

Supplementary Information

Star-shaped Hole Transport Materials with Indeno[1,2-*b*] thiophene or Fluorene on Triazine Core for Efficient Perovskite Solar Cells

Kimin Lim,^{a,b} Moon-Sung Kang,^c Yoon Myung,^d Jong-Hyun Seo,^e Parag Banerjee,^d

Tobin J. Marks^{b,*} and Jaejung Ko^{a,*}

^a Department of Advanced Material Chemistry, Korea University Sejong Campus, Sejong-ro 2511, Sejong City,
339-700, Korea. E-mail: jko@korea.ac.kr

^b Department of Chemistry, Northwestern University, 2145 Sheridan Road Evanston, IL 60208, USA. E-mail: t-
marks@northwestern.edu

^c Department of Environmental Engineering, Sangmyung University, 300 Anseo-dong, Dongnam-gu, Cheonan-
si, Chungnam 330-720, Republic of Korea.

^d Department of Mechanical Engineering and Materials Science, Washington University in St. Louis, St. Louis,
MO 63130, USA

^e Advanced Analysis Center, Korea Institute of Science and Technology, 39-1, Hawolgok-dong, Seongbuk-gu,
Seoul 130-650, Republic of Korea.

General methods

All reactions were carried out under a nitrogen atmosphere. All reagents were purchased from Sigma-Aldrich, Acros, and TCI. Solvents were distilled from appropriate reagents before the use. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer. The chemical shifts (δ) were calibrated against TMS as an internal standard. Elemental analyses were performed with a Carlo Elba Instruments CHNS-O EA 1108 analyzer. The absorption and photoluminescence spectra were obtained using a Perkin-Elmer Lambda 2S UV-visible spectrometer and a Perkin LS fluorescence spectrometer, respectively. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) data were obtained simultaneously using a Sinco N-1000 and N-650, respectively. The electrical sheet resistivity measurements were carried out in a commercial probe station (Janis ST500-1-2CX) with Cu-Be 4 probe tips (the pitch distance of each tips at 100 μm , Fig. S7) and the probes connected to Keithley 2400 Source Measure Unit. All sheet resistivity values were measured at room temperature under ambient pressure. The surface morphology of the mesoporous (mp)- TiO_2 /MAPbI₃/HTMs/Au films were evaluated by using a scanning electron microscopy (SEM, Quanta 3D). Electrochemistry was performed on a C3 Cell Stand Electrochemical Station equipped with BAS Epsilon software (Bioanalytical Systems, Inc., Lafayette, IN) in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in dry dichloromethane. A three-electrode cell was used which was equipped with, a platinum (Pt) wire as a counter electrode and Ag/AgCl in 3 M KCl as a reference electrode. All of the measurements were carried out after nitrogen (N₂) bubbling and under N₂ condition at a scan rate of 100 mV/s. The redox potential of ferrocene/ferrocenium (Fc/Fc⁺) was measured under the same condition for calibration before and after sample measurements, and E_{onset} was located at 0.398 V vs Ag/AgCl electrode. The energy levels of the highest occupied molecular orbital (HOMO) was then calculated by the following equation.¹

$$E_{\text{HOMO}} = - (E_{[\text{onset, ox. vs. Fc/Fc}^+]} + 5.1) \text{ (eV)}$$

Solar cell fabrication

F-doped tin oxide (FTO) glass substrates (TEC-8, Pilkington) were cleaned using a detergent solution in an ultrasonic bath for 30 min and then rinsed with distilled water, acetone and ethanol, and subjected to an O₃/ultraviolet treatment for 15 min. The dense TiO₂ blocking layer was deposited on the FTO substrate by spray pyrolysis at 450 °C using titanium diisopropoxide bis(acetylacetonate) solution diluted in ethanol (1:39, volume ratio) as precursor. After cooling to room temperature (RT), the FTO plates were immersed in 40 mM TiCl₄ aqueous solution at 70 °C for 30 min and then sintered at 500 °C for 30 min. mp-TiO₂ films were layered by spin coating of a diluted TiO₂ paste (18NR-T, 1:3.5 w/w diluted with ethanol, Dyesol) at 6000 rpm for 30 s. After drying at 120 °C the electrodes were then sintered at 500 °C, baked at this temperature for 30 min and cooled to RT. Prior to their use, the films were again dried at 500 °C for 15 min. A PbI₂ in *N,N*-dimethylformamide (DMF) solution (1.0 M) was dropped on the mp-TiO₂ film and then spun at 6500 rpm for 90 s, followed by drying on a hot plate at 70 °C for 30 min. The electrodes were dipped into a CH₃NH₃I in 2-propanol solution (10 mg ml⁻¹) for 25 s, rinsed with 2-propanol, dried by rapid spinning at 3000 rpm for 30 s and then dried at 70 °C for 30 min. For preparing the HTM solutions, 17.5 μl Li-bis(trifluoromethanesulfonyl)imide in acetonitrile (520 mg ml⁻¹) and 28.8 μl 4-*tert*-butylpyridine were added into the 1 ml HTM/chlorobenzene solutions (HTM concentration: spiro-OMeTAD: 60 mM, Triazine-Flu and Triazine-InT: 30 mM) as the additives. The HTM solutions were spin-cast on top of the CH₃NH₃PbI₃/TiO₂/FTO substrate at 3000 rpm for 40 s. The device was pumped down to lower than 10⁻⁶ torr and *ca.* 70 nm thick Au counter electrode was finally deposited on top.

Photovoltaic performance measurements

Photovoltaic performances were characterized under simulated 100 mW cm⁻² AM 1.5G irradiation (1 sun) from a Xe arc lamp with an AM 1.5 global filter. Simulator irradiance was characterized using a calibrated spectrometer and illumination intensity was adjusted using an NREL certified silicon diode with an integrated KG1 optical filter. The spectral mismatch factors were calculated for each device in this report to be less than 5%. Short circuit currents were also found to be well consistent with the values obtained from the integrated external quantum efficiency (EQE) spectra within 5% error. The EQE was measured by under filling the device area using a reflective microscope objective to focus the light output from a 75 watt Xe lamp, monochromator, and optical chopper; photocurrent was measured using a lock-in amplifier and the absolute photon flux was determined by a calibrated silicon photodiode.

HTM synthesis

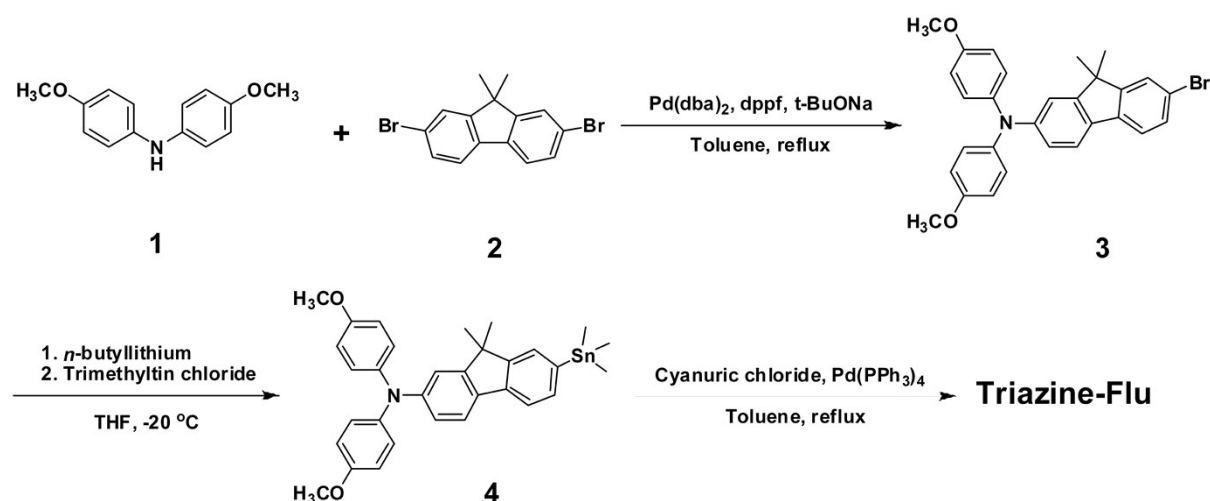


Fig. S1. Schematic diagram for the synthesis of the **Triazine-Flu**.

7-Bromo-*N,N*-bis(4-methoxyphenyl)-9,9-dimethyl-9H-fluorene-2-amine (3)²: A mixture of bis(4-methoxyphenyl)-amine (**1**) (1.15 g, 5.0 mmol), 2,7-dibromo-9,9-dimethyl-9H-fluorene (**2**) (3.52 g, 10. mmol), Pd(dba)₂ (34 mg, 0.075 mmol), dppf (41 mg, 0.75 mmol), and sodium tert-butoxide (0.48 g, 10.5 mmol) in dry toluene was placed in a three-necked flask under a nitrogen atmosphere and was stirred at 110 °C for 15 h. After cooling, the reaction was quenched by adding water, then was extracted with ethyl acetate. The organic layer was dried over anhydrous MgSO₄ and evaporated under vacuum. The product was purified by silica gel column chromatography. (dichloromethane/hexane=1:4, Yield: 53%) ¹H NMR (300 MHz, (CD₃)₂CO): δ 7.63-7.59 (m, 3H), 7.45 (d, 1H, *J* = 7.8 Hz), 7.09-6.90 (m, 10H), 3.81 (s, 6H), 1.39 (s, 6H). Anal. Calcd. for C₂₉H₂₆BrNO₂: C, 69.60; H, 5.24. Found: C, 69.18; H, 6.02.

***N,N*-Bis(4-methoxyphenyl)-4'-(trimethylstannyl)biphenyl-4-amine (4)**: To a solution of 7-bromo-*N,N*-bis(4-methoxyphenyl)-9,9-dimethyl-9H-fluorene-2-amine (**3**) (1.16 g, 2.32 mmol) in dry THF (40 ml) was added 1.6 M *n*-BuLi (1.9 ml, 3.0 mmol) dropwise at -78 °C, and the resulting mixture was stirred for 1 h. The 1.0 M chlorotrimethylstannane solution (3.0 ml, 3.0 mmol) was added quickly to the reaction mixture, and stirring was continued for overnight. The reaction was quenched with saturated ammonium chloride solution, diluted with ethyl acetate, and extracted with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄, and concentrated. The resulting product was used in the next step without further purification. (Yield: 100%) ¹H NMR (300 MHz, (CD₃)₂CO): δ 7.65-7.58 (m, 3H), 7.44 (d, 1H, *J* = 6.9 Hz), 7.08-7.04 (m, 5H), 6.92 (d, 4H, *J* = 9.0 Hz), 6.84 (dd, 1H, *J* = 2.1 Hz, 8.4 Hz), 3.79 (s, 6H), 1.37 (s, 6H), 0.30 (s, 9H).

7,7',7''-(1,3,5-Triazine-2,4,6-triyl)tris(*N,N*-bis(4-methoxyphenyl)-9,9-dimethyl-9*H*-fluoren-2-amine) (Triazine-Flu)³ : To compound cyanuric chloride (0.10 g, 0.54 mmol) dissolved in anhydrous toluene (30 ml), under N₂ gas in round two-bottom flask were added *N,N*-bis(4-methoxyphenyl)-4'-(trimethylstannyl)biphenyl-4-amine (**4**) (1.27 g, 2.17 mmol) and Pd(PPh₃)₄ (94 mg, 0.081 mmol). The resulting mixture was stirred for 4 days at 110 °C. Subsequently, the mixture was cooled down to room temperature. Water was added and the resulting solution was extracted three times with CHCl₃. The combined organic layers were washed with brine, dried over MgSO₄ and evaporated until brown oil appeared. The crude product was purified by column chromatography (dichloromethane/ hexane, 3:1). (Yield: 71%). ¹H NMR (400 MHz, CDCl₃): δ 8.81 (d, 3H, *J* = 8.1 Hz), 8.76 (s, 3H), 7.81 (d, 3H, *J* = 8.4 Hz), 7.62 (d, 3H, *J* = 8.4 Hz), 7.14 (d, 12H, *J* = 7.2 Hz), 7.11 (sd, 3H, *J* = 1.6 Hz), 6.95 (dd, 3H, *J* = 1.6 Hz, 6.8 Hz), 6.88 (d, 12H, *J* = 7.2 Hz), 3.83 (s, 18H), 1.55 (s, 18H). ¹³C NMR (100 MHz, CDCl₃): δ 171.6, 156.2, 155.9, 153.6, 149.4, 143.7, 141.1, 134.2, 131.1, 128.6, 126.6, 122.8, 121.2, 119.9, 119.0, 114.8, 114.7, 55.5, 46.9, 27.2. Anal. Calcd. for C₉₀H₇₈N₆O₆: C, 80.69; H, 5.87. Found: C, 80.38; H, 5.76.

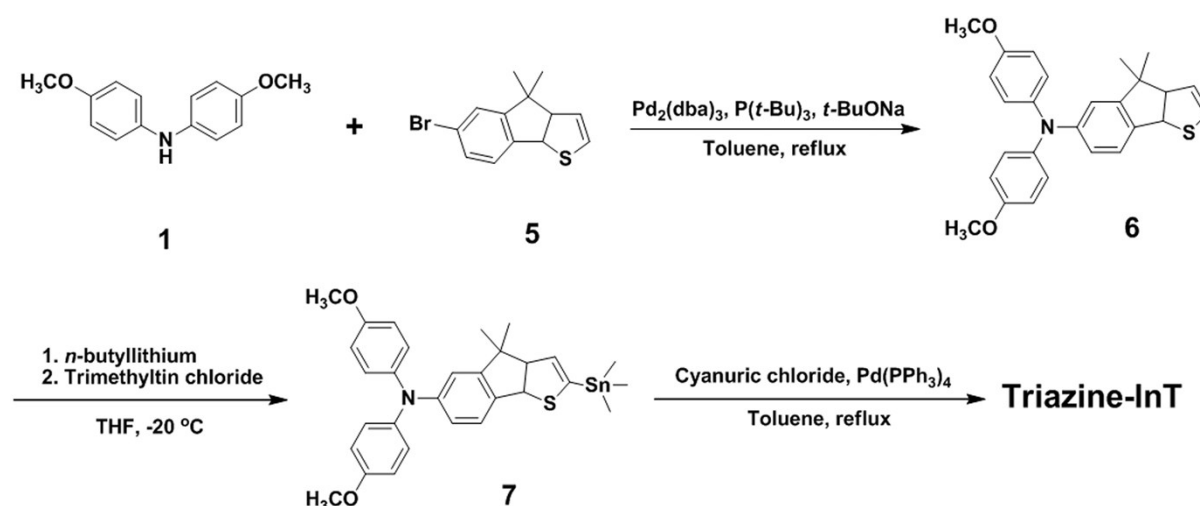


Fig. S2 Schematic diagram for the synthesis of the Triazine-InT.

***N,N*-Bis(4-methoxyphenyl)-4,4-dimethyl-4*H*-indeno[1,2-*b*]thiophen-6-amine (**6**)⁴** : bis(4-methoxyphenyl)-amine (**1**) (0.56 g, 2.43 mmol), 6-bromo-4,4-dimethyl-4*H*-indeno[1,2-*b*]thiophene (**5**)³ (0.75 g, 2.70 mmol), Pd₂(dba)₃ (74 mg, 0.081 mmol), P(*t*-Bu)₃ (16 μl, 0.081 mmol), and sodium tert-butoxide (0.39 g, 4.03 mmol) in dry toluene (30 ml) was stirred and reflux for 8 hrs. After cooling to room temperature, saturated ammonium chloride solution was added to the reaction solution. The solution was extracted with ethyl acetate, dried over MgSO₄. The product was purified by silica gel column chromatography.

(dichloromethane/ hexane=1:4, Yield: 73%) ^1H NMR (300 MHz, $(\text{CD}_3)_2\text{CO}$): δ 7.36 (d, 1H, $J = 5.4$ Hz), 7.29 (d, 1H, $J = 8.7$ Hz), 7.12 (d, 1H, $J = 4.5$ Hz), 7.05-7.02 (m, 5H), 6.91 (d, 4H, $J = 9.3$ Hz), 6.79 (d, 1H, $J = 8.4$ Hz), 3.79 (s, 6H), 1.37 (s, 6H). Anal. Calcd. for $\text{C}_{27}\text{H}_{25}\text{NO}_2\text{S}$: C, 75.85; H, 5.89. Found: C, 75.43; H, 5.42.

***N,N*-bis(4-methoxyphenyl)-4,4-dimethyl-2-(trimethylstannyl)-4*H*-indeno[1,2-*b*]thiophen-6-amine (7)** : To a solution of *N,N*-bis(4-methoxyphenyl)-4,4-dimethyl-4*H*-indeno[1,2-*b*]thiophen-6-amine (6) (0.62 g, 1.32 mmol) in dry THF (30 ml) was added 1.6 M *n*-BuLi (1.2 ml, 1.88 mmol) dropwise at -78 °C, and the resulting mixture was stirred for 1 hour. The 1.0 M chlorotrimethylstannane solution (1.9 ml, 1.9 mmol) was added quickly to the reaction mixture, and stirring was continued for overnight. The reaction was quenched with saturated ammonium chloride solution, diluted with ethyl acetate, and extracted with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 , and concentrated. The resulting product was used in the next step without further purification. (Yield: 100%). ^1H NMR (300 MHz, $(\text{CD}_3)_2\text{CO}$): δ 7.26-7.20 (m, 2H), 7.05-7.02 (m, 5H), 6.90 (d, 4H, $J = 9.3$ Hz), 6.79 (d, 1H, $J = 8.4$ Hz), 3.78 (s, 6H), 1.36 (s, 6H), 0.38 (s, 9H).

2,2',2''-(1,3,5-triazine-2,4,6-triyl)tris(*N,N*-bis(4-methoxyphenyl)-4,4-dimethyl-4*H*-indeno[1,2-*b*]thiophen-6-amine) (Triazine-InT)³ : To compound cyanuric chloride (62 mg, 0.34 mmol) dissolved in anhydrous toluene (20 ml), under N_2 gas in round two-bottom flask were added *N,N*-bis(4-methoxyphenyl)-4,4-dimethyl-2-(trimethylstannyl)-4*H*-indeno[1,2-*b*]thiophen-6-amine (7) (0.8 g, 1.36 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (59 mg, 0.051 mmol). The resulting mixture was stirred for 4 days at 110 °C. Subsequently, the mixture was cooled down to room temperature. Water was added and the resulting solution was extracted three times with CHCl_3 . The combined organic layers were washed with brine, dried over MgSO_4 and evaporated until brown oil appeared. The crude product was purified by column chromatography (dichloromethane/hexane, 3:1). (Yield: 74%). ^1H NMR (400 MHz, CDCl_3): δ 8.16 (s, 3H), 7.34 (d, 3H, $J = 8.4$ Hz), 7.11 (d, 12H, $J = 6.8$ Hz), 7.02 (sd, 3H, $J = 1.6$ Hz), 6.87-6.84 (m, 15H), 3.82 (s, 18H), 1.46 (s, 18H). ^{13}C NMR (100 MHz, CDCl_3): δ 167.4, 158.5, 157.8, 155.9, 148.2, 147.4, 141.9, 141.0, 128.8, 126.5, 124.9, 120.4, 119.7, 115.1, 114.7, 55.5, 45.8, 26.1. Anal. Calcd. for $\text{C}_{84}\text{H}_{72}\text{N}_6\text{O}_6\text{S}_3$: C, 74.31; H, 5.35. Found: C, 73.96; H, 5.09.

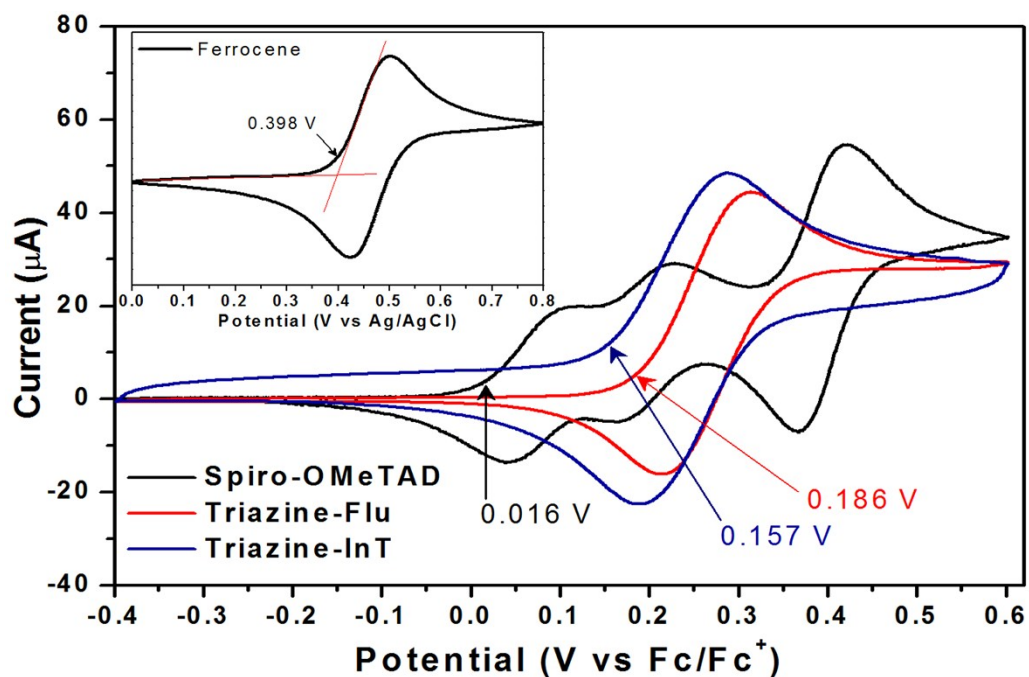


Fig. S3 Electrochemical characterization of **Spiro-OMeTAD**, **Triazine-Flu** and **Triazine-InT** in DCM with 0.1 M $(n\text{-C}_4\text{H}_9)_4\text{NPF}_6$ as supporting electrolyte with scan rate of 100 mV s^{-1}

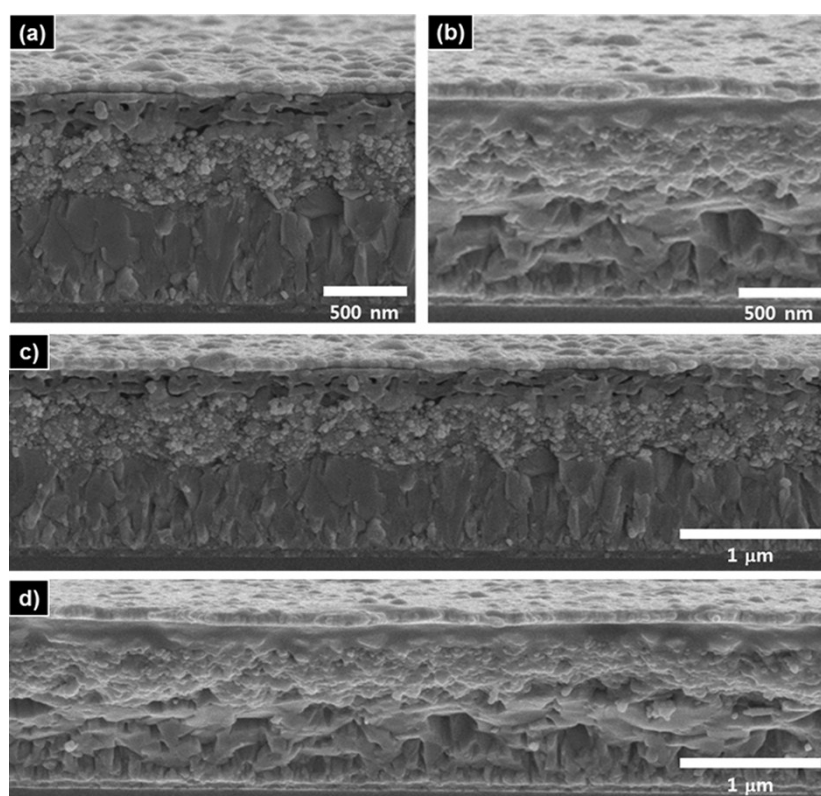


Fig. S4 Cross-sectional scanning electron microscopy (SEM) images under high magnification of the mp-TiO₂ / CH₃NH₃PbI₃ / (a) **Triazine-Flu** and (b) **Triazine-InT** / Au. Cross-sectional SEM images under lower magnification of the mp-TiO₂ / CH₃NH₃PbI₃ / (c) **Triazine-Flu** or (d) **Triazine-InT** / Au.

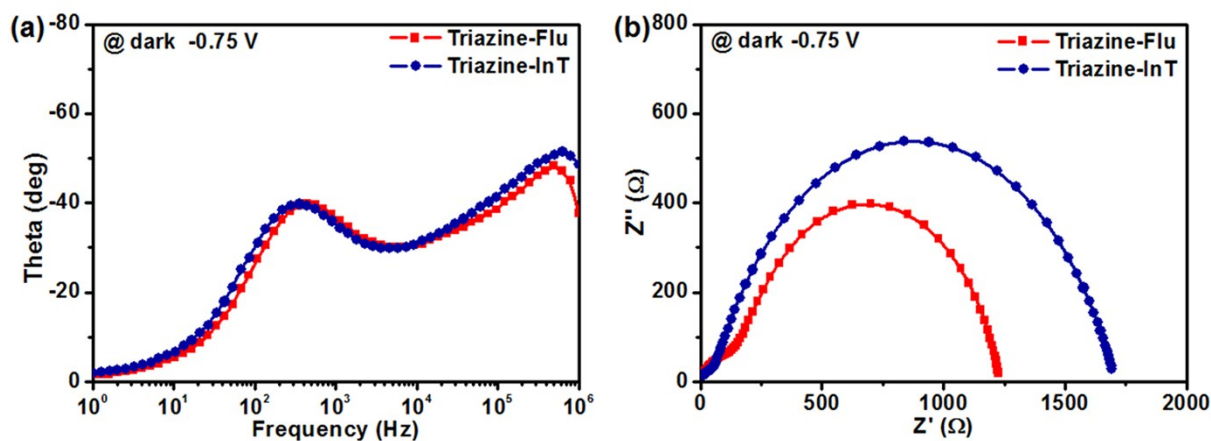


Fig. S5 (a) Nyquist plots of electrochemical impedance spectra measured at forward bias of -0.75 V on $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{HTM}/\text{Au}$ solar cell under dark condition. (b) Bode plots obtained with the same devices.

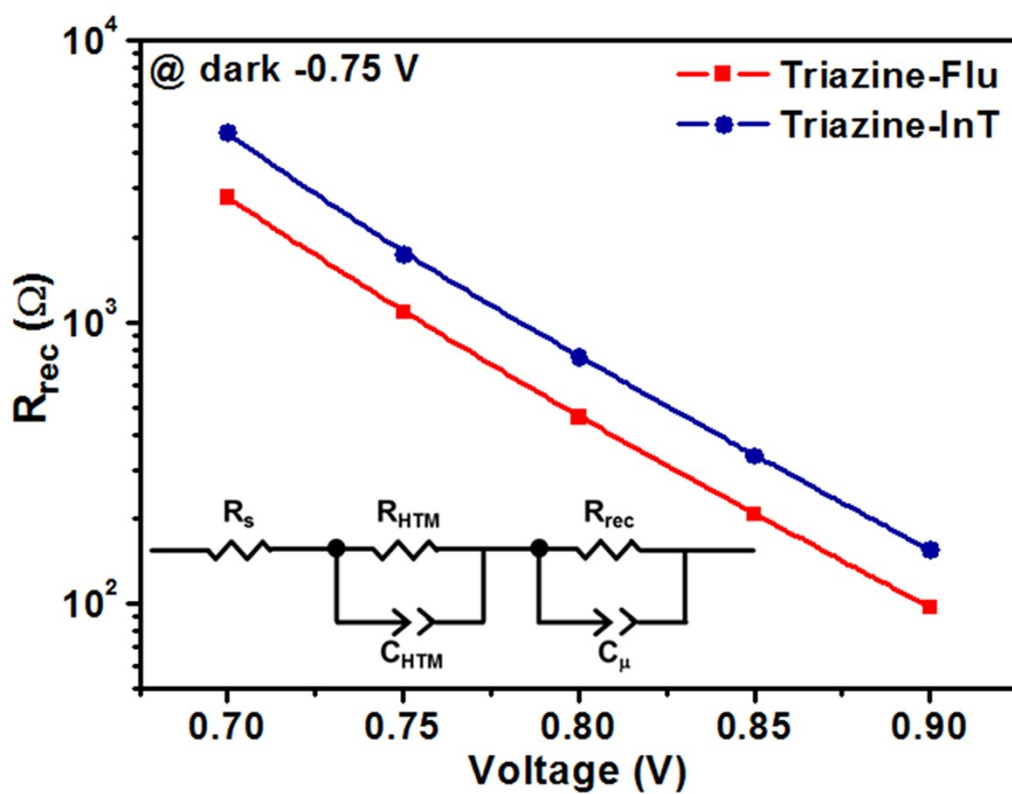


Fig. S6 The plots of resistance vs. voltage for the perovskite solar cells employing several HTMs. (inset) Equivalent circuit model for impedance spectra analysis of the perovskite solar cells.

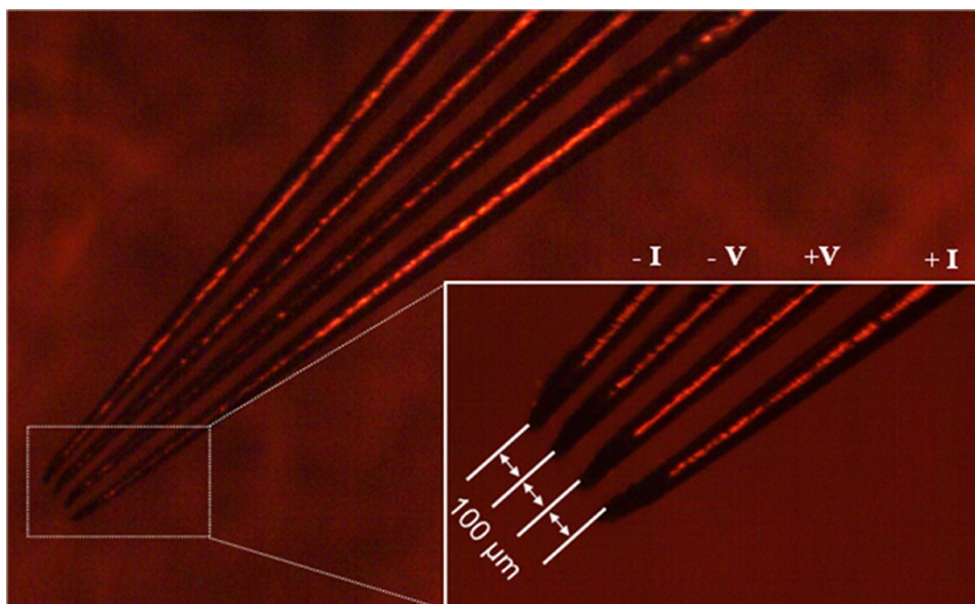


Fig. S7 Optical microscope image of 4 point probe tips and configuration (the pitch distance of each tips at 100 μm). The probe tips are made of Cu-Be. A Keithley 2400 source measure unit attached to the JANIS STX-500-1 is used to make the measurements.

Table S1. Comparison of the sheet resistance and conductivity.

Compounds	Sheet Resistance ($\Omega \text{ sq}^{-1}$)	Conductivity (S cm^{-1})	Thickness (nm)
spiro-OMeTAD	1.65×10^8	3.03×10^{-4}	200
Triazine-Flu	1.47×10^8	3.40×10^{-4}	200
Triazine-InT	1.15×10^8	4.35×10^{-4}	200

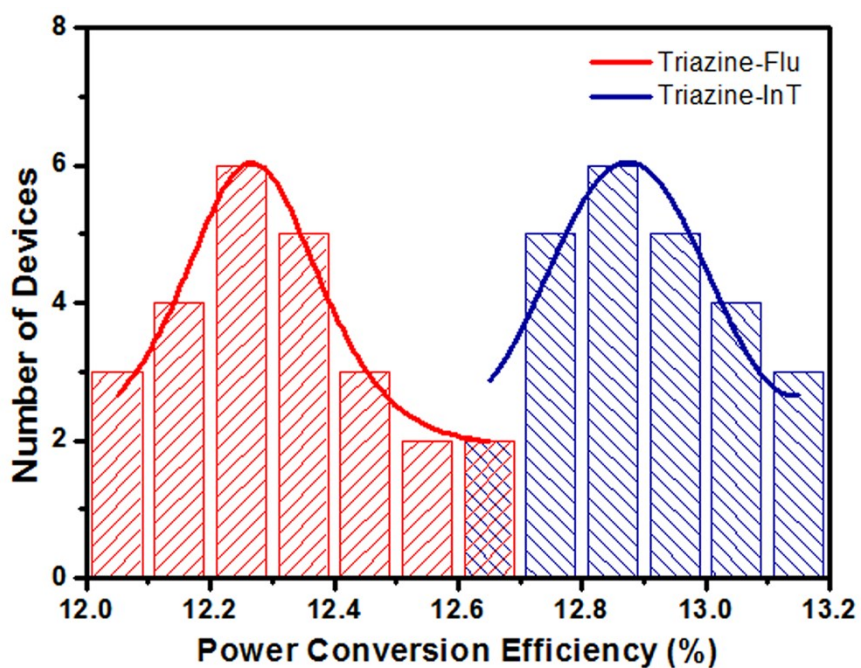


Fig. S8 Histogram of the PCEs obtained from the **Triazine-Flu** (red) and **Triazine-InT** based (blue) hybrid solar cells.

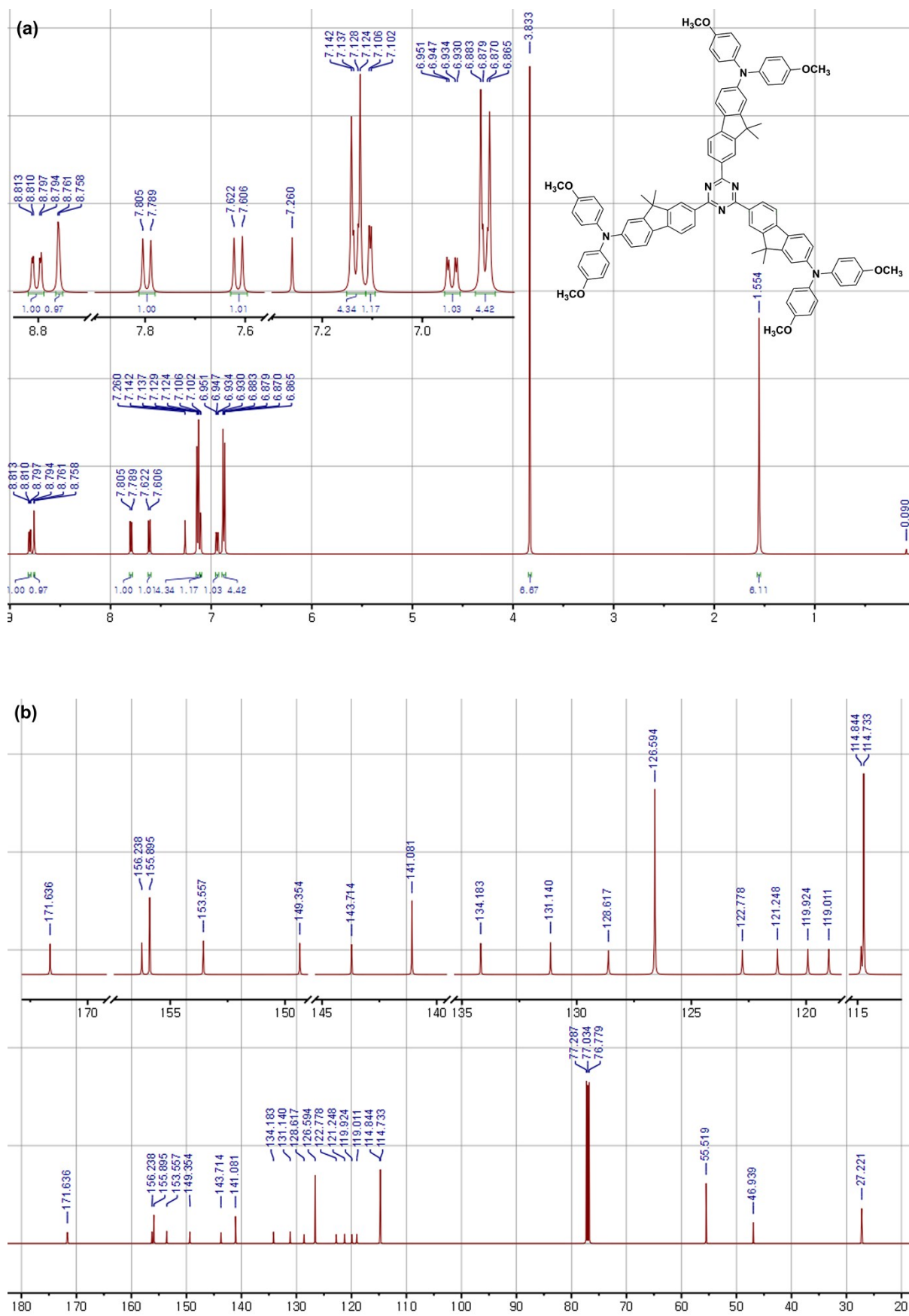


Fig. S10 (a) ^1H NMR and (b) ^{13}C NMR of Triazine-Flu

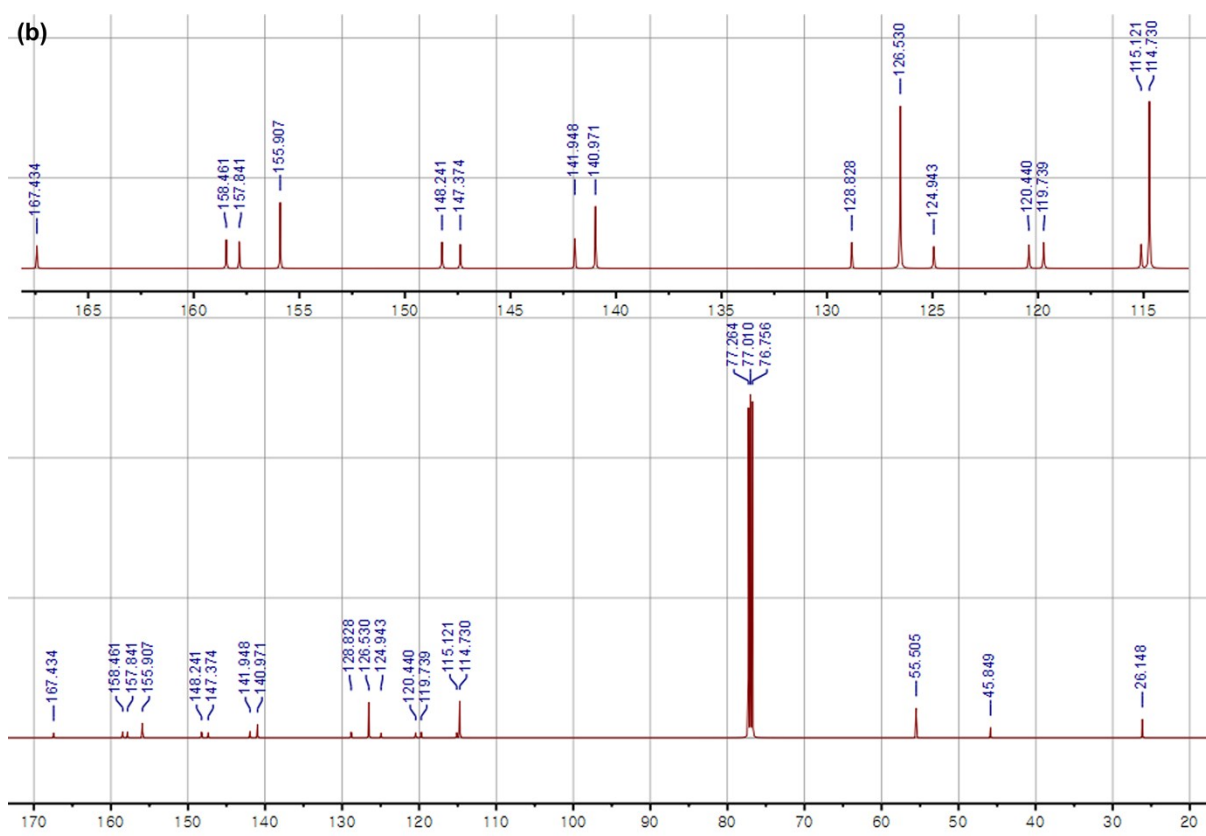
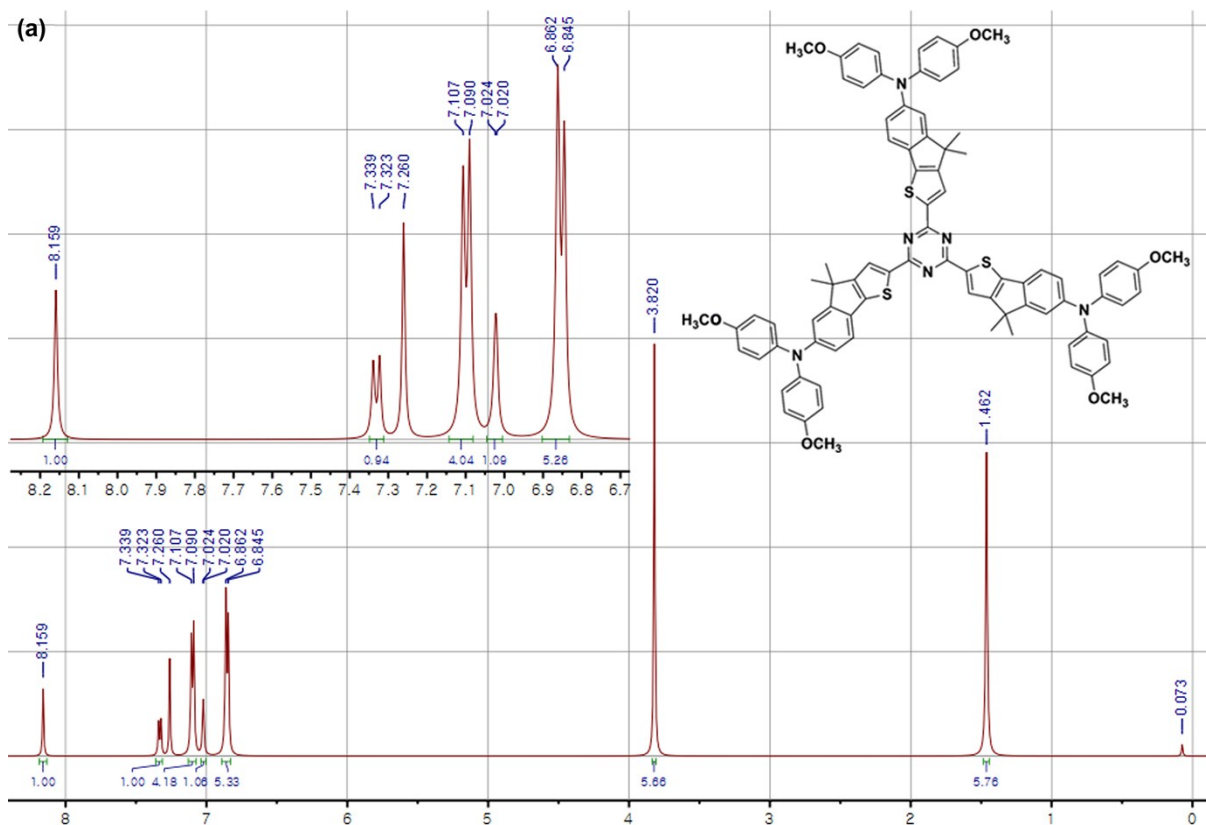


Fig. S11 (a) ^1H NMR and (b) ^{13}C NMR of Triazine-Int

References

1. *Adv. Mater.* 2011, **23**, 2367–2371
2. *Tetrahedron*, 2009, **65**, 9626–9632
3. *J. Am. Chem. Soc.*, 2010, **132**, 10944–10952
4. *ChemSusChem*, 2013, **6**(8), 1425–1431