Electronic Supplementary Information for the manuscript:

Dark ESR spectroscopy for monitoring photochemical and thermal degradation of conjugated polymers used as electron donor materials in organic bulk heterojunction solar cells

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Contents

1. Experimental Procedure

The samples for investigation of photochemical and thermal stability of conjugated polymers were prepared as follows. A weighted portion of conjugated polymer (5-10 mg), cholorobenzene purified by distillation (1.0 mL) and small PTFE-coated magnetic stirrer were placed inside a dark 2 mL glass vial in argon glove box. The solutions were stirred at ca. 50 ^{o}C for 4-5 days until the polymer was completely dissolved. Afterwards, a small portion of the solution (100-200 μL) was introduced into ESR sample tube (operation performed in air with protection from direct light) with a known weight. This sample tube was immediately connected to a vacuum line to remove the solvent under reduced pressure (10^{-1} mbar). Gentle shaking was applied during the solvent evaporation to achieve homogeneous coating of the internal walls with thin polymer film. The resulting films were transferred immediately to argon glove box and dried in high vacuum (10^{-6} mbar) to ensure removal of trace amounts of solvent and absorbed reactive species (oxygen, moisture). The weight of the test tubes with the polymer films was determined with a high accuracy. Then the tubes were closed with plastic stoppers, taken outside and connected to a vacuum/helium line. Multiple successive evacuation (10^{-3} mbar) and filling the tubes with helium provided clean anaerobic atmosphere. The tubes were sealed while being connected to a helium line.

The setup for investigation of photodegradation of conjugated polymers comprised a rotating sample holder and three 150 W halogen lamps arranged at equal distances from the holder inside a 100 L chamber. Rotation of the holder provided equal illumination conditions for all polymer samples. The power of the light flux at the sample holder was about 60 mW/cm^2, the temperature in the sample chamber was 82-85 ^{o}C. All samples were continuously illuminated with except for a time when they were subjected to the ESR measurements. The ESR spectra were recorded using CMS8400 spectrometer (produced in Belorussia, 2012). Integration of the signals observed in the ESR spectra was performed using EPR4K software developed by National Institute of Enviromental Health Science (NIEHS). The concentration of the radical species was expressed as a number of spins per one repeating unit (r.u.) in the polymer chain.

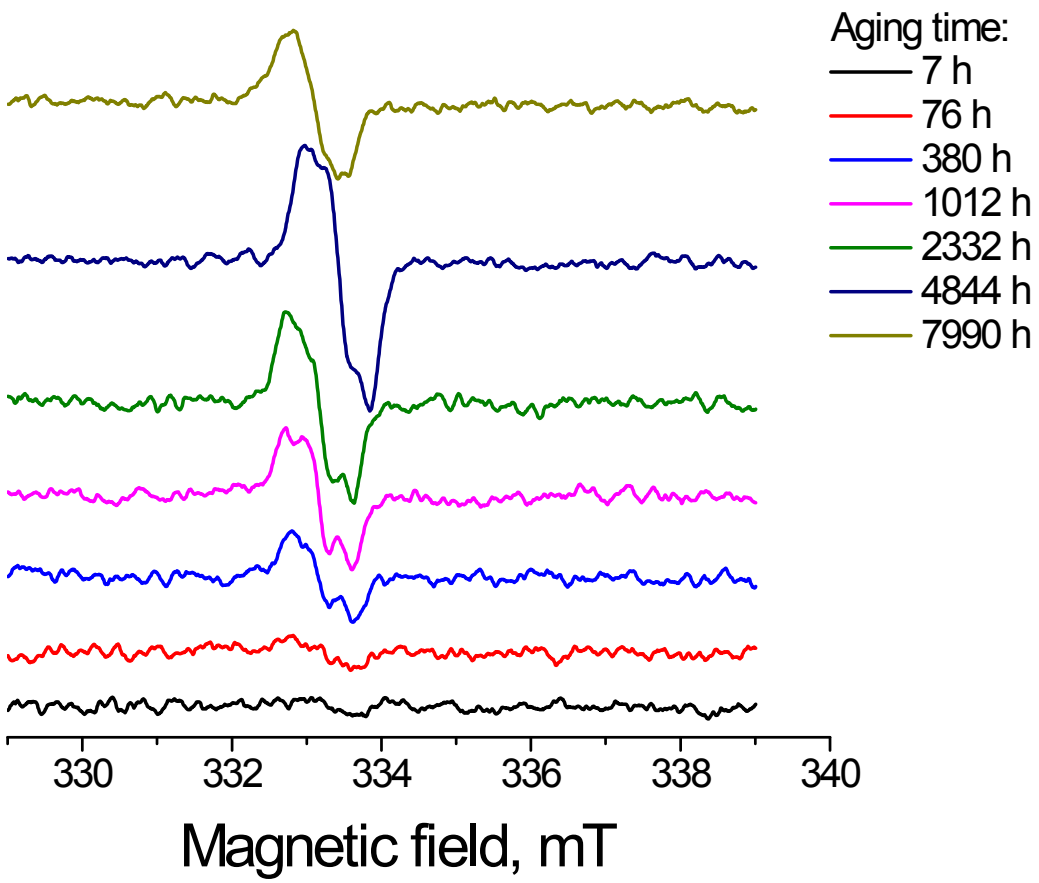

Figure S1. Evolution of the ESR spectra of PBDTTT-CF sample in the course of photothermal aging

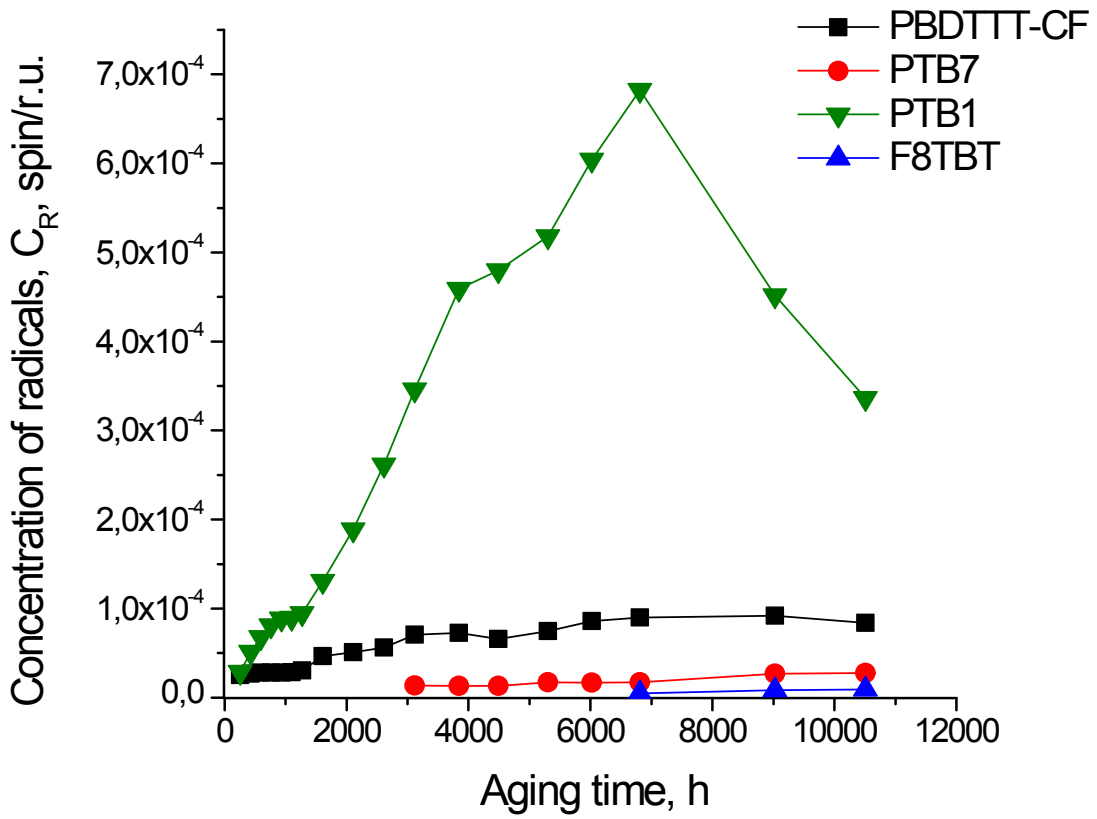

Figure S2. Heat-induced degradation profiles of different conjugated polymers obtained using ESR spectroscopy. The concentration of the radical species is expressed as a number of spins per one repeating unit (r.u.) in a polymer chain.

Table S1. Some quantitative characteristics estimated from the photothermal and thermal degradation profiles obtained for different conjugated polymers using ESR spectroscopy

Polymer	Photothermal degradation				Thermal degradation			
	R_{in},x10^8 spin/r.u.·h^{-1}	T(max), h	C_R(max)x10^4 spin/r.u.	R_{av},x10^8 spin/r.u.·h^{-1}	R_{in},x10^8 spin/r.u.·h^{-1}	T(max), h	C_R(max)x10^4 spin/r.u.	R_{av},x10^8 spin/r.u.·h^{-1}
PCDTBT	2.32	9132	0.67	0.73	-*	-	-	-
P3HT	2.78	9132	1.05	1.15	-	-	-	-
SiPCPDTBT	3.48	3994	1.36	3.40	-	-	-	-
F8TBT	5.92	3994	1.75	4.39	0.12	10512	0.09	0.09
PBDTTT-CF	7.69	3308	1.73	5.23	1.61	3840	0.72	1.89
PTB7	8.71	3308	2.27	6.86	0.22	10512	0.28	0.26
PTB1	32.15	1972	3.08	15.60	11.45	6814	6.82	10.01

* Symbol "-" means that no thermal degradation was revealed for a polymer