Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Title: New method for the synthesis of Highly-conjugated Acene Material and Its application in Perovskite solar cells

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Materials and Methods.

Reagents. All commerically acquired reagents were used as received. Dichloromethane and diethyl ether were used as received. Tetrahydrofuran was dried by passing through a column of activated molecular sieves using a solvent purification system.

Reaction conditions. Reaction requiring inert atmosphere were conducted under nitrogen using standard Schlenk line techniques. All other reactins were performed employing standard organic synthesis protocols.

Chromatography. Thin layer chromatography (TLC) was performed using Merck aluminium-backed plates of TLC Silica gel 60 F_{254}; the plates were revealed using UV light. Standard Flash Column chromatography was accomplished using silica gel (60 Å pore size, 230-400 μm mesh size).

Other analytical techniques. Field emission scanning electron microscopy (SEM) images was observed from Hitachi S-4800 FESEM microscope at an accelerating voltage of 15 kV.

Materials. All the reagents were purchased commercially from Sinopharm Chemical Reagent and used without further purification. All aqueous solutions were prepared with Milli-Q water.

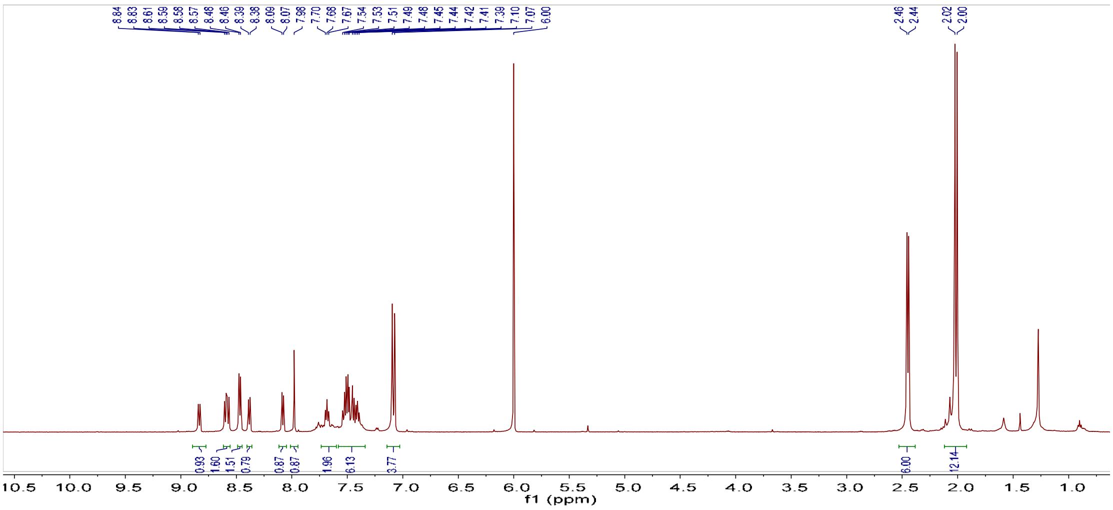
Experimental section

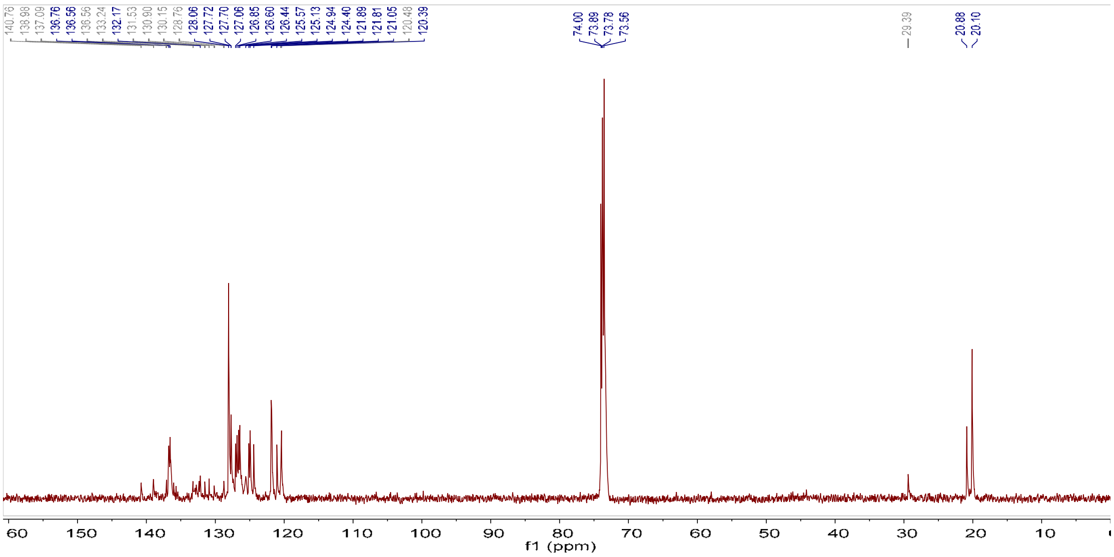
Compound 4,4''-dimesityl-1,1':4',1''-ternaphthalene (1a) and 4,4'''-dimesityl-1,1':4',1'':4'',1'''-quaternaphthalene (2a) were synthesized as per the literature report.[15,16]

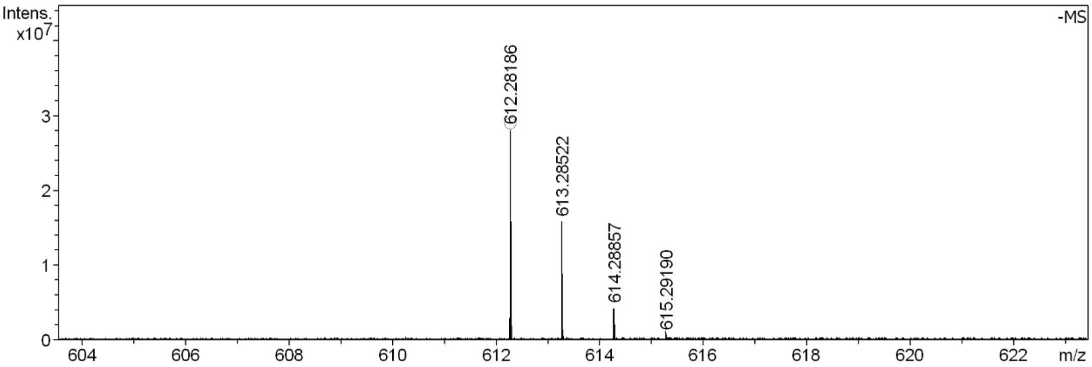
General procedure for the synthesis of 1 and 2

To a stirred solution of oligonaphthalenes (0.1 mmol) in dichloromethane (50 mL), a solution of iron(III) chloride (1 mmol) in nitromethane (10 mL) was added dropwise. A nitrogen stream was bubbled through the mixture throughout the course of the reaction. After stirring for another 2 hours at 40 °C, the reaction was quenched with methanol (10 mL). The resulting mixture was poured into water and extracted with DCM. The extract was purified by column chromatography to afford corresponding 1 and 2.

Compound 1. Brown powder; Yield: 53%; DCM/petroleum ether = 1/5, R_f = 0.21. ^{1}H NMR (500 MHz, $CDCl_2CDCl_2$, 373.2K) δ ppm 8.83 (d, J = 5.0 Hz, 1H), 8.61 - 8.57 (m, 1H), 8.47 (d, J = 10.0 Hz, 1H), 8.38 (d, J = 5.0 Hz, 1H), 8.08 (d, J = 10.0 Hz, 1H), 7.98 (s, 1H), 7.68 (t, J = 10.0 Hz, 2H), 7.54 – 7.39 (m, 6H), 7.09 (d, J = 15.0 Hz, 4H), 2.45 (d, J = 10.0 Hz, 6H), 2.01 (d, J = 10.0 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_2CDCl_2$, 373.2K) δ ppm 140.76, 138.98, 137.09, 136.76, 136.56, 136.56, 133.24, 132.17, 131.53, 130.90, 130.15, 128.76, 128.06, 127.72, 127.70, 127.06, 126.85, 126.60, 126.44, 125.57, 125.13, 124.94, 124.40, 121.89, 121.81, 121.05, 120.48, 120.39, 74.00, 73.89, 73.78, 73.56, 29.39, 20.88, 20.10. HRMS (MALDI-TOF) m/z calcd for $C_{48}H_{36}$ $[M]^+$ 612.2817, found: 612.2819.

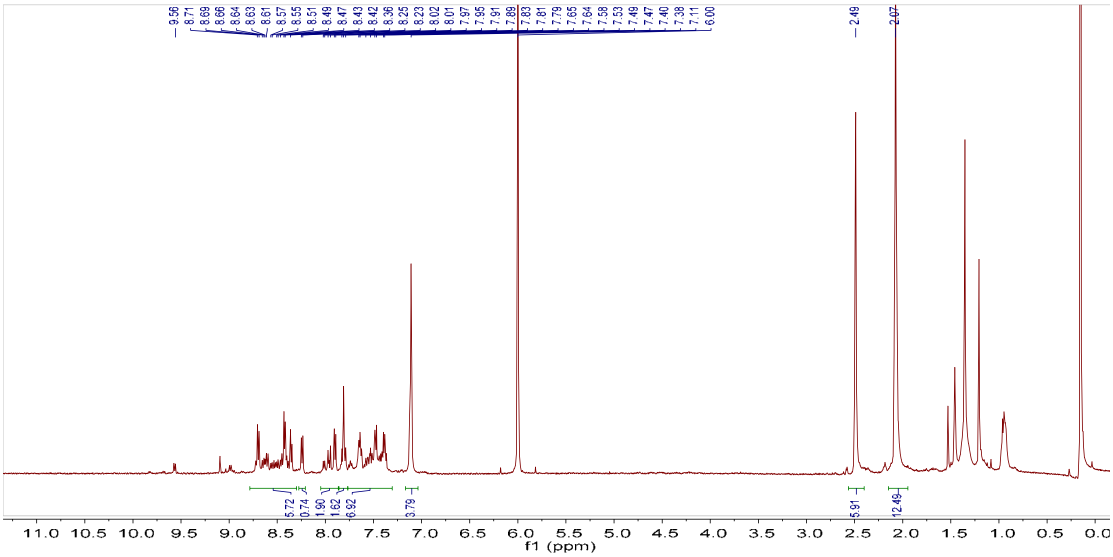


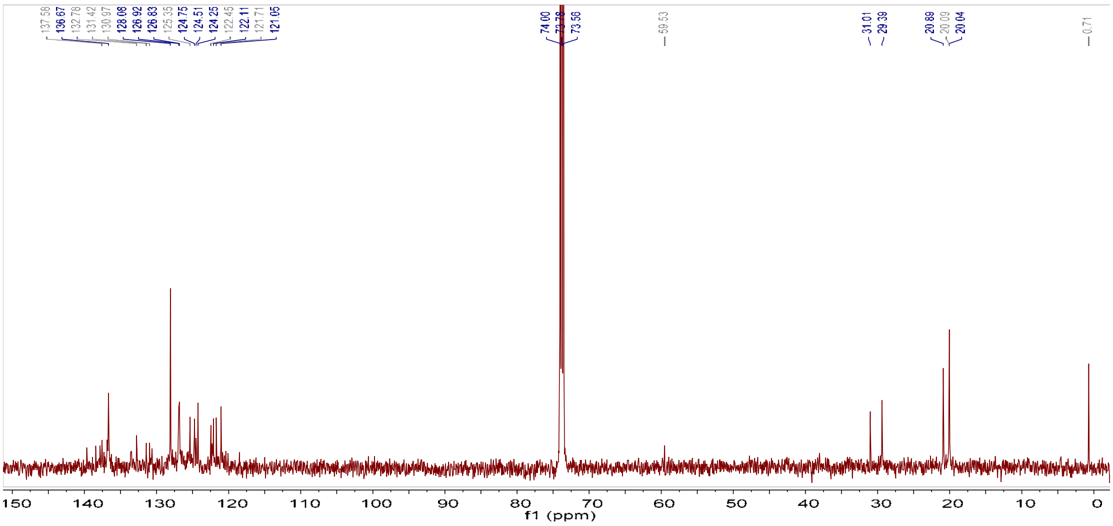


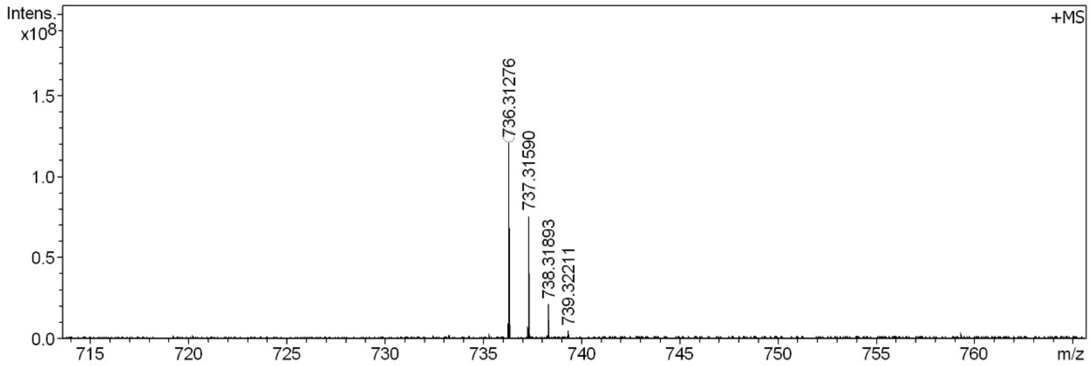


Compound 2. Purple powder; Yield: 65%; DCM/petroleum ether = 1/2, R_f = 0.34. ^{1}H NMR (500 MHz, $CDCl_2CDCl_2$, 373.2 K) δ ppm 8.71 – 8.36 (m, 6H),

8.24 (d, J = 10.0 Hz, 1H), 8.02 - 7.89 (m, 2H), 7.81 (t, J = 10.0 Hz, 2H), 7.66 – 7.38 (m, 7H), 7.11 (s, 4H), 2.49 (s, 6H), 2.07 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_2CDCl_2$, 373.2 K) δ ppm 137.58, 136.67, 132.78, 131.42, 130.97, 128.08, 126.92, 126.83, 125.35, 124.75, 124.51, 124.25, 122.45, 122.11, 121.71, 121.05, 74.00, 73.78, 73.56, 59.53, 31.01, 29.39, 20.89, 20.09, 20.04, 0.71. HRMS (MALDI-TOF) m/z calcd for $C_{58}H_{40}$ $[M]^+$ 736.3130, found: 736.3128.







Perovskite Precursor Preparation. To form the $CH_3NH_3PbI_3$−xClx precursor solution, MAI and $PbCl_2$ (molar ratio 3:1) are dissolved in DMF with final concentrations 2.64 M MAI and 0.88 M $PbCl_2$. This solution was stirred at 60 °C overnight in a N_2-filled glovebox. Prior to device fabrication, the precursor solution was filtered twice with a 0.45 μm PTFE filter.

Device Fabrication. The perovskite solar cells were fabricated on indium tin oxide (ITO)-coated glass substrates (Shenzhen NanBo Group, China, 10 Ω/sq) with the following device configuration: ITO/P3CT-K/Pervoskite/ $PC_{61}BM$ or $PC_{61}BM$:Compound 2/ZnO/Al. The ITO-coated glass substrates were cleaned by sequential ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol for 30 min each and then dried with a nitrogen stream. Then the precleaned ITO glasses were moved into an ultraviolet (UV) chamber for UV−ozone treatment for 20 min. A 35 nm thick P3CT-K was spin-coated onto ITO at 4000 rpm for 60 s and then dried at 140 °C for 10 min in air. All substrates were transferred to the glovebox for further processing. Perovskite precursor solution was spin-coated on the P3CT-K layer at 2000 rpm for 45 s.

After spin-coating, the films were left to dry at room temperature for 30 min to allow slow solvent evaporation. They were then annealed on a hot plate in the glovebox at 80 °C for 120 min to promote crystallization of the CH3NH3PbI3−xClx perovskite and gave the thickness of ~500 nm. The PC$_{61}$BM or PC$_{61}$BM:Compound 2 layer was then spin-coated onto the CH$_3$NH$_3$PbI$_3$−xClx layer at 2000 rpm for 60 s. Finally a 50 nm thick C60 and a 100 nm thick aluminum cathode (deposition rate of 1.0 Å/s)) were deposited on the substrates through a shadow mask to give a device area of 0.06 cm2 under a vacuum level of 10−6 Torr. All device measurements were performed in an inert environment.

Device Characterization. The illuminated current density−voltage ($J-V$) characteristics of the photovoltaic devices were recorded under illumination and dark conditions using a computer-controlled Keithley 2400 source meter under AM 1.5G simulated solar light. The external quantum efficiency measurements were performed with the Newport IQE-200 Measurement System, which equipped a Xe lamp, a monochromator, a current−voltage preamplifier, and a lock-in amplifier.