Fluorination increases the electron mobility of zinc azadipyrromethene-based electron acceptors and enhances performance of fullerene-free organic solar cells

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Characterization of $Zn(WS3)_2 – Zn(L4)_2$

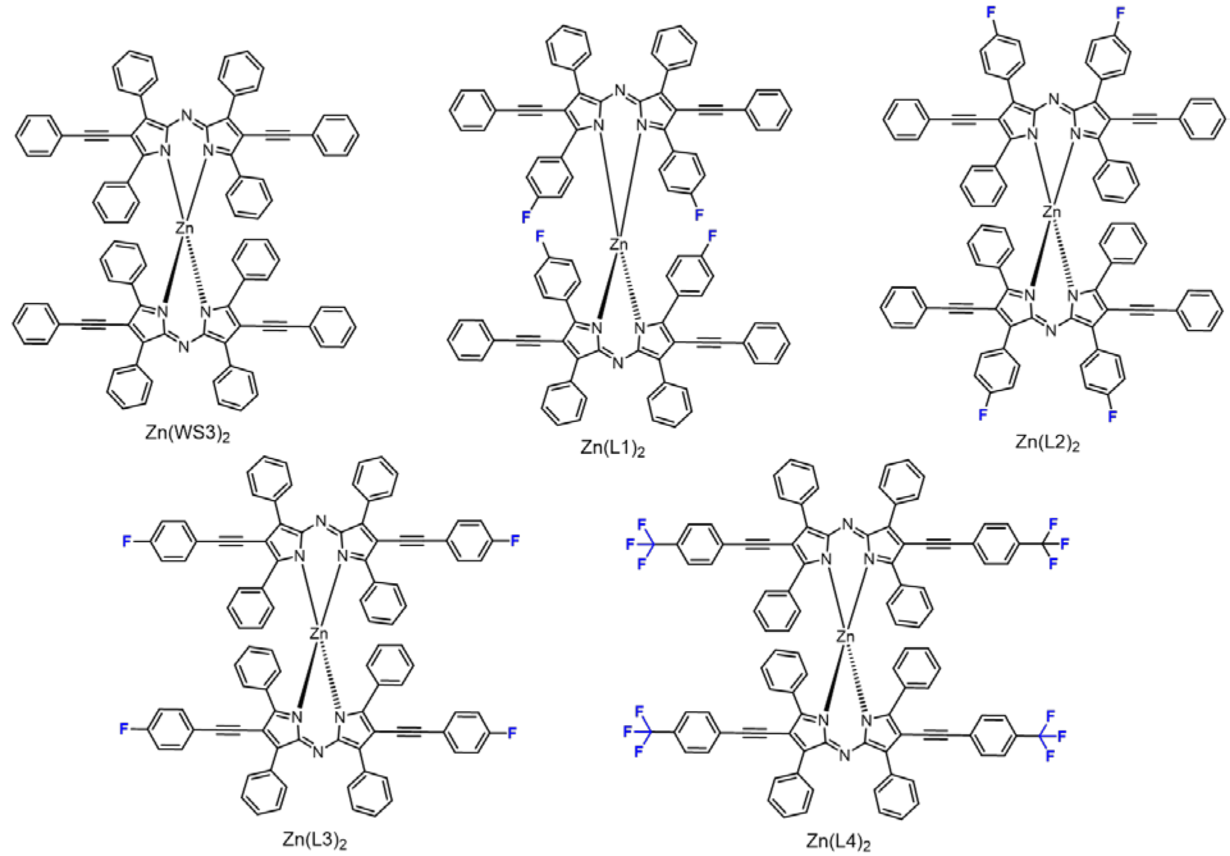

Figure S1. Zinc azadipyrromethene chelates ($Zn(WS3)_2$) and they fluorine derivations ($Zn(L1)_2$ – $Zn(L4)_2$).

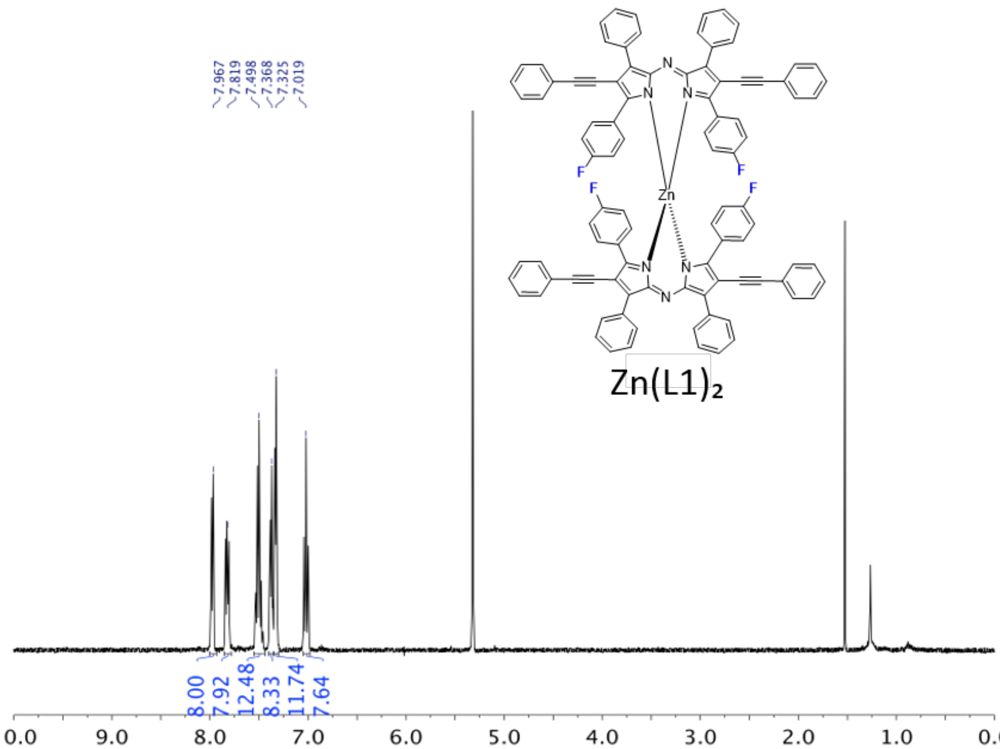

Figure S2. [1]H NMR of Zn(L1)$_2$ (1).

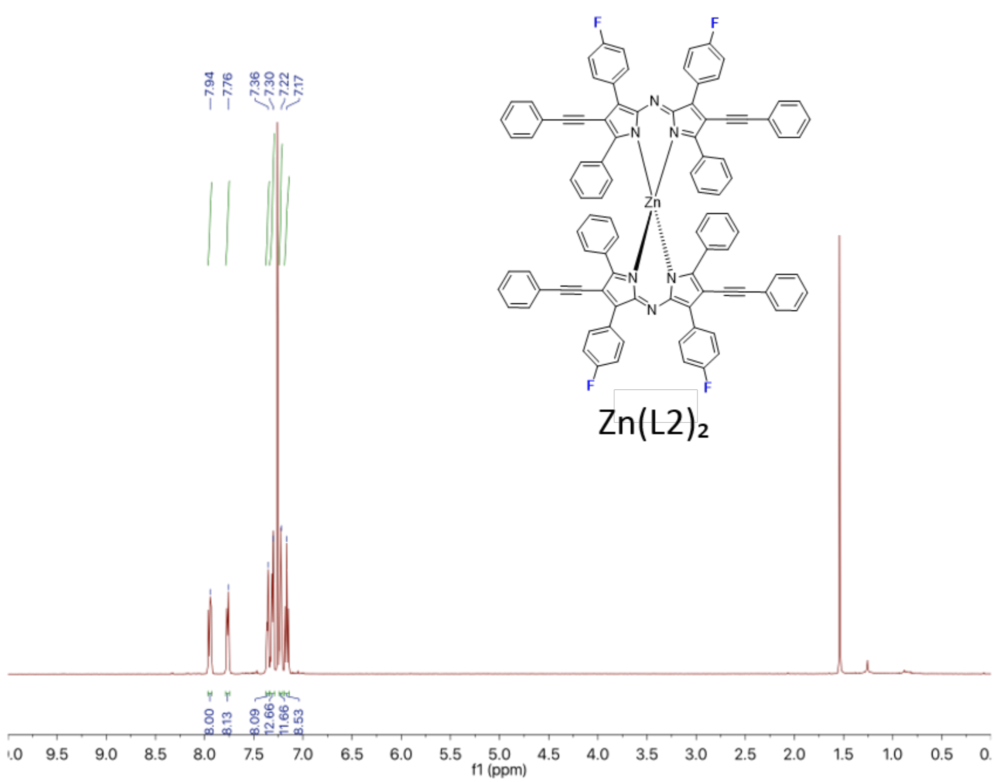

Figure S3. [1]H NMR of Zn(L2)$_2$ (1).

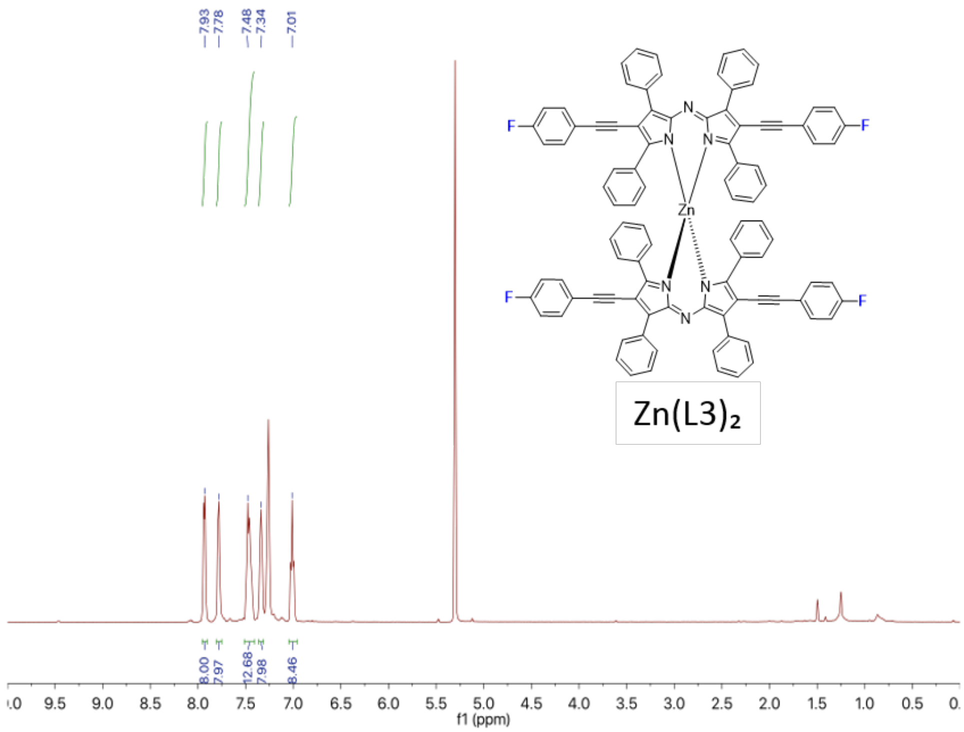

Figure S4. ^{1}H NMR of $Zn(L3)_2$ (1).

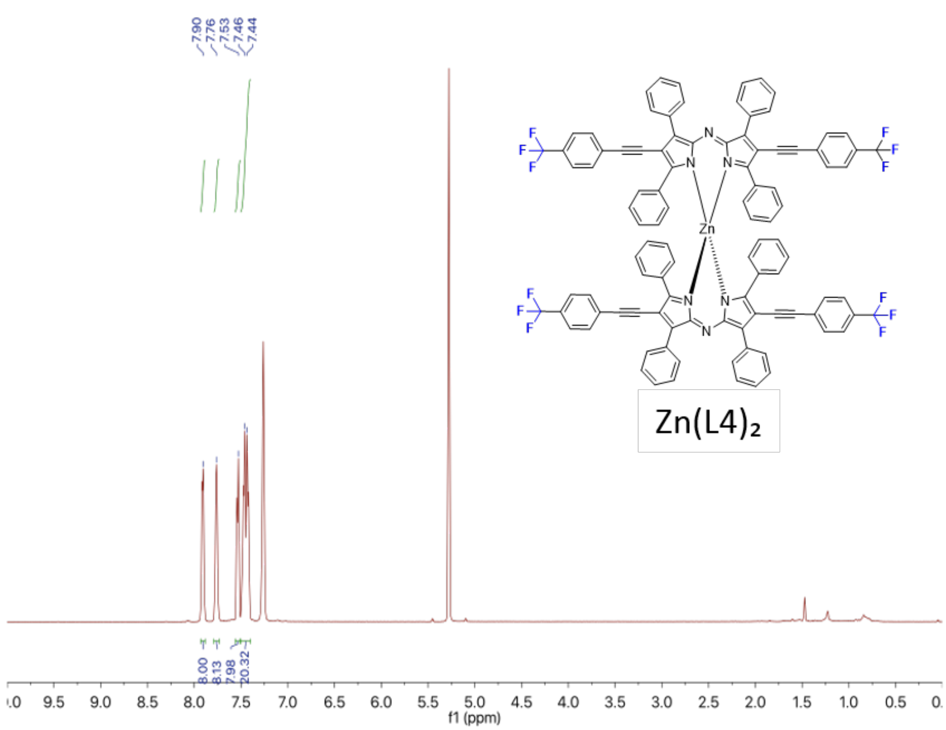

Figure S5. ^{1}H NMR of $Zn(L4)_2$ (1).

Table S1. Elemental analysis of $Zn(L1)_2$ (1).

	Theoretical	**Found**	**Difference**
Carbon	80.36	80.58	0.22
Hydrogen	3.93	4.08	0.15
Nitrogen	5.86	5.89	0.03

Table S2. Elemental analysis of $Zn(L2)_2$ (1).

	Theoretical	**Found**	**Difference**
Carbon	80.36	80.19	0.17
Hydrogen	3.93	4.04	0.11
Nitrogen	5.86	5.78	0.08

Table S3. Elemental analysis of $Zn(L3)_2$ (1).

	Theoretical	***Found***	***Difference***
Carbon	80.36	80.13	0.23
Hydrogen	3.93	4.09	0.16
Nitrogen	5.86	5.69	0.17

Table S4. Elemental analysis of $Zn(L4)_2$ (1).

	Theoretical	***Found***	***Difference***
Carbon	73.46	73.42	0.04
Hydrogen	3.45	3.69	0.14
Nitrogen	5.14	5.06	0.08

Table S5. Electrochemical properties of $Zn(WS3)_2$ – $Zn(L4)_2$ in dichloromethane. All reported values are in V *vs.* Fc/Fc^+ (1).

	$E_{1/2\ ox.}$	$E_{(p,a)}$	$E_{1/2\ red.}$	$E_{(p,c)}$
$Zn(WS3)_2$	0.50, 0.77	0.58, 0.86	-1.25, -1.47	-1.33, -1.55
$Zn(L1)_2$	0.60, 0.78	0.66, 0.87	-1.16, -1.39	-1.11, -1.33
$Zn(L2)_2$	0.54, 0.73	0.58, 0.81	-1.24, -1.45	-1.19, -1.41
$Zn(L3)_2$	0.56, 0.79	0.61, 0.86	-1.23, -1.44	-1.18, -1.39
$Zn(L4)_2$	0.61, 0.84	0.66, 0.88	-1.15, -1.36	-1.11, -1.32

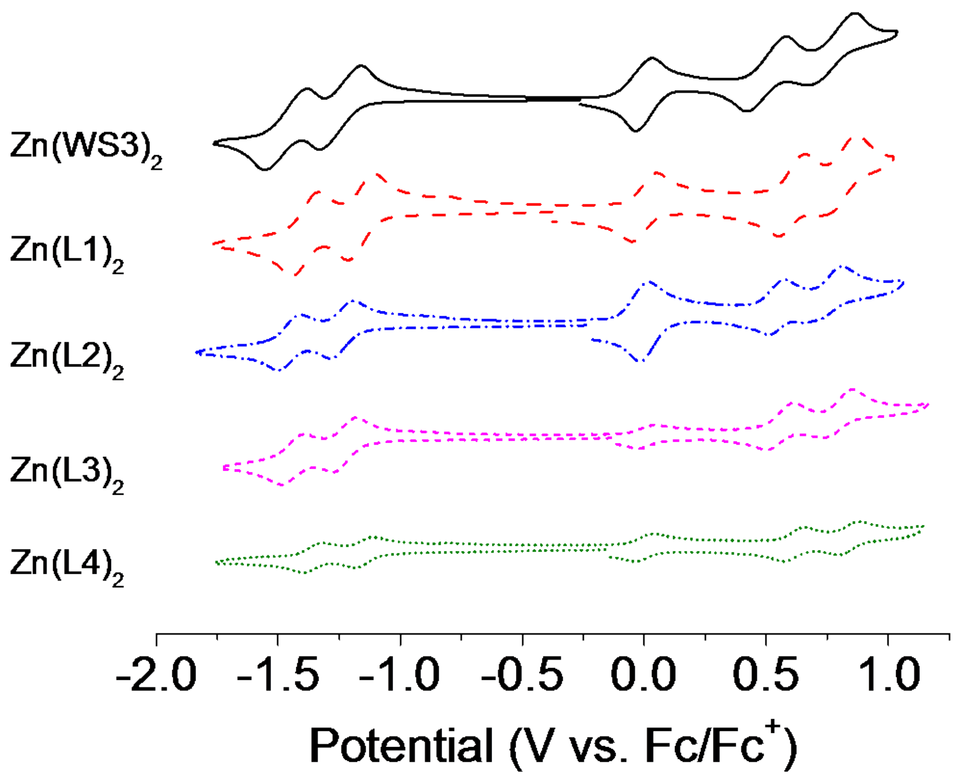

Figure S2. Cyclic voltamograms of $Zn(WS3)_2$ – $Zn(L4)_2$ in 0.1 M $TBAPF_6$ dichloromethane solution with Fc/Fc^+ as an internal standard ($E_{1/2}$ at 0.0 V) (1).

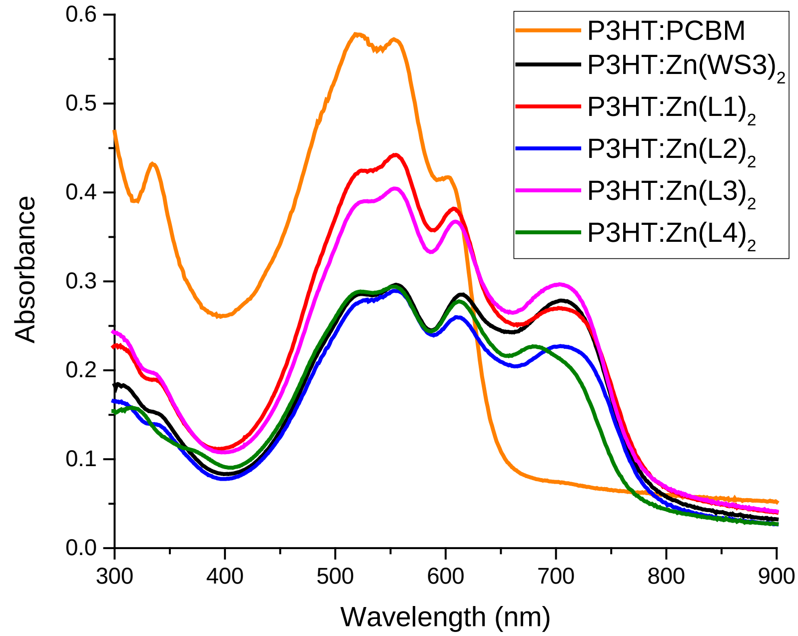

Figure S3. UV-vis absorption spectra of blended P3HT:Acceptor films. Ratios and concentrations vary to match optimized photovoltaic active layers.

Additional atomic force microscopy (AFM) images

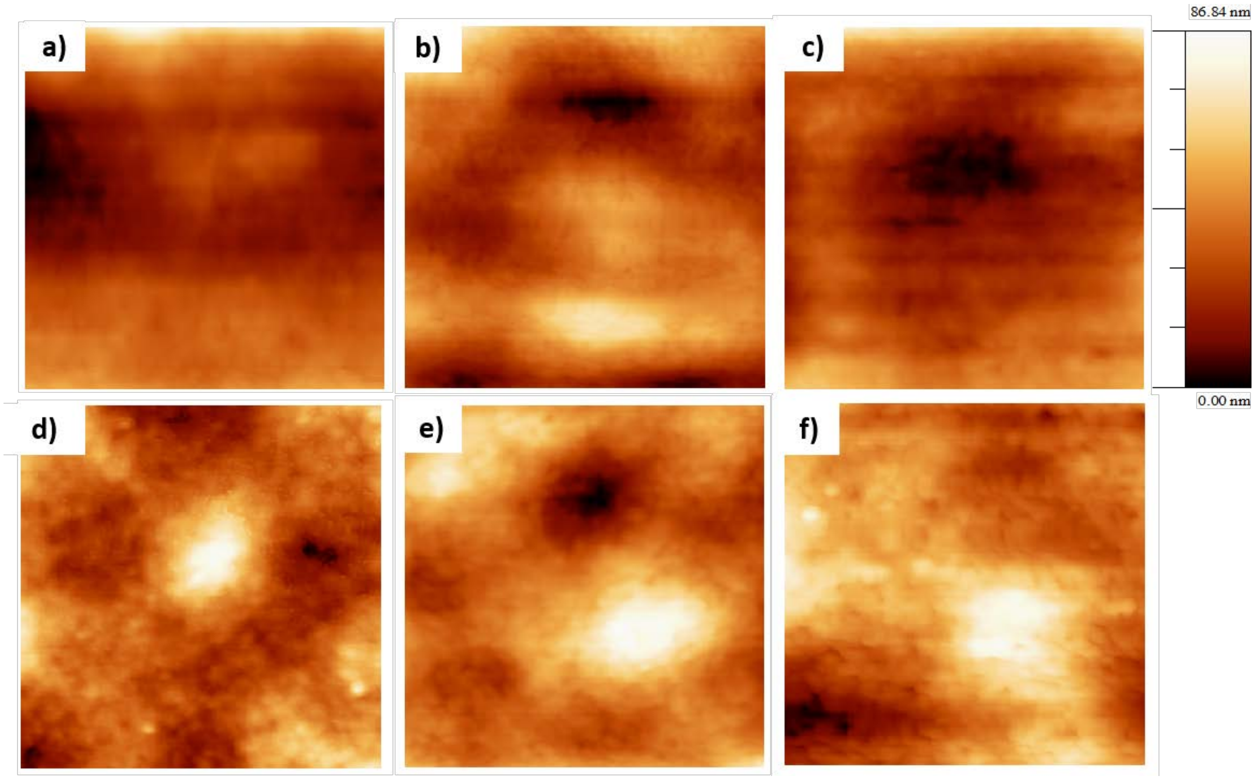

Figure S8. Atomic force microscopy 1 x 1µm height images of blend films of a) P3HT: PCBM b) P3HT: $Zn(WS3)_2$ c) P3HT:$Zn(L1)_2$ d) P3HT:$Zn(L2)_2$ e) P3HT:$Zn(L3)_2$ f) P3HT:$Zn(L4)_2$.

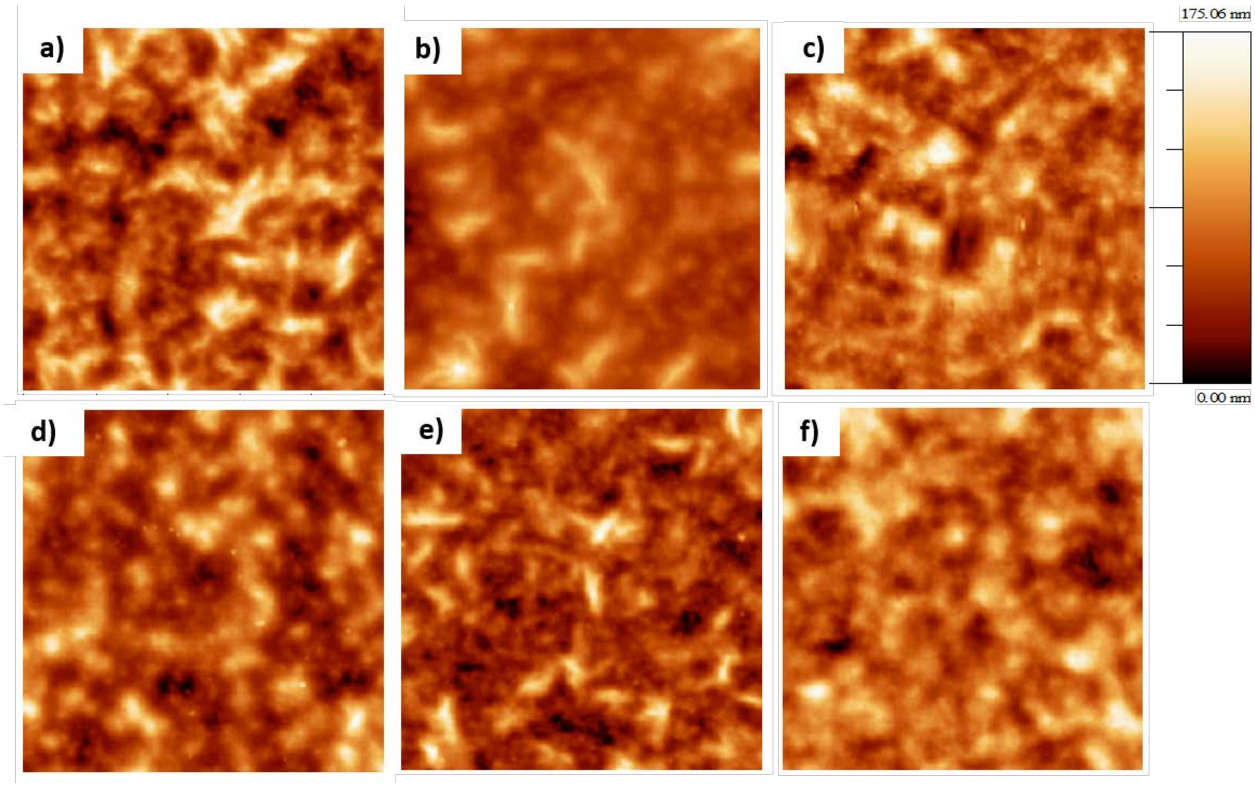

Figure S9. Atomic force microscopy 10 x 10μm height images of blend films of a) P3HT: PCBM b) P3HT: $Zn(WS3)_2$ c) P3HT:$Zn(L1)_2$ d) P3HT:$Zn(L2)_2$ e) P3HT:$Zn(L3)_2$ f) P3HT:$Zn(L4)_2$.

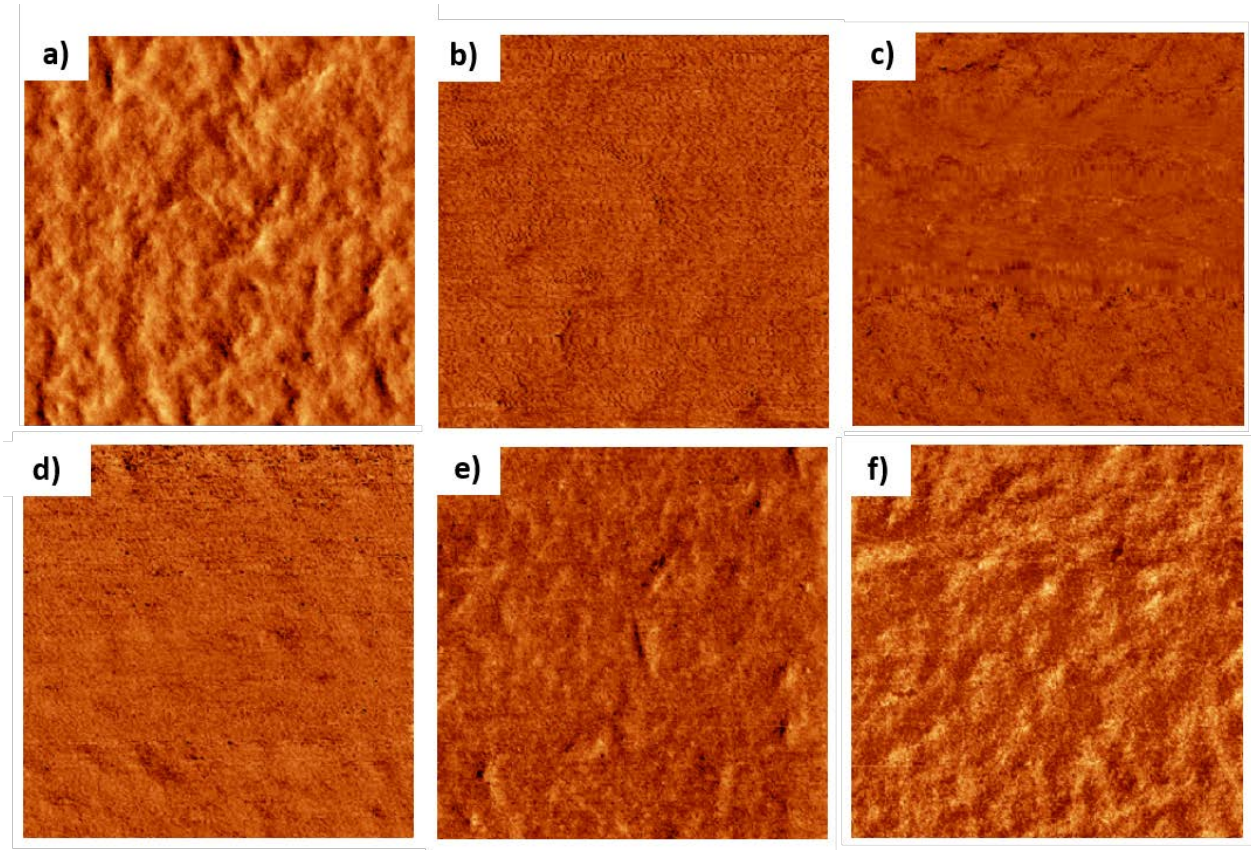

Figure S10. Atomic force microscopy 10 x 10µm phase images of blend films of a) P3HT: PCBM b) P3HT: $Zn(WS3)_2$ c) P3HT:$Zn(L1)_2$ d) P3HT:$Zn(L2)_2$ e) P3HT:$Zn(L3)_2$ f) P3HT:$Zn(L4)_2$.

References

1. Etheridge FS, Fernando RJ, Pejic S, Zeller M, Sauve G. Synthesis and characterization of fluorinated azadipyrromethene complexes as acceptors for organic photovoltaics. *Beilstein J Org Chem*. 2016;12:1925-38.