

# Supporting Information

## Unsymmetrical and Symmetrical Zn(II) Phthalocyanines as Hole-Transporting Materials for Perovskite Solar Cells

Yi Zhang,<sup>†,∇</sup> Sanghyun Paek,<sup>†,∇</sup> Maxence Urbani,<sup>†,‡,§,∇</sup> María Medel,<sup>‡</sup> Iwan Zimmermann,<sup>†</sup> Kyung Taek Cho,<sup>†</sup> Mine Ince,<sup>||,⊥</sup> Mohammad Khaja Nazeeruddin,<sup>\*,†</sup> and Tomás Torres<sup>\*,‡,§,#</sup>

<sup>†</sup>Group for Molecular Engineering of Functional Materials, Institute of Chemical Sciences and Engineering, EPFL, Valais Wallis, Rue de l'Industrie 17, 1950 Sion, Switzerland

<sup>‡</sup>Departamento de Química Orgánica, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain

<sup>§</sup>IMDEA-Nanociencia, Campus de Cantoblanco, 28049 Madrid, Spain

<sup>||</sup>Advanced Technology Research & Application Center, Mersin University, Ciftlikkoy Campus, TR-33343 Mersin, Turkey

<sup>⊥</sup>Department of Energy Systems Engineering Faculty of Tarsus Technology, Mersin University, 33480 Mersin, Turkey

<sup>#</sup>Institute for Advanced Research in Chemical Sciences (IAdChem) Universidad Autónoma de Madrid, 28049 Madrid, Spain

### Author Contributions

<sup>∇</sup>Y.Z, S.P. and M.U. contributed equally to this work.

### Corresponding Authors:

\*Email: [mdkhaja.nazeeruddin@epfl.ch](mailto:mdkhaja.nazeeruddin@epfl.ch) (M. K. Nazeeruddin)

\*Email: [tomas.torres@uam.es](mailto:tomas.torres@uam.es) (T. Torres)

## Experimental Section

### 1. Materials

The synthesis and characterisation of **TT0** and **TT1** were previously reported by us<sup>1</sup> (these Pc compounds were used as mixtures of the corresponding regioisomers). 4-*tert*-butylpyridine (TBP) and bis (trifluoromethylsulfonyl)-imide lithium salt (Li-TFSI) were purchased at *Sigma Aldrich*, tris(2-(1H-pyrazol-1-yl)-4- *tert*butylpyridine) cobalt(III) tri-[bis (trifluoromethane) sulfonimide] (FK 209 Co(III) TFSI salt) at *Dyename*, lead iodide at *TCI*, formamidinium iodide, methylammonium iodine, and the mesoporous TiO<sub>2</sub> paste (30 NR-D) at *Dyesol*.

### 2. Device Fabrication

Conductive FTO glass (NSG10) was cleaned by sonication in a 2 % Helmanex solution for 45 min, and then successively washed with water, ethanol and isopropanol. A further UV/O<sub>3</sub> treatment was done for 30 min to remove any traces of residual organic materials prior to the deposition of the functional layers. Next, a 30 nm TiO<sub>2</sub> blocking layer was applied to the substrates by spray pyrolysis at 450°C from a precursor solution of titanium diisopropoxide bis(acetylacetonate) in anhydrous ethanol. For the mesoporous TiO<sub>2</sub> layer, the TiO<sub>2</sub> paste (30 NR-D) was diluted in ethanol (ratio 1:9 w/w) and then applied to the substrate by spin-coating at 2000 rpm for 10s followed by a sintering step at 500 °C for 20 min. The following steps of the device preparation were done in a glovebox under a nitrogen atmosphere. The precursor solution of the modified perovskite FA<sub>0.1</sub>MA<sub>0.9</sub>PbI<sub>3</sub>, was composed of PbI<sub>2</sub> (1.4 M), methylammonium iodine (1.26 M) and formamidinium iodide (0.14 M) in dimethyl sulfoxide. The solution was heated at 70°C under vigorous stirring for approx. 40 min, and then allowed it to cool at RT prior to use. The perovskite solution was spun at 5000 rpm for 30 s using a ramp of 3000 rpm/s. 15 s prior to the end of the spin-coating sequence, 100 µL of chlorobenzene were poured onto the spinning substrate. Afterwards, the substrates were transferred onto a heating plate and annealed at 100 °C for 45 min. The hole-transporting

material (**TT0** or **TT1**) was prepared in a solution of Chlorobenzene (PhCl) or 1,1,2,2-Tetrachloroethane (TCE). To this solution, were successively added TBP, a 1.8M stock solution of Li-TFSI in AcCN and a 0.25 M stock solution of Co(III)-TFSI in AcCN, as additives. The final concentration of the HTM was 20 mM, 30 mM or 40 mM (see details in Table S1). Two different compositions of additives were used, either standard (A) or enriched (B). In the standard condition (A), 0.5 eq of Li-TFSI, 0.05 eq of Co(III)-TFSI and 3.3 eq of TBP per mol of Pc were added. In condition B, the composition was increased to 0.8 eq of Li-TFSI, 0.08 eq of Co(III)-TFSI and 5.1 eqs of TBP, per mol of HTM. The reference HTM solution was prepared at 60 mM of Spiro-OMeTAD in PhCl, incorporating the standard composition (A) of additives (see above). The HTM solutions were spin-coated onto the perovskite layers at 4000 rpm for 20 s. Finally, the gold electrodes were deposited by thermal evaporation of 100 nm gold using a shadow mask under high vacuum conditions.

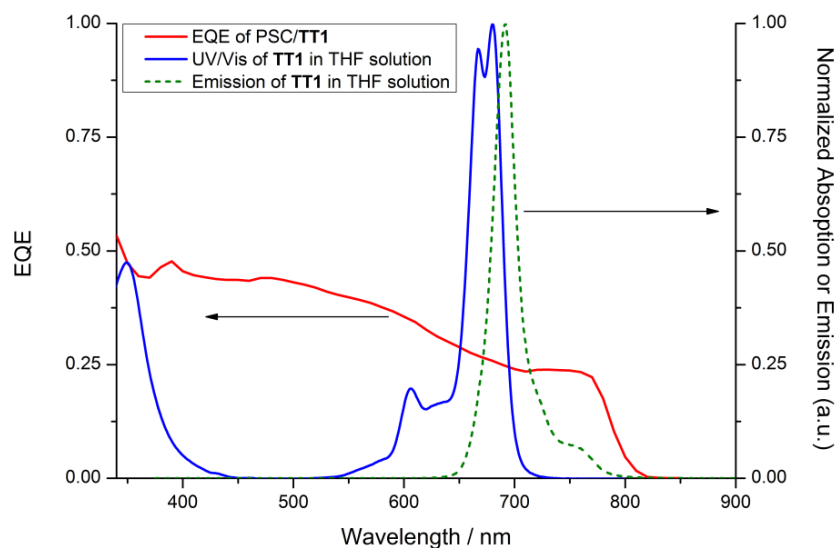
### 3. Characterisation

Current-voltage characteristics were measured in air under AM1.5G simulated sunlight (one sun, 100mW/cm<sup>2</sup>) with a Keithley potentiostat. The light intensity was measured for calibration with an NREL certified KG5 filtered Si reference diode. The solar cells were masked with a metal aperture of 0.16 cm<sup>2</sup> to define the active area. Current–voltage characteristics ( $J/V$ ) of the cells were obtained by applying an external voltage bias while measuring the current response ( $V \rightarrow J_{SC}$ ). The voltage scan rate was 10 mV·s<sup>-1</sup>. Hysteresis curves were recorded scanning at 10 mV·s<sup>-1</sup> from forward scan ( $V \rightarrow J_{SC}$ ) and *vice versa* ( $J_{SC} \rightarrow V$ ; reversed scan), with a preconditioning of the device with light during 4s before each scan. For IPCE characterization, a 300W Xe lamp (ILC Technology) was linked to a Gemini-180 monochromator (Jobin Yvon Ltd.) to tune properly the light beam. 10% of white light bias was applied using an array of white LEDs. SEM cross section images were obtained with

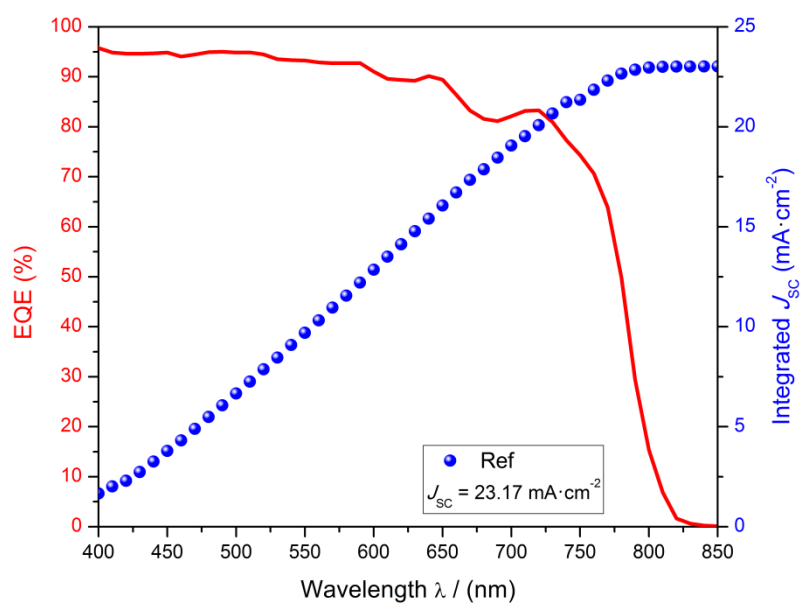
a high-resolution scanning electron microscope (ZEISS Merlin) at accelerating voltage of 5 kV.

#### *4. Conductivity measurements*

The conductivity of **TT0** and **TT1** were measured on substrates having interdigitating gold electrodes with a channel length of 2.5 $\mu$ m. The HTMs were spin-coated onto the substrates from their solutions in chlorobenzene using the same and optimized conditions than those described for the device preparation (40 mM of Pc in PhCl). Current-voltage (IV) curves were recorded in the range from -10 V to 10 V and the corresponding slope was determined using a linear fit. Finally, the conductivity values were obtained using Ohm's law. All these experiments were carried out in inert atmosphere.



**Figure S1.** External Quantum yield Efficiency of PSC/TT1 device (red solid line), and UV-Vis absorption (blue solid line) and emission (dash green line) spectra of TT1 in THF solution.



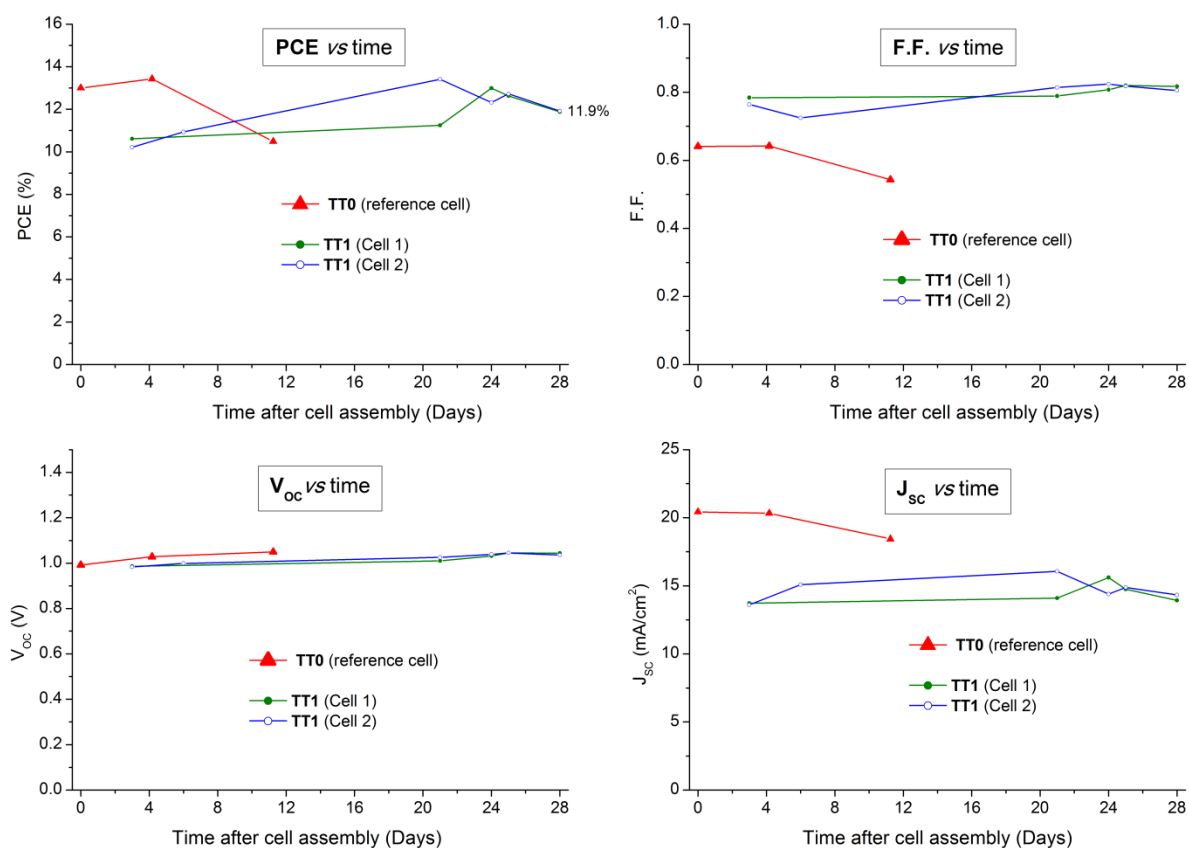
**Figure S2.** External Quantum yield Efficiency of the reference cell PSC/Spiro-OMeTAD device (red solid line), and integrated short-circuit current (blue solid line).

**Table S1.** Summary of the photovoltaic data obtained for all the PSC cells measured under simulated one sun illumination (AM1.5 G conditions).

HTM / Conc.	Uptake Solvent	Additives <sup>a</sup>	Cell	$J_{sc}$ [mA/cm <sup>2</sup> ]	$V_{oc}$ [V]	FF [%]	PCE [%]
<b>TT1</b> / 20 mM	PhCl	A	#1	18.14	0.998	57.7	10.44
			#2	16.51	0.971	48.8	7.82
			<i>Mean</i>	<i>17.3</i>	<i>0.98</i>	<i>53.3</i>	<i>9.1</i>
			$\sigma$	<i>1.2</i>	<i>0.02</i>	<i>6.3</i>	<i>1.9</i>
<b>TT1</b> / 30 mM	PhCl	A	#1	13.67	0.959	61.6	8.08
			#2	12.38	0.971	65.1	7.82
			#3	10.06	0.908	59.3	5.42
			#4	8.62	0.915	66.0	5.21
			<i>Mean</i>	<i>11.2</i>	<i>0.94</i>	<i>63.0</i>	<i>6.6</i>
			$\sigma$	<i>2.3</i>	<i>0.03</i>	<i>3.1</i>	<i>1.5</i>
<b>TT1</b> / 40 mM	PhCl	A	#1	15.05	0.903	49.5	6.73
			#2	13.77	0.829	42.4	4.83
			#3	15.15	0.824	37.4	4.67
			#4	12.96	0.887	39.0	4.48
			#5	18.61	1.007	48.6	9.11
			#6	18.20	0.993	42.8	7.74
			<i>Mean</i>	<i>15.6</i>	<i>0.91</i>	<i>43.3</i>	<i>6.3</i>
			$\sigma$	<i>2.3</i>	<i>0.08</i>	<i>4.9</i>	<i>1.9</i>
<b>TT1</b> / 40 mM	TCE	A	#1	16.66	0.888	43.7	6.47
			#2	14.40	0.469	46.9	6.13
			#3	14.47	0.549	33.2	2.56
			#4	13.58	0.440	33.4	2.00
			<i>Mean</i>	<i>14.8</i>	<i>0.59</i>	<i>39.3</i>	<i>4.3</i>
			$\sigma$	<i>1.3</i>	<i>0.21</i>	<i>7.1</i>	<i>2.3</i>
<b>TT1</b> / 20 mM	PhCl	B	#1	18.79	1.033	66.2	12.85
			#2	18.96	1.018	64.8	12.50
			<i>Mean</i>	<i>18.9</i>	<i>1.03</i>	<i>65.5</i>	<i>12.7</i>
			$\sigma$	<i>0.1</i>	<i>0.01</i>	<i>1.0</i>	<i>0.25</i>
<b>TT1</b> / 40 mM	PhCl	B	#1	17.41	0.962	81.6	13.67
			#2	16.06	1.025	81.4	13.41
			#3	16.76	0.955	82.9	13.27
			#4	15.61	0.807	80.7	12.99
			#5	15.53	0.988	83.6	12.83
			#6	14.90	0.946	83.4	11.75
			<i>Mean</i>	<i>16.0</i>	<i>0.95</i>	<i>82.3</i>	<i>13.0</i>
			$\sigma$	<i>0.9</i>	<i>0.07</i>	<i>1.2</i>	<i>0.7</i>

<b>Spiro</b> / 60 mM	PhCl	A	#1	23.22	1.082	77.1	19.37
			#2	23.48	1.059	77.0	19.14
			#3	23.37	1.056	76.1	18.79
			#4	23.18	1.072	75.2	18.69
			#5	22.20	1.084	76.4	18.38
			#6	21.84	1.058	61.4	14.20
			<i>Mean</i>	22.9	1.07	73.9	18.1
			$\sigma$	0.7	0.01	6.1	1.9
<b>TT0</b> / 20 mM	PhCl	A	#1	19.21	1.021	61.7	12.09
			#2	20.15	1.022	58.0	11.95
			<i>Mean</i>	19.7	1.0215	59.9	12.0
			$\sigma$	0.7	$7.1 \times 10^{-4}$	2.6	0.1
<b>TT0</b> / 40 mM	PhCl	A	#1	20.51	1.042	63.4	13.54
			#2	18.32	0.722	35.5	4.7
			<i>Mean</i>	19.4	0.9	49	9
			$\sigma$	1.5	0.2	20	6
<b>TT0</b> / 40 mM	PhCl	B	#1	20.33	1.028	64.2	13.43
			#2	20.23	1.049	65.9	13.97
			<i>Mean</i>	20.28	1.04	65.1	13.7
			$\sigma$	0.07	0.02	1.2	0.4

<sup>[a]</sup> Additives; Conditions A: Li-TFSI (0.5 eq), Co(III)-TFSI (0.05 eq) and TBP (3.3 eq) per mol of HTM; conditions B: LiTFSI (0.8 eq), Co(III)TFSI (0.08 eq) and TBP (5.1 eq). TCE = 1,1,2,2-tetrachloroethane; PhCl = Chlorobenzene; TFSI = Bis(trifluoromethane)sulfonimide; TBP = 4-tert-butylpyridine.



**Figure S3.** Evolution in time of the photovoltaic characteristics of two optimised **TT1**/PSC devices, measured under simulated one sun illumination (AM1.5G). A reference device made with **TT0** is also given for comparison (fabricated under the same optimized conditions). The non-encapsulated devices were stored inside a home-made dry box, and the  $J/V$  characteristics were measured periodically under ambient atmosphere.

## REFERENCES

(1) Cid, J.-J.; Yum, J.-H.; Jang, S.-R.; Nazeeruddin, M. K.; Martínez-Ferrero, E.; Palomares, E.; Ko, J.; Grätzel, M.; Torres, T., Molecular Cosensitization for Efficient Panchromatic Dye-Sensitized Solar Cells. *Angew. Chem., Int. Ed.* **2007**, 46, (44), 8358-8362.