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Journal Pre-proof



Impact of peripheral groups on novel asymmetric phthalocyanine-based hole-transporting materials for perovskite solar cells

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Abstract:

Three novel asymmetrical substituted phthalocyaninecobalt with nitro and (4-butyl formate) phenoxy, (4-propenyl-2-methoxy) phenoxy or (4-methyl formate) phenoxy as different bulky peripheral groups (CoPcNO₂-OBFPh, CoPcNO₂-OPMPh, CoPcNO₂-OMFPh) are successfully developed and applied as dopant-free hole-transporting materials (HTMs) in perovskite solar cells (PSCs). The impact of the different peripheral groups on properties of these phthalocyanines is also investigated. For the modification of bulky aroxy peripheral groups, all of the three metallophthalocyanines exhibit good solubility, suitable hole mobility, high thermal stability, and appropriate HOMO and LUMO energy levels. The most effective device based on CoPcNO₂-OBFPh demonstrates an impressive power conversion efficiency (PCE) of 13.91% under AM 1.5G standard conditions, while CoPcNO₂-OPMPh and CoPcNO₂-OBFPh devices exhibit relative lower *PCE* of 11.81% and 9.47% respectively. In addition, CoPcNO₂-OBFPh-based PSC shows the best stability after 1008 h in air with 50% relative humidity at room temperature.

Key words: Hole transporting material; Perovskite solar cells; Long-term stability; Peripheral Groups, phthalocyanine

1. Introduction

As the most important natural sources, solar energy is widely studied in the renewable energy field. One of the most effective applications of solar energy is the conversion of solar energy into electricity. For the rapid improvement of device performance [1-4], perovskite solar cells (PSCs) have exhibited as a promising photovoltaic technology with skyrocketed photoelectric conversion efficiency and low-cost solution [5-9]. The high absorption coefficient with adjustable band gap [10], long carrier diffusion length [11], and ambipolar charge transport [12], make perovskite materials appropriate for light harvesting [13-14]. The best power conversion efficiency (*PCE*) of PSCs has achieved 25.2% recently [15].

The durability is an important factor for the application of PSCs. So, many researchers are devoted to the optimizing perovskite composition [16], tolerance factor [17-20], defect passivation [21] and device structures [22]. The hole-transporting material (HTM) of PSCs plays an important role in improving efficiency for the hole extraction. It serves as an effective electron blocking layer to retard charge recombination at the same time [23-25]. A superior HTM should be cost-effective, high-mobility and long-term stability (such as against light, moisture electrical bias, thermal and stress) [26-29]. Unfortunately, (2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD)), the most popular HTM of PSCs, suffers from the deficiencies of unsuitable for commercialization, because of high synthetic cost as well as photothermal and chemical instability [30-33]. Therefore, the replacement of Spiro-OMeTAD with more appropriate alternatives is very urgent.

Phthalocyanines, as attractive organic semiconductor materials, with prominent stability and high mobility, have been used as PSC HTMs [34-37]. But for the planarity of molecular configuration, phthalocyanine shows poor solubility in most organic solvents, unsubstituted phthalocyanine HTMs have to be prepared by vacuum deposition method [38-39]. The introduction of bulky peripheral groups to the phthalocyanine macrocycle, could enhance the solubility, reduce the aggregation, and adjust the HOMO and LUMO energies [40-42]. Subsequently, solution-processed spin coating phthalocyanine films have became possible in PSCs, meanwhile, the performance of PSCs is expected to be improved [43-44]. For phthalocyanine materials, different kinds of peripheral groups can lead to different π - π interaction and enhance their hole mobilities [45-46]. It is reported that [47], an alkoxy group of phthalocyanine can strengthen the electron donating ability, and thus ensure the HOMO level to be located above the valence band of perovskite. We have reported the cobalt (II) phthalocyanine with phenoxy and nitro groups as an efficient HTM in PSCs recently [48]. While, the influence of different peripheral groups on the cobalt (II) phthalocyanine based PSCs have not been studied. The optimization of phthalocyanine properties by substituents such as the mobility and energy levels are needed to be specified.

In this regard, the thermal, electrical and photophysical properties of cobalt (II) phthalocyanine were optimized by introducing peripheral groups of nitro with (4-butyl formate) phenoxy, (4-propenyl-2-methoxy) phenoxy or (4-methyl formate) phenoxy. The dopant-free PSCs with the newly synthesized phthalocyanines as

HTMs and Spiro-OMeTAD controlled device were made under the same conditions. An inspiring efficiency of 13.91% was achieved by the device with CoPcNO₂-OBFPh HTM. The long-term stability test of CoPcNO₂-OBFPh based device retained 75% of the initial efficiency for 1008 h in air of 50% relative humidity, much higher than the other two phthalocyanines. However, only 20% of the initial efficiency with Spiro-OMeTAD device was preserved at the same conditions. Such a noticeable improvement of the device's stability is convinced to be correlated to the extraordinary stability and moisture-proof performance of phthalocyanines. Therefore, this work demonstrated that more bulky substituent of phthalocyanines is preferred as the peripheral group for the design of efficient phthalocyanine HTMs.

2. Materials and methods

2.1. Materials

Materials of Co(OAc)₂·4H₂O, methyl 4-hydroxybenzoate, isoeugenol, butyl 4-hydroxybenzoate, 4-Nitrophthalonitrile and 1,5-diazabicyclo[4.3.0] non-5-ene (DBU) were provided by Aladdin; Spiro-OMeTAD was provided by Advanced Election Technology Co., Ltd. The substance for the preparation of solar cells, PbBr₂ and PbI₂ were purchased from TCI Corporation. 30NRT TiO₂ paste, FAI and MABr were obtained from Great Cell Solar. Patterned fluorine-doped tin oxide coated glass substrates (FTO) were received from Advanced Election Technology Co., Ltd.

2.2. Measurements

The structures of newly synthesized cobalt (II) phthalocyanines were characterized by IR, ¹H NMR spectra and MS. They were recorded on instruments of BIO-RADFIS3000 spectrophotometer, Varian 300 MHz spectrometer and matrix assisted laser desorption Ionization Bruker Autoflex TOF (III) (MALDI-TOF, 2,5-dihydroxybenzoicacid was used as matrix) respectively. Nicoet Evolution 300 spectrophotometer and Fluorolog-Horiba fluoromet were used for the measurement of optical properties in dimethylformamide (DMF) solvent. Q500 thermo gravimetric analyse (TGA) and Q20 differential scanning calorimeter (DSC) were used for the record of thermo properties. In the immersion-lens mode, scanning electron micrograph (SEM, XL30S-FEG) images were performed with 3 kV electron beam voltage and 3 nA current. The cells with an active area of 0.12 cm² were illuminated under 100 mW·cm⁻² (AM 1.5) by an Oriel solar simulator 91192, and the current density-voltage (*J-V*) curve was recorded on Keithley 2400 Source meter.

2.3. Preparation

2.3.1. Preparation of 4-aryloxy phthalonitrile

The intermediates of 4-(4-methyl formate) phenoxy phthalonitrile and (4-(4-butyl formate) phenoxy phthalonitrile were prepared and characterized as reported before [49]. 2-Methoxy-4-(2-propenyl) phenoxy phthalonitrile was obtained as follows. 4-propenyl-2-methoxy phenol (isoeugenol, 8.26 mmol, 1.354 g) and redistilled DMF (40 mL) were put in a two-neck round bottom flask. Under vigorously stirring,

4-nitrophthalonitrile (5.9 mmol, 1.021 g) was added and dissolved. Anhydrous potassium carbonate fine powder (8.26 mmol, 1.140 g) was added portion wise. The reaction was stirred at room temperature till 4-nitrophthalonitrile disappeared completely. The crude product was obtained by disposing the mixture into ice water and dealed with 1% sodium hydroxide for 12 h. The yellowish white product was obtained by recrystallization in methanol. Yield: 1.46 g, 85.6%, m.p. 74–76 °C. IR v_{max}/cm^{-1} (KBr pellet): 3069 (CHar), 2228 (C=N), 1592, 1510, 1481, 1410 (C=C), 1246 (Ph-O-Ar) (Fig. S1).

2.3.2. Preparation of 2,9,16-tri(4-(4-butyl formate) phenoxy)-23-nitrophthalocyaninatocobalt (CoPcNO₂-OBFPh)

In a four-necked round bottom flask, A mixture of 5.0 mmol 4-(4-butyl formate) phenoxy phthalonitrile (1.600 g), 1.7 mmol 4-nitrophthalonitrile 0.294 g) and 1.7 mmol Co(OAc)₂·4H₂O (0.423 g) with 40 mL n-octanol as solvent was put in a 100 mL four-necked round bottom flask. With stirring, catalyst (DBU 10 D) was added to the mixture under nitrogen protection. The reaction performed at the refluxing temperature of octanol for about 30 h till all of the phthalonitriles vanished by TLC detection. Absolute ethanol was introduced to the reaction mixture to precipitate the navy blue product. The crude product was washed by distilled water, ethanol and ethyl acetate respectively. Ethanol and CH₂Cl₂ (volume ratio: 1:30) were used as eluent for further purification of the crude product by column chromatography method. Yield: 0.646 g, 32.5%; IR v_{max} /cm⁻¹ (KBr pellet): 2923 (CHar), 1715 (C=O), 1605-1334 (C=C, Ph), 1269 (Ph-O-Pc), 1000-700 (C=C Pc) (Fig. S2); ¹HNMR (CDCl₃) δ ppm: 0.87 (m, 9H, CH₃), 1.57 (m, 6H, CH₂), 1.88 (m, 6H, CH₂), 3.69 (m, 6H, CH₂), 6.18 (m, 6H, Ph-H), 6.31 (m, 3H, Pc-H), 6.88 (m, 1H, Pc-H), 7.14 (d, 3H, Pc-H), 7.21 (d, 6H, Ph-H), 7.52 (d, 3H, Pc-H), 7.72 (d, 1H, Pc-H), 8.04 (d, 1H, Pc-H); MS (MALDI-TOF) *m/z*: Calc. 1192, Found: 1192.

2.3.3. Preparation of 2,9,16-tri(4-(4-propenyl-2-methoxy) phenoxy)-23-nitrophthalocyaninatocobalt (CoPcNO₂-OPMPh)

The black blue CoPeNO₂-OPMPh was synthesized and purified the same as CoPeNO₂-OBFPh by replacing 4-(4-methyl formate) phenoxy phthalonitrile with 5.0 mmol 2-methoxy-4-(2-propenyl) phenoxy phthalonitrile. Yield: 0.544 g, 29.6%; IR v_{max} /cm⁻¹ (KBr pellet): 2922 (CHar), 1598-1409 (C=C, Ph), 1238 (Ph-O-Pc), 1000-700 (C=C Pc) (Fig. S3); ¹H NMR (CDCl₃) δ ppm: 1.62 (m, 9H, CH₃), 3.63 (m, 9H, OCH₃), 4.92 (m, 6H, =CH₂), 6.22 (m, 6H, Ph-H), 6.40 (m, 3H, Pc-H), 6.96 (m, 1H, Pc-H), 7.21 (d, 3H, Pc-H), 7.31 (d, 6H, Ph-H), 7.36 (d, 3H, Pc-H), 7.88 (d, 1H, Pc-H), 7.91(d, 1H, Pc-H); MS (MALDI-TOF) *m/z*: Calc. 1102, Found: 1102. 2.3.4. Preparation of 2,9,16-tri(4-(4-methyl formate) phenoxy)-23-nitrophthalocyaninatocobalt (CoPcNO₂-OMFPh)

The synthetic and purified method of black blue CoPcNO₂-OMFPh was the same as CoPcNO₂-OBFPh only by replacing 4-(4-butyl formate) phenoxy phthalonitrile with 4-(4-methyl formate) phenoxy phthalonitrile (1.390 g). Yield: 0.476 g, 26.8%; IR v_{max} /cm⁻¹ (KBr pellet): 2926 (CHar), 1716 (C=O), 1597-1335 (C=C, Ph), 1272 (Ph-O-Pc), 1000-700 (C=C Pc) (Fig. S4); ¹H NMR (CDCl₃) δ ppm: 3.65 (m, 9H, CH₃), 6.12 (m, 6H, Ph-H), 6.25 (m, 3H, Pc-H), 6.91 (m, 1H, Pc-H), 7.11 (d, 3H, Pc-H), 7.31 (d, 6H, Ph-H), 7.60 (d, 3H, Pc-H), 7.82 (d, 1H, Pc-H), 8.10 (d, 1H, Pc-H); MS (MALDI-TOF) *m/z*: Calc. 1066, Found: 1066.

2.4. Perovskite Solar cell fabrications

PSCs were fabricated with the structure of FTO/TiO₂(compact) /TiO₂(mesoporous)/Perovskite/HTM/Au according to the reported methods [50]. A thin layer of CoPcNO₂-OBFPh, CoPcNO₂-OPMPh or CoPcNO₂-OMFPh and Spiro-OMeTAD as HTM (40 nm) was spin-coated on perovskite films. Under the same condition, Spiro-OMeTAD HTM based PSC was also fabricated for comparison.

3. Results and discussion

3.1. Synthesis and characterization



Scheme 1. Synthesis route of novel 2,9,16-triaryloxy-23-nitrophthalocyaninatocobalts.

Scheme 1 shows the synthesis route of 2,9,16-triaryloxy-23-nitrophthalocyaninatocobalts. In the solvent of redistilled DMF, 4-aryloxy phthalonitrile intermediates were obtained by the reaction of 4-nitrophthalonitrile and aromatic phenols at room temperature. The cobalt (II) phthalocyanines with different peripheral groups were prepared by the cyclopolymerization of 4-aryloxy phthalonitrile, 4-nitrophthalonitrile and $Co(OAc)_2 \cdot 4H_2O$ salt with the mole ratio of 3:1:1 under nitrogen atmosphere.



Fig. 1 The structure of cobalt phthalocyanine hole transport materials

The structure of 4-Aryloxy phthalonitrile intermediates and novel cobalt (II) phthalocyanine products (Fig. 1) were confirmed by IR, ¹H NMR and MS respectively. Generally speaking, phthalocyanines without peripheral substituents often show poor solubility and aggregation in common solvents [26]. While, the aryloxy substituents make the macromolecule's solubility increased apparently. CoPcNO₂-OBFPh, for the largest

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flexible butyl format, shows the best solubility in dichloromethane, tetrahydrofuran and dimethylformamide solvents. The methyl format has the lowest steric hindrance, CoPcNO₂-OMFPh shows the worst solubility of the three phthalocyanines. The isomers of aryloxy substituents on the different position of phthalocyanine rings will enhance their solubility by disrupting the crystalline order. Therefore, all of the synthesized cobalt (II) phthalocyanines were used for the following studies without further purification.

3.2. Physicochemical properties



Fig. 2 (a) UV-visible absorption spectra in DMF solution; (b) Photoluminescence spectra in DMF solution, excitation wavelengths: 627 nm for CoPcNO₂-OBFPh, 629 nm for CoPcNO₂-OPMPh and 620 nm for CoPcNO₂-OMFPh; (c) Photoluminescence spectra of different phthalocyanines on perovskite film, excitation wavelengths: 500 nm; (d) TRPL decay curves of perovskite film and perovskite films covered by phthalocyanine HTMs; (e) Hole mobility spectra; (f) Energy level diagram of perovskite solar cells with phthalocyanine HTMs

Table 1

The Q band UV-visible absorption data, photoluminescence quenching efficiency and hole mobility

	$\lambda_{ m absQ}$	ε _Q	ϕ^{a}	μ
HTMs	(nm)	$(\mathrm{dm}^3 \cdot \mathrm{mol}^{-1} \cdot \mathrm{cm}^{-1})$	(%)	$(cm^2 \cdot V^{-1} \cdot s^{-1})$
CoPcNO ₂ -OBFPh	674	3.88×10^4	91.50	9.92*10 ⁻⁵
CoPcNO ₂ -OPMPh	670	6.63×10 ⁴	59.83	8.21*10 ⁻⁵
CoPcNO ₂ -OMFPh	675	7.82×10^4	56.36	5.77*10 ⁻⁵

^a ϕ : Photoluminescence quenching efficiency, $\phi = [(I_o - I)/I_o] * 100\%$, I_o : Initial fluorescence intensity, I: Fluorescence intensity after quenching[51].

As shown in Fig. 2a, the appearance of intense B band at around 300 nm and Q-band at around 670 nm shoulder around 620 indicates together with а at nm the formation of novel 2,9,16-triaryloxy-23-nitrophthalocyaninatocobalts. In DMF solution, CoPcNO₂-OBFPh, CoPcNO₂-OPMPh and CoPcNO₂-OMFPh show excellent light absorption abilities in the NIR-infrared region. The Q band molar extinction coefficient (ε) is higher than 10⁴ dm³·mol⁻¹·cm⁻¹ (Table 1). All of the three phthalocyanines exhibit typical photoluminescence spectra with maximum emission peaks at 689, 684, 683 nm respectively (Fig. 2b, Table 1). CoPcNO₂-OBFPh displays the most intense PL intensity and the largest maximum emission wavelength for the largest (4-alkyl format) phenoxy substituents [52], while CoPcNO₂-OMFPh shows the weakest PL intensity and the least maximum emission wavelength for the smallest (4-methyl format) phenoxy substitutes.

Steady-state PL was employed for perovskite film and perovskite film coated by phthalocyanine HTMs. The PL intensity of perovskite layer with phthalocyanines HTMs (Fig. 2c) is quenched significantly than that of pristine perovskite films, indicating that phthalocyanines HTMs are effective in hole extraction. CoPcNO₂-OBFPh shows the greatest fluorescence quenching efficiency (ϕ) of 91.50%. The excellent π - π stacking of CoPcNO₂-OBFPh with bulky peripheral groups leads to the intimate contact of phthalocyanine with perovskite film, which makes the film have good interfacial quality and thus leads to the notable fluorescence quenching. The PSC based on CoPcNO₂-OBFPh as HTM will obtain excellent Jsc and FF. For the ϕ of CoPcNO₂-OPMPh (59.83%) is approximate to that of CoPcNO₂-OMFPh (56.36%), both of them maybe have the similar hole capture rate and thus lead to the similar PSC parameters. The time-resolved photoluminescence (TRPL) decay curve (Fig. 2d) shows a biexponential decay. The CoPcNO₂-OBFPh/perovskite, CoPcNO₂-OPMPh/perovskite and CoPcNO₂-OMFPh/perovskite film respectively show short-lived and long-lived lifetimes ($\tau_1 = 24$ ns, $\tau_2 = 61.1$ ns), ($\tau_1 = 58.6$ ns, $\tau_2 = 143$ ns) and ($\tau_1 = 61.1$ ns, $\tau_2 = 150$ ns) respectively. By contrast, the pristine perovskite film gave $\tau_1 = 91.4$ ns and $\tau_2 = 234.6$ ns. The TRPL decay times for the device mean that all of the three phthalocyaninies can extract the holes from the perovskite effectively. The least lifetime of CoPcNO2-OBFPh/perovskite confirms the fastest hole transport in the CoPcNO₂-OBFPh/perovskite film. While, the similar lifetimes of CoPcNO₂-OPMPh/perovskite and CoPcNO₂-OMFPh/perovskite indicate the similar hole transport ability of them. These are in great agreement with the photoluminescence quenching tests.

3.3. Hole mobility and thermal properties

In order to learn more about the nature of phthalocyanine HTMs, space-charge limited-current (SCLC) model [53] was used for the measurement of hole mobility (μ). As shown in Fig. 2e, hole mobility was calculated from the *J*-*V* curves by fitting to the Mott-Gurney law [54]. For the largest steric hindrance of bulky butyl formate group, CoPcNO₂-OBFPh shows the strongest electron donating effect, least molecular aggregation and therefore the highest μ of $9.92*10^{-5}$ cm²·V⁻¹·s⁻¹. While, Phthalocyanines with

4-(4-propenyl-2-methoxy) phenoxy groups (CoPcNO₂-OPMPh) and (4-methyl formate) phenoxy groups (CoPcNO₂-OMFPh) show relative lower hole motilities of $8.21*10^{-5}$ cm²·V⁻¹·s⁻¹ and $5.77*10^{-5}$ cm²·V⁻¹·s⁻¹ respectively. This is due to steric effects, larger peripheral groups decrease the conformational disorder and thus increase the hole mobility [55]. The high mobility could provide better charge transport capability and might be responsible for the increased *FF* and *J*sc in CoPcNO₂-OBFPh based-PSCs [56-57].

The stability and durability are important factors that influence the commercialization of PSCs. The stability of HTM determines the durability of devices directly. Thermo gravimetric analysis (TGA, Fig. S5) shows that CoPcNO₂-OBFPh, CoPcNO₂-OPMPh and CoPcNO₂-OMFPh exhibit 5% weight loss ($T_{5\%}$) at 309 °C, 390 °C and 394 °C respectively. Decomposition temperatures (T_d) of them are 386 °C, 405 °C, 400 °C respectively, suggesting that all of the three Pcs show more excellent stability than Spiro-OMeTAD [58]. There are 15 °C and 6 °C temperature difference (Δ_t) between $T_{5\%}$ and T_d for CoPcNO₂-OMFPh and CoPcNO₂-OMFPh is 77 °C, indicating that the bigger substituents on benzene ring will decomposed faster than the small ones in the high temperature zone.

In DSC spectra (Fig. S6), all of the three cobalt phthalocyanines show conspicuous peaks around 100 $^{\circ}$ C, which can be attribute to the gasification of water. Meanwhile, CoPcNO₂-OBFPh shows a significant endothermic peak around 140 $^{\circ}$ C, indicating that it can be kept amorphous in the process of device fabrication and measurement [59]. The subtle interplay between the peripheral groups with phthalocyanine rings leads to the difference of stability. The particular thermal stability shows that all of the synthesized phthalocyanines are fit for the application of HTMs.

Table 2

HTMs	XC	$T_{\rm d}^{a}$ (°C)	$HOMO^{b}(eV)$	$LUMO^{c}$ (eV)	E_{g}^{d} (eV)
CoPcNO ₂ -OBFPh		386	-4.95	-3.27	1.68
CoPcNO ₂ -OPMPh		405	-4.94	-3.25	1.69
CoPcNO ₂ -OMFPh		400	-4.96	-3.24	1.72

Thermal and energy level data of phthalocyanines

^a Decomposition temperatures.

^b Measured by photoelectron and CV spectra.

^c $|\text{LUMO}| = |\text{HOMO}| - |E_g|.$

^d Energy gaps calculated from the absorption thresholds (λ_{onset}).

Furthermore, the well-matched energy level between HTM and perovskite film could enhance the overall performance of PSC. Therefore, the energy level of HTMs was obtained by measurement of electrochemical properties with cyclic voltammetry (CV) method. The HOMO levels of CoPcNO₂-OBFPh, CoPcNO₂-OPMPh and CoPcNO₂-OMFPh are -4.95, -4.94 and -4.96 eV (Fig. S7 and Table 2), and the corresponding LUMO

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levels are -3.27, -3.25 and -3.24 eV respectively (Fig. 2f). All of the phthalocyanine HOMO levels are somewhat higher than that of perovskite layer [60]. Thus, hole extraction of all the novel phthalocyanine HTMs is convinced to proceed smoothly from energy level alignment analysis.

3.4. Photovoltaic performances



Fig. 3 Schematic structure of PSCs.



Fig. 4 (a) Cross-sectional SEM image; (b-e) SEM top-image of PSCs fabricated with different HTMs; (f) SEM top-image of perovskite

As reported before, PSC with the configuration of $FTO/TiO_2(compact)/TiO_2(mesoporous)/perovskite/HTM/Au$ was applied for the studying of the different bulkiness of phthalocyanine-HTMs on the performance of devices (Fig. 3) [61]. The cross-sectional scanning electron microscopy (SEM) image of PSC (Fig. 4a) shows a well-defined layer-by-layer structure. The

thickness of TiO₂ compact layer, TiO₂ mesoporous layer, perovskite capping layer, HTM, and gold electrode is determined as 30 nm, 200 nm, 400 nm, 40 nm, 80 nm, respectively (Fig. 4a, Fig. S8 and Table S1). It is reported that [62-63], PSC with poor coverage and rougher surfaces would increase the possibility of interfacial charge recombination, and lead to the decrease of hole extraction, thus result in the reducing of device-performances. Therefore, the photovoltaic performances could be improved by more efficient charge transport efficiency induced by fine PSC morphology with smoother surfaces [64]. SEM top-images of PSCs fabricated with different phthalocyanine and Spiro-OMeTAD HTMs are shown in Fig. 4b-f. CoPcNO₂-OBFPh exhibits a more uniform capping layer and has fewer pinholes on perovskite films than that of CoPcNO₂-OPMPh and CoPcNO₂-OMFPh, because bulky substituents are beneficial to molecular self-assembly and thus increase the π - π stacking of phthalocyanine molecules. Some apparent pinholes on the surface of doped CoPcNO₂-OMFPh may be the reason for the worse photovoltaic performances of corresponding devices.



Fig. 5 J-V hysteresis curves of PSCs with different HTMs (The scan direction is from backward to forward)

Under simulated AM 1.5G solar irradiation at 100 mW·cm⁻² (Fig. 5), the photovoltaic performances of the devices with phthalocyanine and Spiro-OMeTAD as HTMs were characterized by current voltage (*J-V*) measurements. The results are summarized in Table 3. For the prominent hole mobility and uniform PSC morphology, the optimized device with CoPcNO₂-OBFPh as HTM shows a best short-circuit current density (J_{SC}) of 20.88 mA·cm⁻², an open-circuit voltage (V_{OC}) of 1.03 V, a fill factor (*FF*) of 0.65, and most of all, a champion power conversion efficiency (*PCE*) of 13.91%. Compared to CoPcNO₂-OBFPh, the

CoPcNO₂-OPMPh-based PSC exhibits a reduced *PCE* of 11.81% with decreased photovoltaic-parameters (Voc of 0.97 V, Jsc of 20.13 mA·cm⁻², and *FF* of 0.60). CoPcNO₂-OMFPh based PSC shows the worst photovoltaic-parameters (Jsc of 19.57 mA·cm⁻², V_{OC} of 0.92 V, *FF* of 0.53, and *PCE* of 9.47%). The representative *J-V* characteristics and corresponding power conversion efficiency of Spiro-OMeTAD based were also recorded as comparison. As shown in Table 3, Spiro-OMeTAD shows a *PCE* of 19.60% with Voc of 1.12 V, Jsc of 22.69 mA·cm⁻², and *FF* of 0.77. The superior photovoltaic-parameters of CoPcNO₂-OBFPh could be attributed to the higher hole extraction efficiency, better device morphology, higher hole mobility than that of CoPcNO₂-OPMPh and CoPcNO₂-OMFPh.

Table 3

Photovoltaic parameters of different HTM-Based devices

-						
HTMs	$J_{ m SC}$	V _{OC}	FF	PCE	Hysteresis Index	
1111/15	$(mA \cdot cm^{-2})$	(V)	11	(%)	(%)	
CoPcNO ₂ -OBFPh (forward)	20.77	1.03	0.62	13.29	4.45	
CoPcNO ₂ -OBFPh (backward)	20.88	1.03	0.65	13.91		
CoPcNO ₂ -OPMPh (forward)	20.06	0.95	0.57	10.79	8.64	
CoPcNO ₂ -OPMPh (backward)	20.13	0.97	0.60	11.81		
CoPcNO ₂ -OMFPh (forward)	18.9	0.9	0.36	6.15	35.06	
CoPcNO ₂ -OMFPh (backward)	19.57	0.92	0.53	9.47		
Spiro-OMeTAD (forward)	22.73	1.08	0.72	17.65	9.9	
Spiro-OMeTAD (backward)	22.69	1.12	0.77	19.6		

It is reported that [65], the *J*-*V* hysteresis is strongly associated with the nature of the interface between perovskite and HTM layer. *J*-*V* hysteresis of devices with phthalocyanines and Spiro-OMeTAD as HTMs was tested both on forward and backward directions (Fig. 5). CoPcNO₂-OBFPh based on PSC shows the minimal *Hysteresis index* (calculated from equation 1, Table 3) of 4.45%, while CoPcNO₂-OMFPh shows the maximum of 35.06%. Hysteresis and hole mobility are opposite, because that higher hole mobility would be beneficial to hole extraction by reducing the charge accumulation at the interface of the solar absorber and HTM film, and thus lead to less *hysteresis* [66].

$$Hysteresis Index\% = \frac{P backwar - P forward}{P backward}$$
1

The incident photon-to-electron conversion efficiencies (*IPCEs*) of phthalocyanines and Spiro-OMeTAD based perovskite solar cells were also measured to obtain further effects of HTMs on device performance (Fig. 6a). The *IPCE* spectrum displays a wide spectra response in the range of 300 to 800 nm, yielding a broad *IPCE* plateau of around 80%. The *IPCE* values of CoPcNO₂-OBFPh, CoPcNO₂-OPMPh, CoPcNO₂-OMFPh and Spiro-OMeTAD are 20.72, 19.23, 18.06 and 22.01 mA·cm⁻² respectively. They are in great agreement with *J*sc

values of each corresponding PSC.



Fig. 6 (a) IPCE spectra; (b) The stability of PSC under simulated AM 1.5G solar irradiation at 100 mW \cdot cm⁻² without encapsulation; (c) The stability of PSC in air with 50% relative humidity without encapsulation.



3.5 The stability of PSCs

Fig. 7 Contact angles between perovskite/HTMs and water

As shown in Fig. 6b and 6c, long-term stability test of device based on these phthalocyanine HTMs was evaluated. Spiro-OMeTAD HTM based PSC was conducted as the control device for comparison. The stability under simulated AM 1.5G solar irradiation at 100 mW·cm⁻² was tested every 48 h for 240 h at room temperature without encapsulation. The efficiencies of the devices with CoPcNO₂-OBFPh, CoPcNO₂-OPMPh and CoPcNO₂-OMFPh retain 85%, 70% and 64% of the initial value. While, for the device with Spiro-OMeTAD HTM, only 47% of the initial efficiency is retained at the same conditions. However, the durability tests in air with 50% humidity at room temperature (dark state, every 72 h for 1008 h) without encapsulation shows that the efficiencies of the four corresponding devices retain 75%, 59%, 40% and 20% respectively. All of the phthalocyanine based devices represent more superior stability than Spiro-OMeTAD ones. Besides more chemical and thermal stability of phthalocyanines, the largely improved efficiency stability of phthalocyanines based PSCs are also contributed by the hydrophobic nature of phthalocyanine HTMs. As shown in Fig. 3, hydrophobic phthalocyanines films covered well on the surface of the devices that prevented the moisture-labile perovskite layer from being attacked by water. For the maximal contact angles of 91.87° (Fig. 7), CoPcNO₂-OBFPh shows the best hydrophobicity. The better hydrophobicity of phthalocyanines than Spiro-OMeTAD as the protective layer

of perovskite perovskite films.

4. Conclusions

In summary, three novel asymmetric cobalt (II) phthalocyanines (CoPcNO₂-OBFPh, CoPcNO₂-OPMPh and CoPcNO₂-OMFPh) with different bulky peripheral groups were synthesized. All of them show good solubility and high thermal stability. The suitable hole mobility, significant photoluminescence quenching on perovskite film, appropriate HOMO and LUMO energy levels of the three materials indicate good PSC prospect. The dopant-free PSCs based on these phthalocyanine HTMs show satisfactory solar cell performance. The most effective device based on CoPcNO₂-OBFPh with bulky substituents demonstrates an impressive photovoltaic-parameters with *PCE* of 13.91%, *V*_{OC} of 1.03 V, *J*_{SC} of 20.88 mA·cm⁻² and *FF* of 0.65 under AM 1.5G standard conditions. While CoPcNO₂-OPMPh and CoPcNO₂-OMFPh device exhibits relative lower *PCE* of 11.81% and 9.47% respectively. For the least pinholes and the largest contact angle, CoPcNO₂-OBFPh-based PSC shows the best efficiency stability through durability tests. These results ascribe to the fact that the more bulky substitutes are beneficial to molecular self-assembly and thus increase the π - π stacking of HTM molecules. As a result, suitable bulky substitutes are preferred for the developing phthalocyanine-based HTMs for efficient and stable PSCs.

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High lights

- Three Novel asymmetric cobalt phthalocyanines (CoPcNO₂-OBFPh, CoPcNO₂-OPMPh and CoPcNO₂-OMFPh) were synthesized
- They were applied in perovskite solar cells as hole transporting materials
- The *PCE* of the dopant-free device based on CoPcNO₂-OBFPh HTM is up to 13.91%
- The solar cell based on CoPcNO₂-OBFPh shows excellent stability in air at room temperature
- Phthalocyanine HTM with bulky substituent is more beneficial for the improvement of PSC performance

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Conflict of interest

The authors declare that we do not have any commercial or associative interest that represents a Le Wi Junjie Guo conflict of interest in connection with the work submitted.

Author statement

Junjie Guo designed the experiments, carried out the experimental study on device fabrication, and performed stability tests. Mengmeng Sun and Xianfang Meng synthesized and the purified the phthalocyanines. Hongwei Zhu, performed the MS and Hole mobility tests. Chao Ma, Shiyan Hu and Jiaqi Shen performed the Contact angles, SEM, PL, and CV test. Qian Wang performed the thermal perproties test and analyzed the data. Jinghan Gao performed the IR test. Junjie Guo wrote and reviewed the manuscript. All authors made a substantial contribution to the discussion of the content and reviewed and edited the manuscript before submission.