Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Spin dynamics of light-induced charge separation in composites of semiconducting polymers and $PC_{60}BM$ revealed by Q-band pulse EPR

E. A. Lukina[1,2], E. Suturina[3], E. Reijerse[4], W. Lubitz[4], L. V. Kulik[1,2*]

[1] Voevodsky Institute of Chemical Kinetics and Combustion of Siberian Branch of Russian Academy of Sciences, Institutskaya 3, 630090 Novosibirsk, Russia

[2] Novosibirsk State University, Pirogova 2, 630090 Novosibirsk, Russia

[3] School of Chemistry, University of Southampton, Highfield Campus, Southampton, UK

[4] Max Planck Institute for Chemical Energy Conversion, Stiftst. 34-36, D-45470 Muelheim an der Ruhr, Germany

Supporting Information

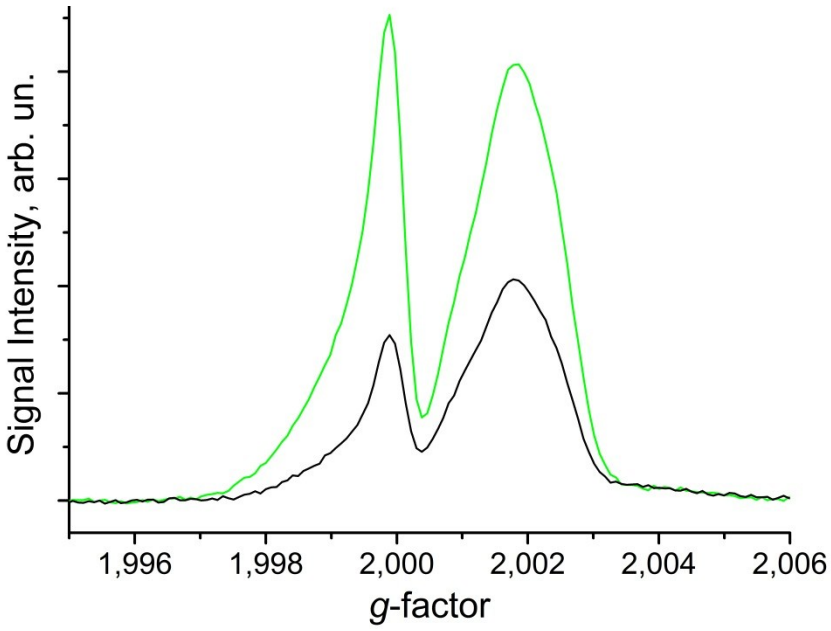

Figure S1. ED EPR spectrum measured in the dark (black line) and under continuous laser

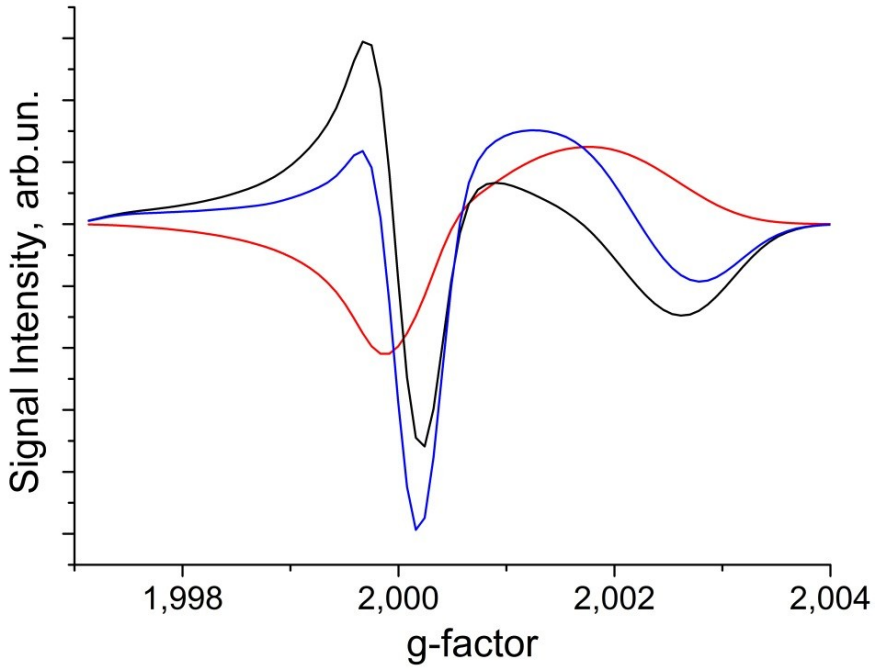

Figure S2. Simulated echo-detected EPR spectra used to mimic extraction of RR-P3HT$^{\bullet+}$/$PC_{60}BM^{\bullet-}$ SCPP signal. The black line shows a spectrum simulated with π/2-τ-π microwave pulse sequence multiplied by $1/2\sqrt{2}$, the blue line corresponds to the spectrum simulated with π/4-τ-π/2 microwave pulse sequence. The simulated extracted spectrum of SCPP (red line) was determined as their difference (see the main text). The simulation was done using parameters of radical species summarized in Table 1 of the main text, dipolar interaction of 5 MHz and exchange interaction of 3 MHz.

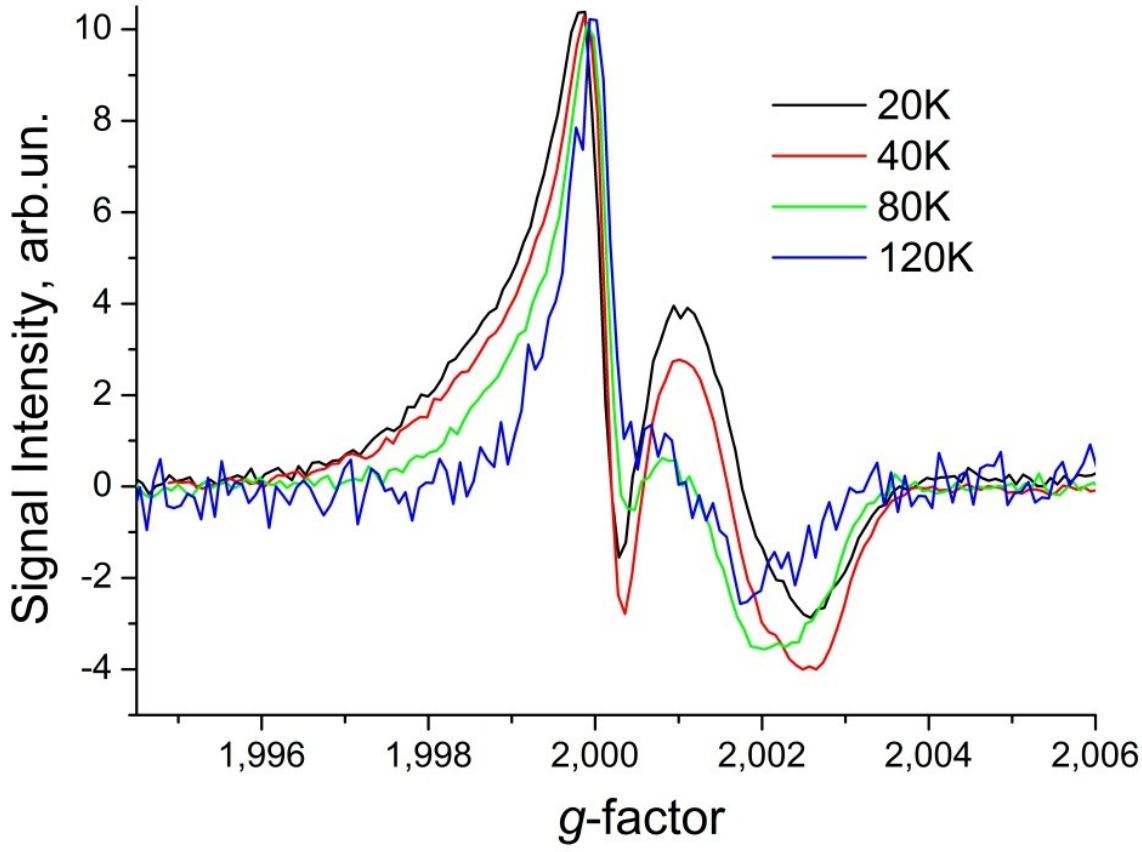

Figure S3. In-phase echo detected flash-induced EPR spectra of RR-P3HT/PC_{60}BM measured at different temperatures. The two-pulse microwave sequence with selective pulses and $\tau = 400$ ns was used for detection. The signal intensity was scaled to the fullerene peak ($g \approx 1.9998$).

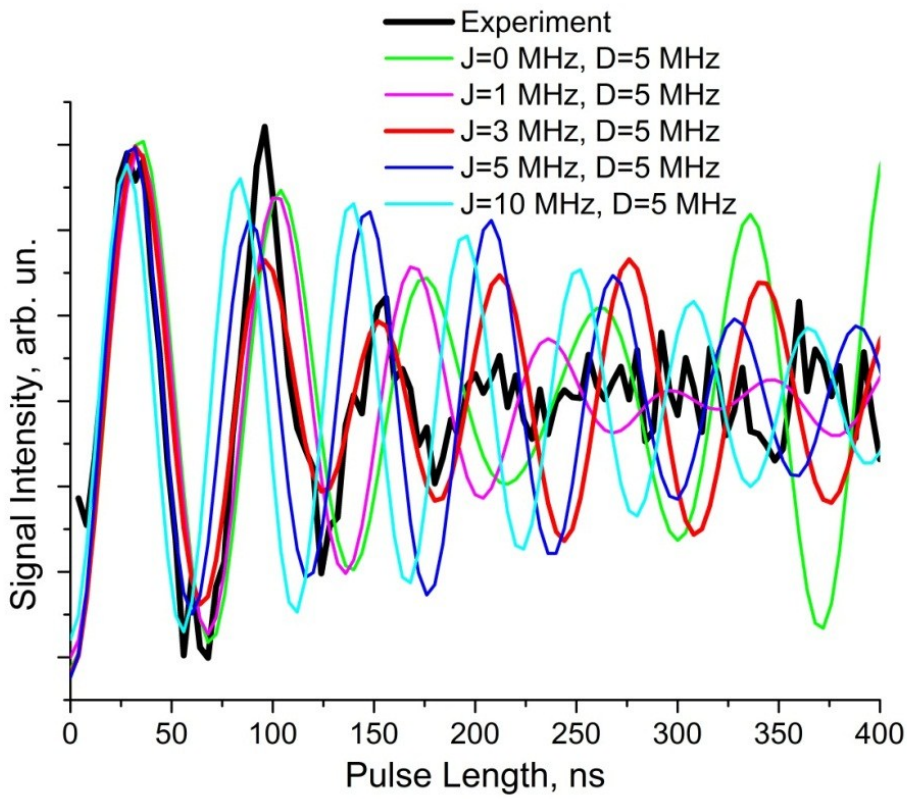

Figure S4. Nutation curves for the SCPP P3HT$^{\bullet+}$/$PC_{60}BM^{\bullet-}$ (pulse sequence 3 and protocol for extracting the SCPP contribution in the main text). The black line shows the experimental nutation of the SCPP signal measured at g = 2.00105 , the other lines show simulated curves calculated using parameters of radical species summarized in Table 1, dipolar interaction 5 MHz and various values of exchange interaction.

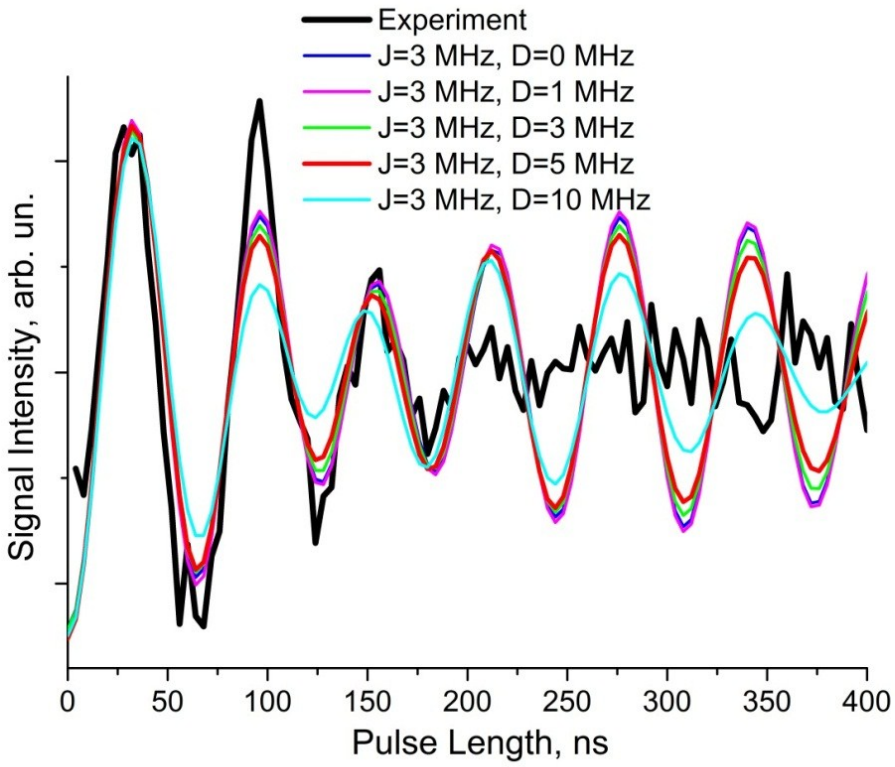

Figure S5. Nutation curves for the SCPP P3HT$^{\bullet+}$/$PC_{60}BM^{\bullet-}$ (pulse sequence 3 and protocol for extracting the SCPP contribution in the main text). The black line shows the experimental nutation of the SCPP signal measured at g = 2.00105 , the other lines show simulated curves calculated using parameters of radical species summarized in Table 1, exchange interaction 3 MHz and various values of dipolar interaction.

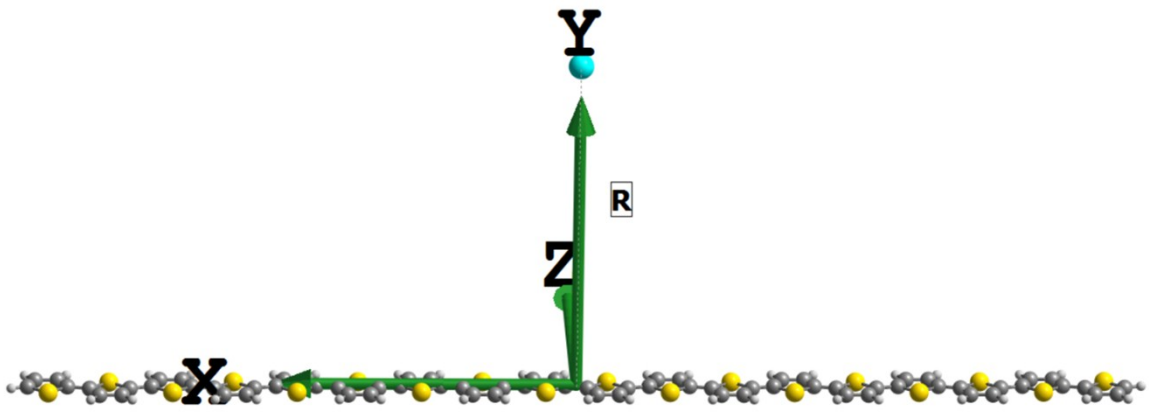

Figure S6. Model system of the positively charged 18 member oligothiophene chain and a negative point charge placed on top of the XZ plane of the molecule at a given distance. *R* is the distance between the point charge and the center of polythiophene molecule.

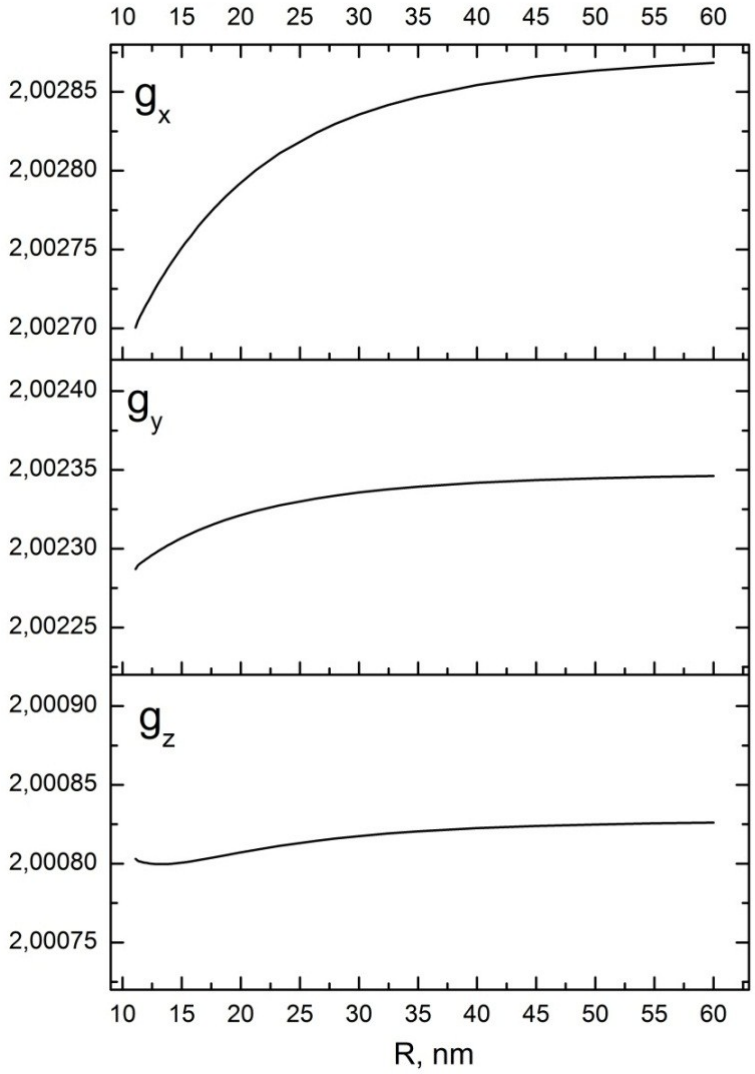

Figure S7. *g*-factors of the positively charged 18 members oligothiophene cation-radical (Fig. S6) as a function of the distance to a negative point charge computed by TPSSh/def2-SVP. The smallest value g_z corresponds to the direction along the chain, the medium value g_y corresponds to the out-of-plane direction, and the largest value g_x corresponds to the in-plane direction of the oligothiophene molecule.

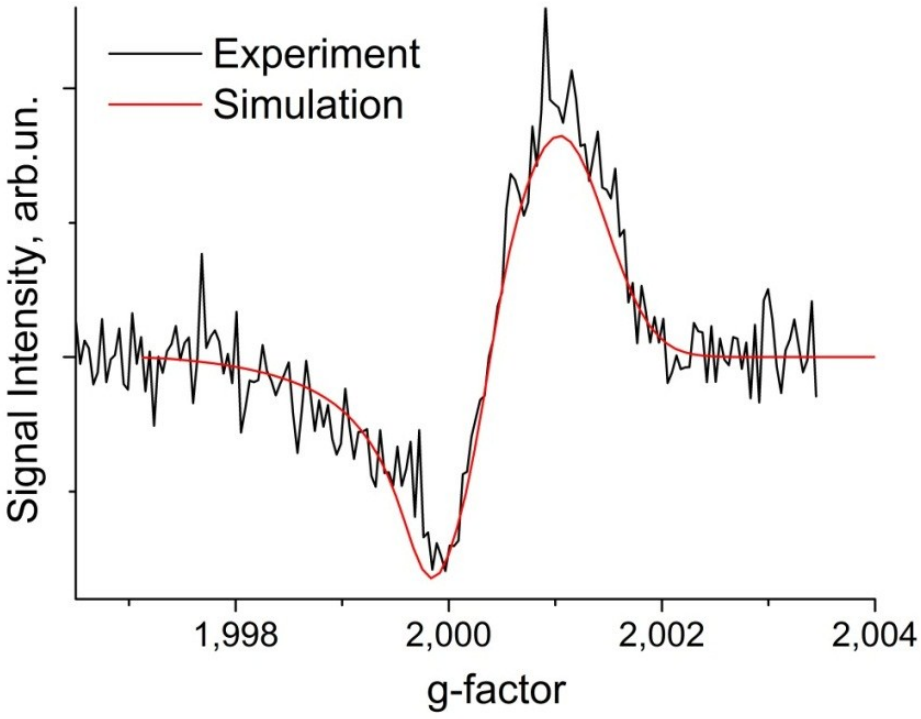

Figure S8. In-phase echo-detected EPR spectrum of the SCPP extracted for RR-P3HT/$PC_{60}BM$ at T_{DAF}=300ns (black line). The red line shows the simulation done using $g_{RR\text{-}P3HT}{}^{\bullet}$+=[2.0012 2.0010 2.0009], the other parameters of polaron species summarized in Table 1 of the main text, dipolar interaction of 5 MHz, exchange interaction of 3 MHz.