Supporting Information

Novel benzodithiophene-TBTBT copolymers: synthesis and investigation in organic and perovskite solar cells

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Table of contents

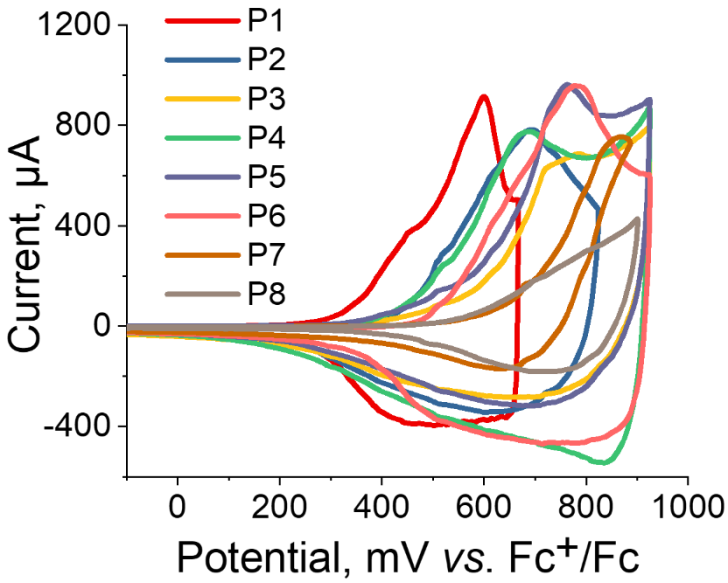

Fig. S1 Cyclic voltammograms of polymers **P1-P8**

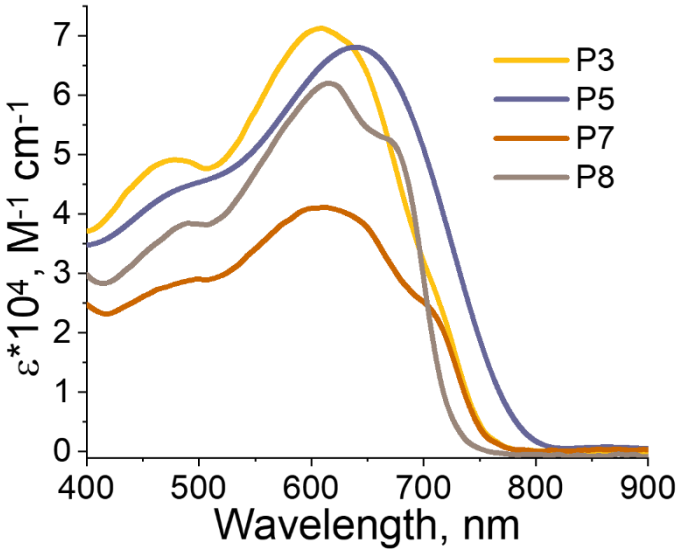

Fig. S2 Absorption spectra of **P3**, **P5**, **P7** and **P8** in solution (chlorobenzene)

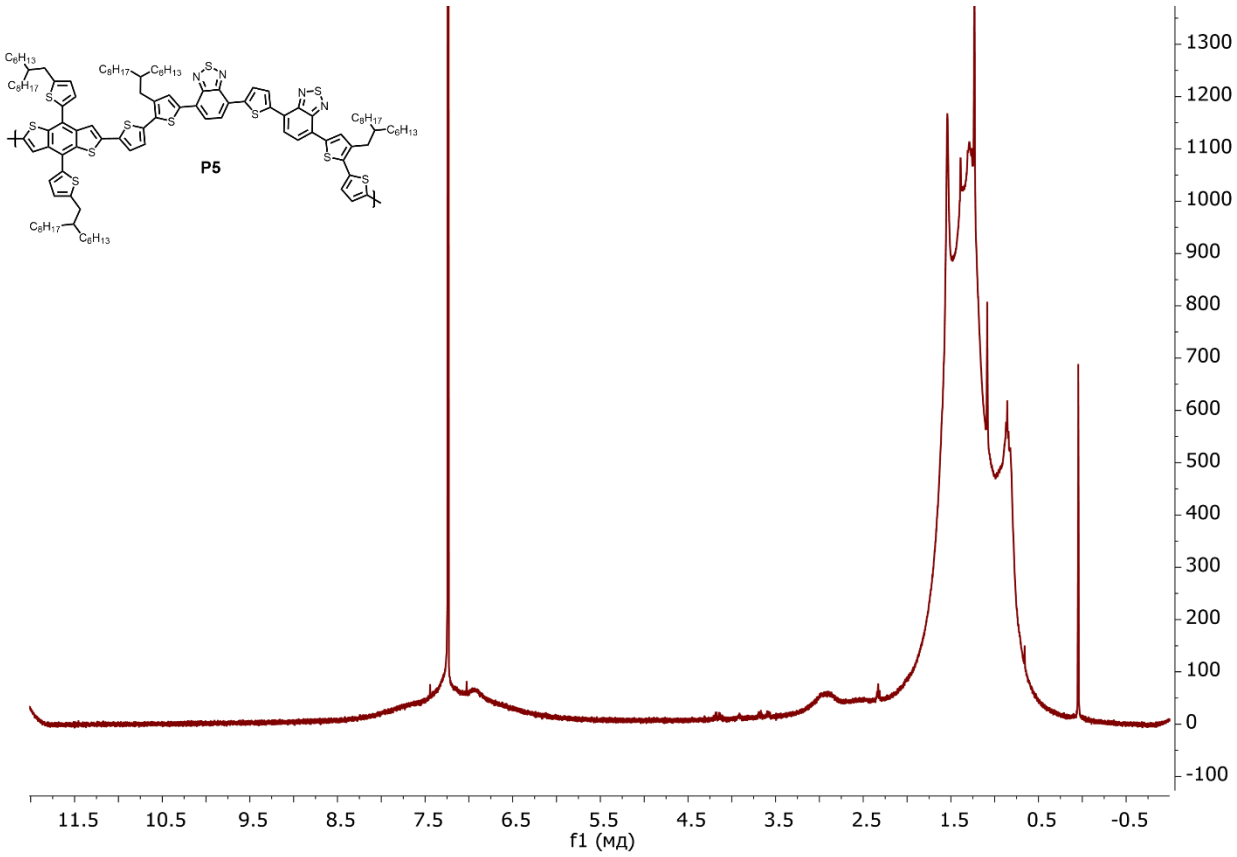

Fig. S3 ^{1}H NMR spectrum of **P5** in $CDCl_3$

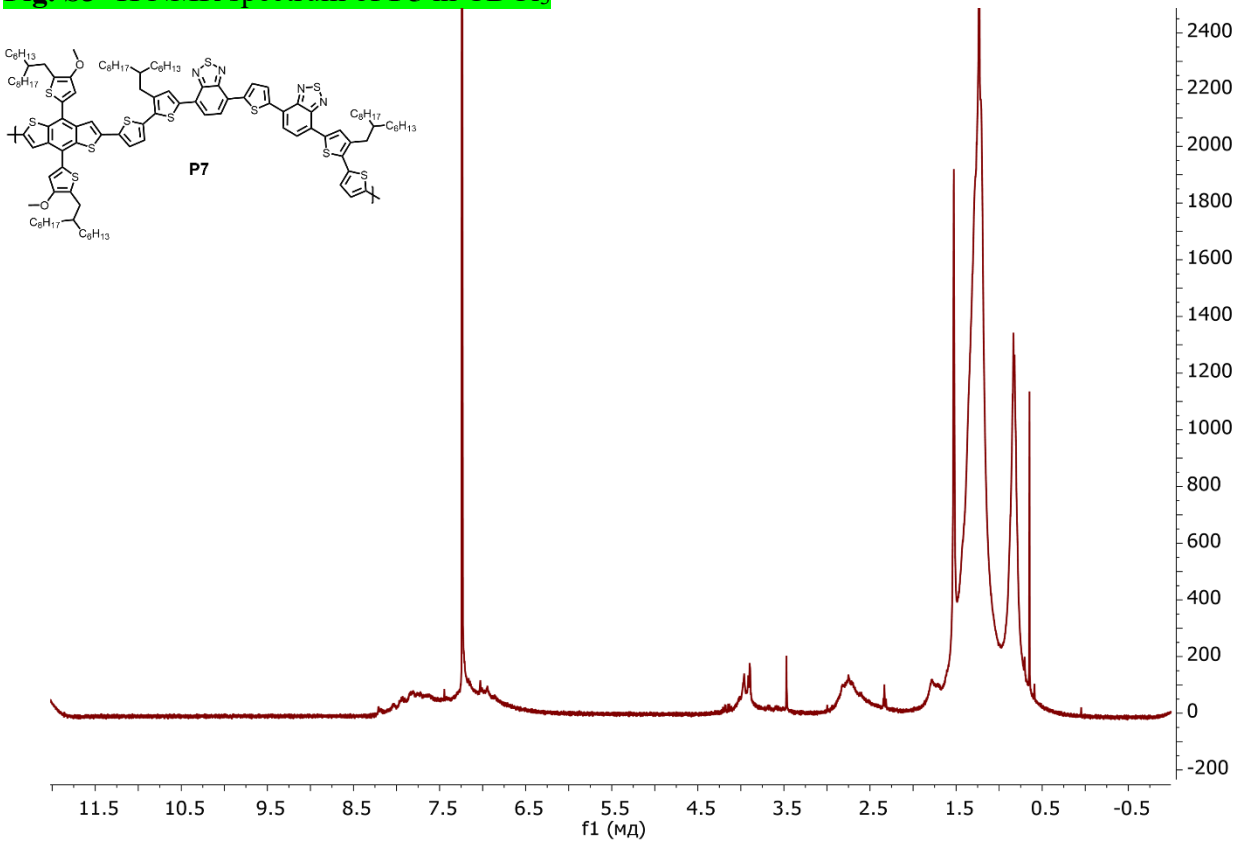

Fig. S4 ^{1}H NMR spectrum of **P7** in $CDCl_3$

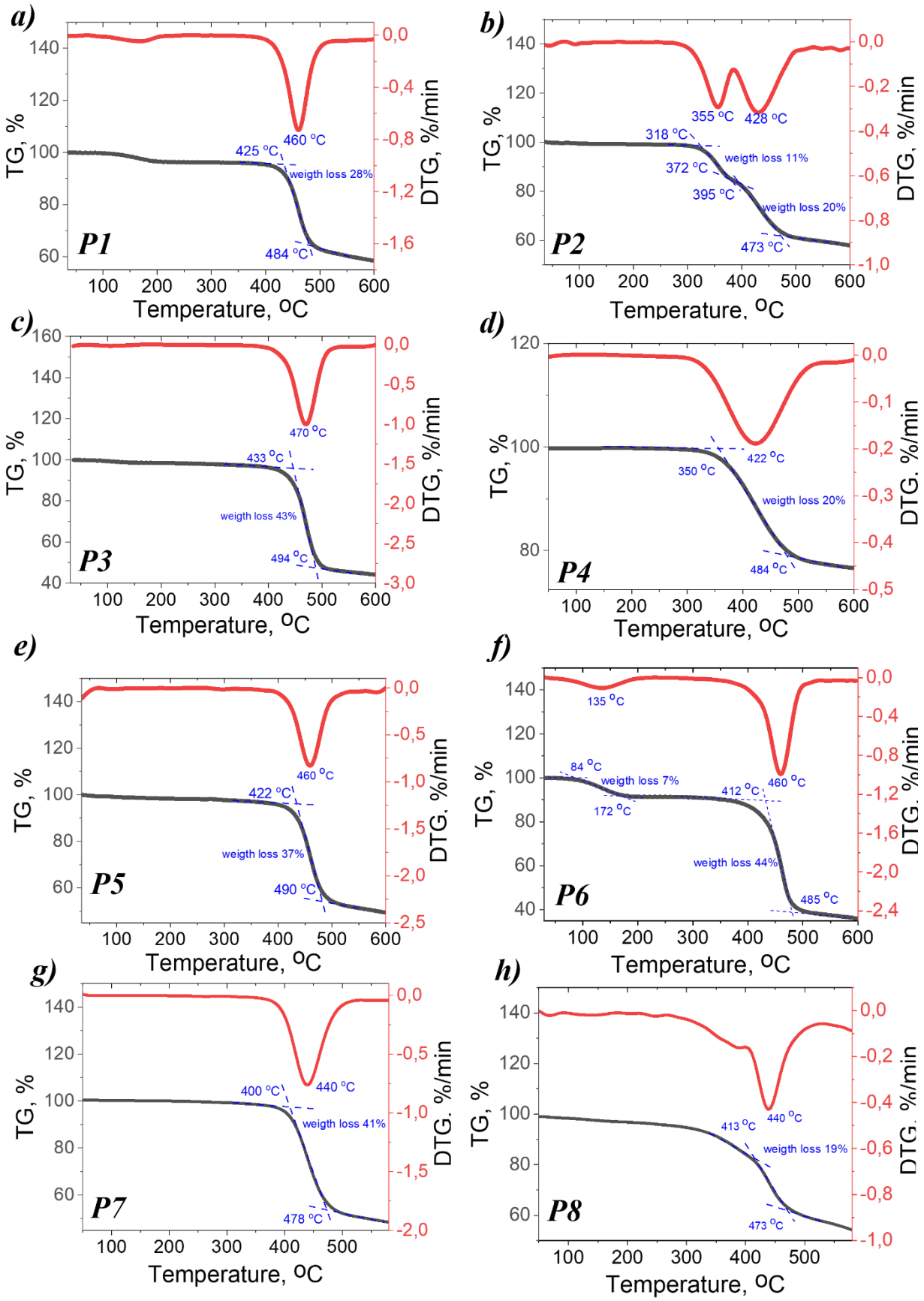

Fig. S5 TG curves of polymers **P1-P8**

Table S1 Processing conditions and performance characteristics of organic solar cells based on polymers **P1-P8**

Donor D	Acceptor A	D : A ratio w/w	Additive	Conditions	V_{OC}, mV	J_{SC}, mA/cm^2	FF, %	η, %
P1	[60]PCBM	1:1	-	10 mg/ml in 1,2,4-TCB[1] at 190°C. DB[2] at 120°C, blade speed 30 mm/s.	362	10.83	29	1.13
		1:2	-		614	10.00	39	2.40
		1:2	CN / 1%		550	12.97	35	2.52
		1:2	DPE / 1%		657	11.54	47	3.60
		1:2	DIO / 1%		647	13.06	57	4.82
		1:2	ODT / 1%		679	13.16	55	4.88
P2	[60]PCBM	1:2	-	8 mg/ml in 1,2,4-TCB at 190°C. DB at 110°C, blade speed 40 mm/s.	467	7.5	31	1.1
		1:1.5	-		506	7.6	36	1.4
		1:1.5	ODT / 1%		589	8.9	45	2.4
P3	[60]PCBM	1:1	-	10 mg/ml in 1,2,4-TCB at 190°C. SC[3] 800 rpm.	619	8	47	2.3
		1:1.5	-		650	10.1	59	3.9
		1:1.5	DPE / 1%		636	9.9	67	4.2
	EH-IDTBR	1:1	-	10 mg/ml in 1,2,4-TCB at 190°C. SC 800 rpm, annealing at 125ºC within 10 min.	788	10.5	48	4
P4	[60]PCBM	1:2	-	10 mg/ml in 1,2-DCB[4] at. SC 900 rpm	601	9.3	44	2.5
		1:1	-		617	10.6	53	3.5
		1:1	-	10 mg/ml in 1,2-DCB at. SC 600 rpm	614	12.1	60	4.5
		1:1	-	10 mg/ml in 1,2-DCB at. SC 900 rpm, annealing at 95ºC within 10 min	614	11.1	54	3.7
		1:1	-	10 mg/ml in 1,2-DCB at. SC 900 rpm, annealing at 95ºC within 10 min, SVA[5] in CH_2Cl_2 within 1 min	593	11.8	60	4.2
		1:1	CN / 1%	10 mg/ml in 1,2-DCB at. SC 900 rpm, annealing at 95ºC within 10 min, SVA in 1% CN	593	12.1	60	4.3
	EH-IDTBR	1:1	-	10 mg/ml in 1,2-DCB at 160°C. SC, 600 rpm	816	8.8	34	2.4
	O-IDTBR	1:1.5	-	10 mg/ml in 1,2-DCB at 160°C. SC, 600 rpm	853	8.8	41	3.1
P5	[60]PCBM	1:1	-		571	9.2	41	2.2

Donor D	Acceptor A	D : A ratio w/w	Additive	Conditions	V_{OC}, mV	J_{SC}, mA/cm^2	FF, %	η, %
		1:1.5	-	10 mg/ml in 1,2-DCB at 160°C. DB at 80°C, blade speed 15 mm/s, annealing at 95ºC within 10 min	635	10	61	3.9
		1:1.5	DIO / 1%	10 mg/ml in 1,2-DCB at 160°C. DB at 80°C, blade speed 50 mm/s, annealing at 95ºC within 10 min	617	10.7	58	3.8
	ITIC-M	1:1	-	10 mg/ml in 1,2-DCB at 160°C. DB at 80°C, blade speed 15 mm/s, annealing at 125ºC within 10 min	737	14.5	50	5.3
	EH-IDTBR	1:1	-		888	12	49	5.3
P6	[60]PCBM	1:2	-	10 mg/ml in 1,2,4-TCB at 190°C. DB at 120°C, blade speed 15 mm/s.	757	7.30	64	3.54
		1:1.5	-		747	8.12	63	3.82
P7	[60]PCBM	1:1	-	10 mg/ml in 1,2-DCB at 160°C. DB at 25°C, blade speed 50 mm/s, annealing at 95ºC within 10 min	717	4	33	1
		1:1.5	-		754	5.3	34	1.4
		1:1.5	ODT / 1%	10 mg/ml in 1,2-DCB at. SC 900 rpm, annealing at 95ºC within 10 min	731	11.6	42	3.6
		1:1.5	DPE / 1%		752	10.3	46	3.6
	EH-IDTBR	1:1	-	10 mg/ml in 1,2-DCB at. SC 1000 rpm, annealing at 125ºC within 10 min	937	8.9	43	3.6
P8	[60]PCBM	1:1.5	-	8 mg/ml in 1,2-DCB at 160°C. DB at 25°C, blade speed 50 mm/s, annealing at 95ºC within 10 min	783	10.1	39	3.1
		1:1	-		822	11.8	49	4.7
		1:1	-	10 mg/ml in 1,2-DCB at 160°C. DB at 25°C, blade speed 20 mm/s, annealing at 95ºC within 10 min	849	12.6	45	4.8
		1:1	-	10 mg/ml in 1,2-DCB at 160°C. DB	811	11.8	53	5.1

Donor D	Acceptor A	D : A ratio w/w	Additive	Conditions	V_{OC}, mV	J_{SC}, mA/cm^2	FF, %	η, %
				at 25°C, blade speed 20 mm/s				
		1:1	ODT / 1%		824	13.7	57	6.5
	ITIC-4F	1:1	-	10 mg/ml in 1,2-DCB at 160°C. DB at 25°C, blade speed 20 mm/s, SVA in 1% $CHCl_3$	729	9.4	46	3.2

[1]1,2,4-Trichlorobenzene; [2]Doctor Blade; [3]spin-coating; [4]1,2-dichlorobenzene; [5]solvent vapor annealing

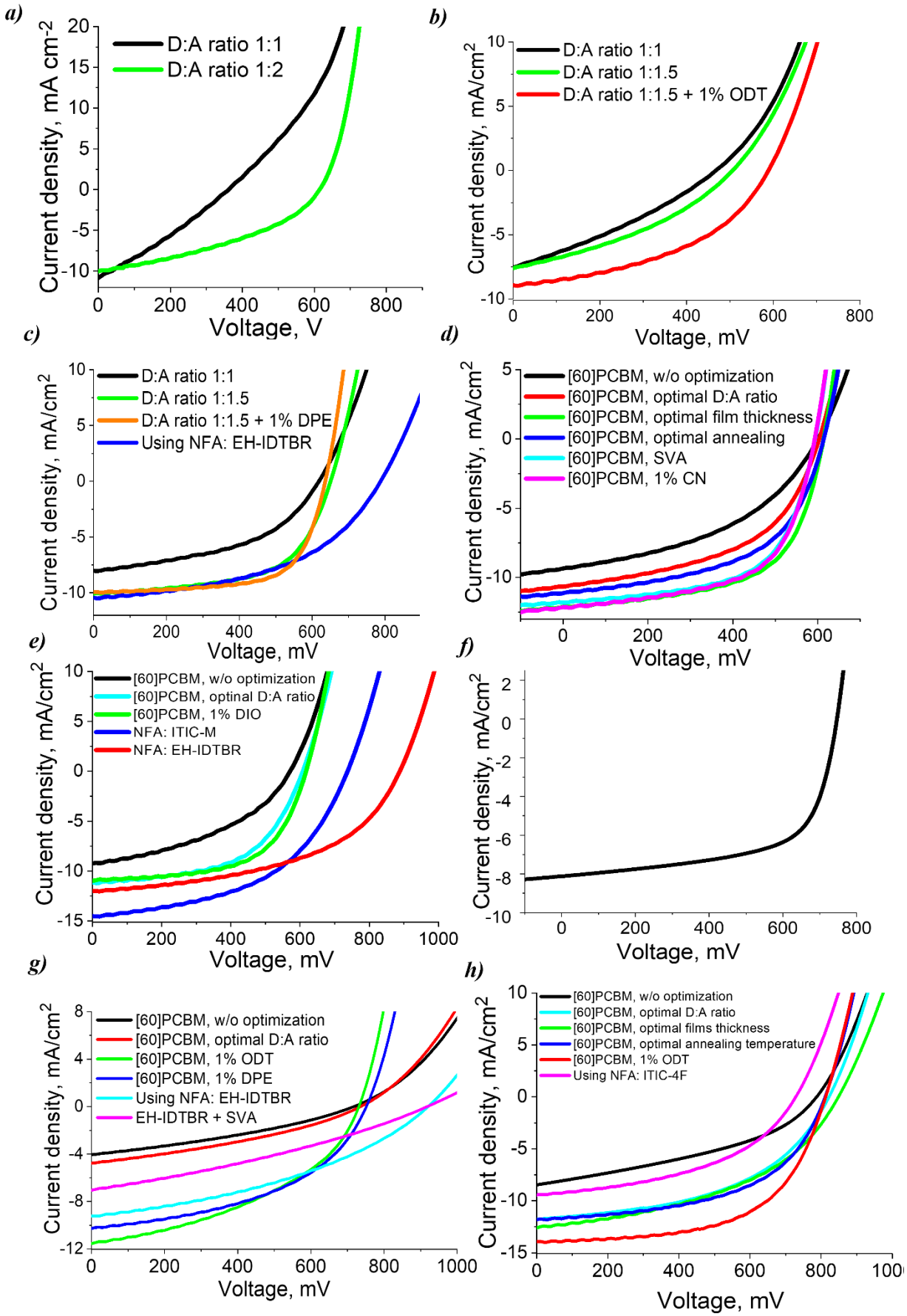

Fig. S6 J-V characteristics (a-h) of OSCs based on **P1** (a), **P2** (b), **P3**(c), **P4**(d), **P5** (e), **P6** (f), **P7** (g) and **P8** (h)

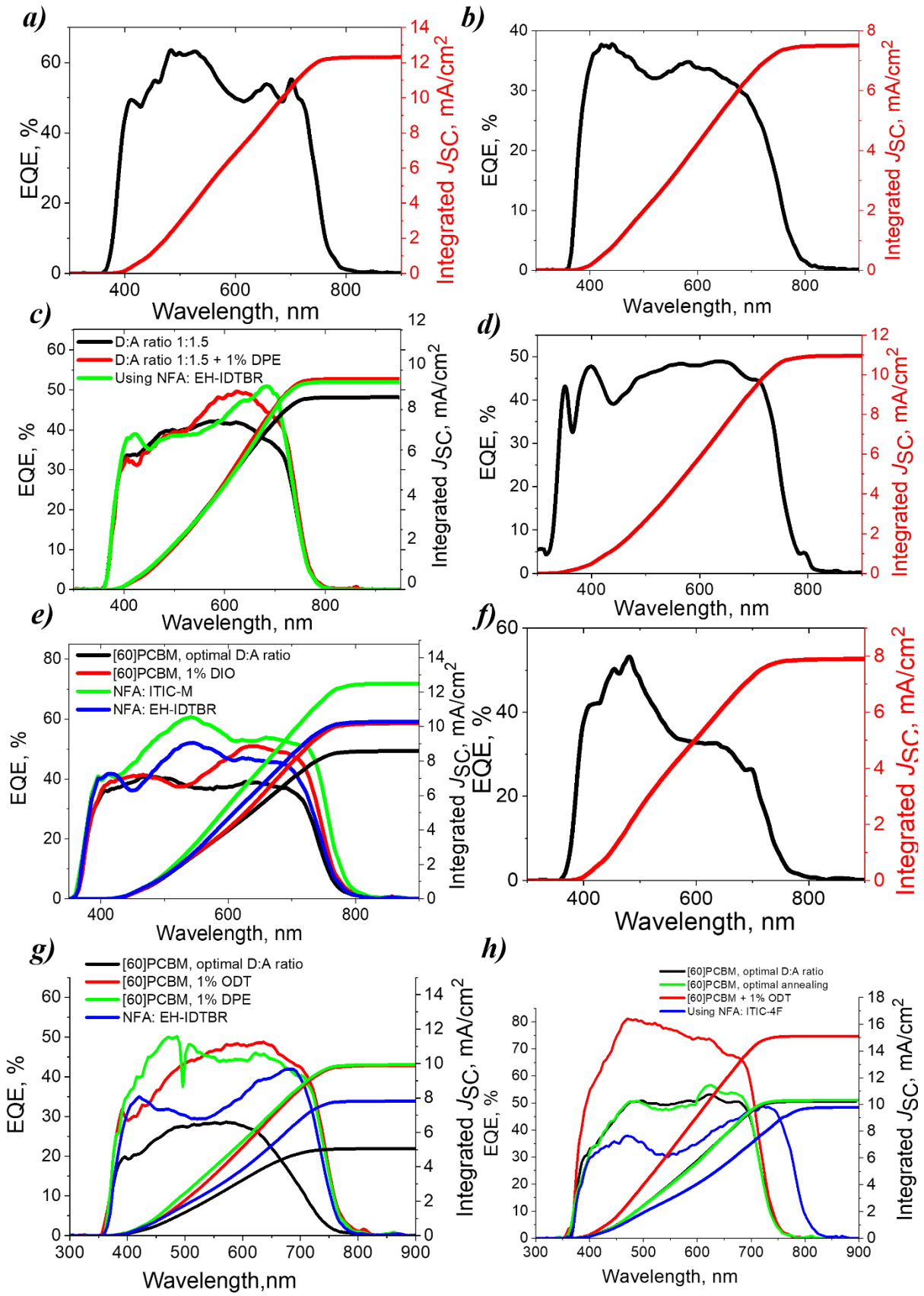

Fig. S7 EQE spectra (a-h) of OSCs based on **P1** (a), **P2** (b), **P3**(c), **P4**(d), **P5** (e), **P6** (f), **P7** (g) and **P8** (h)

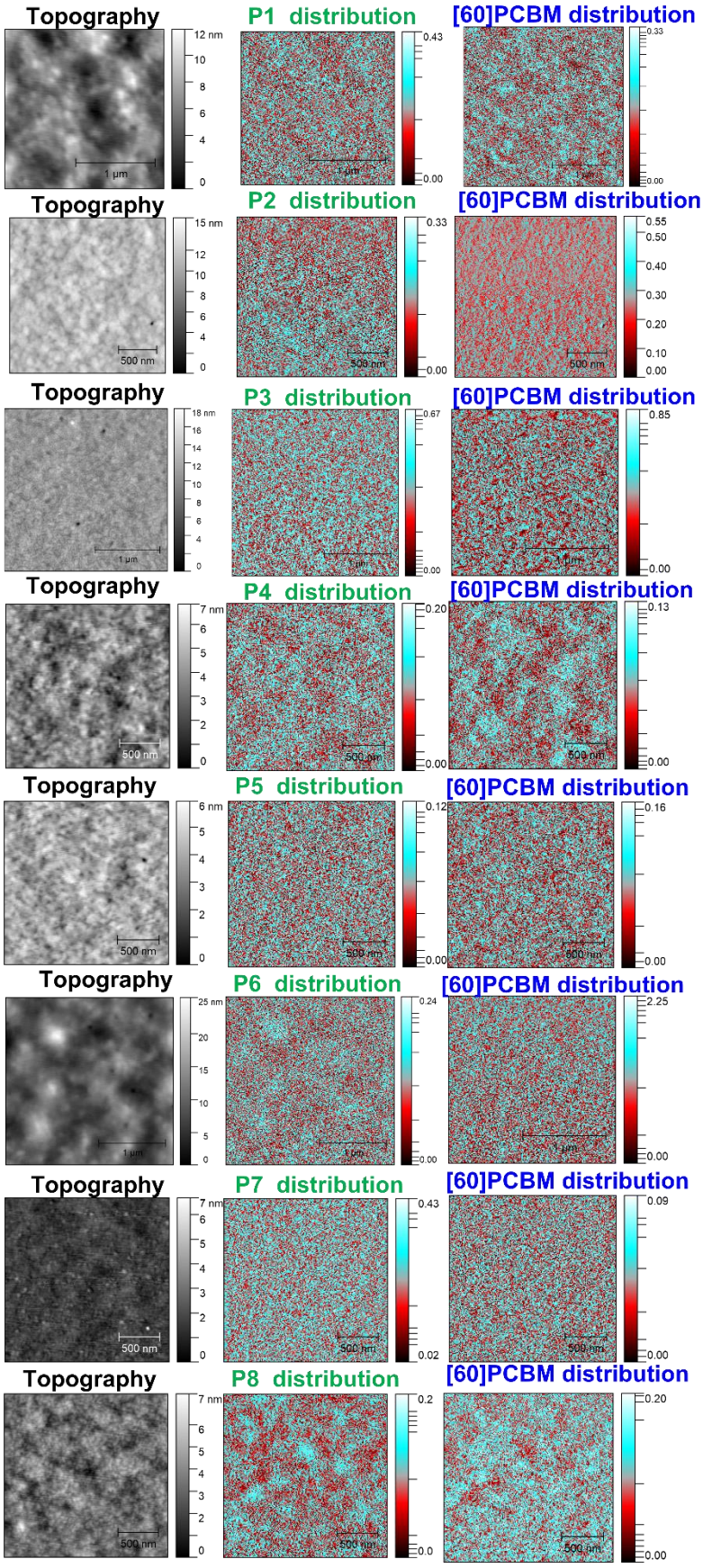

Fig. S8 Topographic images of composite films based on polymers **P1-P8** (left) and the results of IR s-SNOM mapping on the characteristic IR absorption frequencies of the conjugated polymer (center) and the acceptor material (right)

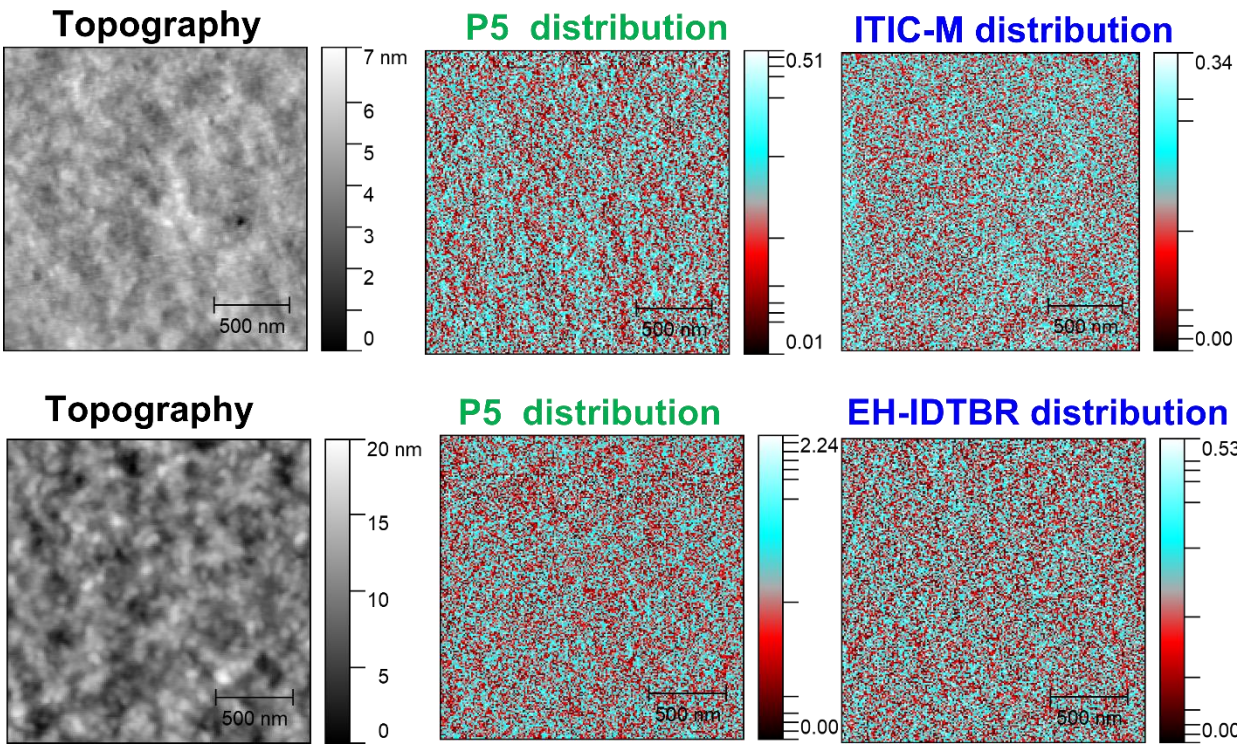

Fig. S9 Topographic images of composite films based on polymers **P5** (left) and the results of IR s-SNOM mapping on the characteristic IR absorption frequencies of the conjugated polymer (center) and the acceptor material (right)

Table S2 Processing conditions and parameters of ITO/SnO_x/PCBA/MAPbI3/HTM/VO_y/Ag perovskite solar cells based on polymers **P1-P8** and reference PTA applied as hole transport materials

HTL	Conditions	Scanning direction	V_{OC}, V	J_{SC}, mA cm^{-2}	FF, %	PCE, %
P1	5 mg/ml in 1,3,5-TCB, 180 °C, 1000 rpm	Forward	1.01	22.6	72.5	16.6
		Reverse	1.01	22.6	71.6	16.4
P2	3 mg/ml in 1,2-DCB, 85 °C, 1000 rpm	Forward	0.91	23.4	63.0	13.4
		Reverse	0.89	23.4	64.0	12.8
P3	7 mg/ml in CB, 25 °C, 1000 rpm	Forward	0.99	23.4	73.3	17.0
		Reverse	0.97	23.3	63.5	14.5
P4	5 mg/ml in CB, 65-70 °C, 1000 rpm	Forward	1.07	23.5	64.6	16.3
		Reverse	1.06	23.4	67.1	16.7
P5	10 mg/ml in CB, 95-100 °C, 5000 rpm	Forward	1.10	22.6	70.4	17.5
		Reverse	1.11	22.5	70.5	17.6
P6	5 mg/ml in CB, 65-70 °C, 1000 rpm	Forward	0.99	23.5	49.3	11.5
		Reverse	0.99	23.4	42.1	10.1
P7	6 mg/ml in CB, 25 °C, 1000 rpm	Forward	1.08	23.5	66.0	16.9
		Reverse	1.08	23.5	65.0	16.8
P8	7 mg/ml in CB, 25 °C, 2000 rpm	Forward	1.07	23,5	75.0	18.8
		Reverse	1.06	23,5	72.0	17.9
PTA	6 mg/ml in CB, 25 °C, 1000 rpm	Forward	1.04	23.4	67.8	16.5
		Reverse	1.03	23.3	64.9	15.5

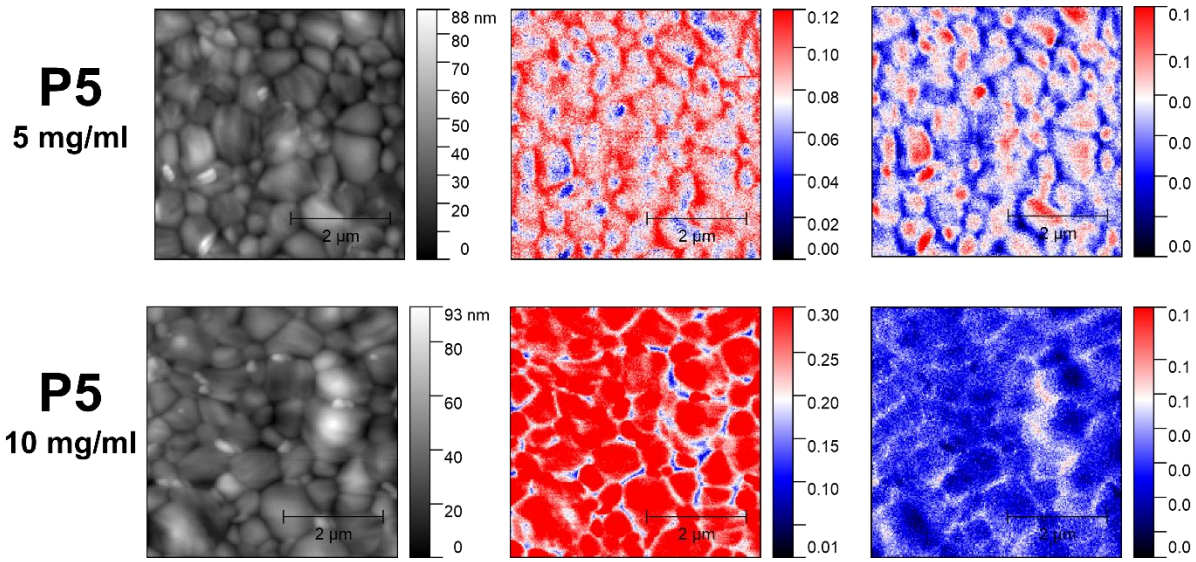

Fig. S10 AFM topography images of **P5** films deposited atop perovskite absorber layer (left) and IR s-SNOM mapping results at the characteristic IR absorption frequencies of conjugated polymer (center) and $MAPbI_3$ perovskite (right)