

## Influence of a Mesogenic Dendrimer on the Morphology of Polymer–Fullerene Composites for Photovoltaics

Olga Kasdorf, Heinz-Siegfried Kitzerow, Julie Lenoble-Zwahlen<sup>1</sup>, and Robert Deschenaux<sup>1</sup>

*Department of Chemistry, University of Paderborn, 33098 Paderborn, Germany*

<sup>1</sup>*Institut de Chimie, Université de Neuchâtel, 2009 Neuchâtel, Switzerland*

The efficiency of “bulk hetero junction”-type plastic solar cells depends crucially on the morphology of an entangled network of two immiscible compounds that serve as electron donor and electron acceptor, respectively. The present work describes preliminary results about the question how the luminescence and the morphology of a composite containing a fullerene C<sub>60</sub> derivative and a *p*-phenylene vinylene (PPV) derivative are altered, when a dendrimer with a fullerene core and mesogenic side-chains is added. Fluorescence quenching and surface topography of the composites indicate that adding the mesogenic dendrimer can result in smaller domain sizes, which may be useful for photovoltaic applications.

### 1. Introduction

Organic photovoltaics has become a topic of extensive research. The very efficient electron transfer from excited organic dye molecules to TiO<sub>2</sub> nanocrystals is utilized in dye-sensitized solar cells,<sup>1,2)</sup> while an organic electron donating compound is combined with an organic electron accepting compound in hetero junction solar cells.<sup>3,4)</sup> Low molar mass compounds,<sup>3,4)</sup> oligomers,<sup>5,6)</sup> polymers,<sup>7,8)</sup> and dendrimers<sup>9,10)</sup> can be employed for organic photovoltaics. A high efficiency has also been reported for certain columnar liquid crystals.<sup>11,12)</sup> In many cases, soluble fullerene derivatives are used as efficient electron acceptors, since the electron transfer from excited conjugated polymer molecules to C<sub>60</sub> is extremely fast.<sup>13)</sup>

Materials and device structures of photovoltaic cells have to provide very high efficiencies of several subsequent processes, namely the absorption of light, generation of charge carriers, separation of the charge carriers of opposite charge, and transport of the charge carriers to the electrodes. Optimization of these processes suffers from competing requirements: Efficient light absorption is favored by a large sample thickness. However, effective charge carrier separation is only possible if the layer thickness of the electron donating layer is smaller than the exciton diffusion length

(10–20 nm), in order to avoid charge carrier recombination. Thus, nanostructured systems have been investigated, which contain, for example, semiconductor nanocrystals,<sup>14)</sup> nanowires,<sup>15,16)</sup> dyad molecules, where both an electron donating and an electron accepting unit are combined in the same molecule,<sup>17)</sup> or diblock copolymers, where the size of the functional units can be tailored appropriately.<sup>18)</sup>

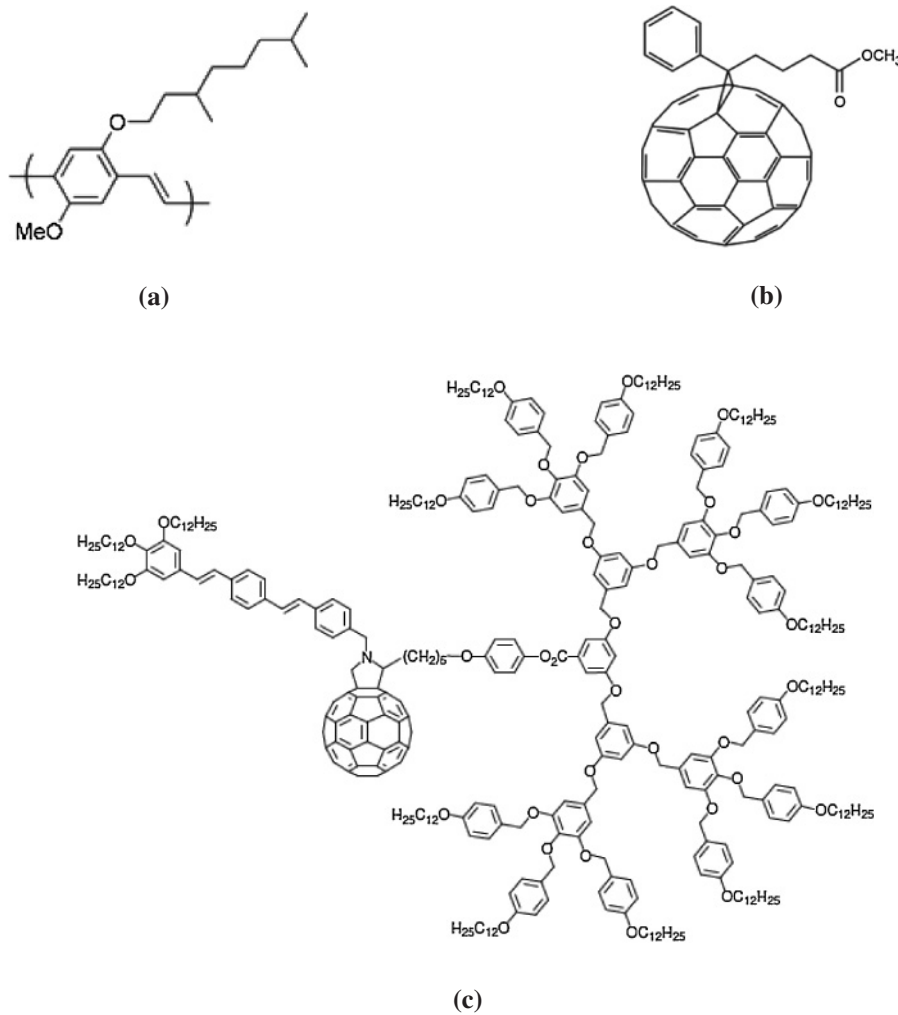
More easily, the problem of limited exciton diffusion length can be solved by means of heterogeneous organic composites.<sup>19,20)</sup> Typically, such heterogeneous composites consist either of two immiscible polymers<sup>19)</sup> or of an electron-donating polymer and a fullerene derivative.<sup>20)</sup> The respective systems are known as inter-penetrating polymer network,<sup>19)</sup> or bulk-hetero junction<sup>20)</sup> photovoltaic cells, respectively. The efficiency of bulk hetero junction photo-voltaic cells<sup>19,20)</sup> is extremely dependent on the morphology of the heterogeneous system,<sup>21)</sup> which in turn depends on the processing parameters. For example, choosing chlorobenzene instead of toluene as a solvent for spin casting a polymer-fullerene composite was found to enhance the

efficiency by almost a factor of 3, mainly due to enlarging the short circuit current.<sup>21)</sup> This dramatic effect motivated many detailed studies on the morphology of polymer–fullerene composites.<sup>22–26)</sup> In addition to the influence of the solvent used for the spin-casting process, also the effect of additives on the morphology was discussed.<sup>25)</sup>

Due to the rapid progress in fullerene chemistry,<sup>27)</sup> many fullerene derivatives, including fullerene-containing dendrimers,<sup>28–31)</sup> have been synthesized. In particular, Janus-type dendrimers,<sup>31)</sup> where different functional units are combined in the dendritic part of the molecule, show a remarkable mesogenic versatility.<sup>31)</sup> In the present paper, we report on the influence of a mesogenic dopant of the latter type on the sample morphology of a composite that has been very well investigated and considered for photovoltaic applications. The system is based on poly[2-methoxy,5-(3,7-dimethyloctyloxy)]-*p*-phenylene vinylene (MDMO-PPV) and [6,6]-phenyl C<sub>61</sub>-butyric acid methyl ester (PCBM). In (1 : 4) mixtures, the latter compound was systematically replaced by the dendrimer compound **1** presented in Fig. 1. In the first part of the experimental section, fluorescence studies are described, which give indirect hints on changes of the morphology. Fluorescence indicates that electrons return from an excited state to the ground state, thereby losing their energy through radiation. This process competes with the charge carrier separation that is necessary for photo-voltaics. Thus, reducing the fluorescence intensity may enhance the photovoltaic efficiency. In the second part of the experimental section, results obtained by atomic force microscopy (AFM) are presented, which give direct evidence for changes of the morphology.

### 2. Experiments and Results

From the compounds shown in Fig. 1, samples with six different compositions were prepared (Table I). All composites contain 20% (by weight) MDMO-PPV. The fraction of PCBM was subsequently replaced by compound **1**. For the sample preparation, indium tin oxide (ITO)-coated substrates were cleaned in an ultrasonic bath for 10 min in acetone, propanol and deionised water. Subsequently, thin films were deposited by spin-coating at 2000 rpm from solutions of 0.5 wt % of the respective mixture in toluene. Photoluminescence spectra (PL) of the resulting samples were measured at room temperature. A 90° geometry between light source, sample and detector and an excitation



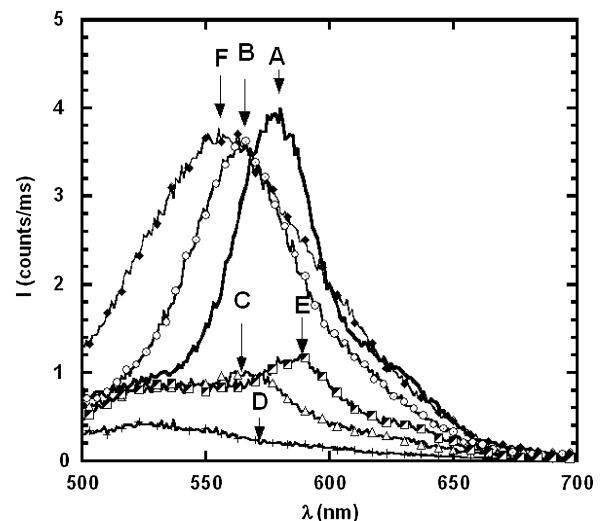
**Fig. 1.** Chemical structures and luminescence wavelengths of the substances. (a) MDMO-PPV:  $\lambda = 580$  nm, (b) PCBM:  $\lambda = 525$  nm, (c) compound 1:  $\lambda = 540$  nm.

**Table I.** Mass fractions of MDMO-PPV, PCBM, and compound 1 in samples A–F that were investigated.

Compound	Sample					
	A	B	C	D	E	F
MDMO-PPV	0.2	0.2	0.2	0.2	0.2	0.2
PCBM	0.8	0.75	0.7	0.6	0.4	0
Compound 1	0	0.05	0.1	0.2	0.4	0.8

wavelength of 480 nm were used. The morphology of the composites was investigated by means of atomic force microscopy in the pulsed-force mode (WiTec Alpha).

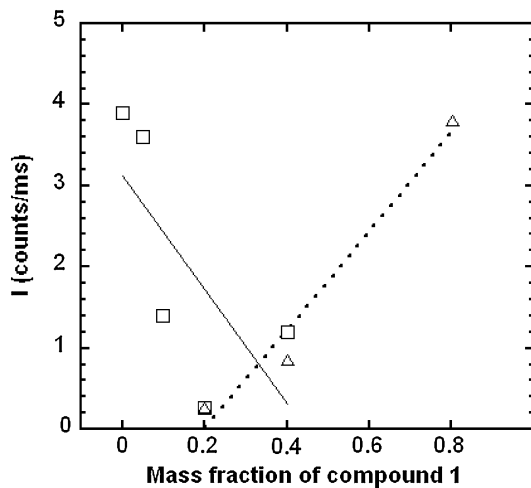
Composites without compound 1 or with a small mass fraction  $x_{m,1}$  of compound 1 show photoluminescence (PL) at 580 nm (Fig. 2). This luminescence indicates that excited molecules can return to their ground state by emitting radiation, a process that competes with charge carrier separation and thus diminishes the potential efficiency of a photovoltaic process. For  $x_{m,1} < 0.1$ , the PL intensity decreases with increasing concentration of compound 1. This decrease indicates more efficient fluorescence quenching, which in turn favors the potential photovoltaic efficiency. However, a slightly different fluorescence peak at 548 nm appears at higher values of  $x_{m,1}$  and increases with increasing



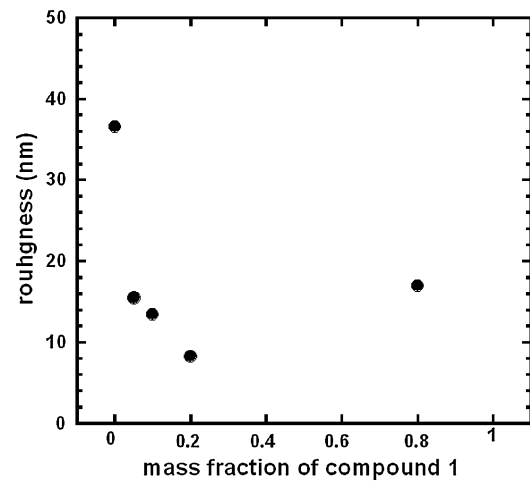
**Fig. 2.** Photoluminescence spectra of the composites for various mass fractions of compound 1.

$x_{m,1}$  (Fig. 3). Thus, replacing PCBM completely by compound 1 does not lead to efficient fluorescent quenching.

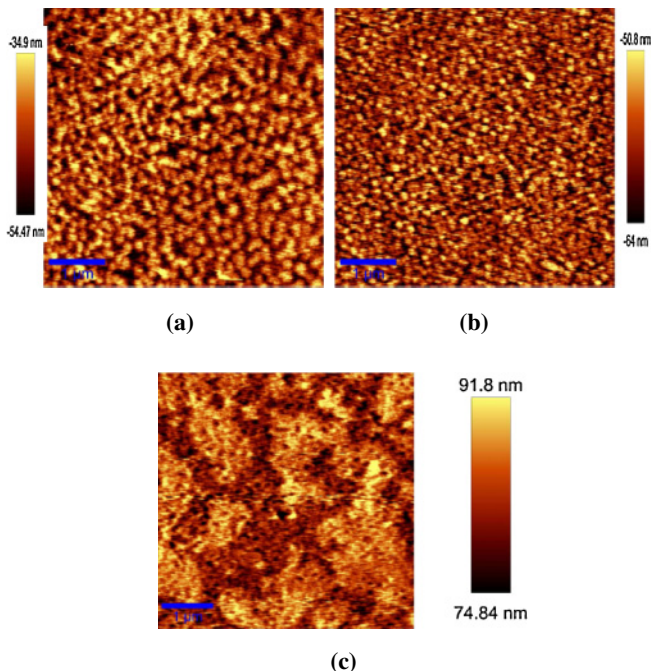
The AFM images for  $x_{m,1} \leq 0.1$  [Figs. 4(a) and 4(b)] indicate that the average size of the islands of the heterogeneous composites decreases with increasing amount



**Fig. 3.** Influence of the mass fraction of compound 1 on the luminescence intensity. (□) Peak at  $\lambda = 580$  nm, ( $\triangle$ ) peak at  $\lambda = 548$  nm.



**Fig. 5.** Roughness of the sample surfaces versus concentration of compound 1.



**Fig. 4.** (Color online) Pulsed-force mode AFM topography scans of the samples A, C, and F. (a) 20% MDMO-PPV:80% PCBM (sample A). (b) 20% MDMO-PPV:70% PCBM:10% compound 1 (sample C). (c) 20% MDMO-PPV:80% compound 1 (sample F).

of compound 1. This result explains the more efficient fluorescence quenching in samples, where a small fraction of PCBM was replaced by the dendrimer 1. However, the AFM image of sample F [Fig. 4(c)] indicates that replacing PCBM completely by compound 1 results in a non-uniform morphology, which is characterized by large islands. The roughness of the surfaces of the different samples (Fig. 5) decreases with increasing mass fraction  $x_{m,1}$  for  $x_{m,1} \leq 0.2$ , and increases again for higher values of  $x_{m,1}$ . This result coincides with the continuous variations of the sample morphology. In addition, it shows that adding small amounts of compound 1 is suitable in order to reduce the surface roughness, which enhances the uniformity of the film thickness and makes the deposition of further functional layers easier.

### 3. Conclusions

In summary, the investigations on the fluorescence and the surface topography of composites with different concentrations indicate, that smaller island sizes, more efficient fluorescence quenching and a smoother surface of MDMO-PPV:PCBM blends can be achieved by doping the system with the mesogenic dendrimer 1. Previous studies<sup>21–25</sup> have indicated that heterogeneous composites containing a conjugated polymer and the fullerene derivative PCBM in a (1 : 4)-ratio consist of PCBM clusters dispersed in a polymer-rich matrix.<sup>24</sup> The influence of the solvent on the domain size<sup>21</sup> was attributed to the respective solubility of PCBM. Thorough studies indicated that the lower solubility of PCBM in toluene as compared to chlorobenzene results in an earlier onset for fullerene precipitation during the phase separation, which in turn results in larger PCBM clusters.<sup>24</sup> The results on the ternary system used in this study reveal that adding a fullerene dendrimer has a similar effect on the morphology of the polymer–fullerene composite as using a better solvent for PCBM. We expect that this additional influence may be suitable to enhance the photovoltaic efficiency of this material system further.

### Acknowledgements

Financial support by the European Science Foundation (EUROCORES/05-SONS-FP-014), the German Research Foundation (KI 411, GRK 1464), and the Swiss National Science Foundation (Grant No. 200020-119648) is gratefully acknowledged.

- 1) B. O'Regan and M. Grätzel: *Nature* **353** (1991) 737.
- 2) U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissörtel, J. Salbeck, H. Spreitzer, and M. Grätzel: *Nature* **395** (1998) 583.
- 3) C. W. Tang: *Appl. Phys. Lett.* **48** (1986) 183.
- 4) M. Riede, T. Mueller, W. Tress, R. Schueppel, and K. Leo: *Nanotechnology* **19** (2008) 424001.
- 5) W. Geens, J. Poortmans, S. C. Jain, J. Nijs, R. Mertens, S. C. Veenstra, W. Krasnikov, and G. Hadziioannu: *Sol. Energy Mater. Sol. Cells* **61** (2000) 43.
- 6) J. L. Segura, N. Martin, and D. M. Guldi: *Chem. Soc. Rev.* **34** (2005) 31.
- 7) N. S. Sariciftci, D. Braun, C. Zhang, V. I. Srdanov, A. J. Heeger, G. Stucky, and F. Wudl: *Appl. Phys. Lett.* **62** (1993) 585.

- 8) S. Günes, H. Neugebauer, and N. S. Sariciftci: *Chem. Rev.* **107** (2007) 1324.
- 9) T. Hasobe, P. V. Kamat, M. A. Absalom, Y. Kashiwagi, J. Sly, M. J. Crossley, K. Hosomizu, H. Imahori, and S. Fukuzumi: *J. Phys. Chem. B* **108** (2004) 12865.
- 10) N. Kopidakis, W. J. Mitchell, J. van de Lagemaat, D. S. Ginley, G. Rumbles, S. E. Shaheen, and W. L. Rance: *Appl. Phys. Lett.* **89** (2006) 103524.
- 11) L. Schmidt-Mende, A. Fechtenkötter, K. Müllen, E. Moons, R. H. Friend, and J. D. MacKenzie: *Science* **293** (2001) 1119.
- 12) T. Habheider, S. A. Benning, M. W. Lauhof, H.-S. Kitzerow, H. Bock, M. D. Watson, and K. Müllen: *Mol. Cryst. Liq. Cryst.* **413** (2004) 461.
- 13) N. S. Sariciftci, L. Smilowitz, A. J. Heeger, and F. Wudl: *Science* **258** (1992) 1474.
- 14) D. S. Ginger and N. C. Greenham: *Synth. Met.* **101** (1999) 425.
- 15) W. U. Huynh, J. J. Dittmer, and A. P. Alivisatos: *Science* **295** (2002) 2425.
- 16) H. Xin, F. S. Kim, and S. A. Jenekhe: *J. Am. Chem. Soc.* **130** (2008) 5424.
- 17) E. H. A. Beckers, P. A. v. Hal, A. P. H. J. Schenning, A. El-Ghayoury, E. Peeters, M. T. Rispens, J. C. Hummelen, E. W. Meijer, and R. A. J. Janssen: *J. Mater. Chem.* **12** (2002) 2054.
- 18) M. Sommer, S. M. Lindner, and M. Thelakkat: *Adv. Funct. Mater.* **17** (2007) 1493.
- 19) J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marsaglia, R. H. Friend, S. C. Moratti, and A. B. Holmes: *Nature* **376** (1995) 498.
- 20) G. Yu and A. J. Heeger: *J. Appl. Phys.* **78** (1995) 4510.
- 21) S. E. Shaheen, C. J. Brabec, N. S. Sariciftci, F. Padinger, T. Fromherz, and J. C. Hummelen: *Appl. Phys. Lett.* **78** (2001) 841.
- 22) T. Röder, H.-S. Kitzerow, and J. C. Hummelen: *Synth. Met.* **141** (2004) 271.
- 23) T. Glatzel, H. Hoppe, N. S. Sariciftci, M. C. Lux-Steiner, and M. Komiyama: *Jpn. J. Appl. Phys.* **44** (2005) 5370.
- 24) H. Hoppe and N. S. Sariciftci: *J. Mater. Chem.* **16** (2006) 45.
- 25) J. K. Lee, W. L. Ma, Ch. J. Brabec, J. Yuen, J. S. Moon, J. Y. Kim, K. Lee, G. C. Bazan, and A. J. Heeger: *J. Am. Chem. Soc.* **130** (2008) 3619.
- 26) S. S. van Bavel, E. Sourty, G. de With, and J. Loos: *Nano Lett.* **9** (2009) 507.
- 27) A. Hirsch: *Fullerene Relat. Struct.* **199** (1999) 1.
- 28) S. Campidelli, J. Lenoble, J. Barberá, F. Paolucci, M. Marcaccio, D. Paolucci, and R. Deschenaux: *Macromolecules* **38** (2005) 7915.
- 29) S. Campidelli, E. Vásquez, D. Milic, J. Lenoble, C. A. Castellanos, G. Sarova, D. M. Guldi, R. Deschenaux, and M. Prato: *J. Org. Chem.* **71** (2006) 7603.
- 30) N. Maringa, J. Lenoble, B. Donnio, D. Guillon, and R. Deschenaux: *J. Mater. Chem.* **18** (2008) 1524.
- 31) J. Lenoble, S. Campidelli, N. Maringa, B. Donnio, D. Guillon, N. Yevlampieva, and R. Deschenaux: *J. Am. Chem. Soc.* **129** (2007) 9941.