Advanced Organic Hole Transport Materials for Solution-Processed Photovoltaic Devices

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To my family

Abstract

Solution-processable photovoltaic devices (PVs), such as perovskite solar cells (PSCs) and solid-state dye-sensitized solar cells (sDSCs) show great potential to replace the conventional silicon-based solar cells for achieving low-cost and large-area solar electrical energy generation in the near future, due to their easy manufacture and high efficiency. Organic hole transport materials (HTMs) play important roles in both PSCs and sDSCs, and thereby can well facilitate the hole separation and transportation, for obtaining high performance solar cells.

The studies in this thesis aimed to develop advanced small-molecule organic HTMs with low-cost, high hole mobility and conductivity for the achievement of highly efficient, stable and reproducible sDSCs and PSCs. In order to achieve these objectives, two different strategies were utilized in this thesis: the development of new generation HTMs with simple synthetic routes and the introduction of cost-effective p-type dopants to control the charge transport properties of HTMs.

In Chapter 1 and Chapter 2, a general introduction of the solution-processed sDSCs and PSCs, as well as the characterization methods that are used in this thesis were presented.

In Chapter 3 and Chapter 4, a series of novel triphenylamine- and carbazole-based HTMs with different oxidation potential, hole mobility, conductivity and molecular size were designed and synthesized, and then systematically applied and investigated in sDSCs and PSCs.

In Chapter 5, two low-cost and colorless p-type dopants AgTFSI and TeCA were introduced for the organic HTM-Spiro-OMeTAD, which can significantly increase the conductivity of the Spiro-OMeTAD films. The doping effects on the influence of sDSC and PSC device performances were also systematically investigated.

Keywords: Hole transport material, Photovoltaic device, Solid-state dye-sensitized solar cell, Perovskite solar cell, P-type dopant, Hole mobility, Conductivity, Solution-processed.
Abbreviations

Al₂O₃  aluminium oxide
AM 1.5G  air mass 1.5 global
AgTFSI  silver bis(trifluoromethane)sulfonimide
BHJ  bulk heterojunction
CB  conduction band
CE  counter electrode
CV  cyclic voltammetry
DCM  dichloromethane
DFT  density functional theory
DMF  N,N-dimethylformamide
dppf  diphenylphosphinoferrocene
DSC  dye-sensitized solar cell
D-π-A  donor-π-linker-acceptor
E₀-₀  energy gap
Eox  oxidation potential
ER  reorganization energy
Fc/Fc⁺  ferrocene/ferrocenium
ff  fill factor
HOMO  highest occupied molecular orbital
HTM  hole transport material
FTO  fluorine-doped tin oxide
IPCE  incident photon-to-current conversion efficiency
ITO  tin-doped indium oxide
Jsc  short circuit current
LHE  light harvesting efficiency
LiTFSI  lithium bis(trifluoromethane)sulfonimide
LUMO  lowest unoccupied molecular orbital
NHE  normal hydrogen electrode
OLED  organic light emitting diode
OFET  organic field-effect transistor
OPV  organic photovoltaic
OS  organic semiconductor
OSC: organic solar cell
PCE: power conversion efficiency
PEDOT: poly(3,4-ethylenedioxythiophene)
PSC: perovskite solar cell
P3HT: poly(3-hexylthiophene-2,5-diyl)
PTAA: poly-triarylamine
Spiro-OMeTAD: 2,2',7,7'-tetrakis(n, n-di-p-methoxy-phenylamine)-9,9'-spirobifluorene
SCLC: space charge limited current
sDSC: solid-state dye-sensitized solar cell
SEM: scanning electron microscopy
TBP: 4-tert-butylpyridine
TeCA: 1,1,2,2-tetrachloroethane
TiO₂: titanium dioxide
T₉: glass transition temperature
Tₘ: melting point
TPA: triphenylamine
VB: valence band
Vₜₒｃ: open circuit voltage
ZnO: zinc oxide
η: power conversion efficiency
μ: hole mobility
ε₀: vacuum permittivity
εᵣ: dielectric constant of the material
σ: conductivity
λ: wavelength
λₐₜ₅: absorption wavelength
λₑₘ: emission wavelength
This thesis is based on the following papers, referred to in the text by their Roman numerals I-V:

   Bo Xu, Haining Tian, Dongqin Bi, Erik Gabrielsson, Erik M. J. Johansson, Gerrit Boschloo, Anders Hagfeldt, Licheng Sun  
   *J. Mater. Chem. A, 2013*, 1, 14467-14470

II. **Integrated Design of Organic Hole Transport Materials for Efficient Solid-state Dye-Sensitized Solar Cells**  
   Bo Xu, Haining Tian, Lili Lin, Deping Qian, Hong Chen, Jinbao Zhang, Nick Vlachopoulos, Gerrit Boschloo, Yi Luo, Fengling Zhang, Anders Hagfeldt, Licheng Sun  

III. **Carbazole-based Hole-Transport Materials for Efficient Solid-state Dye-sensitized Solar Cells and Perovskite Solar Cells**  
   Bo Xu, Esmail Sheibani, Peng Liu, Jinbao Zhang, Haining Tian, Nick Vlachopoulos, Gerrit Boschloo, Lars Kloo, Anders Hagfeldt, Licheng Sun  

IV. **AgTFSI as p-Tpye Dopant for Efficient and Stable Solid-state Dye-sensitized and Perovskite Solar Cells**  
   Bo Xu, Jing Huang, Hans Ågren, Lars Kloo, Anders Hagfeldt, Licheng Sun  
   *ChemSusChem., 2014*, 7, 3252-3256

V. **1,1,2,2-tetrachloroethane (TeCA) as Solvent Additive for Organic Hole Transport Materials and Its Application in Highly Efficient Solid-state Dye-sensitized Solar Cells**  
   Bo Xu, Erik Gabrielsson, Majid Safdari, Ming Cheng, Yong Hua, Haining Tian, James M. Gardner, Lars Kloo, Licheng Sun  

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Paper not included in this thesis:

VI. Initial Light Soaking Treatment Enables Hole Transport Material to Outperform Spiro-OMeTAD in Solid-State Dye-Sensitized Solar Cells
Lei Yang (co-first author), Bo Xu (co-first author), Dongqin Bi, Haining Tian, Gerrit Boschloo, Licheng Sun, Anders Hagfeldt, Erik M. J. Johansson

VII. Solid-State Perovskite-Sensitized p-Type Mesoporous Nickel Oxide Solar Cells
Haining Tian, Bo Xu, Hong Chen, Erik M. J. Johansson, Gerrit Boschloo

VIII. Phenoxazine-based Small Molecule Material for Efficient Perovskite Solar Cells and Bulk Hetero-junction Organic Solar Cells
Ming Cheng, Bo Xu, Cheng Chen, Xichuan Yang, Fuguo Zhang, Qin Tan, Yong Hua, Lars Kloo, Licheng Sun

IX. The Combination of A New Organic D-π-A Dye with Different Organic Hole-transport Materials for Efficient Solid-state Dye-sensitized Solar Cells
Peng Liu, Bo Xu, Martin Karlsson, Jinbao Zhang, Nick Vlachopoulos, Gerrit Boschloo, Licheng Sun, Lars Kloo
J. Mater. Chem. A, 2015, 3, 4420-4427

X. Improved Performance of Colloidal CdSe Quantum Dot-Sensitized Solar Cells by Hybrid Passivation
Jing Huang, Bo Xu, Chunze Yuan, Hong Chen, Junliang Sun, Licheng Sun, Hans Ågren
ACS Appl. Mater. Interfaces, 2014, 6, 18808-18815

XI. Structure and Function Relationships in Alkylammonium Lead(II) Iodide Solar Cells
Majid Safdari, Andreas Fischer, Bo Xu, Lars Kloo, James Michael Gardner
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XII. **Novel Small Molecular Materials Based on Phenoxazine Core Unit for Efficient Bulk Heterojunction Organic Solar Cells and Perovskite Solar Cells**

Ming Cheng, Cheng Chen, Xichuan Yang, Jing Huang, Fuguo Zhang, **Bo Xu,** Licheng Sun


XIII. **Organic Dye-Sensitized Tandem Photoelectrochemical Cell for Light Driven Total Water Splitting**

Fusheng Li, Ke Fan, **Bo Xu,** Erik Gabrielsson, Quentin Daniel, Lin Li, Licheng Sun

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XIV. **Effect of the Cromophores Structures on the Performance of Solid-State Dye Sensitized Solar Cells**

Haining Tian, Andrea Soto Navarro, **Bo Xu,** Licheng Sun, Anders Hagfeldt, Francisco Fabregat, Ivan Mora-Sero, Eva M. Barea

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XV. **Enhancement of p-Type Dye-Sensitized Solar Cell Performance by Supramolecular Assembly of Electron Donor and Acceptor**

Haining Tian, Johan Oscarsson, Erik Gabrielsson, Susanna K. Eriksson, Rebecka Lindblad, **Bo Xu,** Yan Hao, Gerrit Boschloo, Erik M. J. Johansson, James M. Gardner, Anders Hagfeldt, Håkan Rensmo

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Energy and environmental issues are the grand challenges of our time. There are 7.3 billion people on the Earth who use energy everyday to make their lives healthier, richer, more convenient and productive. Most of the energy consumed by humans is produced from fossil fuels, such as coal, petroleum and natural gas, which are also the most important global energy consumption in recent years. According to the statistics, the global consumption of energy in fossil energy has accounted up to 80%. However, with the continuous exploitation from human beings, the depletion of fossil fuels is inevitable by the end of this century. Furthermore, the excessive emission of greenhouse gases into the atmosphere that are caused by burning of massive fossil fuels, results in global warming, threatening our Earth's ecosystems. According to the Intergovernmental Panel on Climate Change’s (IPCC) report, the global average surface temperature on Earth has increased by 0.5~0.8 °C since 1850. Carbon dioxide (CO₂) is considered to be the main culprit of greenhouse, and more than 90% of anthropogenic CO₂ emits from the fossil energy consumption activities. Thus, with the gradual lowering of fossil energy reserves and the world's looming energy crisis, together with climate issues, the development of clean and sustainable energy systems is highly important for human beings.

1.1. Solar energy and photovoltaics

The sustainable energy systems, such as sunlight, geothermal heat, wind, tides and biomass are considered as the most promising energy sources for alleviation of the world’s energy and environment crisis, which have been given more and more attentions in recent years. Due to the tremendous amount of energy that the earth receives daily from the sun, solar energy is deemed as the top candidate among all of these sustainable energy sources.

Solar energy is generated by the continuously inside nuclear fusion reaction of the Sun. The total radiated power of solar energy is about 3.8×10²³ kW, and can be received by the Earth is around 1.7×10¹⁷ kW at the upper atmosphere. Taking into consideration of the reflection of atmosphere and the absorption of clouds, the final solar energy of 8.0×10¹⁶ kW can be received by the oceans and landmasses of the Earth, which is a vast energy source. The International Energy Agency (IEA) reported that the world annual energy consumption in 2012 was equivalent to the solar energy that absorbed by earth in one hour.
One of the most prominent strategies to utilize solar energy is the direct conversion of solar energy into electricity using photovoltaic devices (PVs). The first practical PVs based on silicon p-n junction with power conversion efficiency (PCE) of 6%, was successfully developed by Daryl Chapin et al. at Bell Laboratory in 1954, which was also called the first-generation solar cell.\(^5\)

So far, a tremendous progress has been made in this type of PV technology, the lab record PCE of single-crystalline based silicon solar cell has been increased to 27.6\% (as shown in Figure 1, the blue lines), and the efficiency of commercial single-crystalline silicon solar cell reached to 13\%~17\%.\(^6\) At the same time, the second-generation PV-thin film solar cells, such as Copper Indium Gallium Selenide (CIGS), Cadmium Telluride (CdTe) and Gallium Arsenide (GaAs)-based PVs also exhibited promising photovoltaic performance with lab record PCE of 23.3\%, 19.6\%\(^7\) and 28.8\%\(^8\) were achieved, respectively (as shown in Figure 1, the green lines). All of these conventional inorganic-based photovoltaic technologies (both first-generation and second-generation PVs) that permit efficient conversion of solar energy into electrical power were developed and commercialized long time ago. However, the long energy payback time and high manufacturing costs of these inorganic-based solar cells, as well as the use of toxic and scarce elements in the production processes, significantly limit these types of photovoltaics on a terawatt scale application. Thus, the third-generation solar cells, the so called organic-based PVs have attracted intensive attentions due to their solution-processable encapsulating process.

1.2. Solution-processable photovoltaics

The conventional inorganic semiconductor-based PVs need multistep processes with high temperatures (over 1000 °C) and vacuums in special clean room to produce materials with high-purity for the achievement of high power conversion efficiency, which always require large amount of energy during the production process. However, organic semiconductors have many unique advantages as compared to the inorganic semiconductors, such as the low-cost, solution-processability, infinite variety, non-toxicity, easy fabrication and mechanical flexibility. Thus, the need for cheap and fast processing of larger areas of thin organic-based films has become an increasingly important goal in recent years, and a number of research fields on organic-based photovoltaic technologies have emerged from this idea. The solution-processable encapsulating process of solid-state dye-sensitized solar cells (sDSCs), perovskite solar cells (PSCs) and organic solar cells (OSCs) have great potential for achieving low-cost manufacturing of light-weight, large area and flexible photovoltaics, which have drawn wide concern during the last decade.
Figure 1. The world record efficiencies of different kind of photovoltaic devices. (http://www.nrel.gov/ncpv/images/efficiency_chart.JPG, retrieved 2015-06-16)
1.2.1. **Solid-state dye-sensitized solar cells**

Dye-sensitized solar cells (DSCs) is a photoelectrochemical system that is based on metal oxide semiconductors, such as titanium dioxide (TiO$_2$) and zinc oxide (ZnO) formed between a dye-sensitized photoanode and an electrolyte, which was firstly reported by Gerischer *et al.* in the late 1960s. A significant breakthrough was made by Brian O'Regan and Michael Grätzel in 1991, a power conversion efficiency of 7% was obtained by using ruthenium complex-based photosensitizer absorbed on the nanoporous TiO$_2$ film as photoanode and iodide/triiodide (I$^-$/I$_3^-$) as a redox shuttle. The advantages of DSC are the low-cost materials, high efficiency and mild production conditions; thereby DSCs are considered as one of the promising photovoltaic technologies for the future. Later on, more and more researchers joined in this research field and great progress has been made. To date, the record PCE of DSC has reached 13% by employing a metal complex redox couple-Co(II/III)tris(bipyridyl) and zinc-porphyrin dye (as shown in Figure 1, the red lines). Recently, a PCE of 12.6% has been achieved by using a metal-free N-Annulated perylene dye and cobalt-based complex as redox mediators.

![Spiro-OMeTAD](image)

*Figure 2. Chemical structure of Spiro-OMeTAD.*

However, the potential leakage problems as well as the volatile nature of the liquid electrolyte that used in the DSC device, significantly limit this technology for large-scale applications in the future. In an effort to address these issues, Bach *et al.* successfully developed the first solid-state dye-sensitized solar cells (sDSCs) in 1998 by using a solid-state p-type organic semiconductor termed Spiro-OMeTAD (2,2',7,7'-tetrakis-(N,N-di-p-methoxy-phenyl-amine)) to replace the conventional liquid electrolyte as the hole-transporting conductor and combination with a ruthenium dye, a PCE of 0.74% was achieved. Since
then extensive research efforts have been made in this area. To date, the record efficiency of 7.2% for sDSCs has been achieved by using Spiro-OMeTAD as the hole transport material (HTM) doped with a cobalt-complex and in combination with a high molar extinction coefficient organic dye-Y123, which was reported by Nazeeruddin and co-workers\textsuperscript{14} in 2011.

\textbf{Figure 3.} Device structure of a solid-state dye-sensitized solar cell.

A typical device structure of sDSC is shown in Figure 3, a compact TiO\textsubscript{2} layer (around 150 nm) is deposited on the fluorine-doped tin oxide (FTO) coated glass substrates by spray pyrolysis, which avoids a direct contact between the FTO and the HTM, to prevent the cell short-circuit. The mesoporous TiO\textsubscript{2} film is applied on the top of the blocking layer by screen printing, spin-coating or doctor blading of a commercial TiO\textsubscript{2} paste, such as the Dyesol, 18NR-T, which are sintered together with the compact layer via a heat treatment at 450–500 °C, forming an interconnected network of TiO\textsubscript{2} (the thicknesses of the mesoporous TiO\textsubscript{2} films are around 2 µm.). This network is subsequently decorated with a monolayer of dye molecules during the so-called dye sensitization, which is typically achieved by immersing the substrate in a bath solution of dye molecules. Then, the mesoporous layer with dye absorption on the surface is infiltrated with a transparent organic HTM, typically Spiro-OMeTAD. The device is completed by evaporating a layer of metal as the counter electrode that usually consists of 150–200 nm Ag.

\textbf{Figure 4} shows the working principle of a typical sDSC, and the main processes that occur in a sDSC are as follows:\textsuperscript{15}
1) Upon absorption of light, the dye molecule is excited from the ground state to the excited state;
2) As electron from the excited state dye is injected into the conduction band (CB) of the TiO$_2$ semiconductor;
3) The electron is transported through the semiconductor layer and then outer circuit to the silver counter electrode;
4) The electron at the CB of the TiO$_2$ may undergo recombination with the oxidized dyes;
5) The recombination of the electrons in the TiO$_2$ with the holes in the HTM;
6) The dye is regenerated by the HTM;
7) The positive charge moves by a hopping between neighboring HTM molecules, then is regenerated at the silver counter electrode to complete an electric generation cycle in the sDSCs.

The photovoltage of a sDSC device is determined by the difference in energy between the pseudo-Fermi/conduction band level of the TiO$_2$ and the redox potential of the HTM. The photocurrent of a sDSC is determined by the number of photons absorbed by the dye at the working electrode minus the electrons lost in the recombination reactions.

![Diagram of solid-state dye-sensitized solar cell](image)

**Figure 4. Working principles of a solid-state dye-sensitized solar cell.**
Although solid-state dye-sensitized solar cell has been proposed for a long time, the PCE of this type of photovoltaic device is still less than 8%, which is far below the PCEs of liquid electrolyte-based DSCs. The lower PCE is mainly due to the incomplete light harvesting, resulting in a low photocurrent of the device. The maximum thickness of the nanoporous TiO$_2$ active layer for a sDSC is typically optimized to 2.0 µm, which is far thinner than the thickness required to obtain good light absorption. The limitations of the sDSCs from being more efficient at thicknesses over 2.0 µm primarily attribute to the incomplete filling of the mesoporous TiO$_2$ films with HTMs and fast electron-hole recombination in the device.$^{16-18}$ The manifest solution to these problems is the development of new photosensitizers with high molar extinction coefficients. Some efforts have been devoted into the dye molecule design for sDSCs. The studies showed that the organic dyes, such as LEG4,$^{19}$ D102$^{20,21}$ and D35$^{22}$ (as shown in Figure 5), have much better device performance than the ruthenium complex-based dyes (eg. Z907),$^{23}$ which is mainly due to their higher molar extinction coefficients. In addition, more evidences demonstrate that the long alkyl chains on the photosensitizer play a crucial role in a sDSC device, which can effectively suppress the dye aggregation and prevent the HTMs to approach TiO$_2$, thereby slow down the electron-hole recombination and improve the device performance.

\[ \text{LEG4} \]

\[ \text{D102} \]

\[ \text{D35} \]

\[ \text{Z907} \]

*Figure 5. Chemical structures of the commonly used photosensitizers in solid-state dye-sensitized solar cells.*
However, the intrinsic quality shortcoming of sDSC is the short-electron diffusion length, which will limit this type of device to obtain high efficiency. This has led scientists to concentratedly search novel light harvesting materials for solid-state solar cells, and more recently, a family of organometallic halide perovskite catches people's eyes.

### 1.2.2. Perovskite solar cells

Perovskite solar cell (PSC) is an emerging photovoltaic device in most recent years that employed the organometallic halide perovskite structured compound, such as the methylammonium lead trihalide (CH$_3$NH$_3$PbX$_3$, where $X$ is a halogen ion $\Gamma^-$, Br$^-$ or Cl$^-$), methylammonium tin trihalide (CH$_3$NH$_3$SnX$_3$) and formamidinum lead trihalide (H$_2$NCHNH$_3$PbX$_3$), as the light-harvesting active layer, which have attracted significant attention due to their high intrinsic carrier mobilities, high molar extinction coefficients, long charge diffusion lengths and the strong absorption over most of the visible spectrum.

The first incorporation of organometallic lead halide perovskite into a solar cell was reported by Miyasaka and co-workers$^{24}$ in 2009. The CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbBr$_3$ were used as the photosensitizers and in combination with the iodide/triiodide ($I^-/I_3^-$)-based liquid electrolyte, PCEs of 3.8% and 3.1% were obtained for the triiodide and tribromide PSCs, respectively. Subsequently, Park et al.$^{25}$ further improved the efficiency of the liquid electrolyte-based CH$_3$NH$_3$PbI$_3$ solar cell to 6.5% under simulated AM 1.5G solar irradiance (100 mW·cm$^{-2}$) in 2011, through the photoanode modification and the processing deposition of perovskite crystal. Although promising photoactive properties were obtained in liquid-DSC, the device was further found extraordinarily unstable and the perovskite crystals were easily degraded in liquid electrolytes. Later on, a great breakthrough was made by Park et al.$^{26}$ and Snaith et al.$^{27}$ in 2012. Learning from the solid-state dye-sensitized solar cells, by replacing the liquid electrolytes with the solid-state hole transport materials-Spiro-OMeTAD that undertook hole-transporting, and in combination with the perovskite as the light absorbers, high PCEs exceeding 10% were achieved.$^{26, 27}$ Since then tremendous progresses have been made during the last three years, the overall conversion PCEs of PSCs have been quickly improved to 20.1% (as shown in Figure 1, the red lines),$^{28}$ which were reported and certified by Soek and co-workers. Nowadays, the fast unprecedented increase in PCE of PSCs motivates many research groups to focus on the new HTMs development, new device architecture design, high-quality perovskite film formation and interface engineering of the device etc.

A conventional device structure of a mesoscopic PSC is shown in Figure 6, which is quite similar to a sDSC device. The different part is the commonly
used photosensitizer was replaced by the perovskite light absorber, which can be easily deposited by spin-coating, vapour deposition\textsuperscript{29} or sequential deposition\textsuperscript{30} methods. The photoactive layer of a PSC is around 300 nm, which is much thinner than that of the sDSC (around 2 µm).

![Device structure of a mesoscopic perovskite solar cell.](image.png)

**Figure 6.** Device structure of a mesoscopic perovskite solar cell.

1.3. Organic hole transport materials

Organic HTMs play an important role in the regeneration of the oxidized state light absorbers and transportation of the holes to the counter-electrode both in sDSCs\textsuperscript{15} and PSCs\textsuperscript{31}. In principle, high performance HTM must meet several general requirements in a photovoltaic device:

1) Compatible energy level: the HTM should have a more negative oxidation potential than that of the light harvester so that the oxidized light absorber can be efficiently regenerated;
2) Excellent charge carrier mobility: high hole mobility to satisfy the fast hole transport toward the back contact metal electrode;
3) Good stability: high thermal, photochemical, air- and moisture-stability are required;
4) Solution-processable: high solubility in organic solvents (particularly in toluene and chlorobenzene) to satisfy the solution processing, such as inkjet printing and spin coating;
5) Excellent film forming capacity: the HTM should have low tendency towards crystallization so that it can easily form a high quality of smooth thin layer at the interfaces, in favor of the charge transfer;

6) Low-cost and environment-friendly: the HTM should be easy to synthesize, non-toxic and recyclable;

Incipiently, inorganic p-type semiconductors, such as cuprous iodide (CuI), cuprous bromide (CuBr), cuprous thiocyanate (CuSCN) and nickel oxide (NiO) were introduced as the hole transporters for sDSCs by researchers, and reasonably PCEs around 3% were obtained. However, such inorganic hole conductors suffer from the easy crystallization, poor solubility and insufficient pore filling problems, which are not facile to handle for the fabrication of high-efficiency sDSCs. An exciting result was reported by Kanatzidis and co-workers in 2012, an inorganic p-type semiconductor CsSnI$_3$ (type of perovskite) was employed as the hole conductor for sDSCs and in combination with the ruthenium dye-N719 as the photosensitizer, an inspiringly high PCE of 8.5% was achieved.$^{37}$ The advantages of CsSnI$_3$ are the high hole mobility with the value of 585 cm$^2$V$^{-1}$s$^{-1}$ and excellent solubility in organic solvents. CsSnI$_3$ can be easily dissolved in N,N-dimethylformamide (DMF), γ-Butyrolactone (GBL) and methyl sulfoxide (DMSO) for the solution processing. However, CsSnI$_3$ is sensitive to the oxygen and moisture, which will lead to poor stability and reproducibility of the sDSC device.

Organic HTMs have some unique advantages as compared to the inorganic hole conductors, such as the solution-processability, infinite variety, good stability, low-cost, environment-friendly, easy fabrication, tenability of electronic properties and mechanical flexibility. The triphenylamine (TPA) compounds, no matter small-molecule- or oligomer-based, are the most intensively investigated HTMs in sDSCs. In 2006, a series of TPA-based oligomers (termed HTM1 to HTM6 as shown in Figure 7) with variant polymerization degree and hole mobilities were developed by Durrant and co-workers,$^{38}$ and the best PCE of 2.0% was obtained with these HTMs. The correlation of the hole transfer at the dye/HTM interface with the sDSC device performance was further investigated by the authors. Their result demonstrated no obvious correlation between the hole mobility of the HTM and device performance, and the pore filling properties of the HTM for the device is more important than the hole mobility of the HTM. In order to improve the pore filling of the HTM in the mesoporous TiO$_2$ film, McGehee et al. designed and synthesized two small organic HTMs named AS37 and AS44$^{23}$ (chemical structure shown in Figure 7) in 2012. Through detailed studies, they found that with the introduction of long alkyl chains into the HTM molecular structure, the solubility of HTMs is significantly improved, leading to better pore infiltration of the device. The HTM AS44-based device exhibited higher PCE than that of the state-of-the-art HTM-Spiro-OMeTAD-based one with a 6
µm thick Z907 sensitized TiO$_2$ film was used as the photoanode. Although some other types of TPA-based HTMs$^{39-41}$ were gradually reported in sDSCs, the related device performances are still not as good as Spiro-OMeTAD.

![Chemical structures of the triphenylamine-based small molecule and oligomer hole transport materials that investigated in sDSCs.](image)

As previously discussed, the pore filling of HTMs into the mesoporous TiO$_2$ film is one critical limitation of sDSC for achieving high photocurrent. Thus, the solubility of the HTM should be most taken into consideration during the molecular design.$^{42}$ However, the device structure of a PSC is more similar to a thin film solar cell where the photoactive layer is around 300 nm with full coverage of perovskite crystals. Accordingly, one should consider increasing the charge carrier mobility, leveling up the oxidation potentials and improving
film forming capacity of the HTMs in a PSC, rather than to improve the solubility of the HTMs. In addition, the charge diffusion length\(^{13,44}\) of the perovskite crystal is much longer than the organic-based photosensitizer that used in a sDSC, thus most of the HTMs can work very well in the PSCs. A series of small molecule HTMs using pyrene as the core were reported by Soek and co-workers\(^{45}\) in 2013. One of the pyrene-based HTMs termed Py-C (chemical structure shown in Figure 8) exhibited good PCE of 12.4% in PSCs, which can compete with the PCE of Spiro-OMeTAD based device (12.7%). Later on, several TPA-based HTMs using various thiophene derivatives as cores, such as the ethylenedioxythiophene, thiophene, and swivel-cruiform thiophene (As shown in Figure 8, H101\(^{46}\), H112\(^{47}\) and KTM3\(^{45}\)) were developed, and photovoltaic device performances comparable with Spiro-OMeTAD were obtained in PSCs.

![Py-C](image1.png)  ![KTM3](image2.png)

![H101](image3.png)  ![H112](image4.png)

**Figure 8.** Chemical structures of the triphenylamine-based small molecule hole transport materials that investigated in PSCs.

Compared with small-molecule HTMs, polymer-based HTMs always exhibit remarkably high hole mobility and conductivity, which can be used as effective
hole conductors for PSCs. P3HT (Poly(3-hexylthiophene-2,5-diyl, chemical structure shown in Figure 9) was the first polymer HTM that used in PSCs due to its great successful achievement in OSC-based devices, and PCEs of over 10% could be achieved by the optimization of experimental conditions. Another commercial polymer-PTAA (poly-triarylamine, chemical structure shown in Figure 9) with strikingly high hole mobility ($10^{-3}$~$10^{-2}$ cm$^2$·V$^{-1}$·s$^{-1}$) was introduced in PSCs by Soek and et al., which could present excellent device performance with a maximum PCE of up to 20% under simulated AM 1.5G solar irradiance (100 mW·cm$^{-2}$). Nowadays, more and more polymer-based HTMs for PSCs were developed by researchers, and the main research hotspots are the high hole mobility and conductivity. The high hole mobility and conductivity polymers also can be used as dopant-free HTMs for PSCs.

![Figure 9](image_url)  
*Figure 9. Chemical structures of polymer hole transport materials that investigated in PSCs.*

Although many novel HTMs-based both on small molecule and polymer have been developed, Spiro-OMeTAD is still considered as the most successful HTMs in both sDSCs and PSCs, and the champion efficiencies of these two type of photovoltaic devices have been achieved using Spiro-OMeTAD as the HTM. However, the measured hole mobility and conductivity of Spiro-OMeTAD is around $10^{-4}$ cm$^2$·V$^{-1}$·s$^{-1}$ and $10^{-7}$ S·cm$^{-1}$, respectively, which is much lower than the values of the inorganic semiconductors. This might be a limitation of Spiro-OMeTAD-based photovoltaic devices to obtain the maximum power point in solar cells. More importantly, the harsh reaction conditions and lengthy synthetic route of Spiro-OMeTAD make it impractical for large-scale application in sDSCs and PSCs in the future. Figure 10 shows the synthetic route of Spiro-OMeTAD. The synthesis of Spiro-OMeTAD needs five steps$^{50}$ including the Grignard reaction, cyclization reaction, bromination reaction and Buchwald-Hartwig reaction from commercially available starting materials with total yield less than 50%. In addition, the Grignard reaction used in the synthesis process normally requires harsh reaction conditions. Therefore, the development of new generation HTMs with
easy synthesis, low cost, high hole mobility and conductivity for sDSCs and PSCs is still highly desired.

**Figure 10. Synthetic route of Spiro-OMeTAD.**

1.4. P-type chemical doping of HTMs

Organic semiconductors (OSs) show fascinating application prospects due to their potential fabrication of low-cost, light-weight, large-area and flexible organic electronic devices, such as the organic photovoltaic devices (OPVs), organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs). Although tremendous progresses have been made in this area during the last four decades, some key challenges for further advancement still
remain. One of the biggest challenges is the low charge-carrier mobility, as compared to traditional silicon-based inorganic semiconductors (iOSs). A powerful tool to control and improve the charge carrier transport and the electrical conductivity of organic semiconductors is by using chemical doping.\textsuperscript{51}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{doping_diagram.png}
\caption{Schematic illustration of the doping mechanisms for an organic semiconductor (n-type doping and p-type doping).}
\end{figure}

Generally, the fundamental principle of chemical doping is introducing chemical impurities into the OSs to improve their electrical conductivity. The exact doping mechanism for an OS is illustrated\textsuperscript{51} in Figure 11. The equal number of free holes and electrons occupy at the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the intrinsic OS, respectively. In an n-type doped host OS, the electron donor impurities were introduced to the LUMO of host OS which can contribute extra electron energy levels so that the electrons of dopant can be easily excited into the LUMO of the host OS. Thereby, surplus electrons are formed in the LUMO of host OS, which is called the "majority carriers" for current flow in an n-type semiconductor. In a p-type doped OS, electron acceptor impurities were introduced to the HOMO of OS which can contribute extra hole energy levels so that the electrons of OS can be easily excited into the dopant. Thereby, mobile holes are left in the HOMO of OS, which are called the "majority carriers" for current flow in a p-type semiconductor. The
additional charge carriers (either electron donors or accepters) were introduced into the OSs, which lead to an increased charge carrier density in the host material, resulting in a higher electrical conductivity. This approach has been extensively applied in many p-type and n-type OSs and related electronic devices.

![Chemical structures of different p-type dopants](image)

**Figure 12.** Chemical structures of different p-type dopants that investigated in sDSCs and PSCs.

A number of effective chemical p-type dopants have been developed for the state-of-the-art-HTM Spiro-OMeTAD and successfully applied in sDSCs and PSCs. Tris(4-bromophenyl) ammoniumyl hexachloroantimonate\textsuperscript{13} (p-BrC\textsubscript{6}H\textsubscript{4})\textsubscript{3}NSbCl\textsubscript{6}, as shown in **Figure 12**) was the first p-type dopant that was introduced in Spiro-OMeTAD-based sDSCs by Bach and co-workers in 1998, which also was widely used in OLEDs. In 2011, Gratzel et al. reported a cobalt complex-tris(2-(1H-pyrazol-1-yl)pyridine)cobalt(III) (termed FK102,\textsuperscript{14} as shown in **Figure 12**) as a p-type dopant, which can dramatically increase the conductivity of Spiro-OMeTAD films, resulting in better device performances in sDSCs. Later on, the second generation cobalt(III) complex-based p-type dopant named FK209\textsuperscript{52} (as shown in **Figure 12**) was further developed through molecular engineering and counter ion exchange, which exhibited much better solubility in the Spiro-OMeTAD-based precursor solution. Recently, Snaith et al. demonstrated that lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) also can act as a p-dopant for HTMs in the presence of oxygen atmosphere.\textsuperscript{53,54} However, further study
found that the LiTFSI was easily consumed during the doping process, leading to poor device stability and reproducibility. In addition, some other kinds of p-type dopants also have been successfully developed, such as the 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane\textsuperscript{55} (F\textsubscript{4}TCNQ, as shown in Figure 12), tin(IV) chloride\textsuperscript{56} (SnCl\textsubscript{4}) and protic ionic liquids.\textsuperscript{57} All of these p-type dopants could significantly improve the conductivity of HTM films, including Spiro-OMeTAD and the other HTMs, resulting in good device performance in PSCs and/or sDSCs. However, some of these p-type dopants have a strong color and/or poor solubility in organic solvents, or are not easy to synthesize. Thus, the development of low-cost, solution-processable, colorless, non-toxic and air-stable p-type dopant for high performance PSCs and sDSCs still remains.

1.5. The aim of this thesis

Solution-processed photovoltaic devices, such as sDSCs and PSCs, show great potential for large-scale industrial application in the near future due to their high efficiency and low manufacturing cost. Thus, the aim of this thesis is to develop new generation small-molecule organic HTMs with low cost, high hole mobility and conductivity for application in high performance sDSCs and PSCs. The photoelectrical, photophysical, electrochemical and photovoltaic properties of these HTMs are systematically investigated and calculated. In addition, in order to improve the charge carrier mobility of organic HTMs and enhance the corresponding devices performance, two new p-type dopants with low-cost, colorless and solution-processable are introduced to the well-known organic HTM-Spiro-OMeTAD. The doping effect and the doping concentration of these p-type dopants on the influence of Spiro-OMeTAD-based sDSCs and PSCs are systematically studied.
2. Characterization Methods

2.1. Structural characterization

$^1$H NMR, $^{13}$C NMR and high resolution mass spectrometry of the compounds in this thesis were recorded by Bruker Avance DMX 500 and Waters MALDI Micro MX (MALDI-TOF), respectively.

2.2. Optical characterization

UV-Vis absorption spectra were recorded on a Lambda 750 UV-Visible spectrophotometer. The fluorescence spectra were recorded on a Cary Eclipse fluorescence spectrophotometer. All samples were measured in a 1 cm cell at room temperature with a concentration of $10^{-5}$ M in dichloromethane (DCM).

2.3. Electrochemical characterization

Electrochemical experiments were performed with a CH Instruments electrochemical workstation (model 660A) using a conventional three-electrode electrochemical cell.

Cyclic voltammograms of the HTMs in organic solution: a DCM containing 0.1 M of tetrabutylammoniumhexafluorophosphate ($\text{n-Bu}_4\text{NPF}_6$) was introduced as electrolyte; Ag/0.01 M AgNO$_3$ (acetonitrile as solvent) was used as the reference electrode and a glassy carbon disk (diameter 3mm) as the working electrode, a platinum wire as the counter electrode. The cyclovoltammetric scan rates were 50mV·s$^{-1}$.

Cyclic voltammograms of the HTMs on TiO$_2$ electrode: a ionic liquid 1-Butyl-1-methylpyrrolidinium bis(trifluoromethyl-sulfonyl) imide was used as electrolyte; Ag/AgCl (3 M NaCl) as the reference electrode; FTO/TiO$_2$/HTMs (spin coating with concentration of 5 mg /100μL in chlorobenzene) as the working electrode (area: 1 cm$^2$); a stainless steel plate as the counter electrode. Scan rates: 50mV·s$^{-1}$.

All redox potentials were calibrated vs. normal hydrogen electrode (NHE) by the addition of ferrocene. The conversion $E_{(\text{Fc/Fc}^+)} = 630$ mV vs NHE.
2.4. Hole mobility

Due to the low mobility of charge carriers in organic semiconductors, the injected carrier forms a space charge. This space charge creates a field that opposes the applied bias and thus decreases the voltage drop across junction; as a result, space charge limited currents (SCLCs) have been proposed as the dominant conduction mechanism in organic semiconductors by researchers.\textsuperscript{59} Ohmic conduction can be described by equation (1):

\[
J = \frac{9}{8}\mu\varepsilon_0\varepsilon_r\frac{V^2}{d^3} \quad (1)
\]

where \( J \) is the current density, \( \mu \) is the hole mobility, \( \varepsilon_o \) is the vacuum permittivity (8.85 x 10\textsuperscript{-12} F/m), \( \varepsilon_r \) is the dielectric constant of the material (normally taken to approach 3 for OSs), \( V \) is the applied bias, and \( d \) is the film thickness.

The hole-only devices were fabricated as following: Tin-doped indium oxide (ITO) coated glass substrates were cleaned by using detergent and acetone. The substrates were then treated by a mixture of water, ammonia (25%), and hydrogen peroxide (28%) (5:1:1 by volume). A 40 nm thick PEDOT: PSS layer was spin-coated onto the substrates, which were then annealed at 120 °C for 30 min in air. The substrates were then transferred into a glovebox for further fabrication steps. The HTMs were dissolved in anhydrous chlorobenzene at 70 °C with a solution concentration of 10 mg/ml. This solution was spin-coated at 2000 rpm to yield films. The thicknesses of the films are measured by using a Dektak 6M profilometer. 10 nm of molybdenum trioxide was then evaporated onto the active layer under high vacuum (less than 10\textsuperscript{-6} mbar). Finally, aluminum contact, 90 nm, has been applied via evaporation through a shadow mask. \( J-V \) characteristics of the devices have been measured with a Keithley 2400 Source-Measure unit, interfaced with a computer.

2.5. Conductivity

The electrical conductivities of the HTM films were determined by using two-probe electrical conductivity measurements, which were performed by following a published procedure.\textsuperscript{60} Conductivity devices structure was shown in Figure 13, and the electrical conductivity (\( \sigma \)) was calculated by using the following equation (2):
where $L$ is the channel length 10 mm, $W$ is the channel width 2 mm, $D$ is the film thickness of the TiO$_2$ and HTM, and $R$ is the film resistance calculated from the gradients of the curves.

\[
\sigma = \frac{W}{R L D} \quad (2)
\]

Figure 13. Schematic illustrations of the conductivity device: (a) top-sectional view; (b) cross-sectional view.

The conductivity devices were fabricated as following: Glass substrates without conductive layer were carefully cleaned in ultrasonic bath of detergent, deionized water, acetone and ethanol successively. Remaining organic residues were removed with 10 min by airbrushing. A thin layer of nanoporous TiO$_2$ was coated on the glass substrates by spin-coating with a diluted TiO$_2$ paste (Dyesol DSL 18NR-T) with terpineol (1:3, mass ratio). The thickness of the film is ca. 500 nm, as measured with a DekTak profilometer. After sintering the TiO$_2$ film on a hotplate at 500 °C for 30 min, the film was cooled to room temperature, after that it was subsequently deposited by spin-coating a solution of HTM in chlorobenzene, whereas the concentrations were the same as in case of photovoltaic devices. $J$-$V$ characteristics were recorded by a Keithley 2400 Source-Measure unit. The current was measured when a bias voltage from -2 V to 2 V was applied across the two silver layers. The inverse of the slope obtained from the current-voltage curve is the film resistance.

2.6. Photovoltaic property characterization

The photovoltaic property characterizations of solar cells include the current-voltage (I-V) characteristic and incident-photon-to-electron conversion
efficiency (IPCE). I-V characteristic is determined under simulated sunlight illumination and IPCE is determined under a monochromatic light. In this thesis, the I-V curves were recorded by using a Keithley 2400 Source-Measure unit under simulated sunlight (light intensity of 100 mW·cm⁻²) from a Newport 300 W solar simulator, and the IPCE was recorded by using a monochromatic light from a system consisting of a Xenon lamp, a monochromator and appropriate filters. All of these two systems are calibrated by using a certified silicon solar cell (Fraunhofer ISE, Freiburg, Germany) before use.

2.6.1. Current-voltage measurement

The I-V measurement is the most important technique for the evaluation of the photovoltaic performance of a solar cell. The following parameters, short-circuit current (J_{sc}), open-circuit potential (V_{oc}), fill factor (ff) and efficiency (η), could be obtained from a I-V curve (as shown in Figure 14).

![Figure 14. I-V curve of a DSC device.](image)

The value of J_{sc} can be obtained when the voltage is zero and the value of V_{oc} can be extracted when current is zero from Figure 14. In addition, the maximum power point (P_{max}) also could be found when the product of the photocurrent and voltage reaches its maximum value (J_{max} and V_{max}). The overall light-to-electricity conversion efficiency (η) of a DSC device is therefore defined by the ratio of the maximum power to the power of the incident light (P_{in} = 100 mW·cm⁻², AM 1.5G), as the corresponding equation is given by following:
\[
\eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{J_{\text{sc}} \cdot V_{\text{oc}} \cdot ff}{P_{\text{in}}} \quad (3)
\]

Where the \( ff \) is the ratio of the maximum power to the external short and open circuit values, as described in equation (4):

\[
ff = \frac{J_{\text{max}} \cdot V_{\text{max}}}{J_{\text{sc}} \cdot V_{\text{oc}}} \quad (4)
\]

The fill factor is a parameter to evaluate the deviation of the measured solar cell efficiency from the theoretical maximum power output of the cell.

2.6.2. \textit{Incident photon-to-current conversion efficiency}

The incident photon-to-electron conversion efficiency (IPCE) is defined by the ratio of the number of electrons generated in a solar cell to the number of photons incident on the photoactive surface of the device at a given wavelength that determined under monochromatic illumination, which also can be defined as the following equation (5):

\[
\text{IPCE} = \frac{n_{\text{electrons}}(\lambda)}{n_{\text{photons}}(\lambda)} = \frac{h \cdot c \cdot J_{\text{sc}}(\lambda)}{e \cdot \lambda \cdot P_{\text{in}}(\lambda)} \quad (5)
\]

where \( J_{\text{sc}}(\lambda) \) corresponds to the measured photocurrent, \( P_{\text{in}}(\lambda) \) is the input optical power and \( \lambda \) the wavelength of the incident irradiation. In general the IPCE is measured under short-circuit conditions and is graphically displayed versus the corresponding wavelength in a photovoltaic action spectra. The IPCE corresponds to the photo response or external quantum efficiency.

\[
\text{IPCE} = LHE \cdot \varphi_{\text{inj}} \cdot \varphi_{\text{reg}} \cdot \eta_{cc} \quad (6)
\]

The IPCE is affected by several factors such as the product of the light harvesting efficiency (\( LHE \)), injection efficiency (\( \varphi_{\text{inj}} \)), regeneration efficiency (\( \varphi_{\text{reg}} \)) and charge collection efficiency (\( \eta_{cc} \)), as described in equation (6).
3. Triphenylamine-based HTMs
(Paper I and Paper II)

3.1. Introduction

Triphenylamine derivatives\textsuperscript{61} are well known HTMs that have been widely applied in many organic electronic devices, such as OPVs, OLEDs and OFETs due to their high hole mobility, sufficient thermal stability, non-crystalline or amorphous morphology of thin films and outstanding electrochemical reversibility. The hole transporting properties are undertaken by the nitrogen atom of the TPA unit,\textsuperscript{62} which can be associated into a wide range of small molecules (e.g. TPD, Spiro-OMeTAD) and polymers (e.g. PTAA).

Many TPA-based small molecules and polymers have already been developed and investigated in sDSCs and PSCs during the past decade. Among them, Spiro-OMeTAD has been considered as one of the most successful HTMs, which has yielded the highest power conversion efficiencies both in sDSCs and PSCs. However, the low charge carrier mobility and lengthy synthetic route of Spiro-OMeTAD may make it impractical for industrial applications in the future. In addition, the substantial overpotential required for dye regeneration by Spiro-OMeTAD limits the maximum obtainable voltage of the system, that is, the open-circuit voltage of device could be tuned by adjusting the HOMO of the HTM. Therefore, the aim of this Chapter is to design and synthesize a series of TPA-based oligomers with easy synthetic routes, high charge carrier mobilities and more negative HOMO levels for sDSCs. In addition, the energy level, charge carrier mobility and molecule size of the TPA-based HTMs on the influence of the device performance will be systematically investigated.

![Triphenylamine (TPA)](image)
Figure 15. Molecular structures of X1, X2, X3 and X35; the molecular weights are given in g·mol⁻¹.

3.2. Design and synthesis

It has been discussed in Chapter 1 that the high solubility and charge carrier mobility of HTMs are two important factors for the achievement of high performance sDSC device. The solubility of the TPA-based HTMs can be enhanced by the generation of more extended TPA oligomers. To this end we designed a series of TPA-based HTMs termed X1, X2, X3 and X35 (Figure 15) with different oligomerization numbers.

The synthetic routes of X1, X2, X3 and X35 are described in Figure 16. All of the synthetic procedures of these X-based HTMs have no more than 3 steps, which are more economical than that of the well-known HTM Spiro-OMeTAD. The HTM-X1, X2 and X3 are synthesized straightforwardly by using one or two steps palladium-catalyzed Buchwald-Hartwig reaction with commercial raw materials, rendering overall yield up to 95%, 90% and 91%, respectively. The starburst HTM X35 has the same molecular weight with X3 but different molecular structure, which is synthesized through two-step Suzuki coupling-cross reactions with the final yield of 55%. The introduction of the methoxy groups for the X-HTMs are very important, which has been
reported to have a high tendency to stabilize the radical cations and also increase the hole mobility and solubility.\textsuperscript{16,41,63} All of the intermediates and final products are characterized by $^1$H NMR, $^{13}$C NMR and high resolution mass spectrometry (HR-MS).

\textbf{Figure 16. The synthetic routes of X1, X2, X3 and X35.}
3.3. Material characterization

3.3.1. Computational study

Density functional theory (DFT) calculations were performed at the B3LYP 6-31G (d) level with Gaussian 09 program. The electronic distribution of the HOMOs and the LUMOs of the X-HTMs and Spiro-OMeTAD are shown in Figure 17. The HOMOs of these HTMs are almost delocalized in the whole systems, which forecast good hole transport properties.

![Figure 17. Frontier orbitals of the HTM-X1, X2, X3, X35 and Spiro-OMeTAD.](image)

The charge transport rate of the materials can be calculated by the Marcus rate equation (7).

\[
W_{ji} = \frac{V_{ji}^2}{\hbar} \sqrt{\frac{\pi}{K_B T \lambda}} \cdot \exp \left[ - \frac{(\Delta G_{ji} + \lambda)^2}{4 \lambda K_B T} \right] (7)
\]

where, \( V_{ji} \) is the transfer integral between site \( i \) and site \( j \); \( \lambda \) is the reorganization energy; \( \Delta G_{ji} \) is the site energy difference between the site \( i \) and site \( j \) (normally taken to approach zero for the pure molecular crystals). The charge transfer rate is highly related to transfer integral \( V_{ji} \) and the reorganization energy \( \lambda \), which can be concluded from the equation (7). In general, large transfer integral and small reorganization energy of the HTMs indicates high charge transfer rate for holes or electrons. All of the calculated reorganization energy are listed in Table 1. X3 exhibits the smallest calculated reorganization energy of 119 meV that is expected the fastest hole transport property among all of these HTMs, which might be due to its larger conjugation length as compared to the X1, X2, and Spiro-OMeTAD from the structural point of view. This result also suggests that X3 is expected higher
hole mobility and conductivity than the other HTMs in the devices, which will be discussed later.

**Table 1.** The Reorganization Energy of the different HTMs calculated with four-point method based on the adiabatic potential energy surface.

<table>
<thead>
<tr>
<th>HTMs</th>
<th>X1</th>
<th>X2</th>
<th>X3</th>
<th>X35</th>
<th>Spiro-OMeTAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reorganization Energy (meV)</td>
<td>216</td>
<td>154</td>
<td>119</td>
<td>129</td>
<td>147</td>
</tr>
</tbody>
</table>

The isomers of X3 with different configurations are also calculated by the frozen dihedral angle of the carbon atom 1-2-3-4, which is illustrated with the cyan color in Figure 18. The structure of X3 with different angles from 140.57 to 38.79 degree are optimized, and the corresponding energy values and the three configurations at the minima are shown in Figure 18. Computation showed that X3 existed in three stable configurations at 140.57, 40.57 and 38.79 degree, named Cis, Vert and Trans configuration, respectively. This result implies that the configurations of X3 are chaotic and amorphous in the hole transport films, which is beneficial for the pore penetration and film formation during the device fabrication.

**Figure 18.** Potential energy surface of X3 with different dihedral angles and the configurations of its isomers.
3.3.2. Optical and electrochemical properties

The normalized UV-Visible absorption and photoluminescence spectra of X1, X2, X3 and X35 together with Spiro-OMeTAD are shown in Figure 19, which are recorded in DCM with a concentration of $10^{-5}$ M; the corresponding data are described in Table 2. All of these X-HTMs have similar absorption peaks around 370 nm as well as homologous emission peak around 430 nm, which indicates that the extended TPA unit shows little effect on the photophysical properties of these HTMs. In addition, the optical band gap $E_{o-o}$ of the materials can be obtained from the intersection of absorption and emission spectra, which are listed in Table 2.

![Normalized UV-Visible absorption and photoluminescence spectra of X1, X2, X3 and X35 in DCM (10^{-5} M).](image)

We firstly investigate the oxidation potentials of these HTMs in DCM solution by using cyclic voltammetry (CV), and the corresponding data are recorded in Table 2. The oxidation potentials of the X-HTMs are more positive than that of the Spiro-OMeTAD. However, the overpotentials of the X-HTMs are determined between 160 mV to 110 mV as compared to the oxidation potential of the LEG4 dye,\(^{19}\) which are not sufficient enough for the dye regeneration by the HTMs. Generally, the overpotential between the HTM and dye should be over 180 mV so that the hole transfer from the dye to HTM could be sufficiently achieved.\(^{64,65}\) According to the previous work, the protonation/deprotonation of surface-adsorbed hydroxyl groups has been shown to shift the density of states of the nanocrystalline TiO\(_2\) band and to modulate the reduction/oxidation potentials of dyes and HTMs.\(^{38}\) Subsequently, the oxidation potentials of these HTMs on TiO\(_2\) electrode are
further determined; all of the data are listed in Table 2. All of the HTMs show larger overpotentials from 190 mV to 370 mV compared to that of the LEG4 dye on TiO₂ electrode, thus, the driving force should be sufficient enough to regenerate the oxidized dye in the device. In addition, the oxidation potentials of the X-HTMs are more positive than that of Spiro-OMeTAD in both DCM solution and on TiO₂ electrode; thereby higher open-circuit voltage is expected in the devices under the same conditions, as we will discuss afterwards.

Table 2. Summary of optical and electrochemical data of the HTMs used in this study.

<table>
<thead>
<tr>
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<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>X1</td>
<td>353</td>
<td>434</td>
<td>0.72</td>
<td>0.81</td>
<td>3.12</td>
<td>608.7</td>
</tr>
<tr>
<td>X2</td>
<td>371</td>
<td>429</td>
<td>0.73</td>
<td>0.89</td>
<td>3.06</td>
<td>882.1</td>
</tr>
<tr>
<td>X3</td>
<td>373</td>
<td>429</td>
<td>0.77</td>
<td>0.89</td>
<td>3.03</td>
<td>1155.4</td>
</tr>
<tr>
<td>X35</td>
<td>370</td>
<td>432</td>
<td>0.75</td>
<td>0.93</td>
<td>3.05</td>
<td>1155.4</td>
</tr>
<tr>
<td>Spiro-OMeTAD</td>
<td>385</td>
<td>424</td>
<td>0.63</td>
<td>0.75</td>
<td>3.05</td>
<td>1225.4</td>
</tr>
<tr>
<td>LEG4</td>
<td>514</td>
<td>717</td>
<td>0.88</td>
<td>1.12</td>
<td>2.04</td>
<td>1125.6</td>
</tr>
</tbody>
</table>

a) The values were determined in DCM, detailed procedures have been described in section 2.2.3. b) The values were determined on TiO₂ electrode, detailed procedures have been described in section 2.2.3. c) Calculated from the intersection of the normalized absorption and emission spectra.

3.3.3. Charge carrier mobilities

Charge transport is an important factor to consider in the design of highly efficient HTMs for sDSCs and PSCs. SCLCs is a commonly used method to determine the hole mobility of HTM, which has been discussed in Chapter 2. The measured hole mobility data of the HTMs are described in Table 3. The hole mobility values of X1, X2 and X3 are higher than that of Spiro-OMeTAD, which are in good agreement with the calculated results in the section 3.3.1. Surprisingly, the measured hole mobility of X3 (1.47×10⁻⁴ cm²·V⁻¹·s⁻¹) is almost one order of magnitude higher than that of Spiro-OMeTAD (1.67×10⁻⁵ cm²·V⁻¹·s⁻¹), which might contribute to obtain superior performance in the device.
Figure 20. Current-voltage characteristics of different HTM films (doping with LiTFSI).

Table 3. Hole mobility and conductivity of the HTMs used in this study.

<table>
<thead>
<tr>
<th>HTMs a)</th>
<th>Hole Mobility None Li⁺ doping (cm²·V⁻¹·s⁻¹)</th>
<th>Conductivity None Li⁺ doping (S·cm⁻¹)</th>
<th>Conductivity 30 mM Li⁺ (S·cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X1</td>
<td>6.19×10⁻⁵</td>
<td>4.95×10⁻⁷</td>
<td>3.43×10⁻⁵</td>
</tr>
<tr>
<td>X2</td>
<td>9.82×10⁻⁵</td>
<td>2.75×10⁻⁷</td>
<td>6.96×10⁻⁵</td>
</tr>
<tr>
<td>X3</td>
<td>1.47×10⁻⁴</td>
<td>6.98×10⁻⁷</td>
<td>1.99×10⁻⁴</td>
</tr>
<tr>
<td>X35</td>
<td>1.34×10⁻⁵</td>
<td>4.47×10⁻⁷</td>
<td>1.20×10⁻⁴</td>
</tr>
<tr>
<td>Spiro-OMeTAD</td>
<td>1.67×10⁻⁵</td>
<td>3.54×10⁻⁷</td>
<td>1.37×10⁻⁴</td>
</tr>
</tbody>
</table>

a) The concentrations of the HTMs were the same as in case of photovoltaic devices.

We used two-probe electrical conductivity measurements to investigate the conductivities of the X-HTMs and Spiro-OMeTAD, which has been discussed in Chapter 2. The obtained current-voltage curves are showed in Figure 20, and the corresponding conductivity values of the HTMs (both with and without LiTFSI) are depicted in Table 3. All of the HTMs show poor conductivities in the absence of LiTFSI, which are less than 10⁻⁶ S·cm⁻¹. However, the conductivity can be dramatically improved by two orders of magnitude when doped with LiTFSI. Notably, X₃ exhibits slightly higher conductivity than that
of X1, X2, X35 and Spiro-OMeTAD under both doping and non-doping conditions, most likely due to its better conjugated length, resulting in more efficient π-π stacking in the hole transporting films. Our preliminary data clearly showed that the calculated reorganization energy, measured hole mobility and conductivity of X3 are better than those of the well-known HTM Spiro-OMeTAD as well as X1, X2 and X35. X3 thereby is expected to exhibit a better performance in the photovoltaic devices.

3.3.4. Photovoltaic properties

We employed the high molar extinction coefficient organic D-π-A dye LEG4 as the photosensitizer and fabricated sDSC devices with the above HTMs. It has been widely demonstrated that the LiTFSI plays an important role in sDSC, which is required at the dye-sensitized heterojunction to enhance the charge generation. Most recently, researchers discovered that LiTFSI also can act as a p-type dopant for HTM and can significantly increase the conductivity of the HTM films. Thus, we firstly optimized the doping concentration of LiTFSI for the different HTMs. The final optimal LiTFSI concentration for X1, X2, X3 and X35 based sDSCs were 60 mM, 50 mM, 30mM and 30 mM, respectively, which then yield the best efficiencies for each material. The best doping concentration of LiTFSI for Spiro-OMeTAD is 20 mM that used here according to the published literatures. The J-V characteristics of the sDSCs with those HTMs based under optimal doping concentrations are shown in Figure 21(a); the corresponding parameters are depicted in Table 4. The X3 and X35 based devices obtained the efficiencies of 5.8% and 5.5%, respectively, which are slightly higher than that of the Spiro-OMeTAD based one (5.4%). The devices made with X1 and X2 yielded the PCEs of 4.4% and 5.0 %, respectively, which are lower than that of the X3, X35 and Spiro-OMeTAD based ones. We noted that the inferior device performance of X1 and X2 is mainly attributed to their low Voc. However, the Jsc density of all the devices can reach the same level, around 9.5 mA cm\(^{-2}\) under the best optimal LiTFSI doping concentration, which means that all the X-HTMs can effectively regenerate the oxidation state LEG4 dye. This result is in accordance with the oxidation potential measurement of the X-HTMs on TiO\(_2\) electrode, which has been discussed in section 3.3.2. In addition, the corresponding IPCE spectra of these homologous devices were recorded in Figure 21(b), all of these HTMs based devices exhibit the similar IPCE of 75% at the maximum absorption wavelength of 475 nm.
Figure 21. (a). J-V characteristics of different HTMs based sDSC device measured under standard AM1.5G solar intensity. (b). Corresponding IPCE spectra of the devices.

Table 4. Photovoltaic parameters determined from J-V measurements of the sDSCs doping with different concentration of LiTFSI based on these HTMs. a)

<table>
<thead>
<tr>
<th>HTMs</th>
<th>LiTFSI [mM]</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt; [V]</th>
<th>J&lt;sub&gt;sc&lt;/sub&gt; [mA·cm&lt;sup&gt;-2&lt;/sup&gt;]</th>
<th>ff</th>
<th>η [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>X1&lt;sup&gt;b)&lt;/sup&gt;</td>
<td>60</td>
<td>0.725±0.025 (0.75)</td>
<td>9.26±0.34 (9.47)</td>
<td>0.56±0.06 (0.62)</td>
<td>4.0±0.2 (4.4)</td>
</tr>
<tr>
<td>X2&lt;sup&gt;c)&lt;/sup&gt;</td>
<td>50</td>
<td>0.800±0.015 (0.81)</td>
<td>9.51±0.42 (9.79)</td>
<td>0.60±0.04 (0.63)</td>
<td>4.7±0.3 (5.0)</td>
</tr>
<tr>
<td>X3&lt;sup&gt;d)&lt;/sup&gt;</td>
<td>30</td>
<td>0.880±0.035 (0.91)</td>
<td>9.23±0.45 (9.52)</td>
<td>0.62±0.05 (0.67)</td>
<td>5.4±0.4 (5.8)</td>
</tr>
<tr>
<td>X35&lt;sup&gt;e)&lt;/sup&gt;</td>
<td>30</td>
<td>0.875±0.025 (0.89)</td>
<td>9.62±0.35 (9.81)</td>
<td>0.61±0.03 (0.63)</td>
<td>5.2±0.3 (5.5)</td>
</tr>
<tr>
<td>Spiro-OMeTAD&lt;sup&gt;f)&lt;/sup&gt;</td>
<td>20</td>
<td>0.905±0.025 (0.93)</td>
<td>9.13±0.51 (9.37)</td>
<td>0.58±0.02 (0.62)</td>
<td>5.2±0.2 (5.4)</td>
</tr>
</tbody>
</table>

a) 2.0 µm TiO<sub>2</sub> film; b) 170 mM HTM doped with 200 mM t-BP and 60 mM LiTFSI; c) 130 mM HTM doped with 200 mM t-BP and 50 mM LiTFSI; d) 100 mM HTM doped with 200 mM t-BP and 30 mM LiTFSI; e) 100 mM HTM doped with 200 mM t-BP and 30 mM LiTFSI; f) 150 mM HTM doped with 200 mM t-BP and 20 mM LiTFSI. Note: the values are reported as the average obtained from 8 devices.

As previously discussed, the X-HTMs showed more positive oxidation potentials than that of Spiro-OMeTAD and were expected to obtain higher V<sub>oc</sub> in the devices. However, we noted that the V<sub>oc</sub> of the X-HTMs based devices were still lower than that of the Spiro-OMeTAD-based one, which was reversed to our expectation. This result indicated that some other parameters
beyond the oxidation potential of the HTMs might play important roles in the $V_{oc}$ of sDSC devices.

Generally, the device performance of DSC (both in liquid-electrolyte DSCs and solid-stated DSCs) can be enhanced by addition of lithium salts, such as the LiTFSI and LiClO$_4$. These additives are known to modulate the energetics of the cell components and hence influence the dynamics and yields of the interfacial charge-transfer reactions.$^{67-69}$ More specifically, lithium ions are known to shift the TiO$_2$ conduction-band edge to more positive potentials, and to screen electrostatic interactions, resulting in increased charge-injection efficiency and reduced recombination,$^70$ whereas 4-tert-butyl pyridine (t-BP) shifts the conduction-band edge to more negative potentials,$^71$ leading to an increase of the device $V_{oc}$. In consideration of that the different doping amount of LiTFSI can affect the $V_{oc}$ of the device; we further investigated the HTMs at the same doping conditions.

![Figure 22](image-url)

**Figure 22.** (a) J-V curves of sDSCs with different HTMs doping with 20 mM LiTFSI. (b) Corresponding electron lifetime curves of the sDSCs. (c) J-V curves of sDSCs with different HTMs doping with 30 mM LiTFSI. (d) Corresponding electron lifetime curves of the sDSCs.
Table 5. Photovoltaic parameters determined from J-V measurements of the sDSCs doping with the same concentration of LiTFSI based on these HTMs.\(^a\).

<table>
<thead>
<tr>
<th>HTMs</th>
<th>LiTFSI [mM]</th>
<th>(V_{oc}) [V]</th>
<th>(J_{sc}) [mA·cm(^{-2})]</th>
<th>(ff)</th>
<th>(\eta) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>X1 (^b)</td>
<td>20</td>
<td>0.765±0.45 (0.80)</td>
<td>7.56±0.66 (8.17)</td>
<td>0.50±0.05 (0.55)</td>
<td>3.1±0.5 (3.6)</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.755±0.35 (0.79)</td>
<td>8.11±0.58 (8.64)</td>
<td>0.53±0.04 (0.56)</td>
<td>3.2±0.6 (3.8)</td>
</tr>
<tr>
<td>X2 (^c)</td>
<td>20</td>
<td>0.845±0.25 (0.87)</td>
<td>8.36±0.29 (8.54)</td>
<td>0.56±0.03 (0.58)</td>
<td>3.8±0.5 (4.3)</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.825±0.35 (0.86)</td>
<td>8.95±0.43 (9.30)</td>
<td>0.57±0.02 (0.58)</td>
<td>4.2±0.4 (4.6)</td>
</tr>
<tr>
<td>X3 (^d)</td>
<td>20</td>
<td>0.905±0.025 (0.93)</td>
<td>8.91±0.25 (9.15)</td>
<td>0.56±0.05 (0.61)</td>
<td>4.8±0.4 (5.2)</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.880±0.035 (0.91)</td>
<td>9.23±0.45 (9.52)</td>
<td>0.62±0.05 (0.67)</td>
<td>5.4±0.4 (5.8)</td>
</tr>
<tr>
<td>X35 (^e)</td>
<td>20</td>
<td>0.865±0.045 (0.90)</td>
<td>8.89±0.37 (9.24)</td>
<td>0.55±0.07 (0.62)</td>
<td>4.9±0.3 (5.2)</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.875±0.025 (0.89)</td>
<td>9.62±0.35 (9.81)</td>
<td>0.61±0.03 (0.63)</td>
<td>5.2±0.3 (5.5)</td>
</tr>
<tr>
<td>Spiro-OMeTAD (^f)</td>
<td>20</td>
<td>0.905±0.025 (0.93)</td>
<td>9.13±0.51 (9.37)</td>
<td>0.58±0.02 (0.62)</td>
<td>5.2±0.2 (5.4)</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.875±0.015 (0.89)</td>
<td>9.28±0.41 (9.50)</td>
<td>0.56±0.06 (0.61)</td>
<td>4.8±0.4 (5.2)</td>
</tr>
</tbody>
</table>

\(^a\) 2.0 µm TiO\(_2\) film; \(^b\) 170 mM HTM doped with 200 mM t-BP; \(^c\) 140 mM HTM doped with 200 mM t-BP; \(^d\) 100 mM HTM doped with 200 mM t-BP; \(^e\) 100 mM HTM doped with 200 mM t-BP; \(^f\) 150 mM HTM doped with 200 mM t-BP. Note: the values are reported as the average obtained from 8 devices.

Figure 22(a) and 22(c) showed the J-\(V\) curves of the X-HTMs and Spiro-OMeTAD based devices with addition of 20mM or 30mM LiTFSI and 200 mM t-BP, and the photovoltaic parameters were collected in Table 5. We noted that the \(ff\) and \(J_{sc}\) of X3, X35 and Spiro-OMeTAD-based devices are higher than those of X1 and X2 based ones both under 20 mM and 30 mM doping concentration of LiTFSI, which might be due to the higher conductivity of the formers compared to those of X1 and X2. In general, the higher conductivity of HTM can decrease the hole transfer resistance in cell. Moreover, the \(V_{oc}\) of X1- and X2-based devices are much lower than those of X3, X35 and Spiro-OMeTAD-based devices, which might be in virtue of the small molecule size of X1 and X2. The small HTM molecules are not only easy to permeate into the meso-TiO\(_2\) pores, but also easy to permeate into the lacunas between dye molecules and contact directly with TiO\(_2\) surface, then the
The recombination process between injected electrons and oxidized HTMs is faster. In order to verify this hypothesis, we further used transient photovoltage decay measurement to investigate the electron lifetime ($\tau_e$) of the device with different HTMs under the same doping conditions, the corresponding curves of $\tau_e$ plotted vs. $V_{oc}$ are shown in Figure 22(b) and 22(d). Generally, the lower $\tau_e$ values indicate faster electron recombination in the device. We observed that the $\tau_e$ values of the X3-based device were obviously the highest ones among all the HTMs when doped with 30 mM LiTFSI, while the Spiro-OMeTAD-based device showed the slowest electron recombination when doped with 20 mM LiTFSI. This result suggested that different doping ratios of LiTFSI for the HTM could affect electron recombination in the related devices. Furthermore, we noted that the electron recombination rates of the X1 and X2-based device were much faster than those of X3, X35 and Spiro-OMeTAD-based ones both under low and high concentration of LiTFSI, which is in good agreement with our previous assumption that the HTMs-X1 and X2 with smaller molecule size can more easily permeate into the meso-TiO$_2$ pores and approach to the TiO$_2$ interface, resulting in a fast electron recombination process in the devices. Obviously, the oxidation potential of X1 is more positive than that of the Spiro-OMeTAD, the hole mobility of X1 is also higher, and yet the $V_{oc}$ of the X1-based device is much lower than that of the Spiro-OMeTAD based one both under 20 mM and 30 mM doping concentrations of LiTFSI. This phenomenon most likely are attributed to the small molecular size of X1 less than half of Spiro-OMeTAD. This is a good case to show that a smaller molecular HTM leads to faster electron recombination, giving lower $V_{oc}$ in the device.

![Figure 23](image-url)
The $V_{oc}$ of the devices can be significantly increased upon enlarging the molecular weight of HTMs by oligomerization of TPA units (Figure 23(b)). However, no obvious relationship can be observed from the oxidation potential of the HTMs and the $V_{oc}$ of the devices (Figure 23(a)). At this stage, it is hard to rule out that the more positive oxidation potential of the HTM is a key factor for obtaining a high $V_{oc}$ in a sDSC device. Nevertheless, the above conclusion demonstrated that the smaller molecular size of the HTM induced faster electron recombination in the device, which might indicate that the molecule size of the HTM is an important factor as regarding its impact on the $V_{oc}$ in the device, or even more important than the HOMO level of the HTM.

![Figure 24](image.png)

**Figure 24.** (a). J-V characteristics of the HTMs-based sDSCs measured under standard AM1.5G solar intensity. (b) Corresponding IPCE spectra of the devices.

**Table 6.** The photovoltaic properties of sDSCs devices based on ruthenium dye-Z907 and HTM-X3 and Spiro-OMeTAD.a)

<table>
<thead>
<tr>
<th>Devices</th>
<th>$J_{sc}$ [mA·cm$^{-2}$]</th>
<th>$V_{oc}$ [V]</th>
<th>$ff$</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z907+X3 b)</td>
<td>8.10</td>
<td>0.72</td>
<td>0.63</td>
<td>3.7</td>
</tr>
<tr>
<td>Z907+Spiro-OMeTAD  c)</td>
<td>7.28</td>
<td>0.75</td>
<td>0.64</td>
<td>3.5</td>
</tr>
</tbody>
</table>

a) 2.0 µm TiO$_2$ film; b) 90 mM HTM doped with 200 mM t-BP and 30 mM LiTFSI; c) 150 mM HTM doped with 200 mM t-BP and 20 mM LiTFSI.

In addition, HTM-X3 not only exhibits better performance in the organic dye LEG4-based devices than that of Spiro-OMeTAD, but also showed higher PCE in the ruthenium dye-Z907-based devices (as shown in Figure 24 and Table 6).
3.4. Conclusions

A series of novel triphenylamine-based HTMs with different conjugation length, oxidation potential and hole mobility were designed and synthesized, which also have been successfully applied in sDSCs.

➢ To design high performance HTMs, one should consider the following aspects: small reorganization energy, high hole mobility and conductivity. Typically, the larger conjugation length of the HTM is highly recommended.

➢ The results of transient photovoltage measurements showed that the smaller molecular size of the HTM induced faster electron recombination in the device, which should be avoided in the materials design in the future.

➢ The experiment involving different HTMs using different LiTFSI doping concentrations showed that LiTFSI was a vital part of sDSCs to achieve the optimal efficiency, which provided an effective way to evaluate more HTMs for sDSCs, and eventually materials for perovskite solar cells as well in the future.
4. Carbazole-based HTMs

(Paper III)

4.1. Introduction

During the past two decades, carbazole-based derivatives have been intensively investigated in organic electronic devices due to their interesting properties, such as the low cost raw material of 9H-carbazole, excellent chemical stability of the fully aromatic unit.\textsuperscript{72,73} The most fascinating advantage is the versatility of the carbazole reactive sites that can be substituted with a wide arrange of functional groups,\textsuperscript{74} allowing fine-tune of its photochemical properties, which can be utilized in the molecular design of new types of HTMs in OLEDs\textsuperscript{75,76} and sDSCs\textsuperscript{73}, and as an electron donor group for the development of new organic photosensitizers.\textsuperscript{77}

As discussed in Chapter 3, the reorganization energy, hole mobility, conductivity and molecule size of HTM play critical roles in the device performance of sDSCs. The results demonstrated that the HTM bearing small reorganization energy, high hole mobility, conductivity and large molecule size of HTM is highly expected to obtain better photovoltaic performance in the device. Thus, the aim of this Chapter is to design and synthesize carbazole-based HTMs with high hole mobility, conductivity and large molecule size for the application in sDSCs and PSCs.

\begin{center}
\includegraphics[width=0.2\textwidth]{carbazole.png}
\end{center}

\textbf{Carbazole}
Figure 25. Molecular structures of the target HTM X19, X51; the molecular weights are given in g·mol⁻¹.

4.2. Design and synthesis

Our previous work in Chapter 3 has showed that the HTM with small molecular size induce fast electron recombination in the device. In order to suppress the electron recombination process and obtain higher $V_{oc}$ in sDSCs, we designed a larger HTM termed X51 (chemical structure shown in Figure 25) with molecular weight of 1393.6 g·mol⁻¹, which is higher than that of the well-known HTM Spiro-OMeTAD (1225.4 g·mol⁻¹). In addition, the smaller size HTM-X19 (chemical structure as shown in Figure 25) with molecular weight of 727.8 g·mol⁻¹ was employed as a reference in this study.

The synthetic routes of X19 and X51 are straightforward (as shown in Figure 26). A copper-catalyzed Ullman reaction and a palladium-catalyzed Buchwald-Hartwig reaction were utilized to synthesize the HTM X19 with overall yield up to 81%. Compared to X19, the synthesis of X51 requires one further step of protection and deprotection. All of the materials were characterized by $^1$H NMR, $^{13}$C NMR spectroscopy and high-resolution mass spectrometries HR-MS.
4.3. Material characterization

4.3.1. Computational study

The DFT calculations were carried out by Gaussian 09. The reorganization energy $\lambda$ is determined by the Nelson four-point method. The HOMO and LUMO orbitals are showed in Figure 27. As implied in Table 7, the calculated reorganization energy values of X19 and X51 are smaller than that of Spiro-
OMeTAD, which suggests that the hole mobility of these carbazole-based HTM might be higher than Spiro-OMeTAD. In addition, X51 will exhibit higher hole mobility than X19 as inferred from the calculation, which might be attributed to its larger conjugation length.

<table>
<thead>
<tr>
<th>HTMs</th>
<th>X19</th>
<th>X51</th>
<th>Spiro-OMeTAD</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>HOMO</strong></td>
<td><img src="image" alt="HOMO" /></td>
<td><img src="image" alt="HOMO" /></td>
<td><img src="image" alt="HOMO" /></td>
</tr>
<tr>
<td><strong>LUMO</strong></td>
<td><img src="image" alt="LUMO" /></td>
<td><img src="image" alt="LUMO" /></td>
<td><img src="image" alt="LUMO" /></td>
</tr>
</tbody>
</table>

*Figure 27. Frontier orbitals of the HTM-X19 and X51.*

### 4.3.2. Optical and electrochemical properties

The $E_{ox}$ of these carbazole-based HTMs were determined by the Differential Pulsed Voltammetry (DPV) that was shown in Figure 28(b), and the corresponding data are collected in Table 7. The $E_{ox}$ values were recorded to 0.61 V and 0.64 V vs. NHE in DCM solution for X19 and X51, respectively, which are at the same level with the oxidation potential of Spiro-OMeTAD (0.63 V). In this case, the carbazole-based HTMs and Spiro-OMeTAD should have similar ability for the regeneration of the oxidized state dye, which is good for the comparative study. The UV-Visible absorption and emission spectra of the HTMs are shown in Figure 28(a), and the photophysical data are listed in Table 7. All of these HTMs displayed weak absorption in the visible light region and will not obstruct sunlight from efficiently reaching the sensitizing dye molecules.
Figure 28. (a) Normalized UV-Visible absorption and photoluminescence of X19 and X51 in DCM (10^{-5} M). (b) Normalized differential pulsed voltammetry gravies (DPV) of X19, X51 and Spiro-OMeTAD in DCM (10^{-4} M).

Table 7. Summary of optical, electrochemical, photoelectrical properties and reorganization energy of the HTMs used in this study.

<table>
<thead>
<tr>
<th>HTMs</th>
<th>(\lambda_{\text{abs}}) [nm]</th>
<th>(\lambda_{\text{em}}) [nm]</th>
<th>(E_{\text{ox}}) a) [V vs NHE]</th>
<th>(E_{\sigma-\sigma}) b) [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>X19</td>
<td>310(max)</td>
<td>371</td>
<td>0.61</td>
<td>2.95</td>
</tr>
<tr>
<td>X51</td>
<td>307(max)</td>
<td>365</td>
<td>0.64</td>
<td>2.93</td>
</tr>
<tr>
<td>Spiro-OMeTAD</td>
<td>306</td>
<td>386(max)</td>
<td>0.63</td>
<td>3.05</td>
</tr>
</tbody>
</table>

a) The values were determined in DCM, detailed procedures have been described in section 2.2.3. b) Calculated from the intersection of the normalized absorption and emission spectra.

4.3.3. Charge carrier mobilities

The hole mobilities of the HTMs were determined by using SCLCs, which has been discussed in Chapter 2. Fitting the \(J-V\) curves (Figure 29(a)) for each HTMs to this expression gives the mobility data listed in Table 8. The hole mobility of X51 is slightly higher than that of X19, and both of these carbazole-based HTMs show almost three times higher hole mobility than that of Spiro-OMeTAD. These results are in good agreement with the implications from the computational data showing that the molecule X51 has the lowest calculated reorganization energy.
The conductivities of the HTM films doped with LiTFSI are depicted in Figure 29(b) and Table 8. The conductivity of X51 is slightly higher than that of Spiro-OMeTAD, but much higher than that of X19. This might be relevant to the larger conjugated system in the former molecular material, leading to more efficient \( \pi-\pi \) stacking in HTMs films. This result indicates that the HTM X51 could contribute to better photovoltaic performance as compared to those of X19- and as well as Spiro-OMeTAD-based devices.

![Figure 29](image)

**Figure 29.** (a) J-V characteristic of thin films in hole-conducting only devices. (b) Current-voltage characteristics of different HTM films.
Table 8. Summary of optical, electrochemical, photoelectrical properties and reorganization energy of the HTMs used in this study.

<table>
<thead>
<tr>
<th>HTMs</th>
<th>$E_R$ a) (meV)</th>
<th>Hole Mobility b) (cm$^2$·V$^{-1}$·s$^{-1}$)</th>
<th>Conductivity c) (S·cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X19</td>
<td>395</td>
<td>$1.19 \times 10^{-4}$</td>
<td>$2.88 \times 10^{-5}$</td>
</tr>
<tr>
<td>X51</td>
<td>378</td>
<td>$1.51 \times 10^{-4}$</td>
<td>$1.05 \times 10^{-4}$</td>
</tr>
<tr>
<td>Spiro-OMeTAD</td>
<td>495</td>
<td>$5.31 \times 10^{-5}$</td>
<td>$8.67 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

a) $E_R$: reorganization energy, calculated using the four-point method based on the adiabatic potential energy surface. b) Pure HTM without doping. c) X19 and X51 doped with 30 mM LiTFSI, Spiro-OMeTAD doped with 20 mM LiTFSI.

4.3.4. Photovoltaic properties

As has been dicussed in Chapter 3, the LiTFSI is essential in sDSCs to render a low series resistances and to facilitate photocurrent generation, and different HTMs need different doping concentration of Li$^+$. The final optimal Li$^+$ concentration used for X19- and X51-based cells was 30 mM. The $J$-$V$ curves of the best devices containing different HTMs are shown in Figure 30(a), and the corresponding parameters are stated in Table 9. The X51-based devices yielded the highest efficiency among these HTMs, up to 6.0%, which is slightly higher than that of the standard HTM Spiro-OMeTAD-based one, and much higher than that of the small size HTM X19-based device. We note that the $J_{sc}$ of the all devices are very similar after optimization of the concentration of LiTFSI. However, the $V_{oc}$ of the X19-based devices was 170 mV and 150 mV lower than those of the Spiro-OMeTAD- and X51-based devices, respectively. One explanation might be the HOMO levels of X51 and Spiro-OMeTAD are slightly more negative than that of X19, but the main reason might because of the smaller molecular size of X19 induces faster electron recombination in the device, which has been proposed in Chatper 3. In addition, the transient photovoltage decay measurements (Figure 30(b)) of these devices has clearly showed that the $\tau_e$ values for the X19-based device was much lower than those of X51 and Spiro-OMeTAD-based devices, which indicates that the X19-based device has much faster electron recombination progress. This is in good agreement with our previous conclusion that the HTM-X19 with small molecule size results in a facilitated approach to the TiO$_2$ interface, leading to a fast recombination process in the devices.
Figure 30. (a) J-V characteristics of X19-, X51- and Spiro-OMeTAD-based sDSCs studied under standard AM1.5G solar illumination, (b) Electron lifetime plots of X19-, X51- and Spiro-OMeTAD-based sDSCs at the best optimized conditions.

We also investigated these cabazole-based HTMs in PSCs under the same preparation conditions as used before without any further device optimization; thus, the concentrations of LiTFSI and t-BP were the same as the ones used for the sDSC devices. The J-V curves obtained from the best performing solar cells are showed in Figure 31(a), and the corresponding photovoltaic parameters are summarized in Table 9. We noted that the devices containing the HTM X51 exhibited a higher PCEs of 9.8%, in comparision with that of devices based on the HTM X19 (7.6%), also was comparable to the PCE of 10.2% obtained in devices based on the HTM Spiro-OMeTAD. It was also confirmed that the $J_{sc}$ values of the best performing devices were highly consistent with the results obtained from the IPCE measurements (Figure 31(b)). However, significant deviations were observed for the $V_{oc}$ and fill factor, where X51-based devices exhibited the highest $V_{oc}$ in agreement with the high HOMO energy level of X51. Moreover, the $ff$ of devices based on X51 and Spiro-OMeTAD both in sDSCs and PSCs were considerably higher than devices made with X19, which might be caused by the higher conductivity of the former materials resulting in a lower overall device serial resistance.
Figure 31. (a) J-V characteristics of X19-, X51- and Spiro-OMeTAD-based PSCs investigated under standard AM1.5G solar illumination. (b) Corresponding IPCE spectra of the cells.

Table 9. Photovoltaic parameters determined from J-V measurements of sDSCs based on the HTMs. The results were obtained under simulated AM1.5G solar illumination (100 mW·cm⁻²).

<table>
<thead>
<tr>
<th>Photosensitizers</th>
<th>HTMs</th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA·cm⁻²]</th>
<th>$ff$</th>
<th>$\eta$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>X19 b)</td>
<td></td>
<td>0.75</td>
<td>9.62</td>
<td>0.62</td>
<td>4.5</td>
</tr>
<tr>
<td>LEG4 a)</td>
<td>X51 c)</td>
<td>0.92</td>
<td>9.27</td>
<td>0.70</td>
<td>6.0</td>
</tr>
<tr>
<td>Spiro-OMeTAD d)</td>
<td></td>
<td>0.90</td>
<td>9.22</td>
<td>0.66</td>
<td>5.5</td>
</tr>
<tr>
<td>X19 f)</td>
<td></td>
<td>0.76</td>
<td>17.14</td>
<td>0.58</td>
<td>7.6</td>
</tr>
<tr>
<td>Perovskite e)</td>
<td>X51 g)</td>
<td>0.88</td>
<td>16.79</td>
<td>0.66</td>
<td>9.8</td>
</tr>
<tr>
<td>Spiro-OMeTAD h)</td>
<td></td>
<td>0.83</td>
<td>16.82</td>
<td>0.73</td>
<td>10.2</td>
</tr>
</tbody>
</table>

a) 2.0 µm TiO₂ film; b) 180 mM HTM doped with 200 mM t-BP and 30 mM LiTFSI; c) 90 mM HTM doped with 200 mM t-BP and 30 mM LiTFSI; d) 150 mM HTM doped with 200 mM t-BP and 20 mM LiTFSI; e) 350 nm TiO₂ film; f) 120mM HTM doped with 200 mM t-BP and 30 mM LiTFSI; g) 60 mM HTM doped with 200 mM t-BP and 30 mM LiTFSI; h) 70 mM HTM doped with 200 mM t-BP and 20 mM LiTFSI.
4.4. Conclusions

Two new small-molecule carbazole-based organic HTMs with different molecular weight, oxidation potential, hole mobility and electrical conductivity were designed and synthesized, which also have been successfully applied in both sDSCs and PSCs.

- The HTM-X51 with a larger molecular size exhibited a better performance in both sDSCs and PSCs, mainly due to its smaller reorganization energy, higher hole mobility and conductivity.
- The results of the transient photovoltage measurement showed that the smaller molecular size of the HTM induced faster electron recombination in the device, which is in good agreement with the conclusion obtained in Chapter 3.
- Molecular engineering to develop new and efficient HTMs with high hole mobility and high conductivity is a feasible strategy for the sDSCs and PSCs in the future.
5. P-type Dopants for HTMs

(Paper IV and Paper V)

5.1. Introduction

In Chapter 3 and 4, we have successfully discussed the development of a series low-cost triphenylamine and carbazole-based HTMs for sDSCs and PSCs. However, the low intrinsic electrical conductivity of these organic HTMs is a limitation for the achievement of high performance photovoltaic devices. As discussed in Chapter 1, p-type chemical doping is a powerful method to improve the charge transport and the overall electrical conductivity of HTMs, which has been widely used in p-type organic HTMs, such as Spiro-OMeTAD in sDSCs and PSCs. To date, a number of p-type chemical dopants have been successfully developed and investigated in sDSCs and PSCs by researchers, such as Co(III) complexes-FK102\textsuperscript{14} and FK209\textsuperscript{52} (chemical structures as shown in Figure 12), (p-BrC\textsubscript{6}H\textsubscript{4})\textsubscript{3}NSbCl\textsubscript{6},\textsuperscript{23} F4-TCNQ,\textsuperscript{55} SnCl\textsubscript{4}\textsuperscript{56} and protic ionic liquids\textsuperscript{57}. All of these p-type dopants can dramatically increase the conductivity of Spiro-OMeTAD and allow it to exhibit excellent device performance in sDSCs and PSCs. However, some of these dopants exhibit poor solubility in organic solvents and/or high boiling points, making them unsuitable for the fabrication of solution-processed photovoltaic devices. Most importantly, the majority of the p-type dopants are not easily obtained, and their complicated synthesis and high-cost may offer limitations for future large-scale production. The aim of this Chapter is to develop some low-cost, colorless and solution-processable p-type dopants for high performance sDSCs and PSCs.
5.2. Silver bis(trifluoromethanesulfonyl)imide (AgTFSI)

We determined the oxidation potential of Spiro-OMeTAD as 0.63 V vs NHE in Chapter 3, whereas we also found that the oxidation potential of Ag⁺ is 0.80 V vs. NHE from literature. The formal potential gap of 0.17 V, although the effective difference will depend on the relative concentrations of all the involved redox species in the particular solution used, may supply a driving force for the Spiro-OMeTAD one-electron oxidation reaction with Ag⁺. Thus, we observed a distinct color change when mixed the silver nitrate (AgNO₃) and Spiro-OMeTAD solution without any heating, which indicated that AgNO₃ can oxidize Spiro-OMeTAD at room temperature. However, AgNO₃ has very poor solubility in organic solvent, such as toluene and chlorobenzene, which is not suitable for the solution-processed photovoltaic device fabrication. We further investigated a silver-based organic salt silver bis(trifluoromethanesulfonyl)imide (AgTFSI), which shows good solubility in acetonitrile and also can oxidize Spiro-OMeTAD. Figure 32 clearly shows that the Spiro-OMeTAD-based films become systematically darker upon increasing the concentration of AgTFSI, which is readily attributed to the increasing amount of oxidized Spiro-OMeTAD in the film.

The proposed doping mechanism is:

\[
\text{Spiro-OMeTAD} + \text{AgTFSI} \rightarrow \text{Spiro-OMeTAD}^+\text{TFSI}^- + \text{Ag} \quad (8)
\]

The neutral Spiro-OMeTAD can be oxidized by AgTFSI and form the organic salt matrix Spiro-OMeTAD⁺TFSI⁻. It was previously suggested that the generated organic matrix Spiro-OMeTAD⁺TFSI⁻ in hole transport layer can smooth the potential landscape and increase the probability of intra-molecular charge transfer.
5.2.1. **AgTFSI as p-type dopant for HTMs**

P-type doping can significantly improve the charge-carrier density of the hole transport layer and reduce the series resistances in the sDSC device. We firstly investigated the doping effect of AgTFSI in Spiro-OMeTAD films. **Figure 33(a)** and **33(b)** clearly show that the conductivity of Spiro-OMeTAD films has a significantly increase upon addition of AgTFSI into the deposited HTM/dopant chlorobenzene solution, which indicated that AgTFSI can be used as p-type dopant to improve the conductivity of HTMs.

![J-V curves of Spiro-OMeTAD films with different doping ratios of AgTFSI.](image1)

![Increasing trend curve of conductivity with doping concentration.](image2)

**Figure 33.** (a) J-V curves of Spiro-OMeTAD films with different doping ratios of AgTFSI. (b) Increasing trend curve of conductivity with doping concentration.
5.2.2. Application in photovoltaic devices

We further investigated the influence of different doping levels on the sDSC device performance, whereas LEG4 (chemical structure shown in Figure 5) was employed as the photosensitizer and Spiro-OMeTAD as the hole conductor. Doping concentrations of 1 mM, 5 mM and 8 mM AgTFSI were investigated, and non-doped device (without AgTFSI) was used as a reference. The $J-V$ curves are depicted in Figure 34, and the corresponding photovoltaic parameters are collected in Table 10. We noted that the device without AgTFSI doping shows a low PCE of 4.0% and a low $ff$, which might be due to the low intrinsic conductivity and high charge-transport resistance of the non-doped Spiro-OMeTAD films. Upon the addition of 1 mM, 5 mM and 8 mM AgTFSI to the Spiro-OMeTAD solution, the fill factor values of the devices show a significantly increase from 0.54 to 0.61 and 0.69, respectively, yielding the corresponding efficiencies of 4.4%, 5.4 %, and 6.2%. We observed that the photocurrent of the devices showed a slightly decrease at higher doping concentration, which might be attributed to the strong light absorption of the Spiro-OMeTAD cation radical at 520 nm that can compete with the photosensitizer for light harvesting. The final optimal doping concentration of AgTFSI for the sDSCs is 8 mM.

![Figure 34. J-V characteristics of the devices containing different amounts of AgTFSI recorded under standard AM1.5G light intensity.](image-url)
Table 10. Photovoltaic parameters determined from J-V measurements of sDSCs based on different doping ratios.

<table>
<thead>
<tr>
<th>Doping Ratio [mM]</th>
<th>$J_{sc}$ [mA·cm$^{-2}$]</th>
<th>$V_{oc}$ [V]</th>
<th>$ff$</th>
<th>$\eta$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>9.26</td>
<td>0.87</td>
<td>0.49</td>
<td>4.0</td>
</tr>
<tr>
<td>1</td>
<td>9.31</td>
<td>0.88</td>
<td>0.54</td>
<td>4.4</td>
</tr>
<tr>
<td>5</td>
<td>9.91</td>
<td>0.89</td>
<td>0.61</td>
<td>5.4</td>
</tr>
<tr>
<td>8</td>
<td>9.76</td>
<td>0.91</td>
<td>0.69</td>
<td>6.2</td>
</tr>
</tbody>
</table>

* $\mu$m TiO$_2$ film; LEG4 as photosensitizer; All of the samples contain 150 mM Spiro-OMeTAD, 200 mM t-BP and 20 mM LiTFSI in chlorobenzene, while the only difference is the doping ratio of AgTFSI.

We further investigated this doping method in sDSCs with different organic dyes LEG4 and D102 (chemical structure are shown in Figure 5) under the optimal doping conditions of 8 mM AgTFSI. The oxygen doping devices were employed as the reference. The $J$-$V$ characteristics and IPCE spectra of the champion devices are shown in Figure 35(a) and 35(c), the corresponding photovoltaic parameters are summarized in Table 11. We noted that the LEG4-dye and D102-dye based devices containing AgTFSI as dopant showed PCEs of 6.9% and 4.3%, respectively, which were much higher than those of oxygen-doped devices with conversion efficiencies of 5.5% (LEG4) and 3.0% (D102), respectively. The superior photovoltaic performance of the AgTFSI doped devices is mainly attributed to their high fill factors and low series resistances. Therefore, the results clearly show that this p-type dopant can increase not only the $ff$ of the LEG4 dye-based device but also that of the D102 dye-based solar cells.
Figure 35. (a) J-V characteristics of the devices based on different doping methods and different organic sensitizing dyes; (b) J-V characteristics of the perovskite-based devices obtained using different doping substances. (c) The corresponding IPCE curves of the devices using different doping methods and different organic dyes. (d) The corresponding IPCE curves of the devices using different doping methods with CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ as light absorber.

Our results demonstrated that the AgTFSI can act as a p-type dopant for HTMs and enhance the fill factor of sDSCs, leading to a better photovoltaic performance. We further fabricated the solar cell devices employing the metal-halide perovskite-CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ as light-harvesting material instead of the organic photosensitizer. The addition concentration of AgTFSI in this perovskite type device was the same as the one in sDSC device, without further optimization. The J-V curves and IPCE spectra of the best devices obtained with different doping methods are shown in Figure 35(b) and 35(d), and the photovoltaic parameters are collected in Table 11. The AgTFSI doped device displayed a higher PCE of 12.0% than that of the oxygen doped device with efficiency of 10.1%, which is attributed to the higher fill factor in the former type of cells, leading to superior device performance. Therefore, our study clearly shows that this commercial silver salt AgTFSI can be used as effective p-type dopant in both sDSCs and PSCs.
Table 11. Photovoltaic parameters determined from J-V measurements of sDSCs and PSCs based on different doping methods and different light-harvesting materials.

<table>
<thead>
<tr>
<th>Light-harvesting materials</th>
<th>Doping methods</th>
<th>$J_{sc}$ [mA·cm$^{-2}$]</th>
<th>$V_{oc}$ [V]</th>
<th>$ff$</th>
<th>$\eta$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>D102 (a) Oxygen</td>
<td></td>
<td>6.94 (6.63±0.42)</td>
<td>0.80 (0.78±0.02)</td>
<td>0.54 (0.50±0.04)</td>
<td>3.0 (2.6±0.4)</td>
</tr>
<tr>
<td>D102 (a) AgTFSI(c)</td>
<td></td>
<td>7.29 (7.02±0.31)</td>
<td>0.82 (0.81±0.01)</td>
<td>0.72 (0.68±0.05)</td>
<td>4.3 (4.0±0.3)</td>
</tr>
<tr>
<td>LEG4 (a) Oxygen</td>
<td></td>
<td>9.24 (9.04±0.28)</td>
<td>0.94 (0.91±0.03)</td>
<td>0.63 (0.60±0.03)</td>
<td>5.5 (5.0±0.5)</td>
</tr>
<tr>
<td>LEG4 (a) AgTFSI(c)</td>
<td></td>
<td>10.16 (9.72±0.35)</td>
<td>0.95 (0.92±0.03)</td>
<td>0.71 (0.67±0.05)</td>
<td>6.9 (6.5±0.4)</td>
</tr>
<tr>
<td>perovskite (b) Oxygen</td>
<td></td>
<td>19.95 (18.2±1.93)</td>
<td>0.92 (0.90±0.02)</td>
<td>0.55 (0.48±0.07)</td>
<td>10.1 (9.2±0.9)</td>
</tr>
<tr>
<td>Perovskite (b) AgTFSI(c)</td>
<td></td>
<td>20.95 (19.0±2.21)</td>
<td>0.92 (0.90±0.02)</td>
<td>0.62 (0.57±0.06)</td>
<td>12.0 (11.2±0.8)</td>
</tr>
</tbody>
</table>

a) 2.2 µm TiO$_2$ film, 150 mM Spiro-OMeTAD with 200 mM t-BP and 20 mM LiTFSI in chlorobenzene; b) 400 nm Al$_2$O$_3$ film, 80 mM Spiro-OMeTAD with 200 mM t-BP and 30 mM LiTFSI in chlorobenzene; c) Doping with 8 mM AgTFSI. Note: the values are reported as the average obtained from 8 devices.

5.2.3. Stability

As discussed in Chapter 3 there are two functions of LiTFSI in sDSCs. On the one hand, the lithium ions on the TiO$_2$ surface can influence the local polarity at the dye-sensitized heterojunction and facilitate the photocurrent generation.$^{53}$ On the other hand, LiTFSI also can act as a p-type dopant for HTMs to decrease the series resistances of the devices in the absence of oxygen.$^{53}$ However, the LiTFSI will react with oxygen and form to lithium oxide (Li$_2$O) during the doping process, which would decrease the concentration of lithium ions on the TiO$_2$ surface, resulting in instability of device performance.$^{53}$ Thus, the p-type dopant used in the sDSC may improve not only the device performance but also maximize the cell stability.

The stability of the AgTFSI- and oxygen-doped sDSC devices was further investigated. We stored the unsealed devices in the atmosphere with humidity below 15% and recorded the J-V curves at time interval. The PCE of AgTFSI-doped device degraded by 15%, while the oxygen-doped devices decreased by 40% after 120 days’ aging (as shown in Figure 36). We noted that the $V_{oc}$ of both types of devices show an obvious decrease, which primarily should be
attributed to the volatility of the additive t-BP, leading to a shift of the Fermi level of TiO$_2$ to more positive potential. However, the $J_{sc}$ and the $ff$ of the AgTFSI-doped devices displayed a small degradation during this period, whereas the corresponding parameters of the oxygen-doped devices decreased significantly. This is consistent with the results reported in literature that the lithium ions both in the HTMs layer and on the TiO$_2$ surface were consumed by oxygen after a long time aging, resulting in a lower photocurrent and a high series resistance in the solar cells, thereby reducing the overall efficiency and the stability of the devices. Above all, the preliminary stability data indicate that the p-type dopant AgTFSI has the ability to increase both the efficiencies of sDSCs and PSCs and furthermore enhance the stability of the devices.

![Figure 36](image_url). Time aging test of the LEG4-based sDSC devices containing AgTFSI as dopant (black color) or oxygen as dopant (red color).
5.3. 1,1,2,2-Tetrachloroethane (TeCA)

1,1,2,2-Tetrachloroethane (TeCA) is a chlorinated derivative of ethane with boiling point of 146.5 °C, which is produced by the catalytic addition of chloride to acetylene or through the direct chlorination or oxychlorination of ethylene.\textsuperscript{79,80} It was once widely used as a solvent or as an intermediate in the industrial production of trichloroethylene (TCE) and tetrachloroethylene (PCE),\textsuperscript{81} and has the highest solvent power of any chlorinated hydrocarbon.\textsuperscript{82} It has been reported that the exposure of TeCA to ultraviolet (UV) light, air, heat or moisture causing decomposition and forming hydrogen chloride (HCl), chlorine (Cl\textsubscript{2}) and carbon dioxide (CO\textsubscript{2}) gas.\textsuperscript{83-85}

![Absorption spectra](image)

**Figure 37.** UV-Visible absorption spectra of Spiro-OMeTAD solution for different doping ratios of TeCA (volume ratio relative to the HTM solution). All solutions contained the same concentration of Spiro-OMeTAD (2×10\textsuperscript{-5} M). Each doped solution was illuminated one minute for the generation of Spiro-OMeTAD\textsuperscript{+} by UV light (λ\textsubscript{max} = 400 nm) before measurement.

TeCA also shows strong dissolving capacity of organic semiconductors. At first, we would like to use TeCA as the solvent for Spiro-OMeTAD during the device fabrication. Surprisingly, we noted that the color of Spiro-OMeTAD/TeCA solution changed from light yellow to dark red when it was exposed under light. Further study found that this mixture solution was sensitive to UV light (λ\textsubscript{max} = 400 nm). Figure 37 shows the UV-vis absorption spectral change of the Spiro-OMeTAD solution upon addition of different ratios of TeCA, and following illumination for one minute by UV light (λ\textsubscript{max} = 400 nm) before measurement. We observed a clear decrease of the absorption band intensity at 389 nm and a cointaneous increase of the bands at 521 and 704 nm. The emerging bands belong to the absorption of Spiro-OMeTAD\textsuperscript{+} (521 nm) and Spiro-OMeTAD\textsuperscript{2+} (704 nm), respectively. Our results clearly showed that the additive TeCA can oxidize Spiro-OMeTAD, which can be
used as a p-type dopant for sDSCs. Moreover, the doping effect of this additive is strongly depended on the UV light irradiation and the addition concentration of TeCA.

5.3.1. TeCA as solvent additive for HTMs

In order to investigated the reaction between TeCA and Spiro-OMeTAD, we added the AgNO$_3$ aqueous solution into the illuminated Spiro-OMeTAD/TeCA solution and a white precipitate of silver chloride (AgCl) was observed. This suggested that the TeCA reacted with Spiro-OMeTAD and produced Cl$^-$ during the photoinduced photochemical reactions which could form an organic matrix Spiro-OMeTAD$^+$Cl$^-$ with Spiro-OMeTAD cation. Furthermore, the acidity of the Spiro-OMeTAD/TeCA/H$_2$O solution was monitored by a pH meter and the pH value decreased significantly after irradiation, which might be due to a small quantity of protons (H$^+$) generated by TeCA during the photoinduced photochemical reactions (detailed photochemical reaction investigation is ongoing).$^{85-87}$

The doping effects of the additive TeCA on Spiro-OMeTAD films were investigated by two-probe electrical conductivity measurement. All of the doped Spiro-OMeTAD-solutions were irradiated one minute by UV light ($\lambda_{max} = 400$ nm) before spin-coating. The conductivity of Spiro-OMeTAD films showed a gradual improvement with increasing the doping concentration of TeCA (Figure 38(a) and 38(b)). These suggested that the additive TeCA can be employed as an effective p-type dopant for Spiro-OMeTAD. On the other hand, TeCA is also a good solvent for the dissolution of Spiro-OMeTAD, which might be beneficial for the pore filling of the device during the solution processed spin-coating.
We further investigated this additive in sDSCs, whereas the LEG4 dye was employed as the light absorber and the Spiro-OMeTAD as the HTM. The doping concentrations of 2%, 4% and 6% TeCA (volume ratio relative to the HTM solution) were studied, and a non-doped device (no TeCA) was used as a reference. The obtained $J-V$ curves are shown in Figure 39(a), and the corresponding data are listed in Table 12. The reference device (without TeCA) showed a low efficiency of 3.8% after cell fabrication, which can be ascribed to its low $ff$ of 0.40. This could be attributed to the low intrinsic conductivity and high charge-transport resistance of the non-doped Spiro-
OMeTAD films. We observed that the $J_{sc}$ of the devices showed a notable increase from 0.40 to 0.65, and the $J_{sc}$ were also improved significantly from 9.73 to 10.67 mA·cm$^{-2}$, yielding an overall PCE of 6.5% when 2% TeCA was added into the Spiro-OMeTAD solution. Through further optimizing the concentrations of TeCA, a maximum PCE of 7.0% was achieved for the device based on 4% TeCA doping after device fabrication. The IPCE spectra of the devices under different doping concentration are shown in Figure 39(b), and the corresponding calculated $J_{sc}$ from the IPCE spectrum are listed in Table 12. We noted that the IPCE spectra of the devices have an enhancement as increasing the doping concentration of TeCA, which might be attributed to trace amount of protons (H$^+$) generated by TeCA during the photoinduced photochemical reactions process, and that may intercalate into the dye layers thus shift the pseudo-Fermi/conduction band level of TiO$_2$ to more positive direction. In general, lowering the pseudo-Fermi/conduction band level may result in a more efficient electron injection from the excited state dyes to the metal oxide and thus lead to a higher photocurrent. Correspondingly, the photovoltage of the device decrease from 0.96 V to 0.86 V upon increasing the doping ratio of TeCA, which may be ascribed to the increase in residual H$^+$ in the device, leading to a downshift of the pseudo-Fermi/conduction band level in the TiO$_2$. In principle, the photovoltage of a DSC device is determined by the difference in energy between the pseudo-Fermi/conduction band level of the TiO$_2$ and the redox potential of the HTM.

![Figure 39.](image-url) (a) J-V curves of devices containing different amounts of TeCA (volume ratio relative to chlorobenzene) measured under standard AM1.5G light intensity. (b) The corresponding IPCE spectra.
Table 12. Photovoltaic parameters determined from J-V measurements of sDSCs a) based on different doping ratio of TeCA.

<table>
<thead>
<tr>
<th>Doping ratios b)</th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA·cm$^{-2}$]</th>
<th>$J_{sc}^{cal}$ c) [mA·cm$^{-2}$]</th>
<th>$ff$</th>
<th>$\eta$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.96</td>
<td>9.73</td>
<td>9.45</td>
<td>0.40</td>
<td>3.8</td>
</tr>
<tr>
<td>2 %</td>
<td>0.93</td>
<td>10.67</td>
<td>10.59</td>
<td>0.65</td>
<td>6.5</td>
</tr>
<tr>
<td>4 %</td>
<td>0.90</td>
<td>11.34</td>
<td>11.38</td>
<td>0.69</td>
<td>7.0</td>
</tr>
<tr>
<td>6 %</td>
<td>0.86</td>
<td>11.77</td>
<td>11.82</td>
<td>0.63</td>
<td>6.4</td>
</tr>
</tbody>
</table>

a) 2.5 µm TiO$_2$ film; LEG4 as photosensitizer; 150 mM Spiro-OMeTAD, 200 mM t-BP and 20 mM LiTFSI was used for each sample. b) The doping concentration used here is volume ratio relative to the HTM solution, each doped solution was illuminated one minute for the generation of Spiro-OMeTAD$^+$ by UV light ($\lambda_{max} = 400$ nm) before spin-coating. c) Calculated $J_{sc}$ from the IPCE spectrum.

We further fabricated devices based on two different organic dyes, the D-π-A dye-LEG4 and indoline dye-D102 (chemical structure as shown in Figure 5) under the best doping ratio of 4% TeCA. In addition, the commonly used Cobalt(III)-FK209$^{52}$ (chemical structure as shown in Figure 12) and oxygen doped devices were used as the references. The $J$-$V$ curves, the corresponding IPCE spectra and the integrated $J_{sc}$ of the best devices are shown in Figure 40, and the average photovoltaic parameters are summarized in Table 13. The results clearly show that the new doping method exhibits good universal applicability in both LEG4 and D102 dye-based sDSC device, which not only can enhance the fill factor, but also improve the photocurrent, leading to better overall device performance. Moreover, the PCE of the TeCA-doped device is higher than that of the device using Cobalt(III)-FK209 as the dopant, but much higher than that of the oxygen doped device. Notably, the LEG4-dye-based device employing TeCA as the dopant yielded the highest efficiency of 7.7%, which is also a record efficiency for all reported Spiro-OMeTAD-based sDSCs up to now.
Figure 40. (a) J-V characteristics of devices based on different doping methods and on the LEG4 dye. (b) J-V characteristics of the devices based different doping methods and on the D102 dye. (c) The IPCE spectra and corresponding integrated $J_{sc}$ of the devices based on different doping methods and on the LEG4 dye. (c) The IPCE spectra and corresponding integrated $J_{sc}$ of the devices based on different doping methods and based on the D102 dye.
Table 13. The average and best photovoltaic parameters of the devices based on different doping methods and different photosensitizers (The average values of the LEG4 dye-based sDSCs obtained from 32 devices; the average values of the D102 dye-based sDSCs obtained from 16 devices; ).

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Doping methods a)</th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA·cm$^{-2}$]</th>
<th>$ff$</th>
<th>$\eta$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>D102</td>
<td>Oxygen b)</td>
<td>0.84±0.03 (0.86)</td>
<td>6.83±0.36 (7.05)</td>
<td>0.59±0.03 (0.61)</td>
<td>3.12±0.4 (5 (3.7))</td>
</tr>
<tr>
<td></td>
<td>TeCA c)</td>
<td>0.78±0.04 (0.82)</td>
<td>7.82±0.47 (8.21)</td>
<td>0.69±0.04 (0.74)</td>
<td>4.27±0.3 (1 (5.0))</td>
</tr>
<tr>
<td></td>
<td>Oxygen b)</td>
<td>0.94±0.02 (0.96)</td>
<td>9.57±0.34 (9.77)</td>
<td>0.58±0.04 (0.62)</td>
<td>5.08±0.5 (1 (5.8))</td>
</tr>
<tr>
<td></td>
<td>TeCA c)</td>
<td>0.86±0.03 (0.90)</td>
<td>11.35±0.42 (11.65)</td>
<td>0.68±0.03 (0.73)</td>
<td>7.01±0.3 (5 (7.7))</td>
</tr>
<tr>
<td></td>
<td>FK209 d)</td>
<td>0.95±0.02 (0.97)</td>
<td>9.61±0.40 (9.81)</td>
<td>0.67±0.03 (0.71)</td>
<td>6.24±0.3 (2 (6.8))</td>
</tr>
</tbody>
</table>

a) 2.5 µm TiO$_2$ film, 150 mM Spiro-OMeTAD with 200 mM t-BP and 20 mM LiTFSI was used for each sample; b) The samples were left in a dry box (oxygen atmosphere) in the dark (humidity below 15%) overnight after spin-coating. c) Doping with 4% TeCA (volume ratio relative to the HTM solution), each doped solution was illuminated one minute for the generation of Spiro-OMeTAD$^+$ by UV light ($\lambda_{max}$ = 400 nm) before spin-coating. d) Doping with 10% FK209 (molar ratio relative to Spiro-OMeTAD).

5.3.3. Reproducibility

As mentioned in the introduction part, the LiTFSI is easily consumed during the oxygen doping process, leading to poor device reproducibility and stability. Thus new additives are required. We further investigated the reproducibility of this new doping method, and the commonly used Cobalt(III)-FK209 and oxygen doping methods were employed for the comparison study. Figure 41 shows the histograms of the device efficiencies based on different doping methods. The TeCA doped devices manifested an analogous reproducibility as devices based on FK209 as dopant, and both of the two doping methods render much better reproducibility than the oxygen doping method. In short, our results clearly showed that the TeCA doping method can improve both the device performance and reproducibility as compared to the commonly used oxygen doping method.
Figure 41. Histogram of device efficiencies (LEG4 as photosensitizer) based on different doping methods (32 devices were studied for each doping method).

5.4. Conclusions

In this Chapter, we have successfully developed two low-cost and colorless p-type dopants AgTFSI and TeCA for the organic HTMs-Spiro-OMeTAD, which can significantly increase the conductivity of the Spiro-OMeTAD films and enhance the device performance of sDSCs and PSCs.

- The PCEs of AgTFSI doped devices were improved by 20%, as compared to the commonly used oxygen-doped devices (in the presence of LiTFSI) both in sDSCs and PSCs. Moreover, the sDSCs based on AgTFSI as dopant showed much better stability than those based on the oxygen as dopant.
- The additive TeCA could readily oxidize Spiro-OMeTAD to Spiro-OMeTAD\(^+\) upon UV-light irradiation, and significantly increase the electrical conductivity of the Spiro-OMeTAD films, leading to better device performances. In addition, the TeCA doped sDSCs exhibited better reproducibility than the known p-type dopants-based devices.
- These two low-cost and colorless p-type dopants have potential for the preparation of highly efficient, long-term stable and reproducible sDSCs and PSCs in the future. They may also have potential to apply in the other solution-processed organic electronic devices.
6. Concluding Remarks

The studies in this thesis aimed to develop advanced small-molecule organic HTMs with low-cost, high hole mobility and conductivity for the achievement of high performance, stable and reproducible solution processed photovoltaic devices, such as sDSCs and PSCs. In order to achieve these objectives, two different strategies are utilized in this thesis: the development of new generation HTMs based on triphenylamine and carbazole as core units with simple synthetic routes and the introduction of cost-effective p-type dopants to control the charge transport properties of HTMs.

In Chapter 3, a class of novel triphenylamine-based easily synthesized HTMs with different oxidation potential, conjugation length, hole mobility and conductivity have been presented and systematically investigated in sDSCs. The computational, electrochemical and photophysical properties of all the HTMs were comprehensively studied. The theoretical study showed that HTM-X3 and X35 had smaller reorganization energy than Spiro-OMeTAD due to the larger conjugation length, which implied relative fast hole transport properties. By optimizing aforementioned parameters of the HTMs in conjunction with sDSC operation, PCEs of 5.8% and 5.5% were achieved by X3- and X35-based solar cells when the organic dye LEG4 was employed as photosensitizer, which were slightly higher than that the PCE of 5.4% obtained using the well-known HTM Spiro-OMeTAD, thereby making these new HTMs promising for preparing high performance sDSCs in the future. In addition, the HTM-X3 not only exhibited better performance in the organic dye LEG4-based devices than that of Spiro-OMeTAD, but also showed higher PCE in the ruthenium dye-Z907 based devices. More importantly, the transient photovoltage decay data showed that the smaller molecular size of the HTM induced faster electron recombination in the device, which is probably due to that the small HTM molecules are easy to permeate into the meso-TiO₂ pore and the lacunas between the dye molecules and approach to the TiO₂ surface. These results provide new guidance for the molecular design of efficient HTMs for sDSCs and PSCs in the future.

In Chapter 4, we have designed and synthesized two new carbazole-based small-molecule HTMs termed X19 and X51, with different molecular size, hole mobility and conductivity for sDSCs and PSCs. The HTM-X51-based sDSC devices exhibited higher PCE of 6.0% than those of the smaller HTM-X19-based devices (4.5%) when the organic dye LEG4 was employed as the photosensitizer, which also overplayed the PCE of 5.5% obtained by using the standard HTM Spiro-OMeTAD. When making the same comparison studies in PSCs, devices based on HTM-X51 exhibited higher PCE of 9.8% than those
containing HTM-X19 (7.6%); the former results are comparable to the results of 10.2% obtained when using Spiro-OMeTAD as HTM. These results qualify the new HTM as promising materials for preparing high-efficiency sDSCs and PSCs. Moreover, the results of the transient photovoltage measurement showed again that the smaller molecular size HTM-X19 had faster electron recombination than that of the larger molecular size HTM-X51 in the sDSC devices, which is in good agreement with conclusion obtained in Chapter 3 that the molecule size of the HTM is an important factor as regarding its impact on the $V_{oc}$ in the sDSC device, or even more important than the oxidation potential of the HTM. In addition, X51 exhibited a higher hole mobility and conductivity than X19, leading to better device performance. These results clearly show that molecular engineering is a viable route to develop high hole mobility and high conductivity HTMs for highly efficient sDSCs and PSCs in the future.

In Chapter 5, two low-cost and colorless p-type dopants AgTFSI and TeCA were developed for the organic HTM-Spiro-OMeTAD and successfully applied in sDSCs and PSCs. The silver-based organic salt AgTFSI showed good solubility in organic solvent, which could easily oxidize Spiro-OMeTAD and significantly increase the conductivity of the Spiro-OMeTAD films. The PCEs of AgTFSI-doped devices were improved by 20%, as compared to the device based on the commonly used oxygen doping both in sDSCs and PSCs. Moreover, the sDSC devices exposed to AgTFSI as dopant showed considerably better stability than those of the oxygen doped devices, qualifying this p-type dopant as a promising alterative for the preparation of highly efficient as well as stable sDSCs and PSCs for the future. The chlorinated hydrocarbon-based organic solvent TeCA was employed as an additive for organic HTM-Spiro-OMeTAD, which could readily oxidize Spiro-OMeTAD to Spiro-OMeTAD$^+$ upon UV-light irradiation, and in conjunction also significantly increased the electrical conductivity of the Spiro-OMeTAD films. Subsequently, this additive was successfully applied in the Spiro-OMeTAD-based sDSCs, a record PCE of 7.7% was obtained while employing the D-$\pi$-A-dye LEG4 as photosensitizer under standard solar irradiation. In addition, the TeCA doped sDSCs exhibited better reproducibility than the known p-type dopants-based devices. These results provide new opportunities for the fabrication of low-cost and highly efficient sDSCs and PSCs. It may also have potential for application in solution-processed OFETs and OLEDs.
7. Future Outlook

The solution processable photovoltaic devices, PSCs and sDSCs have great potential for the replacement of conventional inorganic silicon-based solar cells due to their easy manufacture and high efficiency, to achieve low-cost and large-area solar electrical energy generation in the near future. Although considerable progress has been achieved in this field during last five years, some key points still remains.

*Light-harvesting materials.* Although PSCs exhibit attractive prospect, the stability problem and the environmental issue of the perovskite crystal will be a big limitation for the large-scale application. Therefore, future studies should focus on the development of low-cost, stable and environmental friendly light-harvesting materials. For sDSCs, the limitation of the device from being more efficient at thicknesses over 2.0 µm is primarily attributed to the incomplete filling of the mesoporous TiO₂ films with HTMs and fast electron-hole recombination in the device. Thus, the development of high molar extinction coefficient and broad absorption spectrum photosensitizers for sDSCs is highly important in the future.

*Hole transport materials.* Small-molecule arylamine-based HTMs have been intensively developed and investigated in PSCs in recent years. However, most of the arylamine-based HTMs need chemical doping to improve the conductivity of hole-transporting films and enhance the related device performance, which will increase the device manufacturing cost and affect the solar cell stability. Future work should especially focus on the development of cost-effective doping-free HTMs with 2D structure for PSCs. With regard to the sDSCs, the development of high solubility HTMs with 3D structure to improve their pore filling is highly desired.

*P-type dopants.* Despite two low-cost and solution processable p-type dopants were successfully introduced for sDSCs and PSCs in this thesis, several important aspects of the doping mechanism are still not entirely understood. Future studies should focus on elucidating the doping mechanism and investigating the doping effect of these new dopants in different types of HTMs and photovoltaic devices.
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Appendix A

The following is a description of my contribution to Publications I to V, as requested by KTH.

**Paper I:** Major contributed to the initiation of the project. I performed all of the synthesis work, device fabrication and characterization, and wrote the majority of the manuscript.

**Paper II:** Major contributed to the initiation of the project. I performed all of the synthesis work, device fabrication and characterization, and wrote the majority of the manuscript. The DFT calculation was performed by Dr. Lili Lin, and the hole mobility measurement was carried out by Deping Qian.

**Paper III:** Major contributed to the initiation of the project. I performed all of device fabrication and characterization work, and wrote the manuscript. The synthesis work was carried out by Dr. Esmail Sheibani, and the DFT calculation was performed by Peng Liu.

**Paper IV:** Major contributed to the initiation of the project. I performed all of the device fabrication and characterization work, and wrote the manuscript.

**Paper V:** Major contributed to the initiation of the project. I performed all of the device fabrication and characterization work, and wrote the manuscript.
References
