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Advancements in pyridine-based charge transporting materials for perovskite solar cells

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Abstract

The utilization of pyridine derivatives for their donor-acceptor nature has seen an impressive serge in research community over the globe. As these materials offer a variety of applications, ranging from thermally activated delayed fluorescence, organic solar cells, organic light emitting diodes (OLEDs) to even perovskite solar cells (PSCs). These derivatives are well-established as excellent electron transporting materials (ETMs) with better quantum and current efficiency, mainly due to excellent thermal stability of pyridine-based OLEDs devices. Pyridine derivative based hole transporting materials (HTMs) also gained a widespread popularity as charge carriers in PSCs devices. Due to lower quenching of triplet state, uniform thin-films fabrication and low operating voltage, these devices exhibit durable longevity. In this review, we try to connect the structural characteristics and the optoelectrical properties of pyridine-derivatives in PSCs devices. During this journey, we try to highlight recent advancements in designing and synthesizing techniques of pyridine-based derivatives for their improved donor-acceptor nature and their utilization as in HTMs. Those dopants and additive free HTMs could acts as Lewis's acid-base adduct (LABA) in PSCs assembly, where HTMs interacted with metal-iodide and borane-compound to introduced an interface of metal-iodide/HTMs to boost selectivity towards holes in the device.

Keywords: Pyridine Derivatives; Organic Light Emitting Diodes (OLEDS); Perovskite Solar Cells (PSCS); Hole Transporting Materials (HTMS); Lewis's Acid-Base Adduct (LABA)

1. Introduction

The demand of energy and energy harvesting technique faced an unsettling rise in last few decades, this uprising crisis is one of the biggest factor to developing new and efficient energy-technologies.[1–3] In this trend, optoelectronic technologies based devices, such as phototransistors, OLEDs, and PSCs achieved a remarkable place for themselves in this next-generation energy harvesting technology race.[4–6] With tuneable nature and fabrication ease, PSCs devices immerged as phenomenal power conversion devices with standout efficiencies for vast variety of chemical compounds.[7–8] The semiconducting materials of these devices are vital part of the efficient working and the feasible fabrication of these material provides essential mobilities of charge carriers in the devices. Organic semiconducting materials functioned as excellent charge carrier transporter that allowed the recombined process of hole and electron pair with better efficiency to maximize radiative emissions of the process. Extensive research of decades and wide-open opportunity in organic material suggests that there is huge scope of redesigning and synthesizing such organic compounds with higher electron and hole count in material to improve efficient PSCs.[9–13] When voltage applied through the fabricated device, the thin-single layered organic material layer emits light through recombination process.[14–18] This light emitting process might get disturbed in case of imbalanced charge carriers counts, with exceeding numbers of holes than electrons in materials, that results in insufficient efficiency of devices because of restricted charge mobilities

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and reduced recombination rate of charge carriers.[19-23] This structural imperfection of PSCs was improved with the addition of extra layer of electron transporting materials. These charge transporting layers of electrons (electron transport layer, ETL) and/or holes (hole transporting layer, HTL) fabricated over transparent conducting oxide (TCO) classified these PSCs devices into inverted (p-i-p) or normal (n-i-n) PSCs devices.[24]

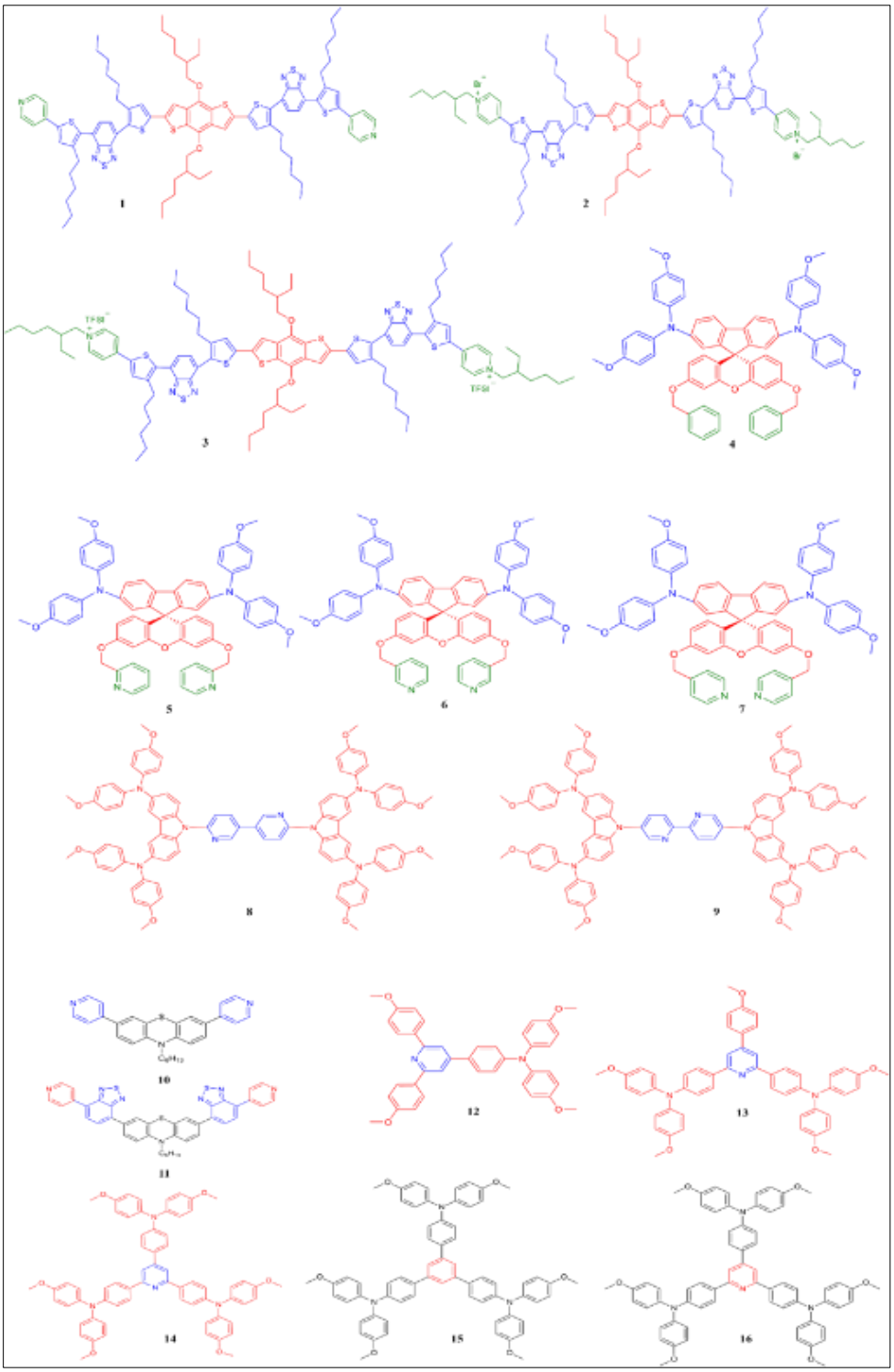

Figure 1 Structure of Pyridine-derivatives based organic compounds utilized as HTMs in PSCs devices (1-16)

The trapping of holes in HTL considered to be one of the pivotal features of these material and we can be understood this from that the highest power conversion efficiency (PCE) for PSCs without HTL is only 20.0% lies far behind the standard PCE of HTL modified PSCs devices for energy harvesting.[25] The appropriate frontier HOMO and LUMO levels

and compatible band gap of HTMs with respect to perovskite layers exhibit excellent hole extraction and minimize the potential loss in these devices to further enriching charge transportation through these layers. Spirobifluorene derivative 2,2',7,7'–Tetrakis[N,N–di(4–methoxyphenyl)amino]–9,9'–spirobifluorene (C81H6-8N4O8), also known as spiro-OmeTAD, is one of the most explored HTM material for PSCs devices fabrication till date, yet it displays an excellent PCE of 25% still the long synthetic route with tedious and costly purification with lower yield make it undesirable for the first choice.[26] Furthermore, it required additional p-dopants, like cobalt(III) complexes, 4-tertbutylpyridine (TBP) and bis(trifluoromethane) sulfonamide lithium salt (LiTFSI), to enrich the hole mobility and conductivity of material, as in the natural state Spiro-compounds accounts very low hole mobility and charge conductivity.[27–30] Although this improved conductivity and better mobility of holes came with significant downsizing, as it compromise the thin film fabrication of PSCs devices results in destabilizing the functionality of entire device.

To address this shortcoming, scientific world has had explored a range of chemicals starting from organometallic complexes to semiconducting inorganic compounds and even small organic molecules to conducting polymers for the betterment of PSCs devices.[31–36] Out of all these explored options, pyridine came out as an exciting option with wide range of possibilities to modification and tunability. As pyridine is a heterocyclic ring that has electron-deficient nature with good wate solubility mainly due to phenomenal H-bonding capacity. Owning to these facts, derivatives of pyridine display excellent conducting properties in various optoelectronic devices. The discovery of polypyridine vinylidene (PPyV) and polypyridine (PPy) by Yamamoto et al, in 1994, was landmark start of utilizing the n-type charge carrier properties of these derivatives.[37] Soon after these developments, a variety of multifunctional pyridine base derivatives were introduced as excellent ETM for advancement in device fabrication with better external quantum efficiency (η_{ext}), via developing improved ETL that has more efficient hole/exciton blocking layers in it. Furthermore, refine tuning to the HOMO energy levels of those pyridine-based derivative was achieved through introducing extra-heterocyclic rings to parent ring. This approach worked well for improving for hole mobility as well as for electron transportation of those materials in PSCs devices. This introduction of extra hetero-ring came with additional electron density from peripheral conjugation system and that came handy when we consider these pyridine-derivatives for electron and hole transporting materials. The interesting combination of pyridine based HTM/ETM produces an efficient methodology to design better photovoltaic devices. The non-hygroscopic HTM in PSCs are better p-dopants relative to hygroscopic, as wet materials compromise stability and quantum efficiency.[38]

This review highlights the recent development on pyridine-derivative based charge transporting materials for PSCs devices and we try to put an outline for the plausible changes in these derivatives for future development in the PSCs devices. During this process, we emphasize the importance of pyridine derivatives based small organic molecules and polymers as charge transporting materials with enhanced charge manoeuvrability. The effect of inter- and intra-molecular interactions in the fabricated thin layers and the classification of those derivatives purely based on linkage sites was considered during this literature survey, so that a better understanding of structure-property relation of electrochemical and thermal properties corelated with photophysical observation in these systems.

2. Pyridine derivatives as Hole Transporting Materials in Perovskite Solar Cells

Over the time, civilizations judged to be advanced or primitive, based on the resources of energy utilized for their energy requirements. In this modern era renewable energy sources are gaining a large chunk of energy consumption and the scientific community working on betterment of existing methodology is need of hours for humankind. Utilization of infinitely available solar energy is one of the hottest topics in modern science that yield in variety of solar cells to harness solar energy. The perovskite-materials based photovoltaic devices emerged as most exciting materials for solar energy harnessing.[39-40] Although these devices exhibit excellent PCE and quantum efficiency, the presence of toxic materials, such as Sn and Pb, in perovskite moieties leads to safety concerns. Using small organic molecules or conducting polymers offers better and safer alternative of these toxic materials in perovskite moieties. Furthermore, small molecules like pyridine and pyridine-based derivatives act as charge transporting materials, all due to their finely tuned bandgap and intermolecular as well as intramolecular interactions for efficient charge mobility.[41] In an organic material-based PSCs, organic HTMs exhibits one of most crucial roles of enhancing charge carriers' mobility and reducing device degradation over the working time. Furthermore, the construction of these PSCs devices started with the fabrication of hole transporting materials as thin film, HTLs, on a transparent conducting oxide (TCO) in normal (n-i-p) PSCs device. This set-up was introduced to perovskite layer, to merge HTL in between perovskite layer and TCO, followed by an electron transporting material as a thin film, ETLs. Lastly this fabricated device was connected to conductive contact, to finally construct the normal PSCs photovoltaic device. Meanwhile, the position of HTLs and ETLs were swapped with each other's position in case of inverted (p-i-n) PSCs devices. Both the ETL and HTL are integral parts of the fabricated device, but hole transportation layer (HTL) effect more than anything else in these devices and the utilization of pyridine derivatives-based materials for HTL offers a marginal difference over other materials. This can be seen that the electron deficiency of heterocyclic pyridine ring and free lone pair of nitrogen in the ring provides

an extra edge to these materials in PSCs devices to counter-balance holes and electron imbalances. It is well established that pyridine based HTM achieved around 20% PCS in traditional set-up of PSCs devices, without any additional p-dopants.

Cheng and co-workers synthesize three pyridines based HTMs and utilized these organic molecules in the PSCs devices.[42] They end-caped a benzodithiophene (BDT) core, which is substituted with ethylhexyloxy units, with pyridine to yield HTM 1 whereas HTM 2 and 3 were synthesized with ionized pyridine derivatives. HTM 1 in dichloromethane (DCM) solution display sharp absorption peaks in UV-Visible spectrum in a range of 300 to 600 nm and the effect of ionization is observed as red shift of 50 nm for HTM 2 and 3. This change hooked peripheral-conjunction of cations, and their absorption peaks reflect in this red shift in those three HTMs. The HOMO-LUMO levels of these materials were calculated from cyclic voltametric data, and frontier energy level of 5.33 eV, 5.28 eV and 5.28 eV as HOMO for HTMs 1, 2, and 3, respectively, with LUMO 3.49 eV, 3.58 eV, and 3.58 eV. The bandgap of 1.84 eV, 1.7 eV, and 1.7 eV was obtained in the optical calculation. Out of all, HTM 2 was fabricated without any additional additives to achieve the highest 17.4% PCE among all the PSCs devices and HTM 3 displays highest calculated hole mobility of 3.48×10−4 cm2 V−1 S−1.

A family of HTMs based on spiro[fluorene-9,9''-ton] (SFX) units was synthesized by Xu et al. for the tBP free PSCs devices, HTM 4, 5, 6 and 7.[43] These HTMs different from each other in terms of linkage of pyridine rings with SFX unit, as ortho, para, and meta. The emission spectra show peak around 425 nm for these HTMs in DMC solution, whereas absorption spectra with a maximum near 385 nm suggesting similar kind of continuous p-conjugated structure in those HTMs. The frontier energy levels, LUMO and HOMO, for all the members of this family was electrochemically recorded at 2.11 eV and 5.15 eV, respectively, and utilized to fabricate photoactive layers for charge carriers in the PSCs device. The bandgap between LUMO and HOMO level of each HTM 4-7 was equivalent to the bandgap of ETL material, C60, utilized in the device, as the energy gap is equivalent in all the HTMs displays similar hole mobility too, 1 ×10−4 cm2 V−1 S−1. The HTM 7 standout among all HTMs with 17.2% valuation in PCE column and that even without any tBP in this planar PSCs using MeNH3PbI3 as perovskite material, under AM 1.5G sunlight with 100 mW cm2. The high PCE value of HTM 7 as compared to equivalent HTMs could be better understood when we take consider of stronger interaction between nitrogen situated at para position in the pyridine ring of HTM 7 and lead (Pb) of perovskite material layer, which was not so effective in other HTMs and Pb of the layer. Moreover, the planar PSCs with mixed ion exhibit a record braking 19.5% PCE without any additive tBP. The free nitrogen of pyridine ring help to achieve higher efficiency for HTMs 4-7, meanwhile Zhu and colleagues explore other options, and they report two HTM (HTM 8 and 9) with bipyridine moiety inverted inside the transporting materials.[44] The group fabricate these HTMs with traditional planar PSCs to yield exceptionally well 17.71 and 18.48% PCE, respectively, and their absorption spectra display almost similar peaks around 300 nm. The stronger electron withdrawing nature of bipyridine ring affect the HOMO energy level of HTM 8 and 9 resulting in enhancement of open circuit voltage (VOC) of the device. Also, the HTM 8 and 9 display stronger tendency of hole transportation capabilities and excellent hole extraction. With excellent thermal stability (Td) up to 442 °C and 380 °C of HTM 8 and 9 and with glass transition temperature (Tg) of 162 °C and 151 °C, respectively, display excellent practicality for device fabrication.

In 2019, Wang and co-worker synthesis two HTMs (HTM 10 and 11) based on phenothiazine units and report NiOX based PSCs device.[45] Wang et al. utilized pyridine rings as terminal of phenothiazine units to enhance interaction among NiOX, HTMs, and perovskite layers to boost charge carriers' mobility and conductivity of the device. This relationship goes hand-in-hand-like manner one pyridine interact with NiOX layer, while other one interacts with Pb from perovskite layer, this bridge enriched the hole transportation process. The valance band (VB) of NiOX (5.19 eV) was higher than the calculated HOMO levels of phenothiazine based HTM 10 (5.28 eV) and 11 (5.36 eV), thus these HTMs fit prefect for device fabrication. PSCs device based on HTM 11 outperformed HTM 10 based device with higher VOC (1.043 V v/s 1.028 V) as well as short circuit current (JSC) of 21.45 compared to 20.91 mA cm−2. The higher value of VOC suggests that higher rate of recombination of charges in HTM 11 than HTM 10 that producing in better PCE for HTM 11.

To study the effects of substitutes on pyridine ring, in 2020, Xue and colleagues utilize 2,4,6-triarylpyridine unit and reported a series of HTMs, HTM 12, 13, and 14.[46] The conjugated system of all these three HTMs strongly corelate with absorption spectra in UV region with two maxima in 320-430 nm and 300-320 nm. The calculated bandgap between frontier energy levels for those HTM were 2.83 eV, 2.75 eV, and 2.86 eV, respectively for HTM 12, 13, 14. It was observed that with each additional bis(4-methoxyphenyl) amine to pyridine ring core, the hole mobility enhanced and ultimately HTM 14 with three additional has higher mobility among all three HTMs. Those addition to pyridine ring made material more hydrophobic and improve contact with perovskite layer, ultimately lowering the recombination rate and enhancing charge transportation. Thus HTM 14 display excellent 18.24% of PCE compared to other members of series. In 2021, Lui and co-worker synthesis two HTMs (HTM15 & 16) of star shaped to analysis core structural features of HTMs in the PSCs devices.[47] The HTM 16 has more planar shape and had better intramolecular interaction in the layer compared to HTM 15, resulting in PCE of 17% for HTM 16. Due to this planar structural integrity HTM 16 had improved

p-conjugation and enhanced hole transportation behaviour, 3.48×10−7 cm2 V−1 S−1 compared to 2.08×10−7 cm2 V−1 S−1 of HTM 15.

3. Conclusion

The properties, such as low turn on voltage, higher power conversion efficiency with promising charge carriers' mobility, and ease of fabrication allow the uprise of optoelectronic devices like phototransistors, OLEDs, and PSCs. The significant upholds of these devices improves thermal stability over a long range of temperature and enhanced driving voltage allow efficient working of these devices. To further improve the PSCs devices a wide array of organic, inorganic, and inorganic-organic hybrid materials has been under consideration and many yet to explored over the globe as ETMs and HTMs. These charge carrier materials exhibit crucial role to boost quantum efficiency of PSCs device alongside improving PCE as well. We have focused, in this review, on pyridine derivatives-based charge carriers HTMs for the PSCs devices and explore the property-structure relationship for all the three possible position available in pyridine molecule, i.e. para, meta, and ortho. We take close look at the electrochemical, photovoltaic, and photophysical properties of those derivatives and summarize their recent development with each feasible substitutions on para, ortho and meta position along with the result in changes of their acceptor and donor nature observed in HTMs layers of the PSCs devices. The conclusive out came of this robust study are following:

- The device fabrication holds one of the most important factors is the carefully choosing materials of effective Frontier Molecular Orbitals that incorporating of intermolecular and intramolecular interaction of strong multiple bonds and their electrical infusion which beneficiate the charge transportation process and ultimately device performance.
- The interaction between molecules and layers in the device can be controlled through introduction of hydrogen bonding elements in the pyridine derivatives. This improve that ability of molecular stacking among themselves and with other molecules/ molecule complexes. The lone pair on nitrogen atom of pyridine is least effective in ortho position for hydrogen bonding, and this reduce the charge transfer ability as compared to meta derivatives, which lower than para derivatives of same molecule in the PSCs device as hydrogen bonding facilitate higher quality of thin film fabrication.
- The introduction of pyridine derivative-based materials as ETMs and HTMs counter the poor hole blocking problem and unreliable mobility of charge carrier of widely used traditional materials in the PSCs devices. This is mainly due to the better fabrication and durability of thin films of pyridine derivative-base materials. Furthermore, the ability of pyridine to make effective LABA with Pb of perovskite layer in these materials offer cost cutting as this eliminating the need of high-costly hygroscopic dopant like LiTESI, Cobalt (III) complexes, and TBP.
- The electron density acceptor nature of pyridine-based derivatives lowers the relative energy levels of HOMO of this material to facilitate equivalent energy levels of perovskite layer of the PSCs device for open-circuit voltage. Meanwhile, the pyridine derivative-based HTMs open new gateway for dopant free PSCs devices which can offers enhanced quantum efficiency and improved thermal stability over a wider range of temperature.
- The performance of PSCs can be improved by enhancing the quality of thin layers of the fabricated devices and their layer dimensions and thermal stability. The LABA of HTMs and Pb from Perovskite material interact in synergetic manner which boost hole transportation and mobility of charge carriers. This synergetic behaviour improves fabrication of thin films that results in smoother morphological surface of hydrophobic nature, and this ultimately enhance longevity and durability of the PSCs devices.

In the nutshell, this review highlights pyridine derivative-based materials as emerging and one of the important ETMs, HTMs materials for the PSCs devices and recent advancement in these materials in contexts of charge carrier thin layers in PSCs fabrication. The design and synthesis of pyridine derivatives with improved photophysical, electrochemical and photovoltaics properties to fabricate enhanced device performance can be achieved through structure-property relationship and better clue should be taken for their synthesis.

Compliance with ethical standards

Conflicts of Interest

There are no conflicts to declare.

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