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

Peng Huang a,f, Manju c#, Samrana Kazim a,b, Gangala Sivakumar c, Manuel Salado a, Rajneesh Misra c*, and Shahzada Ahmad a,b*

a BCMaterials, Basque Center for Materials, Applications and Nanostructures, Martina Casiano, UPV/EHU Science Park, 48940 Leioa, Spain
Tel: +34 946128811 E-mail: shahzada.ahmad@bcmaterials.net;

b IKERBASQUE, Basque Foundation for Science, Bilbao, 48013, Spain

c Department of Chemistry, Indian Institute of Technology, Indore, India
Email: rajneeshmisra@iiti.ac.in

#: Equal contribution

Abstract

Developing cost-effective and rational hole transporting materials is critical for fabricating high-performance perovskite solar cells (PSCs) and to promote 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, electro-optical 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 bandgap 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 are sandwiched between an electron / hole transporting material (ETM/HTM). Perovskite enjoys ambipolar characteristic, thus PSCs without hole selective layers can also be fabricated, but it is not adequate for the fabrication of high performance PSCs, as in perovskite the holes are at low level.\(^6\) The HTMs play pivotal roles in facilitating holes extraction and transportation, and help to retard the degradation of PSCs induced by H\(_2\)O and oxygen.\(^7\)–\(^10\)

Currently, 2,2′,7,7′-tetrakis-(N,N-di-p-methoxyphenylamine)-9,9′-spirobifluorene (Spiro-OMeTAD) is the most investigated 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, additional post-oxidation step, and low charge carrier mobility of Spiro-OMeTAD significantly limit its large-scale commercial endeavor. 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 a rational molecule is a prevailing method to optimize and develop novel HTMs with excellent properties.
Various cores such as triazatruxene, thiophene-based compounds, and carbocyclic moieties have been reported as HTMs, but reports dealing with pyridine as a core for designing HTMs are 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. Besides the core of HTMs, the arm is also vital for optimizing the semiconducting properties of HTMs. Up to now, the bis(N3,N3,N6,N6-tetrakis(4-methoxyphenyl)-9H-carbazole-3,6-diamine) (DANCBZ) moiety have been demonstrated to be a valuable arm for the designing of molecular HTMs owing to their superior charge-transporting ability, stability and low-cost.

More importantly, linking topologies in molecular designing is an effective method to fine-tune electro-optical properties of materials. 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. 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 types 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. Using core-arm type linking topology, HTMs based on thiophene-arylamine and pyrene-arylamine was investigated by Dai et al. and Wang et al., respectively. Considering arylamine-pyrene core-arm as an example, PYP16 with 1,6-arm substitution possessed reduced dihedral angles, lower level of planarity, improved film formation and polarized structure as compared to PYP27 with 2,7-arm substitution. By doing so, the devices with PYP16 presented higher efficiency and stability. To develop pyridine based HTMs and understanding the relationship between structural and chemical properties, and its influence on
device performance, we report the synthesis of two innovative molecules-based on pyridine as core which is end-capped with common DANCBZ as an arm. Such structures have not been designed and investigated to date. We further investigated the effect of the linking topology of core and arm on the properties of pyridine-based HTMs on the opto-electrical, thermal, semiconducting and photovoltaic properties in PSCs.

2. Results and discussion

2.1 Synthesis

The synthetic route for 2,6PyDANCBZ and 3,5PyDANCBZ 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)-9H-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)-9H-carbazole-3,6-diamine) 2,6PyDANCBZ 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)-9H-carbazole-3,6-diamine) 3,5PyDANCBZ with 50% yield. The molecular structures of 2,6PyDANCBZ and 3,5PyDANCBZ were confirmed by various spectroscopic techniques such as \(^1\)H, \(^{13}\)C 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 conjugate 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 donor arm 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_{g}^{opt}) of 2,6PyDANCBZ and 3,5PyDANCBZ were calculated to be around 2.82 eV from the equation (E_{g}^{opt} = 1240/λ_{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 voltammogram 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. The corresponding $E_{\text{HOMO}}$ 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 $E_{\text{HOMO}} = (E^{1/2}_{\text{ox}} + 0.67 + 4.44)$ eV and the data are summarized in Table 1. Both the samples 2,6PyDANCBZ and 3,5PyDANCBZ exhibited similar $E_{\text{HOMO}}$ level of $-5.5$ eV. The lowest unoccupied molecular orbital energy level ($E_{\text{LUMO}}$) was calculated from the equation ($E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g opt}}$) 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, illustrating that the presented HTMs are energetically favourable for hole transportation. More importantly, the large energy barrier between the conduction band of perovskite and $E_{\text{LUMO}}$ of HTMs could efficiently block the undesired photogenerated 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 (Figure 1c and Figure S2). The 2,6PyDANCBZ and 3,5PyDANCBZ exhibit a high glass transition temperature ($T_g$) of 132 and 126 °C, respectively, which are higher than that of Spiro-OMeTAD. The notable high $T_g$ shown by HTMs will prevent any phase change process, suggesting the functioning of devices in the temperature window required for commercial validation.
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 ($\mu$S cm$^{-1}$) | Mobility ($\times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$) |
|-----------|-------------------------------------|-----------|----------------|----------------|-----------|----------------------------------|---------------------------------------------|
| 2,6PyDANCBZ | 284/309/440                        | 2.82$^{a,b}$/3.30$^{b}$ | -5.5$^{a,b}$/4.28$^{b}$ | -2.7$^{a,b}$/0.98$^{b}$ | 132       | 3.9                              | 16                                          |
| 3,5PyDANCBZ | 287/308/440                        | 2.82$^{a,b}$/3.26$^{b}$ | -5.5$^{a,b}$/4.34$^{b}$ | -2.7$^{a,b}$/1.08$^{b}$ | 126       | 3.1                              | 9                                           |

$^aE_{HOMO}$ 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: $E_{LUMO}=E_{HOMO} + E_g$; $^cE_{LUMO} = E_{HOMO} + E_g$ and $E_{HOMO}$ and $E_g$ estimated from the redox potential in cyclic voltammetry and UV–vis absorption spectra, respectively; $^d$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 ($\sigma_0$) was determined by measuring the linear current density-voltage ($J$-$V$) curve of the device in 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 $\sim$ 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 $1.6 \times 10^{-4}$ and $0.9 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, and doped 2,6-Py and 3,5-Py substituted HTM showed the increased mobility values of $2.0 \times 10^{-4}$ and $1.2 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively, which are higher than that of the doped Spiro-OMeTAD ($< 5 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$) reported$^{24,48,49}$ The conductivities and mobilities values of 2,6PyDANCBZ are higher than of 3,5PyDANCBZ, in both doped as well as undoped form.

![Graph](image)

**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 3**a and the values are compiled in Table 1. The $E_{\text{HOMO}}$ level is localized at donor DAnCBZ unit (arm) of pyridine-based HTMs, while the $E_{\text{LUMO}}$ level is localized on acceptor pyridine unit (core). Especially, the $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ energy levels of 3,5PyDANCBZ are slightly stabilized as compared to $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ energy levels of 2,6PyDAnCBZ. The theoretical determined $E_{\text{HOMO}}$ levels of 2,6PyDANCBZ and 3,5PyDANCBZ are –4.28 eV and –4.34 eV whereas $E_{\text{LUMO}}$ 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.](image)
The film-forming abilities of the HTMs were investigated and perovskite/2,6PyDANCBZ represents uniform microstructure while perovskite/3,5PyDANCBZ showed pin-holes, which can also be visualized by the naked eye (Figure 4a). Surface top view images acquired through scanning electron microscopy (SEM) experiments of the perovskite covered with different HTMs are illustrated in Figure 4b and 4c. It can be deducted 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. Our 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) Visual image of perovskite covered with 2,6PyDANCBZ and 3,5PyDANCBZ films, b) SEM images of perovskite with 2,6PyDANCBZ and c) 3,5PyDANCBZ.

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 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 illustrate the $J$-$V$ curves of the PSCs fabricated with developed HTMs under AM 1.5G illumination (100 mW cm$^{-2}$), and the detailed photovoltaic (PV) parameters 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 device with 3,5PyDANCBZ gave a relatively lower PCE of 15.92%, with a $V_{oc}$ of 1043 mV, a $J_{sc}$ of 22.88 mA cm$^{-2}$ and a $FF$ of 66.7%. Expectedly, 3,5PyDANCBZ yielded a lower PCE than 2,6PyDANCBZ and this is ascribed to its high electrical properties and favourable microstructures. Subsequently, it also gave enhanced $FF$ due to higher conductivity of the doped 2,6 Py than 3,5-Py substituted one, thus decreasing the series resistance of the film. The series resistance ($R_s$) and shunt resistance ($R_{sh}$) of 2,6PyDANCBZ and 3,5PyDANCBZ were shown in Table 2. The 2,6PyDANCBZ-based device showed the lower $R_s$ and higher $R_{sh}$ of 27.8 $\Omega$ and 33.9 k$\Omega$ ($J$-$V$ curves in RS condition), whereas 3,5PyDANCBZ showed $R_s$ and $R_{sh}$ of 41.0 $\Omega$ and 12.2 k$\Omega$, respectively. Subsequently, 2,6PyDANCBZ yielded improved PCE with high $FF$, which is due to the lower $R_s$ and higher $R_{sh}$.$^{16,52}$ Besides, the rough microstructure of 3,5-Py substituted HTM leads to unfavourable interfacial contact, which also lowers the $FF$. 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 $J$-$V$ curves. The Spiro-OMeTAD-based device under the same condition gave a PCE of 17.08% with a $V_{oc}$ of 1053 mV, $J_{sc}$ of 21.63 mA cm$^{-2}$ and a $FF$ of 75.0% (Figure 5e). The relatively high performance of 2,6PyDANCBZ-based device is in accordance with the improved semiconducting properties and aligned 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 was studied via measuring the $J-V$ in the 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:

$$HI = \frac{J_{RS}(0.8V_{oc}) - J_{FS}(0.8V_{oc})}{J_{RS}(0.8V_{oc})}.$$ \cite{10,53}

3,5PyDANCBZ-based PSC with slightly high $HI$ (0.305) can be attributed to poor uniformity. Notably, PSCs with 2,6PyDANCBZ presented improved performance than of Spiro-OMeTAD, suggesting its potential as a cost-effective replacement. By further interface optimization and perovskites components tuning, we believe that the PCE of 2,6PyDANCBZ-based PSCs can be substantially improved to achieve state of the art. Further, we have also fabricated the inverted PSCs with architecture (ITO/HTM/perovskite/PC$_{61}$BM/BCP/Ag). The device performance with different HTMs was shown in Figure 5h and Table S3 and the PCE of the PSCs with 2,6PyDANCBZ and 3,5PyDANCBZ are 10.79% and 10.18%, respectively, which is comparable with those of classical PEDOT:PSS (10.66%). Suggesting the suitability of 2,6PyDANCBZ as a competitive candidate to supersede the conventional Spiro-OMeTAD.
Figure 5. Cross-sectional SEM images of the PSCs with a) 2,6PyDANCBZ and b) 3,5PyDANCBZ; J-V hysteresis curves of forward and reverse scans under simulated AM 1.5G illumination for the champion n-i-p devices with different HTMs, c) 2,6PyDANCBZ, d) 3,5PyDANCBZ and e) Spiro-OMeTAD, (f) EQE curves of corresponding PSCs (n-i-p), g) The
stabilized power output of PSCs with 2,6PyDANCBZ and 3,5PyDANCBZ and h) $J$-$V$ curves of the inverted-structure ($p$-$i$-$n$) 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) | $R_{sh}$ (kΩ) | 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         |      |

$^aR_s$ 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 S4a,b showed the typical Nyquist ($Z' - Z''$) and Bode (a’ and b’) plots of impedance spectroscopy for the studied configurations under illumination for different photovoltages. An equivalent circuit was used to extract information about recombination processes as shown in Figure S4a. The resistance and capacitance values are represented in Figure 6. From the equivalent circuit used we derived the resistance and capacitance value, and noted variance in the slope in the recombination vs voltage graph. This can be explained by the calculation of the ideality factor (n=1/$\beta$). The PSCs with 2,6PyDANCBZ and 3,5PyDANCBZ presented $\beta$ values of 0.26 and 0.29, respectively, and the ideality factor increases from 3.45 to 3.85 when 2,6PyDANCBZ was substituted with 3,5PyDANCBZ, suggesting 2,6PyDANCBZ based PSCs reduces the recombination process as compared to 3,5PyDANCBZ. Furthermore, 2,6PyDANCBZ based PSCs illustrated lower capacitance value compared to 3,5PyDANCBZ. The relatively higher ideality factor and lower capacitance values of 2,6PyDANCBZ-based PSCs will allow to improve charge transportation ability and thus enhanced performance of PSCs.
Figure 6. a) Resistance and b) capacitance plots for 2,6PyDANCBZ and 3,5PyDANCBZ-based PSCs. Derived from the fitting of impedance spectroscopy spectra at different illumination intensities through open-circuit regime.

We studied 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 performance of PSCs 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 as 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 developed 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 of a) PSCs with different HTMs vs the storage time and b) contact angle of perovskite with different HTMs.

Developing cost-effective HTMs with excellent properties is an effective methodology to lower the cost of PSCs modules to promote the commercialization. Our results suggest that the pyridine based HTMs are competitive candidates 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.

3. Conclusion

We have designed pyridine bridging diphenylamine-carbazole as hole transporting layers for PSCs. We systematically investigated the core-arm linking topology on the optical and electronic properties of developed HTMs. Our results suggest that the 2,6PyDANCBZ display higher
conductivity due to stronger charge transfer from the donor arm to the core of the acceptor, and uniform film-forming ability. As compared to 3,5PyDANCBBZ, the fabricated PSCs with 2,6Py substitution showed improved performance when integrated into PSCs, and supersede the performance of conventional Spiro-OMeTAD. Our results put forward new design strategies for cost-effective and efficient hole transport materials, and also provide the guiding principle on the molecular design of core-arm linking topology.

**Author Contributions**

P.H. made the experiments, fabricated the devices and prepared the initial draft, Manju synthesized the molecules and made chemical analysis, S.K. performed all the electro-optical measurements, G.S. performed DFT calculation, M.S. performed impedance spectroscopy, R.M. supervised the work of Manju and G.S. and analyse the data, S.A. supervised and directed the research.

**Conflicts of interest**

The authors declare no conflict of interest.

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**Supporting Information**

Device fabrication and characterization methodology, general experimental methods and 1H and 13C NMR and HRMS spectra of the developed compounds, cost calculations.
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