Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Asymmetric triphenylamine –phenothiazine based small molecules with varying terminal acceptor for solution processed bulk heterojunction organic solar cells

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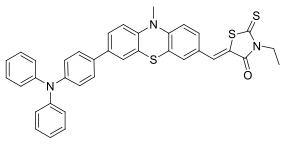
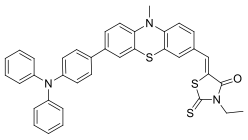
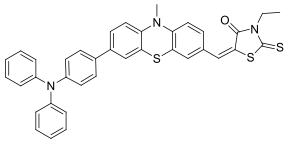
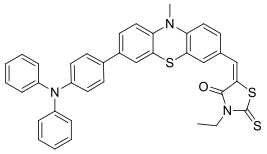
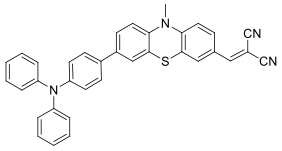
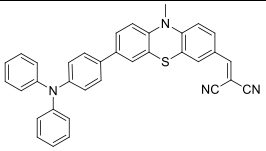
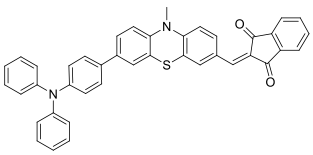
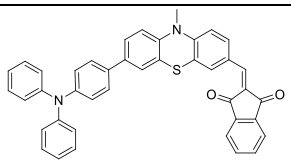
Table S1. B3LYP/6-31G(d) geometry-optimized configurations and conformations of **M1**, **M2** and **M3**, with energy differences, dipole moments, and HOMO/LUMO energy levels.[a]

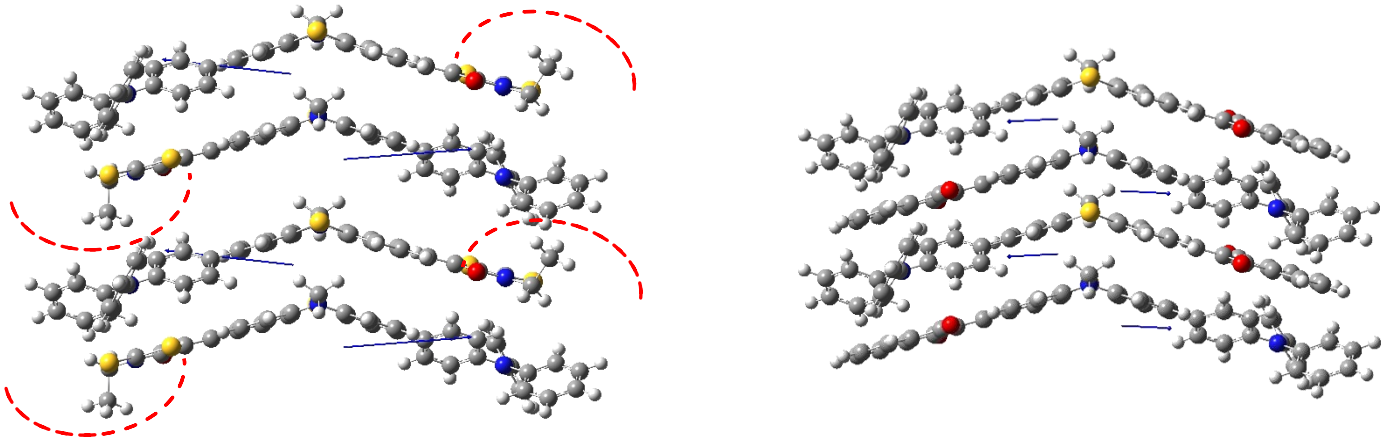
Compound; Configuration or conformation		**DFT-optimized geometry**	**ΔE** (kJ mol^{-1})	**Dipole moment** (D)		**HOMO/LUMO** (eV)
				In vacuo	PCM ε = 4.81	
M1	1		0	6.0	7.2	-4.97/-2.42
	2		0.5	6.7		-4.95/-2.39
	3		14.9	7.1		
	4		15.9	7.2		
M2	1		0	10.2	11.7	-5.08/-2.63
	2		1.4	10.4		-5.04/-2.60
M3	1		0	3.7	4.5	-4.93/-2.39
	2		1.0	3.2		-5.04/-2.60

[a] The DFT calculations were performed with an *N*-methyl group instead of the *N*-ethylhexyl group in the structures of **M1**-**M3**. The PCM calculations of dipole moments were done as single-point calculations on the lowest-energy structure of each compound **M1**-**M3.**

Table S2. Main characteristics of singlet-singlet electronic transitions obtained by TD-DFT calculations for the lowest-energy structure of SMs **M1**, **M2** and **M3**.[a]

	Excitation	Transitions		Wavelength (nm)	Energy (eV)	Oscillator strength
M1	1	163 ->165 164 ->165	-0.10348 0.69637	538.77	2.3012	0.2220
	2	163 ->165 164 ->165	0.68480 0.11277	468.06	2.6489	0.2415
	3	160 ->165 162 ->165 164 ->166 164 ->167	-0.15976 0.61739 0.23607 -0.12176	372.15	3.3315	1.0371
	4	160 ->165 162 ->165 163 ->165 163 ->166 164 ->166 164 ->167	0.11133 -0.22006 -0.10340 -0.14715 0.60873 -0.13780	354.04	3.5020	0.1778
M2	1	139 ->140	0.70182	564.56	2.1961	0.1442
	2	138 ->140	0.68650	473.27	2.6197	0.1880
	3	136 ->140 137 ->140 139 ->141	0.11033 0.54738 -0.40167	360.45	3.4397	0.6775
	4	136 ->140 137 ->140 139 ->141	-0.10563 0.39790 0.54487	348.61	3.5566	0.2646
M3	1	159 ->161 160 ->161	-0.11709 0.69434	546.01	2.2707	0.2715
	2	159 ->161 160 ->161	0.68483 0.12495	477.04	2.5991	0.2122
	3	158 ->161 160 ->163	0.61156 -0.31091	366.52	3.3827	0.7891
	4	157 ->161 158 ->161 160 ->163	-0.17078 0.30111 0.59273	349.87	3.5437	0.2899
	5	157 ->161 159 ->163 159 ->164 160 ->163 160 ->164	0.60845 -0.14830 -0.11002 0.13250 0.17048	327.41	3.7868	0.4580

[a] The table has data for excitations with wavelength > 300 nm and oscillator strength > 0.1



(a) (b)

Figure S1. Proposed π-π-stacking with antiparallel alignment of the individual molecules; (a) **M1**, where the *N*-ethyl group inhibits a tight stacking due to steric hindrance. (b) **M3**, where a steric hindrance such as that of **M1** does not exist.

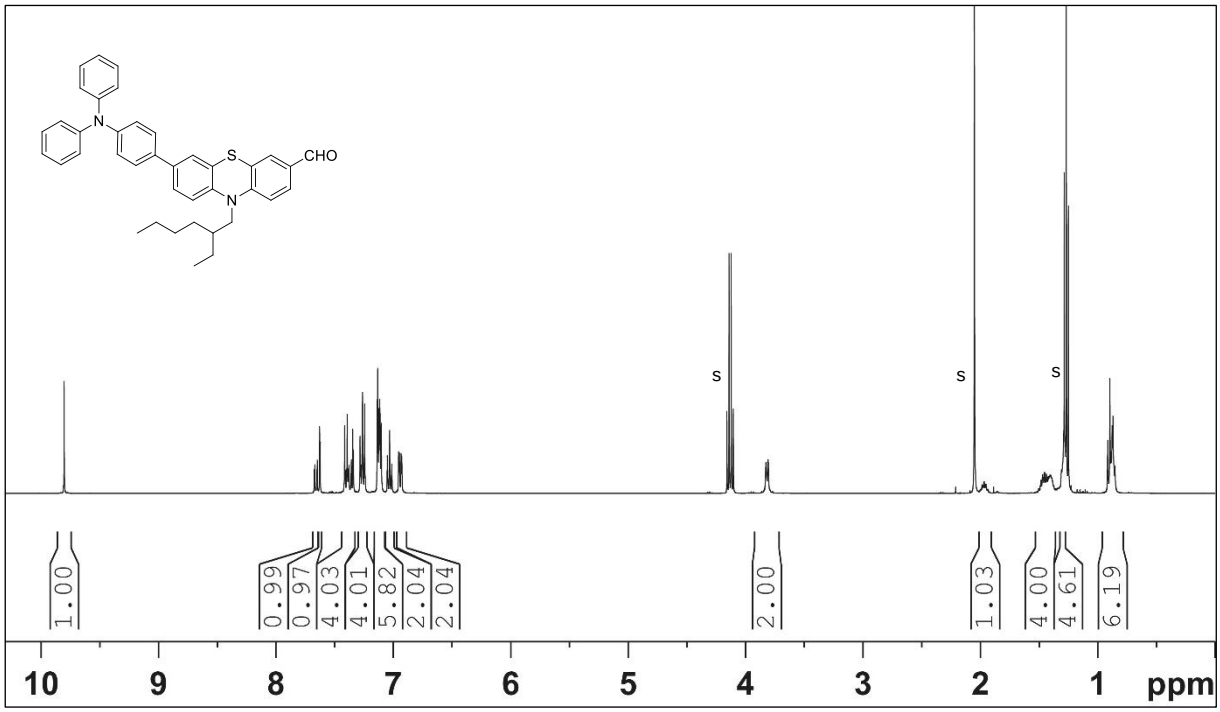


Figure S2. ^{1}H NMR of compound **5**.

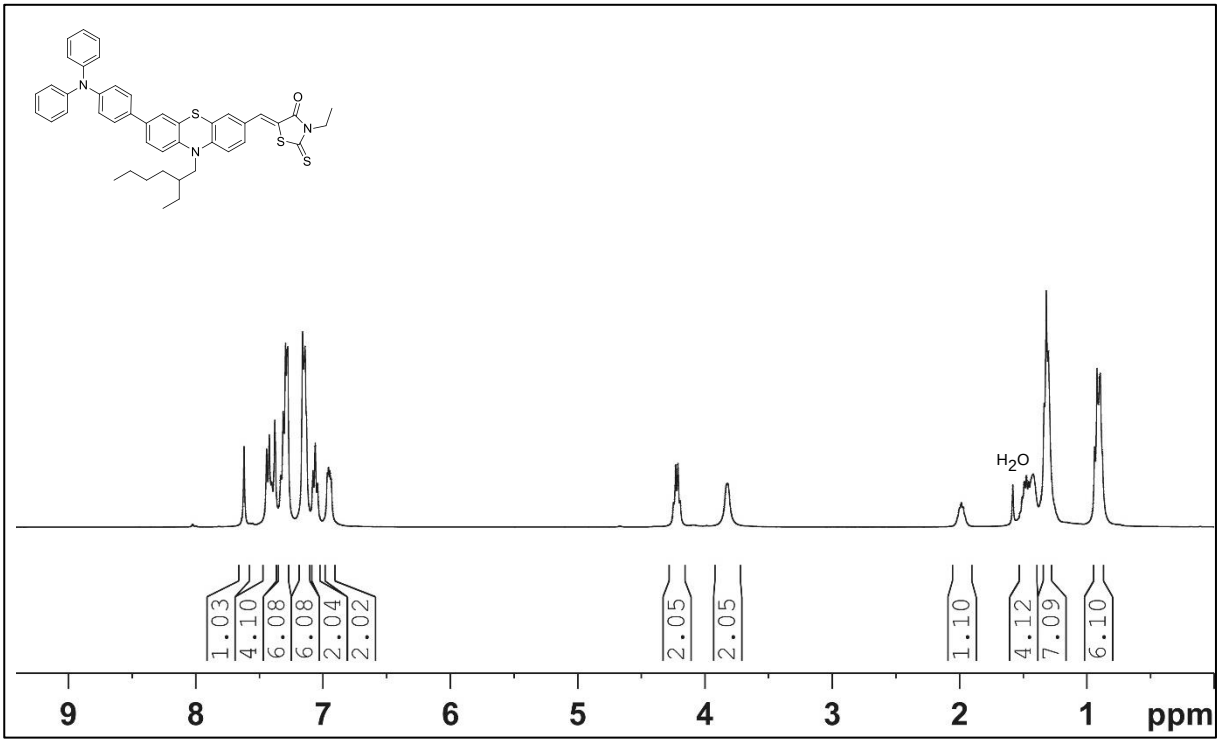


Figure S3. ^{1}H NMR of compound **M1**.

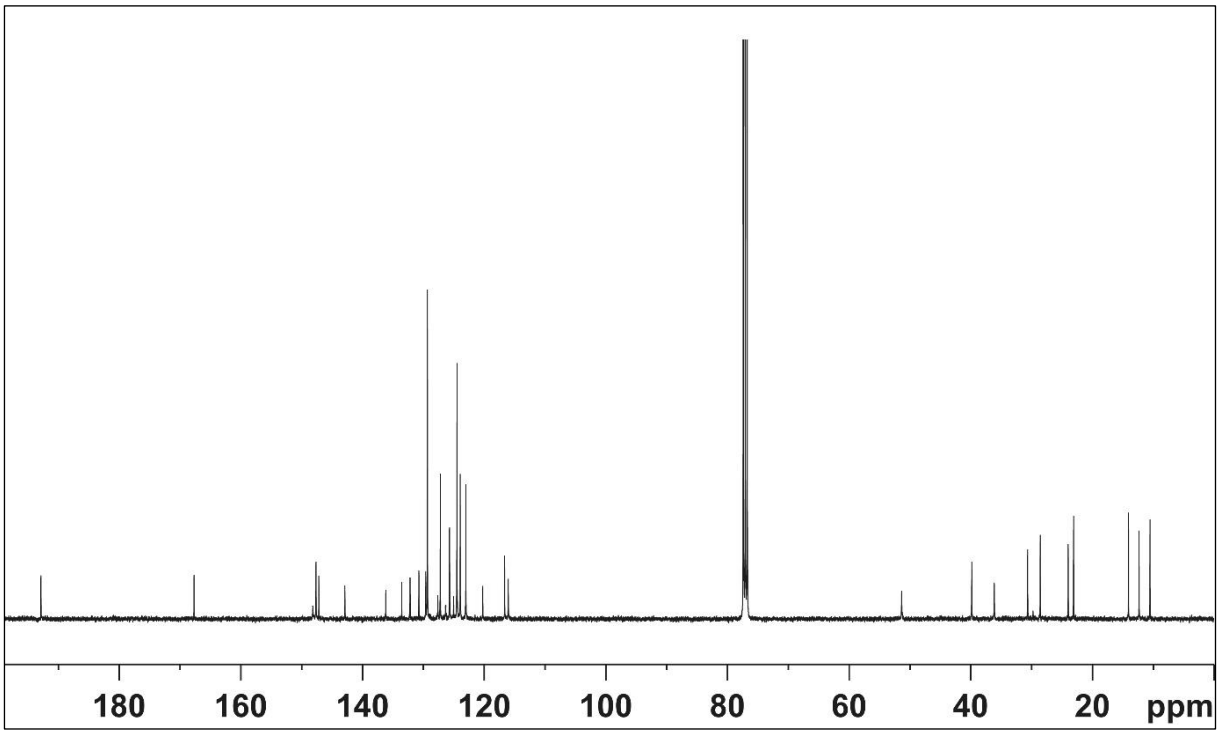


Figure S4. ^{13}C NMR of compound **M1**.

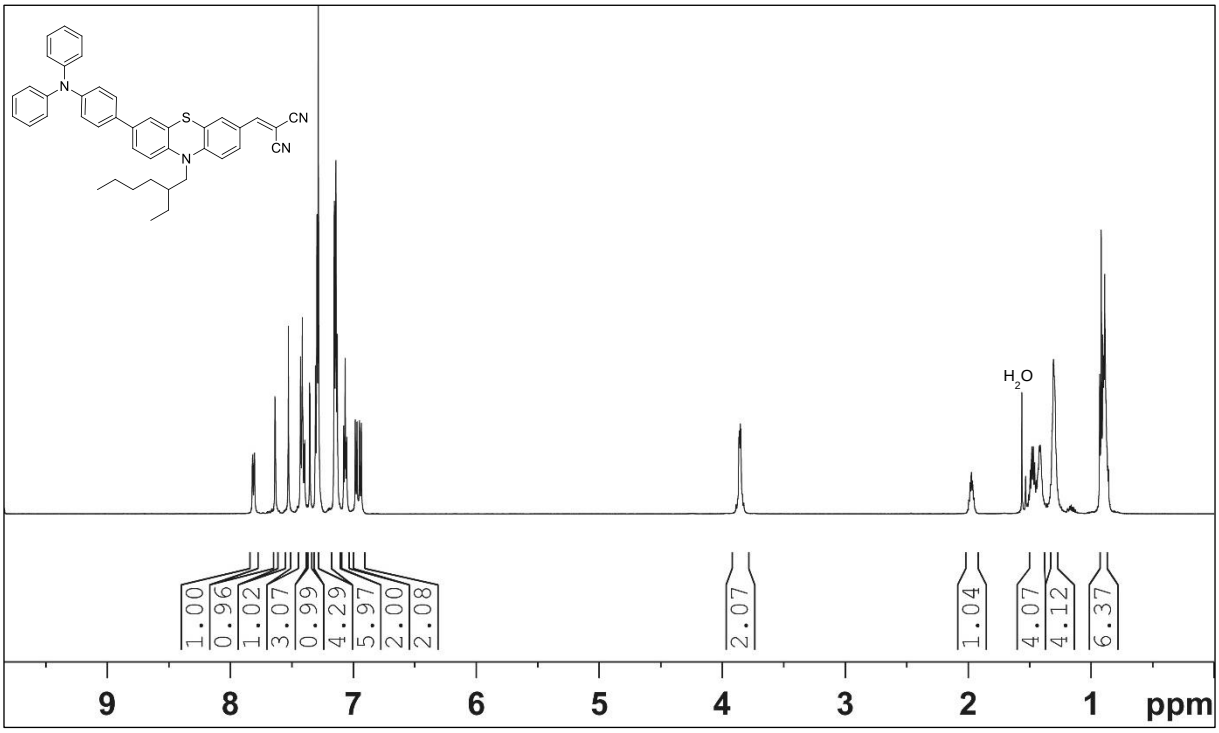


Figure S5. ^{1}H NMR of compound **M2**.

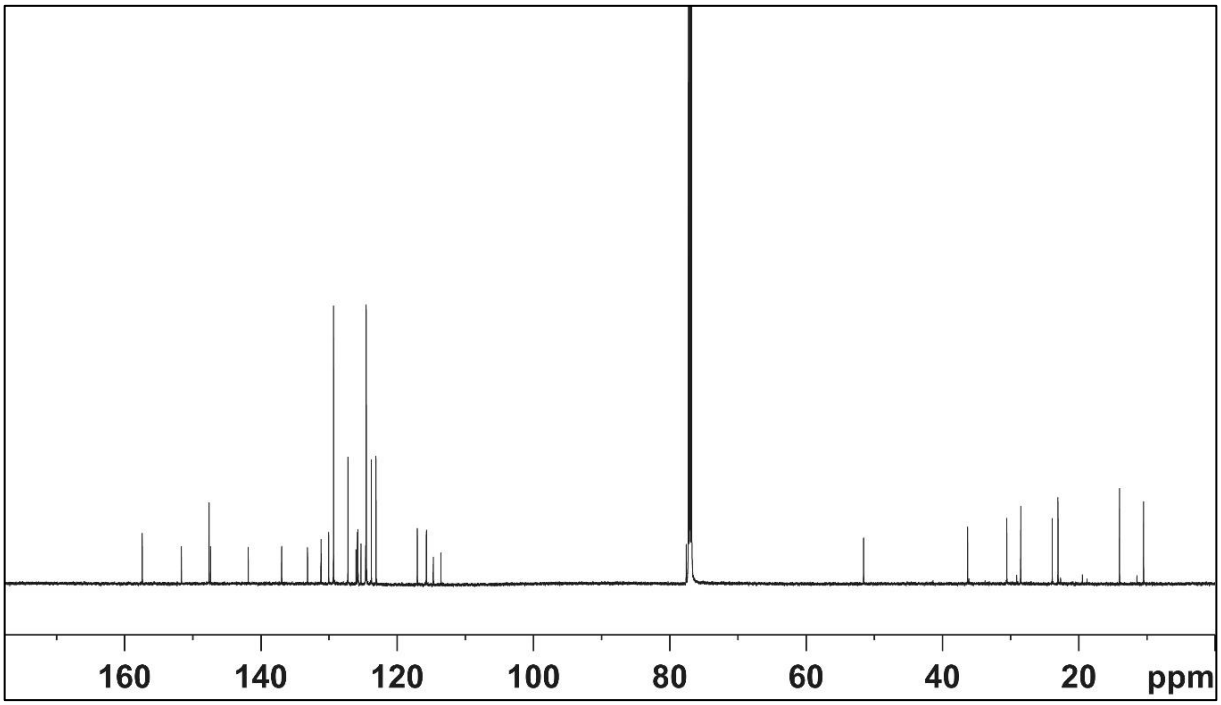


Figure S6. ^{13}C NMR of compound **M2**.

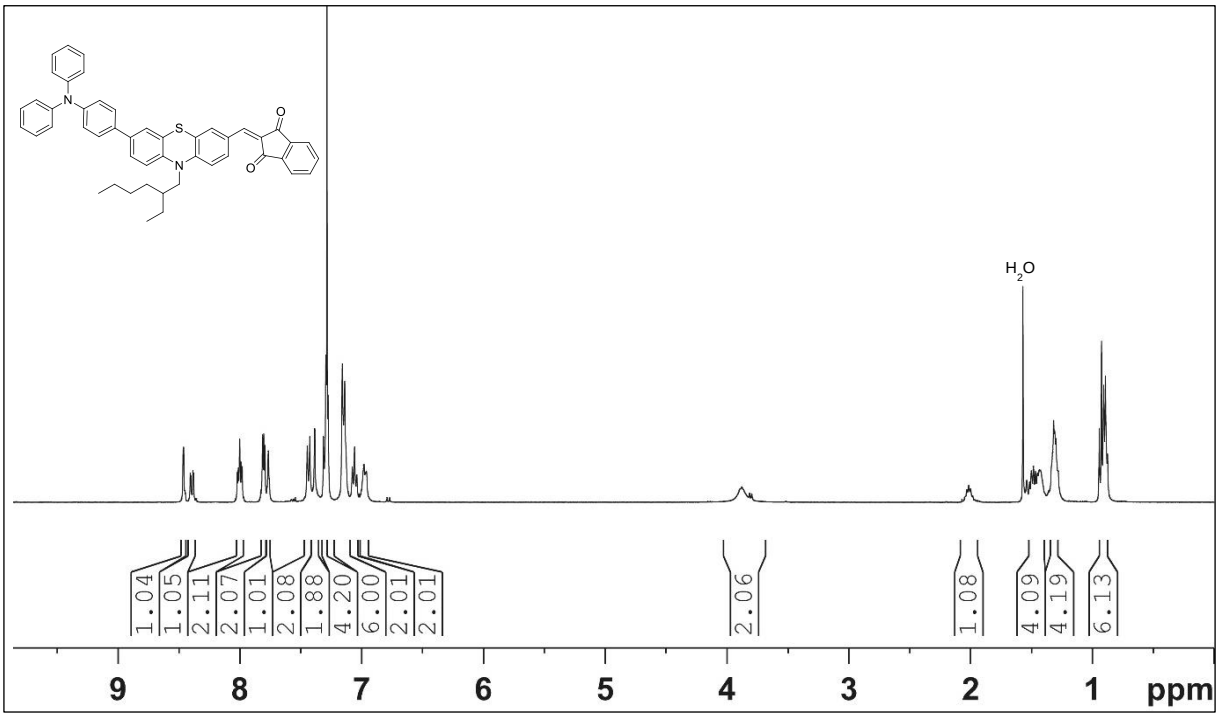


Figure S7. ^{1}H NMR of compound **M3**.

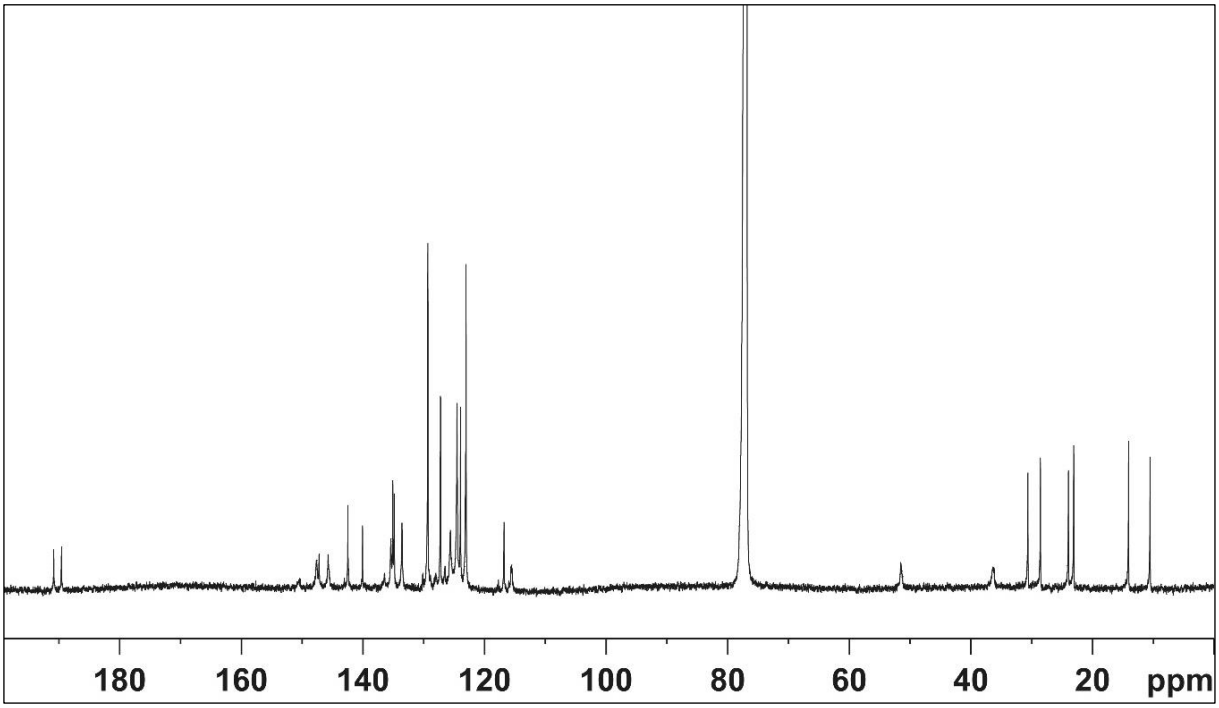


Figure S8. ^{13}C NMR of compound **M3**.

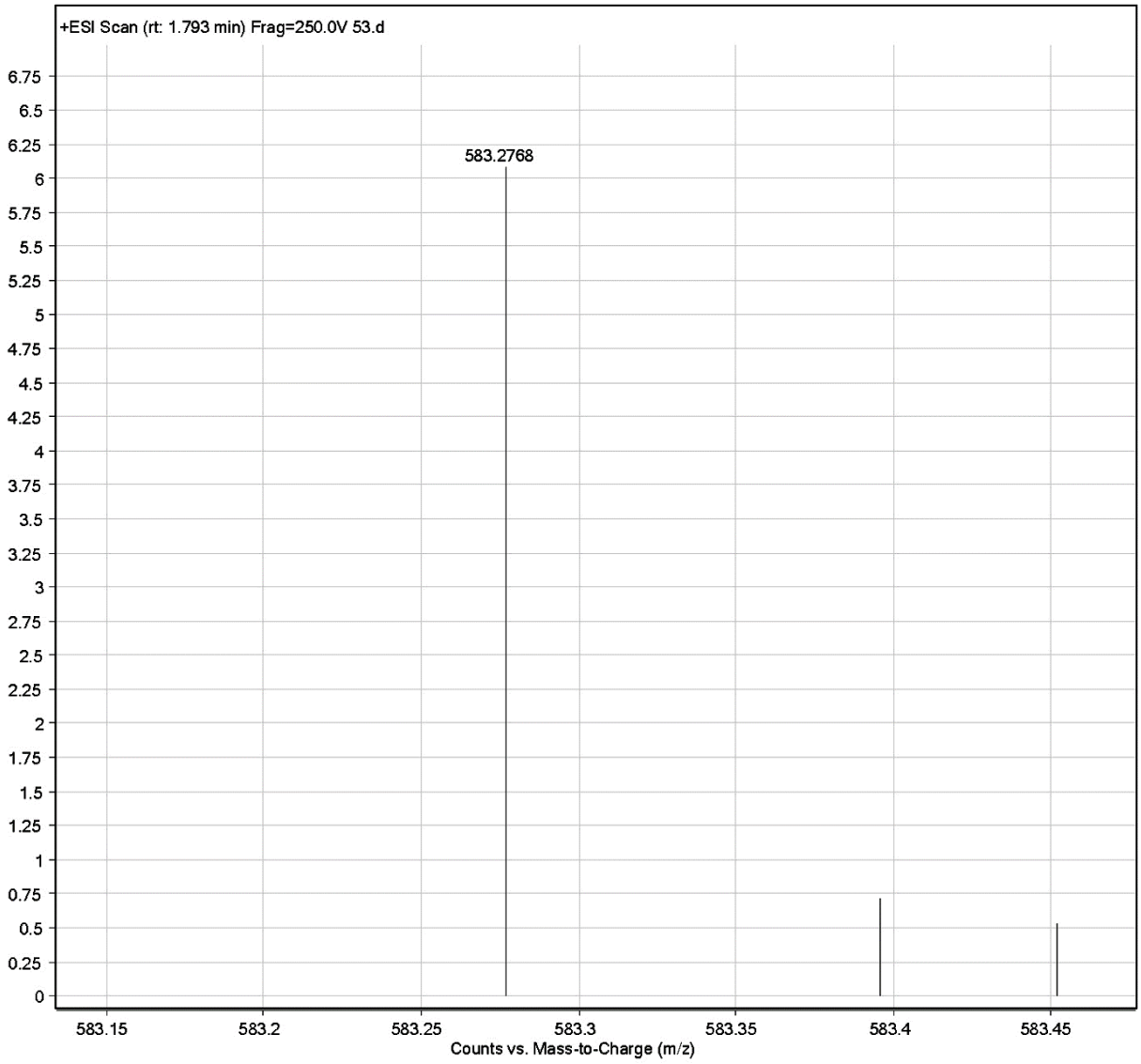


Figure S9. HRMS of compound **5**.

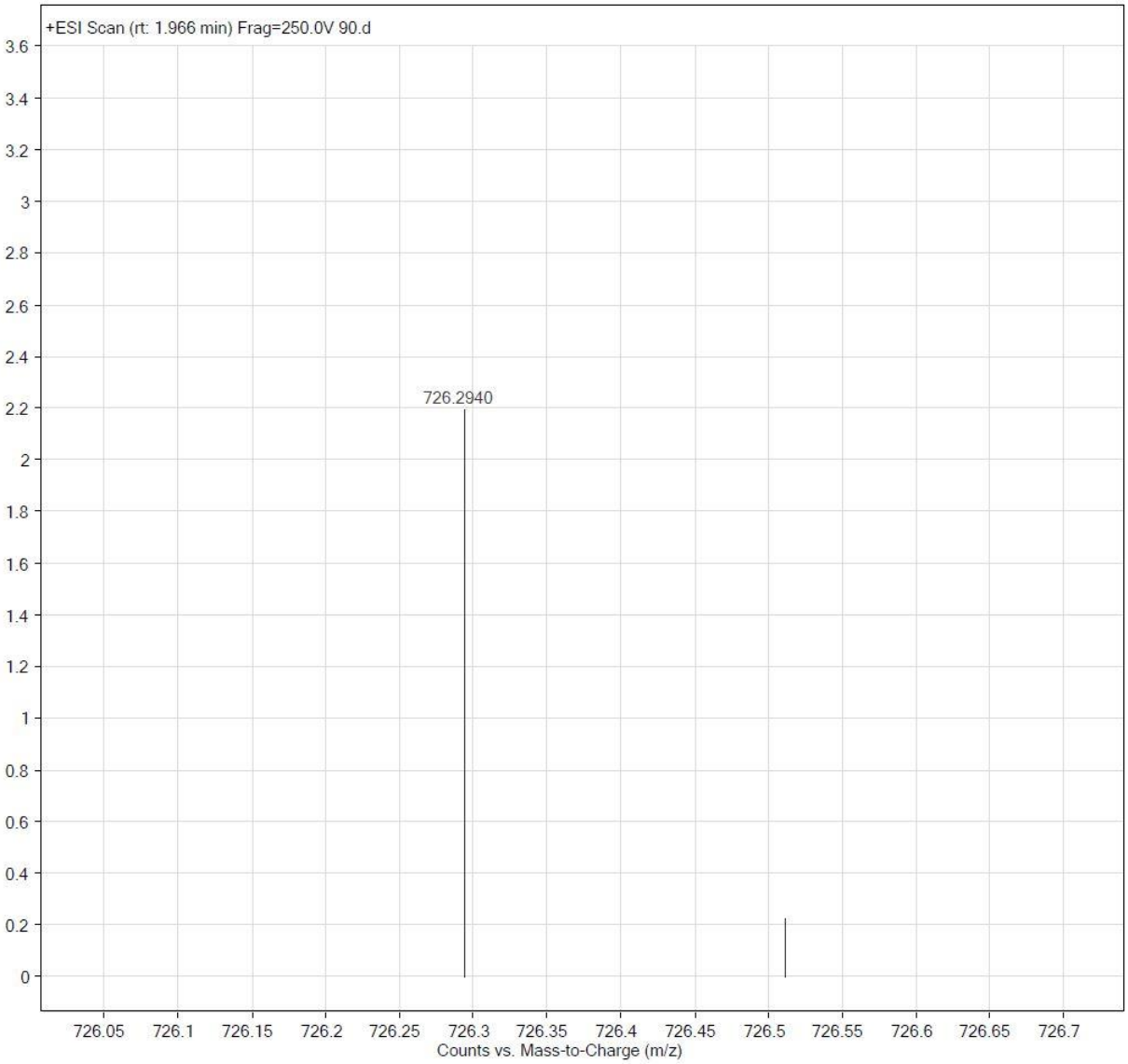


Figure S10. HRMS of compound **M1**.

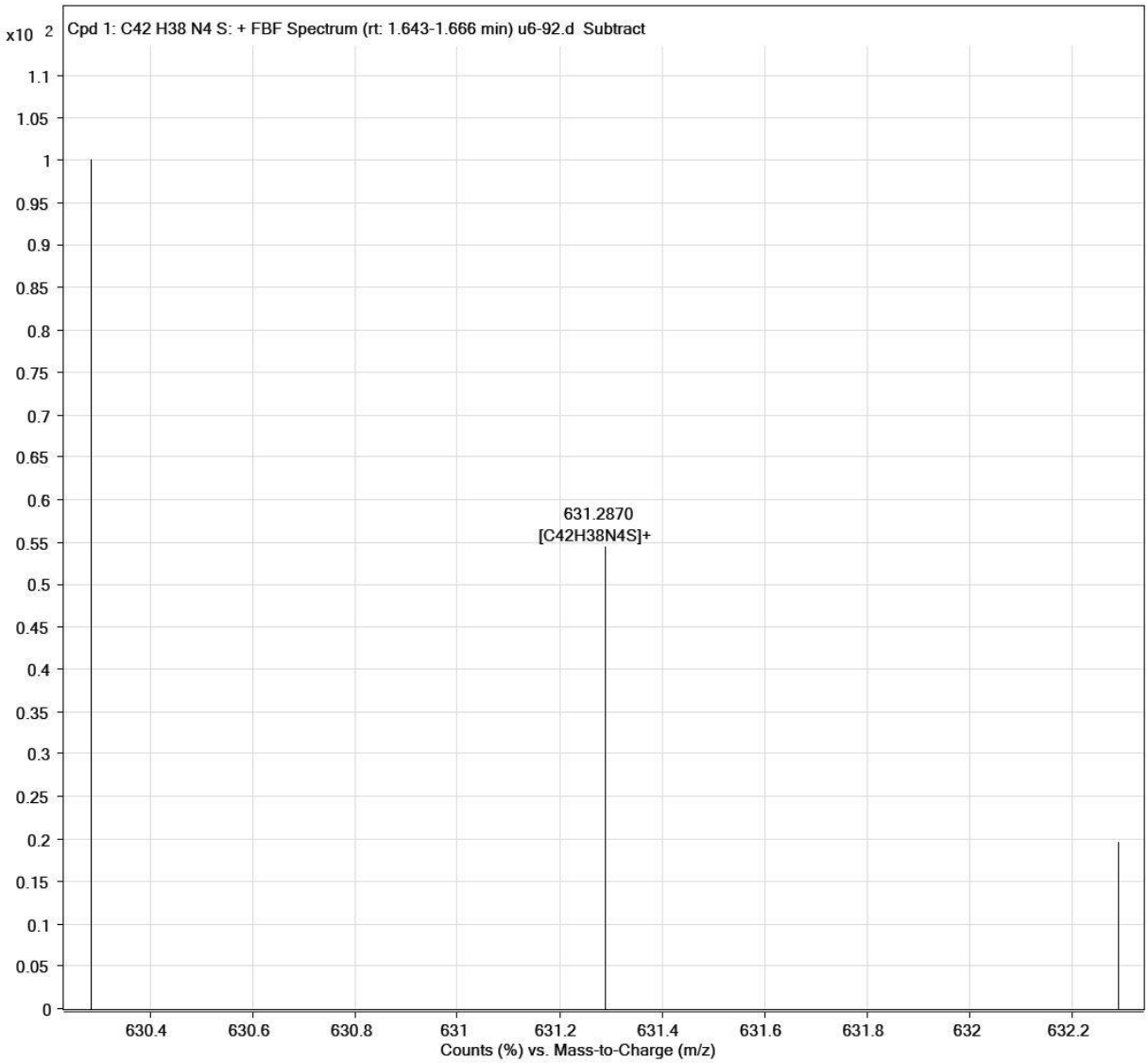


Figure S11. HRMS of compound **M2**.

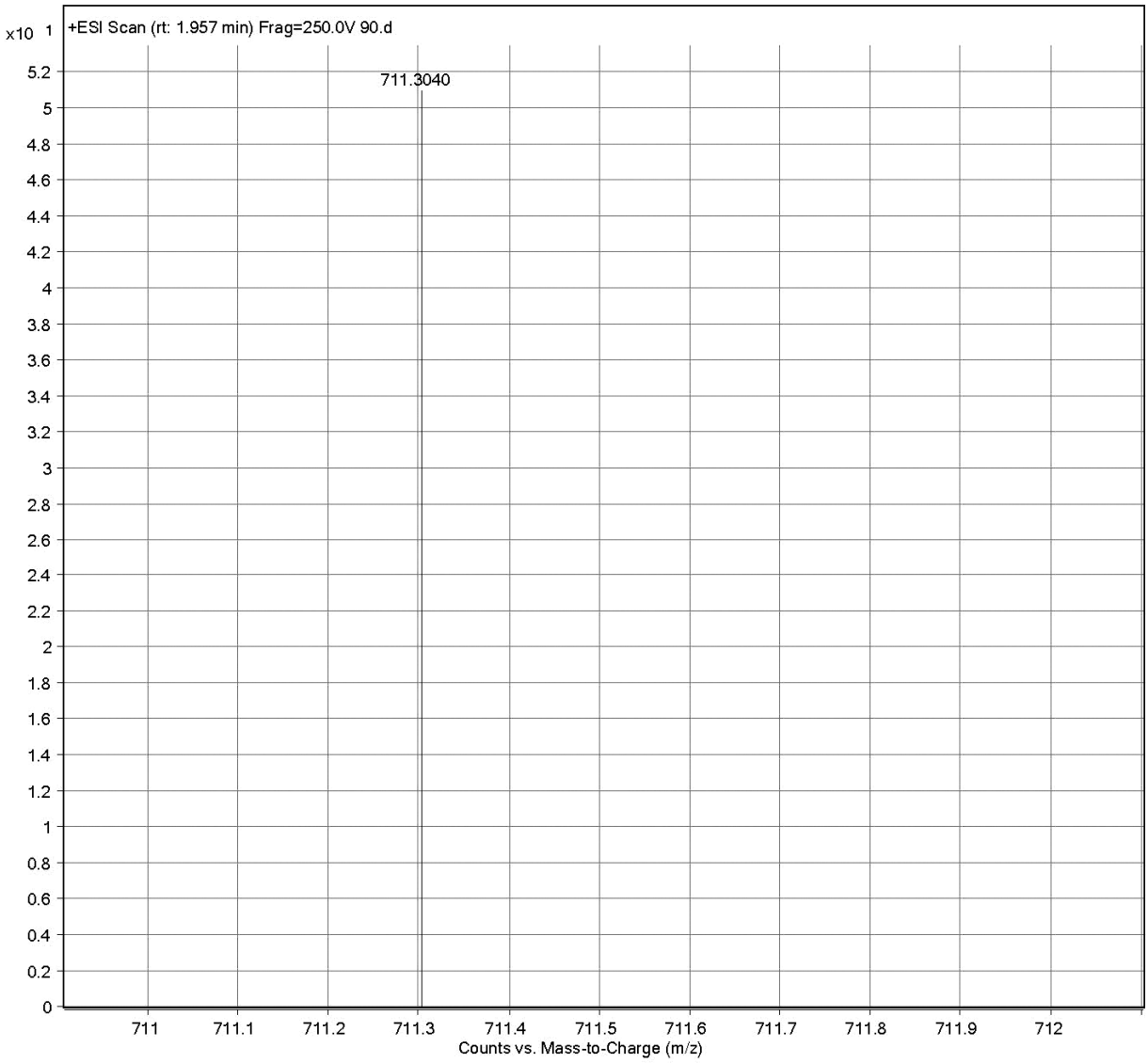


Figure S12. HRMS of compound **M3**.

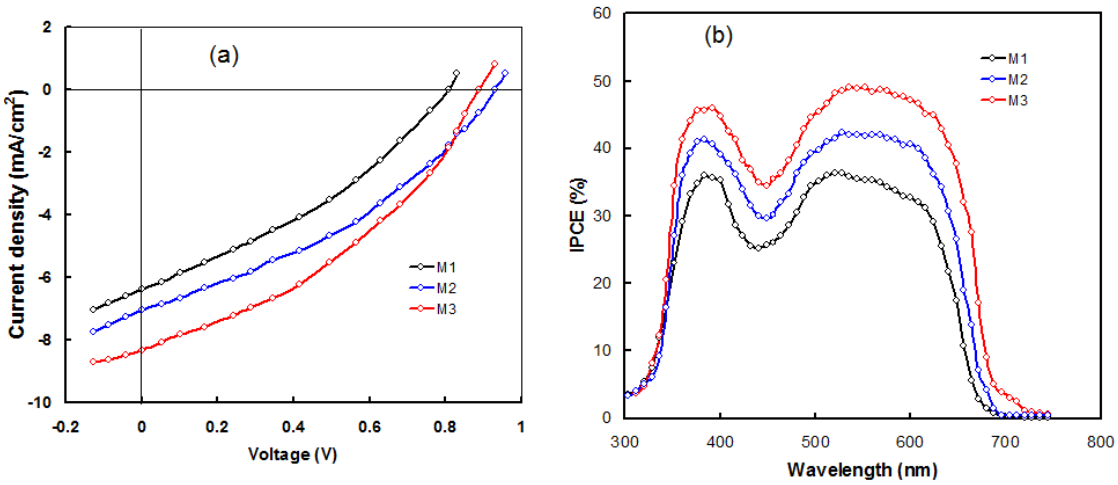


Figure S13. Current-voltage characteristics under illumination of OSCs based on as cast active layers.