

## Supporting Information

### **A Cost-Device Efficiency Balanced Spiro Based Hole Transport Material for Perovskite Solar Cells**

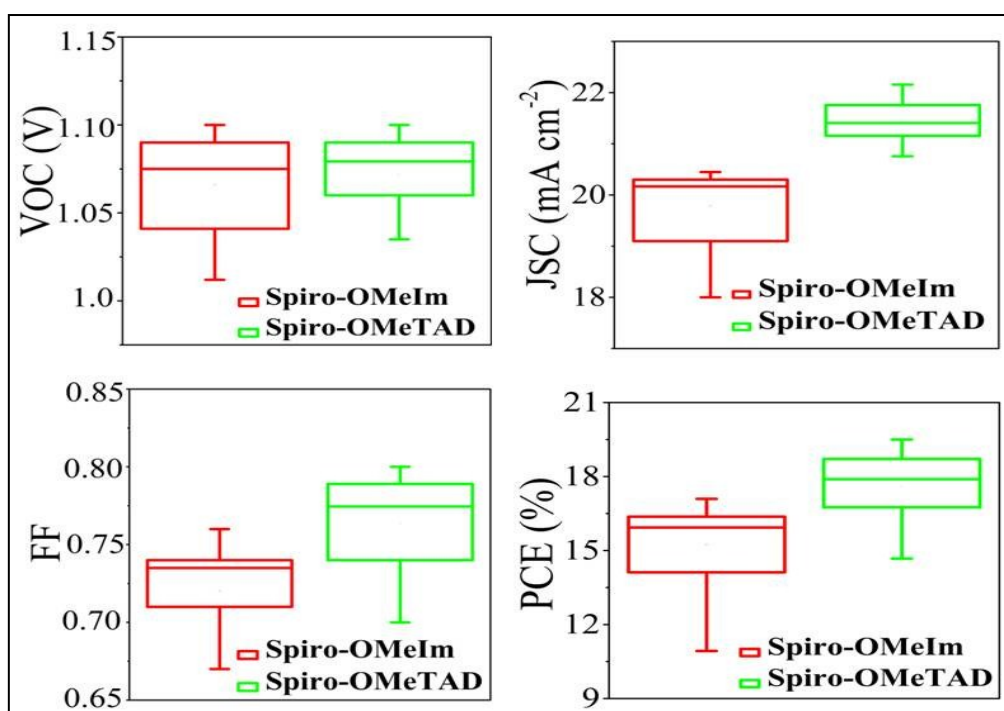
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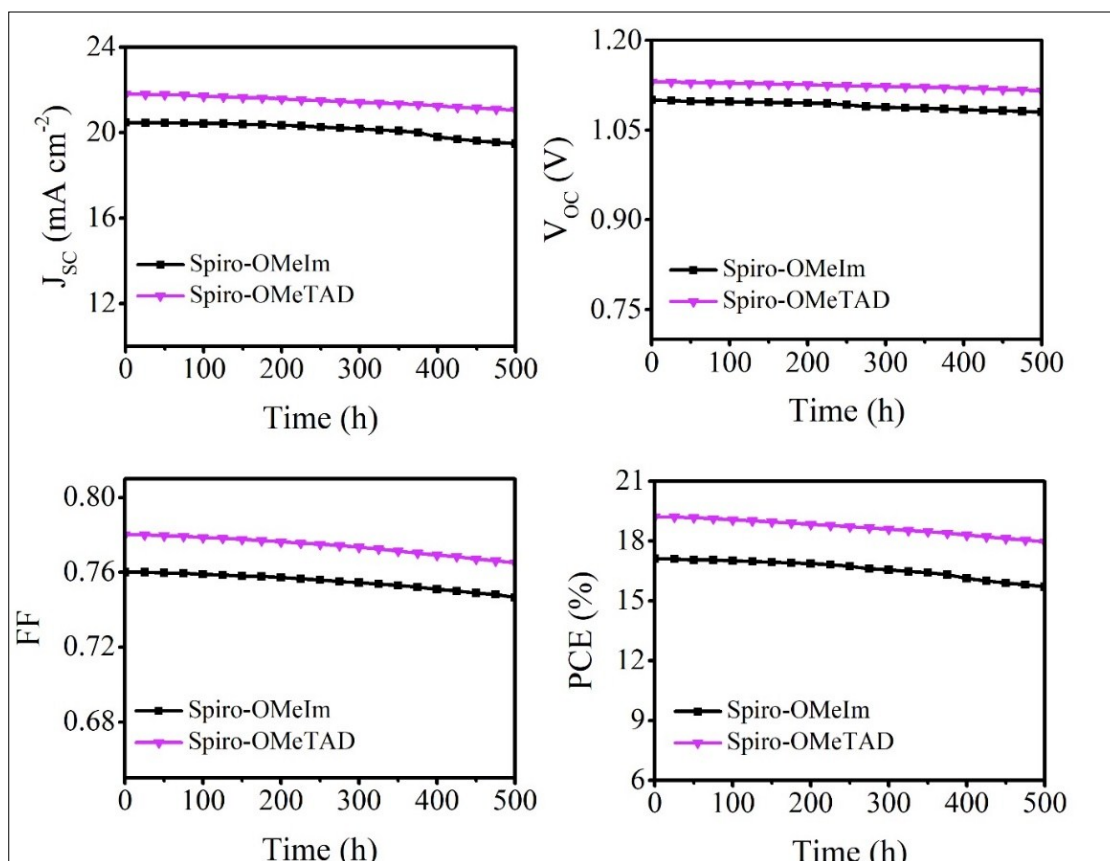
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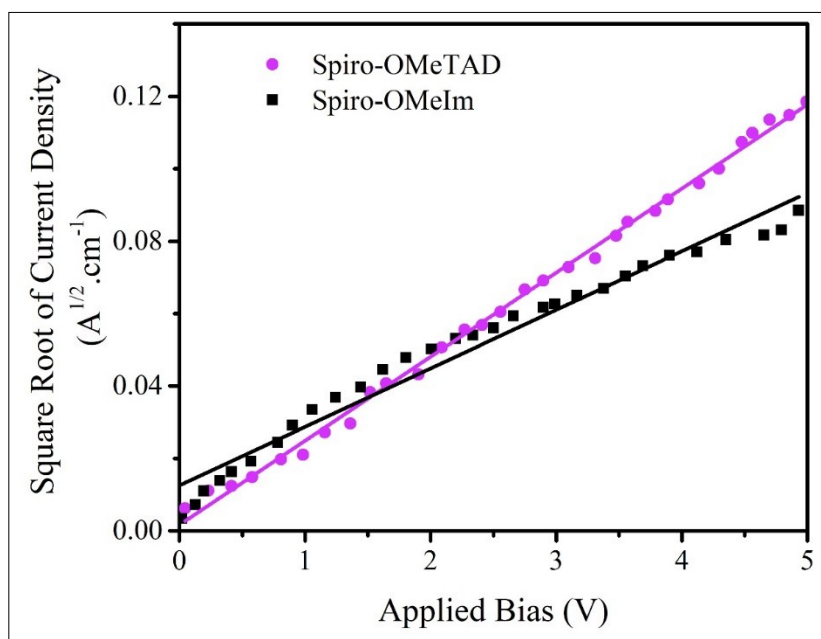
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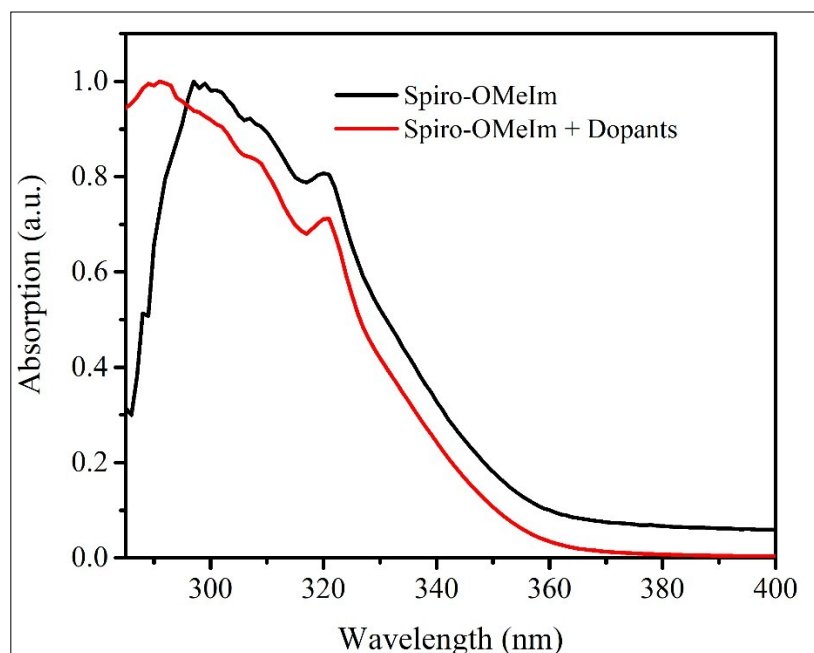
**Figure S1.** Statistical distribution of the performance of 20 perovskite solar cells.



**Figure S2.** Stability of the photovoltaic characteristics over time for the PSCs based on Spiro-OMeIm and Spiro-OMeTAD. The stability test of devices are done under during exposure to full AM 1.5 simulated sunlight for 500 hours (humidity  $\approx$  40%).



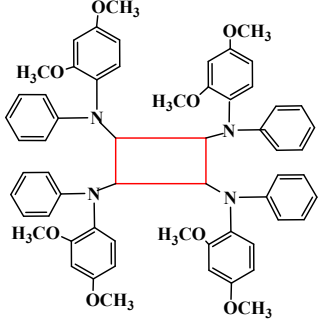
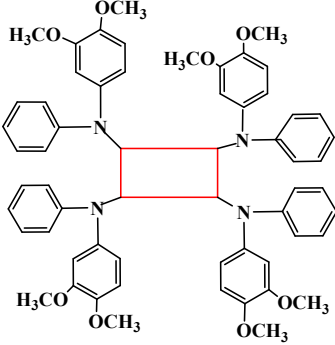
**Figure S3.** J–V characteristic of thin films in hole-conducting only devices based on Spiro-OMeTAD and Spiro-OMeIm (pristine state).



**Figure S4.** UV-Vis spectra of Spiro-OMeIm without and with dopants in  $\text{CHCl}_3$ .

**Table S1.** The photovoltaic performance of previously reported spiro-cyclic HTMs.

HTMs	HTMs	$V_{oc}$ [V]	$J_{sc}$ [ $\text{mA cm}^{-2}$ ]	FF [%]	PCE [%]	Ref.
<p>pp-spiro-OMeTAD (1a): <math>R^1=H, R^2=H, R^3=OCH_3</math>            pm-spiro-OMeTAD (1b): <math>R^1=H, R^2=OCH_3, R^3=H</math>            po-spiro-OMeTAD (1c): <math>R^1=OCH_3, R^2=H, R^3=H</math></p>	pp-spiro-OMeTAD(1)	1	20.7	71.1	14.9	[1]
	Pm-spiro-OMeTAD(2)	1.01	21.1	65.2	13.9	
	po-spiro-OMeTAD(3)	1.02	21.2	77.6	16.7	
<p>spiro-027 (6)</p>	Spiro-027 (4)	1.07	22.07	70	16.6	[2]

 <p style="text-align: center;">2,4-Spiro-OMeTAD (7)</p>	<b>2,4-Spiro-OMeTAD (5)</b>	0.956	25.6	70.1	17.2	[3]
 <p style="text-align: center;">3,4-Spiro-OMeTAD (8)</p>	<b>3,4-Spiro-OMeTAD (6)</b>	0.752	20.1	59.9	9.1	

## References

- [1] N. J. Jeon, H. G. Lee, Y. C. Kim, J. Seo, J. H. Noh, J. Lee and S. I. Seok, *J. Am. Chem. Soc.*, 2014, **136**, 7837.
- [2] Y. Shi, Y. Xue, K. Hou, G. Meng, K. Wang, R. Chi, F. Chen, H. Ren, M. Pang and C. Hao, *RSC Adv.*, 2016, **6**, 96990.
- [3] M.-D. Zhang, D.-X. Zhao, L. Chen, N. Pan, C.-Y. Huang, H. Cao and M.-D. Chen, *Sol. Energy Mater. Sol. Cells*, 2018, **176**, 318.