Supporting Information

Semiconductor Self-Assembled Monolayers as Selective Contact for Efficient PiN Perovskite Solar Cells.

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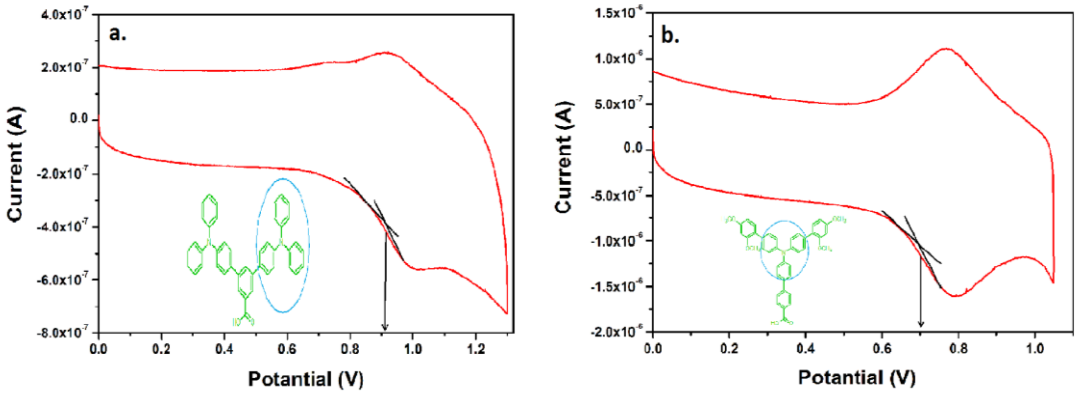

Figure S1. Cyclic Voltammograms of ITO/TPA (a), and ITO/MC-43 (b).

For the electrochemical study, a 3-electrode system was chosen. All measurements were performed in 0.1 M $TBAPF_6$ (tetrabutylammonium hexafluorophosphate) solution. The new HOMO level of modified ITO was found from the inflection point of the voltammograms of individual of ITO/TPA (a) and ITO/MC-43 (b) coatings. The energy of the HOMO level of ITO were calculated from the following formulation using the oxidation potentials of the substrates (Dai et al., 2010):

$$E_{HOMO} = -(E_{1/2(ox.)} + 4.4)\ eV$$

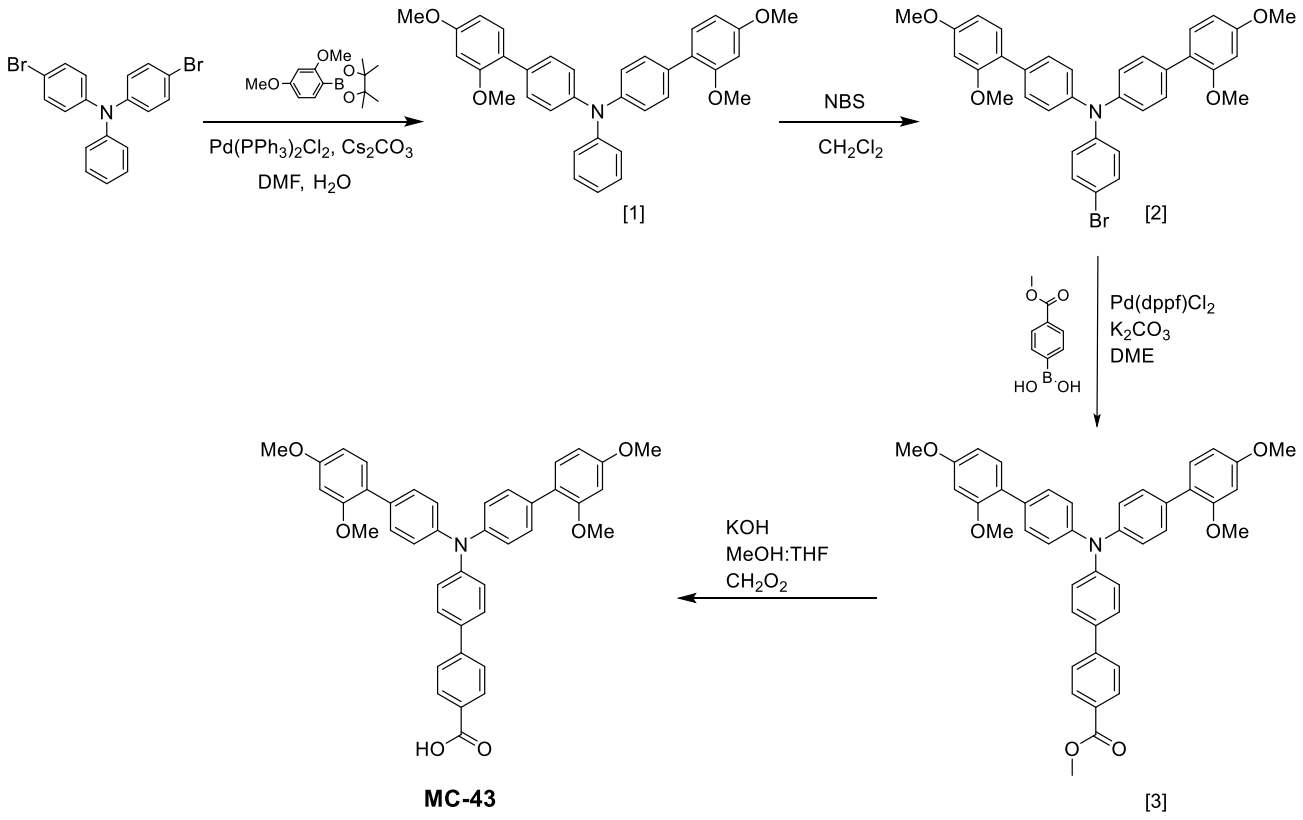

Figure S2. Synthetic route for MC-43.

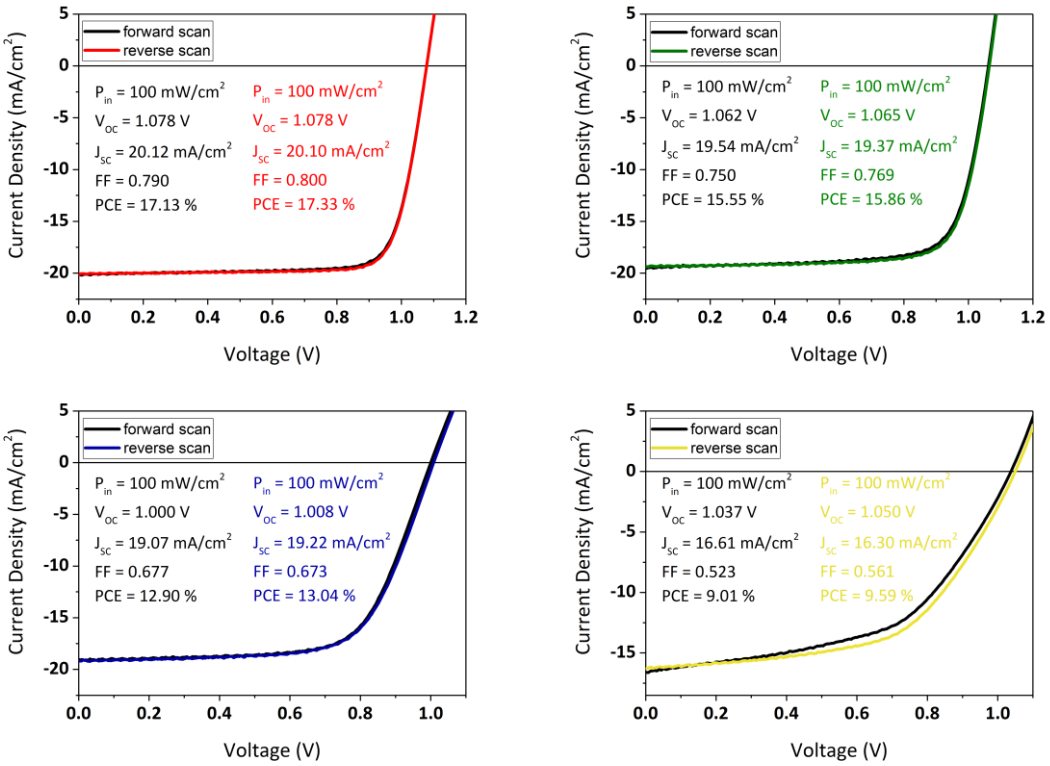

Figure S3. J-V characteristics of best PSC based on MC-43 (red), TPA (green), PEDOT:PSS (blue) and bare ITO (yellow) at 1 sun. Both forward and reverse scans have been performed at a scan rate of 40 mV/s.

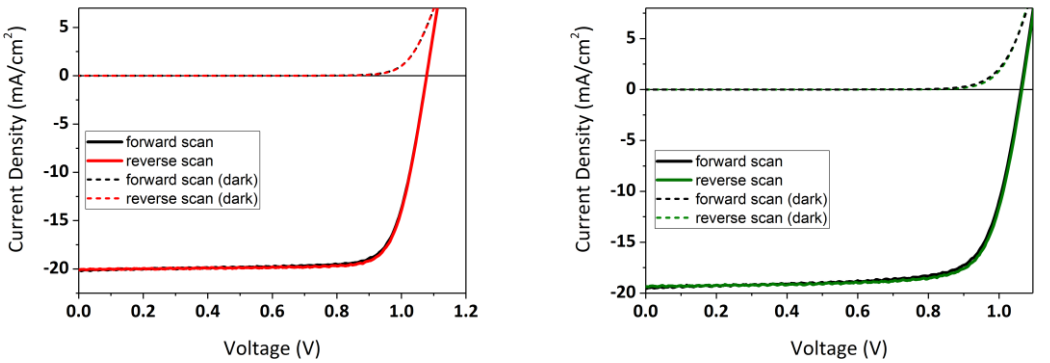

Figure S4. J-V characteristics of best PSC based on MC-43 (red), TPA (green) at 1 sun and dark.

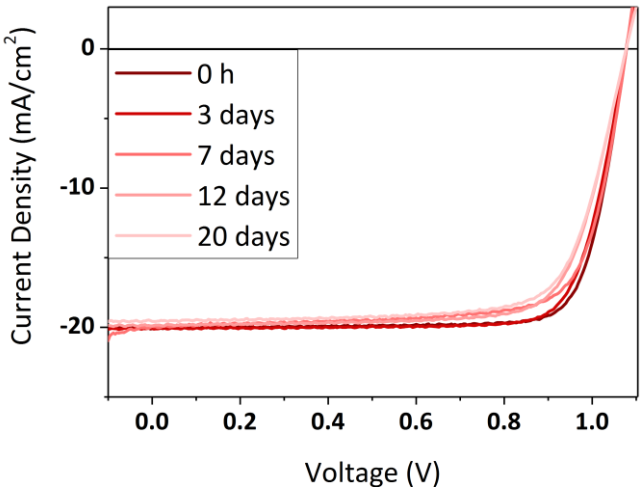

Figure S5. Evolution of the J-V characteristic, measured at 1 sun, for a MC-43 based PSC over 20 days. The device was encapsulated and stored in dark under low humidity conditions.

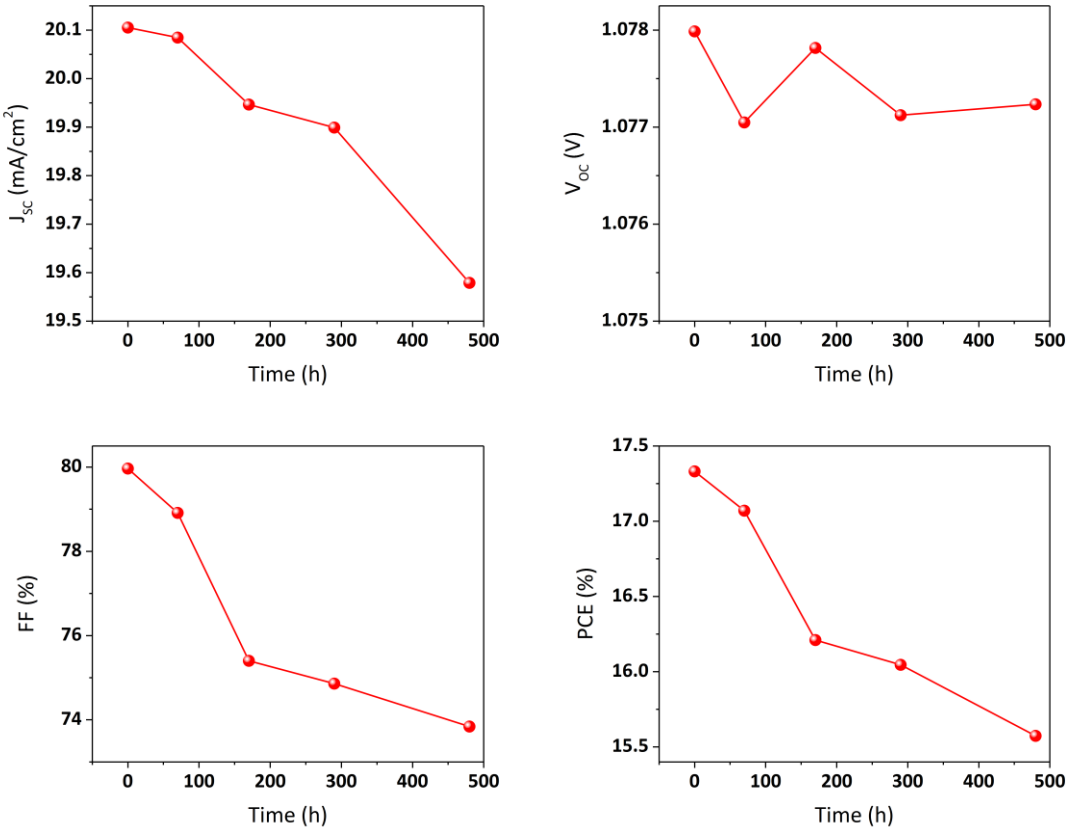

Figure S6. Long-term evolution of photovoltaic parameters of the best MC-43 based PSC measured at 1 sun.

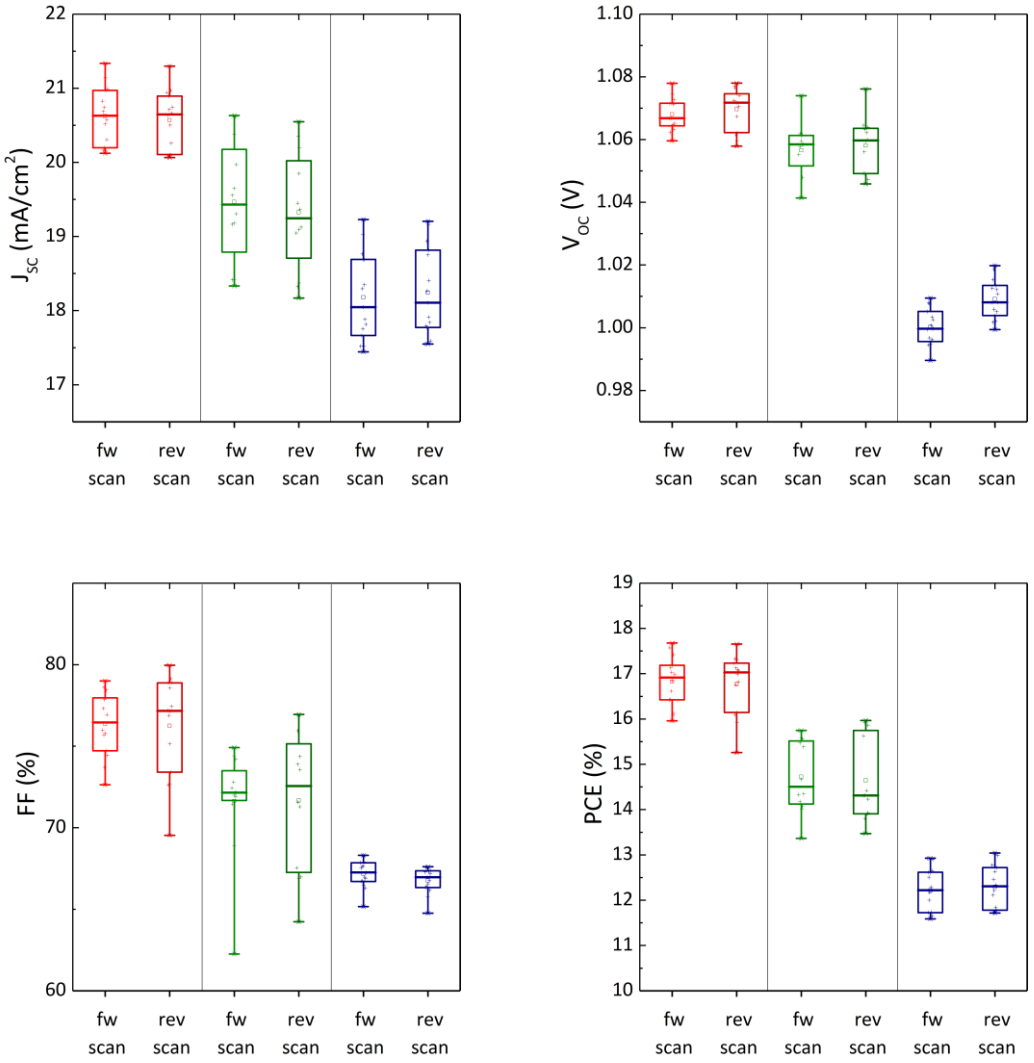

Figure S7. Statistics of photovoltaic parameters for PSCs based on MC-43 (red), TPA (green) and PEDOT:PSS (blue) recorded at 1 sun for both forward and reverse voltage scan.

Table S1. Average values (mean ± std. dev.) for the photovoltaic parameters of the solar cells calculated over 15 individual devices.

Sample	Scan direction	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
PEDOT:PSS	forward	18.18 ± 0.59	1.000 ± 0.006	67.17 ± 0.83	12.21 ± 0.47
	reverse	18.24 ± 0.59	1.009 ± 0.006	66.75 ± 0.78	12.29 ± 0.47
TPA	forward	19.47 ± 0.82	1.057 ± 0.009	71.63 ± 3.34	14.72 ± 0.79
	reverse	19.32 ± 0.80	1.058 ± 0.009	71.68 ± 4.33	14.64 ± 0.93
MC-43	forward	20.62 ± 0.40	1.068 ± 0.005	76.36 ± 1.97	16.82 ± 0.56
	reverse	20.57 ± 0.39	1.070 ± 0.007	76.25 ± 3.10	16.77 ± 0.67

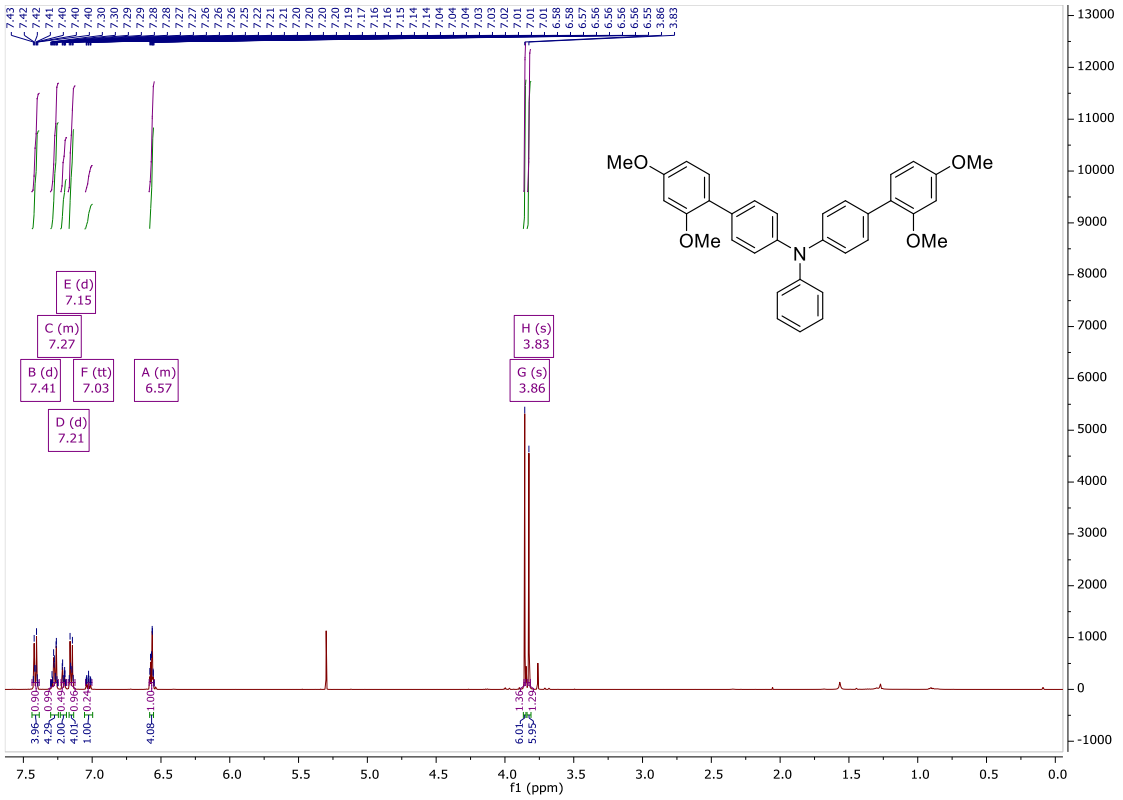

Figure S8. ^{1}H NMR of N-(2',4'-dimethoxy-[1,1'-biphenyl]-4-yl)-2',4'-dimethoxy-N-phenyl-[1,1'-biphenyl]-4-amine [1].

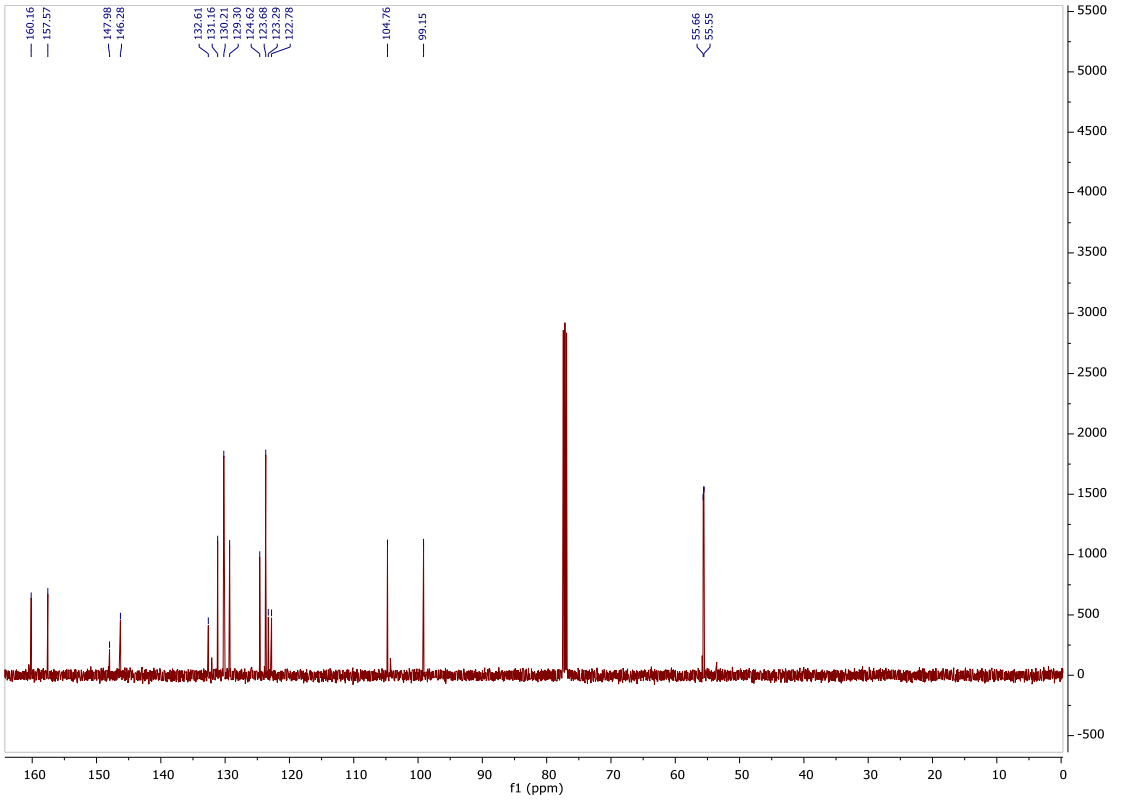

Figure S9. ^{13}C NMR of N-(2',4'-dimethoxy-[1,1'-biphenyl]-4-yl)-2',4'-dimethoxy-N-phenyl-[1,1'-biphenyl]-4-amine [1].

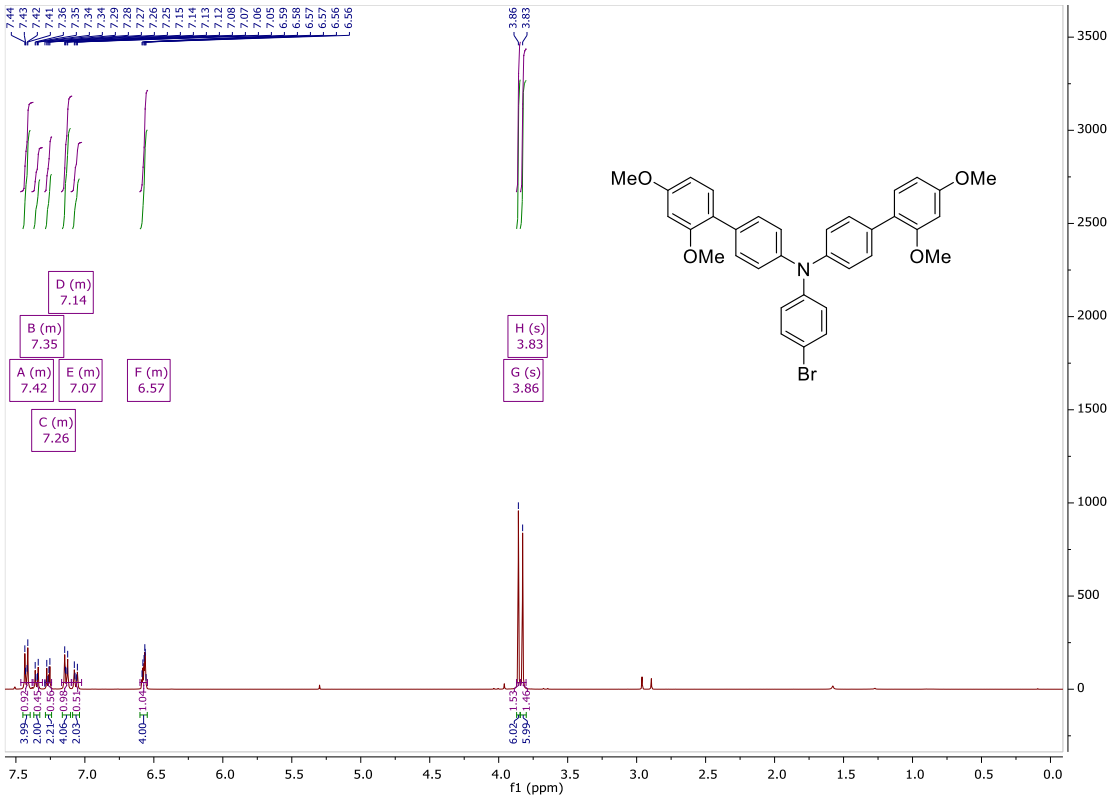

Figure S10. ^{1}H NMR of N-(4-bromophenyl)-N-(3',5'-dimethoxy-[1,1'-biphenyl]-4-yl)-2',4'-dimethoxy-[1,1'-biphenyl]-4-amine [2].

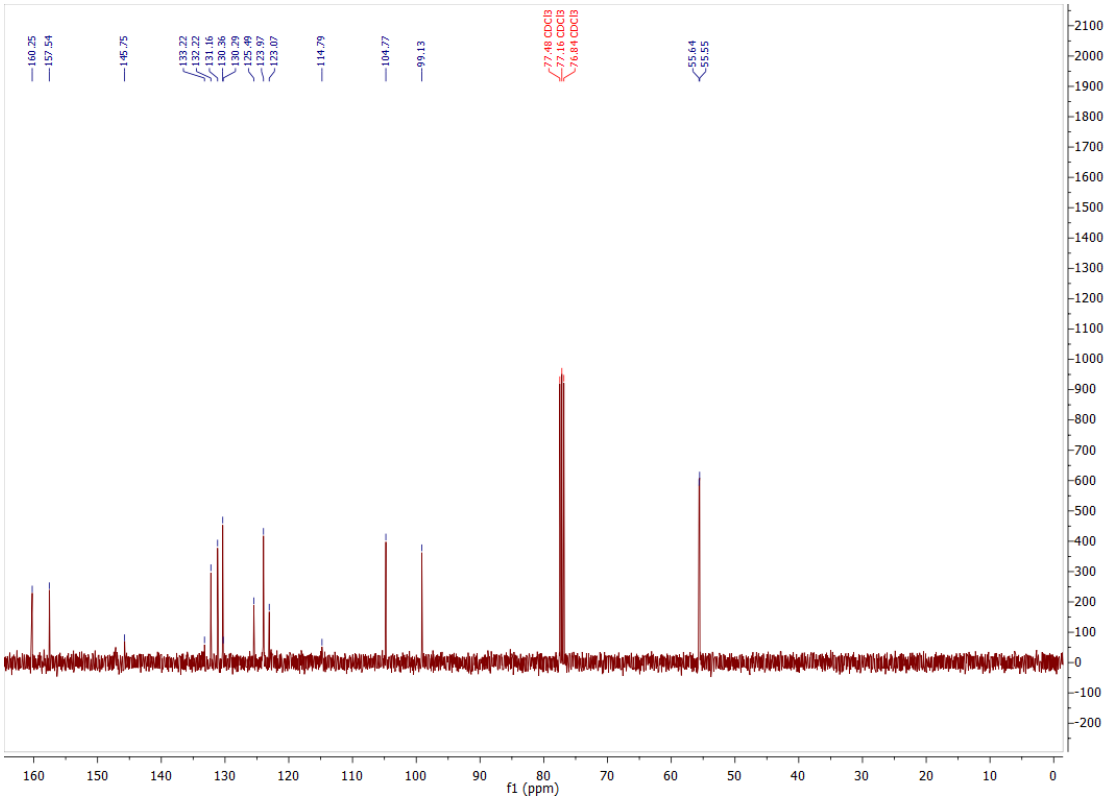

Figure S11. ^{13}C NMR of of N-(4-bromophenyl)-N-(3',5'-dimethoxy-[1,1'-biphenyl]-4-yl)-2',4'-dimethoxy-[1,1'-biphenyl]-4-amine [2].

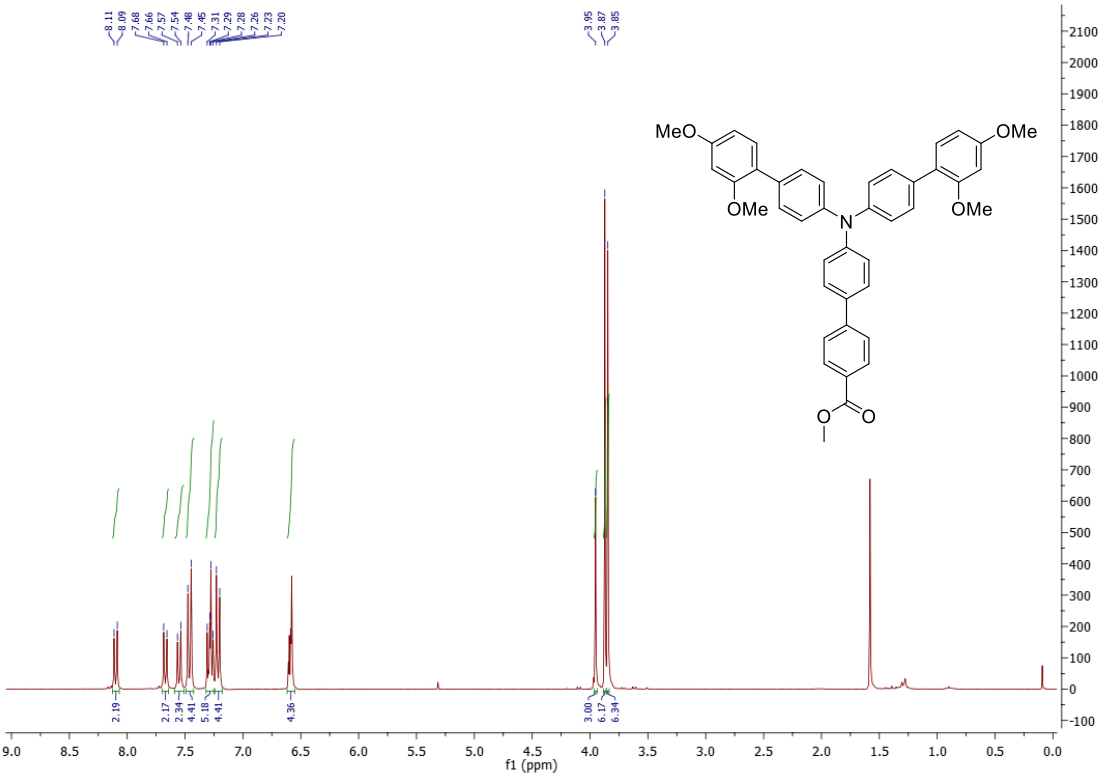

Figure S12. ^{1}H NMR of methyl 4'-[bis(2',4'-dimethoxybiphenyl-4-yl)amino]biphenyl-4-carboxylate [3].

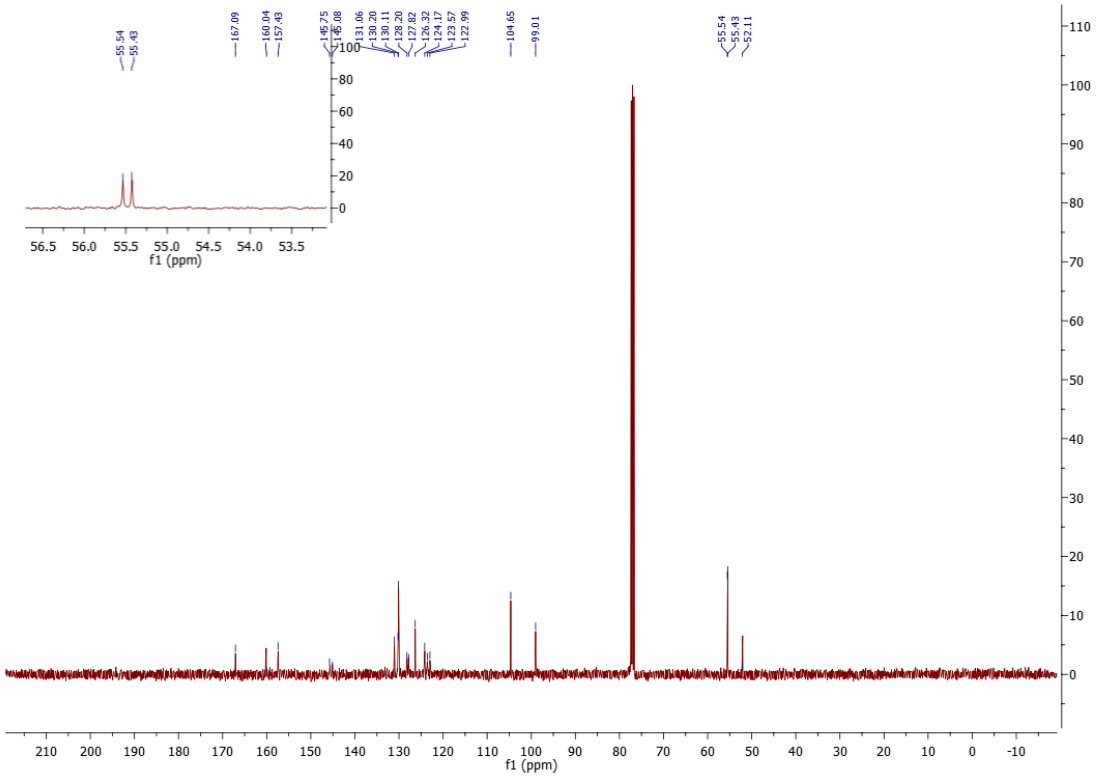

Figure S13. ^{13}C NMR of methyl 4'-[bis(2',4'-dimethoxybiphenyl-4-yl)amino]biphenyl-4-carboxylate [3].

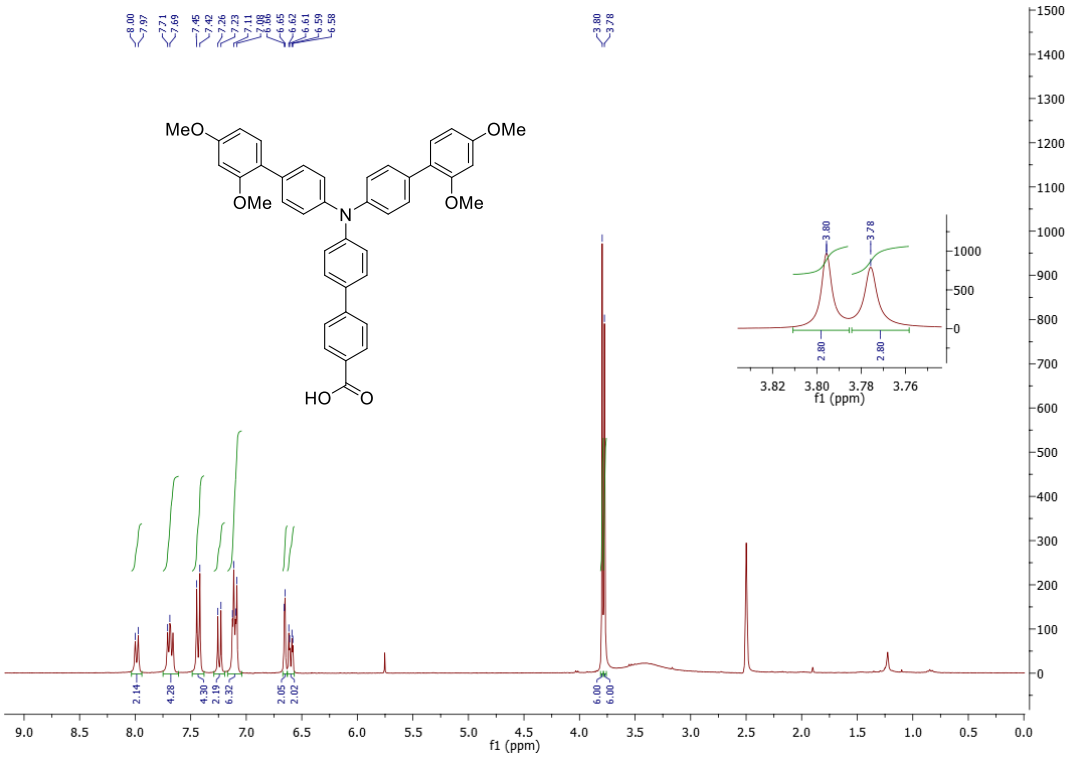

Figure S14. ^{1}H NMR of 4'-[bis(2',4'-dimethoxybiphenyl-4-yl)amino] biphenyl-4-carboxylic acid of MC-43.

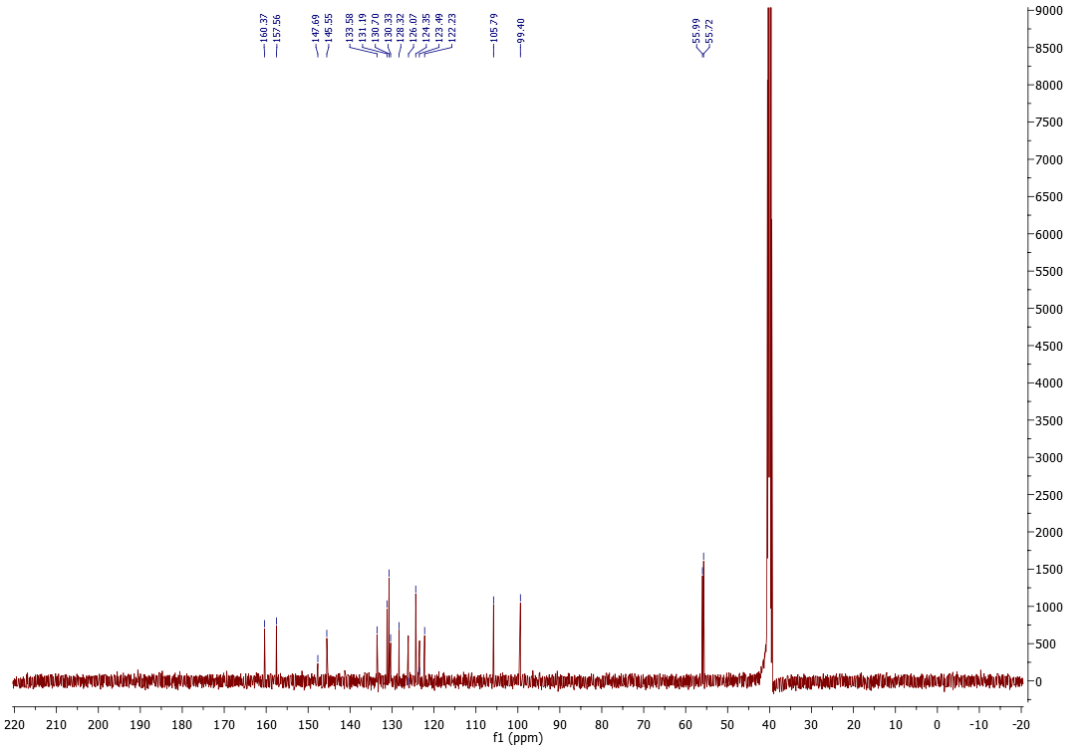

Figure S15. ^{13}C NMR of 4'-[bis(2',4'-dimethoxybiphenyl-4-yl)amino] biphenyl-4-carboxylic acid of MC-43.

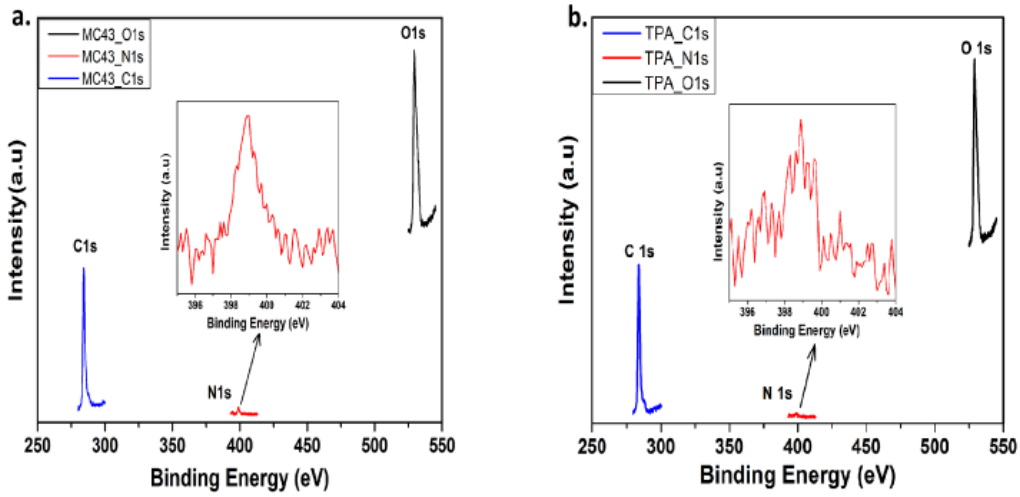

Figure S13. XPS Survey Spectrum of C1s, O1s and N1s for ITO/MC-43 (a) and ITO/TPA (b).

Table S2. The corresponding binding energy of functional groups for ITO/MC-43 and ITO/TPA.

Samples	O1s (eV)		C1s (eV)			N1s (eV)
	O_2^-	C=O	C—C and C—H	C—O—C	O—C=O	
ITO/MC43	529.32	530.96	284.08	285.43	287.41	398.94
ITO/TPA	528.77	530.12	283.95	284.60	287.58	398.89

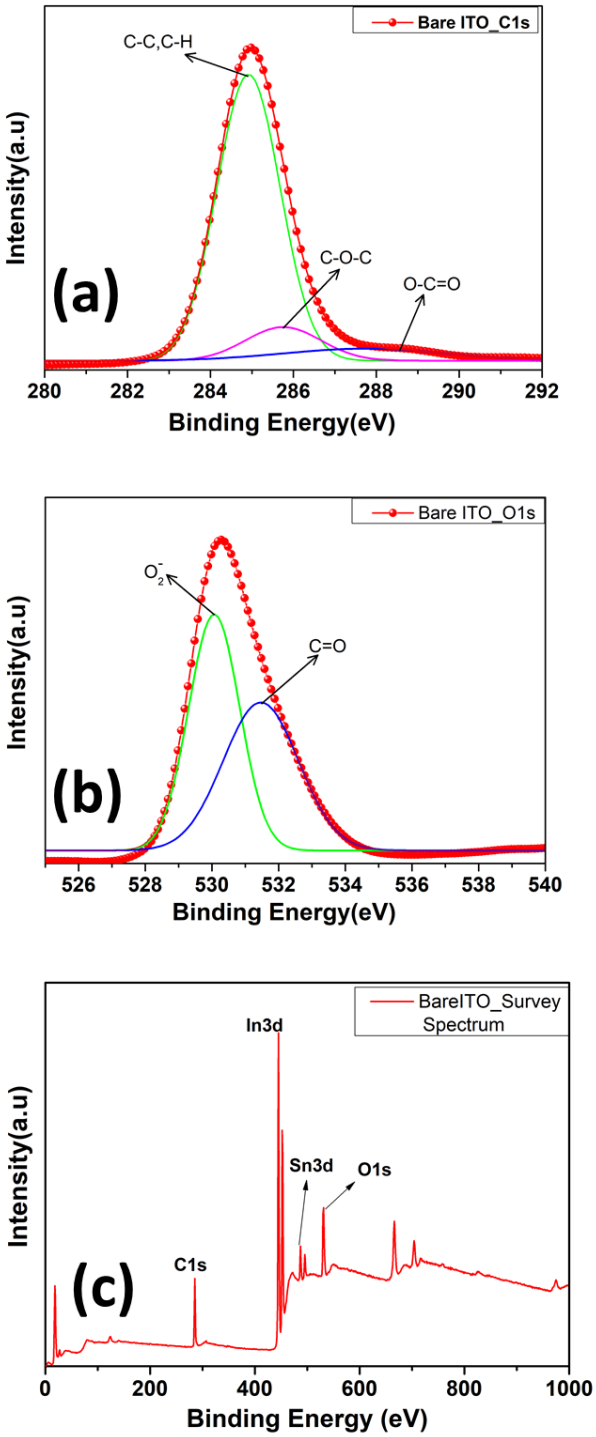

Figure S14. The XPS survey spectrum of bare ITO (c). The measured bands correspond to C1s, In3d, Sn3d and O1s with binding energy of 285.2 eV, 445.01 eV, 487.07eV and 531.03 eV, respectively. High resolution spectrum of C1s and O1s were fitted (a) and (b to analyse the atomic bonds of carbon and oxygen atoms on the ITO. The peaks of C1s at 284.97, 285.70 and 288.50 eV are attributed to C—C or C—H, C—O—C and O—C=O, respectively. The peaks of O1s

at 530.01 eV and 531.50 eV are correspond to lattice oxide O_2^- (present on ITO surface) and C=O group, respectively[1]. As expected , without the SAM's there is not bad for the N1s.

References

1. Havare, A. K.; Can, M.; Demic, S.; Okur, S.; Kus, M.; Aydın, H.; Yagmurcukardes, N.; Tari, S., Modification of ITO surface using aromatic small molecules with carboxylic acid groups for OLED applications. Synthetic Metals 2011, 161, 2397–2404.