Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting information

A Simple Spiro Type Hole Transporting Material for Efficient Perovskite Solar Cells

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Experimental Section

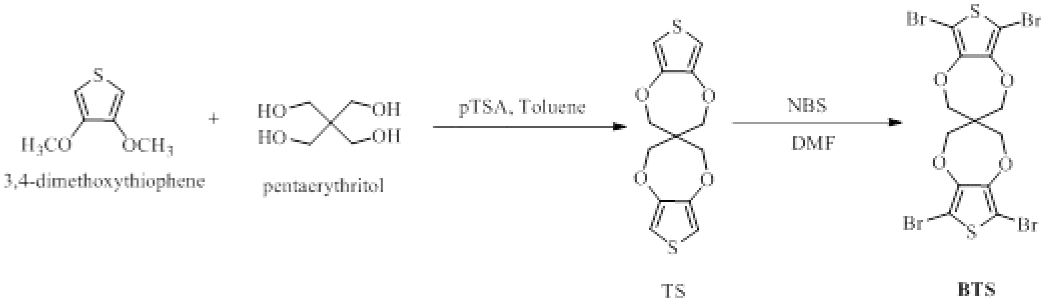
1. Material Synthesis

All chemicals were purchased from either Sigma-Aldrich or TCI and they were used as received without further purication unless otherwise specified

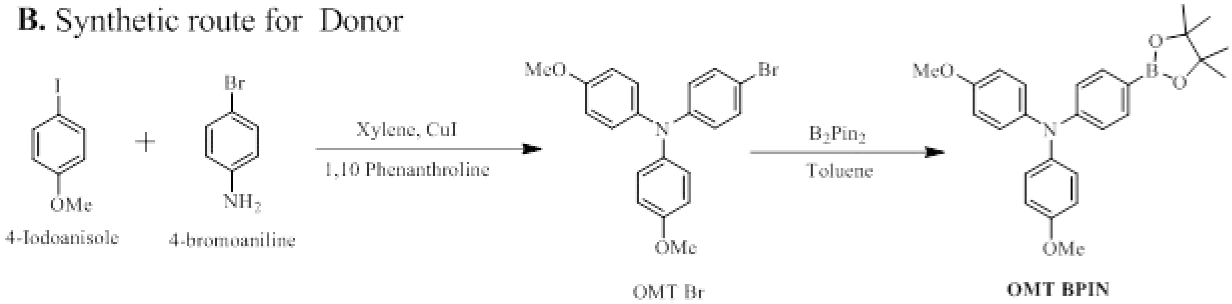
Synthesis of methyl ammonium iodide

CH_3NH_3I was prepared according to the reported procedure [1, 2]. Hydroiodic acid (57 wt. % in water, Aldrich) and methylamine (40% in methanol, TCI) were purchased from Sigma-Aldrich and used without further purification. They were mixed in 1:1 ratio and stirred in the ice bath for 2 h, and then evaporated at 50°C for 1 h with rotary evaporator. It was further washed with diethyl ether multiple times and dried under vacuum.

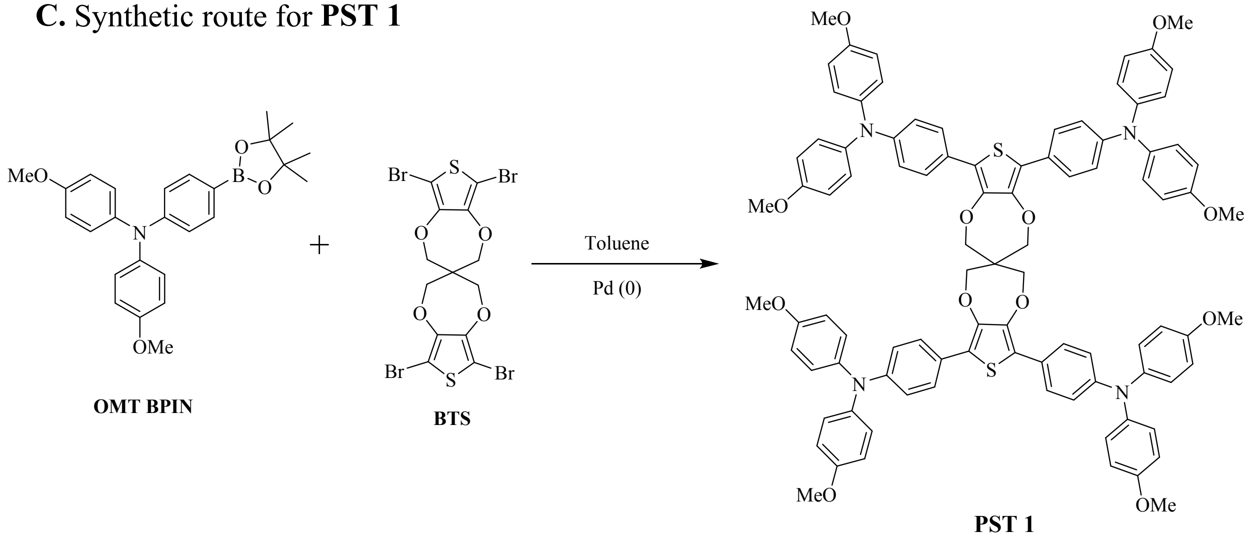
A. Synthetic route for thiophene based spiro compound



B. Synthetic route for Donor



C. Synthetic route for **PST 1**



Scheme S1. Synthesis of PST1.

Synthesis of TS

3,4-dimethoxythiophene (2.0 g, 0.014 mol), *p*-toluenesulphonic acid (0.26 g, 0.00138 mol), pentaerythritol (11.3 g, 0.083 mol), was charged in toluene (250 ml) in a 500 ml round bottomed flask. The reaction mixture was then refluxed under N_2 for 24 h and then cooled to room temperature and washed with water. The organic layer was separated and dried. The resulting crude mixture was purified through a silica gel plug using DCM as eluent. The obtained solid was recrystallized from chloroform to yield white crystals of TS (2.5 g, 61 %). 1H NMR (400 MHz, Chloroform-d) δ 6.49 (s, 2H), 4.08 (s, 8H). 13C NMR ($CDCl_3$) δ (ppm): 50.67, 71.37, 105.39, 149.04.

Synthesis of BTS

N-Bromosuccinimide (1.35 g, 0.0076 mol) in DMF (30 mL) was added to a solution of TS (0.5 g, 0.00169 mol) in $CHCl_3$ (30 mL) over 45 min. The mixture was stirred at room temperature for 6 h and then concentrated under reduced pressure. Water (200 mL) was added into the residue with stirring. The precipitate was filtered and washed with water and methanol, and the crude product was purified by recrystallization from THF/MeOH (1/3) to give BTS as a white crystalline solid (1.2 g, 76%). 1H NMR ($CDCl_3$) δ (ppm): 4.16 (s, 8H). 13C NMR ($CDCl_3$) δ (ppm): 146.07, 91.33, 71.03, 50.84.

Synthesis of OMT Br

4-bromoaniline (5.00 g, 29.2 mmol), 4-iodoanisole (14.4 g, 61.3 mmol), CuI (0.28 g, 1.46 mmol), KOH (12.8 g, 228 mmol), and 1,10-phenanthroline (0.26 g, 1.46 mmol) were added in Xylene (30 mL) and the reaction mixture was heated to 120^{o}C. Reaction was continued for 36 h and then the reaction mixture was cooled to room temperature, diluted with CH_2Cl_2(200 mL), and washed four times with 150 mL portions of water. The combined organic phases were dried over anhydrous $MgSO_4$, and the solvent was evaporated subsequently. Raw product was purified by column chromatography on silica gel using an eluent of DCM: Hexane (1:1) which afforded OMT Br (6.35 g, 57%) as yellow oily liquid. 1H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2H), 7.07 – 7.02 (m, 4H), 6.87 – 6.83 (m, 4H), 6.83 – 6.78 (m, 2H), 3.82 (s, 6H).

Synthesis of OMT BPIN

OMT Br (2.0, 0.0052 mol), Bis(pinacolato)diboron (1.6 g, 0.00625 mol), potassium acetate (1.5 g, 0.0156 mol) were dissolved in dioxane (40.0 ml). This solution was degassed for 20 min under nitrogen and then Pd_2dba_3 (25 mg) and X-Phos (50 mg) were added simultaneously. The reaction was then brought to 80 °C for 12 hours. The reaction was then cooled to RT, and plugged through a thin pad of $MgSO_4$ with DCM. The crude product was purified with gradient silica gel chromatography: 100% hexane to 50:50 Hexane:DCM to give OMT BPIN (1.5 g, 67 %) as yellow solid. 1H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.59 (m, 2H), 7.12 – 7.07 (m, 4H), 6.92 – 6.88 (m, 2H), 6.88 – 6.84 (m, 4H), 3.82 (s, 6H), 1.35 (s, 12H).

Synthesis of PST 1

OMT BPIN (1.1 g, 0.00245 mol), BTS (0.25 g, 0.00041 mol) were dissolved in Toluene (30.0 ml) and 2M K_2CO_3 aqueous solution (10.0 ml). This solution was degassed for 30 min under nitrogen and then Pd (0) (100 mg) was added. The reaction was then brought to 100 ^{o}C and stirred for 24 hours. The reaction was then cooled to RT, and washed with water (100 ml), brine solution (100 ml) and the organic layer was separated and dried. The crude product was purified with gradient silica gel chromatography: 100% hexane to 50:50 Hexane:DCM to give PST 1 (0.31 g, 50%) as yellow solid. 1H NMR (400 MHz, THF-d8) δ 7.52 (d, J = 8.5 Hz, 8H), 7.03 (d, J = 8.6 Hz, 16H), 6.85 (m, J = 6.9 Hz, 24H), 4.24 (s, 8H), 3.76 (s, 24H). 13C NMR (101 MHz, THF-d8) δ = 154.45, 145.75, 142.87, 138.76, 124.98, 124.56, 123.25, 118.11, 116.36, 112.61, 68.77, 52.76, 48.67.

2. Chemical analysis and photophysical and electrochemical characterization

All the compounds synthesized in this thesis work were characterized by 1H NMR, 13C NMR and mass spectrometry. Thin-layer chromatography (TLC) was conducted with Merck KGaA precoated TLC Silica gel 60 F254 aluminum sheets and visualized with UV. Flash column chromatography was performed using Silicycle UltraPure SilicaFlash P60, 40-63 μm (230-400 mesh). 1H and 13C NMR spectra were obtained using a Bruker spectrometer (400 MHz), Bruker AvanceIII-400 (400MHz), Bruker DPX-400 (400 MHz) and are reported in ppm using THF-d8 solvent as an internal standard: Mass spectra were obtained with Bruker daltonics, FT-ICR/APEX II, ESI mode. MALDI-TOF mass spectra were recorded using Micromass Tof Spec 2E instrument. High-resolution mass spectra were obtained at the École Polytechnique Fédérale de Lausanne mass spectrometry laboratory (EPFL). Absorption spectral measurements were recorded using JASCO V630 UV–visible spectrophotometer. Cyclic voltammetry was measured with an Autolab Eco Chemie cyclic voltammeter in dichloromethane solvent. The experimental setup consisted of a glassy carbon working electrode, platinum wire counter electrode and platinum reference electrode. All samples were deaerated by bubbling with pure nitrogen gas for ca. 5min at room temperature. The system was initially calibrated with ferrocene/ferrocenium (Fc/Fc^{+}) redox couple. Differential scanning calorimetry (DSC) measurements were conducted using a DSC8000 (Perkin Elmer) calorimeter at a rate of 10°C min^{-1} from 30 to 200°C under N_2. Approximately 2–5 mg of sample powder was used in each experiment using aluminum pans and lids. The data was recorded and analyzed using Pyris – Instrument Managing Software (Perkin Elmer). The cross-section view of perovskite-based device was taken with a high-resolution scanning electron microscope (ZEISS Merlin).

3. X-ray crystallography

The crystals of **PST1** were invariably twinned pseudo merohedrally and did not scatter well, even at T=170K. This temperature was provided by a CryoStream by Oxford CryoStream. The crystal were taken out of their mother liquors just prior to the data collection, enrobed in a drop of HOSTINERT from HOECHST and immediately brought in the cold stream. X-ray intensities were collected on an IPDS 2T from Stoe, equipped with a XENOCS CuKalpha Beam Delivery System at T=170K. This temperature was maintained with the help of a Cryostream from Oxford Cryostream. The unit cell was determined with the help of the X-Area program, as was the integration. The absorption correction, based on the habitus of the crystal, was computed by means of the XRed32 program. The crystals displayed {100} (platelet face) and {10} pinacoids, and (110), (0) and (1) pedions.

The model was found with the help of SIR2004 and the refinement carried out by SHELXSTL in the space group Cc. A pseudo-inversion centre appeared at $(\frac{1}{4}\frac{1}{4}0)$, but a refinement in the space group $C\frac{2}{c}$ suffers from a major disorder around the common carbon atom of the two dioxepine moieties. For this reason, the non-centrosymmetric refinement was preferred, although that in $C\frac{2}{c}$ resulted in better agreement factors (e.g. R_1~0.014). That these are not so good may, perhaps, be understood by looking at the packing coefficient of ~0.501. Also, precise information on the included solvent molecules is missing. This might also explain the large average U_{iso} values.

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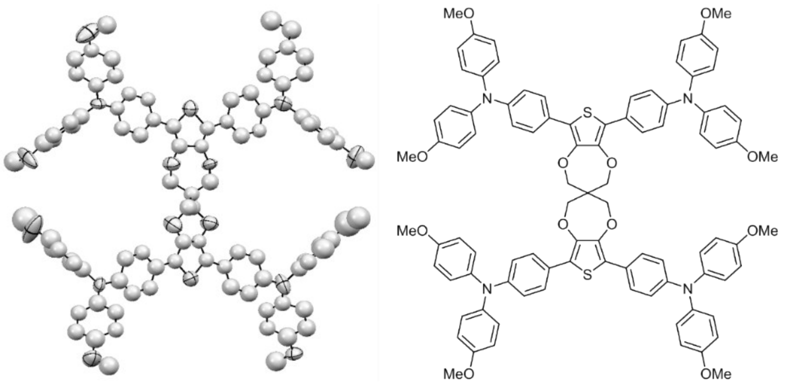
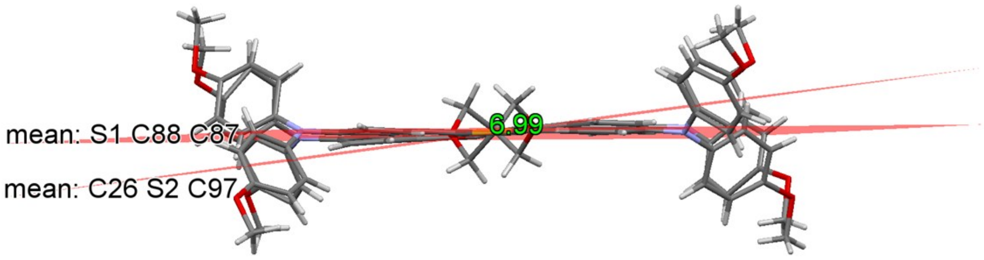
CCDC-1024446 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.





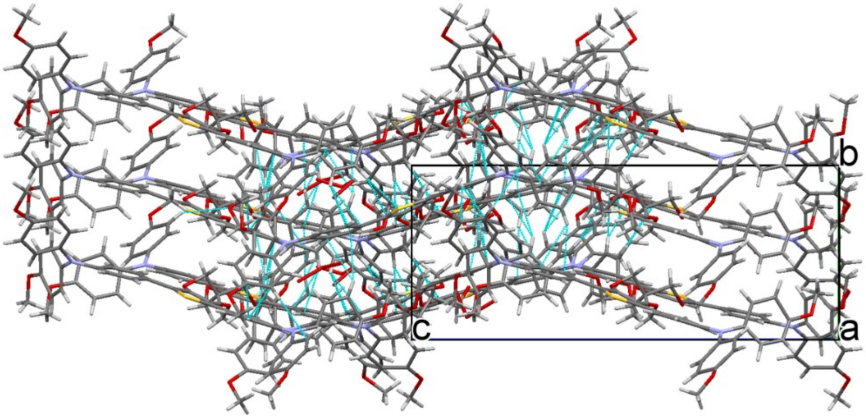


Figure S1. Perspective view, dihedral angle and stacking of PST1.

Intensity data of spiro-OMeTAD single crystal were collected on an Oxford Diffraction KM-4 CCD diffractometer by using graphite-monochromatized Mo Ka radiation (λ=0.71073 Å) at low temperature [140(2) K]. A summary of the crystallographic data, the data collection parameters, and the refinement parameters are given in Table S1.

The data reduction was carried out by Crysalis PRO [4]. The solution and refinement were performed by SHELX [5]. The crystal structure was refined using full-matrix least-squares based on F2 with all non hydrogen atoms anisotropically defined. Hydrogen atoms were placed in calculated positions by means of the "riding" model.

CCDC-1024447 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

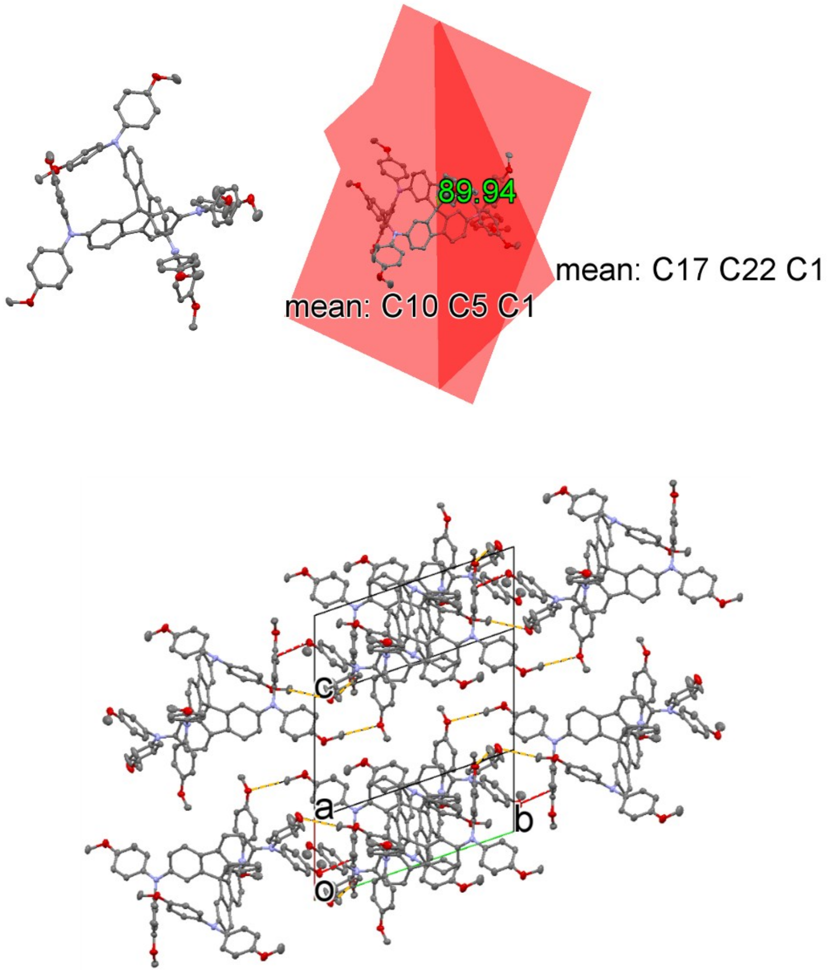


Figure S2. Perspective view, dihedral angle, stacking and S-C short contacts of spiro-OMeTAD.

Table S1. Crystallographic parameters of PST1 and spiro-OMeTAD

	PST1	*spiro-OMeTAD*
Empirical formula	$C_{93}H_{80}N_4O_{12}S_2$	$C_{81}H_{68}N_4O_8$
Formula weight	1509.799	1225.455
Crystal color, habit	Yellow, needle	Colorless, needle
Crystal system	Monoclinic	triclinic
a, Å	43.879(9)	13.1111(7)
b, Å	9.5887(19)	16.1465(7)
c, Å	25.050(5)	16.9214(9)
β, deg	109.94(3)	85.670(4)
V, $Å^3$	9907.76	3358.57
ρ calc, g/cm^3	1.141	1.267
Space group	C c	P -1
Z value	4	2
Temperature, K	170	140
no. of reflections measured	13303	23601
no. of variables	574	909
Residuals: R; wR2	0.1553, 0.3809	0.0419, 0.1068

4. Thermal Analysis

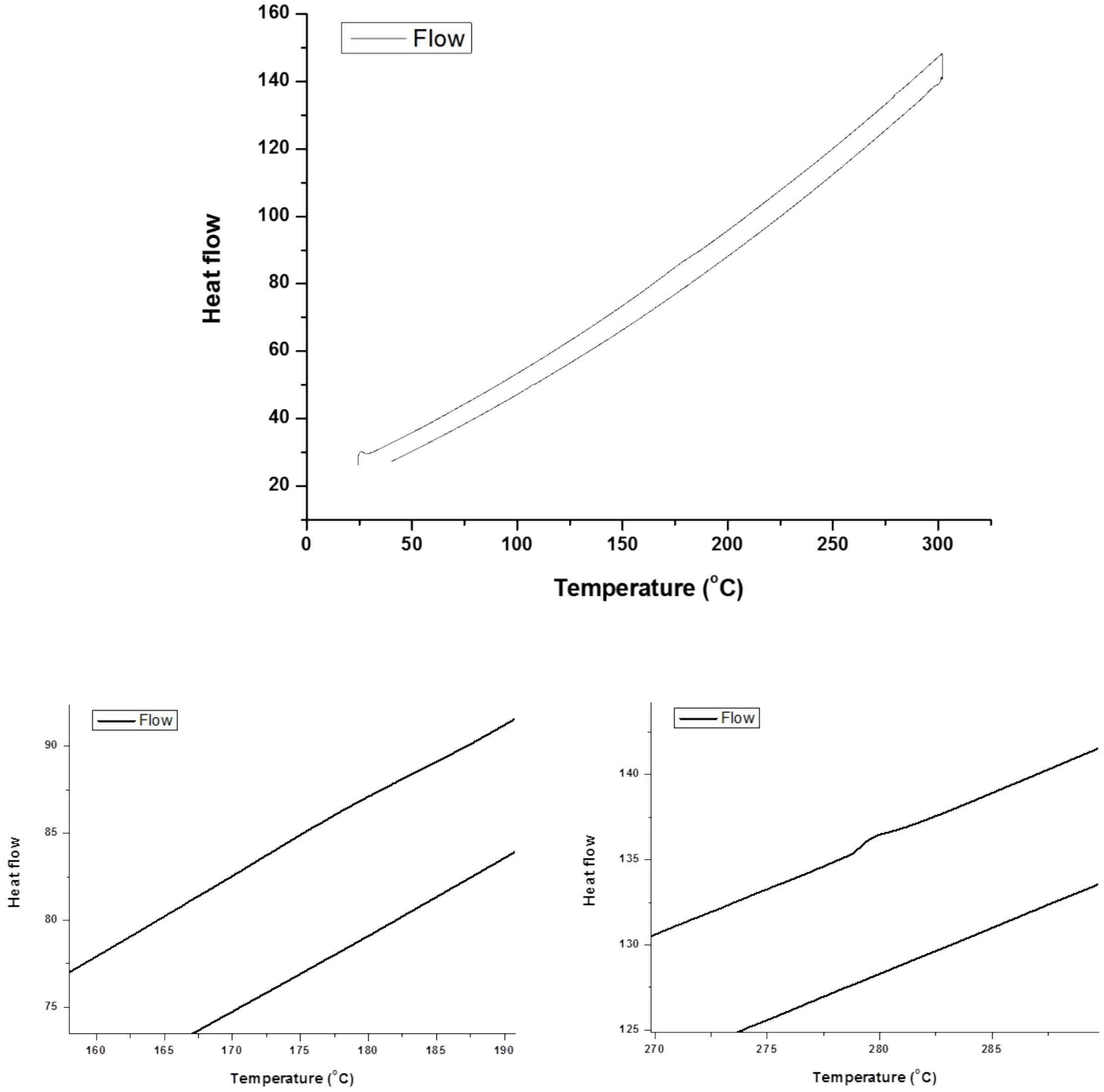


Figure S3. DSC heating and cooling curves for PST1

5. Device fabrication

FTO glasses (NGS 10, resistance ~ 10 ohm/square) were patterned by laser etching to give the desired electrode configuration and cleaned in an ultrasonic bath with Hellmanex soap solution, DI H_2O and ethanol for 15 min, respectively. A dense TiO_2 blocking layer was made by spray pyrolysis process, with titanium diisopropoxide bis(acetylacetonate) (75%, Sigma-Aldrich), mixed with acetylacetone (3:2) and diluted in ethanol (1:9). Nanocrystalline TiO_2 film was made by spin-coating Dyesol 30NRD paste and sintered at 500°C for 15 min. Post-treatment of $TiCl_4$ was done by immersing substrates into 40 mM aqueous $TiCl_4$ solution at 70 °C for 30 min. After rinsing and drying, the films were heated to 500°C for 30 min. After cooling to room temperature, 1.2 M PbI_2 solution was spin-coated onto the mesoporous film and then heated at 70 °C for 30 min. The films were then immersed into 8 mg/ml CH_3NH_3I in IPA solution for 15 min, after which they were rinsed with IPA and dried by spinning at 4000 rpm for 30 s, followed by annealing at 100 °C for 15 min. HTM solution was prepared according to the reported recipe[3]. The as-prepared solution was spin coated onto the film at 4000 rpm for 30 s. Au cathode layer of 80 nm was deposited by thermal evaporation to complete the device.

6. Device characterization

Current–voltage characteristics were recorded by applying an external potential bias to the cell while recording the generated photocurrent with a digital source meter (Keithley Model 2400). The light source was a 450-W xenon lamp (Oriel) equipped with a SchottK113 Tempax sunlight filter (Praezisions Glas & Optik GmbH) to match the emission spectrum of the lamp to the AM1.5G standard. Before each measurement, the exact light intensity was determined using a calibrated Si reference diode equipped with an infrared cut-off filter (KG-3, Schott). IPCE spectra were recorded as functions of wavelength under a constant white light bias of approximately 5 $mW\cdot cm^{-2}$, supplied by an array of white light emitting diodes. The excitation beam coming from a 300-W xenon lamp (ILC Technology) was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd) and chopped at approximately 4 Hz. The signal was recorded using a Model SR830 DSP Lock-In Amplifier (Stanford Research Systems). All measurements were conducted using a non-reflective metal aperture of 0.159 cm^2 to define the active area of the device and avoid light scattering through the sides.

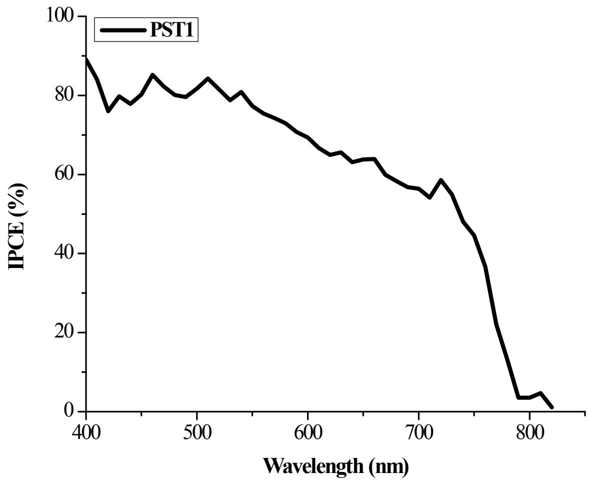


Figure S4. IPCE of the perovskite solar cell made with PST1 as HTM.

7. Device stability test

Normalized cell efficiency plotted as a function of storage time for perovskite solar cells both with PST1 (red cubic) and Spiro-OMeTAD (black circles) as HTM layer. Measurements were made on 3 devices of each type, and the error bars represent plus or minus one standard deviation from the mean.

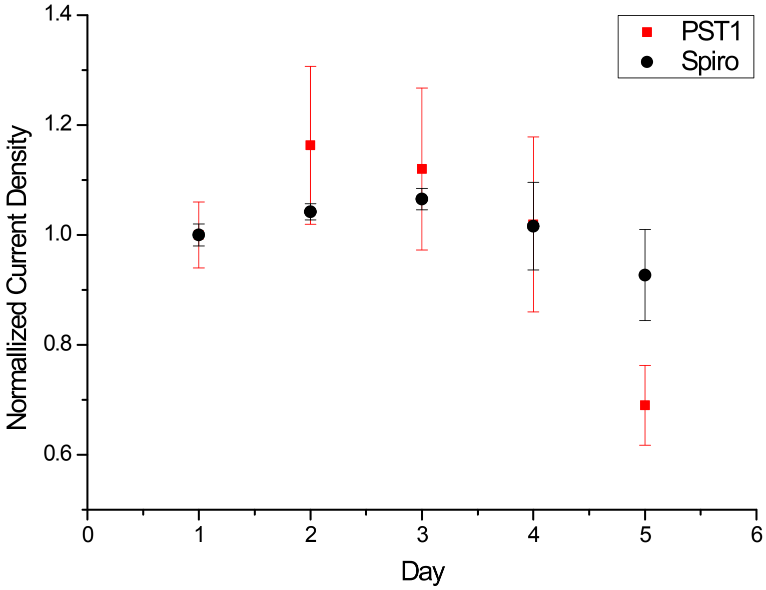


Figure S5. Comparison of J_{SC} change with time

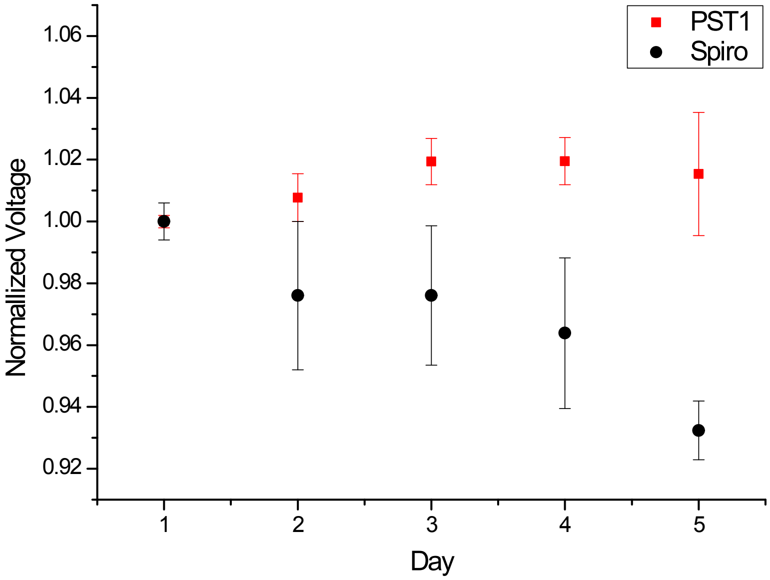


Figure S6. Comparison of V_{OC} change with time

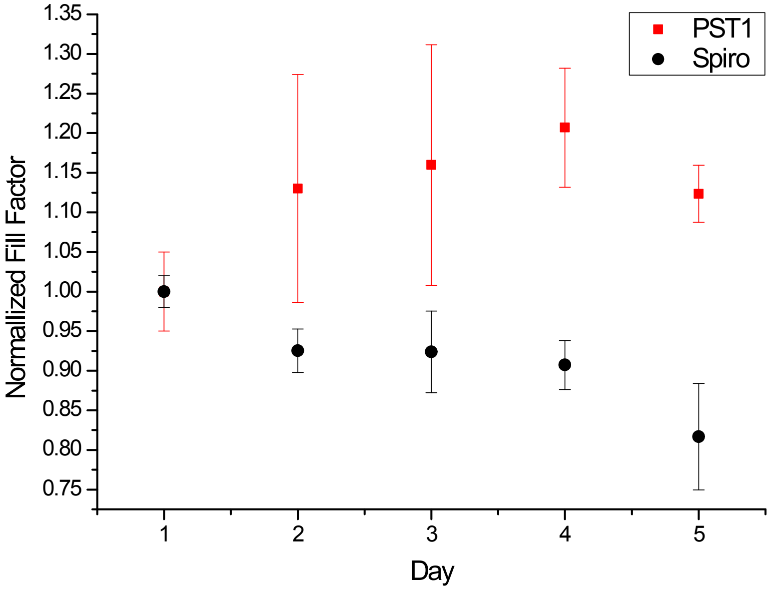


Figure S7. Comparison of FF change with time

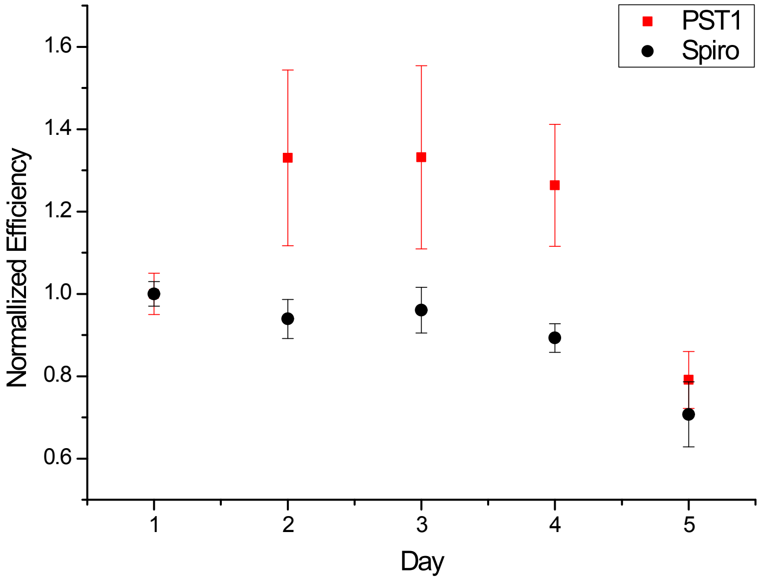


Figure S8. Comparison of efficiency change with time

8. NMR spectra of PST1

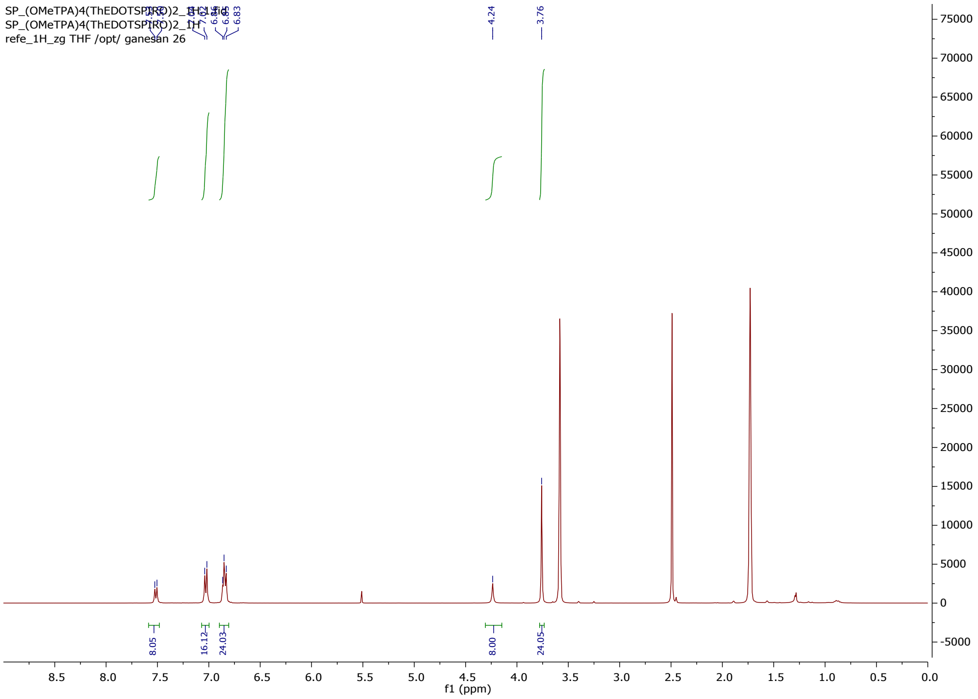


Figure S9. 1H NMR of PST1

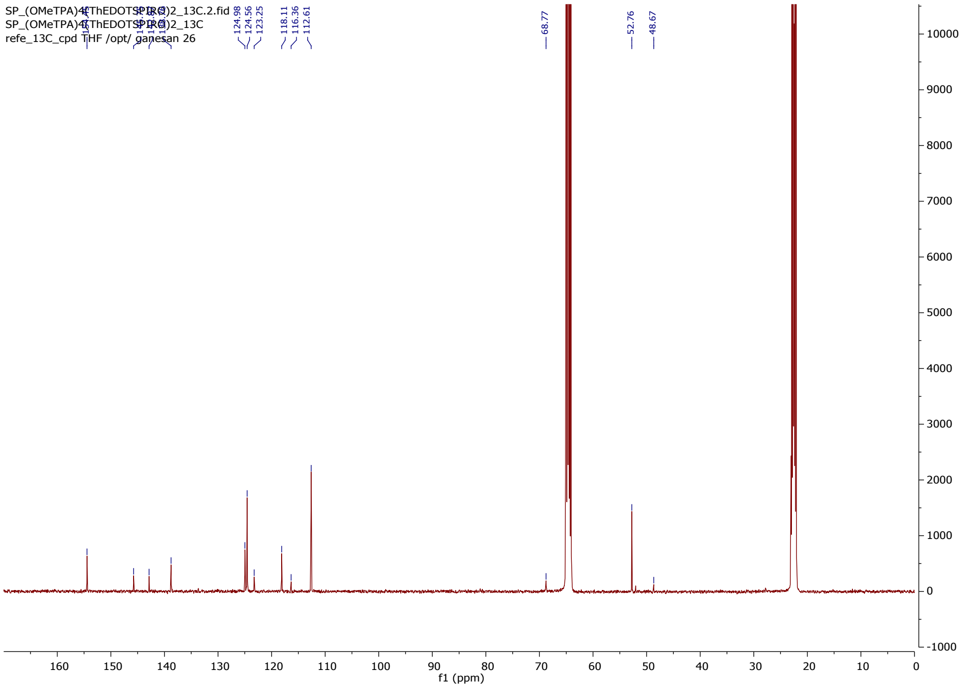


Figure S10. 13C NMR of PST1

References

1. Im, J.H., et al., *6.5% efficient perovskite quantum-dot-sensitized solar cell.* Nanoscale, 2011. **3**(10): p. 4088-93.
2. Kim, H.S., et al., *Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%.* Scientific reports, 2012. **2**: p. 591.
3. Burschka, J., et al., *Sequential deposition as a route to high-performance perovskite-sensitized solar cells. Nature, 2013. 499(7458): p. 316-319.*
4. *Crysalis PRO, Agilent Technologies, release 1.171.37.31, 2014.*
5. *SHELX, G. M. Sheldrick, Acta Crystallogr., Sect. A 2008, 64, 112-122.*