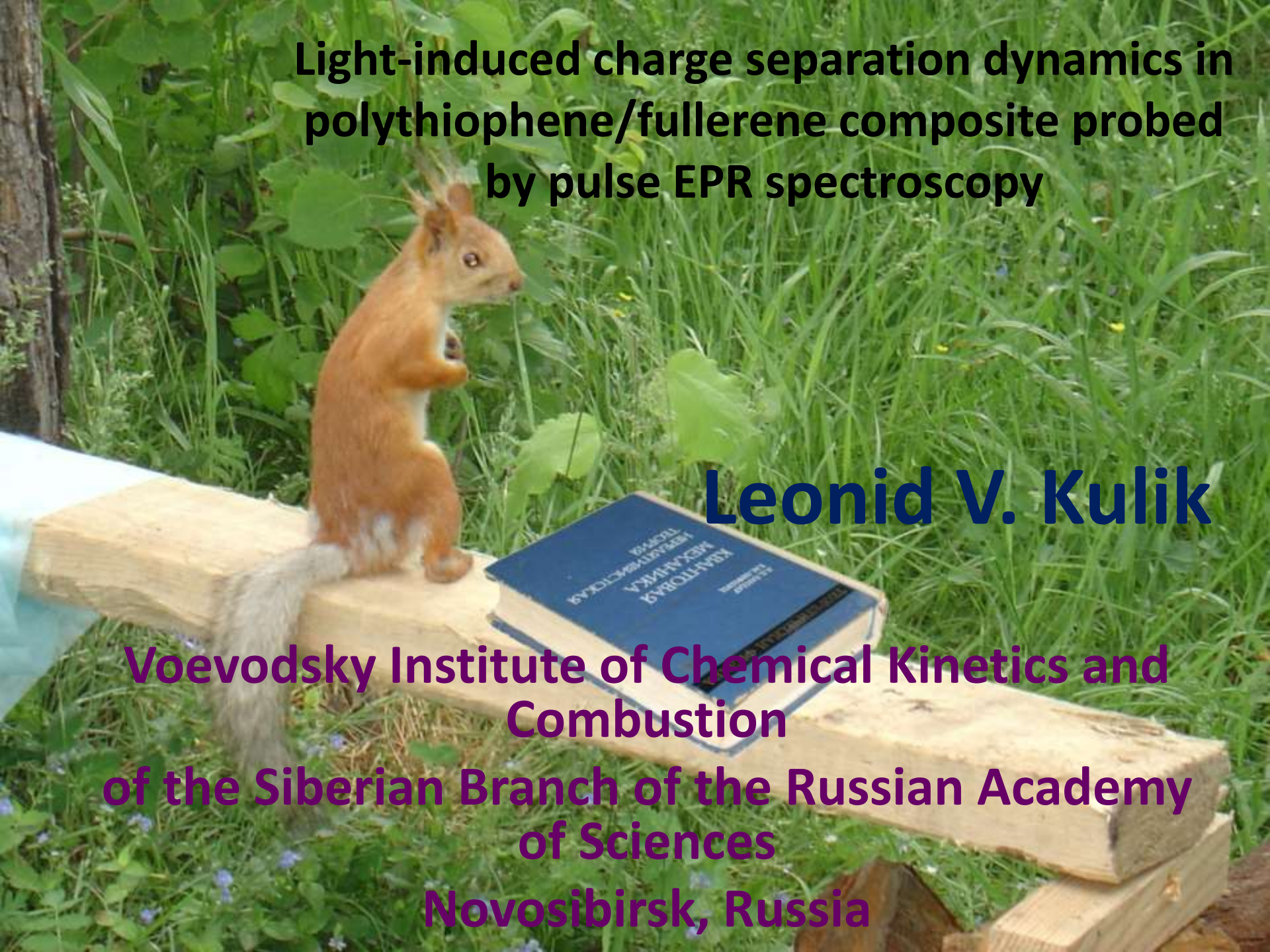
Light-induced charge separation dynamics in polythiophene/fullerene composite probed by pulse EPR spectroscopy



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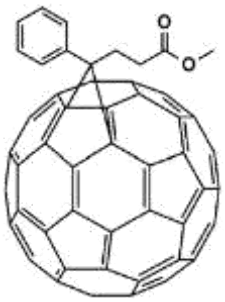
Outline

1. Principles of organic photovoltaics
2. Models of charge separations at donor/acceptor interface
3. Brief introduction into out-of-phase electron spin echo spectroscopy
4. Results: distance- and time-scale of light-induced charge separation in polymer/fullerene composite
5. Conclusions

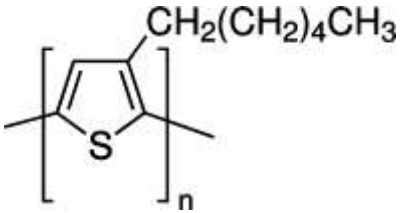
Organic Solar Cells

The main advantages:

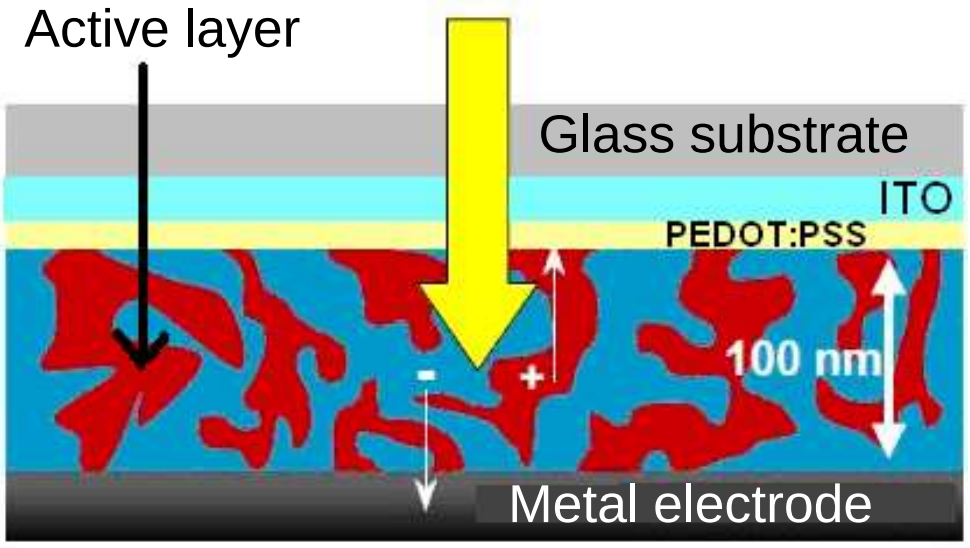
- ❑ flexibility
- ❑ light weight
- ❑ Inexpensive processing by inkjet printing or spray coating techniques



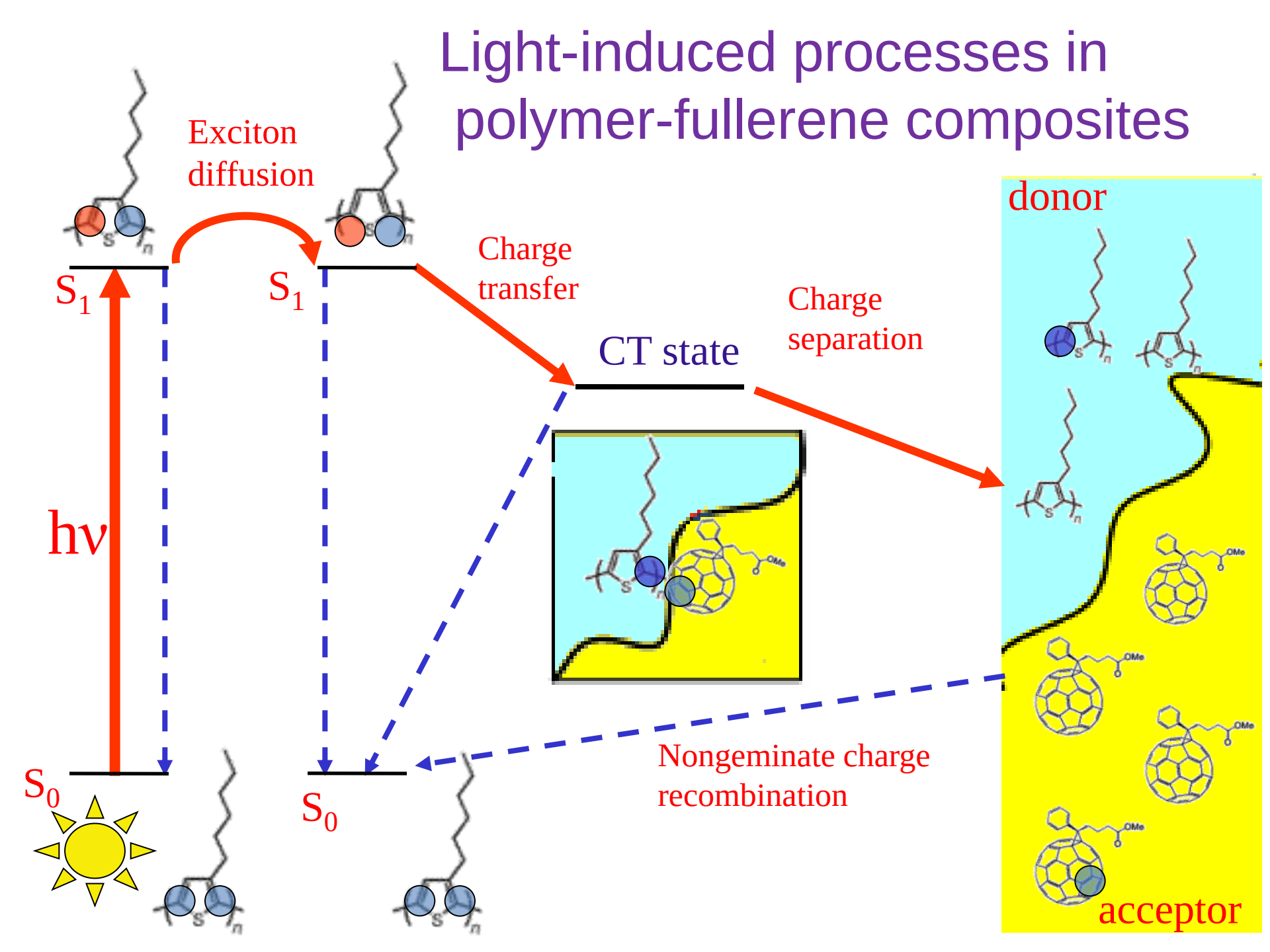
PCBM
[6,6]-phenyl C_{61} butyric acid methyl ester



P3TH
poly(3-hexylthiophene)

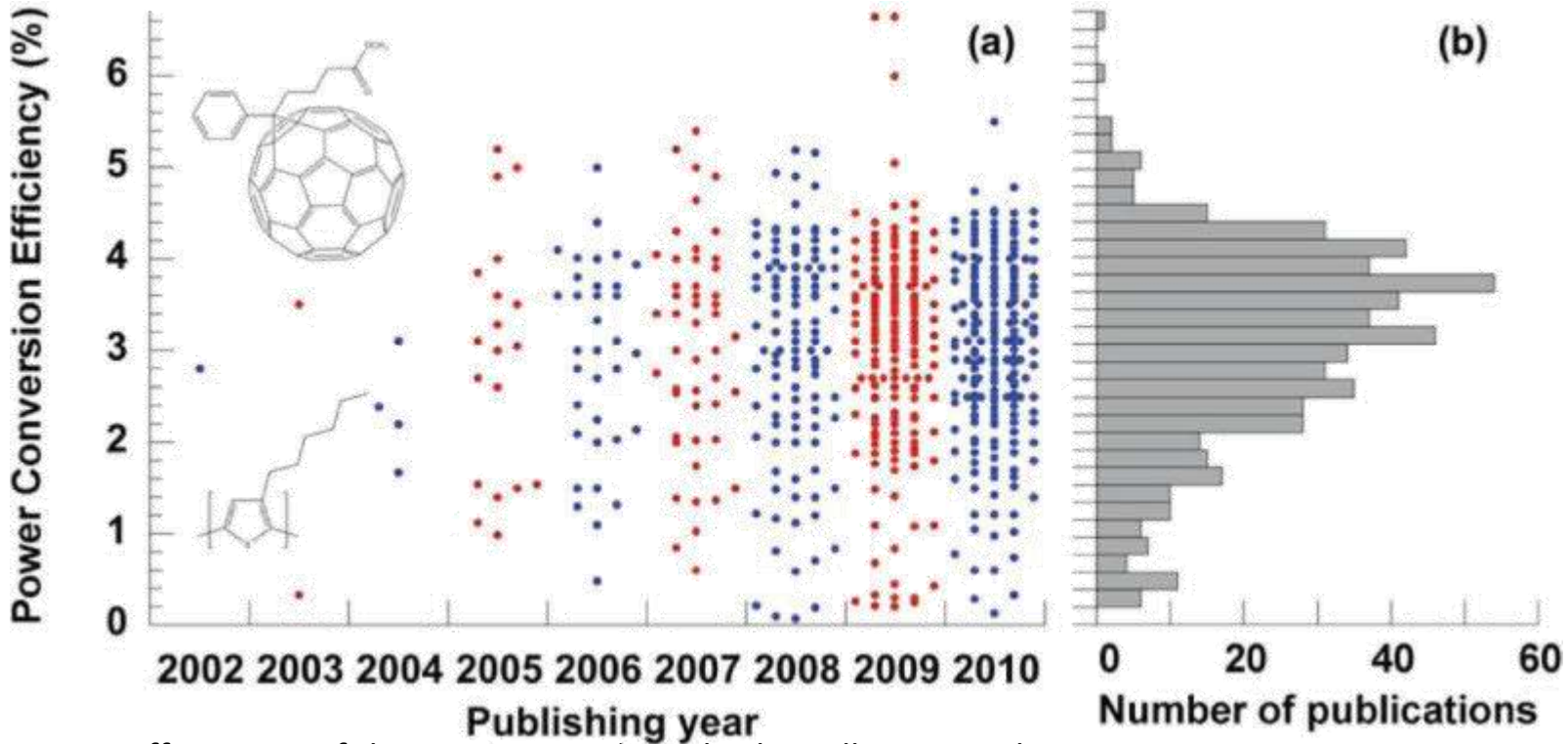


Light-induced processes in polymer-fullerene composites



The benchmark photovoltaic composite P3HT/PC60BM

Dang M.T., Hirsch L., Wantz G. Advanced Materials, 23, 3597 (2011)



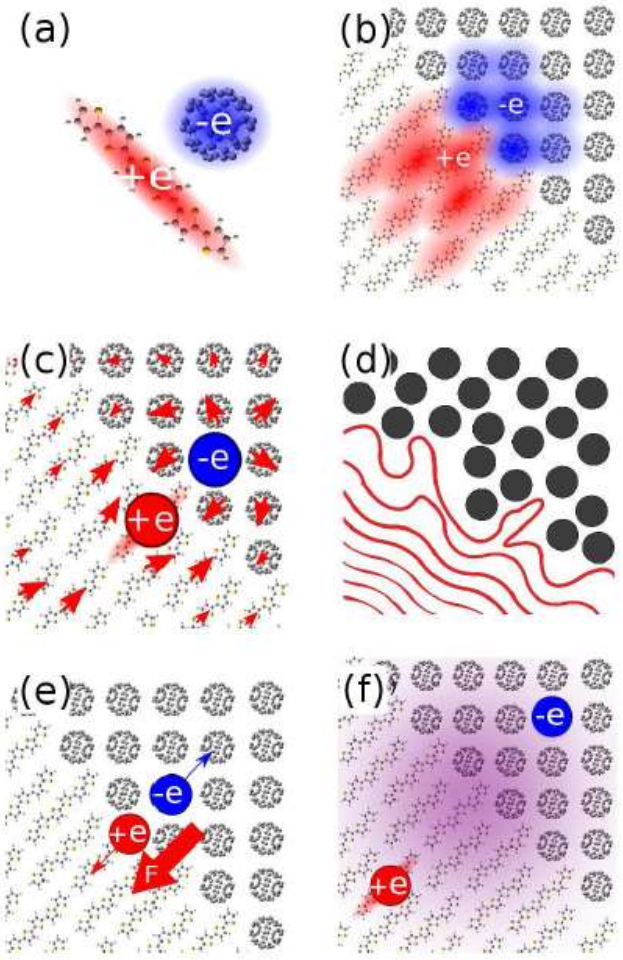
a) Power-conversion efficiencies of the P3HT:PCBM-based solar cells reported in each of the 579 publications screened in this survey. Each dot corresponds to the maximum PCE value reported in each publication The inset shows the chemical structures of P3HT and PCBM. **b)** The overall distribution of PCE values from 2002 to 2010.

Why do charges separate in polymer/fullerene composites?

Coulomb attraction energy is about 0.5 eV if charges are located at neighboring molecules.

Still the charge separation efficiency is close to unity for P3HT/PCBM composite.

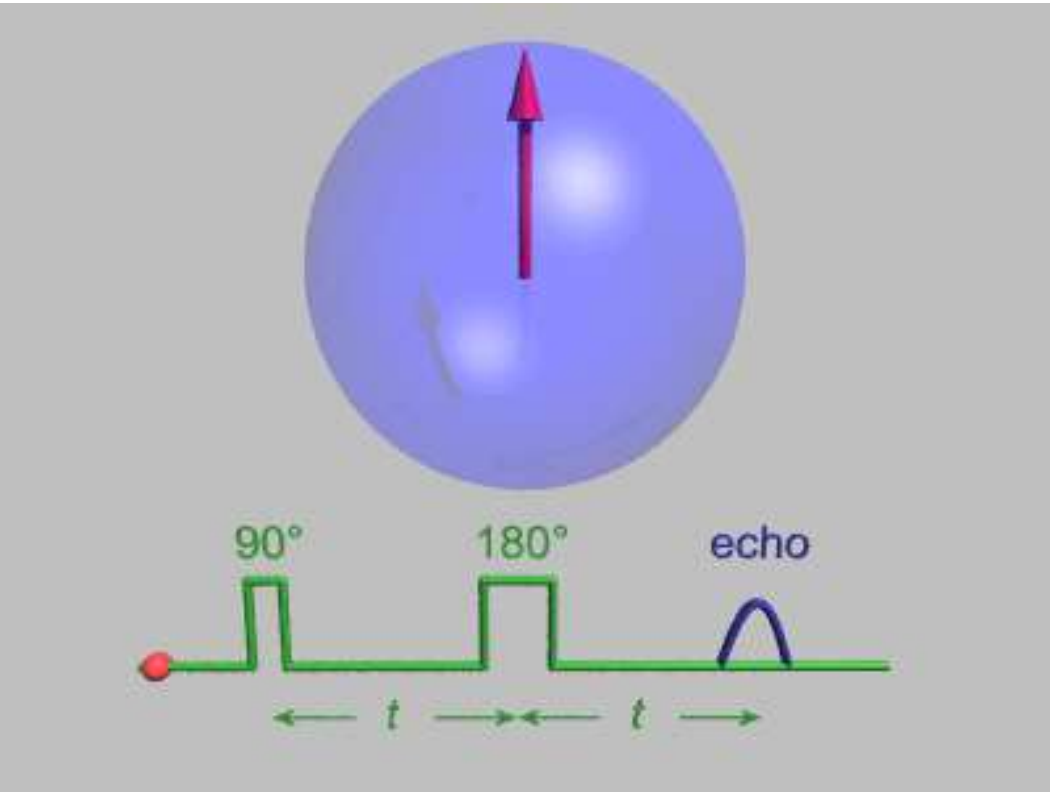
Proposed models for charge separation in polymer-fullerene composite



No experimental technique can measure the distance between the charges in CT state directly except electron spin echo.

S. Few et al., 2014

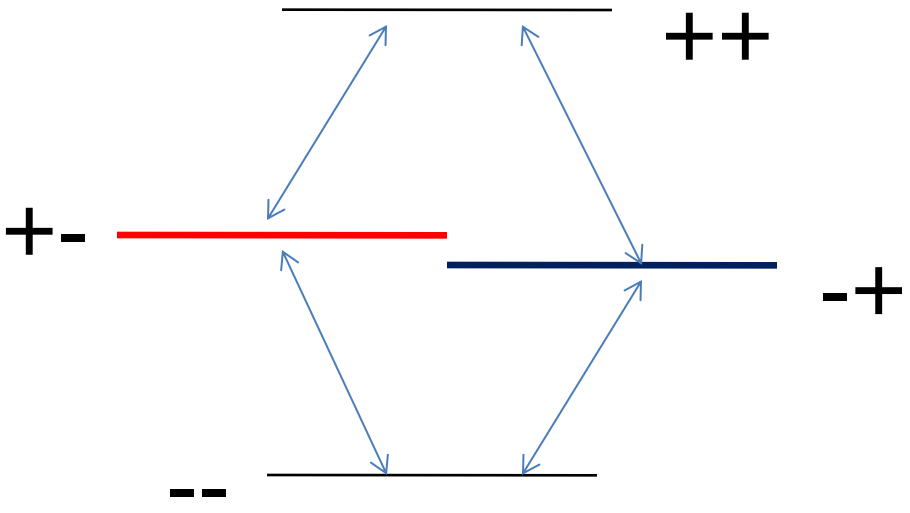
Usual in-phase electron spin echo in rotating frame

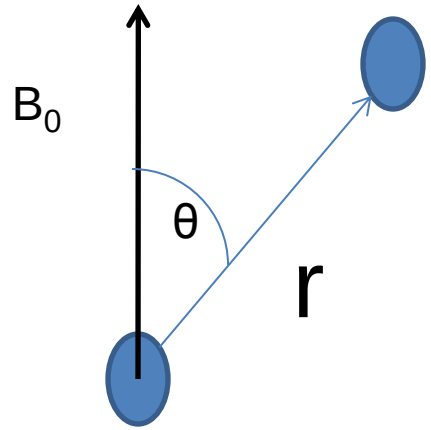


$$B_{eff} = (B_1, 0, B_0 - \omega_0/\gamma)$$

Observed in isolated radicals (S = 1/2) with any spin polarization, thermalized radical pairs, triplets, higher spin systems

Spin-correlated radical pair





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

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

Dipolar splitting *d*

Out-of-phase electron spin echo

Observed in spin-correlated radical pairs.

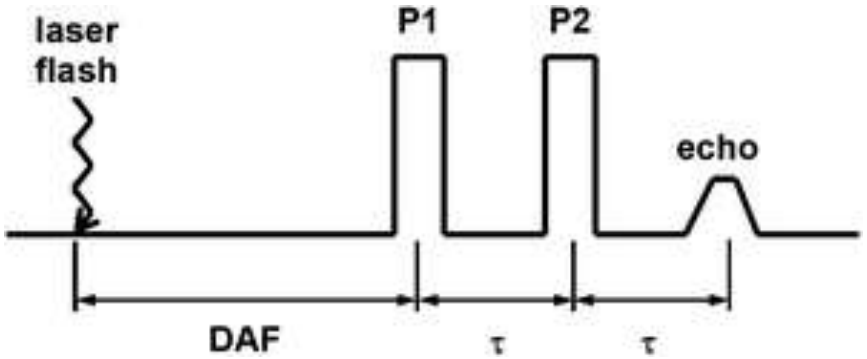
Can be detected only if:

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.

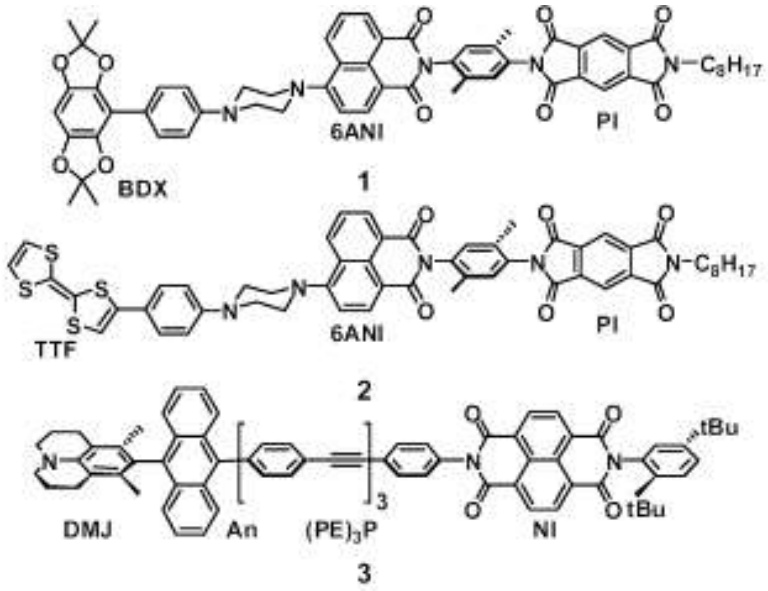
Optimal pulse turning angles: $\pi/4 - \tau - \pi$

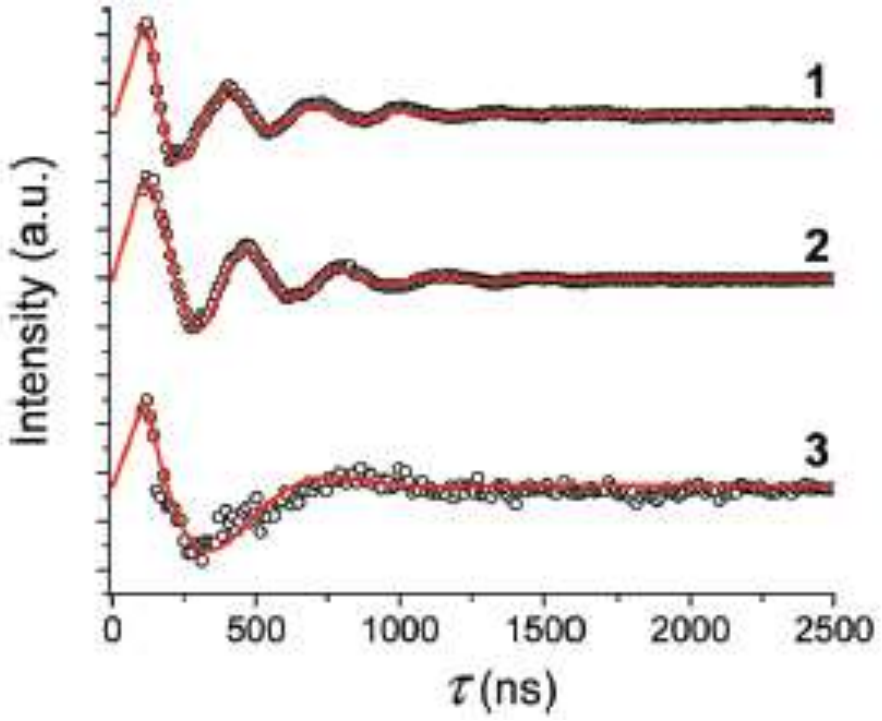
Dependence on τ: $M_X \sim \sin(d\tau)$ $\quad d = \gamma^2/r^3\,(1 - 3\cos^2\theta)/2$

Out-of-phase ESE: examples



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





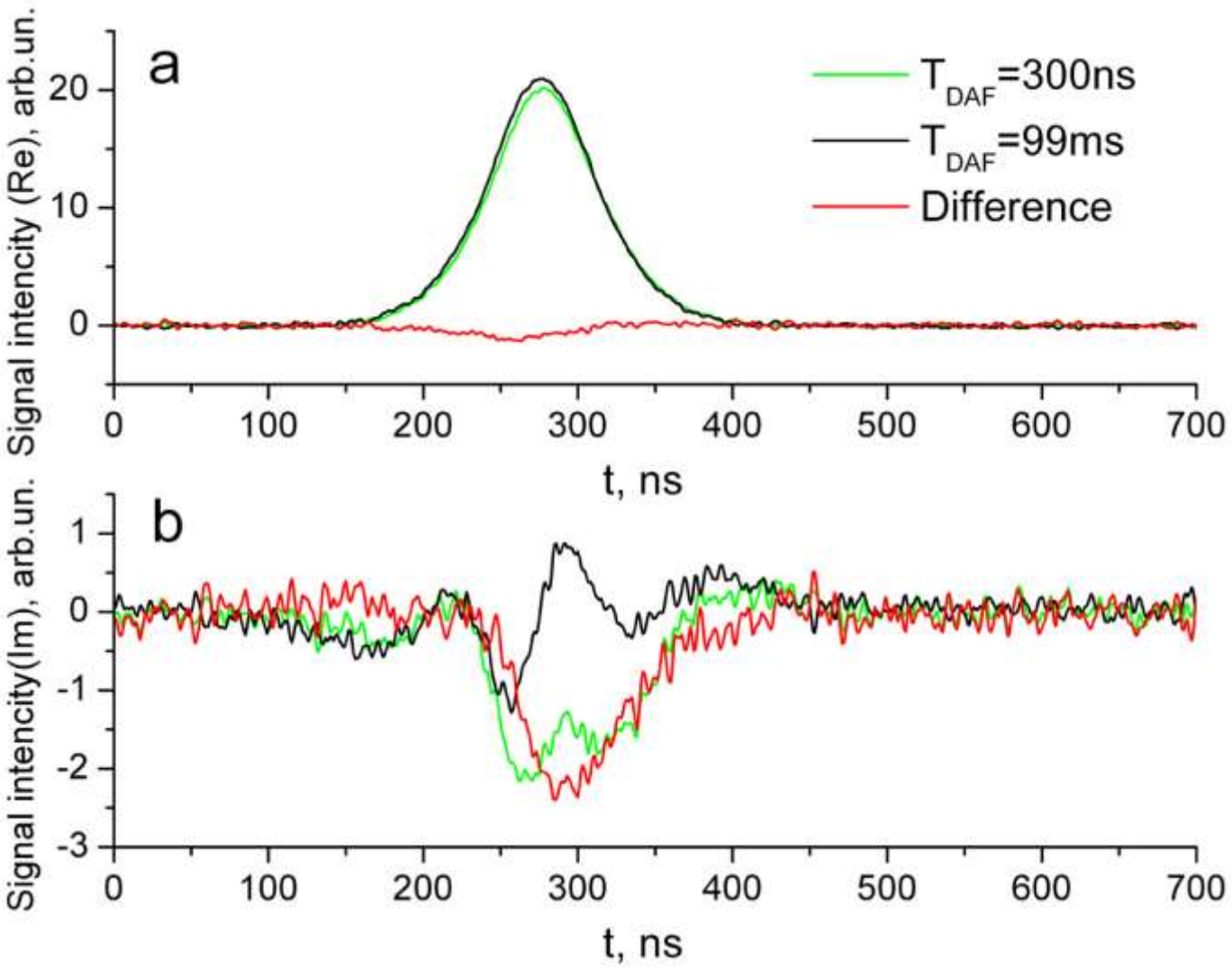
Interspin distances in nanometer range can be determined with angstrom precision!

P3HT/PC70BM composite sample preparation

Prepare 400 ml toluene solution
of P3HT and PC70BM (0,5 mg each)

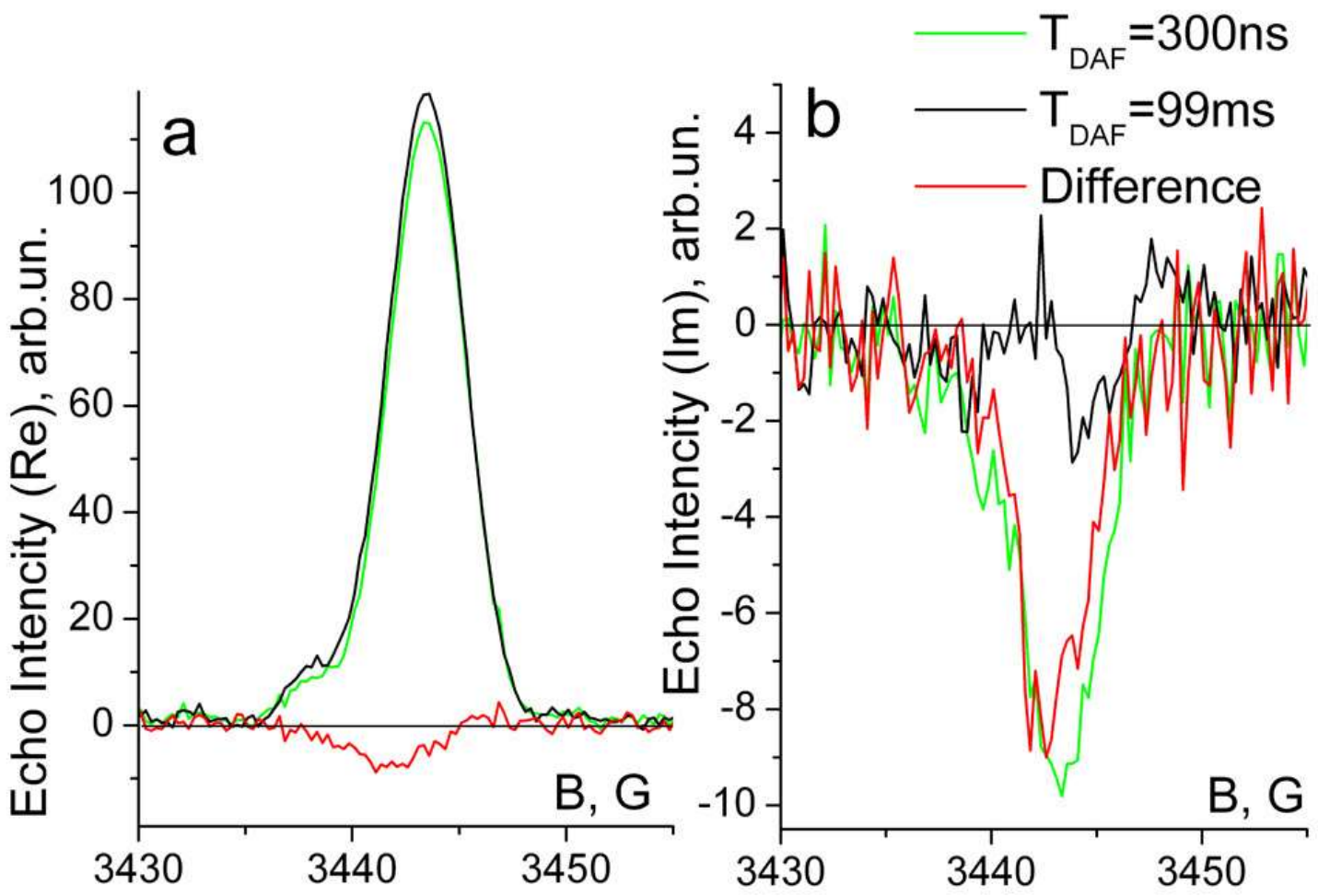
put the solution was into quartz tube,
evaporate toluene ,
the blend with thickness ~ 1 mkm
should be annealed at 150°C
under vacuum of ~ 0.1 torr.

Time domain echo shape of P3HT/$PC_{70}BM$ composite



65 K

Pulse EPR experiments on P3HT/PC70BM composite

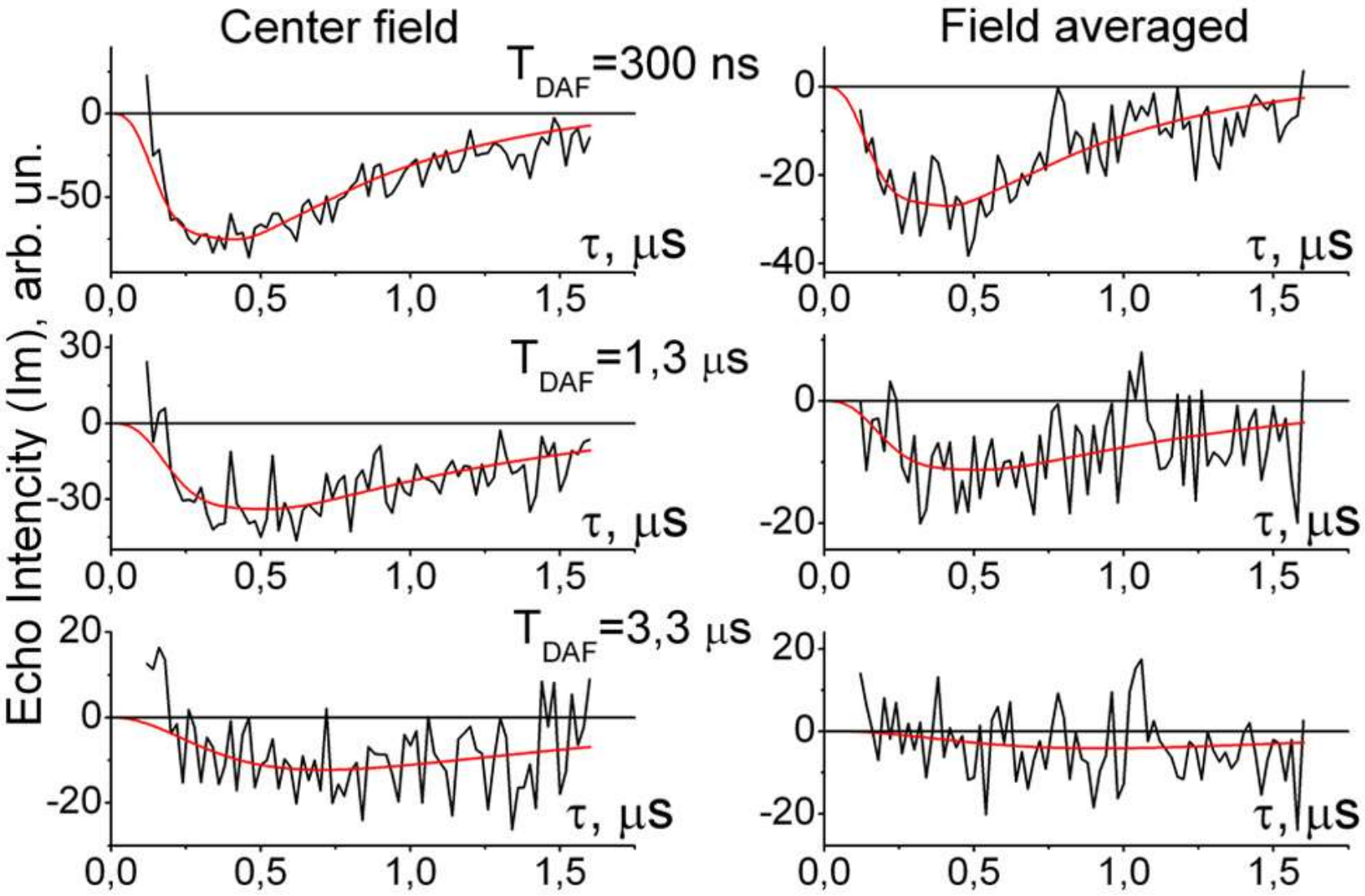


Flash – DAF - π/4 – τ – π – τ – echo

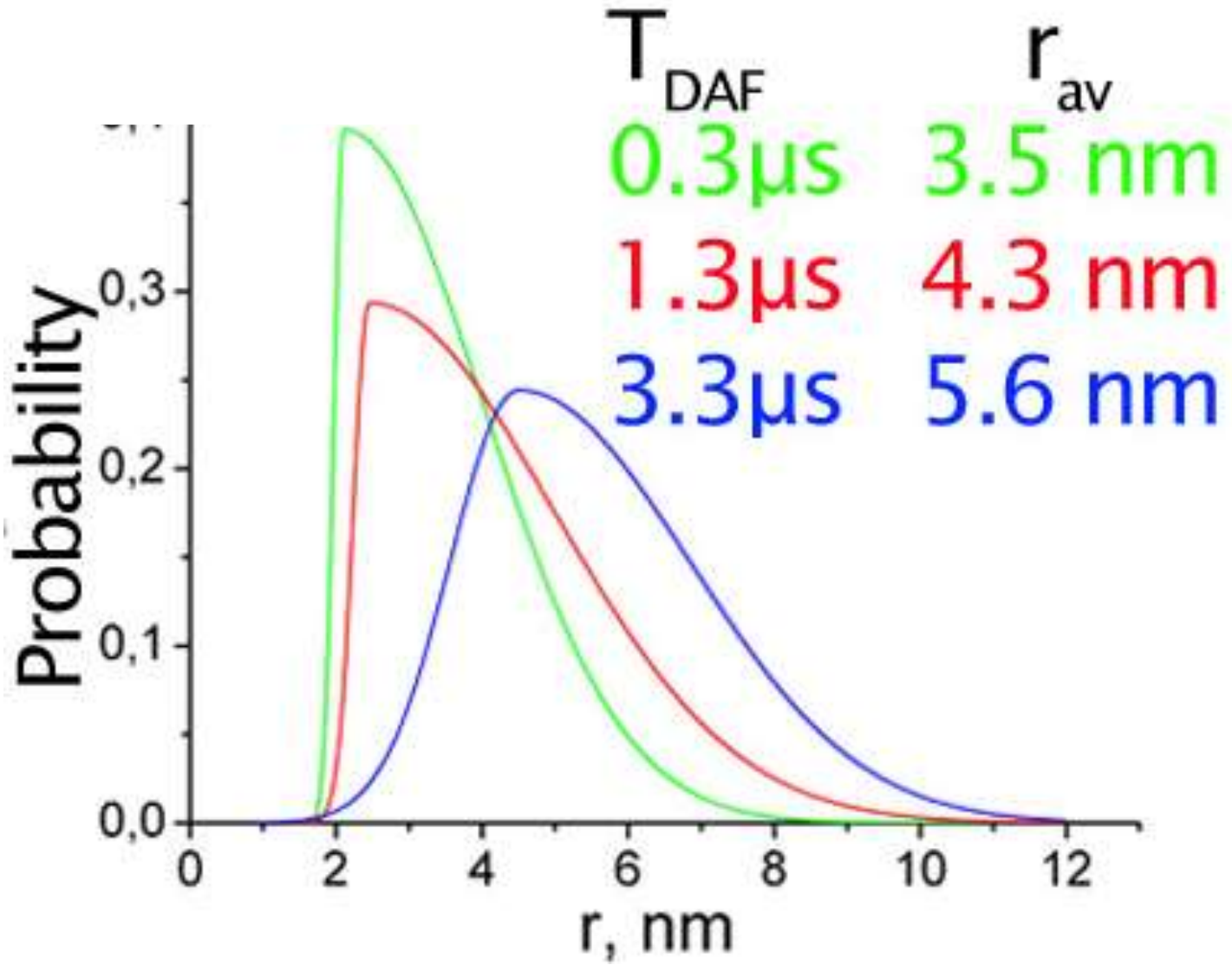
τ=340ns , λ = 532 nm

T = 65K

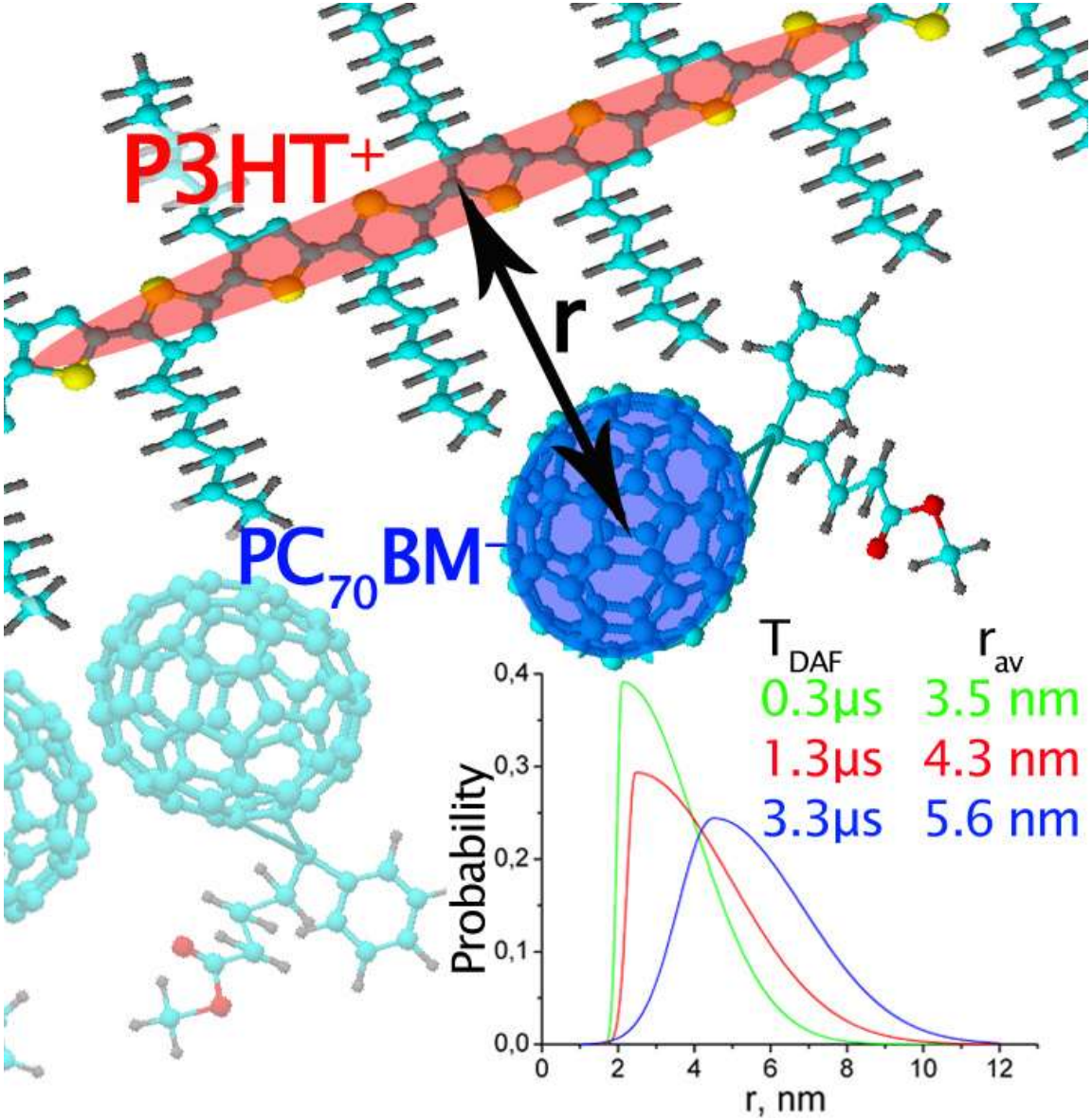
Out-of-phase ESE decay



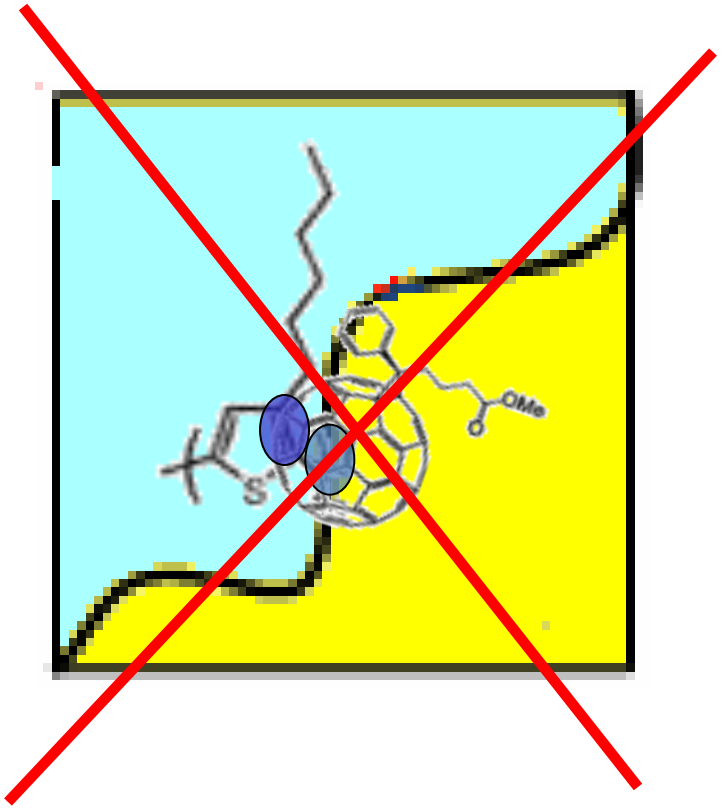
Interspin distance distribution in CT state

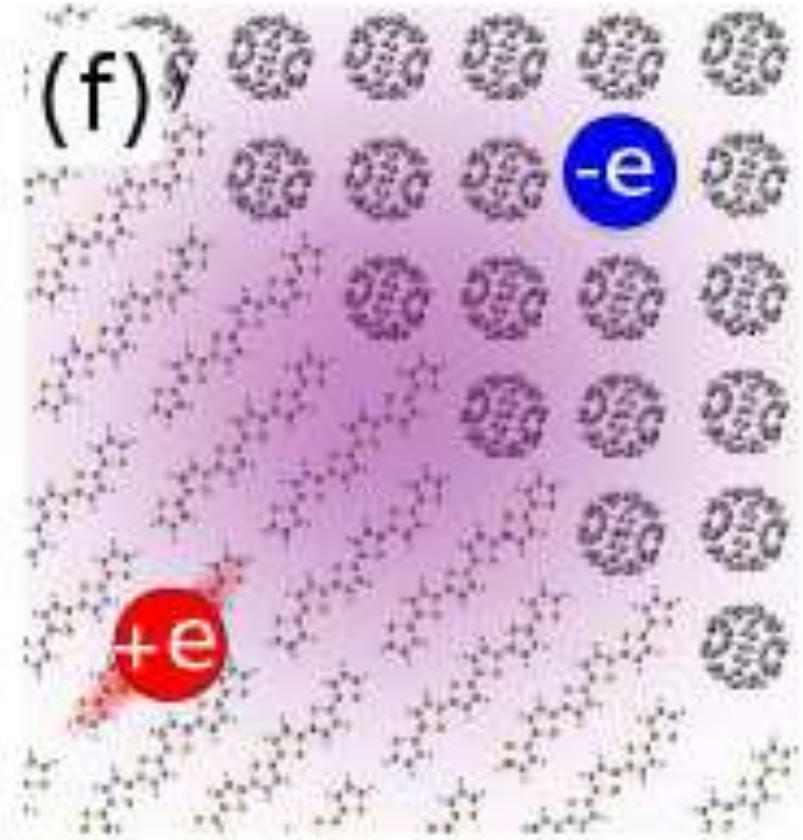


Evolution of interspin distance distribution with DAF increase



Initial distance of charge separation in polymer/fullerene composite is not that small!





Conclusions

Light-induced charge-transfer state in P3HT/PCBM composite is spin-correlated radical pair.

Out-of-phase electron spin echo is the method of choice for study the structure of charge-transfer state in polymer/fullerene composites and the mechanism of charge separation.

From numerical simulation of the ESE evolution for singlet radical pair $P3HT^{+}/PC_{70}BM^{-}$ the distribution of the distance between the radicals in charge-transfer state is obtained at 65K.

The evolution of charge-transfer state is determined by two simultaneous processes: diffusion of the radicals from the polymer/fullerene interface and geminate recombination of radical pairs with small distances between radicals.

Acknowledgements

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Thank you for your attention!


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Key Dates & Information

Registration – June 30
Abstracts – June 30 (Oral); July 31 (Posters)

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