Dynamics of Long – Lived Photoexcitations in SWNT – Polymer Blends

Larry Lüer,[a] Abasi Abudulimu,[a] Florian Spaeth,[b] Imge Namal,[b] Tobias Hertel[b]
[a] *IMDEA Nanociencia, C/ Faraday, 9, 28049 Cantoblanco, Spain, larry.luer@imdea.org*
[b] *Institute of Physical and Theoretical Chemistry, Julius-Maximilians University Würzburg, Germany*

Single-walled carbon nanotubes (SWNT) present favorable properties that encourage their use in organic photovoltaic (OPV) devices, namely, high charge carrier mobilities, near infrared optical absorption and thermal and chemical stability. Nonetheless, the maximum power conversion efficiencies (PCE) of systems comprising SWNT do not yet approach those of the SWNT - free OPV materials. This has been ascribed to the lack of knowledge and control of electronic processes happening on the nanoscale [1]. Elementary processes in organic photovoltaics occur on very different time scales, from femtoseconds to microseconds and must be studied specifically and in relation to sample morphology in order to quantify and overcome the respective loss processes [2]. We have shown that in SWNT, inter-tube singlet exciton transfer can occur in a few femtoseconds [3], and that charge trapping is a subpicosecond process [4]. Recently, photoinduced triplet exciton generation has been demonstrated on SWNT-polymer blends, with yields up to 32% and lifetimes in the microsecond range [5]. Triplet excitons are therefore expected to interfere with charge extraction in SWNT - based OPV devices, making it important to investigate the generation and relaxation pathways of triplet states.

Here, we present recent results on chirality specific triplet exciton dynamics in SWNT-PFO-Bpy blends of different composition. Comparing data from femtosecond transient absorption spectroscopy with recently published spectroelectrochemical data [6], we quantify the amount of transient photobleach associated with charged states and singlet and triplet excitons (Fig. 1a). We show that in samples rich in (6,5) tubes, triplet exciton transfer between (6,5) and (7,5) tubes occurs with first order kinetics with a transfer constant of about 70 ps (Fig. 1b). In contrast, in (7,5) rich samples, we do not observe the analogous transfer of triplet excitons from (7,5) → (8,4) tubes. We find a reduction of the overall triplet yields with pump intensity, an indication that singlet exciton annihilation is competing with triplet formation. We discuss possible mechanisms for triplet generation and inter-tube transfer of triplet excitons.

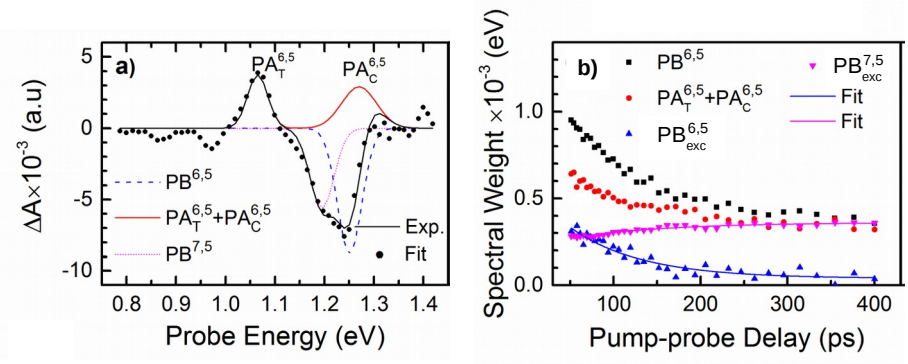

Fig.1 (a). Transient absorption (TA) spectrum of (6,5) rich SWNT-PFO-Bpy blend at t = 167 ps after pumping with 150 fs pulses at λ = 387 nm (symbols). Lines are global spectral fits, using data from [6] as spectral model for charged states considering trion absorption and charge induced absorption in (6,5) tubes ($PA_T^{6,5}$ and $PA_C^{6,5}$, respectively) and transient photobleach PB of (6,5) and (7,5) tubes . b) Spectral weights of the PA and PB bands in panel (a) as function of pump-probe delay. For t > 50 ps, the excess photobleach PB_{exc} is proportional to the number of triplet excitons on the respective chirality. Solid lines are monoexponential fits.

We acknowledge financial support from Autonomous Community of Madrid (Project "FotoCarbon", s2013/Mtr-2841), Ministry of economy and competitiveness (Plan Nacional, Project "MultiCrom"), and the European Commission (ITN "POCAONTAS", Project No: 316633)

[1] M. Gong et al., ACS applied materials & interfaces **7**, 7428 (2015)
[2] S. Karuthedath, T. Sauermann, H. – J. Egelhaaf, R. Wannemacher, C.J. Brabec, L. Lüer, J. Mater. Chem. A, **3**, 3399-3408 (2015)
[3] L. Lüer, J. Crochet, T. Hertel, G. Cerullo, and G. Lanzani, ACS Nano **4(7)**, 4265-4273 (2010)
[4] (a) J. J. Crochet, S. Hoseinkhani, L. Lüer, T. Hertel, S. K. Doorn, and G. Lanzani, Phys Rev Lett **107**, 257402 (2011); (b) B. Yuma et al., Physical Review B **87**, 205412 (2013)
[5] (a) D. Stich, F. Spaeth, H. Kraus, A. Sperlich, V. Dyakonov, and T. Hertel, Nature Photonics **8**, 139 (2014).; (b)F. L. Späth, Doctoral Thesis, Universität Würzburg, Fakultät für Chemie und Pharmazie (2015)
[6] H. Hartleb, F. Späth, and T. Hertel, ACS Nano **9**, 10461 (2015)