Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Cost-Effective Dopant-Free Star-Shaped Oligo-Arylamines for High Performance Perovskite Solar Cells

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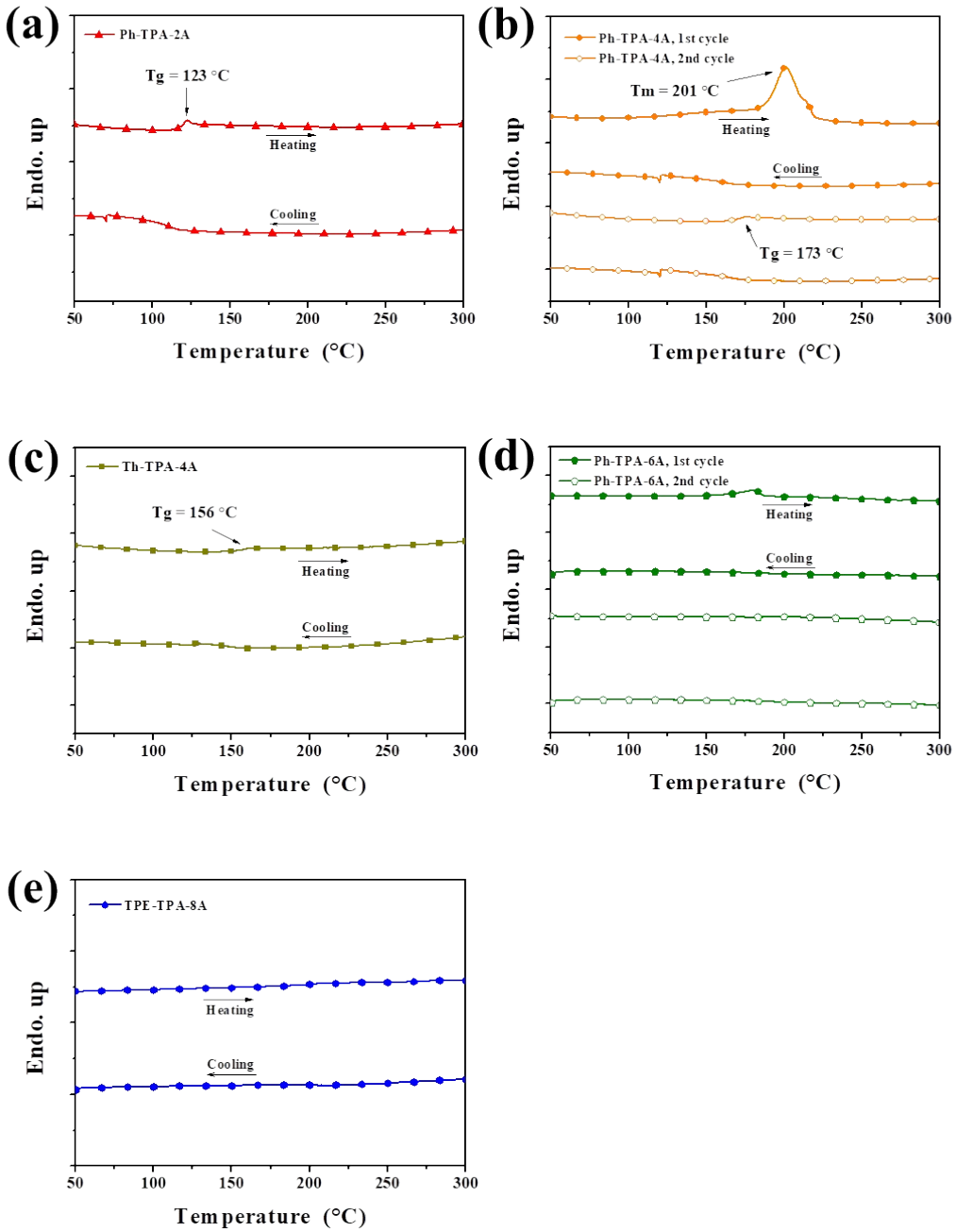


Figure S1. Differential Scanning calorimetry (DSC) thermograms of of HTMs.

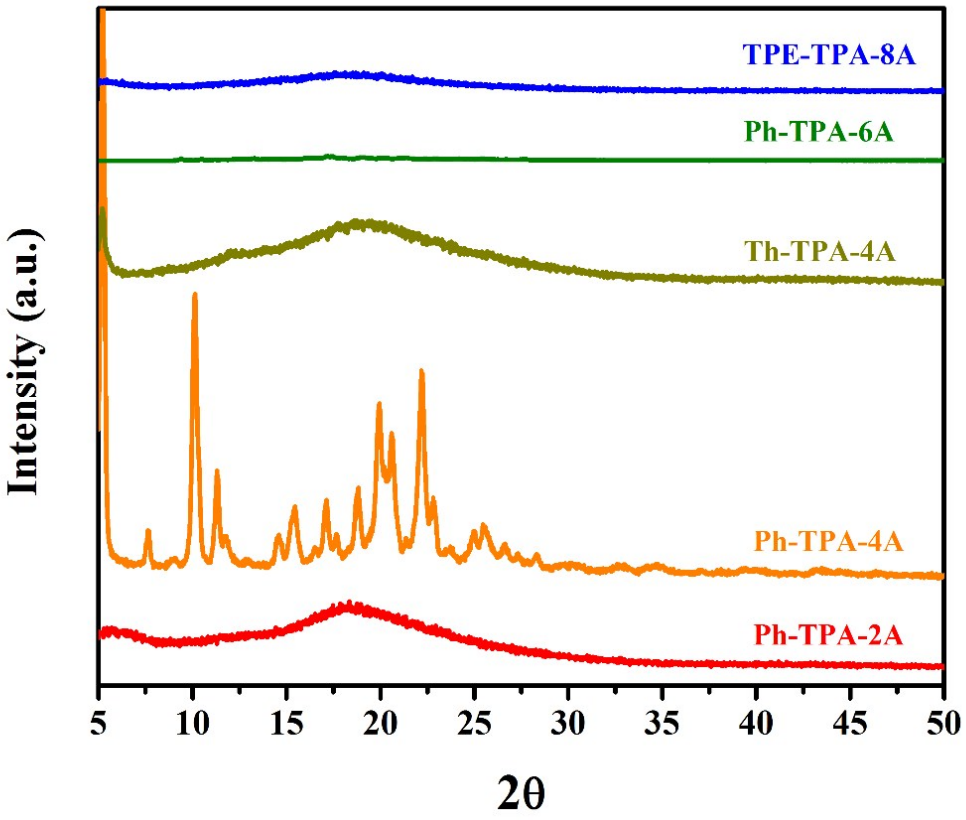


Figure S2. Powder X-ray diffraction patterns of the HTMs.

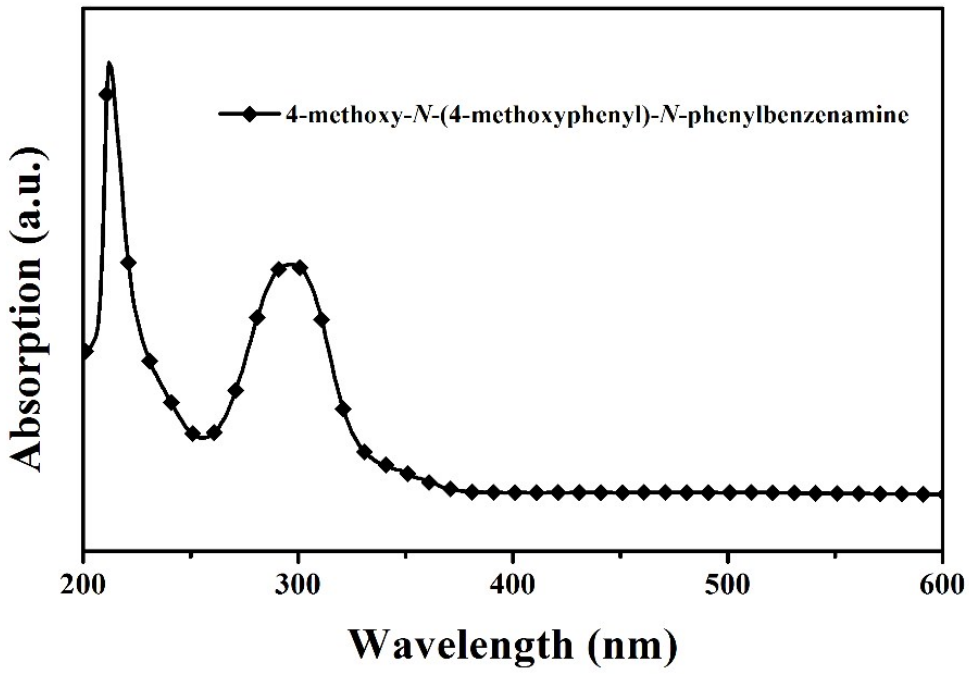


Figure S3. UV-Vis absorption spectrum of 4-methoxy-*N*-(4-methoxyphenyl)-*N*-phenyl-benzenamine.

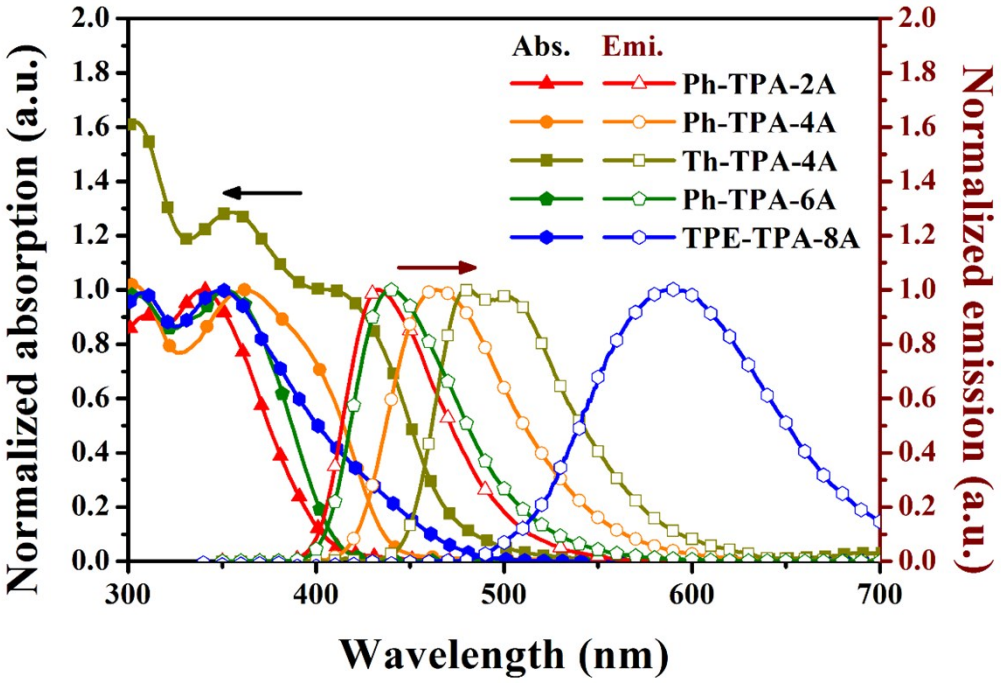


Figure S4. Normalized UV-Vis absorption and emission spectra of HTMs.

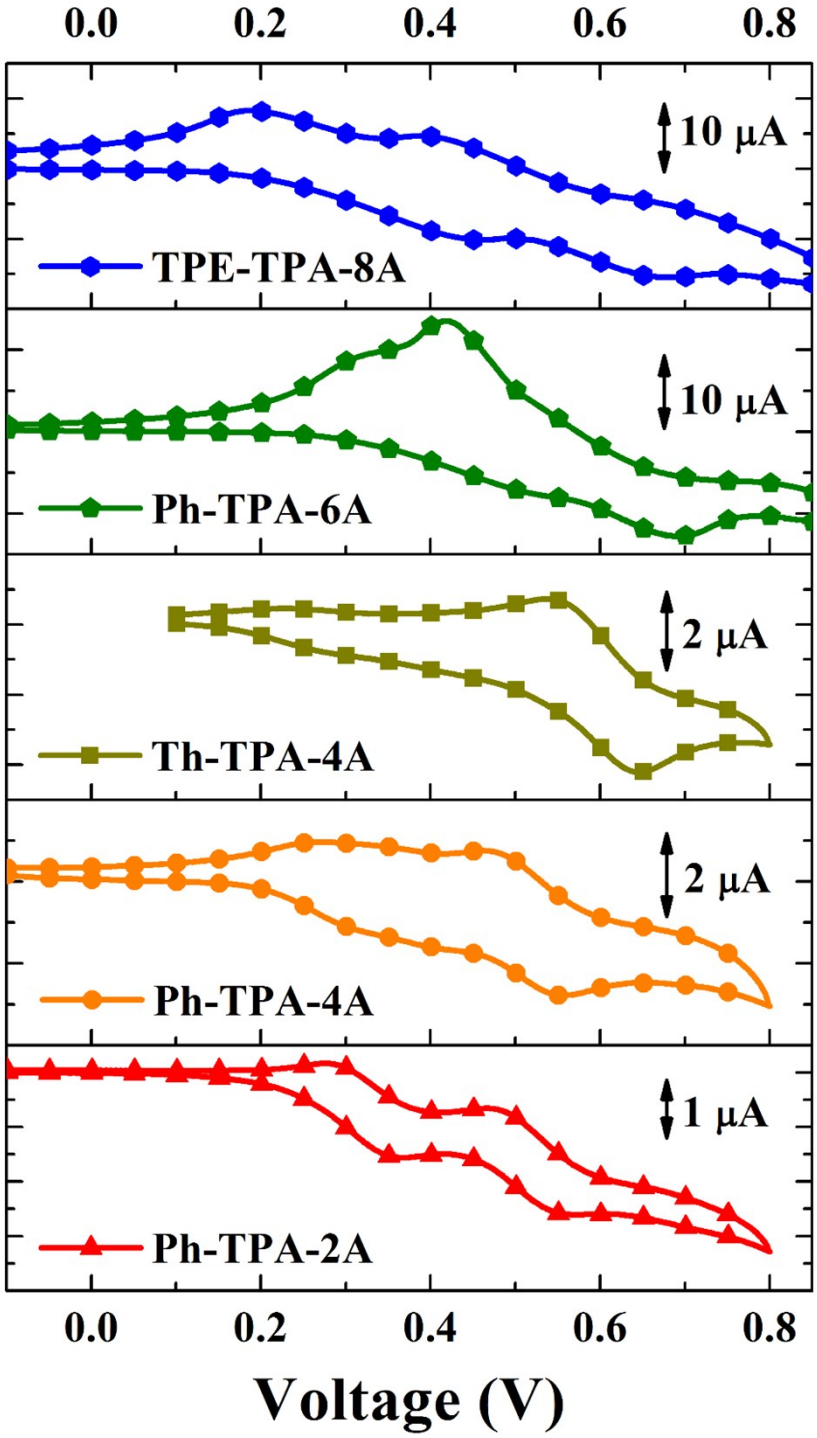


Figure S5. Cyclic voltammograms of HTMs.

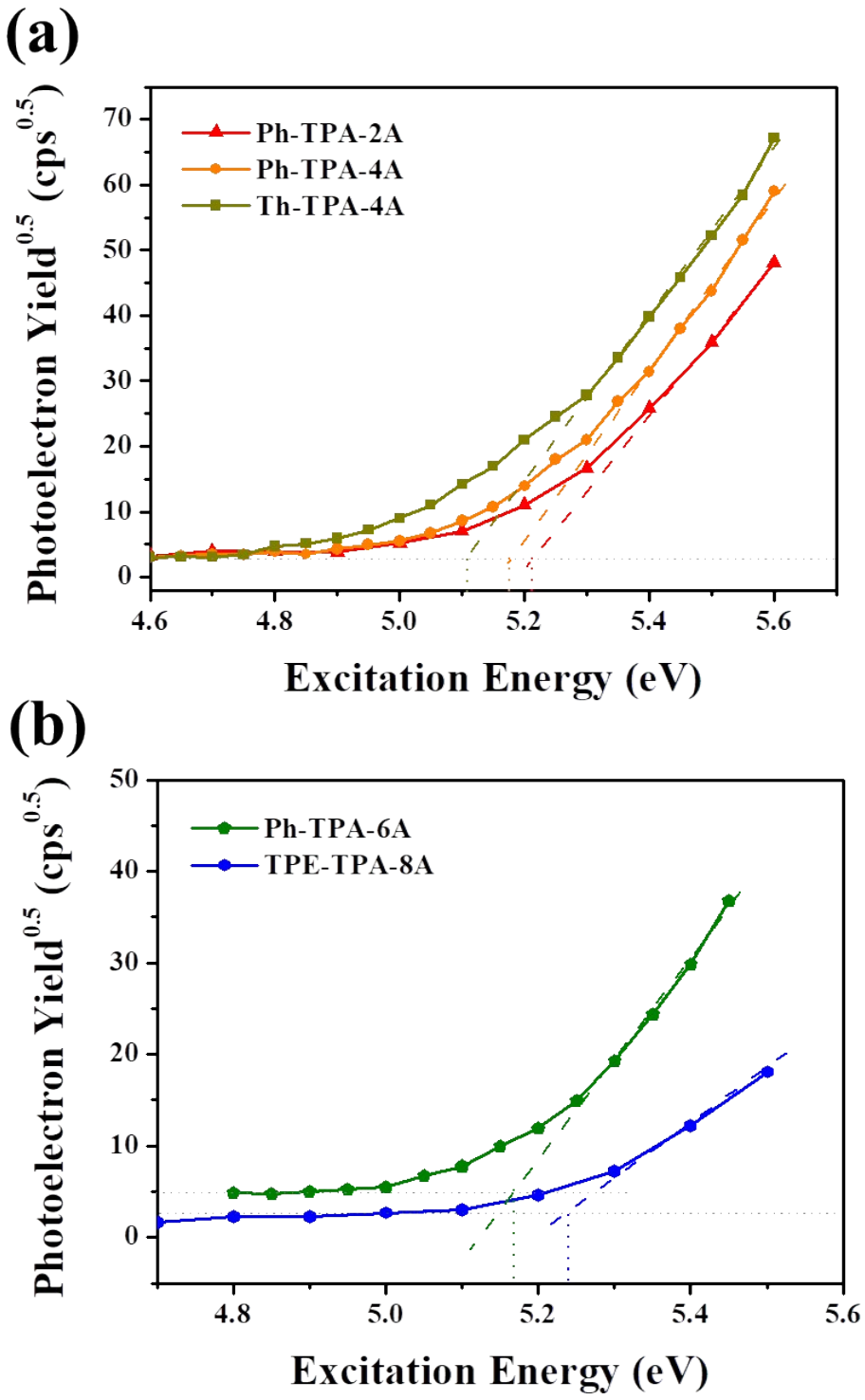


Figure S6. Photoelectron spectra of the HTM films.

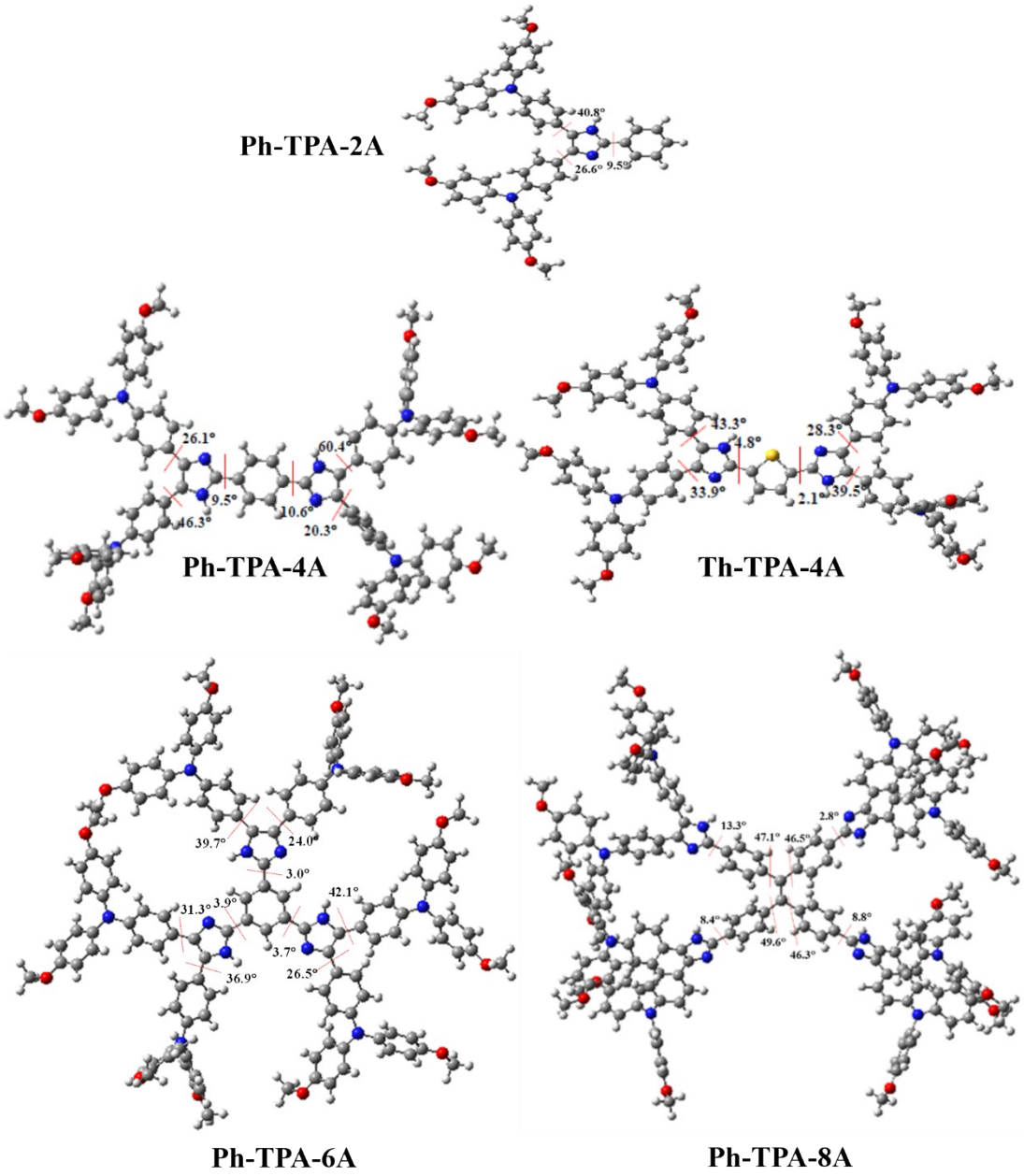


Figure S7. Optimized structures of HTMs.

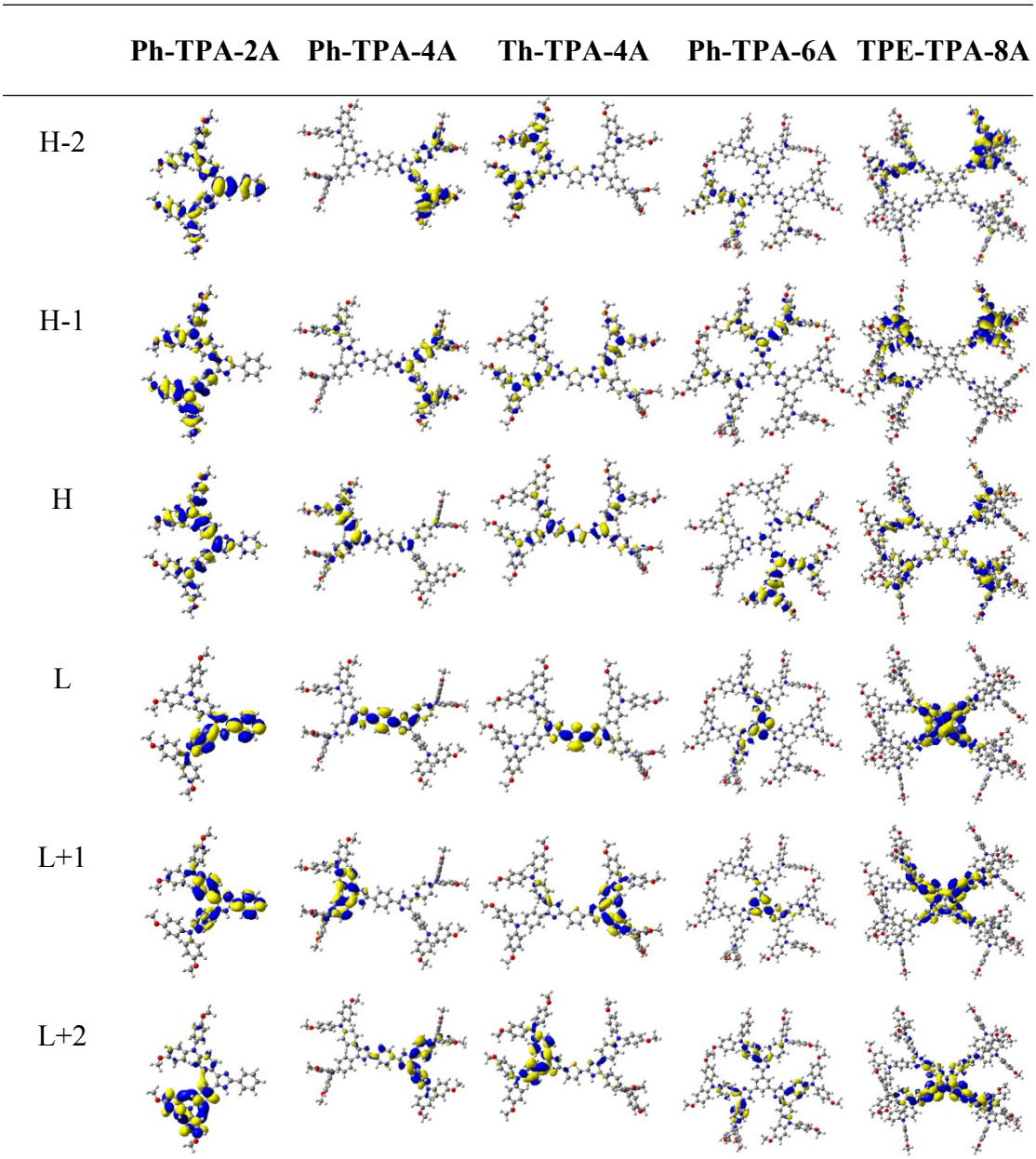


Figure. S8. Frontier orbitals of HTMs.

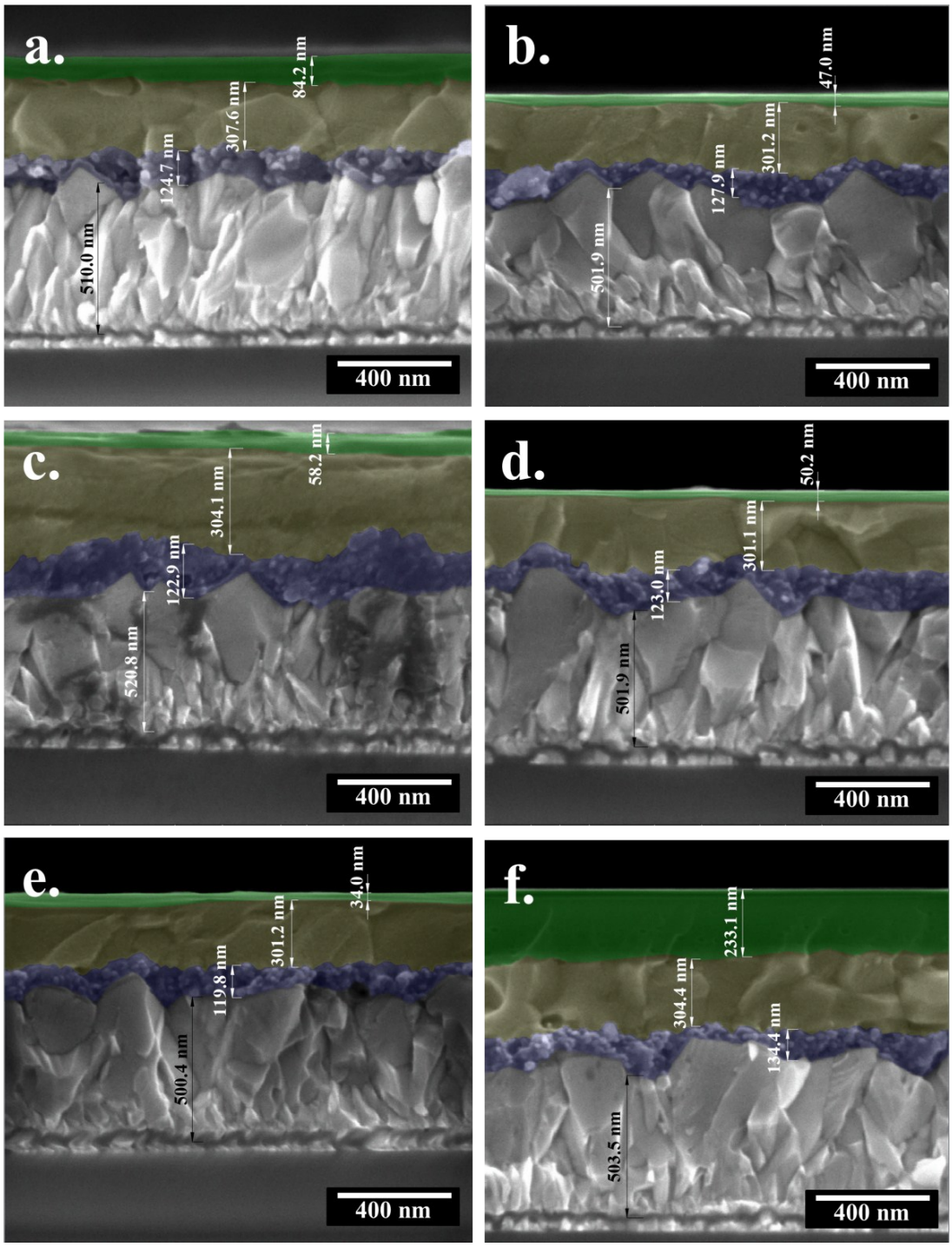


Figure S9. Cross-sectional SEM images using the device structure of FTO/TiO_2/perovskite/HTM, where the HTM is (a) **Ph-TPA-2A**, (b) **Ph-TPA-4A**, (c) **Th-TPA-4A**, (d) **Ph-TPA-6A**, (e) **TPE-TPA-8A**, and (f) Spiro-OMeTAD.

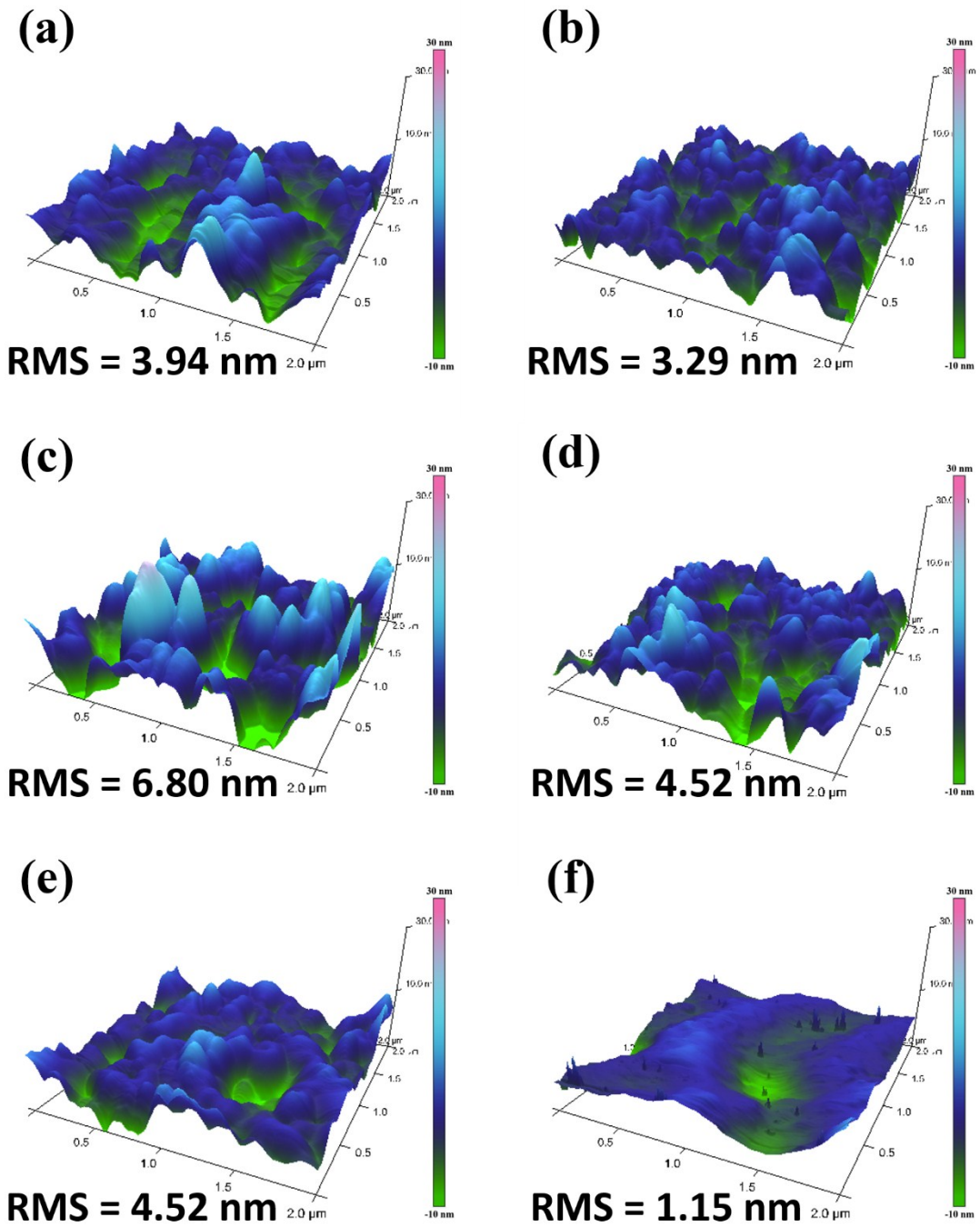


Figure S10 The AFM images using the device structure of FTO/TiO_2/perovskite/HTM, where the HTM is (a) **Ph-TPA-2A**, (b) **Ph-TPA-4A**, (c) **Th-TPA-4A**, (d) **Ph-TPA-6A**, (e) **TPE-TPA-8A**, and (f) Spiro-OMeTAD.

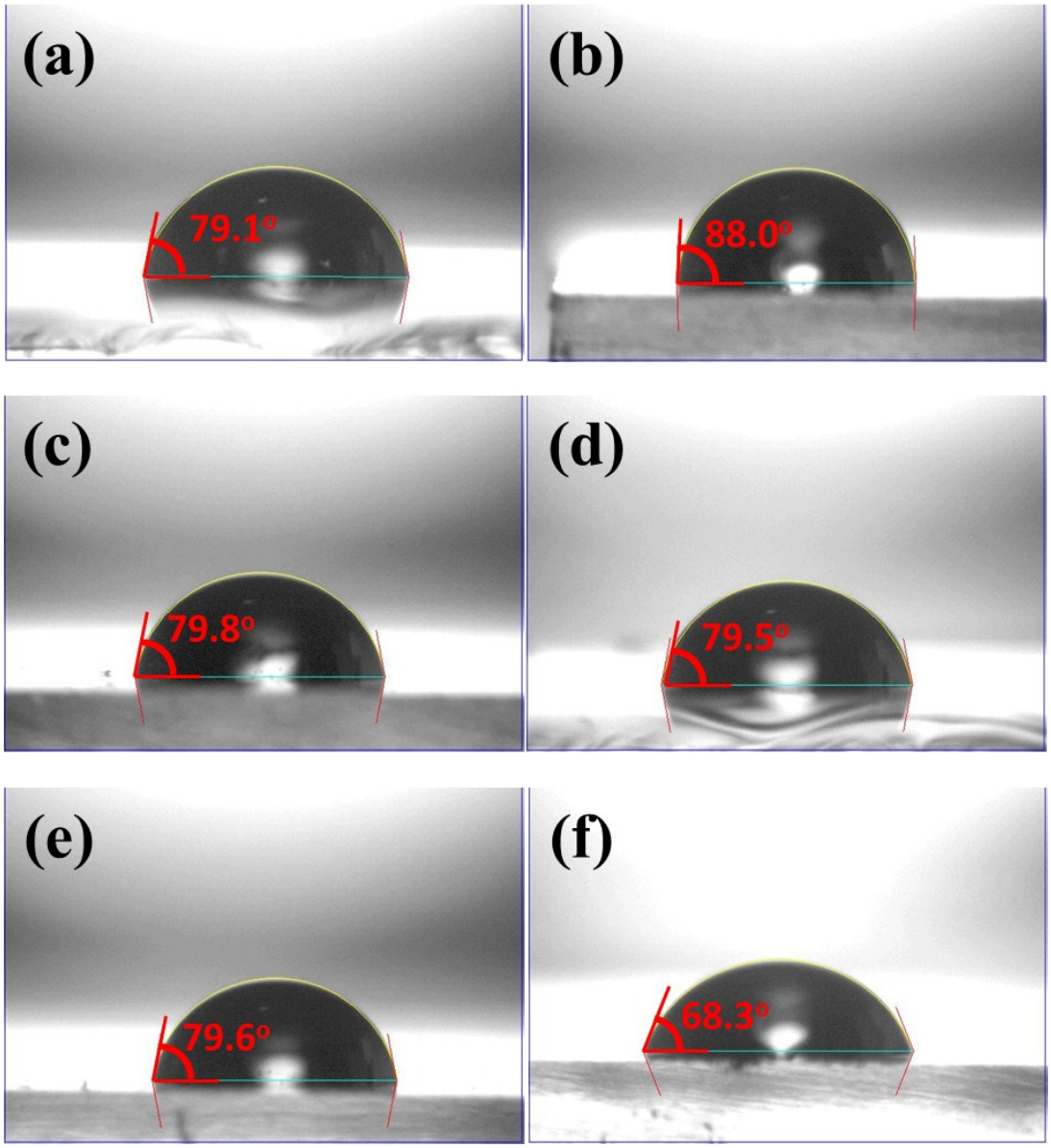


Figure S11. Contact angles of different HTMs on glass. (a) **Ph-TPA-2A**, (b) **Ph-TPA-4A**, (c) **Th-TPA-4A**, (d) **Ph-TPA-6A**, (e) **TPE-TPA-8A**, and (f) spiro-OMeTAD.

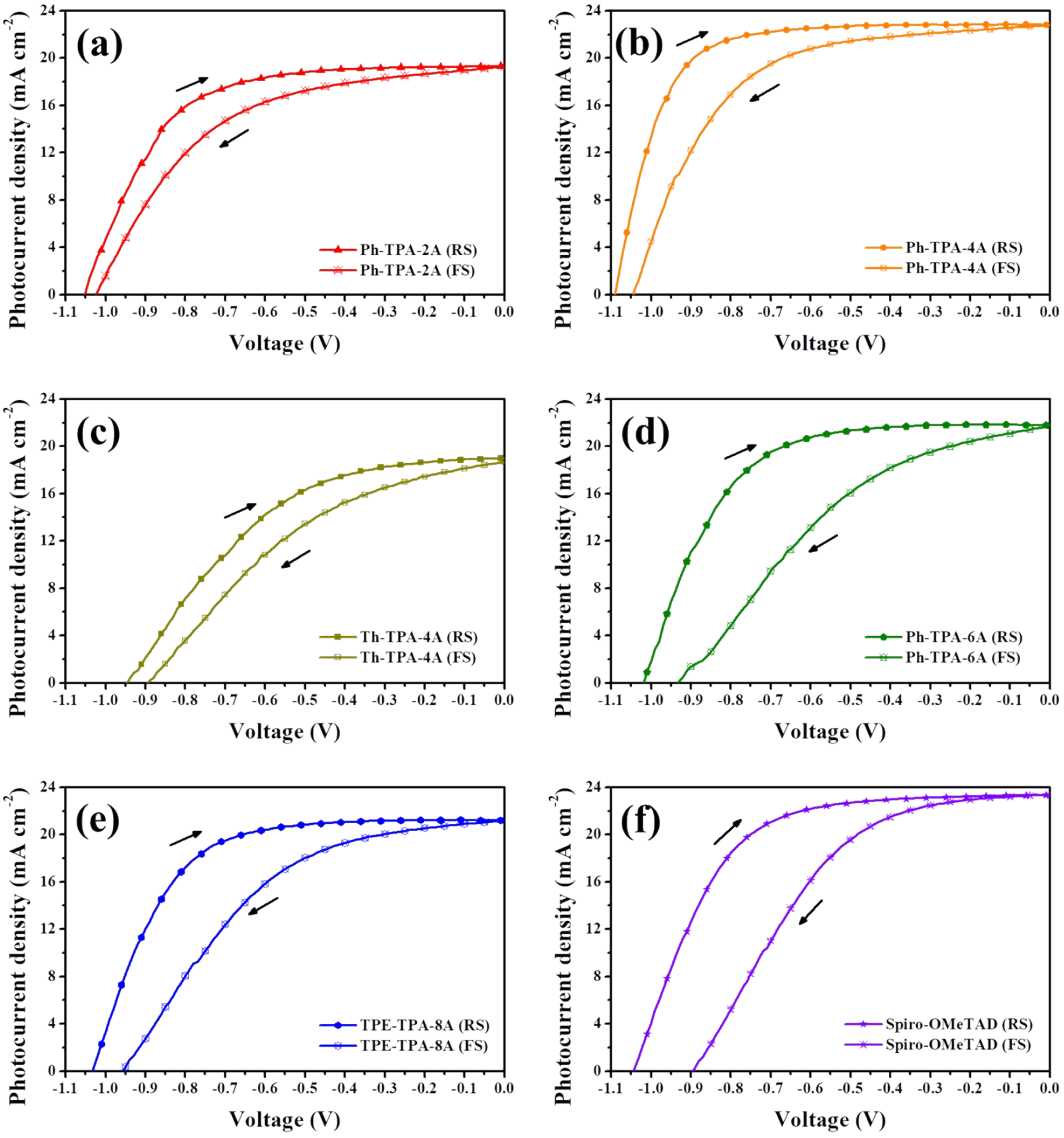


Figure S12. *J–V* plots of HTMs for both forward and reverse scan.

(a) Ph-TPA-2A

						USD				
Step1	Reagent	1	CuI	0.15	g	0.05	71%	OMeTPA		
		2	KO(*t*-Bu)	3.43	g	0.60		1.10	g	
		3	1,10-Phenathraline	0.15	g	0.51				
		4	aniline	0.46	ml	0.08				
		5	4-Iodoanisole	2.39	g	2.23				
	Solvent		toluene	25.28	ml	0.16				
	Workup		MeOH	50.56	ml	0.72				
Step2	Reagent	1	NBS	0.65	g	0.07	92%	OMeTPABr		
	Solvent		$CHCl_3$	12.36	ml	0.43		1.28	g	
Step3	Reagent	1	1,4-dimethylpiperazine-2,3-dione	214.89	mg	0.75	93%	OMeTPAdione		
		2	*n*-BuLi	1.98	ml	0.16		0.93	g	
	Solvent		THF	5.76	ml	0.24				
	Workup		DCM	165.03	ml	2.46				
Step4	Reagent	1	benzaldehyde	0.21	ml	0.01	95%	Ph-TPA-2A		
		2	ammonium acetate	2.46	g	0.21		1.00	g	
	Solvent		HOAc	25.28	ml	0.54		9.31	USD/g	
	Workup		HOAc	4.21	ml	0.09				

(b) Ph-TPA-4A

						USD				
Step1	Reagent	1	CuI	0.18	g	0.06	71%	OMeTPA		
		2	KO(*t*-Bu)	3.98	g	0.70		1.28	g	
		3	1,10-Phenathraline	0.17	g	0.59				
		4	aniline	0.54	ml	0.09				
		5	4-Iodoanisole	2.76	g	2.58				
	Solvent		toluene	29.27	ml	0.18				
	Workup		MeOH	58.54	ml	0.83				
Step2	Reagent	1	NBS	0.75	g	0.08	92%	OMeTPABr		
	Solvent		$CHCl_3$	14.31	ml	0.50		1.48	g	
Step3	Reagent	1	1,4-dimethylpiperazine-2,3-dione	248.78	mg	0.87	93%	OMeTPAdione		
		2	*n*-BuLi	2.29	ml	0.19		1.08	g	
	Solvent		THF	6.67	ml	0.28				
	Workup		DCM	191.06	ml	2.84				
Step4	Reagent	1	terephthalaldehyde	108.94	mg	0.05	86%	Ph-TPA-4A		
		2	ammonium acetate	0.94	g	0.08		1.00	g	
	Solvent		HOAc	32.52	ml	0.69		10.96	USD/g	
	Workup		HOAc	16.26	ml	0.35				

Figure S13. Flow chart for estimation of the synthetic cost for HTMs: (a) **Ph-TPA-2A**, (b) **Ph-TPA-4A**, (c) **Th-TPA-4A**, (d) **Ph-TPA-6A**, (e) **TPE-TPA-8A**.

(c) Th-TPA-4A

						USD				
Step1	Reagent	1	CuI	0.18	g	0.06	71%	OMeTPA		
		2	KO(*t*-Bu)	4.08	g	0.72		1.31	g	
		3	1,10-Phenathraline	0.17	g	0.61				
		4	aniline	0.55	ml	0.09				
		5	4-Iodoanisole	2.83	g	2.65				
	Solvent		toluene	30.00	ml	0.19				
	Workup		MeOH	60.00	ml	0.85				
Step2	Reagent	1	NBS	0.77	g	0.08	92%	OMeTPABr		
	Solvent		$CHCl_3$	14.67	ml	0.51		1.52	g	
Step3	Reagent	1	1,4-dimethylpiperazine-2,3-dione	255.00	mg	0.89	93%	OMeTPAdione		
		2	*n*-BuLi	2.35	ml	0.19		1.11	g	
	Solvent		THF	6.83	ml	0.29				
	Workup		DCM	195.83	ml	2.92				
Step4	Reagent	1	2,5-Thiophenedicarboxaldehyde	116.67	mg	4.40	85%	Th-TPA-4A		
		2	ammonium acetate	0.97	g	0.08		1.00	g	
	Solvent		HOAc	33.33	ml	0.71		15.59	USD/g	
	Workup		HOAc	16.67	ml	0.36				

(d) Ph-TPA-6A

						USD				
Step1	Reagent	1	CuI	0.19	g	0.07	71%	OMeTPA		
		2	KO(*t*-Bu)	4.22	g	0.74		1.35	g	
		3	1,10-Phenathraline	0.18	g	0.63				
		4	aniline	0.57	ml	0.10				
		5	4-Iodoanisole	2.93	g	2.74				
	Solvent		toluene	31.03	ml	0.19				
	Workup		MeOH	62.07	ml	0.88				
Step2	Reagent	1	NBS	0.79	g	0.08	92%	OMeTPABr		
	Solvent		$CHCl_3$	15.17	ml	0.53		1.57	g	
Step3	Reagent	1	1,4-dimethylpiperazine-2,3-dione	263.79	mg	0.92	93%	OMeTPAdione		
		2	*n*-BuLi	2.43	ml	0.20		1.15	g	
	Solvent		THF	7.07	ml	0.30				
	Workup		DCM	202.59	ml	3.02				
Step4	Reagent	1	benzene-1,3,5-tricarbaldehyde	93.10	mg	29.01	83%	Ph-TPA-6A		
		2	ammonium acetate	0.89	g	0.08		1.00	g	
	Solvent		HOAc	34.48	ml	0.74		40.57	USD/g	
	Workup		HOAc	17.24	ml	0.37				

Figure S13. (conti.)

(e) TPE-TPA-8A

						USD				
Step1	Reagent	1	CuI	0.53	g	0.18	71%	OMeTPA		
		2	KO(*t*-Bu)	11.75	g	2.07	→	3.77	g	
		3	1,10-Phenathraline	0.50	g	1.75				
		4	aniline	1.59	ml	0.27				
		5	4-Iodoanisole	8.17	g	7.64				
	Solvent		toluene	86.54	ml	0.54				
	Workup		MeOH	173.08	ml	2.46				
Step2	Reagent	1	NBS	2.22	g	0.23	92%	OMeTPABr		
	Solvent		$CHCl_3$	42.31	ml	1.48	→	4.38	g	
Step3	Reagent	1	1,4-dimethylpiperazine-2,3-dione	735.58	mg	2.56	93%	OMeTPAdione		
		2	*n*-BuLi	6.78	ml	0.56	→	3.20	g	
	Solvent		THF	19.71	ml	0.83				
	Workup		DCM	564.90	ml	8.41				
Step4	Reagent	1	4,4',4",4'"-(ethene-1,1,2,2-tetrayl)tetrabenzaldehyde	521.63	mg	233.85	28%	TPE-TPA-8A		
		2	ammonium acetate	3.62	g	0.31	→	1.00	g	
	Solvent		HOAc	86.54	ml	1.85		265.99	USD/g	
	Workup		HOAc	48.08	ml	1.03				

Figure S13. (conti.)

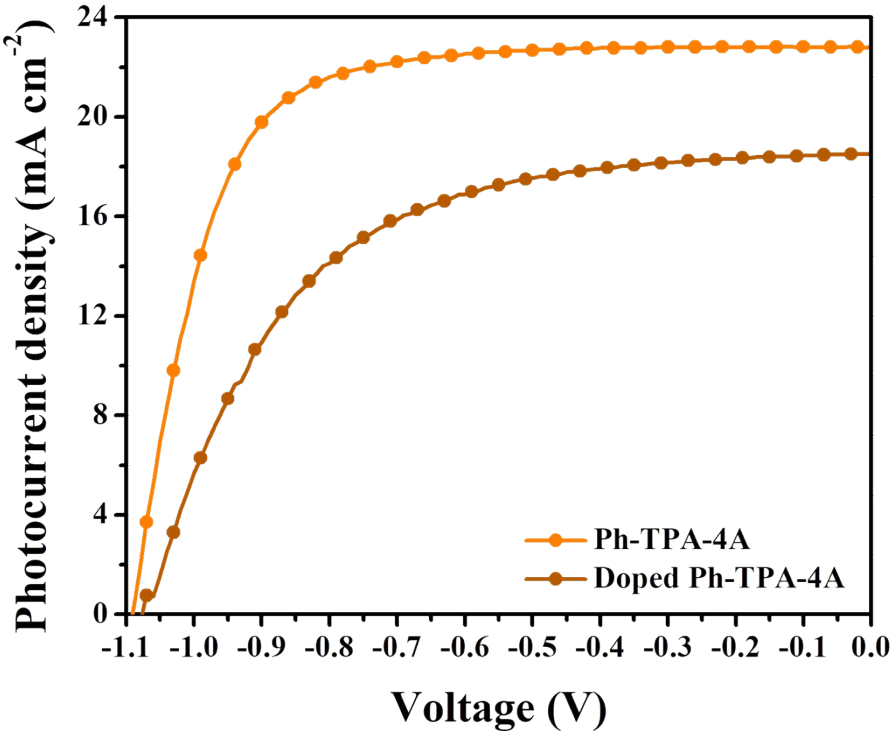


Figure S14. The *J-V* plot of doped **Ph-TPA-4A** compares with non-doped **Ph-TPA-4A**.

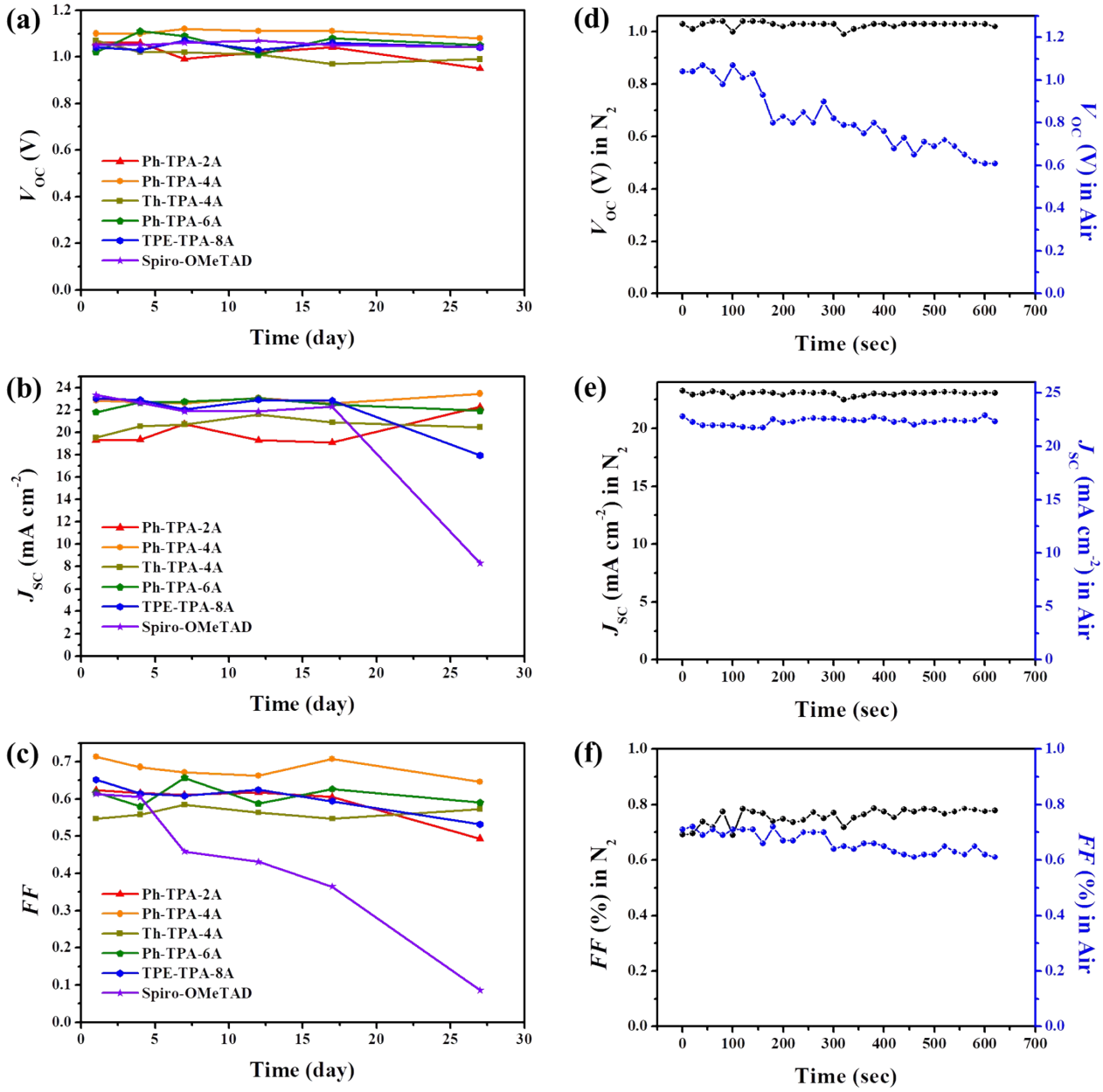


Figure S15. At-rest stability tests of PSCs with various HTMs based on the values of (a) $V_{OC,}$ (b) J_{SC}, and (c) *FF*, measured in a N_2 golve box. Continuous stability test of the **Ph-TPA-4A** PSC under a continuous light soaking (1 sun) for 600 s, based on the values of (a) $V_{OC,}$ (b) J_{SC}, and (c) *FF*, in a N_2 glove box (Black lines) or in air (Blue lines).

Table S1a. Calculated excitation energies for **Ph-TPA-2A** in THF solution.

N_States	*E* (ev)	WL (nm)	*f*	Major Contributions
1	3.01	410.62	0.5652	H→L (89%)
2	3.26	379.38	0.5533	H→L+1 (88%)
3	3.34	371.08	0.0786	H→L+2 (70%), H→L+3 (10%)
4	3.38	366.43	0.2644	H-1→L (80%), H→L+2 (10%)
5	3.43	361.39	0.011	H-1→L+2 (18%), H→L+3 (70%)
6	3.70	334.83	0.0402	H-1→L+1 (95%)
7	3.71	333.67	0.016	H-1→L+2 (67%), H→L+2 (13%)
8	3.88	319.32	0.0159	H-1→L+3 (46%), H→L+6 (26%)
9	3.91	316.65	0.2363	H-1→L+5 (19%), H→L+5 (68%)
10	3.94	314.81	0.1666	H→L+8 (18%), H→L+9 (34%)

WL: wavelength; *f*: oscillator strength; H: HOMO; H-n: HOMO-n; L: LUMO; L+n: LUMO+n.

Table S1b. Calculated excitation energies for **Ph-TPA-4A** in THF solution.

N_States	*E* (ev)	WL (nm)	*f*	Major Contributions
1	2.66	465	1.4123	H→L (93%)
2	2.88	430	0.1073	H-1→L (95%)
3	3.03	408	0.1706	H-2→L (97%)
4	3.08	401	0.1961	H-3→L (76%), H→L+1 (19%)
5	3.15	393	0.485	H-3→L (21%), H→L+1 (67%)
6	3.36	368	0.0299	H→L+3 (67%), H→L+6 (12%)
7	3.37	366	0.4771	H-1→L+2 (37%), H→L+2 (37%)
8	3.42	362	0.2026	H-2→L+4 (12%), H-1→L+4 (40)
9	3.43	361	0.0316	H-3→L+3 (17%), H→L+6 (58%)
10	3.48	356	0.0507	H-2→L+5 (30%), H-1→L+5 (49%)

WL: wavelength; *f*: oscillator strength; H: HOMO; H-n: HOMO-n; L: LUMO; L+n: LUMO+n.

Table S1c. Calculated excitation energies for **Th-TPA-4A** in THF solution.

N_States	*E* (ev)	WL (nm)	*f*	Major Contributions
1	2.49	498	1.2925	H→L (97%)
2	2.73	453	0.0169	H-1→L(99%)
3	2.95	420	0.1921	H-2→L (94%)
4	2.98	415	0.0608	H-3→L (91%)
5	3.11	398	0.2891	H-1→L+1 (13%), H→L+1 (72%)
6	3.15	393	0.876	H-1→L+2 (14%), H→L+2 (67%)
7	3.31	373	0.03	H-1->L+3 (24%), H→L+3 (64%)
8	3.34	371	0.2847	H-4→L (31%), H→L+4 (40%)
9	3.35	370	0.5009	H-4→L (56%), H→L+4 (22%)
10	3.42	362	0.0241	H-1→L+5 (26%), H→L+5 (40%)

WL: wavelength; *f*: oscillator strength; H: HOMO; H-n: HOMO-n; L: LUMO; L+n: LUMO+n.

Table S1d. Calculated excitation energies for **Ph-TPA-6A** in THF solution.

N_States	*E* (ev)	WL (nm)	*f*	Major Contributions
1	2.88	430.49	0.6595	H-2→L (36%), H-1→L+1 (20%), H→L (34%)
2	2.89	428.60	0.4959	H-2→L+1 (15%), H-1→L (35%), H-1→L+1 (13%), H→L+1 (16%)
3	2.90	427.14	0.1116	H-1→L+1 (35%), H→L (28%), H→L+1 (21%)
4	2.96	417.59	0.0824	H-2→L (36%), H-1→L (18%), H-1->L+1 (24%), H→L (15%)
5	2.98	415.99	0.0754	H-2→L (15%), H-2→L+1 (23%), H-1→L (34%), H→L (10%), H→L+1 (13%)
6	2.98	415.22	0.0699	H-2→L+1 (47%), H→L+1 (42%)
7	3.19	388.13	0.4852	H-2→L+2 (12%), H→L+2 (20%), H→L+3 (34%)
8	3.20	387.24	0.5497	H-3→L (10%), H-2→L+2 (15%), H-1→L+4 (19%), H→L+2 (21%)
9	3.21	386.60	0.8732	H-2→L+4 (20%), H-1→L+2 (34%)
10	3.26	380.53	0.3661	H-4→L (20%), H-3→L (42%)

WL: wavelength; *f*: oscillator strength; H: HOMO; H-n: HOMO-n; L: LUMO; L+n: LUMO+n.

Table S1e. Calculated excitation energies for **TPE-TPA-8A** in THF solution.

N_States	*E* (ev)	WL (nm)	*f*	Major Contributions
1	2.37	522.98	0.5342	H→L (95%)
2	2.47	500.78	0.0326	H-1→L (90%)
3	2.48	498.48	0.5542	H-2→L (91%)
4	2.53	489.83	0.004	H-3→L (96%)
5	2.79	444.14	0.0931	H-4→L (90%)
6	2.81	440.82	0.1042	H-5→L (93%)
7	2.82	439.50	0.1029	H-6→L (92%)
8	2.83	437.50	0.0526	H-7→ (91%)
9	2.97	416.91	1.0023	H→ L+1 (78%)
10	2.99	413.63	0.4001	H→ L+2 (70%)

WL: wavelength; *f*: oscillator strength; H: HOMO; H-n: HOMO-n; L: LUMO; L+n: LUMO+n.

Table S1f. Calculated HOMOs and LUMOs energies (eV) of the oligo arylamine HTMs in THF medium using B3LYP function.

	Ph-TPA-2A	**Ph-TPA-4A**	**Th-TPA-4A**	**Ph-TPA-6A**	**TPE-TPA-8A**
H-2	-5.78	-5.04	-5.07	-4.79	-4.78
H-1	-5.09	-4.88	-4.84	-4.77	-4.77
H	-4.77	-4.72	-4.67	-4.76	-4.71
L	-1.30	-1.68	-1.80	-1.49	-2.01
L+1	-1.00	-1.08	-1.11	-1.48	-1.39
L+2	-0.89	-0.91	-1.03	-1.11	-1.36
H-L gap	3.47	3.04	2.87	3.27	2.70

Table S2. The PCE (> 14%) and hole mobility values for HTMs published in 2016–2019.

HTM name	Perovskite	PCE (%)	μ_h ($cm^2\ V^{-1}\ s^{-1}$)	ref.	Molecular structure
	Type I				
$PdMe_2Pc$	$MAPbI_3$	16.28	3.42×10^{-2}	73	
3F-br-4C[a]	$MAPbI_3$	16.9	4.0×10^{-5}	75	
PCA-1	$MAPbI_3$	18.17	2.0×10^{-3} [b]	24	
CuPc-OBu	$(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$	17.6	4.30×10^{-4}	25	
CuPc nanorod	$MAPbI_3$	16.1	10^{-2}	72	
$ZnPcNO_2$-OPh	$(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$	14.35	2.80×10^{-5}	83	
M7-TFSI	$(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$	17.7	3.24×10^{-4}	67	
$DFBT(DTS\text{-}FBTTh_2)_2$	$MAPbI_3$	17.3	1.78×10^{-4}	68	
ACE-QA-ACE	$MAPbI_3$	18.2	2.3×10^{-4}	69	
DERDTS-TBDT	$MAPbI_{3-x}Cl_x$	16.2	1×10^{-4}	70	
KR321	$(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$	19.03	2.6×10^{-4}	39	
FA-CN	$(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$	18.9	1.2×10^{-4}	59	

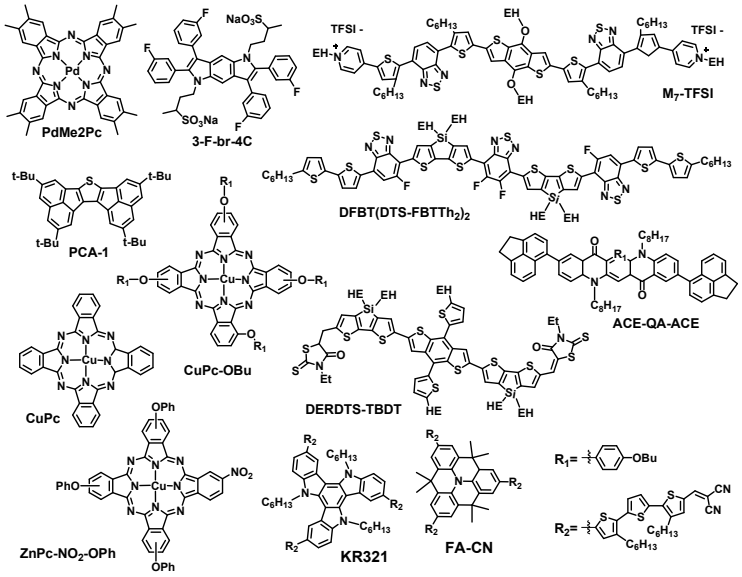


Table S2. (Conti.)

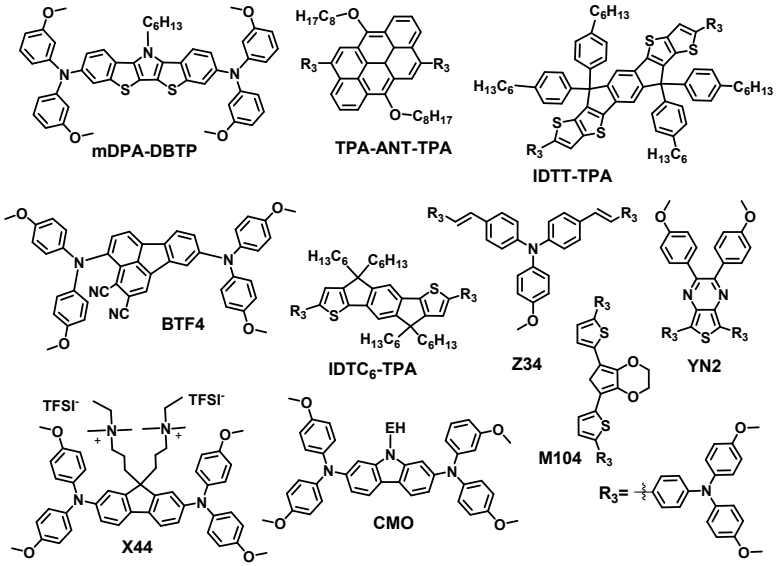
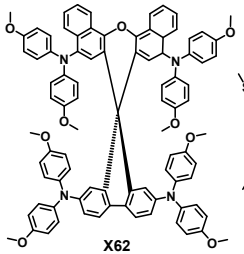
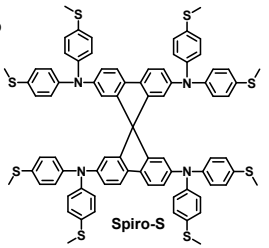
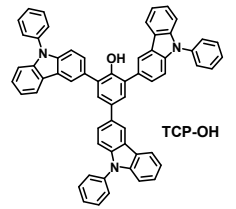
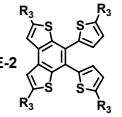
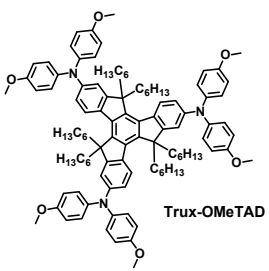
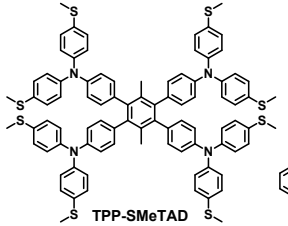
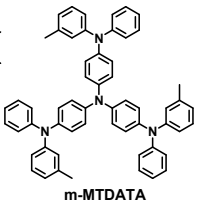
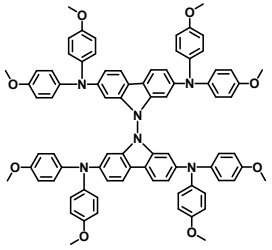
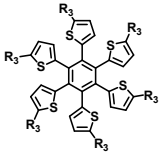
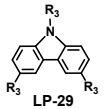
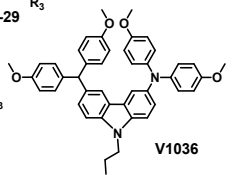
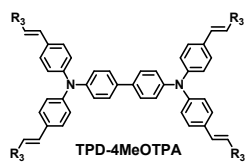
HTM name	Perovskite	PCE (%)	μ_h ($cm^2\ V^{-1}\ s^{-1}$)	ref.	Molecular structure
	Type II				
mDPA-DBTP	$MAPbI_3$	18.09	6.34×10^{-4}	60	
BTF4	$(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$	18.03	1.17×10^{-4}	61	
TPA-ANT-TPA	$MAPbI_3$	17.5	2.6×10^{-4}	62	
YN2	$(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$	19.27	9.65×10^{-4}	63	
Z34	$MAPbI_3$	16.1	7.46×10^{-4}	71	
IDTT-TPA	$MAPbI_3$	15.9	6.46×10^{-4}	79	
X44	$[FA]_{0.85}(MA)_{0.15}Pb(I_{0.85}Br_{0.15})_3$	15.2	-	80	
CMO	$MAPbI_3$	15.92	1.4×10^{-5}	82	
$IDTC_6$-TPA	$MAPbI_3$	14.52	4.26×10^{-4}	84	
M104	$(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$	16.50	1.12×10^{-4}	85	
YN3	$(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$	18.84	2.25×10^{-4}	65	
TPAC-3M	$MAPbI_3$	17.54	1.1×10^{-5}	66	
BTPA-TCNE	$MAPbI_3$	16.94	3.14×10^{-5}	49	
NP2	$Cs_{0.05}(FA_{0.17}MA_{0.83})_{0.95}Pb(Br_{0.17}I_{0.83})_3$	16.4	4.23×10^{-2}	74	

Table S2. (Conti.)

HTM name	Perovskite	PCE (%)	μ_h ($cm^2\ V^{-1}\ s^{-1}$)	ref.	Molecular structure
	Type III				
X62	mixed cation/mixed halide	15.9	7.95×10^{-5}	76	
Spiro-S	$MAPbI_3$	15.92	1.90×10^{-5}	77	
Trux-OMeTAD	$MAPbI_3$	18.6	2×10^{-3}	31	
TTE-2	$(FAPbI_3)_{0.95}(MAPbBr_3)_{0.05}$	20.04	6.18×10^{-4}	38	
HTB-OMe	$MAPbI_3$	17.3	5.48×10^{-4}	34	
TPP-SMeTAD	$MAPbI_3$	16.2	7.4×10^{-5}	84	
2,7-BCz-OMeTAD	$Cs_{0.05}FA_{0.79}MA_{0.16}PbI_{2.49}Br_{0.51}$	17.6	0.95×10^{-4}	37	
***m*-MTDATA**[a]	$Cs_{0.05}(FA_{0.85}MA_{0.15})_{0.95}Pb(I_{0.85}Br0_{.15})_3$	18.12	4.3×10^{-5}	35	
***m*-MTDATA**[a]	$MAPbI_3$	17.73	-	36	
TPD-4MeOTPA	$(FAI)_{0.85}(PbI_2)_{0.85}(MABr)_{0.15}(PbBr_2)_{0.15}$	15.28	4.92×10^{-4}	81	
TCP-OH	$(FAI)_{0.81}(PbI_2)_{0.85}\ (MAPbBr_3)_{0.15}$	16.97	5.85×10^{-6}	33	
LD-29	$(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$	14.29	1.72×10^{-5}	86	
ST1	$MAPbI_3$	15.4	2.57×10^{-4} [c]	78	
	Others				
V1036[a]	$Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})_3$	17.8	-	64	
TAPC[a]	$MAPbI_3$	18.80	4.94×10^{-4} [b]	58	

[a]inverted PSC; [b]annealed HTM film; [c]determined via TOF. EH = 2-ethylhexyl

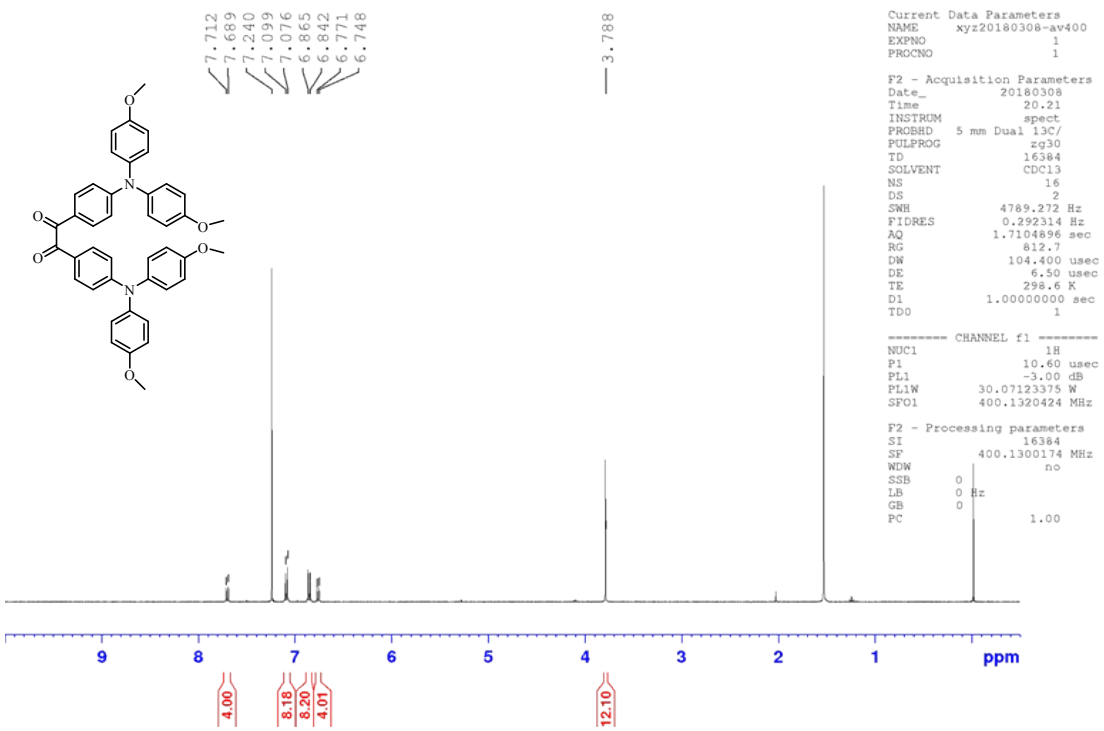


Figure S16. ^{1}H NMR spectrum of **OMeTPA-dione**

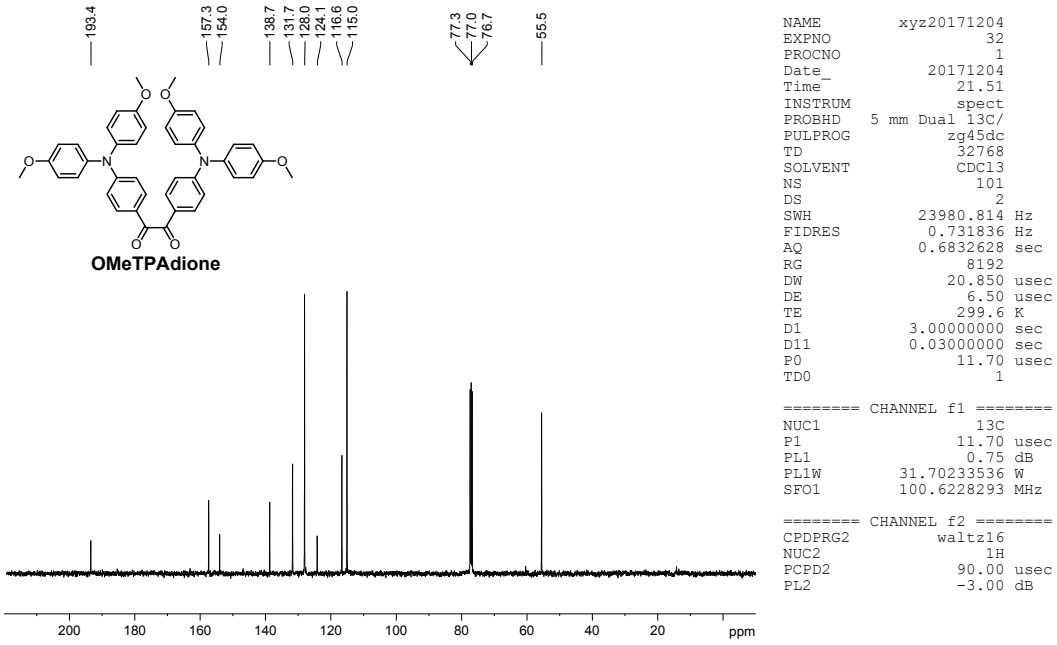


Figure S17. ^{13}C NMR spectrum of **OMeTPA-dione**

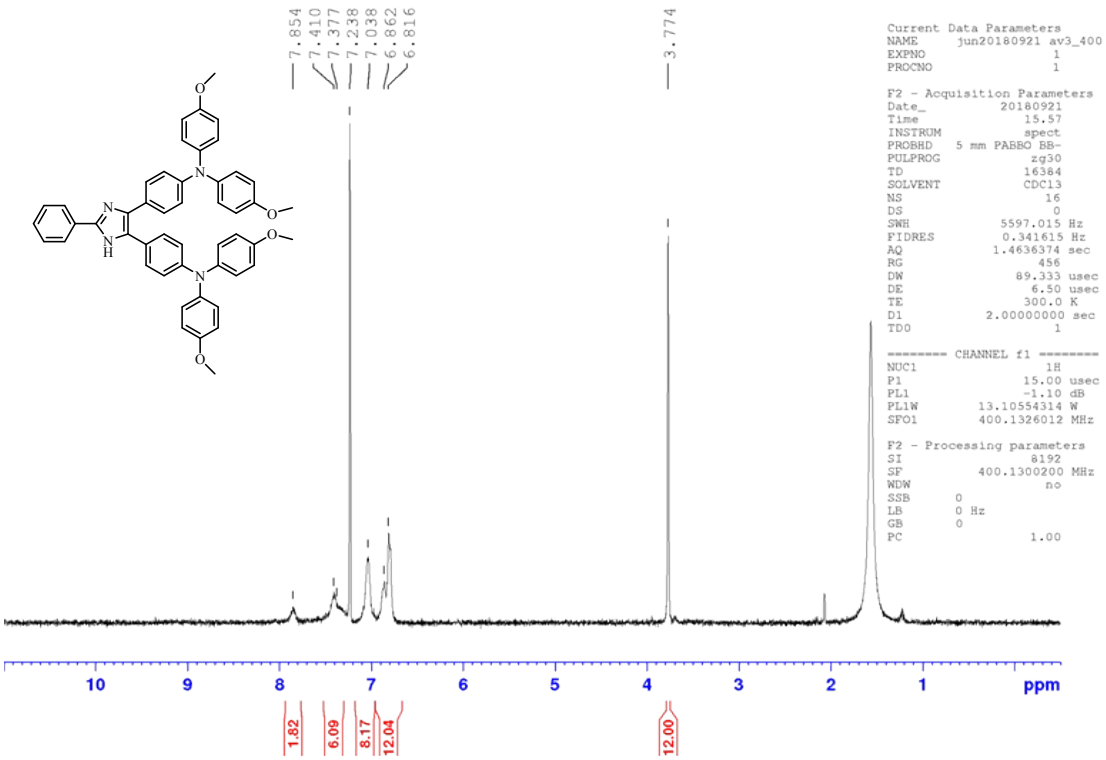


Figure S18. ^{1}H NMR of spectrum of **Ph-TPA-2A**

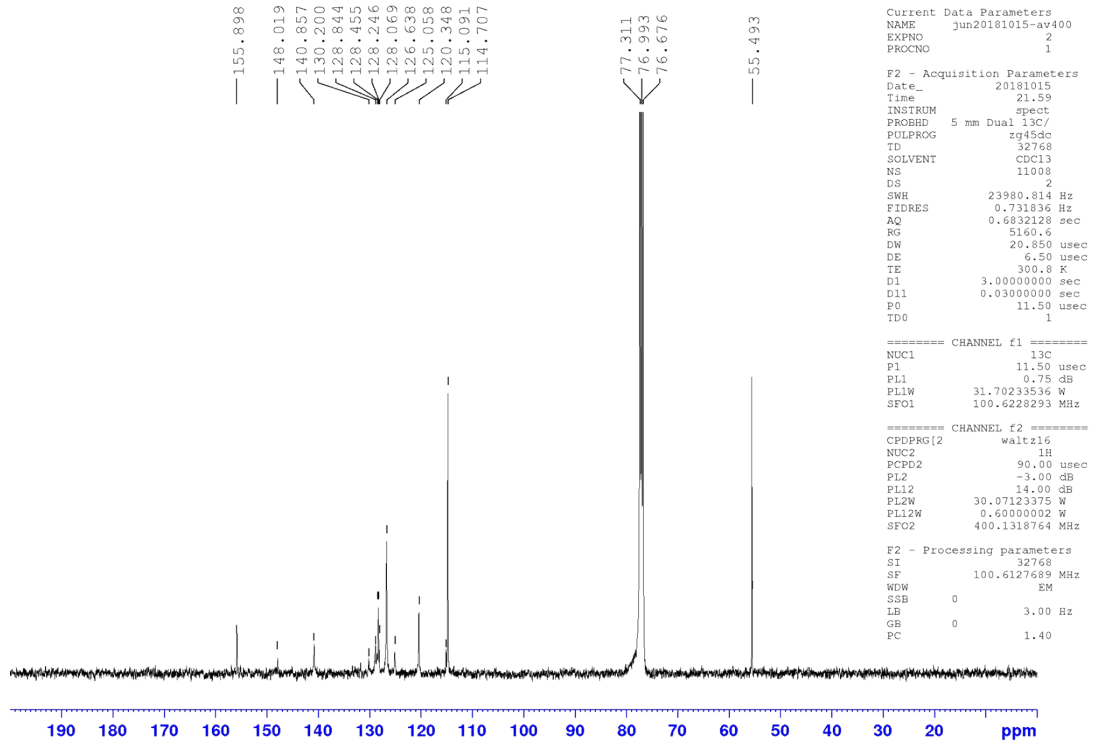
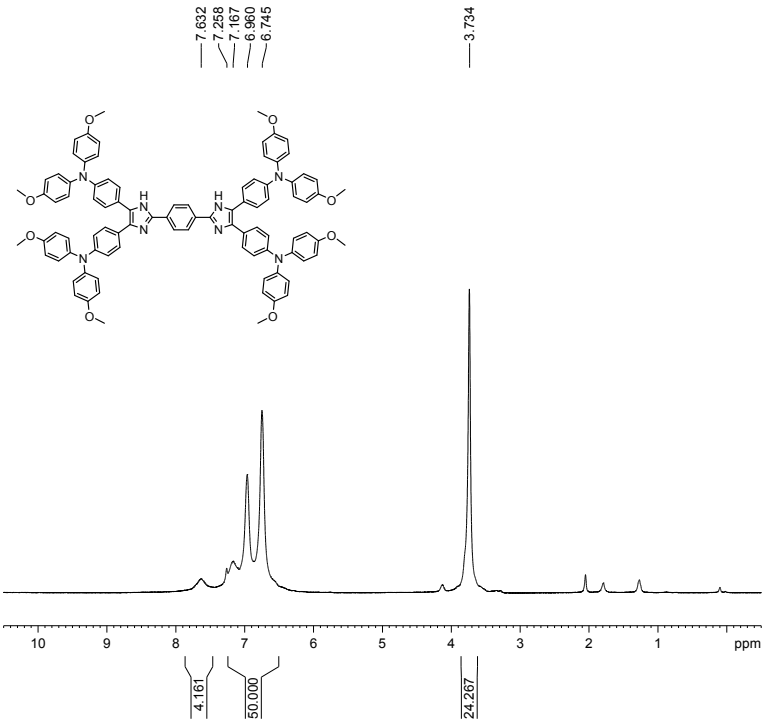


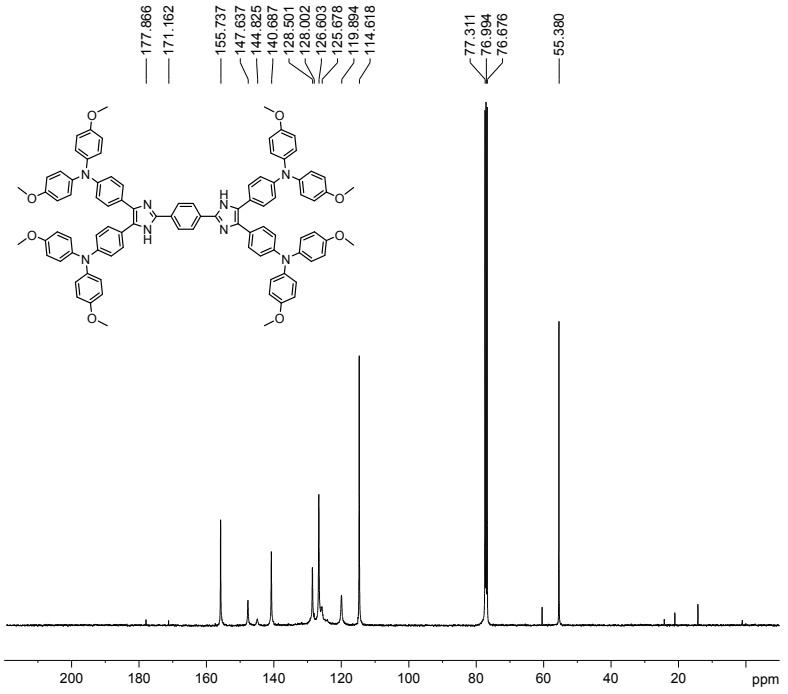
Figure S19. ^{13}C NMR spectrum of **Ph-TPA-2A**




```
NAME         xyz20180101
EXPNO                  1
PROCNO                 1
Date_           20180101
Time               20.02
INSTRUM            spect
PROBHD   5 mm Dual 13C/
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4789.272 Hz
FIDRES          0.292314 Hz
AQ              1.7105396 sec
RG                    64
DW                104.400 usec
DE                  6.50 usec
TE                 298.6 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 15.00 usec
PL1                -2.90 dB
PL1W         29.38673019 W
SFO1         400.1320424 MHz
SI                 16384
SF           400.1300089 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```

Figure S20. ^{1}H NMR spectrum of **Ph-TPA-4A**

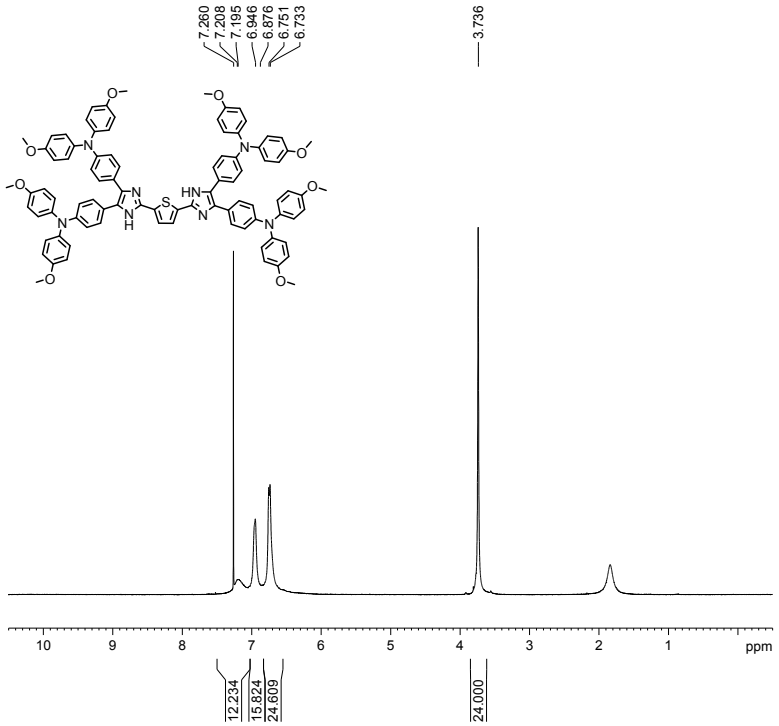



```
NAME         xyz20180101
EXPNO                  2
PROCNO                 1
Date_           20180101
Time               20.07
INSTRUM            spect
PROBHD   5 mm Dual 13C/
PULPROG           zg45ig
TD                 32768
SOLVENT            CDCl3
NS                 14350
DS                     8
SWH            23980.814 Hz
FIDRES          0.731836 Hz
AQ              0.6832628 sec
RG                2896.3
DW                20.850 usec
DE                  6.50 usec
TE                 298.7 K
D1           3.00000000 sec
D11          0.03000000 sec
P0                 11.70 usec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 11.70 usec
PL1                 0.75 dB
PL1W         31.70233536 W
SFO1         100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -3.00 dB
```

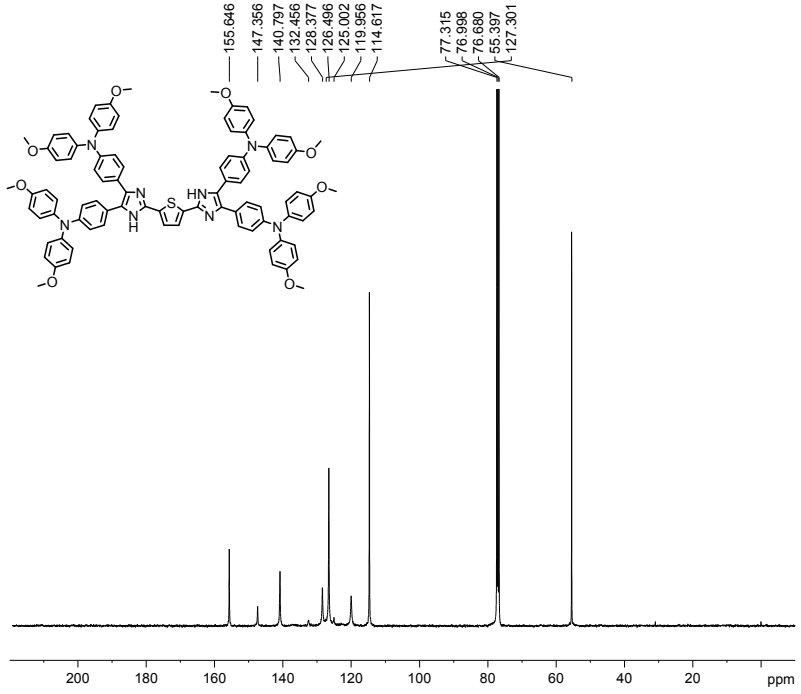
Figure S21. ^{13}C NMR spectrum of **Ph-TPA-4A**




```
NAME      xyz20180716-av400
EXPNO                    12
PROCNO                    1
Date_            20180716
Time                 14.31
INSTRUM              spect
PROBHD   5 mm Dual 13C/
PULPROG               zg30
TD                   16384
SOLVENT              CDCl3
NS                      32
DS                       2
SWH               4789.272 Hz
FIDRES           0.292314 Hz
AQ              1.7105396 sec
RG                     512
DW                 104.400 usec
DE                   6.50 usec
TE                  298.3 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                  10.60 usec
PL1                 -3.00 dB
PL1W          30.07123375 W
SFO1          400.1320424 MHz
SI                   16384
SF            400.1300093 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
```

Figure S22. ^{1}H NMR spectrum of **Th-TPA-4A**

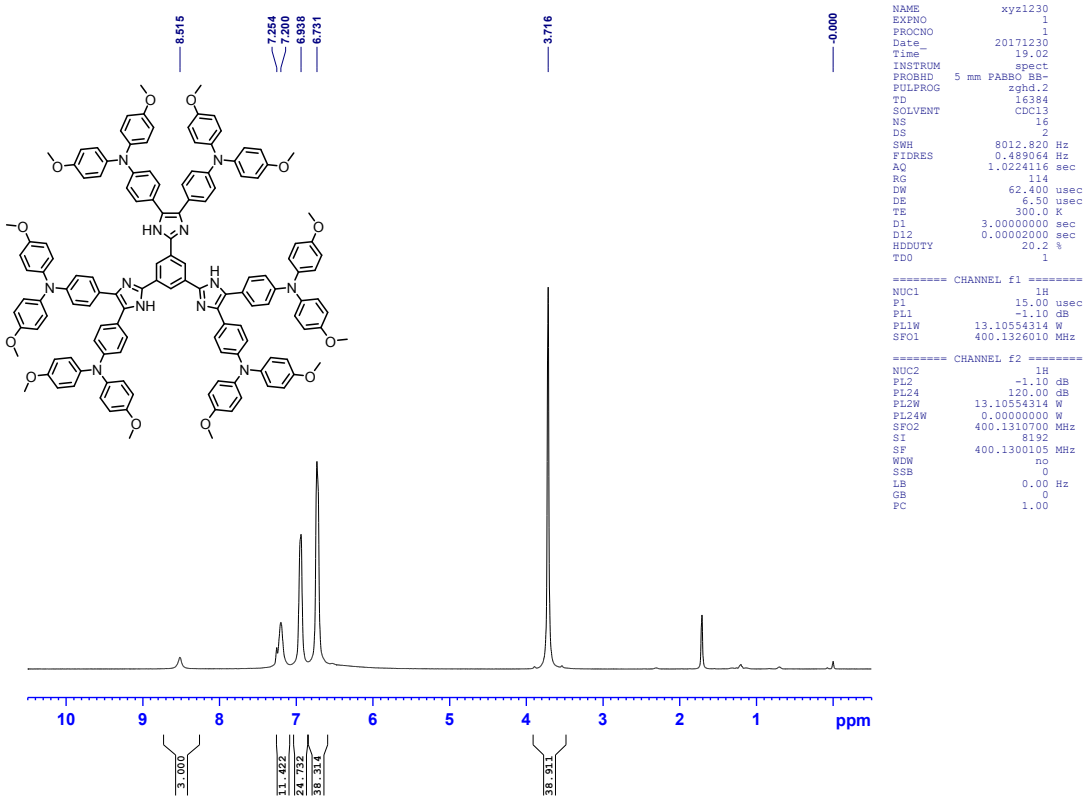



```
NAME      xyz20180321-av400
EXPNO                    12
PROCNO                    1
Date_            20180321
Time                 21.37
INSTRUM              spect
PROBHD   5 mm Dual 13C/
PULPROG            zg45dc
TD                   32768
SOLVENT              CDCl3
NS                   11351
DS                       2
SWH              23980.814 Hz
FIDRES            0.731836 Hz
AQ               0.6832628 sec
RG                    8192
DW                  20.850 usec
DE                   6.50 usec
TE                  299.3 K
D1             3.00000000 sec
D11            0.03000000 sec
P0                  11.00 usec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                  11.00 usec
PL1                  0.75 dB
PL1W          31.70233536 W
SFO1          100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                    1H
PCPD2                70.00 usec
PL2                  -3.00 dB
```

Figure S23. ^{13}C NMR spectrum of **Th-TPA-4A**

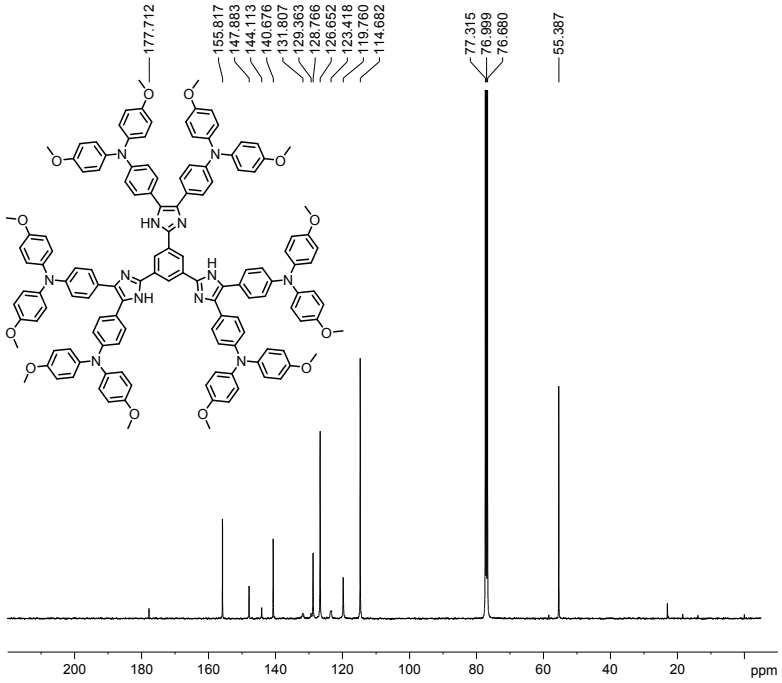



```
NAME              xyz1230
EXPNO                   1
PROCNO                  1
Date_            20171230
Time                19.02
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG             zghd.2
TD                   16384
SOLVENT              CDCl3
NS                      16
DS                       2
SWH              8012.820 Hz
FIDRES           0.489064 Hz
AQ              1.0224116 sec
RG                     114
DW                62.400 usec
DE                 6.50 usec
TE                300.0 K
D1             3.00000000 sec
D12            0.00002000 sec
HDDUTY               20.2 %
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  15.00 usec
PL1                 -1.10 dB
PL1W          13.10554314 W
SFO1         400.1326010 MHz

======== CHANNEL f2 ========
NUC2                   1H
PL2                 -1.10 dB
PL24               120.00 dB
PL2W          13.10554314 W
PL24W          0.00000000 W
SFO2         400.1310700 MHz
SI                   8192
SF           400.1300105 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```

Figure S24. ^{1}H NMR spectrum of **Ph-TPA-6A**




```
NAME              xyz1230
EXPNO                   2
PROCNO                  1
Date_            20171230
Time                19.10
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   32768
SOLVENT              CDCl3
NS                   17954
DS                       0
SWH             23148.148 Hz
FIDRES           0.706425 Hz
AQ               0.7078388 sec
RG                    2050
DW                21.600 usec
DE                 8.50 usec
TE                300.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.00 usec
PL1                 -1.80 dB
PL1W          52.84632492 W
SFO1         100.6238359 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                 -1.10 dB
PL12                13.90 dB
```

Figure S25. ^{13}C NMR spectrum of **Ph-TPA-6A**

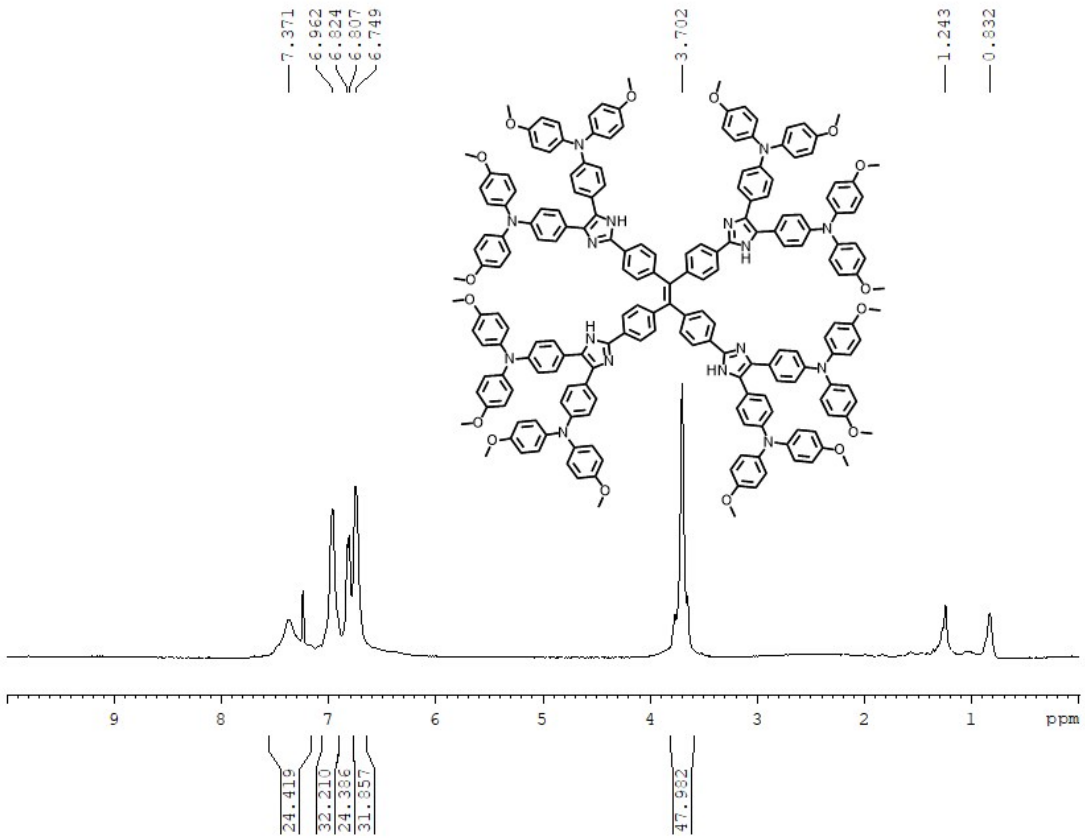


Figure S26. ^{1}H NMR spectrum of **TPE-TPA-8A**

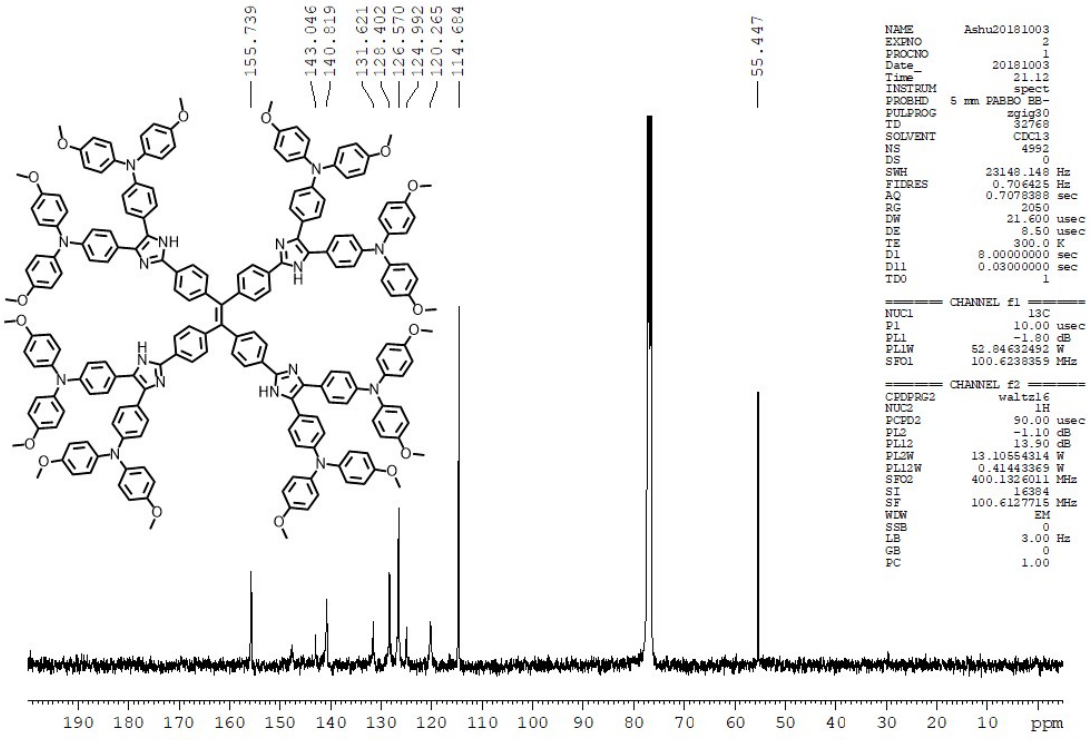


Figure S27. ^{13}C NMR spectrum of **TPE-TPA-8A**

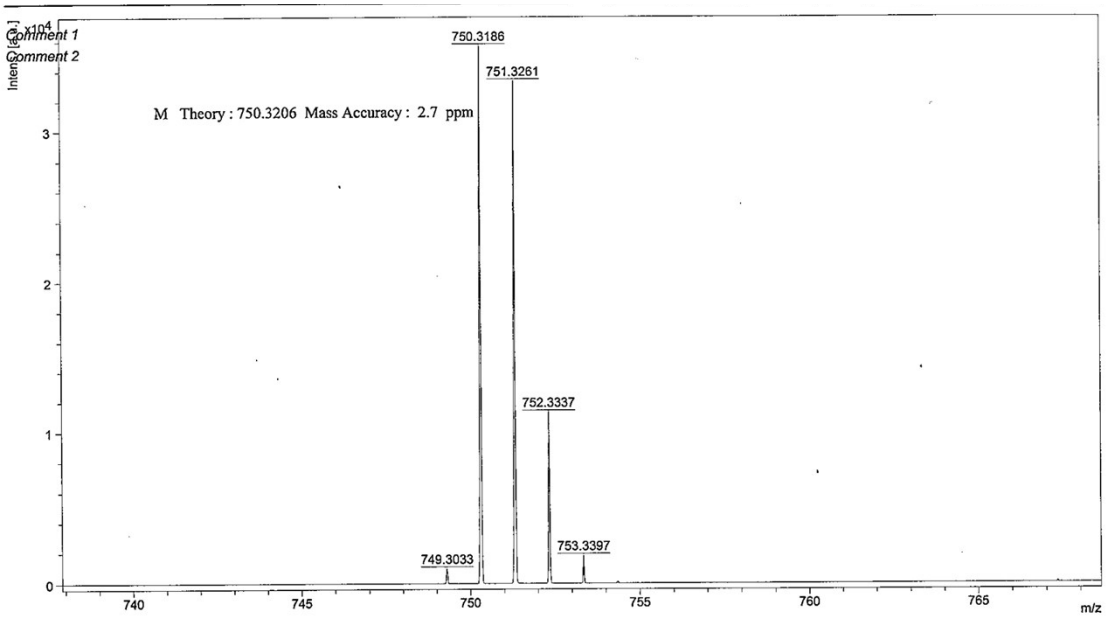


Figure S28. MALDI-TOF mass spectrum of **Ph-TPA-2A**

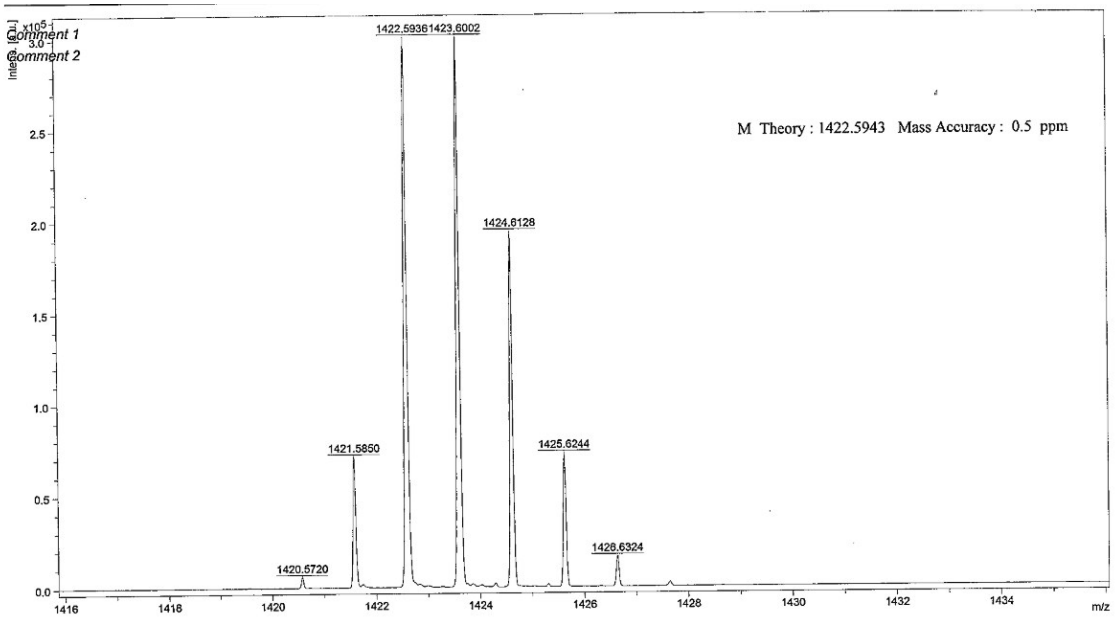
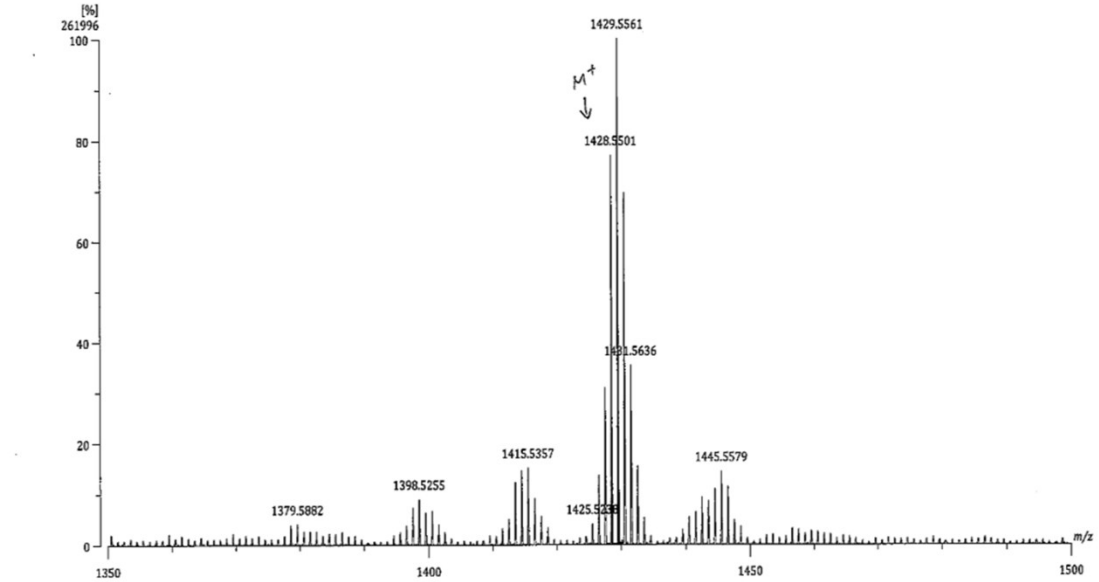


Figure S29. MALDI-TOF mass spectrum of **Ph-TPA-4A**



	Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
1	1428.5501	77.03	-0.4 / -0.6	58.0	C90 H76 N8 O8 S = 1428.5507
2	1429.5561	100.00	-1.7 / -2.4	57.5	C90 H77 N8 O8 S

Figure S30. FAB mass spectrum of **Th-TPA-4A**

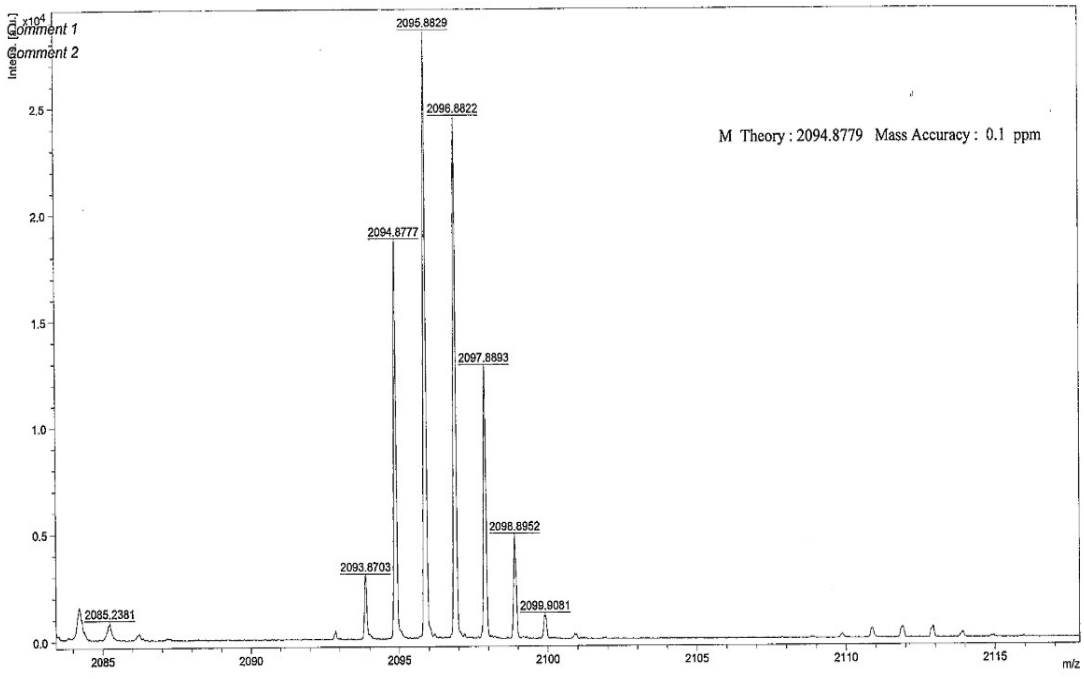


Figure S31. MALDI-TOF mass spectrum of **Ph-TPA-6A**

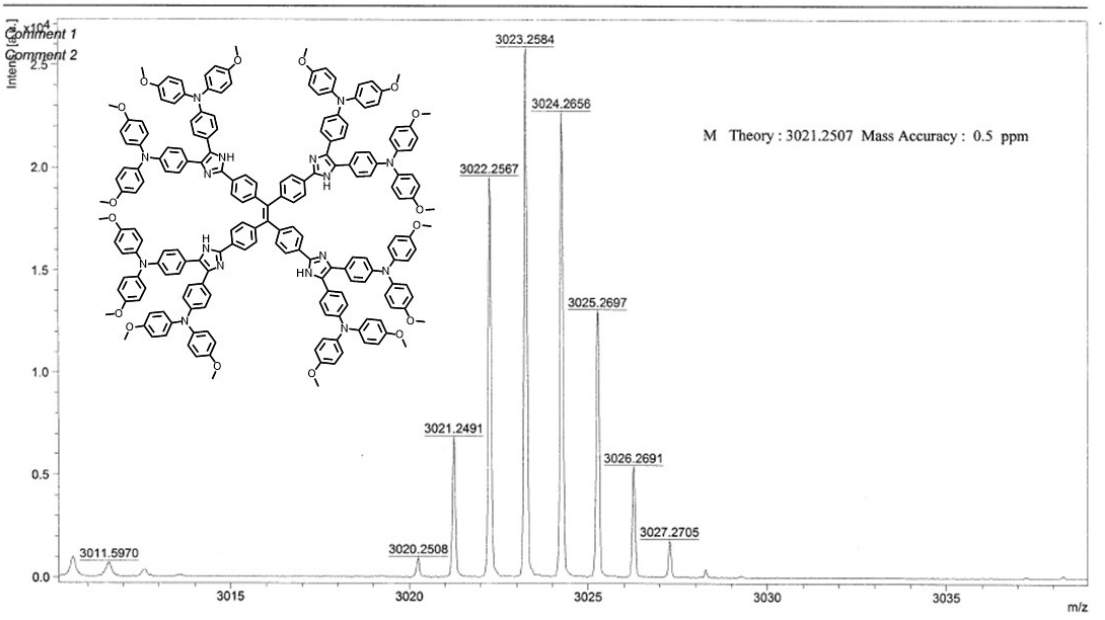


Figure S32. MALDI-TOF mass spectrum of **TPE-TPA-8A**