Short-living charge-transfer state photovoltaic composite (poly-3-hexylthiophene/semiconducting carbon nanotubes) detected by out-of-phase electron spin echo

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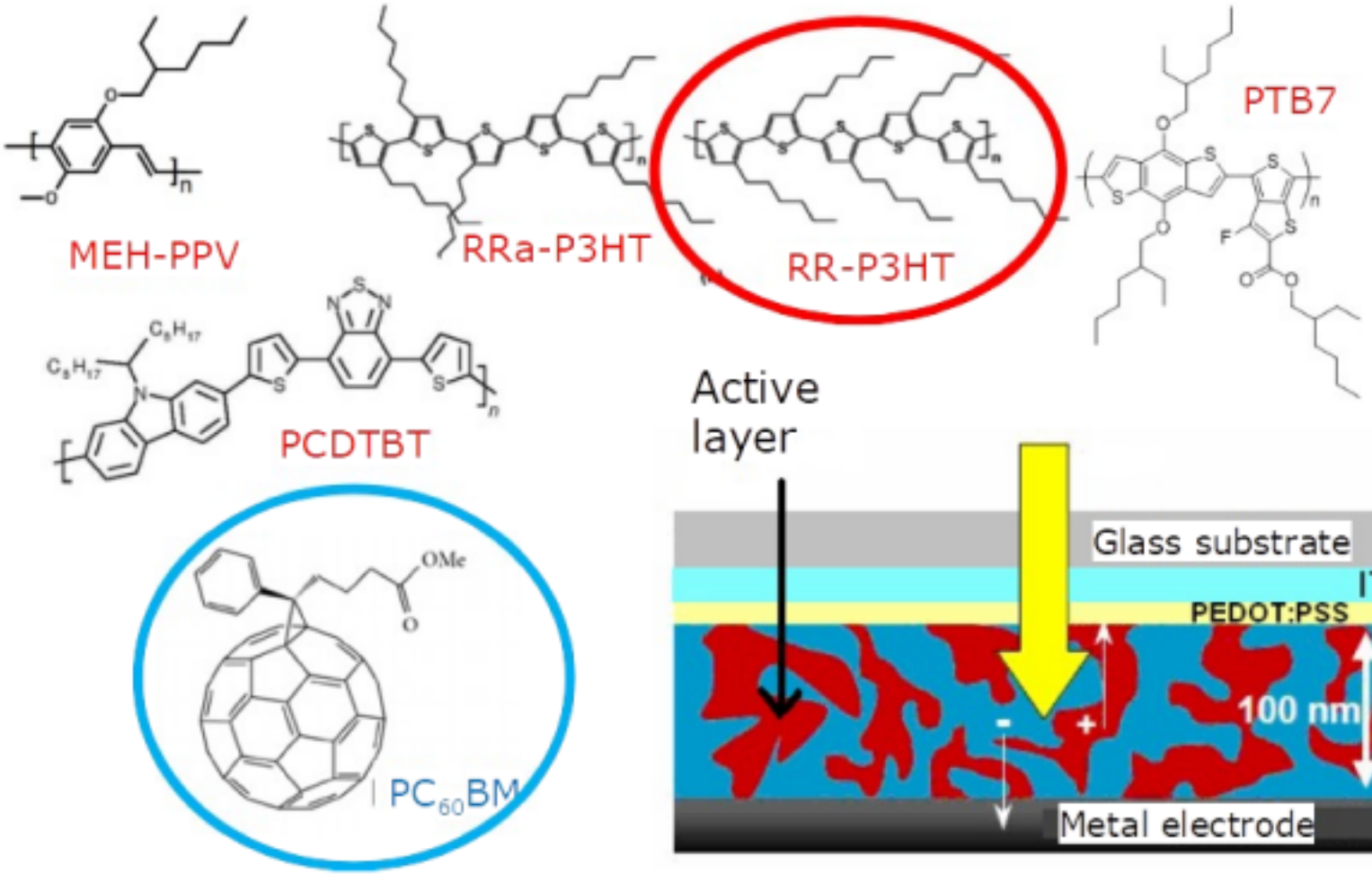
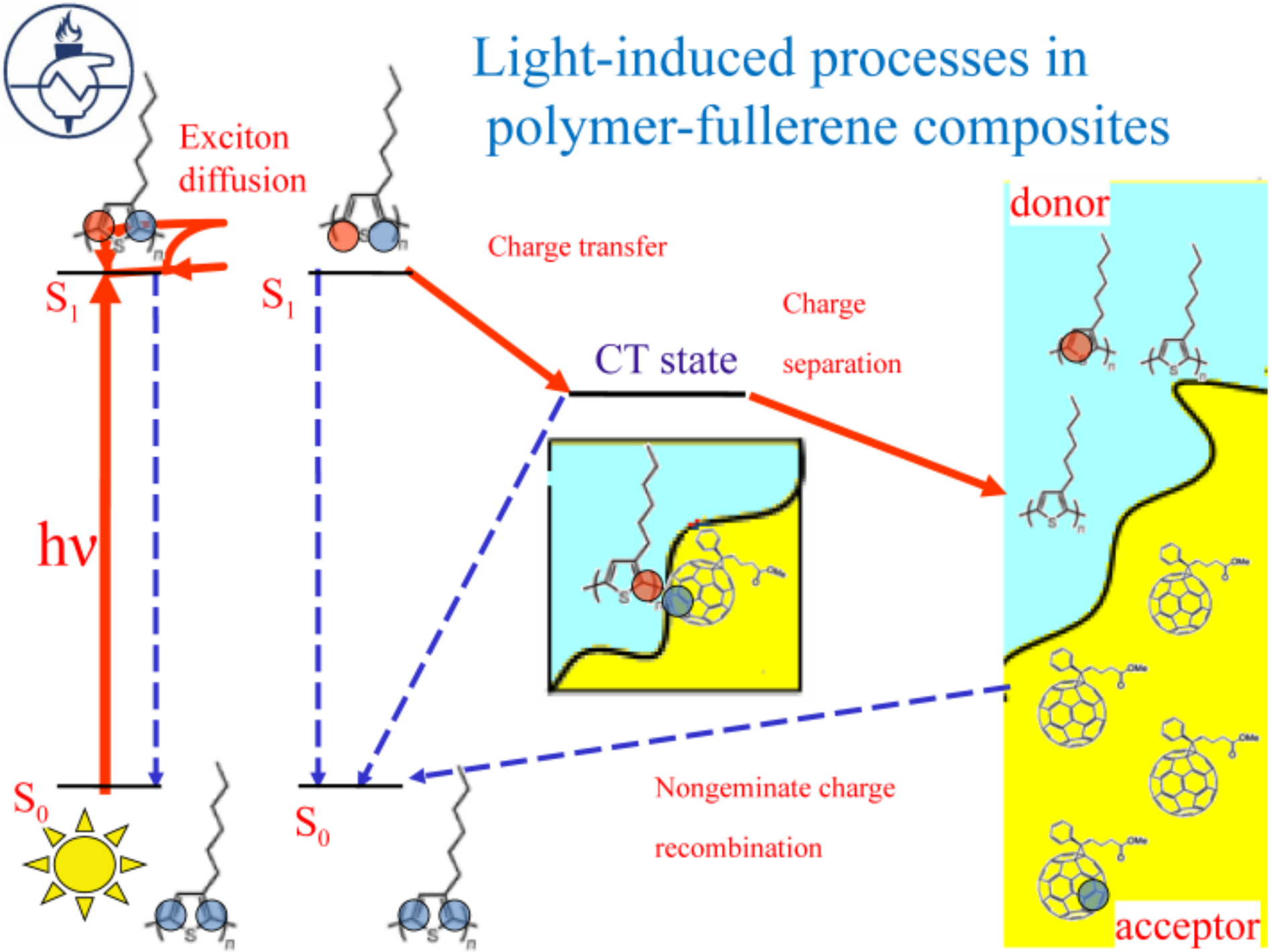
Outline

- 1. Brief introduction into the mechanism of photoelectric conversion in OPV devices
- 2. Motivation: performance of polymer/s-CNT OPV devices
- 3. Introduction into out-of-phase ESE spectroscopy
- 4. In-phase and out-of-phase ESE as tools for study short-living elusive intermediates of photoelectric conversion

Polymer/fullerene OPV devices

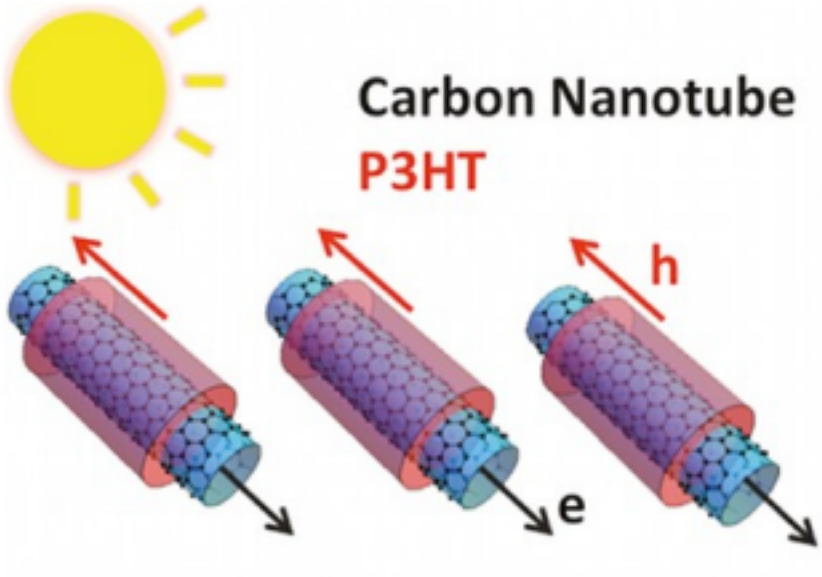


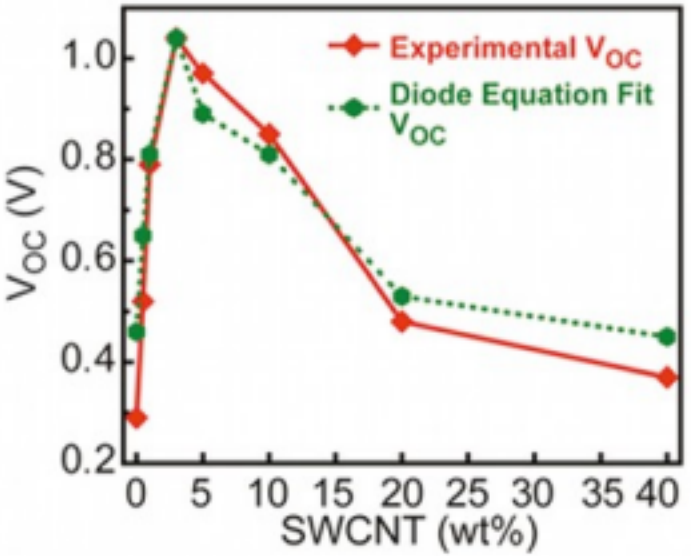
Light-induced processes in polymer-fullerene composites



Motivation:
replace fullerenes with carbon nanotubes

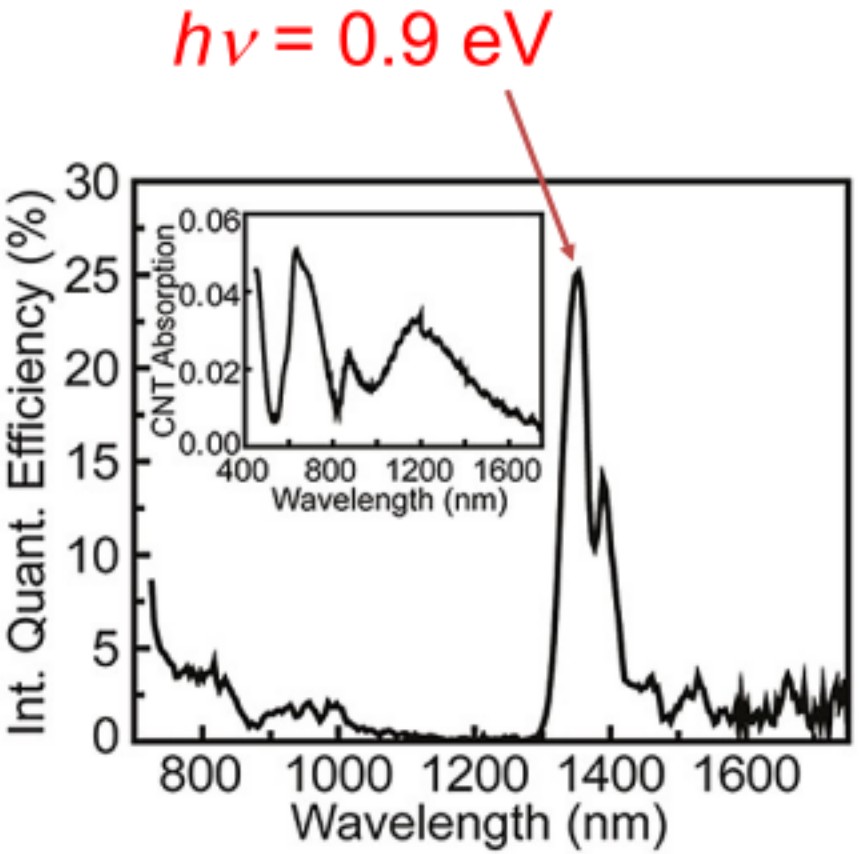
Very high voltage and appreciable photocurrent was reported for semiconducting SWCNT/P3HT bulk heterojunction solar cells.



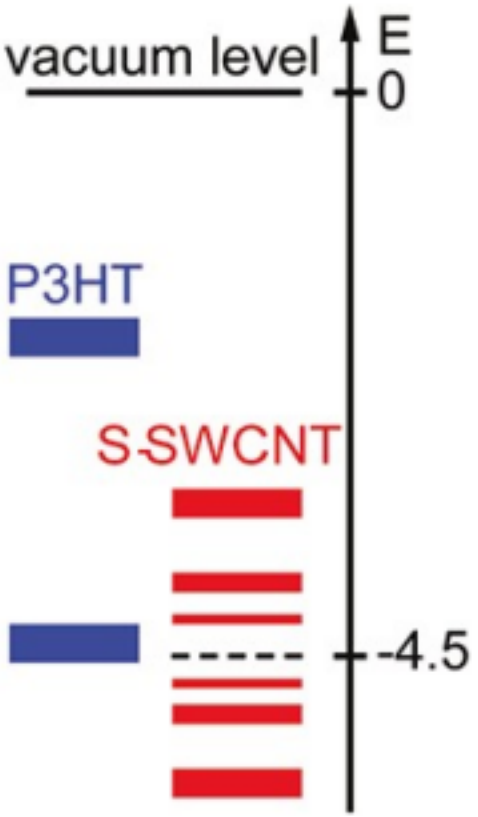


S. Ren *et al., Nano Lett.* **11**, 5316 (2011)

How high open circuit voltage 1.02 eV can be compatible with low driving force of electron transfer?

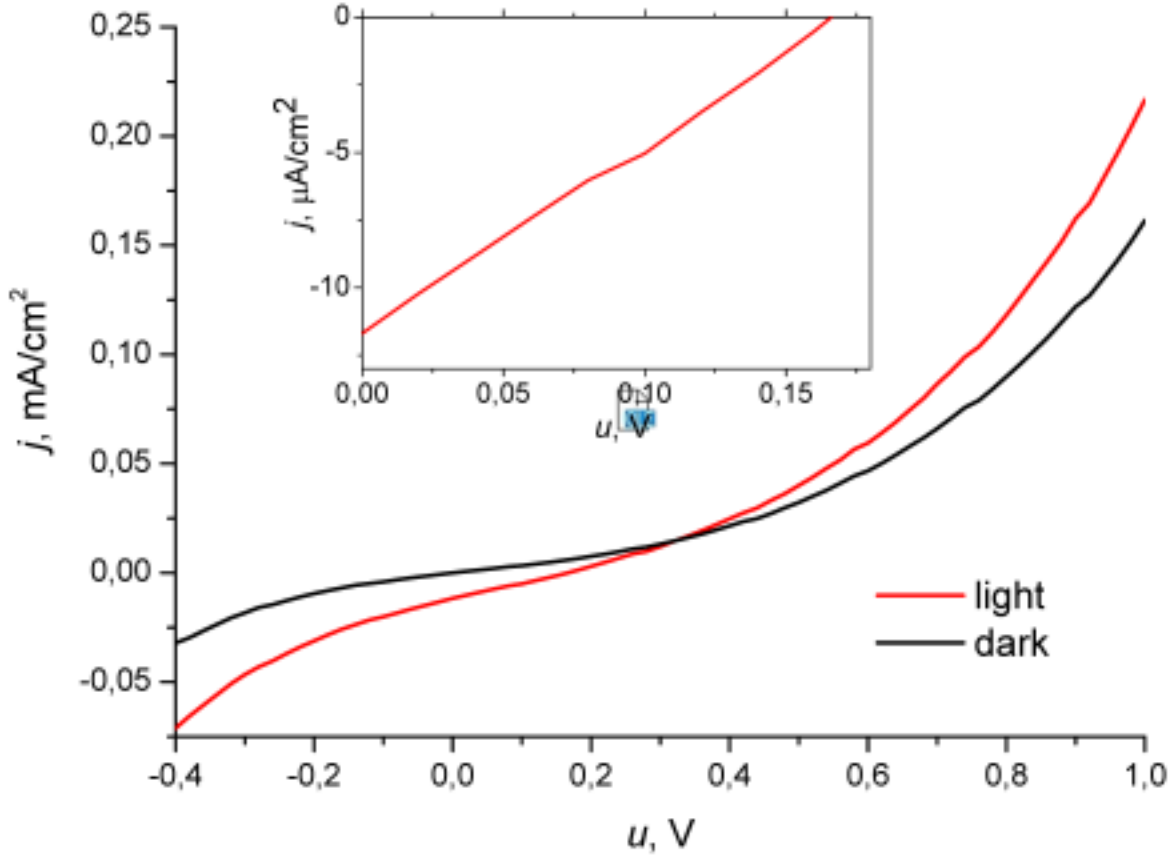


Driving force is less than 1 eV



S. Ren *et al., Nano Lett.* **11**, 5316 (2011)

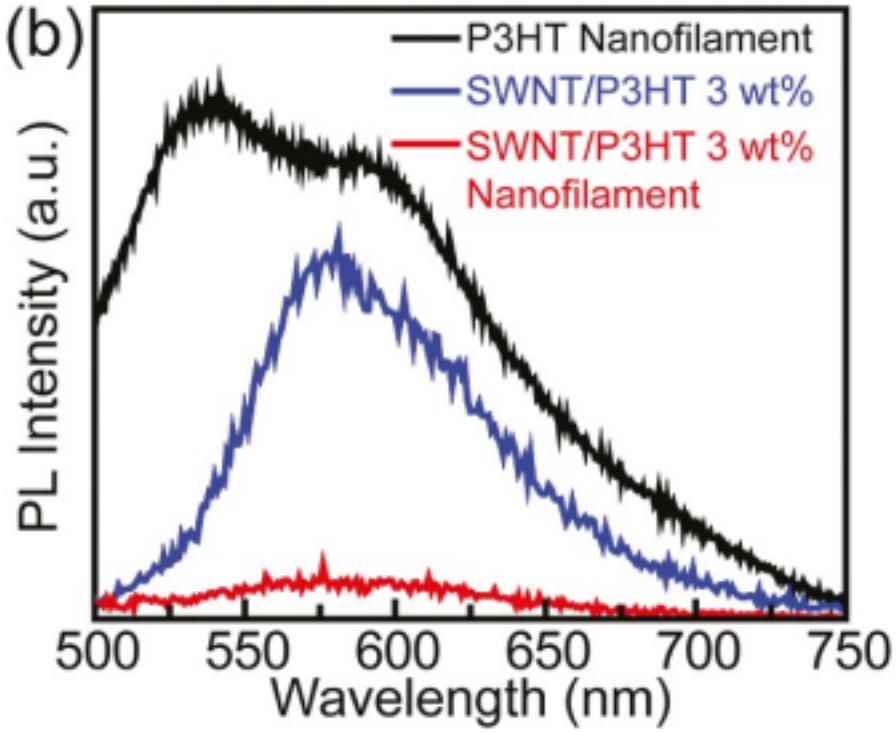
Our experience:
P3HT/s-CNT devices do not work like this



V_{oc} = 0.18V

ITO/PEDOT:PSS/P3HT:sCNT(2%)/BCP/Al device

Why photocurrent is low in P3HT:sCNT OPV devices?

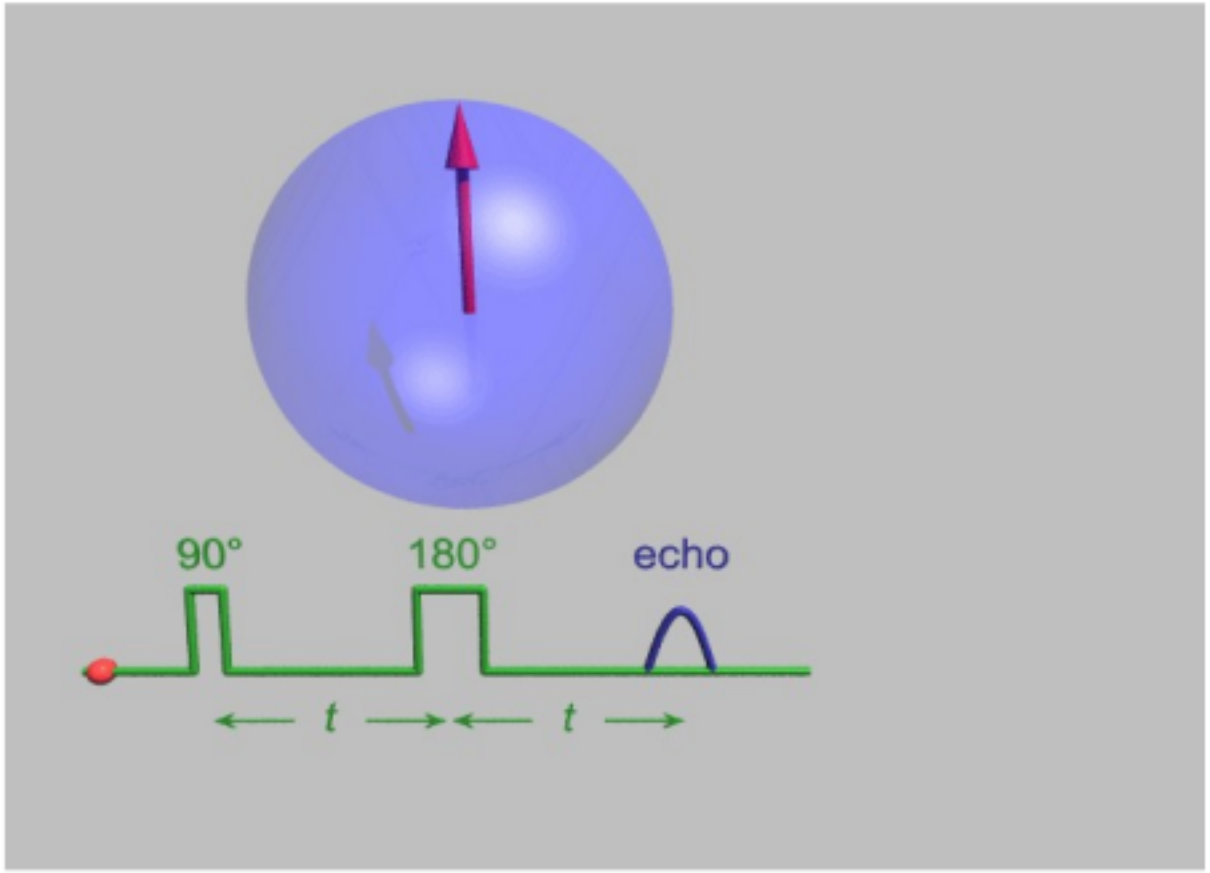


Large fraction of P3HT excitons is quenched upon addition several percent of semiconducting CNT (also reproduced in our experiments).

S. Ren *et al.*, *Nano Lett.* **11**, 5316 (2011)

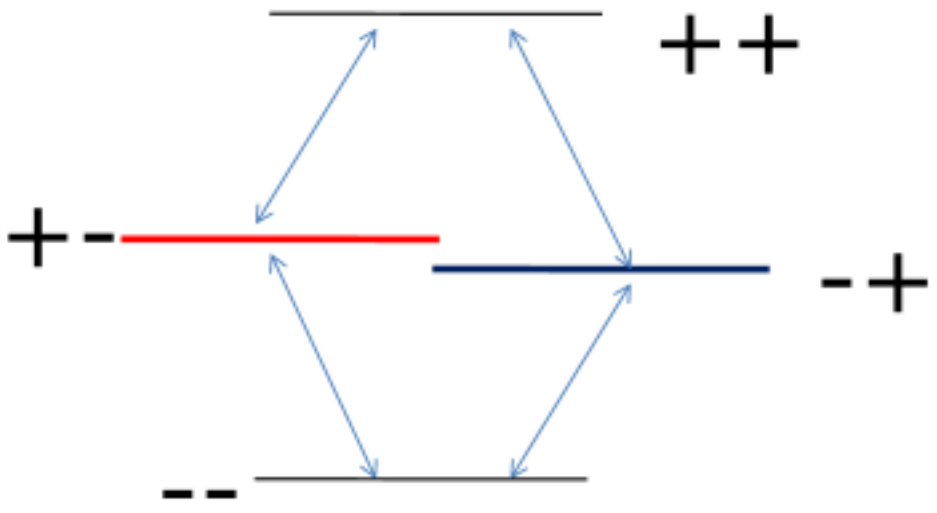
Pulse EPR is needed to trace the fate of photogenerated charges.

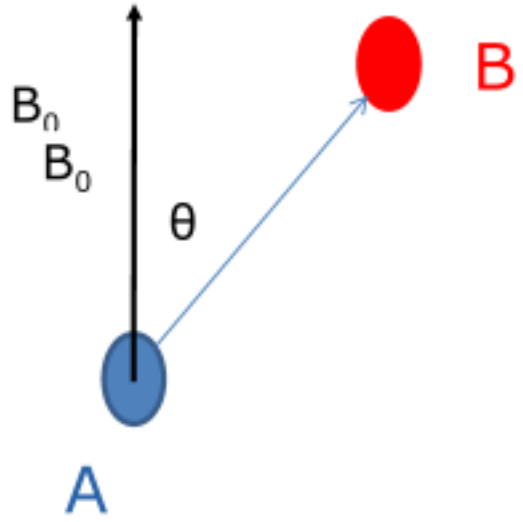
Two-pulse electron spin echo decay



In-phase echo is observed in isolated radicals (S = 1/2) with any spin polarization, thermalized radical pairs, triplets.

Spin-correlated radical pair





$$H = \omega_{Az}S_{Az} + \omega_{Bz}S_{Bz} + dS_{Az}S_{Bz}$$

$$d \sim (1\text{-}3\cos^2\theta)/r^3$$

Features of out-of-phase electron spin echo

OOP ESE can be observed in spin-correlated radical pairs.

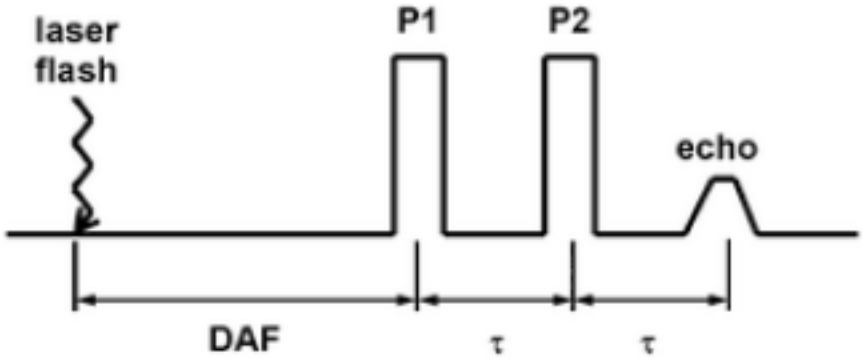
It can be detected only if:

1. Spins of the radicals are correlated (the pair is singlet spin state)
2. Spins experience magnetic interactions (dipolar or exchange)
3. Both spins are excited by microwave pulses.

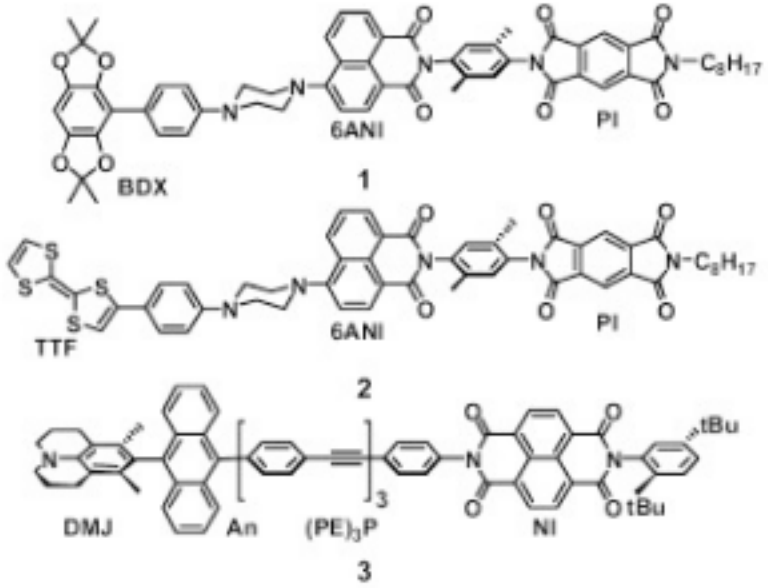
Optimal pulse turning angles: $\pi/4 - \tau - \pi$

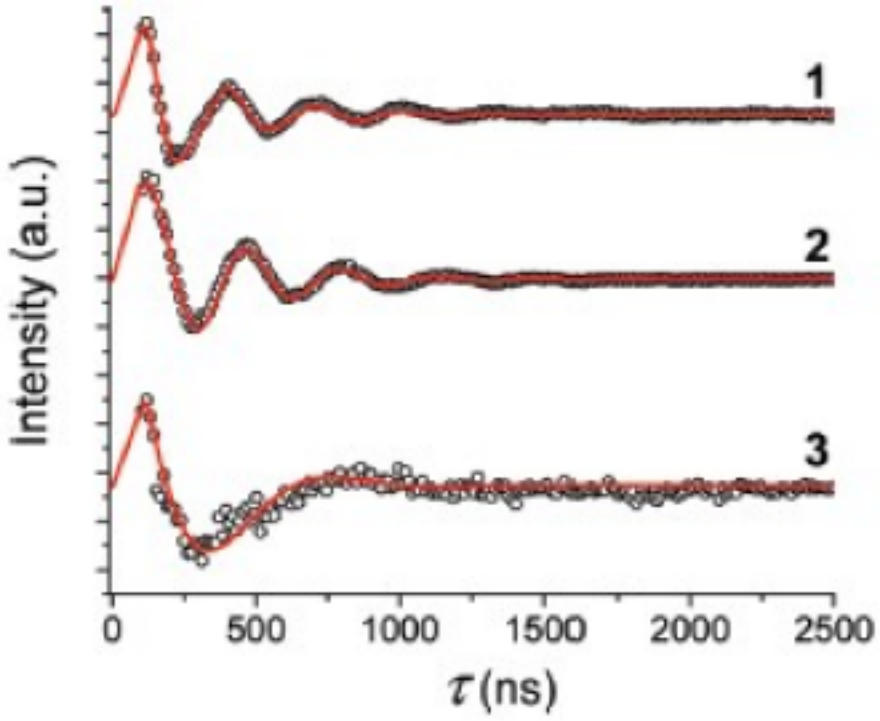
Dependence on τ : $M_x \sim \sin(d\tau)$ $\quad d = \gamma^2/r^3\,(1 - 3\cos^2\theta)/2$

Out-of-phase ESE: example



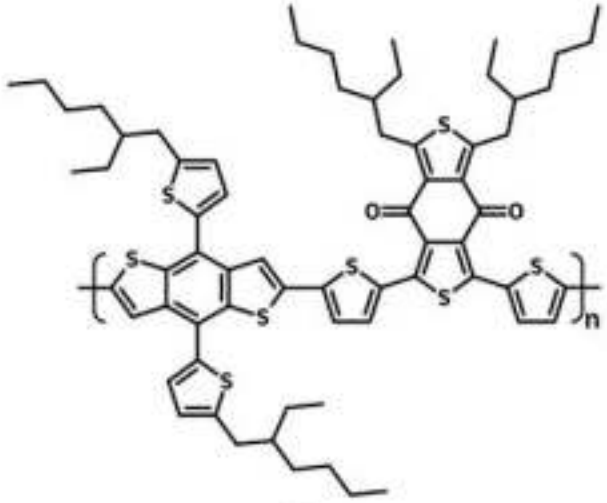
Artificial donor-acceptor systems
R. Carmieli et al. 2009



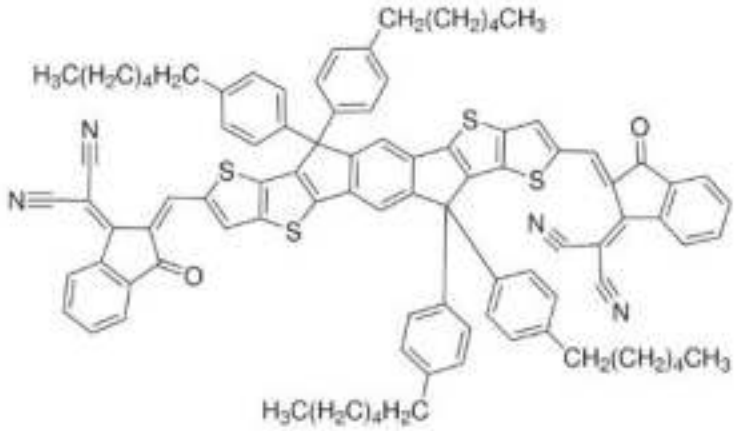


Interspin distances in nanometer range can be determined with angstrom precision!

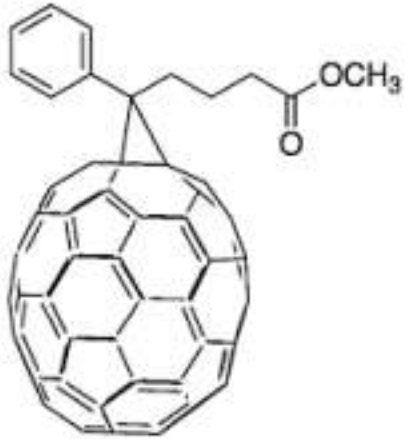
Ternary OPV system PBDB-T/ ITIC:$PC_{70}BM$



PBDB-T



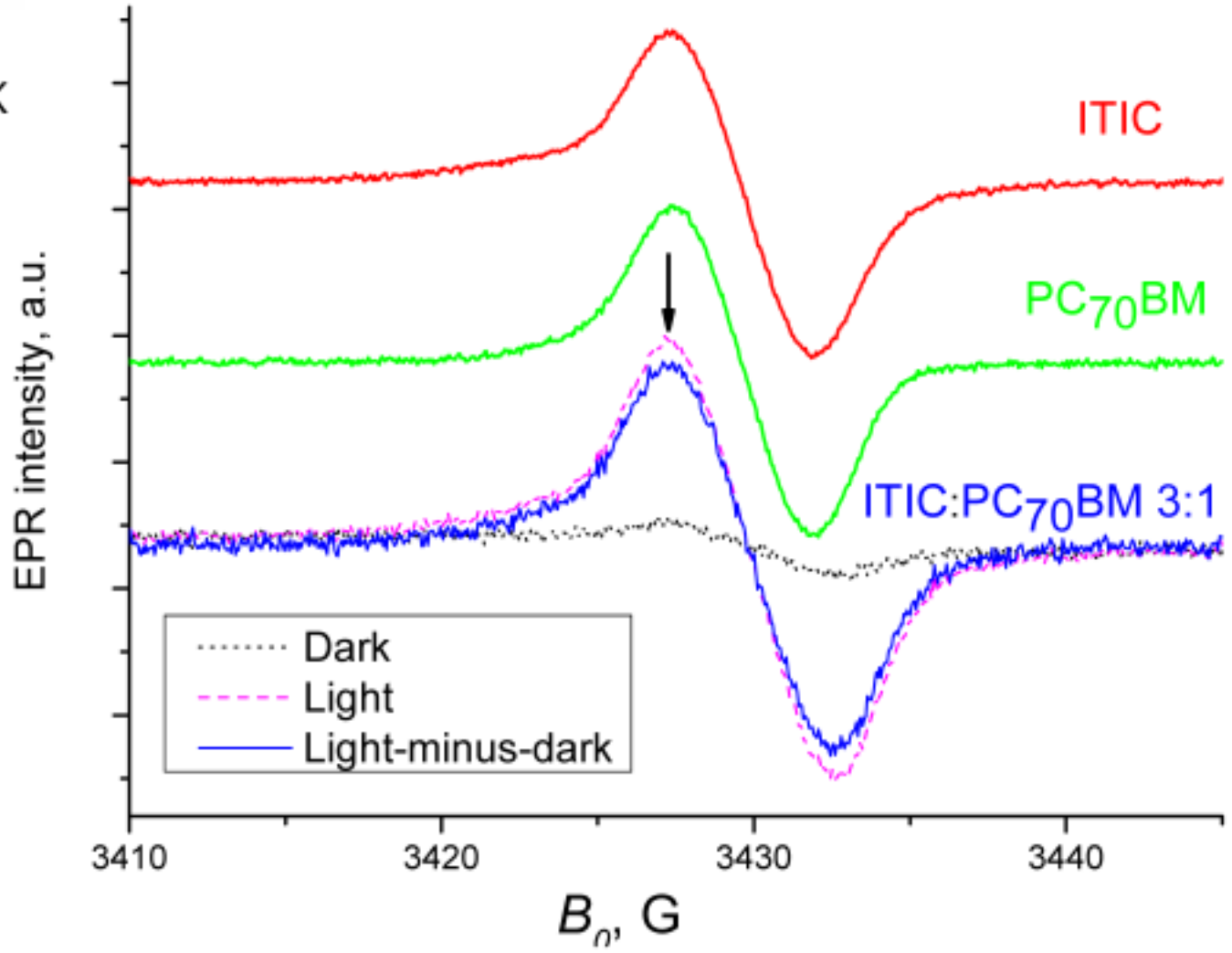
ITIC



$PC_{70}BM$

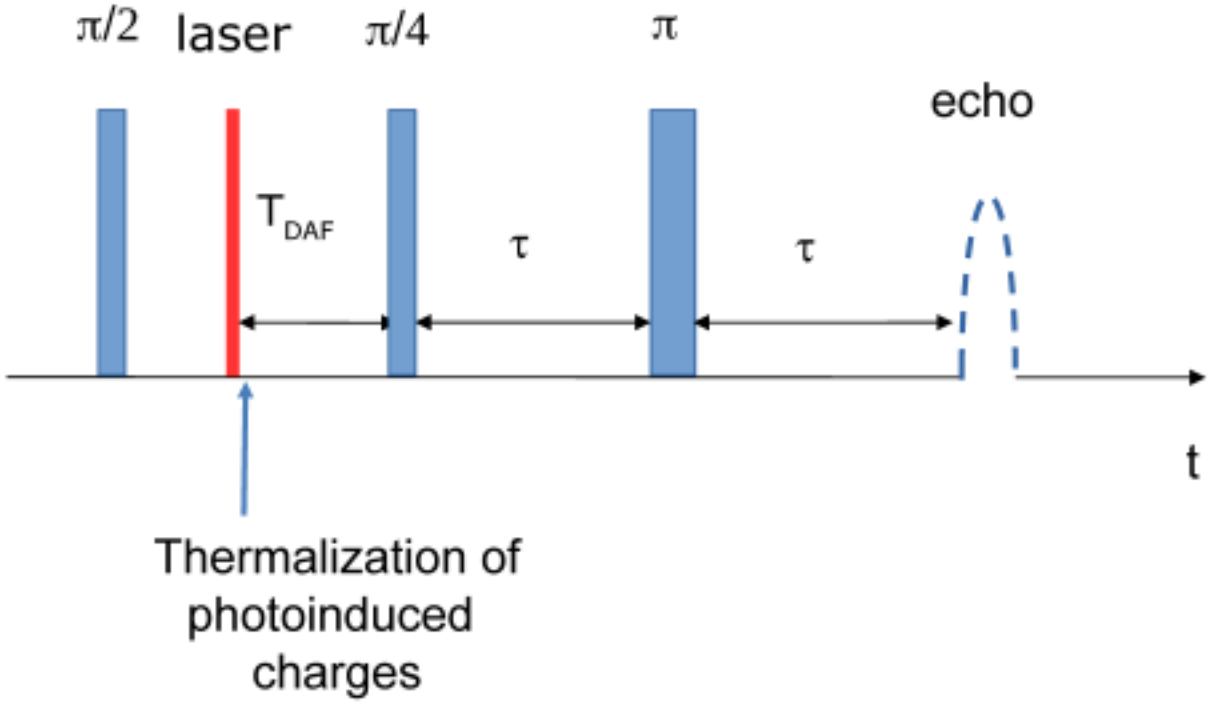
Light-induced EPR spectra

T = 120K



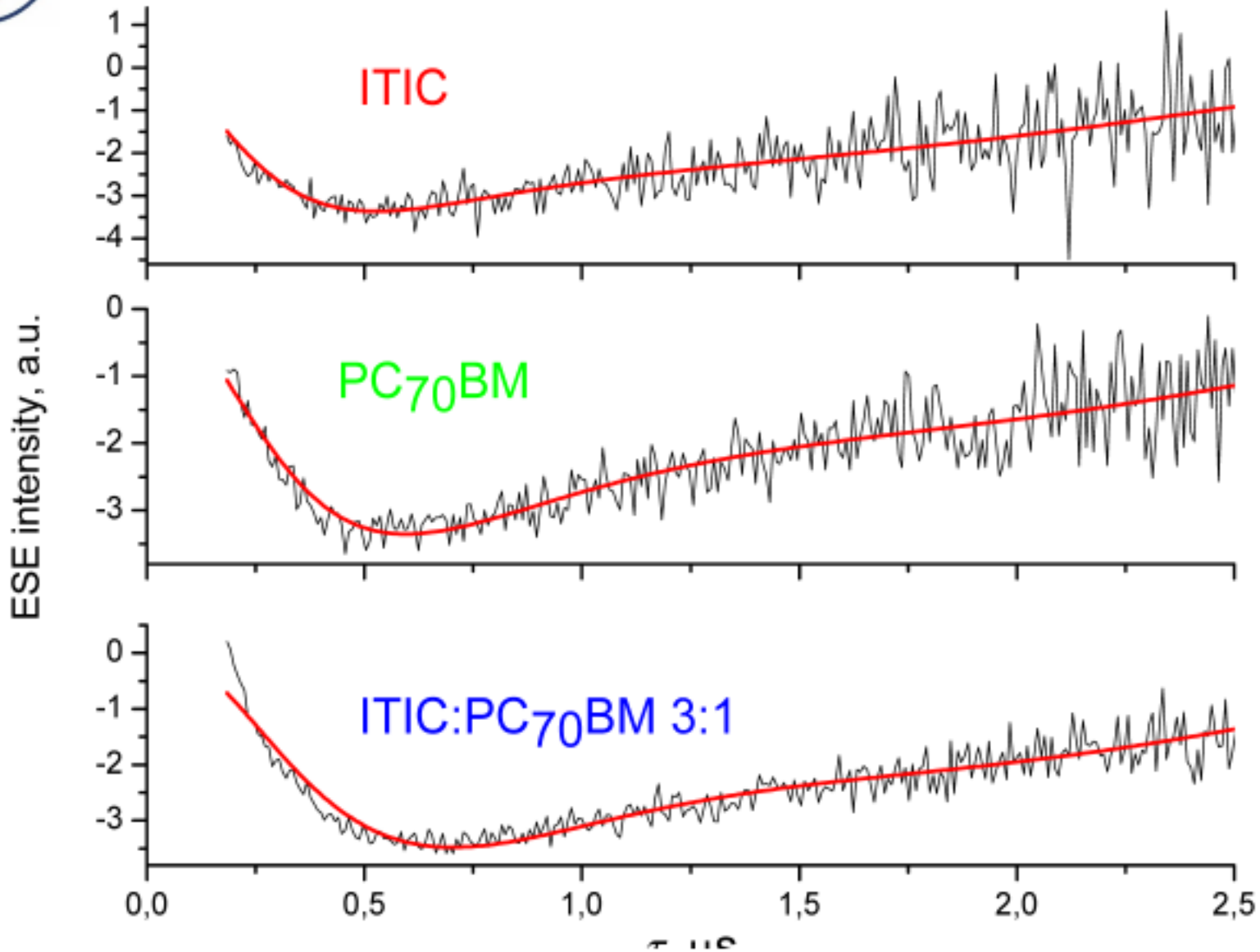
A. A. Popov et al., Synthetic Metals 277 (2021) 116782

Two-pulse ESE with laser excitation and pre-saturation

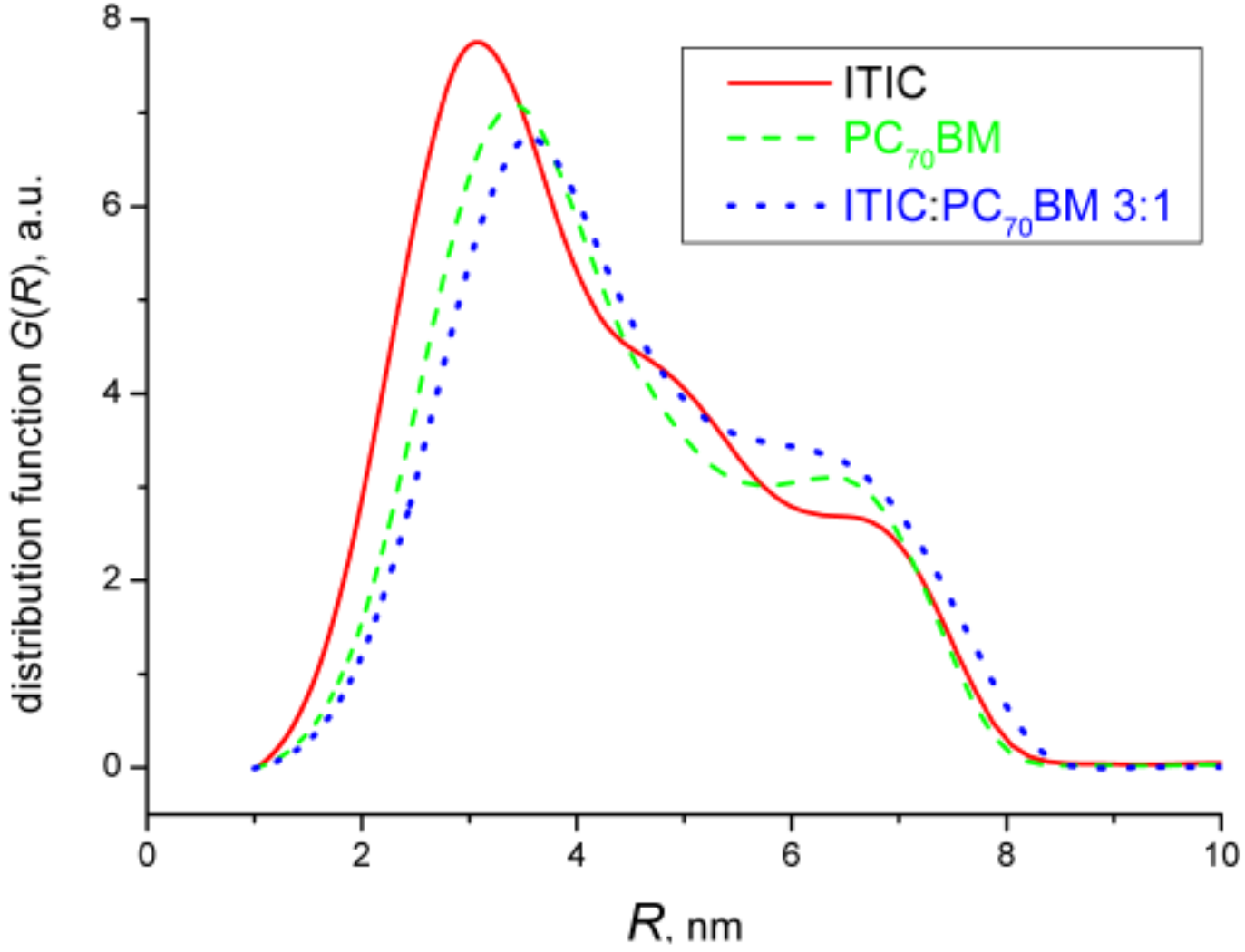


Challenge: sample thickness is less than 1 micron!

«Modulation» of out-of-phase ESE signal

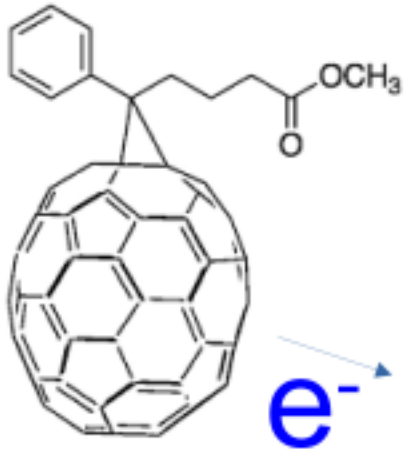


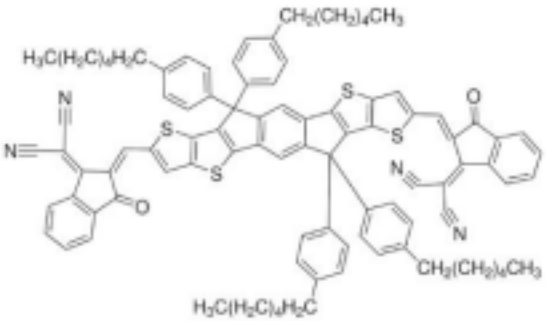
Charge-transfer distance distribution



Typical distances are from 2 to 8 nm.

Cascade electron transfer

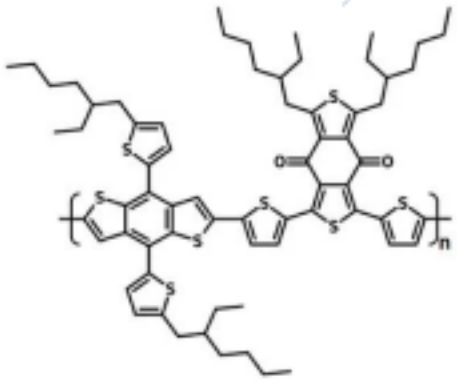




e⁻

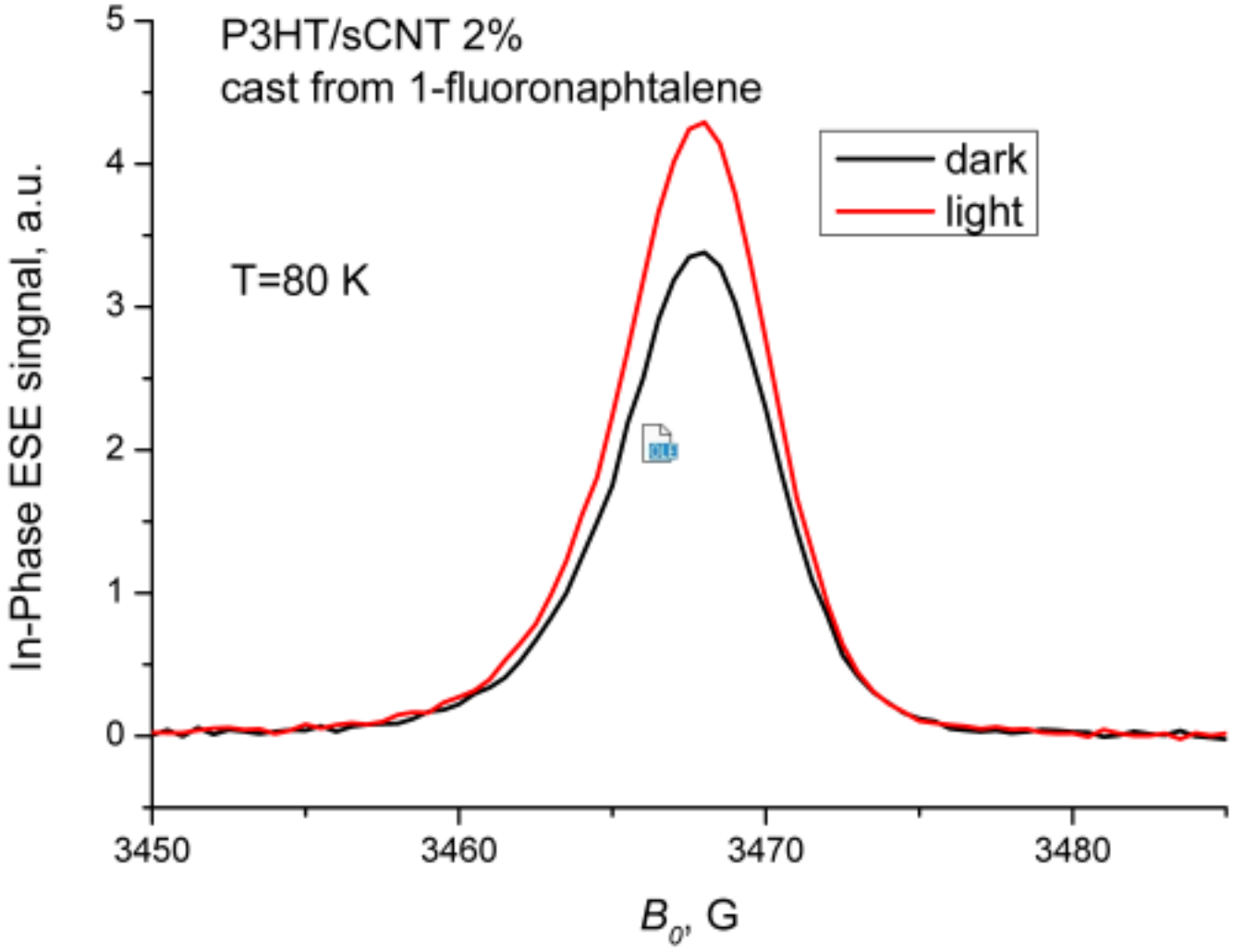
e⁻

hν



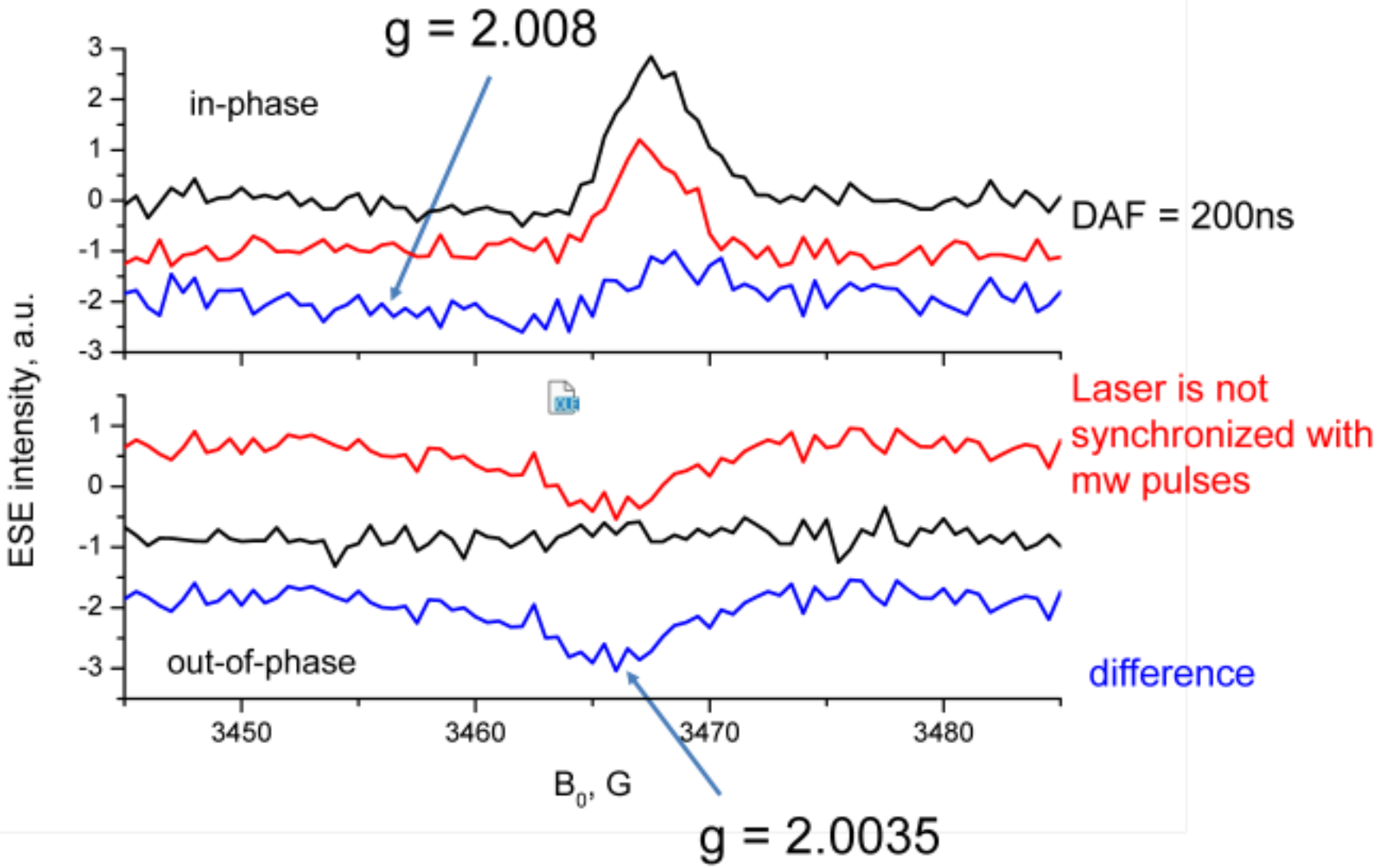
Photovoltaic properties of the ternary composite PBDB-T/ ITIC:PC70BM are improved mainly by increasing the electron transfer distance at the donor/acceptor interface, which leads to a decrease of geminate recombination rate.

Two-pulse light-induced ESE is small for P3HT/s-CNT.

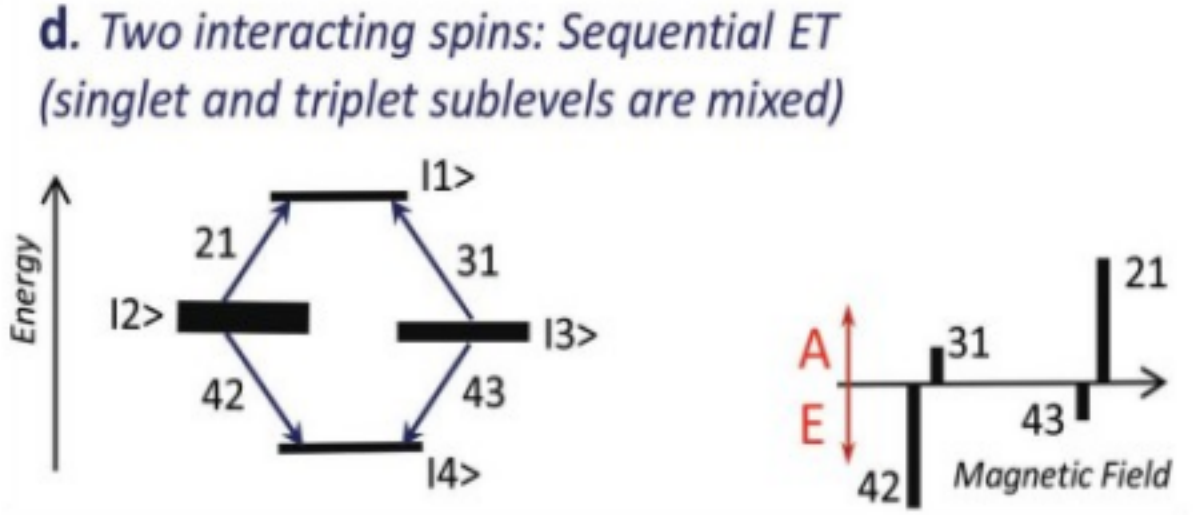


Continuous illumination

Echo-detected EPR spectra with pulse excitation



In-phase ESE: E/A polarization

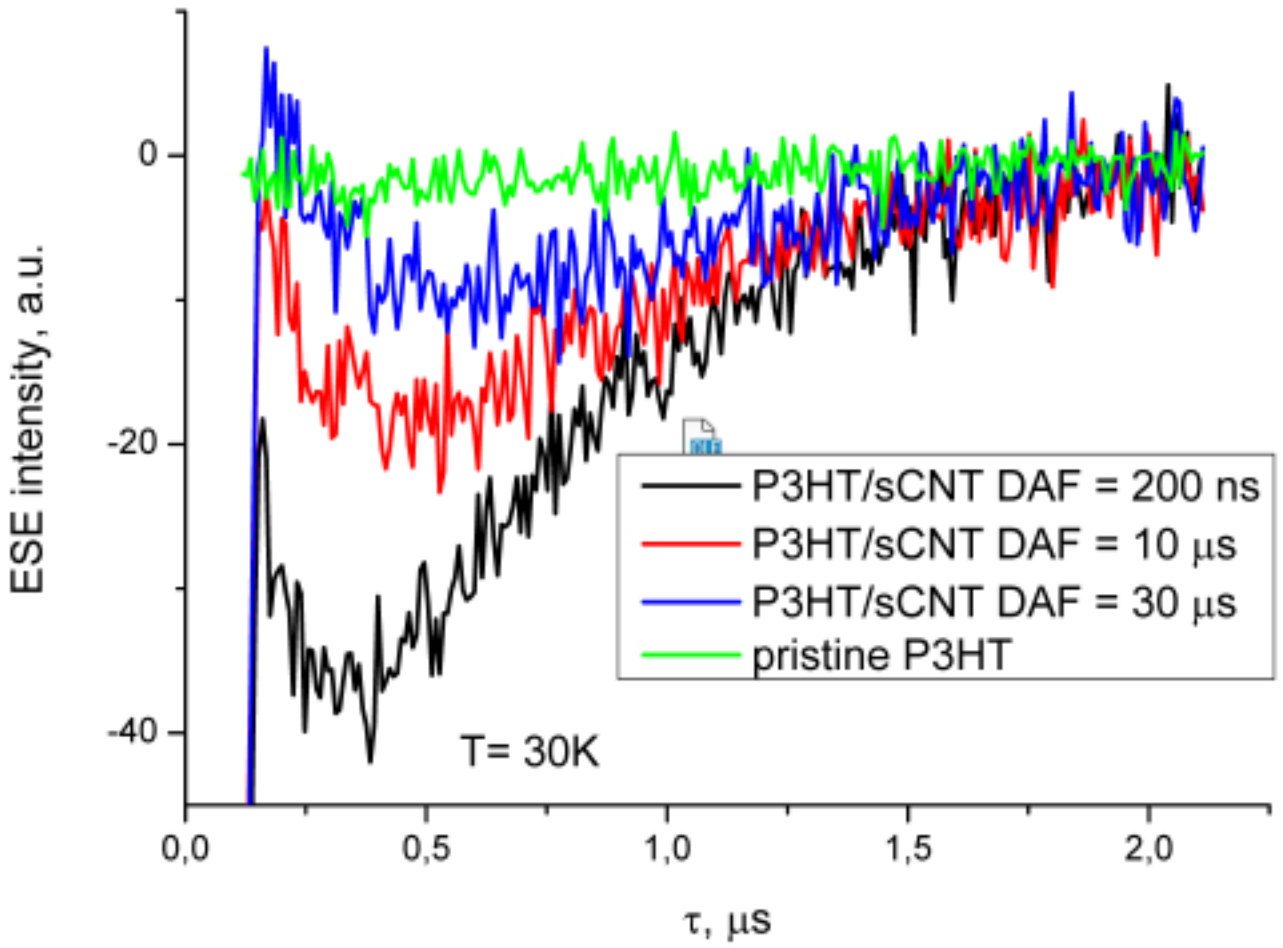


J. Niklas, O. G. Poluektov, Adv. Energy Mat. 1602226 (2017)

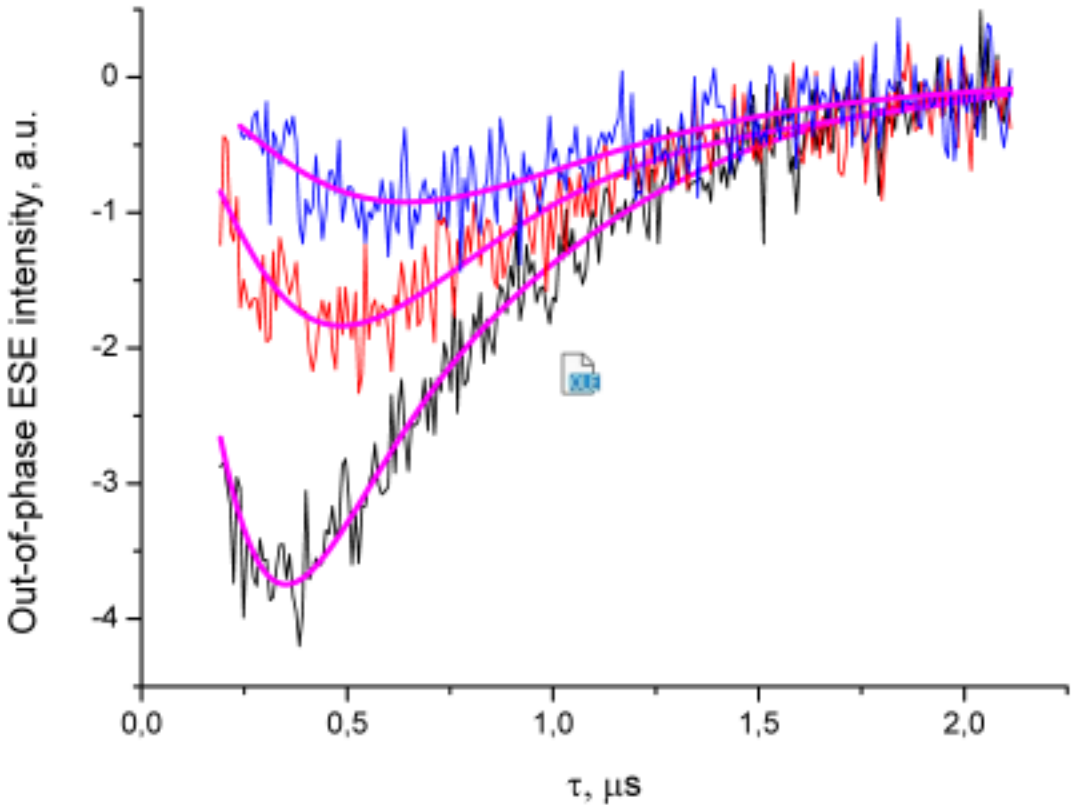
Principal g-values of $P3HT^{+}$ are in the range 2.001 – 2.004
J. Niklas et al. PCCP (2013)

Low-field emissive line with g-value up to 2.008 is assigned to $s\text{-}CNT^{-}$
earlier suggested at J. Niklas et al. JPC Letters (2014)

Out-of-phase ESE: spin-correlated radical pair $P3HT^{+}/s\text{-}CNT^{-}$

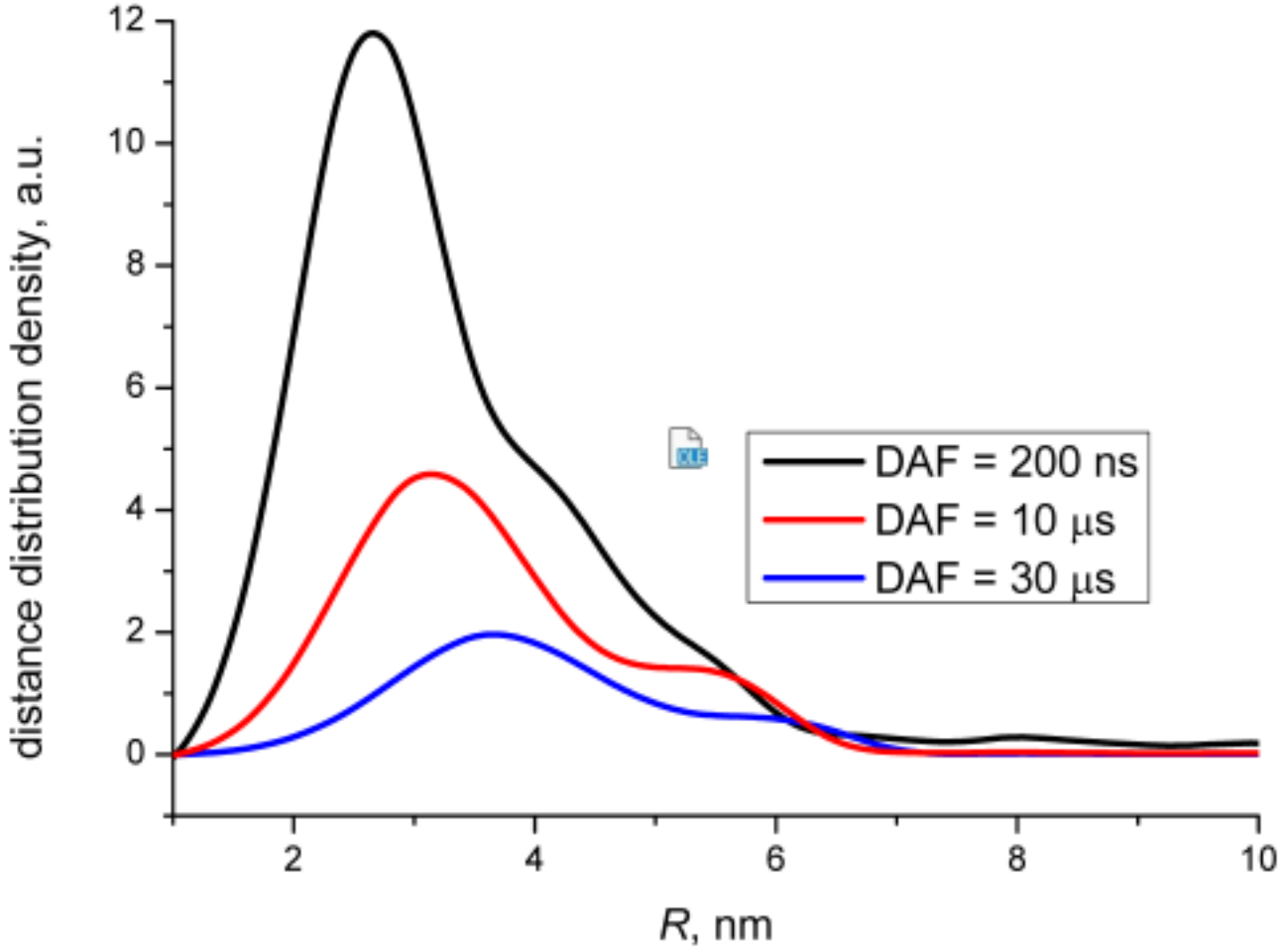


Out-of-phase ESE for P3HT^{+}/s-CNT^{-} : simulation



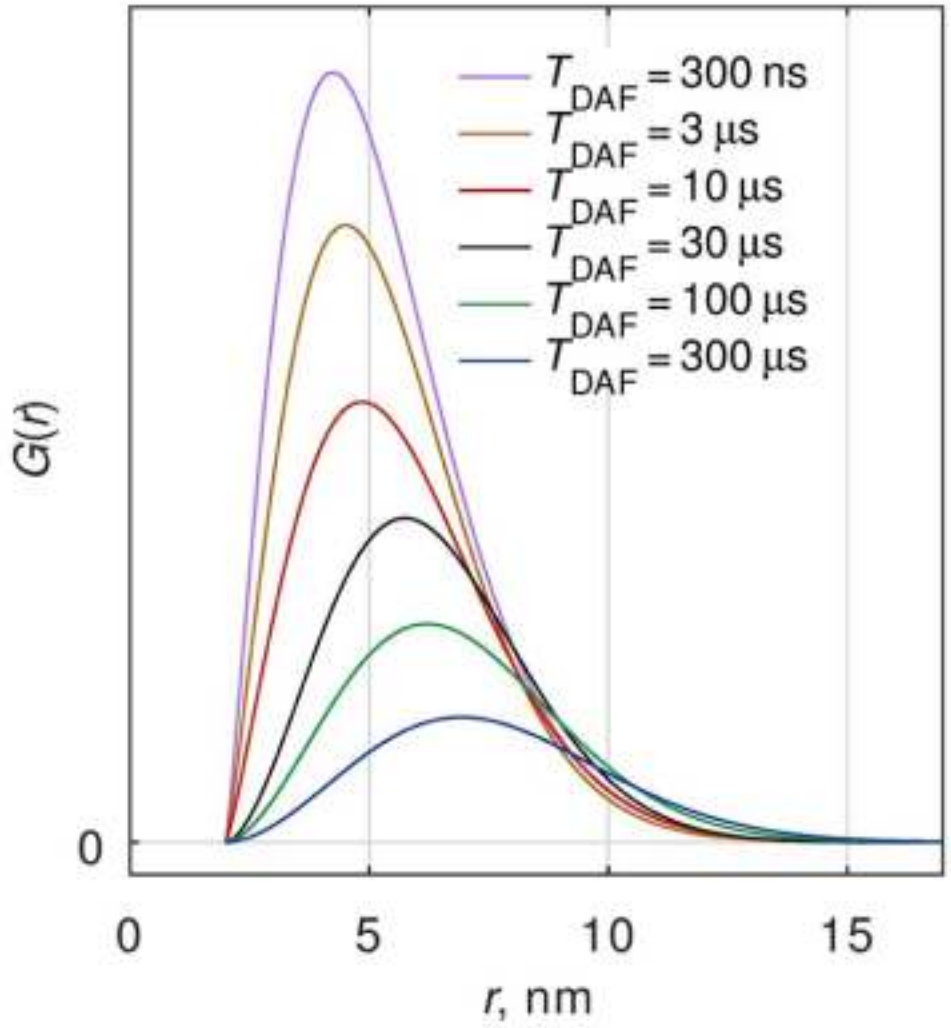
$$(\quad) = \exp(-2 \quad / \quad _2) \int \quad (\quad) \iint s \in [\quad (\quad , \quad , \quad) \quad] \sin(\quad)$$

Evolution of interspin distance distribution in P3HT^{+}/s-CNT^{-} charge-transfer state



Typical distances are from 1.5 to 6 nm.

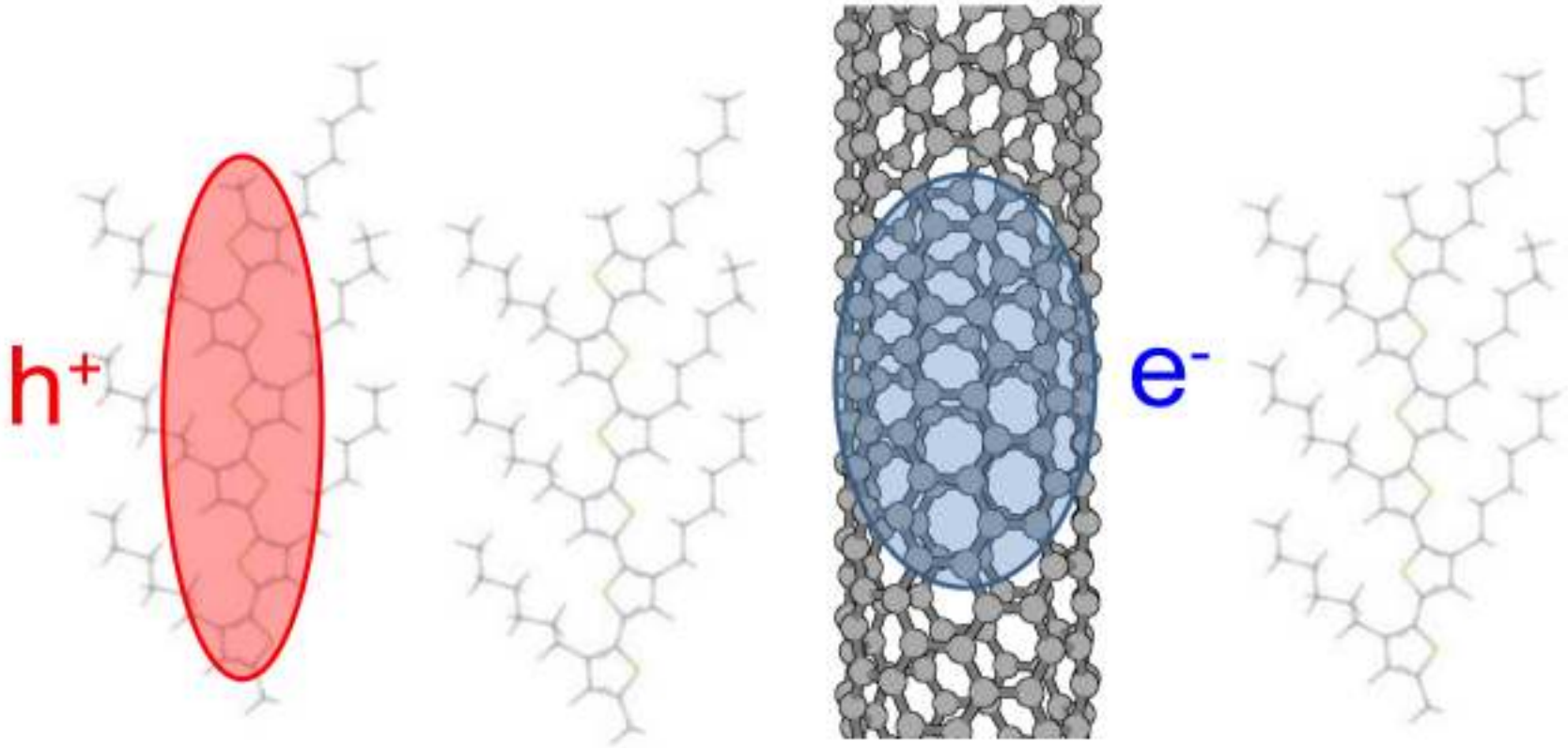
Comparison: evolution of interspin distance distribution in PCDTBT^{+}/PC$_{70}$BM^{-} charge-transfer state



CTS decay is noticeably slower in polymer/fullerene systems.

E. A. Beletskaya et al., J. Chem. Phys. **152**, 044706 (2020)

Reason for CTS formation:
delocalization of electron at s-CNT is suppressed by Coulombic attraction to $P3HT^+$



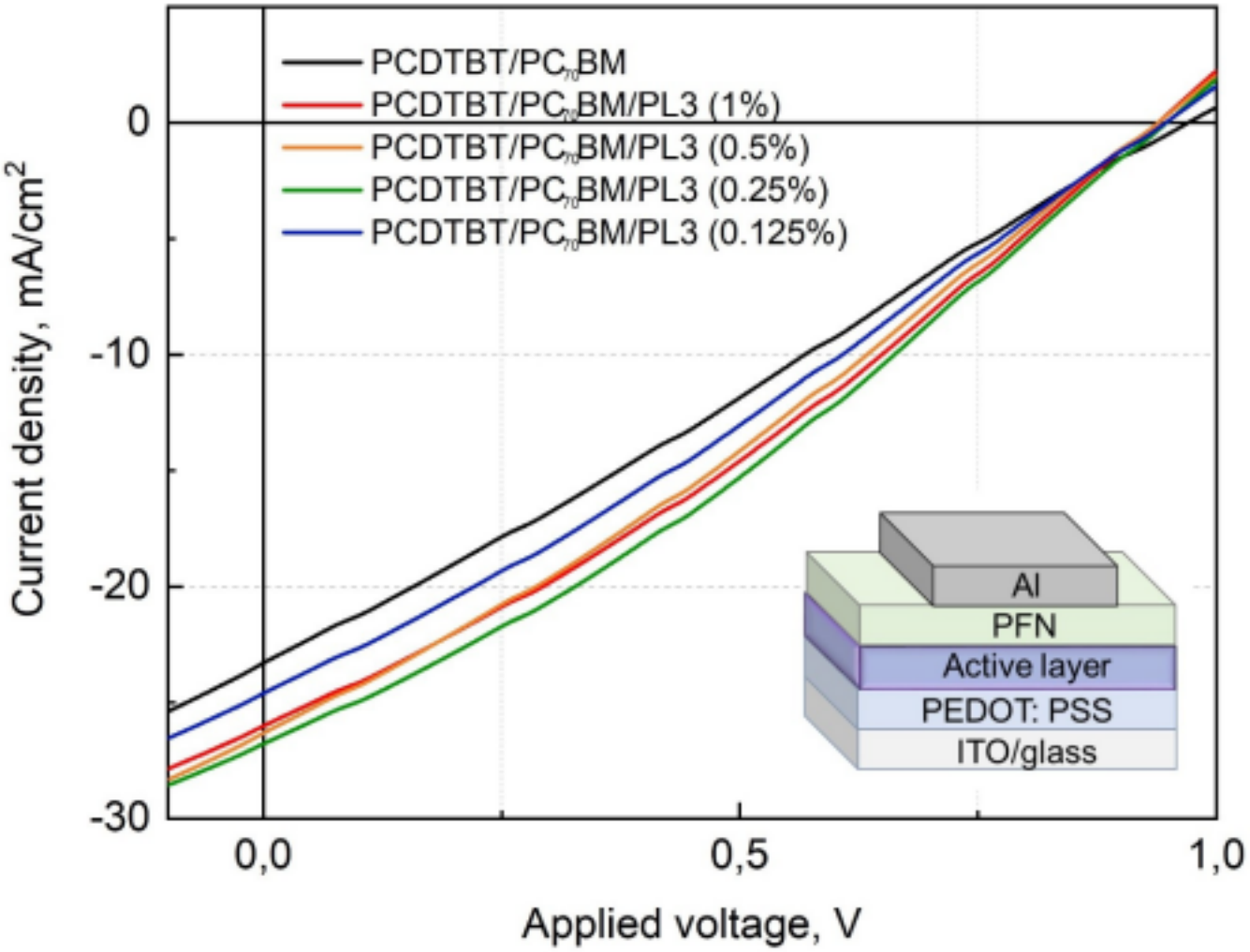
Conclusions

1. Photovoltaic performance of composite of P3HT with semiconducting carbon nanotubes is poor.

- 2. Low charge current density is caused by fast geminate recombination of $P3HT^{+}$/s-CNT^{-} charge-transfer state, detected by out-of-phase ESE spectroscopy

- 3. g-factor of the electron localized at s-CNT is close to that of $PC_{70}BM$ anion.

Fluorinated carbon nanotubes as non-volatile additive to active layer of OPV devices



Reason for increase of J_{SC} – improved connectivity of donor and acceptor domains due to high aspect ratio of CNT.


Thank you for attention!