ChemTech

International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.9, No.03 pp 623-628, 2016

A Brief discussion on Hole-Transport Materials in Solar energy Conversion

S. Sarveswari*

Centre for organic and medicinal chemistry, School of advanced sciences, VIT University, Vellore-14, Tamil nadu, India.

Abstract: This review article highlights the development in the field of solid-state DSSC as an economical renewable energy resource. To harvest the solar energy the solar cells are being fabricated, with five main components among them a liquid redox electrolyte has been replaced with a solid-state hole-transporter material (HTM). Among the reported hole transport materials 2,2,7,7-tetrakis(N,N-di-*p*-methoxyphenylamine)9,9-spirobifluorene(Spiro-OMeTAD) reported to achieve 19.3% efficiency. In this review it was attempted to emphasis the developments in the design and synthesis of organic molecules and polymers to achieve an improved power conversion efficiency (PCE).
Key words: Organic molecules, alternative energy, Solar energy conversion, HTM.

Introduction

The conversion of solar energy into electrical energy has attracted the interest of scientists in order to fulfill the energy needs. A search for an alternative to develop advanced materials to serve the needs of mankind is a never ending process. Recent spectacular developments in the field of synthetic methodologies have made significant contributions to the synthesis of organic molecules with improved properties[1]. A dye sensitized solar cell comprised of the following components (1) a glass substrate coated with transparent conductive oxides; (2) a nanoporous TiO_2; (3) a dye sensitizer adsorbed onto the surface of the semiconductor; (4) a liquid redox electrolyte; and (5) an electric contact capable of regenerating the redox mediator. Grätzel and Snaith [2,3] proposed to replace the liquid electrolyte with a solid-state hole-transporter material (HTM) to get solid-state DSSC (ssDSSC).

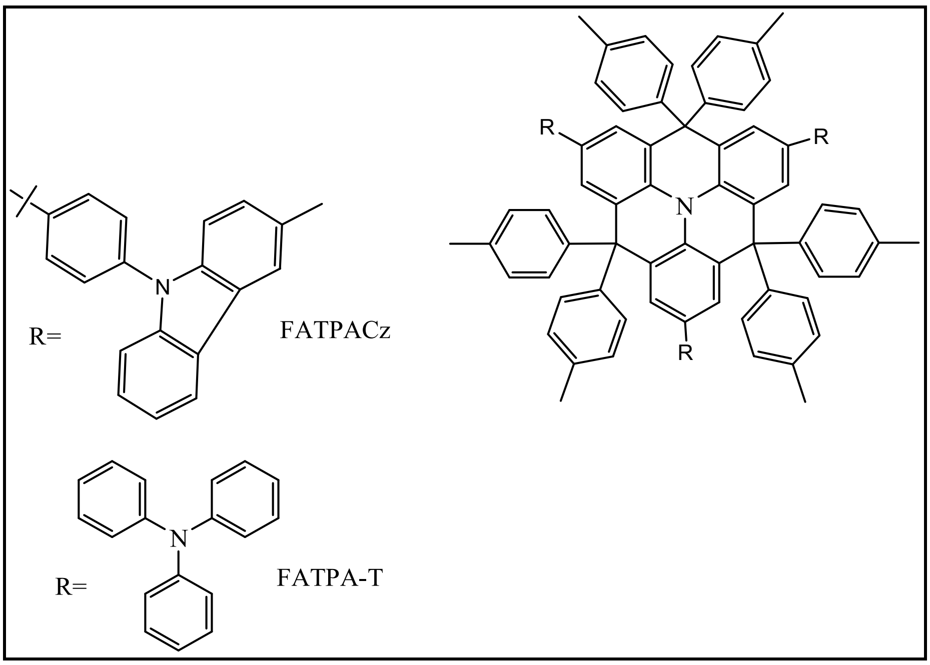
Photovoltaic technologies promisingly meet the intensively increasing demands of renewable energies. The perovskite solar cells have been paid considerable attention due to their economical and highly efficient conversion of solar energy into electricity.[4–8] The perovskite solar cells are composed of a perovskite/

mesoporous TiO_2 layer sandwiched between layers of electron-transporting TiO_2 and a hole transporting material (HTM). Absorption of sunlight by the perovskite generates electron−hole pairs, which then transport through TiO_2 and HTM, before getting collected at the electrodes. Organic HTMs are serving as good candidates for the performance perovskite solar cells[9−14]. For example 2,2′,7,7′-tetrakis(N,N-di-p-methoxy phenylamine) 9,9′-spirobifluorene (Spiro-OMeTAD) has been reported to exhibit higher efficiency (19.3%).[6,7,15] The achievable maximum value of power conversion efficiency (PCE) is 20% , the reported PCE of single cells and polymer tandem solar cells is over 10%. P-type metal oxides, such as NiO, MoO3, and WO3, have been successfully applied as a hole transport layer (HTL) to increase the PCE of PSCs[16]. Apart from inorganic metal oxides, poly(3,4-ethylenedioxythiophene) : poly(styrenesulfonate) reported to show efficient hole extraction and transportation. Due to the strenuous synthetic procedure and the extremely high coast of Spiro-OMeTAD scientists continuously putting their efforts to develop a low cost and effective HTM for the solar energy conversions.

Triphenylamine-based HTMs

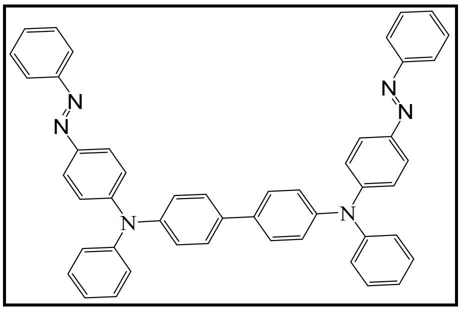
Triphenylamine-based HTMs have shown promising results. Kroeze et al.[17] synthesized and tested different triarylamine oligomers of varying conjugation lengths showing that small, low- molecular-weight hole conductors present the best hole-transfer yields and pore filling in the amorphous phase. Leijtens et al.[18] New hole transport polymers have been prepared through copolymerization of a fluorinated triphenyl diamine derivative and trimethoxyvinylsilane. Organic light-emitting diodes containing these polymers show decreased operating voltages and enhanced operational stability due to improved interfacial contact between the hole transport layer and the anode[19]. A triphenylamine derivative 4,4¢,4¢¢-tris(*N*-3-methylphenyl-*N*-(9-ethylcarbazyl-3)amino)triphenylamine (PCATA) was reported[20] by Jiuyan Li et al. The introduction of PCATA into the standard NPB/Alq3 OLED as the hole injecting and transporting layer reported to enhance the device efficiency to 5.7 cd/A and 2.2 lm/W.

The star-shaped oligo triarylamines with planar triphenylamine core and peripheral triarylamine groups, namely FATPA-T and FATPA-Cz, were reported with the following features: (i) excellent thermal stabilities with quite high glass transition temperatures (ii) good solution-processability; (iii) good hole mobility, efficient hole injection, and electron-blocking functions. Furthermore, their optoelectronic properties can be modulated by the peripheral triarylamine groups. For example, FATPA-T with triphenylamine peripheries shows the significantly red shifted absorption and emission, as well as the small band gap as compared to FATPA-Cz with carbazole peripheries. Double-layer Alq3-emitting OLEDs using FATPA-T or FATPA-Cz as hole transport layer by spin-coating method were fabricated.



According to Zuoquan Jiang et al the optimized three-layer Alq3-emitting OLEDs with FATPA-Cz and NPB as double hole-transport layers exhibit the current efficiency of 6.83 cd/A. The advantages of solution processablity and very high Tg make the star-shaped oligotriarylamines ideal substitutes for conventional arylamines as hole-inject and hole-transport materials[21].

By irradiation with polarized light, azo dyes undergo photoselective isomerization cycles, leading to a reorientation preferably into the plane perpendicular to the polarization direction and therefore to a change in the refractive index ellipsoid. The final orientation is a state in which the molecules cannot be excited again because their transition dipole moment and the polarization direction are perpendicular to each other. By uniform irradiation of an isotropic film with polarized light, uniaxial negative birefringence is induced. Gratings recorded in azo side chain polymers by intensity holography as well as polarization holography using this reorientation principle have been reported by different groups. The *N*,*N*¢-bis(phenyl)-*N*,*N*¢-bis((4-phenylazo)-phenyl)benzidine reported to serves as grating structures in multilayer devices[22].



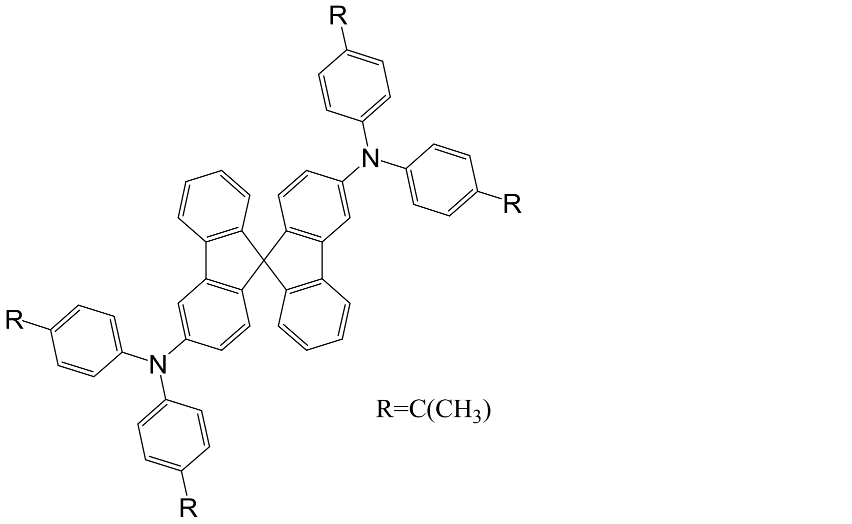
Squaraine-based HTMs

Squaraines are a class of dyes with resonance stabilized zwitterionic structure. Squaraines typically contains an electron deficient central four membered ring and two electron-donating groups in a donor–acceptor–donor (D–A-D) form. They come under the class of functional dyes which are important in photon based technologies for optical data storage and communication. Imaging [23, 24] nonlinear optics[25, 26, 27] photovoltaics,[28, 29, 30] photodynamic therapy[31] and ion sensing.[32]

Spiro compounds as HTMs

It is known that 9,9'-spirobi[9H-fluorene] (SBF) is a spiro-molecule with an orthogonal molecular structure, where two planar fluorene units are connected through a spiro-sp^3 carbon. This rigid and orthogonal core serves as an excellent building block for constructing novel 3D molecules. In addition, a better solubility and less intensive intermolecular interaction of the final molecules would be expected for its nonplanar molecular structure.[33] However, only a few PDI derivatives based on this well-known spiro-core were reported in the literature.[34-37] 9,9'-spirobi[9*H*-fluorene]-cored perylenediimide derivative were synthesized as a non-fullerene acceptor in organic solar cells[38].

Charge carrier mobility was reported to influence the device performance. Among tested organic materials some triaryldiamines exhibit hole mobilities exceeding 10^{-3} cm^2 V^{-1} s^{-1}, were used as hole transporting materials in organic light-emitting diodes (OLED) and in xerography.[39] These compounds, however, often possess poor morphological stability, which results low reliability in optoelectronic devices. Obviously structural modifications on these triaryldiamines will improve the morphological stability. The introduction of spiro-type linkages, covalently bridged orthogonal structural configurations can lead the triarylamine derivatives to exhibit higher values of *T*g. The Salbeck group established a tetrasubstituted spirobifluorene based amine, 2,2′,7,7′-tetrakis(diphenylamino)-9,9′-spirobifluorene (spiro-TAD) with improved morphological stability (*T*g = 133 °C).4 More importantly, the three-dimensional structural feature of spiro-TAD allows it to exhibit remarkable hole transport properties.[40]



2,2Œ-bis[di-(4-tert-butylphenyl)amino]-9,9Œ-spirobifluorene)

The systematic study on the hole transport properties of 2,7- and 2,2′-disubstituted spirobifluorene-based triaryldiamines and the parent nonspiro- linked model compound, *N*,*N*,*N*′,*N*′-tetraphenylbenzidine (TPB) was reported by Yuan-Li Liao et al. They found that the introduction of a spirobifluorene unit as a central core is highly beneficial. The physical properties can be altered through modification of the substitution pattern of the spirobifluorene core and the nature of the aryl groups on the diarylamino substituents. Which provide a better understanding on the structural requirements and hole mobility of spirobifluorene-based triaryldiamine derivatives[41].

Conclusion:

In order to meet the growing needs for energy, finding out the alternative energy resources are must. One of the best alternative resources is solar energy, the conversion of solar energy into electrical energy at reasonably low coast can be achieved by dye sensitized solar cells, and continuous attention is being paid to till date improve the performance and to reduce the coast of production this review has briefly discussed few important compounds of current interest and improvement. The spiro derivatives proved as the better counterparts their combination with pervoskite materials led to increase the life time and efficiency.

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