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SUPPORTING INFORMATION

Silolothiophene-Linked Triphenylamines as Stable Hole Transporting Materials for High Efficiency Perovskite Solar Cells

Antonio Abate,*[1] Sanghyun Paek,[2,5] Fabrizio Giordano,[1] Juan-Pablo Correa-Baena,[3] Michael Saliba,[2] Peng Gao,[2] Taisuke Matsui,[4] Jaejung Ko,*[5] Shaik M. Zakeeruddin,[1] Klaus H. Dahmen,[6] Ulf Anders Hagfeldt,[3] Michael Grätzel,[1] Mohammad Khaja Nazeeruddin*[2]

[1] Laboratory for Photonics and Interfaces, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne, CH-1015-Lausanne, Switzerland.

[2]Group for Molecular Engineering of Functional Materials, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne, CH-1015-Lausanne, Switzerland

[3]Laboratory of Photomolecular Science, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne, CH-1015-Lausanne, Switzerland.

[4]Advanced Research Division, Materials Research Laboratory, Panasonic Corporation
1006 Kadoma, Kadoma City, Osaka 571-8501, Japan

[5]Department of Advanced Material Chemistry, Korea University, 2511, Sejong-ro, Sejong City 339-700 (Republic of Korea)

[6]Qatar Environment and Energy Research Institute, a center of Qatar Foundation for Education, Qatar.

* Corresponding authors: AA antonioabate83@gmail.com; JK jko@korea.ac.kr, MKN mdkhaja.nazzeruddin@epfl.ch.

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Double exponential decay fitting parameters for device A, B and C reported in Figure 2

Device A

Equation	y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0
Adj. R-Square	0.994

	Value	Standard Error
y0	0	0
A1	0.14182	0.00288
t1	6.4026	0.24455
A2	0.85113	9.34E-04
t2	1492.697	20.82155

Fast half-life constant = t1*ln2 = 4 hrs
Slow half-life constant = t2*ln2 = 1035 hrs

Device B

Equation	y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0
Adj. R-Square	0.989

	Value	Standard Error
y0	0	0
A1	0.1904	0.00372
t1	7.90751	0.29269
A2	0.7931	0.00135
t2	2123.056	63.68939

Fast half-life constant = t1*ln2 = 6 hrs
Slow half-life constant = t2*ln2 = 1472 hrs

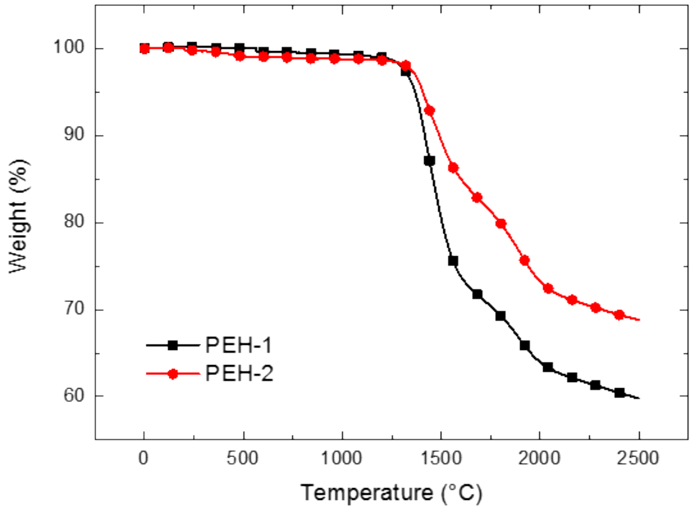
Device C

Equation	y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0
Adj. R-Square	0.987

	Value	Standard Error
y0	0	0
A1	0.22261	0.00601
t1	8.81457	0.45883
A2	0.7519	0.00245
t2	976.2945	25.99587

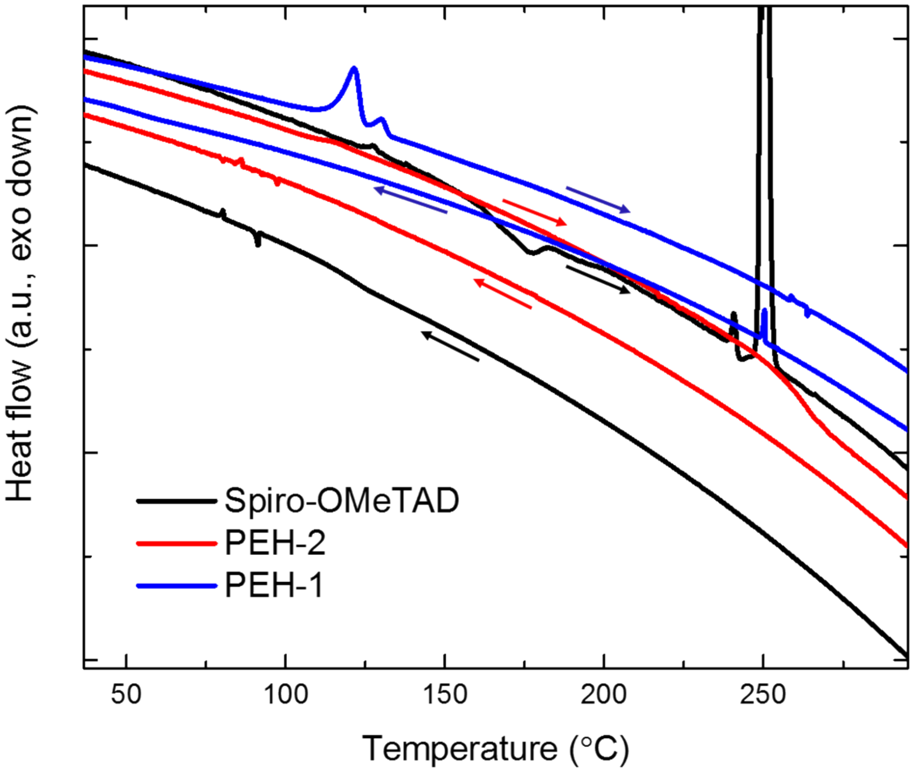
Fast half-life constant = t1*ln2 = 6 hrs
Slow half-life constant = t2*ln2 = 677 hrs

Thermogravimetry analysis of PEH-1 and PEH-2



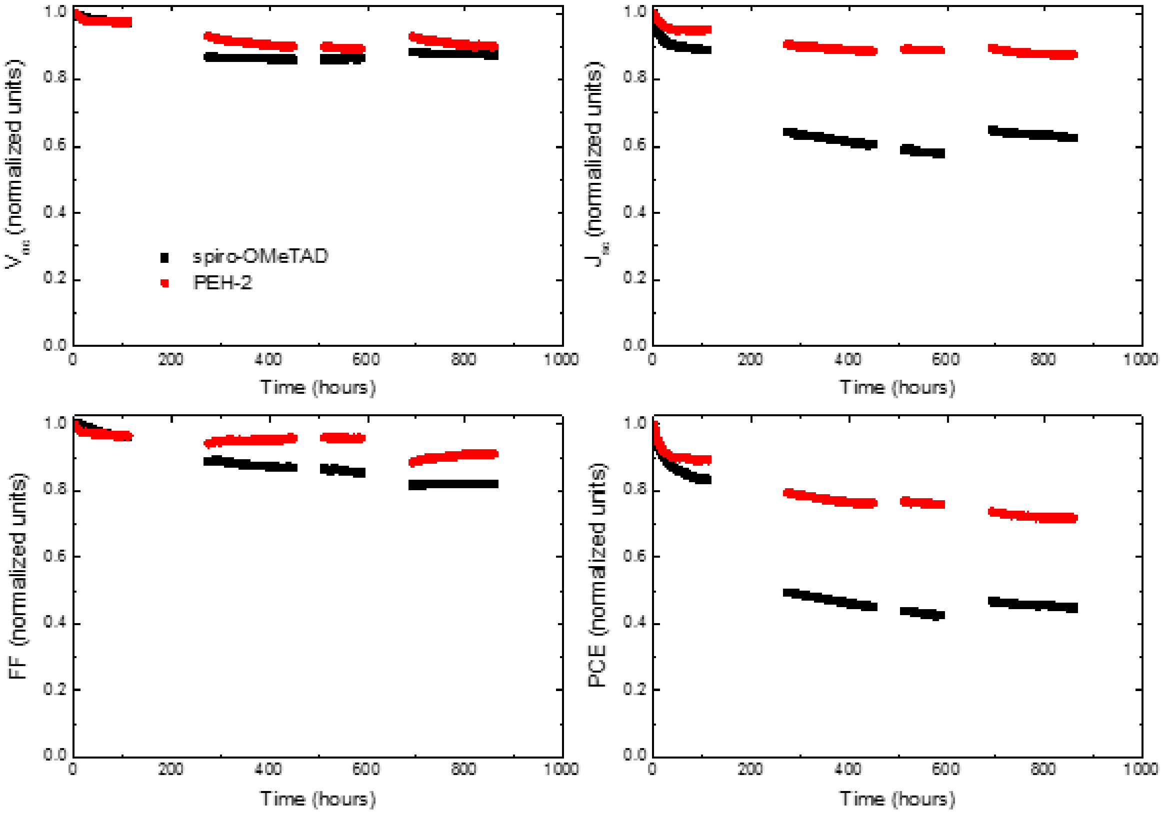
Thermogravimetry analysis (TGA) showed that **PEH-1** and **PEH-2** start to decompose at temperature higher than 500° and they encounter 30% weight loss after 1000°C. In similar experimental conditions, spiro-OMeTAD has been reported losing about 30% of the initial weight at 450° (ACS Appl. Mater. Interfaces 2015, 7, 11107−11116). This demonstrated a superior thermal stability of silolothiophene-linked compared to spiro-linked triphenylamines as hole transporting material for perovskite solar cells. TGA analysis was performed following the same conditions reported in paper published in ACS Appl. Mater. Interfaces 2015, 7, 11107−11116.

Differential scanning calorimetry of PEH-1, PEH-2 and Spiro-OMeTAD



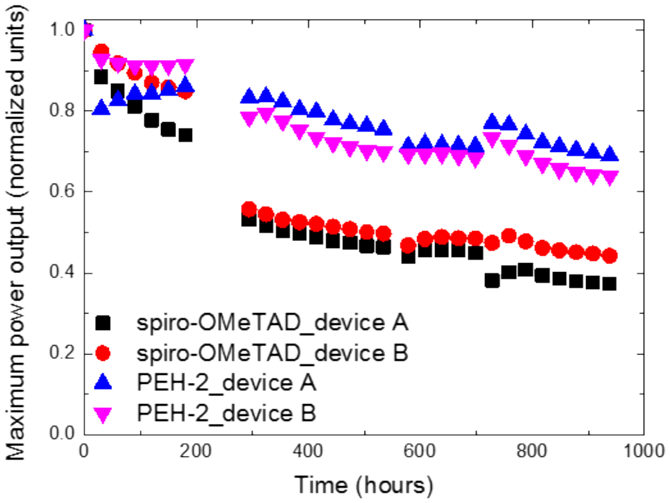
Differential scanning calorimetry (DSC) showed that spiro-OMeTAD processed from solution exhibits a glass transition around 150°C and melting of the crystalline phases around 245°C. As reported in previous studies, spiro-OMeTAD processed from solution to deposit the hole transporting layer in solar cells forms a film predominantly amorphous (ACS Appl. Mater. Interfaces, 2015, 7, 11107–11116). However, even if the glass transition temperature (150°) is significantly higher than room temperature, Malinauskas and co-workers observed the formation of crystalline domains within the amorphous spiro-OMeTAD films after long time ageing the device in working condition (ACS Appl. Mater. Interfaces, 2015, 7, 11107–11116). They demonstrated that the transition from an amorphous to a crystalline phase is responsible for device performance degradation. As a strategy to improve the device lifetime in working condition they propose to implement hole transporting materials with higher glass transition temperture. Notably, **PEH-2** showed a significantly higher glass transition temperature than spiro-OMeTAD and no evidence of melting of a crystalline phase up to 300°C. This suggests that the amorphous phase of **PEH-2** is more stable than spiro-OMeTAD and the formation of crystalline domains is significantly slower in **PEH-2** than in spiro-OMeTAD films. We also reported the DSC trace of **PEH-1** that exhibits no evidence of glass transition between room temperature and 300°C. The endothermic transitions around 120° suggest the presence of crystalline phase at room temperature when the molecule is processed from solution. According to what we discussed before, this may contribute to the rapid degradation we observed in devices prepared with **PEH-1**. All the DSC analysis were performed following the same conditions reported in paper published in ACS Appl. Mater. Interfaces 2015, 7, 11107−11116.

Time dependence of the device performance parameters



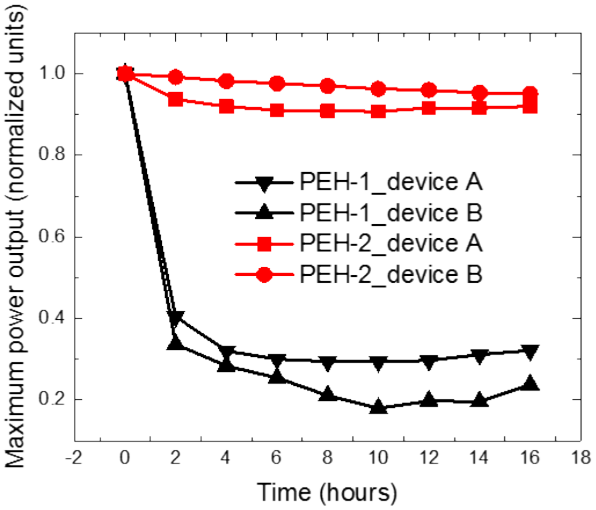
Device performance parameters, open circuit voltage (V_{oc}), short circuit current (J_{sc}), fill factor (FF) and maximum power conversion efficiency (PCE) were monitored by regularly collecting current-voltage (JV) characteristics as reported in the Experimental Section. We note here that the JV characteristic of perovskite solar cells may show relatively large hysteretic behaviour, which makes it ambiguous to estimate the actual PCE from the JV curve. In freshly made devices this problem can be minimized by slowing down the voltage sweep rate to 10 mV s^{-1} (see Figure 6 in the main text), but for aged devices even if the hysteresis of the JV is minimal, the steady-state photocurrent and thus the actual PCE can be significantly lower (see Ref. in the main text Energy & Environmental Science 2015, 8, 995). Nevertheless for the sake of completeness we reported here the device performance parameters extracted from the backward scan of the JV curves collected during the ageing test.

Ageing data reproducibility comparing 4 devices with spiro-OMeTAD and PEH-2



In this figure we reported additional data supporting the trends observed in Figure 7 of the main text. The experimental condition are reported in the Experimental Section of the main text.

Ageing data comparing PEH-1 and PEH-2 based perovskite solar cells



Maximum power output tracking of 4 perovskite solar cells prepared using **PEH-1** and **PEH-2** as hole transporting materials. The power conversion efficiency at time zero was measured after taking the devices in argon and dark for 24 hours and it was over 11 and 14% for **PEH-1** and **PEH-2** respectively. The experimental conditions are reported in the Experimental Section of the main text.