Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Insights into Working Mechanism of Cathode Interlayer in Polymer Solar Cells via $[(C_8H_{17})_4N]_4[SiW_{12}O_{40}]$

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1. Synthesis and characterization of TASiW-12.

0.33 g $(C_8H_{17})_4NBr$ and 0.50 g $H_4SiW_{12}O_{40}$ were dissolved in 15 mL methanol, respectively, and the molar ratio of the organic cations to $H_4SiW_{12}O_{40}$ was controlled by ~ 3.5:1 (charge ratio: ~ 3.5:4). Under vigorous stirring at room temperature, the $(C_8H_{17})_4NBr$ solution was added dropwise to the $H_4SiW_{12}O_{40}$ solution with no significant change in the solution. After stirring at room temperature for 2 h, 30 mL H_2O was added dropwise, generating a white precipitate. The resulted precipitate was filtered, washed with 30 mL H_2O for three times and then dried in vacuum to give TASiW-12($[(C_8H_{17})_4N]_4[SiW_{12}O_{40}]$). Elemental analysis (%) calculated for $C_{128}H_{272}N_4SiW_{12}O_{40}$ (4741.7 g mol^{-1}): C 32.42, H 5.78, N 1.18; Found: C 32.26, H 5.50, N 1.18, corresponding to the chemical formula $[(C_8H_{17})_4N]_4[SiW_{12}O_{40}]$.

2. Ultraviolet-visible absorption spectrum of TASiW-12 film.

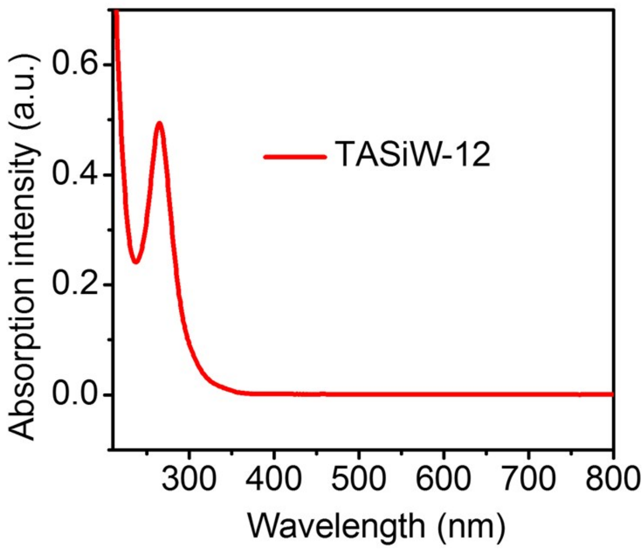


Figure S1. Ultraviolet-visible absorption spectrum of TASiW-12 film.

3. Ionized potential measurements of PDINO film and TASiW-12 film using UPS.

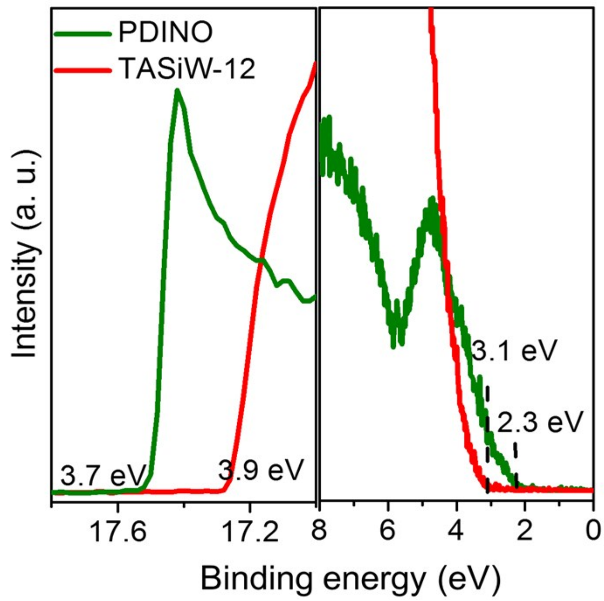


Figure S2. UPS spectra of 15 nm PDINO and 15 nm TASiW-12 films on ITO in the secondary electron cutoff region (left) and valence band region (right). HOMO versus vacuum level of PDINO is 6.0 eV and valence band of TASiW-12 is 7.0 eV.

4. Conductivity measurement of TASiW-12 film.

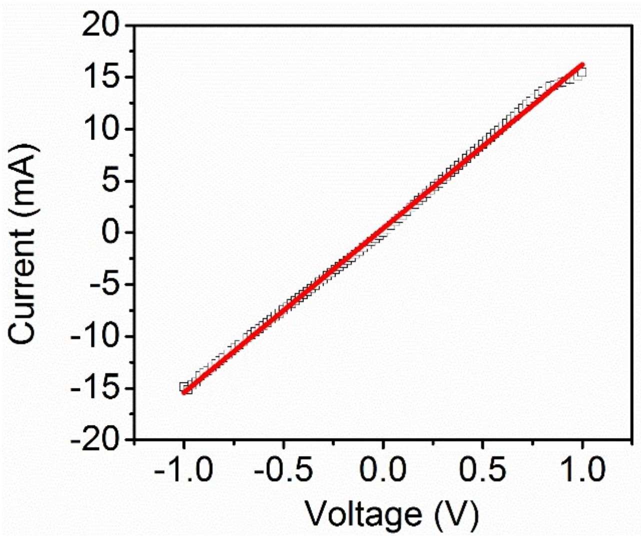


Figure S3. I-V curve of the device for ITO/TASiW-12 (23 nm)/Al in the dark. The conductivity of TASiW-12 is 8.76×10^{-5} S/m.

5. AFM images of $H_4SiW_{12}O_{40}$, TOAB and TASiW-12 on the PTB7:$PC_{71}BM$.

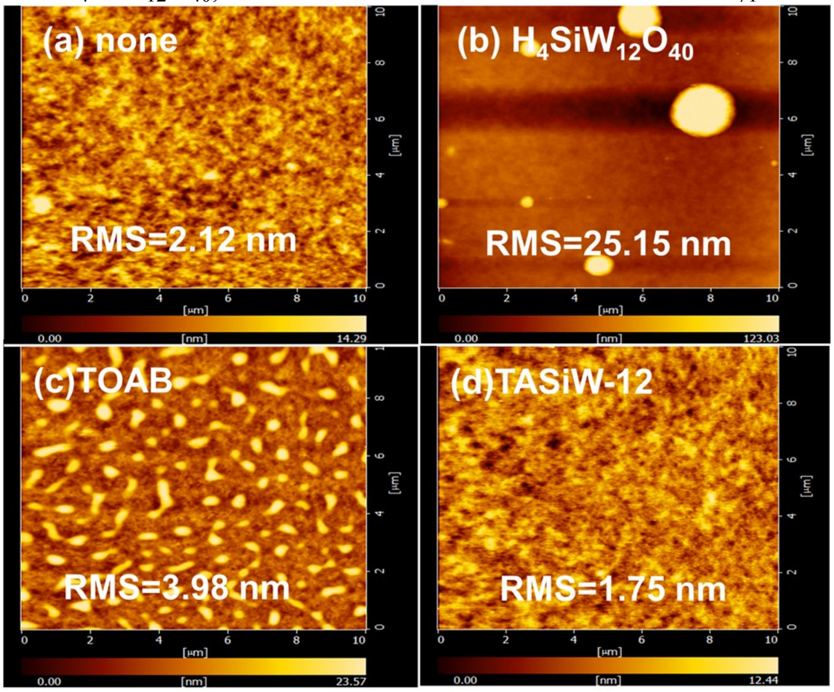


Figure S4. AFM images of the PTB7:$PC_{71}BM$ film (a), $H_4SiW_{12}O_{40}$ on the PTB7:$PC_{71}BM$ film (b), TOAB on the PTB7:$PC_{71}BM$ film (c) and TASiW-12 on PTB7:$PC_{71}BM$ film (d).

6. SEM and SEM-EDS images of TASiW-12 on the PTB7:$PC_{71}BM$.

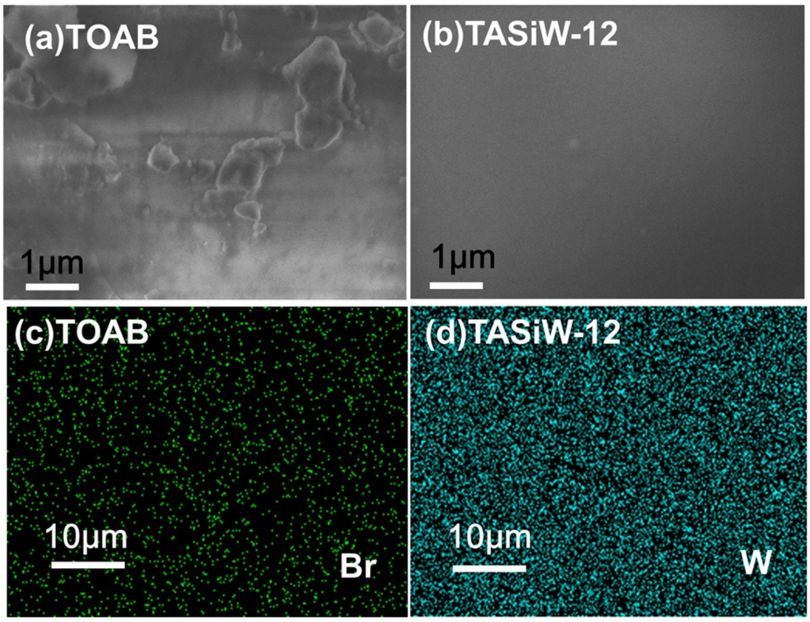


Figure S5. SEM and SEM-EDS images of TOAB on the PTB7:$PC_{71}BM$ film (a for SEM and c for SEM-EDS) and TASiW-12 on PTB7:$PC_{71}BM$ film (b for SEM and d for SEM-EDS). The green dots (c) signify bromine element; The light blue dots (d) signify tungsten element.

7. Performance parameters of different PSCs with error bars.

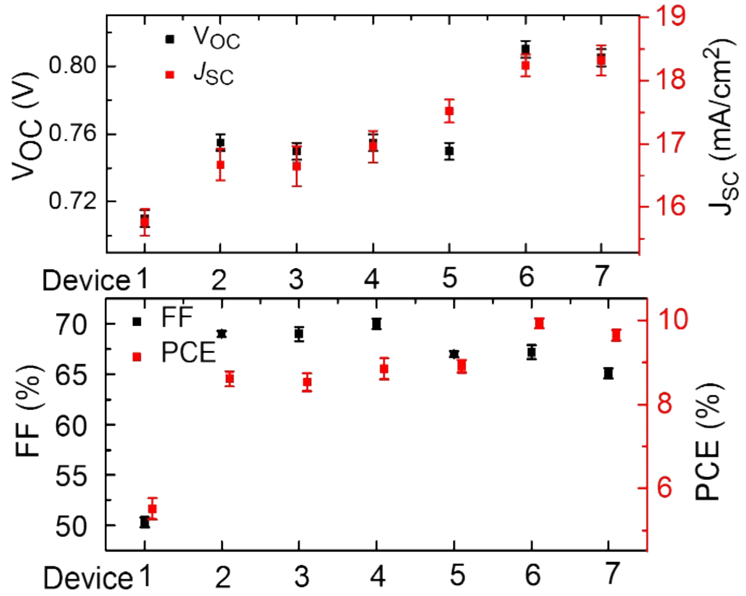


Figure S6. Performance parameters of different PSCs with error bars.

Device 1: ITO/PEDOT:PSS/PTB7:$PC_{71}BM$/Al,
Device 2: ITO/PEDOT:PSS/PTB7:$PC_{71}BM$/LiF/Al,
Device 3: ITO/PEDOT:PSS/PTB7:$PC_{71}BM$/PDINO/Al,
Device 4: ITO/PEDOT:PSS/PTB7:$PC_{71}BM$/TASiW-12/Al,
Device 5: ITO/PEDOT:PSS/PTB7:$PC_{71}BM$/TASiW-12/Ag
Device 6: ITO/PEDOT:PSS/PTB7-Th:$PC_{71}BM$/TASiW-12/Al,
Device 7: ITO/PEDOT:PSS/PTB7-Th:$PC_{71}BM$/TASiW-12/Ag.

8. Device stability of the PTB7:$PC_{71}BM$ based PSCs with TASiW-12/Al as cathode.

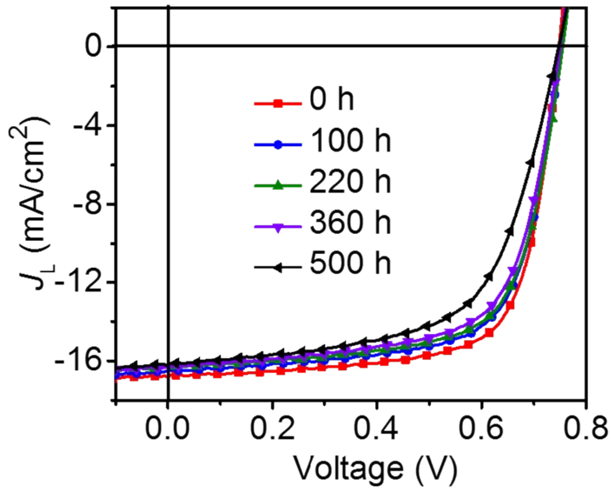


Figure S7. *J*-V characteristics of PTB7:$PC_{71}BM$ based PSCs with TASiW-12/Al measured at different time after encapsulation.

Table S1. Photovoltaic parameters of TB7:$PC_{71}BM$ based PSCs with TASiW-12/Al at different time after encapsulation.

Time (h)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
0	0.745	16.78	71.6	8.95
100	0.745	16.53	69.4	8.55
220	0.750	16.32	69.0	8.45
360	0.750	16.33	67.1	8.22
500	0.745	16.11	65.3	7.84

9. J-V curves of the PSCs based on PTB7:$PC_{71}BM$ with different cathodes in the dark.

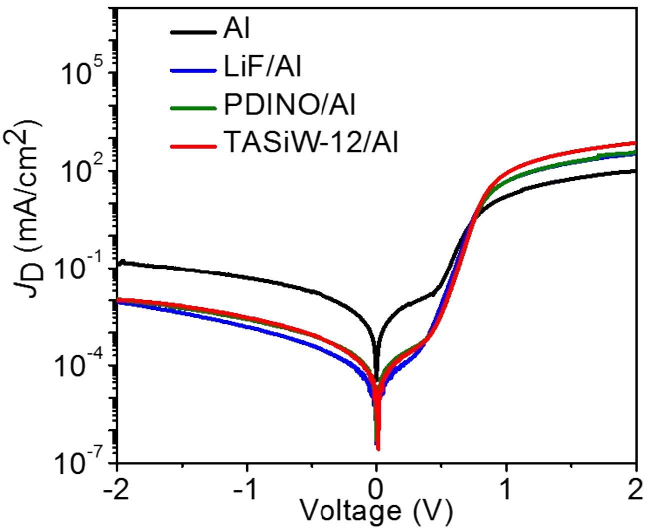


Figure S8. J-V curves of the PSCs based on PTB7:$PC_{71}BM$ with different cathodes in the dark.

Equation S1

$$J_{inj} = J_{0,n}exp(\frac{qV}{nTk_B})$$

$J_{0,n}$ is reverse saturation dark current density, n is diode ideality factor, k_B is Boltzmann constant, T is tempreture, q is elementary charge. J_{inj} is current density of PSCs in the dark.

10. Transient photocurrent measurements of the PSCs based on PTB7:$PC_{71}BM$.

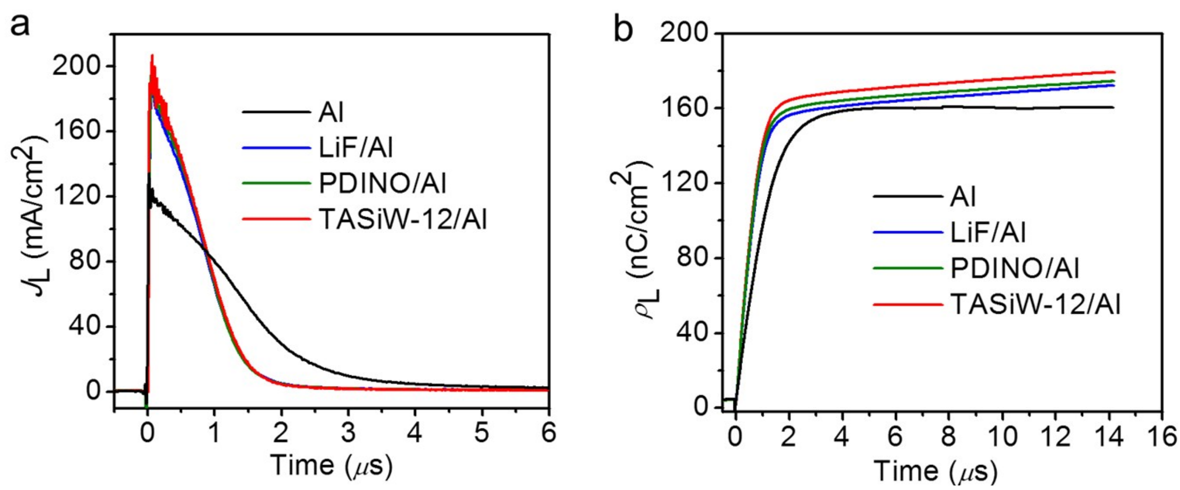


Figure S9. (a) Transit photocurrent and (b) the integrated photocurrent of PTB7:$PC_{71}BM$ based devices with different cathodes.

11. Mobility measurements of electron and hole using space charge limited current (SCLC) method.

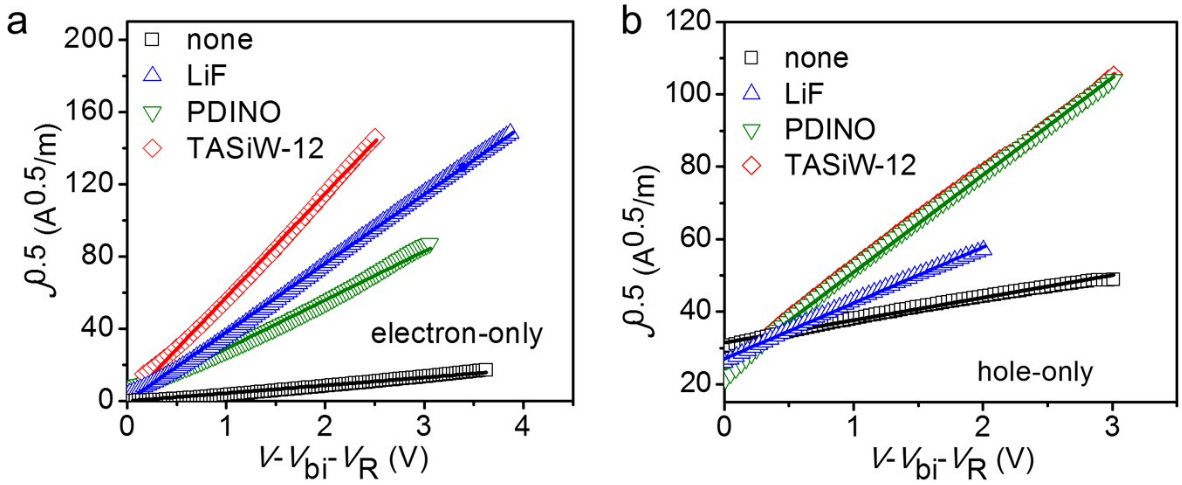


Figure S10. $J^{0.5}$versus V-V_{bi}-V_R plots for the electron-only (a) and the hole-only (b) devices with different CILs.

Equation S2

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V^2}{L^3}$$

ε_0 is the permittivity of free space, ε_r is the dielectric constant of the active layer, μ is the carrier mobility, V is the voltage drop across the device, L is the active layer thickness.

12. Work function measurements of Al, Al/LiF, Al/PDINO and Al/TASiW-12 using UPS.

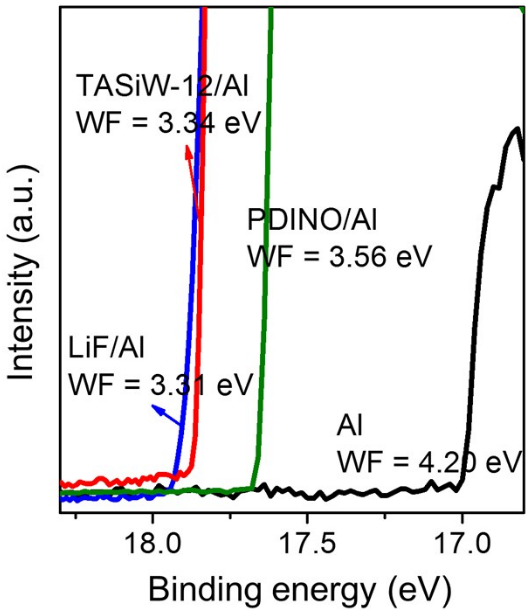
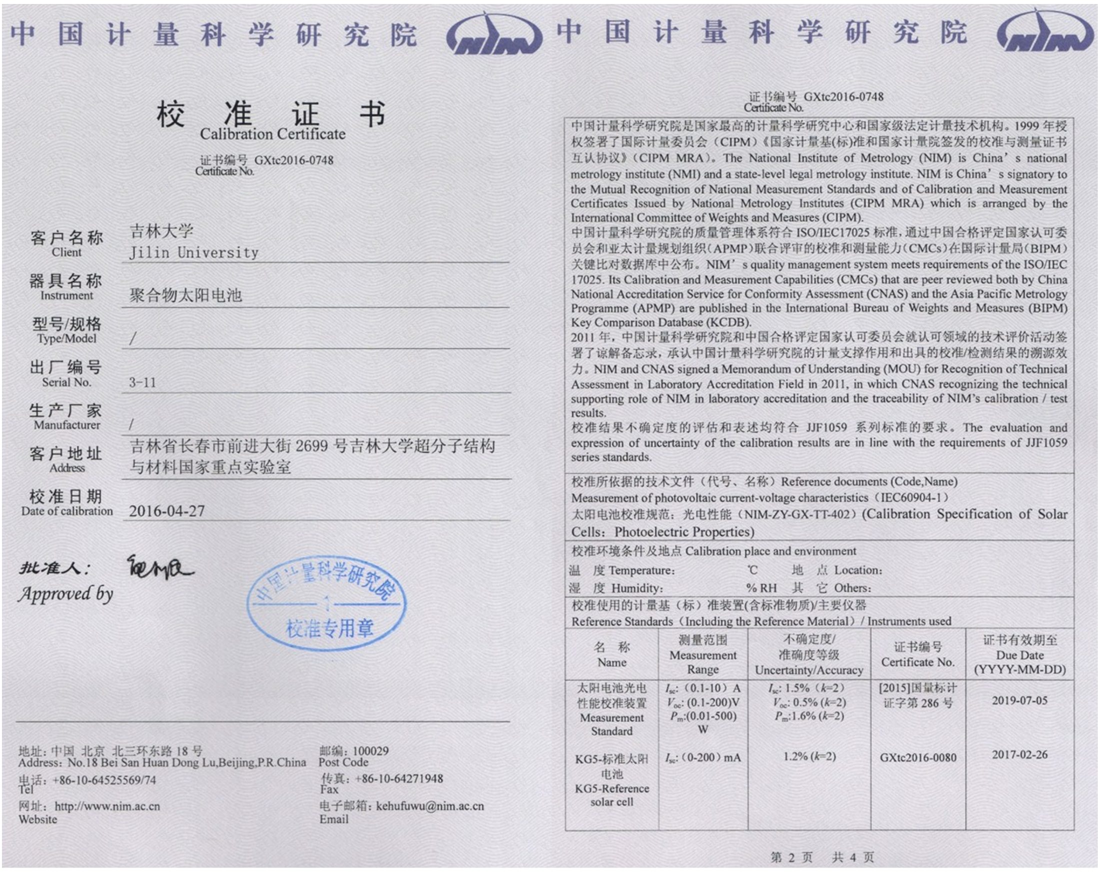


Figure S11. UPS spectra of bare Al, Al covered by 1 nm LiF, 10 nm PDINO and 10 nm TASiW-12 in the secondary electron cutoff region.

13. Certified device performance of the PSC based on PTB7-Th:$PC_{71}BM$ with TASiW-12/Al as a cathode.



中国计量科学研究院 中国计量科学研究院

校准证书
Calibration Certificate

证书编号 GXtc2016-0748
Certificate No.

客户名称 Client	吉林大学 Jilin University
器具名称 Instrument	聚合物太阳电池
型号/规格 Type/Model	/
出厂编号 Serial No.	3-11
生产厂家 Manufacturer	/
客户地址 Address	吉林省长春市前进大街 2699 号吉林大学超分子结构与材料国家重点实验室
校准日期 Date of calibration	2016-04-27

批准人： Approved by

中国计量科学研究院 1 校准专用章

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证书编号 GXtc2016-0748
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中国计量科学研究院的质量管理体系符合 ISO/IEC17025 标准，通过中国合格评定国家认可委员会和亚太计量规划组织（APMP）联合评审的校准和测量能力（CMCs）在国际计量局（BIPM）关键比对数据库中公布。NIM's quality management system meets requirements of the ISO/IEC 17025. Its Calibration and Measurement Capabilities (CMCs) that are peer reviewed both by China National Accreditation Service for Conformity Assessment (CNAS) and the Asia Pacific Metrology Programme (APMP) are published in the International Bureau of Weights and Measures (BIPM) Key Comparison Database (KCDB).
2011 年，中国计量科学研究院和中国合格评定国家认可委员会就认可领域的技术评价活动签署了谅解备忘录，承认中国计量科学研究院的计量支撑作用和出具的校准/检测结果的溯源效力。NIM and CNAS signed a Memorandum of Understanding (MOU) for Recognition of Technical Assessment in Laboratory Accreditation Field in 2011, in which CNAS recognizing the technical supporting role of NIM in laboratory accreditation and the traceability of NIM's calibration / test results.
校准结果不确定度的评估和表述均符合 JJF1059 系列标准的要求。The evaluation and expression of uncertainty of the calibration results are in line with the requirements of JJF1059 series standards.

校准所依据的技术文件（代号、名称）Reference documents (Code,Name)
Measurement of photovoltaic current-voltage characteristics（IEC60904-1）
太阳电池校准规范：光电性能（NIM-ZY-GX-TT-402）(Calibration Specification of Solar Cells：Photoelectric Properties)

校准环境条件及地点 Calibration place and environment
温　度 Temperature：　℃　地　点 Location：
湿　度 Humidity：　% RH　其　它 Others：

校准使用的计量基（标）准装置(含标准物质)/主要仪器
Reference Standards（Including the Reference Material）/ Instruments used

名　称 Name	测量范围 Measurement Range	不确定度/准确度等级 Uncertainty/Accuracy	证书编号 Certificate No.	证书有效期至 Due Date (YYYY-MM-DD)
太阳电池光电性能校准装置 Measurement Standard	I_{sc}:（0.1-10）A V_{oc}: (0.1-200)V P_m:(0.01-500) W	I_{sc}: 1.5%（k=2） V_{oc}: 0.5% (k=2) P_m:1.6% (k=2)	[2015]国量标计证字第 286 号	2019-07-05
KG5-标准太阳电池 KG5-Reference solar cell	I_{sc}:（0-200）mA	1.2% (k=2)	GXtc2016-0080	2017-02-26

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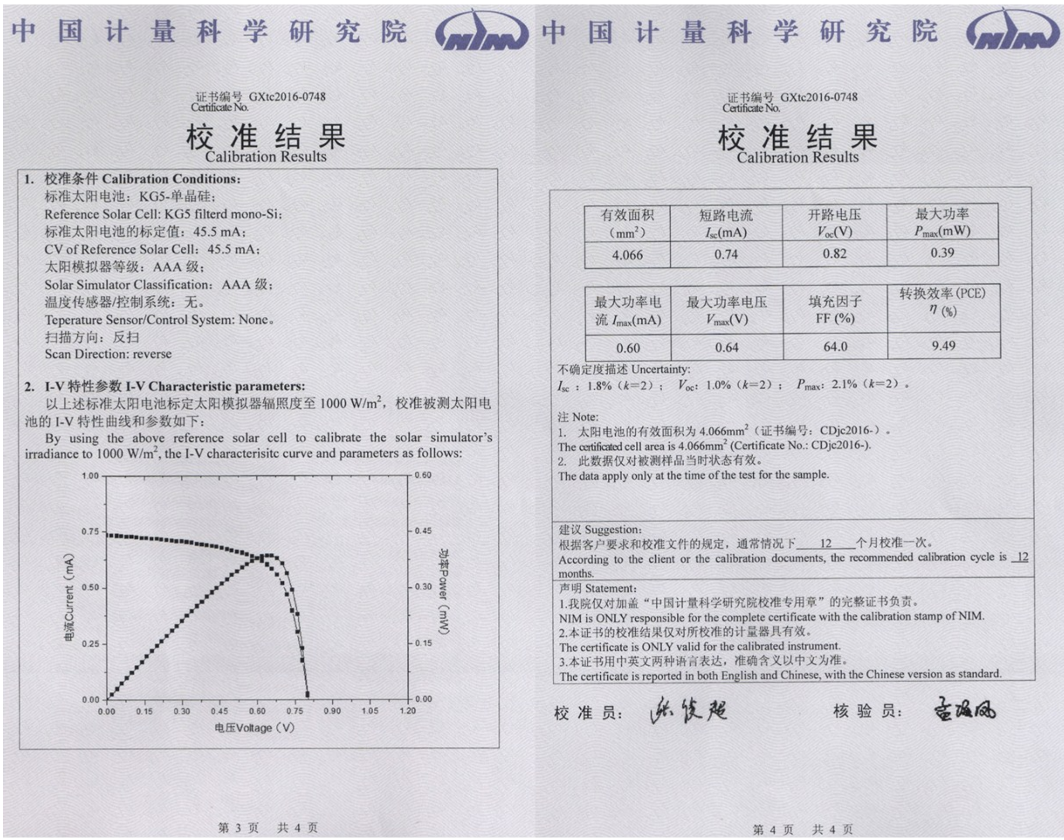

中 国 计 量 科 学 研 究 院

证书编号 GXtc2016-0748
Certificate No.

校 准 结 果
Calibration Results

1. 校准条件 Calibration Conditions:
标准太阳电池：KG5-单晶硅；
Reference Solar Cell: KG5 filterd mono-Si;
标准太阳电池的标定值：45.5 mA；
CV of Reference Solar Cell：45.5 mA；
太阳模拟器等级：AAA 级；
Solar Simulator Classification：AAA 级；
温度传感器/控制系统：无。
Teperature Sensor/Control System: None。
扫描方向：反扫
Scan Direction: reverse

2. I-V 特性参数 I-V Characteristic parameters:
以上述标准太阳电池标定太阳模拟器辐照度至 1000 W/m²，校准被测太阳电池的 I-V 特性曲线和参数如下：
By using the above reference solar cell to calibrate the solar simulator's irradiance to 1000 W/m², the I-V characterisitc curve and parameters as follows:

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中 国 计 量 科 学 研 究 院

证书编号 GXtc2016-0748
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校 准 结 果
Calibration Results

有效面积（mm²）	短路电流 I_{sc}(mA)	开路电压 V_{oc}(V)	最大功率 P_{max}(mW)
4.066	0.74	0.82	0.39

最大功率电流 I_{max}(mA)	最大功率电压 V_{max}(V)	填充因子 FF (%)	转换效率 (PCE) η (%)
0.60	0.64	64.0	9.49

不确定度描述 Uncertainty:
I_{sc}：1.8%（k=2）； V_{oc}：1.0%（k=2）； P_{max}：2.1%（k=2）。

注 Note:
1. 太阳电池的有效面积为 4.066mm²（证书编号：CDjc2016-）。
The certificated cell area is 4.066mm² (Certificate No.: CDjc2016-).
2. 此数据仅对被测样品当时状态有效。
The data apply only at the time of the test for the sample.

建议 Suggestion:
根据客户要求和校准文件的规定，通常情况下 12 个月校准一次。
According to the client or the calibration documents, the recommended calibration cycle is 12 months.

声明 Statement:
1.我院仅对加盖"中国计量科学研究院校准专用章"的完整证书负责。
NIM is ONLY responsible for the complete certificate with the calibration stamp of NIM.
2.本证书的校准结果仅对所校准的计量器具有效。
The certificate is ONLY valid for the calibrated instrument.
3.本证书用中英文两种语言表达，准确含义以中文为准。
The certificate is reported in both English and Chinese, with the Chinese version as standard.

校 准 员： 核 验 员：

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Figure S12. Certified J-V curve and device parameters of the PSC based on PTB7-Th:$PC_{71}BM$ with TASiW-12/Al as a cathode by National institute of metrology, China.

14. *J-V* curves of the PSCs based on PCDTBT:$PC_{71}BM$ with TASiW-12.

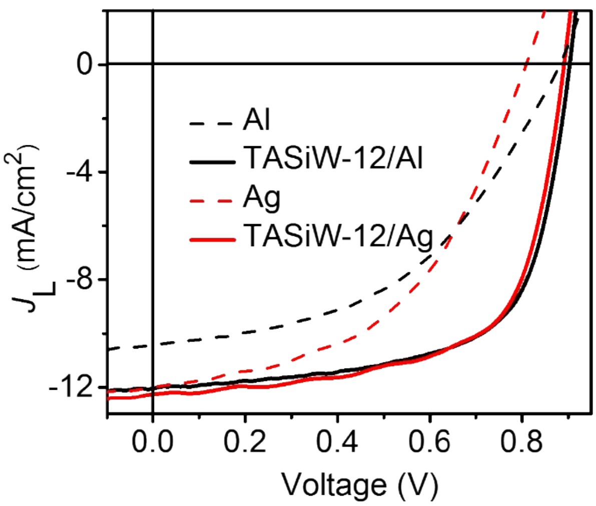

Figure S13. *J-V* curves of PCDTBT:$PC_{71}BM$ based PSCs with TASiW-12/Al or Ag under 100 mW cm^{-2} AM 1.5G illumination.

Table S2. photovoltaic parameters of PCDTBT:$PC_{71}BM$ based PSCs with differnt cathode.

	Cathode	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
PCDTBT:$PC_{71}BM$	Al	0.885	10.43	46.6	4.30
	TASiW-12/Al	0.905	12.10	65.3	7.15
	Ag	0.800	11.98	49.3	4.73
	TASiW-12/Ag	0.890	12.26	65.4	7.14

15. X-ray photoemission spectroscopy (XPS) measurements of Ag/TASiW-12.

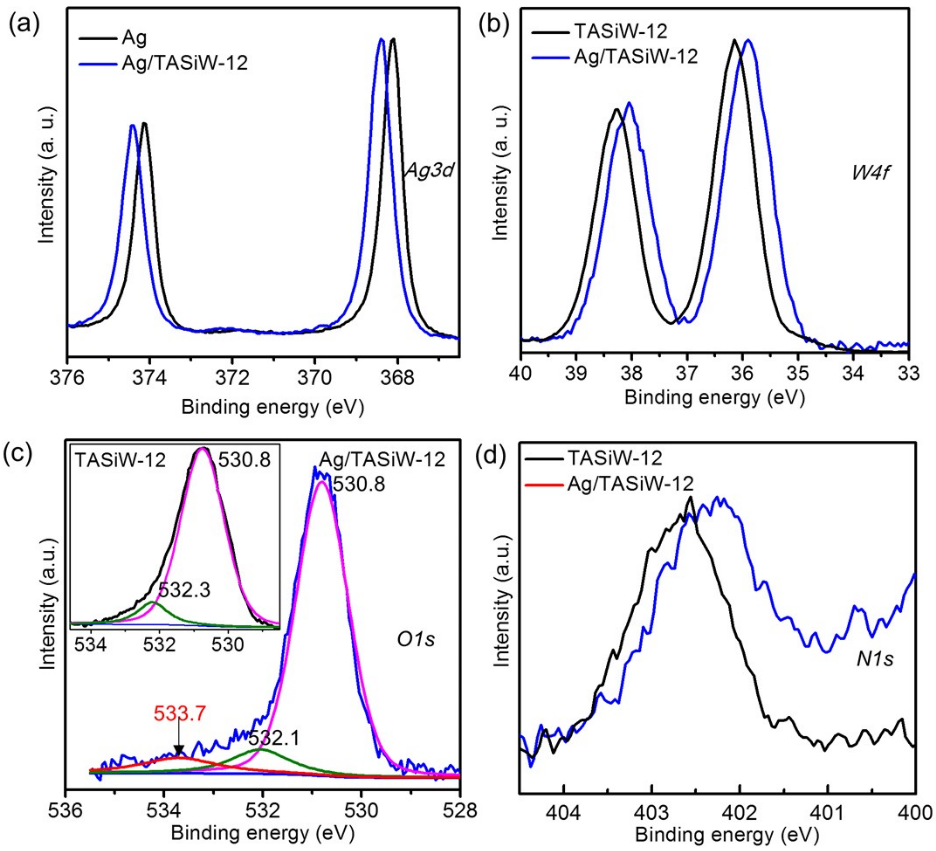

Figure S14. (a) *Ag3d*, (b) *W4f*, (c) *O1s* and (d) *N1s* core-level XPS spectra of Ag, Ag covered by 8 nm TASiW-12 and 40 nm TASiW-12 on ITO.

16. UPS measurements of ITO/TASiW-12.

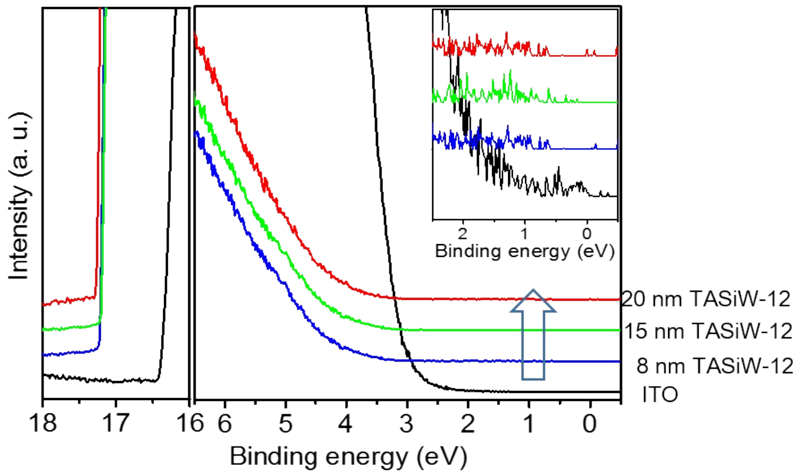

Figure S15. UPS spectra of ITO (black line), 8 nm (blue line), 15 nm (green line) and 20 nm (red line) TASiW-12 on ITO. Insets show the valence band spectra blown up from -0.5 to 2.5 eV.