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Supplementary information for:

Dopant-Free and Low-cost molecular "Bee" Hole-Transporting Materials for Efficient and Stable Perovskite Solar Cells†

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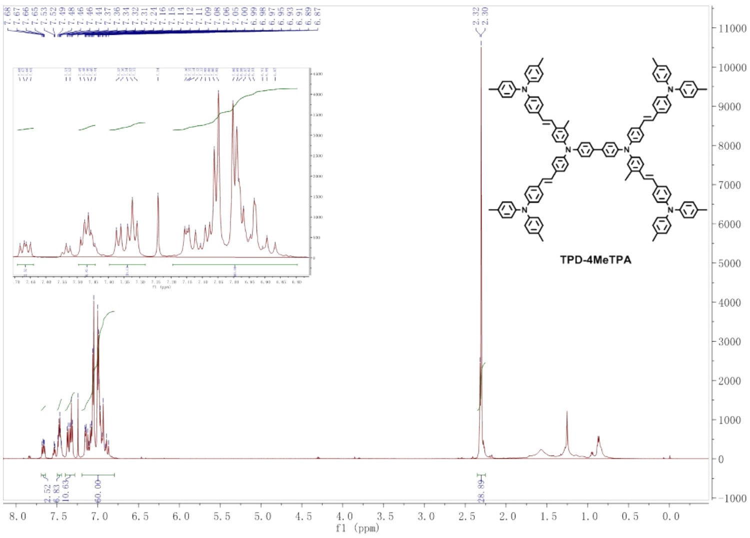
† X. C. Liu and F. Zhang have equivalent contribution.

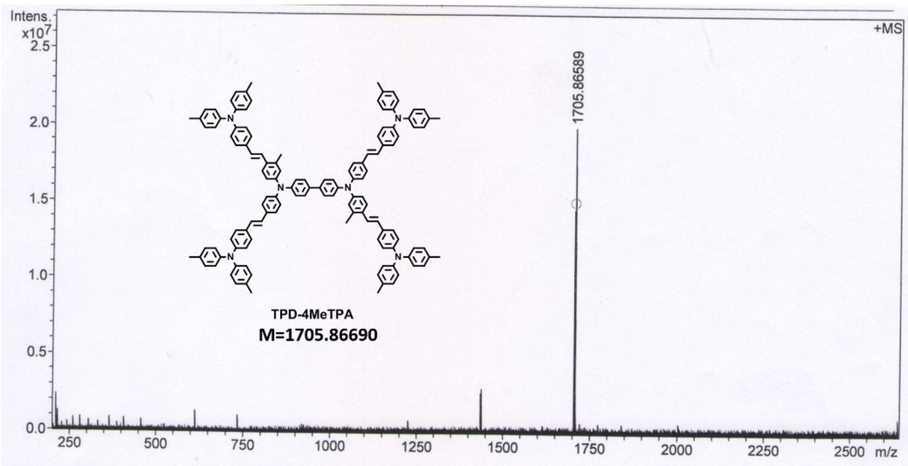
1. Structural characteristics

The structure of as-synthesized HTMs (TPD-4MeTPA, TPD-4MeOTPA, and TPD-4EtCz) were confirmed *via* ^{1}H NMR and HRMS, which agreed well with the proposed molecular structure (**Fig. S1**).

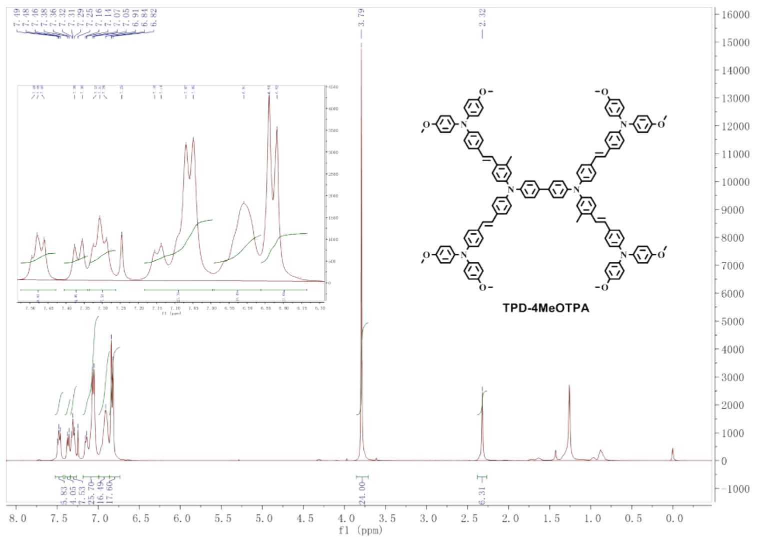
^{1}H NMR of TPD-4MeTPA



HRMS of TPD-4MeTPA



[1]H NMR of TPD-4MeOTPA



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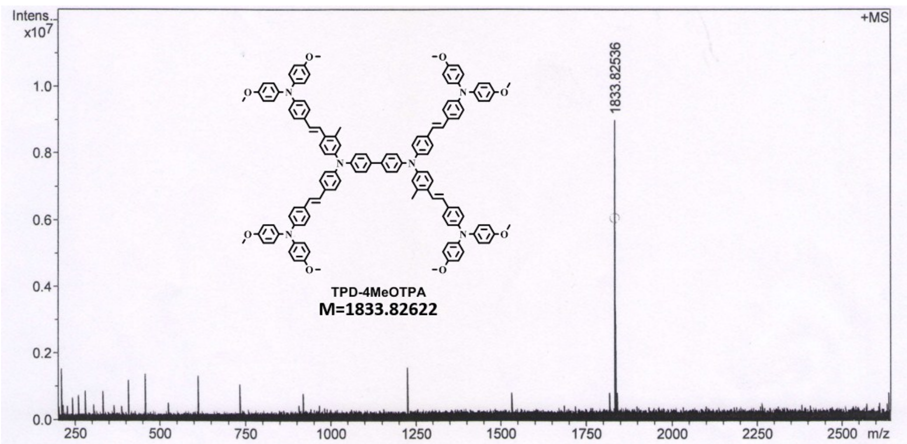
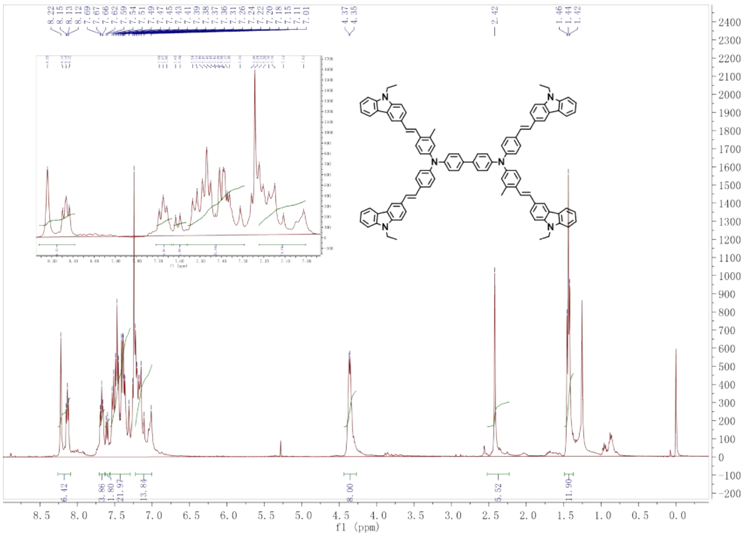


^1H NMR of TPD-4EtCz



HRMS of TPD-4EtCz

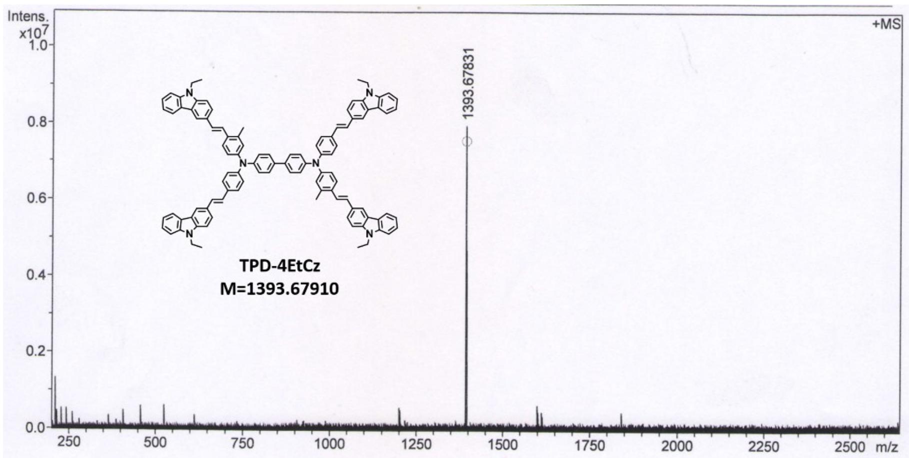


Fig. S1 ^1H NMR and HRMS of the as-synthesized HTMs.

2. Synthesis cost estimation of as-synthesized HTMs

We roughly estimated the synthesis cost of as-synthesized HTMs according to the cost model that was described by Pablo *et al*[1]. and Osedach *et al*[2]. The estimated synthesis cost is 55.59 $/g, 64.47 $/g and 29.66 $/g for TPD-4MeTPA, TPD-4MeOTPA and TPD-4EtCz, respectively. Since these tables do not take into account several important parameters (e.g. energy consumption, waste treatment and labor), it was multiplied by a factor of 1.5 to get a more realistic estimation of lab synthesis costs of 83.39 $/g, 96.71 $/g and 44.49 $/g as reported in the main text (55.59 ∗ 1.5 = 83.39 $/g, 64.47 ∗ 1.5 = 96.71 $/g, 29.66 ∗ 1.5 = 44.49 $/g)[3], which is much cheaper than that of *spiro*-OMeTAD (581.52 $/g).

Table S1 Materials quantities and cost for the synthesis of TPD-4MeTPA

Chemical name	Price of Chemical / $	Weight or amount reagent	Material cost / $
N,N′-diphenyl-*N,N′*-di(*m*-tolyl)benzidine (TPD)	163.80 / 10 g	0.8 g	13.10
Imidazole	12.25 / 25 g	0.5 g	0.25
Acetonitrile	3.06 / 500 mL	30 mL	0.18
Trifluoroacetic Anhydride	45.64 / 750 g	2 mL	0.12
Tetrahydrofuran	3.98 / 500 mL	60 mL	0.48
Hydrochloric Acid	2.76 / 500 mL	10 mL	0.06
4-(di-*p*-tolylamino) benzaldehyde	272.84 / 5 g	0.5 g	27.28
Sodium Borohydride	10.72 / 25g	0.5 g	0.21
Triphenylphosphine Hydrobromide	45.64 / 500 g	3.5 g	0.32
Dichloromethane	11.33 / 5 L	150 mL	0.34
Ether	3.98 / 500 mL	50 mL	0.40
Potassium *tert*-Butanolate (*t*-BuOK)	21.90 / 100 g	2.5 g	0.55
Sodium Hydroxide	4.43 / 500 g	2.0 g	0.02
Silica gel (300-400mesh)	13.52 / kg	0.44 kg	5.95
Petroleum ether	7.35 / 5 L	3 L	4.41
Ethyl acetate	11.49 / 5 L	800 mL	1.84
Ethanol	7.66 / 5 L	50 mL	0.08
Total			55.59 $

Table S2 Materials quantities and cost for the synthesis of TPD-4MeOTPA

Chemical name	Price of Chemical / $	Weight or amount reagent	Material cost / $
N,N′-diphenyl-*N,N′*-di(*m*-tolyl)benzidine (TPD)	163.80 / 10 g	0.8 g	13.10
Imidazole	12.25 / 25 g	0.5 g	0.25
Acetonitrile	3.06 / 500 mL	30 mL	0.18

Trifluoroacetic Anhydride	45.64 / 750 g	2 mL	0.12
Tetrahydrofuran	3.98 / 500 mL	60 mL	0.48
Hydrochloric Acid	2.76 / 500 mL	10 mL	0.06
p-Iodoanisole	69.17 / 10 g	2.6 g	17.98
Phenylamine	7.83 / 500 mL	3.0 mL	0.01
Copper(I) chloride	16.54 / 100 g	1.6 g	0.26
1,10-phenanthroline	3.98 / g	3.0 g	11.95
Dimethylbenzene	5.36 / 500 mL	100 mL	1.07
N,N-Dimethylformamide	15.00 / 100 mL	30 mL	4.50
Phosphorus oxychloride	19.60 / 500 mL	10 mL	0.39
Sodium Borohydride	10.72 / 25 g	0.5 g	0.21
Triphenylphosphine Hydrobromide	45.64 / 500 g	3.5 g	0.32
Dichloromethane	11.33 / 5 L	150 mL	0.34
Ether	3.98 / 500 mL	50 mL	0.40
Potassium *tert*-Butanolate (*t*-BuOK)	21.90 / 100 g	2.5 g	0.55
Sodium Hydroxide	4.43 / 500 g	2.0 g	0.02
Silica gel (300-400mesh)	13.52 / kg	0.44 kg	5.95
Petroleum ether	7.35 / 5 L	3 L	4.41
Ethyl acetate	11.49 / 5 L	800 mL	1.84
Ethanol	7.66 / 5 L	50 mL	0.08
Total			64.47 $

Table S3 Materials quantities and cost for the synthesis of TPD-4EtCz

Chemical name	Price of Chemical / $	Weight or amount reagent	Material cost / $
N,N′-diphenyl-*N,N′*-di(*m*-tolyl)benzidine (TPD)	163.80 / 10 g	0.8 g	13.10
Imidazole	12.25 / 25 g	0.5 g	0.25
Acetonitrile	3.06 / 500 mL	30 mL	0.18
Trifluoroacetic Anhydride	45.64 / 750 g	2 mL	0.12
Tetrahydrofuran	3.98 / 500 mL	60 mL	0.48

Hydrochloric Acid	2.76 / 500 mL	10 mL	0.06
3-Formyl-9-ethylcarbazole	96.07 / 25 g	0.35 g	1.35
Sodium Borohydride	10.72 / 25g	0.5 g	0.21
Triphenylphosphine Hydrobromide	45.64 / 500 g	3.5 g	0.32
Dichloromethane	11.33 / 5 L	150 mL	0.34
Ether	3.98 / 500 mL	50 mL	0.40
Potassium *tert*-Butanolate (*t*-BuOK)	21.90 / 100 g	2.5 g	0.55
Sodium Hydroxide	4.43 / 500 g	2.0 g	0.02
Silica gel (300-400mesh)	13.52 / kg	0.44 kg	5.95
Petroleum ether	7.35 / 5 L	3 L	4.41
Ethyl acetate	11.49 / 5 L	800 mL	1.84
Ethanol	7.66 / 5 L	50 mL	0.08
Total			29.66 $

3. Thermal properties

The glass transition temperatures (T_g) of the new HTMs were determined by differential scanning calorimetry (DSC) and decomposition temperatures (T_d) were determined by thermogravimetric analysis (TGA).

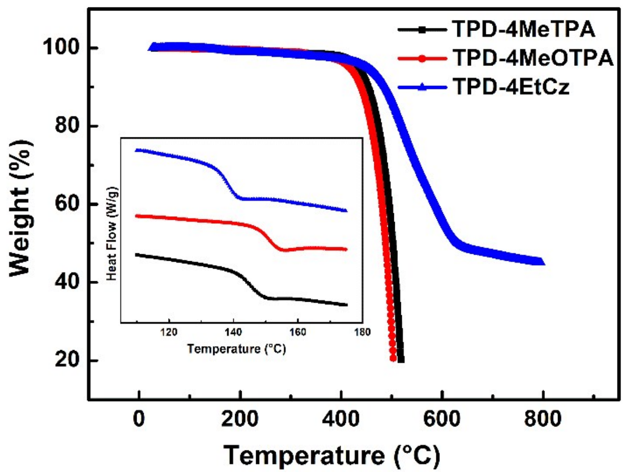


Fig. S2 TGA and DSC curves of the as-synthesized HTMs.

4. PYS measurement

The photoelectron yield spectroscopy (PYS) method as a new tool to study the energy distribution of electronic states can determine the ionization potential (E_{IP})

directly. The Photoelectron yield spectra of spin-coated films are shown in **Fig. S3.** As shown, the threshold energies refer to the E_{IP} of thin films spin-coated with the three new HTMs. The HOMO levels are determined as the minus of E_{IP}, which are –5.33, -5.28, and –5.34 eV for TPD-4MeTPA, TPD-4MeOTPA and TPD-4EtCz, respectively.

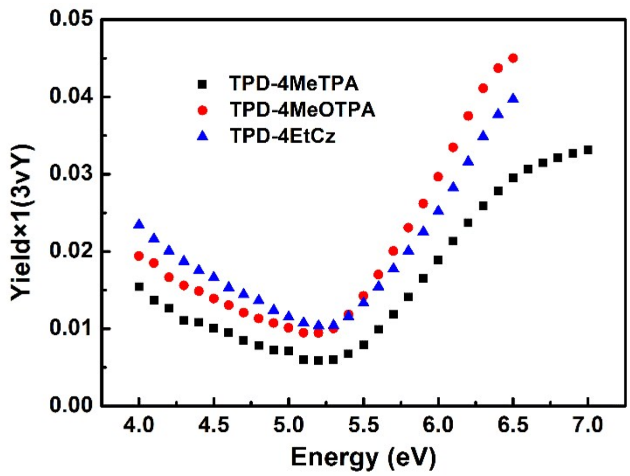


Fig. S3 Photoelectron yield spectroscopy of as-synthesized HTMs.

5. Morphology measurements of films

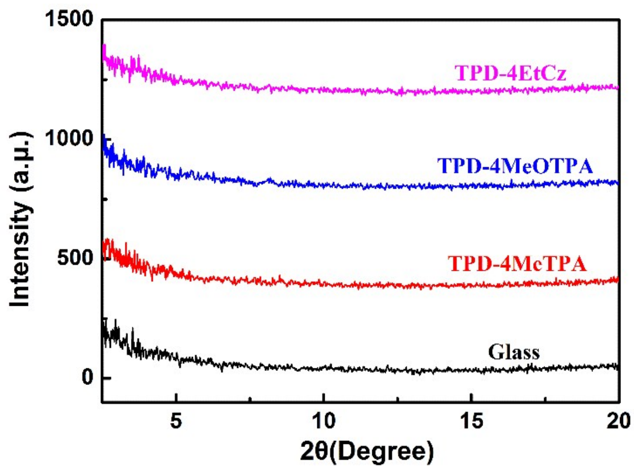


Fig. S4 X-ray diffraction spectra of the thin film samples on glass substrates.

6. Hole Mobilities of HTMs

The hole mobilities of the new HTMs were measured by the time-of-flight (TOF) transient photocurrent technique at room temperature. The transit times (t_T) were obtained from the intersection point of two asymptotes in the double-logarithmic representations (insets of Fig. S5). The hole mobilities (μ) were calculated using the relation $\mu = d^2 / V t_T$, where d is the organic film thickness, V is the applied voltage, and t_T is the transit time.

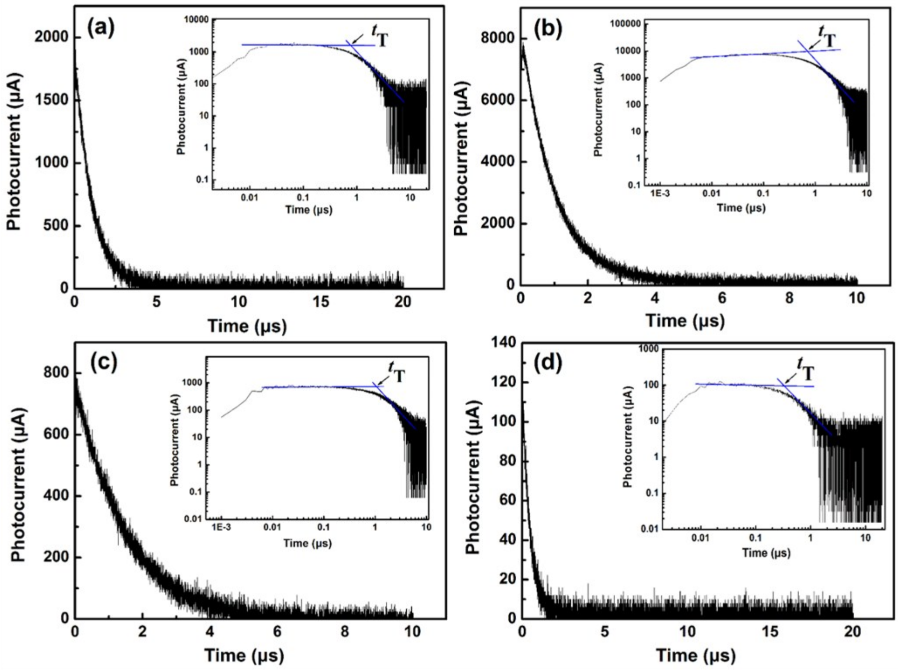


Fig. S5 Representative TOF transients for holes at room temperature ($E = 1.5\times10^5$ V cm^{-1}). Insets are double-logarithmic plots of the data.

7. Characteristics of PSC

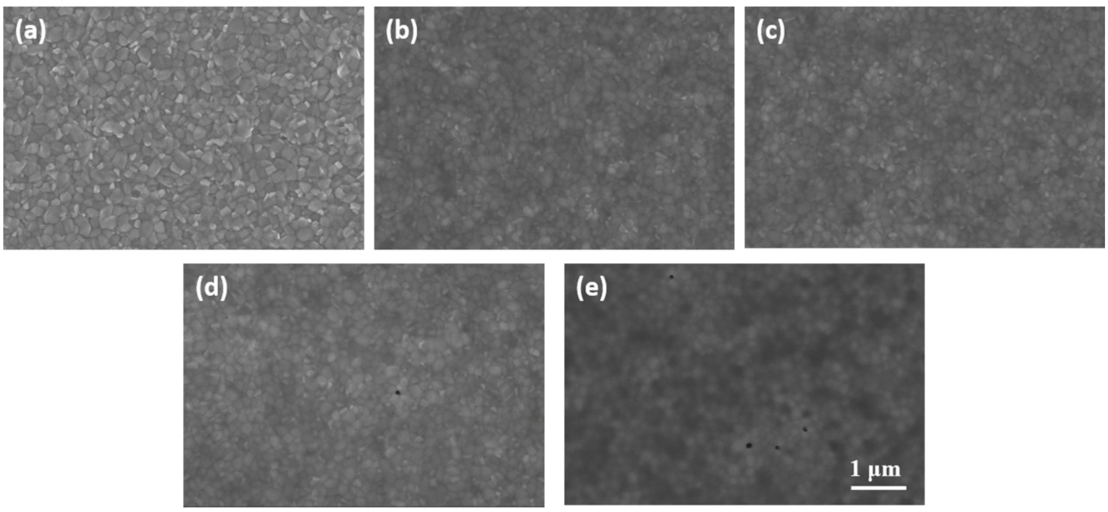


Fig. S6 Surface view SEM images of (a) pristine perovskite ; (b) perovskite /dopant-free TPD-4MeTPA; (c) perovskite / dopant-free TPD-4MeOTPA; (d) perovskite/dopant-free TPD-4EtCz; (e) perovskite / doped TPD-4MeOTPA. Scale bar is 1μm.

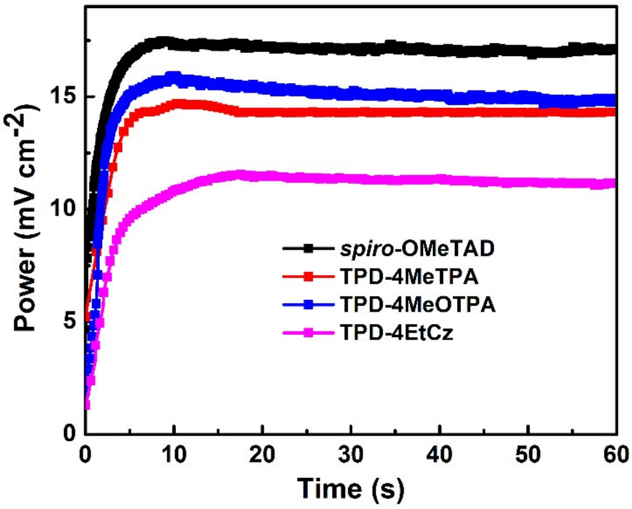


Fig. S7 The stabilized power output of the cell based on the new HTMs and *spiro*-OMeTAD.

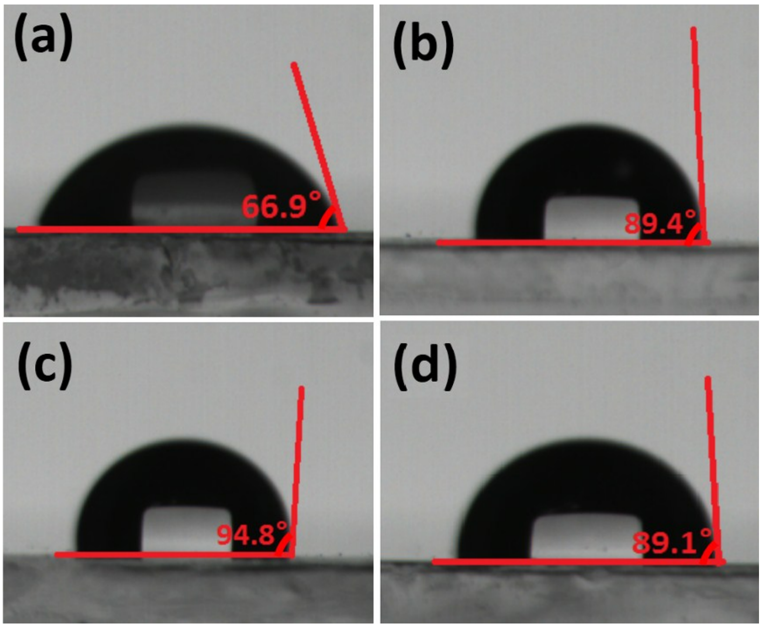


Fig. S8 Contact angles between HTMs and water, (a) *spiro*-OMeTAD doped; (b) ~ (d) TPD-4MeTPA, TPD-4MeOTPA, and TPD-4EtCz dopant-free, repectively.

Table S4 *J-V* curves of doped-HTMs based device under different scan directions

HTM	J_{sc}(mA cm^{-2})	V_{oc}(V)	*FF*	PCE (%)
TPD-4MeTPA++	17.500	0.959	0.447	7.50
TPD-4MeOTPA++	18.540	0.949	0.415	7.29

TPD-4EtCz++	18.830	0.948	0.453	8.09
spiro-OMeTAD	18.132	0.949	0.389	6.69
HTM-free	14.470	0.896	0.475	6.16

+ + = samples include LiTFSI and tBP additives.

Table S5 PL lifetimes of $TiO_2/CH_3NH_3PbI_3$/HTM films

HTM	τ_2 (ns)	τ_1 (ns)
TPD-4MeTPA	74.53	8.50
TPD-4MeOTPA	63.70	7.55
TPD-4EtCz	92.58	12.26
spiro-OMeTAD++	30.26	3.59
HTM-free	171.70	22.14

+ + = samples include LiTFSI and tBP additives.

References

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2 T. P. Osedach, T. L.Andrew and V.Bulovic, *Energy Environ. Sci.*, 2013, **6**, 711-718.

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