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Supporting Information to

Perovskite Solar Cells Involving Poly(tetraphenylbenzidine)s: Investigation of Hole Carrier Mobility, Doping effects and Photovoltaic Properties

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1 Methods

Cyclic voltammograms (CV) were recorded under moisture- and oxygen-free conditions using a standard three-electrode assembly connected to a potentiostat (model 263A, EG&G Princeton Applied Research) and at a scanning rate of 50 mV sec^{-1}. The working electrode was a glassy carbon disk electrode (area ¼ 0.0314 cm^2), a platinum wire was used as auxiliary electrode and the quasi-reference electrode was Ag/Ag+ composed of a Ag wire and $AgNO_3$ in acetonitrile. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M) was used as the conducting salt. Each measurement was calibrated with an internal standard (ferrocene/ferrocenium). The HOMO values were determined from the value of -5.16 eV for ferrocene with respect to vacuum level and correcting for the solvent effects.

Table S1. Oxidation potentials E_{ox} vs. ferrocene in cyclic voltammetry measurements at 50 mV s^{-1} in DCM with 0.1 M tetrabutylammonium hexafluorophosphate and calculated HOMO values for **PTPD2-4**.

Polymer	E_{ox1} vs. Fc [eV]	HOMO[b)] [eV]
PTPD2	0.10	-5.26
PTPD3	0.10	-5.26
PTPD4	0.11	-5.27

2 Size exclusion chromatography

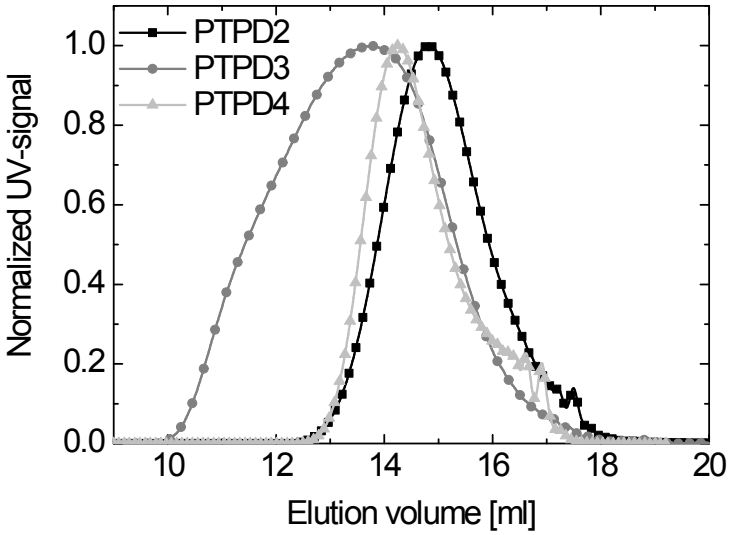

Figure S1. SEC-curves of the polymers **PTPD2**, **PTPD3**, and **PTPD4** measured in THF at room temperature (flow rate: 0.5 ml/min).

3 Differential scanning calorimetry

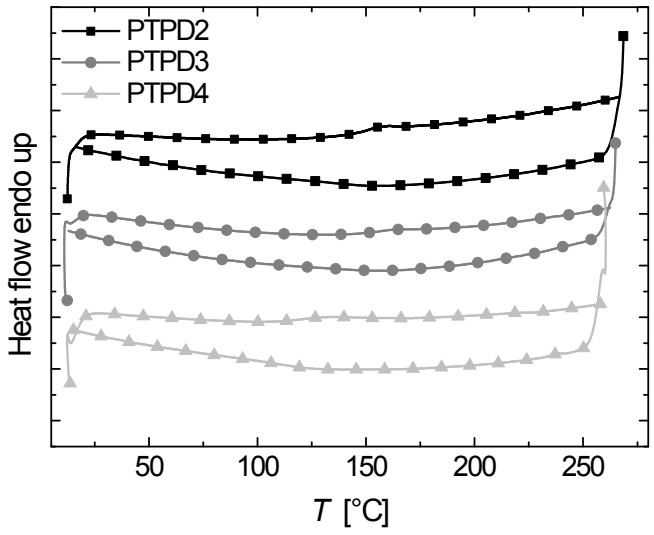

Figure S2. DSC-curves of the polymers **PTPD2**, **PTPD3**, and **PTPD4**. All three polymers show a glass transition.

4 Space charge limited current measurements

4.1 Log-log plots

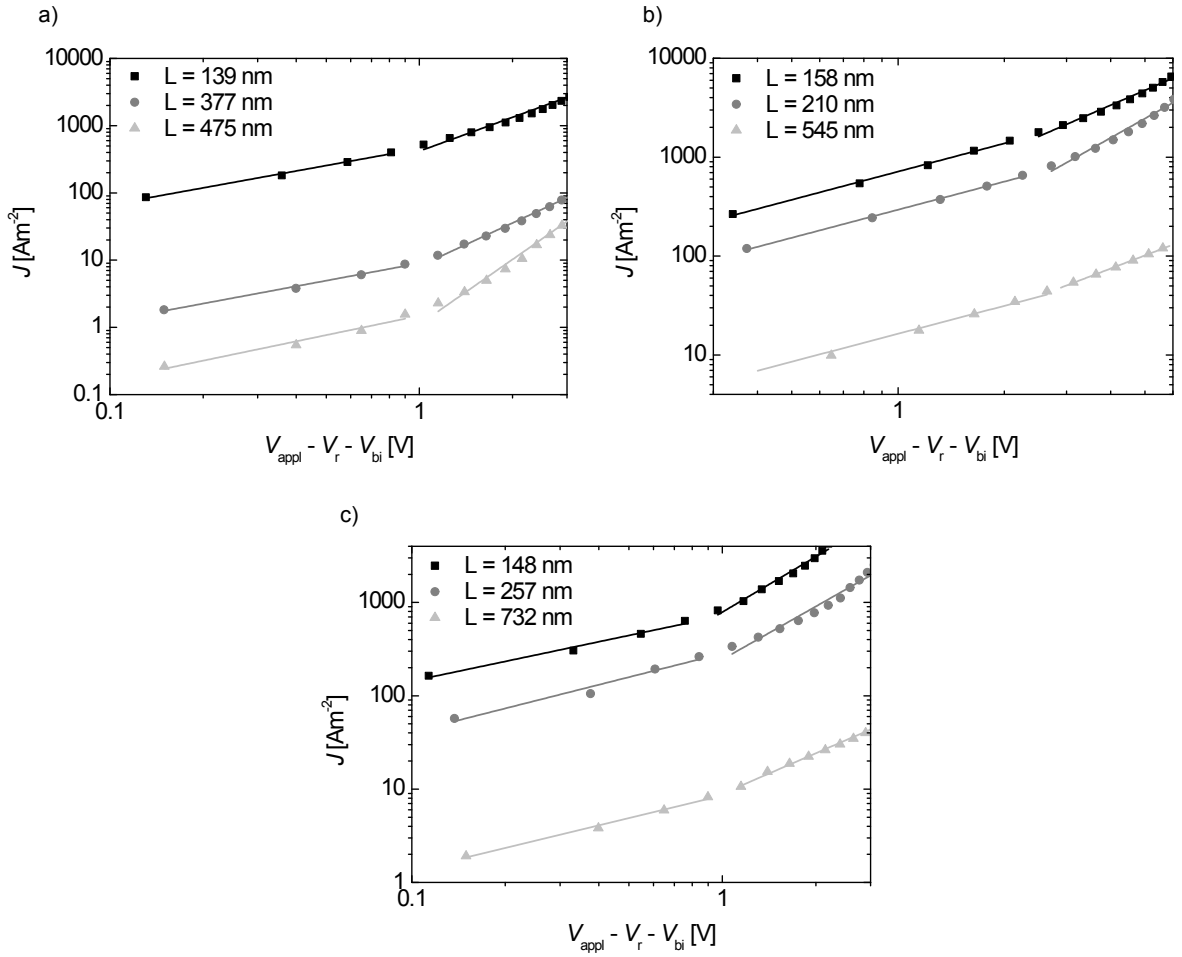

Figure S3. Log-log plots of current density *J* vs. voltage *V* (data points) and fits according to equation 1 (straight lines) at room temperature for the polymers a) **PTPD2**, b) **PTPD3** and c) **PTPD4** for different layer thicknesses.

4.2 Verification of the relation $J \sim V^2 L^3$

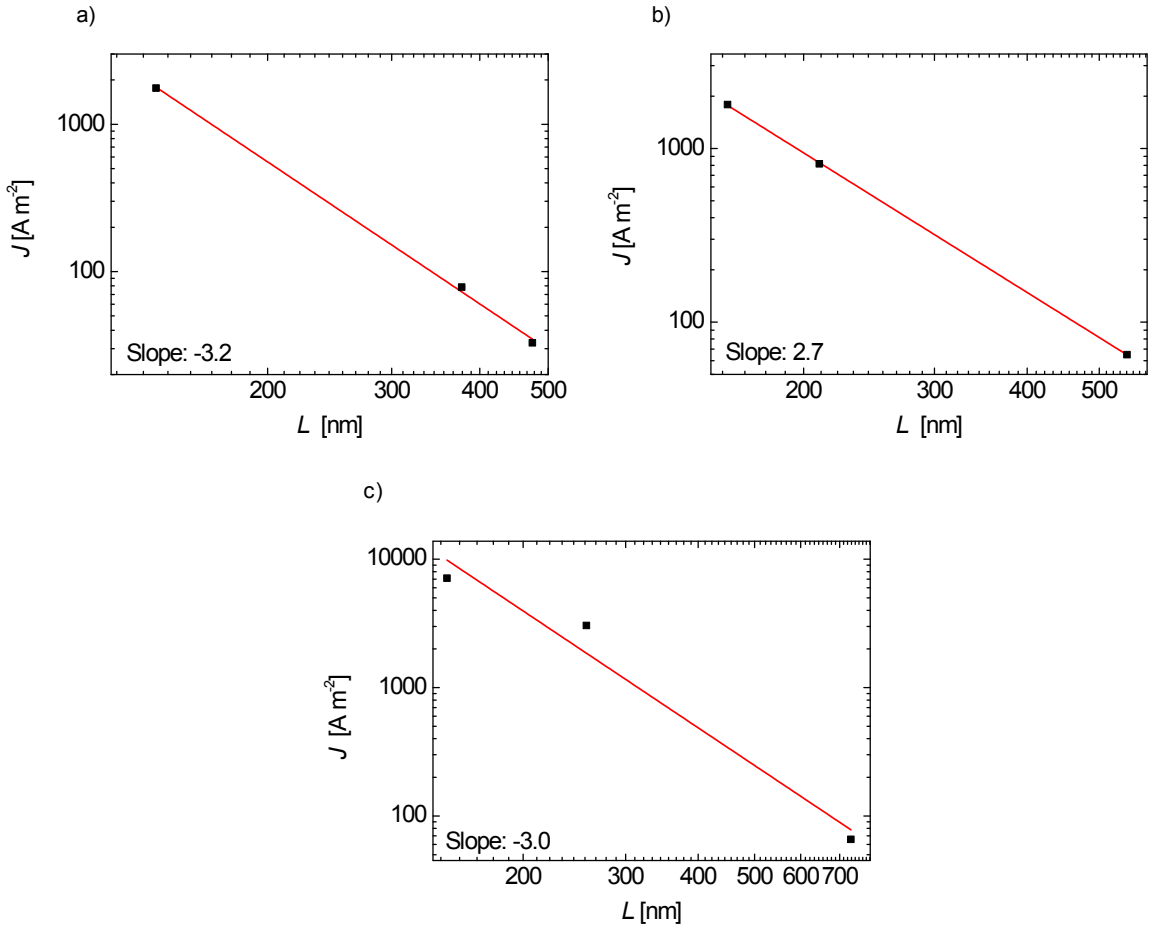

Figure S4. Log-log plot of the thickness dependence of the current density at a fixed bias of 4 V for a) **PTPD2**, b) **PTPD3** and c) **PTPD4** . The squares are experimental data and the solid line is the fit according to relation $J \sim V^2 L^{-3}$, where L is the thickness of the sample.

4.3 SCLC results for different layer thicknesses

Table S2. Calculated hole transport mobilities μ_h for three layer thicknesses and average value for μ_h for **PTPD2**.

PTPD2	Device	*L* [nm]	μ_h [$cm^2V^{-1}s^{-1}$]
	1	139	$1.9 \cdot 10^{-4}$
	2	377	$2.0 \cdot 10^{-4}$
	3	475	$5.6 \cdot 10^{-4}$
	Average		$\boldsymbol{3.2 \cdot 10^{-4}}$

Table S3. Calculated hole transport mobilities μ_h for three layer thicknesses and average value for μ_h for **PTPD3**.

Device	*L* [nm]	μ_h [$cm^2V^{-1}s^{-1}$]
1	158	$1.5 \cdot 10^{-4}$
2	210	$4.1 \cdot 10^{-4}$
3	545	$1.2 \cdot 10^{-4}$
Average		$\boldsymbol{2.3 \cdot 10^{-4}}$

Table S4. Calculated hole transport mobilities μ_h for three layer thicknesses and average value for μ_h for **PTPD2**.

Device	L [nm]	μ_h [$cm^2V^{-1}s^{-1}$]
1	148	$4.9 \cdot 10^{-4}$
2	257	$8.4 \cdot 10^{-4}$
3	732	$5.4 \cdot 10^{-4}$
Average		**$6.2 \cdot 10^{-4}$**

4.4 Effect of doping in SCLC devices

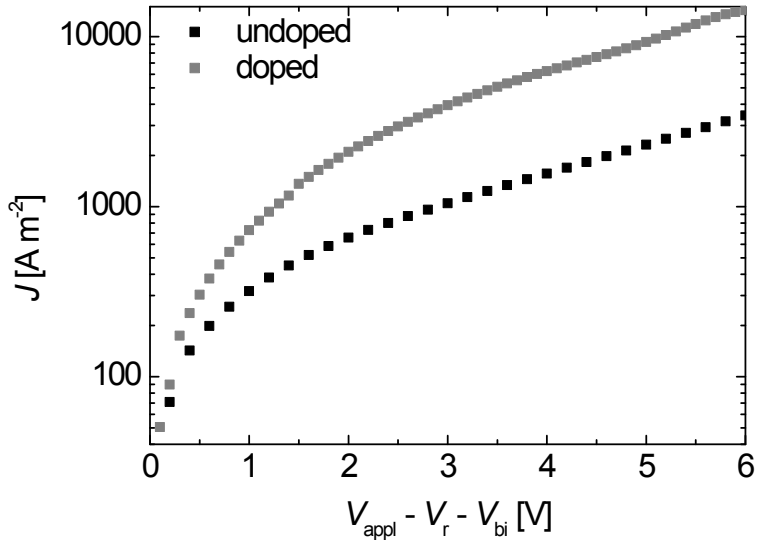

Figure S5. Log-linear-plots of J vs. V for the undoped **PTPD2** and doped SCLC devices with 10 % Co(III)-complex at similar active layer thicknesses of 184 nm.

5 Solar cell characterization

5.1 Summary of photovoltaic parameters

Table S5. Photovoltaic parameters of the devices directly after preparation and stored for 5 month under nitrogen using **PTPD2** doped containing LiTFSI and TBP as additives. The devices were measured under ambient conditions and under nitrogen conditions. The parameters for the best devices and the average values for seven cells are given.

PTPD2 doped + LiTFSI, TBP	J_{sc} [mA cm^{-2}]	V_{oc} [mV]	FF	PCE [%]	R_S [Ω cm^2]	R_{SH} [Ω cm^2]
After preparation measured under air						
Best value	10.54	805	0.60	5.10	12	272
Average value	11.24	815	0.48	4.39	15	149
RMS deviation	± 0.9	± 10	± 0.08	± 0.50	± 3	± 66
Stored 5 month measured under air						
Best value	14.00	910	0.46	5.87	16	179
Average value	13.18	894	0.44	5.12	19	167
RMS deviation	± 1.06	± 32	± 0.04	± 0.55	± 2	± 28
Stored 5 month measured under N_2						
Best value	13.40	918	0.68	7.69	15	8803
Average value	11.62	921	0.54	5.84	19	1665
RMS deviation	± 1.8	± 34	± 0.11	± 1.73	± 3	± 1192

Table S6. Photovoltaic parameters for **PTPD4** doped containing the additives LiTFSI and TBP directly after preparation and stored for 5 months measured under ambient conditions. Stored devices measured under nitrogen atmosphere. Average values for four cells and standard deviation.

PTPD4 doping, LiTFSI, TBP	J_{sc} [mA cm^{-2}]	V_{oc} [mV]	FF	PCE [%]	R_S [Ω cm^2]	R_{SH} [Ω cm^2]
After preparation measured under air						
Best value	9.81	815	0.58	4.62	20	378
Average value	9.62	804	0.58	4.44	15	3010
	± 0.75	± 27	± 0.04	± 0.16	± 1.5	± 1594
Stored 5 month measured under air						
Best	16.65	866	0.45	6.50	15	427
Average	16.17	877	0.42	5.94	25	352
	± 0.34	± 8	± 0.02	± 0.40	± 4	± 41
Stored 5 month measured under N_2						
Best	16.43	955	0.41	6.44	18	223
Average	14.26	931	0.41	5.43	24	222
	± 0.18	± 39	± 0.04	± 0.7	± 7	± 14

Table 7. Comparison of the photovoltaic parameters for devices with **PTPD2** and **PTPD4** both doped and containing the additives LiTFSI and TBP; measured in air under forward bias (f) and backward bias (b).

	V_{oc} [mV]	J_{sc} [mA cm^{-2}]	FF	PCE [%]	R_S [Ω cm^2]	R_{SH} [Ω cm^2]
Under air						
PTPD2 f	910	14.00	0.46	5.87	16	179
PTPD2 b	898	11.41	0.50	5.11	18	219
PTPD4 f	866	16.60	0.45	6.50	20	378
PTPD4 b	910	16.65	0.43	6.47	18	237

5.2 Comparison of the interfaces of PTPD2 and PTPD4

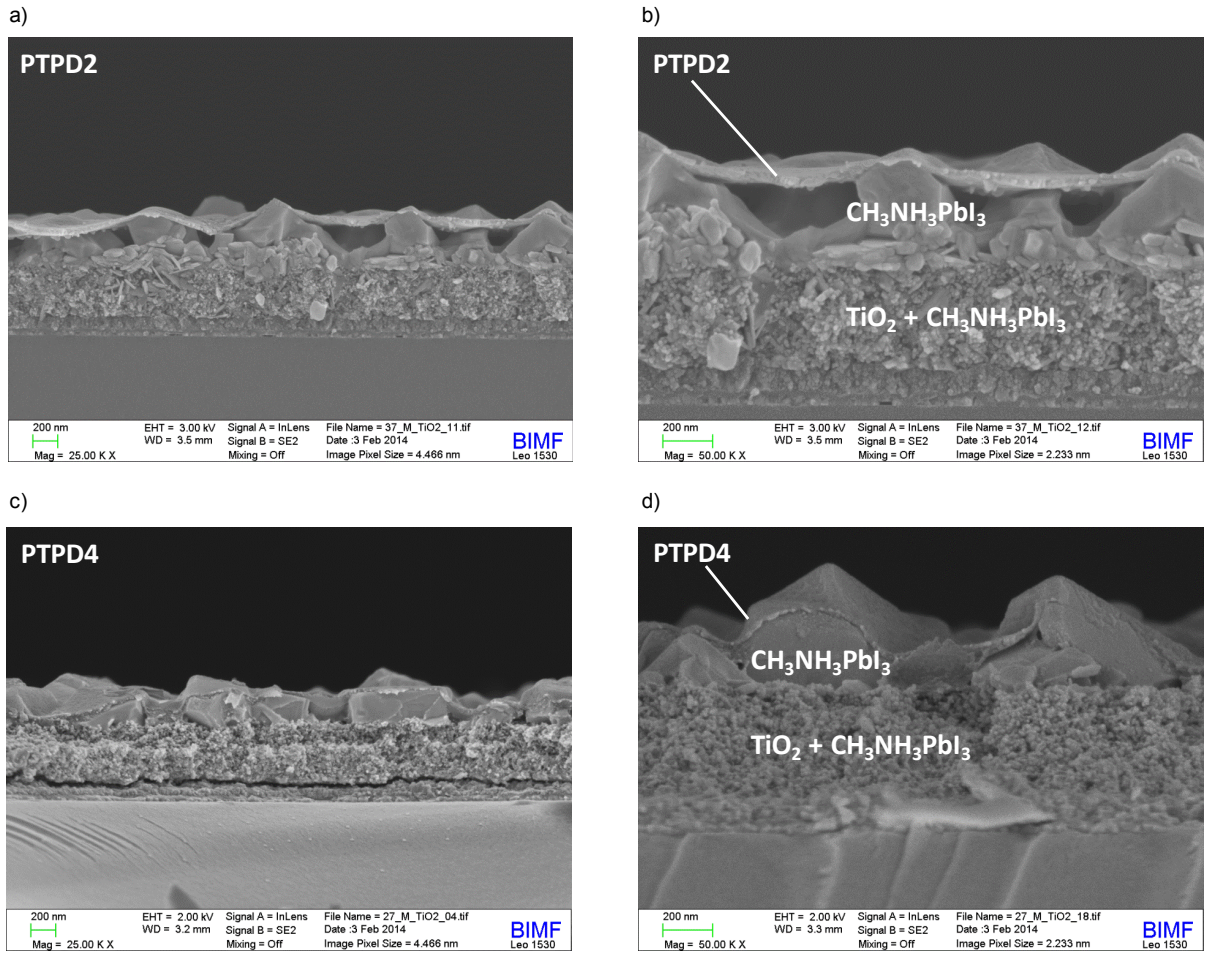

Figure S6. SEM images of devices with **PTPD2** (a) and b)) and **PTPD4** (c) and d)) showing the better compatibility of **PTPD4** with the perovskite crystals.

5.3 Comparison of EQE and UV-vis upon storage for PTPD4

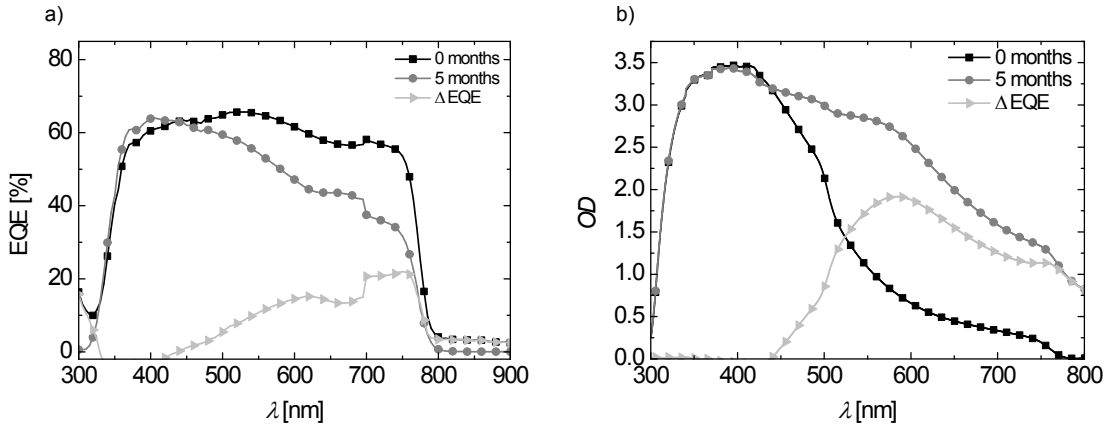

Figure S7. Comparsion of freshly prepared devices (squares) and devices stored for 5 months under nitrogen atmosphere (circles) with undoped **PTPD4** and difference between the two devices (triangles) a) EQE-spectra; The artifact between 650-700 nm is due to the switching of the lamp from one wavelength range to the other. b) UV-vis absorption. All measurements were carried out under ambient conditions.