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Counterions-Tunable N-Type Conjugated Polyelectrolytes for the Interface Engineering of High-Performance Polymer Solar Cells

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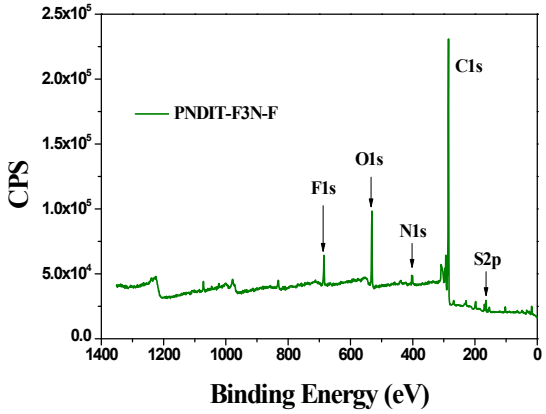
Support Information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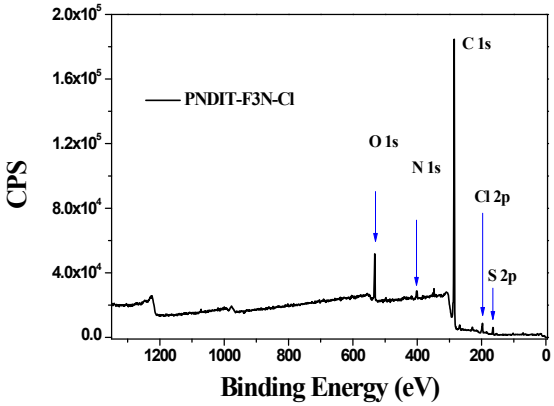
O1s
F1s
N1s
S2p
CPS
Binding Energy (eV)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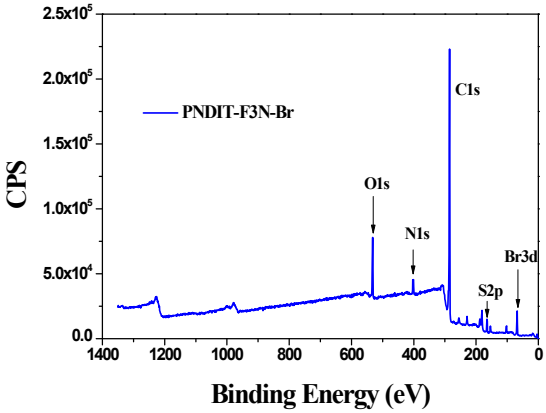
Cl 2p
S 2p
CPS
Binding Energy (eV)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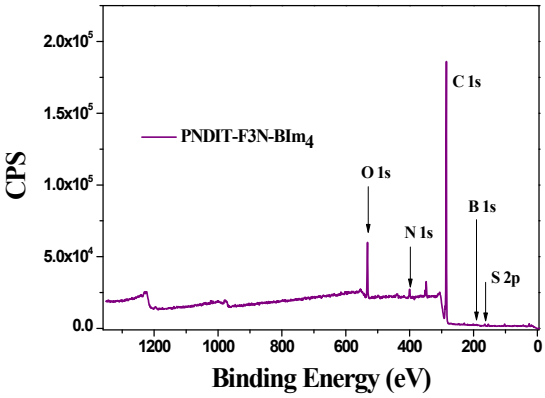
Binding Energy (eV)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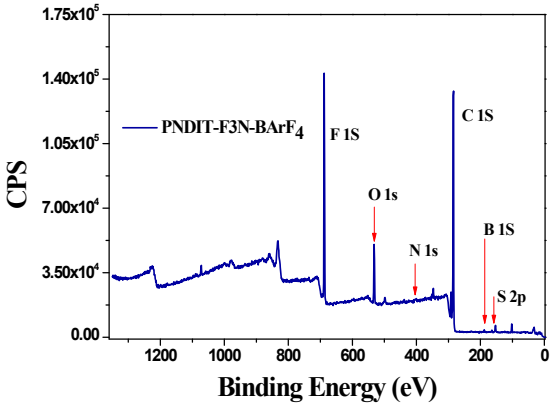
S 2p
CPS
Binding Energy (eV)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O 1s
B 1S
N 1s
S 2p
CPS
Binding Energy (eV)

Fig. S1 The XPS spectra of CPEs in solid state.

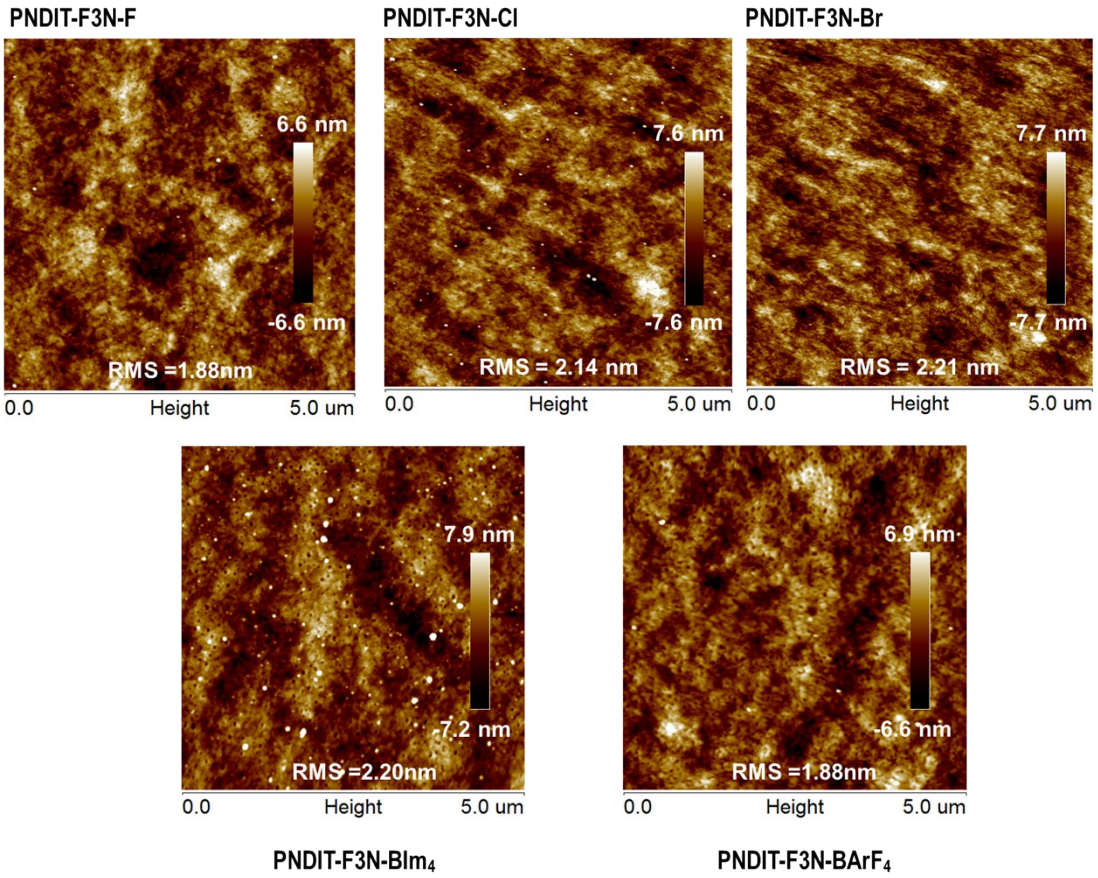


Fig. S2 Atom force microscopy topography of CPEs

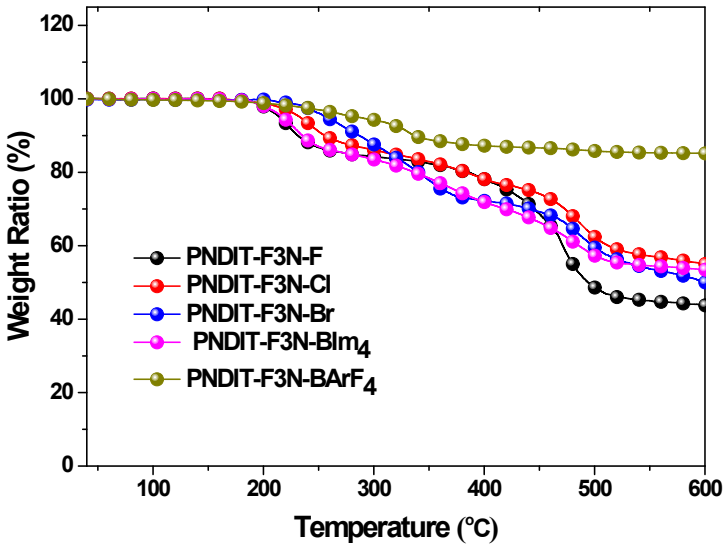


Fig. S3 Thermogravimetric analysis of CPEs.

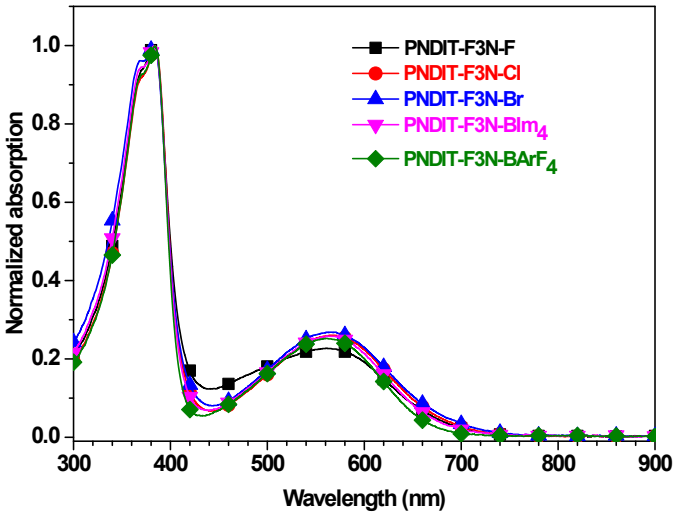


Fig. S4 The UV-vis-NIR absorption spectra of CPEs in methanol solution.

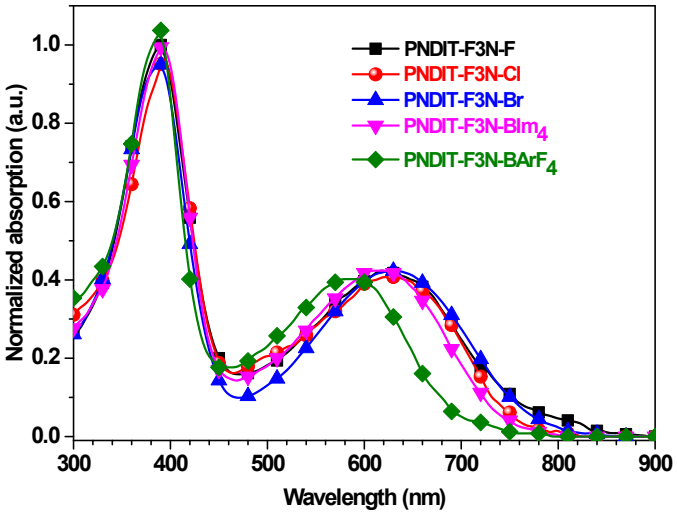


Fig. S5 The UV-vis-NIR absorption spectra of CPEs in heated film.

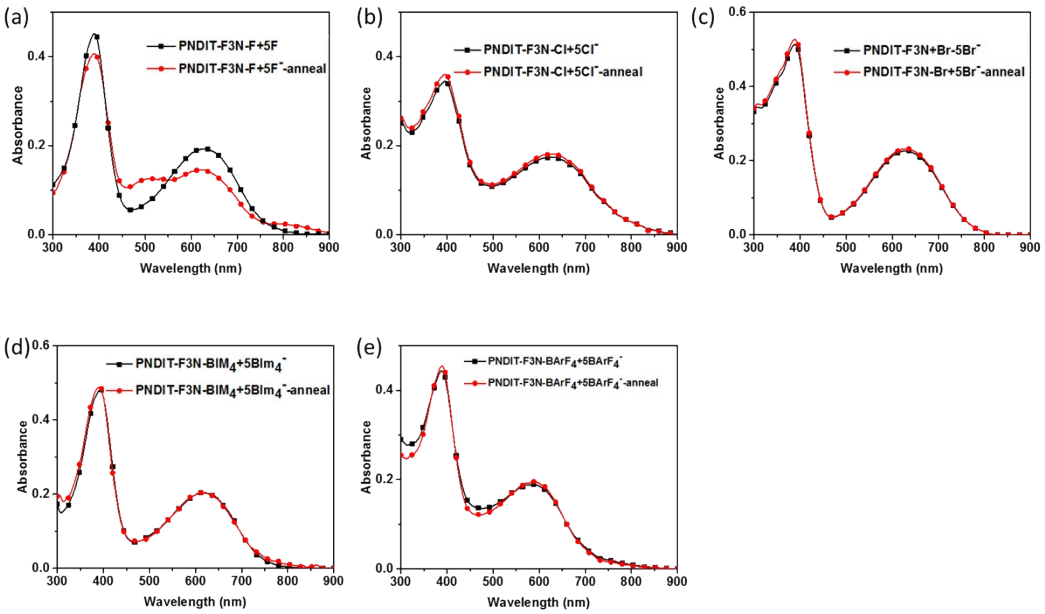
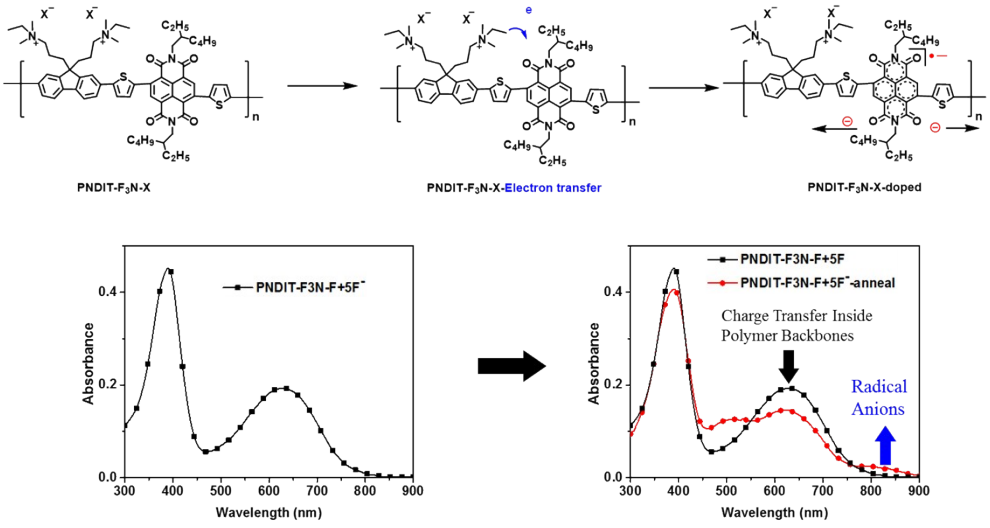


Fig. S6 The UV-vis-NIR absorption spectra of CPEs with excess counterions in heated film.(a) PNDIT-F3N-F + 5TBAF (tetrabutylammonium fluoride); (b) PNDIT-F3N-Cl + 5TBACl (tetrabutylammonium chloride); (c) PNDIT-F3N-Br + 5TBABr (tetrabutylammonium bromide); (d) PNDIT-F3N-BIm_4 + 5$NaBIm_4$ (sodium tetrakis(1-imidazolyl)borate); (e) PNDIT-F3N-$BArF_4$ + 5$NaBArF_4$ (sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate).



Scheme S1 The schematic diagram of doping process between the counterions and n-type backbones (Taking the UV-vis-NIR spectrum of PNDIT-F3N-F as example).

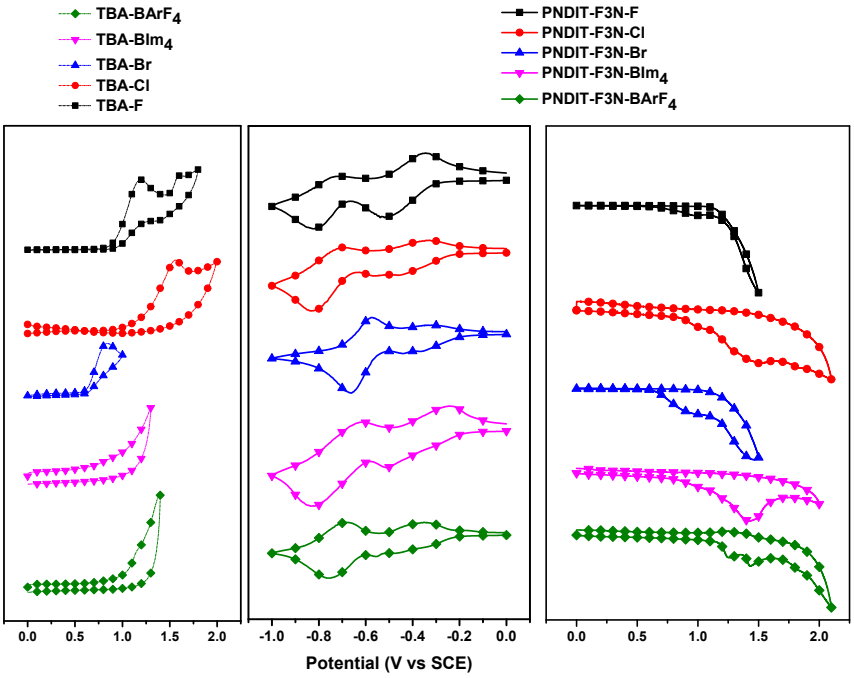


Fig. S7 The cyclic voltammetry curves of these CPEs and tetrabutylammonium salts (TBA-X, X= F, Cl, BIm_4 and $BArF_4$). The lowest unoccupied molecular orbital level (E_{LUMO}) of NDIT-F3N-$BArF_4$ backbone was calculated to be -3.9 eV.

Table S1 The work function (WF) of Ag electrode modified by CPEs with different thickness

	Thickness	PNDIT-F3N-F	PNDIT-F3N-Cl	PNDIT-F3N-Br	PNDIT-F3N-BIm_4	PNDIT-F3N-$BArF_4$
WF of Ag (eV)	5 nm	4.08	4.08	3.99	4.13	5.63
	40 nm	3.81	3.97	3.90	3.99	5.83
	80 nm	3.96	3.98	3.88	3.99	5.85

Table S2 Electron mobility calculated from electron-only devices with structure of ITO/Al/$PC_{71}BM$/CPEs (5 nm)/Al

	$PC_{71}BM$/PNDIT-F3N-F	$PC_{71}BM$/PNDIT-F3N-Cl	$PC_{71}BM$/PNDIT-F3N-Br	$PC_{71}BM$/PNDIT-F3N-BIm_4	$PC_{71}BM$/PNDIT-F3N-$BArF_4$	$PC_{71}BM$
Electron mobility ($\times 10^{-3}$ $cm^2V^{-1}s^{-1}$)	0.39	1.22	2.22	1.10	0.06	0.31

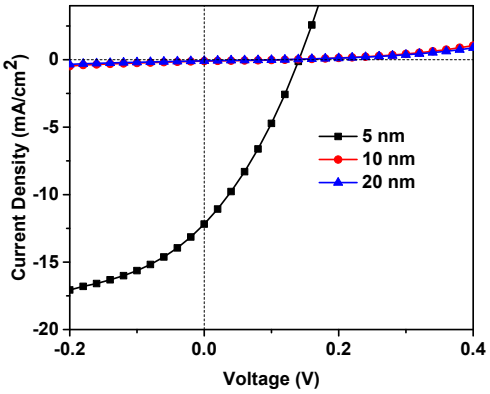


Fig. S8 *J-V* curves of photovoltaic devices with structure of ITO/ PNDI-F3N-$BArF_4$ (5-20 nm)/NT812:$PC_{71}BM$/ PNDI-F3N-Br/Al.

Table S3 Device parameters of PSCs based on NT812/$PC_{71}BM$ with 5-20 nm PNDI-F3N-$BArF_4$ CPEs as HTMs.

HTMs	*Voc* (V)	*Jsc* (mA/cm^2)	FF (%)	PCE (%)
PNDIT-F3N-$BArF_4$ (5 nm)	0.14 ±0.00	11.83 ±0.42	30.43±0.49	0.52±0.02 (0.53) [a]
PNDIT-F3N-$BArF_4$ (10 nm)	0.12±0.01	0.12±0.02	27.43±3.44	0.0038±0.001 (0.0039)
PNDIT-F3N-$BArF_4$ (20 nm)	0.11±0.00	0.08±0.01	26.52±1.59	0.0023±0.0003 (0.0025)

[a] the best PCE of photovoltaic devices