

Electronic Supplementary Information

**Self-Passivation Hole-Transporting Materials with Pyridine-Contained Core for
Antimony Chalcogenide Solar Cells Studied under Dopant-free Conditions**

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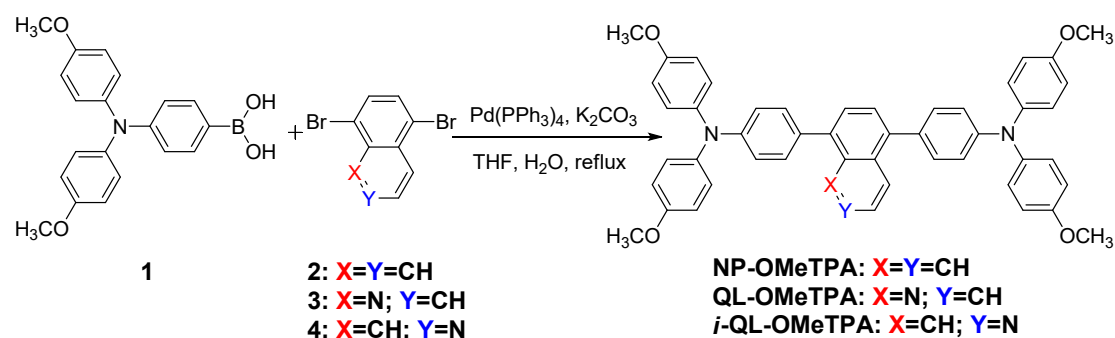
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Experimental

Materials and Characterization

All the reagents and solvent were obtained from Sinopharm Group and used without further purification unless mentioned. The 1,4-dibromonaphthalene, 5,8-dibromoquinoline, 5,8-dibromoisquinoline, (4-(bis(4-methoxyphenyl)amino)phenyl)boronic acid, Potassium antimony (III) L(+)- tartrate hemihydrate ($C_4H_4KO_7Sb \cdot 0.5H_2O$), and sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) were purchased from Innochem Science & Technology co., Ltd, Beijing. The selenourea (CH_4N_2Se) were got from TCI(Shanghai)Development Co., Ltd. The Cadmium(II) nitrate ($Cd(NO_3)_2$), Chromium(II) chloride ($CdCl_2$), thiourea and ammonia were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. The fluorine tin oxide conductive glasses (FTO, transmission >90%, 12~14 Ω per square) were obtained from TEC 15, U.S.A.). the indium-tin oxide conductive glasses (ITO, transmission >90%, 8~9 Ω per square) were obtained from GeAoChem China). The 1H NMR and ^{13}C NMR spectra were measured on the 400 MHz Bruker spectrometer. The UV-vis spectra were tested on U3900H UV-vis spectrophotometer. The HR-MS-ESI was measured on Vanquish Q Exactive Plus (Thermo Fisher Scientific, Germany), The CV measurement (cyclic voltammetry) was recorded by a CHI660d electrochemical analyzer through a standard three-electrode cell with a glassy carbon electrode as working electrode, a Pt wire as counter electrode, and a saturated calomel electrode (SCE) as reference electrode, the ferrocene (Fc/Fc^+) as external reference (*vs.* Fc/Fc^+ +0.63 V *vs.* NHE +4.44 eV).^{S1,S2}

Synthesis details for NP-OMeTPA, QL-OMeTPA and *i*-QL-OMeTPA



Scheme S1. Synthetic Route for NP-OMeTPA, QL-OMeTPA and *i*-QL-OMeTPA

Synthesis of 4,4'-(naphthalene-1,4-diyl)bis(N,N-bis(4-methoxyphenyl)aniline) (NP-OMeTPA): A 50 mL flask with 4-(bis(4-methoxyphenyl)amino)phenylboronic acid (**1**) (366mg, 1.05mmol), 1,4-dibromonaphthalene (**2**) (100mg, 0.35mmol), Pd(PPh₃)₄ (0.016 mmol, 20 mg) and 0.5ml saturated K₂CO₃ aqueous solution in 30ml Tetrahydrofuran (THF) was stirred and reflux for 18 h under N₂ atmosphere. After cooling down to room temperature, the mixture was filtered and extracted with CH₂Cl₂ for three times. The organic layers were collected and dried to solid powder. The purified product was obtained by column chromatography on silica gel using CH₂Cl₂/PE(Petroleum ether) (1/2, v/v) as eluent to yield a faintly yellow powder (160mg, 62%). ¹H NMR (400 MHz, CDCl₃) δ 8.11 (m, 2H), 7.47 (m, 4H), 7.36 (d, *J* = 8.6 Hz, 4H), 7.20-7.17 (m, 8H), 7.07 (m, 4H), 6.92-6.88 (m, 8H), 3.84 (s, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 155.95, 147.96, 141.00, 139.26, 135.78, 132.70, 132.14, 130.69, 127.14, 126.78, 126.56, 126.45, 120.02, 114.78, 114.74, 55.52. HRMS (EIS-TOF, m/z): [M+H] calcd for (C₅₀H₄₂N₂O₄), 735.3223, found 735.3173.

Synthesis of 4,4'-(quinoline-5,8-diyl)bis(N,N-bis(4-methoxyphenyl)aniline) (QL-OMeTPA): The synthetic method of product **QL-OMeTPA** was similar to **NP-**

OMeTPA, with 5,8-dibromoquinoline (**3**) (100mg, 0.35mmol) replacing 1,4-dibromonaphthalene (**2**). The product was obtained by column chromatography using eluent CH₂Cl₂/PE (2/1, v/v) to afford a canary yellow powder (133mg, 52%). ¹H NMR (400 MHz, CDCl₃) δ 8.97 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.43 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.38 (dd, *J* = 8.5, 4.1 Hz, 1H), 7.32 (d, *J* = 8.6 Hz, 2H), 7.22-7.14 (m, 8H), 7.06 (d, *J* = 8.3 Hz, 4H), 6.93-6.86 (m, 8H), 3.84 (s, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 156.09, 155.88, 149.60, 148.33, 147.93, 146.33, 141.03, 140.78, 139.27, 134.79, 131.48, 131.26, 131.16, 130.65, 129.47, 127.27, 126.91, 120.55, 119.86, 119.68, 114.82, 114.69, 55.52. HRMS (EIS-TOF, m/z): [M+H] calcd for (C₄₉H₄₂N₃O₄) 736.3175, found 736.3149.

Synthesis of 4,4'-(isoquinoline-5,8-diyl)bis(N,N-bis(4-methoxyphenyl)aniline) (i-QL-OMeTPA): The synthetic method of product **i-QL-OMeTPA** was resembled that of **NP-OMeTPA**, with 5,8-dibromoisoquinoline (**4**) (100mg, 0.35mmol) replacing 1,4-dibromonaphthalene (**2**). The product was obtained by column chromatography using eluent CH₂Cl₂/PE (4/1, v/v) to afford a light yellow powder (92.3mg, 36%). ¹H NMR (400 MHz, CDCl₃) δ 9.47 (s, 1H), 8.51 (d, *J* = 6.0 Hz, 1H), 7.90 (d, *J* = 6.0 Hz, 1H), 7.67 (d, *J* = 7.4 Hz, 1H), 7.56 (d, *J* = 7.4 Hz, 1H), 7.40-7.31 (m, 4H), 7.23-7.15 (m, 8H), 7.12-7.03 (m, 4H), 6.94-6.87 (m, 8H), 3.84 (s, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 156.12, 151.70, 148.59, 148.44, 142.82, 140.74, 139.87, 137.91, 134.72, 130.77, 130.70, 130.52, 130.31, 127.60, 127.14, 126.94, 126.92, 119.90, 119.86, 118.79, 114.83, 55.52. HRMS (EIS-TOF, m/z): [M+H] calcd for (C₄₉H₄₂N₃O₄) 736.3175, found 736.3147.

Device Fabrication

The $\text{Sb}_2(\text{S,Se})_3$ solar cells were fabricated following the previous report.^{S3} The $\text{Sb}_2(\text{S,Se})_3$ film was deposited through the hydrothermal method using $\text{C}_4\text{H}_4\text{KO}_7\text{Sb}\cdot 0.5\text{H}_2\text{O}$ as Sb-source, $\text{Na}_2\text{S}_2\text{O}_3$ as S-source and $\text{CH}_4\text{N}_2\text{Se}$ as Se-source on FTO conductive glass deposited CdS layer to form the FTO/CdS/ $\text{Sb}_2(\text{S,Se})_3$ framework.^{S4} After the fabrication, the HTMs layers were spin-coated upon the $\text{Sb}_2(\text{S,Se})_3$ film at 3000 rpm for 30 s with 5mg/mL in chlorobenzene, then annealing at 105 °C for 10 min, followed by the thermal evaporation technology of Au counter electrode at high-vacuum. The active area of the solar cells was defined as 0.09 cm².

Device Characterizations

The J-V curves of these solar cells employed using Newport 3A solar simulator. The parameters were obtained with Keithley model 2400 digital source meter. The EQE spectra were measured by Newport IPCE/QE test system. The electrical impedance spectroscopy (EIS) measurements were carried out on CHI660d electrochemical analyzer, with 0.6V voltage bias and frequency from 100 mHz to 1000 kHz, fitted with Z-View software. The time-resolved photoluminescence measurements (TR-PL) with FTO/CdS/ $\text{Sb}_2(\text{S,Se})_3$ /HTM structure were carried out on a LaserStrobe Time-Resolved Spectrofluorometer (Photon Technology International (Canada) Inc.) with a USHIO xenon lamp source, a GL-302 high-resolution dye laser (lifetimes 100 ps to 50 ms, excited by a Nitrogen laser) and a 914 photomultiplier detection system.

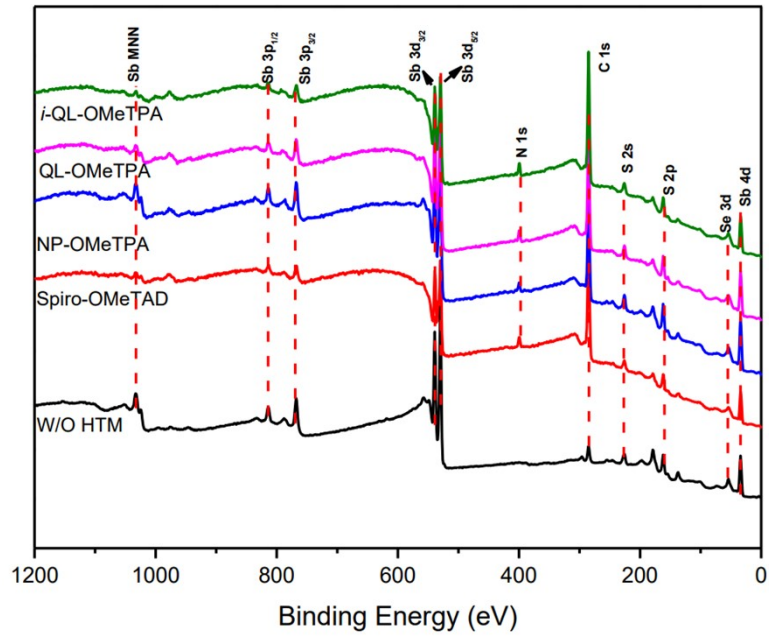


Fig. S1 The total XPS spectra of the pristine $\text{Sb}_2(\text{S,Se})_3$ and $\text{Sb}_2(\text{S,Se})_3$ with these HTMs

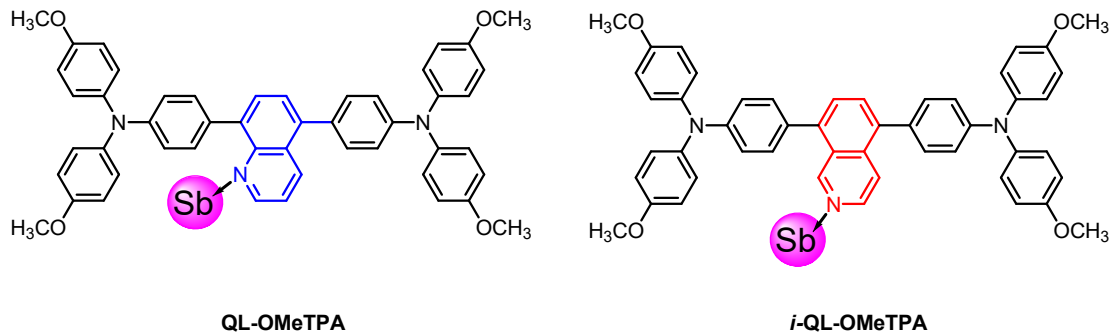


Fig. S2 Schematic illustration of the coordination effect for pyridine moieties with Sb atoms.

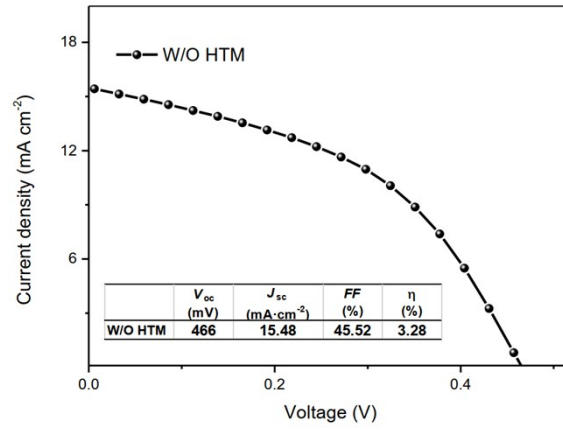


Fig. S3 the J-V curves of the champion solar cells based on $Sb_2(S,Se)_3$ film without HTMs, with an inset table showing the detail parameters.

Table S1 the average paraments of solar cells with NP-OMeTPA, QL-OMeTPA and *i*-QL-OMeTPA as HTMs compared with Spiro-OMeTAD under dopant-free conditions.

HTMs	V_{oc} (mV)	J_{sc} (mA cm ⁻²)	FF (%)	η (%)
NP-OMeTPA	620±12	16.53±0.45	48.38±2.92	4.95±0.22
QL-OMeTPA	629±10	15.70±0.23	50.41±1.57	5.07±0.39
<i>i</i> -QL-OMeTPA	621±11	15.51±0.33	43.78±1.88	4.22±0.14
Spiro-OMeTAD	618±16	15.53±0.65	52.06±1.38	4.99±0.32

Based on 12 cells.

Table S2 the paraments summarized from the EIS and SCLC measurements

HTMs	R_s (Ω)	R_{rec} (Ω)	Hole Mobility (μ_h) (cm ² V ⁻¹ s ⁻¹)
NP-OMeTPA	9.87	1731	6.36×10^{-5}
QL-OMeTPA	8.49	3505	5.41×10^{-5}
<i>i</i> -QL-OMeTPA	16.64	4052	3.59×10^{-5}
Spiro-OMeTAD	8.00	1608	7.33×10^{-5}

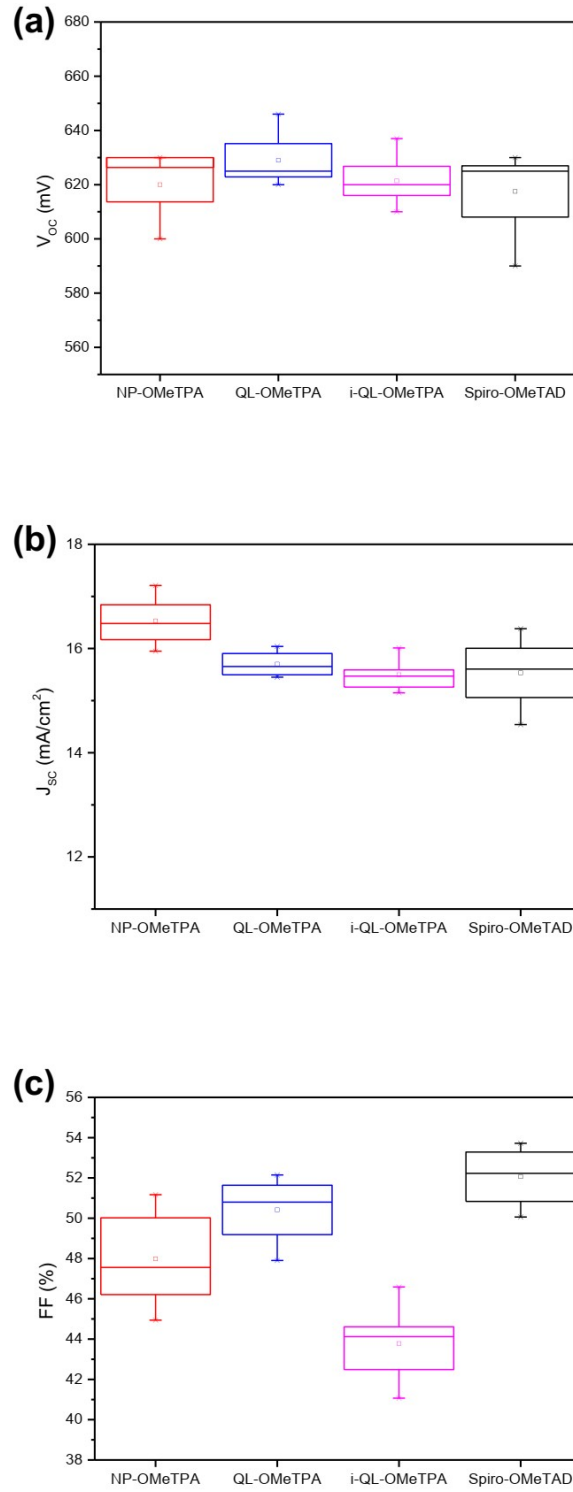


Fig. S4 a) Box plots showing device performance statistical distribution of a) V_{oc} , b) J_{sc} and c) FF based on these HTMs summarized from 12 cells.

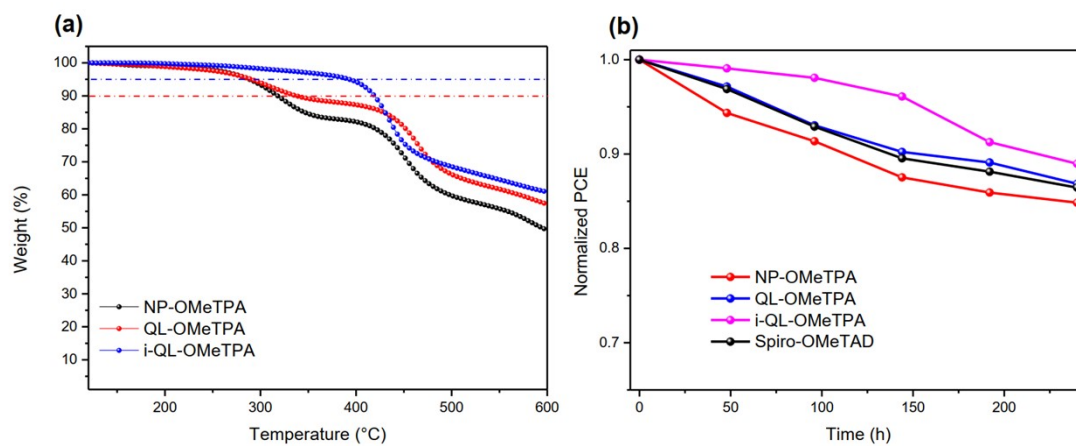


Fig. S5 a) TGA curves of pyridine-contained QL-OMeTPA, *i*-QL-OMeTPA and the reference NP-OMeTPA without pyridine; b) the stability test of $\text{Sb}_2(\text{S,Se})_3$ solar cells based on these HTMs (storage in ambient air, RT, 35-60% humidity)

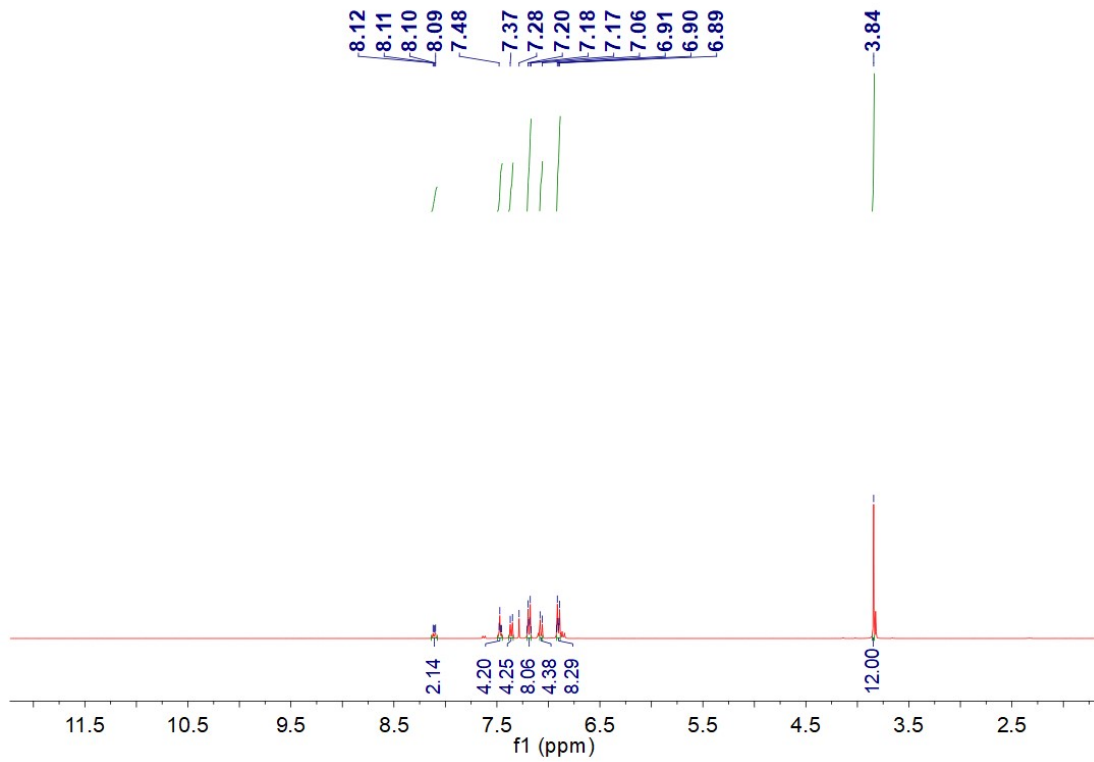


Fig S6. ¹H NMR spectrum of NP-OMeTPA

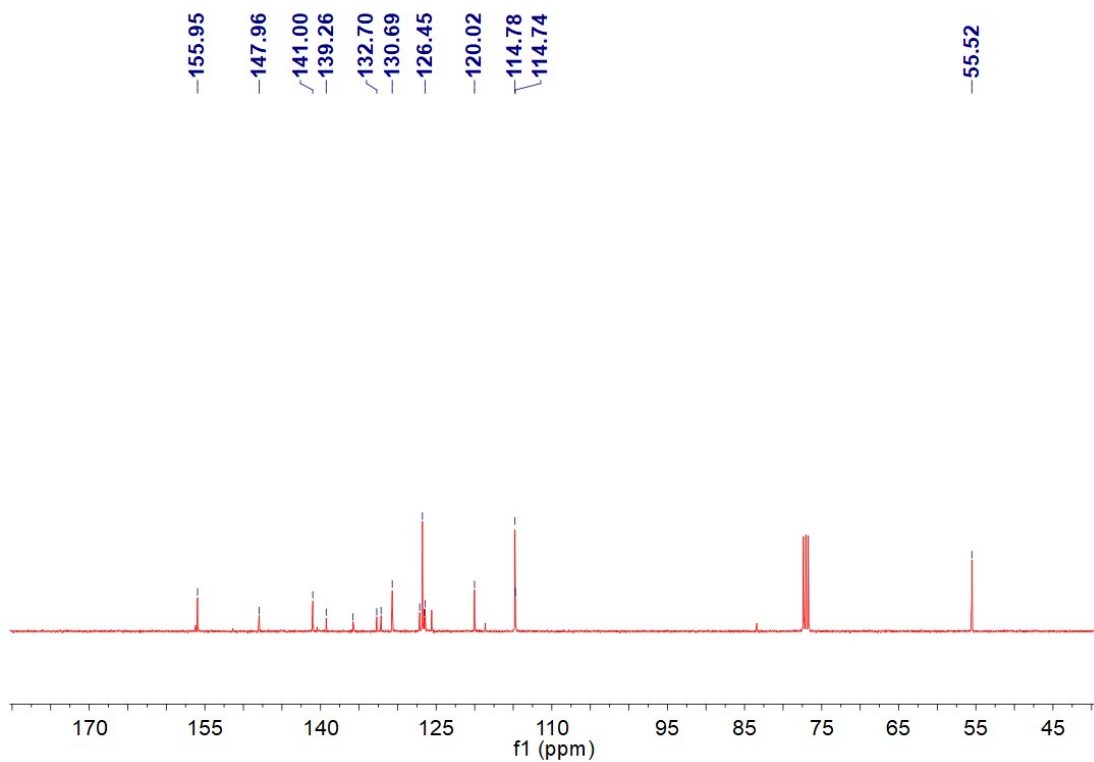


Fig S7. ¹³C NMR spectrum of NP-OMeTPA

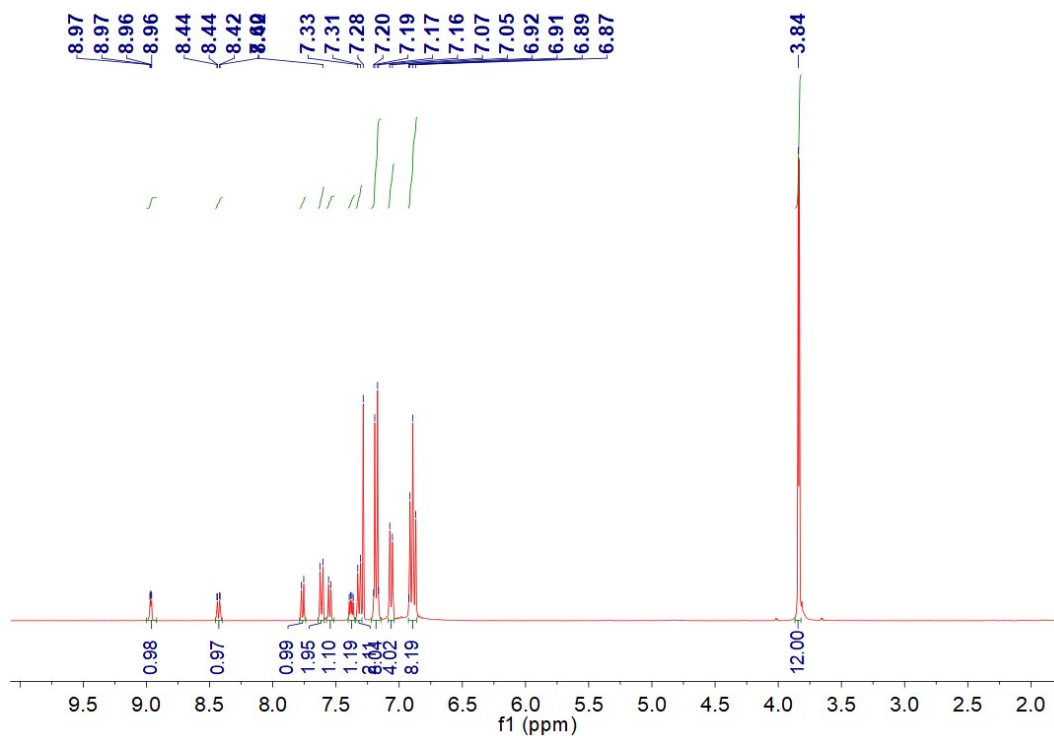


Fig S8. ^1H NMR spectrum of QL-OMeTPA

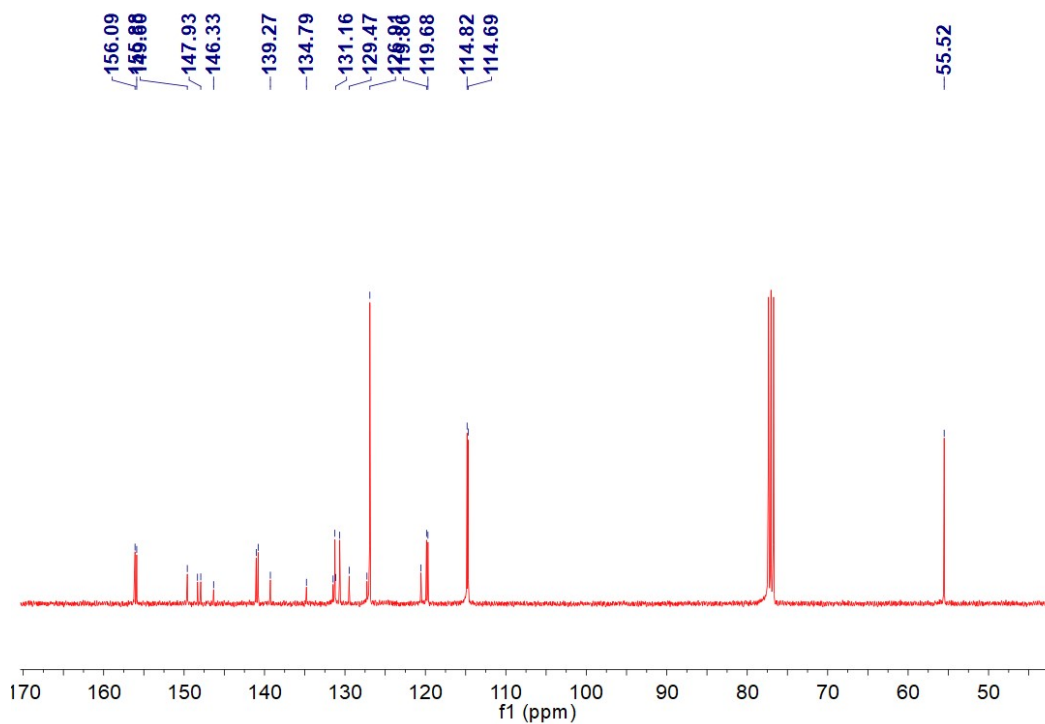


Fig S9. ^{13}C NMR spectrum of QL-OMeTPA

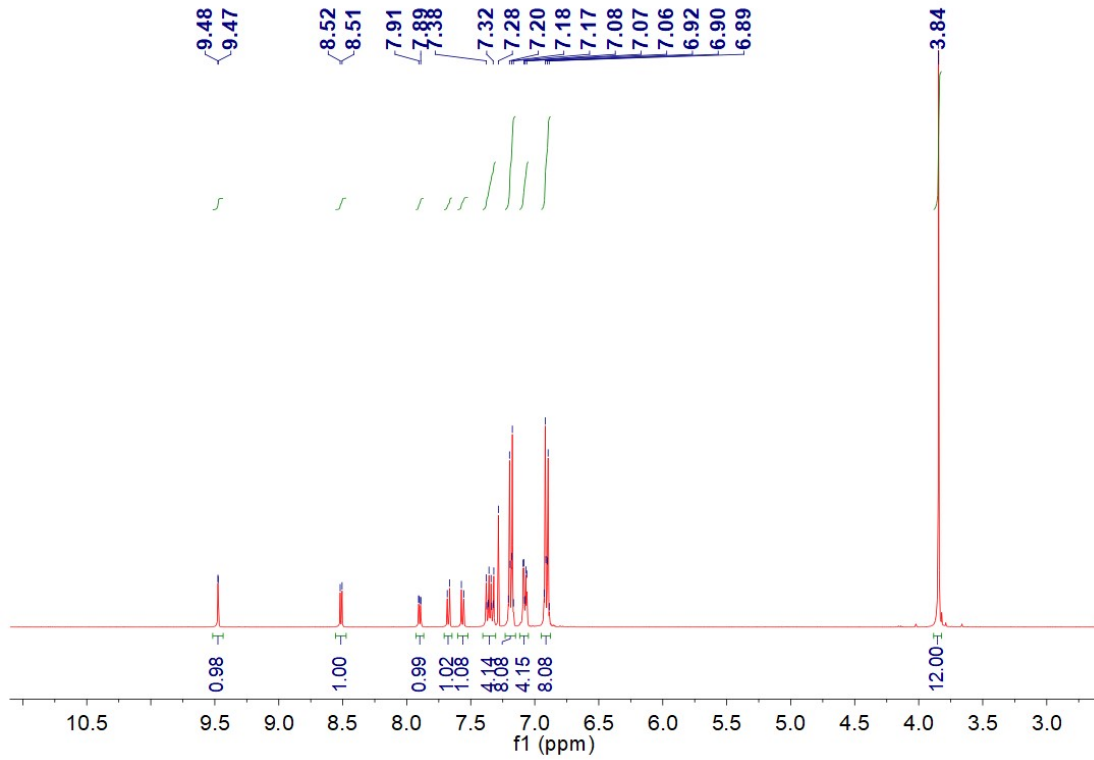


Fig S10. ^1H NMR spectrum of *i*-QL-OMeTPA



Fig S11. ^{13}C NMR spectrum of *i*-QL-OMeTPA

References

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