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Paper:

Sonar, P., Pham, H., Jain, S., Meng, L., Manzhos, S., Feron, K., Pitchaimuthu, S., Liu, Z., Motta, N., et. al. (2019). Dopant-Free, Novel Hole Transporting Materials Based on Quinacridone Dye for High-Performance and Humidity Stable Mesoporous Perovskite Solar Cells. *Journal of Materials Chemistry A*
<http://dx.doi.org/10.1039/C8TA11361K>

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1 **Dopant-Free, Novel Hole Transporting Materials Based on Quinacridone Dye**
2 **for High-Performance and Humidity Stable Mesoporous Perovskite Solar Cells**

3

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23 Electronic Supplementary Information (ESI) available: [details of any supplementary information
24 available should be included here]. See DOI: 10.1039/x0xx00000x

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27

28 **Abstract**

29 This work reports three newly developed dopant free hole transporting materials (HTMs) for
30 perovskite solar cells. The design is based on quinacridone (QA) dye as a core with three different
31 extended end-capping moieties including acenaphthylene (ACE), triphenylamine (TPA) and
32 diphenylamine (DPA) attached to the QA. These HTMs were synthesized and fabricated
33 successfully in mesoscopic TiO₂/CH₃NH₃PbI₃/HTM perovskite devices. Under 100 mW
34 cm⁻² AM 1.5G, the devices achieved a maximum efficiency of 18.2% for ACE-QA-ACE,
35 16.6% for TPA-QA-TPA and 15.5% for DPA-QA-DPA without any additives, while the
36 reference devices with doped Spiro-OMeTAD as HTM showed a PCE of 15.2%. Notably, the
37 unencapsulated devices based on these novel dopant-free HTMs show impressive stability in
38 comparison with the doped Spiro-OMeTAD devices under 75% relative humidity for 30 days.
39 These linear symmetrical HTMs pave the way to a new class of organic hole transporting materials
40 for cost-efficient and large area applications of printed perovskite solar cells.

41

42 Keywords: quinacridone, acenaphthylene, triphenylamine, dopant-free, perovskite solar cells

43 **Introduction**

44 The research efforts related to π -conjugated vat dyes and pigments are burgeoning because
45 of their outstanding properties such as the fused planar aromatic hydrocarbon nature, high
46 backbone rigidity, backbone planarity of the core structures, strong absorption in the visible
47 range, high environmental, thermal and chemical stability and the possibility to tune
48 optoelectronic properties via functionalization with functional groups like ketones,
49 halogens and amines.^{1, 2} Additionally, some of them are very cost-efficient such as
50 carbazole, anthanthrone, quinacridone and so forth. Currently, this type of materials has
51 been employed intensively in organic solar cells (OSC), organic light-emitting diodes
52 (OLEDs), sensors and organic field-effect transistors (OFETs).¹⁻⁵

53 Particularly, the use of inexpensive organic dyes as hole transporting materials (HTMs) for
54 perovskite solar cells (PSCs) has attracted attention because it opens a new way for the
55 development of cost-effective and printable solar cells. Recently, HTM designs based on
56 anthanthrone (ANT),^{3,4} carbazole (CAZ),⁶⁻⁸ diketopyrrolopyrrole (DPP),^{9, 10} and isoindigo (IS)¹¹
57 dyes exhibited promising power conversion efficiencies (PCE) in perovskite devices. Several dye
58 based HTMs are reported in the literature but most of them used dopant as an additive to
59 enhance the power conversion efficiency of PSC.^{7, 8} Though the PCE is enhanced, the
60 presence of salt dopants leads to the decrease in the stability of the devices and the increase
61 in the cost of production. Therefore, the development of novel dopant-free organic dyes-
62 based HTMs is important. As per our knowledge, there are not much reports about using
63 dopant free dyes as a hole transporting materials for perovskite solar cells in the literature.

64 Owing to the high chemical and thermal stability, low cost, planar fused molecular
65 structure, intermolecular hydrogen bond and high charge carrier mobility, in our current
66 work we explored the used of quinacridone (QA) dye as core for the development of new
67 class of HTMs for PSC technology. It has been well documented that QA dye and its
68 derivatives have been widely employed as an active semiconductor in various
69 optoelectronic devices, including organic solar cells, light-emitting diodes, sensors and
70 field-effect transistors.^{2, 12-17} Nevertheless, its use in PSCs has not yet been reported.
71 Interestingly, QA is a well-known acceptor material due to presence of two electron
72 withdrawing ketonic groups in the conjugated backbone. Electron withdrawing QA

73 skeleton leads to a low-lying highest occupied molecular orbital (HOMO) level, which minimizes
74 the energy offset between the valence band maximum of perovskite and the HOMO of hole
75 transporting layers. This boosts the open circuit voltage (V_{oc}) and the efficiency of PSCs as well.^{3,}
76 ¹⁸⁻²²

77 Herein, we are reporting for the first time three novel quinacridone (QA) dye based HTMs
78 where we used a common QA central core as acceptor and three different end capping
79 groups donors such as acenaphthylene (ACE), triphenylamine (TPA) and diphenylamine
80 (DPA). All three materials are coded as 2,9-bis(1,2-dihydroacenaphthylen-5-yl)-5,12-
81 dioctyl-5,12-dihydroquinolino[2,3-*b*]acridine-7,14-dione (**ACE-QA-ACE**), 2,9-bis(4-
82 (bis(4-methoxyphenyl)amino)phenyl)-5,12-dioctyl-5,12-dihydroquinolino[2,3-*b*]acridine-
83 7,14-dione (**TPA-QA-TPA**) and 2,9-bis(bis(4-methoxyphenyl)amino)-5,12-dioctyl-5,12-
84 dihydroquinolino[2,3-*b*]acridine-7,14-dione (**DPA-QA-DPA**). These HTMs are fully
85 characterized and used as the active hole transporting layers in mesoscopic
86 $TiO_2/CH_3NH_3PbI_3/HTM$ solid-state PSCs without using any additives. The aim of this
87 work is to investigate the effect of different end-capping units of QA based HTMs on the
88 PSCs performance. Moreover, the comparison between the efficiency and stability of these
89 new QA based HTMs with the standard 2,2',7,7'-tetrakis(*N,N'*-di-*p*-methoxyphenylamino)-
90 9,9'-spirobiorene (Spiro-OMeTAD) based devices was also studied.

91 **Results and Discussion**

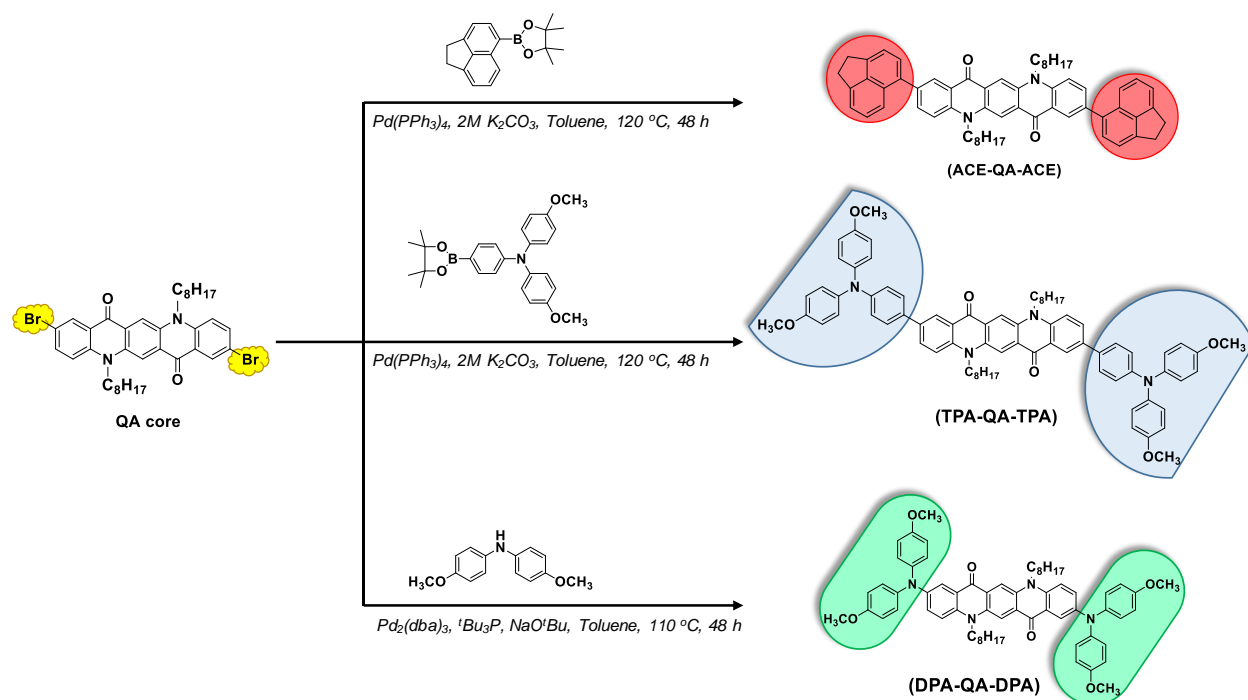
92 **Rational Design and Synthesis**

93 Symmetrical organic semiconductors using planar fused core have been of great benefit to the
94 device performance in optoelectronic applications. Particularly in perovskite solar cells,
95 this kind of geometry is usually used to design organic HTMs because it can improve π - π
96 stacking interactions and high hole mobility.²³⁻²⁵ In this work, QA polyaromatic hydrocarbon
97 selected as the fused central core because of its planar conjugated structure (resemblance to
98 pentacene with exception of nitrogen and ketonic groups present in the backbone).
99 Additionally strong H-bonding properties provide high charge transport abilities and
100 electron deficient core (acceptor) conjugated backbone plays a role of an allowing a Donor-
101 Acceptor-Donor (D-A-D) geometry, which has recently been shown to provide high
102 performance and stability in PSCs.²⁶⁻²⁸ In our current molecular engineering design, we

103 used QA acceptor as core and ACE, TPA and DPA donor groups as end cappers. TPA and
104 DPA moieties have already been widely used as end-capping groups in the design of organic
105 HTMs for PSCs, and devices using such HTMs displayed not only very high efficiency but also
106 superior stability.^{3, 29-33} In contrast, the ACE substituted conjugated HTMs are very rare and our
107 group was the first to report ACE end capping moiety for PSC devices. In our first report, we
108 reported ACE end capped anthranthrone dye which yielded PCE of 13.5% without any additives
109 .⁴ Thus, making a series of different end capping units based on QA dye, which are implemented
110 as HTMs in PSCs, will provide a comparative view about the effect of these promising small
111 molecules on the performance and stability of PSCs.

112 The synthesis routes of **ACE-QA-ACE**, **TPA-QA-TPA** and **DPA-QA-DPA** are illustrated
113 in Scheme 1. The preparation of three precursors, including ACE, TPA and DPA, followed earlier
114 attempts.^{3, 4, 19, 29} The target **ACE-QA-ACE** and **TPA-QA-TPA** compounds were synthesized by
115 Suzuki coupling reaction between ACE and TPA boronic ester starting material in combination
116 with common octyl substituted dibromo QA core using a palladium [Pd(PPh₃)₄] catalyst and 2M
117 K₂CO₃ base at 120 °C for 48 h in the toluene solvent. The synthesis of the target **DPA-QA-DPA**
118 was carried out via Buchwald-Hartwig coupling reaction between dibromo octyl substituted QA
119 and bis(4-methoxyphenyl)amine using tris(dibenzylideneacetone)dipalladium [Pd₂(dba)₃]
120 catalyst, tri-tert-butylphosphine (^tBu₃P), and sodium tert-butoxide (NaO^tBu) at 110 °C for 48 h in
121 anhydrous toluene solvent. After purification, the reaction yield of **ACE-QA-ACE**, **TPA-QA-**
122 **TPA** and **DPA-QA-DPA** was 62%, 54% and 39%, respectively. The purity of these compounds
123 was verified by proton and C¹³ Nuclear Magnetic Resonance (NMR) spectroscopy (Fig. S1 – S3,
124 Supporting Information (ESI[†])). Moreover, the molecular weight of these synthesized materials
125 was confirmed by mass spectroscopy. All these substances are well soluble in most common
126 organic solvents such as chloroform, dichloromethane, and chlorobenzene.

127



128

129 Scheme 1. The synthetic route for QA derivatives. Reagent and conditions: For the synthesis of
 130 **ACE-QA-ACE** and **TPA-QA-TPA**: 2M K₂CO₃, toluene, Pd(PPh₃)₄, 120 °C, 48 h; For the
 131 synthesis of **DPA-QA-DPA**: Diphenylamine, ^tBu³P, NaO^tBu, Pd₂(dba)₃, Toluene, 110 °C, 48 h.

132

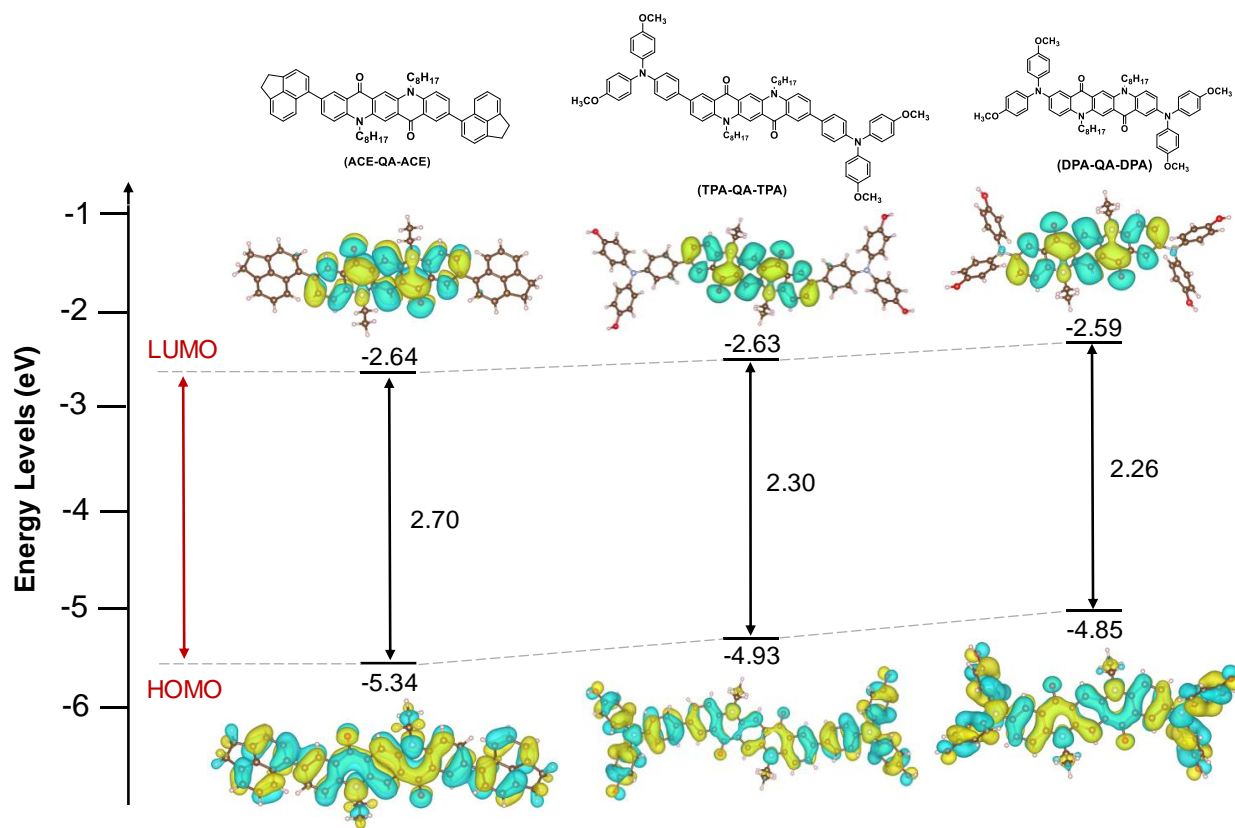


Fig. 1 Calculated electron density of HOMO and LUMO of QA derivatives.

133

134

135

136 **Ab initio Calculations**

137 In order to gain insight about the electron density distribution of key molecular orbitals and their
 138 respective energy level trend among molecules, Density Functional Theory (DFT) calculations at
 139 the B3LYP level using the basis set Lanl2dz³⁴⁻³⁶ and a polarized continuum model of the
 140 chloroform solvent³⁷ were performed. The resulting HOMO and LUMO distributions are
 141 displayed in Fig. 1. The trend in HOMO and LUMO energies among the three molecules are
 142 similar to that observed experimentally (see below). The computed levels are higher than those
 143 measured by PESA likely due to limitations of the approximations used. Generally, three new
 144 substances unveil similarities in both electron densities of the HOMO and the LUMO. While the
 145 electron distribution of the LUMO is primarily localized on the parent quinacridone skeleton, those
 146 of the HOMO are fully delocalized over the entire molecules. This is in good agreement with
 147 previous reports.^{14, 15, 38} The calculated HOMO values of **ACE-QA-ACE**, **TPA-QA-TPA**, and
 148 **DPA-QA-DPA** are -5.34, -4.93 and -4.85 eV, respectively. The LUMO values are -2.64 eV for

149 **ACE-QA-ACE**, -2.63 eV for **TPA-QA-TPA**, and -2.59 eV for **DPA-QA-DPA**. Accordingly, the
 150 band gap is estimated to be of 2.70 eV for **ACE-QA-ACE**, 2.30 eV for **TPA-QA-TPA**, and 2.26
 151 eV for **DPA-QA-DPA**. In addition to above data, the dihedral angle between end capping ACE
 152 and TPA groups with the QA skeleton is computed to be 47° and 28°, respectively whereas the
 153 dihedral angle between QA core and end capping DPA group is not observed.

154 Table 1. Thermal, optical and electrochemical properties of QA derivatives.

HTM	λ_{\max} (nm)		λ_{PL} (nm)	Stoke shift (nm)	λ_{onset} (nm)	E_g^{optc} (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_m (°C)	T_c (°C)	μ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)
	Solution ^{a)}	Film ^{b)}												
ACE-QA-ACE	301	353	558	257	585	2.12	-5.59	-3.47	-5.37	414	-	265	212	2.3×10^{-4}
TPA-QA-TPA	364	368	540	172	626	1.98	-5.41	-3.43	-5.02	424	105	-	-	1.6×10^{-4}
DPA-QA-DPA	360	364	-	-	663	1.87	-5.28	-3.41	-4.93	413	74	215	141	1.2×10^{-4}

155 ^{a)}Absorption spectrum was measured in chloroform (CF) solution; ^{b)}Film was prepared by spin-coating an CF solution
 156 containing the sample onto glass substrate at a spin speed of 1000 rpm at room temperature; ^{c)}Optical bandgap was
 157 calculated from the formula of $1240/\lambda_{\text{onset}}$; ^{d)}The oxidation potential was measured by photoelectron spectroscopy in
 158 air (PESA); $E_{\text{LUMO}}^{\text{PESA}} = E_{\text{HOMO}}^{\text{PESA}} + E_g^{\text{opt}}$; ^{e)}The Oxidation potential of the material was characterized in
 159 dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate at scan speed 100 mV s^{-1} , potentials versus
 160 Fc/Fc^+ .

161 162 **Optical Properties**

163 The absorption properties of **ACE-QA-ACE**, **TPA-QA-TPA** and **DPA-QA-DPA** are
 164 characterized by UV-Vis spectroscopy. The normalized UV-vis absorption spectra in chloroform
 165 (CF) solutions and solid films are shown in Fig. 2a and the data are summarized in Table 1.
 166 Generally, a similar pattern of the spectra between CF solutions and thin films is observed,
 167 suggesting that there is no significant crystallization in thin films.^{29, 39} In addition, the absorption
 168 spectra of samples in CF solutions shows the slight blue shift compared to that of thin films, which
 169 is mainly caused by the intermolecular interactions in the solid state and the increased π -electron

170 density ($\pi-\pi^*$ transitions) of the compound. Obviously, the absorption of **TPA-QA-TPA** is red-
171 shifted compared to that of **DPA-QA-DPA** and **ACE-QA-ACE**, which could be ascribed to the
172 stronger electron-donating ability of TPA unit in comparison with DPA and ACE.^{4, 29}

173 These newly developed materials exhibit three main absorption bands, including 300 – 320 nm,
174 330 – 400 nm, and 400 – 670 nm. This is in good agreement with previous studies related to other
175 derivatives of QA dyes.^{12, 13, 15} The absorption peaks at the region of 300 – 320 nm indicate the
176 absorption of three different end-capping units.^{4, 29} Meanwhile, the impact of the intramolecular
177 charge transfer (ICT) between the QA skeleton and end-capping groups results in the prominent
178 peaks at 330 – 400 nm area. Furthermore, their weak additional absorption band at 400 – 670 nm
179 might be caused by ICT between the electron-accepting carbonyl group (C=O) of the parent QA
180 molecule and end-capping groups.¹⁵ In CF solutions, **ACE-QA-ACE** unveils absorption maxima
181 at 301 nm **whereas** **TPA-QA-TPA** and **DPA-QA-DPA** exhibits at 364 nm and 360 nm
182 **respectively**. In solid thin film, the absorption peaks of these materials are found to be at 353 nm
183 for **ACE-QA-ACE**, 368 nm for **TPA-QA-TPA** and 364 nm for **DPA-QA-DPA**. Certainly, the
184 optical band gaps calculated by using the absorption onset wavelength ($E_g^{opt}=1240/\lambda_{onset}$) of the
185 corresponding absorption spectrum in solid-state are found 2.12 eV for **ACE-QA-ACE**, 1.98 eV
186 for **TPA-QA-TPA** and 1.87 eV for **DPA-QA-DPA**.

187 Furthermore, the photoluminescence (PL) spectra in CF and Toluene solutions of these three new
188 materials was carried out and illustrated in Fig. S5 (ESI†) and the **results are** listed in Table 1.
189 While **DPA-QA-DPA** does not exhibit the emission in CF solution, it shows the emission in
190 Toluene solution which is in good agreement with compound NPh₂-QA in the previous report.¹³
191 On the contrary, the emission maximum of **ACE-QA-ACE** and **TPA-QA-TPA** are found to be
192 558 nm and **540** nm, respectively. According to the maximum of absorption and emission peaks,
193 the Stoke shift is estimated to be 257 nm for **ACE-QA-ACE**, **172** nm for **TPA-QA-TPA** and 269
194 nm for **DPA-QA-DPA** taking first strong absorption peak into an account.

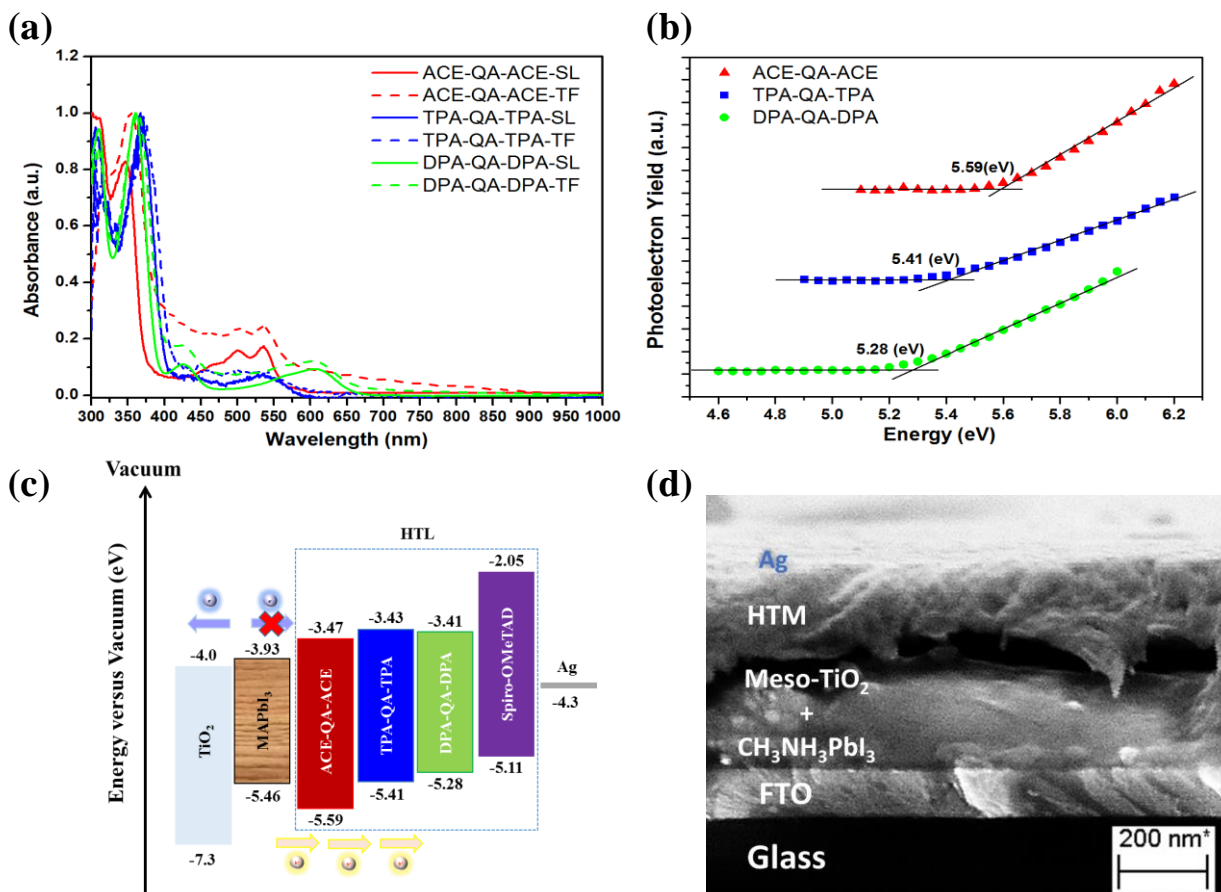
195

196 **Thermal Properties**

197 The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques
198 were used to investigate the 5% weight loss and thermal transition of these new materials. This

199 information will be helpful to determine thermal stability and glass transition temperature, melting
200 temperature and other relevant studies. The corresponding DSC and TGA data are shown in Table
201 1. According to the TGA curves (Fig. S6, ESI†), the decomposition temperature (T_d) of all these
202 compounds is greater than 410 °C, presenting their high thermal stability. The T_d is in the order:
203 **DPA-QA-DPA** (413 °C) = **ACE-QA-ACE** (414 °C) < **TPA-QA-TPA** (424 °C), which is higher
204 than that of original QA skeleton (~370 °C).^{13, 40} The decomposition temperature of TPA-based
205 HTMs is higher than those of DPA and ACE-based ones, which coincides well with previous
206 studies.^{4, 41-43} Thus, the QA cores substituted with ACE, TPA and DPA moieties result in improved
207 thermal stability.

208 The DSC data (Fig. S7, ESI†) exhibits different glass transition temperatures (T_g), melting
209 temperatures (T_m) and crystalline temperatures (T_c) among these compounds. The T_g of **TPA-QA-**
210 **TPA** and **DPA-QA-DPA** is found to be 105 °C and 74 °C, respectively, whereas the T_g of **ACE-**
211 **QA-ACE** is not observed. For T_m , the values of **ACE-QA-ACE** and **DPA-QA-DPA** are estimated
212 to be 265 °C and 215 °C, respectively, which is higher than that of original QA skeleton (179 °C).¹³
213 Meanwhile, the **TPA-QA-TPA** compound doesn't exhibit T_m and it could be higher than
214 instrument measurement range. Moreover, the T_c of **ACE-QA-ACE** and **DPA-QA-DPA** are
215 assessed to be 212 °C and 141 °C, respectively, whereas T_c of **TPA-QA-TPA** is not observed. The
216 melting and crystalline behaviors of **TPA-QA-TPA** are not revealed, suggesting that TPA-QA-
217 TPA is a typical amorphous glass. Interestingly, the appearance of methoxy groups in DPA units
218 of **DPA-QA-DPA** leads to the presence of T_c , the decrease in T_d and the increase in both T_m and
219 T_g in comparison with compound NPh₂-QA, which does not possess methoxy ones, in the previous
220 report.¹³



221
 222 **Fig. 2** (a) The UV-Vis absorption and PL spectra in CF solutions and the UV-Vis absorption in
 223 films; (b) Photoelectron spectroscopy in air (PESA) spectra; (c) Energy level diagram, (d) Cross-
 224 sectional scanning electron microscopy image of PSC of three new materials.

225
 226 **Energy Level Determination**

227 Determining the energy levels of hole transporting materials is quite crucial to estimate the
 228 architecture of the device. In this work, the HOMO values of three new materials are measured by
 229 photoelectron spectroscopy in air (PESA) (Fig. 2b) and cyclic voltammetry (CV) (Fig. S8, ESI†)
 230 methods respectively. The LUMO values of **ACE-QA-ACE**, **TPA-QA-TPA** and **DPA-QA-DPA**
 231 are calculated by using the difference between the HOMO values and the optical band gap via the
 232 equation: $E_{LUMO}^{PESA} = E_{HOMO}^{PESA} + E_g^{opt}$. The corresponding data are shown in Table 1. In this report, the
 233 energy values based on PESA data was used instead of CV one because the PESA measurements
 234 were done in the thin film forms, which are more relevant to the actual devices.^{3, 4} As shown in

235 Fig. 2b, the HOMO values of **ACE-QA-ACE**, **TPA-QA-TPA** and **DPA-QA-DPA** are assessed
236 to be at -5.59 eV, -5.41 eV and -5.28 eV, respectively. These HOMO values are deeper than that
237 of Spiro-OMeTAD (-5.22 eV)^{19, 44} which may lead to more efficient hole-transport ability than
238 conventional Spiro-OMeTAD. The substitution of three different terminating units ACE, TPA and
239 DPA has impacted the low-lying HOMO energy level, proving that the strong electron donating
240 ability displays an order of ACE > TPA > DPA. The stronger electron donating ability of TPA
241 compared to DPA coincides well with the experimental red shifts in UV-Vis spectra of both
242 compounds and the trend observed for the energy levels of other HTMs based on these end-capping
243 moieties in the earlier attempts.^{29, 42, 43, 45, 46} On the contrary, in case of ACE unit, it is not in good
244 accordance with the previous report.⁴ This may be attributed to the weak electron donating ability
245 of QA core in comparison with the strong electron donating ability of ANT one arising from more
246 extended conjugated nature of the core. According to the HOMO values and the optical band gap,
247 the obtained LUMO value is found to be -3.47 eV for **ACE-QA-ACE**, -3.43 eV for **TPA-QA-**
248 **TPA** and -3.41 eV for **DPA-QA-DPA**. These LUMO offset between active perovskite layer and
249 hole transporting material is quite low and this will block the electron movement, which can cause
250 boosting the solar cell efficiency.

251

252 Perovskite Solar Cells

253 The new QA core based small molecules were employed as hole transport materials in the
254 typical mesoporous perovskite solar cells with TiO₂/CH₃NH₃PbI₃/HTM/Ag device architecture.
255 This device architecture allows us to investigate the effect of different end-capping groups on the
256 performance of perovskite solar cells.

257 The mesoporous devices were prepared using the previously reported procedure^{47, 48} which
258 is described in the experimental section above. A compact TiO₂ layer of around 30-40 nm thickness
259 is first deposited on the conducting FTO substrate by spray pyrolysis, then a mesoporous TiO₂ is
260 deposited by using the conventional spin-coating methodology. The CH₃NH₃PbI₃ absorber is then
261 spin-coated using anti solvent treatment. The perovskite solution was prepared by dissolving 50
262 wt % of CH₃NH₃PbI₃ in the mixed dimethyl sulfoxide and gamma butyrolactone (GBL). The
263 sample was annealed for 30 minutes at 100 °C. Once the substrate cooled down, a hole transport

264 layer of 100-120 nm was applied on top of the $\text{CH}_3\text{NH}_3\text{PbI}_3$. At last, the silver (Ag) as a counter
265 electrode was deposited by thermal evaporation.

266 The $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{HTM}/\text{Ag}$ architecture of the PSC devices were kept constant and just
267 the hole transport layers are changed. This allows to isolate the effect of the different HTMs used.
268 The optimized, champion device efficiency and the corresponding photovoltaic performance for
269 all three different dopant-free HTMs and conventional doped Spiro-OMeTAD are shown in Fig.
270 3 and Table 2, respectively. According to Fig. 3a, the non-doped **ACE-QA-ACE** HTM based PSC
271 devices show a record PCE of 18.2% ($J_{\text{sc}}=22.41 \text{ mA cm}^{-2}$, $V_{\text{oc}}=1.06 \text{ V}$ and $\text{FF}=77\%$) whereas
272 lower PCEs are obtained from the devices using **TPA-QA-TPA** and **DPA-QA-DPA** HTMs under
273 similar conditions. The **TPA-QA-TPA** HTM based PSCs yields a PCE of 16.6% ($J_{\text{sc}}=22.4 \text{ mA}$
274 cm^{-2} , $V_{\text{oc}}=0.99 \text{ V}$ and $\text{FF}=75.1\%$) whereas those of **DPA-QA-DPA** HTM displays a PCE of 15.5%
275 ($J_{\text{sc}}=22.38 \text{ mA cm}^{-2}$, $V_{\text{oc}}=0.95 \text{ V}$ and $\text{FF}=73.2\%$). Meanwhile, the control devices based on doped
276 Spiro-OMeTAD show an efficiency of 15.2% with a J_{sc} of 21.46 mA cm^{-2} , a V_{oc} of 1.03 V and a
277 FF of 69.3%. Additionally, all devices made employing different HTMs exhibited very little
278 hysteresis (Fig. S9, ESI[†]). The excessive small band offset between perovskite and the HTL
279 hampers the effective hole transport ability. Our result shows that the higher V_{oc} (1.06 V) obtained
280 by employing **ACE-QA-ACE** HTMs as compared to lower V_{oc} of 0.99 V and 0.95 V obtained by
281 using **TPA-QA-TPA** and **DPA-QA-DPA** respectively, is a result of small band offset and HOMO
282 value difference between these HTMs and perovskite absorber.⁴⁹⁻⁵¹ Moreover, the dopant free
283 **ACE-QA-ACE** HTM based PSCs shows negligible change in short circuit current ($J_{\text{sc}} = 22.41$
284 mA cm^{-2}) compared to the **TPA-QA-TPA** ($J_{\text{sc}} = 22.40 \text{ mA cm}^{-2}$) and **DPA-QA-DPA** ($J_{\text{sc}} = 22.38$
285 mA cm^{-2}). This is due to the shallow HOMO of all QA core based HTMs that allows effective hole
286 transport.

287 The device performance of these new HTMs based devices is in order: **DPA-QA-DPA** <
288 **TPA-QA-TPA** < **ACE-QA-ACE**. The efficiency of **TPA-QA-TPA** HTL based devices is higher
289 than that of **DPA-QA-DPA**, which is in agreement with previous attempts reporting that the PCE
290 obtained using TPA terminating groups-based HTMs is greater than that with DPA in mesoporous
291 layouts under similar characterization conditions.^{29, 41, 42, 46, 52, 53} Furthermore, the PCE of **ACE-**
292 **QA-ACE** HTM-based devices is better than those of **TPA-QA-TPA**, which does not agree well
293 with an earlier study.⁴ This could be ascribed to the different electron accepting/donating ability
294 of quinacridone and anthanthrone cores. **Though both the quinacridone and anthanthrone contains**

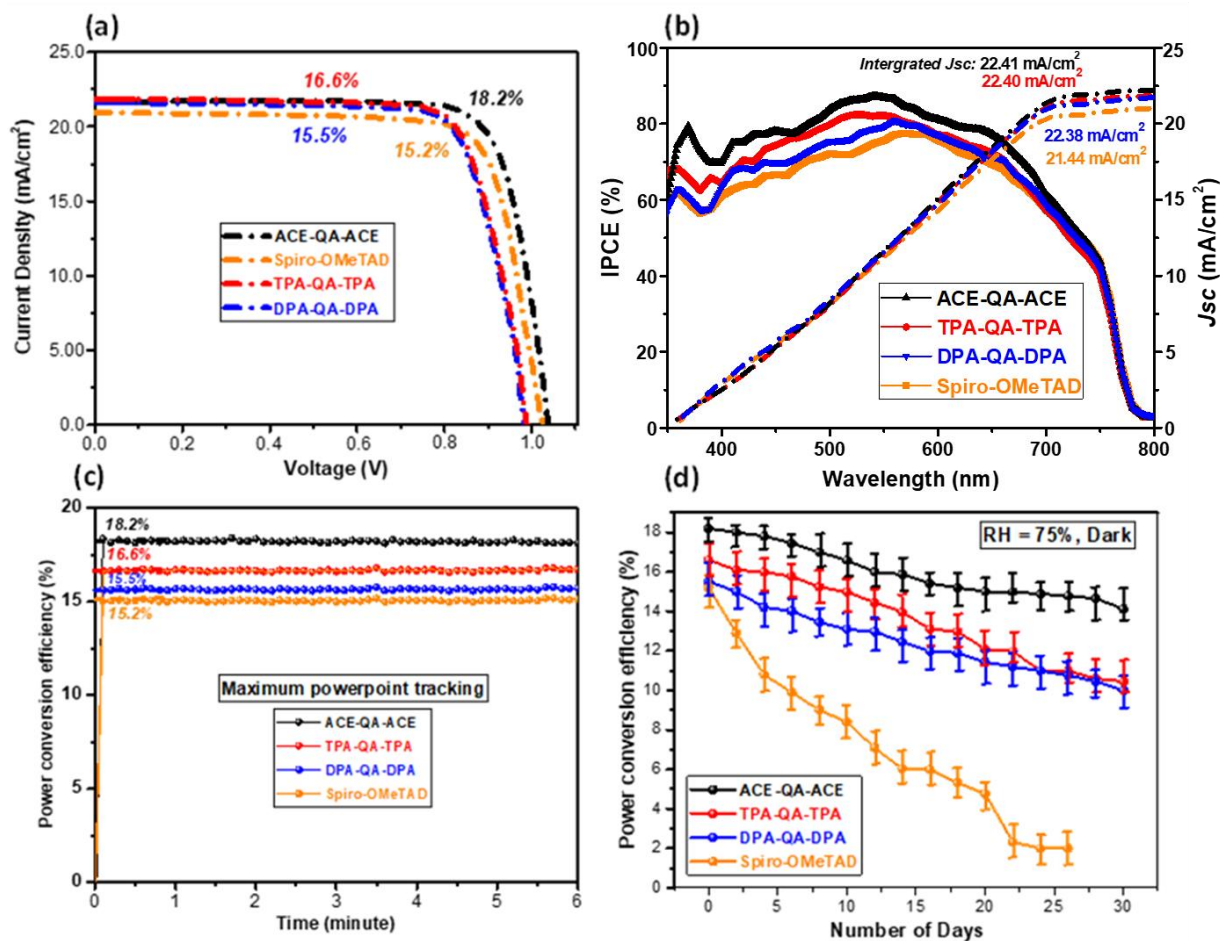
295 two ketonics (C=O) groups but anthanthrone is more fused aromatic with extended conjugation,
296 which possesses more electron donating capability than quinacridone.

297 The space charge limited current (SCLC) method was used to measure the hole transport
298 properties of different hole transport layers. For these measurements, HTMs were spin-coated on
299 top of ITO/PEDOT:PSS substrate and then gold metal contacts were deposited on top by thermal
300 evaporation process. The work function of ITO and gold are close enough to that of the HTMs
301 HOMO level hence this whole assembly acts as a hole-only device from which the mobility can
302 be determined (Table 1 and Fig. S10, ESI†). The highest hole mobility of $2.3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was
303 obtained for **ACE-QA-ACE** and was higher than that of **TPA-QA-TPA** ($1.6 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$),
304 **DPA-QA-DPA** ($1.2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and doped Spiro-OMeTAD ($1.4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). This
305 trend of effective hole transport is well matched with the efficiency obtained employing these
306 HTMs.

307 As shown in Fig. 3b, the devices with **ACE-QA-ACE** HTL exhibit an incident photon-to-
308 current efficiency (IPCE) values around 80-90% from 360 to 650 nm covering the entire UV region
309 with the highest IPCE of 90% observed at 540 nm. The integrated current density calculated from
310 IPCE spectrum presented in Figure 3(b) is in well match to the current density (J_{sc}) values obtained
311 from the IV curves (Figure 3(a))

312 The maximum power point tracking with each HTM is displayed in Fig. 3c. In comparison
313 with other organic dyes employed as small molecular HTMs for perovskite solar cells (Table S2,
314 ESI†), the power conversion efficiency of 18.2% obtained using dopant-free **ACE-QA-ACE** HTM
315 here is the highest reported efficiency. The PSCs prepared using **ACE-QA-ACE**, **TPA-QA-TPA**,
316 **DPA-QA-DPA** and Spiro-OMeTAD show an average device efficiency of 14.7%, 13.0%, 12.1%
317 and 11.4% respectively as shown in Table 2.

318 Perovskite solar cells suffer from rapid degradation when exposed to high humidity
319 conditions. Therefore, a PSCs stability measurement in high humidity is an important aspect to
320 evaluate further. We have kept all our champion devices for 720 hours in 75% relative humidity
321 and checked their performance at regular intervals. Fig. 3d shows aging of perovskite solar cells.
322 PSC made with dopant-free HTMs (**ACE-QA-ACE**, **TPA-QA-TPA** and **DPA-QA-DPA**) shows
323 improved stability over devices prepared using doped Spiro-OMeTAD. In our previous study, the
324 fast degradation of the solar cells which were doped with LiTFSI salt was explained.⁴



325
 326 **Fig. 3** (a) Photovoltaic performance of perovskite devices prepared using Spiro-OMeTAD and QA
 327 derivatives HTMs, respectively illumination; (b) Absolute IPCE spectra (solid line) and integrated
 328 current density calculated for optimized PSCs prepared using different hole transporting layers;
 329 (c) Power output under maximum power point tracking for 360 s, starting from forward bias and
 330 resulting in a stabilized power output of 18.2, 16.6, 15.5 and 15.2% for **ACE-QA-ACE**, **TPA-**
 331 **QA-TPA**, **DPA-QA-DPA** and Spiro-OMeTAD - based devices, respectively. The devices
 332 measured at voltage scan rate of 10 mV s^{-1} ; (d) Aging of champion devices stored in high relative
 333 humidity of 75% and in dark condition for 725 hours (30 days).

481

482

483 **Table 2** Solar cell device performance with different HTMs under 1 sun condition.

HTLs ^{a)}	Scan Direction	V _{oc} [V]	J _{sc} [mA/cm ²]	FF [%]	PCE [%]
ACE-QA-ACE	Forward	1.06	22.41	77.0	18.2
	Reverse	1.06	22.36	76.7	18.0
	Average ^{c)}	1.00	20.32	72.5	14.7
TPA-QA-TPA	Forward	0.99	22.40	75.1	16.6
	Reverse	0.98	22.34	75.0	16.0
	Average ^{c)}	0.95	20.00	69.6	13.0
DPA-QA-DPA	Forward	0.95	22.38	73.2	15.5
	Reverse	0.95	22.34	73.0	15.2
	Average ^{c)}	0.91	19.70	68.1	12.1
Doped Spiro-OMeTAD ^{b)}	Forward	1.03	21.46	69.3	15.2
	Reverse	1.02	21.35	68.4	14.8
	Average ^{c)}	0.93	19.00	65.0	11.4

484

485 ^{a)} Cell size (active area): 0.100 cm². Photovoltaic performance at 1000 Wm⁻² (AM1.5G) and constant scan speed of 10
486 mVs⁻¹ mesoscopic MAPbI₃ devices; ^{b)}with additives: 4-tert-butylpyridine (*t*BP) and Li-bis(trifluoromethanesulfonyl)-
487 imide (LiTFSI); ^{c)}An average device efficiency of a total of 40 devices for each Spiro-OMeTAD and QA derivatives,
488 respectively (Fig. S11, ESI†).

489

490 **Conclusions**

491 In summary, three novel small molecular hole transporting materials based on quinacridone
492 dye, namely **ACE-QA-ACE**, **TPA-QA-TPA** and **DPA-QA-DPA**, were designed, synthesized and
493 characterized successfully. For the first time, they were employed as dopant-free HTMs in the
494 mesoporous perovskite solar cells. In comparison with that of the standard doped Spiro-OMeTAD
495 (15.2%), the perovskite cells prepared using pristine newly developed **ACE-QA-ACE**, **TPA-QA-**
496 **TPA**, and **DPA-QA-DPA** HTMs yielded 18.2%, 16.6% and 15.5%, respectively under 1 sun
497 condition. The resultant devices of new HTMs exhibited negligible hysteresis. As a result of
498 avoiding the use of hygroscopic LiTFSI and TBP additives in our novel hole transport material,
499 the stability of non-encapsulated devices improved significantly vs that of doped Spiro-OMeTAD
500 under similar aging conditions. The champion devices using **ACE-QA-ACE** HTL achieved the
501 highest PCE and retained superior stability to other HTMs due to its higher hole mobility and
502 suitable energy levels. The outstanding result proves that the newly developed HTMs based on
503 quinacridone dyes can boost the efficiency and stability of perovskite solar cell devices.

504 **Experimental**

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

506

507 **Conflicts of interest**

508 There are no conflicts to declare.

509

510 **Acknowledgements**

511 H.D.P and S.M.J. share equal contribution for this work. H.D.P is thankful to QUT for offering
512 here QUTPRA scholarship to conduct his research work. Some of the data reported in this paper
513 were obtained at the Central Analytical Research Facility operated by the Institute for Future
514 Environments (QUT). Access to CARF is supported by generous funding from the Science and
515 Engineering Faculty (QUT). Author S. M. J. is thankful to Welsh assembly Government funded
516 Sêr Cymru Solar project, EPSRC grants [EPSRC Supergen SuperSolar Hub for an International
517 and Industrial Engagement Award](#) (Supergen Solar Challenge) and Marie-Curie COFUND
518 fellowship for financial support. The UKRI Global Challenge Research Fund project SUNRISE
519 (EP/P032591/1). S.M. is supported by the Ministry of Education of Singapore. Additionally, this
520 project has received funding from the European Union's Horizon 2020 research and innovation
521 programme under the Marie Skłodowska-Curie grant agreement No 663830. N.M. acknowledges
522 the support of the Queensland government via the Q-CAS funding scheme. P.S. is thankful to QUT
523 for financial support and to the Australian Research Council for the Future Fellowship grant
524 FT130101337.

525 References

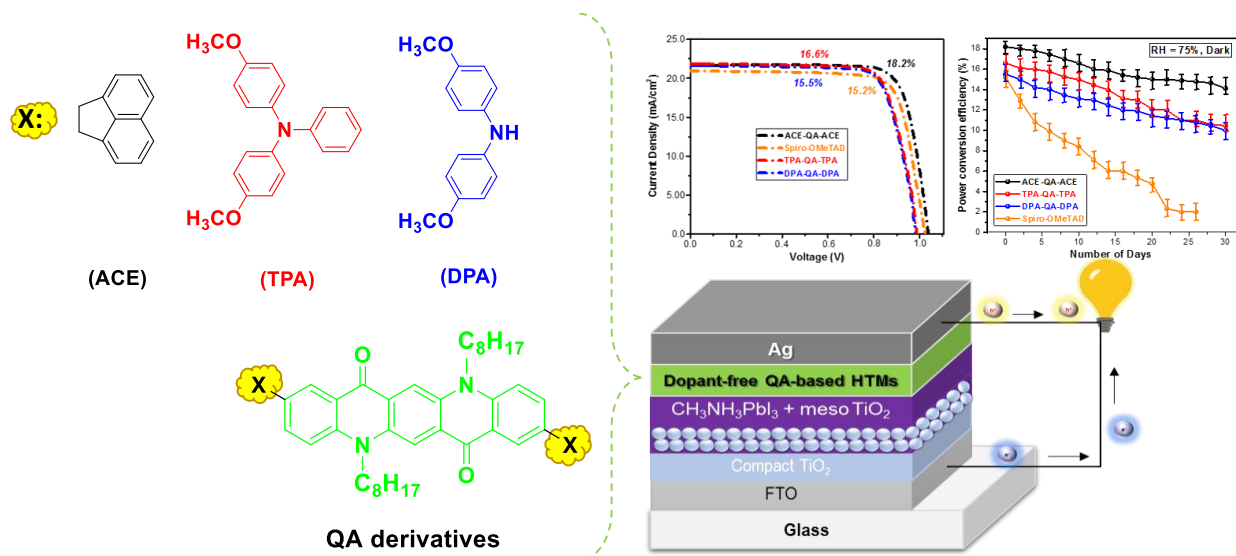
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- 628
- 629

630 **Table of Content Figure**

631 A series of novel pristine hole transporting materials-based quinacridone (QA) dyes is developed
 632 and fabricated in mesoporous perovskite solar cells in the first time. Among them, the devices
 633 using QA core with acenaphthylene (ACE) moieties as terminating units, namely ACE-QA-
 634 ACE, exhibits highest performance with 18.2% efficiency. The resultant devices show the
 635 outstanding efficiency of these new materials and superior stability compared to those of the
 636 standard doped Spiro-OMeTAD ones.



637