Supplementary Materials

Green anisole solvent-based synthesis and Deposition of phthalocyanine dopant-free hole-transport materials for perovskite solar cells

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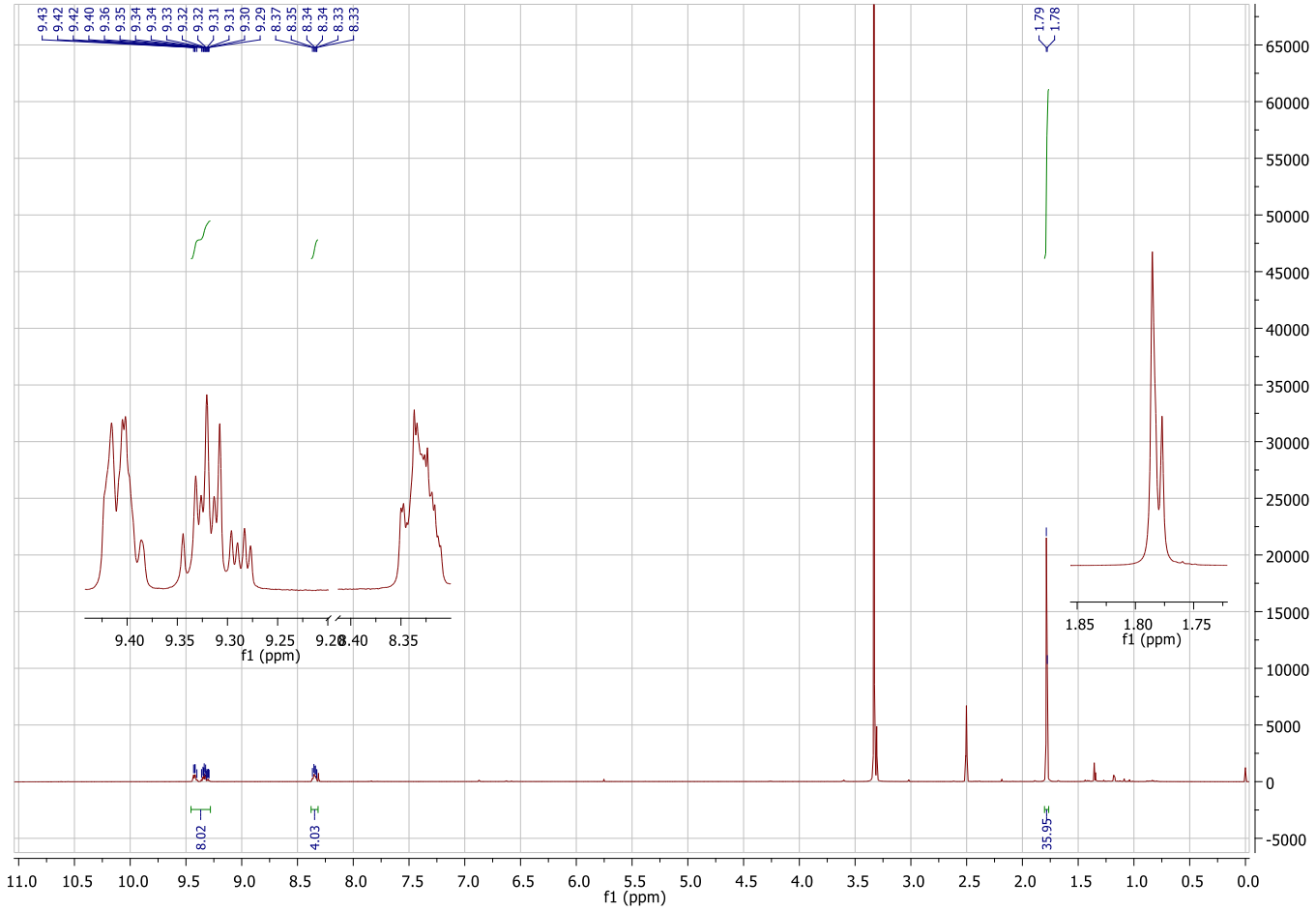


Figure S1*: ^{1}H NMR of TBU4-Zn in DMSO-d6.*

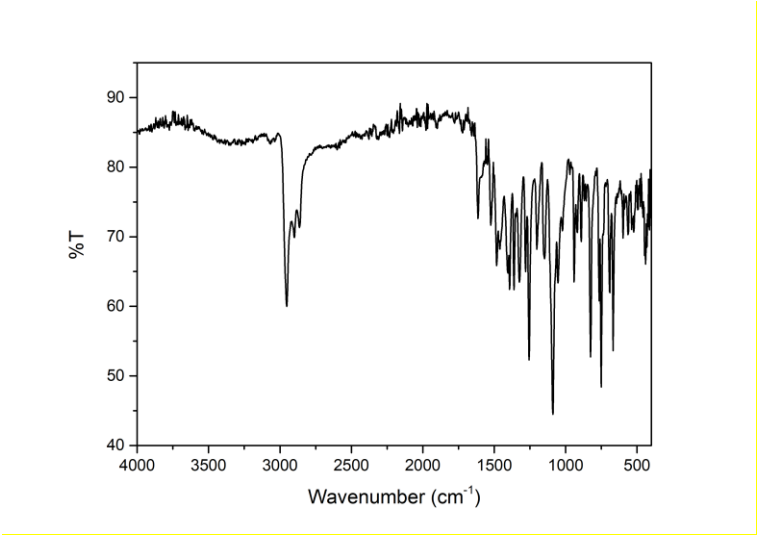


Figure S2a: *IR spectrum of TBU4-Co.*

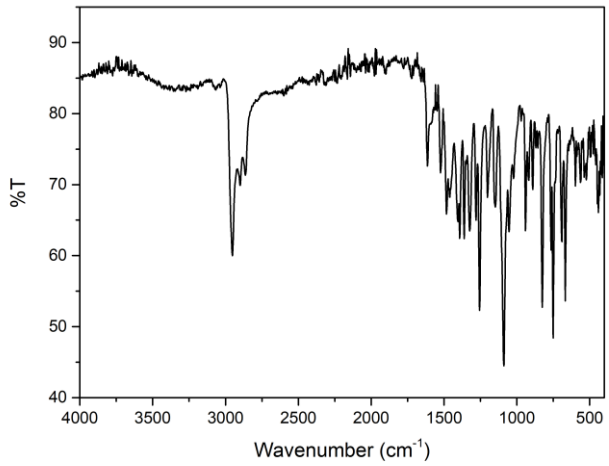


Figure S2b: *IR spectrum of TBU4-Cu.*

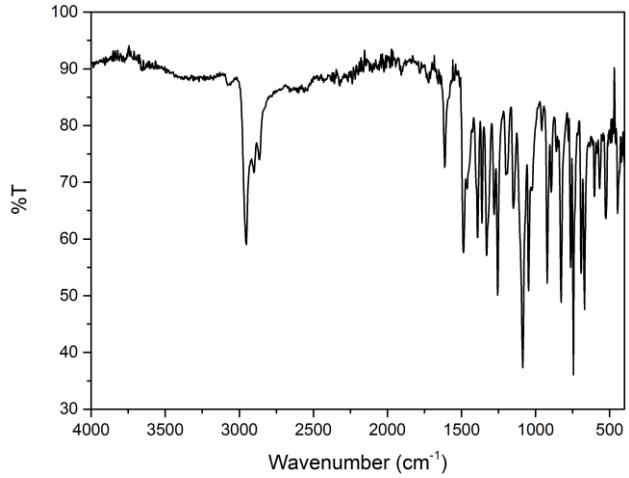


Figure S2c: *IR spectrum of TBU4-Zn.*

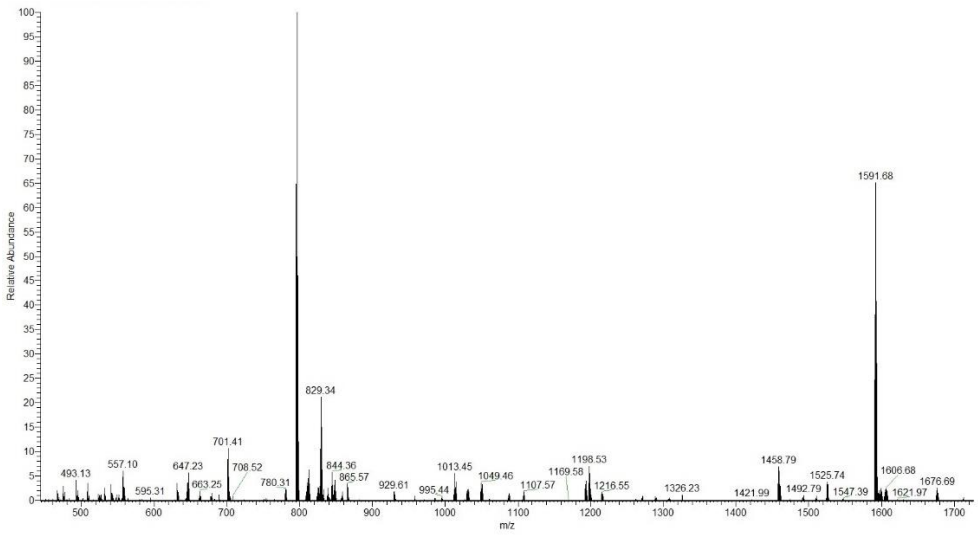


Figure S3a: ESI-MS spectrum of TBU4-Co.

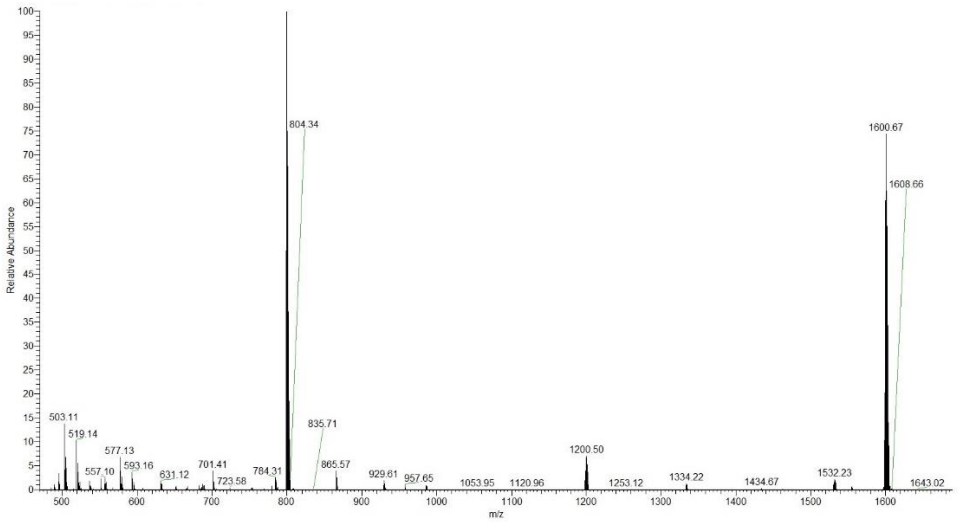


Figure S3b: ESI-MS spectrum of TBU4-Cu.

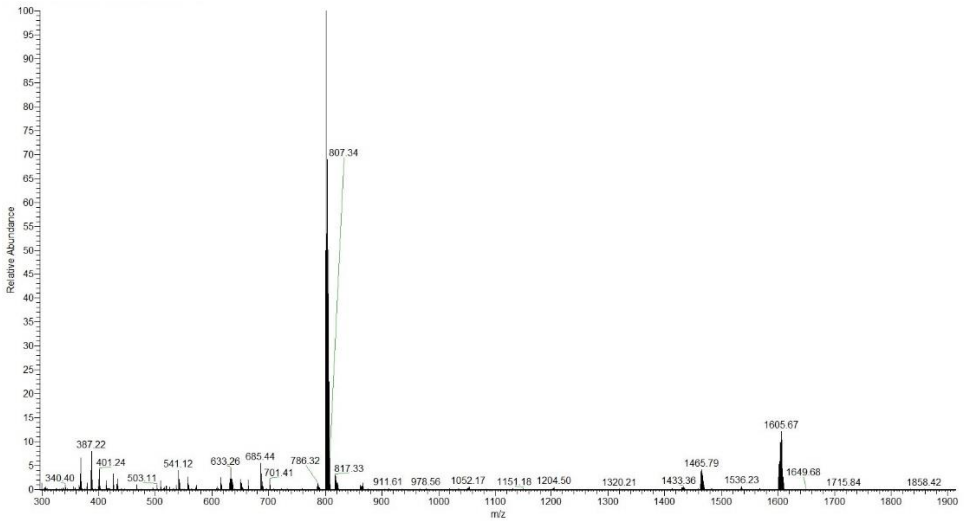


Figure S3c: ESI-MS spectrum of TBU4-Zn.

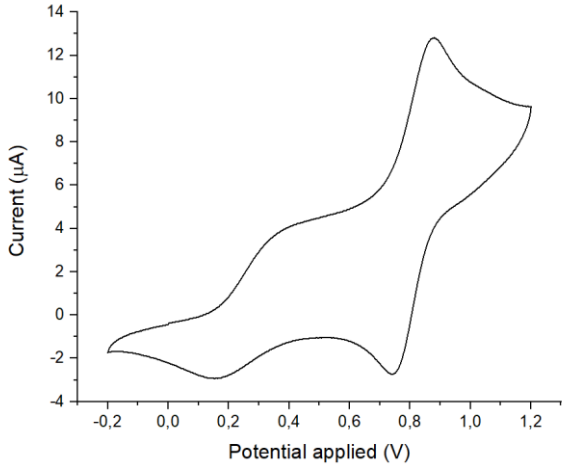


Figure S4a: *TBU4-Co anodic scan in dichloromethane. Scan rate 0.1 Vs^{-1}. The reference Fc^{+}/Fc couple gave a potential of 0.43 V.*

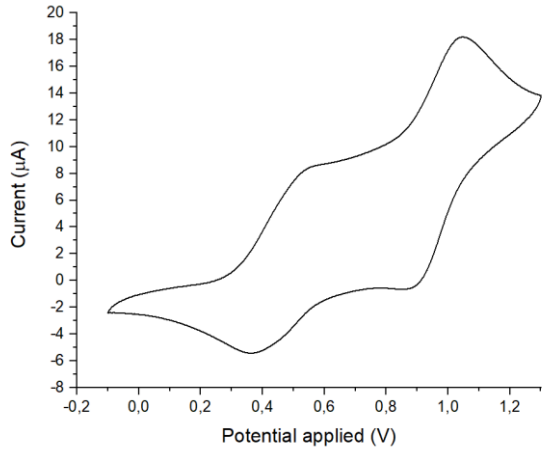


Figure S4b: *TBU4-Cu anodic scan in dichloromethane. Scan rate 0.1 Vs^{-1}. The reference Fc^{+}/Fc couple gave a potential of 0.43 V.*

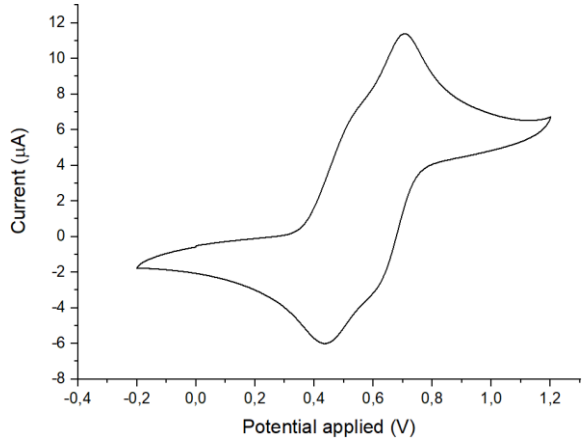


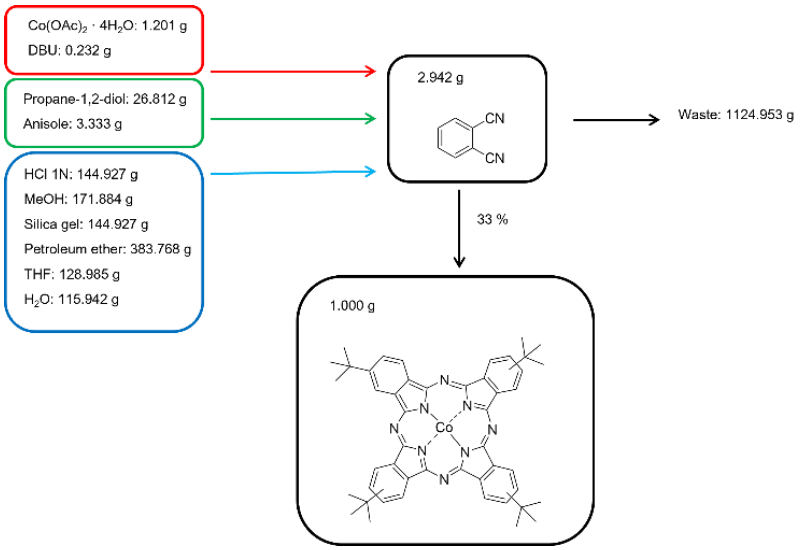
Figure S4c*: TBU4-Zn anodic scan in dichloromethane. Scan rate 0.05 Vs^{-1}.The reference Fc^{+}/Fc couple gave a potential of 0.43 V.*

Cost analysis

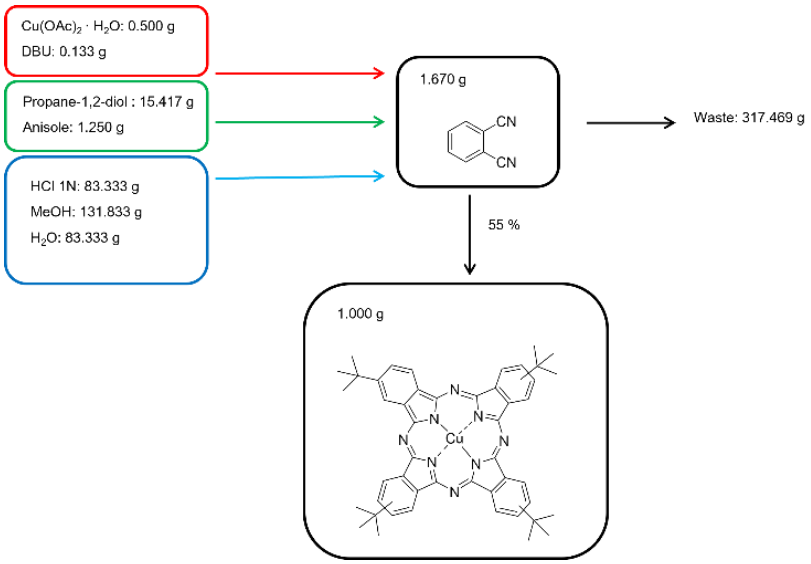
For the sake of simplicity, Merck has been chosen as the only supplier for reagents, solvents, and purification materials (https://www.sigmaaldrich.com/IT/it) except for 4-*tert*-butylphthalonitrile that has been quoted from TCI chemicals (https://www.tcichemicals.com/IT/en/). In all cases, the bulkiest batches available on the online catalogs at a sufficient degree of purity have been chosen and the product number of each chemical has been reported in Table S1 for sake of clarity. The costs of our syntheses have been estimated by calculating the required amounts of chemicals to produce 1 gram of the desired phthalocyanine in the respective yields (see the synthesis flowcharts in Figures S5 a,b,c) and multiplying them by their current prices, rounded to the nearest cent. Prices have been checked on March 10th, 2023.
The density of HCl 1N has been approximated to 1.00 g/cm^3.

Table S1: Overview of the quoted materials

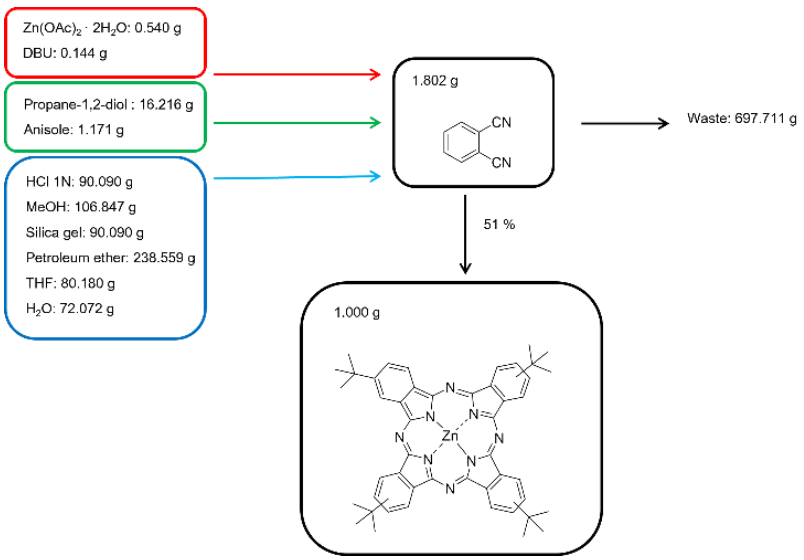
Reagent	quoted price (EUR)	size	EUR/g
4-*tert*-butylphthalonitrile B1334	368.00	25g	14.72
$Co(OAc)_2 \cdot 4H_2O$ 208396-1KG	439.00	1.0 kg	0.44
$Cu(OAc)_2 \cdot H_2O$ 341746-2.5KG	406.00	2.5 kg	0.16
$Zn(OAc)_2 \cdot 2H_2O$ 383058-2.5KG	470.00	2.5 kg	0.19
DBU 8032829050 d= 1.02 g/cm³	2770.00	50 kg	0.055
Anisole 8014529025 d= 0.995 g/cm^3	791.00	25 L 24.875 kg	0.032
Propane-1,2-diol W294004-25KG-K d= 1.035 - 1.040 g/cm³	286.00	25 kg	0.011
Methanol 179337-200L d= 0.791 g/cm^3	1880.00	200 L 158.200 kg	0.012
HCl 30721-2.5L-M d= 1.2 g/cm³	47.00	2.5 L 3.0 kg	0.016
Silica gel 60741-25KG	1610.00	25 kg	0.064
Petroleum ether 50-70 1009106025 d= 0.662 g/cm^3	856.00	25 L 16.55 kg	0.052
THF 360589-20L d= 0.89 g/cm^3	827.00	20 L 17.80 kg	0.047
Chlorobenzene 8017919025 d= 1.11 g/cm^3	307.00	25L 27750 kg	0.011



(a)



(b)



(c)

***Figure S5**: Flowcharts for the synthesis of 1.000 g of (a) TBU4-Co, (b) TBU4-Cu and (c) TBU4-Zn. Reagents are highlighted in red, solvents are highlighted in green and workup/purification materials are highlighted in blue.*

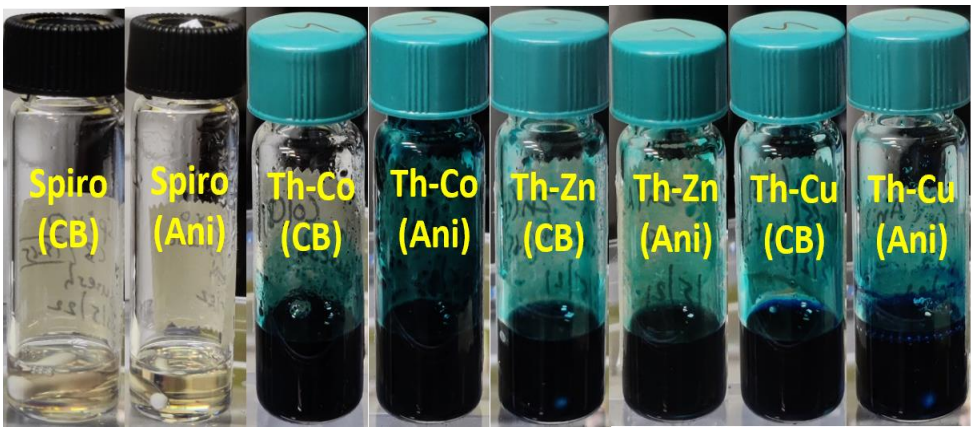


Figure S6*: Solutions of Various HTMs with Chlorobenzene (CB), Anisole (Ani).*

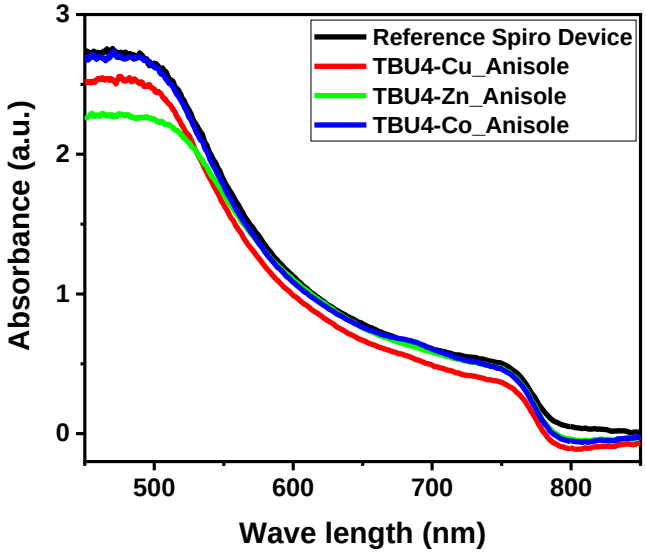


Figure S7*: UV absorption spectra of various HTMs thin films on perovskite (TBU4-Co, TBU4-Zn, TBU4-Cu).*

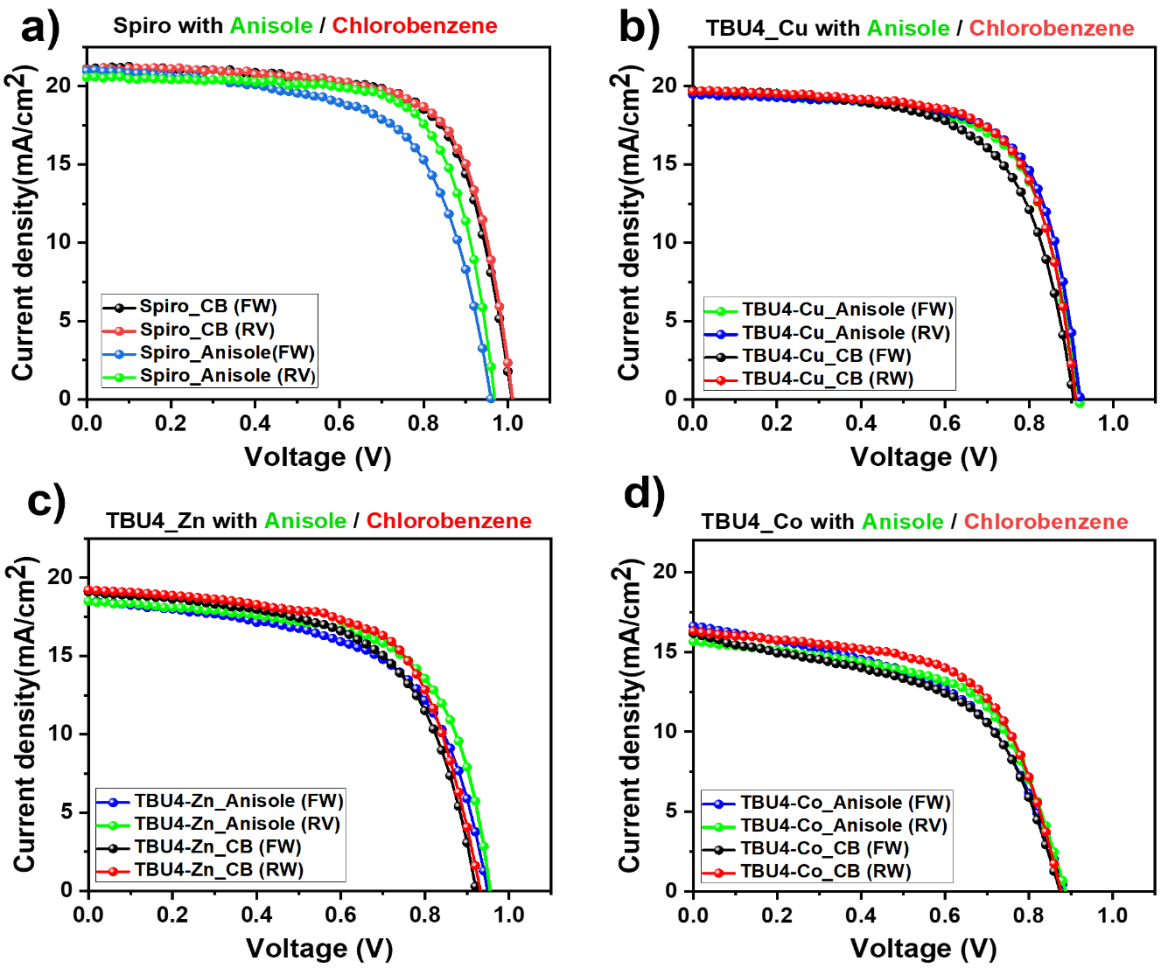


Figure S8: *Anisole- and chlorobenzene-based HTM devices Current density vs voltage curves a) Spiro devices, b) TBU4-Cu devices, c) TBU4-Zn devices, d) TBU4-Co devices.*

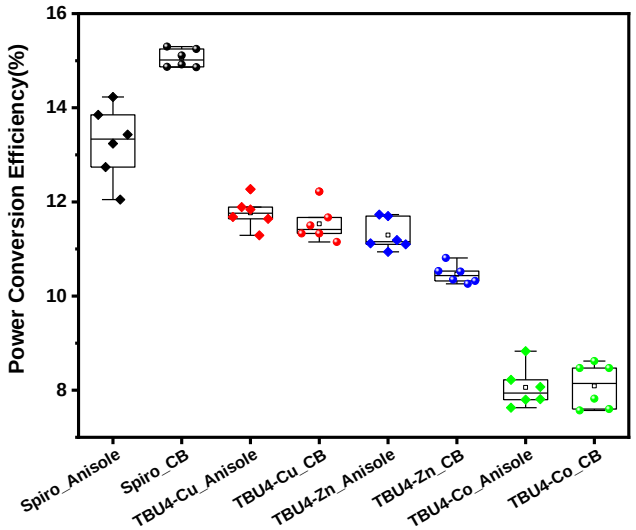
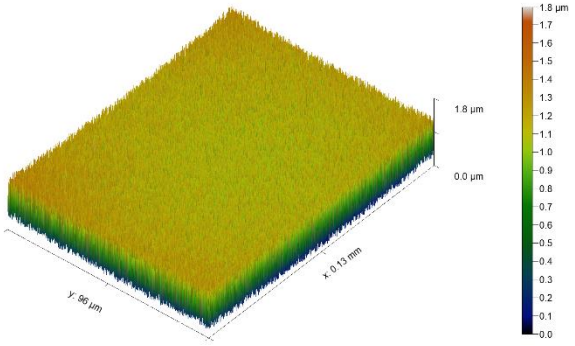
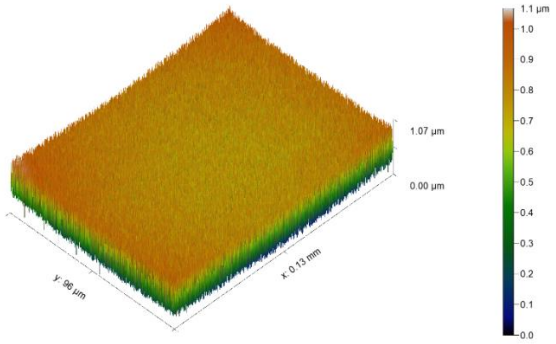


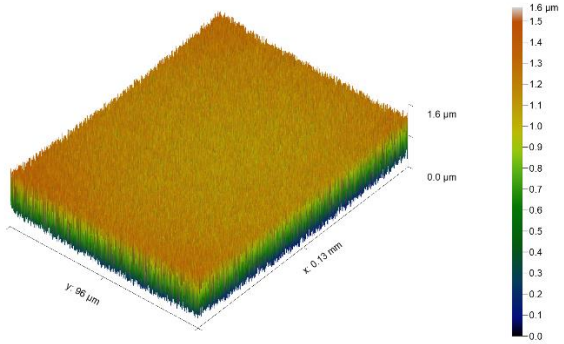
Figure S9: *Statistical evaluation box charts of anisole- and chlorobenzene-based devices (6 samples for each).*



(a) TBU4-Cu Roughness 345.0 ± 7.8 nm



(b) TBU4-Zn Roughness 230.3 ± 5.2 nm



(c) TBU4-Co Roughness 343.6 ± 7.7 nm

Figure S10: *Surface morphologies with roughness values for a) TBU4-Cu, b) TBU4-Zn, c) TBU4-Co*.

Optical images were obtained by Olympus Lext OLS 3100 confocal microscope. Confocal microscopy provides a topographic map by transforming a series of optical sections taken from the surface that can be used to measure surface roughness. Surface roughness measurement from this technique is proved to be comparable to stylus instruments. Gwyddion software was used to calculate surface roughness from confocal microscopy results.