*Supporting Information*

**Molecular Design with Silicon Core: Toward Commercially Available Hole Transport Materials for High-performance Planar *p-i-n* Perovskite Solar Cells**

*Rongming Xue,* [a] *Moyao Zhang,* [a] *Guiying Xu,* [a] *Jingwen Zhang,* [a] *Weijie Chen,* [a]*Haiyang Chen, Ming Yang,* [c] *Chaohua Cui,* [a] *Yaowen Li,** [a] *Yongfang Li**[a, b]

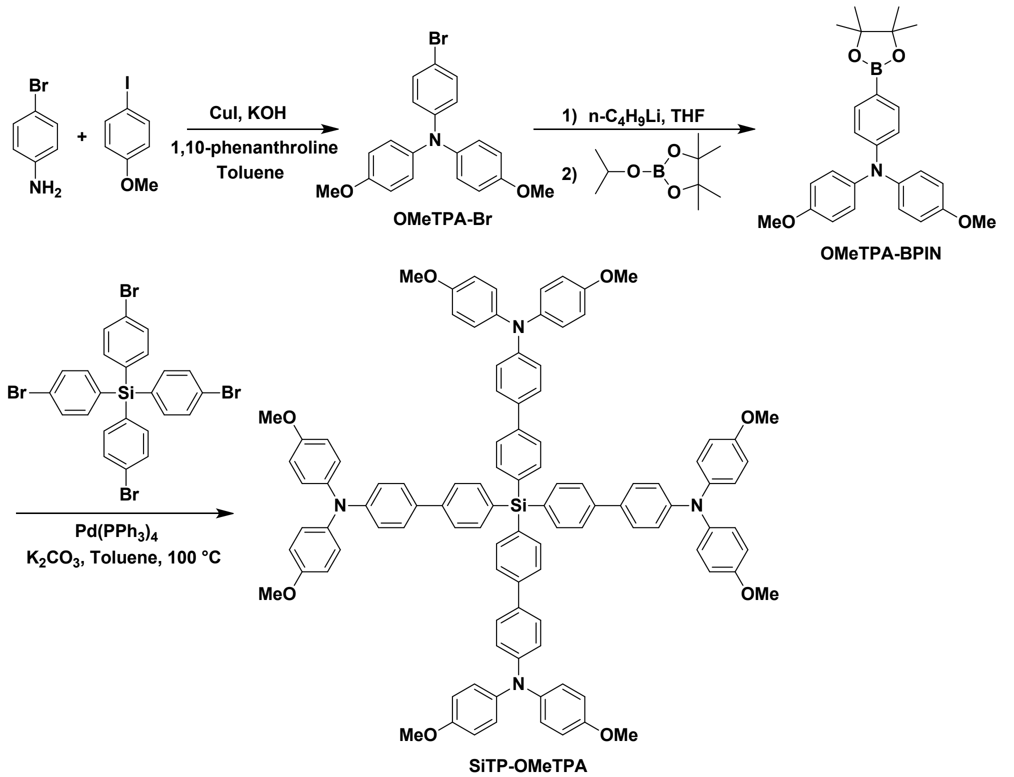
[a] *Laboratory of Advanced Optoelectronic Materials, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China*
*Email:* *ywli@suda.edu.cn* (Li. Y. W.)

[b]*Beijing National Laboratory for Molecular Sciences; Institute of Chemistry, Chinese Academy of* Sciences, Beijing 100190, *China*
*Email:* *liyf@iccas.ac.cn* (Li. Y. F.)

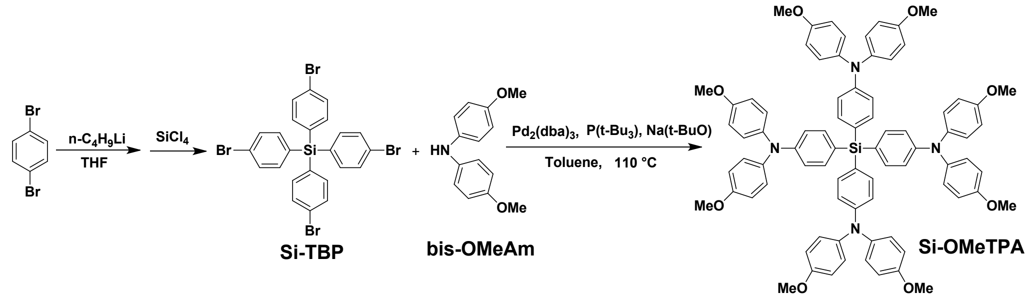
[c] College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

**Materials**.

Lead (II) iodide (ultra-dry, 99.999%) and PTAA (Mw 10,000-100,000 by GPC) Were purchased from Xi'an Polymer Light Technology Corp. MAI (Methanaminium iodide, 99.999%) was purchased from Shanghai Mater. Win New Materials Co. , Ltd. PEDOT:PSS (Clevious P VP AI 4083) was purchased from H. C. Stark company. 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) were purchased from Jilin OLED company. $PC_{61}BM$ was purchased from Solarmer Materials Inc. The ultra-dry solvents used in device fabrication process were purchased from J&K. 1,4-dibromobenzene was purchased from TCI. Bis(4-methoxyphenyl)amine was purchased from Accela ChemBio Co., Ltd. $SiCl_4$ was purchased from Energy Chemical. All the synthetic monomers can be commercially obtained easily and all the materials were used as received without any purification.




**Scheme S1.** Sythesis route of SiTP-OMeTPA.




**Scheme S2.** Synthesis route of Si-OMeTPA.

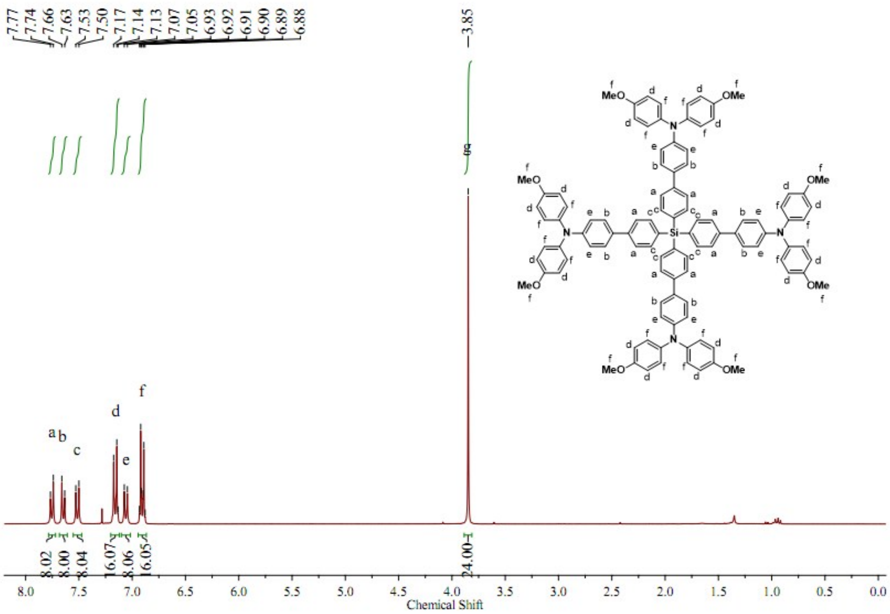



**Fig. S1**. [1]H NMR spectrum of SiTP-OMeTPA.

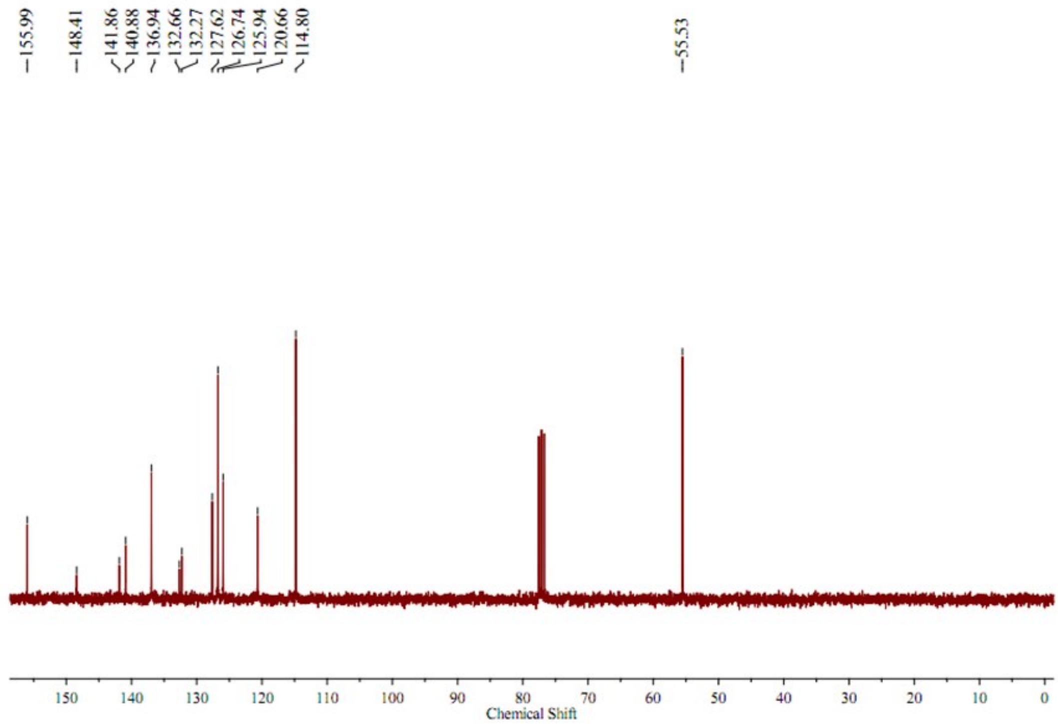



**Fig. S2** $^{13}$C NMR spectrum of SiTP-OMeTPA.

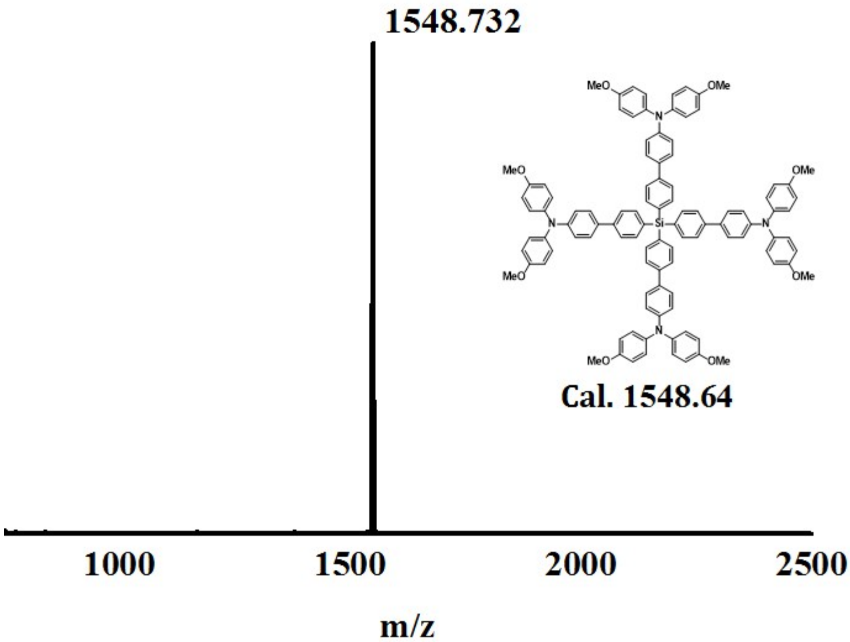



**Fig. S3** MALDI-TOF mass spectrum of SiTP-OMeTPA.

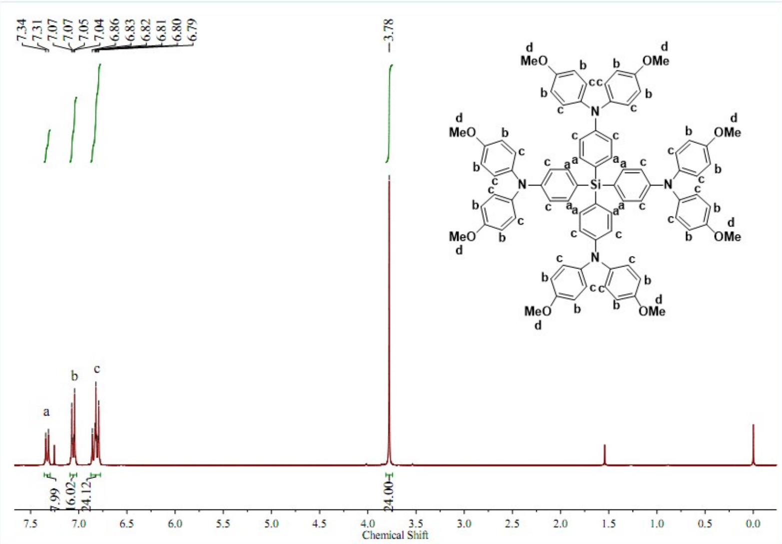



**Fig. S4** $^{1}H$ NMR spectrum of Si-OMeTPA.

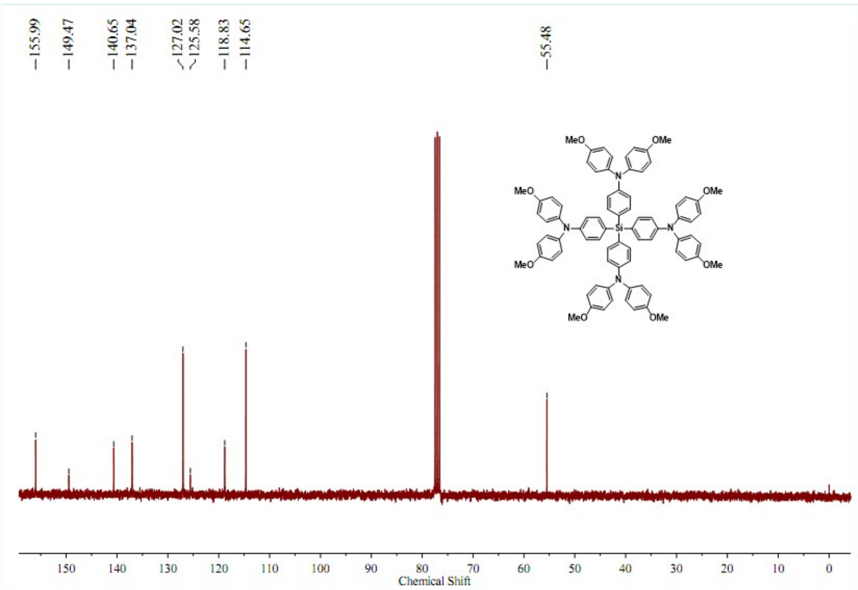



**Fig. S5** $^{13}C$ NMR spectrum of Si-OMeTPA

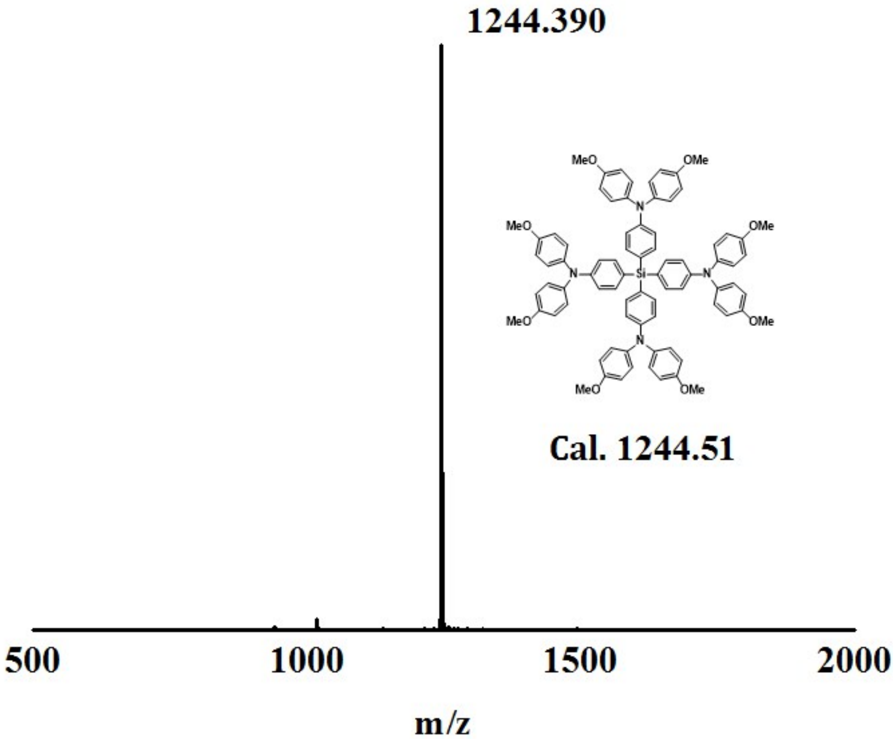


**Fig. S6** MALDI-TOF mass spectrum of Si-OMeTPA.

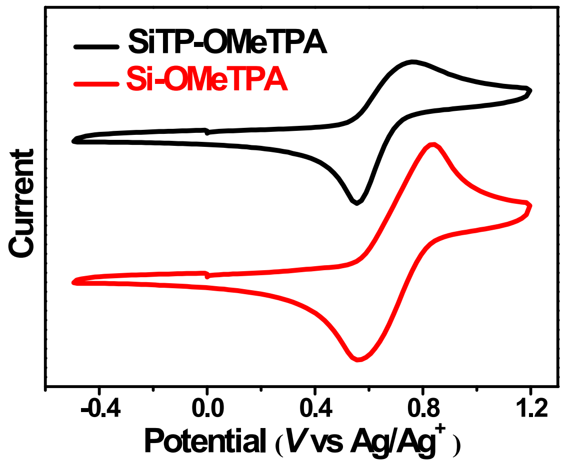



**Fig. S7** Cyclic voltammograms of SiTP-OMeTPA and Si-OMeTPA.

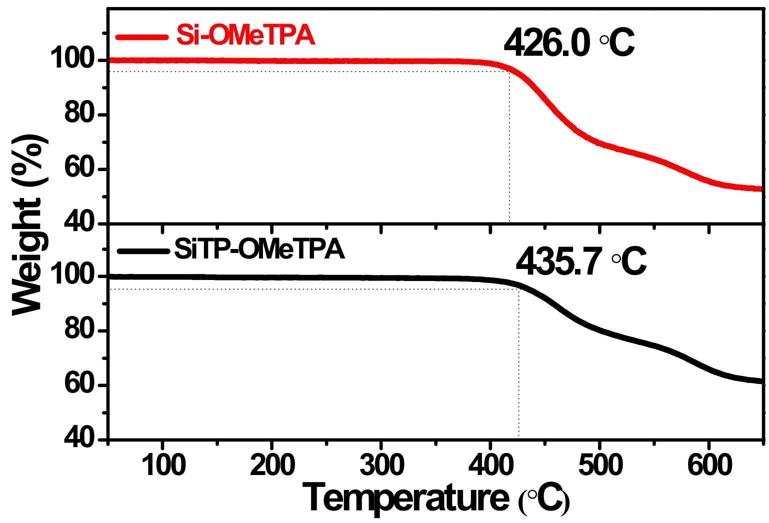



**Fig. S8** TGA thermograms of SiTP-OMeTPA and Si-OMeTPA at a heating rate of 10 °C/min under $N_2$.

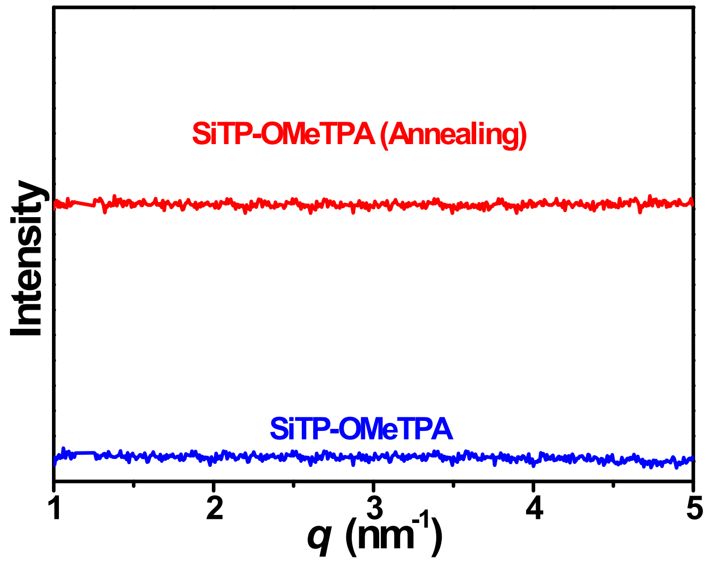



**Fig. S9** XRD patterns of SiTP-OMeTPA films with or without thermal annealing.

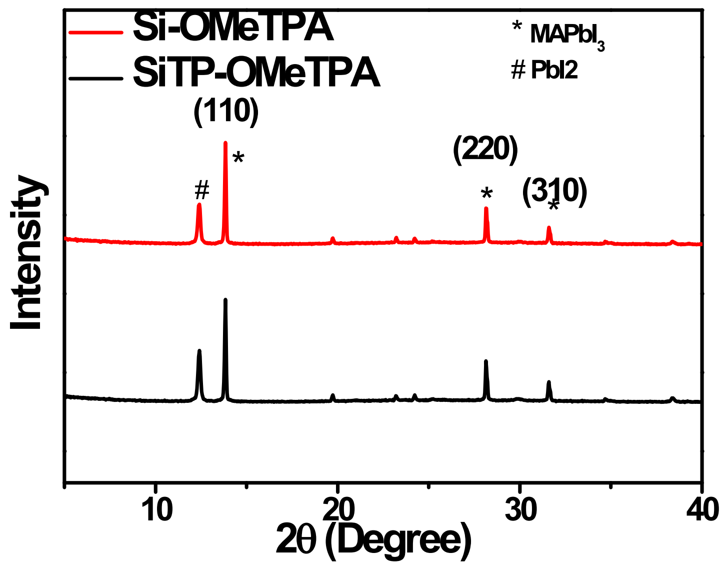



**Fig. S10** XRD patterns of perovskite film grown on SiTP-OMeTPA and Si-OMeTPA HTLs.

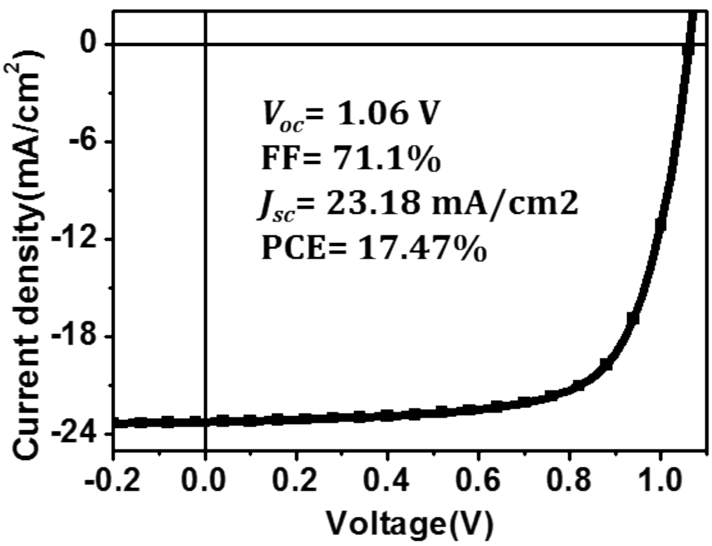



**Fig. S11** PCE of pero-SCs with PTAA HTL, where the PTAA was doped with 1 wt% F4-TCNQ and thermal annealed at 100 $^{o}$C for 10 min.

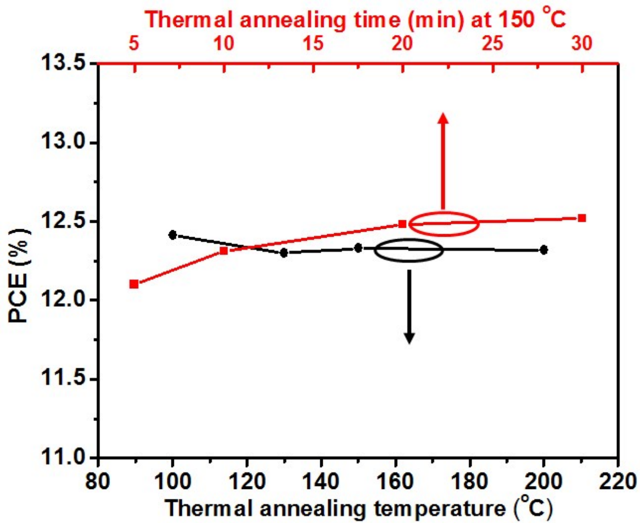



**Fig. S12** PCE evolution of pero-SCs with a 30-nm-thick Si-OMeTPA HTL at different thermal annealing temperatures with different annealing time.

**Table S1.** Values for TRPL characteristics of $MAPbI_3$ grown on different HTLs coated ITO substrate.

| HTL | Treatment | τ (ns) |
|---|---|---|
| none | -- | 95.78 |
| Si-OMeTPA | as-cast | 43.19 |
| Si-OMeTPA | annealed | 24.29 |
| Si-OMeTPA | doped/annealed | 22.35 |
| SiTP-OMeTPA | doped/annealed | 27.62 |

**Synthesis cost estimation of 1-gram HTMs:**

We estimated the synthesis cost of 1-gram Si-OMeTPA and SiTP-OMeTPA using the cost model that was described by Pablo *et al*.[1] and Osedach *et al*.[2] The estimated synthesis cost of Si-OMeTPA and SiTP-OMeTPA is ca. 19.71 $/g and 23.4 $/g, respectively. When further taking several important parameters (e.g. energy consumption, waste treatment and labor) into account, the synthesis cost was multiplied by a factor of 1.5[3] to obtain a more realistic costs of ca. 29.57 $/g and 35.1 $/g, respectively, which are much cheaper than that of PTAA (423.3 $/g)[4].

**Table S2.** Materials quantities and cost for the synthesis of 1-gram Si-OMeTPA

| Chemical name | Price of chemical (RMB/quantity) | Weight or volume of Chemical | Material cost (RMB) |
|---|---|---|---|
| 2.4 M *n*-BuLi | 405.6/500 mL | 4.75 mL | 3.85 |
| silicon tetrachloride | 52.25/25 g | 0.23 g | 0.48 |
| 1,4-dibromobenzene | 54.3/25 g | 1.4 g | 3.04 |
| bis(4-methoxyphenyl)amine | 540/25 g | 1.81 g | 39.1 |
| sodium tert-butoxide | 146.64/100 g | 0.63 g | 0.92 |
| tri-tert-butylphosphine in toluene | 766.16/50 mL | 0.067 mL | 1.03 |
| tris(dibenzylideneacetone)di-palladium (0) | 2346/5 g | 0.032 g | 15.01 |
| petroleum ether | 155/20 L | 3 L | 23.25 |
| dichloromethane | 125/18.9 L | 1.5 L | 9.9 |
| tetrahydrofuran | 18.3/500 mL | 50 mL | 1.83 |
| toluene | 7.11/500 mL | 30 mL | 0.43 |
| magnesium sulphate | 17.77/500 g | 5 g | 0.18 |
| Sodium | 25/250 g | 2 g | 0.2 |
| Silica gel (200-300mesh) | 39/kg | 0.8 kg | 31.2 |
| Total | | | 130.42 RMB/g= 19.71 $/g |

**Table S3** Materials quantities and cost for the synthesis of 1-gram SiTP-OMeTPA

| Chemical name | Price of chemical (RMB/quantity) | Weight or volume of Chemical | Material cost (RMB) |
|---|---|---|---|
| 4-bromoaniline | 136/100 g | 1.95 g | 2.66 |
| 4-iodoanisole | 91.8/25 g | 5.6 g | 20.6 |
| copper(I) iodide | 88.4/50 g | 0.11 g | 0.19 |
| potassium hydroxide | 8.22/500 g | 4.98 g | 0.08 |
| isopropoxyboronic acid pinacol ester | 164.52/25 mL | 1.56 mL | 10.27 |
| potassium carbonate | 16.15/500 g | 2.76 g | 0.09 |
| 2.4 M *n*-BuLi | 405.6/500 mL | 6.38 mL | 5.18 |
| 1,10-phenanthroline | 108.7/25 g | 0.1 g | 0.43 |
| 1,4-dibromobenzene | 54.3/25 g | 1.16 g | 2.52 |
| tetrakis(triphenylphosphine)-palladium(0) | 1262.25/5 g | 0.033 g | 8.33 |
| petroleum ether | 155/20 L | 5 L | 38.75 |
| dichloromethane | 125/18.9 L | 3 L | 19.84 |
| tetrahydrofuran | 18.3/500 mL | 100 mL | 3.66 |
| toluene | 7.11/500 mL | 150 mL | 2.13 |
| magnesium sulphate | 17.77/500 g | 6 g | 0.21 |
| Sodium | 25/250 g | 3 g | 0.3 |
| Silica gel (200-300mesh) | 39/kg | 1 kg | 39 |
| Total | | | 154.64 RMB/g= 23.4 $/g |
| | | | |

## References


1. M. L. Petrus, T. Bein, T. J. Dingemans, P. Docampo, *J. Mater. Chem. A*, 2015, **3**, 12159-12162.
2. T. P. Osedach, T. L. Andrew, V. Bulovic, *Energy Environ. Sci.*, 2013, **6**, 711-718.
3. M. Saliba, S. Orlandi, T. Matsui, S. Aghazada, M. Cavazzini, J. Correa-Baena, P. Gao, R. Scopelliti, E. Mosconi, K. Dahmen, F. D. Angelis, A. Abate, A. Hagfeldt, G. Pozzi, M. Graetzel, M. K. Nazeeruddin, *Nature Energy*, 2016, **1**, 15017.
4. ⟨http://www.p-oled.cn/product/showproduct.php?lang=cn&id=243⟩.