1. Introduction

The preliminary work of perovskite solar cells (PSCs) can be traced back to Miyasaka et al. using perovskite as a dye in dye-sensitized solar cells measuring 3.8% efficiency.\(^1\) Today, the improvement is remarkable with a 25.7% efficiency.\(^2\) This development is due to the unmatched properties of halide perovskites such as a broad absorption spectral range, a long carrier diffusion length, ambipolar charge transport, and solution processability.\(^3\)-\(^5\) These properties, along with ease of fabrication and low cost due to less material usage,\(^6\) make PSCs a promising technology on the way to decreasing carbon emissions.

On the other hand, the development of low-cost, efficient, and stable hole transporting materials (HTMs) is a prerequisite for the commercialization of PSCs. HTMs provide electron blocking and charge extraction at a perovskite/HTM interface, as well as transport holes to the electrode. Furthermore, in an n-i-p configuration, a HTM can increase the stability of a device by protecting the perovskite layer against humidity and oxygen.\(^7\)

2,2’,7,7’-tetrakis(N,N-di-p-methoxyphenylamine)-9,9’-spirobifluorene (Spiro-OMeTAD) is the HTM used par excellence in n-i-p type PSCs, but possesses low hole mobility in its pristine form.\(^8\),\(^9\) To improve its electrical properties, dopants and additives such as lithium bis(trifluoromethanesulfonylimide) (Li-TFSI), a cobalt complex, and 4-tert-butylpyridine (t-BP) have been commonly used. However, doping also accelerates the degradation of perovskite layers due to the hygroscopic nature of dopants and additives that decrease the long-term

Four symmetrically substituted and four asymmetrically substituted fluorinated and non-fluorinated-diarylmphthalocyanines have been designed and utilized as hole transporting materials in perovskite solar cells in a planar n-i-p structure. We established the correlation between the electronic structure, charge mobility parameters, core metal, and substituents in metal phthalocyanines. The fluorinated asymmetrically substituted undoped ZnPc-6 yielded the best power conversion efficiency of 15.40% with an open-circuit voltage (\(V_{oc}\)) of 1016.1 mV, a short-circuit current density (\(J_{sc}\)) of 21.27 mA cm\(^{-2}\), and a fill factor (FF) of 71.25%, followed by the non-fluorinated asymmetrically substituted ZnPc-5 with 14.36%. In the case of symmetrical CuPcs, the best performance was measured using non-fluorinated CuPc-3 and fluorinated CuPc-4 gave 11.53% and 10.90% of PCEs, respectively. Importantly, the devices with MPCs showed improved stability under multi-stress conditions.
stability of PSCs. It is of high research interest to develop dopant-free HTMs that can overcome the limitations of doped HTMs and are UV stable.

Phthalocyanines are synthetic analogs of porphyrins that stand out for their effective photochemical and electrochemical stability. Metal phthalocyanines (MPcs) have recently been used as HTMs in PSCs. Earlier, we reported ZnPc dimers as HTMs, which gave good performance and stability without the addition of dopants, owing to their extended electron delocalization and high charge mobility. On the other hand, the use of various metals, along with different peripheral and nonperipheral substituents, can modify the optical and electrical properties of MPcs and improve their solubility in conventional solvents. Recently, NiPc substituted with four methoxyethoxy groups has been reported and the devices also exhibited good moisture, thermal, and light stabilities.

On the other hand, arylamine groups, particularly triphenylamine (TPA) or diphenylamine (DPA) based compounds, have been extensively utilized as small-molecule HTMs in PSCs due to their excellent hole-transporting properties, electron-donor ability, high stability, and solubility. Reports on employing these groups as substituents for MPcs as HTMs are scarce and not well exploited. Nazeeruddin and co-workers reported PSCs with a PCE of 11.75% using doped DPA-substituted ZnPc. Similarly, a ZnPc having four peripheral TPA substituents in PSCs achieved a PCE of 5.6%. The photovoltaic performance of PSCs fabricated with doped OMe–DPA–CuPc (16.73%) and OMe–TPA–CuPc (19.67%) was compared, featuring four bis-(4-methoxyphenyl)amino substituents and four N,N-bis(4-methoxyphenyl)benzenamino substituents, respectively. Our group studied arylamine-based substituted MPcs as undoped HTMs in PSCs. Recently, it was found that the presence of fluorine atoms in phthalocyanines can up-shift the energy level of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and enhance interfacial charge transfer, this also improves the stability of a device due to the increased hydrophobic character that prevents the entry of moisture. Moreover, efforts to establish a direct relationship between the nature of a metal ion and the phthalocyanine substituents with electronic properties to optimize photovoltaic devices have not been reported. Moreover, in comparison, asymmetric structures tend to have excellent solubility and thermal stability and hold potential for application as HTMs. Yet, asymmetric HTMs have been relatively less studied to date compared to their symmetric counterparts.

In this work, we designed symmetrical and unsymmetrical substituted phthalocyanines to study the effect of the inclusion of fluorine atoms in the arylamino substituents and the variation of the central metal ion on the conductivity and hole mobility and their integration as HTMs in PSCs.

Syntecrical phthalocyanines, ZnPc-1 and CuPc-3, have four diphenylamine (DPA), while ZnPc-2 and CuPc-4 consist of four fluorinated diphenylamine (FDPA) substituents, respectively. In the case of asymmetric ones, ZnPc-5 and CuPc-7 contain one DPA unit and three tert-butyl groups while ZnPc-6 and CuPc-8, are substituted with one fluorinated DPA unit and three tert-butyl groups, which have worked well in previously reported PSCs. Using both families, we have prepared zinc and copper analogs (Fig. 1).

2. Results and discussion

Synthesis of MPcs

Phthalonitriles 1 and 2 were synthesized by a high-yield palladium-catalyzed substitution of 4-iodophthalonitrile with the corresponding secondary amine (Fig. 2). Phthalonitriles 1 and 2 were characterized by 1H-NMR and 13C-NMR spectroscopies. Synthesis of symmetrical MPcs was carried out by cyclotetramerization of the corresponding phthalonitrile (1 or 2) and Zn(OAc)$_2$ or CuCl$_2$ using DMAE as a solvent and DBN as
catalyst. After purification by silica gel column chromatography, ZnPc-1, ZnPc-2, CuPc-3, and CuPc-4 were obtained with a yield of 41%, 27%, 10%, and 10%, respectively. For the synthesis of asymmetrical MPcs, a statistical cyclotetramerization between 4-tert-butylphthalonitrile and the appropriate phthalonitrile (1 or 2) and zinc acetate or Cu(n) chloride was performed. After careful purification by silica gel column chromatography, ZnPc-5, ZnPc-6, CuPc-7, and CuPc-8 were obtained with 14%, 16%, 8%, and 8% yield, respectively. All MPcs were obtained as mixtures of regioisomers (Fig. 2). The yields obtained for copper phthalocyanines are lower because their purification is more difficult, in addition to the fact that copper exerts a worse template effect than zinc in the cyclotetramerization reaction. Asymmetrical MPcs yields are the lowest because all the possible statistical phthalocyanines are formed in the reaction and they must be carefully separated. All the new MPcs are highly soluble in organic solvents such as CHCl₃ and THF; however, they are not solubile in MeOH and hexane. The synthesized MPcs are quite stable and have melting temperatures typically above 300 °C without decomposition.

The ¹H-NMR spectra of ZnPcs in THF- d₈ showed well-defined aromatic and aliphatic signals. The ZnPc-1 spectrum shows six signals from the isoindole units between 9.2–8.6 and 7.6 ppm; regarding the aromatic chain, we can appreciate two multiplets from the phenyl groups between 7.4–7.0 ppm and a singlet from the methoxy groups at 3.86 ppm. The ZnPc-2 spectrum is not as well resolved as the other ZnPcs but we can still appreciate the peaks from the isoindole units a little shifted downfield compared with ZnPc-1. Furthermore, we observe a new peak at 7.2 ppm due to the loss of symmetry on the phenyl group by the fluorine atom (Fig. 3 and ESI†).

From the ZnPc-5 spectrum, the three isoindole units with the tert-butyl groups show three new signals between 9.5–9.2 and 8.3 ppm, a signal at 1.8 ppm from the tert-butyl group, and the peaks from the fourth isoindole unit are shifted downfield compared with ZnPc-1. The ZnPc-6 spectrum is equal to the one of ZnPc-5, except for the loss of symmetry on the phenyl group by the fluorine atom with a new peak at 7.2 ppm as occurs with ZnPc-2. (Fig. 3 and ESI†).

Characterization by NMR experiments could not be achieved for CuPcs due to the paramagnetic character of copper [ii]. Nevertheless, all MPcs were characterized using Fourier transform infrared spectroscopy (FT-IR), high-resolution-matrix-assisted laser desorption ionization time-of-flight mass spectrometry (HR-MALDI-TOF), and UV-vis absorption spectroscopy measurements.

We performed the FT-IR spectra using a KBr pellet (ESI†). From the different signals of the Pes, highlight the peaks at 1263, 1256, 1263, and 1258 cm⁻¹ of ZnPc-2, ZnPc-6, CuPc-4, and CuPc-8, respectively, corresponding to the C–F stretching of the fluorine atoms.

**Electro-optical and physical properties**

The UV-vis absorption spectra measured in DMF solvent show the commonly known Soret and Q bands, at around 350 nm and 600–780 nm, respectively. In addition, we can observe a charge transfer band at 500 nm for the symmetrical MPcs.

The Q bands of the MPcs are shown in Table 1. An increase in the molar extinction coefficient and a small hypsochromic shift are observed in phthalocyanines substituted with fluorinated amines. While, in the case of asymmetric Pcs, a large hypsochromic shift and a minor increase in the molar extinction coefficient can be seen as compared to their symmetric counterparts. Furthermore, we noted a decrease in the molar extinction coefficient when the metal ion is changed from Zn(II) to Cu(II) as well as a hypsochromic shift, which is higher in the symmetrical Pcs (Fig. 4a and b).

The electrochemical characterization was performed by cyclic voltammetry in dry DMF solvent and ferrocene was used as an external standard. The highest occupied molecular orbital energy levels (E_{HOMO}) were calculated from the equation: E_{HOMO} = −4.8 – E_{OX1}, where E_{OX1} is the first oxidation potential. The LUMO energy level (E_{LUMO}) was calculated by adding the optical band gap to the E_{HOMO} value. CuPcs showed lower E_{HOMO} levels compared to ZnPcs. A similar effect can be observed in the asymmetrical substituted Pcs, and with the addition of fluorine atoms to the Pcs. Symmetrical Pcs presented a smaller band gap. Nevertheless, they showed adequate E_{HOMO} energy values for hole extraction from the perovskite.

In a similar fashion, E_{LUMO} energy is appropriate to prevent the flow of the photogenerated electron and will avoid recombination at the perovskite-HTM interface.

In the absorbance spectra of the phthalocyanines deposited as a thin film, a general broadening of the bands and the

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Electro-optical properties of the different MPcs</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPc</td>
<td>Q band</td>
</tr>
<tr>
<td>ZnPc-1</td>
<td>733</td>
</tr>
<tr>
<td>ZnPc-2</td>
<td>726</td>
</tr>
<tr>
<td>CuPc-3</td>
<td>749</td>
</tr>
<tr>
<td>CuPc-4</td>
<td>740</td>
</tr>
<tr>
<td>ZnPc-5</td>
<td>692</td>
</tr>
<tr>
<td>ZnPc-6</td>
<td>690</td>
</tr>
<tr>
<td>ZnPc-7</td>
<td>697</td>
</tr>
<tr>
<td>CuPc-8</td>
<td>694</td>
</tr>
</tbody>
</table>
splitting of the Q-band can be appreciated, phenomena attributable to the formation of aggregates. The shorter wavelength peak is due to aggregate species and face-to-face stacking of the molecules, while the peak at longer wavelengths is due to monomeric species. This phenomenon can be noted in the case of the phthalocyanines CuPc-4, ZnPc-5, and ZnPc-6 (Fig. 5a).

In the perovskite/HTM absorption spectra deposited as a thin film, the contribution of the phthalocyanines to the absorption is observed, as expected, at wavelengths between 700 and 800 nm (Fig. 5b).

Photovoltaic performance of PSCs with MPcs as HTMs

PSCs were fabricated with a planar n–i–p structure of fluorine-doped tin oxide (FTO)/bl-TiO2/SnO2/perovskite/MPc/Au using different MPcs as HTMs to investigate the effect of the core metal and different substitutions on their photovoltaic performance (Fig. 6a). Owing to the superior optical absorption and higher stability, a triple-cation perovskite, with the chemical formula of Cs0.1(FA0.9MA0.1)0.9Pb(I0.9Br0.1)3 was deposited by antisolvent-assisted one step method.30 The concentration of each HTM was maintained at 10 mM for device fabrication. All layers in the device were deposited by the solution process except the gold anode, which is thermally evaporated. The current density–voltage (J–V) curves measured under the reverse scan of the PSCs based on symmetric (Fig. 6b) and asymmetric (Fig. 6c) MPcs are presented. The corresponding photovoltaic parameters derived from the graph are summarized in Table 2.

The reference device using undoped PTAA as HTM gave a PCE of 15.53% (Fig. S44, ESI†). Notably, among all the MPc-HTMs investigated here, the best PV performances were measured from Zn-based asymmetric Pcs, which are on par with the PTAA-based devices. In particular, the ZnPc-6 HTM yielded the maximum PCE of 15.40% with a Voc of 930.72 mV, 20.58 Jsc of 20.6 mA cm−2, and a FF of 66.06%. Contrary to Zn based Pcs, in case of CuPcs, the best efficiencies were noted from the symmetrical Pcs, in which CuPc-3 and CuPc-4 gave 11.53% and 10.90% of PCEs, respectively. A similar trend can be found from the statistical distribution of the PCE of different MPc-HTMs (Fig. 6d and Table S1, ESI†).

Moreover, the measured Jsc from the J–V curve decreases when the coordination metal Zn(II) is switched out for Cu(II). In general, the deeper HOMO state of the HTM relative to the perovskite’s valence band maximum (VBM) (−5.65 eV) would enable a rational energy alignment, which in turn will facilitate charge extraction; subsequently, the smaller the energy barrier between the perovskite and the HTL, the lower the recombination and minimum voltage (Voc) deficit will be.31,32 This behavior can be deduced...
from ZnPcs, where the deeper HOMO levels associated with ZnPc-5 and ZnPc-6 close to the VBM of the triple-cation perovskite facilitate a higher $V_{oc}$ when compared with a shallow HOMO level associated with ZnPc-1 and ZnPc-2. However, the $V_{oc}$ variation cannot be correlated to the HOMO state position of the Cu-based Pc series. This is per similar behavior of Zn- and Cu-based MPcs irrespective of their HOMO state position. Arguably, our finding suggests that the PCE not only depends on the symmetrical nature of the side chain of the MPc but also the metal species attached to it.

The external quantum efficiency (EQE) spectra of the symmetrical (Fig. 6e) and asymmetrical (Fig. 6f) MPc-based PSCs were recorded to examine the photoresponsivity. The integrated current density values are calculated as 19.05, 19.46, 18.65, 16.19, 19.0, 20.23, 14.88, and 16.36 mA cm$^{-2}$ for ZnPc-1, ZnPc-2, ZnPc-5, CuPc-3, CuPc-4, ZnPc-5, ZnPc-6, CuPc-7, and CuPc-8, respectively, which are consistent with the tendency of $J_{sc}$ obtained from $J-V$ curves. All MPc-HTMs exhibit a significant reduction in EQE at wavelengths over 600 nm, which is following the strong absorption band of MPcs in the range of 600–800 nm. The amount of current produced by the second pass of reflected light from the gold electrode can be dramatically reduced by this absorption corresponding to MPcs. Although all MPcs have B-band absorption in a lower wavelength region below 400 nm, the aforementioned effect cannot be seen for high-energy photons since the perovskite layer has a higher absorption coefficient at a shorter wavelength.

The reverse and forward scan $J-V$ profiles were recorded to uncover the hysteresis behavior of each MPc-HTM (Fig. S45 and S46, ESI†) and the hysteresis indices (HIs) are summarized in Table S1 (ESI†). We noted reduced hysteresis from the PSCs incorporating ZnPc-5 and ZnPc-6, though the high efficiencies were noted from ZnPc-2 and CuPc-3 in the symmetric MPc group they also feature considerable hysteresis. Table 2 summarizes the series resistance ($R_s$) and shunt resistance ($R_{sh}$), which were extracted from the slope at $V_{oc}$ and $J_{sc}$, respectively, from the corresponding $J-V$ curve. The device made with ZnPc-5 and ZnPc-6 exhibits a lower $R_s$ and a higher $R_{sh}$, both of which boost the FF and $V_{oc}$ of the PSC by reducing interfacial charge losses and non-radiative charge recombination in the device. Additionally, the stabilized $J_{sc}$ (Fig. 7a) was measured for the initial 300 s for PSCs with ZnPc-2, CuPc-3, ZnPc-5, and ZnPc-6 as HTMs at their maximum power point (MPP) under ambient conditions (40–60% at 28 °C), which is in agreement with $J_{sc}$ measured from their $J-V$ curves. Overall, the best PV performances were observed from ZnPc-6 > ZnPc-5 > ZnPc-2. We also studied the potential of these MPcs as HTL in inverted (p-i-n) PSC with an architect of FTO/MPC/perovskite/PC$_{60}$BM/BCP/Au. The p-i-n device based on ZnPc-2 as HTLs measured a

### Table 2. Performance summary of devices with different MPcs as HTMs

<table>
<thead>
<tr>
<th>HTM</th>
<th>Scan</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>$R_s$ (Ω)</th>
<th>$R_{sh}$ (kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnPc-1</td>
<td>RS</td>
<td>954.9</td>
<td>19.48</td>
<td>55.57</td>
<td>10.34</td>
<td>136.89</td>
<td>7.9</td>
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<tr>
<td>ZnPc-2</td>
<td>RS</td>
<td>930.7</td>
<td>20.58</td>
<td>66.06</td>
<td>12.66</td>
<td>72.10</td>
<td>15.5</td>
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<td>ZnPc-3</td>
<td>FS</td>
<td>932.2</td>
<td>20.48</td>
<td>61.36</td>
<td>11.71</td>
<td>100.42</td>
<td>12.0</td>
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<td>CuPc-3</td>
<td>RS</td>
<td>953.5</td>
<td>19.08</td>
<td>63.35</td>
<td>11.53</td>
<td>109.29</td>
<td>17.6</td>
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<td>946.4</td>
<td>19.12</td>
<td>47.52</td>
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<td>935.5</td>
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<td>70.46</td>
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<td>55.82</td>
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<td>20.55</td>
<td>73.28</td>
<td>15.53</td>
<td>52.15</td>
<td>17.3</td>
</tr>
<tr>
<td>FS</td>
<td>1023.0</td>
<td>20.47</td>
<td>73.90</td>
<td>15.48</td>
<td>53.60</td>
<td>10.0</td>
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</table>
PCE of 9.06% owing to $V_{oc}$ of 901.87 mV, $J_{sc}$ of 16.85 mA cm$^{-2}$, and FF of 59.59% followed by ZnPc-6 with a 5.53% of PCE (Fig. S50 and Table S2, ESI†). However, the ZnPc-5 in the p-i-n configuration yielded only a mere PCE of 3.88%. The observed low $J_{sc}$ values from p-i-n devices could be attributed to the higher optical absorption in the whole visible range of these MPCs before the light reaching to the active perovskite layer, hindering the generation of photo-charges in the perovskite layer.

The charge transport abilities of each MPc were investigated by measuring their conductivity and mobility values. The electrical conductivity ($\sigma$) was extracted from the $I–V$ (current–voltage) curve (Fig. 7b and c) of the device with the configuration of FTO/MPc/Ag along with the relation, $\sigma = (I/V)A$, where $d$ is the thickness of the HTM (avg. thickness of each MPc from the cross-sectional image of the hole-only device as shown in Fig. S51, ESI†) and $A$ is the active area of the devices.$^{34}$

The space-charge-limited-current (SCLC) measurements were performed to evaluate the hole mobility ($\mu$) of MPcs from semi-logarithmic $J_{0.5}–V$ curves (Fig. 7d and e) of the hole-only device (FTO/PEDOT: PSS/MPc/Ag) along with the Mott–Gurney equation.$^{35}$

$$J = \frac{9\varepsilon_0\varepsilon_d V_{app}^2}{8L^3}$$

The obtained values are summarized in Table S3 (ESI†). The highest conductivity was noted for fluorinated asymmetric ZnPc-6 with $1.268 \times 10^{-6}$ S cm$^{-1}$, which also exhibited the best PCE of PSCs. This was followed by ZnPc-2 with a conductivity value of $1.21 \times 10^{-6}$ S cm$^{-1}$ followed by ZnPc-5 with $1.05 \times 10^{-6}$ S cm$^{-1}$; however, their PCE values are not correlated.

Even though CuPc-7 and CuPc-8 show the highest mobility, they featured the lowest PCE. It is interesting to note that the conductivity and mobility values obtained from MPcs do not follow a similar trend of PCEs, suggesting that there is another reason apart from the symmetrical nature and the coordination metal in the MPc influences the PV performances. The lower values obtained in our synthesized MPcs compared with the already published diphenylamino substituted metallophthalocyanines$^{36}$ could be attributed to the effect of the alkox side chains influencing the molecular packing in the solid state of the HTMs, in a way that determined their ability to conduct charges and in the interaction with the perovskite layer.

To further understand photo-induced charge recombination in PSCs, we performed electrochemical impedance spectroscopy (EIS) under dark conditions for the PSCs with both symmetrical (ZnPc-2 and CuPc-3) and asymmetrical (ZnPc-5 and ZnPc-6) categories. The Nyquist plot (Fig. S52, ESI†) at different bias voltages from 0.85–1.05 V is fitted with the equivalent circuit of $R_s + R_{rec}/CPE$ (dots and continuous lines represent raw and fitted curves, respectively), where $R_s$ is the series resistance coming from the external circuit and $R_{rec}$ is the recombination resistance of the PSC. A constant phase element related to carrier diffusion in selective layers and perovskite is assigned as CPE. At a given potential bias, the ZnPc-6-based PSC features a much higher $R_{rec}$ (Fig. S53, ESI†), indicating that ZnPc-6 leads to lower charge recombination and mitigated charge annihilation at the perovskite/HTL interface, which is consistent with the observed reduced $V_{oc}$ losses in the PSC based on ZnPc-6.
The film-forming ability of any HTM is an important criterion to produce high-performance PSCs apart from the band alignment of the transport layer with the perovskite and their charge transportability. It is well known that non-covalent interactions between two or more phthalocyanine (Pcs) molecules cause their derivatives to aggregate, leading to their low solubility in the majority of solvents.37,38 We observed that Cu-based Pcs give poor solubility and make clusters with time in chlorobenzene, a solvent used for device fabrication. Thus, the likely cause of the PV underperformance seen in some MPcs could be attributed to a lesser degree of solubility and the molecular accumulation that prevent the efficient energetic coupling and introduce recombination centers, thus responsible for the lower PCE measured for PSCs. The film-forming ability and the uniformity of MPcs on the perovskite were examined using scanning electron microscopy (SEM) and the surface image (Fig. 8a–i) and the corresponding water contact angle of different HTMs deposited on the perovskite layer is presented. The best performance featured from the ZnPc-6 is ascribed to their uniform film-forming ability on the perovskite without any visible defects and pinholes, and this is further supported by a maximum water contact angle of 97 ± 1°. Further, ZnPc-5, CuPc-3, and ZnPc-2 show uniform film coverage on the perovskite with the water contact angles of 91 ± 1°, 94 ± 1°, and 93 ± 1°, respectively. Different from this, an inhomogeneous surface with pinholes and aggregated molecular clusters could be observed from the CuPc-7 and CuPc-8 samples, which also results in a lower water contact angle owing to the higher wettability of the defective surfaces. Even though CuPc-7 and CuPc-8 produce significantly higher mobility, their reduced homogeneity on the perovskite layer induces a possible shunting pathway as indicated by their lower shunt resistance value and non-radiative charge recombination at the perovskite/HTM interface. This might be the plausible reason for the low PV performance noted from PSCs based on these two MPcs.

We also studied the long-term operational stability of the un-encapsulated devices (ZnPc-5 and ZnPc-6) from the MPc series with reference PTAA device at their maximum power point (MPP) under ambient conditions (relative humidity of 45–60% and 300 K) under white LED light (Fig. 8j). While the PSCs based on ZnPc-5 showed stabilized current density just below 70% of its initial value after rapid performance degradation at the early stage of the experiment, ZnPc-6 performed better and showed a nearly linear response, holding around 70% of its initial current density for around 60 h. Particularly, the reference device based on pristine PTAA featured 70% of its original performance up to 30 h and speedy performance lost thereafter.

3. Experimental
Synthesis of phthalocyanines
All chemicals and solvents were purchased from Sigma Aldrich (Merck) and TCI and were used without further purification unless otherwise stated.
Lead iodide (PbI₂, 99.9%) was procured from Tokyo Chemical Industry (TCI). Other chemicals for perovskite were purchased from Greatcell Solar and employed without further purification. PTAA (Mn = 5000–15000 by GPC) was obtained from Xi’an Polymer Light Technology Corp. [60]PCBM >99.5% and Bathocuproine (BCP) were purchased from Solenne BC and TCI, respectively. Tin (IV) oxide, dissolved in H₂O colloidal dispersion, was obtained from Alfa Aesar. Chlorobenzene (CB, 99%), isopropanol (IPA, 99.9%), ethanol (EtOH, 99%), anhydrous dimethyl sulfoxide (DMSO, 99.8%), and N,N-dimethylformamide (DMF, 99.8%) were purchased from Acros Organics.

NMR spectra were recorded using a BRUKER AVANCE NEO 400 spectrometer. UV-vis spectra were recorded using a Perkin-Elsmer Lambda 35 spectrophotometer. Fluorescence spectra were recorded using a HORIBA scientific SAS spectrophotometer. High-resolution mass spectra were obtained using a Bruker Microflex LRF20 matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) using dithranol as a matrix. IR spectra were recorded using a Nicolet Impact 400D spectrophotometer. Voltammetry was measured in a conventional three-electrode cell using the supporting electrolyte. Platinum as the working electrode, (0.04 mmol) of RuPhos Pd G4, 18.6 mg (0.04 mmol) of RuPhos of 3-fluoro-4-methoxy-N-(4-methoxypheny)laniline, 33.8 mg (0.04 mmol) of RuPhos Pd G4, 18.6 mg (0.04 mmol) of RuPhos and 518.2 mg (1.59 mmol) of Cs₂CO₃ were dissolved in 10 mL of deaerated toluene and heated to reflux in argon atmosphere for 24 hours. After cooling down to room temperature, H₂O was added to the crude product and it was extracted with DCM two times, dried with Na₂SO₄, filtered, and concentrated. It was purified by column chromatography (Hexane:AcOEt/8:2) obtaining 238 mg (85%) as a yellow powder. ¹H-NMR (400 MHz, CDCl₃): δ = 3.83 (s, 3H), 3.91 (s, 3H), 6.90–6.95 (m, 6H), 7.04 (d, J = 2.5 Hz, 1H), 7.08–7.11 (d, J = 8.9 Hz, 2H), 7.44–7.46 (d, J = 8.8 Hz, 1H), ¹³C-NMR (100 MHz, CDCl₃): δ = 55.7, 56.7, 103.6, 114.5, 114.6, 115.0, 115.2, 115.9, 115.9, 116.6, 117.0, 119.8, 120.8, 122.5, 122.4, 128.3, 134.5, 136.8, 137.3, 137.4, 146.6, 146.7, 151.7, 152.0, 154.2, 158.6.

Synthesis of ZnPc-1
35 mg (0.10 mmol) of 1 and 9 mg (0.05 mmol) of Zn(OAc)₂ in 200 μL of DMAE and one drop of DBN under an inert atmosphere were stirred at 130 °C for 16 hours. The purple mixture was cooled at room temperature, concentrated under vacuum, and purified by column chromatography (Hex: Dioxane/55:45) yielding 15 mg of ZnPc-1 (43%) as a purple solid. ¹H-NMR (400 MHz, THF-d₈): (mixture of regioisomers), δ = 3.86 (d, J = 6.5 Hz, 2H), 7.03–6.97 (m, 16H), 7.37–7.28 (m, 16H), 7.60–7.54 (dd, J = 8.5, 1.8 Hz, 2H), 7.67–7.62 (dt, J = 8.4, 2.2 H, 2H), 8.70–8.67 (d, J = 12.5 Hz, 2H), 8.87–8.84 (dd, J = 11.0, 2.1 Hz, 2H), 8.96–8.92 (dd, J = 8.4, 5.3 Hz, 2H), 9.10–9.07 (dd, J = 8.4, 3.4 Hz, 2H). HR-MALDI-TOF (dithranol): m/z for C₈₈H₆₈CuN₁₂O₈: calculated 1483.4573 [M⁺]; found, 1483.4652. UV-vis (DMF) λmax/nm (log ε): 371 (4.77), 511 (4.14), 659 (4.47), 733 (5.13). FT-IR: ʋmax/cm⁻¹: 3038, 2995, 2950, 2907, 1604, 1507, 1487, 1440, 1396, 1332, 1272, 1242, 1180, 1089, 1036, 883, 826, 756, 667, 585, 524, 434. Mp > 300 °C.

Synthesis of ZnPc-2
50 mg (0.13 mmol) of 2 and 12.28 mg (0.07 mmol) of Zn(OAc)₂ in 500 μL of DMAE and one drop of DBN under an inert atmosphere were stirred at 130 °C for 16 hours. The purple mixture was cooled at room temperature, concentrated under vacuum, and purified by column chromatography (Hex: Dioxane/55:45) yielding 14 mg of ZnPc-2 (27%) as a purple solid. ¹H-NMR (400 MHz, THF-d₈): (mixture of regioisomers), δ = 3.86 (s, 12H), 3.92 (s, 12H), 7.40–6.9 (m, 32H), 7.65–7.62 (m, 4H), 9.05–8.74 (m, 8H). HR-MALDI-TOF (dithranol): m/z for C₈₈H₆₈Cu₂N₁₂O₈Zn: calculated 1556.4192 [M⁺]; found, 1556.4285. UV-vis (DMF) λmax/nm (log ε): 372 (4.87), 495 (4.24), 653 (4.58), 726 (5.25). FT-IR: ʋmax/cm⁻¹: 3058, 2999, 2952, 2908, 2835, 1606, 1507, 1488, 1398, 1333, 1263, 1243, 1181, 1089, 1032, 985, 828, 756, 664, 629, 584, 523, 437. Mp > 300 °C.

Synthesis of CuPc-3
200 mg (0.56 mmol) of 1 and 38 mg (0.28 mmol) of CuCl₂ in 500 μL of DMAE and one drop of DBN under an inert atmosphere were stirred at 130 °C for 16 hours. The purple mixture was cooled at room temperature, concentrated under vacuum, and purified by column chromatography (Hex: Dioxane/55:45) and washed with MeOH, yielding 20 mg of CuPc-3 (10%) as a purple solid. HR-MALDI-TOF (dithranol): m/z for C₈₈H₆₈CuN₁₂O₈: calculated 1483.4573 [M⁺]; found, 1483.4652. UV-vis (DMF) λmax/nm (log ε): 343 (4.88), 501 (4.35), 671 (4.49), 749 (5.02). FT-IR: ʋmax/cm⁻¹: 3059, 2995, 2929, 2832, 1605, 1506, 1404, 1338, 1272, 1241, 1179, 1094, 1035, 892, 826, 758, 589, 525, 424. Mp > 300 °C.
Synthesis of CuPc-4

100 mg [0.27 mmol] of 2 and 18 mg [0.13 mmol] of CuCl₂ in 500 µL of DMAE and one drop of DBN under an inert atmosphere were stirred at 130 °C for 16 hours. The purple mixture was cooled at room temperature, concentrated under vacuum, and purified by column chromatography (CHCl₃ : MeOH/99 : 1) and washed with MeOH, yielding 10 mg of CuPc-4 (10%) as a purple solid. HR-MALDI-TOF (dithranol): m/z for C₅₈H₅₂CuF₄N₂O₈: calecd 1555.4197 [M⁺]; found, 1555.4241. UV-vis (DMF) λ_max/nm (log ε): 346 (4.92), 498 (4.36), 666 (4.52), 740 (5.10). FT-IR: ν_max/cm⁻¹: 3059, 2998, 2932, 2834, 1607, 1506, 1404, 1339, 1263, 1243, 1181, 1093, 1032, 826, 758, 629, 524, 436. Mp > 300 °C.

Synthesis of ZnPc-5

90 mg [0.25 mmol] of 1 186.63 mg [1.01 mmol] of 4-tert-butylphthalonitrile and 92.92 mg [0.51 mmol] of Zn(OAc)₂ in 750 µL of DMAE and two drops of DBN under inert atmosphere were stirred at 130 °C for 16 hours. The blue mixture was cooled at room temperature, concentrated under vacuum, and purified by column chromatography (Hx : Dioxane/75 : 25) yielding 34 mg of ZnPc-5 (14%) as a blue solid. ¹H-NMR (400 MHz, THF-d₈): (mixture of regioisomers), δ = 1.80–1.77 (m, 27H), 3.89 (s, 6H), 7.08–7.04 (m, 4H), 7.43–7.39 (m, 4H), 7.73–7.71 (m, 1H), 8.30–8.20 (m, 3H), 8.96–8.92 (m, 1H), 9.21–9.27 (m, 1.5H), 9.40–9.32 (m, 3H), 9.54–9.50 (m, 2.5H). HR-MALDI-TOF (dithranol): m/z for C₅₈H₅₃N₉O₂Zn: calecd 971.3608 [M⁺]; found, 971.3896. UV-vis (DMF) λ_max/nm (log ε): 353 (4.71), 624 (4.41), 692 (5.14). FT-IR: ν_max/cm⁻¹: 3066, 2955, 2903, 2865, 2834, 1610, 1506, 1489, 1441, 1393, 1329, 1281, 1242, 1181, 1090, 1047, 922, 889, 829, 747, 693, 709, 576, 527, 445. Mp > 300 °C.

Synthesis of CuPc-7

90 mg [0.24 mmol] of 2 137.67 mg [0.75 mmol] of 4-tert-butylphthalonitrile and 88.45 mg [0.48 mmol] of Zn(OAc)₂ in 750 µL of DMAE and two drops of DBN under inert atmosphere were stirred at 130 °C for 16 hours. The blue mixture was cooled at room temperature, concentrated under vacuum, and purified by column chromatography (Hx : Dioxane/75 : 25) yielding 38 mg of ZnPc-6 (16%) as a blue solid. ¹H-NMR (400 MHz, THF-d₈): (mixture of regioisomers), δ = 1.80–1.77 (m, 27H), 3.89 (br, 3H), 3.95 (br, 3H), 7.09–7.06 (m, 2H), 7.20–7.17 (m, 3H), 7.43–7.39 (m, 2H), 7.79–7.74 (m, 1H), 8.31–8.21 (m, 3H), 9.00–8.97 (m, 1H), 9.25–9.19 (m, 1.5H), 9.40–9.33 (m, 3H), 9.55–9.51 (m, 2.5H). HR-MALDI-TOF (dithranol): m/z for C₅₈H₅₂CuFN₉O₂: calecd 1488.3519 [M⁺]; found, 1488.3596. UV-vis (DMF) λ_max/nm (log ε): 346 (4.89), 626 (4.52), 694 (5.19). FT-IR: ν_max/cm⁻¹: 3068, 2956, 2903, 2866, 1611, 1507, 1407, 1326, 1258, 1243, 1153, 1092, 1034, 930, 829, 749, 694, 530, 435. Mp > 300 °C.

Synthesis of CuPc-8

100 mg [0.27 mmol] of 2, 173 mg [0.94 mmol] of 4-tert-butylphthalonitrile and 72 mg [0.54 mmol] of CuCl₂ in 750 µL of DMAE and one drop of DBN under an inert atmosphere were stirred at 130 °C for 16 hours. The blue mixture was cooled at room temperature, concentrated under vacuum and purified by column chromatography (CHCl₃ : MeOH/99 : 5 : 0.5) and washed with MeOH, yielding 21 mg of CuPc-7 (8%) as a blue solid. HR-MALDI-TOF (dithranol): m/z for C₅₈H₅₂CuF₄N₂O₈: calecd 1970.3613 [M⁺]; found, 1970.3705. UV-vis (DMF) λ_max/nm (log ε): 345 (4.86), 628 (4.49), 697 (5.14). FT-IR: ν_max/cm⁻¹: 3060, 2954, 2902, 2833, 1614, 1506, 1406, 1325, 1282, 1241, 1181, 1092, 1038, 930, 827, 749, 671, 575, 530. Mp > 300 °C.

Device fabrication

n-i-p device. Following successive sonication with Hellmanex II (2 vol% in deionized water), deionized water, ethanol, acetone, and isopropanol, the laser-etched FTO-coated glass substrates (TEC15) were dried using compressed airflow. Before usage, the substrates underwent further treatment with UV-ozone for 30 minutes. Spray pyrolysis at 500 °C with 1/19 mL of titanium(Ⅳ) disopropoxide bis(acetylacetonate) precursor solution (75% in 2-propanol) in pure ethanol was used to produce a compact TiO₂ blocking layer onto FTO substrates. The electron transport layer (ETL) was fabricated using colloidal SnO₂ 2.67% water solution via spin coating at 5000 rpm for 30 s, followed by annealing at 180 °C for 1 h in air. Once cooled down to room temperature, the samples were transferred to the Argon-filled glovebox (H₂O level: <1 ppm and O₂ level: <10 ppm). C₆₀, (FA₆,MA₆)₀.₄₉PB₆₀ (FA₆,MA₆,Br₁)₉ perovskite precursor solution was prepared according to the previous report.²⁹ The perovskite precursor solution was spin-coated on the as-prepared SnO₂ ETL in an antisolvent-assisted two-step spin-coating program set at 1000 rpm and 6000 rpm for 10 and 30 s followed by annealing at 100 °C for 1 h to induce perovskite crystallization. 10 mM of each MPe-HTM in chlorobenzene was spin-coated on perovskite at 4000 rpm for 20 s at room temperature. Pristine PTA (10 mg ml⁻¹ in toluene) was spin-coated at 3000 rpm for 35 s to construct the reference device. ~70 nm gold electrode was evaporated (~1 Å s⁻¹) by thermal evaporation under low vacuum conditions below 10⁻⁶ Torr as a final electrode.

p-i-n device. The device was fabricated according to the previous report with modification noted herein.³⁹ 2 mM of each MPe-HTM in chlorobenzene was spin-coated atop the cleaned FTO substrates at 3000 rpm for 30 s. C₆₀, (FA₆,MA₆)₀.₄₉PB₆₀ (FA₆,MA₆,Br₁)₉ perovskite film was achieved as described previously. The PCBM solution of 15 mg ml⁻¹ in chlorobenzene...
was spin-coated at room temperature on perovskite film at 1000 rpm (500 rpm s\(^{-1}\)) for 20 s followed by annealing at 90 °C for 10 min. A thin layer of BCP (0.5 mg mL\(^{-1}\) in IPA) was deposited atop PCBM by spin coating at 5000 rpm for 40 s. The device fabrication was completed by evaporating Ag (100 nm, < 1 Å s\(^{-1}\)) in a thermal evaporator under low vacuum conditions (below 10\(^{-6}\) Torr).

Thin-film characterization and device characterization

To quantify absorption spectra, a Varian Cary 50 UV-vis spectrophotometer was used. We utilized field emission scanning electron microscopy to assess the surface microstructure (Hitachi S-4800). The current–density (J–V) curves were recorded using a Keithley 2400 source meter with a solar simulator (Newport, Oriel AAA solar simulator) under irradiation of 100 mW cm\(^{-2}\) (AM1.5). An NREL-certified calibrated monocrystalline silicon solar cell was used for the calibration. The generated photocurrent was recorded at a scan rate of 100 mV s\(^{-1}\) (pre-sweep delay: 10 s) and a 0.09 cm\(^2\) black metal mask was used as an active area of the devices. The external quantum efficiency (EQE) spectra were carried out using a BioLogic SP-300 impedance analyser in the frequency range of 2 MHz–1 Hz under the ac signal in a faradaic chamber, and the resulting data were fitted with EC-Lab software.

4. Conclusions

We have synthesized eight different arylamino MPcs, to provide a molecular guideline for the designing of MPcs as hole-selective materials for the fabrication of perovskite solar cells. We unravel the influence of the number of aryl amino groups, the presence of fluorine atoms, the central metal, and the symmetry of the molecule on photovoltaic performance. The incorporation of the fluorine atom into arylamino-substituted MPcs is an effective strategy for the performance and stability enhancement in perovskite solar cells. We noted that the PCE not only depends on the symmetrical nature of the side chain of the MPc but also the metal species attached to it. A higher conductivity is found for asymmetric fluorinated ZnPc-6 and it also translates into high PV performance suggesting the variation in the energy level of the perovskite impacts the PV performances apart from the symmetrical nature and the coordination metal in MPc.

Author contributions

A. H. and J. O. carried out the synthesis and characterization of all the compounds. N. H. H and A. H. S. K. performed the experiments, fabricated the devices, and analysed the data. A. H., J. O., and N. H. H prepared the initial draft. S. K., J. O., S. A., and A. S. S. supervised, drafted, and directed the research.

All authors contributed to the draft and prepared the final version.

Conflicts of interest

There are no conflicts to declare.

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