Synthesis and optoelectronic properties of quinoidal 2,2',6,6'-tetraphenyldipyranylidene towards photovoltaic applications

Courté, Marc

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**SYNTHESIS AND OPTOELECTRONIC
PROPERTIES OF QUINOIDAL 2,2',6,6'-
TETRAPHENYLDIPYRANYLIDENE TOWARDS
PHOTOVOLTAIC APPLICATIONS**

COURTÉ MARC PATRICK

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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COURTÉ MARC PATRICK

School of Physical and Mathematical Sciences

Department of Physics and Applied Physics

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Abbreviations

AFM: Atomic force microscopy

AM_x: Air mass coefficient

AO: Atomic orbital

BHJ: bulk heterojunction

BPA: Biphenylamine

CB: Conduction band

DFT: Density functional theory

DIPO-Ph₄: 2,2',6,6'-tetraphenyldipyranylidene

DIPEA: N,N-Diisopropylethylamine

DSSC: Dye-sensitized solar cell

DMF: Dimethylformamide

DMSO: Dimethyl sulfoxide

EA: Electronic affinity

E_F: Fermi level

EQE: External quantum efficiency

ETL: Electron transporting layer

FAI: Formamidinium iodide

F(ε): Fermi Function

FF: Fill factor

FTO: Fluorine-doped tin oxide

HMDS: Hexamethyldisilazane

HTL: Hole transporting layer

HTM: Hole transporting material

HOMO: Highest occupied molecular orbital

ICBA: indene-C60 bisadduct

IP: Ionization potential

IPCE: Incident-photon conversion efficiency

ITIC: 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexyl phenyl) -dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene)

ITO: Indium tin oxide

Jsc: Short-circuit current density

LiTFSI: Lithium bis(trifluoromethanesulfonyl)imide

LUMO: Lowest unoccupied molecular orbital

MAI: Methylammonium iodide

MDMO-PPV: Poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene)

MO: Molecular orbital

OLED: Organic light-emitting diode

OSC: Organic solar cell

OTS: Octadecyltrichlorosilane

PSC: Perovskite solar cell

PCE: Power conversion efficiency

PANI: Polyaniline

PBDB-T: Poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)))]

PEDOT:PSS : Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate

P3HT: Poly-3-hexylthiophene

PF10TBT: Poly[2,7-(9,9-didecylfluorene)-alt-5,5-(4,7-di-2-thienyl-2,1,3-benzothiadiazole)]

PTAA: Poly(triarylamine)

Poly-TPD: Poly[N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)benzidine]

PTB7: Poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]]

PV: Photovoltaic

PVT: Physical vapor methods

RFID: Radio frequency identification

RMS: Root mean square roughness

R_{sh} : Shunt Resistance

R_s : Series Resistance

SCLC: Space charge limited current

SEM: Scanning electron microscope

Spiro-OMETAD: 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine) 9,9'-spirobi-fluorene

TPA: triphenylamine

(TBP)r: 4-tertbutylpyridine

TCO: Transparent conductive oxide

TGA: Thermal gravimetric analysis

UPS: Ultraviolet photoelectron spectroscopy

VB: Valence band

V_{oc} : Open-circuit voltage

XRD: X-ray diffraction

ϕ : Working function

Abstract

Organic solar cells (OSCs) and more recently perovskite solar cells (PSCs) have attracted a great attention in the scientific field of photovoltaics due to their potential low cost, simple fabrication process and promising power conversion efficiency (PCE). With excitons photogeneration processes, the charge carrier extraction is an essential step in the good operation of photovoltaic solar cells. Interfacial layers, such as hole transporting layer are commonly used to promote the charge diffusion towards the electrodes, resulting of a higher photocurrent. Consequently, the development of novel hole transport materials (HTMs) with suitable optoelectronics properties, low-cost and simple synthetic pathway is a major ongoing research to achieve highly efficient OSCs and PSCs.

In this thesis, 2,2',6,6'-tetraphenyldipyranylidene (DIPO-Ph₄), a large quinoidal planar π -conjugated heterocycle is presented. The synthesis and characteristics of DIPO-Ph₄ are described in details, in particular the electrical characteristics which are investigated in a field-effect transistor configuration. A suitable HOMO level energy and good hole transport properties make DIPO-Ph₄ a potential candidate to be used as an efficient hole-transporting material (HTMs) in organic or perovskite solar cells. The presented results will demonstrate that dipyranylidene core could be an excellent building block for high mobility HTMs.

Keyword: Organic solar cells, perovskite solar cells, hole transport materials, small molecules, dipyranylidenes

Chapter 1

Introduction

The 20th century has seen the evolution of electronics from vacuum tube technology, through the invention of transistors by J. Bardeen, W. Brattain and W. Shockley in 1947 to the modern microelectronics.^{1,2} Since the invention of the first integrated circuits in 1959, silicon materials have been responsible for the rise of modern microelectronics. However, with the quest for miniaturized chipsets, further innovations become more challenging. On the other hand, alternative materials are emerging, such as organic semiconducting materials or 2D materials (graphene).

In fact, the first record of semiconducting characteristics within an organic material is dated from the middle of 19th century when H. Letheby observed the electro-activity of polyaniline.³ Nonetheless, the progress on organic semiconductors remained relatively slow due to their high resistivity. One century later, the semiconducting property of organic compounds has been distinctly observed on a charge–transfer complex from anthracene and halogen derivative.⁴ On the same time, A. Bernanose detected for the first time some electroluminescence properties on acridine.⁵ These observations triggered intense investigations on organic materials for electronic applications. In 1977, the field took a new turn with the discovery of high conductivity in a conjugated polyacetylene film⁶ for which A. J. Heeger, A. G. MacDiarmid and H. Shirakawa received the Nobel Prize.⁷ These results represented a major milestone in the quest of organic electronics. Nearly ten years later in

1986, the first organic transistor made of polythiophene has been realized via electrochemical process.⁸ Following this work, later in 1990, first flexible all-organic transistor was fabricated.⁹ These achievements, in addition to the remarkable properties of organic compounds, attracted great attention from academic and industrial researchers.

The principal advantages of organic electronics are:

- ◆ **Large area:** Conventional semiconductor technologies are limited by the wafer size, (e.g.400 mm). In contrast, organic materials can be deposited by roll-to-roll or slot die-coating technics to manufacture large-area devices.
- ◆ **Structural flexibility:** Organic materials exhibit good mechanical characteristics due to the weak Van der Waals interaction between molecules. Therefore, they have generally good bendable properties with higher resistance to cracking. These flexibility properties are beneficial for the portability and the robustness of devices and open the door to flexible electronic applications, such as e-paper.
- ◆ **Tunability:** The physical and optoelectrical properties, such as absorption, band gap or solubility of organic materials can be easily tuned using chemistry tools.
- ◆ **Low-temperature process:** The conventional silicon technologies use high temperature (>1,000°C) for the preparation of single-crystal wafers. Even for a standard process like the fabrication of flat-panel displays, amorphous silicon is deposited at 360°C. In contrast, organic materials can be processed at low temperature (around 100–150°C) using solution methods.

- ◆ **Low-cost:** In theory, organic materials can be mass-produced at low-cost using chemical synthesis methods. These carbon-based materials are abundant and do not impact the depletion of natural resources.

Actually, organic semiconducting materials are used for the following applications:

- ◆ **Solar cells:** Organic materials received a high interest for photovoltaic applications due to the strong and wide absorption in the visible range of some dyes. The low-cost fabrication process makes them attractive to compete with standard silicon-based photovoltaic cells. In addition, the flexibility properties of organic materials allow niche market applications such as portable battery, e-clothes (Fig.1.1).
- ◆ **Screen display:** Organic screen or OLED displays technology is already mature. These devices are light, flexible and more resistant to crack as compared to standard glass and are now largely used by industry (ex: smartphone, TV, e-paper, Fig 1.2).

Figure.1.1: Left) Power plastic photovoltaic material produced by roll-to-roll manufacturing process (Konarka). Middle) Dye-sensitized solar cells (DSSCs) windows installed in the façade of the EPFL's Convention Center. Right) backpack integrating an organic solar panel.

Figure.1.2: *Left) 55-inches concave and convex bendable OLED TV made from printing technology (Panasonic). Middle) HD flexible OLED panel made of plastic substrates. Right) 18-inches OLED e-paper that can be rolled into a tight cylinder presenting by LG in 2014.*

- ◆ **Lighting:** Like flat panel display, organic light emitting diodes (OLEDs) have great potential to replace traditional lighting devices. OLEDs can be used to make flexible and transparent panels (Fig.1.3). OLED lightings are already commercialized by several companies (Philips, Konica Minolta, LG).

Figure.1.3: *Left) flexible organic light-emitting diodes (OLED) lighting, the device is totally bendable, favorable for new design (LG Chem). right) Blue OLED lighting made from nanotechnology process (Pixelligent).*

- ◆ **Other applications:** Using the singular properties of organic materials, a wide range of electronic applications are explored such as sensors or RFID. For example, organic materials possess high switching ratio which is mandatory for new generation memory devices. Besides, their non-toxicity makes them interested for biocompatible devices such as e-skin (fig.1.4).

Figure.1.4: *Left) A fully flexible, 64-bit organic RFID tag consisting of three foils being the antenna foil, the organic rectifier foil and the 64-bit organic digital logic foil. Middle) A large area, flexible sensor matrix with organic field-effect transistors for artificial skin applications. Right) Ultrathin electronic skin made for medical or sport applications (Someya Group).*¹⁰

Despite their uses in various electronic applications, organic semiconducting devices still require further development in term of materials and device performances in order to be competitive with standard electronic technologies. Actually, their main drawbacks are their low electrical conductivity and their long-term stability, in particular in presence of oxygen and moisture. Consequently, the investigation of new type of organic materials with adequate optoelectronics properties is still necessary. These materials require high stability and simple synthetic pathway in the perspective of applications.

Thesis focus and organization

The main scope of study of this thesis is the optimization of emerging solar cells, in particular organic (OSCs) and perovskite solar cells (PSCs). Within photovoltaic devices, the charge extraction is an essential process which influences drastically the device performances. The use of interfacial layers; hole transporting layer (HTL) and electron transport layer (ETL) is crucial to achieve highly efficient solar cells.

The presented work will focus on the development of novel hole transporting materials (HTMs). Currently, spiro-OMETAD is the standard HTM for PSCs. However this material has poor electrical properties and above all, a high cost due to burdensome synthesis and purification methods. In alternative of spiro-OMETAD, various types of material (inorganic, polymers, small molecules) have been investigated resulting of comparable or slightly better performance. At the moment, no rational guidelines have been developed for the molecular design and majority of the reported HTMs are using similar building blocks. Therefore, the development of novel classes of organic HTMs is still necessary; firstly to achieve higher device performances and secondly to determine some structure-property relationship for the design of efficient HTMs. The following chapter will introduce the general background of photovoltaic solar cells and present an overview of the different types of photovoltaic devices. The importance of the hole transporting layer (HTL) within OSCs and PSCs will be discussed and the most relevant type of HTMs that have been investigated will be presented in a literature survey.

Small planar π -conjugated molecules are generally highly stable, with good electrical properties which makes them suitable to be used as a HTM. In this thesis, the use of a small

quinoidal molecule, namely tetraphenyldipyranylidenes (DIPO-Ph₄) will be investigated as a HTM for organic and perovskite solar cells. This type of molecules has been rarely investigated for photovoltaic application. However, dipyranylidene molecules are isoelectronic of tetrathiafulvalene (TTF) which had been well-study for its excellent donor characteristics. Therefore, DIPO-Ph₄ should show good donor properties. Besides, DIPO-Ph₄ is a stable molecule in ambient air with a high melting temperature and can be synthesized easily in mass scale with a good yield. The molecular structure and the synthetic pathway, as well as the physical properties of DIPO-Ph₄ will be introduced in chapter 3. The chapter 4 will focus essentially on the study of the electrical properties in thin film and single crystal field effect transistors and will show that DIPO-Ph₄ has suitable optoelectronic properties to be used within a photovoltaic device. The chapter 5 will present the photovoltaic characteristics of the fabricated devices integrating DIPO-Ph₄ as HTM. At first, DIPO-Ph₄ has been used in combination of PEDOT:PSS in a classical bulk heterojunction (P3HT:PCBM) OSCs. In a second time, we inserted a pristine DIPO-Ph₄ layer in a mesoscopic PSC. The presented results will demonstrate that dipyranylidene could be an excellent core for high mobility HTMs for organic or perovskite solar cells.

Chapter 2

Organic photovoltaic solar cells

Photovoltaic cells use solar radiation to produce electricity based on the photovoltaic effect discovered in 1839 by E. Becquerel.¹¹ The first photovoltaic cell appeared around 1880 and was made of a selenium wafer. Nowadays, the most mature technology uses silicon. Silicon-based solar devices have high manufacturing cost. Thus, intensive research is being conducted on alternative systems, called “*3rd generation solar cells*”, such as organic or perovskite solar cells. This chapter will introduce the basic concepts associated to photovoltaic solar cells and the working principle of organic and hybrid organic-inorganic photovoltaic devices will be described in details. Finally, the last part will focus on the role of the interfacial layers and present the current state-of-art on design of novel HTMs.

2.1. The Sun, an energy source

The Sun produces an enormous amount of energy (3.826×10^{26} joules per second) from nuclear fusion which is conveyed towards Earth by electromagnetic radiation called photons. The Sun with a temperature of 5,250°C is considered as a black body which irradiates from ultraviolet to infrared with an emission peak at 550 nm (fig.1).¹² The photon energy is dependent of the wavelength (λ) and is characterized by the following relation:

$$E(\lambda) = \frac{hc}{\lambda} \quad (h = \text{Planck constant; } c = \text{speed of light}) \quad (\text{eq.2.1})$$

Figure.2.1: Solar radiation spectrum at the top of atmosphere (yellow) and at the sea level (red). The black line represents a 5,250°C blackbody spectrum. At sea level, the absorption bands of water, ozone and carbon dioxide are clearly observed.

At the top of the atmosphere, the solar spectrum matches well the 5,250°C blackbody spectrum. Before reaching the earth surface, part of the photons are absorbed by atmospheric molecules such as ozone and water. At sea level, the solar spectrum is composed of 3% UV, 44% of visible and 53% of infrared light and the total irradiance is reduced approximately by 30% compared to the top of the atmosphere. The parameter **AM_x**, called air mass coefficient, is used to take into account the fluctuation on the direct optical path length through the Earth's atmosphere. It is defined by the following equation:

$$AM_x = \frac{1}{\cos\theta} \quad (\text{eq.2.2})$$

where θ represents the angle between the sun and the zenith.

By definition, the **AM0** referring to “zero atmosphere” corresponds to the solar spectrum of the top of the atmosphere. When the sun has an angle of 48.2° with the zenith, the light has travelled through 1.5 atmospheres and it is noted **AM1.5**. The **AM1.5G** represents the yearly average irradiance for mid-latitudes ($I=1000 \text{ W.m}^{-2}$ at the sea level) and it is used as a universal standard for terrestrial solar cells characterization (ASTMG173-03: standard from American Society for Testing and Materials). The **AM1.5G** is a global standard spectrum and takes into consideration diffuse and reflected light, as opposed to the direct **AM1.5D** spectrum.

Figure.2.2: Schematic representation of the air mass coefficient (AM_x).

2.2. P-n junction and photovoltaic effect

Before describing in details the working principles of a photovoltaic solar cell, some essential concepts related to quantum theory and solid state physics are introduced for the sake of a better understanding.^{13,14}

2.2.1. General background

Atomic orbitals, molecular orbitals

Atoms are composed of electrons bound to a nucleus. Instead of classical mechanics where each body has a well-defined location and movement, electrons follow the rules of quantum mechanics and are described by atomic orbitals (AOs). These orbitals reflect the probability of an electron to be found within this region (Fig.2.3). Each orbital possesses their own energy and shape. They are characterized by four quantum numbers n (the principal quantum number, describing the potential energy of the electron), l (the azimuthal quantum number, describing the magnitude of the angular momentum of the electron and the shape of the orbital), m_l (the magnetic quantum number, describing the direction of angular momentum of the electron and thus the orientation of the orbital) and m_s (the spin quantum number). From the Pauli Exclusion Principle, each AO can accept only two electrons with an opposite spin.

Figure.2.3: Schematic representation of the 2s and 2p atomic orbitals (AO). For the 2p orbital, the (+) and (–) represent the phase of the different AOs.

When two atoms with similar energy are close enough to overlap their AOs, new orbitals, called molecular orbital (MO) are formed from the combination of these AOs. These MOs can be bonding or antibonding, depending of the constructive or destructive interactions between the AOs. Bonding orbitals have high electron density between the two nuclei, shielding their Coulombic repulsion and thus resulting in a lower energy system than that of the individual AOs. Conversely, antibonding orbitals have low electron density in the region between the nuclei, leading to an unstable higher energy state. MOs that are symmetrical around the axis connecting the two nuclei are known as σ bonds and can be either bonding (σ) or antibonding (σ^*) in nature. Molecular orbitals which are not symmetrical about this axis are known as π bonds. Again these can be bonding or antibonding, and due to the location of their electron density away from the axis joining the two nuclei, their strength is significantly lower than that of σ bonds (Fig.2.4).

Figure.2.4: Schematic representation of bonding and antibonding MOs formed by the interaction between two 1s AOs (Left) and $2p_z$ AOs (right).

Band structure and semiconducting properties

In general, a solid is constituted of an ordered arrangement of atoms or molecules which are bonded together by a succession of MOs. As mentioned previously, the interaction of two AOs leads to their splitting into bonding and antibonding MOs. The Pauli's Exclusion Principle excludes two electrons from having the same quantum numbers, thus the succession of MOs results in the formation of discrete states having slightly different energies. When the number of MOs becomes too great, these discrete states become really close in energy and form a continuum, called on energy band.

In a solid, the highest energy band filled with electrons is called the valence band. By contrast, the conduction band refers to the first unoccupied band. The energy difference between the highest occupied energy state of the valence band and the lowest unoccupied state of the conduction band is called the band gap. The band structure and the band gap are at the origin of the electrical characteristics of each material and particularly their conductive properties.

For a material, if the valence band and the conduction band overlap, the material is considered to be a metal and has high conductivity. By contrast, insulators are characterized by a large band gap (typically $> 4\text{eV}$); a large amount of energy is required to move electrons into the conduction band, resulting in a poor conductive property. Materials having their band gap in between these are called semiconductors (Fig.2.5).

Semiconductors possess remarkable electrical characteristics, essential for optoelectronics devices. Their band gap is small enough to allow electrons to jump from the valence band to the conduction band, these excited electrons produce vacancies in the valence band, called

Figure.2.5: *Simplify representation of a band diagram showing the three classes of materials (metal, semiconductor and insulator).*

holes. This electron transfer can be stimulated by external perturbations, such as thermal energy as well as electric field or light. Thus, at a non-zero temperature, there is a probability that some electrons are located in the conduction band. This probability is described by the Fermi function $F(\varepsilon)$ which gives the probability that a given available electron energy state is occupied at a given temperature, and follows the Fermi-Dirac distribution (eq.2.3). This equation allows the determination of the Fermi level defined by the hypothetical energy level of an electron, such that at thermodynamic equilibrium this energy level would have a 50% probability of being occupied at any given time.

$$F(\varepsilon) = \frac{1}{e^{(\varepsilon - E_F)/kT} + 1} \quad (\text{eq.2.3})$$

Note that the Fermi level also exists for metals and insulators. However, metals are generally characterized by their working function. This is defined as the minimum thermodynamic work

required to remove an electron to infinity from a solid and expressed by the following relation:

$$\phi = E_{\text{vide}} - E_F = E_F \quad (\text{with } E_{\text{vide}} = \text{vacuum energy}) \quad (\text{eq.2.4})$$

When the Fermi function $F(\epsilon)$ is equal to 0.5, the Fermi level is located exactly at the middle of the energy gap, and the carrier concentrations on the valence band (holes) and on the conduction band (excited electrons) are equal. This is characteristic of an intrinsic semiconductor (Fig.2.6). Besides, the concentration of electrons or holes in a semiconductor can be adjusted. For example, in inorganic semiconductors such as silicon, impurities, called dopants are introduced into their crystal lattice. Electron donor dopants, such as phosphorus for silicon are inserted to obtain a higher electron carrier concentration. On the contrary, some electron acceptor dopants, such as boron are used to increase the hole carrier concentration. These semiconductors are called extrinsic semiconductors and arranged in two types:

- ◆ **N-type semiconductors:** They have a larger electron concentration than hole concentration. In *n*-type semiconductors, electrons are the majority carriers and holes are the minority carriers. The Fermi level is greater than that of the intrinsic semiconductor and lies closer to the conduction band than the valence band. They are commonly considered as an acceptor material.
- ◆ **P-type semiconductors:** As opposed to *n*-type semiconductors, *p*-type semiconductors are considered as a donor material and have a larger hole concentration than electron concentration. In *p*-type semiconductors, holes are the majority carriers and electrons

are the minority carriers. For p -type semiconductors, the Fermi level is below the intrinsic Fermi level and lies closer to the valence band than the conduction band.

Figure.2.6: Band diagram with their respective Fermi levels of the three types of semiconductors (intrinsic, n-type, p-type). The carrier concentrations at the thermal equilibrium are determined by the product of energy distribution $N(\epsilon)$ and the Fermi-Dirac function $F(\epsilon)$.

Metal-semiconductor contact

The charge carrier concentration in semiconductors is smaller by many orders of magnitude than in metals. When a semiconductor and a metal are brought in contact, the majority charge carriers of the semiconductor diffuse into the metal in order to reach a thermodynamic equilibrium, resulting in an alignment of the Fermi levels.¹⁵ This charge transfer leads to the formation of a space charge zone at the semiconductor-metal interface.

This zone can extend to a certain depth (W), and hence creates a bending of the energy bands of the semiconductor. Two types of electrical contacts can occur depending of the relative position of the Fermi levels of the semiconductor ($E_{F,sc}$) and the metal ($E_{F,m}$), or more accurately of the working function of both them (ϕ_{sc} and ϕ_m).

If $\phi_{sc} < \phi_m$, the electrons from the valence band of the semiconductor diffuse into the metal, and an accumulation of holes occurs at the interface. In this case, there is no potential barrier between the two materials, and the charge can circulate following Ohm's law. The junction is called an ohmic junction (Fig.2.7, top).

Figure.2.7: Representation of the two types of contact happening between a metal and p-type semiconductor. On top) An ohmic junction with no barrier of potential, the charge carriers can diffuse freely across the interface. On bottom) A Schottky junction: a depletion zone (W) occurs at the interface, the charge carriers require an external potential to flow.

If $\phi_{sc} > \phi_m$, electrons from the metal flow into the semiconductor, or conversely holes from the semiconductor diffuse through the metal. The charge carriers cannot cross the interface due to a potential barrier, known as a Schottky barrier and so accumulate at both sides of the interface, leading to the formation of an insulating boundary, called a depletion region. In order to allow the charge diffusion, an external potential is required to overcome the Schottky barrier. This type of semiconductor–metal contact is called a Schottky junction and acts as a rectifier (Fig.2.7, bottom).

P-n junction

When a p-type semiconductor is brought into contact with an n-type semiconductor, a *p-n* junction is formed, resulting in an alignment of their Fermi levels, similar to a Schottky junction. Indeed, the electrons from the n-type semiconductor diffuse towards the *p*-type semiconductor, whereas the holes diffuse in the opposite side. This diffusion current will depopulate the majority charge carriers of each semiconductor, forming a depletion zone with a defined width (*W*) at the interface (Fig 2.8). The internal electric field is directed from the *n*-type semiconductor toward the *p*-type semiconductor. It is in opposition to the diffusion current of the majority charge carrier of each material. Outside the depletion region, the electric field is considered to be constant.

If a negative bias (V_{app}) is applied, the overall electric field at the junction increases. Thus, the potential barrier that the majority charge carriers need to overcome increases. If a positive bias (V_{app}) is applied, the barrier height decreases and the diffusion current of the

majority charge carriers is promoted. Therefore, a p - n junction is commonly used as a diode, allowing the current to flow in one direction but not in the other direction

Figure.2.8: Band diagram representing the formation of a p - n junction between two semiconductors. Left) The n -type and p -type semiconductors just before contact. Middle) The two semiconductor are just in contact. The majority charge carriers from each semiconductor diffuse into the other one. Right) At equilibrium, the Fermi level of the two semiconductors line up and a depletion zone takes place at the interface of the p - n junction.

2.2.2. Photovoltaic effect

By definition, the photovoltaic effect is the generation of an electric field in a semiconductor by absorption of a photon. A photon with an energy E_{ph} can be absorbed by a semiconductor only if its energy E_{ph} is superior to the band gap (E_g) of the semiconductor (Fig 2.9.). The absorption of a photon by a semiconductor provokes the excitation of an electron from the valence band to the conduction band, and so the formation of a hole in the valence band. This electron-hole pair, called an exciton, is bounded together by Coulombic attraction.

For high energy (or short wavelength) photons, with $E_{ph} > E_g$, there is enough energy to promote an electron across the band gap and also to impart additional energy to one or both of the charge carriers. Then the carriers with excess energy will relax to the edge of the band, giving up their energy primarily by the emission of phonons; this energy excess is thus simply converted into heat (thermalisation) in the photoactive material which is unfavorable for the charge diffusion.

Figure.2.9: Representation of the interaction between a photon with an energy E_{ph} and a semiconductor with a band gap E_g . When the energy of the photon is superior to the band gap, a photon is absorbed by the semiconductor forming an excited electron-hole pair.

Typical photovoltaic cells are formed by the combination of a p-type semiconductor and an n-type semiconductor sandwiched between two metals. The two semiconductors form a p-n junction and are considered as the active layers, whereas the metals act as electrodes. In this case, both metal-semiconductor junctions form an ohmic junction. Generally, one of the

electrodes is made of a transparent material (e.g: a transparent conductive oxide (TCO) such as Indium Tin oxide (ITO) or fluorine-doped tin oxide (FTO)), whereas the other electrode has a mirror-like surface in order to reflect the photons towards the active layer. Inside a photovoltaic cell, the process to convert light energy into electric current can be dissociated in five major steps (Fig 2.10):

Figure.2.10: Left) Typical device architecture of a photovoltaic solar cell. Right) Band diagram representing the different processes happening in a photovoltaic solar cell.

(1) Photons absorption and formation of excitons: The incident photon captured by the semiconductor leads to the formation of an exciton. Excitons possess a binding energy on the order of 20 meV to 1 eV and a short lifetime (less than microseconds). They can recombine easily by radiative processes such as phosphorescence or fluorescence. Recombination processes are not favorable for efficient photovoltaic cells.

(2) Excitons diffusion: The photogenerated exciton diffuses until it reaches a donor/acceptor interface or the constituent electron and hole recombine. The exciton diffusion length is an

intrinsic property of a material and varies from few nanometers for organic materials to several micrometers for inorganic semiconductors.

(3) Exciton dissociation and charge separation: When an exciton reaches the p-n interface, the separation of the exciton is induced by the internal electric field occurring in the depletion region. The excited electron is transferred into the conduction band of the n-type semiconductor, whereas the hole remains in the valence band of the p-type semiconductor. The n-type semiconductor is considered as an electron acceptor, in opposition to the p-type semiconductor which is an electron donor. Note that the exciton dissociation takes place if it is energetically favorable, specifically the difference between the ionization potential (IP) of the donor and the electronic affinity (EA) of the acceptor is higher than the binding energy of the exciton.

(4) Charge transport: Driven by the inbuilt field arising from the difference in work function between the cathode and the anode, free electrons travel through the acceptor domains to the cathode whilst free holes travel through the donor domains to the anode.

(5) Charge extraction: Charge extraction can occur once free carriers have successfully reached their respective electrodes. In order to ensure the high efficiency of this process it is important that the appropriate energy levels are well matched, that is, the work function of the anode to the valence band level of the donor (for hole extraction) and the work function of the cathode to the conduction band level of the acceptor (for electron extraction). In situations where this occurs, the contacts between the semiconductor and the electrodes have low resistance and are considered as ohmic.

2.2.3. Device characterization

Photovoltaic devices are ordinarily characterized by measuring their current-response in the dark and under illumination (AM1.5G, 1000 W.m⁻²).¹² The measurement in dark is performed in order to confirm the good diode behavior of the device and respect the Shockley equation (Fig.2.11, blue curve).

$$I_d = I_s \times (e^{\left(\frac{eV}{nkT}\right)} - 1) \quad (\text{eq.2.5})$$

where “ I_s ” is the reverse bias saturation current, “ n ” the ideality factor. In the case of ideal diode, n is equal to 1.

When the device is under the illumination, the free charge carriers coming from the photogenerated excitons generate an additional current (I_{ph}) which add up to the diode current. Thus, the current in a photovoltaic devices respects the following equation (Fig.2.11, red curve):

$$I_d = I_s \times (e^{\left(\frac{eV}{nkT}\right)} - 1) - I_{ph} \quad (\text{eq.2.6})$$

The power conversion efficiency (PCE) representing the overall efficiency of a solar cell is the ratio between the output power and the incident light power. The PCE of a solar cell refers only to the efficiency of an active area on which the incident light is focused. Then for the sake of comparison, the intensity of the current is expressed in term of current density (J(mA/cm²)). The PCE is directly extracted from the current-voltage curve using the short-circuit current density (J_{sc}), the open-circuit voltage (V_{oc}) and the fill factor (FF) (Fig.2.11) and is defined by equation 2.7.

Figure.2.11: Typical current–voltage characteristics of a photovoltaic solar cell measured in the dark (blue curve) and under AM1.5G light illumination (red curve). The short-circuit current (J_{sc}), the open-circuit voltage (V_{oc}), the fill factor (FF), as well as the shunt and series resistance are pointed out on the graph.

$$PCE = \frac{P_{out}}{P_{in}} = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}} \quad (\text{eq.2.7})$$

Short-circuit current density (J_{sc}): The J_{sc} represents the current density when no external voltage is applied to the device. The current arises from the photogenerated charge carriers which are driven by the built-in potential. The J_{sc} is highly dependent on the absorbance of the active layer, of the generation and transport of the charge carrier. Recombination processes affect considerably the J_{sc} .

Open-circuit voltage (V_{oc}): The V_{oc} is the applied voltage at which no current flows. The applied voltage cancels out the built-in voltage of the cell, so the diffusion of photogenerated charge carriers toward the electrode is impossible due to the absence of a driving force. The V_{oc} of an ideal cell is determined by the difference between the ionization potential of the

donor and the electronic affinity of the acceptor, or more precisely, between the valence band of the donor and the conduction band of the acceptor. The V_{oc} is also influenced by recombination processes, the solar device architecture and by the working function of the electrodes.

Fill factor (FF): The FF is the ratio between the maximum power and the theoretical power output by the V_{oc} and J_{sc} (eq.2.8). It shows the quality of the solar cell. Typically Fill Factors are in the range of 50–80%.

$$FF = \frac{J_{max} \times V_{max}}{J_{sc} \times V_{oc}} \times 100 \quad (\text{eq.2.8})$$

Shunt Resistance (R_{sh}) & Series Resistance (R_s): Photovoltaic mechanism involves several physical processes at different interfaces. These different processes are generally not ideal, resulting of some energy dissipation. These losses can be interpreted in term of resistances, designated as shunt resistance or series resistance. The shunt resistance is inversely proportional to the slope at the J_{sc} , whereas the series resistance is inversely proportional to the slope at the V_{oc} . The shunt resistance is generally coming from the fabrication process. R_{sh} with a low value is indicative of alternative pathways for the charge carrier within the active layer, resulting in a decrease of the FF. By contrast, the series resistance arises from charge recombination at the different interfaces and a low value will increase the FF, resulting in better performance.

External Quantum Efficiencies (EQE) or incident-photon conversion efficiency (IPCE): EQE is calculated by the ratio of the number of carriers collected by the solar cell to the number of photons of a given energy (eq.2.9). It reveals the contribution on the generated current of

each photon with a given energy. The J_{sc} observed in the J-V characteristic can be obtained by the integration of the EQE spectrum.

$$EQE(\lambda) = \frac{J_{sc}(\lambda) \times h \times c}{P_{in}(\lambda) \times q \times \lambda} \quad (\text{eq.2.9})$$

where h is the Planck constant, c the velocity of light in vacuum, q the charge of electron and $P_{in}(\lambda)$ the incident power at a given wavelength.

2.3. Categories of photovoltaic solar cells

Since the discovery of photovoltaic effect, various materials have been explored such as selenium¹⁶ or copper oxide¹⁷ to fabricate efficient photovoltaic devices. An important moment occurred in 1954 with the fabrication of the first efficient solar cell (PCE =6%) made from silicon in Bell laboratories.¹⁸ leading to the development and industrialization of the silicon technologies. However various alternative materials have been investigated in the laboratory, their evolution along the last 50 years are summarized in Figure 2.3. Nowadays, photovoltaic cells are classified into four different families:

- ◆ **Silicon-based solar cells:** It is the most mature technology and comprises the majority of the commercialized PV panels. This family is subdivided into three different groups depending on the quality of the silicon layer. Amorphous silicon with low efficiency (PCE = 6-8 %) is mainly used for portable electronic devices such as calculator or batteries. Polycrystalline silicon with a photoconversion efficiency PCE = 15-18% are the most suitable for domestic solar panels. Monocrystalline silicon cells have a higher efficiency

PCE =25-27%, however their production cost is high due to strenuous extraction and purification processes.

- ◆ **Thin film technologies:** They emerged with the progress of vacuum deposition techniques. These devices are mostly composed of chalcogenide (CdTe or CdSe) or copper gallium indium selenide (CGIS). They have high efficiency (PCE=22%) and easier fabrication process which are suitable for power plant applications (example: Topaz Solar Farm (USA, 2014) and Desert Sunlight Solar Farm (USA, 2015) are using CdTe modules). The toxicity of their components is an impediment to their development.
- ◆ **High-efficiency solar cells:** Multijunction solar cells possess the record efficiency for photovoltaic cells (PCE=46%). They are made of complex stacking of inorganic semiconductor (GaAs, GaP, Ge) in order to absorb all over the solar spectrum. They are principally used for space applications due to their extremely high cost of fabrication.
- ◆ **Emerging PV:** These devices, generally composed of organic materials, are attractive for industrial due to their low-cost process. This family is subdivided into two main groups:
 - Dye-sensitized solar cells (DSSC) developed by Graetzel's group in 1991 combined an n-type oxide (TiO₂, ZnO), with an organic dye which has the task of collecting photons.¹⁹ DSSC rises to a maximum efficiency of 13.4%. It has been supplanted by perovskite solar cells which benefit of the expertise from DSSC to reach in few years extremely high efficiency (PCE =22.7%).²⁰
 - Organic semiconductors have been investigated for photovoltaic applications since 1950's.¹⁹ At that time, a typical cell was formed of an organic monolayer sandwiched

between a low work function metal, such as aluminum and a high work function metal like gold or TCO deposited on transparent glass substrate. This type of the devices had very poor performance in the range of 10^{-4} – to 10^{-1} % and the photoelectrical behavior of organic materials was not perfectly understood.²⁰ A major breakthrough was made with the fabrication of the first efficient organic cells with an efficiency of 1% by Tang's group.²³ This device was composed of the superposition of two organic layers (copper phthalocyanine and a perylene tetracarboxylic derivative) which act similarly as a p-n junction. Thenceforth, the research on organic photovoltaics has been stimulated with the considerable progress during the 1990's with the development of the bulk heterojunction as well as the development of *n*-type semiconductors from buckminsterfullerene.^{22,23} After several years of optimization, a great improvement was made by using a blend of {poly(2-methy-5-(3,7-dimethyl-octyloxy)- 1,4-phenylene vinylene (MDMO-PVV) / 6,6-phenyl- C_{61} -butyric acid methyl ester (PCBM))}.²⁶ From that moment, a large range of organic materials has been experimented in various configurations (bulk heterojunction or bilayer). The active layer is typically composed of a mixture of a fullerene derivative associated with a *p*-type organic semiconductor, such as Poly-3-hexylthiophene (P3HT),^{27–29} phthalocyanine,³⁰ oligothiophene^{31,32} Nowadays, the highest efficiency reported is over 13% for a tandem cell containing a {PBDB-T:ITIC} blend³³ While their efficiencies are inferior to inorganic cells, they remain of a high interest due to their potential low manufacturing cost and large-scale solution processing. This type of device is described more in detail in the following part.

Figure 2.12: Research cell record efficiency chart for different photovoltaic technologies from National Renewable Energy laboratory (NREL, USA; July 2017; <https://www.nrel.gov/pv/assets/images/efficiency-chart.png>).

2.4. Organic solar cells

2.4.1. Organic semiconductors

Organic semiconductors are essentially composed of π -conjugated materials and are classified into two different families: polymers and small molecules (Fig 2.13).³⁴ Polymers are formed from a monomeric unit which is repeated numerous times (1,000-100,000), resulting in a high molecular weight. Polymer thin films are commonly prepared from solution methods, such as spin-coating or dip-coating, forming amorphous or low crystallinity films. By opposition, small molecules possess low molecular weight and can be deposited by sublimation methods, resulting in highly crystalline films.

Figure.2.13: Chemical structures of various small molecules (on top) and polymers (at the bottom) used in organic electronic devices

π -conjugation & band structure

The common characteristics in all organic semiconductors are the presence of π -conjugated electrons in the form of double bond, aromatic or quinoidal groups.

The conjugation properties are coming from the electronic structure of carbon atoms. The valence orbital of carbon is composed of four electrons with the $2s^2 2p^2$ electronic configuration. The 2s electrons energy are sufficiently close to the 2p to interact with them, forming a hybrid orbital molecular, called sp .³⁵ This hybridization is the origin of double bonding, triple bonding and the tetravalent property of carbon atoms. The formation of a double bond between two carbons involves three hybrid orbitals, resulting in a change in the splitting of the MOs (Fig.2.13). The carbon-carbon bond is then constituted of one σ and two π -orbitals for which the latter act as the frontier orbitals.

Figure.2.14: Left) Bond structure and right) energy levels for a C=C double bond. Hybridized sp^2 orbital (yellow) form a σ bond between the carbons atoms (red) whilst the unhybridized p_z orbital forms a π bond between (purple). The HOMO and LUMO levels are respectively formed of π -bonding and π^* antibonding orbitals.

A molecule is π -conjugated when it is formed by the alternation of double bond and single bond such as in polyacetylene. Besides, an aromatic compound is defined as a cyclic and planar π -conjugated molecule following the Hückels rule (the molecule should possess $4n+2$ π -electrons).^{36,37}

For a large π -conjugated molecule, the succession of π -MOs formed a band structure, similar to inorganic semiconductors. However, these bands are narrower due to the size of the molecule. So, the highest occupied molecular orbital (HOMO) corresponding to π -bonding orbitals refers to the valence band. The energy level immediately above this is the lowest unoccupied molecular orbital (LUMO), corresponding to the π -antibonding orbital, denoted π^* , and refer to the conduction band. The difference between these two energy levels refers to the band gap of the molecule. In general, the band gap of a molecule decreases with the number of π orbitals. The π -electrons orbitals overlap is weaker than σ -orbitals, this favor the delocalization of the electrons within the molecule and the formation of resonance structures. This resonance is at the origin of the charge transport properties within the molecule. Note that in an aromatic compound, the electrons are totally delocalized which facilitates the charge diffusion and charge transfer.

Charge carriers transport

At the moment, there is still no well-established theory for the charge carrier transport in organic semiconductors. The charge carrier transport properties are highly affected by the molecular geometry and the crystalline structure, which lead to a complex mixture of various types of transport.³⁸ The charge carrier transport within an organic semiconductor appears with the creation of free charges by doping. This doping is realized by applying an

electrochemical field, by light irradiation or from chemical impurities, such as oxygen. The free charges, also called polarons are located within the molecule or polymer (Fig 2.15).^{39,40} The charge carrier transport in small molecule materials are commonly guided by intermolecular transport where charges diffuse from one molecule to another. In case of semiconducting polymers, intermolecular transport is also essential, however the elongated π -conjugated structure allows the free charges carrier to diffuse intramolecularly along the chain.⁴¹ Several mechanisms have been used to describe the charge transport inside organic semiconductors:

Figure.2.15: *Different types of charge carriers on a conjugated polymer (sexithiophene). Unpaired neutral spins are represented by black dots, positive defects by positive charge and negative defects by negative charge. The external charge induces a deformation of the molecular geometry with the formation of quinoidal bonds.*

- ◆ **Hopping:** In organic semiconductors, the molecules are bonded together by weak van de Waals forces (<10 kcal/mol), resulting in high disorder. Molecules are small entities, a large number of localized states are distributed in the band tails where the charge carriers cannot move freely. Thus charge carriers can only transfer by hopping, either to the nearest neighboring localized states (nearest neighbor hopping) or to the smallest barrier sites (energy hopping).^{42,43} The hopping rate depends of the charge carrier concentration^{44,45} and can be also enhanced by phonon vibrations.
- ◆ **Polaronic transport:** In this regime, the charge carriers are self-trapped in an initial site and transfer to another neutral site by tunneling, due to the lattice vibration. In the single-crystal rubrene OFETs, the application of high pressure tunes the intermolecular distance and leads to a linear increase of the carrier mobility. This is in agreement with the Holstein-type small polaron model,⁴⁶ which predicts that the mobility should be proportional to the square of the transfer integral and thus linearly increases with the pressure for a small variation in the intermolecular distance. The resulting mobility by this transport model is small, comparable to that by phonons assisted hopping.⁴⁷
- ◆ **Band-like transport:** In organic semiconductors, the mean free paths of carriers are often comparable or less than the intermolecular spacing, the band-like transport is not believed to be a major transport mechanism. However, in highly pure organic single crystal, such as TCNQ,⁴⁸ TIPS-pentacene,⁴⁹ dicyanoperylene derivatives⁵⁰, high carrier mobility has been observed with metallic-like conduction at low temperature.⁵¹

2.4.2. Organic solar cells-operation principles.

Organic solar cells share some certain basic device operation principles with standard photovoltaic cells as described previously. However some important differences take place due to the particular physical properties of organic materials (Fig.2.16).^{52–58} Organic molecules, like dyes, can have strong absorption with high molar absorption coefficient ($\epsilon > 10^5 \text{ L.mol}^{-1} \text{ cm}^{-1}$), which favor the photons absorption. Due to the weak interaction between molecules, the photogenerated excitons are localized within or to the neighboring molecule. Excitons type depends of the medium, in particular the dielectric constant. The dielectric constant in organic materials is generally lower than in silicon ($\epsilon_r=11.7$), resulting of a strong columbic attraction between the electron and the hole. These excitons are tightly bond, and

Figure.2.16: Left) Typical device architecture of a bulk heterojunction solar cell. Right) Band diagram representing the different processes happening in a BHJ solar cell. (1) Exciton generation from an absorbed photon in the donor material. (2) Exciton diffusion to the acceptor interface. (3) Exciton dissociation by electron transfer to the acceptor molecules. (4) Charge transport by hopping mechanism. (5) Charge extraction and generation of photocurrent.

are described as Frenkel excitons.^{59–61} These Frenkel excitons have a stronger binding energy in the range of 0.1 to 2 eV, (as opposed to inorganic semiconductor excitons with a binding energy of few meV) and are not easily dissociated by thermal energy (26 meV at room temperature). Thus, a driving force is required to promote the charge dissociation. In organic material, the excitons lifetime is short (few nanoseconds), resulting in a short diffusion length L_d (around 10 nm). Therefore most excitons generated at a distance greater than L_d from the donor-acceptor interface will simply recombine.^{62,63} The bulk heterojunction (BHJ) have been developed in order to overcome this exciton-diffusion issue. The intermixed phase allows the excitons to reach the donor-acceptor interface more easily.^{64–66} After the dissociation of excitons and the separation of the polaron pair, the charge can be transported towards the respective electrodes.

Depending on the nature of the organic material, the charge transport would be generally described as a hopping mechanism. During the transport process, the charge carriers can recombine when a positive and negative charge from two different precursors are brought together.⁶⁷ This process is called non-geminate recombination as opposed to geminate recombination happening during polaron pair dissociation. This process is more frequent in BHJ due to the presence of isolated aggregates in which charge are trapped.

2.4.3. Device optimization and importance of interfacial layer

Photovoltaic devices involve at least a p - n heterojunction and two metal-semiconductor junctions. The p - n interface plays an important role on the V_{oc} ⁶⁸ whereas the J_{sc} is substantially affected by the semiconductor-metal interface.

Indeed, the V_{oc} is extracted from the HOMO energy of the donor and the LUMO energy of the acceptor. The value of the V_{oc} has been quantified by Sharber et al. for an organic solar cell by the equation (eq.2.10).⁶⁹

$$V_{oc} = \left[\frac{1}{q} \times (E_{HOMO}(D) - E_{HOMO}(A) - 0.3) \right] \quad (\text{eq 2.10})$$

Where the 0.3 eV comes from the non-ideal character of the diode.

The improvement of V_{oc} in a solar device requires new donor or acceptor molecular architectures. In one hand, a large range of donor polymers has been explored, especially low band gap polymers.^{70–72} On the other hand, fullerene derivatives are still widely used as an acceptor, however their LUMO energy is difficult to lower, with a maximum change of only a few tenths of eV.^{73,74} Therefore, alternative fullerene-free n-type semiconductors, such as perylene bisimide have been explored in order to replace standard PCBM, resulting in efficiencies higher than 10% with high V_{oc} =0.8–1 V in the best devices.^{108–111}

The current density J_{sc} is directly correlated to the absorption of the active layer. If more photons are collected, more charge will be produced. In general, acceptor materials have a large band gap and contribute only to the near-UV absorption. Donor materials having a wide absorption (low band gap) are generally used to match the solar spectrum. However, a band gap inferior to 1–1.2 eV is not suitable for good photovoltaic performance, as it will result of a low V_{oc} and the infrared photons absorption will increase the thermalization and recombination process.

The absorption spectra of the {donor:acceptor} system allow to predict the maximum current density J_{max} of the device by considering 100 % photons absorption of the solar spectrum and that all the absorbed photons participated to the current generation. In reality,

a major party of the absorbed photons would not contribute to the current and the created excitons will recombine. The recombination rate is highly dependent on the charge carrier density within the organic material. This latter parameter is regulated by the charge transport properties of the active layer^{79,80} and by the metal-semiconductor interface.⁸¹

In general, the hole mobility of the common polymers used for efficient solar cells is low ($\mu_h=10^{-3}-10^{-7} \text{ cm}^2.\text{V}^{-1}.\text{s}^{-1}$), due to the particular transport mechanism of organic materials. For examples, the hole mobilities of P3HT are in the range of $\mu_h= 10^{-4}-10^{-1} \text{ cm}^2.\text{V}^{-1}.\text{s}^{-1}$.^{80,82} In contrast, the electron mobilities in PCBM are in the range of $\mu_e=10^{-3}-10^{-7}\text{cm}^2.\text{V}^{-1}.\text{s}^{-1}$ ⁸³ Within an organic solar cell, the hole and electron transport are generally unbalanced, resulting in a charge accumulation at the metal-semiconductor interface. This phenomenon is particularly marked at the anodic side. In order to promote the charge extraction to the electrode, an interfacial layer is inserted between the active material and the electrodes. This layer is usually called hole transporting layer (HTL) when it is located at the donor-anode interface, as opposed to the electron transporting layer (ETL) located between the acceptor and the cathode. The properties of the hole transporting layer will be described in details in the **Section.2.6.**

2.5. Perovskite solar cells

Beside organic photovoltaic cells, a new type of device based on organic-inorganic hybrid perovskites emerged less than a decade and rapidly supplanted all emerging photovoltaic solar cells with photo-conversion efficiency exceeded 20%. The remarkable properties of perovskite are presented in the following section.

2.5.1. Introduction

The perovskite refers to a class of ABX_3 compounds which have the same crystal structure. Initially, the term perovskite designated calcium titanium oxide ($CaTiO_3$) for which the name had been given in honor of Lev Perovski.⁸⁴ Inorganic perovskites have been largely studied such as $BaTiO_3$, $PbTiO_3$ or $LaAlO_3$ for ferroelectric and ferromagnetic properties^{85–88} while the organic lead halide perovskite received recently a high interest for optoelectronic devices. The crystal structure is defined as a cubic structure in which the center of the cube is filled with the metal cation (Pb, Sn), the organic cations are located at the corner of the cube and the halide at the center of each face of the cube (Fig.2.17). methylammonium lead iodide ($CH_3NH_3PbI_3$ or $MAPbI_3$) or mixed halide, ($CH_3NH_3PbI_{3-x}Cl_x$) perovskites have been highly investigated for photovoltaic applications.

The first efficient solar devices using $CH_3NH_3PbI_3$ perovskite have been reported by Miyasaka's group with a PCE of 3.8% using a mesoscopic TiO_2 layer.⁸⁹ After further

Figure.2.17: Schematic representation of hybrid organic-inorganic methylammonium lead perovskite ($CH_3NH_3PbI_3$).

optimization, Park's group pushed the efficiency up to 6.5%.⁹⁰ Based on DSSCs, These devices used a liquid electrolyte made of lithium halide which reduced drastically the stability of the solar cells by dissolving the perovskite layer. The replacement of the electrolyte by solid state hole transport layer has been the basis of the fast development of PSCs. After the first report of a solid state perovskite cell with 9,2% efficiency,⁹¹ the performance increased quickly up to 12.3% using a mix halide $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ perovskite, reported by Seok and Grätzel's groups.⁹²

Nowadays, highly efficient PSCs with PCE higher than 22% have been obtained after intensive investigations and device optimizations.^{93–99} These devices are generally constituted of high

Figure.2.18: Summaries of the different solution methods using spin-coating for high-quality perovskite films: the two-step methods (top) and single step method with anti-solvent treatment (bottom). Both methods require an annealing process to completely remove the solvent and form crystalline perovskite.

crystalline perovskite made of complex mixed halide/mixed organic cation $(\text{FAPbI}_3)_{1-x}(\text{MAPbBr}_3)_x$ (FA stands for formamidium or $\text{NH}_2\text{CH}=\text{NH}_2^+$). The perovskite film preparation is a key component toward high efficiencies. It can be prepared by vapor deposition^{100–102} or by solution method using the single¹⁰³ or two steps methods (Fig.2.18).^{104,105} Solvent engineering, in particular anti-solvent treatment, are an efficient method to obtain high-quality films with large perovskite grains.^{106,107}

2.5.2. Optoelectronic properties of organometal halide perovskites

Methylammonium lead halide perovskite has a wide absorption range up to 800 nm ($E_g = 1.5\text{--}1.6\text{ eV}$) and a relatively high absorption coefficient ($6 \times 10^4\text{ cm}^{-1}$ at 600 nm).¹⁰⁸ The charge separation is achieved more easily in organometal halide perovskites than in organic solar cells. The binding energy of excitons in $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films has been measured in the range of 20 meV to 50 meV, depending on the characterization methods (optical absorption,¹⁰⁹ magneto-absorption,¹¹⁰ temperature dependent PL¹¹¹). These values are comparable to the thermal energy at room temperature (26 meV). Thus, the excitons have a high probability to dissociate into free charge, without the need for a donor-acceptor interface to drive this process.¹¹²

Once the excitons are dissociated, the charge transport and extraction happen similarly as organic solar cells. However, the charge diffusion follows a band-like conduction behavior due to the crystalline structure of the perovskite. The charge carrier mobility is significantly higher (in the order of $10\text{--}20\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) than in typical organic semiconductors.^{113,114} These

high mobilities allow the electrons and holes to diffuse along large distance with a low recombination rate. The electron-hole diffusion lengths can reach up to 100 nm for $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite film¹⁰⁸ and up to 1 μm for a mixed halide $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$.¹¹⁵ Therefore, the thickness of the perovskite layer is not limited as in organic solar cells (e.g 100-200 nm) and are generally thicker (e.g. 500 nm) in order to increase photon absorption.

In conclusion, these remarkable properties of the perovskites make them highly attractive for solar applications. Despite of the exceptional progress made in a quick period, a number of barriers still remain present and need to be further overcome to validate their commercial relevance. Among them, the major issue is the stability of PSCs which degrade easily under exposition to moisture. The presence of lead in PSCs which are water soluble and extremely toxic upon human exposure is also a major concern. Various metallic cations have been investigated such tin^{116,117} or bismuth,^{118,119} however the obtained perovskites are extremely unstable or showing poor device performances. Finally, the interfacial layers, in particular the hole transporting layer are a critical importance towards further development of PSCs and will be extensively discussed in the following section.

2.6. Hole transporting materials

In this part, we will determine what is the relevant properties to design an efficient HTMs for both organic and perovskite solar cells. As these two type of devices are working on the same principles, the primary requirements for the HTMs are similar. Novel HTMs were initially developed for organic solar cells. However at that time, the active layer was still the limiting factor and the majority of the research were focused on it. With the emergence of high-

efficiency PSCs, the development of the HTM layer is now crucial to improve the device performances. Thus a large number of HTMs have been explored in the recent years for PSCs. In fact, in order to ensure an optimal charge extraction from the active layer, the HTMs have to follow some precise requirements:

- ◆ **Energetic properties:** The charge extraction process constrains the HOMO level of the HTM to be close to the HOMO level of the donor material. Precisely, the HOMO level of the HTM should be slightly higher than the HOMO of the donor and slightly lower than the working function of the anode in order to create an ohmic contact. Ideally, the HOMO energy level of the HTMs should be located no more than 0.3 eV higher than the HOMO of the donor.
- ◆ **Transport properties:** The HTM acts as a ramp access for holes toward the conductive metal electrode. The hole transport mobility of the HTM should not be a limitation and it is required that the HTM possesses a high hole mobility, at least superior to $10^{-3} \text{ cm}^2/\text{V.s}$ to avoid any charge accumulation at the HTM-donor interface. In addition, the HTM has to be selective and blocks the electron diffusion.
- ◆ **Stability:** The HTM requires a good thermal stability, at least superior at 150°C . Indeed, annealing process is generally performed during device fabrication and partial decomposition can easily deteriorate the device performances. Besides, solar panels stand under sun irradiation in ambient atmosphere, therefore the HTM should not be affected by the thermal heat, UV irradiation, air or moisture contamination.
- ◆ **Morphological properties:** The HTMs should form homogeneous films and adhere to the electrode or the active layer surface. Furthermore, TCO electrodes possess generally a

high roughness with a lot of grain boundaries that can affect the charge extraction process. The HTM layer should also be able to smooth the surface of the TCO. Besides, nanostructured HTMs can be developed in order to increase the surface contact between the donor and the HTL to enhance the charge extraction. These nanostructured HTMs have been mainly investigated for OSCs.

- ◆ **Optical properties:** Depending on the device configuration, the HTL can be located between the transparent electrode and the active layer and affect the optical pathway of photons. Thus it is preferable that HTMs have a good optical transmission.
- ◆ **Synthetic accessibility:** the HTMs should be easy to synthesize on a large scale, environment-friendly and possess low toxicity.

The ideal HTM which respect all these requirements has not been developed yet. HTMs can be classified into three categories: inorganic, polymeric and small molecule HTMs.

It is generally not trivial to compare HTMs between them because experimental conditions are generally different. For example, PSCs can be fabricated in three different conditions: mesoscopic cells (meso), planar configuration (P), inverted planar configuration (IP), while OSC can be fabricated in BHJ or bilayer (BL) in standard (S) or inverted configuration (I). In this literature review, we will focus mostly on PSC mesoscopic and standard bulk heterojunction configuration because those are the configurations that we investigate for our devices.

2.6.1. Inorganic HTMs

This category of HTMs is described succinctly as these materials are out of scope of this thesis. Metal oxides have a good stability and high charge carrier mobilities as compared to

organic materials. These inorganic materials required a high work function to makes them potential candidates. However, inorganic materials a generally deposited at high temperature by vacuum techniques such as thermal evaporation or pulsed laser deposition which are expensive and not compatible with the used of flexible substrates. Therefore, one main challenge is to develop alternative deposition techniques using low-temperature process such as solution techniques. MoO_x ¹²⁰ NiO_x ,¹²¹ or VO_x ¹²² , copper-based solutions^{123,124} or polyoxometalates¹²⁵ have attracted some high interest due to their low-cost. In organic solar cells, those materials show good performance comparable to the ubiquitous PEDOT:PSS. For examples, solution processed NiO shows in a blend {pDTG-TPD:PC₇₁BM} BHJ a maximum efficiency of 7.82%.¹²⁶ Besides, Jaseniak reported the use of MoO_x from a methanol solution resulting of PCE up to 3.5% for a P3HT:PCBM based solar cells.¹²⁷ Actually, the champion cell for organic solar cells are using MoO_3 as HTL.³³ These materials have been also tested within perovskite solar cells.^{128–130} copper-based materials such as Cu_2O , CuI have shown good performances.^{131–133} Graetzel's group reported the use of copper thiocyanate deposited by solvent removal methods with PCE up to 20.2% and a stability over 1000 h.¹³⁴ This CuSCN HTM offers better device stability than standard spiro-OMetad and it is actually the most promising inorganic HTM for PSCs.

2.6.2. Polymeric HTMs

Since the early development of organic solar cells, p-doped semiconducting polymers have been widely used as HTM in organic electronic devices for the hole extraction. Among them, Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) has been the most

widely employed^{135–137}. Other p-doped semiconducting polymers, such as polyaniline (PANI)^{138,139} or poly(diphenylamine)¹⁴⁰ have been also investigated with decent performances. Water/alcohol soluble conjugated polymers composed of polar pendant groups on their side chains received a large interest. For example, hydrochloric acid doped polyanilines (HAPAN) were utilized as *p*-type electrode buffer layer in highly efficient polymer solar cells (PSC) based on PBDTTT-EFT with PCE up to 9%.¹³⁹

PEDOT:PSS is a polymer electrolyte consisting of positively charged conjugated PEDOT and negatively charged saturated PSS. It has a high electrical conductivity up to 10^3 S.cm^{-1} , which is comparable to ITO ($\sigma=2000 \text{ S.cm}^{-1}$). In addition, this polymer is almost transparent in the visible (90 % transmission at 550 nm) and highly stable in air which made it really attractive at that time. However, it is now well-known that PEDOT:PSS suffers from several drawbacks: Its acidic character (pH=1-2) etches the ITO electrode and considerably shortens the long-term stability of the devices. Furthermore, PEDOT:PSS films are hygroscopic and exhibit weak electron blocking properties.^{141–143} Finally, PEDOT:PSS thin films often possess important structural and electrical inhomogeneities that are not compatible with reproducible device performances.

In term of performance, PEDOT:PSS has been used with various {donor:acceptor} group in BHJ solar cells. The table 2.1 summarized the photovoltaic characteristics of BHJ OCSs integrating PEDOT:PSS. The blend {P3HT:PCBM} has been the most prominent reported system in BHJ solar cells and is generally used as a benchmark, therefore we have selected this system in this study. For {P3HT:PCBM} system, the maximum efficiency reported is 6.53%¹⁴⁴. This high efficiency has been obtained after fine-tuning, especially by using the

reflectivity properties of the metal electrode to increase the light absorption. Despite this record efficiency, it is generally difficult to reproduce such high efficiency in laboratory. In average, {P3HT:PCBM} devices show an efficiency in the range of 3% to 4% with an open circuit voltage around 0.60 V and a fill factor around 60 for optimized condition, the short-circuit current fluctuates in the range of 8-12 mA/cm² depending on the device configuration.¹⁴⁰ The performance of the {P3HT:PCBM} devices are limited by the small open circuit voltage, and also by the weak absorption of P3HT over 650 nm. The intensive research on new acceptor or donor polymers with smaller band gap allowed to overpass these limitations. Nowadays, a large range of donors and acceptors are accessible. Listed all of them would be superfluous and out of scope of this thesis. However for the sake of comparison, we incorporate some major donors (PTB7,¹⁴⁶ PF10TBT¹⁴⁷ or PBnDTDTBT,¹⁴³ MDMO-PPV¹⁴⁹) and major acceptors (ICBA)^{144,145} that are now usually used in BHJ solar cells (Fig.2.19).

Table.2.1: Photovoltaic parameters of PEDOT:PSS with various (donor:acceptor) blend in standard BHJ OCSs.

Device structure (in standard configuration)			V _{oc} V	J _{sc} mA.cm ⁻²	FF	PCE %	Ref	years
HTL	Active layer	ETL						
ITO/PEDOT:PSS	P3HT/PCBM	Ca/Al	0.59	8.95	60	3.2	¹⁵²	2006
ITO/PEDOT:PSS	P3HT/PCBM	Ca/Al	0.58	10.8	62	3.8	¹⁴²	2010
ITO/PEDOT:PSS	P3HT/PCBM	LiF/Al	0.65	15.36	66	6.5	¹⁴⁴	2009
ITO/PEDOT:PSS	P3HT/ICBA	Ca/Al	0.84	9.67	67	5.4	¹⁵⁰	2010
ITO/PEDOT:PSS	P3HT/IC70BA	Ca/Al	0.87	11.35	75	7.4	¹⁵¹	2012
ITO/PEDOT:PSS	PF10TBT:PCBM	LiF/Al	0.99	7.7	54	4.2	¹⁴²	2007
ITO/PEDOT:PSS	PTB7:PC71BM	Ca/Al	0.76	15,4	70	8.2	¹⁴⁶	2012
ITO/PEDOT:PSS	PBnDTDTBT:PCBM	Ca/Al	0.90	12.2	62	6.6	¹⁴⁸	2013
ITO/PEDOT:PSS	MDMO-PPV:PCBM	LiF/Al	0.77	7.6	51	3.0	¹⁴⁹	2003

Figure.2.19. Molecular structures of PEDOT:PSS (top left), selected fullerene acceptors (top right) and conjugated polymer donors (bottom) used in bulk heterojunction solar cells.

The use of semiconducting polymers as HTMs has been not exhaustive for BHJ solar cells as compare to PSCs.^{136,153,154} In fact, a majority of polymers used as donor materials in organic solar cells has been later tested in PSCs, particularly polymers which have a suitable band alignment with the HOMO of the MAPI perovskite. P3HT have been investigated in various configuration with decent performance. Nia *et al.* studied the influence of the molecular weight of P3HT and reported an maximum efficiency of 16.2% in mesoscopic PSCs with a V_{oc} of 1.03 V and a J_{sc} of 23.19 mA/cm².¹⁴⁹ While Yan *et al.* reported the used of ultrathin P3HT layer in a planar inverter configuration with an overall efficiency of 15.4%, a V_{oc} = 0.99 V and J_{sc} =20.3 mA/cm².¹⁵⁶ Besides, PTB7-Th with a suitable HOMO of -5.2 eV and a good hole

mobility of $1.5 \times 10^{-2} \text{ cm}^2/\text{V.s}^1$ has been incorporated in a planar perovskite configuration in combination of ZnO/PCBM ETL, resulting of efficiency of 11.04 % with a moderate current density ($J_{sc}=14.53 \text{ mA}/\text{cm}^2$).¹⁵¹ Among the donor polymers, poly(triarylamine) PTAA showed the highest certified efficiency reported at the moment (PCE=22.2%; Voc=1.10 V; $J_{sc}=25.0 \text{ mA}/\text{cm}^2$).²²⁰ This remarkable performance are obtained after optimization of all the different layer. Indeed, additives such as lithium salt (LiTFSI) and 4-tertbutylpyridine (TBP)r are incorporated into the PTAA polymers. This widespread strategy are commonly used during device fabrication in order to increase the conductivity of the HTM layer.^{158–160} However, these dopants are hydrophilic, which compromises the stability of the solar cell (organic-inorganic lead halide perovskite are susceptible to moisture).¹⁶¹ In general, semiconducting polymers have weak hole mobility and thus the use of dopants is inherent. Undoped polymers have been seldom reported. For examples, the use Poly[N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)benzidine] (poly-TPD) shows efficiency up to 15.3%¹⁶² while donor-acceptor polymers 4,8-dithien-2-yl-benzo[1,2-*d*;4,5-*d'*]bistriazole-*alt*-benzo[1,2-*b*:4,5-*b'*]dithiophenes (pBBTa-BDTs) presents a stabilized PCE up to 12.3%.¹⁶³ Besides, the synthesis of polymers are costly with low efficiency and suffers from batch-to-batch inconsistency due to the polydispersity.

2.6.3. Small molecules HTMs

In contrast, small molecules are generally easy to design by using simple cross-coupling synthesis methods. The report of small molecules as HTM in organic solar cells are not exhaustive until recently. In contrast, surprisingly, a large number of small molecules HTMs

has been reported for perovskite solar cells. The major reason is that perovskite solar cells development have followed the research on solid-state DSSC for which the small molecules 2,2',7,7'-Tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) have been the prevalent hole transport material. Nowadays, spiro-OMeTAD is mainly used as a benchmark for perovskite solar cells, like PEDOT:PSS in organic solar cells.

Small molecules HTMs for organic solar cells

Small molecules have been mainly used to modify the work function of the anode or as a surface modifier. In general, these small molecules are composed of aromatic moieties in order to favor the charge transfer. Some alkyl groups are commonly used to increase the solubility of the π -conjugated system.

Solution-processed materials brought a large interest due to the ease of fabrication. Among them, electron rich building block such as biphenylamine or triphenylamine (BPA or TPA) moieties have been widely investigated as a building-blocks for HTMs (Fig.2.20). triphenylamine-containing polyperfluorocyclobutane (TPA-PFCB) has been used as a double HTL in combination of PEDOT:PSS with relatively good performance (PCE=3.5 % for {P3HT:PCBM} devices, Table.2.2).¹⁶⁴ Lu *et al.* reported the use of various *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD) compounds with a maximum PCE=3.03 % (V_{oc} =0.55 V; J_{sc} =8.62 mA.cm⁻²).¹⁶⁵ Triindoles and triazatruxene have also been reported in inverted BHJ. The triindole molecule has a unique discotic π -extended aromatic structure with excellent charge carrier selectivity.¹⁶⁶ However, the devices show poor performances which are attributed to the weak hole mobilities (1×10^{-4} cm²/v.s). Besides,

Hains *et al.* reported the use of a blend of poly[9,9-dioctylfluorene-co-N-[4-(3-methylpropyl)]-diphenylamine](TFB) and 4,4'-bis[(p-trichlorosilylpropyl)phenyl]-phenylamino]bi-phenyl (TPDSi₂). These materials possess a good charge-blocking capacity and high temperature stability. The presence of silyl groups on TPDSi₂ promotes a good compatibility with the ITO surface. (Si forms a covalent bond with the hydroxyl group of ITO) which can favor the charge extraction¹⁶¹. Finally, conductive conjugated polyelectrolyte (CPE-K) reported by Heeger's group showed the best performances with an overall efficiency up to 8.2 % (Voc=0.71 V; Jsc=16.29 mA.cm⁻²).¹⁶⁸ The use of CPE-K as HTM in {PTB7:PC71BM} BHJ devices promotes the charge extraction toward the cathode by reduction of the series resistance. In addition, this conjugated polyelectrolytes HTMs are deposited from aqueous/alcohol solutions and has a neutral pH which makes it intrinsically superior to PEDOT:PSS. It could be noted that conjugated polyelectrolytes have been also used as an ETL in BHJ with excellent performances.^{169,146}

Figure.2.20. Molecular structures of HTMs used in BHJ OSCs.

Table.2.2: Photovoltaic parameters of various small molecules HTMs in standard BHJ OCSs.

Device structure			V _{oc} V	J _{sc} mA.cm ⁻²	FF	PCE %	Ref	years
HTLs	Active layer	ETL						
ITO/TPA-PFCB/ PEDOT:PSS	P3HT:PCBM	Ca/Al	0.61	9.43	67	3.9	¹⁶⁴	2010
ITO/TPDB	P3HT:PCBM	LiF/Al	0.55	8.62	64	3.03	¹⁶⁵	2013
Au/TAT	P3HT:PCBM	TiO ₂ /ITO	0.43	8.04	39	1.34	¹⁶⁶	2012
TPDSi ₂ :TFB	MDMO-PPV:PCBM	Li/Al	0.86	4.72	53	2.17	¹⁶⁷	2010
ITO/CPE-K	PTB7:PC71BM	Ca/Al	0.71	16.29	66	8.2	¹⁶⁸	2014
ITO/pentacene: PEDOT:PSS	P3HT:PCBM	Al	0.58	15.31	57	5.25	¹⁷⁰	2012

Curiously, the use of planar aromatic molecules as HTMs has been rarely reported. This type of materials has been highly investigated in field effect transistor for their high mobilities (pentacene, rubrene, etc). Kim *et al.* reported the use of pentacene in combination of PEDOT:PSS in a {P3HT:PCBM} system with a maximum efficiency up to 5.25 % and current density up to 15.31 mA.cm⁻². This remarkable device performances have been explained by a decrease of the work function and an increase of the charge mobility which promote the charge extraction.¹⁷⁰

Small molecules HTMs for perovskite solar cells

As mentioned at the beginning of this section, spiro-OMeTAD is the most commonly used HTM in PSCs.¹²⁸ However, its high cost due to a non-trivial synthesis combined with the need to mix it with various dopant materials, is a major hindrance towards cost-effective PSCs. Then it is mandatory to develop alternative HTMs having good transport properties and being easy to synthesize. Organic small molecule are preferred because they offer some unique advantages such as the possibility to tune their electronic properties by chemical design, few-

steps and low-cost synthetic pathways, solution processability, good stability, and often are environmentally friendly.^{165–167} At the moment, no organic HTM has yet clearly emerged in terms of cost, efficiency and stability. Various classes of HTMs based on thiophene,¹⁷⁴ carbazole,¹⁷⁵ triazatruxene,¹⁷⁶ star-shaped molecules,¹⁷⁷ fluorinated indolo[3,2-b]indole,¹⁷⁸ or triptycene,¹⁷⁹ have been recently investigated in PSCs. However, it appears that a number of these HTMs possess a non-planar molecular conformation thus inducing large intermolecular distances in the solid state, a typical example being HTMs based on triarylamine.^{180–182} As a result, these HTMs suffer from a low hole mobility or conductivity in their pristine form that limits device performance.¹⁸³ On the majority of the case, a doping process is needed to promote the charge carrier extraction and achieve high devices performances. For example, devices using pristine spiro-OMetad (Figure.2.21) shows extremely low performances (PCE=5-7%) with low current densities and poor fill factor as compared to doped Spiro-OMetad (Table 2.3).

Recently a large number of dopant-free HTMs have been reported for PSCs (Fig.2.21). An analog of spiro-OMetad using a cyclopentadithiophene (SBCPT, table 2.3) core instead of the bifuorene. The thiophene core has a higher electron density than bifuorene which promotes the charge transport and reduces the internal series resistances at the perovskite-HTM interfaces. Devices performed with these HTMs show relatively good performances with PCE up to 10.3% which are almost twice higher than pristine spiro-OMetad.¹⁸⁴ The triangular pyramid configuration of spiro moieties induce a large steric hindrance and intermolecular distance, resulting of poor crystallinity and low charge carrier mobility. Therefore, HTMs with less compact structure have been developed. Gong *et al.* reported the use of “X” swivel-

cruciform structure using bithiophene (DEPT-SC).¹⁸⁵ This HTM has almost a planar structure which can promote intermolecular π - π stacking and should favor higher mobility. However the hole mobilities measured using space charge limited charge are comparable to spiro-OMetad. Devices using pristine DEPT-SC shows performance slightly lower than SBCPT with PCE=9.7%. Besides, undoped 4-methoxytriphenylamine-based molecules have been reported by Graetzel's group, showing good performance with PCE up to 15.9% and long-term stability up to 1.000 h.¹⁸⁶ Donor-acceptor structure composed of electron donating benzodithiophene (DERDTS-TBDT) has been employed as HTM with efficiency up to 16.2%.¹⁸⁷ By replacing the electron donating benzodithiophene core by an electron withdrawing group such as difluorobenzothiadiazole, the device performances decreases drastically with a maximum up to 6.2 %. This low photovoltaic performance is ascribed to the deep HOMO level (-5.5 eV) which prevent the charge extraction and low hole transport mobilities. Furthermore, acceptor-donor-acceptor (A-D-A) structure has been also investigated for dopant-free HTMs by Cheng *et al.*¹⁸⁸ The undoped HTMs (M1) composed of a benzodithiophene (BDT) central building block and a phenoxazine linker shows an efficiency of 13.2 % with a V_{oc} =1.01 V and J_{sc} =19.1 mA.cm⁻². Finally, a large donor-acceptor star shapes molecules composed of a flattened triarylamine core (fused-F) have been reported with an efficiency of 12.8 %¹⁸⁹ Among all these HTMs, we can note some similarities on the physical properties: firstly their HOMO level is always between -5.0 eV and -5.3 eV which is lower than the perovskite and allow a good charge extraction. Secondly, the hole mobilities of these HTMs are very low in the range of 10^{-4} - 10^{-5} which are comparable to spiro-OMetad. Only few HTMs with a high hole mobility have been reported.

Figure.2.21. Molecular structures of HTMs for PSCs.

One promising strategy to improve charge transport is to use small π -planar conjugated molecules which assemble into π -stacks in the solid state thus exhibiting favorable intermolecular electronic coupling.¹⁹⁰ Kazim *et al.* reported on the use of pristine TIPS-pentacene with a maximum efficiency of 11.51% (Figure.2.22).¹⁹¹ Recently, the Zou's group reported on the use of rubrene in a planar inverted configuration PSC device with a PCE as high as 15.83%.¹⁹² Besides, quinoidal small planar molecules have been rarely reported as HTMs in PSCs, only alkylated tetrathiafulvalene derivatives (TTF-1; PCE=11.03%),¹⁹³ 5,5',5'',5'''-(tetrathiafulvalene-2,3,6,7-tetrayl)tetraisophthalic acid (TTFA; PCE= 16.7 %)¹⁹⁴ and 3,6-di(2H-imidazol-2-ylidene)cyclohexa-1,4-diene (PCE=11.6%).¹⁹⁵

Table.2.3: Photovoltaic parameters of various dopant-free small molecules HTMs in perovskite solar cells.

HTMs	HOMO eV	Hole mobility* cm ² /V.s	perovskites	V _{oc} V	J _{sc} mA.cm ⁻²	FF	PCE %**	Ref.
Spiro-OMetad	-5.07	10 ⁻⁴ -10 ⁻⁵	MAPbI ₃	0.88	15.1	46	6.2	193
Spiro (doped)				0.91	19.8	63	11.4	193
SBCPT	-5.28	3.5 × 10 ⁻⁵	MAPbI ₃	0.90	16.3	70	10.3	184
DEPT-SC	-5.14	2.1 × 10 ⁻⁶	MAPbI ₃	0.85	16.5	69	9.7	185
Z34	-5.14	7.5 × 10 ⁻⁴	MAPbI ₃	1.09	21.3	69	15.9	186
DERDTS-TBDT	-5.09	2.1 × 10 ⁻⁶	MAPbI _{3-x} Cl _x	1.05	21.2	73	16.2	187
M1	-5.28	2.7 × 10 ⁻⁴	MAPbI ₃	1.01	19.1	68	13.2	188
Fused-F	-5.23	3.5 × 10 ⁻⁵	MAPbI ₃	1.03	17.9	68	12.8	189
TIPS-pentacene	-5.40	>1 [#]	MAPbI ₃	0.96	20.8	61	11.8	191
Perylene	-5.40	9.6 × 10 ⁻⁴	MAPbI _{3-x} Cl _x	1.15	6.2	52	3.7	196
Het-pentacene	-5.20	9.6 × 10 ⁻⁵	MAPbI ₃	0.95	16.5	72	11.2	197
rubrene	-5.40	17 [#]	MAPbI _{3-x} Cl _x	0.98	21.8	74	15.8	192
TTF-1	-5.05	0.1 [#]	MAPbI ₂ Cl	0.86	19.9	64	11.0	193
TTF-A	-5.26	9.7×10 ⁻⁴	MAPbI ₃	1.04	20.4	78	16.7	194
DIQ-C12	-5.43	4.0 × 10 ⁻⁴	MAPbI ₃	0.91	19.7	65	11.6	195

*The hole transport properties are determined using space charge limited current (SCLC) model.

**the efficiencies presented in this table show the average value; # value from literature

Figure.2.22. Molecular structures of small planar HTMs for PSCs.

2.7. Conclusions

Within this Chapter, relevant background information and underlying physical principles relating to the topics covered in this thesis have been presented. A major point was to introduce the state of art of photovoltaic solar cells and present the working principles of a photovoltaic device with a large focus on organic and perovskite solar cell devices. Besides, the crucial role of the HTMs toward high efficiency cell has been exposed. A literature survey present an overview of the various HTMs investigated in OSCs and PSCs. Among small molecules, planar structures molecules has showed some promising results with good device performances. Small π -planar conjugated molecules can assemble into π -stacks leading to high transport mobility. The SCLC mobilities measured for this HTMs are one or two order higher than for spiro-OMetad. Therefore the design of novel molecules with a planar structures can be strategy to develop high mobility HTMs.

Chapter 3

Dipyranylidenes

Small π -conjugated molecules present intrinsic advantages for organic electronics.^{198–200} As compared to conjugated polymers, there are monodisperse in nature and present in general simple synthetic pathway. In addition, small π -conjugated molecules have a tendency to crystallize more easily. The use of planar structure molecules leads to a good crystalline packing, which can enhance the charge carrier diffusion within the material.

Dipyranylidene molecules are constituted of two pyran heterocycles that are linked together by an exocyclic C=C double bond in para-position relative to the O-atom (Fig. 3.1). The quinoïdal structure of the dipyranylidene core is reminiscent of the well-known tetrathiafulvalene (TTF).

Figure.3.1: Chemical structures of dipyranylidene ($X=O$), dithiapyranylidene ($X=S$), dithienopyranylidene ($X=Se$) and tetrafulvalene (TTF).

TTF has been highly employed as a strong donor in charge transfer complex salt in the development of electrically conductive material. Indeed, the first “organic metal” discovered

in 1970 by Wudl is constituted of tetrathiafulvalene-tetracyano-p-quinodimethane (TTF-TCNQ) salt.²⁰¹ Since then, a large number of studies has been carried out to enhance the electron donating power of TTF analogues.^{202,203} Moreover, with the popularity of TTF, a large chemistry has been developed opening this material to other applications such as, multifunctional switchable architectures, sensing.^{204–206}

In contrast and despite the structural similarity, dipyranylidene derivatives have been rarely investigated. Only a few reports of these compounds have been found in the literature and it has been rarely used for its semiconducting properties in electronic devices. This chapter presents the synthesis methods and detailed discussion on the intrinsic properties of 2,2',6,6'-tetraphenyldipyranylidene (DIPO-Ph₄, Figure.3.2)

Figure.3.2: Chemical structure of 2,2',6,6'-tetraphenyldipyranylidene (DIPO-Ph₄).

3.1. Synthesis of DIPO-Ph₄

The synthesis of dipyranylidenes has been reported for the first time by Hünig in 1970.²⁰⁷ Dipyranylidenes possess three oxidation levels which are stable and can be isolated. At that time, the cationic forms brought more interest for the development of high conductivity

organic materials from charge transfer salt.^{208–212} Indeed, dipyranylidenes have a high polarizability due to the presence of heterocycles and low ionization potential.

Dipyranylidenes are generally synthesized by reductive coupling from pyrylium salt.^{213,214} Pyrylium salts have been widely investigated since a long time and used as a precursor in organic chemistry, leading to a large range of possibility for the synthesis reaction^{183–185} Other methods have been explored using chalcogenapyranones, however these methods present complex synthesis and low efficiency (Fig.3.3).^{186,187}

Figure.3.3: *Different synthetic pathways for the formation of dipyranylidene.*

In this chapter, we focus exclusively on 2,2',6,6'-tetraphenyldipyranylidene (DIPO-Ph₄). Anterior works showed that DIPO-Ph₄:TCNQ complex has high conductivity, superior to other dipyranylidene-based complexes.²⁰⁸ the donor character is fortified by the presence of four phenyl groups in the α position, leading to a higher number of delocalized π -electrons. Furthermore, the study of its sulfur analog, tetrathiadipyranylidene showed excellent donor properties with high hole mobilities.^{220,221}

Note that this chapter summarizes the synthesis of DIPO-Ph₄ but did not present an exhaustive overview of dipyranylidene synthesis. Other derivatives have been synthesized during my Ph.D but the details are not presented in this thesis. The aim of the thesis is to demonstrate the potential of dipyranylidenes as a functional semiconducting material for

organic electronics. Therefore, the synthesis method has been chosen in order to obtain DIPO-Ph₄ in a large scale with an efficient and simple way. DIPO-Ph₄ has been synthesized in a three-step reaction with an overall synthesis yield of 31.2% (Fig.3.4, appendix A.1).

Figure.3.4: Synthetic pathway of 2,2',6,6'-tetraphenyldipyranylidene (DIPO-Ph₄).

The first reaction step is an acylation of Friedel-Craft in order to functionalize the commercial glutaryl chloride precursor (**1**). This classic reaction allows the functionalization of aromatic moieties by electrophilic substitution in presence of strong Lewis acid (AlCl₃) (Fig.3.5). This reaction works well with aromatic compounds and the double functionalization of the compound (**1**) is effective with a good yield. However, this reaction is not suitable for deactivated arenes (e.g: when electrophilic groups are attached to aromatic ring).²²² Thus, the functionalization of compound **1** with halogenated arenes requires alternative approaches.^{221,223} The compound (**2**) cyclizes easily in acidic medium to form the desired pyrylium-tetrafluoroborate salt (**3**) (fig. 3.6). The latter compound forms the dimer by reductive coupling. The pyrylium salt reacts firstly with an organophosphorous such as triphenylphosphine or tributylphosphine, then the phosphonium salt is reduced in ylide in

the presence of a ternary amine (triethylamine, N,N-Diisopropylethylamine (DIPEA)), which condenses forming the desired compound (Fig.3.7).²¹⁴

Figure.3.5: Friedel-Craft acylation mechanism of glutaryl chloride.

Figure.3.6: Reactional mechanism of the formation of pyrylium salt with a Lewis acid.

Figure.3.7: Reactional mechanism of the formation of DIPO- Ph_4 from pyrylium salt by reductive coupling.

3.2. Physical properties of DIPO-Ph₄

3.2.1. Quinoidal character

DIPO-Ph₄ is a stable molecule with a high melting point of 330°C as determined by TGA (Fig.A3.a). DSC measurement shows only the peak of recrystallization at 323.2°C (Fig.A3.b). This relatively high melting temperature arises from the intrinsic quinoidal character of DIPO-Ph₄.

Polyaromatic semiconductors can have two resonance structures for the ground state within non-degenerate energy (Fig.3.8): the aromatic structure formed by the confined π -electrons within the heterocycle; the quinoidal structure originated from the delocalization of the flowing π -electrons, which convert a double to a single bond and vice-versa. In general, the aromatic conformation is energetically more stable, while the quinoidal conformation has a higher energy.^{224,225}

Figure.3.8: Aromatic and quinoidal resonance in poly(*p*-phenylene) (top) and polythiophene (bottom).

Commonly, as discussed in the previous chapter, the doping by external electric field or irradiation of π -conjugated organic semiconductors induce the formation of polarons. These

polarons reside on sizeable quinoidal structures which facilitate the charge delocalization within the material. In addition, the quinoidal conformation increases the planarity of the molecule. Planar molecules can stack easily by interaction of π -orbital, known as π - π stacking. The π - π -stacking is a noncovalent attractive force which promote a strong coupling between two conjugated molecules and thus favorize intermolecular charge transport process such as hopping.^{226–228} Finally, it has been demonstrated that in conjugated polymers composed of aromatic ring, the bandgap decrease in function of the quinoidal character of the material.^{229,230} Therefore, the quinoidal conformation represents an attractive character and has been widely as a strategy to obtain low bandgap material.^{231–235}

3.2.2. Solid state properties of DIPO-Ph₄

Organic semiconductors require a high purity in order to be used for electronic applications. Therefore, before employment in optoelectronics devices, DIPO-Ph₄ is purified by Soxhlet extraction, and a dark powder with shiny metallic reflections is obtained. This powder can crystallize easily in the form of one-dimensional needle when it is dissolved until saturation in a hot solvent such as acetonitrile (fig.3.9). These crystalline needles grow from microsizes to several millimeters.

Besides, DIPO-Ph₄ is a highly stable small molecule and can be easily evaporated using vacuum techniques. Physical vapor methods (PVT) is a well-known method to form large size crystal with high purity and lattice perfection. This method uses the sublimation property of the material. The source is placed in source tube inside a reactor, generally a quartz tube and are heated until sublimation. The sublimated molecules under the carrier

Figure.3.9: *Images of DIPO-Ph₄ single crystal obtained by solution methods from hot acetonitrile (70°C; concentration≈5 g/mL). The images have been recorded through optical microscope and scanning electron microscopy (SEM) respectively.*

gas transport move to a lower temperature zone in which the crystallization process will occur. The nucleation process is dependent on the nature of the gas, the gas flow and the temperature distribution.^{236–241} By using PVT method in two-zone fully transparent furnace, large DIPO-Ph₄ crystals, with size up to 1 cm long are obtained (Fig.3.10).

Figure.3.10: *Images of DIPO-Ph₄ single crystal obtained by vapor phase transport. The images have been recorded with a standard camera, microscope respectively.*

Polymorphism

Due to the weak interaction energies, organic molecules are prone to polymorphic formation in the solid state. The polymorphism is defined by the ability of a material to exist in more than one crystal structure. Polymorphism can result from the existence of different conformers, in that case we are talking about conformational polymorphism, while packing polymorphism result from the difference in the crystal packing. The polymorphisms within organic materials have been observed since a long time and the number of reported organic polymorphs to lend credence to the widely quoted statement by McCrone (1963) that ‘virtually all compounds are polymorphic and the number of polymorphs of a material depends on the amount of time and money spent in research on that compound’.^{242–245}

The polymorphism behavior highly affects the physical properties of a material, such as the color or the electronic properties.^{246–249} Indeed, charge transport properties are highly dependent on the crystal packing, so the study of polymorphism is a pertinent matter to examine the influence of the molecular conformation on the charge transport properties in organic semiconductors.

DIPO-Ph₄ single crystals conformations

X-ray diffraction (XRD) has been performed on both types of DIPO-Ph₄ crystal. The DIPO-Ph₄ single crystals present a clear packing polymorphism. DIPO-Ph₄ crystals grown by PVT adopt a triclinic phase (*α-phase*) whereas those grow from acetonitrile solution possess a monoclinic phase (*β-phase*). This latter structure is comparable the one reported by Chasseau et al. in 1982.²⁵⁰ The crystallographic parameters are summarized in the Table 3.1.

Table.3.1: Crystallographic parameters extracted from XRD of the two DIPO-Ph₄ polymorphs. Early parameters reported in 1982 by Chasseau et al. on DIPO-Ph₄ crystals grown from a CH₃CN solution are also shown for comparison.²⁵⁰

	α phase	β phase	From ref. 192
Crystal system	Triclinic	Monoclinic	Monoclinic
Group of symmetry	P-1	P1 21/n 1	P21/c,a
a (Å)	10.3715	6.0757	6.046
b (Å)	10.4260	16.4664	17.070
c (Å)	13.2917	11.9301	14.139
α	92.1911°	90°	90°
β	108.3364°	98.440°	123.44°
γ	108.6554°	90°	90°
V (Å ³)	1181.03	1180.63	1217.6
Z	2	2	2
F(000)	488	488	488
D (mg/cm ³)	1.306	1.307	1.266

Bond lengths and angles of both DIPO-Ph₄ crystals are summarized in Tables A1 and A2 as well as the computational DFT calculation using the B3YLP/6-311G* basis set and the early X-ray values obtained by Chasseau et al. on DIPO-Ph₄ grown from solution.²⁵⁰ The molecular geometry is comparable for both polymorphs. The two pyranilidene rings possess two localized double bonds (C7=C8) and (C10=C11) with a bond length of 1.35 Å while the C–C bonds have the characteristic of a single bond (d = 1.45 Å) (Table.A.1). The exocyclic fulvenic C=C double bond which connects the two pyranilidenes measure 1.39 Å and so presents an

intermediate character between single and double bond. This partial delocalization of electrons allows to interconnect electronically both the pyranilidenes. The strong character of the C=C double bonds provides a planar geometry of the dipyranylidene core. Note that for the α -phase polymorph, the dipyranylidene plan is slightly twisted of 3.5°.

The four phenyl groups attached to the dipyranylidene core are slightly elongated due to the presence of the O atoms. The torsion angle between the pyranilidene core and each phenyl is a significant disparity between this two polymorphs. In the α -phase, the phenyls have a higher degree of rotation and four different torsion angles (15.3°, 17.7°, 22.0°, and 23.3°). In contrast, the phenyls in the β -phase have a smaller torsion angle (8.9° and 11.6°), resulting in a quasi-planar molecular conformation. By opposition of the α -phase, the β -phase possesses a center symmetry located on the fulvenic C=C bond. Besides, the optimized geometry of an isolated DIPO-Ph₄ molecule as determined by density functional theory (DFT) (B3LYP/631G method) leads to a unique torsion angle (22.53°) which is larger than the two polymorphs. Thus, the crystallization process leads to a flattening of the molecules. The degree of rotation of the phenyl rings during the growth process, either in the gas phase or in solution, naturally affects the final crystal packing.

Indeed, on the one hand, the α phase forms a “brickwork” packing where molecules stand parallel to each other to form a stack of superimposed layers. This stacking can be considered of a repeating unit formed by three molecules of DIPO-Ph₄ with a lateral shift of 5.1 Å and an intermolecular distance of 3.3 Å (Fig.3.11). On this configuration, the π -orbital of the oxygen atom of one DIPO-Ph₄ molecule overlap the fulvenic bond of the adjacent molecule. On the other hand, the β phase crystallizes in a sandwich herringbone arrangement with an angle of

63.1°. In this conformation, the molecules are aligned face-to-face with an intermolecular distance of 3.4 Å. Similarly to α phase, DIPO-Ph₄ molecule has the same lateral shift of 5.1 Å.

The intermolecular distance for both polymorph is similar (3.3–3.4 Å) and is characteristic of a π – π stacking revealing a strong coupling between each molecule.^{251–253} Hunter and Sanders presented a large overview of aromatic interactions and provide a qualitative model for predicting the offset stacked or T-shaped geometries which are observed exclusively with most aromatic.²⁵⁴ In addition, they demonstrated the important role of solvent (polarity or solvation properties) on aromatic interactions. Thus, the origin of the β -phase polymorph can come from the acetonitrile properties which is a highly polar solvent.

Figure.3.11: Crystal structure of the α -phase DIPO-Ph₄ (triclinic configuration) showing the packing arrangement a) along the b axis (slightly tilted for the sake of clarity) and b) along the c axis. The DIPO-Ph₄ molecules are organized in intermolecular brickwork packing. The distances between molecules are measured considering oxygen atoms. The shading pictures the depth.

Figure.3.12: *Crystal structure of the β -phase DIPO-Ph₄ (monoclinic configuration) showing the packing arrangement a) along the c axis and b) along the a axis. DIPO-Ph₄ molecules are organized in a herringbone packing. The distances and angle between molecules are measured considering oxygen atoms.*

3.2.2. Electronic structure of DIPO-Ph₄

The UV-visible absorption spectrum of DIPO-Ph₄ as recorded in dichloromethane (Fig.3.13) shows a wide peak in the visible range (λ_{max} =456 nm) with a high molar extinction coefficient 9×10^4 l/mol.cm. An absorption tail of weak intensity is observed from 500 to 600 nm. Photoluminescence spectra in solution shows a sharp peak at 606 nm. The HOMO-LUMO band gap of DIPO-Ph₄ (E_g = 2.4 eV) is determined from the edge of the absorption spectrum.

Cyclic voltammetry (Fig.3.13. right) shows two reversible oxidation waves at respectively 0.24 V and 0.5 V, corresponding to the successive formation of the radical cation and dication. The HOMO energy level is estimated at -4.6 eV from the first oxidation peak at 0.24 V.²⁵⁵ In comparison, DIPO-Ph₄ has a slightly lower oxidation potential as compared to that of its sulfur analog (E_{ox} = 0.30 eV).

Figure.3.13: Left) Optical absorption (blue) and photoluminescence (red) spectra of DIPO-Ph₄ a) in solution in dichloromethane. Inserts: photographs of the respective DIPO-Ph₄ solution at low concentration ($C=10^{-4}$ mol.L⁻¹). Right) Cyclic voltammogram of DIPO-Ph₄ recorded in DMF (scan rate 200 mV/s).

The electronic density distribution of frontier orbitals of DIPO-Ph₄ is calculated by DFT using B3LYP/631G method (Fig.3.14). The electron density in the LUMO wave function is delocalized over the whole molecular backbone, whereas the HOMO electron density is mainly localized on the dipyranylidene core.

Figure.3.14: Electronic density distribution of the HOMO and LUMO levels of DIPO-Ph₄ calculated by DFT using the B3LYP/631G method.

The HOMO level calculated by DFT of DIPO-Ph₄ (−4.03 eV) is slightly higher than that the one obtained experimentally. The hole reorganization energy (λ_{hole}) extracted from DFT calculations by withdrawing one electron from DIPO-Ph₄ is 0.29 eV, while electron reorganization energy ($\lambda_{\text{electron}}$) is 0.31 eV. Note that a small hole reorganization energy implies a fast transfer rate, thus having important consequences on charge transport in the condensed phase. The electronic parameters of DIPO-Ph₄ are summarized in table 3.2.

Table.3.2: Summary of electronic properties of DIPO-Ph₄.

	λ_{onset}	$^a E_g$	$E_{\text{HOMO,exp}}$	$^c E_{\text{HOMO,Calc}}$	$^b E_{\text{LUMO,exp}}$	$^c E_{\text{LUMO,calc}}$	$\lambda_{\text{hole,calc}}$	$\lambda_{\text{electron,calc}}$
DIPO-Ph₄	637 nm	1.95 eV	−4.60 eV	−4.03 eV	−2.7 eV	−1.48 eV	0.29 eV	0.31 eV

^a Optical band gap E_g obtained from the onset of absorption (λ_{onset}). ^b LUMO calculated by $E_{\text{LUMO}}=E_{\text{HOMO}}+E_g$. ^c HOMO calculated from DFT using the B3LYP/631G method.

3.3. Conclusions

In this chapter, the synthesis and physical properties of DIPO-Ph₄ are presented. DIPO-Ph₄ is a small planar quinoidal molecule which can crystallize easily in one dimensional needle-like solid. X-ray diffraction performed on the two types of crystal shows a clear polymorphism behavior. Crystals grown from PVT methods (α -phase) adopt a triclinic phase while crystals grown from solution method (β -phase) present a monoclinic structure. The differences in their packing organization have been discussed in detail. A clear π – π stacking is observed for both polymorphs.

Chapter 4

Electrical properties of DIPO-Ph₄ measured by field-effect transistors

This chapter will focus firstly on the elaboration of DIPO-Ph₄ thin films. The different deposition methods which are employed and their implication on the morphology of DIPO-Ph₄ are discussed. The second part of this chapter examines the electrical characteristics of DIPO-Ph₄ thin films through field effect transistors measurements.

4.1. Formation of DIPO-Ph₄ thin films

4.1.1. Organic thin film processes

Organic molecules can be either deposited by solution or by vacuum deposition methods,²⁵⁴ both methods have their own advantages: On one hand, solution phase methods are attractive because of the ease of the process on a large surface area. The processing methods are really simple. A small quantity of an organic material (around 10-100 mg/mL) is simply dissolved into a solvent and a small volume (≈ 0.1 mL) of this solution is dropped on a substrate. The formation of a homogenous organic thin film is induced by the spreading of the solution using different techniques such as spin-coating, dip-coating or doctor-blading (Fig.4.1). The formation of the film is commonly followed by an annealing process in order to

remove any traces of solvents. However, these methods suffer from few disadvantages. Firstly, the material has to be soluble in order to be deposited. Large aromatic compounds and polymers are generally insoluble in common solvents unless side chain substitutions are incorporated into the molecular structures.^{225–227} However, the addition of side chains can interfere with the molecular packing, and thus decrease the charge carrier mobility. The P3HT is a well-known example for which hexyl side chains have been integrated to the polythiophene structure without detrimental effects on the molecular order.^{82,260,261} On top of that, the solvent can damage the morphology of the layer on which the solution is spin coated.

Figure.4.1: Schematic of the deposition processes (spin-coating, thermal evaporation, doctor blading) commonly used for the formation of organic films.

On the other hand, sublimation method allows to deposit small molecules onto various substrates under high vacuum (in the range of 10^{-7} mbar). The sublimation rate is monitored by quartz microbalance (Fig.4.1) which gives a sub-Ångstrom resolution. Thus, the formation of an organic thin film can be meticulously controlled with high resolution. Contrary to solution methods, here the thickness can be adjusted precisely from few nanometers up to few hundred nanometers. In general, organic films obtained by this method have a better quality with higher crystallinity degree, resulting of a better electronic performance. Pentacene,^{31,262} or oligothiophenes^{30,200,231}, such as sexithiophene^{265–267}, are molecules which are commonly deposited using evaporation method. Note that some molecules will decompose when they are heated and will not sublime. Nonetheless, the cost of the equipment, as well as the severe requirements of vacuum process, can be a limitation towards industrialization.

For the elaboration of DIPO-Ph₄ thin films, both methods have been considered. DIPO-Ph₄ is a highly stable small molecule and thus can be easily deposited by thermal evaporation. This method seems to be more appropriate for device fabrication. Nevertheless, solution methods can adduce various advantages, in particular, for the ease of the process during devices fabrication. While DIPO-Ph₄ thin films have been successfully obtained by thermal evaporation (Fig.4.2), the solution methods seem not adequate for the formation of DIPO-Ph₄ thin films. The DIPO-Ph₄ has a low solubility, even in strong polar solvents, and has the tendency to crystallize easily. We can observe on figure 4.2 that the uniform DIPO-Ph₄ film is in fact constituted of an amalgam of micro-sized DIPO-Ph₄ crystals. Therefore, thermal evaporation method has been selected for the fabrication of DIPO-Ph₄ films.

Figure.4.2: Optical images of left) a 50 nm DIPO-Ph₄ film deposited on silicon glass by vacuum evaporation and right) a non-homogenous DIPO-Ph₄ film prepared by spin-coating from a DMF solution (2 mg/mL).

4.1.2. Vacuum deposited DIPO-Ph₄ thin films

Morphological characteristics

The DIPO-Ph₄ thin film prepared by slow vacuum-deposition (0.1 Å/s) onto (100) silicon wafers are characterized morphologically by scanning electron microscope and atomic force microscopy (AFM). Note that the (100) Silicon wafers are treated beforehand by Hexamethyldisilazane (HMDS_ in order to improve the interface dielectric/organic. This surface treatment by organosilanes, such as octadecyltrichlorosilane (OTS) or HMDS, is a well-known method to enhance the organic film quality. Indeed, the SEM image deposited on HMDS modified silicon wafer reveals the better quality of the DIPO-Ph₄ film with no pinholes as compared to DIPO-Ph₄ films deposited directly on a silicon wafer. AFM reveals a highly homogenous surface made of monodisperse grains having an elongated needle shape (Fig.4.3). A distribution of the number of grains in function of their height shows an average

height around 50 nm, a root-mean-square (RMS) roughness of 11.2 nm. The highest grains can reach 80 nm. The XRD measured on vacuum-deposited DIPO-Ph₄ thin films presents a weak peak at 8.92° corresponding to the (001) plane (Fig.4.5, left). The d-spacing calculated from Bragg Law is 0.9 nm. The molecular length obtained from single crystal X-ray analysis is 1.19 nm (chapter 3.2) which suggest that the molecule has a tilt angle of 41° with the substrates.

Fig.4.3: SEM images of a 50 nm-DIPO-Ph₄ thin film vacuum-deposited on left) a SiO₂/Si wafer and right) an HMDS-treated SiO₂/Si wafer. The DIPO-Ph₄ thin film deposited on an HMDS-treated wafer (right image) possesses a uniform surface with no pinholes.

Annealing treatment

Annealing treatment is a common process used in device fabrication in order to improve the crystallinity and enhance the electrical properties of organic films.^{268,269,262}. The effect of the annealing has been investigated on various DIPO-Ph₄ thin films from room temperature to 200°C (Fig.4.5). For higher temperature, the DIPO-Ph₄ film starts to decompose and becomes inhomogeneous. From AFM images, we observed that the annealing promotes the

formation of elongated needle-like grains which are vertically aligned. The heights of this grains are temperature-dependent. Therefore, the annealing increases the roughness of the DIPO-Ph₄ film. As DIPO-Ph₄ crystallizes in one-dimensional needle-like structure, we can infer that these elongated grains are composed of crystallized DIPO-Ph₄ molecules.

Figure.4.4: a) 3D lateral view of an AFM image ($5 \times 5 \mu\text{m}^2$) recorded in tapping-mode of a 50 nm-DIPO-Ph₄ thin film vacuum-deposited on a Si/SiO₂/HMDS wafer. b) Median height grain distribution and c) grain surface area distribution, extracted from a typical AFM image. d) XRD of DIPO-Ph₄ deposited on HMDS-treated SiO₂/Si wafers.

Figure.4.5: *Topological AFM images (top) and 3D lateral view of the corresponding AFM image (bottom) ($10 \times 10 \mu\text{m}^2$) recorded in tapping-mode of a 50 nm-vacuum-deposited DIPO-Ph₄ thin film after annealing at different temperatures: non-annealed (left), 150°C (middle) and 200°C (right) under N₂.*

Optical properties

UV-visible measurement (Fig.4.6, left) on vacuum-deposited DIPO-Ph₄ thin films shows a much broader absorption over almost the entire visible range, with an absorption edge at 640 nm assignable to more intense absorption bands. The band gap of DIPO-Ph₄ film, calculated from the absorption edge is 1.94 eV. The HOMO level of DIPO-Ph₄ films is located at -4.74 eV as determined by ultraviolet photoelectron spectroscopy (UPS, Fig.4.7). The HOMO levels obtained for DIPO-Ph₄ is 0.14 eV lower than the one obtained from solution. The photoluminescence of DIPO-Ph₄ thin film presents two peaks at the 636 nm and 686 nm which are bathochromically shifted as compared to measurement in solution.

Figure.4.6: Optical absorption (left) and photoluminescence (right) spectra of a 50 nm-thin film vacuum-deposited on quartz. Dotted curves show the optical properties of DIPO-Ph₄ in solution.

Figure.4.7: Ultraviolet photon spectroscopy (UPS) spectra of a 50 nm-DIPO-Ph₄ thin film vacuum-deposited on FTO. The onset of the curve is used to determine the Fermi level and the HOMO level of DIPO-Ph₄ (E_F =Energy of Fermi level, WF=work function, VBM=valence band maximum).

4.2. DIPO-Ph₄-based field effect transistors

4.2.1. Field effect transistors

Field effect transistors (FET) is the major constituent of modern electronic devices.²⁷⁰ The fundamental function of a transistor is the modulation of the current flow between two ohmic contacts, by applying a bias to a third electrode. Furthermore, FET provides an important insight into transport properties in a material. Indeed, it is a common method to determine the charge carrier mobility of a semiconducting film. Single crystal rubrene possesses one of the highest hole mobilities reported at room temperature in an organic material (around $20\text{-}40\text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$),¹⁹⁰ while some polymers shows almost similar value, even non-certified value reaching $100\text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ with on/off ratio in the range of $10^5\text{-}10^7$.²⁷¹⁻²⁷³ A large number of organic materials present hole mobilities superior to $1\text{ cm}^2/\text{V}\cdot\text{s}$. Amorphous silicon has hole mobility around $1\text{ cm}^2/\text{V}\cdot\text{s}$, therefore in term of electronics applications, an organic material can be considered as good hole transporter if the mobility is superior to the units. In the following part, the working principle of organic field effect transistor will be presented. Then DIPO-Ph₄ has been integrated into a field effect transistor in order to determine its charge transport properties.

Working principle

Organic field effect transistors are composed of three electrodes (source, drain and gate), an organic semiconductor and an insulating dielectric layer. The dielectric layer is generally composed of SiO₂ (or PMMA in case of fully flexible transistors). The transistor is then called

MISFET or MOSFET when the dielectric is an oxide (stand for metal-insulator-semiconductor or metal-oxide-semiconductor). The dielectric layer is directly in contact with the gate electrode and the semiconductor, while the source and drain electrodes are in ohmic contact with the organic semiconductor. The area between these two electrodes forms a channel with a width W (channel width) and distance L (channel Length) which are the parameters of the FET. Organic FET has different configurations depending on the location of the electrodes (Fig.4.8). The configuration is chosen by ease/constraints of processing and

Figure.4.8: *Different configurations of organic field effect transistor: a) bottom gate/bottom contact; b) bottom gate/top contact; c) top gate/bottom contact; d) top gate/top contact.*

most of the OFET devices are in bottom gate/bottom electrode or bottom gate/top electrode configuration.^{274,270,275} Typically, the source electrode acts as a charge injecting electrode and is always grounded ($V_s=0$ V), while the voltage biases of V_g and V_d are applied to the gate and drain electrodes, respectively. Similar to the working principle of a capacitor, negative (electrons) or positives (holes) charges will be injected from the grounded electrode and accumulated at the semiconductor/insulator interface when a positive or negative voltage is applied to the gate. Part of the induced charges at the interface have to fully occupy deep

traps and any additional induced charges are mobile and contribute to the current. Hence, the mobile charges at the interface are proportional to the capacitance per unit area C_i and the effective gate voltage ($V_{gs} - V_{th}$), where threshold voltage V_{th} is defined to account for filling of charges in those traps.

Without source-drain bias, charge carriers will be evenly distributed along the transistor channel. With small source-drain voltage ($V_{ds} \ll V_g$) bias, a linear charge density gradient will be formed from source to drain, as shown in Fig.4.9 (1). So, the current is directly proportional to drain-source bias V_{ds} . Local potential (ϕ) also decreases linearly from the drain electrode to V_{ds} at the source. This regime is known as linear regime and the transfer characteristics I_d - V_G can be expressed by:

$$I_{ds} = \frac{W}{L} [(V_g - V_{th})V_{ds} - \frac{1}{2}V_{ds}^2] \quad (\text{eq.4.1})$$

where W and L are the channel width and length, respectively. C_i is the unit area capacitance of the gate dielectric, μ is the effective mobility.

The channel is “pinched off” when the applied source-drain bias reached $V_{ds} = V_g - V_{th}$ and a depletion region is formed next to the drain, as shown in Fig.4.9 (2). This is due to the difference between the local potential (ϕ) next to the drain and the gate voltage is now below the threshold voltage. In this regime, the relatively high electric field in the depletion region will only drive the space-charge-limited saturation current I_{ds} , to flow across the narrow depletion region. No substantial increase in the current level with subsequent increase in applied source-drain bias in this regime. Instead, the channel will be shortened due to the expansion of depletion region. Therefore, the drain-source current saturates at a level I_{ds} ,

Figure.4.9: Working principle of organic FET. 1) Linear operating regime. 2) Beginning of the saturation regime. A depletion region appears next to the drain electrode the channel is pinched-off. 3) Saturating operating regime. The depletion regime expands towards the source electrode which slightly shortens the channel.

since the potential at the pinch-off point remains $V_g - V_{th}$, while the potential drop between that point and the source electrode stays around the same potential (Fig.4.10 (3)). In this saturation regime, the transfer characteristics I_d - V_G is expressed by:

$$I_{ds,sat} = \frac{W}{2L} \mu_{sat} C_i (V_g - V_{th})^2 \quad (\text{eq.4.3})$$

4.2.2. Electrical properties of DIPO-Ph₄ field effect transistors

For DIPO-Ph₄ thin film

The transport properties of DIPO-Ph₄ film are investigated in a field-effect transistor configuration. The output and transfer characteristics performed on bottom-gate/bottom-contact OFET devices show a typical p-type behavior (Fig. 4.10). The maximum carrier mobility calculated is $2 \times 10^{-2} \text{ cm}^2/\text{V.s}$ with an on/off current ratio of 6×10^4 . The OFET characteristics in function of the annealing temperature are summarized in Table 4.1. After annealing at 200°C, an increase of almost one order of magnitude is observed for the mobility and on/off ratio. Moreover, the threshold voltage is shifted from 7.5 V towards -7.5 V and the subthreshold voltage is reduced to -4.6 V/decade which indicates a higher degree of crystallinity of the organic film, as it was assumed from the AFM study.

Fig.4.10: Left) Output I_d/V_d curves of the corresponding 200°C annealed DIPO-Ph₄-based OFET. Right) Transfer curves (red) with their respective $(I_d)^{0.5}$ (blue) of the DIPO-Ph₄ based OFET layer for different annealing temperatures, 200°C (straight line), 150°C (dots line) and non- annealed (dash line).

Table.4.1: Summary DIPO-Ph₄ based OFET characteristics.

Annealing temperature (°C)	Mobility (cm ² /V.s)	On/off ratio	Subthreshold voltage (V/decade)	Threshold voltage (V)
No annealing	6.2×10 ⁻³	2.8×10 ³	-16.2	7.5
150	9.1×10 ⁻³	1×10 ⁴	-9.1	-0.5
200	0.02	6.2×10 ⁴	-4.6	-7.5

For DIPO-Ph₄ single crystal

Single crystals are seen as a model system for charge transport as they are free of grain boundaries. Thus, it is interesting to investigate the charge transport properties for both polymorphs of DIPO-Ph₄ in a FET configuration. The OFETs were prepared in a bottom gate/top contact configuration with a channel length of 20 μm. The channel width is determined by the width of the DIPO-Ph₄ crystal (e.g: Fig.4.11, W=6.5 μm).

Figure.4.11: SEM images of DIPO-Ph₄ single-crystal FET. The DIPO-Ph₄ single crystal and gold electrodes deposited on top of the crystal through deposition mask are highlighted in red and yellow respectively. The length of the channel is 20 μm and the width of the single crystal is used as the channel width.

The output and transfer characteristics of both α -phase and β -phase polymorphs are presented in the Fig.4.12. For the α -phase, the maximum carrier mobility calculated is $0.3 \text{ cm}^2/\text{V.s}$ with an on/off current ratio of 85, while for the β -phase, the maximum carrier mobility calculated is $0.64 \text{ cm}^2/\text{V.s}$ with an on/off current ratio of 35. The β -phase DIPO-Ph₄ polymorph present therefore a hole mobility twice as high as the α -phase DIPO-Ph₄ polymorph.

Figure.4.12: Left) Output I_d/V_d and right) transfer I_d/V_g curves with their respective $(I_d)^{0.5}$ (blue) of the α -phase (top) and the β -phase (bottom) DIPO-Ph₄-based single crystal FET.

4.3. Theoretical modelling of hole transport of DIPO-Ph₄ polymorphs

The experimentally measured hole mobility in polymorphs of DIPO-Ph₄ exhibit very interesting structure-property relationship which is induced by slight molecular structure changes and relevant changes of molecular packing. Therefore we carried out density functional theory (DFT) based calculations in conjunction with a 1D polaron transport model (Fig.4.13, detailed in annexe.A.4). The calculated values of hole transfer integrals, as well as the hole-phonon coupling strength are given in Table.4.2. The data listed in Table 4.2 suggested that the higher hole mobility in DIPO-Ph₄ crystal can be explained by a larger hole transfer integral (maximum t_h in β -phase is almost five times higher than the one in α -phase) and lower hole-phonon coupling strength. It is found that

Figure.4.13: Dimer schemes of DIPO-Ph₄ polymorphs for DFT calculations of hole transfer integrals.

Figure.4.14: Vibrational frequency dependent Huang-Rhys factors and polaron binding energies for holes in optimized molecular structures of DIPO-Ph₄ polymorphs. Vector plots of normal modes with $S > 0.2$ for both cases are also plotted.

Table.4.2: Calculated hole transfer integral t_h of various dimers, polaron binding energy E_{pol} , Huang-Rhys factor S , and hole mobility of DIPO-Ph₄ polymorphs. Experimentally measured maximum mobilities are listed for comparisons.

Polymorph	Dimer Name	t_h (meV)	E_{pol} (meV)	S	μ^{Theory} (cm ² V ⁻¹ s ⁻¹)	$\mu^{Max}_{experiment}$ (cm ² V ⁻¹ s ⁻¹)
α -phase (triclinic)	D1/D4	18.7	162.1	4.35	0.01 ^a -0.15	0.3
	D2/D5	0.04				
	D3/D6	8×10^{-5}				
	D7/D8	4				
β -phase (monoclinic)	D1/D4	91.6	150.8	1.33	0.31-0.46	0.64
	D2/D5	9.8				
	D3/D6	6.3				

^a: 0.01 is the value of hole mobility for the transport channel along D7/D8 directions.

Figure.4.15: Hole transport anisotropy in β -phase (ab -plane) and α -phase (ab -plane) of DIPO-Ph₄ polymorphs. The respective definition of angles is listed in the supporting information.

strong hole-phonon coupling in α -phase may originate from a few low-frequency normal modes with large asymmetric out of plane vibration around the quinoidal core as shown in Fig.4.14. These modes are not shown to be coupled with the holes in the β -phase. Strong hole-phonon coupling is also observed for high-frequency modes around 1725 cm^{-1} , which corresponds to in-plane stretching of the pyranilidenes atoms. In both cases, these modes have a similar coupling strength, indicating that the quinoidal core is not involved in the conformation difference between the α - and β -phase polymorphs. Thus, this difference is mainly coming from the phenyl dihedral angles, which diminished the hole-phonon coupling in the quinoidal core.

Hole transfer integrals of dimers in both DIPO-Ph₄ structures exhibit strong anisotropy characteristics, thus we further calculated the hole transport anisotropy based on the equations listed in the annexes A. The calculated hole transport anisotropy can be found in Fig.4.15. It is clear that that the maximum hole mobility for α -phase is along its closest-packing direction. It is also interesting to note that maximum hole mobility for β -phase is not along the closest-packing direction, instead, the maximum hole mobility transport channel exhibit an angle of about 100° from the closest-packing direction.

Another interesting point on the transport properties of DIPO-Ph₄ polymorphs is that the β -phase with higher hole mobility exhibit band-like dominant behavior while the α -phase with lower hole mobility exhibit hopping dominant behavior as revealed by the individual components of the calculated mobility as suggested in Table.S1. It is shown in Table.S1 that band-like and hopping mobility for the β -phase is 0.20 v.s. $0.06\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, while for the α -phase, the value is $2.8 \times 10^{-7}\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ v.s. $0.147\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.

These interesting behaviors can be understood from the values of Huang-Rhys factors, which shows intermediate and strong hole-phonon coupling in the α -phase and β -phase, respectively. Strong hole-phonon coupling will usually lead to the formation of small polarons localized on each DIPO-Ph₄ molecule in α -phase crystal, therefore hopping becomes the major mechanism for the small hole-polaron to move around. However in the case of β -phase, relatively strong hole coupling in D1/D4 dimers as well as intermediate hole-phonon coupling is helpful for the spreading of holes across a few neighboring DIPO-Ph₄ molecules along the D1/D4 direction, thus leading to band-like transport behavior.

4.4. Conclusions

In this chapter, we focus on the electrical properties of DIPO-Ph₄ thin films. We show that vacuum deposited DIPO-Ph₄ thin films present a good p-type behavior. FET measurements reveal in maximum hole mobility of 0.64 cm²/V.s measured in the β -phase polymorphs. Finally, we determined by DFT calculations the conduction mechanism of DIPO-Ph₄ in solid state. α -phase polymorph presents a hopping dominant behavior, while β -phase polymorph presents a band-like behavior.

Chapter 5

DIPO-Ph₄ as a hole transport material

The good hole transport property of DIPO-Ph₄ has been demonstrated in the previous chapter. Additionally, the HOMO level of DIPO-Ph₄ thin film has been determined as -4.74 eV. In organic solar cells, the majority of the *p*-type materials has a HOMO level below -5 eV. Thus, DIPO-Ph₄ thin films have suitable characteristics to act as an efficient hole-transporting material in organic solar cells.

In this chapter, we will present the performances of the DIPO-Ph₄ thin film as a hole transport layer in emerging photovoltaic devices. This vacuum-deposited organic thin film has been integrated into two different types of devices: full organic solar cells and hybrid organic-inorganic perovskite solar cells.

5.1. Organic solar cells

In the previous chapter, it has been demonstrated that DIPO-Ph₄ thin films act an excellent *p*-type semiconductor in a FET configuration with a maximum hole mobility of $0.02 \text{ cm}^2/\text{V.s}$. In this configuration, the device is in a coplanar geometry which allows the determination of the electrical transport parallel to the substrate. When DIPO-Ph₄ is used as an HTM in a photovoltaic device, the holes are transported vertically to the substrate, therefore it is

crucial to determine the vertical mobility of DIPO-Ph₄. When DIPO-Ph₄ is sandwiched between two electrodes, the vertical charge carrier mobility can be easily extracted from current-voltage (J-V) characteristics in the dark by space-charge-limited-current (SCLC) technique using the Mott-Gurney equation^{276,277}

$$J = \frac{9}{8} \epsilon \epsilon_0 \mu \frac{V^2}{L^3} \quad (\text{eq.5.1})$$

where J is the current density, V is the voltage and L is the thickness of hole transporting material. The ϵ is the dielectric constant of the material, which for organic semiconductors usually equals to 3 and ϵ_0 is electric constant. To obtain an accurate value of the SCLC mobility, the J-V characteristics should be in the SCLC regime in which the scaling exponent is equal to 2 (Fig.5.2.b). Using a {FTO/PEDOT:PSS/DIPO-Ph₄/Ag} configuration, a hole mobility of about $2.49 \times 10^{-4} \text{ cm}^2/\text{V.s}$ were determined, which are two orders of magnitude lower than the mobility calculated in FET configuration. This large difference could originate from the anisotropic structural properties of DIPO-Ph₄. However several parameters can also affect the SCLC measurement, such as the device structure or the thickness of the organic layer. It should be noted that SCLC measurements are more accurate for a thick layer for which the contribution of the interfacial layers are weaker and the bulk properties predominant.^{278–280} The presence of traps is also a factor detrimental for high SCLC mobility.

As shown by AFM (Fig.5.2), DIPO-Ph₄ thin film has a relatively high root-mean-square (RMS) roughness (13 nm) which is much higher than PEDOT:PSS film.^{241,242} This particular nanomorphology of DIPO-Ph₄ can considerably increase the contact area between the active material and the anode, thus greatly enhancing hole extraction.

Figure.5.1: *J-V curves of the {FTO/PEDOT:PSS/120 nm thick DIPO-Ph₄/Ag} devices for space charge limited current (SCLC) measurements.*

Figure.5.2: *Tapping-mode AFM images of a) a 10 nm thin DIPO-Ph₄ film vacuum-deposited on ITO and b) an ultrathin film of PEDOT:PSS deposited on top of DIPO-Ph₄.*

Current-sensing atomic force microscopy (CS-AFM) images of DIPO-Ph₄ films are recorded in contact mode using either positive or negative tip voltages (Fig.5.3, left and middle). For a -0.3 V tip voltage the CS-AFM images exhibit high and homogeneous hole conduction with current intensities up to 10 nA. The hole conduction has preferential pathways through the

grain boundaries. In comparison, CS-AFM images recorded on PEDOT:PSS films reveal insulating region and the holes are only diffused in some localized pathways which correspond to individual PEDOT domain (Fig.5.3, right). Current mapping recorded at +0.3 V shows a much weaker conduction of electrons as compared to holes.

However, in order to protect the nanostructure from partial dissolution by the organic solvent during spin-coating deposition of the P3HT:PCBM active layer, a 5 nm thin layer of PEDOT:PSS is spin-coated (from an aqueous solution) on top of the DIPO-Ph₄ films. AFM images (Fig.5.1, right) confirm that the DIPO-Ph₄ morphology is preserved (RMS=11.3 nm). A practical advantage of PEDOT:PSS film is its robustness towards organic solvents during the fabrication process, making it compatible with most of the organic photoactive materials.

We inserted a 10 nm vacuum-deposited DIPO-Ph₄ film as an anodic HTL in combination with a PEDOT:PSS layer (5 nm) into P3HT:PCBM-based OSC devices (Fig.5.4)

Figure.5.4: *left) Scheme of a solar cell using a double HTL: DIPO-Ph₄ (10 nm, red needles) and PEDOT:PSS (5 nm, dark grey coating). Right) Band diagram of a solar cell using a DIPO-Ph₄ (10 nm)/PEDOT:PSS (5 nm) double HTL.*

and compared the PV performance with those of reference cells using a PEDOT:PSS-only HTL. All devices have an open circuit voltage (V_{oc}) of ≈ 0.6 V in agreement with usual values reported for P3HT:PCBM-based devices. The short-circuit current density of the reference cells is $J_{sc}=7.6$ mA.cm⁻², resulting in a power conversion efficiency (PCE) of 2.8% (Fig. 5.5, left, blue curve). With a 10 nm thin layer of DIPO-Ph₄, the organic solar cell exhibit higher current density. Typical devices exhibit an average current density of $J_{sc}=9.5$ mA.cm⁻² and an average PCE of 3.8% (Fig.5.5, left, red curve). These characteristics correspond to a PCE increase of 35% as compare to the reference cell using a PEDOT:PSS-only HTL.

Figure.5.5: *left) J-V curves measured in the dark and under white light illumination (AM 1.5G; 70 mW/cm²) of {P3HT:PCBM} based solar cells using DIPO-Ph₄ (10 nm; red and cyan lines)/PEDOT:PSS (5 nm) or DIPO-Ph₄ (15 nm; green line) /PEDOT:PSS (5 nm) as a double hole injecting HTL. A typical reference cell using a PEDOT:PSS-only HTL is shown for comparison (blue line). Right) EQE spectrum (red) of a PV cell using a DIPO-Ph₄ (10 nm)/PEDOT:PSS (5 nm) double HTL. The dashed blue line represents the integrated current density corresponding to the red J-V curve. The PV characteristics of our devices are summarized in Table.5.1.*

Table.5.1: Photovoltaic characteristics of P3HT:PCBM-based solar cells using a DIPO-Ph₄/PEDOT:PSS double HTL.

HTL		Voc (V)	Jsc (mA/cm ²)	FF	R _s (Ω/cm ²)	R _{sh} (Ω/cm ²)	PCE (%)
PEDOT:PSS	Average values*	0.60	7.6	0.44	16.2	222.7	2.8±0.3
DIPO-Ph ₄ (10nm)/ PEDOT:PSS (5nm)	Average values*	0.58	9.5	0.50	10.0	214.6	3.8±0.8
	Maximum values	0.60	11.5	0.47	9.3	162.6	4.6
DIPO-Ph ₄ (15nm)/ PEDOT:PSS	Average values*	0.55	8.1	0.40	19.5	156.9	2.5±0.5

*The average values have been determined from more than 20 devices.

In the course of our experiments several double-HTL devices exhibit higher current densities up to Jsc=11.5 mA.cm⁻² with a PCE of 4.6% (Fig.5.5, left, light blue curve) corresponding to a 64% increase as compared to OSCs using a PEDOT:PSS-only HTL. We assign the enhanced Jsc to the high hole conduction of the DIPO-Ph₄ films, as revealed by CS-AFM (Fig.5.3). However, these higher characteristics are sample-dependent due to the difficulty in controlling rigorously the nanomorphology of the DIPO-Ph₄ films, in particular the precise height, shape and density of the crystalline needles. These parameters are extremely sensitive to slight variations in the deposition rate, quality of the substrate and purity of the starting materials. Indeed, devices using higher DIPO-Ph₄ thicknesses (15 nm) show lower Voc (Fig.5.5, left, green curve) and thus a decrease in efficiency (PCE=2.5%).

5.2. Perovskite solar cells

Perovskite solar cell (PSC) devices were fabricated in a typical configuration (FTO/TiO₂/CH₃NH₃PbI₃/HTM/Au) using mesoporous TiO₂ (mp-TiO₂) (Fig.5.6). The cross-sectional SEM image of the device shows well-defined layers and clear interfaces. CH₃NH₃PbI₃ was prepared by performing a single-step method using a solvent treatment, forming shiny dark-brown films. Top-view SEM images reveal homogenous films (Fig.5.7, left). A chlorobenzene treatment allows the formation of large grains up to 500 nm in size. The X-ray diffraction pattern (Figure.5.7, middle) reveals a polycrystalline structure with a strong orientation in the (110) plane. The UV/Vis spectrum shows a broad absorption on the visible range up to 800 nm, which is in good agreement with the literature (Fig.5.7, right).¹⁰⁴ The DIPO-Ph₄ thin films were deposited by thermal evaporation on top of the perovskite layer

Figure.5.6: Left) Optical image of a perovskite solar cell prepared in our laboratory. Middle) Cross-sectional SEM image of a typical device. The thicknesses of TiO₂ and perovskite are 250 nm and 400 nm respectively. Right) Band diagram of a perovskite solar cell using DIPO-Ph₄ as a dopant-free HTM.

Figure.5.7: Left) top view SEM images of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite film. Middle) XRD spectra of the same $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite film. Right) Absorption spectrum of our $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films deposited on mesoporous TiO_2 .

The J - V characteristics of PSCs using either pristine DIPO- Ph_4 with various film thicknesses (30, 40, 50, 80 nm) or doped and undoped spiro-OMeTAD as HTMs were recorded under white-light illumination (AM1.5G, 100 mW cm^{-2} ; Fig.5.8).

Figure.5.8: Left) J - V characteristics and right) IPCE spectra of perovskite solar cells fabricated using 40 nm thick DIPO- Ph_4 , doped-spiro-OMeTAD, undoped-spiro-OMeTAD and without HTM, under illumination (AM 1.5G, 100 mW cm^{-2} , active area = 0.2 cm^2).

Performances of all devices are summarized in Table.5.2. PSCs without any HTM show poor characteristics with a PCE of only 4.5%. PSCs that integrate a dopant-free DIPO-Ph₄ thin film show higher performance. The optimized thickness of DIPO-Ph₄ film is 40 nm. For this configuration, the highest PCEs are as high as 10.1% with J_{sc} =19.52 mA.cm⁻², V_{oc} =0.93 V, and

Table.5.2: Summary of device parameters V_{oc} , J_{sc} , FF and PCE of PSCs using either dopant-free DIPO-Ph₄, doped spiro-OMeTAD, dopant-free spiro-OMeTAD or without HTM. Measurements are performed under white light illumination (AM1.5G, 100 mW/cm²). For the sake of comparison, all reported values have been obtained in our laboratory. The standard deviation of PCEs is based on the experimental results obtained on six devices for each type of PSC.

HTM	Thickness (nm)	Area (mm ²)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	R_s (Ω /cm ²)	R_{sh} (Ω /cm ²)	PCE
HTM free	–	20	0.80	10.27	54.61	19.2	986.2	4.5 ± 0.5
Dopant-free spiro-OMeTAD	100	20	0.94	15.38	35.58	41.3	116.5	5.1 ± 0.3
DIPO-Ph ₄	30	20	0.80	15.95	40.50	21.1	90.95	5.18 ± 0.4
	40	20	0.92	18.11	50.70	18.6	917.4	8.5 ± 0.3
	40	7	0.93	19.52	55.42	15.6	370.3	10.1 ± 0.4
	50	20	0.93	18.49	44.72	23.3	196.6	7.7 ± 0.9
	80	20	0.85	17.68	45.76	19.3	207.7	6.9 ± 0.6
Doped spiro-OMeTAD	100	20	1.00	18.95	58.06	17.6	703.72	11.0 ± 0.8

a fill factor FF=55.4%. For thinner DIPO-Ph₄ films (30 nm), the J_{sc} , V_{oc} and FF values are slightly reduced to 15.95 mA^{cm}⁻², 0.80 V, and 40.5 %, respectively. This suggests that for low DIPO-Ph₄ thicknesses, that is, below 30 nm, the films are inhomogeneous and the interface with the perovskite layer is of lower quality. For DIPO-Ph₄ films thicker than 40 nm (i.e., 80 nm), we also observe a lower V_{oc} (0.85 V) due to a higher recombination rate in DIPO-Ph₄. In comparison, devices using dopant-free and doped spiro-OMeTAD as the HTM show a PCE of 5.1 % and 11.0 %, with a J_{sc} of 15.38 and 18.95 mA^{cm}⁻², respectively. Thus, PSCs using DIPO-Ph₄ present J_{sc} values that are higher than those with dopant-free spiro-OMeTAD.

The origin of the improved J_{sc} of DIPO-Ph₄-based PSCs lies in its higher HOMO level (−4.74 eV) compared to that of spiro-OMeTAD (−5.44 eV) in combination with a hole mobility that is higher by two to three orders of magnitude. The higher HOMO level allows a stronger driving force for charge transfer from the perovskite to the HTM. However, PSCs using DIPO-Ph₄ show a slightly lower V_{oc} =0.93 V than those with doped spiro-OMeTAD (V_{oc} =1.00 V). As V_{oc} depends on multiple factors such as the splitting of the Fermi levels for photogenerated charges, the recombination rate, and the energetics of the device, the slightly lower V_{oc} might be due to the higher HOMO level.¹⁷⁹ The lower FF compared to doped spiro-OMeTAD can be attributed to the high series resistance of the DIPO-Ph₄ films.

Incident photon-to-electron conversion efficiency (IPCE) spectra (Figure.5.8) are in agreement with the J -- V curves, revealing similar trends. The integrated J_{sc} well match with J_{sc} measured under white-light illumination and fits entirely the absorption spectra of the perovskite. The similar shapes of the IPCEs for all samples suggest that light absorption by the

HTM has a negligible effect on the performance. However, as DIPO-Ph₄ thin films strongly absorb over most of the visible range up to approximately 650 nm, the contribution of DIPO-Ph₄ in the overall photocurrent needs to be considered. Therefore, we fabricated TiO₂/DIPO-Ph₄ bulk heterojunctions (i.e., free of perovskite), in which the DIPO-Ph₄ thin film is expected to function both as the light-harvesting material and the HTM. The recorded photocurrent is as low as $J_{sc}=0.09 \text{ mA}\cdot\text{cm}^{-2}$, showing that only UV light contributes to J_{sc} (Figure.5.9), which excludes any contribution from DIPO-Ph₄ light absorption in the J_{sc} of PSCs.

Figure.5.9: Left) *J-V characteristics of TiO₂/ DIPO-Ph₄ solar cells under illumination (AM1.5G, 100 mW cm⁻², active area=20 mm²). Right) IPCE spectrum of TiO₂/DIPO-Ph₄ bulk heterojunction solar cell.*

Stability is crucial for the development of PSCs, moisture being one of the major causes for their degradation. Spiro-OMeTAD needs to be doped with materials that are hygroscopic and therefore induce device degradation. As shown in Fig.5.10, the devices fabricated using DIPO-Ph₄ exhibit a much slower degradation compared to spiro-OMeTAD-based devices. The devices were kept at a relative humidity of roughly 30% and were tested for 600 h. The DIPO-Ph₄-based PSCs show only an approximately 20 % decrease in PCE compared to an

approximately 60 % degradation with spiro-OMeTAD. This enhanced stability in DIPO-Ph₄ devices can unambiguously be attributed to the absence of deliquescent additives or dopants. These encouraging results suggest that dipyranylidene can be used as a core for dopant-free HTMs for stable PSCs.

Figure.5.10: *Stability of perovskite solar cells using doped spiro-OMeTAD and DIPO-Ph₄ as HTM. The cells are stored at room temperature with a relative humidity of $\approx 30\%$. Measurements are performed under continuous white light illumination (AM 1.5 G, 100 mW.cm^{-2}) over 600 hours.*

Chapter 6

Conclusions and perspectives

In this thesis, we focused on the understanding and optimization of charge extraction in photovoltaic solar cells. This study concentrates on the dipyranylidene family, in particularly on 2,2',6,6'-tetraphenyldipyranylidene (DIPO-Ph₄). This family of compounds possesses a quinoidal core, analog to tetrathiafulvalene (TTF), and show a strong donor character. The first part of this thesis introduced the state of art of organic semiconductors and pointed out the crucial role of the hole transporting layer in photovoltaic devices.

The second part of the thesis presented the synthesis methods and described the physical properties of DIPO-Ph₄. The synthesis consists in a straightforward three-step pathway starting from inexpensive compounds, leading to an efficient and large-scale production. DIPO-Ph₄ molecules presents a good absorption in the visible range with a high molar absorption coefficient. Moreover, the small planar quinoidal structure allows to crystallize easily in one-dimensional needle. These needle-like crystals can have different crystalline structures depending on the fabrication methods (physical vapor transport (PVT) or solution). Indeed, X-ray diffraction performed on the two types of crystal shows a clear polymorphism behavior. Crystals grown from PVT methods (α -phase) adopt a triclinic phase while crystals grown from solution method (β -phase) present a monoclinic structure. For both polymorphs, a clear π - π stacking are observed, which allows good electrical properties of DIPO-Ph₄ in the solid state.

The third part of the thesis focused on the electrical properties of DIPO-Ph₄. We showed that vacuum-deposited DIPO-Ph₄ thin film measured in a field effect transistors configuration presents good *p*-type semiconducting properties. The hole mobility calculated is $2 \times 10^{-2} \text{ cm}^2/\text{V.s}$ with an on/off current ratio of 6×10^4 . The effect of the annealing treatment has been investigated. The annealed samples show an increase of almost one order of magnitude of the hole mobility and a higher on/off ratio. Furthermore, the maximum hole mobility of $0.64 \text{ cm}^2/\text{V.s}$ has been measured in the β -phase DIPO-Ph₄ single crystal, while the α -phase polymorph presents a slightly lower mobility of $0.3 \text{ cm}^2/\text{V.s}$. The conduction mechanism of DIPO-Ph₄ in solid-state has been analyzed by DFT. The calculation results show that the α -phase polymorph presents a hopping dominant behavior, while β -phase polymorph presents a band-like behavior which explained the higher mobility of the β -phase. Finally, XRD of DIPO-Ph₄ thin film reveals that DIPO-Ph₄ molecules tend to organize in herringbone conformation like in the β -phase polymorphs, and thus the conduction mechanism inside DIPO-Ph₄ thin film follows a band-like behavior.

The good hole transport property of DIPO-Ph₄, in addition with a proper HOMO level (-4.74 eV), makes DIPO-Ph₄ a potential candidate as an efficient hole-transporting material in a photovoltaic solar cell. Therefore, the performance of DIPO-Ph₄ has been investigated in photovoltaic solar cell in two different configurations:

- ◆ In organic solar cell, highly crystalline thin films of DIPO-Ph₄ have been used in organic solar cells. The DIPO-Ph₄ thin films are made of vertically-aligned nano-needles. Current-sensing atomic force microscopy (CS-AFM) reveals a considerable increase of the hole-carrying pathways in DIPO-Ph₄ thin films as compare to PEDOT:PSS, thus revealing their

hole transporting/electron blocking properties. Inserting a 10 nm thick of DIPO-Ph₄ in combination with a 5 nm thick PEDOT:PSS between the ITO electrode and the P3HT:PCBM film leads to photocurrent densities up to 11.5 mA/cm² under AM1.5G and conversion efficiencies up to 4.6%, that is substantially higher than PEDOT:PSS-only devices.

- ◆ In perovskite solar cell, the DIPO-Ph₄ has been inserted as a dopant-free hole transporting material. DIPO-Ph₄ based PSCs show PCEs up to 10.1%, that is two times higher than those obtained with undoped spiro-OMeTAD (5.1%), still retaining J_{sc} and V_{oc} comparable to those of standard doped spiro-OMeTAD based devices. Moreover, DIPO-Ph₄ based devices showed better stability compared to spiro-OMeTAD devices, at a relative humidity of 30%.

In conclusion of this thesis, we demonstrated the excellent donor properties of DIPO-Ph₄ and show its efficient use as a hole transport material in organic solar and perovskite solar cells. These encouraging results suggest that dipyranylidene can be used as a core for dopant-free HTMs in either organic solar cell or perovskite solar cell.

On the perspective of this work, some alternative molecules are in preparation in order to improve the device performance. One strategy is to lower the HOMO level in order to obtain a better band alignment with the *p*-type material. Halogenated groups like fluoride are well-known acceptor and commonly use in organic synthesis to lower the HOMO level of the molecule (Fig.6.1, **1**). Besides, the solubility of DIPO-Ph₄ is a real issue for the formation of homogeneous film made by solution process. The solubility of an organic compound is generally increased by the addition of long alkyl chain (Fig.6.1, **2**). However, this long alkyl

chains can interfere with the packing structure and the charge carrier properties. Thus, the addition of alkyl groups into the DIPO-Ph₄ requires thorough investigation.

Fig.6.1: Chemical structure of 2,2',6,6'-tetraphenyldipyranylidene derivatives.

Finally, DIPO-Ph₄ has a high absorption coefficient, however IPCE measurement shows that any photocurrent is generated from these absorbed photons. This can be explained by a high recombination process or a short exciton lifetime. The photoluminescence properties of DIPO-Ph₄ need to be investigated in details. The synthesis of dissymmetrical dipyranylidene with an acceptor group in one side and a donor group in the other side can result in an interesting push-pull system (Fig.6.1, **3**, **4**). Despite of the challenging synthesis, these materials should present intramolecular charge transfer^{280,281}, leading to longer exciton lifetime and promote the charge generation.

Appendix

Experimental Methods

A.1. Synthesis of DIPO-Ph₄

A.1.1. Materials and synthesis

All commercial reagents were used without further purification. All solvents are distilled under N₂ before utilization. All reactions relating to air and moisture-sensitive reagents were performed in vacuum-dried reaction vessels under argon atmosphere. Column chromatography was carried out on silica gel 40–63 mesh as the stationary phase. Glutaryl chloride, AlCl₃, BF₃·Et₂O, Pbu₃, DIPEA and all solvents are purchased from commercial sources (Sigma-Aldrich, Alfa Aesar).

Scheme.A1: Synthetic pathway to 2,2',6,6'-tetraphenyldipyranylidene (DIPO-Ph₄).

A.1.2. Synthesis of 1,5-diphenyl-1,5-pentadione

In a two-neck round bottom flask of 50 mL, AlCl_3 (150 mmol; 20.01 g) is dissolved in benzene under N_2 . Glutaryl Chloride (60 mmol; 7.65 mL) is added dropwise to the solution and the mixture is stirred under reflux for 12 h. After return to ambient temperature, the mixture is poured into a diluted HCl solution (10 %). The organic phase is extracted with CH_2Cl_2 and dried over MgSO_4 . The organic product is purified by column chromatography (hexane:ethyl acetate at a ratio=95:5) and a white solid is collected (12.01 g, yield=80 %). ^1H RMN (CDCl_3 , 300 MHz) δ =8.00 (d, 4H), 7.57 (t, 2H), 7.47 (t, 4H), 3.15 (t, 4H), 2.23 (quint, 2H).

A.1.3. Synthesis of 2,6-diphenylpyrylium fluoroborate

In a two-neck round bottom flask of 50 mL, 1,5-diphenyl-1,5-pentadione (13.7 mmol, 3.47 g) is dissolved in distilled toluene under N_2 . Then $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (41.2 mmol, 5.09 mL) is added drop by drop to the solution. The slightly red solution is refluxed at 130°C during 12 h process. After cooling down to room temperature, 5 mL of acetone is added to the solution and poured in 100 mL of diethyl ether. A yellow precipitate is filtered and dried overnight under vacuum (2.05 g; yield=46%). ^1H NMR (D_2O , 300 Mhz) δ =ppm: 8.89 (t, 1H), 8.47 (d, 2H), 8.26 (d, 4H), 7.77 (t, 2H), 7.68 (t, 4H).

A.1.4. Synthesis of 2,2',6,6'-tetraphenyldipyranylidene (DIPO- Ph_4)

2,6-Diphenylpyrylium fluoroborate (8.21 mmol, 2.65 g) is dissolved in distilled CH_3CN (50 mL). Pbu_3 (16.4 mmol, 4.1 mL) is added to the solution and during 2 h at room temperature.

DIPEA (41.06 mmol, 7 mL) is added to the yellow solution and the mixture is heated at 90°C under N₂ during 18 h. After the return to room temperature, the red solid formed is filtered and washed with ethyl acetate. The final compound is a dark red powder (m=1.62 g, yield=85%). The raw product is purified by Soxhlet extraction in acetonitrile during several days. The final compound is a highly crystalline deep red powder with shiny metallic reflections. mp=325°C. ¹H NMR (acetone, 500 MHz): δ = 8.02 (d, 8H), 7.51 (dd, 8H), 7.42(t, 4H), 7.18 (s, 4H); MS (ESI+): m/z 464.

Figure.A2: Optical images of DIPO-Ph₄ after Soxhlet purification (left) and after crystallization by vapor methods (right)

A.1.5. Single-crystal growth of DIPO-Ph₄

DIPO-Ph₄ single crystals are prepared by two methods. In one hand, 1D single crystals of DIPO-Ph₄ are prepared by physical vapor transport. The purified materials are put into a two-zone transparent furnace for single crystal growth. Preliminarily, the organic powder is purged under argon gas (flow ~40 cc/min) for 10 hours before crystal growth to remove air

in the two-zone fully transparent furnace, and then placed in the high-temperature zone (250°C). The crystal growth happens in the low-temperature zone (180°C). After few days, centimeter size needle crystals are appeared in the low-temperature zone. After crystal growth, the temperature of the furnace was cooled to room temperature. On the other hand, single crystal of DIPO-Ph₄ are obtained from a solution methods. DIPO-Ph₄ is dissolved in acetonitrile until saturation. Then solution is heated below melting point (70°C, concentration = 5 g/mL) in order to solubilize all the DIPO-Ph₄. The solution is cooled down at a slow rate, large needle-like crystals are formed and dried after filtration of the acetonitrile solution. Besides, micro-needle crystals are obtained by casting DIPO-Ph₄ solution on silicon substrates.

A.1.6. Characterization

¹H and ¹³C NMR (nuclear magnetic resonance) spectra were recorded on a Bruker BBFO-400 instrument at room temperature by using CDCl₃ as a solvent. Chemical shifts were recorded in parts per million (ppm) relative to tetramethylsilane (δ = 0.00 ppm) and chloroform (δ = 7.26 ppm). ¹H NMR splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet), etc. ¹³C NMR spectral values are reported relative to CDCl₃ (δ = 77.00 ppm). Thermal gravimetric analysis (TGA) is performed on a TA Instruments 2920 at a heating rate of 10°C/min under nitrogen. Cyclic voltammetry measurements have been recorded with electrochemical station (model CHI760d) on a three-electrode cell composed of glassy carbon as working electrode and Pt electrode as auxiliary electrode. A calomel electrode is used as a reference electrode. The electrolyte is composed of 0.5 mM of compound and 0.1 M Bu₄NClO₄ in DMF. The scan rate was 200 mV/s. Absorption

spectra of DIPO-Ph₄ solution and thin films are measured by a UV–VIS spectrophotometer (Shimadzu, UV-2501PC), besides absorption spectra of DIPO-Ph₄ single crystals have been measured with microspectrophotometer (Jasco MSV-5200). The morphology of the DIPO-Ph₄ single crystal is characterized with a field-emission scanning electron microscopy (JEOL, JSM-6700F). DIPO-Ph₄ crystalline structure of the two polymorphs of DIPO-Ph₄ single crystal are determined by X-Ray diffraction (Bruker X8 CCD Diffractometer). DSC measurement was performed in nitrogen flow at heating and cooling rate of 10°C/min (TA Instruments Q10 DSC).

Figure.A3: a) Thermal gravimetric analysis (TGA) and b) differential scanning calorimetry of DIPO-Ph₄ performed under nitrogen.

A.2. Parameters of DIPO-Ph₄ single crystals

A.2.1. X-ray measurements

(α -phase) DIPO-Ph₄ single crystals made by physical vapor transport

A red plate like specimen of C₃₄H₂₄O₂, approximate dimensions 0.005 mm × 0.040 mm × 0.420 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total of exposure time was 9.30 hours. The frames were integrated with Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using triclinic unit cell yielded a total of 27809 reflections to a maximum θ angle of 66.85° (0.84 Å resolution), of which 4043 were independent (average redundancy 6.878, completeness = 96.0%, $R_{\text{int}} = 6.87\%$, $R_{\text{sig}} = 4.08\%$) and 3320 (82.12% were greater than $2\sigma(F^2)$). The final cell constants of $a = 10.3715(4)$ Å, $b = 10.4260(3)$ Å, $c = 12.2917(4)$ Å, $\alpha = 92.1911(17)^\circ$, $\beta = 108.3364(17)^\circ$, $\gamma = 108.6554(17)^\circ$, volume = 1181.03(7) Å³, are based upon the refinement of the XYZ-centroids of 9935 reflections above $2\sigma(I)$ with $7.669^\circ < 2\theta < 133.3^\circ$. Data were corrected for absorption effects using the Multiscan methods (SADABS). The ratio of minimum to maximum apparent transmission was 0.687. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7800 and 0.9970.

The structure was solved and refined using the Bruker SHELXTL Software Package, using space group P-1, with $Z = 2$ for the formula unit, C₃₄H₂₄O₂. The final anisotropic full-matrix least-squares refinement on F^2 with 325 variables converged at $R1 = 4.52\%$, for the observed

data and $wR2 = 13.49\%$ for the all data. The goodness-of-fit was 1.063. The largest peak in the final difference electron density synthesis was $0.224 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.264 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.053 \text{ e}^-/\text{\AA}$. On the basis of the final model, the calculated density was 1.306 g/cm^3 and $F(000)$, 488 e^- .

(β -phase) DIPO-Ph₄ single crystals made from acetonitrile

A red needle-like specimen of $\text{C}_{34}\text{H}_{24}\text{O}_2$, approximate dimensions $0.010 \text{ mm} \times 0.020 \text{ mm} \times 0.420 \text{ mm}$, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total of exposure time was 14.34 hours. The frames were integrated with Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using monoclinic unit cell yielded a total of 2666 reflections to a maximum θ angle of 27.41° ($0.77 \text{ \AA}$ resolution), of which 2666 were independent (average redundancy 1.000, completeness = 99.1% , $R_{\text{int}} = 9.38\%$, $R_{\text{sig}} = 119.56\%$) and 880 (33.01% were greater than $2\sigma(F^2)$). The final cell constants of $a = 6.0757(4) \text{ \AA}$, $b = 16.4664(11) \text{ \AA}$, $c = 11.9301(8) \text{ \AA}$, $\beta = 98.440(2)^\circ$, volume = $1180.62(14) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 7192 reflections above $2\sigma(I)$ with $6.033^\circ < 2\theta < 54.63^\circ$. Data were corrected for absorption effects using the Multiscan methods (SADABS). The ratio of minimum to maximum apparent transmission was 0.752. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9670 and 0.9990.

The structure was solved and refined using the Bruker SHELXTL Software Package, using space group $P-1$ $21/n$ 1, with $Z = 2$ for the formula unit, $\text{C}_{34}\text{H}_{24}\text{O}_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 163 variables converged at $R1 = 7.65\%$, for the

observed data and $wR2 = 27.71\%$ for the all data. The goodness-of-fit was 0.848. The largest peak in the final difference electron density synthesis was $0.361 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.436 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.129 \text{ e}^-/\text{\AA}$. On the basis of the final model, the calculated density was 1.307 g/cm^3 and $F(000)$, 488 e^- .

A.2.2. DIPO-Ph₄ structure parameters

Figure.A4: Representation of DIPO-Ph₄ with the labelled C and O atoms. H-atoms are omitted for clarity.

Table.A1: Bond lengths extracted from DFT calculations and X-ray diffraction for the two DIPO-Ph₄ polymorphs. Early molecular parameters reported in 1982 on DIPO-Ph₄ crystals grown from solution are also shown for comparison.²⁵⁰

All values in Å		DFT	α phase	β phase	From ref. 192
Fulvenic C=C bond	C9-C9	1.38	1.39	1.39	1.39
Bond lengths in pyranilidene	C7-C8	1.34	1.35	1.35	1.34
	C8-C9	1.45	1.45	1.46	1.45
	C9-C10	1.45	1.45	1.43	1.44
	C10-C11	1.34	1.35	1.36	1.33
	C11-O	1.38	1.38	1.40	1.39
	O-C7	1.38	1.38	1.37	1.38
Bond lengths pyranilidene core to phenyl groups	C6-C7	1.47	1.47	1.49	1.47
	C11-C12	1.47	1.47	1.45	1.48
Bond lengths within the phenyl groups	C1-C2	1.39	1.39	1.41	1.40
	C2-C3	1.39	1.40	1.36	1.36
	C3-C4	1.39	1.40	1.36	1.35
	C4-C5	1.38	1.39	1.40	1.39
	C5-C6	1.38	1.41	1.38	1.38
	C6-C1	1.40	1.41	1.40	1.38
	C13-C14	1.39	1.39	1.36	1.39
	C14-C15	1.38	1.40	1.39	1.38
	C15-C16	1.39	1.40	1.40	1.38
	C16-C17	1.38	1.39	1.35	1.39
	C17-C12	1.40	1.41	1.41	1.40
	C12-C13	1.40	1.41	1.41	1.40

Table.A2: Bond angles extracted from by DFT calculations and by X-ray diffraction for the two DIPO-Ph₄ polymorphs. Early parameters reported in 1982 on DIPO-Ph₄ crystals grown from solution are shown for comparison.²⁵⁰

All values are in degrees		DFT	α phase	β phase	From ref. 192
Torsion angles between phenyl groups and pyranilidene core	Ph1 (C5-C6-C7-C8 plan)	22.0	22.53	11.6	10.2
	Ph2 (C10-C11-C12-C17 plan)	15.3	22.53	8.9	7.6
	Ph3 (C10-C11-C12-C17 plan)	17.7	22.53	8.9	7.6
	Ph4 (C5-C6-C7-C8 plan)	23.5	22.53	11.6	10.2
Dipyranylidenes torsion		3.5.	0	0	0
Angles within pyranilidene	O	117.7	118.9	118.8	118.2
	C7	122.0	121.4	122.2	121.4
	C8	122.7	122.6	121.9	122.7
	C9	122.8	119.9	112.9	113.0
	C10	122.7	122.6	124.1	123.2
	C11	122.1	121.4	119.9	121.2
Angles between the pyranilidene core and the phenyl rings	C6-C7-C8	126.1	126.4	125.8	127,4
	C10-C11-C12	125.9	126.4	128.1	128.4

All values are in degrees		DFT	α phase	β phase	From ref. 192
Angles within the phenyl rings	C1	120.5	120.6	119.6	119.7
	C2	120.2	120.5	121.8	120.8
	C3	119.8	119.4	120.3	120.2
	C4	120.2	120.3	119.3	120.1
	C5	120.7	120.8	121.8	120.9
	C6	118.6	119.4	119.4	118.2
	C13	120.1	120.6	122.2	120.3
	C14	120.7	120.5	120.9	120.4
	C15	129.6	119.4	117.8	119.4
	C16	120.0	120.3	121.4	121.2
	C17	121.0	120.8	122.1	119.9
	C12	118.5	119.4	115.7	118.7

A.3. DIPO-Ph₄-based optoelectronics devices

A.3.1. DIPO-Ph₄ thin films fabrication and morphology characterization

The crystalline DIPO-Ph₄ is finely divided in a mortar and placed in a quartz boat. DIPO-Ph₄ is evaporated at a slow rate (0.1 Å/s) in a thermal vacuum chamber ($P_0 \sim 10^{-4}$ Pa) and the thickness is monitored by a quartz microbalance (Inficon X TM/2). DIPO-Ph₄ molecules are evaporated at a slow rate of 0.2 Å.s⁻¹ under high vacuum ($P \approx 10^{-4}$ Pa). The morphology of

vacuum-deposited DIPO-Ph₄ films (50 nm) is analyzed by AFM (Bruker, Dimension V) and scanning electron microscopy (Jeol, JSM-6700F).

A.3.2. DIPO-Ph₄ based OFET fabrication

DIPO-Ph₄ molecules are evaporated on single sided n-type low resistivity (0.01–0.02 $\Omega\cdot\text{cm}^{-1}$) Si (100) wafers (Silicon Valley Microelectronics, SVM) with a 300 nm thick SiO₂ grown on top using dry oxidation. Before usage, the substrates were sonicated using ethanol, acetone and isopropyl alcohol for 10 minutes each and treated by UV-ozone for 15 minutes and treated with HMDS (Sigma-Aldrich, > 99%) or OTS (sigma aldrich >90%). HMDS solution was spin-coated at 3,000 rpm for 60 seconds and annealed at 100°C for 10 minutes. While OTS treatment was obtained by immersing the silicon substrate in OTS solution for over 12 h. Then, the samples were rinsed several times with toluene and dried at 110°C for several hours. FET devices were fabricated in top contact configuration by deposition of 85 nm gold layer through a metallic mask leading to a channel width $W=4,000\ \mu\text{m}$ and different channel lengths $L=75, 100, 125, 150, 175$ and $200\ \mu\text{m}$ (Scheme 2a). The FET characteristics are recorded under inert atmosphere using a probe-station (Anexus) and a source-meter (Agilent, B2902A).

A.3.3. Single-crystal field-effect transistors fabrication

Organic field-effect transistor (OFET) were fabricated in both top and bottom configuration on single sided n-type low resistivity (0.01–0.02 $\Omega\cdot\text{cm}^{-2}$) Si (100) wafers (Silicon Valley Microelectronics, SVM) with a 600 nm thick SiO₂ grown on top using dry oxidation. Before

usage, the Si wafers were sonicated using ethanol, acetone and isopropyl alcohol for 10 minutes each. The silicon wafers were dehydrated on a hot plate for 10 minutes followed by UV-ozone treatment for 15 minutes. The silicon substrate was treated with OTS firstly before growth of the DIPO-Ph₄ crystal. Finally, 80 nm thick gold layer was deposited through copper grid mask to act as the source and drain electrodes (scheme 2). The single crystal FET properties are recorded using a probe-station (Anexus) and a source-meter (Agilent, B2902A) on our bottom-gate/top contact-electrode devices in a glovebox under N₂.

A.3.4. Space-charge-limited-current (SCLC) devices

Fluorine-doped tin oxide (FTO, <14 Ω /square, 3 mm thick) substrates were etched to form the desired pattern, which were subsequently cleaned by sonication in 2% Hellmanex aqueous solution, deionized water, and ethanol respectively. A 20 nm thick PEDOT:PSS (Sigma-Aldrich; water solution 1.3 % in weight) is spin-coated on top of FTO substrate followed by an annealing at 120°C under argon for 30 min. DIPO-Ph₄ molecules are evaporated at a slow rate of 0.2 $\text{\AA}\cdot\text{s}^{-1}$ under high vacuum ($P \approx 10^{-4}$ Pa). Finally, the devices are completed by thermal evaporation of Ag (100 nm) through shadows mask with a diameter of 7 mm².

A.3.4. Elaboration of organic photovoltaic solar cells

ITO-coated glass substrates (Sigma-Aldrich; 2.5×2.5 cm²; R=70-100 Ω /cm²) are patterned by chemical etching with HCl (5 % aq.) and sonicated in successively ethanol and acetone during 10 mins. The samples are finally exposed to UV-ozone during 10 minutes in order to remove

organic impurities and improve the hydrophilicity of the substrates. DIPO-Ph₄ thin film are deposited as mentioned previously. Then, a 5 nm layer of PEDOT:PSS (Sigma-Aldrich; water solution 1.3 % in weight) is spin-coated on top of DIPO-Ph₄ thin film. P3HT/PCBM bulk layer is prepared by spin-coating from a solution of P3HT (Sigma-Aldrich; purity >98.5 %) and PCBM (nano-C; purity 99+ %) dissolved in dichlorobenzene (ratio of 1:0.8 P3HT-PCBM) and sonicated beforehand during 10 minutes to obtain a homogenous blend solution. The spin-coating conditions are adjusted to obtain 120 nm P3HT/PCBM thick films. The organic films undergo post-annealing at 110°C under argon during 10 min. The devices are completed by successive thermal evaporation of LiF (7 Å) and Al (100 nm) through shadows mask with a diameter of 7 mm². The reference cells were prepared by deposition of 20 nm film of PEDOT:PSS on ITO followed by an annealing at 120°C under argon for 30 min. Successive layers are deposited under the same conditions.

A.3.5. Elaboration of perovskite solar cells

Fluorine-doped tin oxide (FTO, <14 Ω/square, 3 mm thick) substrates were etched to form the desired pattern, which were subsequently cleaned by sonication in 2% Hellmanex aqueous solution, deionized water, and ethanol respectively. A thin compact layer of TiO₂ as a blocking layer between FTO and perovskite was deposited by atomic layer deposition (ALD). The mesoporous TiO₂ layer composed of 30 nm-sized particles was deposited by spin coating at 6000 rpm for 30 s using a commercial TiO₂ paste (Dyesol DSL 30 NRD) diluted in ethanol (2:7, weight ratio). After drying at 70°C, the TiO₂ films were gradually heated to 500°C, baked at this temperature for 30 min and cooled to room temperature. An organic-inorganic

perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ was deposited by single step method with solvent treatment.¹⁰⁶ After spin coating the samples were annealing at 100°C for 30 min. The Spiro-OMeTAD were dissolved in chlorobenzene (100 mg/ml) respectively and spin-coated on these substrates. Additives like Li-TFSI, *t*-BP and tris(2-(1H-pyrazol-1-yl)pyridine)cobalt(III) (FK 102) dopant were added to the above solution as stated in literature.¹⁰⁴ The DIPO was deposited on perovskite via vacuum evaporation. The substrates were placed in a thermal evaporator for gold (Au) deposition via shadow masking. Thickness of the Au electrode was about 100 nm and an active area of 0.2 cm^2 was defined by the overlap of TiO_2 and Au.

A.3.6. Solar cell characterizations

TiO_2 thickness is determined by Alpha-Step IQ surface profiler (KLA-Tencor). The morphology was characterized with a field-emission scanning electron microscopy (FESEM, FEI SIRION). The photocurrent-voltage characteristics of the solar cells were measured with an electrochemical workstation (Zahner zennuim, Germany) under AM 1.5G solar simulator (100 mW cm^{-2} , Newport, calibrated with a silicon reference cell). The incident photon-to-current conversion efficiency (IPCE) was measured with a 300 W Xenon lamp and a monochromator controlled by TracQ Basic software (QEPVSI-b Measurement System, Newport).

A.4. DFT calculations

A.4.1. Introduction of the polaron transport theory based on canonical transformation of the holstein hamiltonian

A detailed description of the theory can be found out in on this works.^{282,283} We describe here some essential components of the theory. The electron transport is calculated based on a temperature dependent canonical transformation of Holstein Hamiltonian.²⁸⁴ Charge carrier mobility is related to the diffusion coefficient through Einstein relationship as $\mu=e\beta D$, where e is the charge of the electron, $\beta=1/(k_B T)$. The diffusion coefficient can be obtained with:

$$D = a^2 \langle \langle v_k^2 / (G_{kk} + G_0) + \gamma_{kk} \rangle \rangle \quad (\text{eq.A1})$$

where a is the nearest neighbor distance, k is the wave vector and $v_k = \nabla_k E_k$ is the polaron band velocity, Γ_0 is the scattering rate due to static disorder. The double bracket denotes the thermal average of the polaron state E_k , where Γ_{kk} and γ_{kk} are the scattering and hopping rates.

$$\Gamma_{kk} = N^{-1} \sum_{k \neq k'} W_{k,k;k',k'} \quad (\text{eq.A2})$$

$$\gamma_{kk} = \frac{1}{2} \nabla_q^2 \text{Re} \left(\frac{1}{2} W_{k,k;k'+q,k'+q} - W_{k,k+q;k',k'+q} \right) \Big|_{q=0} \quad (\text{eq.A3})$$

where $W_{k,k+q;k',k'+q}$ crucial to the calculation of diffusion coefficient are given by:

$$W_{k,k+q;k',k'+q} = \int_0^\infty dt \left\{ \langle V_{k'+q,k+q} V_{k,k'}(t) \rangle \exp[-i(E_{k'+q} - E_{k+q})t] + \langle V_{k'+q,k+q}(t) V_{k,k'} \rangle \exp[-i(E_k - E_{k'})t] \right\} \quad (\text{eq.A4})$$

The single bracket indicates the average of the residual interaction. Here the single angular bracket denotes the average of the residual interaction $V_{k,k'}(t)$ over phonon states. This residual interaction originates from the temperature dependent canonical transformation. The major model parameters have been listed in Table.4.2 of the main text. Other model parameters involved are: a finite phonon bandwidth of $\Delta\omega = 0.1 \omega_0$ (in which ω_0 is the characteristic phonon frequency, which describe the overall effect of all phonon modes and has the relationship of $E_{\text{pol}}=S\omega_0$) and a constant scattering rate Γ_0 (which can take the effects of impurities and static disorder on band-like mobilities). ω_0 takes different values for the DIPO-Ph₄ polymorphs, calculated as ω_0 (α -phase DIPO-Ph₄)=292.8 cm⁻¹, ω_0 (β -phase DIPO-Ph₄)=913.6 cm⁻¹, The value of Γ_0 has been set to 0.001 ω_0 for both cases considering potentially higher crystal quality in these systems.

A.4.2. Calculation of hole transport anisotropy

The calculation of hole transport anisotropy follows a widely applied method.^{285,286} Based on the measured angles of q_1 and q_2 , as well as calculated maximum hole mobility along each dimer direction, we are able to calculate overall mobilities for different systems as:

$$\mu_{\alpha\text{-phase}} = 0.146 \cos^2 \Phi + 0.000 \cos^2(53 - \Phi) + 0.000 \cos^2(69 + \Phi) \quad (\text{eq.A5})$$

$$\mu_{\beta\text{-phase}} = 0.26 \cos^2 \Phi + 0.20 \cos^2(70 - \Phi) + 0.31 \cos^2(70 + \Phi) \quad (\text{eq.A6})$$

The units for hole mobility are cm² V⁻¹ s⁻¹.

A.4.3. Details of DFT calculations

The CP2K package has been used to relax the XRD-determined unit cells of the DIPO-Ph₄ polymorphs with lattice parameters fixed to their experiment values. The convergence criteria have been set to that when both total force and RMSD force are lower than $1 \times 10^{-4} \text{ bohr}^{-1} \text{ Ha}$. Besides force criteria, maximum displacement and RMSD displacement should also reach that lower than $1 \times 10^{-3} \text{ bohr}$. The electronic self-consistent (SCF) convergence criterion has been set to that $< 1 \times 10^{-7} \text{ Ha}$. A global energy cut-off of 300 Ha has been adopted. As for the pseudopotential, we have chosen GTH^{287–289} potential from Perdew-Burke-Ernzerhof (PBE) density functional with Grimme's dispersion correction (G06).^{290,291} Hole transfer integrals were calculated via the VOTCA package²⁹² by adopting the method described by Valeev.²⁴⁹ Dimers were extracted from close packing planes of optimized cells of DIPO-Ph₄ polymorphs according to schematics shown in Fig.4.13. Molecular orbital needed were obtained from SCF calculation at the level of PW91/6-311G using Gaussian 09 (G09).²⁹⁴

Another important parameter is the Huang-Rhys' factor S for holes. Here we applied the DUSHIN code²⁹⁵ in conjunction with Gaussian 09 (G09) calculations at the PBE0/6-31G(d,p) level.²⁹⁶ Both geometries of DIPO-Ph₄ polymorphs extracted from respective optimized crystal structures with and without positive charge were further optimized free of symmetry constraints using closed-shell and open-shell (with spin multiplicity set to $S=1/2$) methods, respectively. G09 optimized molecular structures are given in Figure 3.14, together with their respective HOMO orbital isosurface. Optimized geometries were then used for frequency calculations at the same level. We are able to calculate for the normal mode displacement Δ_k

for the k_{th} vibrational mode with frequency ω_k of the charged state with respect to the neutral state geometry, based on the geometries of the DIPO-Ph₄ polymorphs at their charged and charge neutral states, as well as their respective vibrational frequencies. Therefore we can calculate their Huang-Rhys factor as $S_k = \Delta_k^2/2$. Base on both Huang-Rhys factor of the k_{th} vibrational mode and their respective frequencies we can get the value of polaron binding energy E_{pol} easily with $E_{pol} = \sum_k S_k \omega_k$. With the calculated values of transfer integral and Huang-Rhys factor, we are able to calculate for the hole mobilities of DIPO-Ph₄ polymorphs at room-temperature using the 1D polaron transport model via the Einstein relationship of $\mu = e\beta D$, where e is the charge of a hole and $\beta = 1/k_B T$, with k_B as the Boltzmann constant. D here stands for the diffusion coefficient of the hole polaron at room-temperature.

List of publications

Manuscript in preparation

1. **Marc Courté**, Hui Jiang, Ye Jun, Rakesh Ganguly, Shen Chao, Christian Kloc, Denis Fichou; Impact of crystal packing on the hole mobility in two organic single crystal polymorphs; in preparation.
2. Shasha Tang, Yongqi Zhang, **Marc Courté**, Haiyong He, Hongjin Fan, Denis Fichou; Design of cobalt-based catalysts towards overall water splitting; in preparation.

Journal publications

This thesis is based on the following papers and reprints were made with permission from the respective publishers.

1. **M. Courté**; S. G. Surya; R. Thamankar; C. Shen; V. R. Rao; S. G. Mhaisalkar; D. Fichou, A non-volatile resistive memory effect in 2,2',6,6'-tetraphenyl-dipyranilidene thin films as observed in field-effect transistors and by conductive atomic force microscopy. *RSC Advances*, **2017**, 7, 3336-3342.
2. **M. Courté**, C. Shen, A. Krishna, S.Tang, D. Fichou, Quinoidal 2,2',6,6'-Tetraphenyl-Dipyranilidene as a Dopant-Free Hole-Transport Material for Stable and Cost-Effective Perovskite Solar Cells. *Energy Technology*, **2017**, 5, 1852-1858, (Invited article with Front cover).

3. **M. Courté**; M. Alaaeddine; V. Barth; L. Torteche; D. Fichou, Structural and electronic properties of 2,2',6,6'-tetraphenyl-dipyranylidene and its use as a hole-collecting interfacial layer in organic solar cells. *Dyes and Pigments*, **2017**, 141, 487-492.

I am also a co-author of the following papers which are not included in this thesis.

4. C. Shen; X. Wang; S. Tang; **M. Courté**; D. Fichou, Phenoxazine Derivative Operates as an Efficient Surface-Grafted Molecular Relay to Enhance CdS and CdSe-Sensitized TiO₂ Solar Cells Performances and Stability. *ChemPhysChem*, **2017**, 18, 1302-1307.
5. V. Rajeshkumar; **M. Courté**; D. Fichou; M. C. Stuparu. Synthesis and Properties of Large Polycyclic Aromatic Hydrocarbons with Planar and Non-Planar Structural Motifs. *European Journal of Organic Chemistry*, **2016**, 36, 6010-6014.
6. A. Efrem; **M. Courté**; K. Wang; D. Fichou; M. Wang. Synthesis and Characterization of γ -Lactone-Pechmann Dye Based Donor–Acceptor Conjugated Polymers. *Dyes and Pigments*, **2016**, 134, 171-177.
7. V. Rajeshkumar; **M. Courté**; D. Fichou; M. C. Stuparu. Synthesis and Properties of a Buckybowl/ Buckyball Dyad. *Synlett*, **2016**, 27, 2101-2104.
8. I. Mínguez-Bacho; **M. Courté**; H. J. Fan; and D. Fichou. Conformal Cu₂S-Coated Cu₂O Nanostructures Grown by Ion Exchange Reaction and Their Photoelectrochemical Properties. *Nanotechnology*, **2015**, 26, 185401 (front cover).
9. I. Mínguez-Bacho; **M. Courté**; C. Shi; D. Fichou. Controlling the Nanomorphology of Thin Conformal Cu₂S Overlayers Grown on Cu₂O Compact Layers and Nanowires. *Materials Letters*. **2015**, 159, 47-50

Conference talk presentations

1. **M. Courté**, M. Alaaeddine, V. Barth, L. Tortech, D. Fichou. *Structural and electronic properties of 2,2',6,6'-tetraphenyldipyranylidene and its use as a hole-collecting interfacial layer in organic solar cells*. 9th International Conference on Materials for Advanced Technologies (ICMAT), Suntec, Singapore, June 18-23, **2017**.
2. **M. Courté**, C. Shen, A. Krishna, S. Tang, D. Fichou. *A dipyranylidene derivative as an efficient hole transporting material for stable perovskite solar cells*; European Materials research Society Spring meeting (EMRS), Strasbourg, France, May 22-26, **2017**.
3. **M. Courté**, S. G. Surya, R. Thamankar, C. Shen, V. R. Rao, S. G. Mhaisalkar, D. Fichou. *A non-volatile resistive memory effect in 2,2',6,6'-tetraphenyl-dipyranylidene thin films as observed in field-effect transistors and by conductive atomic force microscopy*; 7th International Conference on Key Engineering Materials (ICKEM2017), USM, Penang, Malaysia, March 11-13, **2017**.
4. **M. Courté**, I. Mínguez-Bacho, H. J. Fan, D. Fichou. *Controlled conformal coating of Cu₂S on Cu₂O nanostructures and their photoelectrochemical properties*; International Conference on Electronic Materials (ICEM2016), Suntec, Singapore, July 4-8, **2016**.

Conference poster presentations

1. **M. Courté**, C. Shen, A. Krishna, S. Tang, D. Fichou. *Quinoidal 2,2',6,6'-tetraphenyldipyranylidene as an efficient and low-cost dopant-free hole transporting material for stable perovskite solar cells*. 9th International Conference on Materials for Advanced Technologies (ICMAT), Suntec, Singapore, June 18-23, **2017**.

2. **M. Courté**, S. G. Surya, R. Thamankar, C. Shen, V. R. Rao, S. G. Mhaisalkar, D. Fichou. *A non-volatile resistive memory effect in 2,2',6,6'-tetraphenyl-dipyranylidene thin films as observed in field-effect transistors and by conductive atomic force microscopy*; European Materials research Society Spring meeting (EMRS), Strasbourg, France, May 22-26, **2017**.
3. **M. Courté**, S. G. Surya, R. Thamankar, C. Shen, V. R. Rao, S. G. Mhaisalkar, D. Fichou. *A non-volatile resistive memory effect in 2,2',6,6'-tetraphenyl-dipyranylidene thin films as observed in field-effect transistors and by conductive atomic force microscopy*; Institute of Physics Singapore Meeting (IPS2017), Yale-NUS College, National University of Singapore, Singapore, February 22-24, **2017**.
4. C. Shen, X. Wang, S. Tang, **M. Courté**, D. Fichou. *Phenoxazine derivative operates as an efficient surface-grafted molecular relay to enhance CdS and CdSe-sensitized TiO₂ solar cells performances and stability*; 9th Asian Photochemistry Conference (APC2016), School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore, December 4-8, **2016**.
5. **M. Courté**, I. Minguez Bacho, Chen Shi, H.J. Fan, D. Fichou, *Cu₂S-coated Cu₂O photocathode for photoelectrochemical applications*, Institute of Physics Singapore Meeting (IPS2017), School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore, March 4-6, **2015**.

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