Pyridine Bridging Diphenylamine-Carbazole with Linking Topology as Rational Hole Transporter for Perovskite Solar Cells Fabrication

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Abstract

Developing low-cost and rational hole transporting materials is critical for fabricating high-performance perovskite solar cells (PSCs) and promoting their commercial endeavor. We have designed and developed pyridine (core) bridging diphenylamine-substituted carbazole (arm) small molecules, named as **2,6PyDANCBZ** and **3,5PyDAnCBZ**. The linking topology of core and arm on their photophysical, thermal, semiconducting and photovoltaic properties were probed systematically. We found that the **2,6PyDANCBZ** shows higher mobility and conductivity along with uniform film-forming ability as compared to **3,5PyDAnCBZ**. The PSCs fabricated with **2,6PyDANCBZ** supersede the performance delivered by Spiro-OMeTAD, and importantly also gave improved long-term stability. Our findings put forward small molecules based on core-arm linking topology for cost-effective hole selective layers designing.

Keywords: Carbazole; hole transport materials, perovskite solar cells, charge transport, electrooptical properties

1. Introduction

Organic-inorganic hybrid perovskite solar cells (PSCs) have attracted tremendous interests due to their power conversion efficiency (PCE) soaring from 3.8% to 25.2% in a decade. These achievements are attributed to distinctive opto-electrical properties of organic-inorganic perovskites, such as suitable direct band gap for sufficient utilization of solar energy and high charge mobility/long carrier diffusion length for effective photo-generated charge-carrier extraction and transportation.¹⁻⁵ In a typical PSC architect, perovskite layers is sandwiched between an electron / hole transporting material (ETM/HTM). Perovskite enjoys ambipolar characteristic, thus PSCs without hole selective layers can also yield competitive efficiency, but it is not sufficient for the fabrication of high performance PSCs, as in perovskite the holes are at low level.⁶ The HTMs act as pivotal roles in facilitating holes extraction and transportation, and help to retard the degradation of PSCs induced by H₂O and oxygen.⁷⁻¹⁰

Currently, 2,2',7,7'-tetrakis-(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD) is the most studied HTM for PSCs fabrication due to its optimized recipe, ease of implementation to fabricate high performance devices. Kim and Seok et.al independently reported PSCs employing Spiro-OMeTAD as an effective HTM to yield >24% efficiency.^{11,12} However, tedious synthesis process, expensive purification techniques, high cost, necessary hydrophilic dopants, additional post-oxidation step, and low charge carrier mobility of Spiro-OMeTAD significantly limit its large-scale commercial endeavor. Other alternatives, such as small-organic molecules, conjugated semi-conductive polymers, organometallic compounds, and inorganic *p*-type semiconductors, have been developed to replace Spiro-OMeTAD.¹³⁻¹⁵ Among them, small-organic molecules attracted widespread attention due to the choice of molecular building blocks, tunable semiconducting properties, purification and minimum batch-to-batch variation.¹⁶⁻¹⁹ A designed strategy to develop rational molecule is a powerful method to optimize and develop novel HTMs with excellent properties.

Various cores such as triazatruxene,²⁰ thiophene-based compounds,^{21,22} and carbocyclic moieties²³ have been reported as HTMs,¹⁴ but reports dealing with pyridine as a core for designing HTMs is scarce. The pyridine moiety in these HTM can act as a Lewis base and which in turn can assist defect passivation of perovskite and π -conjugation effect.^{24–28} Besides the core of HTMs, the arm is also vital for optimizing semiconducting properties of HTMs. Up to now, the bis(*N*³,*N*³,*N*⁶,*N*⁶-tetrakis(4-methoxyphenyl)-9*H*-carbazole-3,6-diamine) (DANCBZ) moiety have been demonstrated to be a useful arm for the design of small molecule based HTMs owing to their superior charge-transporting ability, stability and low-cost.^{29 30 31 32 33 34 3536}

More importantly, linking topologies in molecular designing is an effective method to fine-tune electro-optical properties of materials.^{37–41} For example, Sun *et al.* systemically studied the impact of linking topology of carbazole-based arm on basic properties, found that HTMs based on carbazole-based arm with 2,7-substitution display higher hole mobility and conductivity than that of HTMs with 3,6-substitution.⁴¹ While linking topology of core and arm are vital to determine properties of HTMs via developing continuous π -conjugation between core and arm, and tuning dihedral angles of small molecules, trivial attention has been made to the linking topology effect of core and arm. For example, Lee and co-workers synthesized two kinds of deep-blue emitter: 26BTPIPy with *meta*-linking and 25BTPIPy with *para*-linking, the front, and the corresponding device showed excellent performance because of relatively planar structure leading to considerable overlapping of its frontier molecular orbitals.³⁸ Recently, following core-arm linking topology, designing HTMs based on thiophene-arylamine and pyrene-arylamine have been investigated by Dai *et al.* and Wang *et al.*, respectively.^{39,40} Take materials with arylamine-pyrene core-arm as examples, PYP16 with 1,6-arm substitution possessed smaller dihedral angles, lower level of planarity, better film formation and a more polarized structure compared with PYP27 with 2,7-arm substitution, and then the device with PYP16 presented higher efficiency and long-term stability. To develop new HTMs with pyridine and better understanding the relationship between

chemical structure, chemical properties, and device performance, we reported the synthesis of two innovative molecules-based on pyridine few reported as core which is end-capped with common DANCZ as an arm. We further investigated the effect of the linking topology of core and arm on the properties of pyridine-based HTMs on the optoelectrical, thermal, semiconducting and photovoltaic properties in PSCs.

2. Results and discussion

2.1 Synthesis

The synthetic route for **2,6PyDANCZ** and **3,5PyDANCZ** is as outlined in **Scheme 1** and the details are described in the Supporting Information. *N*³,*N*³,*N*⁶,*N*⁶-tetrakis(4-methoxyphenyl)-9*H*-carbazole-3,6-diamine (**3**) was synthesized according to reported procedure.^{42–44} The Buchwald–Hartwig amination reaction of **3** with **2,6-dibromopyridine** resulted in the final desired product 9,9'-(pyridine-2,6-diyl)bis(*N*³,*N*³,*N*⁶,*N*⁶-tetrakis(4-methoxyphenyl)-9*H*-carbazole-3,6-diamine) **2,6PyDANCZ** with 46% yield. Similarly, the Buchwald–Hartwig amination reaction of **3** with **3,5-dibromopyridine** generated 9,9'-(pyridine-3,5-diyl)bis(*N*³,*N*³,*N*⁶,*N*⁶-tetrakis(4-methoxyphenyl)-9*H*-carbazole-3,6-diamine) **3,5PyDANCZ** with 50% yield. The molecular structures of **2,6PyDANCZ** and **3,5PyDANCZ** were confirmed by various spectroscopic techniques such as ¹H, ¹³C NMR spectroscopy and MALDI (supporting information). Both the small molecules are readily soluble in polar solvents such as dichloromethane, chloroform, ethyl acetate, 1,4-dioxane, *etc.*

Scheme 1. Molecular structures and synthetic route of **2,6PyDANCBZ** and **3,5PyDANCBZ**.

2.2 Opto-electrical, thermal, semiconducting and photovoltaic properties

The normalized UV-vis absorption spectra of **2,6PyDANCBZ** and **3,5PyDANCBZ** in dichloromethane at room temperature were investigated (**Figure 1a**) and the data are compiled in **Table 1**. The absorption of **2,6PyDANCBZ** and **3,5PyDANCBZ** HTMs containing pyridine displayed a peak maximum at 309 and 308 nm, respectively, which is attributed to the π - π^* electron transition of the large molecular conjugated system. The molecular structures of **2,6PyDANCBZ** and **3,5PyDANCBZ** exhibit absorption peaks in longer wavelength regions (350-400 nm) which could be due to the intramolecular charge transfer from donor to acceptor moieties. The relatively high intensity of shoulder band of **2,6PyDANCBZ** compared to that of **3,5PyDANCBZ** suggests that the **2,6PyDANCBZ** has a stronger charge transfer from the arm donor to the core acceptor unit. The onset absorption wavelengths (λ_{onset} , around 440 nm) of **2,6PyDANCBZ** and **3,5PyDANCBZ** are presented here. The optical bandgap ($E_{\text{g}}^{\text{opt}}$) of **2,6PyDANCBZ** and **3,5PyDANCBZ** were calculated to be around 2.82 eV from the equation ($E_{\text{g}}^{\text{opt}} = 1240/\lambda_{\text{onset}}$). The highest occupied molecular orbital energy level (E_{HOMO}) of

2,6PyDANCBZ and **3,5PyDANCBZ** were evaluated by cyclic voltammetry (Figure 1b). Both **2,6PyDANCBZ** and **3,5PyDANCBZ** exhibit reversible cyclic voltammograms and the oxidation cycle contain two reversible oxidation potentials corresponding to the formation of the radical cation of the carbazole moiety and the dication quinonediimine, respectively.⁴⁵ The corresponding E_{HOMO} values were estimated from the half-wave oxidation value ($E^{1/2}_{\text{ox}}$) of the first oxidation waves, considering 0.67 eV versus a normal hydrogen electrode (NHE) and 4.44 eV versus vacuum, by using the equation $E_{\text{HOMO}} = (E^{1/2}_{\text{ox}} + 0.67 + 4.44) \text{ eV}$ and the data are summarized in Table 1.^{40,46} Both the samples **2,6PyDANCBZ** and **3,5PyDANCBZ** exhibited similar E_{HOMO} level of -5.5 eV and -5.5 eV , respectively. The lowest unoccupied molecular orbital energy level (E_{LUMO}) was calculated from the equation ($E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g}}^{\text{opt}}$) to be -2.7 eV . Figure S1a shows the energy level diagram of fabricated device, where valence and conduction band of mixed-cation perovskite films is -5.9 and -4.4 eV , respectively,⁴⁷ illustrating that the presented HTMs are energetically favourable for hole transportation. More importantly, the large energy barrier between the conduction band of perovskite and E_{LUMO} of HTMs could efficiently block the undesired photo-generated electron transfer and particularly decrease charge recombination rate at the perovskite/HTM interface. The thermal stability of HTMs were evaluated by employing differential scanning calorimetry (DSC) measurements and suggested thermal stability (Figure 1c and Figure S2). The **2,6PyDANCBZ** and **3,5PyDANCBZ** exhibit a high glass transition temperature (T_{g}) of 132 and $126 \text{ }^{\circ}\text{C}$, respectively, which are higher than that of Spiro-OMeTAD.⁴⁸ This notable high T_{g} of both new HTMs would prevent crystallization process and keep them in an amorphous phase, indicating that these HTMs based PSCs may have an improved device performance.

Figure 1. (a) Normalized UV-Vis absorption spectra of **2,6PyDANCBZ** and **3,5PyDANCBZ** in dichloromethane. (b) Cyclic voltammetry of **2,6PyDANCBZ** and **3,5PyDANCBZ** materials. (c) Differential scanning calorimetry of seconding heating curves of **2,6PyDANCBZ** and **3,5PyDANCBZ** materials.

Table 1. Photophysical, thermal, and semiconducting characteristics of the new **2,6PyDANCBZ** and **3,5PyDANCBZ**.

HTM	$\lambda_{max}/\lambda_{onset}$ (nm)	E_g (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	T_g (°C)	Conductivity (μS cm^{-1})	Mobility ($10^{-4} cm^2 V^{-1} s^{-1}$) ^d
2,6PyDANCBZ	284/309/440	2.82 ^a /3.30 ^b	-5.5 ^a /- 4.28 ^b	-2.7 ^c /- 0.98 ^b	132	3.9	1.6
3,5PyDANCBZ	287/308/440	2.82 ^a /3.26 ^b	-5.5 ^a /- 4.34 ^b	-2.7 ^c /- 1.08 ^b	126	3.1	0.9

^a) E_{HOMO} is estimated with $E^{1/2}_{ox}$ versus the ferrocene redox couple (Fc/Fc^+) + 0.67 eV versus a normal hydrogen electrode (NHE; + 4.44 eV versus vacuum); ^b) DFT calculations of HTMs: $E_{LUMO} = E_{HOMO} + E_g$; ^c) $E_{LUMO} = E_{HOMO} + E_g$, and E_g estimated from the redox potential in cyclic voltammetry and UV-vis absorption spectra; ^d) HTMs without dopant.

We study the influence of linking topology of these HTMs on electrical properties, such as conductivity and charge carrier mobility. The conductivity (σ_0) was determined by measuring the linear current density-voltage (J - V) curve of the device with a simple structure (ITO/HTM/Ag) and calculated by the equation of $\sigma_0 = JdV^{-1}$. The J - V curves was tested under the dark and ambient condition as shown in **Figure 2a**. The conductivity values of undoped **2,6PyDANCBZ** and **3,5PyDANCBZ** were ~ 3.7 and $3.1 \mu S cm^{-1}$, these values increases to 5.5 and $4.7 \mu S cm^{-1}$ in the case of doped **2,6PyDANCBZ** and **3,5PyDANCBZ**, respectively. We noted slightly higher

conductivity of both **2,6-Py** and **3,5-Py** substituted based HTM in doped form. Space charge limited current (SCLC) method was used to evaluate hole mobility of the synthesized HTMs using hole-only device structure of ITO/PEDOT:PSS/HTM/Ag and J - V curves were tested under the dark and ambient condition as shown in **Figure 2b**. The hole mobility values of HTMs were calculated from the slope of the $J^{1/2}$ - V curves (Figure S3) according to Mott-Gurney law ($J=9\varepsilon\varepsilon_0\mu V_{\text{app}}^2/8L^3$) and the data were collected in Table 1. The calculated hole mobility values of undoped **2,6-Py** and **3,5-Py** substituted HTM were 1.4×10^{-4} and $0.9 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and doped **2,6-Py** and **3,5-Py** substituted HTM showed the increased mobility values of 2.0×10^{-4} and $1.2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ respectively, which is higher than that of the doped Spiro-OMeTAD ($< 5 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) reported.^{24,48,49} The conductivities and mobilities of 2,6PyDANCBZ are higher than those of 3,5PyDAnCBZ, whether dopants are employed or not.

Figure 2. (a) J - V curves from conductivity measurements (device structure: ITO/HTM/Ag) of the small molecules, (b) The J - V curves of the **2,6PyDANCBZ** and **3,5PyDANCBZ** HTM based hole-only device with structure: ITO/PEDOT:PSS/HTM/Ag. The inset depicts the enhancement in the current after doping.

To gain insight into the structural and electronic properties difference of the **2,6PyDANCBZ** and **3,5PyDANCBZ** compounds, density functional theory (DFT) calculations were performed at

the B3LYP/6-31G(d) level. The calculated frontier molecular orbitals are depicted in **Figure 3a** and the values are compiled in Table 1. The E_{HOMO} level is localized at donor DAnCBZ unit (arm) of pyridine-based HTMs, while the E_{LUMO} level is localized on acceptor pyridine unit (core). Especially, the E_{HOMO} and E_{LUMO} energy levels of **3,5PyDAnCBZ** are slightly stabilized as compared to E_{HOMO} and E_{LUMO} energy levels of **2,6PyDAnCBZ**. The theoretical determined E_{HOMO} levels of **2,6PyDAnCBZ** and **3,5PyDAnCBZ** are -4.28 eV and -4.34 eV whereas E_{LUMO} levels are -0.98 eV and -1.08 eV, respectively. The HOMO and LUMO are well separated allowing distinct intra-molecular charge transfer from the donor DAnCBZ arm to the acceptor pyridine core. In order to investigate the influence of linking topology on molecular structure, we calculate the representative dihedral angles between the pyridine core and DAnCBZ arm. As shown (Figure 3b), the **2,6PyDAnCBZ** with 56.76° and 35.95° dihedral angles owns a lower level of planarity as compared to **3,5PyDAnCBZ** with 46.61° and 38.58° dihedral angles, which reduces the molecular stacking and helps in the formation of uniform film in **2,6PyDAnCBZ**.^{50,51}

Figure 3. (a) Energy level diagram showing the HOMO and LUMO levels of **2,6PyDAnCBZ** and **3,5PyDAnCBZ** as determined at the B3LYP/6-31G(d) level and (b) dihedral angles of the **2,6PyDAnCBZ** and **3,5PyDAnCBZ** materials.

The film-forming abilities of the HTMs were investigated and perovskite/**2,6PyDANCBZ** image represents a uniform morphology while perovskite/**3,5PyDANCBZ** image present pinholes, which can be deduced by naked eye also (**Figure 4a**). Top surface scanning electron microscope (SEM) images of the perovskite covered with different HTMs (Figure 4b and 4c). It can be deduced that the perovskite/**3,5PyDANCBZ** film with pinholes and voids was rougher than perovskite/**2,6PyDANCBZ**. Arguably, the smooth nature of **2,6PyDANCBZ** film will enhance the interfacial contact between the perovskite and HTM layer, avoid direct contact of perovskite with electrode and improve the performance of corresponding devices. These results suggest that the linking topology on core and arm can significantly affect the film-forming abilities, although these HTMs have similar photophysical, electrochemical, thermal and electrical properties.

Figure 4. (a) Photos of perovskite covered with **2,6PyDANCBZ** and **3,5PyDANCBZ** films. SEM images of perovskite with **2,6PyDANCBZ** (b) and **3,5PyDANCBZ** (c) films.

2.2 Device performance

To elucidate the influence of side arm of HTM on the performance of PSCs, we fabricated planar devices with an architect of ITO/SnO₂/perovskite/HTM/Au, introducing **2,6PyDANCBZ**,

3,5PyDANCBZ and Spiro-OMeTAD as HTMs. Device schematic with HTM is shown in Figure S1b.^{7,8} The cross-sectional SEM image of devices with **2,6PyDANCBZ** and **3,5PyDANCBZ** (Figure 5a and 5b) depicts a conformably stacked structure, having a ~ 440 nm-thick perovskite film, and a thick film 127 nm of **2,6PyDANCBZ** and 113 nm of **3,5PyDANCBZ** film, respectively. Figure 5c and 5d illustrates the *J-V* curves of the champion PSCs with doped HTMs under AM 1.5G illumination (100 mW cm⁻²), and the detailed photovoltaic (PV) characteristic data are summarized in Table 2. The best device employing **2,6PyDANCBZ** under reverse voltage scan yields a high PCE of 17.78%, with a *V*_{oc} of 1061 mV, a short-circuit current (*J*_{sc}) of 22.13 mA cm⁻² and a fill factor (*FF*) of 75.7%, while the champion device with **3,5PyDANCBZ** shows a lower PCE 15.92%, with a *V*_{oc} of 1043 mV, a *J*_{sc} of 22.88 mA cm⁻² and a *FF* of 66.7%. As expected, **3,5PyDANCBZ** yields a lower efficiency than **2,6PyDANCBZ** and the higher efficiency performance of **2,6PyDANCBZ**-based device can be ascribed to high conductivity/mobility and favourable film morphology of **2,6PyDANCBZ**. The enhanced *FF* of **2,6PyDANCBZ**-based device can be attributed to the lower conductivity of the doped **3,5-Py** substituted HTM than the **2,6 Py** substituted one, thus increasing the series resistance of the film. The series resistance (*R*_s) and shunt resistance (*R*_{sh}) of **2,6PyDANCBZ** and **3,5PyDANCBZ** were calculated and shown in Table 2. **2,6PyDANCBZ**-based devices showed the lower *R*_s and higher *R*_{sh} of 27.8 Ω and 33.9 kΩ (*J-V* curves in RS condition), whereas **3,5PyDANCBZ** showed *R*_s and *R*_{sh} of 41.0 Ω and 12.2 kΩ, respectively. Subsequently, **2,6PyDANCBZ** yielded improved efficiency with high *FF*, which can be ascribed to the lower *R*_s and higher *R*_{sh}.^{16,52} Besides, the rough film morphology of **3,5-Py** substituted HTM result in worse interfacial contact and then lower *FF*. The average and detailed PV parameters are summarized in Table S1 and S2. To evaluate the performance of the devices with different HTMs, the stabilized power output tracking was evaluated and were 17.7% and 13.1% for PSCs based on **2,6PyDANCBZ** and **3,5PyDANCBZ**, respectively (Figure 5g), consistent with the efficiency obtained from *J-V* curves. The Spiro-OMeTAD-based device under the same

condition gave a PCE of 17.08% with a V_{oc} of 1053 mV, a J_{sc} of 21.63 mA cm⁻² and a FF of 75.0% (Figure 5e). Compared to the standard device, the relatively high performance of **2,6PyDANCBZ**-based device is in good accordance with the unique semiconducting properties and well-matched energy level. Figure 5f presents the external quantum efficiency (EQE) spectra and the integrated current density of corresponding PSCs. The integrated current density values of PSCs with **2,6PyDANCBZ**, **3,5PyDANCBZ** and Spiro-OMeTAD are 21.73, 21.62 and 21.16 mA cm⁻², respectively, which are in agreement with the J_{sc} value measured under the standard solar AM 1.5G.

The hysteresis index (HI) in devices were studied via measuring the J - V in forward scan (FS) and reverse scan (RS) direction. The **2,6PyDANCBZ**-based device gave low HI (0.033) as compared to Spiro-OMeTAD (0.060), the HI was calculated according to the following equation:

$$HI = [J_{RS}(0.8V_{oc}) - J_{FS}(0.8V_{oc})] / J_{RS}(0.8V_{oc}).^{10,53}$$

3,5PyDANCBZ-based PSC with slightly high HI (0.305) can be attributed to poor layer deposition. Notably, solar cells devices with **2,6PyDANCBZ** presented better performance than of Spiro-OMeTAD, and shows potential for its replacement as cost-effective materials. By further interface optimization and perovskites components tuning, we believe that the efficiency of **2,6PyDANCBZ**-based PSC devices with over 24% is reachable. More importantly, the inverted PSCs with architecture (ITO/HTM/perovskite/PC₆₁BM/BCP/Ag) were also fabricated. The device performance with different HTMs was shown in Figure 5h and Table S3 and the efficiencies of the device with **2,6PyDANCBZ** and **3,5PyDANCBZ** are 10.79% and 10.18%, respectively, which is comparable with those of common PEDOT:PSS (10.66%). In all, these results proved that **2,6PyDANCBZ** is a hopeful candidate for superseding common Spiro-OMeTAD for normal-structure device and PEDOT:PSS for normal-structure device, respectively.

Figure 5. Cross-sectional SEM images of the PSCs with 2,6PyDANCBZ (a) and 3,5PyDANCBZ, (b) $J-V$ hysteresis curves of forward and reverse scans under simulated AM 1.5G illumination for the champion normal architecture devices with different HTMs, (c) 2,6PyDANCBZ, (d) 3,5PyDANCBZ and (e) Spiro-OMeTAD and (f) EQE curves of

corresponding PSCs. (g) The stabilized power output of PSC devices with **2,6PyDANCBZ** and **3,5PyDANCBZ**. (h) J - V curves of the inverted-structure devices with different HTMs.

Table 2. Photovoltaic parameters of the PSCs with different HTMs.

HTMs	direction	V_{oc} (mV)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	R_s (Ω)	R_{sh} (k Ω)	HI
2,6PyDANCBZ	FS	1053	22.20	73.4	17.16	28.6	7.6	0.033
2,6PyDANCBZ	RS	1061	22.13	75.7	17.78	27.8	33.9	
3,5PyDANCBZ	FS	987	22.95	56.5	12.78	49.3	5.0	0.305
3,5PyDANCBZ	RS	1043	22.88	66.7	15.92	41.0	12.2	
Spiro-OMeTAD	FS	1060	21.69	69.8	16.05	27.9	5.8	0.060
Spiro-OMeTAD	RS	1053	21.63	75.0	17.08	31.7	18.0	

^a R_s and R_{sh} of PSCs with different HTMs were estimated by slope of the J - V curves near V_{oc} and J_{sc} , respectively.

Electrical impedance spectroscopy (EIS) analysis was conducted to understand the charge transport mechanisms (interface recombination, diffusion, *etc.*) of devices with pyridine-based HTMs. Figure S4 showed the typical Nyquist (Z' - Z'') (a and b) and Bode (a' and b') plots of impedance spectroscopy for the studied configurations under illumination at various photo voltages at open-circuit conditions. An equivalent circuit was used to extract information about recombination processes as shown in Figure S4a in the Supporting Information. The resistance and capacitance values are represented in **Figure 6**. By deriving the resistance and capacitance values from the equivalent circuit, we noted a difference in the slope in the recombination *vs* voltage graph. This can be explained⁵⁴ by the calculation of the ideality factor ($n=1/\beta$). The devices with **2,6PyDANCBZ** and **3,5PyDANCBZ** presented β values of 0.26 and 0.29, respectively, and the ideality factor increases from 3.45 to 3.85 when **2,6PyDANCBZ** was replaced by **3,5PyDANCBZ**. This suggest that **2,6PyDANCBZ** based-device reduces the recombination process as compared to **3,5PyDANCBZ**. Furthermore, **2,6PyDANCBZ**-based devices possess a lower capacitance value compared to **3,5PyDANCBZ**-based device. The relatively higher ideality

factor and lower capacitance values of **2,6PyDANCBZ**-based device resulted in an improved charge transportation ability and thus performance of devices.^{55,56}

Figure 6. (a) Resistive and (b) capacitive behaviours for **2,6PyDANCBZ** and **3,5PyDANCBZ**-based devices, as indicated, from the fitting of impedance spectroscopy spectra at different illumination intensities through open-circuit regime.

We further study the long-term stability of PSCs with different HTMs. The un-encapsulated devices were stored in a dry box (40-50% relative humidity, room temperature) and measured in an ambient condition. The PCE values of the devices with **2,6PyDANCBZ** and **3,5PyDANCBZ** maintained at 79.6% and 75.6% of their initial values after 5,500 h, respectively (**Figure 7**). In contrast, the efficiency of the device with Spiro-OMeTAD degraded to 70.5% of its initial value during this time. The result demonstrates PSCs with pyridine based HTMs shows improved device stability compared to Spiro-OMeTAD. The plausible reasons for improved stability are as follows: the perovskite/**2,6PyDANCBZ** and perovskite/**3,5PyDANCBZ** show a higher water contact angle of 91° and 86° compared to that of Spiro-OMeTAD (76°), the excellent hydrophobic nature of new HTMs can effectively block the water penetration into perovskite layers. Another supporting explanation is that the pyridine core of HTMs acts as a passivating agent for the perovskite layer and perovskite/HTM interface.^{57–59}

Figure 7. Plots of normalized PCE (a) of PSCs with different HTMs vs the storage time and (b) contact angle of perovskite with different HTMs films.

Developing cost-effective HTMs with excellent properties is an effective method to steeply decrease the cost of perovskite modules and can promote the commercialization of PSCs.⁶⁰ Our results suggest that the pyridine-based HTMs are competitive for high-performance PSCs fabrication. The cost of laboratory synthesis and purification of **2,6PyDANCBZ** and **3,5PyDANCBZ** is estimated, and the detailed cost calculations are shown in the supporting information. The cost of **2,6PyDANCBZ** and **3,5PyDANCBZ** is about 28.1 € and 27.0 € per gram, respectively, which is significantly lower than that of Spiro-OMeTAD (~ 400 € per gram, Sigma-Aldrich). Additionally, the optimal concentration of **2,6PyDANCBZ** (39.6 mg mL⁻¹) was almost half of Spiro-OMeTAD solution (72.3 mg mL⁻¹), this will further allow to achieve lower the material cost during device fabrication. (1.11 € per mL of **2,6PyDANCBZ** vs 21.7 € per mL of Spiro-OMeTAD solution), suggesting the usage of **2,6PyDANCBZ** as a promising candidate for hole extraction materials.¹³

3. Conclusion

We have developed pyridine bridging diphenylamine-carbazole as hole transporting layers for PSCs. We have systematically investigated the core-arm linking topology on optical and

electronic properties of novel HTMs. These results indicated that the **2,6PyDANCBZ** display higher conductivity due to stronger charge transfer from the arm donor to the core acceptor, and good film-forming ability. As compared to **3,5PyDANCBZ**, the fabricated PSCs with **2,6PyDANCBZ** shows improved performance, which supersede the performance of conventional Spiro-OMeTAD. Our results put forward design strategies for cost-effective and efficient hole transport materials, and also provide the guide principle on molecular design of core-arm linking topology.

Conflicts of interest

The authors declare no conflict of interest.

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Supporting Information

Detailed device fabrication and characterization, General experimental methods and ^1H and ^{13}C NMR and HRMS spectra of all the new compounds, cost calculations, computational results.

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