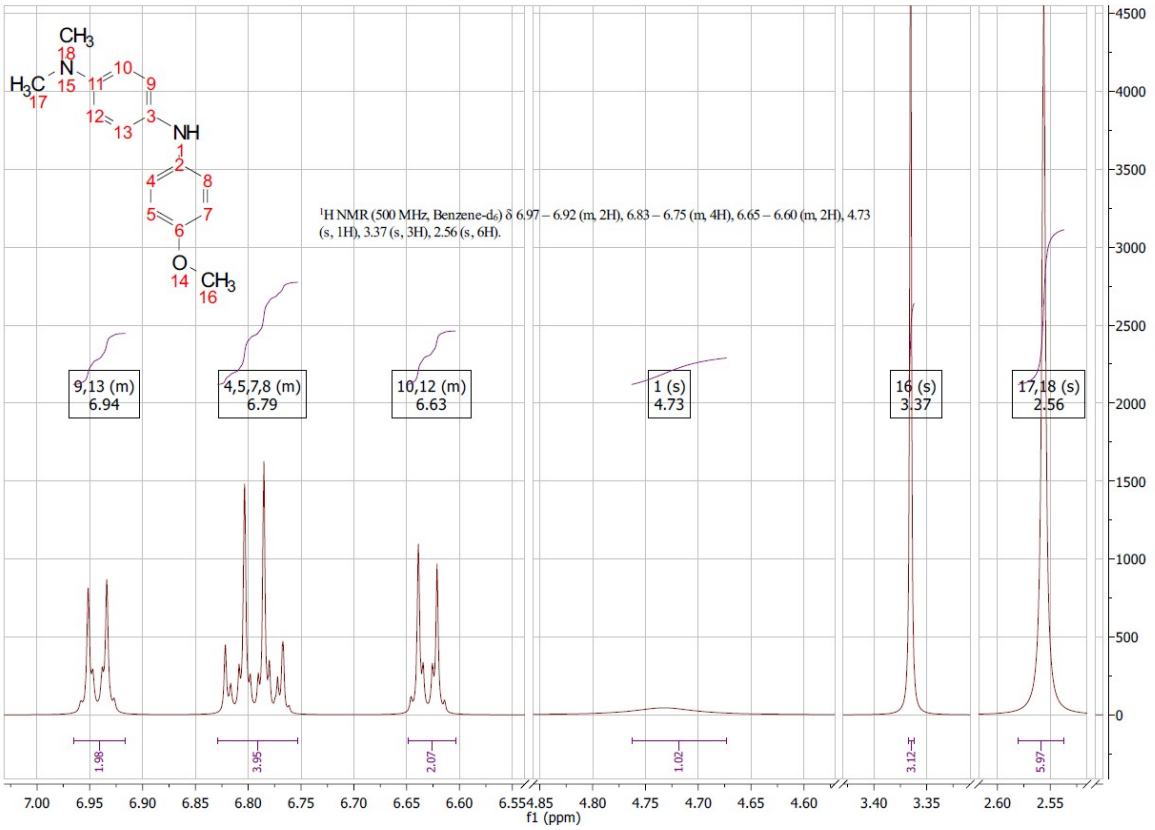
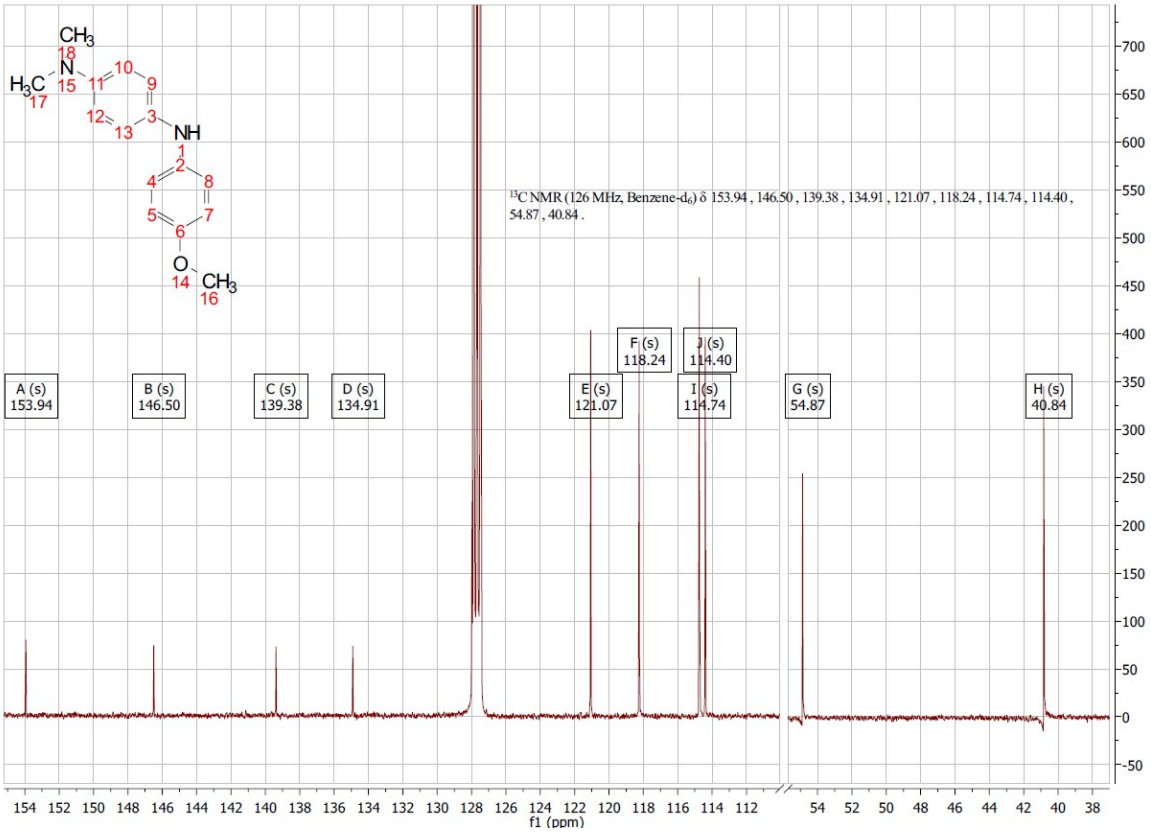
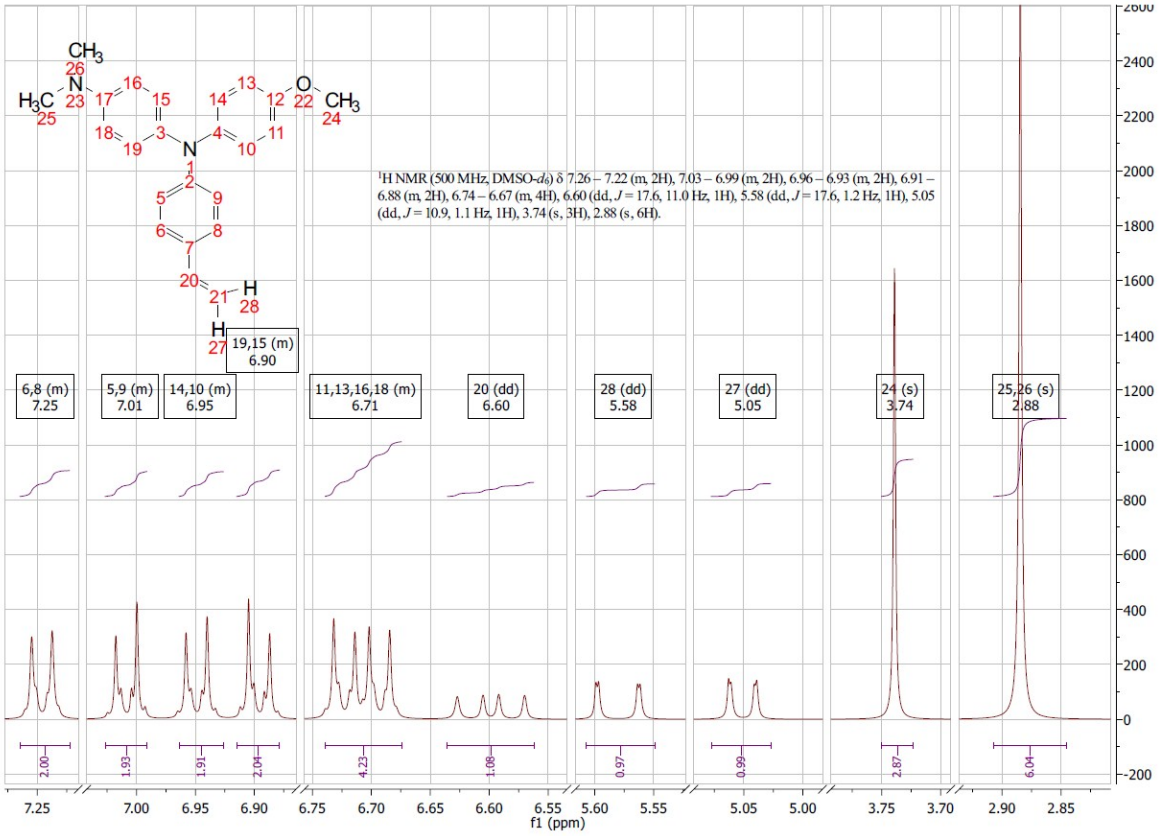
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

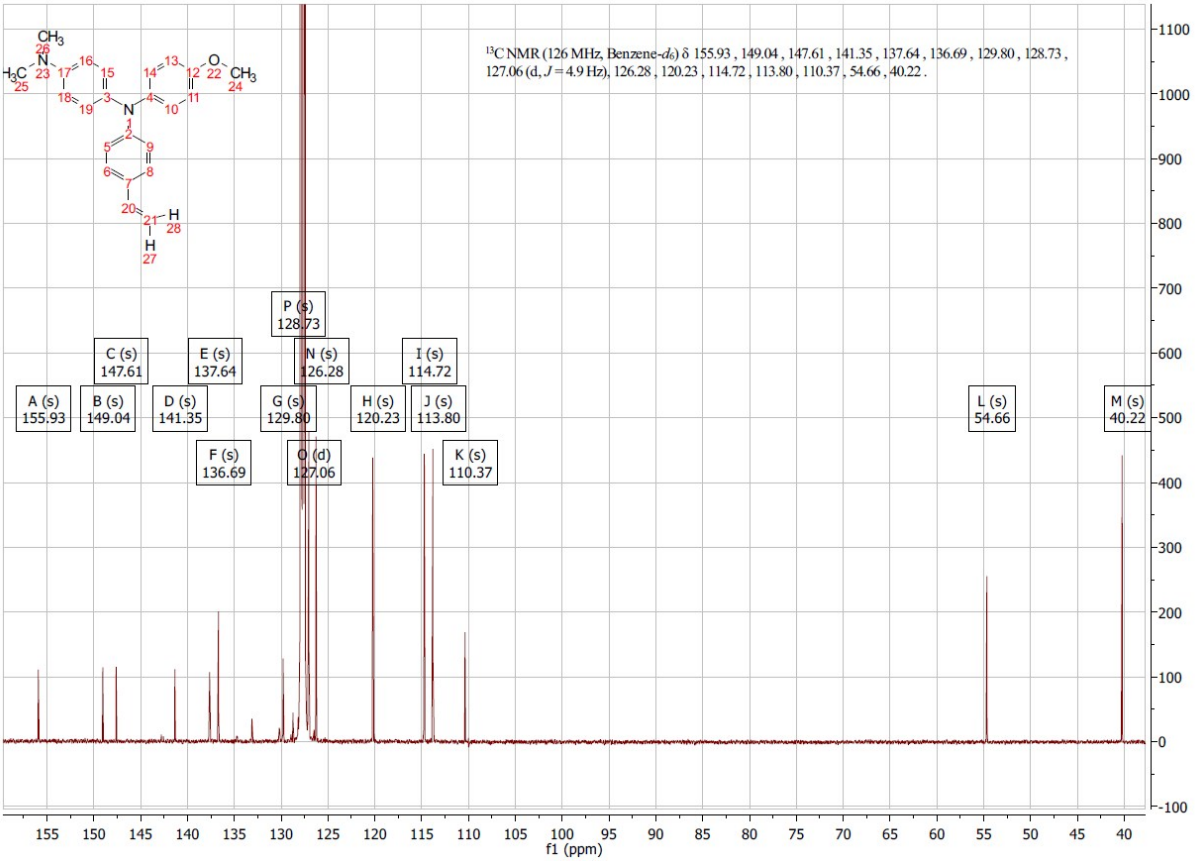
Supporting information

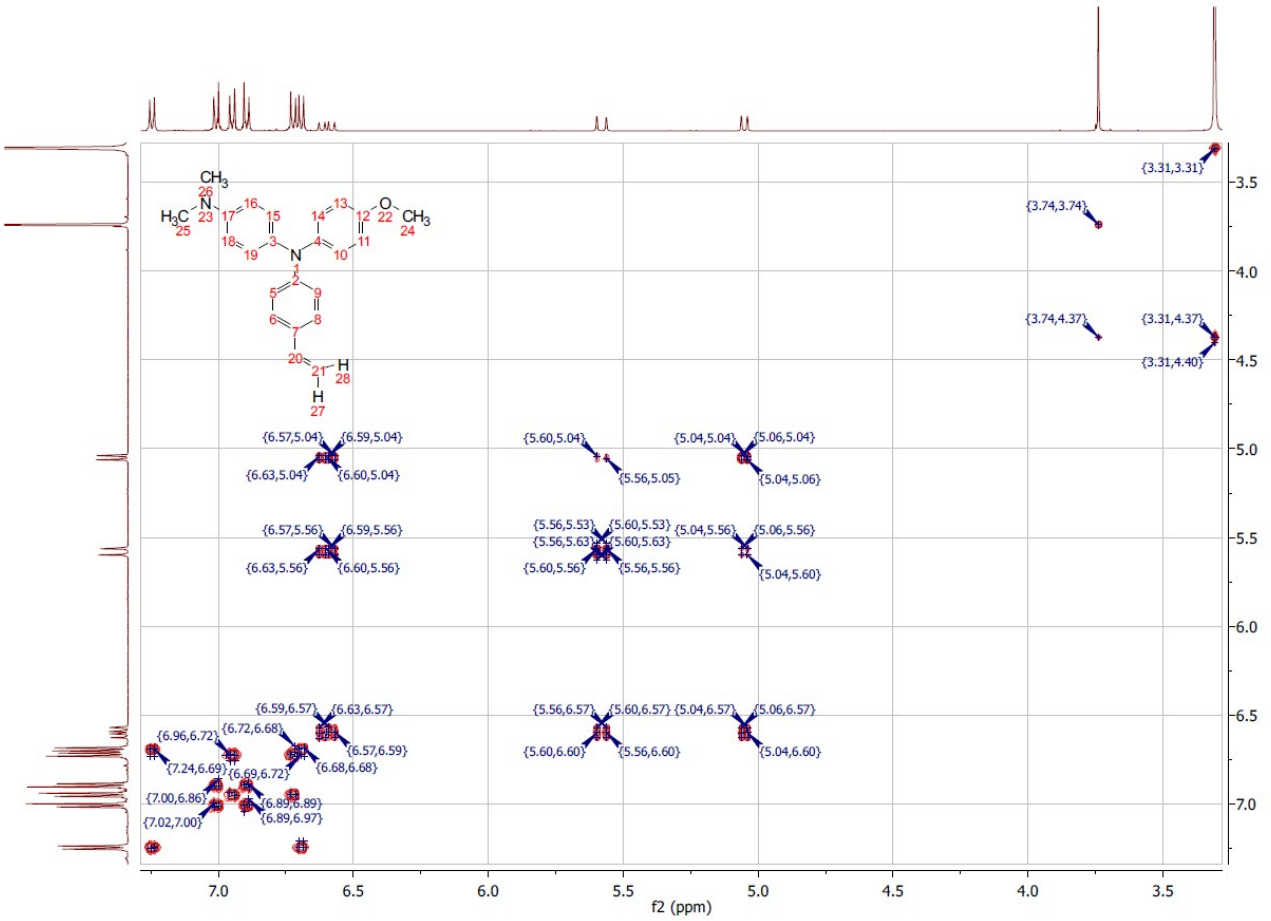

^{1}H NMR (500 MHz, Benzene-d$_6$) δ 6.97 – 6.92 (m, 2H), 6.83 – 6.75 (m, 4H), 6.65 – 6.60 (m, 2H), 4.73 (s, 1H), 3.37 (s, 3H), 2.56 (s, 6H).
9,13 (m) 6.94
4,5,7,8 (m) 6.79
10,12 (m) 6.63
1 (s) 4.73
16 (s) 3.37
17,18 (s) 2.56
f1 (ppm)

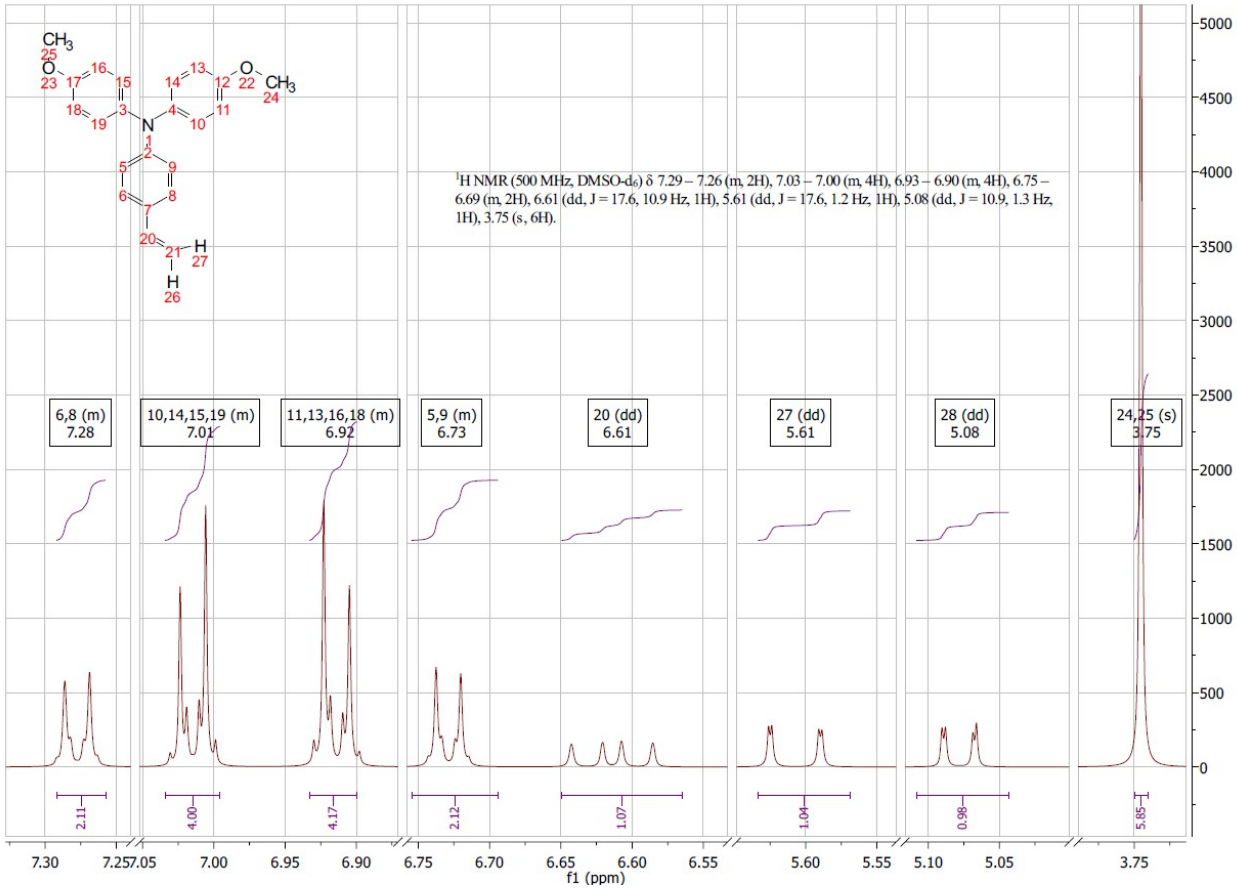

^{13}C NMR (126 MHz, Benzene-d$_6$) δ 153.94 , 146.50 , 139.38 , 134.91 , 121.07 , 118.24 , 114.74 , 114.40 , 54.87 , 40.84 .
A (s) 153.94
B (s) 146.50
C (s) 139.38
D (s) 134.91
E (s) 121.07
F (s) 118.24
I (s) 114.74
J (s) 114.40
G (s) 54.87
H (s) 40.84
f1 (ppm)

1. NMR

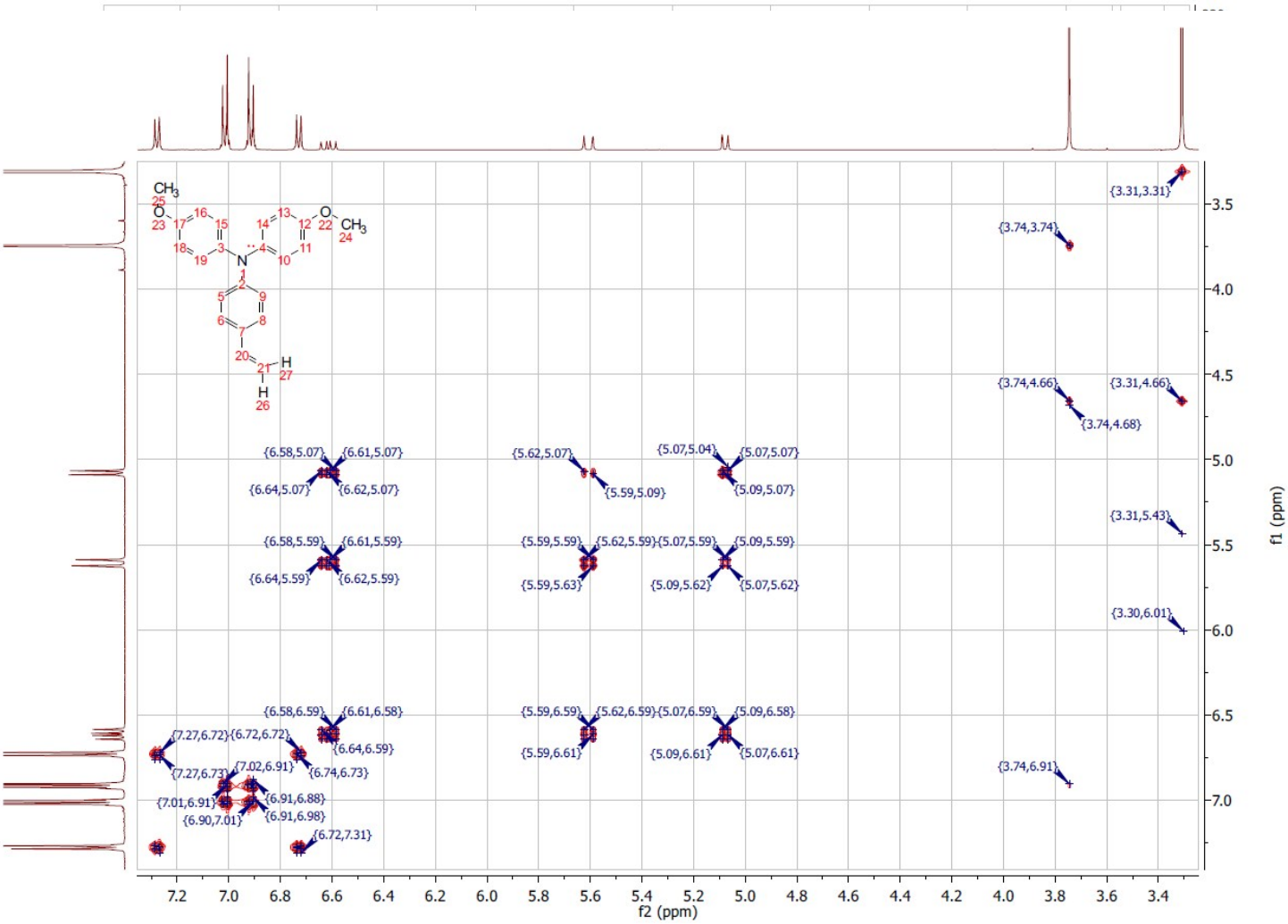

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.26 – 7.22 (m, 2H), 7.03 – 6.99 (m, 2H), 6.96 – 6.93 (m, 2H), 6.91 – 6.88 (m, 2H), 6.74 – 6.67 (m, 4H), 6.60 (dd, J = 17.6, 11.0 Hz, 1H), 5.58 (dd, J = 17.6, 1.2 Hz, 1H), 5.05 (dd, J = 10.9, 1.1 Hz, 1H), 3.74 (s, 3H), 2.88 (s, 6H).
6,8 (m) 7.25
5,9 (m) 7.01
14,10 (m) 6.95
19,15 (m) 6.90
11,13,16,18 (m) 6.71
20 (dd) 6.60
28 (dd) 5.58
27 (dd) 5.05
24 (s) 3.74
25,26 (s) 2.88
f1 (ppm)


^{13}C NMR (126 MHz, Benzene-d_6) δ 155.93 , 149.04 , 147.61 , 141.35 , 137.64 , 136.69 , 129.80 , 128.73 , 127.06 (d, J = 4.9 Hz), 126.28 , 120.23 , 114.72 , 113.80 , 110.37 , 54.66 , 40.22 .
A (s) 155.93
B (s) 149.04
C (s) 147.61
D (s) 141.35
E (s) 137.64
F (s) 136.69
G (s) 129.80
O (d) 127.06
P (s) 128.73
N (s) 126.28
H (s) 120.23
I (s) 114.72
J (s) 113.80
K (s) 110.37
L (s) 54.66
M (s) 40.22
f1 (ppm)





^{1}H NMR (500 MHz, DMSO-d_6) δ 7.29 – 7.26 (m, 2H), 7.03 – 7.00 (m, 4H), 6.93 – 6.90 (m, 4H), 6.75 – 6.69 (m, 2H), 6.61 (dd, J = 17.6, 10.9 Hz, 1H), 5.61 (dd, J = 17.6, 1.2 Hz, 1H), 5.08 (dd, J = 10.9, 1.3 Hz, 1H), 3.75 (s, 6H).


f2 (ppm)
f1 (ppm)
{3.31,3.31}
{3.74,3.74}
{3.74,4.66}
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{3.74,4.68}
{6.58,5.07}
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{6.58,5.59}
{6.61,5.59}
{6.64,5.59}
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{5.62,5.59}
{5.59,5.63}
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{5.09,5.62}
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{6.58,6.59}
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{7.27,6.72}
{6.72,6.72}
{7.27,6.73}
{7.02,6.91}
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{7.01,6.91}
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{5.59,6.59}
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{3.74,6.91}

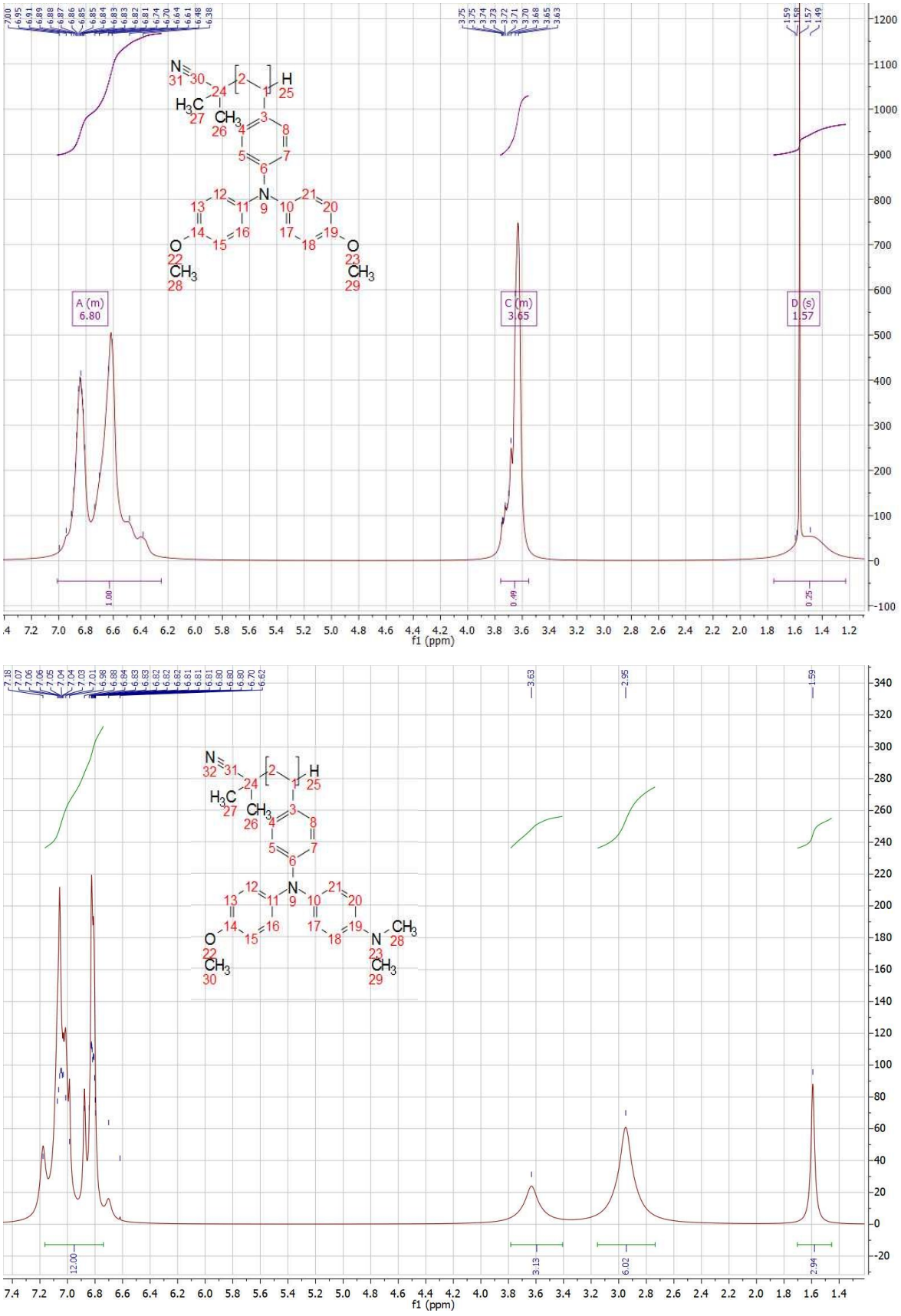


Figure S1: NMR Spectra

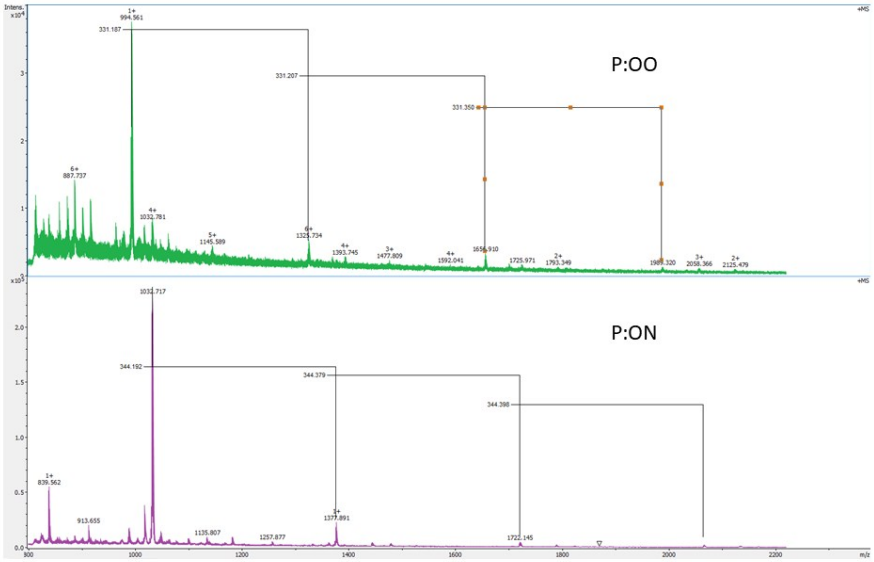


Figure S2: MALDI-TOF mass spectrometry of polymer samples

2. Cyclic Voltammetry and UV/Vis

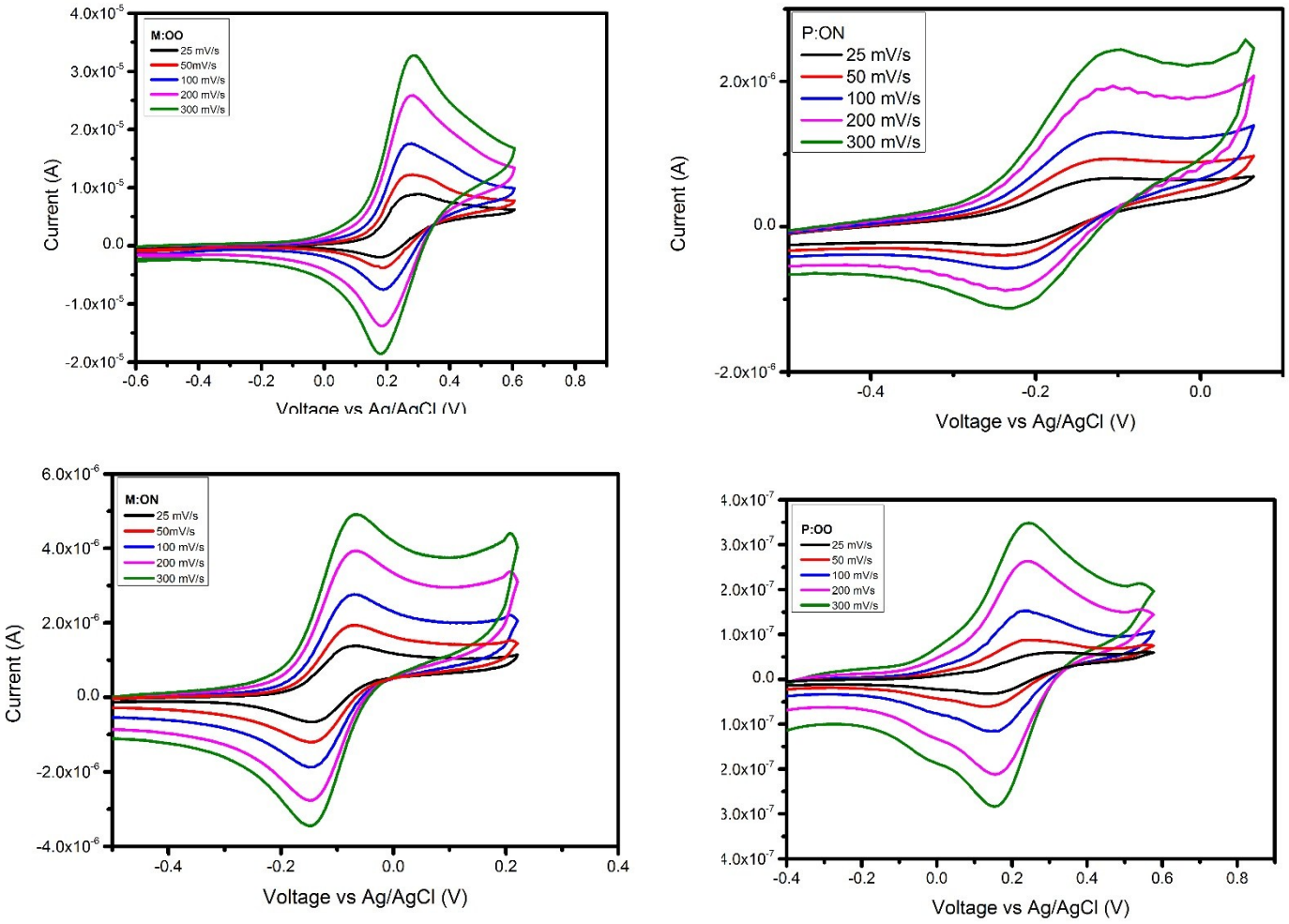


Figure S3a. Cyclic voltammetry traces at different scan rates of M:OO, P:OO, M:ON and P:ON.

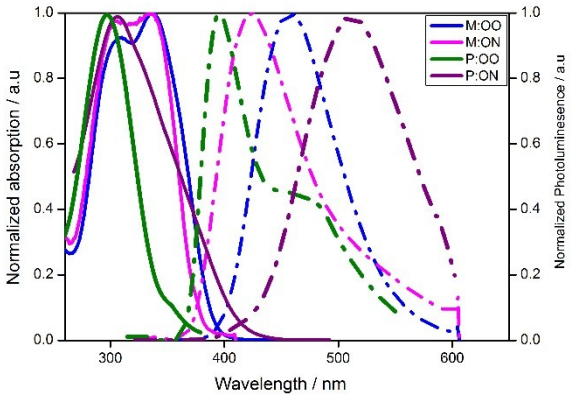


Figure S3b. Normalized UV-Vis absorption (solid line) and emission (dashed line) of monomers and polymers in dichloromethane solution. M:ON was found to be somewhat unstable over time and those data should be treated with caution.

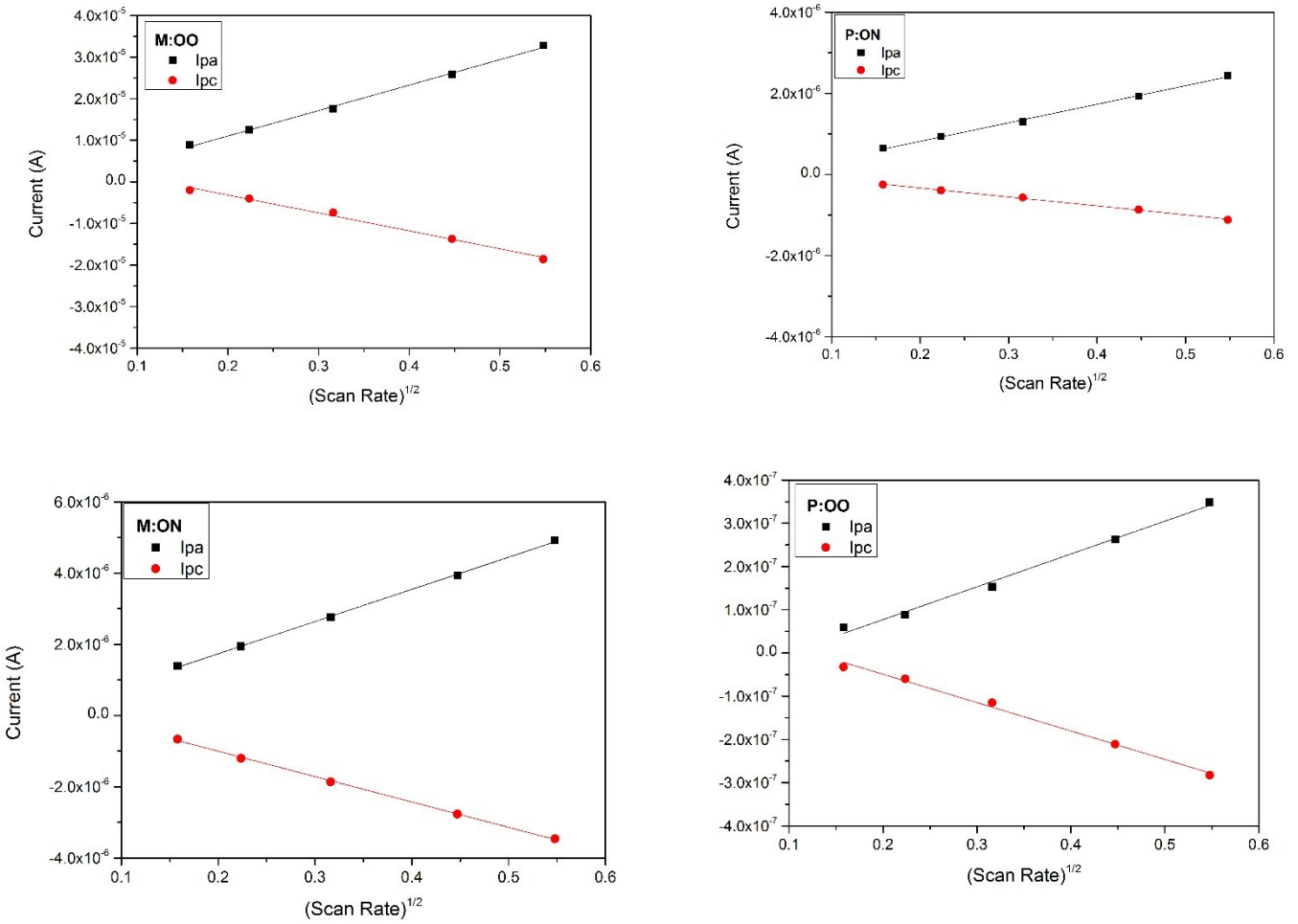


Figure S4. Plot of ipa(black line) and Ipc (red line) versus (scan rate)$^{1/2}$ for M:OO, M:ON, P:OO and A:ON (from 0.025 V/s to 0.3 V/s) from cyclic voltammograms

3. Thermal properties

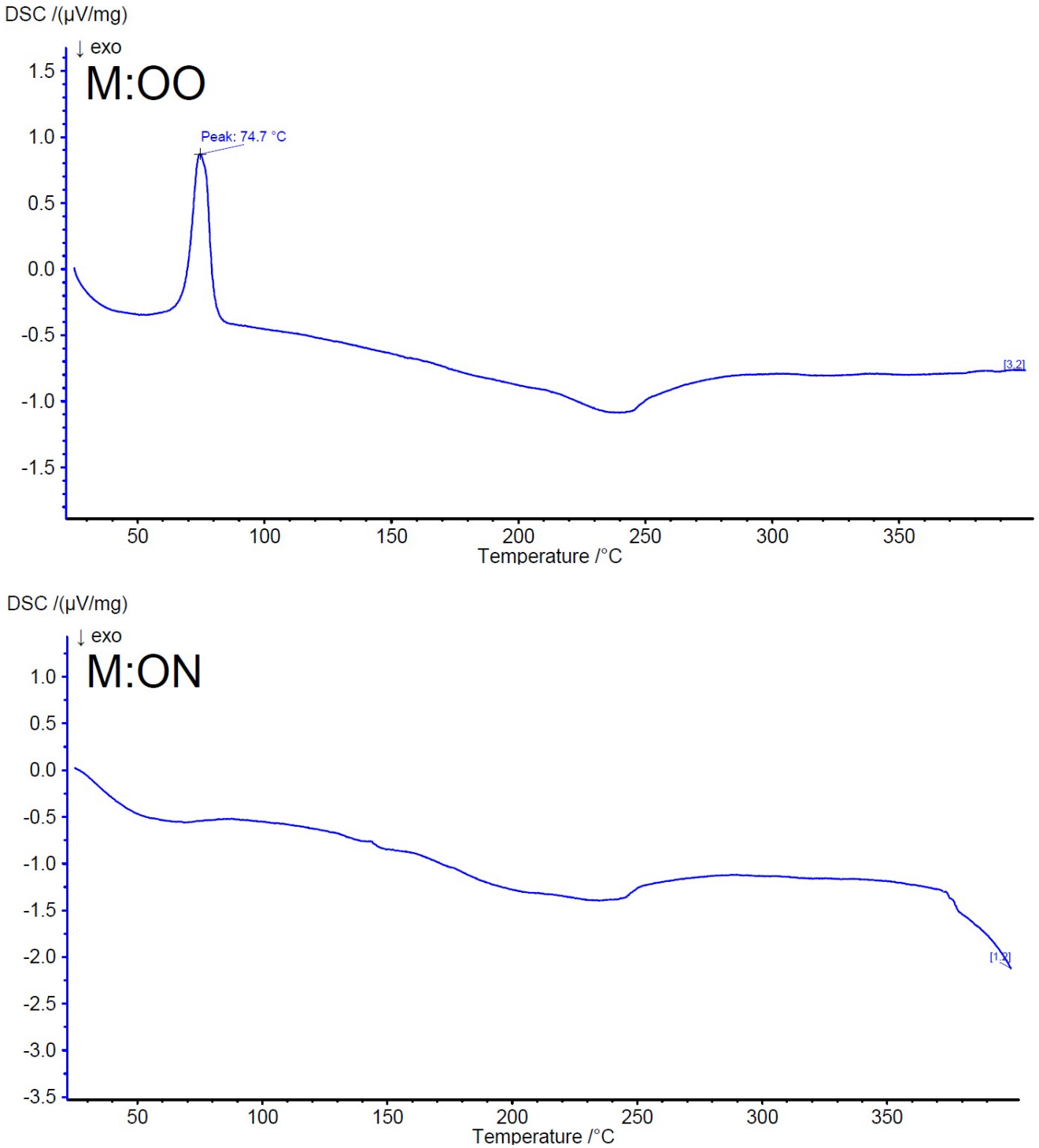
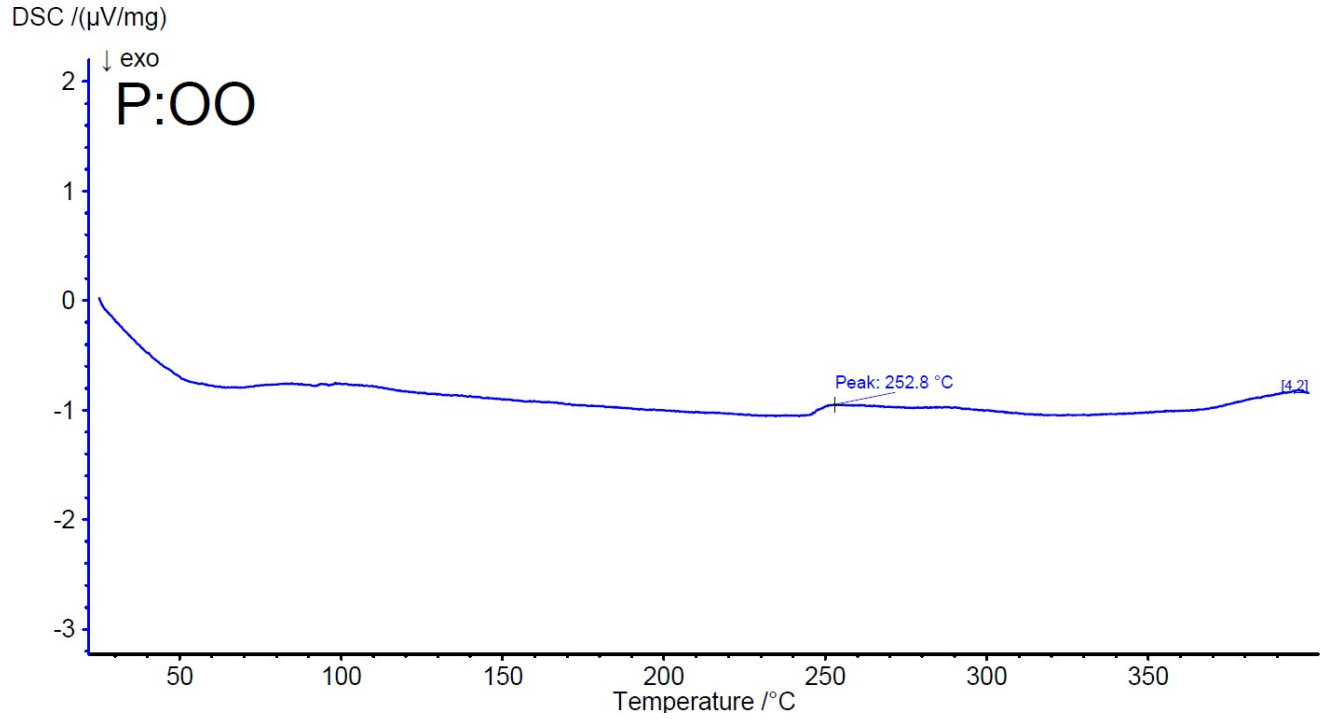


Figure S5 Differential scanning calorimetry curves of M:OO and M:ON



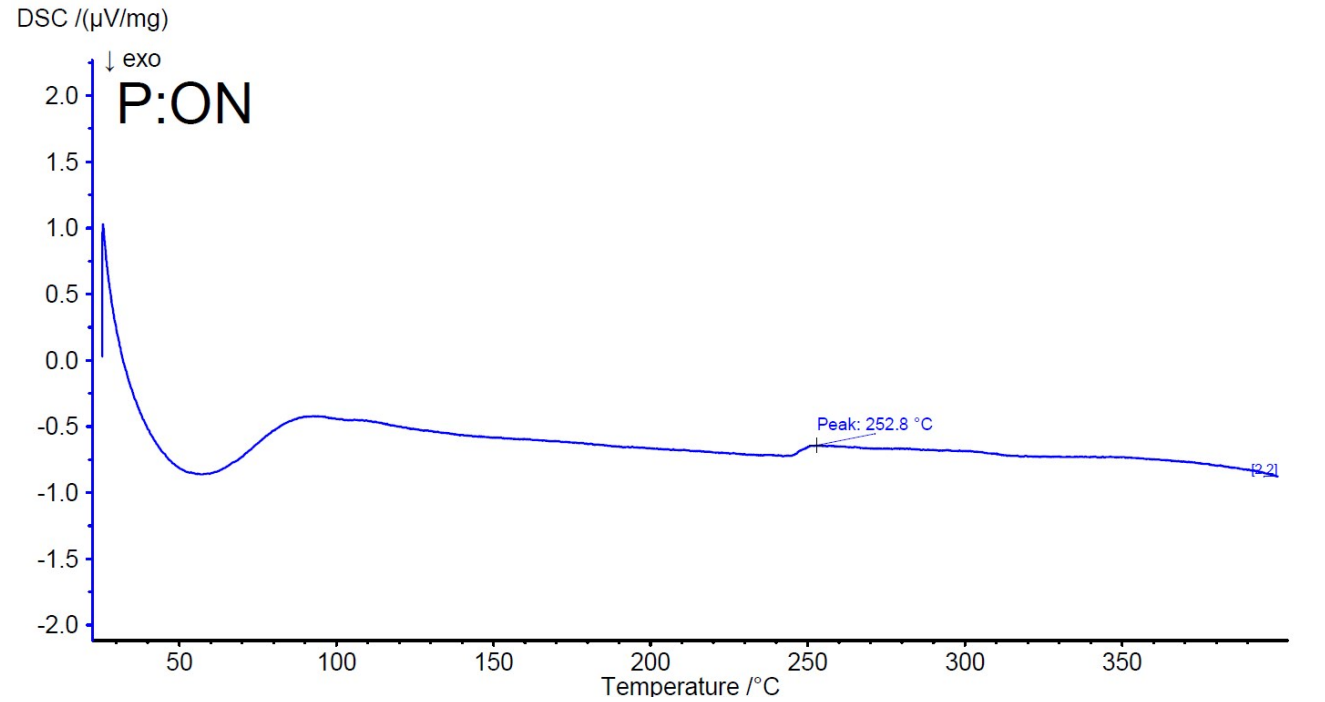


Figure S6 Differential scanning calorimetry curves of P:OO and P:ON

4. Steady-State Photoluminesence

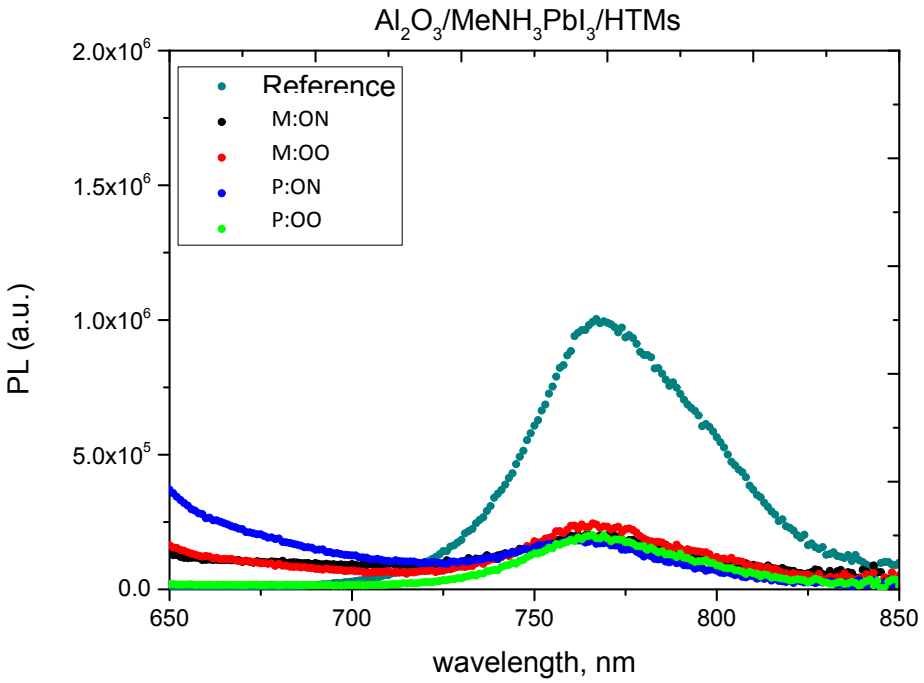


Figure S7. Steady-State Photoluminescence in a $Al_2O_3/MeNH_3PbI_3$/HTM architecture of M:ON (black line), M:OO (red line), P:ON (blue line) and P:OO (green line). The reference is $Al_2O_3/MeNH_3PbI_3$

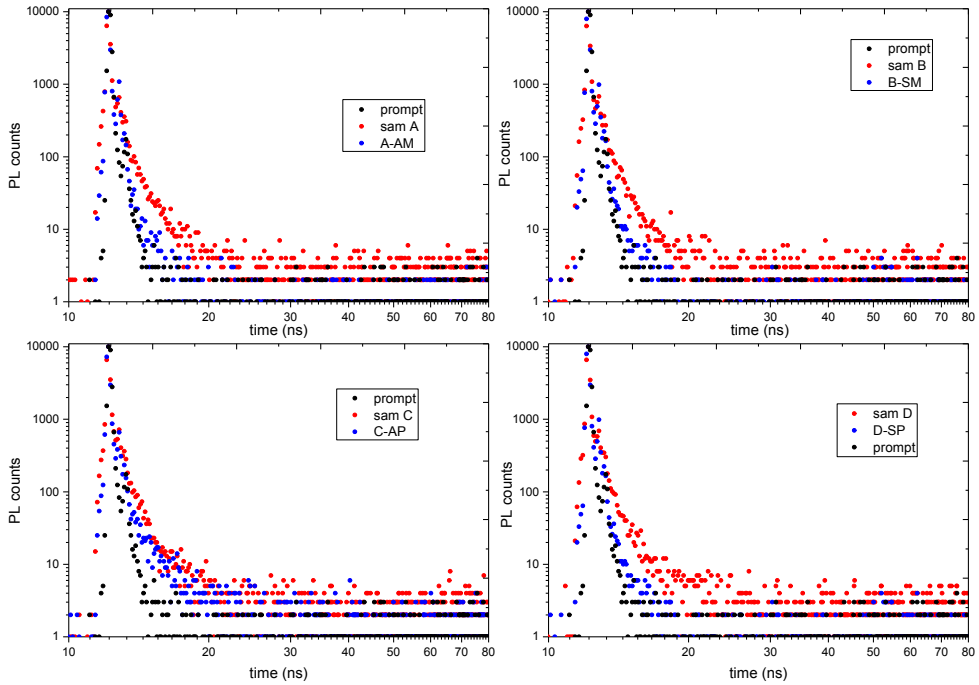


Figure S8. Transient PL decay of monomers and polymers

	M:ON	M:OO	P:ON	P:OO
$1-\tau_q/(\tau_0+\tau_q)$	0,61±0,01	0,88±0,03	0,53±0,02	0,85±0,05

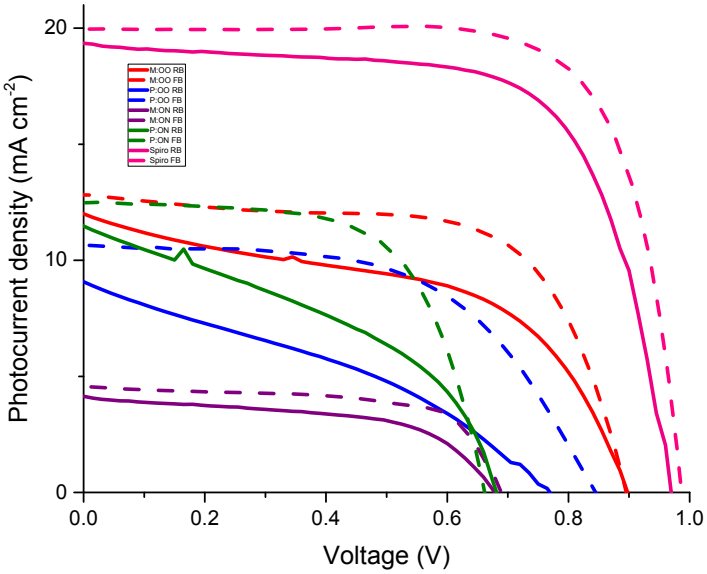
	τ_0 (ns)	τ_q (ns)
M:ON	3,49±0,03	2,24±0,05
M:OO	3,89±0,70	0,53±0,20
P:ON	3,73±0,08	3,28±0,06
P:OO	4,96±0,07	0,86±0,40

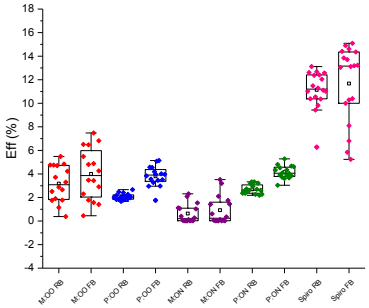
Table S1: Lifetimes (s) obtained from fitting of the perovskite emission decays, with and without HTM and resulting hole-extraction yields (above).

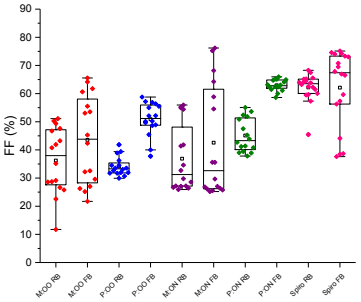
5. Solar cells parameters

Table S2. Summary of the device performance parameters

HTM	PCE (%)	Jsc (mA cm^{-2})	Voc (V)	FF (%)
M:OO	4.24±2.03	10.74±1.71	0.84±0.054	44.67±15.54
P:OO	3.94±0.68	9.58±0.63	0.78±0.035	51.31±6.41
M:ON	1.03±1.23	3.29±1.99	0.38±0.28	43.67±19.98
P:ON	4.22±0.48	10.68±1.11	0.62±0.023	63.24±1.71
Spiro-OMeTAD	11.71±2.96	20.37±0.80	0.93±0.038	62.92±14.67







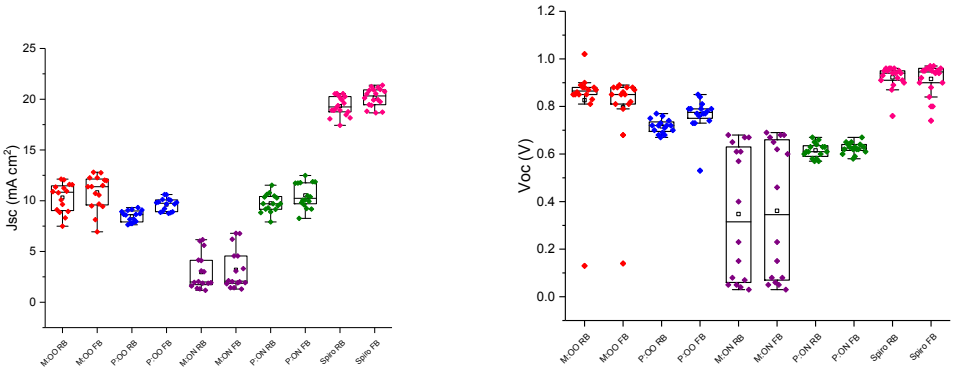


Fig. S9: J-V Curves and hysteresis