View Article Online

Journal of Materials Chemistry A

Materials for energy and sustainability

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: H. Shahroosvand, B. Pashaei, M. Ameri, E. Mohajerani and M. K. Nazeeruddin, *J. Mater. Chem. A*, 2019, DOI: 10.1039/C9TA05121J.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/materials-a

Sequential Condensation Route as a Versatile Platform for Low Cost and Efficient Hole Transport Material in Perovskite Solar Cell

Babak Pashaei,^a Hashem Shahroosvand^a*, Mohsen Ameri,^b Ezeddin Mohajerani^b, Mohammad Khaja Nazeeruddin^{e*}

^aGroup for Molecular Engineering of Advanced Functional Materials (GMA), Chemistry Department, University of Zanjan, Zanjan, Iran

^b Photonics of Organic Materials and Polymers (POMP lab), LASER & Plasma research institute, Shahid Beheshti University, Iran

^c Group for Molecular Engineering of Functional Materials, Institute of Chemical Sciences and Engineering, Ecole polytechnique fédérale de Lausanne, CH-1951 Sion, Switzerland

Abstract: in an effort to diminish the cost of perovskite solar cells (PSCs) with regards to the hole transport materials (HTMs), we employed an easily attainable condensation route to synthesis a cheap and efficient HTM. Using newly engineered small organic molecule, N,N'-(naphthalene-1,5-diyl)bis(1-(2,3-

diphenylquinoxalin-6-yl)-1-phenylmethanimine), coaded as BEDN, the power conversion efficiency (PCE) reached to 17.85%, comparable to the state-of-the-art HTM spiro-OMeTAD (19.50%). The BEDN's estimated cost is 1.38 (\$/g), which is considerably cheaper than spiro-OMeTAD, 92 (\$/g). The low cost and high efficiency are promising perspective in commercialization of perovskite solar cells.

Introduction

The rapid development of organic/inorganic metal-halides perovskite solar cells (PSCs) has amazed the solar cells research community.¹⁻² Only after seven years from the beginning, more than ten thousand researchers are currently being involved in PSCs progress, worldwide.3 The rapid growth of efficiency, reaching from about 3.8%⁴ to phenomenal value of 24.2%,⁵ in just a few years from the discovery of the first perovskite nanocrystals as a light absorber in DSSCs in 2009,⁴ has turned this field to a "gold rush "6. PSCs have the potential to operate efficiently for widespread deployment, but several obstacles still exist. Firstly, achieving a reliable judgment about the long-term stability under extensive light soaking at a temperature of 60 °C is seemingly a challenging step.7-12 In recent years, a number of strategies and protocols have been reported to address this issue in the near future.¹³ Secondly, the environmental issues with the materials at the heart of PSCs, namely lead metal, cannot be neglected.¹⁴ Hence, fundamental understanding of the mechanism of degradation and composition of employed materials could be useful to reach to novel formulations and materials with the reduced cost and higher efficiencies.¹⁵⁻¹⁶.¹⁷ As of the essential requirement to fabricate an efficient device is to minimize the charge recombination losses and to control the trapping phenomena at the perovskite/hole transport materials (HTMs) interface.¹⁸⁻¹⁹ Accordingly, the discovery of new HTMs to employ in optoelectronic devices is still an open issue, and an enormous improvement on the efficiency is achieved by identifying novel HTMs including polymers, small organic molecules, and inorganic materials.²⁰ In this paradigm, small organic molecules have remarkable advantages such as the facility in the synthesis process with high yield and purity, which is of great interest for industrial production.²¹ The most well-known organic-HTM in PSCs is spiro-OMeTAD, which has recorded a high power conversion efficiency (PCE) in the early days of PSC research.²² However, the big problem to the commercialization of spiro-OMeTAD is its costly synthesis process with costly sublimation steps for purification. In particular, six difficult steps of synthesis and purification process is needed to obtain pure spiro-OMeTAD along with highly cost Pd catalyst in inert atmosphere condition.²³⁻

²⁶ The total estimated material cost for 1 gram of spiro-OMeTAD is about 92 \$. Moreover, total estimated chemical waste for the synthesis of 1 gram of spiro-OMeTAD is 3.6 (kg/g). Finally, the commercial price for 1 gram of spiro-OMeTAD reach to 170-425 \$.²⁶⁻²⁷ Besides the high price of spiro-OMeTAD, stability in PSC, is the main limitation for commercialization.

The main strategy to synthesize small molecule HTMs is employing palladium-catalyzed C–N cross-coupling using an expensive catalyst such as Pd/BINAP.²⁸⁻³⁰ Therefore, the actual promising way to reduce the cost of reaction pathway is replacing of Pd catalyst with a cheap and efficient catalyst or completely removing it. Interestingly, a large number of condensation methods do not need to use any catalyst or hard condition.³¹⁻³² Newly synthesized HTM based on the condensation procedure is less prone to undergo undesirable side reactions which seen in the corresponding catalyzed–base reactions due to diminished yields or catalyst deactivation, leading to achieving high product yield (> 80%). Therefore, the specific property of newly synthesized HTM based on condensation methods is the simplified synthesis process compared to other HTM, which are known to date.

Despite the development of several newly synthesized small organic HTMs based on C-N cross coupling for PSCs application,²⁰ the finding of new strategies to facilitate the synthesize pathways needs more efforts. Herein, we introduce an exceedingly cheap PSC device using new HTM based on sequential condensation of phenanthrene ligand. Only two sequent ketone-amine condensations without adding any catalyst or additive at mild condition were carried out to obtain BEDN with high purity and product yield.

Results and discussion

The synthetic routes of BEDN are shown in Scheme 1. The total yield of BEDN is 60%, which was prepared by a straightforward two-step condensation synthesis. BEDN was purified by recrystallization and characterization (¹H NMR, see the ESI[†] Figures S1andS2).



Scheme 1. Molecular structure and synthetic routes for BEDN.

To get more insight about the activity of newly investigated HTM, we compared the differences and similarities in all photophysical, photochemical and photoelectrochemical properties of BEDN with a reference spiro–OMeTAD. The UV-Vis spectra of newly synthesized HTM exhibit similar absorption peaks as spiro–OMeTAD as summarized in Table 1.



Figure 1. (a) UV-Vis and photoluminescence spectra of BEDN and spiro-OMeTAD in CHCl₃ (Inset: the zoomed image of the visible region of absorption spectra of BEDN and spiro-OMeTAD). (b) Cyclic voltammograms of BEDN and spiro-OMeTAD. (c) Differential scanning calorimetry of BEDN and spiro-OMeTAD (Mentioned value in the image is related to glass transition temperature (T_g)). (d) The contact angle of BEDN.

The inset of Figure 1a depicts the absorption band of BEDN and spiro-OMeTAD at the visible region, which shows that the ε of BEDN is smaller than corresponding spiro-OMeTAD.33 The photoluminescence (PL) of BEDN and spiro-OMeTAD recorded in chloroform shows a strong band at 427 and a shoulder at 575 nm, while spiro-OMeTAD exhibited only one emission band at 421 nm, which is in agreement with earlier references.³⁴ The electrochemical behaviors of BEDN and spiro-OMeTAD have been investigated by using cyclic voltammetry (CV) and BEDN exhibited quasi-reversible oxidation/reduction processes in the positive potential range (Figure 1b). The first oxidation half-wave of BEDN was observed at 0.58 V vs Ag/AgCl which is 0.02 V lower than spiro-OMeTAD, confirming that BEDN more easily oxidized to BEDN+ than spiro-OMeTAD to spiro-OMeTAD+.35 UV-Vis, PL and CV spectra were employed to estimate the HOMO, LUMO and band gap of newly investigated HTM, which is summarized in Table 1. Differential scanning calorimetry (DSC) measurements indicated that BEDN has higher 136 °C glass transition temperature (T_g) than spiro-OMeTAD (T_g = 125 °C; Figure 1c),¹⁴ which confirms a higher thermal stability of BEDN with respect to spiro. DSC also proved that BEDN starts crystallization at 164 °C and spiro-OMeTAD at 158 °C, which are both far above temperatures for conventional device operation. To examine the hydrophobicity properties of BEDN, the water contact angle measurement was carried out (Figure 1d). The water contact angle for BEDN coated films was 83.2, as is shown in Figure 1d.

DOI: 10.1039/C9TA05121J This result indicates that the new HTM presents a good hydrophobicity and can be used as suitable HTM in PSCs. This means that new HTM prevents water penetration to the perovskite surface below the HTM, and thus does not destroy the perovskite, which is highly sensitive to moisture. To address the film forming ability and distribution of new HTM on the surface, FE-SEM of glass/BEDN and glass/TiO₂/BEDN was compared to spiro-OMeTAD which shown that there is not any pin-hole or defect on the coated layers (ESI-Figures S3-S5).



Figure 2. Device architecture based on $FTO/compactTiO_2/meso-TiO_2/(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}/BEDN/Au.$ (b) The relative energy levels in the PSCs based on BEDN and spiro-OMeTAD. (b) Cross-sectional SEM image of PSCs devices based on BEDN.

The newly investigated small-molecule BEDN was tested as HTMs in solution-processed PSC devices. A stack of thin layers onto fluorine-doped tin oxide (FTO) coated glass was prepared that serves as the backbone of device. The device was made as standard configuration including TiO₂-blocking layer/TiO₂-mesoporous layer as electron-transporting layer (ETM)/perovskite absorber ((FAPbI₃)_{0.85}(MAPbBr₃)_{0.15}) and the newly engineered molecule as HTM.³⁶ The solubility of BEDN in chlorobenzene (CB) is very good which supports the uniformity of deposited HTM layer. To enhance the conductivity of cells, a small amount of dopants was used in both cases, BEDN and spiro-OMeTAD. For a purposeful comparison, solar cells with spiro-OMeTAD based HTM and without any HTM were also fabricated.

Published on 22 August 2019. Downloaded on 8/23/2019 3:28:45 AM.

 Table 1. Spectroscopic and electrochemical data for BEDN and spiro-OMeTAD.

HTM	$\lambda_{abs^{a)}}$ (nm)	$\lambda_{em^{b)}}$ (nm)	E _{o-o} c) (eV)	E _{ox} ^{d)} (V)	E _{HOMO} ^{e)} (eV)	E _{LUMO} ^{f)} (eV)	T _g (°C)	$\eta_{ ext{quenching}}$	Hole Mobility ^{g)} (cm ² V ⁻¹ s ⁻¹)	Conductivity ^{g)} (S cm ⁻¹)
BEDN	301, 357 (sh), 532 (sh)	427	3.14	0.58	-5.18	-2.02	136	0.94	9.08 × 10 ⁻⁵	6.2 × 10 ⁻⁵
spiro-OMeTAD	304, 388, 525 (sh)	421	3.04	0.6	-5.21	-2.17	125	0.89	4.10 × 10 ⁻⁵	$3.4 imes 10^{-5}$

^{a,b)}In CHCl₃ solutions (1×10⁻⁵ M). ^{c)}E_{o-o} was calculated from the intersection of absorption and emission spectra. ^{e)}From CV measurements, $E_{1/2} = 1/2(E_{pa}+E_{pc})$; 0.1 M acetonitrile/tetrabutylammonium perchlorate (TBAP) versus Ag/AgCl at scan rate of 80 mV/s. ^{e)}E_{HOMO} = -(E_{1/2} (vs. Fc/Fc⁺) + 4.8). ^{f)}E_{LUMO} = E_{HOMO} + E_{o-o}. ^{g)}Pure HTM without doping.

The schematic illustration and the cross-section scanning electron microscopy (SEM) images (the different layers can be seen from displayed in Figure 2b. The current density over the applied voltage figure of PSC devices is shown in Figure 3a and the obtained data are summarized in Table 2. Obviously, all photovoltaic performances of PSC devices based on molecularly engineered HTM are significantly improved compared to the PSC without HTM, confirming the effective role of BEDN in device. On the other hand, compared with spiro-OMeTAD, which exhibited a J_{SC} of 22.16 mA cm⁻², V_{OC} of 1.10 V and consequently PCE of 19.50% which are close to the BEDN-based device with J_{SC} of 20.64 mA cm⁻² and V_{OC} of 1.03 V and PCE of 17.85%.

 Table 2.
 Summarized photovoltaic parameters derived from current–voltage curves for the best samples.

UTMa	V _{oc}	J _{SC}	FF	PCE
11111115	[V]	[mA cm ⁻²]	[%]	[%]
RS-BEDN	1.03	20.60	79	16.76
FS-BEDN	1.03	20.64	84	17.85
RS-spiro-OMeTAD	1.10	22.14	76	18.51
FS-spiro-OMeTAD	1.10	22.16	80	19.50

These results are particularly interesting since the PCE of PSC based on BEDN was almost doubled compared to PSC without HTM. PSCs for 20 samples of BEDN and spiro-OMeTAD in the same condition were also fabricated (ESI.S2). The general trend in PCE for both BEDN and spiro-OMeTAD was the same with the maximum values ones.



Figure 3. J-V (a) and IPCE (b) curves of PSCs based on BEDN and spiro-OMeTAD HTMs. Forward and reverse scanning of J-V is shown in Figure 3(a) by doted and solid lines, respectively.

In order to investigate reproducibility of PSCs based on BEDN, at least 15 individual devices were fabricated using BEDN and spiro-OMeTAD. Statistical distribution of the device performances is shown in Figure 6. The average of performance of PSCs of the devices with BEDN and spiro-OMeTAD are 16.05% and 17.60%, respectively. The general trend in PCE for both BEDN and spiro-OMeTAD was the same with the maximum values ones. The hysteresis parameter of both BEDN and spiro-OMeTAD was

investigated by recording forward and reverse scanning of current against applied voltage (Figure 3(a)). The results shown that the forward scanning mode is slightly lower than reverse ones, indicating the hysteresis phenomenon, which is about less than 1% in both samples.

Figure 3b shows the incident photon-to-current efficiency (IPCE) of the PSCs based on BEDN and spiro-OMeTAD as a function of wavelength, indicating the good agreement between the J_{SC} obtained from the IPCE and J-V measurement. Obviously, the IPCE from BEDN HTM is similar to spiro-OMeTAD, reaching above to 85% conversion. However, as shown in the IPCE spectra, there is a loss in photon conversion in the range of 550–750 nm for the BEDN, which is not the case for spiro-OMeTAD. We attribute this loss to the existence of traps and recombination sites at the perovskite/HTL interface, compared to spiro-OMeTAD.³⁷



Figure 6. Statistical distribution of perovskite solar cells performance with BEDN and spiro-OMeTAD.

After observing the J-V and IPCE spectra, we hypothesized that perhaps the reason for the difference in the photovoltaic performance was due to inefficient hole transport.¹⁹ To test this behavior, the dynamics of hole transfer from perovskite to HTM was investigated by employing steady state PL of the TiO₂/perovskite and TiO₂/perovskite/HTM. As shown in Figure 4a, samples have shown a PL peak at 760 nm originated from the perovskite layer, the perovskite PL quantum yield of perovskite/BEDN film was significantly decreased in respect to the bare perovskite film.





Figure 4. (a) The PL of the substrate $FTO/TiO_2/HTMs$ and $FTO/TiO_2/perovskite$. (b) Time resolved PL spectra measured at a wavelength near band gap that yields maximum PL signal upon exciting pristine and BEDN and spiro-OMeTAD coated perovskite samples at 405 nm.

Compared with the spiro-OMeTAD based cell, which acquires a PL quenching efficiency ($\eta_{quench} = 0.89$), the BEDN-based cell records a substantially higher $\eta_{quench} = 0.94$ (by 11%). The origin of the quenching of PL spectrum of perovskite/BEDN can be attributed to charge carrier extraction across the interface between BEDN and (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15}.²⁵ For a deeper understanding of the charge transfer dynamics in the newly investigated HTM, the time resolved photoluminescence spectroscopy (TRPLs) was also performed. A bi-exponential decay function was employed to fit the lifetime of the perovskite/HTM because the TRPS shown a non-exponential decay. The value of τ_2 of (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15}, BEDN/(FAPbI₃)_{0.85}(MAPbBr₃)_{0.15} and spiro-OMeTAD/(FAPbI₃)_{0.85}(MAPbBr₃)_{0.15} is 16.20, 10.15 and 9.95 ns, respectively. From the results of steady-state PL and TRPS, the difference of charge separation ability in BEDN and spiro-OMeTAD is quite small.³⁶ The electronic structures of the spiro-OMeTAD and BEDN HTMs calculated by density functional theory (DFT) are shown in Figure 5. As seen in the Figure, the HOMO and LUMO of BEDN are separately localized on the naphthalene core and the DPDA moieties, respectively. The BEDN HOMO is stabilized slightly compared to spiro-OMeTAD, which can be seen in their oxidation potential. The higher calculated oxidation potential for BEDN (0.1 eV) relative to spiro-OMeTAD (0.03 eV) indicates that the higher energy is required to oxidize the molecule. This higher potential in BEDN is probably due to the lack of repulsive interactions between the two molecular halves in spiro-OMeTAD.33 Although the PCE of the BEDN HTM is not higher than that of spiro-OMeTAD, the comparable efficiency still supports that the BEDN is a promising HTM for PSC.

Published on 22 August 2019. Downloaded on 8/23/2019 3:28:45 AM.



Figure 5. HOMO–LUMO molecular distribution, energy levels and calculated oxidation potentials of the spiro-OMeTAD and BEDN. $\Delta G_{\alpha x}$ is the Gibbs free energy of oxidation.

Charge transport properties is another important parameter to consider in the design of new HTMs in PSCs. The hole mobility values of the pristine HTMs were measured by a space-charge limited currents (SCLCs) method according to literature^{12,38-41} (ESI[†]. Figure. S6,) and the data is listed in Table 1. The mobility of spiro-OMeTAD is similar to the data reported in the literature, indicating the reliability of the SCLC technic.⁴²⁻⁴³ The extracted hole mobility for pristine BEDN is 9.08×10^{-5} cm² V⁻¹ S⁻¹, which is almost five times higher than that of spiro-OMeTAD (4.10×10^{-5}) cm² V⁻¹ S⁻¹). The high hole mobility and PCE of this new engineered molecule make it good candidate to work in PSCs. The conductivity of pristine BEDN is also slightly higher than that of pristine spiro-OMeTAD (Table 1). The conductivity of BEDN after addition additive was 1.2×10^{-4} S cm⁻¹. The PSC based on dopantfree BEDN presented the better performance in comparison with dopant-free spiro-OMeTAD (ESI, Figure S8, Table S2). However, in spite of showing high conductivity and hole mobility of BEDN without additives, spiro-OMeTAD showed a slightly better performance after the addition of LiTFSI and t-BP additives. Furthermore, the durability of photovoltaic performances of

devices based on BEDN and spiro-OMeTAD was further probed under standard conditions (Figure 7). The performances of devices based on two HTMs decreased very slowly in 500 h. After this time, BEDN and spiro-OMeTAD based devices retained 93% and 90% of initial PCEs.



Figure 7. Changes with time of the photovoltaic performance parameters of the PSC devices with BEDN and Spiro-OMeTAD.

Table 3 shown that the price of newly engineered HTM is much lower than spiro-OMeTAD.²³⁻²⁶ (Please see supplementary, S2 for more details).

 Table 3. Survey of estimated chemical synthesis cost and waste streams for different HTMs.

НТМ	Steps	Material Cost (\$/g)	Cost per m ² (\$/m ²)	Chemica1 Waste (kg/g)	Commercial Price (\$/g)
BEDN	2	1.38	0.2	0.25 (0.0)	-
spiro-OMeTAD	6	92	39.46	3.6 (1.0)	170-425

Conclusion

Published on 22 August 2019. Downloaded on 8/23/2019 3:28:45 AM

In summary, to achieve a low cost HTM for using in efficient PSCs, we successfully replaced the palladium-catalyzed C-N coupling pathway with a simple sequential condensation route. Surprisingly, this newly designed pathway included only two-step without any purification, hard condition and catalyst. In particular, the PCE of PSC based on molecularly engineered HTM is comparable with benchmark spiro-OMeTAD, resulting in 17.85 and 19.50%, respectively.

Experimental

All starting materials were purchased from Aldrich Chemical and Merck Companies and used without further purification. ¹H and ¹³C NMR spectra were recorded on Bruker Advance 250 MHz spectrometers with CDCl₃ and D₆-DMSO as solvent. Chemical shifts were calibrated against TMS as an internal standard. UV/Vis and emission spectra were measured using an Ultrospec 3100 pro spectrophotometer and AvaSpec-125 spectrophotometer in CHCl₃ solution. E_{o-o} obtained using interception of absorption and emission spectra. The Electrochemical studies were accomplished by using SAMA500 potentiostat electrochemical analyzer with conventional three electrode cell, a Pt disk as the working electrode, a Pt wire as the counter electrode. Ag/AgCl was used as the reference electrode and the supporting electrolyte was 0.1 M tetrabutylammonium perchlorate (TBAP) in chloroform. The current density–voltage (J–V) curves were measured using a solar simulator (Newport, Oriel Class A, 91195A) with a source meter (Keithley 2420) under 100 mA cm⁻² illumination (AM 1.5G) and a calibrated Si-reference cell certificated by NREL. The J–V curves of all devices were measured by masking the active area with a metal mask of area 0.096 cm².

Synthesis of N,N'-(naphthalene-1,5-diyl)bis(1-(2,3diphenylquinoxalin-6-yl)-1-phenylmethanimine) (BEDN)

The synthesis of newly investigated HTM is based on simple condensation between carbonyl and amine moieties without any future column chromatography. First, BED precursor was prepared from the condensation of benzil (420 mg, 2 mmol) with DPDA (424mg, 2 mmol) in the mixture of 50 ml ethanol and 2 ml of acetic acid. The mixture was refluxed for 4 h and then the yellow precipitated solid was filtered and washed with cold ethanol to remove the unreacted ligands. In following, the pure BED precursor was achieved through the crystallization of product in ethanol (700 mg, 90 %). Analysis data: 1H NMR (250 MHz, CDCl₃), 8.53 (s, 1H), 8.28 (s, 2H), 7.7.89-7.92 (d, 2H), 7.26-7.64 (m, 13H). 13C NMR (250 MHz, CDCl₃), 195 (C=O), 155, 154, 138, 132.81, 132.45, 130, 129.88, 129.86, 129.76, 129.16, 128.51, 128.37.

Finally, condensation between synthesized BED (386 mg, 1 mmol) and diamine naphthalene (78 mg, 0.5 mmol) in acetic acid for 12 h produced yellow precipitated BEDN. After washing and recrystallization in acetic acid, pure BEDN was achieved (285 mg, 60 %). Analysis data: 1H NMR (250 MHz, CDCl₃), 8.30 (d, 1H), 8.26 (s, 1H), 8.17 (d, 1H), 7.81-7.84 (d, 3H), 7.71 (t, 2H), 7.58-7.61 (m, 2H), 7.43-7.46 (m, 4H), 7.34-7.36 (m, 4H). 13C NMR (250 MHz, CDCl₃), 195.43, 155.28, 154.73, 142.56, 139.89, 138.78, 138.38, 137.07, 133.56, 131.77, 130.19, 130.10, 129.88, 129.65, 129.52, 129.17, 128.55. CHN: Anal. calcd. For C₆₄H₄₂N₆ (%): C, 85.882; H, 4.734; N, 9.391 Found (%): C, 85.889; H, 4.739; N, 9.398 ESI-MS: m/z 894.34, [M-H]⁺.

Fabrication of Cell

Perovskite solar cells were fabricated on fluorine-doped tin oxide (FTO) coated glass substrates. Part of the glass substrate coated with FTO was etched with Zn powder and HCl 2 M ethanol solution. Then, the substrates were washed carefully with distilled water, detergent, acetone, ethanol, isopropanol and then treated with an ultraviolet/O₃ cleaner for 15 min. On these substrates, a solution of HCl and titanium diisopropoxide bis(acetylacetonate) in anhydrous ethanol was coated with spin-coating method at 2000 r.p.m. for 30 s. Then, the substrates were heated at 500 °C for 30 minutes and cool down to room temperature. Mesoporous TiO₂ layer diluted in ethanol was deposited by spin-coating at 2000 r.p.m. for 10 s to achieve 300-400 nm thick layer. After that, the substrates were sintered again at 500 °C for 30 minutes. The PbI₂ solution was coated on mesoporous TiO₂ layer for 5 s at 6500 r.p.m. and dried at 70 °C. The mixed perovskite precursor solution was prepared by dissolving PbI₂ (1.15 M), FAI (1.10 M), PbBr₂ (0.2 M), and MABr (0.2 M) in a anhydrous solvent DMF:DMSO=4:1 (volume ratio). The perovskite solution was spin-coated in a twostep procedure at 1,000 and 6,000 r.p.m. for 10 and 30 s respectively. Chlorobenzene (110 μ l) was dropped on the spinning substrate at the 20 s in the second step and then films were annealed at 100 °C for 90 min in the glove box. Following this step, the BEDN and spiro-OMeTAD were deposited by spin-coating at 4000 r.p.m. for 20 s. The HTM solutions were prepared by dissolving the HTM in chlorobenzene at a concentration of 78 mM, with the

5

addition of 18 μ L LiTFSI (from a stock solution in acetonitrile with concentration of 1.0 M), 29 μ L of tert-butyl pyridine (from a stock solution in chlorobenzene with concentration of 1.0 M). Finally, a 80 nm Au electrode was deposited by thermal evaporation under high vacuum.^{33,44}

Computational method details

The ground-state geometries were fully optimized using density functional theory (DFT) with the B3LYP hybrid functional at the basis set level of 6-31G*, and the frontier molecular orbitals were drawn using an isovalue of 0.03 a.u. All calculations were performed using Gaussian 09 package in the PowerLeader workstation. The molecular orbitals were visualized using Gauss View 5.0.8.

PL quenching efficiency

PL quenching efficiency was calculated using the following formula:

$$\eta_{quench} = rac{PL_{bare} - PL_{quench}}{PL_{bare}}$$

Where PL bare and PL quench are integrated PL intensities of perovskite on sapphire substrates without and with the quenching HTM layer.

Synthesis cost estimation of 1 gram BEDN

We estimated the synthesis cost of 1 gram BEDN according to the cost models of Pablo et al.²⁴ and Osedach et al.²³ The price of the materials used has been obtained from Merck, Sigma Aldrich, DeJong companies. We compared the price of 1 gram of this new HTM with the price of 1 gram of spiro-OMeTAD, which is reported in the literature (Please see the ESI, Table S1).^{33,45}

Conductivity Measurements

Glass substrates without conductive layer were cleaned carefully with detergents, deionized water, acetone and ethanol, respectively. Then to remove remaining organic residues, the substrates were sintered at 500 °C. A thin layer of nanoporous TiO₂ was coated on the glass substrates by spin-coating with a diluted TiO₂ paste (PST-20T) with ethanol (1:3, mass ratio). After that, TiO₂ film was sintered in the oven at 500 ° C. Then a solution of HTM in chlorobenzene (concentrations similar to photovoltaic devices) was deposited by spin-coating on TiO₂ layer. Finally, an Au layer was deposited on top of the HTM layer by thermal evaporation.

Mobility Measurements

The hole mobility of HTMs has been investigated according to literature.³⁹⁻⁴⁰ The devices of BEDN and spiro-OMeTAD were fabricated with the structure ITO/PEDOT:PSS/HTM/Au. The hole mobility values were calculated using the Mott–Gurney law.⁴¹

References:

- F. De Angelis, D. Meggiolaro, E. Mosconi, A. Petrozza, M. K. Nazeeruddin and H. J. Snaith, *ACS Energy Lett.*, 2017, **2**, 857-861.
 M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami and H. J. Snaith, *Science*, 2012, 1228604.
- 3. F. De Angelis and P. Kamat, *ACS Energy Lett.*, 2017, **2**, 1674-1676.

- 5. Best Research-Cell Effciency Chart reported by NREL, https://www.nrel.gov/pv/cell-efficiency.html, 2019.
- 6. M. Saliba, T. Matsui, J.-Y. Seo, K. Domanski, J.-P. Correa-Baena, M. K. Nazeeruddin, S. M. Zakeeruddin, W. Tress, A. Abate and A. Hagfeldt, *Energy Environ. Sci.*, 2016, **9**, 1989-1997.
- 7. A. Dualeh, N. Tétreault, T. Moehl, P. Gao, M. K. Nazeeruddin and M. Grätzel, *Adv. Funct. Mater.*, 2014, **24**, 3250-3258.
- 8. J. W. Lee, D. J. Seol, A. N. Cho and N. G. Park, *Adv. Mater.*, 2014, **26**, 4991-4998.
- 9. N. Pellet, P. Gao, G. Gregori, T. Y. Yang, M. K. Nazeeruddin, J. Maier and M. Grätzel, *Angew. Chem.*, 2014, **126**, 3215-3221.
- 10. M. Hu, L. Liu, A. Mei, Y. Yang, T. Liu and H. Han, *J. Mater. Chem. A*, 2014, **2**, 17115-17121.
- 11. G. E. Eperon, S. D. Stranks, C. Menelaou, M. B. Johnston, L. M. Herz and H. J. Snaith, *Energy Environ. Sci.*, 2014, **7**, 982-988.
- 12. T. Leijtens, S. D. Stranks, G. E. Eperon, R. Lindblad, E. M. Johansson, I. J. McPherson, H. Rensmo, J. M. Ball, M. M. Lee and H. J. Snaith, *ACS Nano*, 2014, **8**, 7147-7155.
- 13. N. H. Tiep, Z. Ku and H. J. Fan, *Adv. Energy Mater.*, 2016, 6, 1501420.
- 14. B. Hailegnaw, S. Kirmayer, E. Edri, G. Hodes and D. Cahen, *J. Phys. Chem. Lett.*, 2015, **6**, 1543-1547.
- 15. Z. Hawash, L. K. Ono, S. R. Raga, M. V. Lee and Y. Qi, *Chem. Mater.*, 2015, **27**, 562-569.
- 16. L. K. Ono, S. R. Raga, M. Remeika, A. J. Winchester, A. Gabe and Y. Qi, *J. Mater. Chem. A*, 2015, **3**, 15451-15456.
- 17. T. A. Berhe, W.-N. Su, C.-H. Chen, C.-J. Pan, J.-H. Cheng, H.-M. Chen, M.-C. Tsai, L.-Y. Chen, A. A. Dubale and B.-J. Hwang, *Energy Environ. Sci.*, 2016, **9**, 323-356.
- 18. M. Grätzel, Nat. Mater., 2014, 13, 838.
- 19. Y. H. Lee, J. Luo, R. Humphry-Baker, P. Gao, M. Grätzel and M. K. Nazeeruddin, *Adv. Funct. Mater.*, 2015, **25**, 3925-3933.
- 20. C. Rodríguez-Seco, L. Cabau, A. Vidal-Ferran and E. Palomares, *Acc. Chem. Res.*, 2018, **51**, 869-880.
- 21. A. Magomedov, S. Paek, P. Gratia, E. Kasparavicius, M. Daskeviciene, E. Kamarauskas, A. Gruodis, V. Jankauskas, K. Kantminiene and K. T. Cho, *Adv. Funct. Mater.*, 2018, **28**, 1704351.
- 22. N. J. Jeon, J. Lee, J. H. Noh, M. K. Nazeeruddin, M. Grätzel and S. I. Seok, J. Am. Chem. Soc., 2013, **135**, 19087-19090.
- 23. T. P. Osedach, T. L. Andrew and V. Bulović, *Energy Environ. Sci.*, 2013, **6**, 711-718.
- 24. M. Petrus, T. Bein, T. Dingemans and P. Docampo, *J. Mater. Chem. A*, 2015, **3**, 12159-12162.
- 25. K. Rakstys, M. Saliba, P. Gao, P. Gratia, E. Kamarauskas, S. Paek, V. Jankauskas and M. K. Nazeeruddin, *Angew. Chem.*, 2016, **128**, 7590-7594.
- 26. A. J. Huckaba, P. Sanghyun, G. Grancini, E. Bastola, C. K. Taek, L. Younghui, K. P. Bhandari, C. Ballif, R. J. Ellingson and M. K. Nazeeruddin, *ChemistrySelect*, 2016, **1**, 5316-5319.
- 27. A. T. Murray, J. M. Frost, C. H. Hendon, C. D. Molloy, D. R. Carbery and A. Walsh, *Chem. Commun.*, 2015, **51**, 8935-8938.
- 28. J. P. Wolfe and S. L. Buchwald, *J. Org. Chem.*, 1997, **62**, 1264-1267.
- 29. J. P. Wolfe and S. L. Buchwald, J. Org. Chem., 2000, 65, 1144-1157.
- 30. P. Ruiz-Castillo and S. L. Buchwald, *Chem. Rev.*, 2016, **116**, 12564-12649.
- 31. C. Peng, G.-H. Ning, J. Su, G. Zhong, W. Tang, B. Tian, C. Su, D. Yu, L. Zu and J. Yang, *Nat. Energy*, 2017, **2**, 17074.
- 32. Y. Zeng, R. Zou, Z. Luo, H. Zhang, X. Yao, X. Ma, R. Zou and Y. Zhao, *J. Am. Chem. Soc.*, 2015, **137**, 1020-1023.

View Article Online

Published on 22 August 2019. Downloaded on 8/23/2019 3:28:45 AM.

33. M. Saliba, S. Orlandi, T. Matsui, S. Aghazada, M. Cavazzini, J.-P. Correa-Baena, P. Gao, R. Scopelliti, E. Mosconi and K.-H. Dahmen, *Nat. Energy*, 2016, **1**, 15017.

34. I. Zimmermann, J. Urieta-Mora, P. Gratia, J. Aragó, G. Grancini, A. Molina-Ontoria, E. Ortí, N. Martín and M. K. Nazeeruddin, *Adv. Energy Mater.*, 2017, **7**, 1601674.

35. K. Rakstys, A. Abate, M. I. Dar, P. Gao, V. Jankauskas, G. n. Jacopin, E. Kamarauskas, S. Kazim, S. Ahmad and M. Grätzel, *J. Am. Chem. Soc.*, 2015, **137**, 16172-16178.

36. J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin and M. Grätzel, *Nature*, 2013, **499**, 316.

37. M. Salado, J. Idigoras, L. Calio, S. Kazim, M. K. Nazeeruddin, J. A. Anta and S. Ahmad, *ACS Appl. Mater. Interfaces*, 2016, **8**, 34414-34421.

38. H. J. Snaith and M. Grätzel, Appl. Phys. Lett., 2006, 89, 262114.

39. T. Leijtens, I.-K. Ding, T. Giovenzana, J. T. Bloking, M. D. McGehee and A. Sellinger, *ACS Nano*, 2012, **6**, 1455-1462.

B. Xu, E. Sheibani, P. Liu, J. Zhang, H. Tian, N. Vlachopoulos,
 G. Boschloo, L. Kloo, A. Hagfeldt and L. Sun, *Adv. Mater.*, 2014,
 26, 6629-6634.

41. V. D. Mihailetchi, H. Xie, B. de Boer, L. A. Koster and P. W. Blom, *Adv. Funct. Mater.*, 2006, **16**, 699-708.

42. B. Xu, H. Tian, L. Lin, D. Qian, H. Chen, J. Zhang, N. Vlachopoulos, G. Boschloo, Y. Luo and F. Zhang, *Adv. Energy Mater.*, 2015, **5**, 1401185.

43. C. Huang, W. Fu, C.-Z. Li, Z. Zhang, W. Qiu, M. Shi, P. Heremans, A. K.-Y. Jen and H. Chen, *J. Am. Chem. Soc.*, 2016, **138**, 2528-2531.

44. K. Rakstys, S. Paek, P. Gao, P. Gratia, T. Marszalek, G. Grancini, K. T. Cho, K. Genevicius, V. Jankauskas and W. Pisula, *J. Mater. Chem. A*, 2017, **5**, 7811-7815.

45. B. Xu, D. Bi, Y. Hua, P. Liu, M. Cheng, M. Grätzel, L. Kloo, A. Hagfeldt and L. Sun, *Energy Environ. Sci.*, 2016, **9**, 873-877.