

## Supporting Information

### Ionization of Hole-Transporting Materials as a Method for Improving the Photovoltaic Performance of Perovskite Solar Cells

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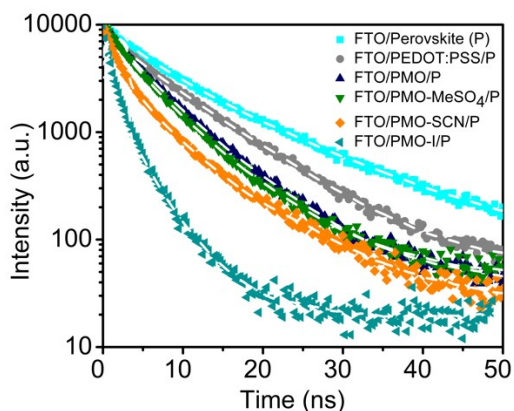
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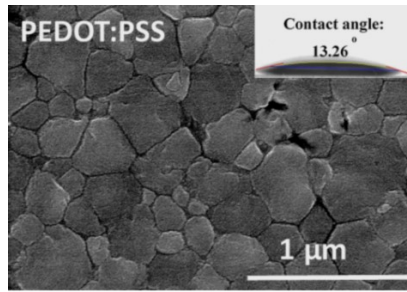
## Supplementary Figures



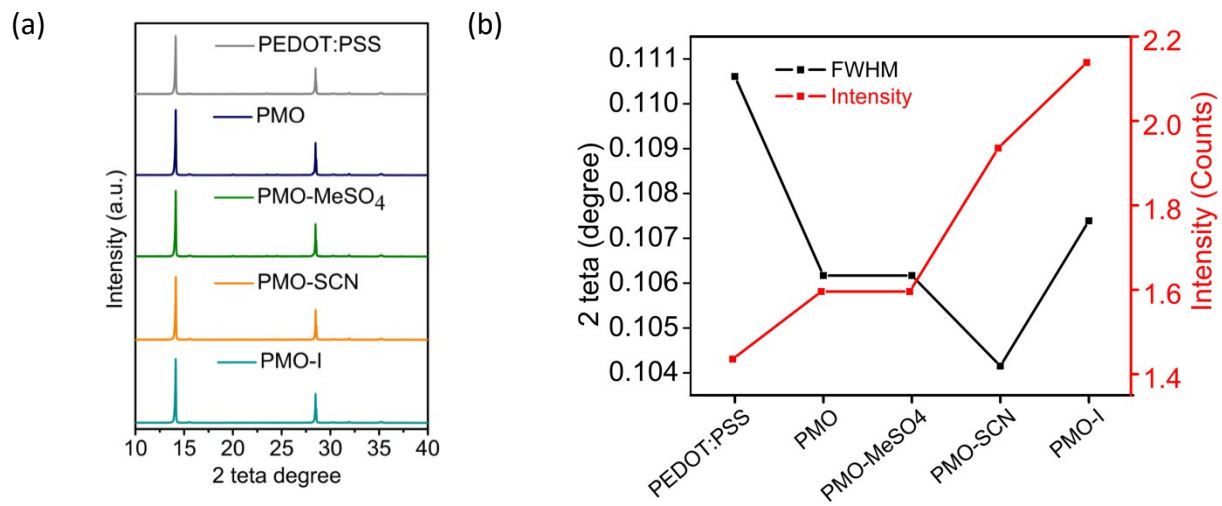
**Figure S1.** Time-resolved photoluminescence for perovskites and perovskites/HTM interface.

**Table S1.** The detailed parameters of PL obtained by fitting the TRPL of **PEDOT:PSS**, **PMO**, **PMO-MeSO<sub>4</sub>**, **PMO-SCN** and **PMO-I**.

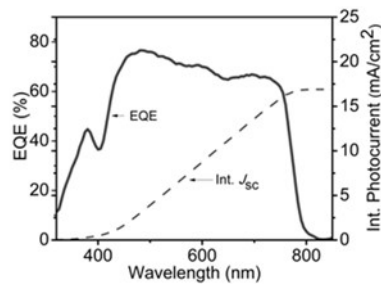
HTM	$A_1$	$\tau_1$	$A_2$	$\tau_2$	$\tau_{Avg}$
<b>FTO</b>	6827.6	6.0261	3025.2	17.46	9.539
<b>PEDOT:PSS</b>	1976.6	1.7197	7534.3	8.3250	6.952
<b>PMO</b>	4996.3	3.3416	5037.3	7.3400	5.349
<b>PMO-MeSO<sub>4</sub></b>	5765.80	3.2037	4246.2	7.4159	4.990
<b>PMO-SCN</b>	6472.00	1.5049	3648.3	6.7962	3.412
<b>PMO-I</b>	5765.49	0.6980	3985.9	2.6811	1.509



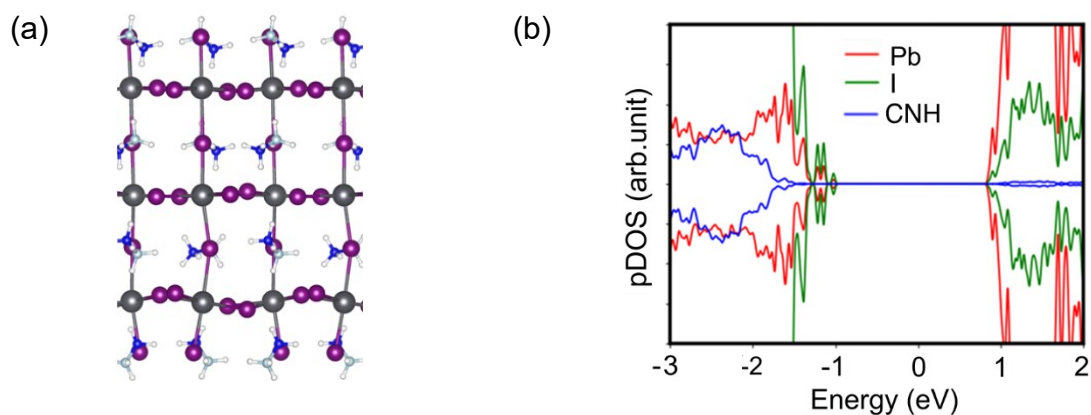
**Figure S2.** Scanning electron microscopy top-view image, with inset water contact angle, of PEDOT:PSS film.



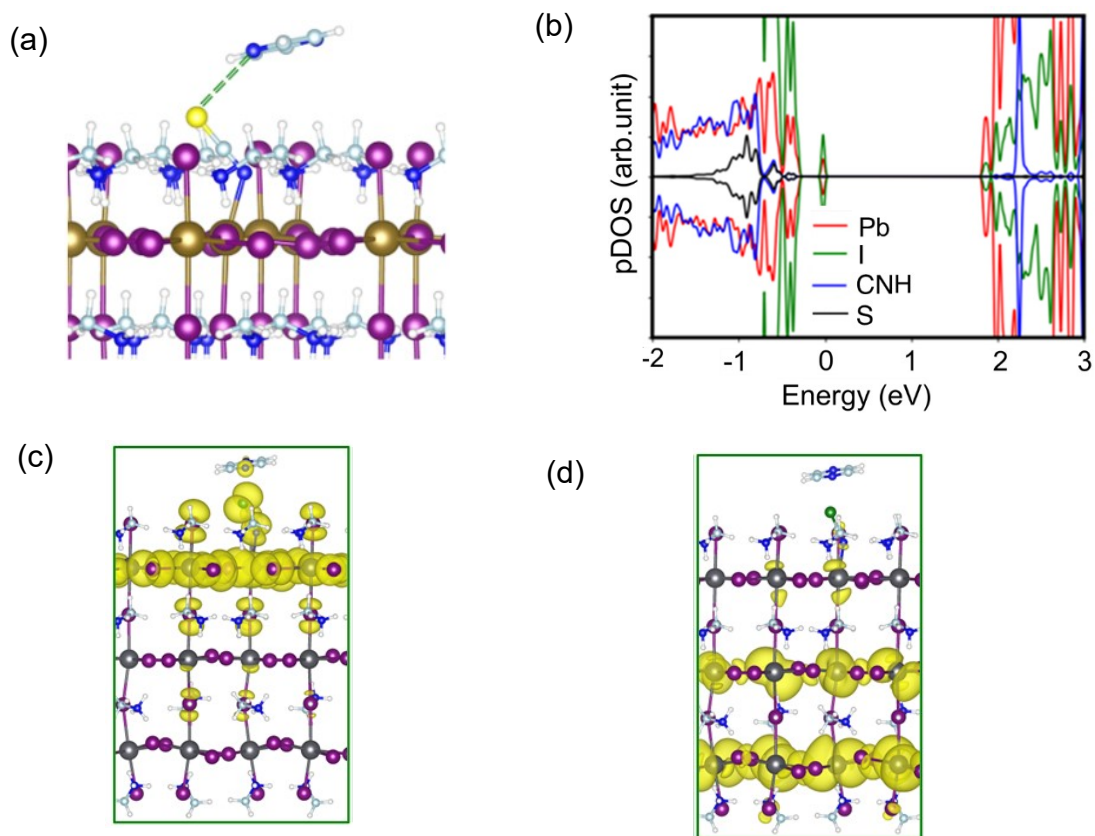
**Figure S3.** (a) X-ray diffraction of perovskite films atop of different HTM films. (b) Fitted results of X-ray diffraction ratio.



**Figure S4.** EQE spectra with integrated  $J_{sc}$  of the PSCs with PEDOT:PSS.

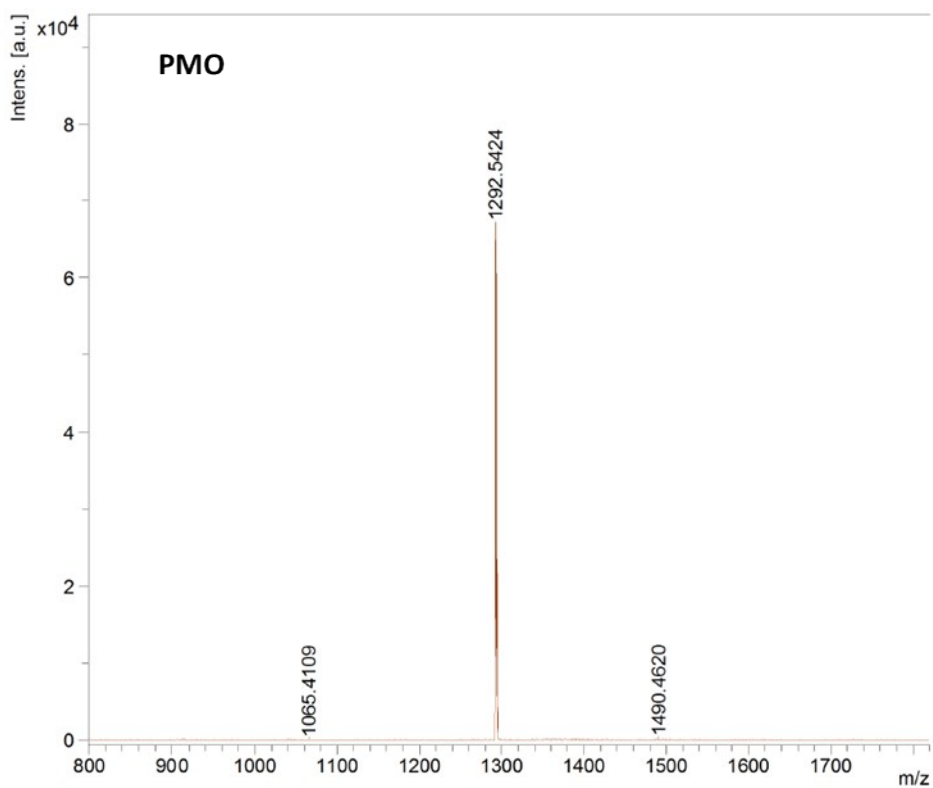
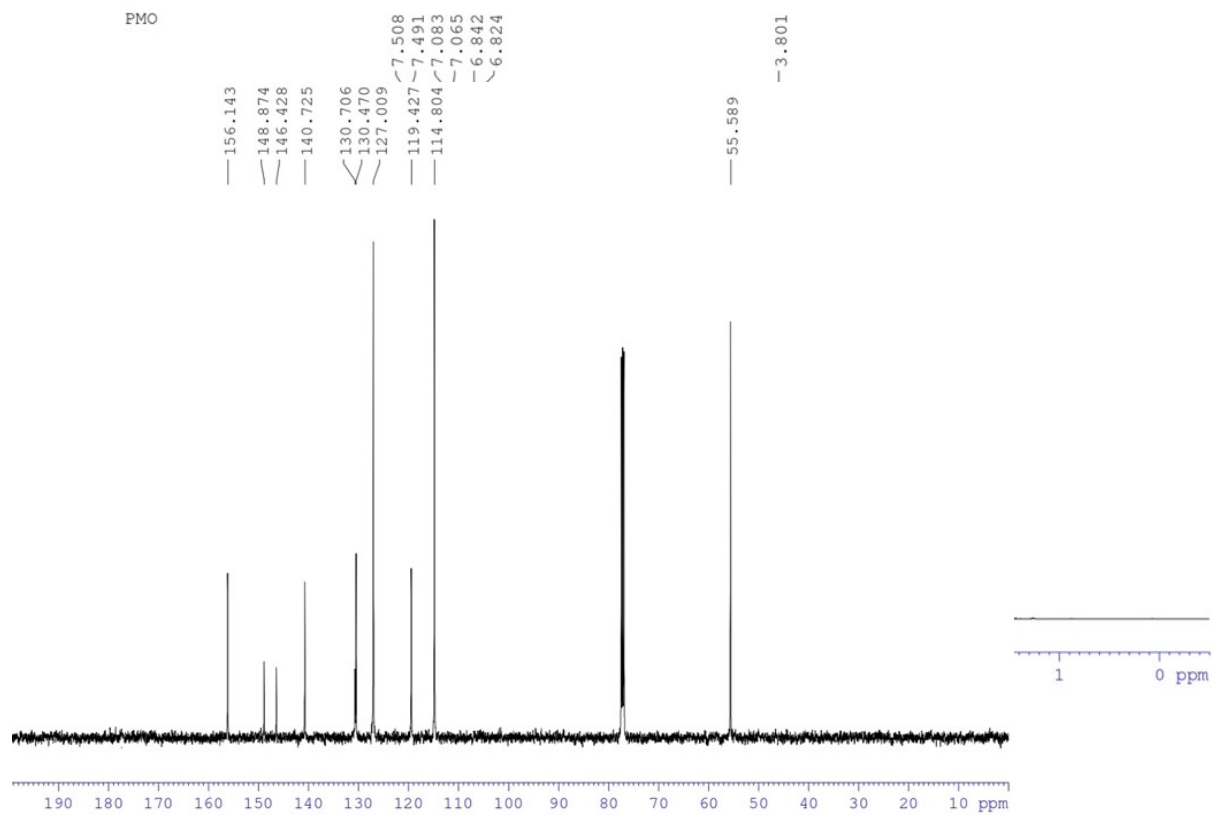


**Figure S5.** The (a) optimized structure and (b) partial density of states (pDOS) of pristine MAPbI<sub>3</sub> slab. The slab has four layers of PbI<sub>2</sub>. The pDOS depicts that there is no surface induced state(s) appear inside the bandgap of MAPbI<sub>3</sub>.



**Figure S6.** The (a) optimized structure and (b) partial density of states (pDOS) of **PMO-SCN** passivated MAPbI<sub>3</sub> slab. The charge densities of the (c) VBM and (d) CBM. The wavefunctions of the band edge states show significant delocalization. Key: Sulphur (green).

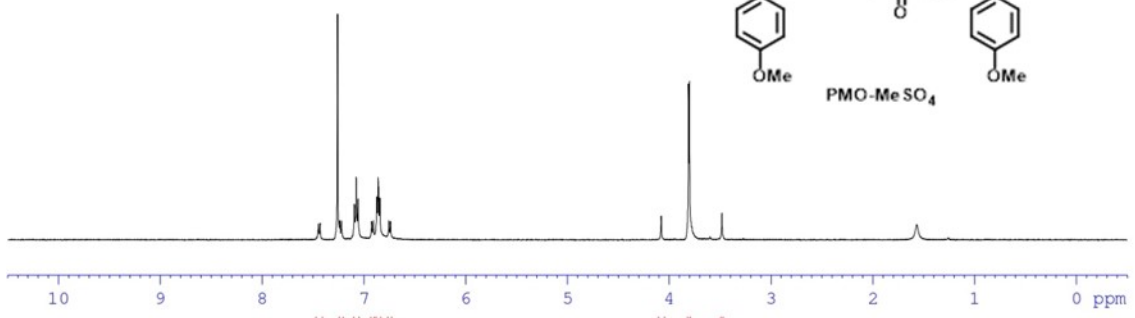
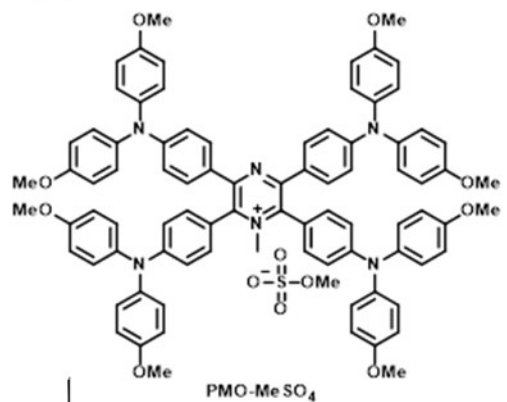
# H<sup>1</sup> and C<sup>13</sup> NMR



PMO-MeSO<sub>4</sub>

7.449  
7.431  
7.237  
7.219  
7.094  
7.075  
7.057  
6.924  
6.907  
6.874  
6.860  
6.857  
6.843  
6.756  
6.738

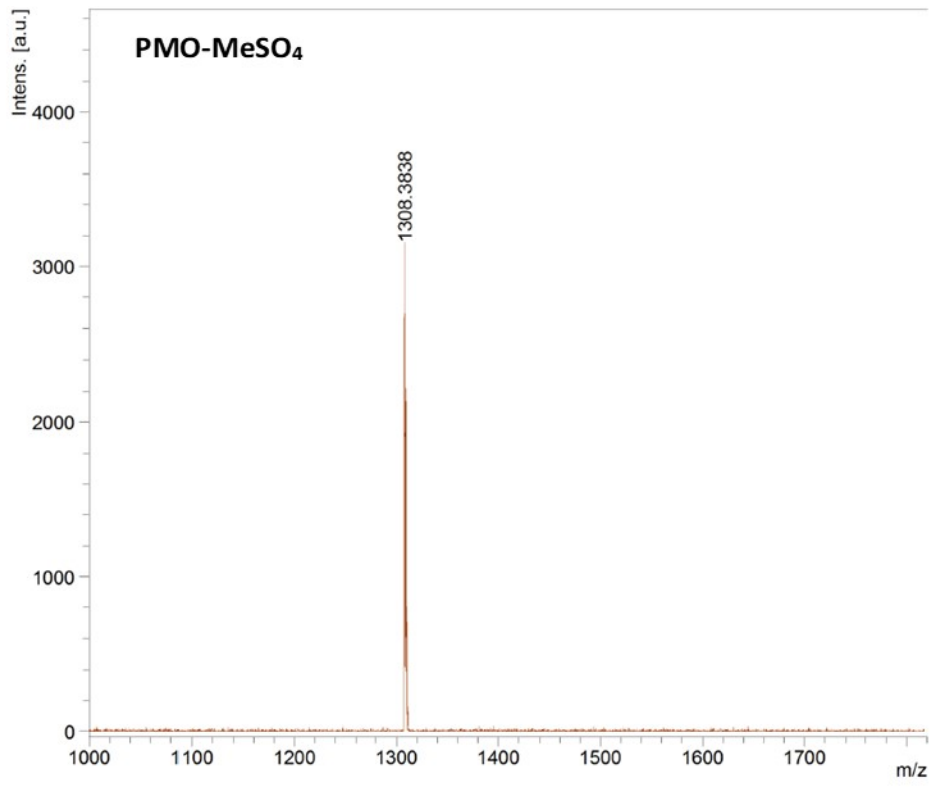
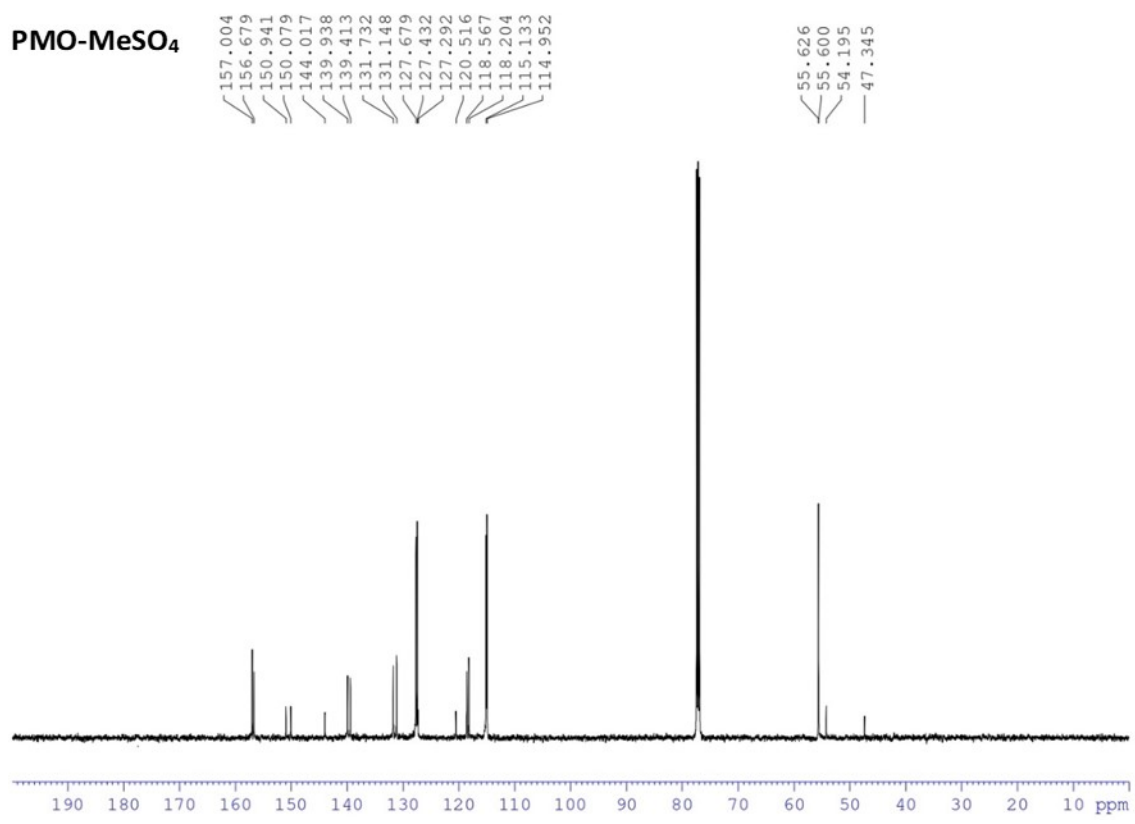
4.079  
3.809  
3.801  
3.482



4.000  
4.107  
16.037  
4.027  
16.422  
4.384

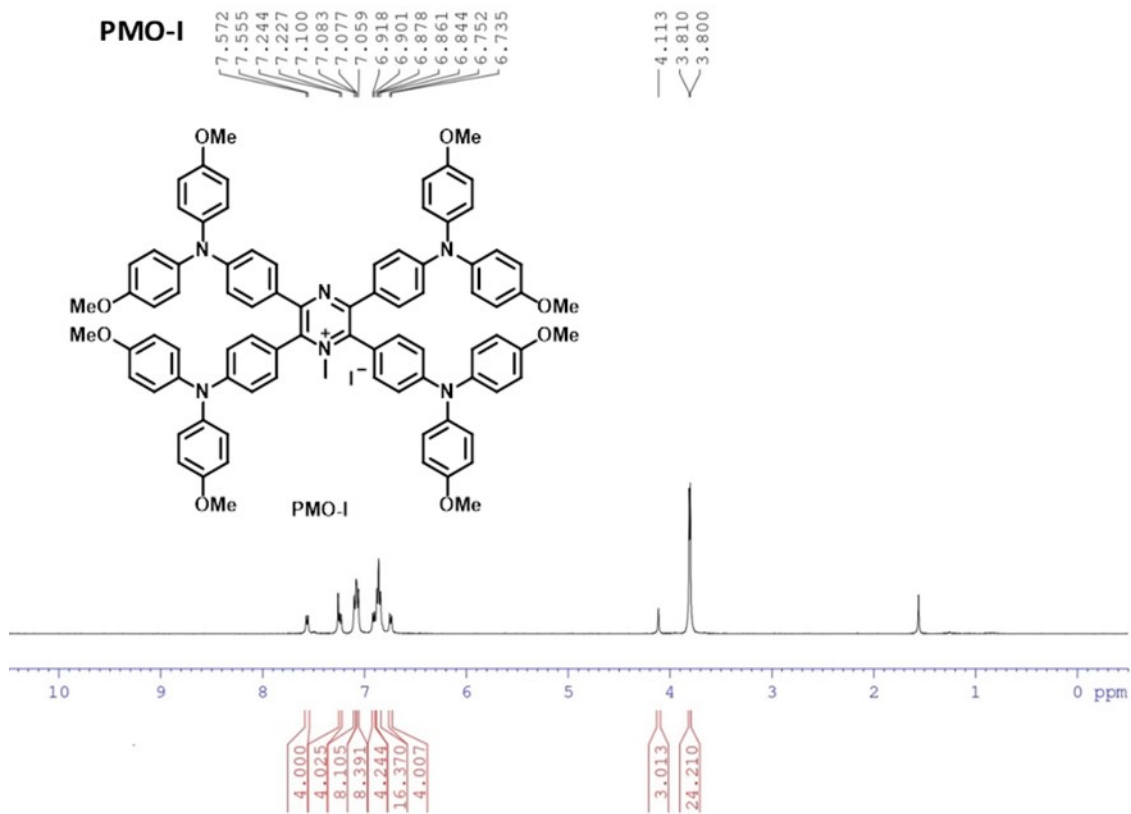
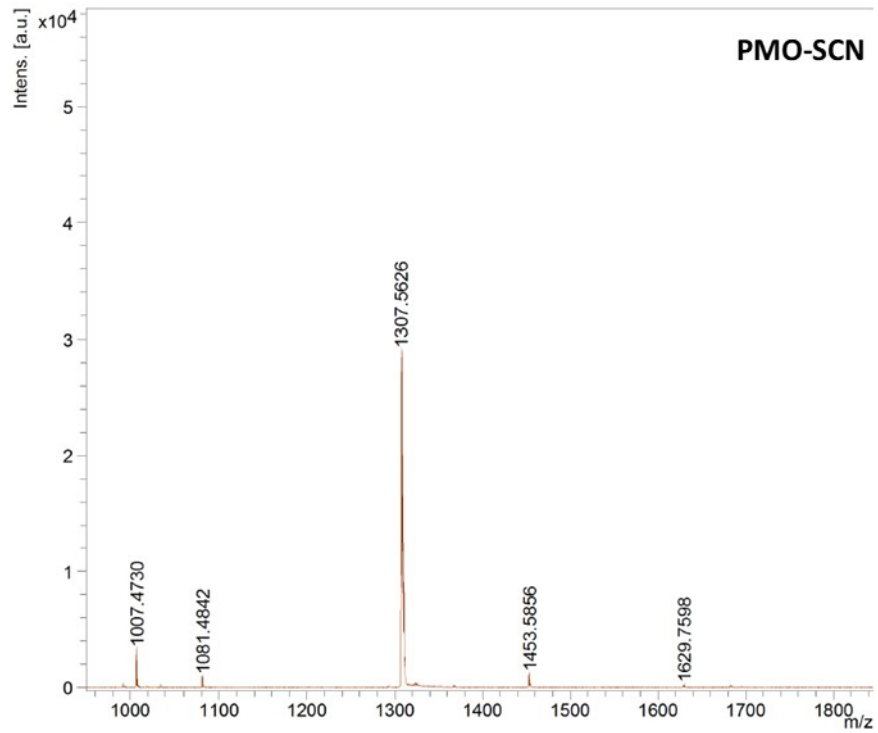
2.821  
24.000  
3.027

PMO-MeSO<sub>4</sub>









PMO-I

