Out-of-phase electron spin echo spectroscopy of short-living charge-transfer state in organic photovoltaic composite of P3HT and semiconducting carbon nanotubes

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Carbon nanotubes (CNT) are an interesting alternative to fullerenes or small molecules as electron acceptor material for active layer of organic solar cell. Promising results were obtained some time ago for bulk heterojunction blend of poly-3-hexylthiophene (P3HT) and semiconducting CNTs (s-CNT), with specially separated s-CNT from statistical mixture of metal CNT and s-CNT [1]. However, paramagnetic intermediates of photoelectric conversion (either free photogenerated charges or charge-transfer states) were not detected for such blends. Thus, the mechanism of photoelectric conversion in such polymer/s-CNT systems is unclear, which complicates their further optimization.

Using out-of-phase electron spin echo (ESE) technique with photoexcitation of P3HT/s-CNT blend by laser flash we detected the signal of the charge-transfer state. Two-pulse sequence $\pi/4 - \tau - \pi - \tau -$ echo was used. No out-of-phase ESE signal was detected in the same experiment with pristine P3HT film without s-CNT. Appearance of out-of-phase ESE signal is a solid proof that spin-correlated pair $P3HT^{+}$/s-CNT^{-} is formed upon photoexcitation. The out-of-phase ESEEM trace for this system is surprisingly close to that of P3HT/$PC_{70}BM$ [2], which implies similar distance of initial charge separation of 3 – 4 nm. However, out-of-phase electron spin echo signal decay with delay-after-flash (DAF) increase for P3HT/s-CNT blend is much faster, with characteristic time of 10 μs at 30K. This point to higher geminate recombination rate for this system, which may be one of the reason of relatively poor photovoltaic performance of P3HT/s-CNT blend [1].

[1] S. Ren *et al.*, *Nano Lett.* **2011**, *11*, p. 5316.
[2] E.A. Lukina *et al.*, *PCCP* **2016**, *18*, p. 28585.