Supplementary Information

Inverted Planar Perovskite Solar Cells with Dopant Free Hole Transporting Material: Lewis Base-Assisted Passivation and Reduced Charge Recombination

Sang Jin Park,[1,†] Seolhee Jeon,[2,†] In Kyu Lee,[2,†] Jing Zhang,[1] Huiseong Jeong,[1,3] Ji-Yong Park,[1,3] Jiwon Bang,[4] Tae Kyu Ahn,[5] Hee-Won Shin,[5] Bong-Gi Kim[2,*] and Hui Joon Park[1,6,*]

[1]Department of Energy Systems Research, Ajou University, Suwon 16499, Republic of Korea

[2]Department of Organic and Nano System Engineering, Konkuk University, Seoul 05029, Republic of Korea

[3]Department of Physics, Ajou University, Suwon 16499, Republic of Korea

[4]Nano convergence Materials Center, Korea Institute of Ceramic Engineering & Technology, Jinju 52851, Republic of Korea

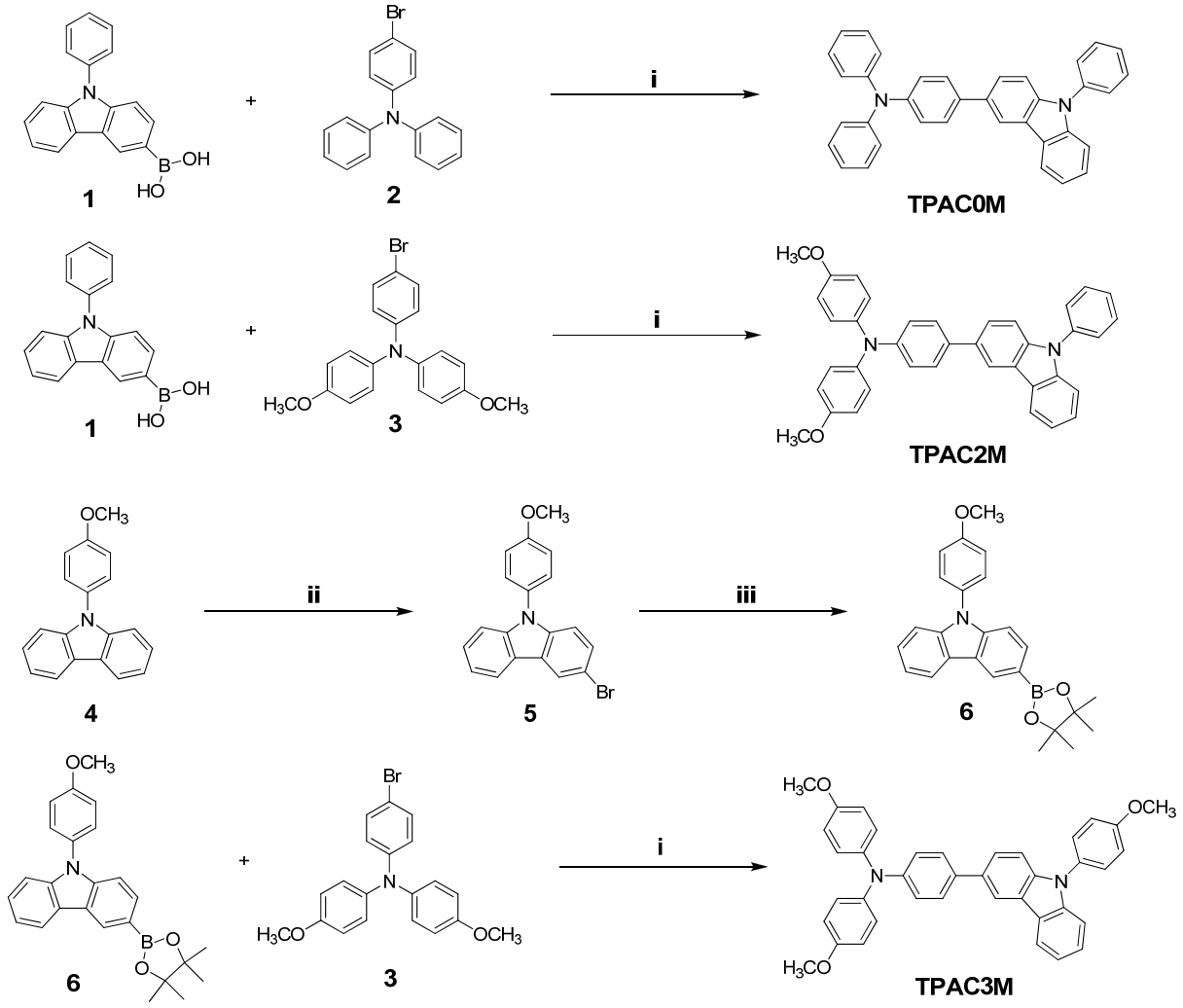
[5]Department of Energy Science, Sungkyunkwan University, Suwon 16419, Republic of Korea

[6]Department of Electrical and Computer Engineering, Ajou University, Suwon 16499, Republic of Korea

*Corresponding Authors: huijoon@ajou.ac.kr, bgkim2015@konkuk.ac.kr

[†]S.J.P., S.J. and I.K.L. contributed equally to this work.

Keywords: triarylamine, dopant free hole transporting material, perovskite solar cell, charge recombination, organic electronics



Scheme S1. Chemical structures and detailed synthetic routes of TPAC series. i) K_2CO_3, Pd(0), THF, 60 °C, 8 hours; ii) NBS, $CHCl_3$, from 0 °C to 60 °C; iii) n-BuLi, 2-isopropyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, from -78 °C to room temperature, overnight.

Synthesis. As shown in Scheme S1, three different triarylamine derivatives and all starting materials were purchased from commercial supplier (Aldrich and TCI). Synthesized compounds were fully characterized with ^{1}H NMR and GC-mass. Compound **4** was prepared as previously described manner.[S1]

3-bromo-9-(4-methoxyphenyl)-9H-carbazole (5). Compound **4** (5.52g, 20.195mmol) was added to round bottom flask and dissolved into chloroform anhydrous (85mL) under Ar atmosphere. After cooling down to 0℃, NBS (3.954g, 22.215g) was added and the reaction mixture was stirred for 2 hours. Then, the mixture was warmed up to 60℃ slowly and stirred overnight. After pouring the mixture into distilled water, the organic layer was extracted with methylene chloride several times, and the combined organic layers was dried with $MgSO_4$. After evaporating the solvent, final compound 5 was obtained through recrystallization into methylene chloride/hexane mixture. ^{1}H-NMR (400MHz, $CDCl_3$) δ 8.25 (d, 1H), 8.09 (d, 1H), 7.47 (d, 1H), 7.45-7.37 (m, 3H), 7.33-7.27 (m, 2H), 7.19 (d, 1H), 7.11 (d, 2H), 3.92 (s, 3H) and m/z EIMS 352.

9-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (6). To a solution of compound **5** (5.49g, 15.586mmol) in anhydrous THF (140mL) was added dropwise n-BuLi (7.80 mL, 2.5 M in hexane) at -78 °C under Argon conditions. The reaction mixture was kept at -78 °C for 1 hour and slowly warmed up to room temperature. After additional stirring for 1 hour at room temperature, the mixture was cooled down to -78℃ again and 2-Isopropyl-4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolane (3.18mL) was added drop-wise. Then, the reaction mixture was warmed up to room temperature and stirred overnight. After pouring the mixture into distilled water, organic layer was extracted with methylene chloride several times and the combined organic layers were dried with $MgSO_4$. Solvent was evaporated and final product **6** was obtained through recrystallization into methanol/tetrahydrofuran mixture. ^{1}H-NMR (400MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.17 (d, 1H), 7.85 (d, 1H), 7.44 (d, 2H), 7.39 (d, 1H), 7.34-7.27 (m, 3H), 7.12 (d, 2H), 3.92 (s, 3H), 1.41 (s, 12H) and m/z EIMS 399.

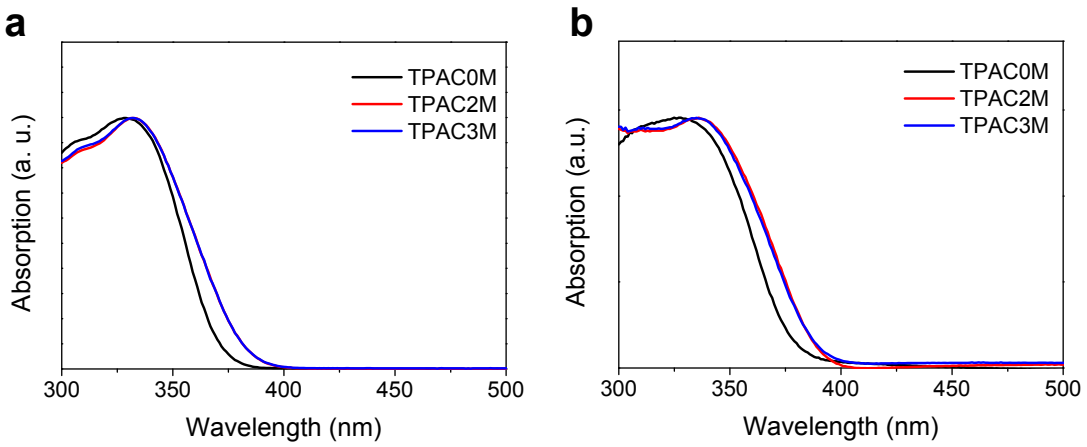


Fig. S1. UV-vis. absorption spectra of obtained TPAC series a) in solution and b) in film states, respectively.

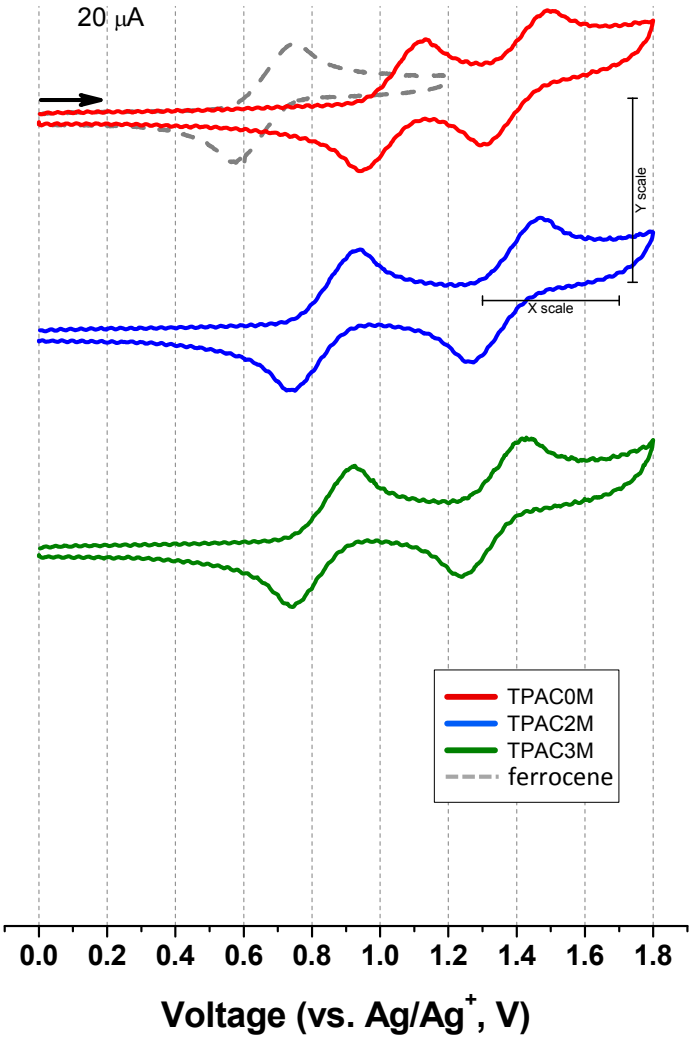


Fig. S2. Oxidation potential of obtained TPAC series. Oxidation was monitored with same concentration (1.0 mM in methylene chloride) in 0.1 M TBAHFP as a supporting electrolyte, under same scan rate (100 mV/s).

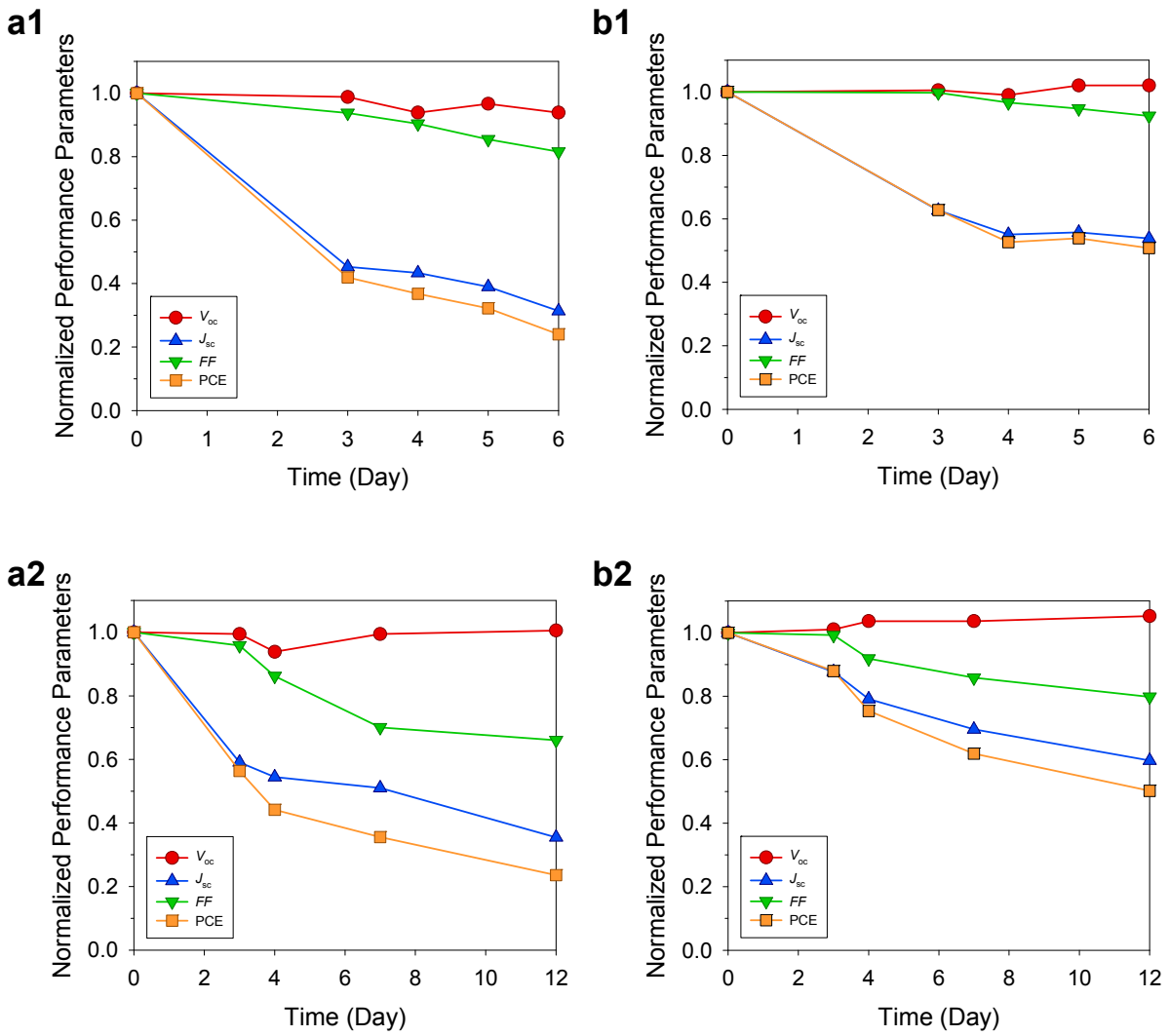


Fig. S3. Stability perovskite solar cells (PSCs) with different hole transport materials: (a1, a2) PEDOT:PSS, (b1, b2) TPAC3M. (a1,b1) PSCs fabricated on the hole transport materials, exposed to air (25 °C and 35% relative humidity) during a certain amount of time. (a2,b2) PSCs stored in N_2 box without encapsulation.

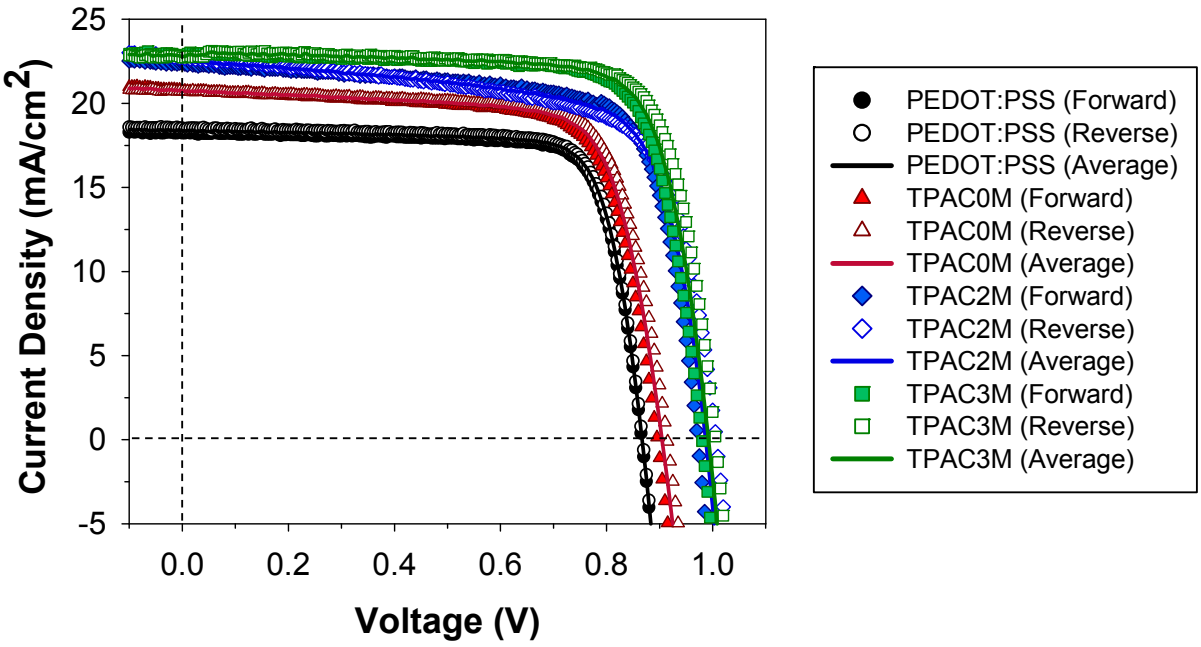


Fig. S4. The symbols represent experimentally measured *J-V* curves, scanned in forward and reverse directions. The lines are average values of experimental data, obtained by scanning in forward and reverse directions. All data were measured at AM 1.5 G with an intensity of 100 $mW \cdot cm^{-2}$.

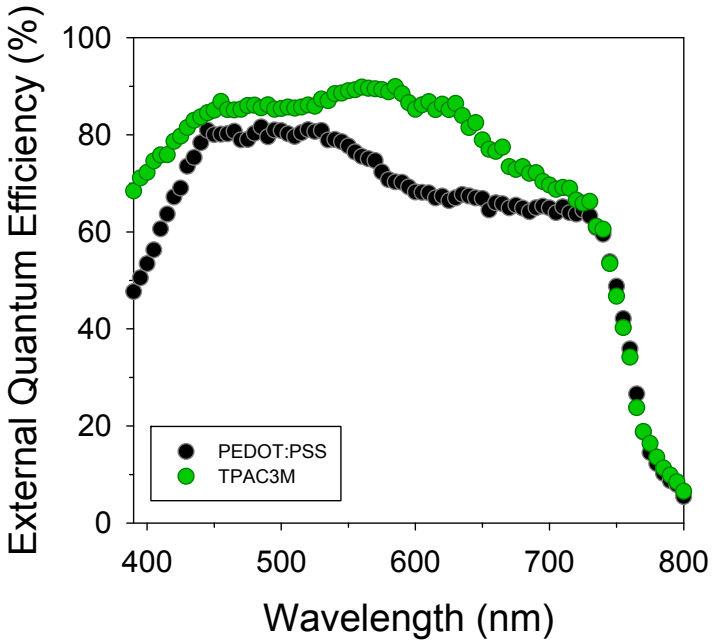


Fig. S5. External quantum efficiency (EQE) spectra of PSCs with PEDOT:PSS and TPAC3M hole transport materials.

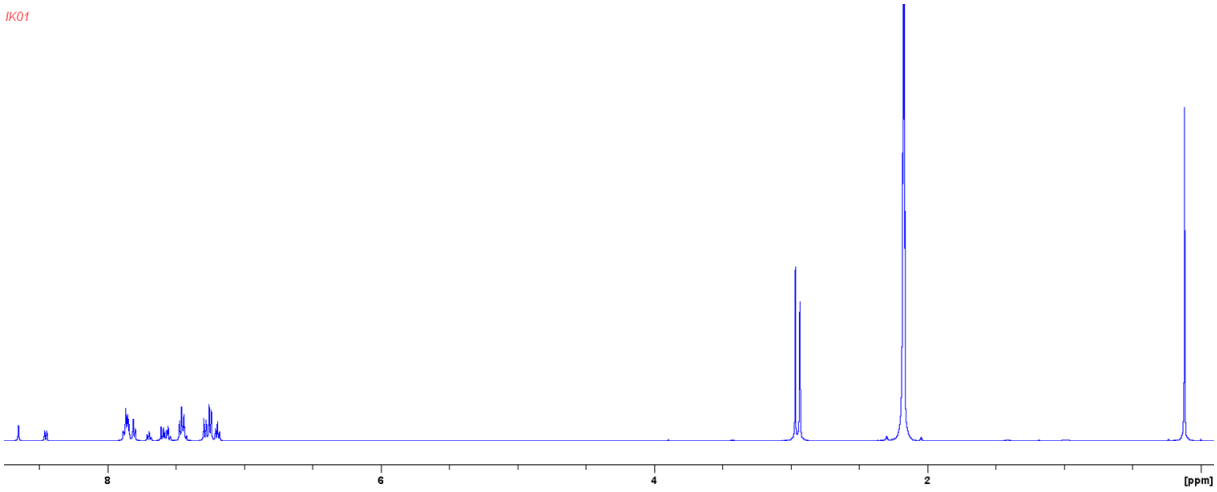


Fig. S6. ^{1}H-NMR spectrum of TPAC0M

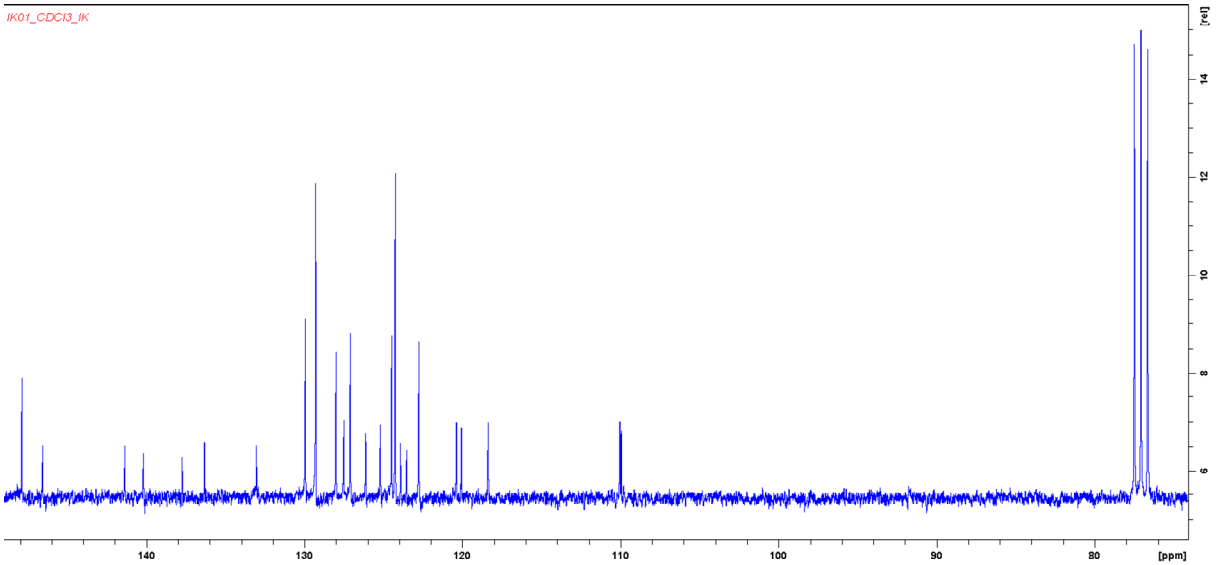


Fig. S7. ^{13}C-NMR spectrum of TPAC0M

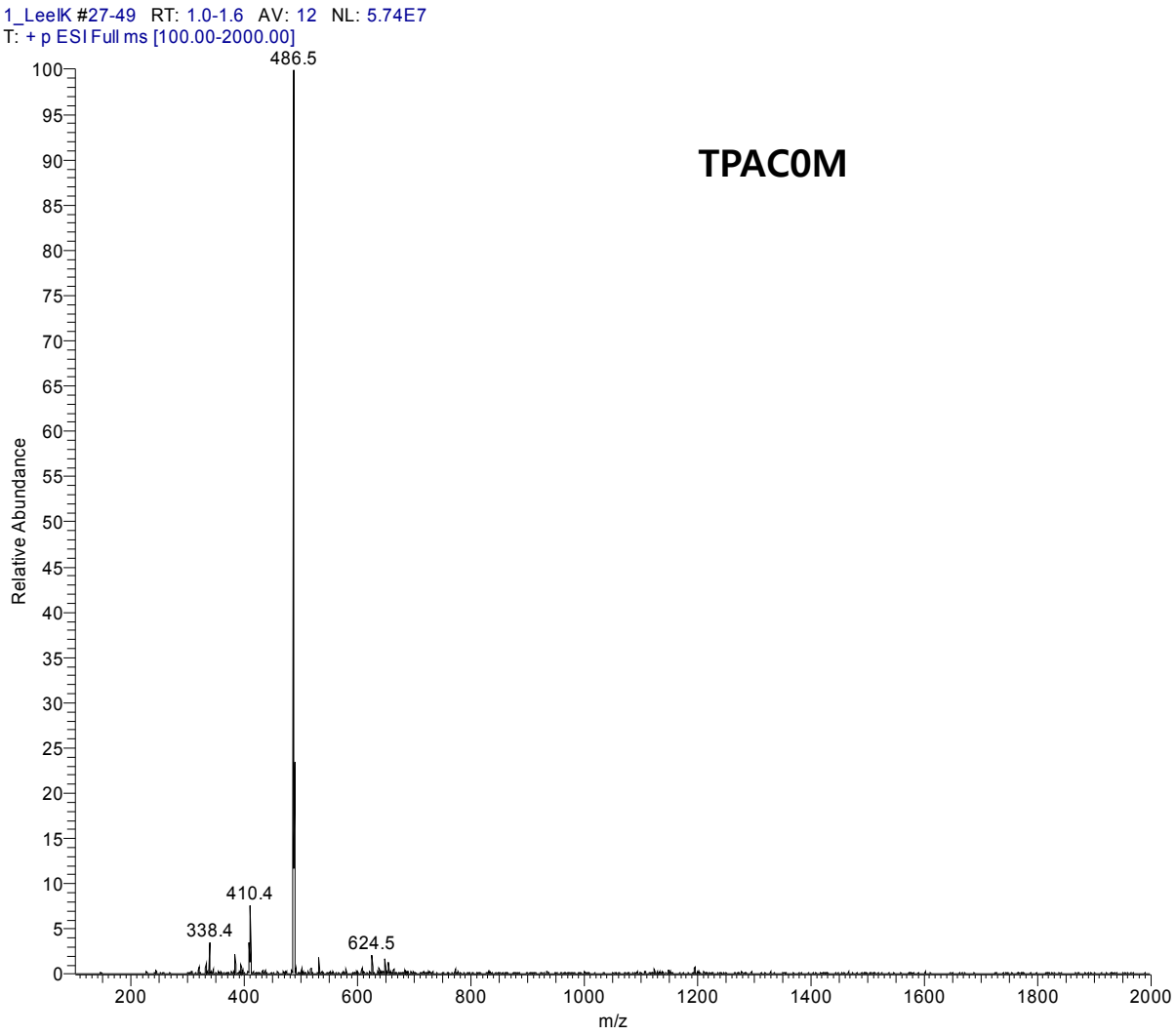


Fig. S8. Analysized LC-mass spectrum of TPAC0M

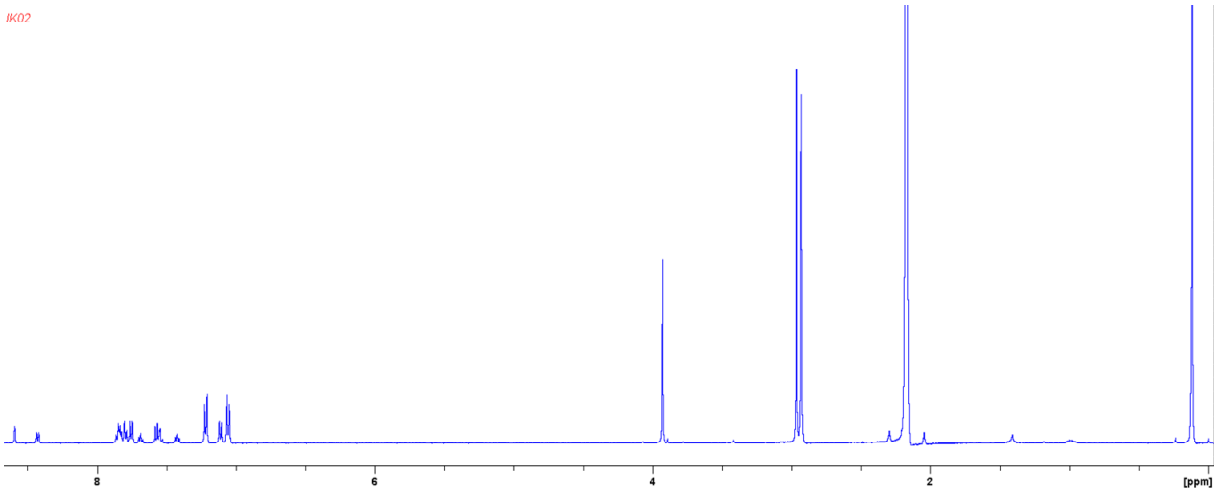


Fig. S9. ^{1}H-NMR spectrum of TPAC2M

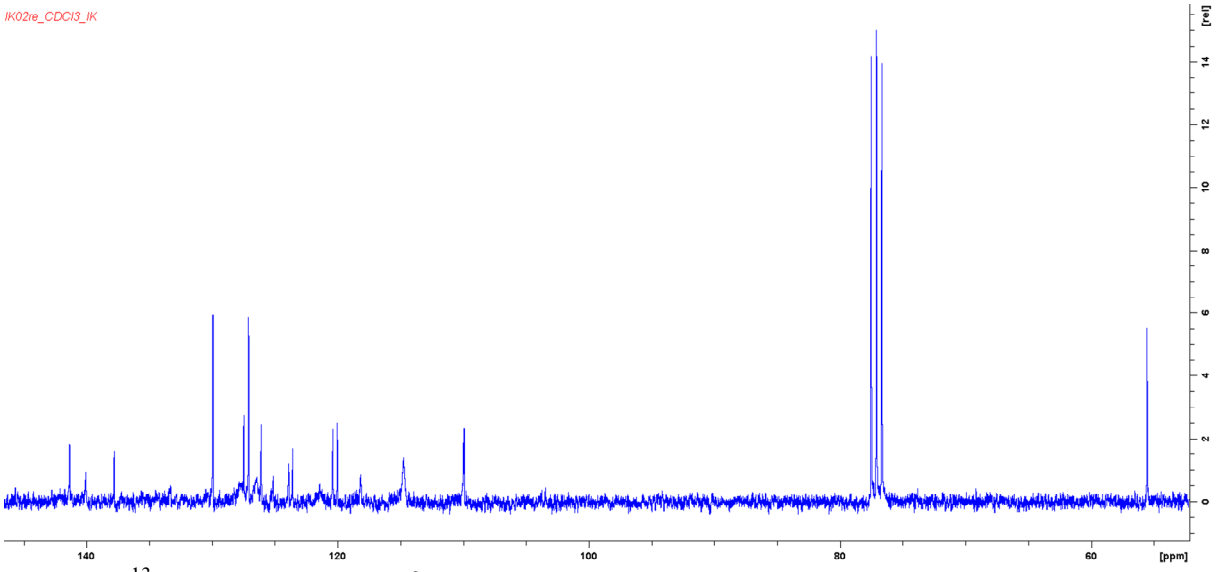


Fig. S10. ^{13}C-NMR spectrum of TPAC2M

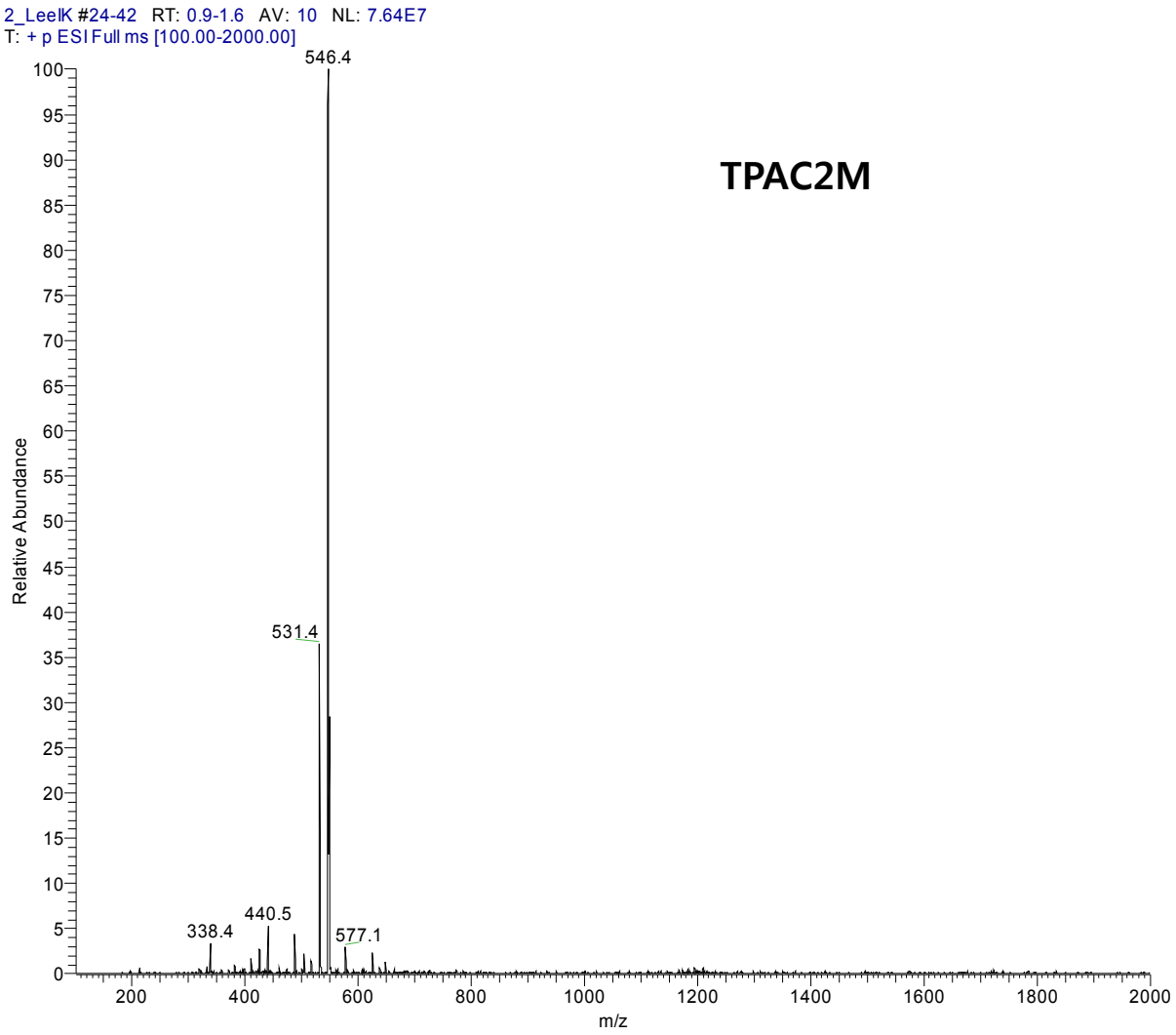


Fig. S11. Analysized LC-mass spectrum of TPAC2M

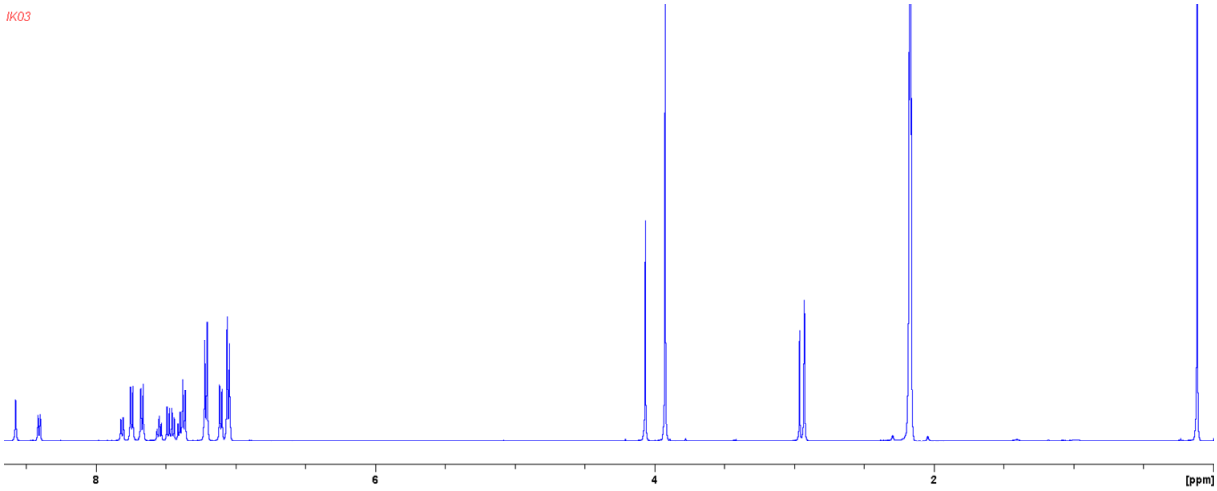


Fig. S12. ^{1}H-NMR spectrum of TPAC3M

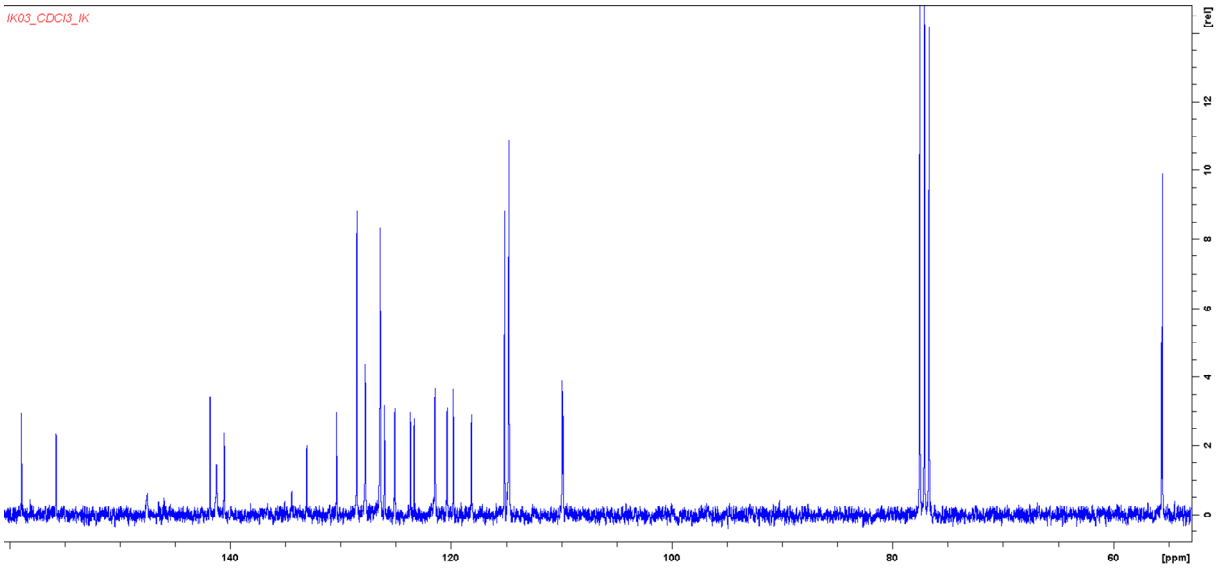


Fig. S13. ^{13}C-NMR spectrum of TPAC3M

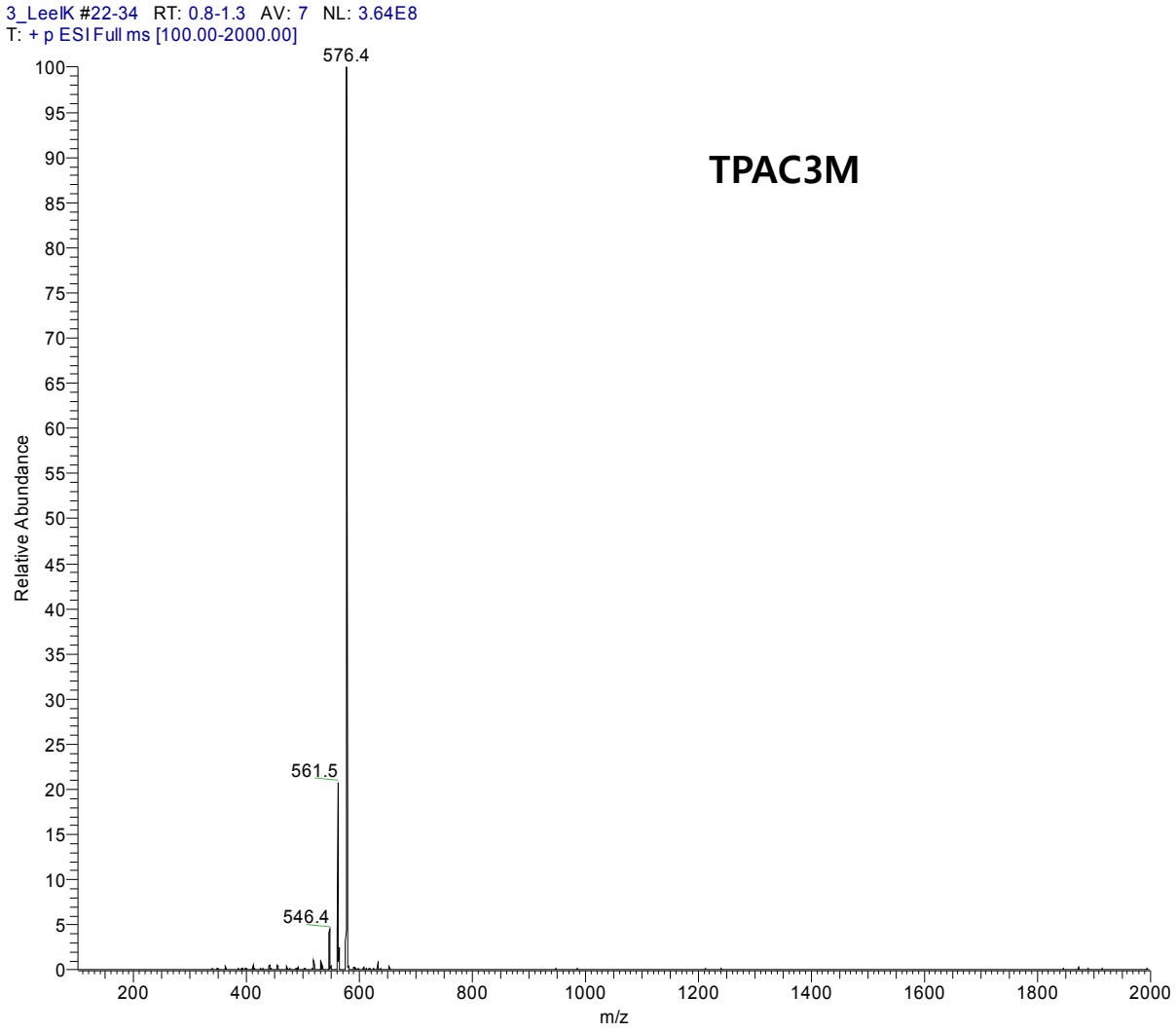


Fig. S14. Analysized LC-mass spectrum of TPAC3M

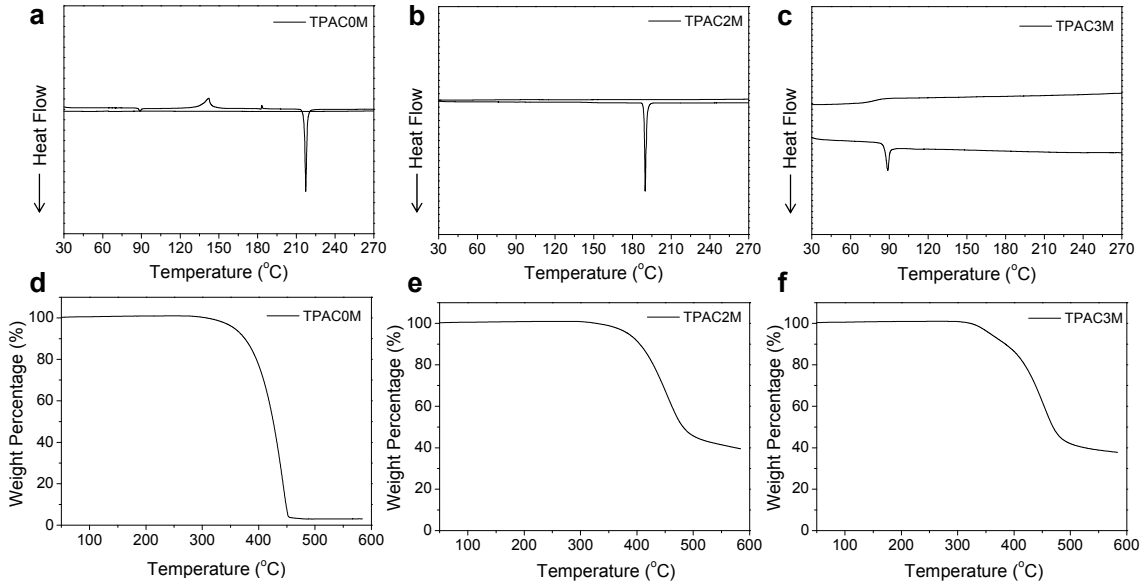


Fig. S15. DSC and TGA thermograms of (a and d) TPAC0M, (b and e) TPAC2M and (c and f) TPAC3M.

Table S1. Summary of device performances of perovskite solar cells adopting different hole transporting materials according to their solution concentration

HTM Materials	Concentration (mg/ml)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)
TPAC0M	10	0.82	21.23	0.69	11.94
	20	0.92 (0.91)	19.80 (20.73)	0.72 (0.74)	12.92 (13.92)
	30	0.91	17.93	0.69	11.23
	40	0.82	16.83	0.66	9.11
TPAC2M	10	0.73	20.62	0.69	10.28
	20	0.98 (0.99)	21.68 (22.58)	0.72 (0.71)	15.20 (15.77)
	30	0.96	18.87	0.72	13.06
	40	0.89	17.95	0.66	10.52
TPAC3M	10	0.68	20.82	0.65	9.07
	20	0.99 (1.00)	22.11 (22.79)	0.75 (0.78)	16.58 (17.54)
	30	0.97	19.52	0.73	13.77
	40	0.92	18.04	0.66	10.79

Numbers are average values of forward and reverse scan data, measured from over 30 devices for each condition (values in parentheses are from the best performing devices).

Table S2. Fitted parameters of all PL decay curves (the values of the goodness-of-fit parameter (χ^2) are all close to 1.0)

	A_1	τ_1(ns)	A_2	τ_2(ns)	τ_{avg}(ns)
PEDOT:PSS	48 %	2.1	52 %	12.1	7.34
TPAC0M	80 %	2.8	20 %	13.5	4.98
TPAC2M	80 %	1.4	20 %	16.2	4.27
TPAC3M	83 %	1.5	17 %	14.5	3.68

where, $Counts(t) = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$

τ_{avg}: amplitude weighted average lifetime

Reference

[S1] J. Keruckas, J. Grazulevicius, D. Volyniuk, V. Cherpak, P. Stakhira, *Dyes and Pigments*, 2014, **100**, 66.