Supporting Information

Boosting Inverted Perovskite Solar Cells Performance by Using Functionalized 9,9-bis(4-diphenylaminophenyl)fluorenes with Triphenylamine as Dopant-free Hole Transporting Materials

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Experimental details

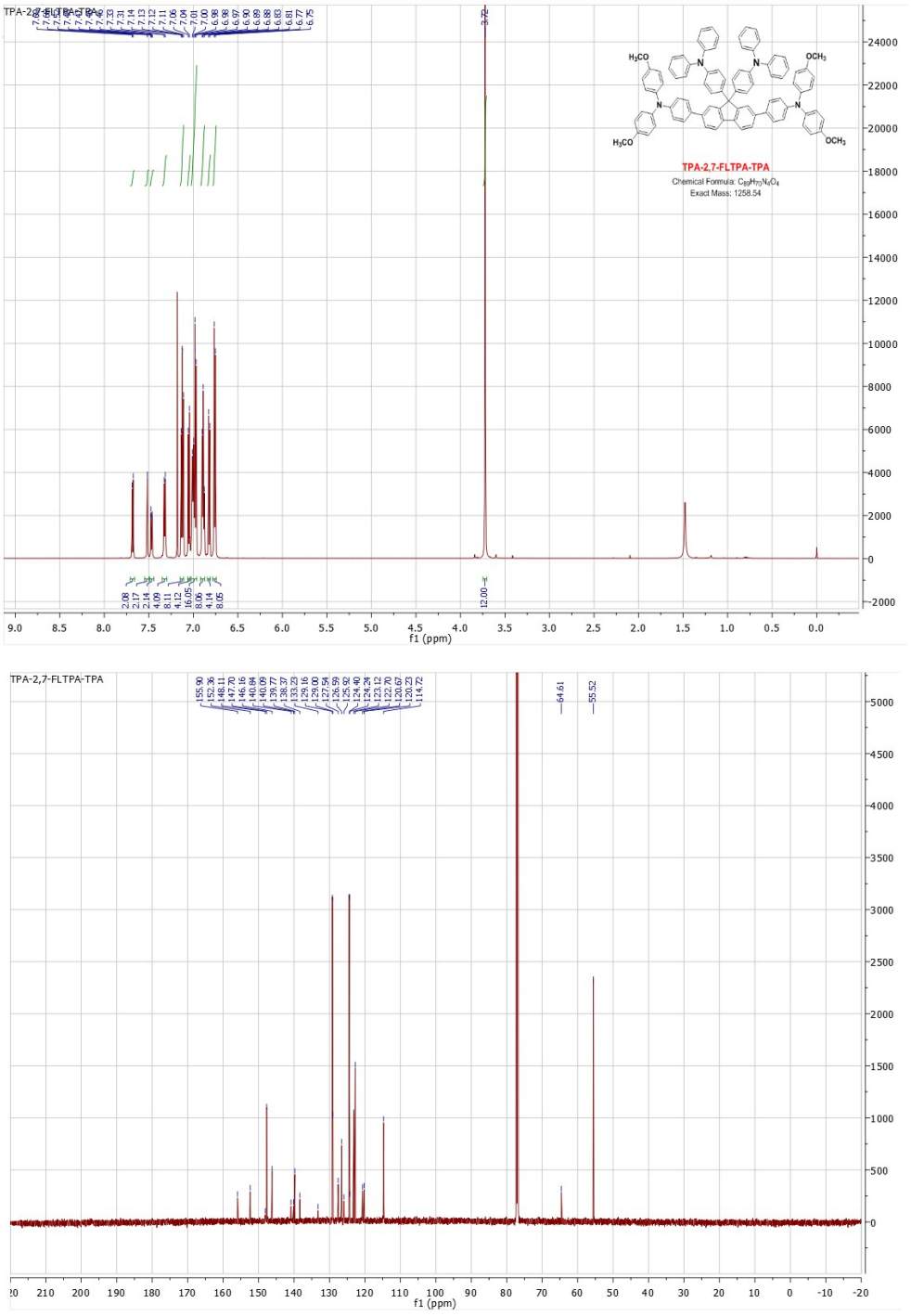


Figure S1. ^{1}H (600 MHz, $CDCl_3$) spectrum of **TPA-2,7-FLTPA-TPA**.

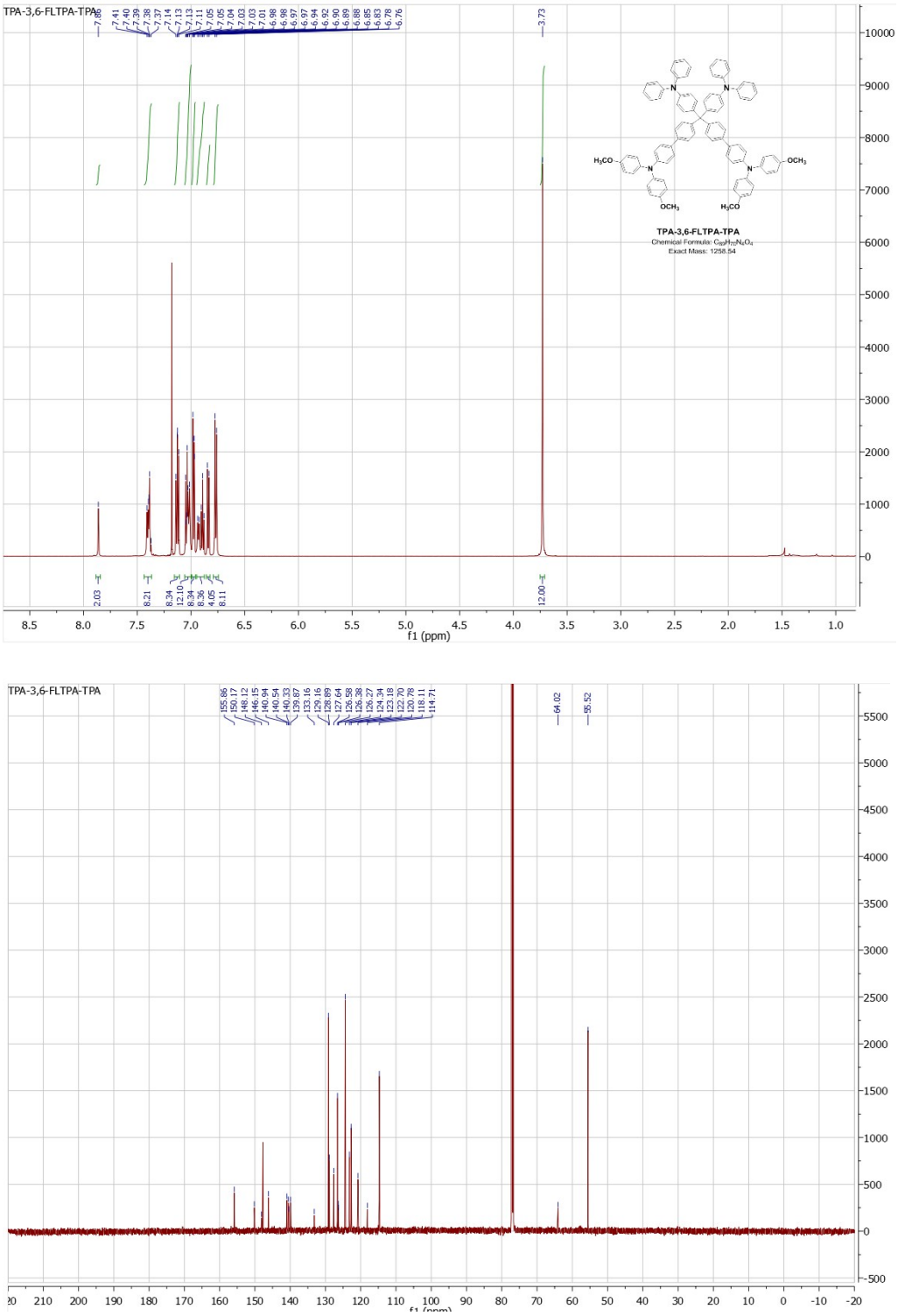


Figure S2. ^{1}H (600 MHz, $CDCl_3$) spectrum of **TPA-3,6-FLTPA-TPA**.

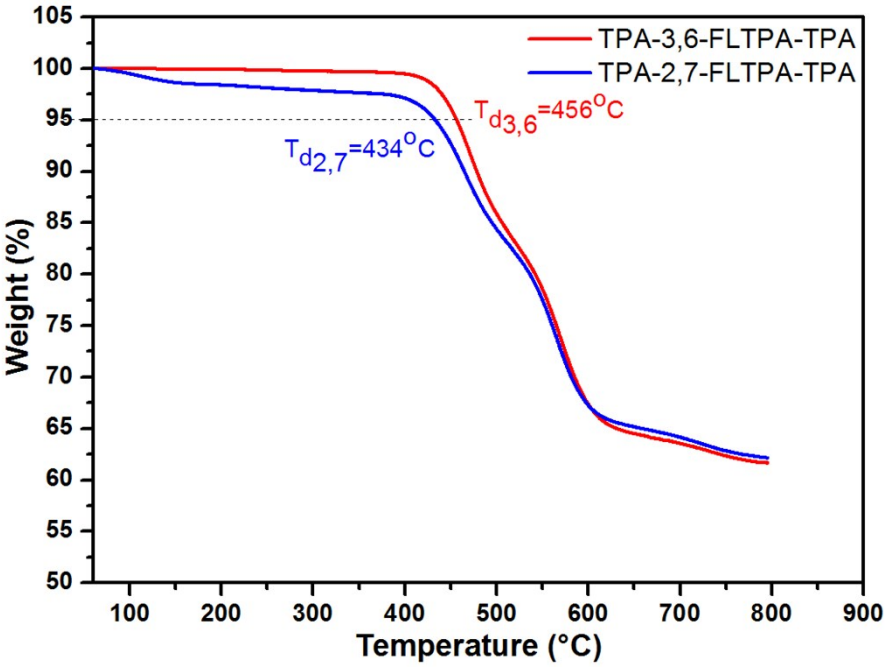


Figure S3. Thermogravimetric analysis (TGA) curve of **TPA-2,7-FLTPA-TPA** and **TPA-3,6-FLTPA-TPA**.

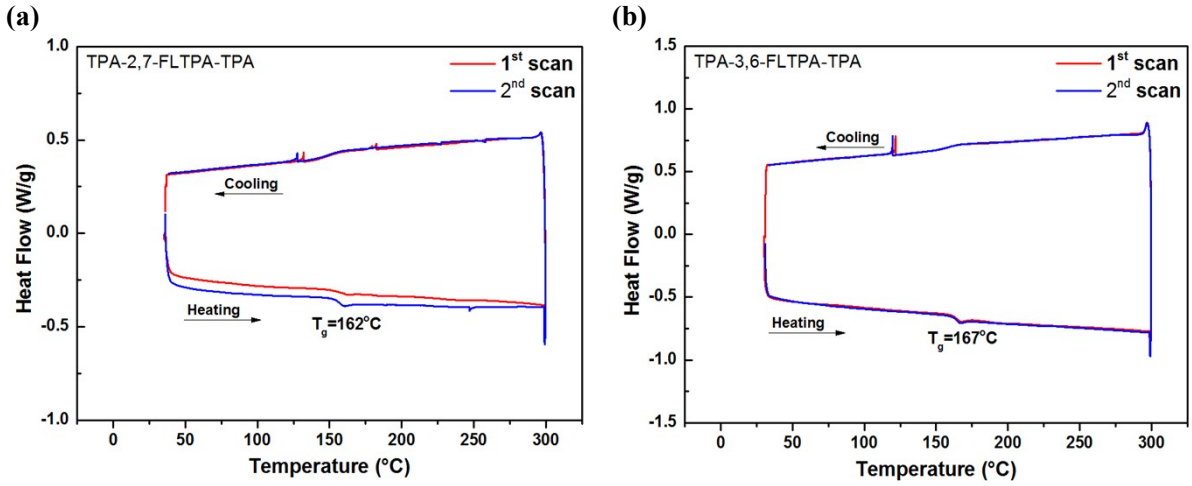


Figure S4. Differential scanning calorimetry (DSC) of (a) **TPA-2,7-FLTPA-TPA** and (b) **TPA-3,6-FLTPA-TPA** with scan rate of 10 °C/min under N_2 atmosphere.

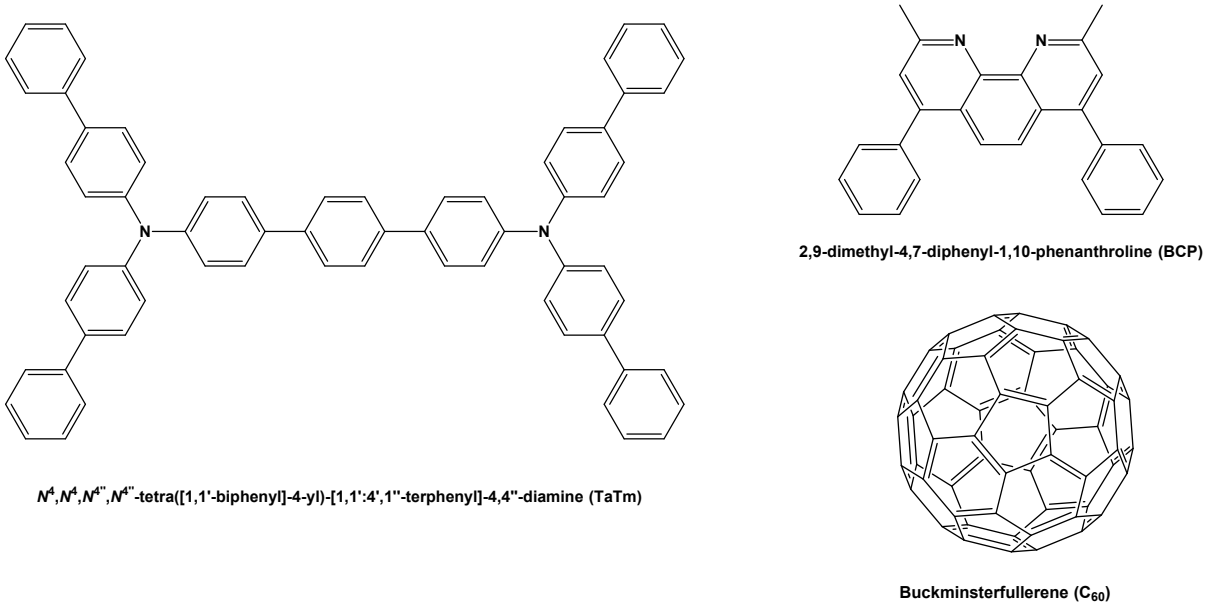


Figure S5. The structures of molecules used in PSC devices.

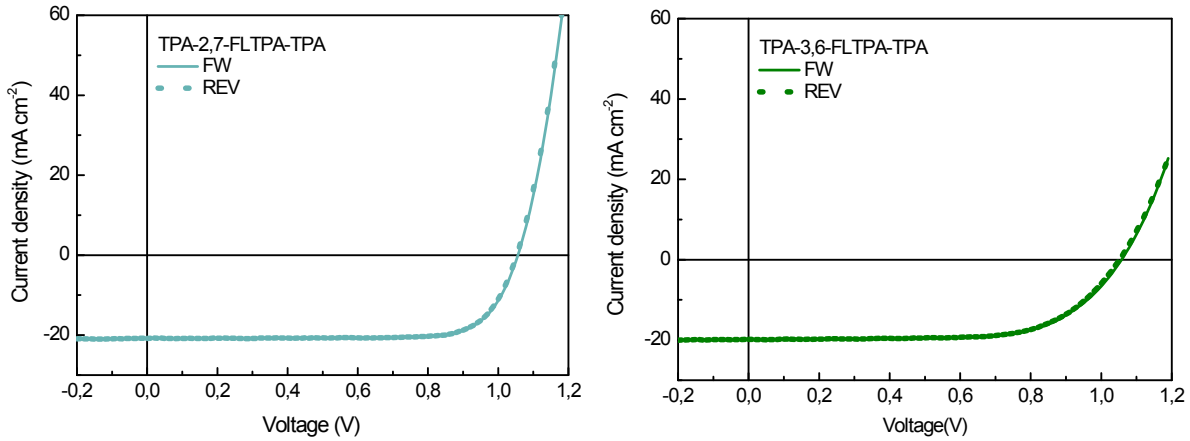


Figure S6. Forward and reverse current density versus voltage curves for the perovskite solar cells. Scan speed was 0.01 V/s.

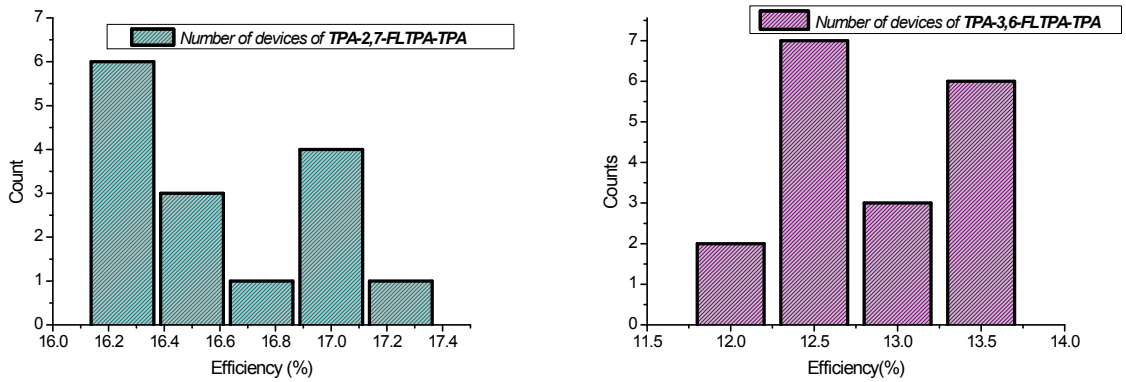


Figure S7. Statistics of the PCE for the two different HTMs based devices (8 cells of each HTM).

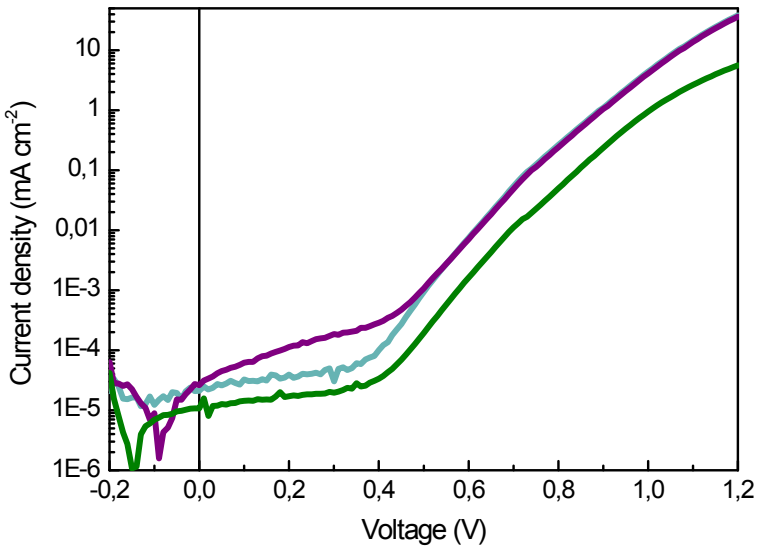


Figure S8. Current density versus voltage plotted on a semilog scale.

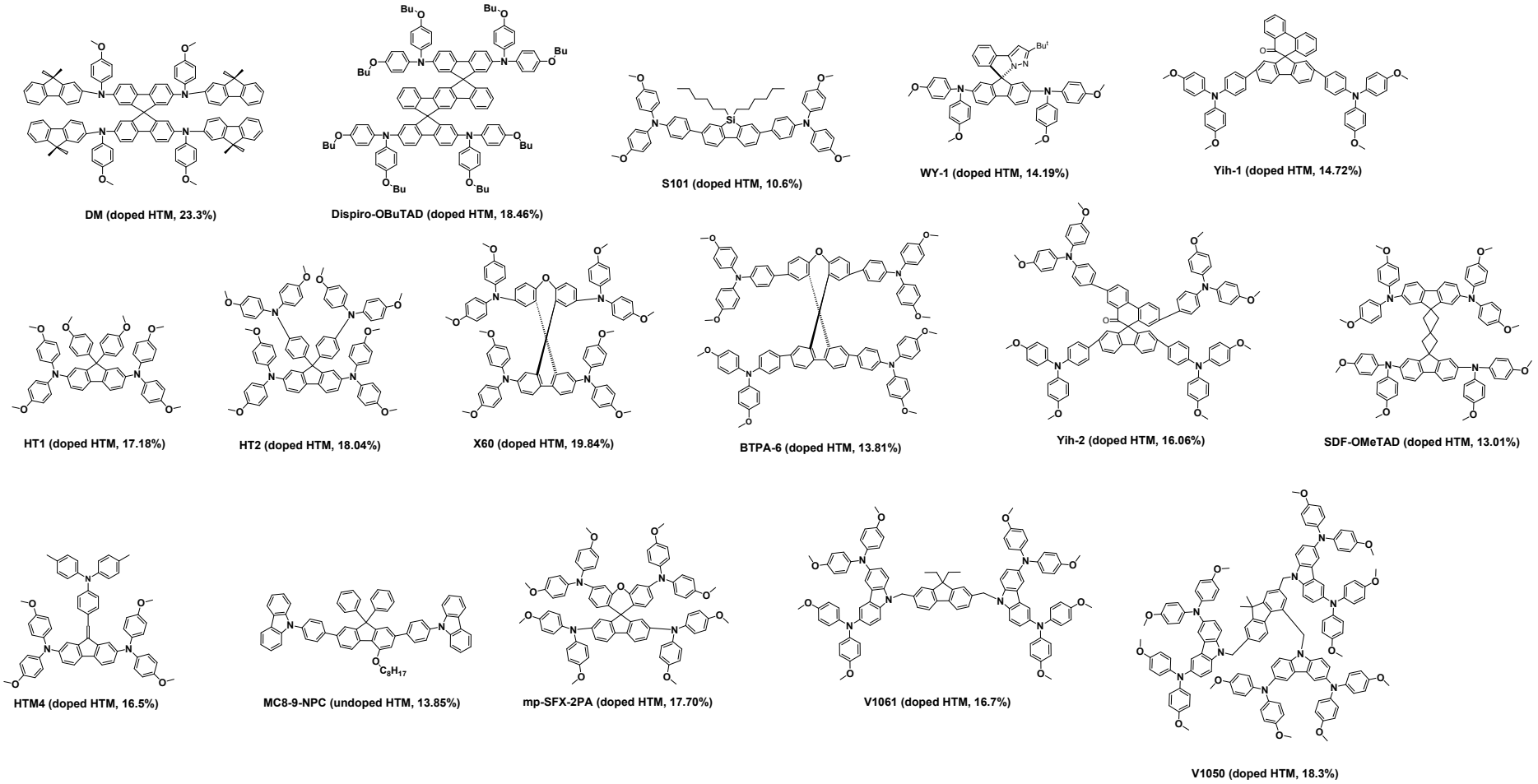


Figure S9. Chemical structures of reported small molecular fluorene-based hole transporting materials.

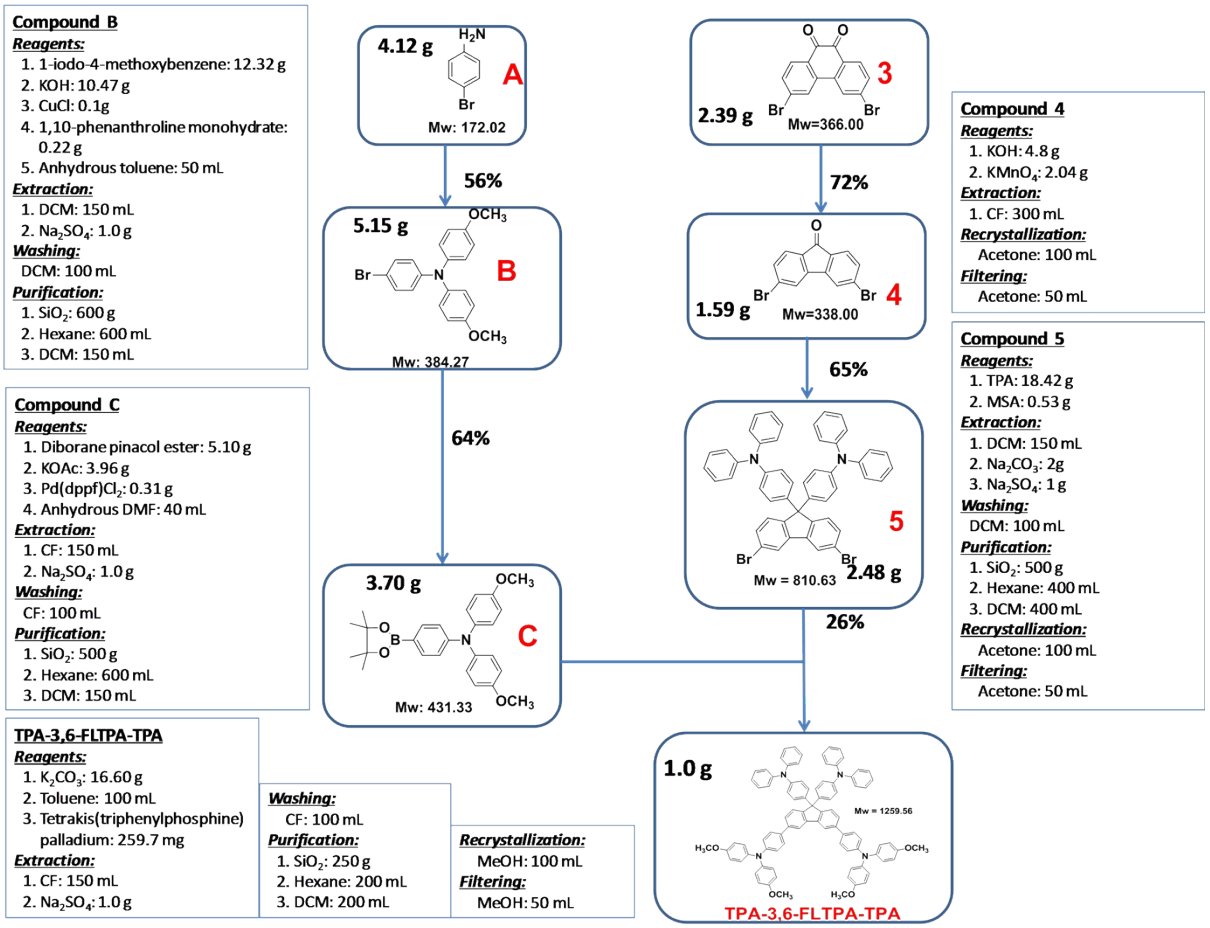


Figure S10. Flowchart describing the synthesis of 1g of TPA-3,6-FLTPA-TPA.

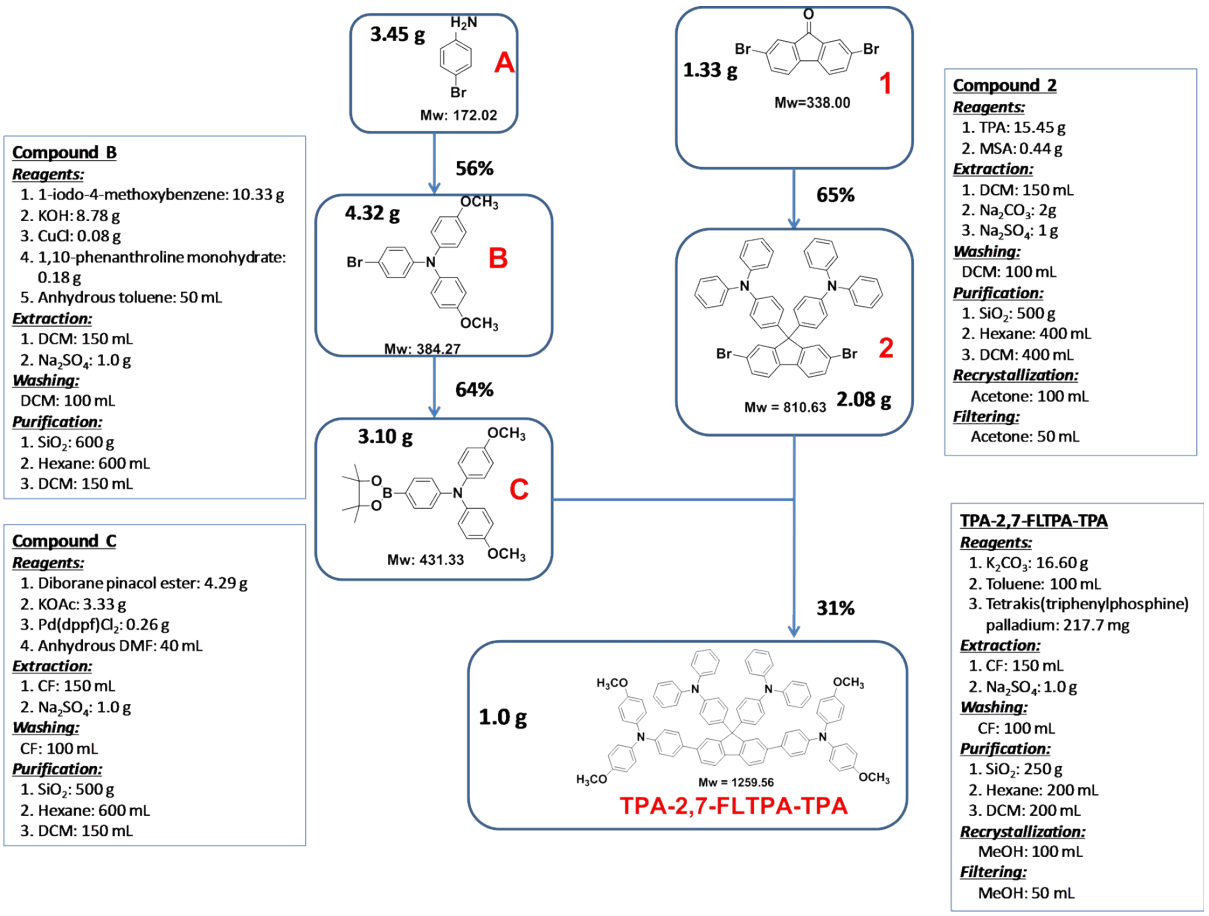


Figure S11. Flowchart describing the synthesis of 1g of TPA-2,7-FLTPA-TPA.

Table S1. Density functional theory (DFT) calculations of **TPA-2,7-FLTPA-TPA** and **TPA-3,6-FLTPA-TPA**

Compound	TPA-2,7-FLTPA-TPA	TPA-3,6-FLTPA-TPA
HOMO, eV	-4.85	-4.92
LUMO, eV	-1.56	-1.29
gap, eV	3.29	3.63
VIS peak, nm	431	384
osc strength	1.6251	0.5552
composition	H->L	H->L 81%
VIS peak, nm		380
osc strength		0.6395
composition		H-1>L 88%
Dihedrals angle		
FLTPA core to TPA end-capping unit	31	31
FL penta core to inside TPA unit	21	20

Table S2. A summary of fluorene-based hole transporting materials for perovskite solar cells.

HTM	Role of Fluorene	HOMO [eV]	T_d [°C]	T_g [°C]	Hole mobility [$10^{-4}cm^2V^{-1}s^{-1}$]	Device structure	Active area [cm^2]	Additives	V_{oc} [V]	J_{sc} [$mAcm^{-2}$]	FF [%]	PCE [%][b)]	References
TPA-2,7-FLTPA-TPA	Central core	-5.45	434	162	-	ITO/MoO_3/HTM/$MAPbI_3$/C_{60}/BCP/Ag	0.01	None	1.052	20.82	78	17.1 (15.9)[c)]	This study
TPA-3,6-FLTPA-TPA	Central core	-5.57	456	167	-	ITO/MoO_3/HTM/$MAPbI_3$/C_{60}/BCP/Ag	0.01	None	1.051	19.85	67	13.9 (15.9)	This study
DP	End-capper	-5.27	460	161	-	c-TiO_2/mp-TiO_2/$(FAPbI_3)_{0.95}(MAPbBr_3)_{0.05}$/HTM/Au	0.0939	Li-TFSI + *t*BP	1.144	24.91	81.29	23.2 (23.05)	[1]
Dispiro-OBuTAD	Central core	-5.16	420	98	0.102	FTO/TiO_2/$MAPbI_3$/Dispiro/Au	-	Li-TFSI + *t*BP	1.08	22.79	75	18.46 (17.82)	[2]
S101	Central core	-5.32	124	45	0.72	c-TiO_2/mp-TiO_2/$MAPbI_3$/HTM/Au	0.2	Li$(CF_3SO_2)_2N$ + *t*BP + FK102	0.92	18.9	65	10.6 (12.0)	[3]
V1050	Central core	-5.11	400	166	1.7	FTO/SnO_2/$FA_{0.83}Cs_{0.17}Pb(I_{0.8}Br_{0.2})_3$/HTM/Au	0.0913	Li-TFSI + *t*BP + Co[t-BuPyPz]$_3$[TFSI]$_3$	1.05	22.0	79.5	18.3 (18.9)	[4]
V1061	Central core	-5.10	420	146	2.0	FTO/SnO_2/$FA_{0.83}Cs_{0.17}Pb(I_{0.8}Br_{0.2})_3$/HTM/Au	0.0913	Li-TFSI + *t*BP + Co[t-BuPyPz]$_3$[TFSI]$_3$	0.96	21.6	79.7	16.7 (18.9)	[4]
Yih-1	Central core	-5.34	435	114	0.336	c-TiO_2/$MAPbI_3$/HTM/Au	-	Li-TFSI + *t*BP	1.03	20.91	68	14.72 (16.08)	[5]
Yih-2	Central core	-5.35	427	159	0.494	c-TiO_2/$MAPbI_3$/HTM/Au	-	Li-TFSI + *t*BP	1.02	22.18	71	16.06 (16.08)	[5]
X60	Central core	-5.61	-	-	1.9	c-TiO_2/mp-TiO_2/$(FAPbI_3)_{0.95}(MAPbBr_3)_{0.05}$/HTM/Au	0.16	Li-TFSI + *t*BP + FK209	1.14	24.2	71	19.84	[6]
MC8-9-NPC	Central core	-5.51	-	-	-	ITO/HTM/$MAPbI_3$/PC_{61}PM/Al/LiF	0.05	-	0.90	20.80	74	13.85 (11.90)	[7]

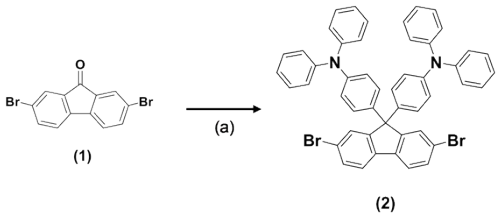
HT1	Central core	-	-	-	1.12	c-TiO_2/mp-TiO_2/$(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$/HTM/Au	0.16	Li-TFSI + *t*BP + FK209	1.12	21.91	70	17.18 (18.27)	[8]
HT2	Central core	-	-	-	1.04	c-TiO_2/mp-TiO_2/$(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$/HTM/Au	0.16	Li-TFSI + *t*BP + FK209	1.11	22.26	73	18.04 (18.27)	[8]
SDF-OMeTAD	Central core	-5.28	400	-	-	FTO/SnO_2/$MAPbI_3$/HTM/Au	0.09	Li-TFSI + *t*BP	1.10	19.06	62	13.01 (17.13)	[9]
SDF-OMeTAD	Central core	-5.28	400	-	-	FTO/SnO_2/$MAPbI_3$/HTM/Au	0.09	-	1.01	19.02	25	4.83 (4.27)	[9]
HTM4	Central core	-	413	89	0.22	c-TiO_2/mp-TiO_2/$(FAPbI_3)_{0.95}(MAPbBr_3)_{0.05}$/HTM/Au	0.16	Li-TFSI + *t*BP + FK209	1.052	21.3	75	16.5 (17.88)	[10]
WY-1	Central core	-5.16	401	122	-	FTO/c-TiO_2/ mp-TiO_2/$MAPbI_3$/HTM/Au	0.1	Li-TFSI + *t*BP	1.053	19.48	69.1	14.19 (14.84)	[11]
BTPA-6	Central core	-5.34	400	143	-	FTO/c-TiO_2/ mp-TiO_2/$MAPbI_3$/HTM/Au	1.02	Li-TFSI + *t*BP	1.036	20.61	64.7	13.81 (13.25)	[12]
mp-SFX-2PA	Central core	-5.06	410	-	0.3	FTO/c-TiO_2/ mp-TiO_2/$MAPbI_3$/HTM/Au	0.1	Li-TFSI + *t*BP	1.023	21.17	77.44	16.77 (15.45)	[13]
mp-SFX-2PA	Central core	-5.06	410	-	0.3	c-TiO_2/mp-TiO_2/$(FAPbI_3)_{0.95}(MAPbBr_3)_{0.05}$/HTM/Au	0.1	Li-TFSI + *t*BP	1.083	20.87	78.31	17.70 (17.64)	[13]

[a] Photovoltaic parameters of the solar cells with HTMs evaluated under 1 sunlight illumination (100 mW cm^{-2}) condition.

[b] The best PCE of the HTMs based devices

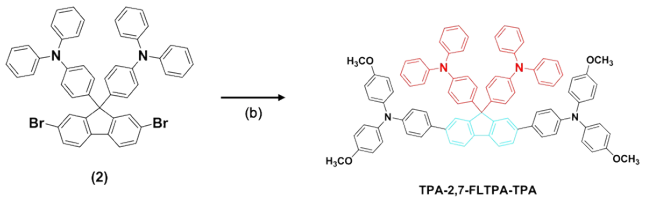
[c] The best PCE of standard conventional HTMs

Table S3. Materials quantities and cost evaluation for the synthesis of 4,4'-(2,7-dibromo-9*H*-fluorene-9,9-diyl)bis(*N*,*N*-diphenylaniline) (**2**)



Chemical Name	Weight reagent [g]	Weight solvent [mL]	Weight of workup [g or mL]	Price of chemical [AUD/g or AUD/mL]	Material Cost [AUD/g product]	Cost per step [AUD/step]
2,7-dibromo-FN	1.33			180	2.39	30.38
TPA	15.45			194	5.99	
methane sulfonic acid	0.44			147	0.13	
DCM		250		15.5	1.55	
Na_2SO_4			1	10.9	0.02	
Na_2CO_3			2	67	0.27	
SiO2			500	704	14.08	
Hexane			400	16.05	2.57	
DCM			400	15.5	2.48	
Acetone			150	14.85	0.89	

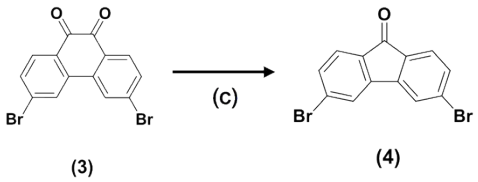
Table S4. Materials quantities and cost evaluation for the synthesis of 4,4'-(2,7-bis(4-(bis(4-methoxyphenyl)amino)phenyl)-9*H*-fluorene-9,9-diyl)bis(*N*,*N*-diphenylaniline) (**TPA-2,7-FLTPA-TPA**)



Chemical Name	Weight reagent [g]	Weight solvent [mL]	Weight of workup [g or mL]	Price of chemical [AUD/g or AUD/mL]	Material Cost [AUD/g product]	Cost per step [AUD/step]
K_2CO_3	16.60			171	2.84	29.16
Tetrakis(triphenyl-phosphine)palladium	0.22			120	5.28	
Toluene		100		71.5	7.15	
CF		250		18.5	1.85	
Na2SO4			1	10.9	0.02	
SiO2			250	704	7.04	
Hexane			200	16.05	1.28	
DCM			200	15.5	1.24	
Methanol			150	41	2.46	

Total cost is ~119.83 AUD/g. It is equal to ~92.89 $/g.

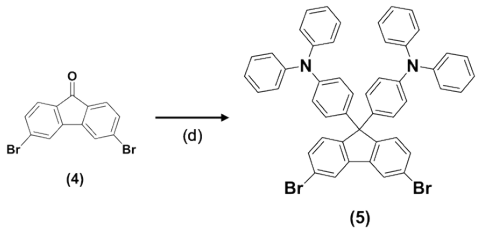
Table S5. Materials quantities and cost evaluation for the synthesis of 3,6-dibromo-9*H*-fluoren-9-one (**4**)



(3) (4)

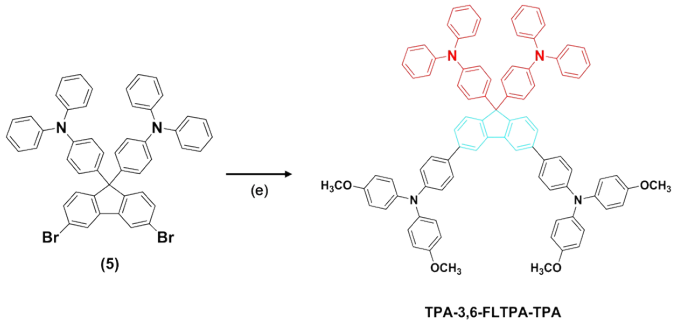
Chemical Name	Weight reagent [g]	Weight solvent [mL]	Weight of workup [g or mL]	Price of chemical [AUD/g or AUD/mL]	Material Cost [AUD/g product]	Cost per step [AUD/step]
Compound 3	2.39			542	12.95	16.59
KOH	4.80			11	0.11	
$KMnO_4$	2.04			103	0.42	
CF		300		18.5	2.22	
Acetone			150	14.85	0.89	

Table S6. Materials quantities and cost evaluation for the synthesis of 4,4'-(3,6-dibromo-9*H*-fluorene-9,9-diyl)bis(*N,N*-diphenylaniline) (**5**)



Chemical Name	Weight reagent [g]	Weight solvent [mL]	Weight of workup [g or mL]	Price of chemical [AUD/g or AUD/mL]	Material Cost [AUD/g product]	Cost per step [AUD/step]
TPA	18.42			194	7.15	29.16
methane sulfonic acid	0.53			147	0.16	
DCM		250		15.5	1.55	
Na_2SO_4			1	10.9	0.02	
Na_2CO_3			2	67	0.27	
SiO2			500	704	14.08	
Hexane			400	16.05	2.57	
DCM			400	15.5	2.48	
Acetone			150	14.85	0.89	

Table S7. Materials quantities and cost evaluation for the synthesis of 4,4'-(3,6-bis(4-(bis(4-methoxyphenyl)amino)phenyl)-9*H*-fluorene-9,9-diyl)bis(*N*,*N*-diphenylaniline) (**TPA-3,6-FLTPA-TPA**)



Chemical Name	Weight reagent [g]	Weight solvent [mL]	Weight of workup [g or mL]	Price of chemical [AUD/g or AUD/mL]	Material Cost [AUD/g product]	Cost per step [AUD/step]
K_2CO_3	16.60			171	2.84	30.12
Tetrakis(triphenyl-phosphine)palladium	0.26			120	6.24	
Toluene		100		71.5	7.15	
CF		250		18.5	1.85	
Na2SO4			1	10.9	0.02	
SiO2			250	704	7.04	
Hexane			200	16.05	1.28	
DCM			200	15.5	1.24	
Methanol			150	41	2.46	

Total cost is ~136.17 AUD/g. It is equal to ~105.56 $/g.

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