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1 **Molecular Engineering Using an Anthanthrone Dye for Low**
2 **Cost Hole Transport Materials: A Strategy for Dopant Free,**
3 **High Efficiency and Stable Perovskite Solar Cells**

4
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24 Abstract

25 In this report, we are presenting highly efficient and humidity-resistant perovskite solar cells
26 (PSCs) using two new small molecule hole transporting materials (HTM) made from a cost-
27 effective precursor anthanthrone (ANT) dye, namely ACE-ANT-ACE and TPA-ANT-TPA.
28 We have systematically compared our newly developed HTMs with the conventional
29 2,2',7,7'-tetrakis(N,N'-di-p-methoxyphenylamino)-9,9'-spirobiuorene (Spiro-OMeTAD).
30 ACE-ANT-ACE and TPA-ANT-TPA were used as a dopant free HTMs in mesoscopic
31 TiO₂/CH₃NH₃PbI₃/HTM solid-state PSCs, and the performance as well as stability were
32 compared with Spiro-OMeTAD based PSCs. After extensive optimization of the metal oxide
33 scaffold and device processing conditions, dopant-free novel TPA-ANT-TPA HTM based
34 PSCs devices achieved a maximum PCE of 17.5% with negligible hysteresis. An impressive
35 current of 21 mA/cm² obtained is also confirmed from photocurrent density with a higher fill
36 factor of 0.79. The obtained PCE of 17.5% utilizing TPA-ANT-TPA is higher performance
37 than the devices prepared using doped Spiro-OMeTAD (16.8%) as hole transport layer at 1
38 sun condition. It is found that doping of LiTFSI salt increases hygroscopic characteristics in
39 Spiro-OMeTAD this leads to the fast degradation of solar cells. While, solar cells prepared
40 using undoped TPA-ANT-TPA shows dewetting and improved stability. Additionally, the
41 new HTMs form a fully homogeneous and completely covering thin film on the surface of
42 the active light absorbing perovskite layers that acts as a protective coating for underlying
43 perovskite films. This breakthrough paves the way for development of new inexpensive,
44 more stable, and highly efficient ANT core based lower cost HTMs for cost effective
45 conventional and printable PSCs.

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47

49 Photovoltaic or solar cells are currently considered as the possible and suitable alternative for
50 traditional non-conventional energy harvesting technology to tackle the issues of
51 environmental pollution, climate change and potential future shortage of hydrocarbon-based
52 energy supply. With the goal of making this alternative feasible, much research on various
53 solar cell technologies has been performed. The main challenges include reducing the cost,
54 increasing the power conversion efficiency (PCE) values, and improving stability to enable
55 large-scale commercial manufacturing for public use. Apart from conventional high
56 performance and stable silicon based inorganic solar cells,^[1] dye sensitised solar cells
57 (DSSC),^[2] organic solar cells (OSCs)^[3] and perovskite solar cells(PSCs)^[4, 5] are some
58 emerging technologies where the active light absorbing layer can be deposited on large scale
59 using either pure organic or organic-inorganic solution processable light absorbing
60 semiconducting layer. These technologies are becoming attractive options due to the potential
61 for lower cost, optoelectronic tunability (energy levels and optical band gap), high efficiency
62 and opportunities to scale them up in the form of flexible prototypes using roll to roll
63 printing.^[4, 6] Among various organic based light absorbing semiconductors, metal-free
64 organic dyes are prospective candidates on account of their practical advantages, including
65 high molar absorption coefficients, facile structure tuning, easy charge carrier mobility
66 modulation, and simple and inexpensive syntheses.^[7] The dye-based semiconductors have
67 been employed successfully in various solar cell devices either as donors (p-type materials)
68 or acceptors (n-type materials). Among various and numerous types of dyes, recently, some
69 of the key dyes such as the dark red diketopyrrolopyrrole (DPP) and isoindigo (IS) have been
70 widely used as a significant building blocks for designing and synthesizing high performance
71 low band gap materials for organic and dye sensitized solar cells.^[8] In addition to OSCs and
72 DSSCs, recently, carbazole-based low cost dyes have been successfully used as hole-
73 transporting materials (HTMs) in PSCs and an impressive PCE has been achieved.^[9]

74 Recently, dibenzo[*def,mno*]chrysene (anthanthrene), one type of polycyclic aromatic
75 hydrocarbons, has been used intensively as a versatile building block for designing advanced
76 functional materials for organic field-effect transistors (OFETs), organic light emitting diodes
77 (OLED) and organic solar cells (OSCs) devices, due to its outstanding properties.^[10, 11, 12] The
78 commercially available anthanthrene dye is not only cost-effective but also possesses a good
79 environmental stability and provides good solubility. Among anthanthrene derivatives, 4,10-
80 dibromoanthanthrone, named as VAT Orange 3 (Scheme 1), is a useful scaffold due to its
81 various exciting features. Firstly, the conjugation backbone of the dye can be extended and its
82 optoelectronic properties can be tuned easily via functionalization of any chemical moiety
83 (either aliphatic or aromatic depending on requirements) at the possible 4, 10 and 6, 12
84 axes.^[13-15] Secondly, the solution processibility aspect can be enhanced by introducing either
85 longer straight or branched alkyl chains via the bromine atoms at the 4 and 10 positions or at
86 the 6 and 12 positions via alkylation.^[13] Thirdly, the possibilities of tuning the starting n-type
87 material (due to two ketonic groups at 6 and 12) to p-type organic semiconductors by
88 introducing electron donating groups.^[14] In addition to the above features, the central fused
89 aromatic six-membered rings in the centre deliver structural planarity leading to ordered
90 morphology in thin films which is essential for better charge delocalization and transport.^[12]
91 Furthermore, this compound seems to be crystallized simply due to its symmetrical structure
92 and can provide ample opportunities to vary the UV-visible absorption range based on rigid
93 and extended π -conjugated backbone.^[16] Although a handful of anthanthrone derivatives
94 were used successfully in OFETs, OLED and OSCs, till date there are no reports using this
95 cost-efficient dye and its derivatives as a hole transporting material in the fast moving PSCs
96 technology.

97 In recent years, PSCs have gained enormous attention from both academia and industry
98 due to their easy processibility, potentially lower cost and ability to reach the performance

99 close to the solar cell technologies currently used globally. The rapid development of this
100 technology is almost comparable to common and traditional solar energy technologies, such
101 as copper indium gallium selenide (CIGS), cadmium telluride (CdTe) and silicon. From the
102 first initial PCE of 3.8% reported in 2009,^[17] the power conversion efficiency (PCE) of PSCs
103 has now reached 22.1%.^[18] One of key points resulting in the rapid success is the presence of
104 a hole-transporting layer (HTL) in the devices. This layer not only assists to transport the
105 holes after exciton dissociation but also plays a significant role in controlling the stability,
106 suppressing charge recombination and preventing the perovskite layer from the invasion of the
107 moisture/oxygen and electrode penetration.^[19, 20] Earlier works showed that while the PCE of
108 perovskite devices with a HTL has recorded greater than 20%,^[21-23] the efficiency in the
109 absence of this layer has been around 14%.^[24] In terms of designing materials for the HTL,
110 various inorganic,^[25] small molecular,^[26, 27] and polymeric^[28] HTMs have been developed.
111 Among them, small molecules are more attractive and can offer considerable benefits such as
112 simplicity of purification, high purity, definite molecular weight, promising tunable highest
113 occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)
114 energy levels and good batch-to-batch reproducibility.^[29] Also, small molecular HTMs have
115 been proven to be one of the best choices of materials till date compared to other type of
116 HTMs. The 2, 2', 7, 7'-tetrakis-(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spiro-bifluorene
117 (Spiro-OMeTAD) has been recognized as one of the key candidates which has achieved the
118 highest PCE close to 20.8% in PSCs.^[21] However, the major drawback of Spiro-OMeTAD is
119 that it gives such a high performance only in combination with some dopants, which are often
120 vulnerable to moisture, and this critically determines the stability of solar cell devices.^[26, 30]
121 In addition, tedious synthesis and a cost too high for commercial use have impeded overall
122 PSC development.^[22, 26]

123 In order to replace Spiro-OMeTAD, researchers worldwide have been designing and
124 developing alternative HTMs. Among them, the triphenylamine (TPA) based HTMs in
125 combination with various different π -functional moieties have shown remarkable success due
126 to simplicity in synthesis and promising PCE value upward growth.^[31, 32-35] Thus, our group
127 has designed HTMs by using anthanthrone dye as a starting cut-rate central core decorated
128 with TPA end-capping groups at 4 and 6-positions. This is the first report of using this dye in
129 PSC devices.

130 Herein, we have designed and synthesized two innovative and **cost effective HTMs**,
131 namely, 4,4'-(6,12-bis(octyloxy)-6,12-dihydronaphtho[7,8,1,2,3-*nopqr*]tetraphene-4,10-
132 diyl)bis(*N,N*-bis(4-methoxyphenyl)aniline) (TPA-ANT-TPA) and 4,10-bis(1,2-
133 dihydroacenaphthylen-5-yl)-6,12-bis(octyloxy)-6,12-dihydronaphtho[7,8,1,2,3-
134 *nopqr*]tetraphene (ACE-ANT-ACE) using low cost anthanthrone core as starting material (as
135 shown in Scheme 1). Apart from the novelty of using the anthanthrone dye as a precursor, we
136 have used for the first time 1,2-dihydroacenaphthylene (ACE) functional group as an end
137 capping group as well as TPA. TPA-ANT-TPA and ACE-ANT-ACE have been successfully
138 used as HTL in conventional n-i-p perovskite devices. The device structure includes
139 glass/FTO/compact-TiO₂/Mesoporous-TiO₂/CH₃NH₃PbI₃/HTL/Ag. First, fluorine doped tin
140 oxide (FTO) commercially available substrates were used as a transparent conducting anode
141 followed by deposition of titanium dioxide (TiO₂) electron transporting compact layer, active
142 perovskite layer and TPA-ANT-TPA & ACE-ANT-ACE based new HTL thin films,
143 respectively. Lastly, silver (Ag) as a cathode electrode was deposited to complete the device
144 fabrication. Further fabrication procedure details can be found in the Supporting Information
145 (ESI†). Under standard illumination (AM 1.5G and 100 mW cm⁻²), the average PCE of
146 devices using ACE-ANT-ACE and TPA-ANT-TPA HTMs have achieved 11.4% and 16%,
147 respectively. Interestingly, these PCE values are without any additives and they are

148 comparable to that of doped Spiro-OMeTAD (16.8%) devices under similar working
149 condition. Additionally, after first 20 h in the ambient environment (room temperature, 58%
150 humidity), while the PCE of unsealed Spiro-OMeTAD based devices retained 2% of its initial
151 value, that of TPA-ANT-TPA still retained 80% of its original performance which is one of
152 the most important striking features of our newly developed HTM. After extensive
153 optimization of the metal oxide scaffold and device processing conditions, novel TPA-ANT-
154 TPA HTM based PSCs devices achieved a maximum PCE of 17.5%. The overwhelming
155 advantages such as high performance and higher stability make our newly developed HTMs
156 promising candidates for low cost perovskite solar cell devices.

157 Novel anthanthrone core derivatives end capped with methoxy triphenylamine at both
158 ends (TPA-ANT-TPA and ACE-ANT-ACE have been designed (**Figure 1**) and synthesized
159 by classical Suzuki coupling. The synthesis is quite straightforward and various steps
160 involved are shown in Scheme 1. Initially, the reaction of 4-bromoaniline (**1**) with 1-iodo-4-
161 methoxybenzene, strong base KOH, CuCl, and 1,10-phenanthroline monohydrate in toluene
162 produced the intermediate 4-bromo-*N,N*-bis(4-methoxyphenyl)aniline (**2**). Afterwards, in
163 presence of bis(pinacolato)diboron, strong base potassium acetate, 1, 1'-
164 bis(diphenylphosphino)ferrocene]dichloropalladium(II) catalyst in dimethyl formamide
165 solution, the compound **2** was converted to 4-methoxy-*N*-(4-methoxyphenyl)-*N*-(4-(4,4,5,5-
166 tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (**3**) at 120 °C overnight. Meanwhile, the
167 alkylation of 4,10-dibromoanthanthrone (**4**) at 2 and 6 positions aimed to enhance the
168 solubility and make dibromoanthanthrone become the electron rich unit. The alkylation was
169 operated under base environment of aqueous sodium hydroxide and Aliquat 336, catalyst of
170 sodium dithionite and 1-bromooctane at 80 °C overnight. Then 4,10-dibromo-6,12-
171 bis(octyloxy)anthanthrene (**5**) was collected with high yield. The final HTMs TPA-ANT-
172 TPA and ACE-ANT-ACE were produced based on the Suzuki coupling reaction (2M

173 potassium carbonate as a base, tetrakis (triphenylphosphine) palladium (0) as catalyst in
174 toluene solvent). ACE-ANT-ACE was synthesized from compound 5 and 2-(1,2-
175 dihydroacenaphthylen-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, whereas TPA-ANT-
176 TPA was made from compound 5 and compound 3. All reactions were stirred at 120 °C for
177 48 h. After purification, TPA-ANT-TPA and ACE-ANT-ACE's yield was to be of 60% and
178 65%. Their purity was proved by proton and C13 nuclear magnetic resonance (NMR)
179 spectroscopy (Figure S1-S5, ESI[†]). The solubility of these anthanthrone derivatives was
180 extremely good in most common organic solvents such as chloroform, dichloromethane, and
181 chlorobenzene.

182 To understand the structures and electronic properties of these molecules, density
183 functional theory (DFT) calculations at the B3LYPr level of theory using the basis set 6-
184 31g(d, p) were performed. A PCM model of the chloroform solvent was used.^[36] The results
185 are shown in **Figure 1** and summarized in Table S1 (ESI[†]). The electron density of the
186 LUMO is primarily distributed over the π -conjugated system through the anthanthrone
187 (ANT) core in both molecules. The HOMO of ACE-ANT-ACE has the electron density
188 localized mainly on the ANT unit, whereas for TPA-ANT-TPA, electron density delocalized
189 over the entire molecule including the electron-rich TPA unit as expected. The lack of
190 HOMO density on the ACE moiety is not unusual, as bonded fused aromatic units tend to
191 preserve their HOMO-like orbitals which become HOMO-*n* in the bonded system.
192 HOMO/LUMO energy levels for ACE-ANT-ACE are -4.80/-2.06 eV whereas for TPA-ANT-
193 TPA, is they are -4.67/-2.04 eV respectively. Consequently, the band gap of ACE-ANT-ACE
194 and TPA-ANT-TPA is calculated to be 2.74 and 2.63 eV, respectively. Optical absorption
195 maxima were at 474 nm for ACE-ANT-ACE (HOMO→LUMO dominated) and at 482 nm
196 for TPA-ANT-TPA (dominated by two transitions, HOMO→LUMO at 524 nm and HOMO-
197 2→LUMO at 467 nm), giving optical band gaps of 2.61 and 2.58 eV respectively which are

198 in a good agreement with the experimentally estimated optical gaps of 2.56 and 2.48 eV
199 (**Table 1**).

200 The normalized UV-vis absorption (**Figure 2a**) and emission (Figure S6, ESI[†]) spectra
201 of ACE-ANT-ACE and TPA-ANT-TPA in chloroform (CF) solutions and thin films were
202 measured and the relevant data was listed in Table 1. The pattern of the spectra in the thin
203 films is the same as those of the solutions, which implies that no significant crystallization in
204 thin films.^[37] The optical absorption of both materials exhibits strong peaks in the ultraviolet
205 (300 – 350 nm) region and lower ones in the visible (400 – 500 nm) region, which has been
206 noticed in the past attempt regarding small molecular ANT derivatives.^[10] Compound ACE-
207 ANT-ACE exhibits the absorption maxima at 461 nm for solution and 467 nm for thin film
208 respectively. The thin film absorbance data of ACE-ANT-ACE is blue-shifted in UV region
209 and slightly red shifted in visible area compared to the solution data. Compound TPA-ANT-
210 TPA unveils absorption maxima at 465 nm for solution and 473 nm for thin film respectively.
211 The absorption spectra of solid-state films illustrate slightly red-shifted and little broadened
212 absorption than those measured in the solution, as is expected due to intermolecular
213 interactions in the solid state. Moreover, the optical absorption spectrum of TPA-ANT-TPA
214 is slightly red-shifted in comparison to ACE-ANT-ACE, which could be ascribed to the
215 higher conjugation and higher electron-donating ability of TPA moiety compared to the 1,2-
216 dihydroacenaphthylene (ACE) moiety. The optical band gap of ACE-ANT-ACE and TPA-
217 ANT-TPA are found to be 2.56 and 2.48 eV, respectively, which was estimated from the
218 onset of solid-state absorption.

219 As shown in Figure S6 (ESI[†]), the emission maximum of ACE-ANT-ACE and TPA-
220 ANT-TPA are depicted at 480 and 553 nm, respectively. Stokes shifts were estimated from
221 the gap between the maximum of absorption and emission spectra. These materials possessed
222 a large Stokes shift of 157 and 228 nm compared to that of Spiro-OMeTAD (44 nm)^[38]. A

223 large Stoke shift implies the different and large geometrical changes between the ground- and
224 excited-state geometry and is a reflection of molecular flexibility. This property also
225 enhances the pore filling of a hole transport ability of materials.^[38-40]

226 The thermogravimetric analysis (TGA) was operated under a nitrogen atmosphere in
227 order to investigate the thermal stability of new molecules, which lost less than 5% weight
228 upon heating. The TGA curves were shown in Figure S7 (ESI[†]) and recorded in Table 1. The
229 decomposition of ACE-ANT-ACE and TPA-ANT-TPA started at temperatures 265 °C and
230 280 °C, respectively, which shows that the small molecules are thermally stable HTMs for
231 PSCs devices. Upon evaluating these materials in DSC measurement (Figure S8, ESI[†]), the
232 glass transition temperature (T_g) was not observed but the melting points were measured at
233 215 °C for ACE-ANT-ACE and 265 °C for TPA-ANT-TPA, respectively. The observed
234 melting temperatures of both compounds are comparable to that of Spiro-OMeTAD (248
235 °C).^[40]

236 The experimental estimation of the HOMO and LUMO energy levels of ACE-ANT-
237 ACE and TPA-ANT-TPA were performed using photoelectron spectroscopy in air (PESA)
238 (Figure 2b) and cyclic voltammetry (CV) (Figure S9, ESI[†]) techniques. The HOMO and
239 LUMO energy level values are presented in the Table 1. In comparison to the HOMO value
240 of active perovskite layer (-5.46 eV), the HOMO value of ACE-ANT-ACE (-5.32 eV) is
241 greater, whereas for TPA-ANT-TPA, the HOMO value (-5.41 eV) is higher than but very
242 close to the perovskite HOMO value. The HOMO values obtained by CV data are also in a
243 good agreement with PESA data. Since the PESA measurements were done in the thin film
244 form they are more relevant to actual devices. As per an earlier report, the hole transport
245 ability can be impeded by an excessively small band offset of the HOMO between
246 perovskite and hole injection layers, whereas a very large band offset could cause the
247 reduction of the open-circuit voltage (V_{oc}).^[41] Meanwhile, all LUMO values of HTMs are

248 greater than that of the perovskite layer (-3.93 eV) proving that the new HTMs can block
249 electron transfer to HTL.

250 After characterizing both new small molecules optically, thermally and
251 electrochemically, the conventional perovskite devices were fabricated with the aim of to
252 study the effect of the hole transport layers on the device performance. PSC devices with the
253 same architecture (FTO/compact-TiO₂/Mesoporous-TiO₂/CH₃NH₃PbI₃/HTL/Ag), and
254 different HTM layers were prepared as previously described.^[42] The configuration of
255 mesoscopic heterojunction perovskite solar cells was characterized by the cross-sectional
256 scanning electron microscopy (SEM) and shown in Figure 2d. A dense compact-TiO₂
257 blocking layer (~30 to 40 nm) is first deposited on the FTO substrate by spray pyrolysis,
258 while a mesoporous n-type mp-TiO₂ layer is formed by spin-coating of diluted TiO₂ paste.
259 The CH₃NH₃PbI₃ absorber layer was then applied on mesoporous TiO₂ by solvent
260 engineering reported by Seok's group.^[43] The perovskite solution was prepared by dissolving
261 50 wt% of CH₃NH₃PbI₃ in the mixed dimethyl sulfoxide (DMSO) and γ -butyrolactone
262 (GBL) DMSO/GBL. Around 120 nm thick HTLs were applied to the top CH₃NH₃PbI₃ layer
263 by spin coating. Finally, silver as a counter electrode was deposited by thermal evaporation.
264 The thickness of mesoporous TiO₂ and perovskite is ~550 nm, whereas the capping layer of
265 perovskite is estimated to be ~100 nm. Bigger crystals of TiO₂ in the capping layer assist in
266 saturated light absorption and enhancing the external quantum efficiency (EQE) in the red-
267 light range.

268 For a valid comparison of performance in terms of PCE and stability, we prepared new
269 dopant-free HTMs based devices and standard devices with dopant using conventional Spiro-
270 OMeTAD (with additional additives, including *t*BP and LiTFSI) as the HTM. The optimized
271 champion device efficiency for three different HTMs and corresponding photovoltaic
272 performance parameters are shown in **Figure 3a, b** and **Table 2**. The TPA-ANT-TPA HTM

273 based PSC device (Figure 3a) shows the highest champion device efficiency of 17.5% ($J_{sc} =$
274 21.07 mA cm^{-2} , $V_{oc} = 1.03 \text{ V}$ and $FF = 79.6$) whereas a bit lower PCE of 13.1% is recorded
275 with $J_{sc} = 18.7 \text{ mA cm}^{-2}$, $V_{oc} = 1.03 \text{ V}$ and $FF = 67$ in case of ACE-ANT-ACE (Figure 3a).
276 Meanwhile, doped Spiro-OMeTAD-based device performance (Figure 3b) approaches the
277 PCE of 16.8% with J_{sc} of 21.09 mA cm^{-2} , $V_{oc} = 1.04 \text{ V}$ and $FF = 76.8$. In addition, there is a
278 no hysteresis on the reverse scan (0 V to V_{oc}) at low scan speed of 0.1 V/s for TPA-ANT-
279 TPA and Spiro-OMeTAD based devices. However, for ACE-ANT-ACE HTM based devices,
280 a negligible hysteresis resulted in a lowered PCE from 13.1% to 11%. As per previous
281 discussion, an excessively small band offset of the HOMO between perovskite and HTL may
282 hamper the effective hole transport ability.^[41] However, our study significantly showed that
283 even though the work function of TPA-ANT-TPA is very close to that of perovskite active
284 layer, still the better PCE than that of ACE-ANT-ACE could be achieved. The lower V_{oc} of
285 ACE-ANT-ACE is due to the large band offset and HOMO value difference between this
286 compound and active layer perovskite.^[41] Furthermore, TPA-ANT-TPA based PSCs shows
287 improvement in short circuit current ($J_{sc} = 21.07 \text{ mA cm}^{-2}$) compared to ACE-ANT-ACE (J_{sc}
288 $= 18.7 \text{ mA cm}^{-2}$) which is due to the shallower HOMO of TPA-ANT-TPA that allows an
289 effective hole extraction.

290 To the best of our knowledge, the obtained PCE of 17.5% using TPA-ANT-TPA HTM
291 is very high compared to other HTMs reported in the literature taking dopant-free aspect into
292 account.^[19, 26, 44, 45] The hysteresis behaviours of champion devices and statistics of a total of
293 90 devices prepared using three different hole transporting layers is shown in Figure S13,
294 Table 2 and S11 respectively (ESI[†]). The statistics of total 90 PSCs prepared using TPA-
295 ANT-TPA, ACE-ANT-ACE and Spiro-OMeTAD exhibits an average device efficiency of
296 16%, 11.4% and 13.8% respectively. As shown in Figure 3c, the devices with TPA-ANT-

297 TPA exhibit EQE values above 78 to 82% from 365 nm to 650 nm covering the entire UV
298 region with the highest EQE of 82% observed at 470 nm.

299 To measure the hole transport properties, a space charge limited current (SCLC)
300 method was used. A spin-coated layer of the HTMs on an ITO/PEDOT-PSS substrate,
301 followed by an evaporated gold counter electrode was prepared for measurements. As the
302 ITO and gold work functions are close to the HTM's HOMO level, this creates a hole-only
303 device from which the mobility can be determined. The highest hole mobility (Table 2,
304 Figure S14 (ESI[†])) of $2.6 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was obtained with TPA-ANT-TPA and was
305 higher than that with Spiro-OMeTAD ($1.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and ACE-ANT-ACE (2.4×10^{-5}
306 $\text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). This is consistent with the good fill factor and efficiency performance shown by
307 perovskite devices prepared utilizing TPA-ANT-TPA as HTL.

308 The stability of PSC devices is one of the most critical parameter and most discussed
309 parameter in perovskite solar cell community. Perovskite solar cell stability is also one of the
310 major hurdles to commercialize this technology for the industrial scale. Ambient humidity is
311 one of the most important factors responsible for the quick degradation of PSCs and this is
312 due to the salt type nature of $\text{CH}_3\text{NH}_3\text{PbI}_3$ active layer in PSC.^[46-48] We studied the stability
313 of fabricated champion devices without any encapsulation at high humidity conditions
314 (relative humidity (RH) $\geq 58\%$, temperature = 22°C , in dark condition) for our newly
315 developed ACE-ANT-ACE, TPA-ANT-TPA and standard classical Spiro-OMeTAD HTMs
316 (as shown in **Figure 4**). A simple stability setup used is shown in Figure S12c, d (ESI[†]) and
317 photovoltaic performance was measured at 1000 W m^{-2} (AM1.5G) using regular aging
318 intervals. In particular, photovoltaic properties of our novel **TPA-ANT-TPA** and Spiro-
319 OMeTAD in the aging test are detailed in Figure 4a, b. Additionally, the efficiency of all
320 HTMs based devices are evaluated under identical conditions and depicted in Figure 4. The
321 degradation test results show that the Spiro-OMeTAD HTM based devices degraded at a

322 faster rate compared to **TPA-ANT-TPA** and **ACE-ANT-ACE** HTM based devices.
323 Additionally, we have tested the champion devices using all three HTLs under continuous 1
324 sun illumination in ambient air for 200 hours exposure (Figure S15, (ESI[†])) and found the
325 TPA-ANT-TPA and ACE-ANT-ACE HTM based devices shows a smaller drop in
326 efficiency, and still sustain improved stability over Spiro-OMeTAD based devices.

327 Moreover, the novel ANT core along with extended TPA groups offers a better surface
328 coverage and in addition the absence of the Li salt also gives better stability^[4, 49] for TPA-
329 ANT-TPA and ACE-ANT-ACE HTM based PSCs than that of Spiro-OMeTAD HTL based
330 PSCs. It can be seen that the PCE values diminished rapidly down to ~2% (after only 10
331 hours) for Spiro-OMeTAD based devices. However, the devices based on TPA-ANT-TPA
332 are seen to be more stable with observed efficiency reduced to ~14% (after >50 hours
333 exposure to 58% RH conditions) and 15% (after 200 hours of continuous illumination to 1
334 sun in ambient air).

335 The overall superior performance of PCE and stability of TPA-ANT-TPA over Spiro-
336 OMeTAD provide a promising alternative replacement for high performance perovskite solar
337 cells. The reason for the dramatic improvement in stability of TPA-ANT-TPA based PSCs
338 (compare to Spiro-OMeTAD and ACE-ANT-ACE) and improvement in efficiency from 13%
339 with ACE-ANT-ACE to 17.5% with TPA-ANT-TPA are further investigated by steady state
340 photoluminescence (**Figure 5a**) and morphological measurements (**Figure 6**).

341 The measurement of steady state photoluminescence based on a simple architecture:
342 Glass/CH₃NH₃PbI₃/HTM is shown in Figure 5a. In order to eliminate any quenching effect
343 related to electron transfer to the oxide layer, we avoided to use of a TiO₂ layer while doing
344 PL measurements. During these PL measurements, we have to make sure that the
345 photoluminescence quenching is only caused by the hole transport layer and is not due to any
346 other materials. All the HTL thin films were excited at 550 nm wavelength. From the data, it

347 is quite clear that the bare perovskite film without any HTM (black curve) exhibits a high PL
348 emission intensity as a result of the formation of good quality (crystallinity and homogeneous
349 surface) perovskite film. Such observations are similar to our earlier studies and they are also
350 comparable with reported data.^[42, 50] Upon deposition of HTM on the perovskite layer, a
351 significant reduction in PL emission was observed. Perovskite films covered with TPA-ANT-
352 TPA (blue curve) and ACE-ANT-ACE (green curve) HTL's display a stronger PL quenching
353 (~95 to 80%) than the films covered with Spiro-OMeTAD (~60 to 65%) HTL. These results
354 clearly indicate a higher PL quenching ability of our newly developed TPA-ANT-TPA and
355 ACE-ANT-ACE materials compared to Spiro-OMeTAD. Between the two materials, TPA-
356 ANT-TPA exhibits more efficient exciton dissociation efficiency and ensures a more efficient
357 charge generation and high hole mobility as well as low recombination at the TPA-ANT-
358 TPA/CH₃NH₃PbI₃ interface.

359 The time resolved photoluminescence **measurement** was performed and shown in
360 Figure 5b to verify the improved hole transport properties. Bare perovskite films deposited on
361 glass substrate as well as with different hole transport layers show biphasic kinetics. The fast
362 component decays in picosecond (due to 80 ps laser pulse) and the slower component has a
363 time constant of 10-15 ns. The fast component represents trap filling. As the hole transfer
364 films are deposited on bare glass - perovskite layer for direct probing, this gives us a good
365 estimation about quenching of the photoluminescence due to hole transport layers. As shown
366 in our previous work, a good quality glass-perovskite sample shows a lifetime of 8-10 ns.^[50]
367 In this case, similarly we have obtained 8 ns lifetime for the bare perovskite sample (without
368 the hole transporting layer). This, along with the high intensity PL, further confirms the
369 quality of the perovskite film. Bare perovskite films show an average life time of 200 ns.
370 After the introduction of TPA-ANT-TPA hole transporting layer above the perovskite layer
371 the average decay time (T) shortened to ~20.2 ns. The fast decay lifetime (T_1) of all 3 hole

372 transporting materials decreased from 33 ns (bare perovskite without HTL) to 20 ns for ACE-
373 ANT-ACE, to 12 ns for Spiro-OMeTAD and 6 ns for TPA-ANT-TPA hole transporting
374 layer. At the same time the weight fraction increased from 3% (bare perovskite film) to 15%
375 for ACE-ANT-ACE hole transport layer, 27.2% for Spiro-OMeTAD and 32.5% for TPA-
376 ANT-TPA hole transport layers. This clearly shows improved hole extraction as well charge
377 dissociation from perovskite to deposited hole transport layers. The order of effective hole
378 extraction follows a trend: TPA-ANT-TPA > Spiro-OMeTAD > ACE-ANT-ACE.

379 Figure 6 exhibits scanning electron microscope (SEM) images recorded on the
380 perovskite thin film deposited on top of FTO/compact TiO₂/mesoporous TiO₂ substrates,
381 TPA-ANT-TPA and ACE-ANT-ACE on perovskite layer, respectively. Figure 6a clearly
382 shows the perovskite film with a high coverage and a crystal size ranging from 100 to 300
383 nm. Figure 6b, c, and d1 illustrate similar surface thicknesses of TPA-ANT-TPA, Spiro-
384 OMeTAD, and ACE-ANT-ACE HTM layers under the same magnification. Among all of the
385 data, Figure 6b obviously shows uniform, defect-free coverage of TPA-ANT-TPA HTM. For
386 Spiro-OMeTAD HTM, weak hydrogen bonding between active CH₃NH₃PbI₃ layer and HTM
387 might be responsible factor for poor morphology than TPA-ANT-TPA. Interface between
388 HTM and CH₃NH₃PbI₃ helps in stabilization of the perovskite phase with a uniform and
389 dense morphology as well as improved crystallites. Such arrangement is responsible for the
390 highly-improved cell performance. Relatively less homogeneous surface is seen for ACE-
391 ANT-ACE HTL whereas for Spiro-OMeTAD, the surface is more inhomogeneous with a
392 rough surface morphology (Figure 6d) and at some point, showing crystallization possibly
393 caused by the use of dopants (Figure 6d1). Spin coated Spiro-OMeTAD HTL shows oriented
394 aggregation or crystallization due to its intrinsic features.^[51] Also, spin coated films of ACE-
395 ANT-ACE and TPA-ANT-TPA films shows small particles which could be attributed with
396 aggregation.

397 These electron microscope observations strongly correlate with the perovskite solar cell
398 stability trends observed in Figure 4. The improved coverage of the TPA-ANT-TPA films
399 resulted in devices with much higher stability whereas the HTM films with small to large pin-
400 holes exhibited lower stability. The good coverage of the HTM on the perovskite layer is an
401 extremely important parameter besides its hole transporting ability. It assures protection of
402 the perovskite thin film layer from the exposure to oxygen,^[47] humidity,^[48, 52] and heat.^[52]
403 These external exposures are main culprits for the quick degradation of PSCs under ambient
404 conditions. In addition to the surface morphology of HTMs on perovskite layer, we also
405 performed contact angle measurements (Figure S10, ESI†) on TPA-ANT-TPA and ACE-
406 ANT-ACE deposited thin films on perovskite layer to confirm the hydrophobicity of the
407 surface. The obtained data show a bad wetting behaviour with an elevated angle (85°) of
408 water droplets for TPA-ANT-TPA surface, whereas a good wetting was observed with a
409 lower contact angle (47°) for the Spiro-OMeTAD layer. The higher stability of TPA-ANT-
410 TPA based PSCs is due to its higher hydrophobic nature that will protect the perovskite layer
411 underneath. To further investigate the stability of all three HTMs, TPA-ANT-TPA, ACE-
412 ANT-ACE and Spiro-OMeTAD are deposited on the perovskite layer and are subjected to 1
413 sun (AM 1.5G) continuous illumination for two weeks.

414 The crystalline and absorbing characteristics of the perovskite covered with the three
415 different HTLs before and after 1 sun illumination for 2 weeks are measured using XRD and
416 UV-visible spectroscopy as shown in Figure S16, ESI†. The perovskite covered with TPA-
417 ANT-TPA and ACE-ANT-ACE does not show any sign of degradation and perovskite layers
418 underneath continue to show high crystallinity and absorbance after 2 weeks of continuous 1
419 sun illumination (Figure S16(a), (b), (c), (d), ESI†). However, the perovskite layer covered
420 with Spiro-OMeTAD shows complete degradation of the perovskite to PbI₂ as observed from
421 Figure S16(c), (f), ESI†.

422 A comparison of lab cost difference between TPA-ANT-TPA and Spiro-OMeTAD
423 HTMs is given in Table 3. The synthesis cost of TPA-ANT-TPA is estimated by using the
424 price of chemical suppliers in Australia and following previous attempts.^[53, 54] Its further
425 details can be found in Table S2-5 (ESI[†]). The flowchart describing the synthesis of 1g of
426 TPA-ANT-TPA was illustrated in Figure S17 (ESI[†]). Meanwhile, the price of synthetic
427 Spiro-OMeTAD's HTM is surveyed from earlier reports and its commercial price is also
428 mentioned.^[53, 55] The cost of our newly developed high performance TPA-ANT-TPA HTM
429 (taking both efficiency and stability into an account) is roughly two third that of synthetic
430 Spiro-OMeTAD and it can further drop if large scale synthesis is performed.

431 A brief comparison among dopant-free HTMs using TPA moiety as either the central
432 core or the end-capping groups has been conducted and listed in **Table 4**. These preferred
433 HTMs have similar device structure: FTO/compactTiO₂/mesoporous
434 TiO₂/CH₃NH₃PbI₃/HTM/cathode with approximately equivalent working area. Their
435 photovoltaic parameters of the solar cells were evaluated under 1 sunlight illumination (100
436 mW cm⁻²) condition. Overall, the device with TPA-ANT-TPA as HTM displays the highest
437 FF whereas the V_{oc} and J_{sc} are among the best values in comparison with other ones. This
438 material also possesses the impressive hole mobility which may be a trigger to the superior
439 values of the FF and J_{sc} . Even though the TPA-CN and TPA-ANT-TPA based devices
440 exhibited the similar efficiency (17.5%), the performance of TPA-CN was lower than that of
441 the reference device based on Spiro-OMeTAD under similar conditions.^[35] During the ageing
442 test without encapsulation at room temperature, the PCE achieved using our TPA-ANT-TPA
443 as HTM maintained 80% of the initial value. Even though this may be lower than that of
444 Z34, Me-QTPA, EDOT-OMeTPA, and Z1011, their initial performance was worse than that
445 of our material based devices. According to the tabular comparison, our novel TPA-ANT-
446 TPA HTM can become a suitable and promising alternative to Spiro-OMeTAD.

447 Overall, the better performance and stability properties of PSCs made using TPA-
448 ANT-TPA based hole transport layers are due to the following factors: (a) better charge
449 extraction - the experimental photoluminescence spectroscopy shows enhanced quenching for
450 TPA-ANT-TPA based perovskite devices due to better hole transfer. Additionally, it is also a
451 result of close alignment of HOMO energy levels of the HTM and perovskite with minimal
452 band offset; (b) stability improvement - the improved morphology, uniformity and a good
453 surface coverage of the capping layer of TPA-ANT-TPA. The hydrophobic nature of the
454 TPA-ANT-TPA surface as seen from contact angle measurements makes the PSCs made
455 from TPA-ANT-TPA HTM more stable than Spiro-OMeTAD based devices. Moreover,
456 avoiding the use of dopants such as LiTFSI enhances the stability (salts often reacts quickly
457 with moisture).

458 In this work, we have successfully designed and synthesized two new small molecular
459 TPA-ANT-TPA and ACE-ANT-ACE HTMs based on an innovative anthanthrone dye as a
460 core. The syntheses of both materials were conducted via a simple coupling protocol using a
461 common anthanthrone dye as a central core and two different tri-phenylamine and
462 acenaphthylene end-capping units. A detailed comparison on optoelectronic properties of
463 TPA-ANT-TPA and ACE-ANT-ACE based PSCs has been performed and it is found that a
464 HOMO energy level of TPA-ANT-TPA is close to the active perovskite energy level for
465 better hole transport with minimal energy offset. Upon evaluating both TPA-ANT-TPA and
466 ACE-ANT-ACE as hole transporting materials in perovskite solar cell devices, the highest
467 power conversion efficiency of 13% and 17.5% has been achieved, respectively. The TPA-
468 ANT-TPA HTM not only exhibits high performance showing champion efficiency of 17.5%
469 and average efficiency of 16% with increased reproducibility of PSCs as compared to Spiro-
470 OMeTAD based PSCs but also shows a lower cost and straightforward synthesis with easy
471 purification. One of the most important striking features of TPA-ANT-TPA based PSC

472 devices is its environmental stability which is much higher than that with classical Spiro-
473 OMeTAD. This is a most critical parameter, and the most discussed aspects in the perovskite
474 solar cell community. The significantly higher stability of the TPA-ANT-TPA based devices
475 is due to the hydrophobic nature and homogeneous coverage as a result of more extended
476 chemical structure of TPA on the perovskite capping layer. The TPA-ANT-TPA HTM
477 without additives resulted in increased V_{oc} and improved moisture resistance of PSCs, as a
478 result of more uniform formation of TPA-ANT-TPA capping layer on the surface of
479 perovskite leading to a more efficient hole transport than with Spiro-OMeTAD. The
480 improved charge collection efficiency in devices prepared with TPA-ANT-TPA HTL (as
481 seen from effective PL quenching) compared to that of ACE-ANT-ACE and Spiro-OMeTAD
482 HTL leads to higher short circuit current and photovoltage. In summary, we successfully
483 demonstrated the great potential of a low cost anthanthrone dye as a starting precursor for
484 designing highly efficient HTMs for stable and low cost efficient PSCs. Using such efficient,
485 stable and low cost HTMs, it must be possible to produce the large-scale roll-to-roll printed
486 perovskite solar cell modules and prototypes for commercialization and energy harvesting
487 application.

488 **Experimental Section**

489 Detailed experimental methods can be found in the Supporting Information.

490 **Supporting Information**

491 Supporting Information is available from the Wiley Online Library or from the author.

492

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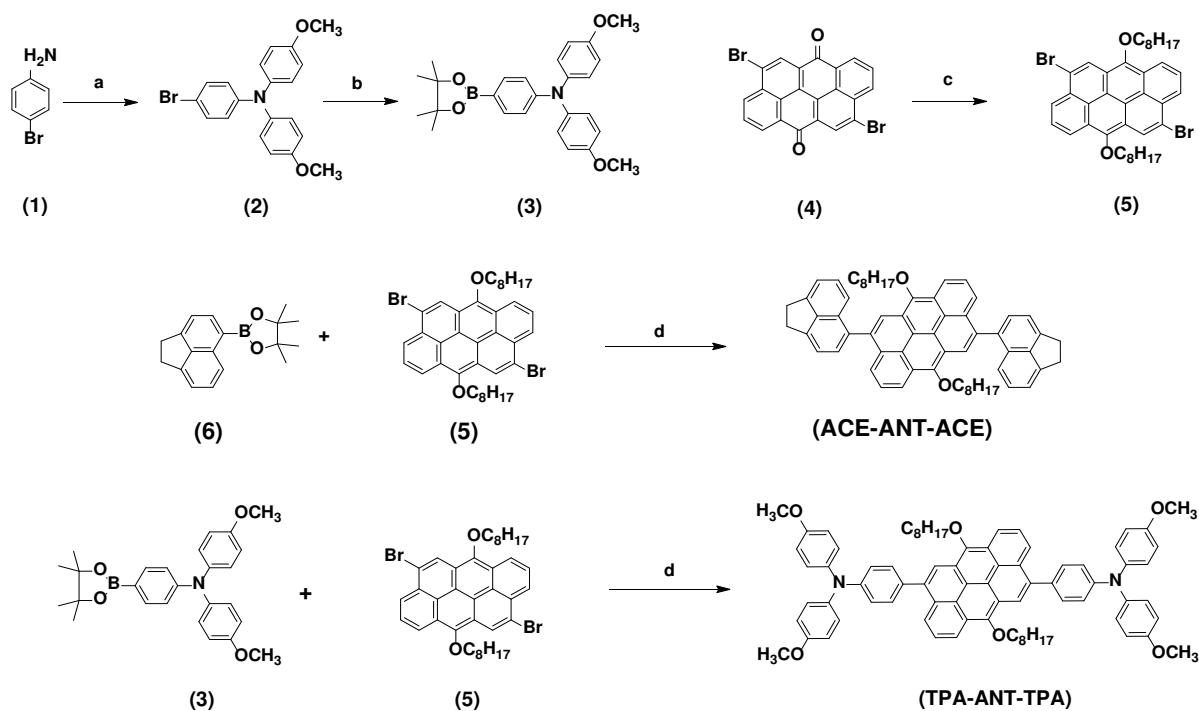
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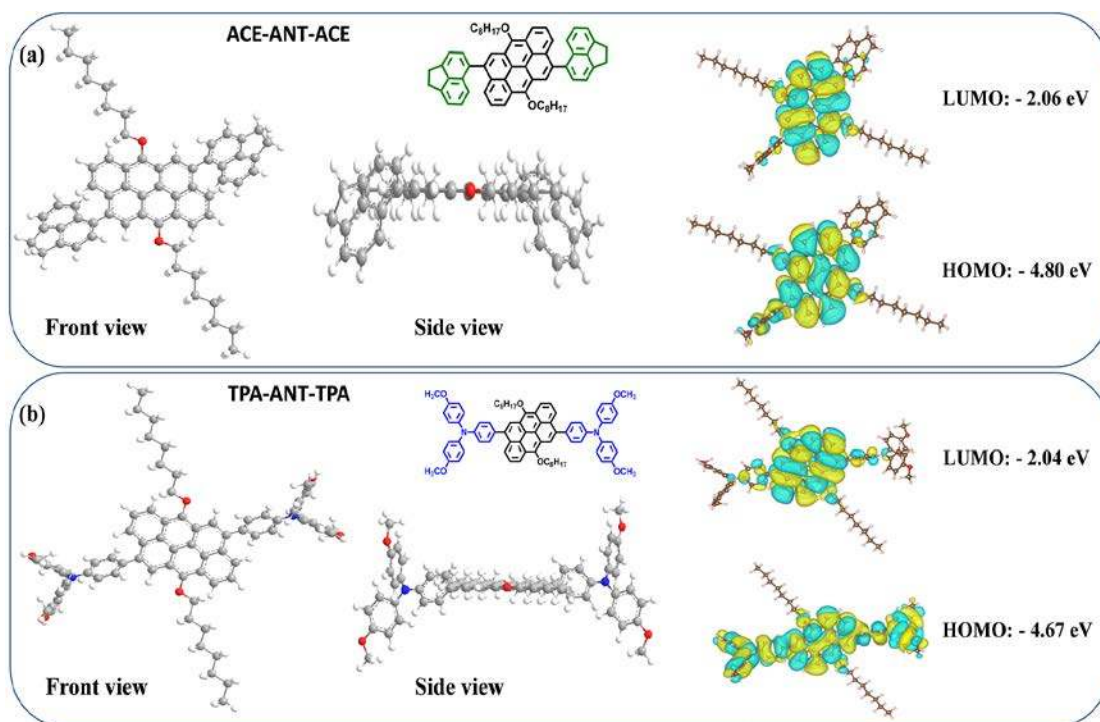
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657



658 **Scheme 1.** Synthetic approach to ACE-ANT-ACE and TPA-ANT-TPA. Reagent and
 659 conditions: (a) 1-iodo-4-methoxybenzene, KOH, CuCl, 1,10-phenanthroline monohydrate,
 660 toluene, 120 °C, overnight; (b) bis(pinacolato)diboron, KOAc, Pd(dppf)Cl₂, DMF, 120 °C,
 661 overnight; (c) Na₂S₂O₄, C₈H₁₇Br, aliquat 336, NaOH (aq.), 120 °C, overnight; (d) 2M K₂CO₃,
 662 toluene, Pd(PPh₃)₄, 120 °C, 48 h.

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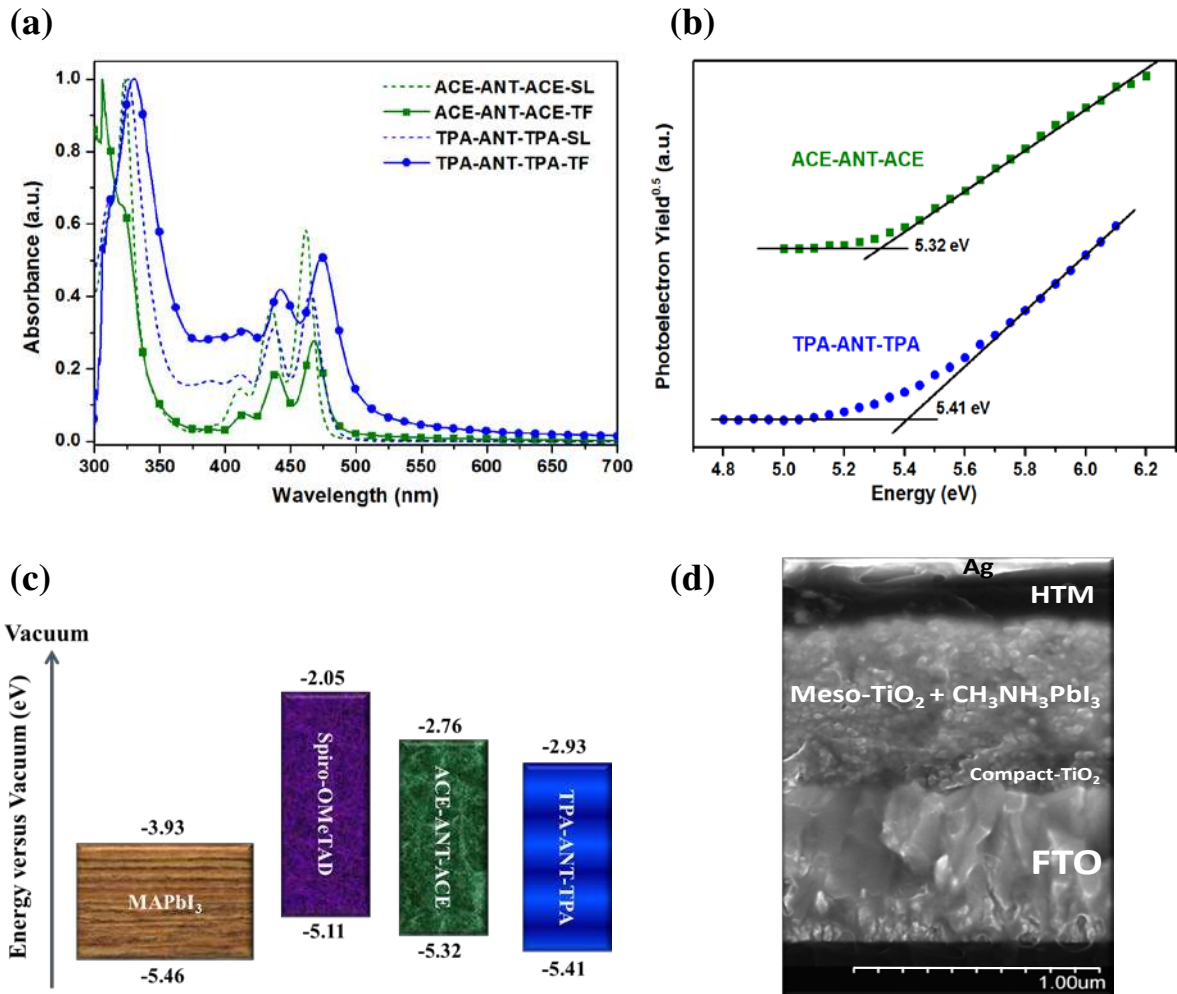


664

665 **Figure 1.** Chemical structures, geometrical configuration (front view and side view), and
 666 calculated isosurfaces and energy levels of HOMO and LUMO orbital surfaces of (a) ACE-
 667 ANT-ACE and (b) TPA-ANT-TPA.

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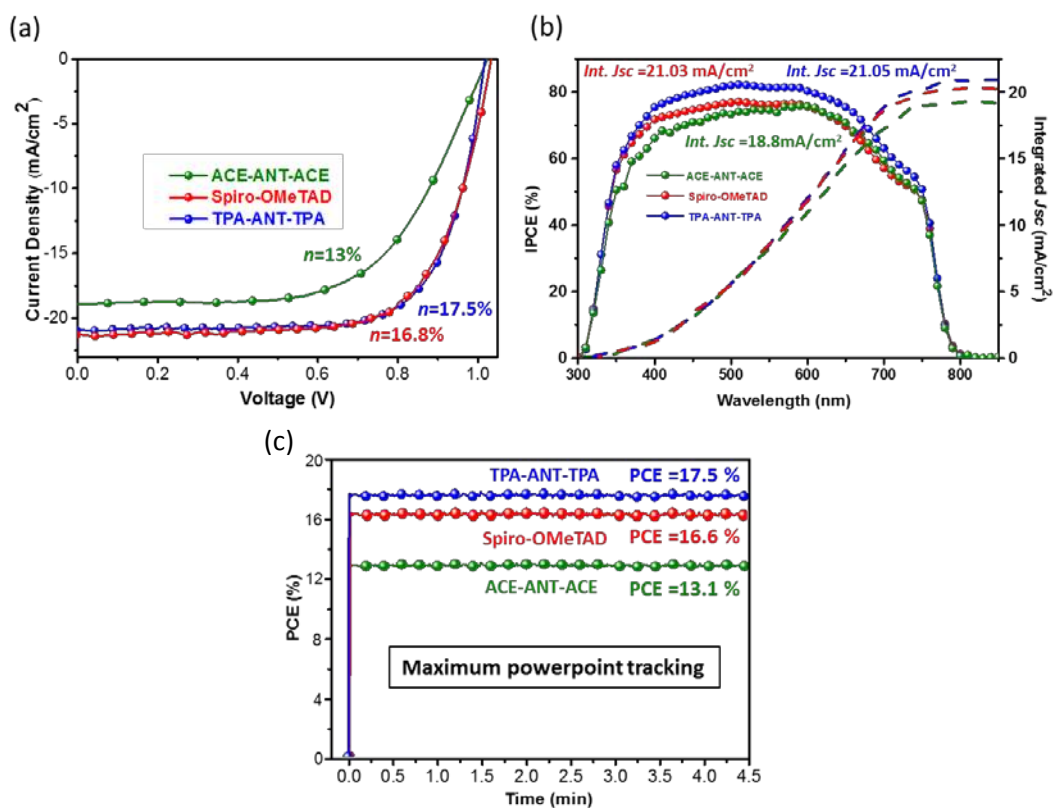
671 **Figure 2.** (a) UV-Vis absorption spectra in CF solutions (dash line) and films (solid line), (b)

672 Photoelectron spectroscopy in air (PESA) spectra, (c) Energy level diagrams, (d) Cross-

673 sectional scanning electron microscopy image of PSC without dopants.

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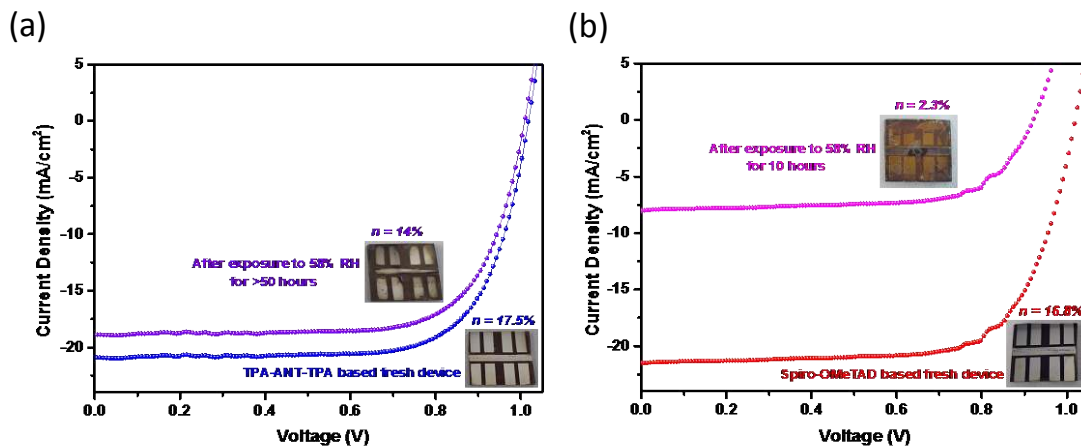


676

677 **Figure 3.** Photovoltaic performance with hysteresis of optimized champion PSC devices
 678 made using different hole transport layers: (a) Using ACE-ANT-ACE (green curve) TPA-
 679 ANT-TPA (blue curve) as the hole transporting layer and Spiro- OMeTAD (red curve and
 680 black curve) as the hole transporting layer; and (b) Absolute EQE spectra (solid line) and
 681 integrated current densities (dashed lines) of optimized PSC solar cells prepared using
 682 different hole transporting layers as ACE-ANT-ACE (green), TPA-ANT-TPA (blue) and
 683 Spiro-OMeTAD (red). (c) Power output under maximum power point tracking for 270 s,
 684 starting from forward bias and resulting in a stabilized power output of 17.5%, 16.6% and
 685 13% for TPA-ANT-TPA, ACE-ANT-ACE and Spiro-OMeTAD based devices respectively
 686 (at 960 mV). The voltage scan rate for all scans was 10 mVs^{-1} and no device preconditioning,
 687 such as light soaking or forward voltage bias applied for a long time, was applied before
 688 starting the measurement.

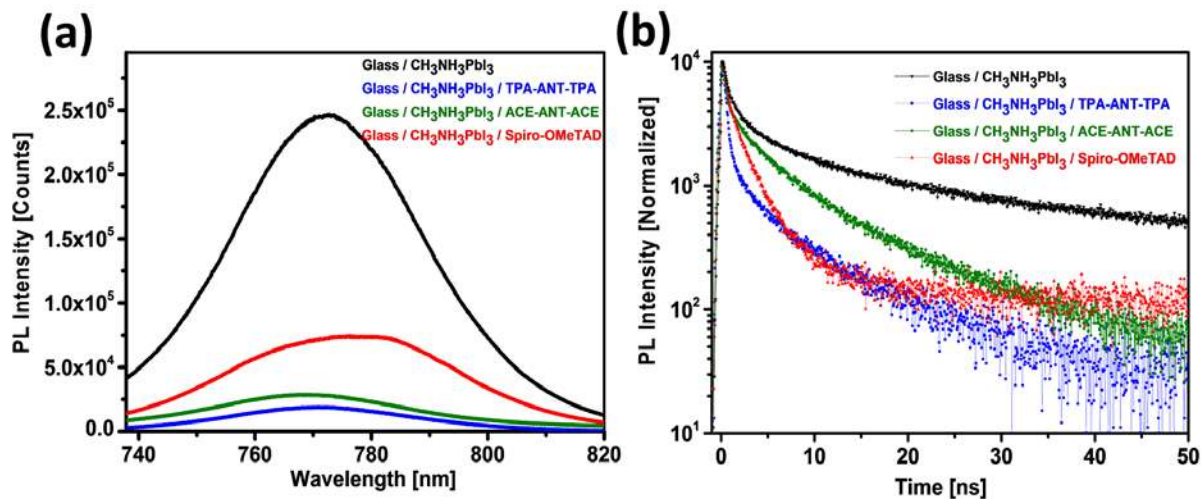
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692 **Figure 4.** Photovoltaic performance of TPA-ANT-TPA (a) and Spiro-OMeTAD (b) based
693 $\text{CH}_3\text{NH}_3\text{PbI}_3$ PSC devices respectively on aging in humidity $\geq 58\%$ (the fresh and aged PSC
694 devices shown in satellite pictures); Stability test/aging for 50 hours: without encapsulation
695 for, TPA-ANT-TPA and Spiro-OMeTAD based $\text{CH}_3\text{NH}_3\text{PbI}_3$ PSC devices at RH \geq
696 58%, After each consecutive measurement, the PSCs are kept in an ambient humidity setup
697 of RH $\geq 58\%$, Temperature = 22 °C, in dark condition. Grey colour scale represents humid
698 condition RH $\geq 50\%$, Temperature = 22 °C, in dark condition.

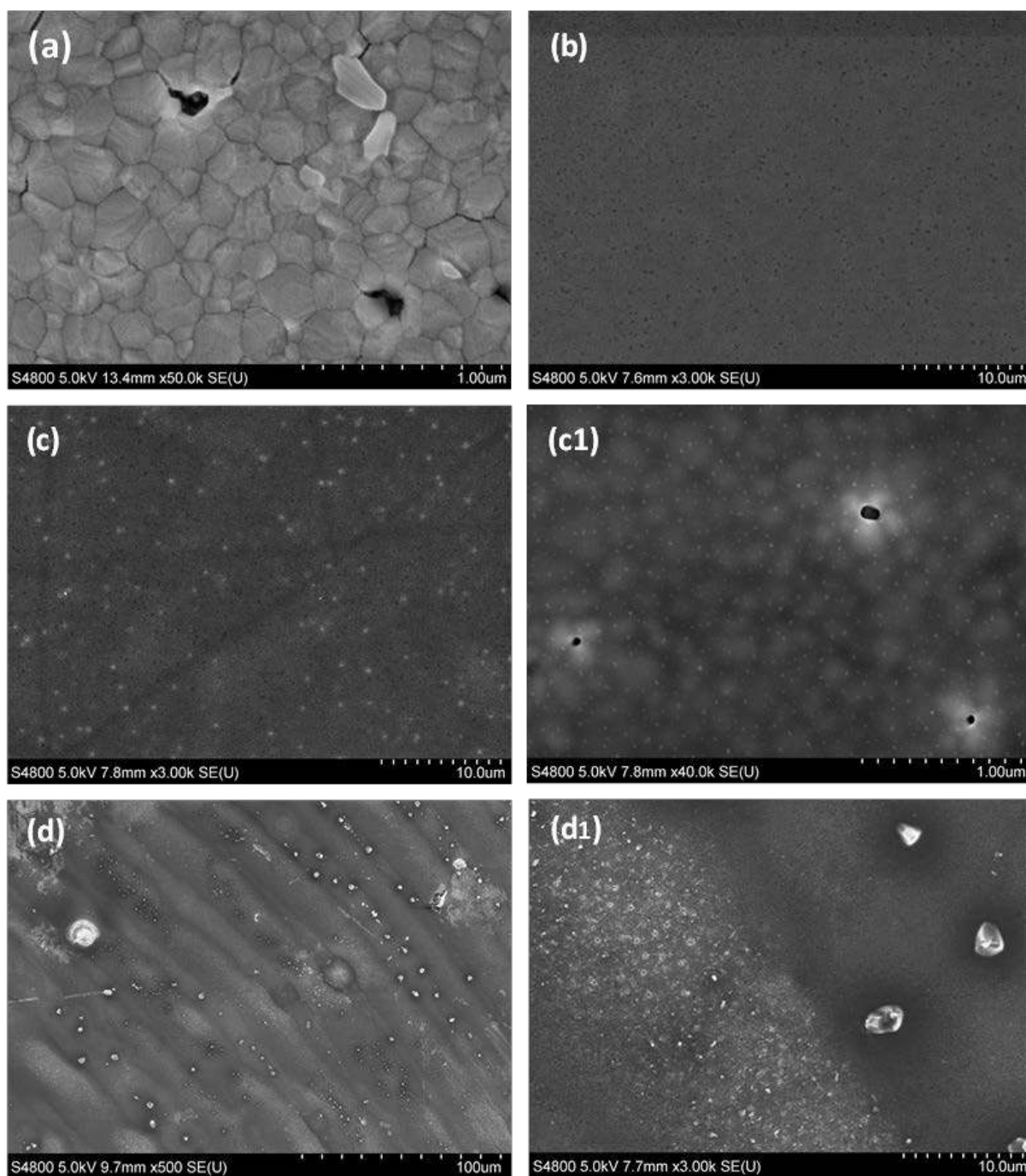


699

700 **Figure 5.** (a) Steady state Photoluminescence (PL) measured on bare perovskite film (black),
 701 and hole transport layer deposited on the perovskite. Red, green, and blue curves represent
 702 Spiro-OMeTAD, ACE-ANT-ACE, TPA-ANT-TPA, respectively, deposited on perovskite.
 703 (b) Time resolved PL taken at excitation wavelength of 765 nm of the perovskite films with
 704 different hole transport layers. A 5 mW picosecond pulsed diode laser at 635 nm excited on
 705 the perovskite and hole transport layer side.

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708

709 **Figure 6.** (a) Surface image of perovskite films deposited on top of FTO/compact
 710 TiO_2 /mesoporous TiO_2 ; (b) Top view of TPA-ANT-TPA on a perovskite layer; (c), and (c1)
 711 top view of ACE-ANT-ACE on a perovskite layer; (d) and (d1) top view of Spiro-OMeTAD
 712 on a perovskite layer.

713

714 **Table 1.** Thermal, optical and electrochemical properties of ACE-ANT-ACE and TPA-ANT-
 715 TPA

HTMs	λ_{\max} [nm]		$\lambda_{\text{PL}}^{\text{c)}$	$E_g^{\text{optd)}$	$E_{\text{HOMO}}^{\text{e)}$	$E_{\text{LUMO}}^{\text{e)}$	$E_{\text{HOMO}}^{\text{f)}$	T_d	T_m
	Solution ^{a)}	Film ^{b)}	[nm]	[eV]	[eV]	[eV]	[eV]	[°C]	[°C]
ACE-ANT-ACE	461	467	480	2.56	-5.32	-2.76	-5.28	265	215
TPA-ANT-TPA	465	473	553	2.48	-5.41	-2.93	-5.40	290	256

716 ^{a)}Absorption spectrum was measured in chloroform (CF) solution; ^{b)} Film was prepared by spin-
 717 coating an CF solution containing the sample onto glass substrate at a spin speed of 1000 rpm at room
 718 temperature; ^{c)}Emission spectrum was analysed in CF solution; ^{d)}Optical bandgap was calculated from
 719 the formula of $1240/\lambda_{\text{onset}}$; ^{e)}The oxidation potential was also measured by photoelectron spectroscopy
 720 in air (PESA); $E_{\text{LUMO}}^{\text{PESA}} = E_{\text{HOMO}}^{\text{PESA}} + E_g^{\text{opt}}$; ^{f)} Oxidation potential of the material was characterized in
 721 dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate at scan speed 100 mV/s,
 722 potentials vs. Fc/Fc⁺.

723 **Table 2.** Summary of champion as well average photovoltaic performance and hole mobility
 724 of PSC devices prepared with different HTLs as ACE-ANT-ACE, TPA-ANT-TPA and
 725 Spiro-OMeTAD.^{a)}

HTLs	Scan Direction	V _{OC} [V]	J _{SC} [mA/cm ²]	FF [%]	PCE [%]	Hole mobility [cm ² V ⁻¹ s ⁻¹]
ACE-ANT-ACE ^{b)}	Forward	1.03	18.7	67.1	13.1	2.4 x 10 ⁻⁵
	Reverse	1.03	17.9	65.3	12.7	
	Average ^{d)}	0.99	17.8	65	11.4	
TPA-ANT-TPA ^{b)}	Forward	1.03	21.07	79.6	17.5	2.6 x 10 ⁻⁴
	Reverse	1.03	21.05	79.6	17.5	
	Average ^{d)}	1.00	21.03	76.5	16	
Spiro-OMeTAD ^{c)}	Forward	1.04	21.09	76.8	16.8	1.5 x 10 ⁻⁴
	Reverse	1.04	21.08	76.8	16.8	
	Average ^{d)}	0.98	20.0	70.2	13.8	

726 ^{a)}Cell size (active area): 0.100 cm². Photovoltaic performance at 1000 w m⁻² (AM1.5G) and
 727 constant scan speed of 0.1 V/s mesoscopic CH₃NH₃PbI₃ devices; ^{b)}without additives; ^{c)}with
 728 additives: 4-tert-butylpyridine (*t*BP) and Li-bis(trifluoromethanesulfonyl)-imide (LiTFSI);
 729 ^{d)}An average device efficiency of total 81 devices.

730

731 **Table 3.** Comparison of lab synthesis costs of TPA-ANT-TPA and Spiro-OMeTAD.

Compound	Material cost [\$/g]	Commercial price [\$/g]
TPA-ANT-TPA	67	-
Spiro-OMeTAD	91.67 ^[53, 55]	170-475 ^[53, 55]

732

733

734 **Table 4.** The comparison of small molecular triphenylamine derivatives based dopant-free
 735 HTMs^{a)}

HTM	HOMO [eV]	Hole mobility [$10^{-4}\text{cm}^2\text{V}^{-1}\text{s}^{-1}$]	Active area [cm^2]	V_{oc} [V]	J_{sc} [mAcm^{-2}]	FF [%]	PCE [%] ^{e)}	Stability test ^{g)}	References
TPA-ANT-TPA ^{b)}	-5.41	2.6	0.1	1.03	21.07	79.6	17.5 (16.8) ^{f)}	80% (14%) ^{h)}	This study
1 ^{b)}	-5.00	6.0	0.16	0.971	19.3	72	13.4 (15)	-	[45]
Z34 ^{b)}	-5.14	7.46	0.16	1.053	21.27	69	15.9 (16.7)	100% (85%)	[33]
TPB-2-MOTPA ^{b)}	-5.28	0.77	-	0.927	17.37	69	11.06 (13.28)	99% (92%)	[56]
MeO-BPZTPA ^{b)}	-5.29	4.80	0.1	0.917	16.89	66.9	10.36 (13.65)	-	[57]
TAE-1 ^{b)}	-5.32	0.592	-	0.885	17.22	72.2	11.02% (13.53%)	-	[58]
H101 ^{b)}	-5.09	-	0.2	0.99	20.11	59	11.03% (13.7%)	-	[40]
EDOT-OMeTPA ^{b)}	-5.28	-	0.0831	0.95	18.9	61	11% (11.9%)	90% (90%)	[53]
OMeTPA-FA ^{b)}	-5.14	3.67	0.16	0.905	19.42	63	11.07% (14.68%)	88% (89%)	[59]
HTM2 ^{b)}	-5.23	12.7	0.08	0.921	18.1	68	11.63% (12.08%)	-	[60]
2TPA-2-DP ^{c)}	-4.96	1.09	0.08	0.974	18.8	70.7	12.96% (11.46%)	-	[61]
Me-QTPA ^{c)}	-5.25	-	0.1	0.917	14.58	67.8	9.07% (13.65%)	100% (38%)	[62]
apv-EC ^{c)}	-5.28	7.23	0.08	0.932	18.4	70	12.0% (13.1%)	-	[63]
ST1 ^{d)}	-5.24	4.57	0.16	1.059	21.07	66	15.4 (16.3)	85% (63%)	[64]
TPA-CN ^{d)}	-5.38	1.1	0.16	1.09	20.85	77	17.5 (19.2)	-	[35]
TPI ^{d)}	-5.18	0.441	0.16	0.956	20.23	63	12.63 (14.93)	70% (52%)	[65]
TBPC ^{d)}	-5.33	4.04	0.08	0.942	19.32	72	13.10% (13.28%)	-	[66]
Z1011 ^{d)}	-5.21	8.49	0.16	1.096	20.52	70	16.3 (16.5)	97% (30%)	[32]
Z1013 ^{d)}	-5.14	6.67	0.16	1.027	21.33	70.2	15.4 (16.7)	- (60%)	[34]

736 ^{a)}Device structure: FTO/compact TiO₂/mesoporous TiO₂/CH₃NH₃PbI₃/HTM/Cathode; photovoltaic parameters
 737 of the solar cells with HTMs evaluated under 1 sunlight illumination (100 mW cm⁻²) condition.

738 ^{b)}TPA with OMe used as end-capping groups

739 ^{c)}TPA without OMe used as end-capping groups

740 ^{d)}TPA used as the central core

741 ^{e)}The best PCE of the HTMs based devices

742 ^{f)}The best PCE of standard doped SPIRO-OMeTAD

743 ^{g)}The percentage of the retaining performance after the ageing test (unsealed devices, at room temperature)

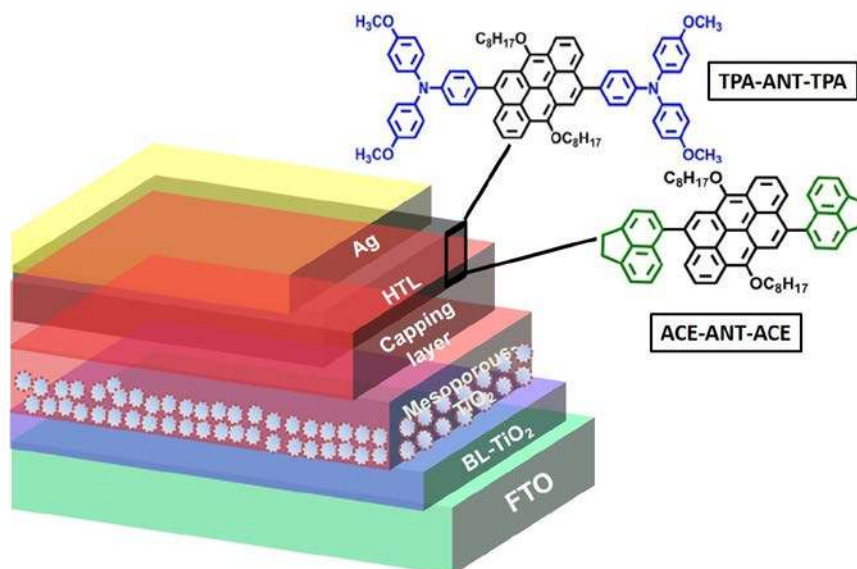
744 ^{h)}The percentage of the retaining performance of standard SPIRO-OMeTAD

745

746 **Table of Content Figure**

747 First time a low cost anthanthrone dye based hole transporting materials **ACE-ANT-ACE**
748 and **TPA-ANT-TPA** end capped with dihydroacenaphthylene and triphenyleamine groups
749 were designed and synthesized respectively. Among both, **dopant-free TPA-ANT-TPA** cut-
750 rate HTM (**\$67/g**) exhibits higher performance with 17.5% efficiency and retains respectable
751 performance after 50 hours in 58% relative humidity than conventional expensive SPIRO-
752 OMeTAD.

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Supporting Information

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Molecular Engineering Using an Anthanthrone Dye for Low

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Cost Hole Transport Materials: A Strategy for Dopant Free,

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High Efficiency Perovskite Solar Cells

760

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779	Content	
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828	methoxyphenyl)aniline (2).....64
829	Table S3. Materials quantities and cost evaluation for the synthesis of 4-methoxy- <i>N</i> -(4-
830	methoxyphenyl)- <i>N</i> -(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (3).....65
831	Table S4. Materials quantities and cost evaluation for the synthesis of 4,10-dibromo-6,12-
832	bis(octyloxy)anthanthrene (5).....66
833	Table S5. Materials quantities and cost evaluation for the synthesis of 4,4'-(6,12-
834	bis(octyloxy)-6,12-dihydronaphtho[7,8,1,2,3- <i>nopqr</i>]tetraphene-4,10-diyl)bis(<i>N,N</i> -bis(4-
835	methoxyphenyl)aniline) (TPA-ANT-TPA)67
836	

837 **Experimental details**

838

839 **1. Materials and Instruments**

840 All chemicals and reagents were purchased from commercial company and used directly
841 without any further purification. Synthesized compounds were characterized by $^1\text{H-NMR}$ and
842 $^{13}\text{C-NMR}$ spectrum, which were obtained with a Varian-400 spectrometer or a Bruker 600
843 MHz spectrometer. High-resolution mass spectra were acquired on an LTQ Orbitrap Elite
844 mass spectrometer (Thermo Fisher Scientific, Bremen, Germany) equipped with an
845 electrospray ionisation (ESI) source, operating in the positive ion mode at a resolution of
846 120,000 (at m/z 400). Reserpine ($[\text{M}+\text{H}]^+$, m/z 609.28066) was used as a lock mass calibrant
847 to increase the measurement accuracy. Thermal analysis was performed using a Pegasus
848 Q500TGA thermogravimetric analyzer under nitrogen atmosphere at a heating rate of 10
849 $^\circ\text{C}/\text{min}$. Differential scanning calorimetry (DSC) was conducted under nitrogen using a
850 Chimaera instrument Q100 DSC. The sample was heated at 10 $^\circ\text{C}/\text{min}$ from 30 $^\circ\text{C}$ to 300 $^\circ\text{C}$.
851 Absorption spectra were recorded on a Shimadzu UV-1800 spectrometer. Photoelectron
852 spectroscopy in air (PESA) measurements were conducted using on an AC-2 photoelectron
853 spectrometer (Riken-Keiki Co.). The cyclic voltammetry (CV) was performed by a
854 Potentiostat Galvanostat with a three electrode cell in a solution of Bu_4NPF_6 (0.1M) in
855 freshly distilled DCM at a scan rate of 100 mV/s. The counter electrode was a Pt wire, the
856 working electrode was glassy carbon and an Ag/Ag^+ electrode was used as the reference
857 electrode.

858

859 **2. Synthesis**860 **Synthesis of 4-bromo-*N,N*-bis(4-methoxyphenyl)aniline (2)**

861 Compound **1** (2 g, 11.6 mmol), 1-iodo-4-methoxybenzene (5.97 g, 25.5 mmol.), KOH (5.1 g,
862 90.5 mmol), CuCl (0.05 g, 0.5 mmol) and 1,10-phenanthroline monohydrate (0.1 g, 0.5
863 mmol) were dissolved in anhydrous toluene. After being degassed by argon for 20 min, the
864 reaction mixture was heated at 120 °C overnight. Then the mixture was cooled to room
865 temperature (RT). Excessive potassium hydroxide (KOH) was neutralized by water. After
866 that, the mixture was extracted by dichloromethane (DCM). The organic layer was dried over
867 anhydrous sodium sulphate (Na₂SO₄) and concentrated by evaporation. The crude product
868 was purified by silica gel chromatography using a mixture of hexane and DCM as eluent to
869 obtain product as a white crystal (2.5 g, 56%). ¹H NMR (600 MHz, CDCl₃, ppm): δ 7.16 (d, *J*
870 = 9.0 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 4H), 6.75 (d, *J* = 8.4 Hz, 4H), 6.72 (d, *J* = 8.4 Hz, 2H),
871 3.72 (s, 6H).

872 Synthesis of 4-methoxy-*N*-(4-methoxyphenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-
873 2-yl)phenyl)aniline (**3**)

874 In a Schlenk flask, compound **2** (2.5 g, 6.5 mmol) was mixed with diborane pinacol ester (2.5
875 g, 9.8 mmol), KOAc (1.9 g, 19.6 mmol) and Pd(dppf)Cl₂ (1.2 g, 1.6 mmol) in 50 mL
876 dimethylformamide (DMF). Then, the mixture was heated overnight at 80 °C. After cooling
877 to RT, the reaction mixture was extracted by chloroform (CF) and water. Subsequently, it
878 was dried over anhydrous Na₂SO₄ and then concentrated by evaporation. The residue was
879 purified by silica gel chromatography using a mixture of hexane and DCM as eluent to obtain
880 product as a white crystal (1.8 g, 64%). ¹H NMR (600 MHz, CDCl₃, ppm): δ 7.53 (d, *J* = 7.2
881 Hz, 2H), 6.98 (m, 4H), 6.78-6.74 (m, 6H), 3.72 (s, 6H), 1.24 (s, 12H).

882 Synthesis of 4,10-dibromo-6,12-bis(octyloxy)anthanthrene (**5**)

883 Compound **4** (2.0 g, 4.3 mmol), aqueous sodium hydroxide (0.2 M, 20 mmol), Aliquat 336
884 (2.1 g, 5.2 mmol), sodium dithionite (1.9 mg, 11.1 mmol), and 1-bromooctane (6.6 g, 34.3

885 mmol) were added into a round bottom flask and then degassed by argon for 20 min. The
886 mixture was stirred at 80 °C overnight. The crude component was extracted by water and
887 methanol. The organic layer was dried over anhydrous Na₂SO₄ and concentrated by
888 evaporation. Purification by using column chromatography yielded the main product as an
889 orange solid (2.4 g, 80%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.78-8.75 (m, 4H), 8.63 (d, *J*
890 = 7.6 Hz, 2H), 8.22-8.18 (t, *J* = 8.0 Hz, 2H), 4.34-4.31 (t, *J* = 6.4 Hz, 4H), 2.15 (m, 4H), 1.76
891 (m, 4H), 1.37-1.24 (m, 16H), 0.94-0.91 (t, *J* = 6.8 Hz, 6H).

892 Synthesis of 2-(1,2-dihydroacenaphthylen-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6) :

893 Into a Schlenk flask, commercially available 5-bromo-1,2-dihydroacenaphthylene (2.89 g,
894 12.4 mmol) was mixed with diborane pinacol ester (3.29 g, 13 mmol), KOAc (3.31 g, 33.6
895 mmol) and Pd(dppf)Cl₂ (271 mg) in 80 mL dioxane. Then, the mixture was heated overnight
896 at 80°C . After cooling to RT, the reaction mixture was extracted by chloroform (CF) and
897 water. Subsequently, it was dried over anhydrous magnesium sulphate and then concentrated
898 by evaporation. The residue was purified by silica gel chromatography using a mixture of
899 hexane and ethyl acetate as eluent to obtain product 2-(1,2-dihydroacenaphthylen-5-yl)-
900 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6) as a white powder (1.8 g, 51%). ¹H NMR (400
901 MHz, CDCl₃, ppm): δ 8.36 (d, *J* = 8.4 Hz, 1H), 8.04-8.02 (d, *J* = 6.8 Hz, 1H), 7.50-7.47 (m,
902 1H), 7.29-7.27 (d, *J* = 7.2 Hz, 2H), 3.38 (s, 4H), 1.40 (s, 12H).

903 Synthesis of 4,10-bis(1,2-dihydroacenaphthylen-5-yl)-6,12-bis(octyloxy)-6,12-
904 dihydronaphtho[7,8,1,2,3-nopqr] tetraphene (ACE-ANT-ACE)

905 In a round bottom flask, compound 5 (200 mg, 0.290 mmol), compound 6 (245 mg, 0.875
906 mmol), and 2M aqueous K₂CO₃ solution (12 mL) were dissolved in degassed toluene (18
907 mL). The solution was purged with argon for 15 minutes, then
908 tetrakis(triphenylphosphine)palladium (16.18 mg 0.014 mmol) was added. The reaction was

909 stirred at 120 °C for 2 days. After the reaction mixture was cooled to room temperature and
910 extracted with chloroform and water. The organic layer was dried over anhydrous Na₂SO₄
911 and concentrated by evaporation. The solvent was evaporated and the crude product
912 recrystallized from hot acetone to yield the desired compound as a yellow solid (205 mg,
913 65%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.81 (d, *J* = 8.0 Hz, 2H), 8.57 (s, 2H), 8.01-7.98
914 (t, *J* = 8.0 Hz, 2H), 7.92 (d, *J* = 7.2 Hz, 2H), 7.79 (d, *J* = 6.8 Hz, 2H), 7.55-7.54 (d, *J* = 7.2
915 Hz, 2H), 7.44-7.42 (m, 2H), 7.37-7.31 (m, 4H), 4.42-4.38 (t, *J* = 6.8 Hz, 4H), 3.58 (m, 8H),
916 2.08 (m, 4H), 1.63 (m, 4H), 1.26 (m, 16H), 0.88-0.84 (t, *J* = 6.8 Hz, 6H). ¹³C NMR (CDCl₃,
917 ppm): δ 149.55, 146.20, 146.12, 139.47, 137.96, 134.18, 132.25, 131.40, 129.74, 129.68,
918 127.95, 125.93, 125.71, 124.38, 123.68, 123.90, 121.90, 121.66, 120.47, 120.05, 119.48,
919 119.31, 119.24, 31.79, 30.71, 30.31, 29.52, 29.28, 26.19, 22.65, 14.10. ESI-MS: C₆₂H₆₀O₂⁺
920 *m/z* 836.4587 (calculated *m/z* 836.4588).

921 Synthesis of 4,4'-(6,12-bis(octyloxy)-6,12-dihydronaphtho[7,8,1,2,3-*nopqr*]tetraphene-4,10-
922 diyl)bis(*N,N*-bis(4-methoxyphenyl)aniline) (TPA-ANT-TPA)

923 In a round bottom flask, compound **5** (200 mg, 0.290 mmol), compound **3** (313 mg, 0.725
924 mmol), and 2M aqueous K₂CO₃ solution (12 mL) were dissolved in degassed toluene (18
925 mL). The solution was purged with argon for 15 minutes, then
926 tetrakis(triphenylphosphine)palladium (16.18 mg 0.014 mmol) was added. The reaction was
927 stirred at 120 °C for 2 days. After the reaction mixture was cooled to room temperature and
928 extracted with chloroform and water. The organic layer was dried over anhydrous Na₂SO₄
929 and concentrated by evaporation. The solvent was evaporated and the crude product
930 recrystallized from hot acetone to yield the desired compound as a yellow solid (200 mg,
931 60%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.81 (d, *J* = 8.0 Hz, 2H), 8.41 (s, 2H), 8.38 (d, *J*
932 = 7.2 Hz, 2H), 8.14-8.10 (t, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 4H), 7.25-7.21 (m, 8H), 7.15
933 (d, *J* = 8.4 Hz, 4H), 6.92 (m, 8H), 4.40-4.37 (t, *J* = 6.8 Hz, 4H), 3.83 (s, 12H), 2.14 (m, 4H),

934 1.72 (m, 4H), 1.31 (m, 16H), 0.90-0.87 (t, $J = 6.4$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3 ,
935 ppm): δ 155.97, 148.27, 140.87, 139.72, 132.72, 131.54, 130.65, 126.91, 126.00, 125.96,
936 125.59, 124.38, 123.11, 122.19, 121.89, 120.40, 119.85, 119.73, 114.76, 55.51, 31.87, 30.80,
937 29.71, 29.61, 29.36, 26.35, 22.69, 14.16. ESI-MS: $\text{C}_{78}\text{H}_{78}\text{N}_2\text{O}_6^{+}$ m/z 1138.5857 (calculated
938 m/z 1138.5854).

939

940 **3. Substrates Preparation:** A patterned FTO-coated glass ($13 \Omega \text{ sq}^{-1}$, Aldrich) was etched by
941 Zn powder and 2 M HCl diluted in deionized water. Subsequently, the substrates were
942 cleaned with detergent diluted in deionized water, rinsed with deionized water, acetone and
943 ethanol, and dried with clean dry air. A compact blocking layer of TiO_2 (40 nm, c- TiO_2) was
944 deposited on the fluorine doped SnO_2 (FTO, Pilkington, TEC8) substrate by spray pyrolysis
945 using a 20 mM titanium di-isopropoxide bis(acetylacetonate) solution (Aldrich) at 500°C for
946 30 minutes.^{[1] [50] [50] [50] [50] [50] [50] [50] [50]} To deposit the mesoporous TiO_2 layer, Dyesol DSL
947 30 NR-D paste is dissolved in anhydrous isopropanol and kept for sonication for 1 hours.
948 Once the solution is homogeneous it is ready to deposit on FTO/Compact TiO_2 substrate by
949 spin coating at 3000 rpm for 30 second followed by annealing at 550°C estimated to give
950 ~ 400 nm thick layer.^[2]

951 **4. Fabrication of Devices:** The PSCs were prepared by one step spin coating of a
952 $\text{CH}_3\text{NH}_3\text{PbI}_3$ solution. The solution was prepared in DMF/DMSO = 6:4 by mixing $\text{CH}_3\text{NH}_3\text{I}$
953 (0.199 gm) and PbI_2 (0.600 gm). The solution was heated at 60°C for 3 hours for mixing.
954 Then the solution was spin coated using Chlorobenzene as antisolvent at rpm of 4000 for 30
955 s, and annealed for 30 minutes at 100°C on a hotplate. The absorber perovskite material with
956 electrode (FTO/Compact- TiO_2 /Mesoporous TiO_2) is ready after the above annealing
957 procedure. The electrodes with the absorber material were allowed to cool down to room
958 temperature. A solution containing 2-7,7-tetrakis(N,N-di-*p*-methoxyphenylamine)-9,9 17-

959 spirobifluorene (Spiro-OMe-TAD) in chlorobenzene and additives ($10 \mu\text{l ml}^{-1}$ *t*BP, $32 \mu\text{l ml}^{-1}$
960 Li-TFSI solution: 600 Mm in acetonitrile) was spin coated onto the perovskite film at 5000
961 rpm, for 30 second. Finally, 80 nm thick silver contacts were evaporated at 10^{-4} torr.

962 Similarly, other hole transporting materials, TPA-ANT-TPA and ACE-ANT-ACE were
963 dissolved in 60 mg in 1 ml chlorobenzene and kept for sonication for 30 minutes. The
964 solution was filtered (0.45 μm) before use and spin coated on top of perovskite absorber at
965 5000 rpm for 30 seconds.

966 **5. Power Conversion Efficiency and Incident Photon to Current Conversion Efficiency**

967 **(IPCE):** Masked devices (0.100 cm^2) were tested under a class AAA solar simulator
968 (Newport Oriel Sol3A) at AM1.5 and 100 mW cm^{-2} illumination conditions calibrated
969 against a KG5 filtered silicon reference cell (Newport Oriel 91150-KG5) using a Keithley
970 2400 source meter. Current–voltage sweeps were performed from forward-to-reverse bias at a
971 rate of 0.1 V s^{-1} .

972 **6. Stability Measurements: Humidity test :** Stability tests on optimized champion devices

973 without encapsulation for different hole transporting material were performed. The solar cells
974 were kept in relative humidity of $>580\%$ at room temperature in the dark. The simple setup is
975 shown in Figure S12.

976 **Continuous 1 sun illumination:** The non-encapsulated cells are placed in a cell holder with
977 a glass cover and are in direct contact with ambient atmosphere. For the stability the cells are
978 kept at 35°C temperature, under 1sun illumination using Solar simulator class A 1.5 M at full
979 sun under short circuit condition for 200 hours. IV curves were characterized by an electronic
980 system using 22 bits delta-sigma analogic to digital converter. For IV curves measurement, a
981 scan rate of 10 mV s^{-1} with a step of 5 mV was used, maintaining the temperature of the
982 holder to 35°C while the temperature of the cells was measured around 45°C . The system

983 comprises a set of I–V curves at different light intensities (dark current, 10 and 100 mW cm⁻²)
984 ²). Between each measurement the cells are maintained at the maximum power point using a
985 MPPT algorithm under 100 mW cm⁻². A reference Si-photodiode is placed in the holder to
986 verify the stability of the light. The same setup was used to do the aging of all three HTLs,
987 which are covered on perovskite material (Figure S15).

988 **7. Characterisation:**

989 **Scanning Electron Microscopy (SEM):** high magnification observations of the hole
990 transport materials and device cross sections were acquired using a Hitachi S-4800 field
991 emission gun-scanning electron microscope (5 kV, WD-8 mm)

992 **Photoluminescence Measurements:** Steady state emission measurements were done on the
993 Horiba Fluoromax-4 spectrofluorometer equipped with double-grating at the excitation
994 wavelength of 550 nm on the 3-layer assembly Glass/CH₃NH₃PbI₃/HTM with different
995 HTMs (TPA-ANT-TPA, ACE-ANT-ACE, and Spiro-OMeTAD). Front face illumination
996 with respect to the incident beam was used to minimize the inner filter effects.

997 **Contact Angle Measurements:** Contact angle measurements were performed using a
998 simple home built instrument. High resolution images of water droplets on the surface of hole
999 transport layers deposited on the perovskite sample were collected using Nikon DSL90
1000 camera, as shown in Figure S11.

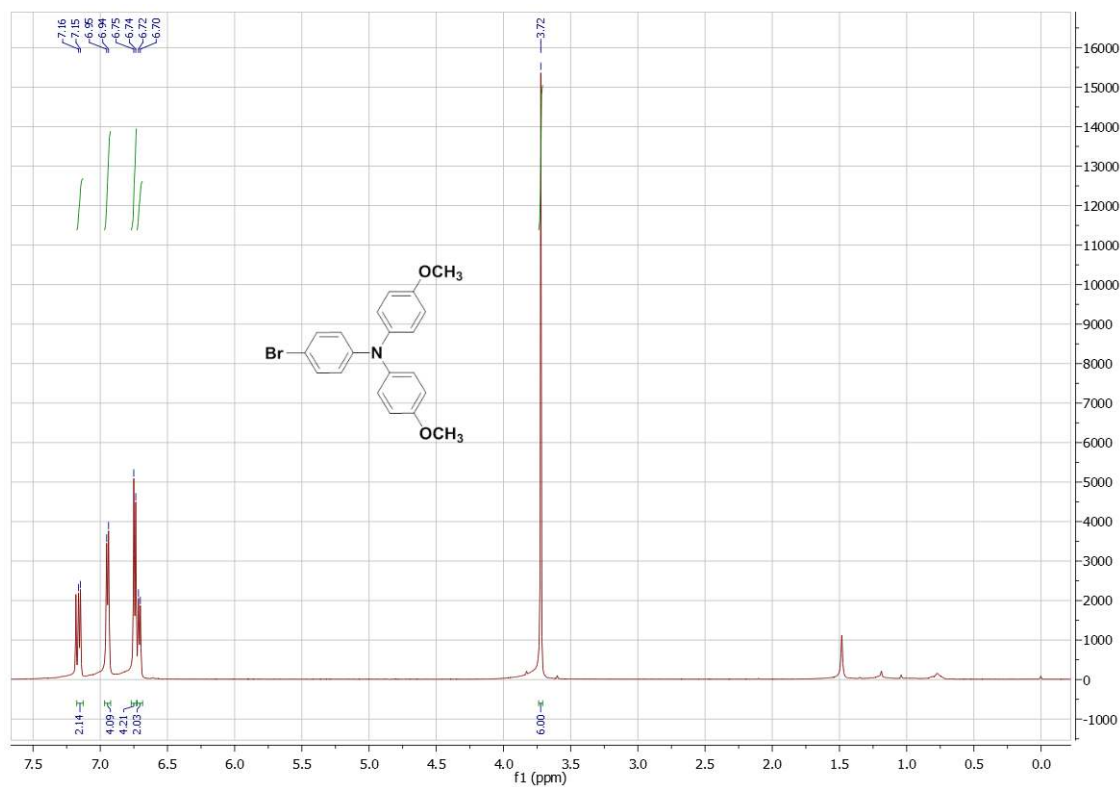
1001 **Time Correlated Single Photon Counting (TCSPC):** Time Correlated Single Photon
1002 Counting measurements were performed on Horiba Jobin Yvon Fluorolog system. Steady
1003 state photoluminescence measurements were done on perovskite and hole transport layers
1004 with < 200 ps pulses of 635 nm excitation from a picosecond diode laser (NanoLED source).
1005 The laser pulse excitation density was 2.3x10¹⁴ cm⁻³, Rep.rate:1MHz. Measurements were
1006 done in reverse mode at 1 MHz rep. rate. A cutoff filter (OG575) was used to block the stray

1007 excitation light. To increase the sensitivity of measurements, all wavelengths transmitted by
1008 cutoff filter were collected without the use of any monochromator.

1009 **Hole transport measurements : space charge limited current (SCLC) method**

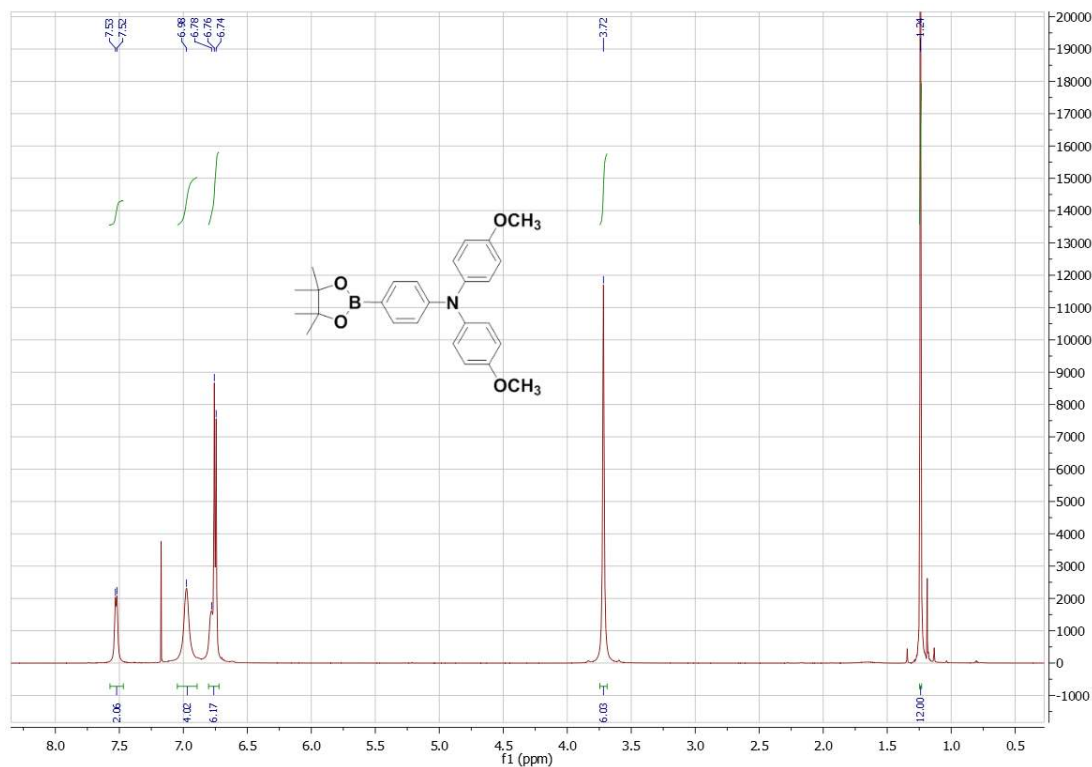
1010 PEDOT: PSS (Poly(3,4-ethylenedioxythiophene)–poly (styrene sulfonate)) was spin-coated
1011 onto indium tin oxide substrate (ITO) and dried at 130 °C for 20 minutes in vacuum. The
1012 purpose of PEDOT: PSS layer (40 nm) was to reduce the roughness of ITO as well as to
1013 improve the work function, achieving enhanced hole-only device properties. The HTMs were
1014 spincoated onto PEDOT: PSS from chloroform solution (30 mg/mL) in a nitrogen
1015 atmosphere. Finally, Au contacts (400 nm thick) were applied via thermal evaporation
1016 through a shadow mask in 2×10^{-6} Torr vacuum. The work function of Au and ITO are close
1017 to the HOMO energy level of the HTM as well as far below the LUMO energy level.
1018 Therefore, the electron injection barrier is higher than the corresponding hole injection
1019 barrier. As a result, the transport is dominated by holes. The J–V characteristics of the sample
1020 was measured with a Keithley 2420 source meter unit at room temperature. The device
1021 configuration and equations to extract mobility has been reported by us previously.^[3]

1022



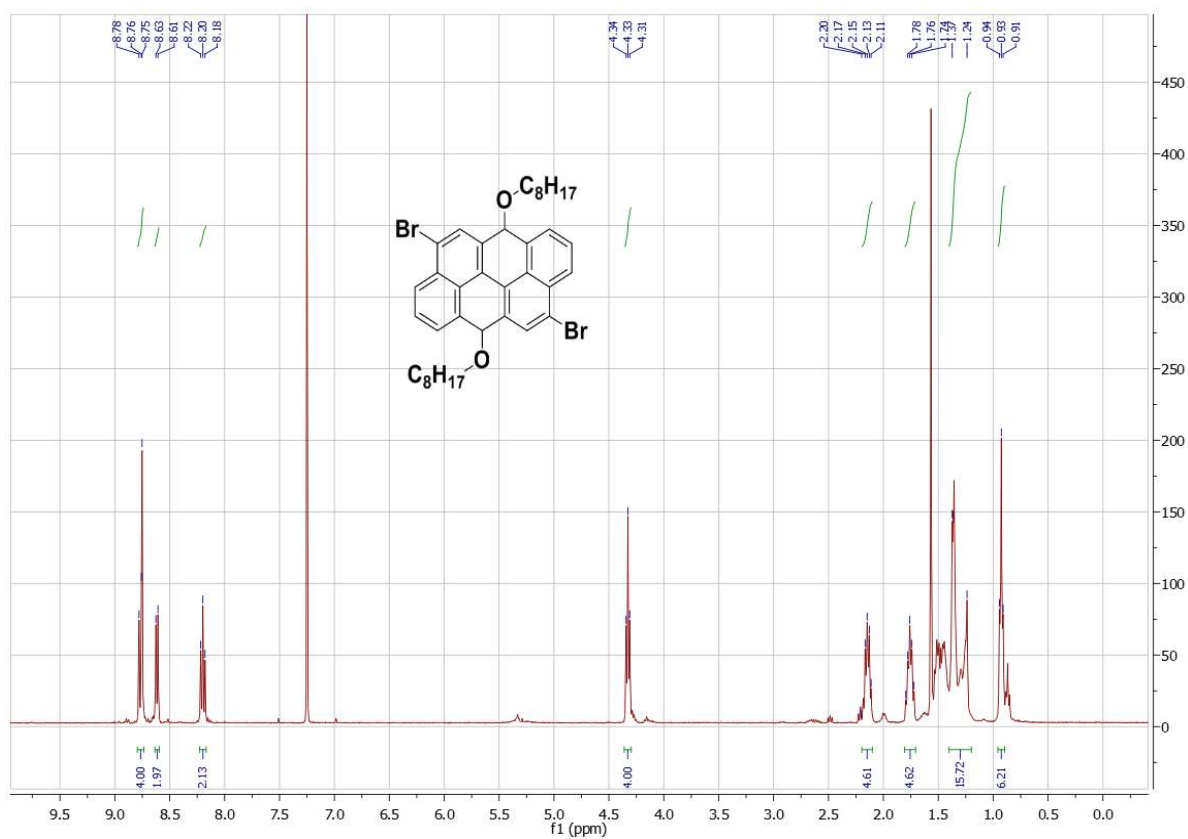
1023

1024 **Figure S1.** ^1H (600 MHz, CDCl_3) spectrum of 4-bromo-*N,N*-bis(4-methoxyphenyl)aniline
 1025 (2).



1026

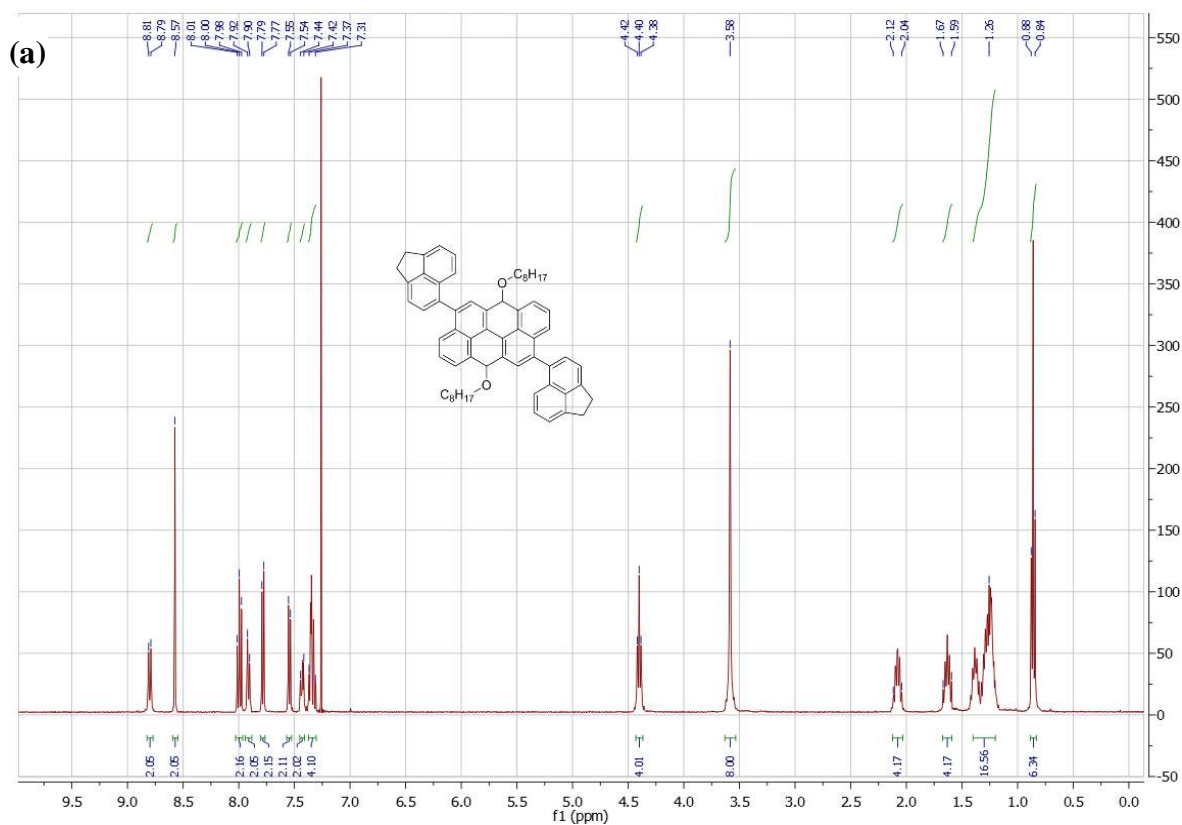
1027 **Figure S2.** ^1H (600 MHz, CDCl_3) spectrum of 4-methoxy-*N*-(4-methoxyphenyl)-*N*-(4-
 1028 (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (3).



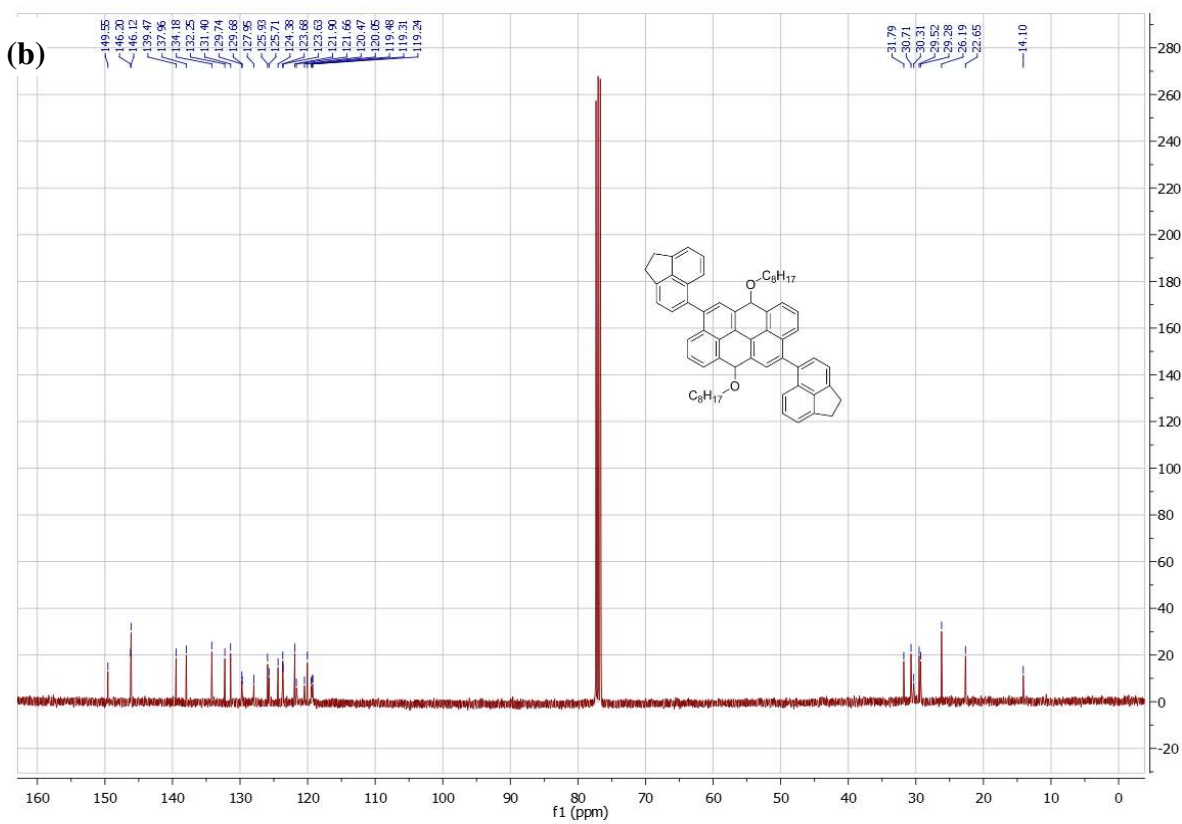
1029

1030 **Figure S3.** ^1H (400 MHz, CDCl_3) spectrum of 4,10-dibromo-6,12-bis(octyloxy)-6,12-
1031 dihydronaphtho[7,8,1,2,3-nopqr]tetraphene (5).

1032

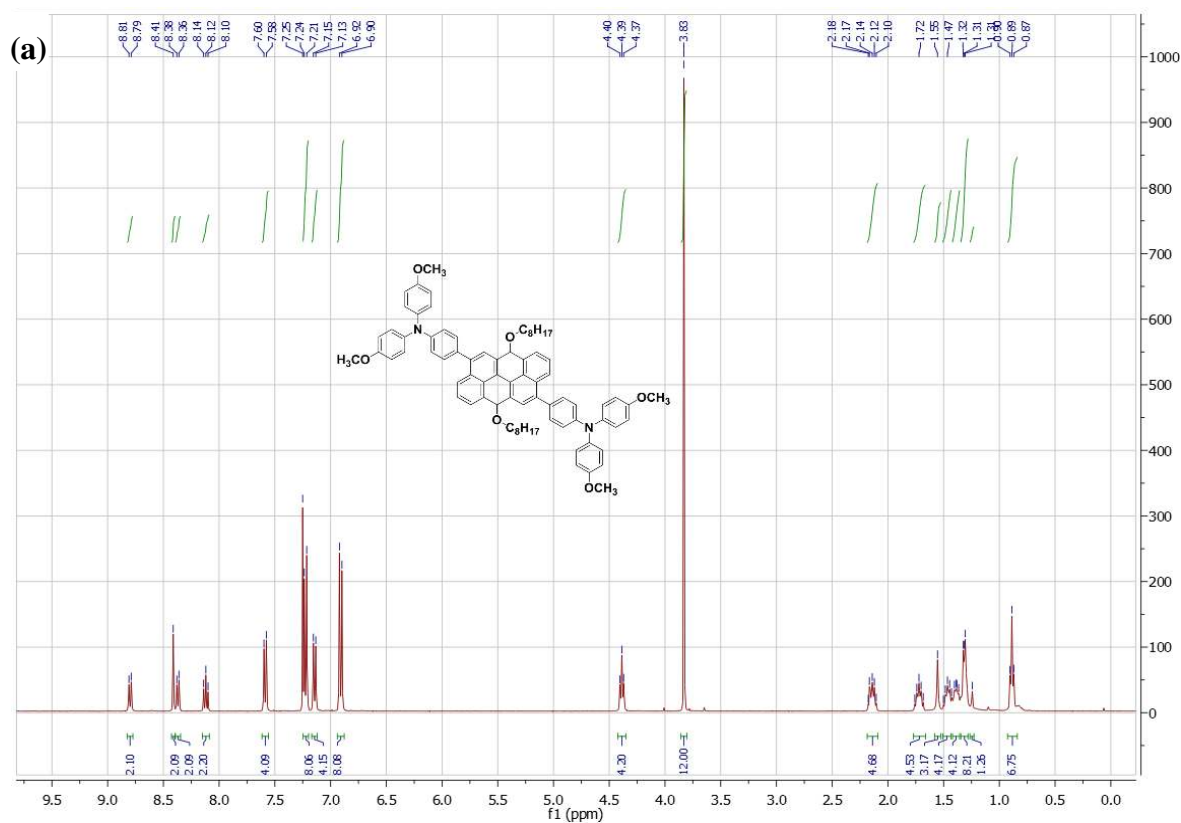


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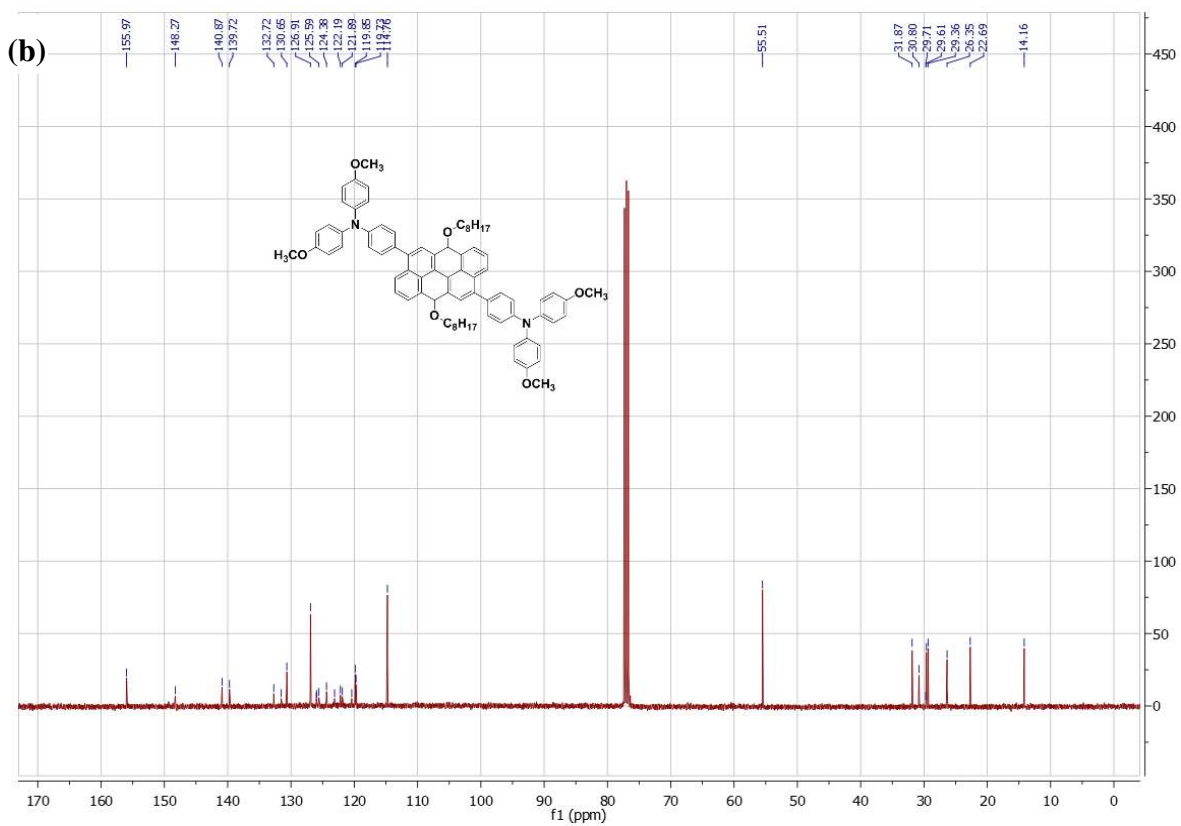


1034

1035 **Figure S4.** (a) ¹H (400 MHz, CDCl₃) spectrum and (b) ¹³C NMR (100 MHz, CDCl₃)
1036 spectrum of ACE-ANT-ACE.

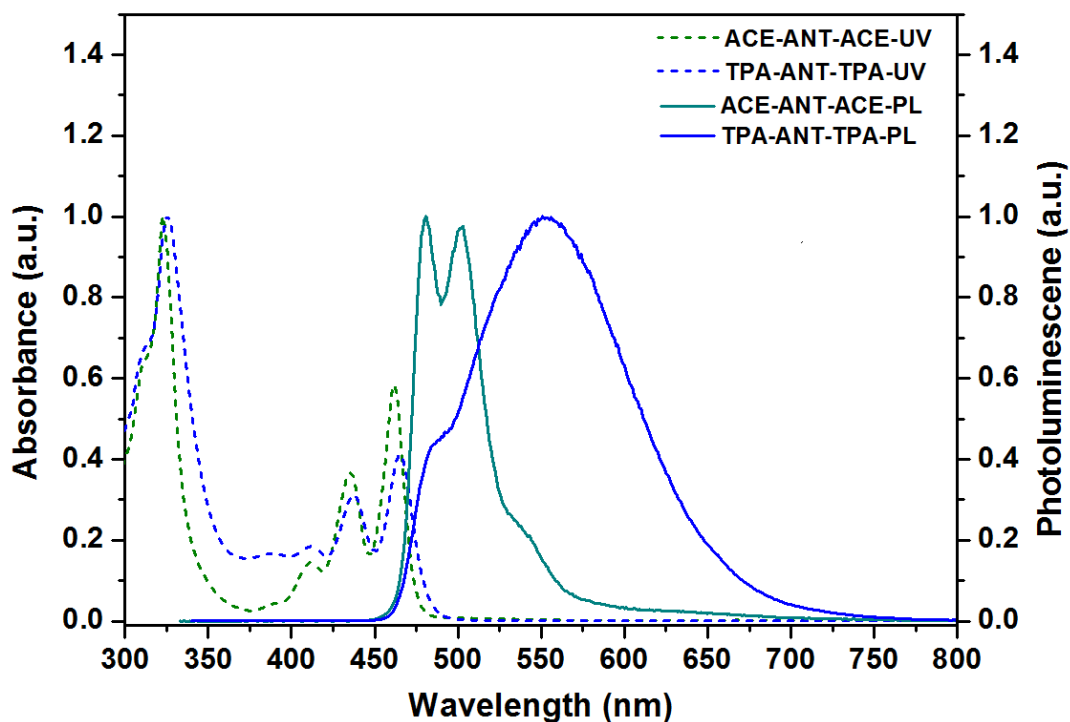


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1038

1039 **Figure S5.** (a) ¹H (400 MHz, CDCl₃) spectrum and (b) ¹³C NMR (100 MHz, CDCl₃)
 1040 spectrum of TPA-ANT-TPA.

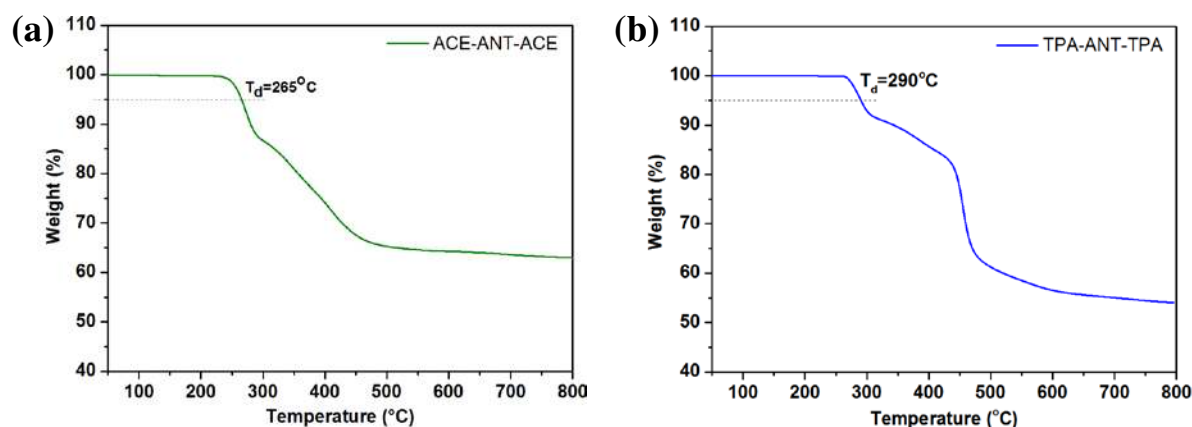


1041

1042 **Figure S6.** Normalised absorption and emission spectra of ACE-ANT-ACE and TPA-ANT-
 1043 TPA in CF solution.

1044

1045



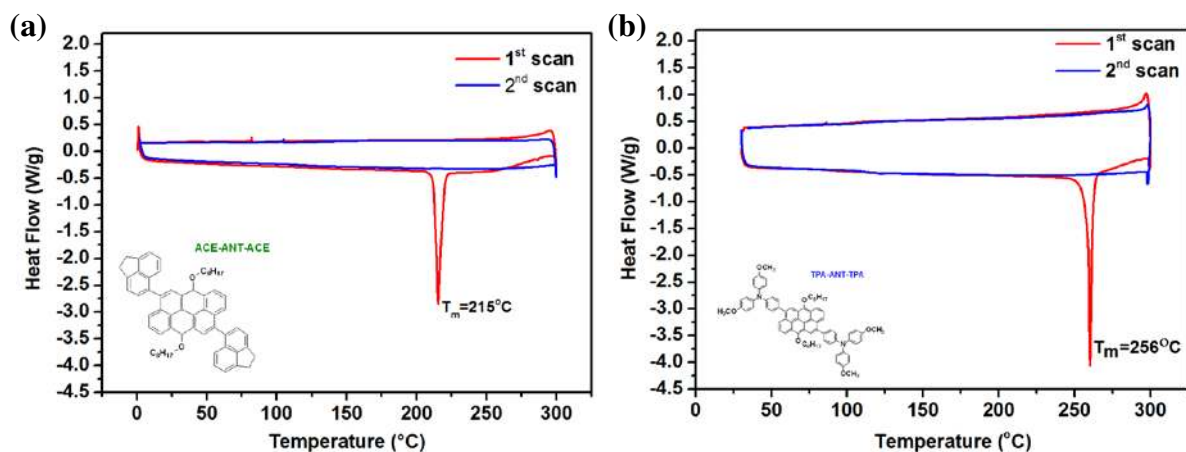
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1047 **Figure S7.** Thermogravimetric analysis (TGA) curve of (a) ACE-ANT-ACE and (b) TPA-
 1048 ANT-TPA.

1049

1050

1051



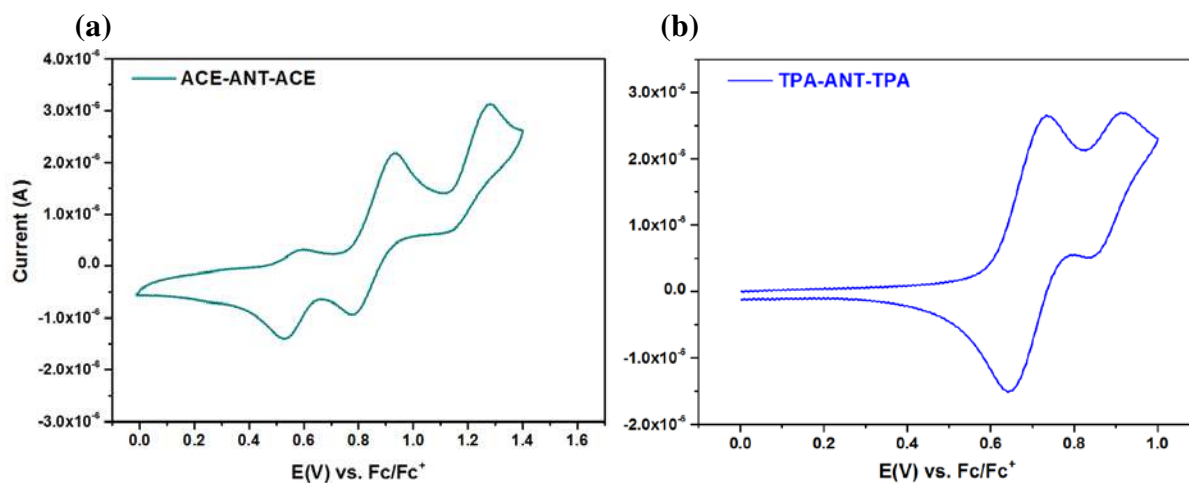
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1053

1054 **Figure S8.** Differential scanning calorimetry (DSC) of (a) ACE-ANT-ACE and (b) TPA-
 1055 ANT-TPA with scan rate of 10 °C/min under N₂ atmosphere.

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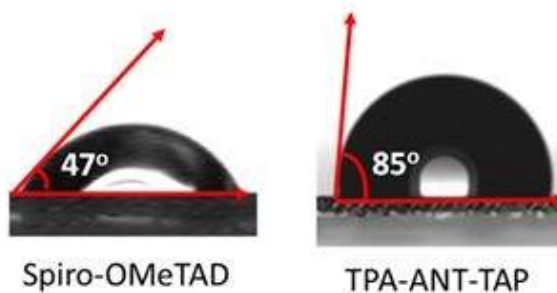


1058

1059 **Figure S9.** Cyclic voltammograms of (a) ACE-ANT-ACE and (b) TPA-ANT-TPA. The
 1060 oxidation was measured in DCM/0.1M Bu₄NPF₆ at a scan rate of 100 mV/s.

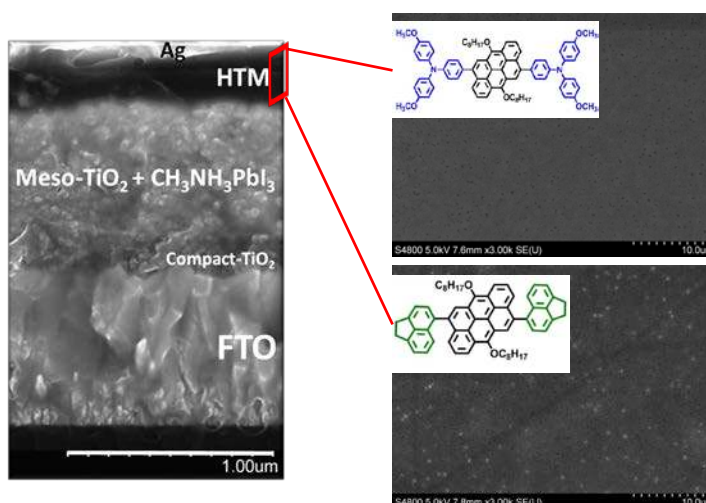
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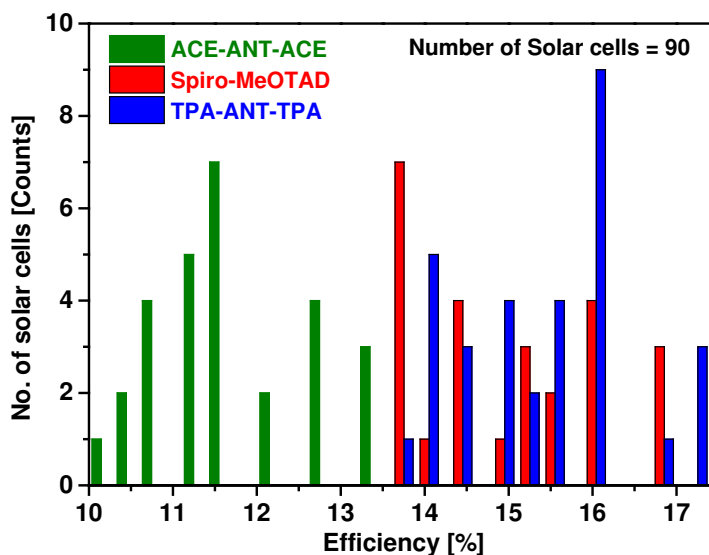


1063

1064 **Figure S10.** Contact angle measurements performed on Spiro-OMeTAD and TPA-ANT-TPA
 1065 surface deposited on $\text{CH}_3\text{NH}_3\text{PbI}_3$.



1066

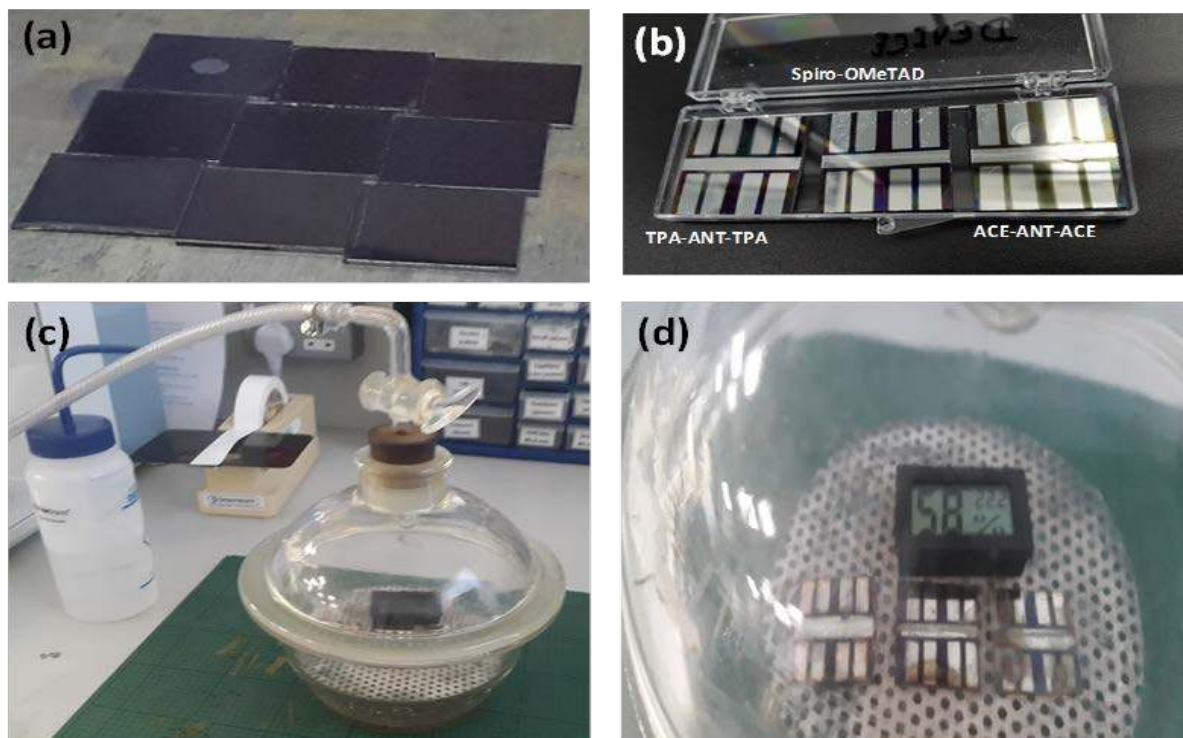


1067

1068 **Figure S11.** SEM cross sectional image of perovskite device with thin film morphology
 1069 comparison of both HTM (upper) and statistics of 90 PSC devices prepared using (i) ACE-
 1070 ANT-ACE (green bars); (ii) TPA-ANT-TPA (blue bars) and (iii) Spiro-OMeTAD (red bars)
 1071 as hole transporting materials (lower)

1072

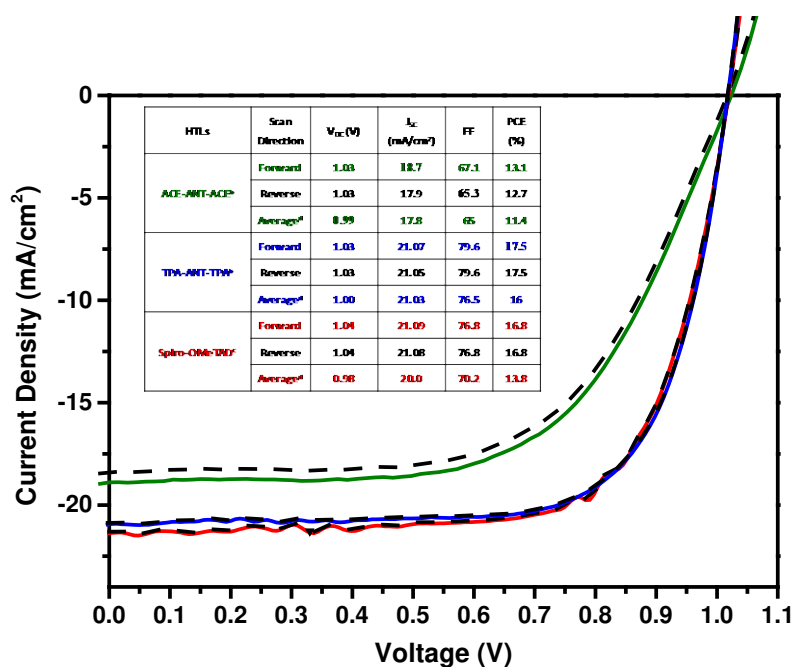
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1074

1075 **Figure S12.** (a) FTO/Compact-TiO₂/Mesoporous TiO₂/CH₃NH₃PbI₃ assemblies after
1076 annealing; (b) Perovskite devices with 3 different hole transport layers; (c) and (d) Simple
1077 stability measurement setup in a humidified desiccator for aging of PSCs in the dark and in
1078 >50% humidity.

1079

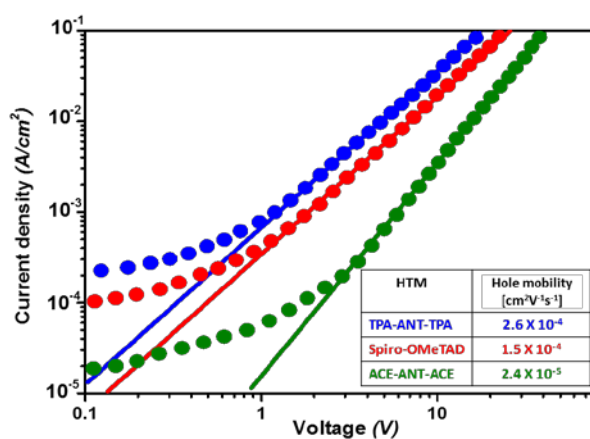


1080

1081 **Figure S13.** Hysteresis behaviour of champion solar cells made using TPA-ANT-TPA (blue
 1082 curve), ANT-ACE-ANT (green curve) and Spiro-OMeTAD (red curve) as HTLs. Scan from
 1083 0 V to V_{oc} at a constant scan speed of 0.1 V/s. Device performance parameters represented in
 1084 the insert table.

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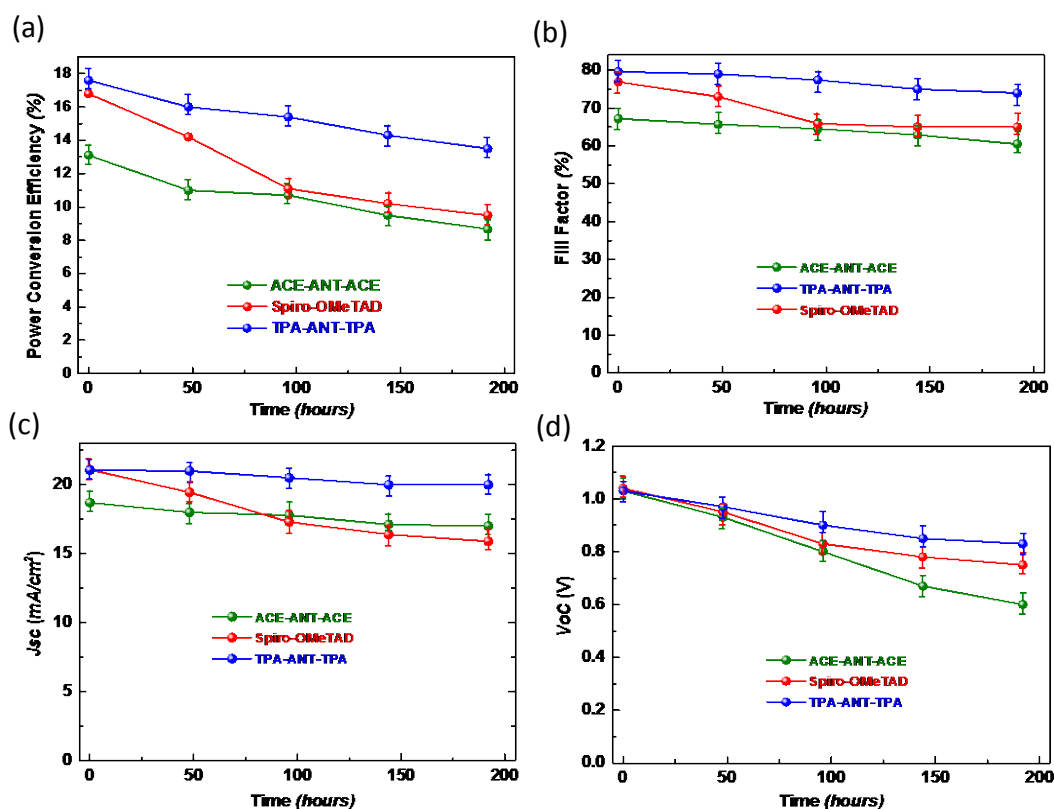
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1089 **Figure S14.** J-V data for space charge limited current (SCLC) method of hole-mobility
 1090 determination. The resulting mobilities of TPA-ANT-TPA (blue line), ACE-ANT-ACE
 1091 (green line) and Spiro-OMeTAD (red line) were 2.6×10^{-4} , 2.4×10^{-5} , 1.5×10^{-4} cm²V⁻¹s⁻¹
 1092 respectively.

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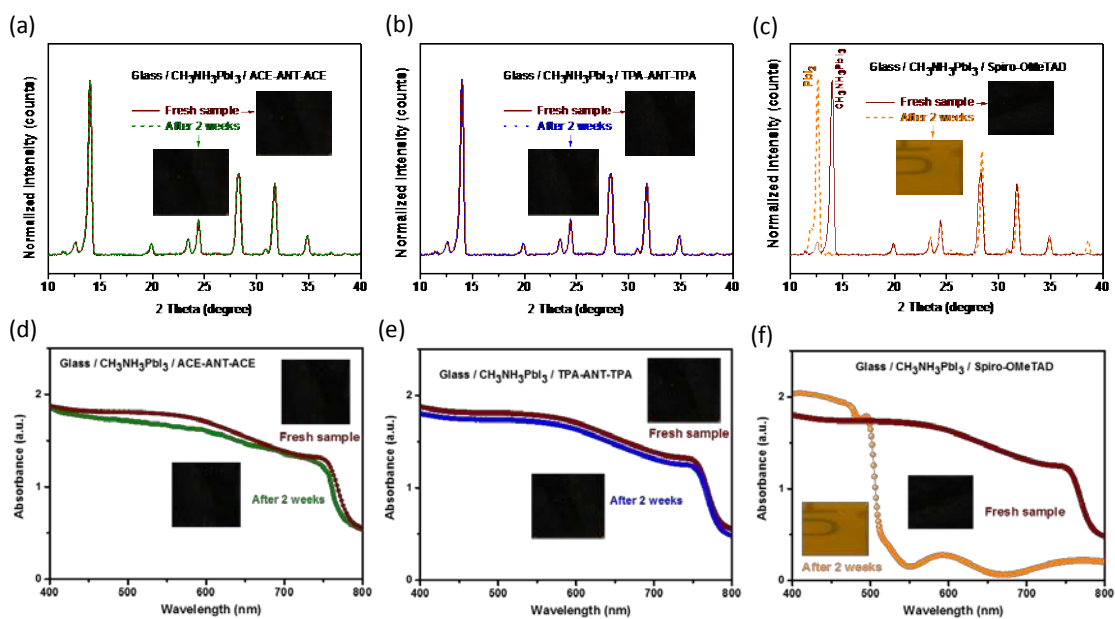
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1097 **Figure S15.** Stability measurements of champion devices under continuous 1 sun, AM 1.5 G
 1098 illuminations and at short circuit conditions. comparison of the aging of (a) PCE, (b) Fill
 1099 factor, (c) Current and (d) open circuit voltage of devices prepared using HTMs, TAP-ANT-
 1100 TPA (blue line), ACE-ANT-ACE (green line) and Spiro-OMeTAD (red line).

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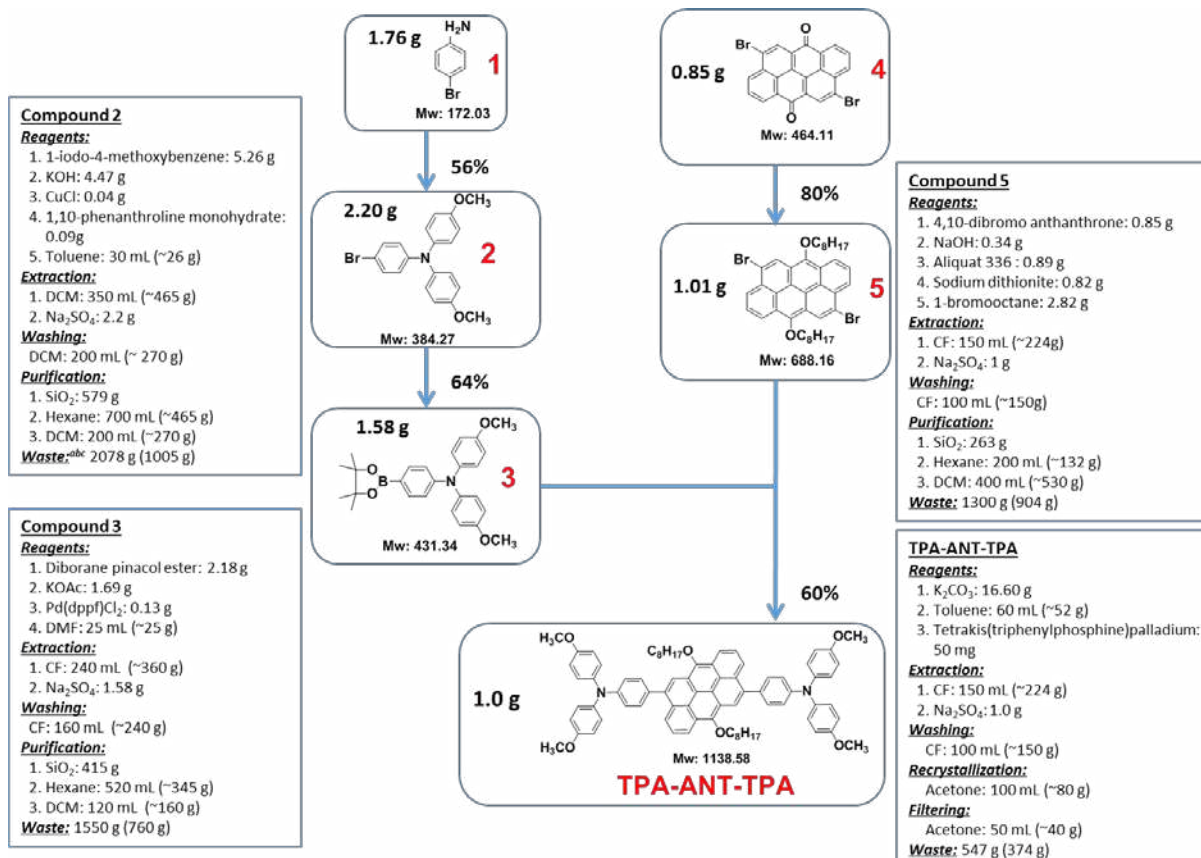
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1105 **Figure S16.** (a),(b),(c) XRD and (d), (e), (f) UV-visible degradation study of all three
 1106 respective HTMs deposited on glass / perovskite assembly. All samples kept under
 1107 continuous 1 sun illumination, in ambient air and at $\sim 35^{\circ}\text{C}$ (sample temperature measured
 1108 during illumination).

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1110



1111

1112 ^aTotal estimated weight of chemical waste, including solvents and precipitate, for the synthesis of 1 gram of
 1113 product.

1114 ^bTotal estimated weight of halogenated solvents (such as CF and DCM) is given in parentheses for the synthesis
 1115 of 1 gram of product.

1116 ^cThe density of solvents (Toluene, DMF, DCM, CF, Hexane, Acetone) are referenced from Sigma-Aldrich
 1117 supplier.

1118

1119

Figure S17. Flowchart describing the synthesis of 1g of TPA-ANT-TPA.

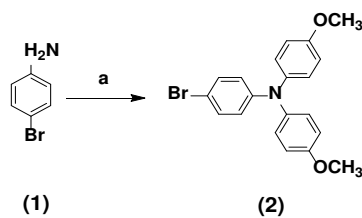
1120 **Table S1.** Density Functional Theory (DFT) calculations of ACE-ANT-ACE and TPA-ANT-
 1121 TPA.

Compound	ACE-ANT-ACE	TPA-ANT-TPA
HOMO, eV	-4.80	-4.67
LUMO, eV	-2.06	-2.04
gap, eV	2.75	2.63
VIS peak(s), nm	476	524, 467
osc strength	0.4569	0.228, 0.3535
composition	H->L 100%	H->L 85%, H-2->L 83%
PL peak(s), nm	542	633, 571, 512
osc strength	0.5789	0.0812, 0.1212, 0.5186
composition	H->L 100%	H->L 100%, H-1->L 86%, H-2->L 85%
dipole moment, D	0.16	0.17
dihedrals (counted from centre. TPA not counted)		
1	67, 71	51, 53
2	n/a	n/a

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1124 **Table S2.** Materials quantities and cost evaluation for the synthesis of 4-bromo-*N,N*-bis(4-
 1125 methoxyphenyl)aniline (**2**)



1126

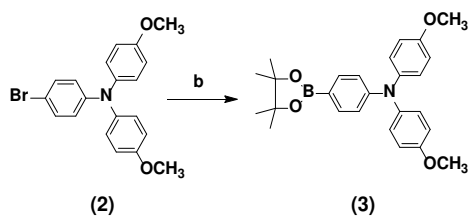
Chemical Name	Weight reagent [g]	Weight solvent [mL]	Weight of workup [g or mL]	Price of chemical [AUD/g or AUD/mL]	Material Cost [AUD/g product]	Cost per step [AUD/step]
4-bromoaniline	1.76			0.32	0.57	31.91
1-iodo-4-methoxybenzene	5.26			0.65	3.40	
KOH	4.47			0.02	0.10	
CuCl	0.04			3.27	0.14	
1,10-phenanthroline monohydrate	0.09			0.78	0.07	
anhydrous Toluene		30.00		0.07	2.15	
DCM		550.00		0.01	3.41	
Na ₂ SO ₄			2.2	0.02	0.05	
SiO ₂			579	0.03	16.30	
Hexane			700	0.01	4.49	
DCM			200	0.01	1.24	

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1130 **Table S3.** Materials quantities and cost evaluation for the synthesis of 4-methoxy-*N*-(4-
 1131 methoxyphenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (**3**)



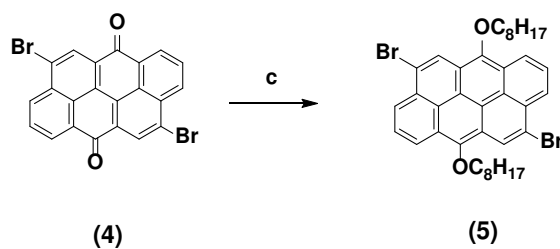
1132

Chemical Name	Weight reagent [g]	Weight solvent [mL]	Weight of workup [g or mL]	Price of chemical [AUD/g or AUD/mL]	Material Cost [AUD/g product]	Cost per step [AUD/step]
diborane pinacol ester	2.18			0.65	1.41	28.38
KOAc	1.69			0.22	0.37	
Pd(dppf)Cl ₂	0.13			32.40	4.07	
DMF		25.00		0.15	3.78	
CF		400.00		0.01	2.96	
Na ₂ SO ₄			1.58	0.02	0.03	
SiO ₂			415	0.03	11.69	
Hexane			520	0.01	3.34	
DCM			120	0.01	0.74	

1133

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1135 **Table S4.** Materials quantities and cost evaluation for the synthesis of 4,10-dibromo-6,12-
 1136 bis(octyloxy)anthanthrene (**5**)



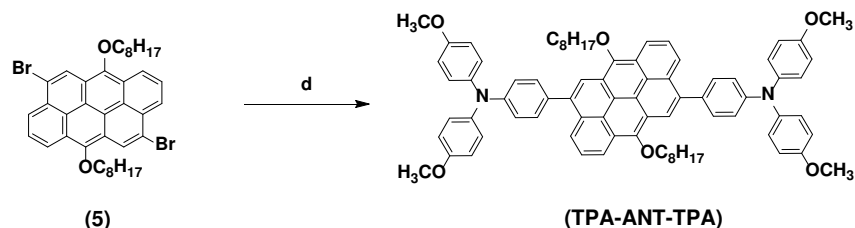
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Chemical Name	Weight reagent [g]	Weight solvent [mL]	Weight of workup [g or mL]	Price of chemical [AUD/g or AUD/mL]	Material Cost [AUD/g product]	Cost per step [AUD/step]
4,10-dibromo anthanthrone	0.85			0.21	0.18	14.51
NaOH	0.34			0.02	0.01	
Aliquat 336	0.89			0.50	0.51	
sodium dithionite	0.82			0.10	0.08	
1-bromooctane	2.82			0.25	0.70	
CF		250.00		0.01	1.85	
Na ₂ SO ₄			1	0.02	0.02	
SiO ₂			263	0.03	7.41	
Hexane			200	0.01	1.28	
DCM			400	0.01	2.48	

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1139

1140 **Table S5.** Materials quantities and cost evaluation for the synthesis of 4,4'-(6,12-
 1141 bis(octyloxy)-6,12-dihydronaphtho[7,8,1,2,3-*nopqr*]tetraphene-4,10-diyl)bis(*N,N*-bis(4-
 1142 methoxyphenyl)aniline) (**TPA-ANT-TPA**)



1143

Chemical Name	Weight reagent [g]	Weight solvent [mL]	Weight of workup [g or mL]	Price of chemical [AUD/g or AUD/mL]	Material Cost [AUD/g product]	Cost per step [AUD/step]
K ₂ CO ₃	16.60			0.17	2.84	11.09
tetrakis(triphenylphosphine)palladium	0.05			24.00	1.20	
Toluene		60.00		0.07	4.29	
CF		250.00		0.01	1.85	
Na ₂ SO ₄			1	0.02	0.02	
Acetone			150	0.01	0.89	

1144

1145 Total cost is ~86 AUD/g. It is equal to ~67 \$/g.

1146

1147 Reference:

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