[34,35] again with multiple lifetimes be-
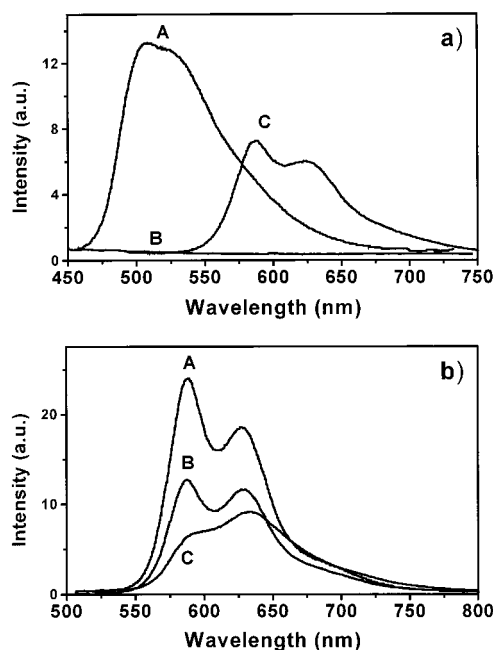

Figure 6. Luminescence spectra for excitation at 430 nm. (a) Film of polymer **1**: A, pristine; B, with 10% PCBM; C, with 10% MDMO−PPV. (b) Film of MDMO−PPV: A, pristine; B, with 10% polymer **1**; C, with 10% monomer **2**.

tween some 100 μs and some milliseconds, as generally observed for charged excitations in conjugated polymers films.

3.2.2. Luminescence Quenching.

The room-temperature luminescence spectrum of a pristine polymer **1** film excited close to the absorption maximum at 2.88 eV is shown in Figure 6a. The luminescence starts at 460 nm (2.7 eV), shows two peaks at 507 and 525 nm (2.45 and 2.36 eV) and extends until some 700 nm. Addition of 10 mol % of the fullerene derivative PCBM quenches the polymer luminescence down by at least a factor of 10. Rapid charge transfer leads to a quenching of the singlet state population of the polymer and with this of the luminescence.

In Figure 3b, there is a PIA signal at 1.65 eV (Figure 3b). This peak is assigned to a triplet−triplet absorption of the polymer due to above-discussed reasons. However, the origin of this triplet−triplet absorption in the mixtures remains unclear. The interpretation of an indirect formation of polymer triplet by recombination of separated charges in composites would explain both the intensity and frequency dependence of this PIA peak, which reflects bimolecular recombination for the mixed polymer/fullerene films and shows preferably monomolecular recombination behavior for the PIA triplet peaks of the pristine polymer (Figure 4). Frankevich and co-workers proposed the geminate recombination of triplet polaron pairs leading to the formation of intrachain triplet excitons in films of pristine conjugated polymers. Pairs of triplet excitons may annihilate in a bimolecular way. This series of processes has been proposed to explain the photoluminescence detected magnetic resonance (PLDMR) signals of conjugated polymer films and their temperature and excitation intensity dependencies.[36,37] Whether this interpretation is also valid for the charge-separated polaron/fullerene anion excited states is not known. Especially the energetics of the charge-separated state versus the triplet state has to be determined to underline this proposition.

The PIA signal in Figure 3b at 1.65 eV may also originate from charged excitations such as polarons, but this leaves the question open for the absence of the lower energy polaron peak, which should show up somewhere below 0.8 eV, although to

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get real evidence for either of the two possibilities requires further experimental observations in particular ODMR and/or ADMR measurements.

For a film of polymer **1** blend with 10 mol % MDMO−PPV, the luminescence of polymer **1** is also quenched (Figure 6a). Only the MDMO−PPV luminescence survives showing an onset around 540 nm and two peaks of vibronic origin at 585 and 625 nm. So most of the singlet state excitation of polymer **1** is transferred to the MDMO−PPV singlet state, whereas the photoinduced triplet−triplet absorption of polymer **1** is still observable (Figure 5a). Excitation energy is transferred from polymer **1** to MDMO−PPV. Via this process the luminescence of polymer **1** is quenched. At the same time a partial charge transfer produces free polarons as well as polaron pairs and gives rise to the weak PIA features in Figure 5a. Bimolecular and/or geminate recombination of the latter leads to the formation of triplet states (triplet excitons). This may on one hand explain why the triplet−triplet absorption in Figure 5b,c follows a bimolecular and not as expected a monomolecular recombination behavior and on the other hand explain why the luminescence is quenched while the triplet PIA remains more or less unchanged.

For MDMO−PPV blended with polymer **1** and monomer **2** slight luminescence quenching is observed as shown in Figure 6b. Addition of 10 mol % of the monomer **2** or the polymer **1** reduces the luminescence of MDMO−PPV to one-third and one-half, respectively. This again might indicate a small charge transfer interaction as seen in weak feature around 0.95 eV in PIA spectra (Figure 5) but is not dominant. Accompanying the quenching of the luminescence, the relative intensities of the vibronic peaks are also changed (Figure 6b). This may be ascribed to emission from different conformations of the polymer influencing the Franck−Condon factors for different vibronic satellites.[45]

3.3. Solar Cells and Light-Emitting Diode Devices.

We tried both using polymer **1** as electron donor in combination with the fullerene derivative PCBM and as electron acceptor together with MDMO−PPV. Functioning photovoltaic devices could be realized only by the combination of polymer **1** with PCBM as electron acceptor. We achieved only low-energy conversion efficiencies (around 0.01%) in these devices, indicating that the electron-donating and/or -accepting properties and/or the charge transport properties of this new polymer **1** are not sufficiently high (as comparison, for example in the well-known MDMO−PPV/PCBM solar cells devices, power conversion efficiencies up to 2.5% [46] have been reported recently). Figure 7 shows a current−voltage characteristics of a polymer **1**/PCBM solar cell compared to a conventional MDMO−PPV/PCBM solar cell. Polymer **1** photovoltaic devices show only weakly pronounced diode behavior with rectification ratios of the order of 3 in the dark (Figure 7a), whereas for the MDMO−PPV device rectification ratios up to 50 are observed (Figure 7b), although under forward bias (positive voltage at ITO) both samples show similar dark *I/V* curves. For higher illumination intensities the rectification of the devices decreases and the *I/V* curve becomes more symmetric between forward and backward bias. The open circuit voltage (V_{oc}) saturates at higher light intensities with 0.36 V for the polymer **1** solar cell as compared to 0.75 V for the reference cell. The short circuit current (I_{SC}) for a 0.15 cm² device was measured with 4 μA, whereas the standard device showed 150 μA at an illumination intensity of about 60 mW/cm² from a tungsten−halogen lamp. This result shows, neglecting some differences in the filling factors, a power conversion efficiency of the solar cell built from the new
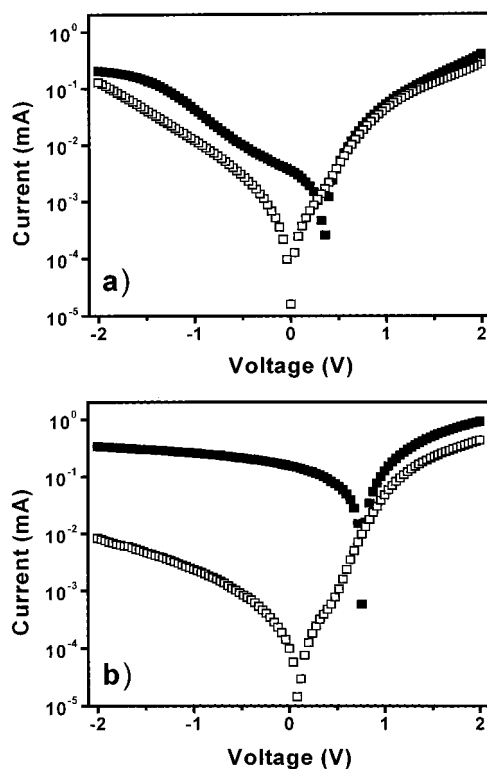
Figure 7. Current−voltage characteristics of photovolatic devices: (a) 1:3 polymer **1**: PCBM, light (filled squares), dark (open squares); (b) 1:3 MDMO−PPV:PCBM, light (filled squares), dark (open squares).

polymer **1**/PCBM that is at least 2 orders of magnitude lower as compared to the conventional solar cells made from MDMO−PPV/PCBM. It is however noted that the high energy absorption of polymer **1** and the consecutive energy transfer onto MDMO−PPV might be useful for harvesting a large area of the solar spectrum.

LED devices have been fabricated and tested using polymer **1** alone. Applying a forward potential of 8 V (positive on ITO) to a LED device built on the base of polymer **1** gives rise to the blue-green electroluminescence as shown in Figure 8a. No luminescence was observed for applying up to 15 V in backward direction. Similar to the photoluminescence in Figure 6a the electroluminescence peaks around 500 nm and extends until 700 nm. One striking feature is the onset voltage of the electroluminescence of only +3 V, which is relatively low for an unoptimized LED in the blue color range. (Figure 8b). A typical *I/V* curve for such a device recorded at room temperature is also shown in Figure 8b. The electroluminescence intensity follows the current−voltage characteristics up to 10 V before it saturates. For this applied voltage an estimated value for the external quantum efficiency between 10^{-4} and 10^{-3} has been achieved. These values are comparable with the 1.5×10^{-3} external quantum efficiency for single layer, blue-green emitting, LED devices based on binaphthalene-containing polymers.[47,48] These authors improved the efficiency by more than a factor of 10 using fluorinated copper phthalocyanine as electron injection/transport layer on top of the polymer. Our not optimized devices with relatively low efficiency still effectively demonstrate that blue LED's can be fabricated with a low turn on voltage using this novel material (polymer **1**).

4. Conclusions

Photoinduced charge transfer and energy transfer in composites of the newly synthesized cyano-substituted naphthalene−
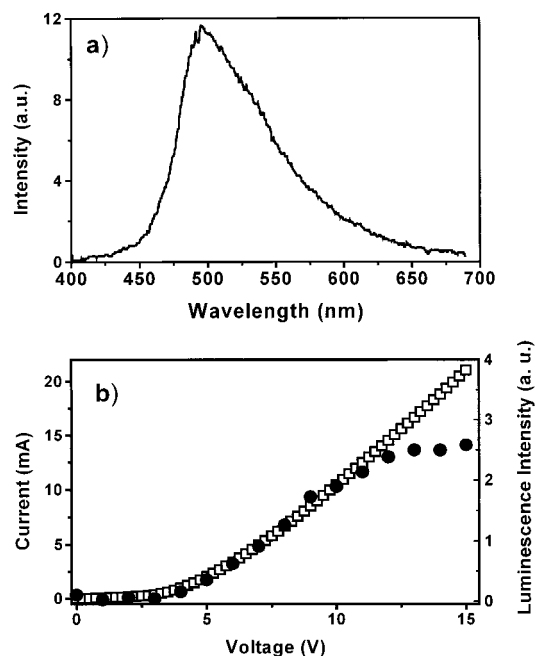
Figure 8. Electroluminescence from LED made of polymer **1**: (a) electroluminescence spectra for a forward bias of 8 V; (b) current/voltage curve (open squares, left scale) and luminescence−intensity/voltage behavior (circles, right scale).

vinylene type conjugated polymer **1** with fullerenes and in blend films with MDMO−PPV were studied. All spectroscopic investigations show that the polymer **1**/fullerene composites as well as blend samples of polymer **1** with MDMO−PPV exhibit only weak photoinduced charge transfer interaction compared to composites of soluble alkoxy PPVs with fullerenes. For the blend polymer films the complete quenching of the luminescence of polymer **1** may be explained by energy transfer to MDMO−PPV. Photovoltaic devices of polymer **1** mixed with PCBM were prepared but resulted only in weak quantum efficiencies, and furthermore, blue-green-emitting LED devices with a low turn on voltage ($\approx$3 V) have been fabricated using the pristine material itself.

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