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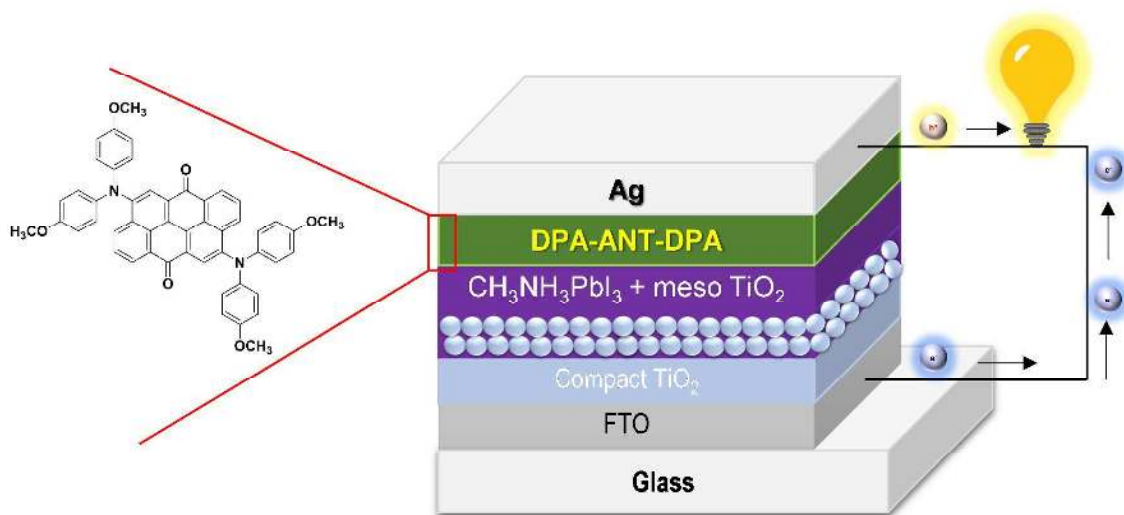
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1

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2 A new kind of a straightforward synthesized and dopant-free hole transporting material
3 designed based on cost efficient anthanthrone dye was implemented successfully in
4 mesoporous perovskite solar cells. This Donor-Acceptor-Donor HTM based device achieves
5 an overall efficiency of 11.5% under 1 sun condition and retains impressive performance
6 during 58% relative humidity than traditional costly SPIRO-OMeTAD.



7

8

9

1 **One Step Facile Synthesis of Novel Anthanthrone Dye Based,**
2 **Dopant-Free Hole Transporting Material for Efficient and Stable**
3 **Perovskite Solar Cells**

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22 information available should be included here]. See DOI: 10.1039/x0xx00000x

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25

26

Abstract:

27 Perovskite solar cell (PSCs) technology has made a tremendous impact in the solar cell
28 community due to their exceptional performance, as the power conversion efficiency (PCE)
29 surged to world record 22% within just last few years. Despite this high efficiency value, the
30 commercialization of PSCs for large area applications at affordable prices is still pending due
31 to the low stability of devices in ambient atmospheric conditions and a very high cost of the
32 hole transporting materials (HTM) used as the charge transporting layer in such devices. To
33 cope with these challenges, the use of cheap HTMs can play a dual role in terms of lowering
34 the overall cost of the perovskite technology as well as protecting the perovskite layer to
35 achieve higher stability. In order to achieve these goals, various new organic hole
36 transporting materials (HTMs) have been proposed. In this work we use a unique and novel
37 anthanthrone (ANT) dye as a conjugated core building block and an affordable moiety to
38 synthesize a new HTM. The commercially available dye was functionalized with an extended
39 diphenylamine (DPA) end capping group. The newly developed HTM, named DPA-ANT-
40 DPA, was one-step synthesized and used successfully in mesoporous perovskite solar cell
41 devices, achieving a PCE of 11.5% under 1 sun condition with impressive stability. The
42 obtained device efficiency is amongst the highest, as per D-A-D molecular design and low
43 band gap concern. Such kind of low cost HTM based on inexpensive starting precursor
44 anthanthrone dye paves the way for economical and large-scale production of stable
45 perovskite solar cells.

46

47 Introduction

48 The number of potentially economic solar cell technologies is increasing every year, in
49 search of the Holy Grail of maximum conversion efficiency and minimum production
50 cost. In the area of low cost solar cells, which includes as organic solar cells and dye
51 sensitized solar cells (DSSC), organic–inorganic halide perovskite solar cells (PSCs)
52 have gained much attention from the scientific community as scientists have been able
53 to quickly achieve record performances, unparalleled in organic and DSSC. After the
54 first breakthrough in 2013, the power conversion energy (PCE) for PSCs achieved a
55 value of 22.1%,^{1, 2} very close to that of traditional silicon solar cells. Nevertheless, a
56 few major obstacles are yet to be addressed before the commercial application of this
57 technology. The first challenge is to improve the stability of the solar cells. The second
58 one is how to enhance the performance in terms of PCE. The hole transporting layer
59 (HTL) plays an extremely important role in both stability and performance of the
60 perovskite solar cells. It improves the device stability by preventing the contact of the
61 active perovskite layer with the metal electrode, blocking moisture and oxygen
62 penetration.³ HTL is also instrumental in suppressing charge recombination allowing
63 to achieve a higher open-circuit photovoltage (V_{oc}), which leads to greater efficiency.⁴⁻
64 ⁶ One of the key components responsible for the high cost of perovskite solar cells, is
65 the hole transporting materials (HTL): in fact the most efficient and widely used HTL
66 is the molecule: 2, 2', 7, 7'-tetrakis-(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spiro-
67 bifluorene (Spiro-OMeTAD). Unfortunately, the very high cost of the Spiro-OMeTAD
68 molecule (400 USD per gram) limit the large scale production of perovskite solar
69 cells. In order to make this technology more economical viable, there is a great need to
70 find alternative HTLs with lower cost, simple synthesis, which would also be easily
71 scalable and which can achieve equal or higher performance than the Spiro-OMeTAD.
72 Currently, several economical organic hole transporting materials (HTMs) employed
73 in PSCs show respectable efficiency and higher stability compared to Spiro-
74 OMeTAD. Among them, small molecular HTMs are advantageous compared to
75 polymeric counterparts because of their high purity, defined molecular structure,
76 promising yield, and better batch-to-batch reproducibility.⁷⁻⁹

77 In the group of small molecules, abundant rational molecular design strategies,
78 including donor- π -donor (D- π -D), acceptor-donor-acceptor (A-D-A) and donor- π -
79 acceptor (D- π -A) moieties, have been intensively used for synthesis. Perovskite

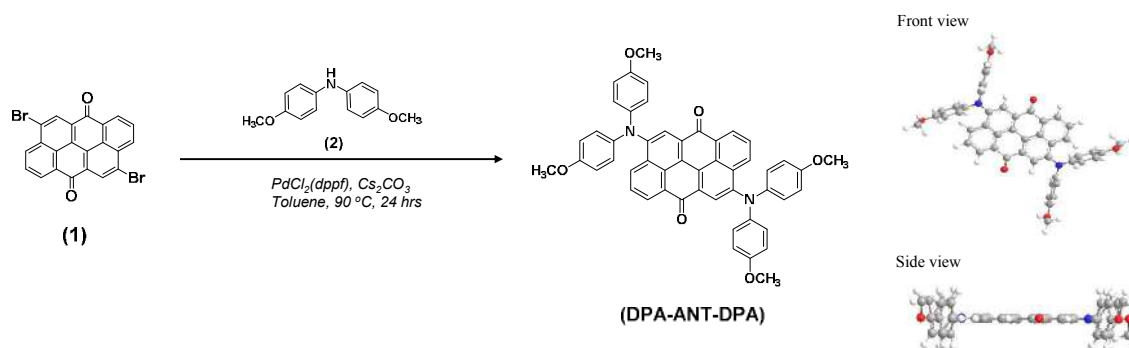
80 devices with higher performance and better stability have been fabricated successfully
81 using such HTMs. For example, (*E*)-4',4'''-(ethene-1,2-diyl)bis(*N,N*-bis(4-
82 methoxyphenyl)-[1'',1'''-biphenyl]-4-amine) (TPA-BPV-TPA) (16.42%),¹⁰ 2',7'-
83 bis(bis(4-methoxyphenyl)amino)spiro[cyclopenta[2,1-b:3,4-b']dithiophene-4,90-
84 fluorene] (FDT) (20.2%),¹¹ *N*-(4-(9*H*-carbazol-9-yl)phenyl)-7-(4-(bis(4-
85 methoxyphenyl)amino)phenyl)-*N*-(7-(4-(bis(4-methoxyphenyl)amino)phenyl)-9,9-
86 dioctyl-9*H*-fluoren-2-yl)-9,9-dioctyl-9*H*-fluoren-2-amine (CzPAF-TPA) (15.71%),¹²
87 4,4'-(5,5'-(7,7'-(5,5'-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-
88 diyl)bis(3-hexylthiophene-5,2-diyl))bis(benzo[c][1,2,5]thiadiazole-7,4-diyl))bis(4-
89 hexyl-thiophene-5,2-diyl))bis(1-(2-ethylhexyl)pyridin-1-ium) bis(trifluoromethane
90 sulfonimide) (M7-TFSI) (17.4%),¹³ and 2,2',2''-(((5,10,15-trihexyl-10,15-dihydro-5*H*-
91 diindolo[3,2-a:3',2'-c]carbazole-3,8,13-triyl)tris(3,3''-dihexyl-[2,2':5',2''-terthiophene]-
92 5'',5-diyl))tris(methanylylidene))trimalononitrile (KR321) (19.03%).¹⁴ These HTMs
93 can lead an efficiency in the range of 16-20%. However, there are few new HTMs
94 based on D-A-D structure reported until now, including 4,4'-(1,3,4-Oxadiazole-2,5-
95 diyl)bis(*N,N*-bis(4-methoxyphenyl)aniline) (H1),¹⁵ 4,4'-(5,6-
96 dimethoxybenzo[c][1,2,5]oxadiazole-4,7-diyl)bis(*N,N*-bis(4-methoxyphenyl)aniline)
97 (BTPA-3),⁶ (9,9'-((benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(4,1-
98 phenylene))bis(*N*³,*N*³,*N*⁶,*N*⁶-tetrakis(4-methoxyphenyl)-9*H*-carbazole-3,6-diamine)
99 (JY5)¹⁶ and (9,9'-((5-fluorobenzo[c][1,2,5]thiadiazole-4,7-diyl)bis(4,1-
100 phenylene))bis(*N*³,*N*³,*N*⁶,*N*⁶-tetrakis(4-methoxyphenyl)-9*H*-carbazole-3,6-diamine)
101 (JY6).¹⁷ The D-A-D structure has been designed by introducing an electron-deficient
102 unit as the core with two strong electron-rich end-capping groups in order to obtain a
103 deeper highest-occupied molecular orbital (HOMO) level, thereby improving the V_{oc} .¹⁸
104 This strategy is expected to result in a higher PCE.^{5, 10, 19-21} In addition, compared to
105 the D- π -D type molecules, the intramolecular charge transfer (ICT) from the electron-
106 donating unit to the electron-withdrawing unit can be boosted via the D-A-D one.⁶

107 In this work, we report one-step facile synthesis of a novel dopant-free D-A-D
108 HTM based on a low cost anthanthrone (ANT) dye as the core and diphenylamine
109 (DPA) as an efficient end-capping conjugated building block. The compound, namely
110 4,10-bis(bis(4-methoxyphenyl)amino)naphtho[7,8,1,2,3-*nopqr*]tetraphene-6,12-dione
111 (DPA-ANT-DPA) is synthesized using standard Buchwald coupling between the
112 halogenated derivative and the amine group; the synthesis details are shown in Scheme

113 1. In this D-A-D type structure, 4,10-dibromoanthanthrone, named as VAT Orange 3
 114 (Compound 1 in Scheme 1) low cost starting precursor was introduced as a strong
 115 electron-withdrawing ketone unit in the core due to its π -conjugated nature and a large
 116 conjugated planar structure.²²⁻²⁴ This is profitable for obtaining a low-lying HOMO
 117 energy level,²⁵ improving intermolecular interactions such as π - π interactions²² and
 118 achieving the high performance of organic optoelectronic devices.²⁵

119 Results and Discussion

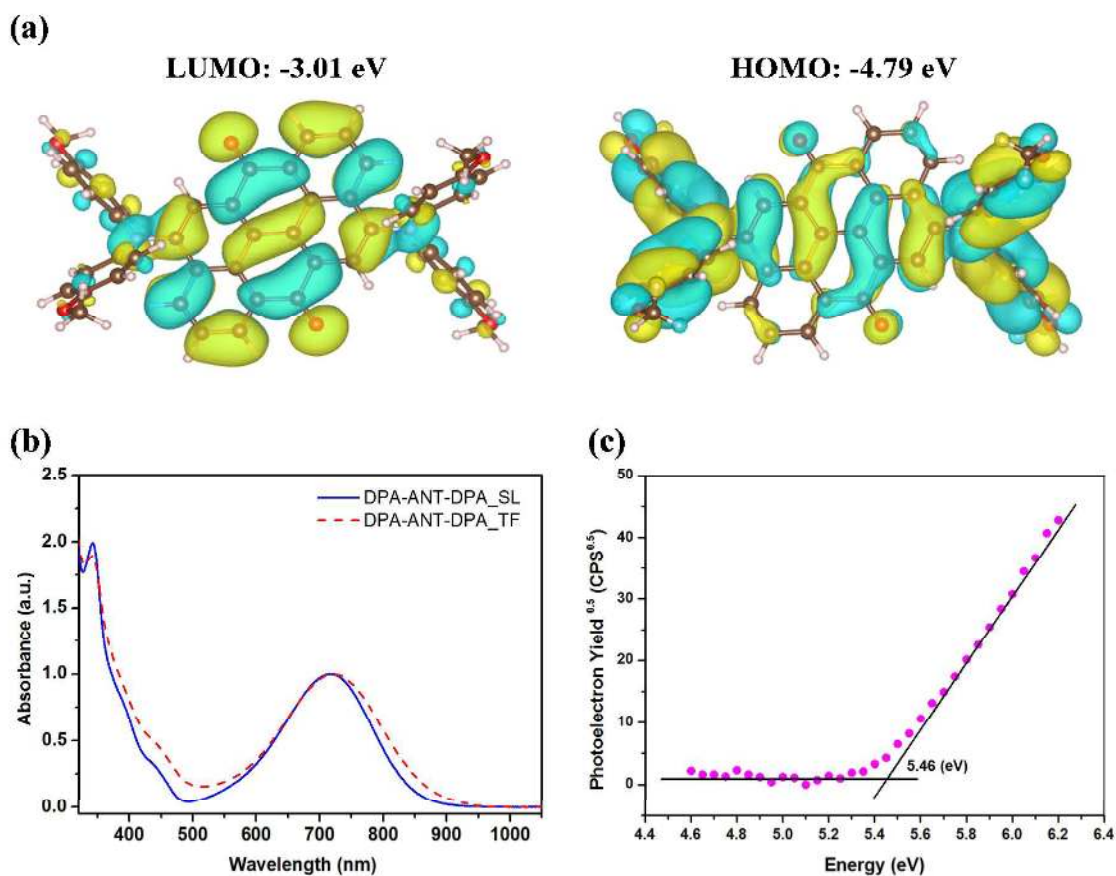
120 The synthesis of DPA-ANT-DPA is straightforward and follows Buchwald-Hartwig coupling
 121 reaction. Compound 1 and 2 were mixed with [1,1'-Bis(diphenylphosphino)ferrocene]
 122 dichloropalladium(II) [PdCl₂(dppf)] catalyst at 90 °C for 24 h in anhydrous toluene solvent as
 123 the earlier attempt.²⁶ After purification by column chromatography, the yield of the reaction
 124 was found to be of 80%, leading to potential large-scale application in the future. The purity
 125 was confirmed by proton and carbon NMR spectroscopy, the results of which are shown in
 126 Fig. S1 (Supporting Information, ESI†). The synthetic procedure is detailed in the ESI†. The
 127 material exhibited good solubility in most common organic solvents such as chloroform,
 128 dichloromethane and chlorobenzene.



130 Scheme 1. A single-step synthetic route for DPA-ANT-DPA and the geometrical
 131 configuration (front and side view).

132 To gain insight into the electronic structure of this material, density functional theory
 133 (DFT) calculations were performed at the B3LYP level of theory using the basis set 6-
 134 31g+(d,p).²⁷⁻²⁹ As shown in Fig. 1a, while the electron density of the HOMO is fully
 135 delocalized over the entire molecules, the lowest unoccupied molecular orbital (LUMO) is
 136 primarily distributed over the π -conjugated system through the ANT core. According to DFT
 137 calculations, the HOMO and LUMO value are assessed to be -4.79 eV and -3.01 eV
 138 respectively. As a result, the band gap is found to be of 1.78 eV. In addition, the optical

139 absorption maxima were at 892 nm, resulting to the optical band gap of 1.39 eV. The DFT-
140 calculated data differs slightly from the experimental values due to the gaseous state
141 assumptions, but the result is still in a good agreement (Table 1).



142

143 Fig. 1 (a) The calculated isosurfaces of electron density of HOMO and LUMO, (b) UV-Vis
144 absorption spectra in CF solutions (solid line) and films (dash line), (c) Photoelectron
145 spectroscopy in air (PESA) spectra of DPA-ANT-DPA.

146 The absorption of DPA-ANT-DPA in chloroform solution and in thin film on glass were
147 measured and shown in Fig. 1b. All the data is listed in Table 1. In the low wavelength
148 region, DPA-ANT-DPA reveals absorption maxima at 344 nm for the solution and 343 nm
149 for thin film respectively. Meanwhile, it shows broaden absorption in the visible range with
150 maxima peak at 717 nm in solution and 724 nm in solid-state film respectively. The
151 electronic absorption in the near-infrared (NIR) region is attributed with the ICT band due to
152 the introduction of strong electron donating DPA end capping units and strong electron
153 accepting ANT core.^{30, 31} The slight red shift of the absorption band in films compared with
154 solution indicates very weak intermolecular interactions in the solid state. Such weak solid-

155 state interaction is also arising due to the presence of two distorted phenylene units. Such
 156 propeller structure could be beneficial to form a better interface with three dimensional
 157 photoactive perovskite layers in the devices, which can promote charge transport effectively.
 158 The optical band gap of DPA-ANT-DPA compound, calculated using the solid-state
 159 absorption onset values at 869 nm, is 1.43 eV. This low band gap implies a strong
 160 intramolecular D-A interaction in relative to the amine and quinone units as mentioned
 161 previously.²⁶ To the best of authors knowledge, it is the lowest band gap HTM for PSCs
 162 compared to other low band gap HTMs (1.47 – 1.50 eV) reported previously.^{30, 32, 33}

163 Table 1 Thermal, optical and electrochemical properties of DPA-ANT-DPA.

HTMs	λ_{\max} (nm)		λ_{onset} (nm)	E_g^{opt} (eV)	$E_{\text{HOMO}}^{\text{d)}$ (eV)	$E_{\text{LUMO}}^{\text{d)}$ (eV)	$E_{\text{HOMO}}^{\text{e)}$ (eV)	T_d (°C)	T_g (°C)	T_c (°C)	T_m (°C)	$\mu^{\text{d)}$ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)
	Solution ^{a)}	Film ^{b)}										
DPA-ANT-DPA	292	294	869	1.43	-5.46	-4.03	-5.2	377	148	244	294	1×10^{-4}

164 ^{a)}Absorption spectrum was measured in chloroform (CF) solution; ^{b)}Film was prepared by spin-coating an CF
 165 solution containing the sample onto glass substrate at a spin speed of 1000 rpm at room temperature; ^{c)}Optical
 166 bandgap was calculated from the formula of $1240/\lambda_{\text{onset}}$; ^{d)}The oxidation potential was also measured by
 167 photoelectron spectroscopy in air (PESA); $E_{\text{LUMO}}^{\text{PESA}} = E_{\text{HOMO}}^{\text{PESA}} + E_g^{\text{opt}}$; ^{e)}Oxidation potential of the material
 168 was characterized in dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate at scan speed 100
 169 mV/s, potentials vs. Fc/Fc⁺; ^{f)}hole mobility was measured by space charge limited current (SCLC) method.

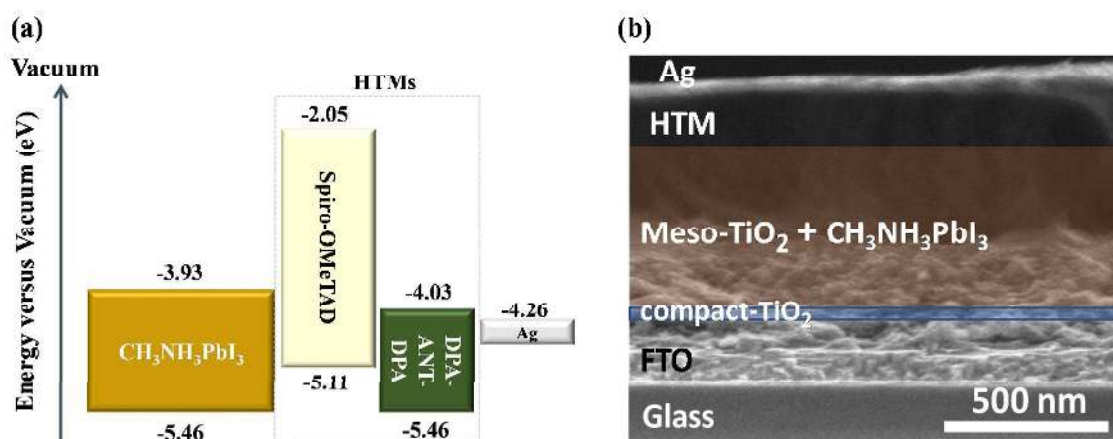
170

171 In this work we determine the HOMO value of DPA-ANT-DPA experimentally using two
 172 methods such as photoelectron spectroscopy in air (PESA) (Fig. 1c) and cyclic voltammetry
 173 (CV) respectively (Fig. S2, ESI†). All these parameters are shown in Table 1. The HOMO
 174 value of DPA-ANT-DPA is estimated to be -5.46 eV, being similar to the valence band
 175 maximum (VBM) of the perovskite layer. The reduced energy gap between the HTL and the
 176 active layer guarantees a high valued for of V_{oc} and also keeps efficient hole extraction.
 177 Meanwhile, the respective LUMO level of this compound was estimated, based on E_{LUMO}
 178 $= E_{\text{HOMO}} + E_g^{\text{opt}}$, to be found of -4.03 eV. This low-lying LUMO energy level is below the
 179 conduction band minimum (CBM) of the perovskite, which allows part of undesired electron
 180 transport to occur and then cause to the low efficiency. While the LUMO value obtained by
 181 CV data is in consistent with the calculation one from PESA data, the HOMO values from
 182 both techniques are slightly different. This may be caused by the energy values of sample in
 183 CV technique which was performed in dichloromethane solution with tetrabutylammonium

184 hexafluorophosphate. Whereas, in PESA, the sample is deposited in thin film and then
 185 exposed to ultraviolet light with certain intensity in air. The HOMO energy value data from
 186 the PESA technique is more relevant since the actual devices in solid state and the PESA
 187 measurement also performed in thin film form.

188 The thermal properties of DPA-ANT-DPA were determined by using thermogravimetric
 189 analysis (TGA) and differential scanning calorimetry (DSC), which are shown in Fig. S3
 190 (ESI†) and summarized in Table 1. According to the TGA curve, this compound has an
 191 extremely good thermal stability, and is stable up to 377 °C. The thermal transitions were
 192 investigated by DSC with two scan cycles. The melting temperature (T_m) (294 °C) is
 193 observed during the first and second heating scans whereas the glass transition (T_g) (148 °C)
 194 is only noticed during the second heating scan. Furthermore, the crystallization temperature
 195 (T_c) is witnessed at 244 °C during the second heating scan. It turns out that the material has
 196 some crystalline phases and this might be arising from donor-acceptor interaction and fused
 197 core nature of ANT conjugated building block.³⁴ This is in good agreement with the
 198 observation of the needle-like crystals' formation during drying process of DPA-ANT-DPA
 199 solution in the glass tube (Fig. S4, ESI†). Meanwhile, there is no crystallization peaks
 200 perceived during the cooling step. Furthermore, X-ray diffraction (XRD) was performed with
 201 the result shown in Fig. S5 (ESI†). The primary intense peak at $2\theta = 9.34^\circ$ was observed,
 202 leading to a d-spacing (the lamellar repeating distance between the compound chains) of 1.1
 203 nm calculated by using Bragg equation.

204



205

206 Fig. 2 (a) Energy level diagrams, (b) Cross-sectional scanning electron microscopy image of
 207 PSC of DPA-ANT-DPA.

208

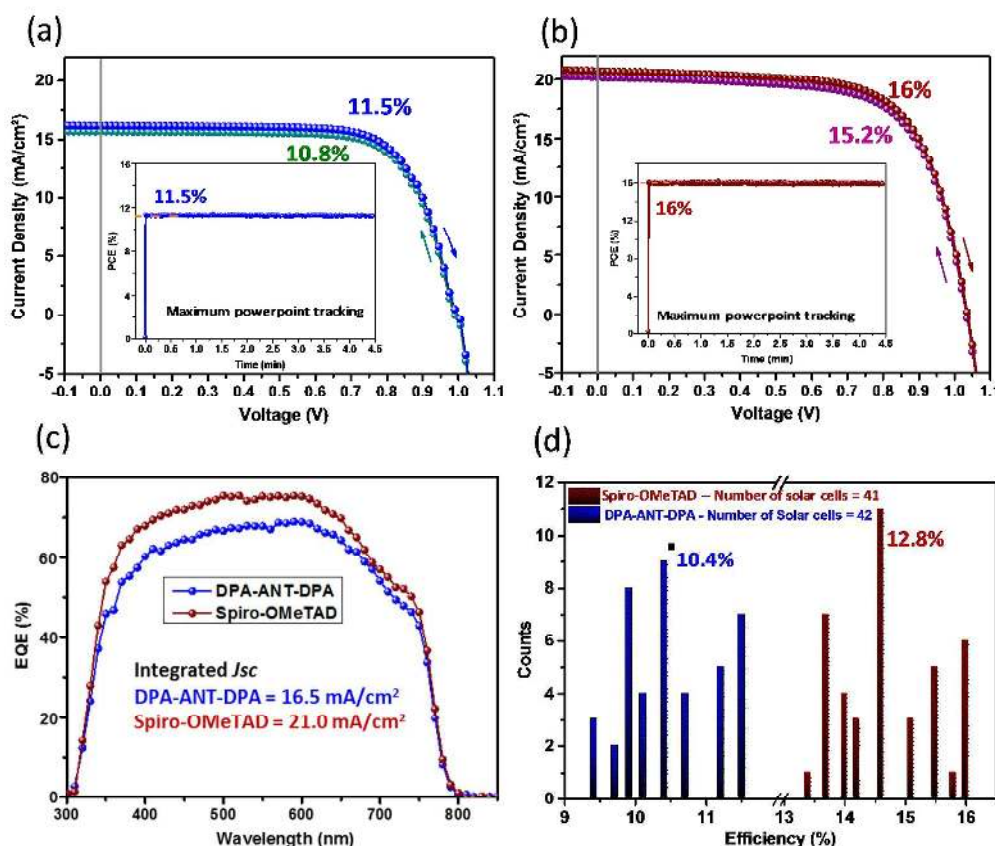
209 In order to evaluate the effect of such crystalline phases on the charge carrier transport, we
210 used DPA-ANT-DPA material as an active layer in organic field-effect transistor (OFET)
211 devices using bottom gate top contact devices. The OFET device fabrication is described in
212 ESI†. Its data is shown in Table 1 and illustrated in Fig. S6 (ESI†). The hole mobility of
213 DPA-ANT-DPA was calculated using output and transfer characteristics. The mobility of
214 DPA-ANT-DPA was calculated to be $2.6 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is higher than that of Spiro-
215 OMeTAD ($\mu = 1.69 \times 10^{-6} - 2.3 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)^{35, 36} measured with a similar experimental
216 technique (using OFET devices). Furthermore, we measured and compared the hole mobility
217 of our newly developed DPA-ANT-DPA and of the traditional Spiro-OMeTAD hole
218 transport layers (Fig. S7, ESI†) using hole only space charge limited current method using
219 identical conditions. The hole mobility for DPA-ANT-DPA is $1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ whereas for
220 Spiro-OMeTAD it is 1.6×10^{-4} respectively measured by SCLC method. As per solar cell
221 devices concern, SCLC measurement is most relevant techniques which give correct charge
222 carrier mobility since the charge transport occurs vertically. The details of sample preparation
223 and SCLC measurement can be found in supporting information (ESI†). Both OFET and
224 SCLC techniques confirms the better charge carrier mobility of our newly developed hole
225 transport layers DPA-ANT-DPA .

226 After the optical, thermal and electrochemical characterization of the new small molecule,
227 the DPA-ANT-DPA layer was fabricated within the conventional perovskite devices
228 processing as HTM, with the main aim to study the effect of the hole transport layers on the
229 device performance. PSC devices with the FTO/compact-TiO₂/Mesoporous-
230 TiO₂/CH₃NH₃PbI₃/HTL/Ag device architecture were fabricated as per previously reported
231 procedure.³⁷ The configuration of mesoscopic heterojunction perovskite solar cells was
232 characterized by the cross-sectional scanning electron microscopy (SEM) and shown in Fig.
233 2b. A dense compact-TiO₂ blocking layer (~30 to 40 nm) is first deposited on the FTO
234 substrate by spray pyrolysis, while a mesoporous n-type mp-TiO₂ layer is formed by spin-
235 coating of diluted TiO₂ paste. The CH₃NH₃PbI₃ absorber layer was then applied on
236 mesoporous TiO₂ by solvent engineering reported by Seok's group.³⁷

237 The perovskite solution was prepared as per standard procedure and details can be found
238 in the supporting information (ESI†). Around 120 nm thick HTLs were applied to the top
239 CH₃NH₃PbI₃ layer by spin coating. Finally, silver as a counter electrode was deposited by
240 thermal evaporation. The thickness of mesoporous TiO₂ and perovskite is ~550 nm, whereas

241 the capping layer of perovskite is estimated to be ~ 100 nm. Bigger crystals of TiO_2 in the
242 capping layer assist in saturated light absorption, which enhances the external quantum
243 efficiency (EQE) in the red-light range.

244 For a valid comparison of performance in terms of PCE and stability, we prepared new
245 dopant-free HTMs based devices and standard devices with dopant using conventional Spiro-
246 OMeTAD (with additional additives, including *t*BP and LiTFSI) as the HTM. The optimized
247 champion device efficiency for DPA-ANT-DPA and Spiro-OMeTAD HTMs and
248 corresponding photovoltaic performance parameters are shown in Fig. 3 and Table 2.



249
250 Fig. 3 Current–voltage scans for the best performing perovskite devices made using (a) DPA-
251 ANT-DPA as hole transport layer and (b) Spiro-OMeTAD as hole transport layer showing
252 PCEs 11.3% and 14.3% respectively. The full hysteresis loop is reported in Table 2. The inset
253 shows the power output under maximum power point tracking for 270 s, starting from
254 forward bias and resulting in a stabilized power output of 11.5% and 16% for DPA-ANT-
255 DPA and Spiro-OMeTAD hole transport based devices respectively. The constant scan rate
256 for all scans was 10 mV s^{-1} , (c) External quantum efficiency of perovskite devices prepared
257 using DPA-ANT-DPA and Spiro-OMeTAD hole transport materials. The integrated short

258 circuit current density of 16.5 mA/cm^2 and 21 mA/cm^2 follows the JV scans from the solar
259 simulator, (d) Statistics, and the average device efficiency of a total of 83 solar cells prepared
260 using DPA-ANT-DPA and Spiro-OMeTAD as hole transport materials.

261

262 The non-doped DPA-ANT-DPA HTM based PSC devices (Fig. 3a) shows the highest
263 champion device efficiency of 11.5% ($J_{sc} = 16.2 \text{ mA cm}^{-2}$, $V_{oc} = 1.0 \text{ V}$ and $FF = 71\%$).
264 Whereas the doped Spiro-OMeTAD-based device performance (Fig. 3b) approaches a PCE
265 of 16 % with J_{sc} of 21 mA cm^{-2} , $V_{oc} = 1.03 \text{ V}$ and $FF = 74\%$. The hysteresis behaviour of
266 champion devices and statistics of the total of 42 devices prepared using DPA-ANT-DPA and
267 41 devices using Spiro-OMeTAD as hole transporting layers is shown in Table 2 and Fig.
268 3(a),(b) respectively.

269

Table 2 Solar cell device performance with DPA-ANT-DPA HTMs.

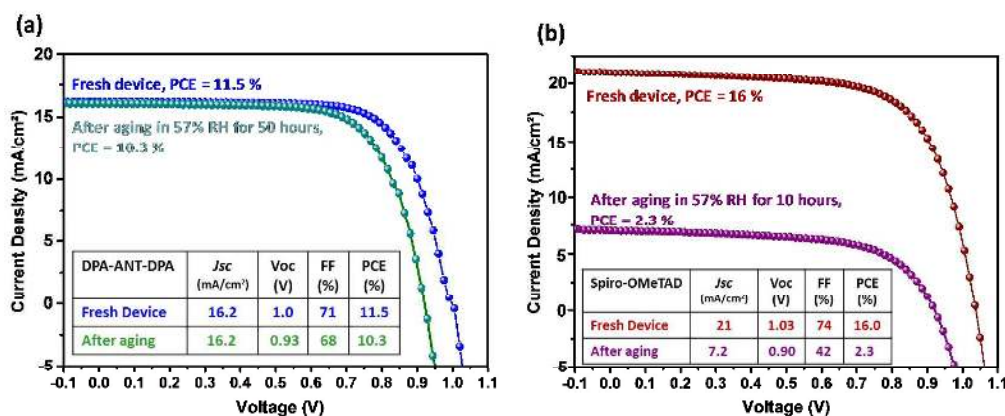
HTLs	Scan Direction	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
DPA-ANT-DPA ^{b)}	Forward	1.00	16.2	71	11.5
	Reverse	0.98	15.8	69	10.8
	Average ^{d)}	0.97	15.0	69	10.4
Spiro-OMeTAD ^{c)}	Forward	1.03	21.0	74	16.0
	Reverse	1.03	20.4	72	15.2
	Average ^{d)}	0.99	18.2	71	12.8

270 ^{a)} Cell size (active area): 0.100 cm^2 . Photovoltaic performance at 1000 nm^{-2} (AM1.5G) and constant scan speed
271 of 10 mV s^{-1} mesoscopic $\text{CH}_3\text{NH}_3\text{PbI}_3$ devices; ^{b)}without additives; ^{c)}with additives: 4-tert-butylpyridine (*t*BP)
272 and Li-bis(trifluoromethanesulfonyl)-imide (LiTFSI); ^{d)}An average device efficiency of a total of 41 and 42
273 devices for Spiro-OMeTAD and DPA-ANT-DPA, respectively.

274

275 We observed a negligible hysteresis on the reverse scan (0 V to V_{oc}) at a low scan speed of 10
 276 mV s^{-1} for DPA-ANT-DPA and Spiro-OMeTAD based devices that results in the efficiency
 277 decrease from 16% to 15.2% for Spiro-OMeTAD based and 11.5% to 10.8% for DPA-ANT-
 278 DPA HTM based perovskite solar cells. The excessively small band offset of the HOMO
 279 between perovskite and DPA-ANT-DPA HTL (as shown in Fig. 2(a)), may hamper the
 280 effective hole transport ability.³⁸ We observed that even though the work function of DPA-
 281 ANT-DPA is very close to that of the perovskite active layer, a respectable PCE could still be
 282 achieved, without doping. The good comparable V_{oc} of 1.0 V for DPA-ANT-DPA to that of
 283 Spiro-OMeTAD based devices is due to the very small band offset and HOMO value
 284 difference between this compound and perovskite active layer.³⁸ Furthermore, the non-doped
 285 DPA-ANT-TPA based PSC shows a short circuit current ($J_{sc} = 16.2 \text{ mA cm}^{-2}$) comparable to
 286 that with Spiro-OMeTAD ($J_{sc} = 21 \text{ mA cm}^{-2}$) which is due to the shallower HOMO of DPA-
 287 ANT-DPA that allows for effective hole extraction.

288 The PCE of 11.5%, obtained using non-doped DPA-ANT-DPA HTM, is high compared to
 289 other HTMs reported in the literature taking dopant-free aspect into account.^{4, 39-41} As shown
 290 in Fig. 3c, the devices with DPA-ANT-DPA exhibit external quantum efficiency (EQE)
 291 values above 65 to 70% from 365 nm to 650 nm covering the entire UV region with the
 292 highest EQE of 70% observed at 470 nm. The statistics of total 83 PSCs prepared using
 293 DPA-ANT-DPA and Spiro-OMeTAD as shown in Fig. 3d exhibits an average device
 294 efficiency of 10.4% and 12.8% respectively.



295

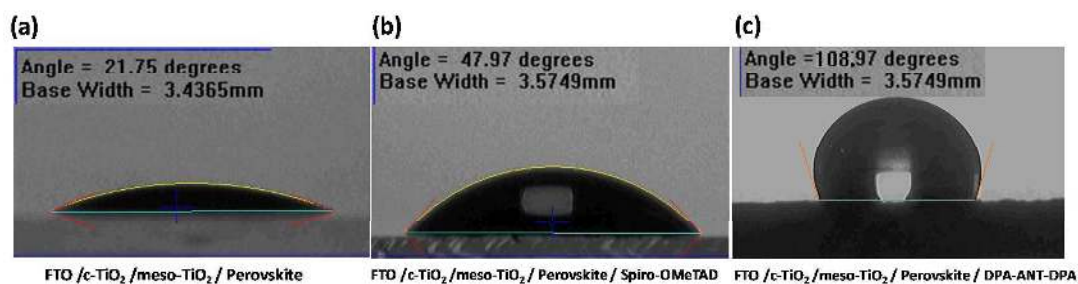
296 Fig. 4 Photovoltaic performance of DPA-ANT-DPA (a), and Spiro-OMeTAD (b) based
 297 $\text{CH}_3\text{NH}_3\text{PbI}_3$ PSC devices respectively on aging in humidity $\geq 57\%$ (the fresh and aged PSC
 298 devices performance is shown in satellite table); Stability test/aging for 50 hours for DPA-
 299 ANT-DPA HTM based cells and 10 hours for Spiro-OMeTAD HTM based PSC: without

300 encapsulation. After each consecutive measurement, the PSCs are kept in an ambient
301 humidity setup of RH of 57%, Temperature = 22 °C.

302

303 The stability of PSCs is one of the most discussed issues within the perovskite solar cell
304 community and a major hurdle for commercialization. Since the active layer in perovskite
305 devices is an organometallic salt, it has a strong tendency to absorb water. Among different
306 degradation factors, ambient humidity is one of the most critical parameters being for the
307 degradation of Spiro-OMeTAD based PSCs and this is due to the hydrophilic nature of the
308 active layer used in PSC.⁴²⁻⁴⁴ Taking these parameters into account, we studied the stability of
309 fabricated champion devices without any encapsulation at high humidity conditions (relative
310 humidity (RH) = 57%, temperature = 22 °C, in dark condition) for our newly developed
311 DPA-ANT-DPA and standard Spiro-OMeTAD HTMs (as shown in Fig. 4).

312 A simple stability setup used is shown in Fig. S8 a,b (ESI†) and the photovoltaic
313 performance was measured at 1000 wm^{-2} (AM1.5G) using regular aging intervals. The
314 photovoltaic properties of our novel DPA-ANT-DPA and Spiro-OMeTAD in the aging test
315 are detailed in Fig. 4a and 4b. Additionally, the efficiency of all HTMs based devices is
316 evaluated under identical conditions and depicted in Fig. 4. The degradation test results show
317 that the Spiro-OMeTAD HTM based devices degraded at a faster rate compared to DPA-
318 ANT-DPA based devices. The Spiro-OMeTAD HTM based devices showed a rapid drop in
319 PCE from 14.2% (Fresh device) to 2.3% after aging in 57% RH, for only 10 hours. Spiro-
320 OMeTAD HTM based devices showed significant drop in current from $J_{sc} = 21$ to 7.1
321 mA/cm^2 . On the other hand, the DPA-ANT-DPA HTM based devices maintained the J_{sc} of
322 16 mA/cm^2 with a very small drop in open circuit voltage V_{oc} from 1.0 to 0.93 V. This
323 resulted in a small drop in PCE from 11.5% to 10.3%, this is even after prolonged exposure
324 of 50 hours to high relative humidity of 57%. This clearly shows improved device stability of
325 PSCs made using DPA-ANT-DPA HTM over Spiro-OMeTAD based devices.



326

327 Fig. 5 Contact angle measurements performed on (a) $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite, (b) Spiro-
328 OMeTAD and (c) DPA-ANT-DPA surface, deposited on FTO/c-TiO₂/meso-TiO₂ substrate.

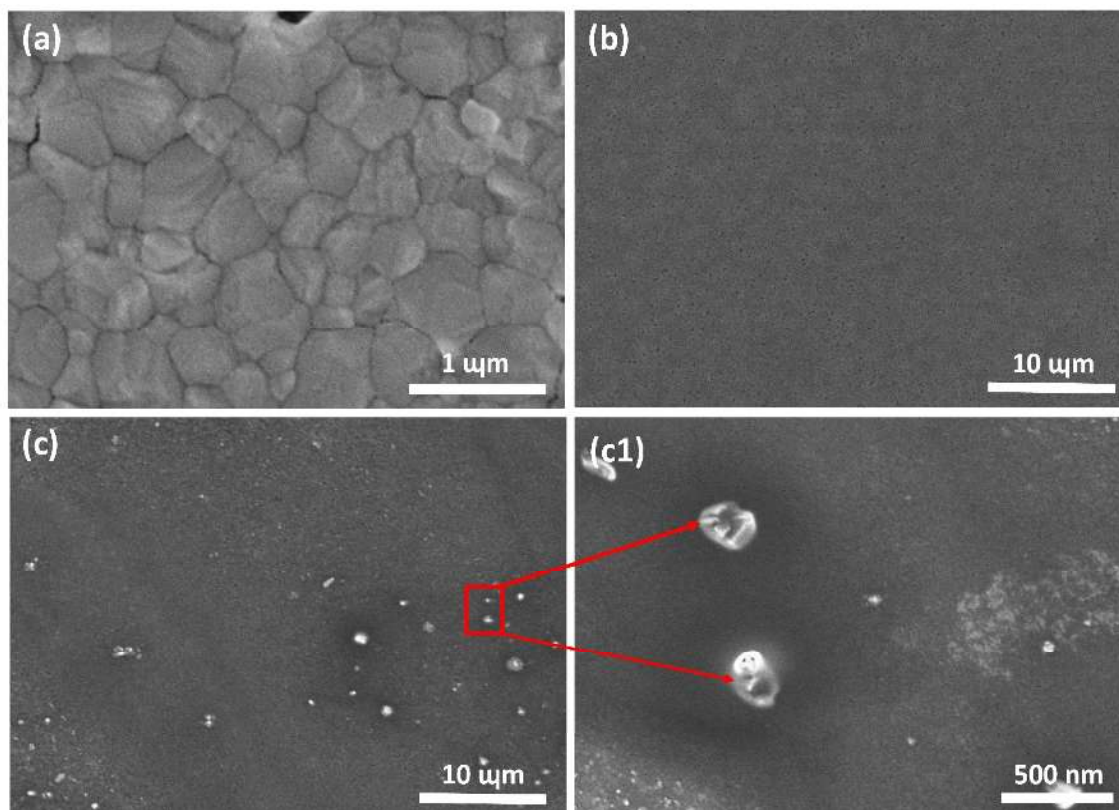
329

330 To further investigate the reason for the dramatic improvement in stability of DPA-ANT-
331 DPA (compare to Spiro-OMeTAD) based PSCs. Considering that the top layer of the
332 perovskite solar cell device plays an important role in preventing water ingress,⁴⁵ we
333 performed contact angle measurements (as shown in Fig. 5(a-c)) as well morphological
334 measurements on the top surface of PSCs, which is the surface of HTMs (as shown in Fig. 6).

335 Fig. 5 (a) shows a low contact angle of 21° of a water droplet on $\text{CH}_3\text{NH}_3\text{PbI}_3$ surface, this
336 confirms the good wetting behaviour, high hydrophilic nature of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite
337 active layer used in this study. Doped Spiro-OMeTAD layers, deposited on top of the
338 perovskite shows a contact angle of 47.9°, indicating a reduced albeit still high degree of
339 hydrophilicity of the overall device. Snaith et al already demonstrated the cause behind
340 hydrophilic nature of Spiro-OMeTAD based HTM devices and this is mainly due to the
341 doping of Spiro-OMeTAD using hygroscopic LiTFSI salts.⁴⁵ We would like to make clear
342 that though the Spiro-OMeTAD molecule itself is non-polar by nature due to the presence of
343 four methoxy groups on phenylene units, it becomes hydrophilic owing to the addition of
344 dopant salts. The contact angle measured using our newly developed DPA-ANT-DPA HTMs
345 surface without using any dopant leads to an impressive elevated contact angle of 108° with
346 lower wetting (enhancing hydrophobicity); this is likely mainly responsible for higher
347 stability of reported devices here using our new HTM.

348 Moreover, it is further necessary to study the surface morphology of the HTMs in order to
349 understand the different wetting, de-wetting behaviour and hence to probe the reason for the
350 hygroscopic nature of the films. Fig. 6 shows surface morphology of the perovskite, DPA-
351 ANT-DPA and Spiro-OMeTAD hole transport layer. The $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite film Fig. 6
352 (a) shows good quality, larger crystalline grains ranging from 500 - 800 nm. The good quality
353 of the perovskite film is further confirmed from high photoluminescence (PL) intensity
354 obtained (Fig. 7). The HTM DPA-ANT-DPA deposited on perovskite shows homogeneous,
355 uniform surface coverage over a large area (Fig. 6(b)), while the Spiro-OMeTAD deposited
356 on perovskite shows inhomogeneous and rough surface also formation of small aggregates at
357 intervals, as shown in Fig. 6(b-c). These are possibly the crystals formed due to doping of
358 LiTFSI.⁴⁶ This is further confirmed from the observation that in absence of doping with

359 tertiary butyl pyridine (*tBP*) and LiTFSI salts in Spiro-OMeTAD, we have not observed such
360 aggregate formation.



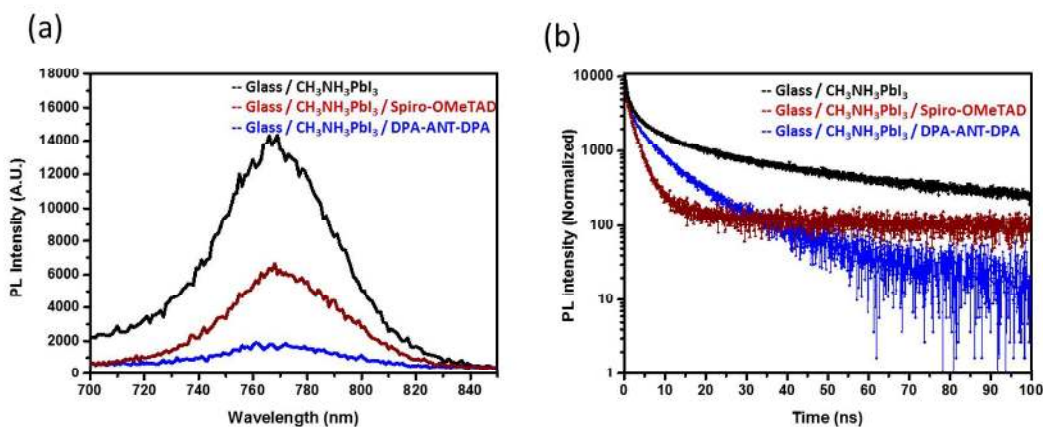
361

362 Fig. 6 (a) Surface image of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite film deposited on top of FTO/compact-
363 TiO_2 /mesoporous- TiO_2 ; (b) Top view of DPA-ANT-DPA on perovskite layer; (c) top view of
364 Spiro-OMeTAD on perovskite, and (c1) zoomed in of top view of Spiro-OMeTAD layer, red
365 mark highlights crystals formed due to addition of dopant. To mimics the device architecture
366 all the layers are deposited on FTO/compact- TiO_2 /mesoporous- TiO_2 substrate.

367

368 These electron microscope observations along with the contact angle measurements clearly
369 correlate with the higher perovskite solar cell stability observed for DPA-ANT-DPA HTM
370 based solar cells as compared to Spiro-OMeTAD HTM based solar cells. The improved
371 homogeneous coverage of the DPA-ANT-DPA films along with de-wetting, hydrophobic
372 nature as observed from contact angle measurements resulted in devices with much higher
373 stability, whereas the Spiro-OMeTAD HTM films with rough, in-homogeneous surface,
374 small to large pin-holes and increased wetting and hydrophilic nature exhibited lower
375 stability. The good coverage along with hydrophobic nature of the DPA-ANT-DPA HTM on

376 the perovskite layer assures protection of the perovskite thin film layer from exposure to
 377 oxygen,^{44, 45} humidity,⁴³ and heat.⁴⁷ In summary, the homogeneous surface morphology and
 378 de-wetting characteristics offered by the novel anthanthrone (ANT) core with extended
 379 Diphenylamine (DPA) in DPA-ANT-DPA films have contributed significantly to protecting
 380 the underneath perovskite layer from degradation.



381

382 Fig. 7 (a) Steady state Photoluminescence (PL) measured on bare perovskite film (black), and
 383 hole transport layer deposited on the perovskite. Brown curve represent Spiro-OMeTAD,
 384 blue curve represents DPA-ANT-DPA, respectively, deposited on perovskite. (b) Time
 385 resolved PL taken at excitation wavelength of 765 nm of the perovskite films with different
 386 hole transport layers. A 5 mW picosecond pulsed diode laser at 635 nm was used to irradiate
 387 the perovskite and hole transport layer side.

388

389 Steady state and time resolved photoluminescence based on a simple architecture:
 390 Glass/CH₃NH₃PbI₃/HTM is shown in Fig. 7. In order to eliminate any quenching effect
 391 related to electron transfer to the oxide layer, we avoided to use of a TiO₂ layer while doing
 392 PL measurements. During these PL measurements, we have to make sure that the
 393 photoluminescence quenching is only caused by the hole transport layer and is not due to any
 394 other materials. All the HTL thin films were excited at 635 nm wavelength. From the data, it
 395 is quite clear that the bare perovskite film without any HTM (black curve) exhibits a high PL
 396 emission intensity as a result of the formation of good quality (crystallinity and homogeneous
 397 surface) perovskite film, which is also seen from the surface morphology of the perovskite
 398 film (Fig. 6a). On deposition of HTM on the perovskite layer, a significant reduction in PL
 399 emission was observed. Perovskite films covered with DPA-ANT-DPA HTL (blue curve)

400 display a stronger PL quenching (~90%) than the films covered with Spiro-OMeTAD (~60%)
401 HTL. This effective quenching indicates a higher PL quenching ability of our newly
402 developed DPA-ANT-TPA compared to Spiro-OMeTAD. The DPA-ANT-DPA HTM
403 exhibits efficient exciton dissociation efficiency, comparable to that of doped Spiro-
404 OMeTAD. This ensures a efficient charge generation and high hole mobility as well as low
405 recombination at the DPA-ANT-DPA/CH₃NH₃PbI₃ interface.

406 The time resolved photoluminescence was performed to verify the improved hole transport
407 properties; the results are shown in Fig. 7b. Bare perovskite films deposited on glass substrate
408 as well as with different hole transport layers show biphasic kinetics. The fast component
409 decays in picoseconds (due to 80 ps laser pulse) and the slower component has a time
410 constant of 10-15 ns. The fast component represents trap filling. As the hole transfer films are
411 deposited on bare glass - perovskite layer for direct probing, this gives us a good estimation
412 of quenching of the photoluminescence due to hole transport layers only.

413 For bare perovskite sample (glass/perovskite) we have obtained high PL intensity and
414 lifetime of 8 ns. As shown previously⁴⁸ highly crystalline, good quality perovskite sample
415 shows a life time of ~ 8-10 ns, this confirms the quality of the perovskite films we used in
416 this study. After the introduction of DPA-ANT-DPA hole transporting layer above the
417 perovskite layer the average decay time (τ) shortened to ~20.2 ns. The fast decay lifetime
418 (τ_1) of both hole transporting materials decreased from 33 ns (bare perovskite without HTL)
419 to 18 ns for DPA-ANT-DPA and 16 ns for Spiro-OMeTAD hole transporting layer. At the
420 same time the weight fraction increased from 3% (bare perovskite film) to 23.5% for DPA-
421 ANT-DPA and 25.7% for Spiro-OMeTAD hole transport layers. This clearly shows the
422 complete hole extraction as well charge dissociation exerted by our novel undoped DPA-
423 ANT-DPA HTM is competent the traditional doped Spiro-OMeTAD.

424 Currently, among reported competitive D-A-D type HTMs in the literature using both
425 planar and mesoporous devices, JY5 and JY6 HTMs in planar devices^{16, 17} and BTPA-3 and
426 H1 HTMs based mesoporous layouts exhibit lower performance.^{6, 15} A brief comparison
427 based on the similar device structure and approximately equivalent working area among our
428 new HTM, DPA-ANT-DPA, with BTPA-3 and H1 is made and shown in Table 3. Overall,
429 the photovoltaic performance of DPA-ANT-DPA based devices achieves the highest PCE of
430 11.5% among all these materials without any additives, whereas the BTPA-3-based device
431 exhibits a close PCE of 9.81% with Li-TFSI and *t*BP as dopants. Notably, though the novel
432 DPA-ANT-DPA and H1 have the similar HOMO energy levels, the PCE of H1 based devices

433 is very low (~5.8%) due to its small J_{sc} and the use of different type of perovskite as active
434 layers. Moreover, the device with new DPA-ANT-DPA HTM has a superior stability in
435 comparison with the reference device based on Spiro-OMeTAD.

436 **Table 3.** The comparison among promising D-A-D HTMs.

HTM ^{a)}	HOMO (eV)	Perovskite materials	Active area (cm ²)	Additives ^{b)}	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF (%)	PCE (%)	Stability test ^{d)}	References
DPA- ANT- DPA	-5.46	CH ₃ NH ₃ PbI ₃	0.1	None	1.00	16.2	71	11.5 (16.0) ^{c)}	66% (14%) ^{e)}	This study
BTPA-3	-5.42	CS _{0.05} (MA _{0.17} FA _{0.83}) _{0.95} Pb(I _{0.83} Br _{0.17}) ₃	0.16	Li-TFSI <i>t</i> BP	1.09 1.44	19.9 6.66	53.4 61.5	9.81 (13.2) 5.91 (5.61)	84% (98%) 75% (91%)	6
H1	-5.46	CH ₃ NH ₃ PbBr ₃	0.16	Li-TFSI <i>t</i> BP FK209	1.43	5.50	72	5.80 (6.12)	-	15

437 ^{a)}A typical mesoporous architecture, including FTO/compact TiO₂/mesoporous TiO₂/Perovskite/HTM/cathode,
438 was used in these studies. While Ag was the cathode in this study, Au were employed in other citations (H1,
439 BTPA-3).

440 ^{b)}bis(trifluoromethylsulfonyl)imide lithium salt (Li-TFSI), 4-*tert*-Butylpyridine (*t*BP), tris(2-(1*H*-pyrazol-1-yl)-
441 4-*tert*-butylpyridine)cobalt(III) tri[hexafluorophosphate] (FK209)

442 ^{c)}PCE of standard Spiro-OMeTAD

443 ^{d)}The percentage of the retaining performance after the ageing test (unsealed devices)

444 ^{e)}The percentage of the retaining performance of standard Spiro-OMeTAD

445

446 Conclusions

447 In summary, we have successfully designed and synthesized a new highly scalable
448 small molecular DPA-ANT-DPA HTM based on an innovative low cost anthanthrone
449 dye as a core using D-A-D molecular design. The synthesis of DPA-ANT-DPA was

450 elegantly conducted in a single step via a simple coupling protocol using a common
451 anthanthrone dye as a central core and diphenylamine as end-capping units. A detailed
452 comparison on optoelectronic properties of DPA-ANT-DPA and traditional Spiro-
453 OMeTAD based PSCs has been performed and it has found that a HOMO energy level
454 of DPA-ANT-DPA is close to the active perovskite energy level, guaranteeing a better
455 hole transport ability with minimal energy offset. Upon evaluating DPA-ANT-DPA as
456 hole transporting material, without doping in perovskite solar cell devices, the highest
457 power conversion efficiency of 11.5% has been achieved. The DPA-ANT-DPA HTM
458 not only exhibits a respectable performance in comparison to other undoped hole
459 transport materials, but shows also an increased reproducibility of PSCs as compared
460 to Spiro-OMeTAD based PSCs and a lower cost and straightforward one-step
461 synthesis with easy purification. One of the most important features of DPA-ANT-
462 DPA based PSC devices is their environmental stability, much higher than that of
463 classical Spiro-OMeTAD. The reason behind the significantly higher stability of our
464 new DPA-ANT-DPA based devices has been also investigated in detail and it was
465 found that the hydrophobic nature and homogeneous coverage are responsible factors
466 and they are a result of chemical structure of the central ANT core and more extended
467 structure of DPA on the perovskite capping layer. The DPA-ANT-DPA HTM without
468 additives resulted in V_{oc} of 1.0 V. The improved charge collection efficiency in devices
469 prepared with DPA-ANT-DPA HTL (as seen from effective PL quenching) compared
470 to that of the Spiro-OMeTAD HTL leads to higher short circuit current and
471 photovoltage. By using such low cost fused anthanthrone dye, it is be possible to
472 design new efficient, stable and low cost scalable HTMs for roll-to-roll printed
473 perovskite solar cell modules and prototypes for large area application.

474

475 **Experimental**

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

477

478 **Conflicts of interest**

479 There are no conflicts to declare.

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493

494

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