Electronic supplementary information

ESR spectroscopy as a powerful tool for probing the quality of conjugated polymers designed for photovoltaic applications

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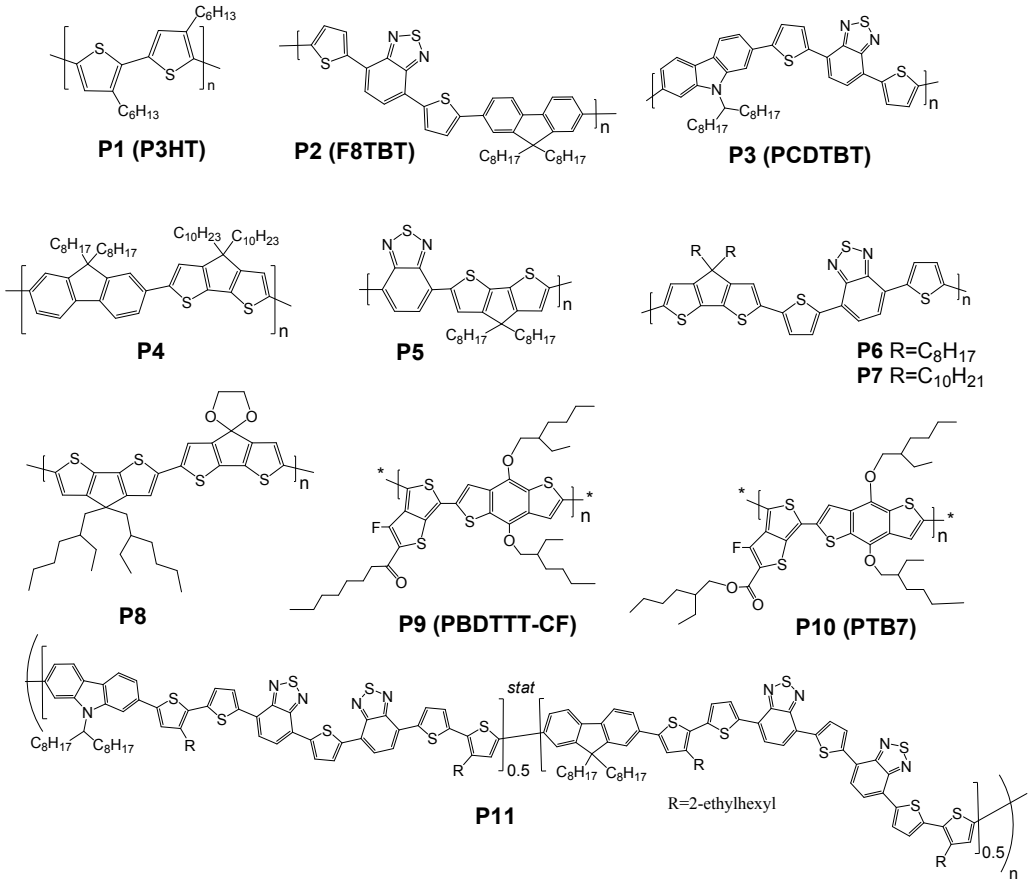

Figure S1. Molecular structures of the investigated polymers

1. Synthesis of conjugated polymers and their characteristics.

The P3HT batches investigated in this work were obtained from commercial sources such as Rieke Metals (12 batches), Aldrich (2 batches) and Merck (5 batches). PBDTTT-CF and PTB7 were obtained from Solarmer Energy and One Material, respectively. All other conjugated polymers were synthesized using Suzuki-Miyamura polycondensation reaction according to the following general procedure.

Monomers **I** (657.6 mg) and **II** (1063 mg) were introduced into a 50 mL round-bottom three necked flask equiped with a thermometer and reversed condenser. Toluene (25 mL), 2M aqueous solution of K_2CO_3 (2 mL), aliquat 336 (1 drop, ca. 80 mg) and tetrakis(triphenylphosphine)palladium(0) (10 mg) were added in the listed here sequence. The reaction mixture was deaerated, immersed into an oil bath and heated at reflux for 3-6 hours. The molecular weight characteristics of the formed product were controlled every 30 min. The reaction was stopped when the weight average molecular weight M_w reached ca. 150000 g/mol or did not show further increase within 3-4 hrs. To terminate the reaction, we introduced 0.1 mmol of phenylboronic acid, heated the mixture at reflux for additional 1 h and then introduced 2 mmol of bromobenzene and continued the heating for additional 2 h. Afterwards, the reaction mixture was cooled down to room temperature, the polymer was extracted with 500 mL of toluene, the resulting solution was washed 3 times with deionized water (250 mL), dried and concentrated in vacuum (rotary evaporator) to 40 mL. Addition of 150 mL of methanol precipitated the crude polymer. Subsequent purification was achieved using several additional dissolving/precipitation cycles. Finally, the precipitated polymer flakes were filtered to the cellulose thimble and processed using Soxhlet extraction with hexanes (12 h), acetone (12 h), dichloromethane (12 h), chloroform (8 h) and chlorobenzene (12 h). The chlorobenzene extract was concentrated in vacuum and precipitated in methanol. The obtained solid was collected by filtration and dried in vacuum. The resulting crude polymer was further purified from the residual Pd catalyst as described in K. T. Nielsen, K. Bechgaard, F. C. Krebs, *Macromolecules* **2005,** *38,* 658-659 and K.T. Nielsen, K. Bechgaard, F.C. Krebs, *Synthesis* **2006**, 10, 1639-1644. The total yield of the purified polymers varied between 50 and 90% depending on the initial molecular weight and number of the applied dissolving/precipitation cycles. All prepared polymer samples were transferred immediately inside argon glove box where they were stored in the absence of direct light.

2. General procedure used for analysis of the polymer samples by ESR

A portion of the polymer (10-20 mg) was introduced inside the ESR tube of a known weight. The tube was closed inside an argon glove box and then taken outside for the measurements. The measurements of each sample were performed in parallel on two instruments: CMS8400 spectrometer (produced in Belorussia, 2012) and Radiopan SE/X 2544 instrument (Poland). Before the measurements, the reference sample containing ca. 0.05 mg of $CuSO_4*5H_2O$ was measured on each instrument. Afterwards, the ESR spectra of each polymer sample were obtained on both instruments inside a dark room. Typically, the measurements were performed with gain values of ca. 10^3, sweep time was ca. 50-60 s, number of averaged spectra (number of passes) was equal to 10. Finally, the obtained spectra were treated using EPR4K software form National Institute of Enviromental Health Science (NIEHS). Concentrations of the radical species in the reference sample and some of the analyzed samples were additionally cross-checked using X-band ESR spectrometer ELEXSYS-II E500 (Bruker, Germany, 2013). The obtained results were in a full agreement with the data provided by the CMS8400 and Radiopan SE/X 2544 instruments.

Table S1. Characteristics of the investigated samples of conjugated polymers

#	*Sample*	*Mw*	M_w/M_n	C_R *(spin/g)*	*Fullerene component*	V_{OC}, *mV*	J_{SC}, *mA/cm²*	*FF, %*	η_{exp}, *%*	η_{max}, *%*	*Ref. for* η_{max}
1	**P1-1**	n/a	n/a	1.64E+16	[60]PCBM	623	10.05	60	3.8	4.0	Exp. [1] and this work
2	**P1-2**	n/a	n/a	1.01E+16	[60]PCBM	598	10.13	59	3.6	4.0	
3	**P1-3**	n/a	n/a	7.83E+15	[60]PCBM	626	10.51	59	3.9	4.0	
4	**P1-4**	n/a	n/a	9.18E+15	[60]PCBM	580	10.52	58	3.5	4.0	
5	**P1-5**	n/a	n/a	7.65E+15	[60]PCBM	654	10.20	58	3.9	4.0	
6	**P1-6**	n/a	n/a	8.05E+15	[60]PCBM	629	10.95	57	3.9	4.0	
7	**P1-7**	n/a	n/a	1.15E+16	[60]PCBM	587	11.13	58	3.8	4.0	
8	**P1-8**	n/a	n/a	4.53E+16	[60]PCBM	627	9.30	58	3.4	4.0	
9	**P1-9**	n/a	n/a	1.44E+16	[60]PCBM	621	10.68	61	4.0	4.0	
10	**P1-10**	n/a	n/a	7.54E+15	[60]PCBM	605	11.04	59	3.9	4.0	
11	**P1-11**	n/a	n/a	8.34E+17	[60]PCBM	570	7.24	57	2.3	4.0	
12	**P1-12**	n/a	n/a	1.51E+16	[60]PCBM	604	10.60	59	3.8	4.0	
13	**P1-13**	n/a	n/a	1.76E+17	[60]PCBM	540	10.00	63	3.4	4.0	
14	**P1-14**	n/a	n/a	2.17E+17	[60]PCBM	541	9.44	64	3.3	4.0	

#	*Sample*	*Mw*	M_w/M_n	C_R *(spin/g)*	*Fullerene component*	V_{OC}, *mV*	J_{SC}, *mA/cm²*	*FF, %*	η_{exp}, *%*	η_{max}, *%*	*Ref. for* η_{max}
15	**P1-15**	n/a	n/a	2.86E+17	[60]PCBM	566	8.67	64	3.2	4.0	
16	**P1-16**	n/a	n/a	4.24E+17	[60]PCBM	532	8.79	62	2.9	4.0	
17	**P1-17**	n/a	n/a	5.58E+17	[60]PCBM	555	8.24	59	2.7	4.0	
18	**P1-18**	n/a	n/a	6.27E+17	[60]PCBM	557	8.28	61	2.8	4.0	
19	**P1-19**	n/a	n/a	6.71E+17	[60]PCBM	543	8.24	60	2.7	4.0	
20	**P2-1**	12860	1.96	5.28E+16	[60]PCBM	760	5.0	47	1.8	4.0	Exp. [2]
21	**P2-2**	6250	1.18	1.56E+16	[60]PCBM	900	8.65	40	3.1	4.0	
22	**P2-3**	15700	1.68	1.01E+16	[60]PCBM	860	8.98	43	3.3	4.0	
23	**P2-4**	14830	1.48	2.30E+16	[60]PCBM	885	8.28	45	3.3	4.0	
24	**P2-5**	15570	1.76	2.71E+16	[60]PCBM	833	7.24	43	2.6	4.0	
25	**P3-1**	27200	7	1.73E+16	[60]PCBM	828	8.56	49	3.5	5.0	Exp., this work
26	**P3-2**	52300	6	1.26E+16	[60]PCBM	864	8.95	59	4.6	5.0	
27	**P3-3**	55500	4.4	1.30E+16	[60]PCBM	810	8.7	55	3.9	5.0	
28	**P3-4**	56360	3.9	3.50E+16	[60]PCBM	731	3.10	32	0.72	5.0	
29	**P3-5**	12441	2.1	2.82E+16	[60]PCBM	805	6.73	46	2.5	5.0	
30	**P3-6**	230000	3.0	1.07E+16	[70]PCBM	784	12.4	58	5.7	6.5	Exp., this work
31	**P3-7**	299000	2.2	3.19E+15	[70]PCBM	836	11.9	60	6.0	6.5	
32	**P3-8**	310000	3.6	9.74E+14	[70]PCBM	862	12.0	63	6.5	6.5	
33	**P3-9**	317000	3.4	3.54E+15	[70]PCBM	820	12.5	62	6.3	6.5	
34	**P4**	13540	1.85	2.69E+16	[60]PCBM	760	4.48	44	1.5	2.8	Theor. estim. following [3]
35	**P5-1**	12500	2.0	6.79E+16	[60]PCBM	600	4.80	34	1.0	2.7	Exp. [4].
36	**P5-2**	18340	2.3	7.97E+16	[60]PCBM	520	3.55	32	0.6	2.7	
37	**P5-3**	26200	1.9	9.56E+16	[60]PCBM	634	6.60	44	1.9	2.7	
38	**P5-4**	25600	2.8	1.24E+17	[60]PCBM	587	5.80	37	1.3	2.7	
39	**P6-1**	34300	2.19	2.07E+17	[60]PCBM	440	10.30	37	1.7	3.5	Exp., this work and theor. estim. following [3] and using data from [5]
40	**P6-2**	3400	1.36	3.51E+16	[60]PCBM	560	3.95	32	0.7	3.5	

#	*Sample*	*Mw*	M_w/M_n	C_R *(spin/g)*	*Fullerene component*	V_{OC}, *mV*	J_{SC}, *mA/cm²*	*FF, %*	η_{exp}, *%*	η_{max}, *%*	*Ref. for* η_{max}
41	**P7-1**	132700	3.7	1.90E+16	[60]PCBM	558	8.59	56	2.7	3.5	Exp., this work and theor. estim. following [3] and using data from [5]
42	**P7-2**	130150	3.3	3.62E+16	[60]PCBM	551	9.29	55	2.8	3.5	
43	**P7-3**	133400	4,5	9.69E+15	[60]PCBM	597	10.5	52	3.3	3.5	
44	**P7-4**	120640	4.6	6.14E+16	[60]PCBM	560	9.20	54	2.8	3.5	
45	**P7-5**	99600	4.1	4.25E+16	[60]PCBM	561	7.74	51	2.2	3.5	
46	**P8-1**	9950	1.50	1.93E+17	[60]PCBM	504	2.45	29	0.4	4.0	Theor. estim. following [3] and using data from [6]
47	**P8-2**	30200	2.83	2.38E+19	[60]PCBM	378	0.95	26	0.1	4.0	
48	**P8-3**	9640	1.39	8.26E+17	[60]PCBM	385	0.63	28	0.1	4.0	
49	**P9-1**	n/a	n/a	3.47E+16	[70]PCBM	668	16.90	53	6.0	7.7	Exp. [7]
50	**P9-2**	53200	1.4	2.82E+17	[70]PCBM	706	12.70	51	4.6	7.7	
51	**P10-1**	40500	2.9	7.46E+16	[70]PCBM	680	8.90	56	3.4	7.4	Exp. [8]
52	**P11-1**	37200	5.7	6.02E+17	[60]PCBM	601	3.5	33	0.7	6.0	Theor. estim. following [3]
53	**P11-2**	160600	2.1	8.43E+16	[60]PCBM	766	9.20	57	4.0	6.0	
54	**P11-3**	99000	6.1	6.86E+16	[60]PCBM	762	10.70	47	3.9	6.0	
55	**P11-4**	174500	2.5	3.68E+16	[60]PCBM	756	9.70	54	3.9	6.0	
56	**P11-5**	199200	2.9	8.73E+16	[60]PCBM	787	10.20	57	4.6	6.0	
57	**P11-6**	n/a	n/a	6.20E+16	[60]PCBM	782	10.60	52	4.3	6.0	
58	**P11-7**	168400	6.2	1.96E+17	[60]PCBM	766	9.78	52	3.9	6.0	

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