

Triplet Exciton Generation and Electron Back Transfer  
in Photovoltaic Bulk-Heterojunctions  
with Endohedral Fullerenes

Andreas Sperlich and Vladimir Dyakonov

Experimental Physics VI, Julius Maximilian University of  
Würzburg, 97074 Würzburg, Germany

To increase the power conversion efficiency of organic solar cells it would be extremely advantageous to improve harvesting of singlet as well as charge transfer (CT) excitons. Decay of CT states into free charge carriers or, alternatively, electron back transfer (EBT) reactions depends on the energy levels of constituting donor and acceptor molecules, on microscopic structure of blends but also on the relative spin orientation of charges carriers within the e-h pair. Attempting to improve the performance of organic solar cells, a novel acceptor was introduced, the endohedral fullerene 1-[3-(2-ethyl)hexoxy carbonyl] propyl-1-phenyl-Lu<sub>3</sub>N@C<sub>80</sub>. [1] This molecule in combination with the conjugated polycrystalline polymer P3HT enabled high open circuit voltage above 0.8 V, i.e. 0.3 V higher than in devices with [6,6]-phenyl-C[61]-butyric acid methyl ester (PC<sub>60</sub>BM), although resulting in a similar power conversion efficiency of 4%. Hence the limitations are suggested to be on the photogeneration side. To address this issue, we applied optical, current-voltage, morphology, and spin-sensitive techniques. On the whole, the blends with Lu<sub>3</sub>N@C<sub>80</sub> show the photo- and electrophysical behaviour resembling the one in P3HT:PC<sub>60</sub>BM. In blends containing Lu<sub>3</sub>N@C<sub>80</sub>-PCBEH, we found slightly weaker photoluminescence quenching, i.e. the remainders of interchain excitons, and, most remarkably, triplet excitons formed on the polymer chain, which were absent in the reference system P3HT:PC<sub>60</sub>BM. We show that EBT to the triplet state in P3HT:Lu<sub>3</sub>N@C<sub>80</sub> may be responsible for the reduced photocurrent.[2] We offer a physical picture on how pushing up the LUMO level of acceptors may end up in an unwanted reduction of the overall performance of the bulk-heterojunction solar cells. Furthermore, in blends of the novel benzodithiophene PTB7 in combination with the fullerene-derivative PC<sub>70</sub>BM with efficiency above 7%, we found a significant increase of triplet exciton generation by changing the blend morphology with 1,8-diiodooctane, which strongly suppressed the degree of phase segregation. In summary, the fundamental understanding of the processes involving the charge transfer and triplet states and their relation to nanoscale morphology and/or energetics is essential for the optimization of the performance of molecular photovoltaic devices.

1. Ross, R. B.; Cardona, C. M.; Guldi, D. M.; Sankaranarayanan, S. G.; Reese, M. O.; Kopidakis, N.; Peet, J.; Walker, B.; Bazan, G. C.; Keuren, E. V.; Holloway, B. C.; Drees, M. *Nat. Mater.* 2009, 8, 208.
2. Liedtke, M.; Sperlich, A.; Kraus, H.; Baumann, A.; Deibel, C.; Wirix, M.; Loos, J.; Cardona, C.; Dyakonov, V. *J. Am. Chem. Soc.* 2011, 133, 9088.

