Supplementary Material

DFT and EPR study of spin-assisted processes in poly(3-alkylthiophene) oligomers and their composites

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Table S-1. Band parameters, HOMO, LUMO, and E_g (all in eV) calculated for polyacene (PA), triphenyle (TP), and polycyclic aromatic hydrocarbon (PH) additives in the absence of an external magnetic field.

Additive	HOMO	LUMO	*E*g
PA1	-6.911	-0.117	6.794
PA2	-5.828	-1.224	4.604
PA3	-5.207	-1.905	3.302
PA4	-4.816	-2.337	2.480
PA5	-4.555	-2.627	1.928
PA6	-4.372	-2.830	1.542
PA7	-4.239	-2.979	1.261
PA8	-4.140	-3.089	1.051
PA9	-4.064	-3.174	0.890
PA10	-4.006	-3.240	0.765
TP4	-6.007	-1.299	4.708
TP7	-5.458	-2.106	3.353
TP10	-4.924	-2.602	2.322
TP13	-4.608	-2.902	1.706
PH5	-4.908	-2.213	2.695
PH6	-4.866	-2.268	2.598
PH7	-5.546	-1.551	3.996
PH8	-4.359	-2.808	1.550
PH9	-4.665	-2.508	2.157
PH10	-4.965	-2.198	2.767

Additive	HOMO	LUMO	*E*g
PH11	-4.860	-2.312	2.548
PH12	-4.330	-2.899	1.431
PH13	-4.591	-2.638	1.954
PH14	-4.781	-2.427	2.354
PH15	-4.161	-3.099	1.061
PH16	-4.153	-3.138	1.015
PH17	-4.787	-2.420	2.367
PH18	-4.892	-2.338	2.554
PH19	-4.993	-2.255	2.738
PH20	-4.038	-3.293	0.745
PH21	-3.978	-3.325	0.652
PH22	-3.950	-3.366	0.584
PH23	-4.332	-2.975	1.357
PH24	-3.947	-3.399	0.548
PH25	-3.954	-3.410	0.544
PH26	-3.891	-3.455	0.435
PH27	-3.888	-3.468	0.421
PH28	-3.887	-3.478	0.408
PH29	-3.893	-3.485	0.408
PH30	-3.900	-3.492	0.408

Note: The index of additives means a number of phenyl circles *n* (see Fig. 1).

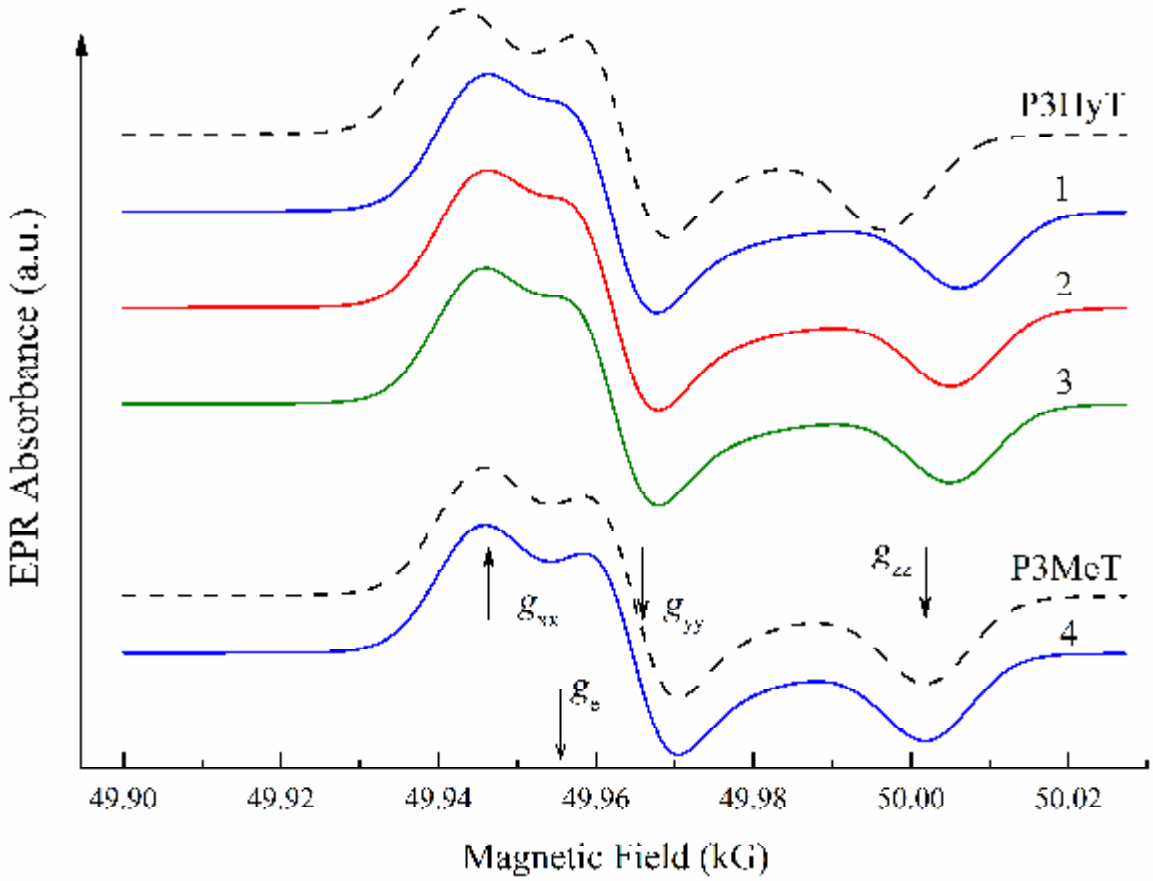
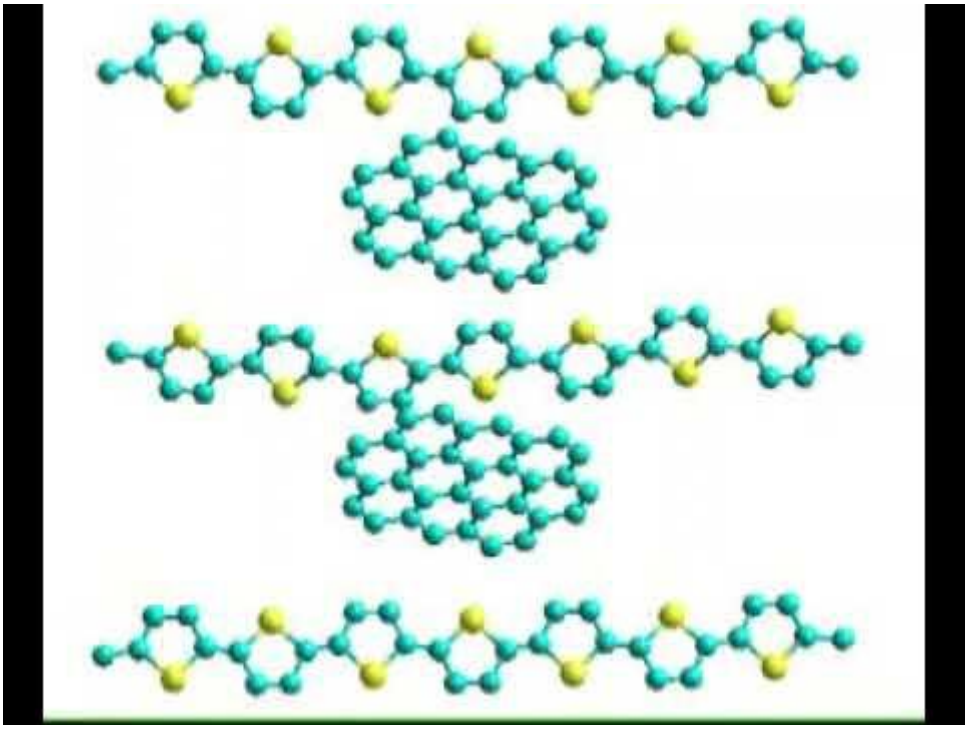


Fig. S-1. D-Band EPR spectra calculated by the EasySpin program packet for polarons initiated in the P3HyT, P3HyT:PA1 (1), P3HyT:PA2 (2), P3HyT:PA3 (3), P3MeT, and P3MeT:PA1 (4) systems by using their resonant parameters summarized in Table S-2 according the procedure described in the Methodical section.

Table S-2. The main and averaged/isotropic values of spin-spin hyperfine coupling constants A_i (all in MHz) and ***g***-tensors calculated for some initial oxidized P3HyT and P3MeT oligo7mers complexed with different polyacenes PA using the Orca software package according the procedure described in the Methodical section.

Complex	A_x	A_y	A_z	A_{iso}	g_{xx}	g_{yy}	g_{zz}	g_{iso}
P3HyT	1.168	-0.743	-1.021	-0.199	2.002857	2.001999	2.000651	2.001836
P3HyT:PA1	1.244	-0.411	-0.822	0.004	2.002746	2.002058	2.000272	2.001692
P3HyT:PA2	1.186	-0.333	-0.629	0.075	2.002745	2.002050	2.000318	2.001705
P3HyT:PA3	1.164	-0.371	-0.689	0.035	2.002756	2.002049	2.000320	2.001708
P3MeT	1.953	1.566	2.320	1.946	2.002946	2.001946	2.000947	2.001946
P3MeT:PA1	1.293	0.827	0.897	1.005	2.002747	2.001948	2.000445	2.001713



Movie M-1. Self-assembly crystallization/structurization of exemplary P3HyT:PH10 complex due to spin-assisted intermolecular π-π-coupling.