Supporting Information

Catechol derivatives as dopants in PEDOT:PSS to improve the

performance of *p-i-n* perovskite solar cells

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Dopant	PCE with neat film (%) F	CE with doped film (%)	Reference
polyethylene oxide	11.41	16.52	1
glycerol	8.57	11.41	2
imidazole	12.70	15.70	3
PSS-Na	12.35	15.56	4
DMSO + Zonyl	-	12-12.5	5
graphene oxide + glucose	9.4	12.8	6
MoO _x	13.90	15.79	7
TiO ₂ -MoO ₃ core-shell NPs	8.98	13.63	8
Ag NPs	11.33	12.68 ± 0.86	9
isopropanol	-	13.01	10
F4-TCNQ	13.30	17.22	11
ammonia	14.40	15.5	12
DMSO	11.8	16.70	13
dopamine (HCl)	15.2	16.65	14
TS-CuPC	13.29	17.29	15

Table S1. PEDOT: PSS doped with different materials as HTLs and corresponding photovoltaic parameters.



Fig. S1 *J-V* curves of Pero-SCs depend on the concentration of catechol derivatives in the aqueous solution of PEDOT:PSS.

Table S2. Optimization of dopant content in PEDOT:PSS solutions. Photovoltaic characteristics extrapolated from *J-V* curves of the Pero-SCs depend on the concentration of catechol derivatives in the aqueous solution of PEDOT:PSS.

Dopant in	Concentration (mg mL ⁻		/ (m / cm ⁻²)	FF (0/)		
HTL	¹)	$V_{\rm oc}$ (V) $J_{\rm sc}$ (r		FF (%)	PCE (%)	
DOPA	3	1.00	19.56	72.22	14.12	
	6	1.02	20.43	71.14	14.85	
	10	1.02	20.18	66.53	13.71	
	2	0.98	18.27	64.75	11.58	
NE	6	0.97	20.58	71.98	14.40	
	10	0.99	21.06	61.64	12.88	
	6	1.04	20.69	77.56	16.73	
DOBD	9	1.04	21.45	78.57	17.46	
	12	1.03	21.28	76.72	16.85	



Fig. S2 EQE spectra of Pero-SCs with PEDOT:PSS, DOPA-, NE- and DOBD-PEDOT:PSS as HTL.



Fig. S3 Hysteresis assessment of the influence of catechol derivatives on the performance of the Pero-SCs. The measurement was conducted under the illumination of AM 1.5G, 100 mW cm⁻² at both forward and reverse scans with a rate of 20 V s⁻¹.

Table S3. Photovoltaic characteristics of the Pero-SCs obtained with forward and reverse scans.

Dopant in HTL-scan direction	V _{oc} (V)	J _{sc} (mA cm⁻²)	FF (%)	PCE (%)
DOBA Forward	1.02	20.42	71 1	14.95
DOPA-FOI walu	1.02	20.45	/1.1	14.65
DOPA-Reverse	1.02	20.02	69.5	14.25
NE-Forward	0.97	20.58	72.0	14.40
NE-Reverse	0.97	20.01	70.4	13.72
DOBD-Forward	1.04	21.45	78.6	17.46
DOBD-Reverse	1.04	21.40	77.6	17.28

Table S4 The percentage of PEDOT and PSS and the ratio of PEDOT / PSS in different films surface.

	W/O	DOP	NE	DOBD	
DEDOT	42.2	45.0	447	44.0	
PEDOT	12.3	15.8	14.7	14.9	
PSS	87.7	84.2	85.3	85.1	
PEDOT /	0 1/	0 19	0 17	0 18	
PSS	0.14	0.15	0.17	0.10	



Fig. S4 FTIR spectra of neat PEDOT:PSS and DOPA-, NE- and DOBD-PEDOT:PSS films.



Fig. S5 Typical *J-V* curves of Pero-SCss with neat PEDOT:PSS and DOPA-, NE- and DOBD-PEDOT:PSS as HTLs measured in the dark.



Fig. S6 Stability assessment of the Pero-SCs with neat PEDOT:PSS and DOPA-, NE- and DOBD-PEDOT:PSS as HTLs. Normalized photovoltaic parameters depend on the storage time in the glovebox filled with nitrogen: (a) V_{oc} , (b) J_{sc} , (c) FF, and (d) PCE.

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