Tuning of physical properties of Van Der Waals bonded materials through charge transfer

Hu, Peng

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**Tuning of Physical Properties of Van der Waals Bonded
Materials through Charge Transfer**

HU PENG

School of Materials Science and Engineering

2017

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School of Materials Science and Engineering

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Abstract

Organic semiconductors are attractive for electronics applications due to soluble process, low cost and large area processing. Compared with polycrystalline materials, single crystals allow investigation of intrinsic properties and relationship between molecular packing and properties, due to nearly perfect structures and low concentration of structure imperfections. Charge transfer compounds, formed by molecules, exhibit electrons transfer from donor to acceptor. Such compounds show lots of special electrical properties, such as ambipolar properties, high conductivity, even superconductivity. Charge transfer compounds also show unique properties, such as ferromagnetic properties in C₆₀-TDAE, bound states with multiple excitons in anthracene-TMDA and ferroelectrics in lock arm supramolecular ordering system. It is an effective way to tuning the physical properties through charge transfer.

Perylene-TCNQ charge transfer compound single crystals with different stoichiometry were grown from solution. The stoichiometries of final perylene-TCNQ charge transfer compound depend on the using solvent, but not depend on the starting stoichiometry of perylene and TCNQ. (Perylene)₁(TCNQ)₁ (P1T1) is grown from toluene and (perylene)₃(TCNQ)₁ (P3T1) is grown from benzene, no matter what stoichiometry of perylene and TCNQ are used in the beginning. The reason for such phenomenon is that the crystals with lower solubility will precipitate first. As a result, only P1T1 is formed from toluene because P1T1 is less soluble than P3T1 in this solvent. As P3T1 is less soluble than P1T1 in benzene, only P3T1 was crystallized from benzene. By using PVT method, a mixture of monomolecular crystals and all three charge transfer compound single crystals (P1T1, P2T1 and P3T1) are obtained. Field-effect transistors on the single crystal surfaces of P1T1, P2T1 and P3T1 have been made. The results reveal that P1T1 is typically an n-type semiconductor, P3T1 showed p-type behavior, whereas P2T1 showed ambipolar properties. From P1T1 to P3T1, the increase of perylene molecules in the unit cell may lead to the transformation of the single crystal from n-type to p-type.

The methodology of searching for novel organic charge transfer binary compounds and crystal growth was made in the case that only the two starting organic substances are known but the phase diagram is not known, the thermodynamic data of the binary compound are not known and even the existence of new binary compounds is not known.

Kinetically lowering the sublimation rate was the key factor for growing large-size charge transfer compound single crystals. By using this concept, crystals of novel perylene-F₁TCNQ, perylene-F₂TCNQ and perylene-F₄TCNQ charge transfer binary compounds were obtained by decreasing the evaporation area of the individual components. Perylene-F₄TCNQ shows room temperature ferromagnetism, which is undiscovered before. The larger charge transfer degree may play an important role in expressing the properties in perylene-F₄TCNQ. On the other hand, the weak acceptor, TCNQ, does not cause ferromagnetism in perylene-TCNQ because the degree of charge transfer is too low.

Triangle monolayer WS₂ and MoS₂ were grown using the chemical vapor deposition (CVD) method. The formation of the monolayers was confirmed by both AFM and Raman spectra. The PL increased after a thin layer of F₄TCNQ was deposited on the surface of the WS₂ and MoS₂ monolayers. The reason for such an increase is the dissociation of trions. The charged excitons, trions, lose electrons during the charge transfer from monolayer WS₂ and MoS₂ to F₄TCNQ. Meanwhile, the weaker exciton-phonon interaction of WS₂ results in narrower PL peaks with larger amplitudes. Therefore, the charge transfer of electrons to the acceptor, such as F₄TCNQ, from CVD-grown monolayer WS₂ and MoS₂ enhances the PL, and materials with weaker exciton-phonon interactions show a stronger PL intensity.

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Abbreviations

α -6T	α -hexathiophene
AFM	Atomic force microscopy
BEDSe-TTF	Bis(ethylenediselena)tetrathiafulvalene
BEDT-TTF	Bis(ethylenedithio)tetrathiafulvalene
Ben-OTS	Phenyltrichlorosilane
BN	Boron nitride
C ₆ H ₆	Benzene
Cl ₂ TCNQ	2,5-dichloro-7,7,8,8-tetracyanoquinodimethane
CS ₂	Carbon disulfide
CVD	Chemical vapor deposition
DBTTF	Dibenzotetrathiafulvalene
DDQ	2,3-dichloro-5,6-dicyano-p-benzoquinone
DPTTA	Meso-diphenyltetrathia[22]annulene[2,1,2,1]
DTTCNQ	4,8-bis(dicyanomethylene)-4,8-dihydrobenzo[1,2-b:4,5-b']-dithiophene
EDO-TTF	Ethylenedioxytetrathiafulvalene
F ₁ TCNQ	2-fluoro-7,7,8,8-tetracyanoquinodimethane
F ₂ TCNQ	2,5-difluoro-7,7,8,8-tetracyanoquinodimethane
F ₄ TCNQ	2,3,5,6-tetrafluoro-7,7,8,8- tetracyanoquinodimethane
FET	Field effect transistor
F-OTS	Perfluorodecyltrichlorosilane
HOMO	Highest occupied molecular orbital
IPA	Isopropyl alcohol
IR	Infrared
KBr	Potassium bromide
K _{sp}	Solubility product constant
LUMO	Lowest unoccupied molecular orbital
MoO ₃	Molybdenum trioxide
Nd:YAG	Neodymium-doped yttrium aluminum garnet
OSCFET	Organic single crystal field effect transistor

OTS	Octadecyltrichlorosilane
P3HT	Poly(3-hexylthiophene)
PCBM	Phenyl-C61-butyric acid methyl ester
PDOS	Partial density of states
PF ₆	Hexafluorophosphate
PL	Photoluminescence
PMDA	Pyromellitic acid dianhydride
PMDS	Polydimethylsiloxane
PMMA	Poly(methylmethacrylate)
PPMS	Physical property measuring system
PVT	Physical vapor transport
SAED	Selected-area electron diffraction
SAM	Self-assemble monolayers
TCNE	Tetracyanoethylene
TCNQ	7,7,8,8-tetracyanoquinodimethane
TDAE	tetrakis(dimethylamino)ethylene
TDOS	Total density of states
TEM	Transmission electron microscopy
TGA	Thermo-gravimetric analysis
TMTSeF	Tetramethyltetraselenafulvalene
TMTSF	Ditetramethyltetraselenafulvalene
TTF	Tetrathiafulvalene
VSM	Vibrating sample magnetometer
WO ₃	Tungsten trioxide

Chapter 1

Introduction

This chapter shows a short background of organic charge transfer single crystal research which introduces the advances of organic electronics, advantages of single crystals and the importance of organic charge transfer single crystals. Then it followed with the hypothesis: “The physical properties of Van der Waals bonded materials can be tuned through charge transfer.” To address the hypotheses, the objectives and scope are divided into four aspects: 1. Growth of charge transfer compound single crystals from gas phase and solution phase; to obtain different stoichiometry organic charge transfer single crystals between donors and acceptors. 2. LUMO-HOMO gap measurements of the charge transfer compound single crystals. 3. Investigation of physical properties of charge transfer single crystals, especially its charge transport properties, ferromagnetic properties, piezoelectric properties and so on. In order to find how stoichiometry effect on the properties and find new properties. 4. Fabricate the organic-inorganic charge transfer samples to evaluate the properties changes. Then, it follows a short summary of the entire doctoral thesis. Finally, the novel achievements of this research work are summarized.

1.1 Background

Organic semiconductors are more and more attractive for electronics applications due to their many fundamental benefits compared with inorganic ones¹. Firstly, most of them are soluble allowing fabrication of devices by many unconventional methods, for example, solution casting², inkjet printing^{3,4}, stamping⁵, spin coating⁶. Secondly, organic semiconductors are low cost, which is good for large area semiconductor electronics^{7,8}. The last but not the least, organic semiconductor devices can make lots of applications, which is not only in the bendable displays⁹, solar cells^{10,11}, flexible electrodes¹², but also in wearable electronics¹³, chemical sensors¹⁴, skin for robots¹⁵ and so on (Figure 1.1). Some organic semiconductors have already been used in light emitting diode displays¹⁶ while some of them such as rubrene¹⁷ and pentacene¹⁸ have outperformed the amorphous silicon field effect transistors applications.

Compared with other forms of materials, single crystals allow investigation of intrinsic properties¹⁹ like charge transport, anisotropy. Because single crystals have nearly perfect structures and minimum concentration of structure imperfections (i.e. grain boundaries) and impurities, which decrease the charge trapping and scattering and improve the intrinsic properties. Thus, single crystals always present superior intrinsic properties so that it gives the opportunity to design the new organic semiconductors and high performance devices²⁰. From single crystal X-ray diffraction, the molecular packing is easy to obtained, and it enables the study of the relationship between molecular packing and charge transport in materials²¹⁻²³.

Charge transfer compounds exhibit electrons transfer from donor to acceptor²⁴. They are formed by molecules²⁴, which are important in many fields, such as bio-electrochemical energy transfer process²⁵, surface chemistry²⁶, non-linear optical materials²⁷ as well as solar energy storage²⁸. Investigation of charge transfer compounds offers basic information²⁹ like electronic band formation and the conductivity can vary from insulating³⁰ to superconducting³¹. In charge transfer compounds, the electronic bands are always based on the molecular orbitals³². Thus, it is very convenient to control the band structure by changing the donor or acceptor molecules and modifying the crystal structure as well as molecular packing arrangements. The stability of charge transfer compounds is enhanced due to the increase of the electron density³³. The charge transfer compounds

give two main information³⁴: (1) Fermi energy controlled by the mean charge on molecules, and (2) the overlap between molecular orbitals depends on the molecular packing arrangements (i.e. the angles and distances between neighboring molecules).

Figure 1.1 Application of organic semiconductors^{3-9,17,24}. (a) solar cell; (b) flexible electronics; (c) bendable displays; (d) wearable sensors.

Charge transfer compound single crystals show lots of special electrical properties, such as superconductivity, ambipolar properties and so on. Therefore, they are used for many applications. For example, water/moisture-resistant nanoelectronic devices³⁵, organic electrodes³⁶, organic-based photovoltaics^{37,38}. Sometimes, charge transfer compound single crystals offer great versatility as a plaything for studying the formation of band structure and new properties in organics. For example, organic ferroelectric structures based on intermolecular charge transfer^{39,40}, multiple excitons formed in organic charge transfer compounds⁴¹, neutral π -radical conducting organic charge transfer compounds⁴² and soft ferromagnetism⁴³. Therefore, charge transfer is an effective way to tune the physical properties of an organic semiconductor.

1.2 Hypothesis

Before bringing together the charge transfer pairs, donor and acceptor have their LUMO and HOMO. When charge transferred from donor to acceptor, their resulting compounds will have new LUMO and HOMO. Consequently, the charge transfer compounds have a new smaller band gap compared with donor and acceptor. Schematic diagram of LUMO-HOMO engineering is shown in Figure 1.2, which illustrates the basic conception of organic single crystal charge transfer compounds LUMO-HOMO engineering. The possibility of charge transfer is determined by the ionization energy of donor and electron affinity of acceptor. The ionization energy controls the ability of donor to give electrons, while electron affinity governs the ability of acceptor to obtain electrons. The larger electron affinity of acceptor and smaller ionization energy of donor will increase the possibility to form charge transfer compounds. If the energy difference between electron affinity of acceptor and the ionization energy of donor is too large, the charge transfer compounds will not form.

Figure 1.2 LUMO-HOMO engineering of an organic single crystal charge transfer compound.

There are two ways to control the properties of organic single crystals charge transfer compounds. The first way is changing the molecular of donors and/or acceptors. For examples, adding new side chains, replacing the carbon atom to other atoms, new types of donor or acceptors and so on. The second way is to change the stoichiometry of donors and acceptors.

Charge transfer compounds sometimes show unique properties in organics. Ferromagnetic properties are easy to obtain in inorganics, such as iron, nickel and cobalt. However, ferromagnetism of metal-free organic is very rare. The first example is TDAE-C₆₀ organic charge transfer compounds at few degrees Kelvin. Furthermore, in conventional organic semiconductors, more than two excitons formed intermediate bound state are not formed. Nevertheless, the bound states with multiple excitons are found in an organic charge transfer solids.

Charge transfer is not only formed between two organic species, but also can form between organic and inorganic. The charge transferred between inorganic and organic can lead to an improvement of some properties.

Therefore, the following hypotheses have been formulated: “The physical properties of van der Waals bonded materials can be tuned through charge transfer.” It can be detailed as follow:

1. The LUMO-HOMO gap will decrease after charge transfer from donor to acceptor.
2. The physical properties, especially the electrical properties of organic single crystal charge transfer compound can be controlled by the stoichiometry of donors and acceptors.
3. The organic single crystal charge transfer compounds may express some new physical properties.
4. The charge transfer between organic and inorganic will change some physical properties, such as electrical properties or optical properties.

1.3 Objectives and Scope

To address the hypotheses mentioned above, the following studies were made:

1. Growth of charge transfer compound single crystals from gas phase and solution phase. To obtain different stoichiometry organic charge transfer single crystals between donors and acceptors.
2. LUMO-HOMO gap measurements of the charge transfer compound single crystals.
3. Investigation of physical properties of charge transfer single crystals, especially

its charge transport properties, ferromagnetic properties, piezoelectric properties and so on. In order to find how stoichiometry effect on the properties and find new properties.

4. Fabricating the organic-inorganic charge transfer samples to evaluate the properties changes.

1.4 Dissertation Overview

Chapter 1 shows a short background of organic charge transfer single crystal research. Then it followed with hypothesis, objectives and scope and a short summary of the entire doctoral thesis.

Chapter 2 reviews organic charge transfer compound theory, single crystal growth techniques of organic charge transfer compound, history and the basic principle of organic field effect transistors, history and the basic principle of organic magnets and recent research on charge transfer single crystals.

Chapter 3 discusses the experimental apparatus and basic principle of characterization techniques. It includes materials purification, single crystal growth, FET device fabrication and principles of characterization.

Chapter 4 firstly investigates the crystal growth and charge transport properties of perylene and TCNQ single crystals. Further, perylene-TCNQ charge transfer compound single crystals with different stoichiometry were grown from solution. We found that the stoichiometry of final perylene-TCNQ charge transfer compound is dependent on the solvent used, but not depend on the starting stoichiometry of perylene and TCNQ. (perylene)₁(TCNQ)₁ (P1T1) is grown from toluene and (perylene)₃(TCNQ)₁ (P3T1) is grown from benzene, no matter what stoichiometry of perylene and TCNQ are used in the beginning. The reason for such phenomenon is explained by solubility data and optical spectrum. By using PVT method, a mixture of monomolecular crystals and all three charge transfer compound single crystals (P1T1, P2T1 and P3T1) are obtained. Beside P1T1 and P3T1, (perylene)₂(TCNQ)₁ (P2T1) is a new phase, which is not published. After that, the charge transfer and charge transport properties of all three compounds are investigated. It shows that from P1T1 to P3T1, the increase of perylene molecules in the unit cell may lead to the transformation of the single crystal from n-type to p-type.

Chapter 5 firstly investigates the crystal growth and charge transport properties of

F₄TCNQ single crystals. A methodology of searching for novel organic charge transfer binary compounds and crystal growth was supposed, which in the case that only the two starting organic substances are known but the phase diagram is not known, the thermodynamic data of the binary compound are not known and even the existence of new binary compounds is not known were studied. By using this concept, crystals of novel perylene-F₁TCNQ perylene-F₂TCNQ and perylene-F₄TCNQ charge transfer binary compounds were obtained by decreasing the evaporation area of the individual components. We found that kinetically lowering the sublimation rate was the key factor for growing large-size charge transfer compound single crystals. Field-effect behavior was not observed in perylene-F₄TCNQ FETs. However, we found that the strong acceptor F₄TCNQ transfers sufficient charge from perylene to cause room-temperature ferromagnetism. On the other hand, the weak acceptor, TCNQ, does not cause ferromagnetism in perylene-TCNQ because the degree of charge transfer is too low. These results explain previous observations of ferromagnetism in metal-free organics and enable the design of novel ferromagnetic compounds due to strong charge transfer. Such compounds may be vital components for room temperature spintronic devices.

Chapter 6 investigates the charge transfer from the CVD-grown monolayer MoS₂ or WS₂ to F₄TCNQ, which increases the photoluminescence intensity dramatically. We found that the photoluminescence of this CVD-grown triangle monolayer of MoS₂ and WS₂ is enhanced by the deposition of F₄TCNQ on these monolayer surfaces. The intensity of the photoluminescence after deposition increases sharply. We concluded that charge transfer from the monolayer MoS₂ or WS₂ to F₄TCNQ is the key reason. Charge transfer increases the formation of neutral excitons at the expense of charged excitons.

Chapter 7 draws together the study by summarizing the results and suggesting future research directions. The main findings are discussed with reflect in the original hypothesis, which is thus verified.

1.5 Findings and Outcomes/Originality

The novel achievements of this research work are:

1. Growth new high-quality organic charge transfer single crystals of perylene-TCNQ and perylene-F_xTCNQ (x=1,2,4).
2. Explaining the organic solvent-dependent stoichiometry of single crystals by using

classical inorganic precipitation-dissolution theory in the perylene-TCNQ system.

3. Correlating the charge transport properties with the stoichiometry of donor and acceptor in perylene-TCNQ charge transfer single crystals.
4. Establishing a method to grow large organic charge transfer single crystals when only the two starting organic substances are known but the phase diagram is not known, the thermodynamic data of the binary compound are not known and even the existence of new binary compounds is not known.
5. Discovery of the room-temperature ferromagnet of metal-free organic charge-transfer compounds of perylene-F₄TCNQ.
6. Correlating the charge transfer degree of perylene-F₄TCNQ with the magnetic properties.
7. Establishing a method to enhance the photoluminescence intensity dramatically of MoS₂/WS₂ monolayers.

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Chapter 2

Literature Review

In this chapter, the history of organic charge transfer compound is firstly reviewed. After that, the theory of organic charge transfer compound is introduced. It presents the definition and determination method of charge transfer. Single crystal growth techniques by using gas and solution methods of organic charge transfer compound are introduced. Field effect transistors and magnetic properties of organic charge transfer single crystal compound were measured in this thesis. Therefore, the history and basic principle of organic field effect transistors and the history and basic principle of organic magnets were exhibited. Finally, the recent research on charge transfer single crystals is reviewed.

2.1 Charge transfer compound

2.1.1 History

In 1927, Pfeiffer¹ found that some aromatic hydrocarbons undergo additive combination with certain organic molecules, which are not obeying existing rules of chemical bonds. After that, a large number of this kind of compounds was found. Such compounds are always containing two parts: one part can share their π electrons while another part has the capacity of accepting π electrons^{2,3}. Such compounds are named charge transfer compounds. Some papers are addressing these compounds as charge transfer complex, charge transfer salt, charge transfer co-crystal and so on⁴. In my entire thesis, the name “charge transfer compound” is used.

2.1.2 Definition and theory

Charge transfer compounds⁵ exhibit electrons transfer from one component (the donor) to another (the acceptor). The component can be molecules or ions, or both, without a covalent bond involved. The amount of electron transferred from donor to acceptor can in principle vary from zero to one whole electron.

The ground state of charge transfer compounds with one donor and one acceptor can be written by its wave function as follow^{6,7}:

$$\psi_n(D, A) = a\psi_0(DA) + b\psi_1(D^+A^-)$$

Where D is donor and A is acceptor; ψ_0 is the wave function for no electrons transferred; ψ_1 is the wave function for one electron transferred from donor to acceptor; a and b are coefficients.

The excited state is:

$$\psi_e(D, A) = a^*\psi_1(D^+A^-) - b^*\psi_0(DA)$$

With charge transfer compounds having slightly charge transferred, $a \gg b$, so that:

$$\psi_n \approx \psi_0(DA) \text{ and } \psi_e \approx \psi_1(D^+A^-)$$

It means when $b \gg a$, the charge transfer compounds have a stable ionic bond.

The energy of charge transfer compound is determined by ionization energy of donor molecular and electron affinity of acceptor molecular. The ionization energy (I) is the ability of donor to give electrons, while electron affinity (E_a) controls the ability of acceptor to obtain electrons. Thus, the optical energy requirement of charge transfer

compounds can be written as:

$$h\nu = I - E_a - W$$

where h is Planck's constant, ν is the transition frequency, I is ionization energy of donor, E_a is electron affinity of acceptor and W is the dissociation energy of the charge transfer compound.

Figure 2.1 gives the ionic potential and electron affinity of some organic molecules.

Figure 2.1 Ionic potential and electron affinity of some organic molecules⁸⁻¹⁴.

2.1.3 Determination of charge transfer

A quantum-mechanical form^{7,15} to represent the ground state of a charge transfer complex:

$$\Psi \sim \Psi_0 + b\Psi_D$$

where Ψ_0 and Ψ_D are the wave functions for no-bond and dative state, respectively. Ignoring overlap, the dative coefficient is

$$b = \frac{H_{OD}}{W}$$

where $H_{OD} = \int \Psi_0 H \psi_D d\tau$, and $W = I - (E_a + C)$; I , E_a , C are the ionization energy of the donor, electron affinity of the acceptor and the coulomb of other energy terms, respectively. The dipole moment of the complex is

$$\mu_0 = b^2 \mu_D$$

where μ_D is the moment of the complex in the zero order dative state. The binding energy is

$$E_c \cong b^2 W$$

The ultraviolet absorption frequency is

$$h\nu_{uv} = W(1 + 2b^2)$$

From this calculation, the decrease of the frequency and increase of the intensity of a certain stretching vibration can be observed by different spectroscopy methods.

Spectrophotometry is an extremely convenient method for determining the formation of a charge transfer complex. The displacement of electron density accompanying the formation of such a complex corresponds to a considerable change not only in the absorption but also in its increasing intensity. Measurements of the change in the absorption electronic spectra of the complexes are widely used.

S. P. McGlynn³ supposed that the following effects should be considered in the charge transfer complexes: (a) Some bond length of donors or acceptors should be increased. (b) When the charge transfer occurred, vibrational frequencies of some vibration modes should be decreased due to such modes are sensitive to active orbitals. (c) Some modes are unobserved in donor or acceptor because of symmetry forbiddances. However, when the charge transfer occurred, total symmetry is usually decreased. It is to be expected that some vibrational modes in charge transfer compounds will appear in the spectrum.

From above, there are two ways to confirm charge transfer. The first is checking some bonds length of donors or acceptors; the second is to find a new peak in the optical spectrum.

In TCNQ based charge transfer compounds, the length of bonds is especially sensitive to the negative charge on molecules^{16,17}. The population of electrons in TCNQ is increasing the length of two bonds (a and c) while decreasing the length of the other two bonds (b and d)¹⁸. The a, b, c, d bonds are shown in Figure 2.2. By measuring the length of these bonds, the charge transfer effect can be estimated.

Figure 2.2 Illustrated structure of TCNQ molecular.

When charge has transferred from donor to acceptor, the intensities of molecular vibration bands will be enhanced. Thus, electron transferred from a bonding orbital of donor to an anti-bonding orbital of acceptor³. It is properly to be considered as an “electron-vibration” spectrum, since infrared absorption is due to electron motion. Therefore, infrared spectroscopy has been employed to investigate the donor-acceptor interaction of charge transfer complexes.

In the example of 2-methyl pyridine-iodine charge transfer compound¹⁹, the two new peaks were observed. One is near 180 cm^{-1} and the other broader band is in the range 65 to 95 cm^{-1} . Absorption bands in the region of 180 cm^{-1} have been observed previously²⁰ for iodine complexes and have been allocated to the stretching vibration of iodine molecule, which turns to infrared active when the complex is formed. The new band which is observed at lower frequencies must be associated with an intermolecular vibration of the complex, and its nature will depend on the geometric form of the charge transfer complex.

Another example is the mirtazapine based system²¹, as shown in Figure 2.3. Compared with pure mirtazapine, all the charge transfer compounds show a new peak in the region of 2000 cm^{-1} to 2500 cm^{-1} . This new peak strongly supports that the charge transfer effect occurs between donors and acceptors. Furthermore, in the compounds, the peak of donor and acceptor shows both position shift and intensity change as a consequence of molecular symmetries and electronic structures changes.

Not only infrared spectroscopy can identify charge transfer effects, but also other kinds of spectrophotometry can be used, such as Raman. The Raman spectrum can probe vibration modes in a system and provide a fingerprint of crystals. When charge transfer occurs, between donor and acceptor, new vibration will appear by changing the environment of donor and acceptor. Thus, new Raman peak will be detected and some of

the peaks identified for the pure compounds will shift^{22,23}.

Figure 2.3 FT infrared spectroscopy of mirtazapine based charge transfer compounds²¹ in the range of 2500-500 cm^{-1} . (a) Pure mirtazapine; (b) Mirtazapine - DDQ charge transfer compound; (c) Mirtazapine - TCNE charge transfer compound; (d) Mirtazapine - TCNQ charge transfer compound.

2.2 Solution method growth of charge transfer compound single crystals

Compared with growth of monomer organic crystals, charge transfer takes effect between acceptors and donors. Therefore, the crystal growth methods should be modified. Charge transfer compound single crystals growth methodologies by solution methods are introduced in the following sections.

2.2.1 Slowing cooling method

This method requires that the solubility of acceptor and donor is larger than charge transfer compound. Meanwhile, the solubility of donor, acceptor and charge transfer compound decreases significantly with temperature decreases. The basic arrangement is shown in Figure 2.4.

Figure 2.4 Basic arrangement of slow cooling method.

First, both donor and acceptor are added into a test tube. Then, selected solvent is dropped into the tube. Donor and acceptor will dissolve in the tube and the charge transfer effect occurs. A color change is observed to make sure that the charge transfer compounds were formed. Then, the test tube is heated to a high temperature. After that, a saturated solution of charge transfer compound should be obtained at high temperature. The last, single crystal appears at the bottom of test tube through cooling down procedure. The cooling rate must be very slow to obtain good charge transfer compound single crystals. Thus a water bath with the accurate cooling system is required. The freezer can be used if crystal growth below ambient temperature. This method is the easiest way to get single crystals of charge transfer compounds. There are several examples, such as TTF - TCNQ²⁴, (BEDT-TTF) - (Cl₂TCNQ)²⁵, (BEDSe-TTF) - (F₄TCNQ)²⁶. Surprisingly, this simple method sometimes works well and yields large crystals with good quality. Nevertheless, the solvent molecules may incorporate into the crystal structure. The most common material is fullerene²⁷ (C₆₀), for example, DBTTF - C₆₀ - C₆H₆ and TMTSeF - C₆₀ - (CS₂)₂.

2.2.2 Slow evaporation method

The method is similar to slow cooling in view of the apparatus requirements (Figure 2.5). It is more suitable to grow crystals which solubility unvaried with changing temperature or have very small temperature coefficient of stability. Instead of a full closed cap, the cover needs some small holes in order to make slow evaporation of solvent. The temperature is fixed constantly in order to make solvent evaporation. It is always at low temperature, or even in a refrigerator, to slow down the evaporation rate of selected solvent. Typical growth conditions require temperature stabilization to about $\pm 0.005^{\circ}\text{C}$ and evaporation rates to a few milliliters per day. M. Schröder²⁸ and Nanova²⁹ grew thioether-iodine and DBTTF-TCNQ and by using this method, respectively.

Figure 2.5 Basic arrangement of slow evaporation method.

2.2.3 Vapor diffusion method

Vapor diffusion method is more suitable to use when only milligram materials are available. Typical equipment setups are shown in Figure 2.6.

Figure 2.6 Basic arrangement of slow evaporation method.

One solvent requires volatile so as to diffusion is carry out. A small amount of donor and acceptor put in a tube with dissolving in solvent A and then placing this tube into a large vial which contains solvent B. The outer vial is then sealed. The two liquids start to equilibrate via vapor diffusion. If solvent A is more volatile, A molecules will evaporate into solvent B, therefore the concentration of charge transfer compound is increased. Then, the crystal will grow in solvent A. The amount of donor and acceptor by using this method should be in milligrams level. If more materials are used, it is always inappropriate and increases the chance for intergrowth of charge transfer compound single crystals. The slower diffusion rate benefits the crystal growth. A transparent tube is recommended by using this method. It will supply a chance for continuous checking the crystal growth process.

Table 2.1 Recommended solvents for vapor diffusion.

Solvent A	Solvent B
Tetrahydrofuran	Cyclohexane
Ethanol	Cyclohexane
Methanol	Hexane
Acetonitrile	Tetrahydropyran
Acetone	Chloroform
Water	Dioxane

B. Spingler³⁰ gives some recommended solvents shown in Table 2.1 which is helpful to select solvent A and B. The solvent in the outer vial must be removed when the crystals formed in the inner tube, which is helpful to prevent crystallization with unknown impurities. (EDO-TTF) - TCNQ³¹ single crystal is also grown by this approach. But it is quite difficult to find two suitable solvents.

2.2.4 Liquid-liquid interface method

Donor and acceptor were dissolved in two immiscible solvents separately. Usually, charge transfer effect occurs at the interface between two solvent. Without disturbing the interface, the resulting interface is stored at low temperature for a long time to crystal growth. Then the charge transfer compound single crystals will form at the interface. Figure 2.7 shows the schematic diagram.

Figure 2.7 Schematic diagram of liquid-liquid interface method.

Sometimes, donor and acceptor were dissolved in one solvent to form charge transfer compound. Then, another solvent was slowly added into the solution which contains charge transfer compound. After that, the crystal was grown at the interface. This method is useful to grow some charge transfer compound single crystals, such as fullerene-cobalt porphyrin³² and fullerene-ferrocene³³.

2.3 Vapor method growth of charge transfer compound single crystals

Compared with solution methods, organic single crystals grown from gas phase are widely believed to be much cleaner. Such crystals have better performance in device because no solvent molecules affect the crystals. Organic materials always have low melting point and low sublimation temperature, thus PVT method is always employed to grow organic single crystals. C. Kloc et al. firstly designed the system to grow centimeter-sized crystals of α -6T³⁴. Then, this method successfully applied to grow other high-quality monomer organic crystals, such as anthracene³⁵, tetracene³⁶, pentacene³⁷, rubrene³⁸ and so on. There are two different PVT methods³⁹ frequently used to grow monomer crystals: open system and close system. For charge transfer single crystal growth by PVT method, the methods need to be modified. The modified apparatus are shown in Figure 2.8.

Figure 2.8 Scheme of the PVT growth method. (a) Open system; (b) Close system.

In an open system (Figure 2.8a), the speed of sublimation and crystal growth is controlled by the carrier gas. Zone 1 and Zone 2 are high temperatures for donor and acceptor, respectively. The donor (acceptor) sublimated at Zone 1 and acceptor (donor) molecule sublimated at Zone 2. The temperature in Zone 2 should be higher than Zone 1, in order to prevent the materials in Zone 1 crystallized in Zone 2. Therefore, materials in Zone 2 should have a higher sublimation temperature compared with materials in Zone 1. The sublimation temperature difference of donor and acceptor should be small. Then, charge

transfer occurs between donor and acceptor, the charge transfer single crystals crystallized at Zone 3. Zone 3 always has the lowest temperature in the three zones. Crystals and impurities deposited in the different positions in zone 3 due to the difference in their molecular weight. The carrier gas plays an important role, which can prevent organic materials from oxidizing.

In a closed system (Figure 2.8b), the mixture of donor and acceptor are sealed in a glass or quartz ampoule under vacuum so as to nothing can escape from the ampoule in the whole crystal growth process. When temperature increased to sublimation temperature of donor and acceptor in Zone 1, the donor and acceptor molecules will charge transfer with each other. Zone 2 is set at a lower temperature than Zone 1. With temperature gradient, the crystals will crystalize in the low temperature zone. By using the close system, it requires that the sublimation temperature of donor and acceptor have small differences. Otherwise, the low sublimation temperature materials will firstly crystallize in the low temperature zone.

In the vapor phase, it is difficult to control the morphology and the crystals are difficult to be implanted in devices. Therefore, there are still rare publications about charge transfer compound single crystal growth by using PVT method and most cases are still using solution methods.

2.4 Organic single crystal field effect transistor

2.4.1 Definition and basic principle

A transistor is an electrical device, which contains three terminals. The electric current flowing between two terminals and it is controlled by the third terminal. A FET is using electrical field to control the conductivity in semiconductor materials. While using organic single crystals as semiconductor materials, the device is named OSCFET. Schematic picture of OSCFET device is shown in Figure 2.9. The two electrodes on the single crystal are called source and drain and the single crystal between the two electrodes are named channel. The source and drain electrodes are the same in the device, but source electrode is always grounded. There should be an applied bias voltage between source and drain to get current. This current is modulated by the different voltage which is applied from the third electrode called gate.

Figure 2.9 Typical structures of OSCFET devices.

2.4.2 Basic parameters

Before discussing the basic parameter, two important measurement curves should be understood: output curve and transfer curve, as shown in Figure 2.10.

Output curve shows the current between source and drain electrodes (I_{SD}) varies with the voltage between source and drain electrodes (V_{SD}) under different gate voltage (V_G). There are two regions in the output curve: linear region and saturation region (Figure 2.10a). Transfer curve gives the current between source and drain electrodes (I_{SD}) varies with gate voltage (V_G) under different voltage between source and drain electrodes (V_{SD}), as shown in Figure 2.10b. The three basic parameters can be obtained by these two curves.

2.4.2.1 Field effect mobility

Field effect mobility shows how strong the electrons or holes in channel are modulated by applying gate voltage. In FET, field effect mobility is always indicated with the short term “mobility”. If the carrier is hole (electron), the “hole (electron) mobility” will be used. Mobility is determined from the FET characterization and with units of $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$.

There are two methods to calculate the mobility from the transfer curve of the device. The first method is to estimate mobility by using the linear region. Another method is to

calculate the mobility by using the saturation region.

Figure 2.10 Output curve (a) and transfer curve (b) of OSCFET devices.

When in the linear region, the following equation is applied:

$$\mu = \frac{L}{WC_i V_{SD}} \cdot \frac{\partial I_{SD}}{\partial V_G}$$

Where L is the channel length, W is the channel width. C_i is the capacitance of dielectrics.

When in the saturation region, the saturated mobility can be extract from the following

equation:

$$\mu = \frac{2L}{WC_i} \cdot \left[\frac{\partial \sqrt{I_{SD}}}{\partial V_G} \right]^2$$

The calculated linear mobility is always smaller than calculated saturation mobility. The mobility of FET is influenced by semiconductor materials, temperature, types of electrodes, contact between single crystals and electrodes, device configuration, and so on.

2.4.2.2 On-off ratio

On-off ratio is the ratio of switch-on drain current and switch-off drain current. The value is calculated from the transfer curve of devices. The value is the ratio of the maximum current between source and drain electrodes and the current when the gate voltage is equal to zero. The Higher on-off ratio is leading to higher device stability and anti-jamming capability.

2.4.2.3 Threshold voltage

Threshold voltage is the minimum gate voltage to accumulate the carriers enough to form current between source and drain electrodes. If the threshold voltage is close to zero, the device can be operated at low voltage. Therefore, from practical application, the threshold voltage must be decreased. The value of threshold voltage is calculated from the intersection point of linear fitting of $I_{SD}^{1/2}$ - V_G and the axis of V_G .

2.4.3 History and current research

The first description of organic FET was reported in 1970 by Westgate et al⁴⁰. They performed field-effect measurements on single crystals of metal-free phthalocyanine in high vacuum. The first realistic organic FET device was reported in 1986⁴¹. They used polythiophene thin film as semiconducting materials and found the mobility of this material is around $10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Due to the single crystals are very fragile and incompatible with conventional microelectronic process⁴², the FET based on single crystals was reported very late compared with organic thin film FET. The first OSCFET was reported by Kouki in 1996⁴³. They used sexithiophene as single crystal and PMMA as insulating layer. The mobility of sexithiophene was $0.075 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, and the on/off

ratio was above 10^4 . After that, several reports on OSCFET were published, but the mobility was below $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Until 2003, Podzorov et al⁴⁴ reported the rubrene single crystal FET device using parylene as dielectric. The results showed that the mobility is around $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and the on/off ratio is about 10^4 . Then, another group⁴⁵ improved the mobility value for rubrene single crystal FET. The mobility reaches $18 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $40 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ by using two-terminal and four-terminal measurements, respectively. After that, the mobility could reach $58 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at 225K for pentacene single crystal FET⁴⁶. They found that the purity of single crystals affects the properties dramatically. The highest mobility of OSCFET published is $94 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for $\kappa\text{-(BEDT-TTF)}_2 - \text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ by using a four-terminal measurement⁴⁸.

FET studies based on organic charge transfer single crystals are rather rare. In 1994⁴⁷, the first charge transfer compound thin film FET was published. After that, lots of such thin film FET based on TCNQ were reported⁴⁸⁻⁵¹. Up to 2004, first organic charge transfer single crystals was fabricated⁵² based on (BEDT-TTF) - F_2TCNQ . This material showed ambipolar field effect carrier at 2K. Theoretical calculation⁵³ indicates the charge transfer compound single crystals should have ambipolar properties due to both donor and acceptor unit in the molecular packing. Several research confirms this calculation. Fullerene-cobalt porphyrin³² charge transfer compound single crystals shows that the electron and hole mobilities are relatively low and around 10^{-5} and $10^{-6} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively. The interesting materials are sulfur-bridged annulene based charge transfer single crystals. DPTTA - TCNQ single crystals⁵⁴ gives electron and hole transport of $0.03 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $0.04 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively. DPTTA - C_{60} single crystals displays electron and hole mobility of $0.01 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $0.3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively. Furthermore, DPTTA - DTTCNQ shows remarkable high ambipolar transport characteristics. It exhibits a high electron mobility of $0.24 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and hole mobility of $0.77 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in ambient atmosphere. Researchers⁵⁵ found that the electrodes of the charge transfer OSCFET affected the transport properties. In this experiment, six types of organic metals were used as electrode for DBTTF - TCNQ FET devices and they found the charge transport properties were tuned from n-type to p-type.

2.5 Organic magnets

2.5.1 Basic magnetic theory

This part is only describing the basic magnetic definition and classifies related to organic magnets.

Magnetic induction ($\mathbf{B}$) is the response of material when a magnetic field ($\mathbf{H}$) is applied to the material. The relationship between $\mathbf{B}$ and $\mathbf{H}$ is a property of the material, shown as follow:

$$\mathbf{B} = \mathbf{H} + 4\pi\mathbf{M}$$

where $\mathbf{M}$ is the magnetization of the material. $\mathbf{M}$ is defined as the magnetic moment per unit volume. It shows the magnetic strength of the material. Magnetization depends on the individual magnetic moment of the atoms or molecules and the interaction between neighboring atoms or molecules.

Figure 2.11 Schematic illustrations of spin interactions. (a) Paramagnetic; (b) Antiferromagnetic; (c) M - H curve.

The magnetic behavior of material is determined by how and how strong the unpaired electron spins interact with each other. The magnetization curve (M - H curve) can be used to identify the magnetic behavior of the materials. The symbol “ $\uparrow$ ” is used to represent the unpaired electron spins. Figure 2.11 shows the spin interaction and M - H curve of paramagnetic and antiferromagnetic behavior. If the spins do not have interact with each other, they will show paramagnetic (Figure 2.11a). The spins are random while the

external magnetic field is applied. If the spins are antiparallel with each other, this phenomenon is called antiferromagnetic (Figure 2.11b). In both two cases, the magnetization increases with applied magnetic field increases.

Figure 2.12 Schematic illustrations of spin interactions. (a) Ferromagnetic; (b) Ferrimagnetic; (c) M - H curve.

Figure 2.13 M - H curve of a ferromagnet or ferrimagnet showing hysteresis⁵⁶.

Ferromagnet shows the spins are correlated with each other with external magnetic field applied (Figure 2.12a). While ferrimagnet is a net moment form when the materials have a different spin domain and can not cancel antiferromagnetic ordering completely (Figure

2.12b). The magnetization of Ferromagnetic and ferrimagnetic increases with field increases in low magnetic field. After further increase of the field, the magnetization will saturate. A diamagnet shows that the magnetization decreases with field increases.

Most ferromagnetic/ferrimagnetic materials show hysteresis (Figure 2.13). First, magnetization increases with field increases until to saturation. Then, when field decreases to zero, the curve follows a different curve and the materials still have a remnant magnetization. If the M-H curve is plotted for all section of applied magnetic field, the result shows hysteresis.

2.5.2 History and current research

The first molecule-based organic magnet⁵⁷ is $\text{Fe}^{\text{III}}(\text{S}_2\text{CNEt}_2)_2\text{Cl}$ with $T_c=2.46\text{K}$ reported in 1967. Then, lots of organic magnets with T_c less than 10K were published, such as $\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$ ⁵⁸ with $T_c=5.5\text{K}$, $[\text{Fe}(\text{C}_5\text{Me}_5)_2] - [\text{TCNQ}]$ ⁵⁹ with $T_c=2.55\text{K}$, $[\text{Fe}(\text{C}_5\text{Me}_5)_2] - [\text{TCNE}]$ ⁶⁰ with $T_c=4.8\text{K}$. The first organic polymer magnet reported in 1987⁶¹. Due to no *d*-electrons can be involved in the spin correlation, the reason is the radicals in polymer contribute to magnetic properties. In 1991, first room-temperature organic magnet was discovered, $[\text{V}(\text{TCNE})_x]_y(\text{CH}_2\text{Cl}_2)^{62}$ with $T_c=400\text{K}$. The author concluded that it resulted from three-dimensional antiferromagnetic exchange of donor and acceptor spins. In the same year, metal-free organic charge transfer magnet, $\text{C}_{60} - \text{TDAE}$ ⁶³, was reported with $T_c=16\text{K}$. It is the first organic metal free molecular weak ferromagnet. In 1995, $\text{V}^{\text{II}}_{0.42}\text{V}^{\text{III}}_{0.58}[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.86} \cdot 2.8\text{H}_2\text{O}$ ⁶⁴ was reported as the second room-temperature molecule-based magnet with $T_c=315\text{K}$. Furthermore, in 2007, the high-temperature metal-organic magnets $[\text{Ni}_2\text{TCNQ} \cdot (\text{O})_x \cdot (\text{H}_2\text{O})_y \cdot (\text{OH})_z]$ were reported with $T_c=480\text{K}$. However, a metal-free organic room temperature molecule-based magnet is not reported until now.

2.6 Recent research on charge transfer single crystals

Charge transfer compounds study of FET and magnetic are discussed in Chapter 2.4.2 and 2.5.2. In this section, the conductivity, superconductivity and some new properties in organic charge transfer compounds are reviewed.

Organic compounds are good insulators due to van der Waals interaction. In the early of

20th century, McCoy and Moore⁶⁵ predicted that people could not synthesize organic conductors. Until 1973, TTF - TCNQ⁶⁶ charge transfer compounds were synthesized, it is the first organic conductor with $\rho=500$ S/cm. After that, lots of researchers are jumping into the field to find new conductors to increase the conductivity, even superconductors. In 1980, Bechgaard et al. found that (TMTSF)₂-PF₆⁶⁷ charge transfer compounds show superconductivity below 0.9 K under 1.2×10^9 Pa. It is the first organic charge transfer compound which shows superconductivity. In 1990, the superconducting critical temperature was increased to 12.5 K in κ -(BEDT-TTF)₂-Cu[N(CN)₂]⁶⁸ organic charge transfer compounds. Organic conductors and superconductors are very important to electronic applications because they are not only as good as metals, but also more light and flexible. Recent research is focused on how to improve conductivity, multifunctionality, stability.

The exchange interaction between two electrons can bind together, forming biexcitons. But in organic semiconductors, two excitons bind together were not found. In 2002⁶⁹, the first direct evidence, by X-ray diffuse scattering, of lattice-relaxed charge transfer exciton strings was reported, which are one-dimensional self-trapped multiadjacent excitons. The result provides a new way to get multiple excitons bound state in organic semiconductors.

Organic ferroelectrics are rare. The first ferroelectric organics was discovered in 1920⁷⁰. The transition temperature is always below room temperature. Organic charge transfer compounds provide a possibility to room temperature organic ferroelectrics. The regular intermolecular separation of $\cdots\text{DA}\cdots\text{DA}\cdots$ sequence is leading a symmetry broken to form a polar chain⁷⁰. In very recent, charge transfer compound of pyromellitic diimide-TTF⁷¹ shows room temperature ferroelectricity. The organic charge transfer compounds provide the flexibility of designing new devices due to its unique correlated electron dynamics⁷⁰.

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Chapter 3

Experimental Methodology

In this chapter, the experimental apparatus and basic principle of characterization techniques will be introduced. It includes: 1. Materials purification method and apparatus; 2. Solution growth apparatus of organic single crystal; 3. Vapor growth apparatus of organic single crystal; 4. FET device fabrication and surface modification; 5. Characterization method: powder X-ray diffraction, single crystal X-ray diffraction, Infrared spectroscopy, Raman spectroscopy, photoluminescence spectroscopy, thermogravimetric analysis, atomic force microscopy and vibrating sample magnetometer.

3.1 Chemicals

Chemicals used in this thesis are listed below (Table 3.1).

Table 3.1 Chemicals used in this thesis.

Reagent	Purity	Company
Perylene	99%	Sigma-Aldrich
TCNQ	99%	Sigma-Aldrich
F ₄ TCNQ	99%	Jilin OLED
Perfluorodecyltrichlorosilane	97%	Sigma-Aldrich
WO ₃	99.99%	Sigma-Aldrich
MoO ₃	99.99%	Sigma-Aldrich
Sulphur	99.99%	Sigma-Aldrich
F ₁ TCNQ	99%	TCI, Japan
F ₂ TCNQ	99%	TCI, Japan

3.2 Organic chemical purification

Organic materials dislike inorganic ones; always have low purity due to catalyst in the synthesis process, oxidation products, and side products. These impurities will affect the crystal growth process, which lead a bad quality of crystals. Thus, it is important to remove some impurities from source materials before single crystal growth.

Vacuum purification was employed to purify the source materials. The apparatus is shown in Figure 3.1. One end of the quartz tube is sealed, and the other end is connected to a high-vacuum pump, which removes volatile impurities. The source materials put in a tube and then put the tube in the semi-open tube located in Zone 1. Then, the open side is connected to a vacuum pump. The vacuum is 10^{-5} bar. Then the temperature in Zone 1 is increased to the sublimation temperature of source materials. In vacuum, the sublimation temperature of materials will be lower than in the atmosphere. When heating the source materials, the solid source will transform to gas and deposit at low temperature zone (Zone 2). Due to the molecular weight of target materials and impurities are different, the purified materials sublime in zone 2 of the furnace and impurities deposited upstream or downstream. Purified F₄TCNQ and impurities separated along quartz tube are shown in

Figure 3.2. The impurity in F₄TCNQ shows yellow and green colour in the downstream position of the quartz tube. The purified F₄TCNQ shows orange and red colour in the upstream zone.

Figure 3.1 Vacuum purification apparatus (a) and temperature-furnace length profile (b).

Figure 3.2 F₄TCNQ after vacuum purification.

All organic materials were purified in this thesis, the purify vacuum is 10^{-5} bar. Different chemicals have different sublimation temperature leads the purification temperature changed. The details of purification temperatures are listed in Table 3.2.

Table 3.2 Purify temperatures parameter of Zone 1 and Zone 2.

Materials	Temperature in Zone 1	Temperature in Zone 2
Perylene	160 °C	120 °C
TCNQ	160 °C	120 °C
F ₄ TCNQ	180 °C	120 °C
F ₁ TCNQ	180 °C	120 °C
F ₂ TCNQ	180 °C	120 °C

3.3 Single crystal growth by solution

Slow cooling method was used to grow charge transfer single crystal compounds. A precise temperature-controlled water bath was employed. The optical photo was shown in Figure 3.3.

Figure 3.3 Slow cooling growth apparatus.

Figure 3.4 Precise temperature control profile for charge transfer single crystal growth. The temperature sequences are: 1, temperature increasing from room temperature to 80 °C by 2 hours; 2, dwells at 80 °C for 1 hour to equilibrium; 3, slow cooling rate at 1 °C/hour or lower.

Precise temperature control is achieved with the heating tube and temperature feedback system (red square in Figure 3.3). The temperature decreasing rate can be as slow as 0.5 °C/hour. In the experimental process, the plot of temperature versus time shows in Figure 3.4. In the beginning, the temperature is increased to 80 °C to dissolve more solute in the solvent. Then the system is achieved equilibrium at 80 °C for one hour. After that, the cooling rates are set as 1 °C/hour or lower to grow the single crystals. This system can avoid the temperature fluctuations, which can increase the chance of growing high quality charge transfer single crystals.

3.4 Single crystal growth by vapour phase

A two-zone tube furnace was used to grow charge transfer compound single crystals. The optical photo shows the setup in Figure 3.5.

The temperature increase rate is about 10-20 °C/min and the dwell temperature is set and control by the temperature controller. The setting temperatures of Zone 1 and Zone 2 are determined by the sublimation point of organic materials. This information can be obtained from literature or TGA measurement.

Figure 3.5 A two-zone furnace set-up. Two-zone gold coated furnaces are hung and the temperature of the two zones controlled by a temperature feedback system (indicates as red).

3.5 Field effect transistor device fabrication

3.5.1 Device configuration

Compared with TFT, OSCFET has the similar device configuration¹. Two common device structures are used in this thesis. They are top-contact, bottom-gate structure and bottom-contact, bottom-gate structure, as shown in Figure 3.6.

Figure 3.6 Different OSCFET configurations. (a) top-contact, bottom-gate; (b) bottom-contact, bottom-gate.

In both configurations, Si / SiO₂ substrate is easy to realize the FET device. Doped-Si used as gate electrode and a 600 nm oxidation layer used as dielectrics. In a top-contact, bottom-gate structure, single crystal firstly aligns onto the substrate. Then, source and drain electrodes are directly deposited on the surface of the crystals (Figure 3.6a). Different metals are selected to tune the work function to the LOMO and HOMO of organic materials which can improve the injection from electrode to organic materials². The most common way to get the source and drain electrodes is thermal evaporation or e-beam deposition. However, thermal evaporation of metals is always designated due to less harmful to single crystals. Generally, a cleaned or surface modified Si / SiO₂ substrate was put into the crystal growth quartz tube. After crystal growth, crystals can directly grow onto the Si / SiO₂ substrate, as shown in Figure 3.7a. Then, a mask was

used to get a pattern onto the surface of crystals (Figure 3.7b). After gold deposition, source and drain electrodes were obtained by removing the mask (Figure 3.7c). In a bottom-contact, bottom-gate structure, source and drain electrodes are firstly deposited onto the Si / SiO₂ substrate. After that, a very thin and surface smooth crystal laminated on the electrodes (Figure 3.6b). The thickness of crystals are less than 500 micrometers is favorable. The thin crystal with a smooth surface will adhere to the Si / SiO₂ substrate naturally due to electrostatic forces. While, thick crystals are very difficult to adhere to the Si / SiO₂ substrate.

Figure 3.7 Crystal growths on the Si / SiO₂ substrate (a); cover with a mask (b); after deposition gold and remove mask (c).

3.5.2 Si / SiO₂ substrate cleaning

No matter what configuration is used, Si / SiO₂ substrate need clean enough to avoid other contaminants on the surface influence the device performance. The cleaning procedure of Si / SiO₂ substrate is shown in Figure 3.8.

Figure 3.8 Procedure of cleaning the Si / SiO₂ substrate.

3.5.3 Si / SiO₂ substrate surface modification

OH group forms on the surface of SiO₂ due to the non-bridging oxygen in the films³. It is considered as an electron trap, which can decrease the performance in an OSCFET⁴. Therefore, elimination the OH group on the surface of Si / SiO₂ substrate is necessary. Self-assembled monolayers methods are commonly used to avoid the OH group forming. Such SAM molecules contain a head with a functional group which can react with OH group on the surface and a long tails to avoid OH group forming again. The devices with SAM substrate always shown higher mobility compared with non-SAM substrate ones⁵⁻⁷. The most common used SAM molecular is OTS, which has a head with Si and Cl and an 18 C alkyl tail. The structure of OTS and self-assemble schematic diagram are shown in Figure 3.9.

Figure 3.9 Octadecyltrichlorosilane molecular structures (a); Self-assembly on the Si / SiO₂ substrate (b).

Figure 3.10 Molecular structure of OTS (a); Ben-OTS (b) and F-OTS (c)

Due to the OH group is not form on the surface of Si / SiO₂ substrate, the surface is hydrophobic. Therefore, the contact angle is a good way to the check the surface whether

the surface is well self-assembled. More hydrophobic means larger contact angle, which means better self-assemble quality. When changing the head function, the self-assembled quality is also changed. Accordingly, three different SAM molecules (shown in Figure 3.10) were tested to determine which one shows the best self-assemble quality. The contact angle images of the three molecules are shown in Figure 3.11.

Figure 3.11 Contact angle of bare Si / SiO₂ substrate (a); Ben-OTS modified (b); OTS modified (c) and F-OTS modified (d).

From the contact angle result, the non-modified substrate shows lowest contact angle, which means OH group formed on the surface. After SAM modified, the surface turns to hydrophobic. The OTS and F-OTS (structure in Figure 3.10) modified surface shows larger contact angle, which is suitable for device fabrication. F-OTS is selected for SAM in this thesis. The SAM procedure is relative simple. Cleaned Si / SiO₂ substrates were put in a glass petri dish and then put into a vacuum oven for 1 hours at 120 °C for removal of free water molecules. After that, 50 mL F-OTS solution drop quickly in the center of the petri dish. When finished the drop process, the system was put in vacuum again. The temperature is maintained at 120 °C for 2 hours for the hydrolysis reaction between the

SiCl₃- group and the SiO₂ surface. When the SAM process finished, the Si / SiO₂ substrates are rinsed and ultrasonicated in chloroform and IPA for 5 minutes in order to remove excess F-OTS molecules. Then, the substrates are dried under N₂ flow for device fabrication.

3.6 Characterization

3.6.1 Powder X-ray diffraction

The electrons in an atom can scatter light and such atoms can diffract light if they are periodically arranged. The wavelength of X-rays ($\sim 1 \text{ \AA}$) is similar with the distance between atoms. Therefore, from the atoms, scattering of X-rays produces a diffraction pattern when Bragg's Law is satisfied. Generally, an X-ray tube, a sample holder and an X-ray detector are the basic parts in an X-ray diffractometers. Two configurations are always used in an X-ray diffractometers: θ - θ and θ - 2θ configuration. In a θ - θ configuration, both the detector and X-ray tube make the same angle θ movement and the sample holder is fixed. In a θ - 2θ configuration, the X-ray tube is fixed and the detector moves the angle of 2θ while sample just moves θ (shown in Figure 3.12). The powder X-ray diffraction data are used to identify the phase, crystallinity, lattice parameters, particle size and so on. Furthermore, by using Rietveld method, the refined structure can be also obtain from the powder X-ray diffraction data.

Figure 3.12 Schematic diagram of a simple X-ray powder diffractometer with θ - 2θ configuration.

In this thesis, the powder X-ray diffraction data were obtained with a Bruker D8 Advance diffractometer ($\text{CuK}\alpha=1.5406\text{\AA}$ radiation at 45kV, 30mA). The ranges from 5° to 40° with a step size of 0.02° and a dwell time of 10 seconds per step.

3.6.2 Single crystal X-ray diffraction

More reliable atomic parameters, such as positional and thermal, can be obtained by using a single crystal X-ray diffractometer. The summary of this technique is shown in Figure 3.13⁸. The same as powder X-ray diffraction, diffraction pattern with positions and intensities is obtained when Bragg's Law is satisfied. Then the electron density distribution is obtained by mathematics calculation. The atoms are positioned at the maximum position of electron density. Then, from a structural model, the atoms position, atomic coordinates, bond length are determined.

Figure 3.13 Summary diagram of a single crystal X-ray diffraction technique.

In this thesis, the single crystal structures were collected using Bruker SMART APEX II single crystal diffractometer (X-ray radiation, $\text{Mo K}\alpha$, $\lambda=0.71073\text{\AA}$).

3.6.3 Infrared spectroscopy

Figure 3.14 shows the whole electromagnetic spectrum, while infrared spectrum is just part of that between the visible regions and microwave regions. Infrared spectroscopy is analyzing the infrared light interact with molecules. The molecules absorb specific frequencies, which are the characteristic frequencies of specific bonds vibration. It means

the absorbed radiation is matching the energy of the bond vibrations. In other words, when an infrared light goes through a sample, some frequencies are absorbed by the sample, while some frequencies are passed through the sample without absorption. Different vibration modes have different absorption frequencies. Wavenumber, cm^{-1} , is preferred to be the unit of infrared spectrum. Especially in organic charge transfer compound, the infrared spectrum is always used to determine the occurrence of charge transfer and calculate the degree of charge transfer.

One common method for solid sample is to grind small amount samples with KBr to fine particles. Then, the mixture is mechanically pressed into a transparent pallet, which can let the infrared light pass by.

Figure 3.14 Electromagnetic spectrum.

In this thesis, IR measurements were taken using a Perkin Elmer Spectrum GX spectrometer with a spectral resolution of 2 cm^{-1} in a range of $400\text{--}4000 \text{ cm}^{-1}$. The single crystals mixed with KBr (Sigma-Aldrich) were completely grounded and then pressed into pellets for measurement.

3.6.4 Raman spectroscopy

Both infrared and Raman are common vibrational spectroscopies for identifying molecules. Some vibrational modes of molecules are infrared active and some vibration

modes are Raman active. Figure 3.15 shows the energy-level diagram involved in Raman signal. A laser (monochromatic light source) was used produce light to expose on the surface of the sample. Then, the sample scatters the light. The majority of scattering light have the same frequency as the excitation light, called Rayleigh scattering. The rest of the scattering light is changing the frequency due to the incident electromagnetic waves interact with vibrational energy of the molecules of the sample. If the excitation frequency is larger than scattering frequency, it is named Stokes Raman scattering. Otherwise, it called anti-Stokes Raman scattering. Compared with infrared, Raman shows the properties by scattering the light of the sample against absorbing the light. Therefore, Raman spectroscopy can measure without sample preparation and it is insensitive to the water absorption bands. It makes the Raman measurement directly on the sample surface without damage. In Raman spectroscopy, some Raman active modes are sensitive to polarized light. The crystal symmetry and orientation information can be obtained from the polarization of Raman peaks.

Figure 3.15 Energy-level diagrams for Rayleigh and Raman scattering.

In this thesis, Raman spectra were recorded using a Renishaw Raman microscope

configured with a charge-coupled device array detector with the excitation laser line of 532 nm.

3.6.5 Photoluminescence spectroscopy

Photoluminescence spectroscopy is a method to probe the electronic structure of materials, which is contactless and non-destructive. An electron is excited from valance band to excited state by photon. The excited state has higher energy than conduction band. The excited electron will relax to the conduction band through non-radiative relaxation. When the electron falls to the valence band, the energy will transform into a luminescent photon. The photon is emitted from materials and the energy is band gap. The detail process is shown in Figure 3.16.

From the length of lifetime, photoluminescence can be divided into two forms: fluorescence and phosphorescence. Fluorescence undergoes an internal energy transition with shorter lifetime, while phosphorescence undergoes an intersystem crossing with a longer lifetime, as shown in Figure 3.17 lifetime of fluorescence is around 10^{-8} to 10^{-4} seconds and that of phosphorescence is 10^{-4} - 10^{-2} seconds.

Figure 3.16 Energy scheme of photoluminescence.

Figure 3.17 Energy scheme of fluorescence (a) and phosphorescence (b).

In this thesis, the laser beams (solid-state laser, 473 nm and Nd:YAG solid-state laser, 532 nm) were collimated and focused through a $\times 100$ objective onto the sample surface. All the photoluminescence spectra were collected using a confocal triple-grating spectrometer (Horiba-JY T64000).

3.6.6 Thermo-gravimetric analysis

Thermo-gravimetric analysis is a technique, which measures the weight loss or gain of samples in the heating or cooling process with temperature or time in a selected atmosphere. In order to obtain the weight change, a precision balance is used. The mass changes of the sample are recorded during the experiment. Purging gas controls the atmosphere, such as argon, oxygen. Thermo-gravimetric analysis can provide not only physical phenomena including adsorption, sublimation, absorption, vaporization; but also chemical phenomena like decomposition.

In this thesis, sublimation rates were not measured during the crystal growth process but were measured as a function of time in a thermal gravimetric analyzer, TGA. (TA Instruments, Model Q500). Platinum TG pans were filled with samples for TGA measurement. In TGA experiments, a purge gas of argon with 40 mL/min was used.

3.6.7 Atomic force microscopy

Atomic force microscopy is one kind of scanning probe microscopy. It shows very high resolution with nanometres resolution and obtains the surface information of samples. A typical working mechanism scheme of AFM is shown in Figure 3.18.

The AFM tips interact with the surface of the sample by surface force when it is scanning the sample surface. When the topography is changing, the atomic force also changes. Such changed atomic force causes the bending of the cantilever. Therefore, a laser beam focusing on the cantilever is used to supply a signal. The signal is then reflected to a position sensitive photodetector. After that, the photodetector gives feedback signal to the scanner to make a constant force on the tip. Such information finally transferred to a topography image. Two work modes are always used: contact mode and non-contact mode. The contact mode is to keep the cantilever at a constant position, so called static mode. Non-contact mode makes the tip oscillated at resonance frequency and the amplitude of the oscillation is kept constant.

Figure 3.18 Schematic operation of atomic force microscopy.

In this thesis, atomic force microscopy was performed on a Digital Instruments 3100.

3.6.8 Vibrating sample magnetometer

Magnetic properties of materials with temperature or magnetic field can be measured by

a vibrating sample magnetometer. A typical vibrating sample magnetometer schematic diagram is shown in Figure 3.19.

When a magnetic material is put into a uniform magnetic field, the materials will be magnetized by the uniform magnetic field through aligning the magnetic spins. The magnetization of the materials is determined by the applied field. The stronger applying field, the larger magnetization will obtain. The magnetic moment of the materials will generate a magnetic field around the materials. Such generated magnetic field will be changed by moving up and moving down of the materials. These changes can be detected by the pickup coils, shown in Figure 3.18. The alternating magnetic field causes the electric field changes in the pickup coils due to Faraday's Law of Induction. Therefore, the current or voltage in the pickup coils can be obtained. The current or voltage is proportional to the magnetization of materials, but does not rely on the applied field. Generally, the greater magnetization brings lager induced current or voltage.

Figure 3.19 Schematic diagram of vibrating sample magnetometer.

In this thesis, magnetic measurements were carried out with a Physical Property Measuring System, PPMS (Quantum Design Inc., USA) equipped with a vibrating sample magnetometer (VSM) probe.

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Chapter 4

Perylene-TCNQ charge transfer compound single crystals

In this chapter, the crystal growth and charge transport properties of perylene and TCNQ single crystals are investigated. Further, perylene-TCNQ charge transfer compound single crystals with different stoichiometry were grown from solution. We found that the stoichiometry of final perylene-TCNQ charge transfer compound depends on the using solvent, but not depends on the starting stoichiometry of perylene and TCNQ. (perylene)₁(TCNQ)₁ (P1T1) is grown from toluene and (perylene)₃(TCNQ)₁ (P3T1) is grown from benzene, no matter what stoichiometry of perylene and TCNQ are used in the beginning. The reason for such phenomenon is explained by solubility data and optical spectrum. By using PVT method, a mixture of monomolecular crystals and all three charge transfer compound single crystals (P1T1, P2T1 and P3T1) are obtained. Beside P1T1 and P3T1, (perylene)₂(TCNQ)₁ (P2T1) is a new phase, which is not published. After that, the charge transfer and charge transport properties of all three compounds are investigated. It shows that from P1T1 to P3T1, the increase of perylene molecules in the unit cell may lead to the transformation of the single crystal from n-type to p-type.

4.1 Introduction

TCNQ (the molecular structure is shown in Figure 4.1b) is firstly synthesized in 1962¹. After that, lots of properties about TCNQ were published, such as optical properties^{2,3}, electrical properties⁴, charge transport properties⁵, photo-electrical properties⁶ and so on. TCNQ is a good n-type semiconductor and shows a mobility of $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ by using free-space gate dielectrics⁵. TCNQ shows an electron affinity around $3.0 \text{ eV}^{7,8}$, which is a good acceptor to form charge transfer compounds with donors. TCNQ based charge transfer compounds single crystals are widely investigated due to the finding of the organic metal TTF-TCNQ in 1973⁹. TTF-TCNQ shows highest conductivity with a value of $1.4 \times 10^4 \Omega^{-1}\text{cm}^{-1}$ at 66K^9 compared with other TCNQ based charge transfer compound single crystals. However, some TCNQ based charge transfer compounds show metal-insulator transition^{10,11}. TCNQ based charge transfer compounds also show special magnetic properties, such as meta-, ferro- or para-magnets¹².

Perylene (the molecular structure is shown in Figure 4.1a) is a planar organic assembled with five benzene rings. It is a donor with high ionization energy¹³, about 6.96 eV . Perylene is often used as a basic block for synthesise new compounds, which is widely used as transistors¹⁴⁻¹⁶, solar cells¹⁷, gas sensors¹⁸ and so on.

Figure 4.1 Molecular structure of perylene (a) and TCNQ (b).

Perylene and TCNQ form two types of binary compounds with different stoichiometries, P1T1 (perylene1:TCNQ1) and P3T1 (perylene3:TCNQ1). These two stable charge transfer compounds were previously reported: P1T1^{19,20} and P3T1^{21,22}. Solution methods were employed to grow these two compounds. Tetrahydrofuran and a mixed solvent of benzene and acetonitrile in a 5:1 mole ratio was used to grow P1T1, while benzene was used to grow P3T1. However, the effect of stoichiometry and molecular packing on the charge transport properties as a function of composition was not reported.

Figure 4.2 Possible ways to change the properties of charge transfer compound single crystals.

Most of the reported organic charge transfer compound single crystals are binary ones. Compared with the case of the inorganic binary compounds, where well-documented libraries of phase diagrams provide useful information on the stoichiometry control and phase co-existence, it is striking that such phase diagrams for *organic* binary compounds are rather rare²³⁻²⁸. Nevertheless, the availability of this information is extremely crucial in controlling the properties of single crystals of charge-transfer binary compounds due to such properties are strongly linked to the crystal structures. One example is the charge transfer degree, which is coupled to the electrical properties²⁹. That, in turn, is affected not only by the type of molecules of which the binary compound is built, but also by the molecular packing and the molecular stoichiometry^{29,30}. Figure 4.2 shows the possible

way to change the properties of charge transfer compound single crystals. The easiest way is to change the properties of donors and acceptors. There are several methods: 1) Design new structure which does not a modification of known structure. For example, C₆₀ is a new structure compared with aromatic structure. 2) Add side chains or groups to a known framework. Such as pentacene, 6,13-Bis(triisopropylsilylethynyl)pentacene. 3) Substitute the carbon atoms to sulfur, nitrogen, selenium and so on. Besides changing the properties of donors and acceptors, varies of the stoichiometry between donors and acceptors still provide a method to tuning the properties.

In this chapter, TCNQ and perylene individual single crystals were grown and the charge transport properties were investigated. After that, the charge transfer compound single crystals of perylene and TCNQ were grown by solution method and vapor method. It was also shown that the stoichiometry of a binary organic charge-transfer compound depends upon the stoichiometry of the starting materials^{31,32}. Nevertheless, by using solution method, we observed an interesting phenomenon: the final stoichiometries of single crystal P1T1 and P3T1 are not affected by the stoichiometry of the starting materials, but by the solvent which we choose for the growing of perylene-TCNQ crystals. The P1T1 crystals were grown from toluene, whereas the P3T1 crystals were grown from benzene regardless of the acceptor/donor stoichiometry in the starting materials. Furthermore, by utilizing the PVT method, a mixture of monomolecular crystals, P1T1 (perylene1:TCNQ1), P2T1 (perylene2:TCNQ1) and P3T1 (perylene3:TCNQ1) is obtained. The solubility data is used to analyze the effect of the selection of solvent on the stoichiometry of the perylene-TCNQ charge transfer single crystals. Steady-state optical spectra and time-resolved fluorescence were measured in a mixture of perylene and TCNQ in toluene and benzene, revealing that the difference in the solubilities of TCNQ in benzene and toluene leads to different fluorescence spectra due to selective crystallization of P1T1 and P3T1 from toluene and benzene. The charge transfer properties and electrical transport properties of the charge transfer single crystals by using two methods were evaluated and compared.

4.2 Experimental Methods

4.2.1 Chemicals and materials

TCNQ (>99%), perylene (>99%), toluene (>99%), benzene (>99%), chlorobenzene (>99%), xylene (>99%) and acetonitrile (>99%) were purchased from Sigma-Aldrich. Perylene and TCNQ were purified at 180 °C and 220 °C via PVT³³, respectively. The solvents (toluene, benzene and acetonitrile) were used without further purification.

4.2.2 SiO₂/Si substrates clean procedure

All the SiO₂/Si substrates were firstly immersed H₂O₂ /H₂SO₄ (1 volume / 4 volume) for 10 min at 160 °C in order to remove organic compound physically absorbed on the substrates. Then, they were successively cleaned with distilled water and isopropyl alcohol in an ultrasonic bath for 5 min and then dried in ambient N₂. F-OTS was used to modify the surface of the substrates by PVT method.

4.2.3 Solution growth of TCNQ and perylene single crystals

Perylene or TCNQ was dissolved in acetonitrile in a test tube. After ultrasonication at room temperature for 15 min, the test tubes were placed in a temperature-controlled water bath (see Chapter 3, Figure 3.3). The initial temperature of the water bath was set at 80 °C, with a cooling rate of 0.5 °C/hr. The starting materials were nearly all dissolved at 80 °C after 2 hrs. A small quantity of precipitated starting materials remained in the tube indicating that the solution was saturated. Single crystal growth was observed with decreasing temperature and crystals were isolated from the solution when the bath reached 20 °C.

For crystals directly grown on the substrate, perylene or TCNQ saturated solution were utilized. The saturated solution (acetonitrile and benzene as solvent were used) was heated to 60 °C for several minutes. A small quantity of precipitated starting materials remained in the tube at 60 °C indicating that the solution was saturated. 100 µL saturated solution were directly dropped onto the substrate. With slowly evaporation of the solvent, the crystals were formed on the surface of substrate.

4.2.4 PVT growth of TCNQ and perylene single crystals

The growth apparatus is shown in Chapter 3, Figure 3.5. Perylene or TCNQ was placed in Zone 1 with temperature 200 °C and the temperature of Zone 2 was set at 120 °C. Argon was fed as carrier gas with a flow rate at 60 sccm in the whole process. The crystal growth time is around 1 to 2 hours.

4.2.5 Solution growth of P1T1 and P3T1 single crystals

Perylene and TCNQ with mole ratios of 1:1, 2:1 and 3:1 were weighed and put in capped test tubes. Benzene or toluene was added to each test tube for crystal growth. After ultrasonication at room temperature for 15 min, the test tubes were placed in a temperature-controlled water bath (see Chapter 3, Figure 3.3). The initial temperature of the water bath was set at 80 °C, with a cooling rate of 0.5 °C/hr. The starting materials were nearly all dissolved at 80 °C after 2 hrs. A small quantity of precipitated starting materials remained in the tube indicating that the solution was saturated. Single crystal growth was observed with decreasing temperature and crystals were isolated from the solution when the bath reached 20 °C.

4.2.6 PVT growth of P1T1, P2T1 and P3T1 single crystals

The growth apparatus is shown in Chapter 3, Figure 3.5. Perylene was placed in Zone 1 with temperature 200 °C and TCNQ was placed in Zone 2 with temperature 210 °C. Argon was fed as carrier gas with a flow rate at 60 sccm in the whole process. The crystal growth time is around 4 to 6 hours.

4.2.7 Solubility measurements for perylene, TCNQ, P1T1 and P3T1

To measure the solubility of the charge transfer compounds and individual components, solvent was added to a known quantity of single crystal in a sealed test tube to avoid evaporation of the solvent. The temperature was slowly increased to the target temperature. Then, the solution was stirred at target temperature overnight (longer than 20 hours). Saturation was confirmed by the presence of residual undissolved crystals. Then, 1-mL quantities of the saturated solutions were placed into glass bottles and weighed before and after solvent evaporation. The solubility of the single crystal was

calculated from the difference in weight. The same procedure was repeated for benzene and toluene.

4.2.8 Device fabrication and electrical measurements

OSCFETs were fabricated on a 600 nm SiO₂/Si substrate. The Si is heavily n-type doped, which is used as gate electrode. A thin bar copper grid (model: M200-CR) was used as mask. Gold was as electrode materials.

I-*V* characteristics of all the OSCFETs were measured using a Keithley 4200-SCS and a micromanipulator probe station with a shielded box at room temperature in atmosphere.

4.2.9 Characterization

The crystal structures of perylene, TCNQ, P1T1, P2T1 and P3T1 single crystals were obtained using a Bruker SMART APEX II single crystal diffractometer (X-ray radiation, Mo K α , $\lambda = 0.71073$ Å). The steady-state fluorescence emission and excitation spectra were recorded on a spectrofluorometer (Fluorolog-3, HORIBA Jobin Yvon). The time-resolved fluorescence measurements were carried out at room temperature by the time-correlated single photon counting (TCSPC) technique with a resolution of 10 ps (PicoQuant PicoHarp 300). The second harmonic of a titanium-sapphire laser (Chameleon, Coherent Inc.) at 400 nm (100 fs, 80 MHz) was used as the excitation source.

4.3 Results and discussion

4.3.1 Perylene and TCNQ single crystals growth and structures

The perylene single crystals were grown from benzene and TCNQ single crystals were grown from acetonitrile by slow cooling. The perylene crystals show planar morphology and TCNQ is needle-like, as shown in Figure 4.3. The maximum length of TCNQ is around 5 millimeters. The maximum perylene crystal is 3 mm $\times$ 3 mm square. However, the perylene crystals are very thick.

By using PVT method, the morphology of perylene and TCNQ is quite the same as solution method. Perylene shows square planar and TCNQ is also needle-like, shown in Figure 4.4. TCNQ shows longer length with 1.5 centimeters and perylene shows larger

area compared with solution method. Meanwhile, the perylene crystals are thinner than solution growth ones. The planar structure of the perylene molecules is leading the formation of planar single crystals.

Figure 4.3 Optical images of perylene (a) growth in benzene and TCNQ (b) grown in acetonitrile.

Perylene crystals can directly grow on the SiO_2/Si substrate. The acetonitrile, chlorobenzene, toluene and xylene are used as solvent to prepare saturated perylene solution. Then, the solution is directly dropped on the substrate. The optical images of perylene single crystals are shown in Figure 4.5. All the perylene single crystals have the same parallelogram morphology. The size of the solution drop-casted single crystals is about $100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$. Some crystals are very thin and some are thick. Meanwhile, the surface of the thin perylene crystals is very flat. By solution drop-casting, the largest crystals can reach $2.5\text{ mm} \times 2.5\text{ mm}$ (Figure 4.6). However, the surface is not perfectly smooth.

AFM images of a thin perylene single crystal grown by solution drop-casting method on a SiO_2/Si substrate were shown in Figure 4.7. The thickness of the crystals is around 170 nm. The thickness of perylene single crystals can vary from 50 nm to several micrometers by solution drop-casting method. The mean roughness of most thin crystals was less than 1 nm, which indicates that such surface is atomically flat. From Figure 4.5, some thick perylene crystals can also obtain in the same procedure, which due to the crystal is grown along the thickness direction.

Figure 4.4 Optical images of perylene (a) and TCNQ (b) grown by PVT.

Figure 4.5 Optical images of perylene single crystals by solution drop-casting method on a SiO_2/Si substrate. (a) use acetonitrile as the solvent; (b) use xylene; (c) use toluene; (d) use chlorobenzene.

Figure 4.6 Optical images of the largest perylene crystal by solution drop-casting of saturated xylene solution.

Figure 4.7 AFM images of a thin perylene single crystal grown by solution drop-casting method on a SiO_2/Si substrate (xylene used as solvent) and the corresponding section analysis.

The TCNQ crystals can also grow through solution drop-casting method. The optical images are shown in Figure 4.8. Several researchers indicated that the solvent plays an important role in organic molecular crystallization^{34,35}. Four solvent (acetonitrile, chlorobenzene, toluene and xylene) are used to grow TCNQ crystals directly on the SiO_2/Si substrate. However, TCNQ crystals were successfully grown only by using acetonitrile as solvent. The TCNQ single crystals exhibit rhombus morphology and the thickness is several micrometers.

Figure 4.8 Optical images of TCNQ single crystals by solution drop-casting method on a SiO₂/Si substrate. (a) low magnification; (b) high magnification.

Table 4.1 Crystallographic data for perylene and TCNQ derived from single-crystal X-ray diffraction data.

	Perylene	TCNQ
Formula	C ₂₀ H ₁₂	C ₁₂ H ₄ N ₄
Crystal system	Monoclinic	Monoclinic
Space group	P 1 21/c 1	C 1 2/c 1
Lattice parameter a (Å)	10.250(9)	8.891(4)
Lattice parameter b (Å)	10.818(3)	7.050(10)
Lattice parameter c (Å)	11.253(6)	16.394(2)
Lattice parameter (degree)	90	90
Lattice parameter (degree)	100.523(3)	98.530(3)
Lattice parameter (degree)	90	90
Cell volume (Å ³)	1227.0(2)	1016.29(4)
Formula units per cell Z	4	4
Temperature (K)	300K	300K
R-factors	0.0544	0.0348

Perylene crystals have two types of polymorphic modifications: the α phase and the β phase^{36,37}. In this thesis, the perylene crystals show α phase, no matter what method was

used to grow the single crystals. The perylene single crystals displayed a monoclinic symmetry, which belonged to the $P2_1/c$ space group with $a = 10.250(9)$ Å, $b = 10.818(3)$ Å, $c = 11.253(6)$ Å and $\beta = 100.523(3)^\circ$. The TCNQ single crystals also showed a monoclinic symmetry, which belonged to the $C2/c$ space group with $a = 8.891(4)$ Å, $b = 7.050(10)$ Å, $c = 16.394(2)$ Å and $\beta = 98.530(3)^\circ$. The selected crystal structure information is listed in Table 4.1. The molecular packing of perylene and TCNQ along a different direction is shown in Figure 4.9 and 4.10, respectively.

Figure 4.9 Molecular packing of perylene. (a) along (100) direction; (b) along (010) direction; (c) along (001) direction; (d) along (111) direction.

Figure 4.10 Molecular packing of TCNQ. (a) along (100) direction; (b) along (010) direction; (c) along (001) direction; (d) along (111) direction.

4.3.2 Charge transport properties of perylene and TCNQ single crystals

Perylene single crystal field effect transistor was fabricated with a top-contact, bottom-gate configuration, as shown in Figure 4.11. Gold is used as the source and drain electrodes.

Figure 4.11 Schematic device configuration (a) and the optical image of perylene field effect transistor (b).

The transfer curve and output curve of perylene transistor are shown in Figure 4.12. It shows p-type behavior. The average mobility of the devices is around $0.02 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in the linear region and $0.05 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in the saturated region. The maximum mobility is $0.05 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in the linear region and $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in the saturation region. The on-off ratio and the threshold voltage of the device are 3×10^4 and -31V , respectively.

Figure 4.12 Transfer curve (a) and output curve (b) of perylene transistor.

We found that our measured highest mobility is around 100 times higher than the published data³⁸. Several reports^{39,40} indicated that the surface of the perylene crystals is crucial for charge transport properties. The perylene transistor shows low mobility or even no field effect performance if the surface of the perylene crystals is rough.

TCNQ single crystal field effect transistor was fabricated with a top-contact, bottom-gate configuration, the same as perylene transistors shown in Figure 4.11. Gold is used as the source and drain electrodes.

Figure 4.13 Transfer curve (a) and output curve (b) of TCNQ transistor.

The transfer curve and output curve of TCNQ transistor are shown in Figure 4.13. It shows n-type behavior and the average mobility of the devices is $0.008 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The maximum mobility and on-off ratio are $0.02 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and 10^4 , respectively. The mobility is much lower than the reported value ($1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$)⁵, due to the use of different dielectrics. However, by using the same dielectrics, the mobility value is well agreed with the published data⁶.

4.3.3 P1T1, P2T1 and P3T1 single crystals growth and structures

By solution method, the single-crystal charge-transfer compounds (perylene)_n-(TCNQ)₁ with perylene and TCNQ stoichiometries of 1:1 (P1T1) and 3:1 (P3T1) were grown from toluene and benzene, respectively, for all three ratios of starting materials. The stoichiometry of the final single crystals was found to be influenced only by the solvent, not by the stoichiometry of the starting materials. Needle-like P1T1 single crystals (see Figure 4.14a) were grown from toluene, and cube-like P3T1 (Figure 4.14b) were grown from benzene.

Figure 4.14 Optical images of P1T1 crystals (a) and P3T1 crystals (b).

Figure 4.15 A mixture of perylene, TCNQ, P1T1, P2T1 and P3T1 by phases grown in an open PVT system with flowing argon gas.

By using PVT method, a mixture of monomolecular crystals, P1T1, P2T1 and P3T1 are obtained. An optical image of the mixture is shown in Figure 4.15. The yellow crystals are the starting materials: perylene and TCNQ. The dark color crystals are the charge transfer compounds. Needle-like P1T1 is easy to distinguish from plate-like P2T1 and cube-like P3T1 crystals. However, P2T1 and P3T1 have the same morphology and they can only distinguish with each other by single X-ray diffraction. It is important to know that P3T1 is often obtained while P2T1 is occasionally grown. Meanwhile, single crystalline P2T1 was never detected among the crystals grown by the solution method. The optical image of P2T1 is shown in Figure 4.16. The crystal is belt like and much smaller than P1T1 and P3T1.

The P1T1 single crystals displayed a monoclinic symmetry, which belonged to the $P2_1/c$ space group with $a = 7.3116(19) \text{ \AA}$, $b = 10.858(3) \text{ \AA}$, $c = 14.500(4) \text{ \AA}$ and $\beta = 90.276(5)^\circ$. The P2T1 single crystals showed a triclinic symmetry, which belonged to the $P-1$ space group with $a = 7.181(2) \text{ \AA}$, $b = 11.080(5) \text{ \AA}$, $c = 11.904(4) \text{ \AA}$, $\alpha = 103.81(4)^\circ$, $\beta = 102.91(3)^\circ$, and $\gamma = 101.32(1)^\circ$. The P3T1 single crystals also showed a triclinic symmetry, which belonged to the $P-1$ space group with $a = 10.411(3) \text{ \AA}$, $b = 10.862(1) \text{ \AA}$, $c = 12.574(2) \text{ \AA}$, $\alpha = 66.456(1)^\circ$, $\beta = 66.295(3)^\circ$, and $\gamma = 89.225(4)^\circ$. The selected crystal

structure information is listed in Table 4.2. The molecular packing of perylene and TCNQ along a different direction is shown in Figure 4.17, 4.18 and 4.19.

Figure 4.16 Optical image of P2T1.

The molecular packing of the three charge transfer compound single crystals are quite different. In the P1T1 crystals, the layers of perylene molecules are separated by layers of TCNQ molecules. The molecules of perylene and TCNQ are arranged mainly face-to-face “ π - π ” stacking (Figure 4.17b). In P2T1, two perylene molecules are inserted between adjacent TCNQ molecules. One perylene molecule is still face-to-face “ π - π ” stacking with near one TCNQ molecule, but between two “ π - π ” planes, another perylene molecule is “herringbone” packing with the near two TCNQ molecules (Figure 4.18b). The molecular packing of P3T1 is that two perylene molecules are located between each pair of TCNQ molecules, and a third perylene molecule is located between the perylene-TCNQ stacks. Two perylene molecules are respectively standing at the both sides of one TCNQ molecule and they are still face-to-face “ π - π ” stacking, but the third perylene molecule is “herringbone” packing with nearest two TCNQ molecules (Figure 4.19b).

Table 4.2 Crystallographic data for P1T1, P2T1 and P3T1 derived from single-crystal X-ray diffraction data.

	P1T1	P2T1	P3T1
Formula	$C_{32}H_{16}N_4$	$C_{52}H_{28}N_4$	$C_{72}H_{40}N_4$
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	P 21/c	P -1	P -1
Lattice parameter a (Å)	7.3116(19)	7.181(2)	10.411(3)
Lattice parameter b (Å)	10.858(3)	11.080(5)	10.862(1)
Lattice parameter c (Å)	14.500(4)	11.904(4)	12.574(2)
Lattice parameter (degree)	90	103.81(4)	66.456(1)
Lattice parameter (degree)	90.276(5)	102.91(3)	66.295(3)
Lattice parameter (degree)	90	101.32(1)	89.225(4)
Cell volume (Å ³)	1151.2(5)	864.8(6)	1175.1(4)
Formula units per cell Z	2	1	1
Temperature (K)	293	293	293
R-factors	0.0450	0.0412	0.0496

Figure 4.17 Molecular packing of P1T1. (a) along (100) direction; (b) along (010) direction; (c) along (001) direction; (d) along (111) direction.

Figure 4.18 Molecular packing of P2T1. (a) along (100) direction; (b) along (010) direction; (c) along (001) direction; (d) along (111) direction.

Figure 4.19 Molecular packing of P3T1. (a) along (100) direction; (b) along (010) direction; (c) along (001) direction; (d) along (111) direction.

4.3.4 Solvent-Dependent Stoichiometry of P1T1 and P3T1

By using solution method, we observed an interesting phenomenon: the final stoichiometries of single crystal P1T1 and P3T1 are not affected by the stoichiometry of the starting materials, but by the solvent which we choose for the growing of perylene-TCNQ crystals. The P1T1 crystals were grown from toluene, whereas the P3T1 crystals were grown from benzene regardless of the acceptor/donor stoichiometry in the starting materials, as shown in Figure 4.20. Furthermore, we dissolved P1T1 crystals in benzene to make a saturated solution at 80 °C and placed the test tubes in a temperature-controlled water bath. The initial temperature of the water bath was set at 80 °C, with a cooling rate of 0.5 °C/hr. When the solution returned to room temperature, we obtained P3T1 crystals. Similarly, we dissolved P3T1 crystals in toluene to make a saturated solution at 80 °C and cooled it slowly to room temperature obtaining P1T1 crystals.

Figure 4.20 Solution-grown charge transfer single crystals of P1T1 and P3T1 exhibit a stoichiometry which depends on the solvent used, and not on the initial stoichiometry of the perylene and TCNQ.

Precipitation-dissolution equilibrium theory is widely used to explain the salt effect and common-ion effect in a separate precipitation of ionic compounds from solution^{23,26,27,41,42}. Recently, it has been successfully applied to organic co-crystals^{23,43}. Therefore, the same theory was employed to understand the growth of the organic charge

transfer compounds. Donors partly transfer electrons to acceptors; thus, the donors are partly positively charged (δ^+), while the acceptors are partly negatively charged (δ^-). Therefore, the precipitation-dissolution equilibrium theory can also be applied to organic charge transfer systems. The charge transfer compound can be written as D_nA_m , in which D represents the donor, A the acceptor and n and m describe the stoichiometry of the donors and acceptors. Thus, the precipitation-dissolution equilibrium of D_nA_m in a given solvent can be presented as follows:

The solubility product constant (K_{sp}) is

$$K_{sp} = [D]^n [A]^m \quad (4-2)$$

in which $[D]$ is the donor concentration and $[A]$ is the acceptor concentration in the solvent.

In a precipitation-dissolution equilibrium state, the following relationship between the donor and acceptor is attained:

$$m[D] = n[A] \quad (4-3)$$

Equation (4-2) can be presented as follows:

$$K_{sp} = \left\{ \frac{n}{m} [A] \right\}^n [A]^m = \left[\frac{n}{m} \right]^n [A]^{m+n} \quad (4-4)$$

The relationship between the solubility and solubility product constant is

$$s = \frac{[A]}{m} = \frac{[D]}{n} = \sqrt[m+n]{\frac{K_{sp}}{(n/m)^n m^{m+n}}} = \sqrt[m+n]{\frac{K_{sp}}{m^m n^n}} \quad (4-5)$$

For P1T1 and P3T1, the precipitation-dissolution equilibrium equations are as follows:

Therefore, according to Equation (4-5), the relationships between the solubility and the solubility product constant for P1T1 and P3T1 are

$$s(P1T1) = \sqrt{K_{sp}} \quad (4-8)$$

$$s(P3T1) = \sqrt[4]{\frac{K_{sp}}{27}} \quad (4-9)$$

The enthalpy and entropy for reactions (6) and (7) can be calculated from the solubility product constant according to the following equation⁴²:

$$\ln K_{sp} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (4-10)$$

Equation (10) is linear in $1/T$ with a slope equal to $-\Delta H/R$ and a y-intercept of $\Delta S/R$. The enthalpy and entropy of dissolution can be calculated using the temperature dependence of the solubility product constant.

The solubility data of P1T1 and P3T1 are listed in Table 4.3. Note that in solution the chemicals with low solubility will precipitate first⁴⁴. The solubility of P1T1 is greater than that of P3T1 in benzene and lower in toluene. Consequently, P1T1 will precipitate first in toluene, and P3T1 will precipitate first in benzene.

Table 4.3 Solubility of P3T1 and P1T1 in toluene and benzene at different temperatures (mol/L)

		40 °C	50 °C	60 °C	70 °C	80 °C	40 °C
Toluene	P1T1	0.0006(7)	0.0008(3)	0.0008(6)	0.0009(2)	0.0010(1)	0.0006(7)
	P3T1	0.0029(6)	0.0031(7)	0.0037(4)	0.0048(3)	0.0056(7)	0.0029(6)
Benzene	P1T1	0.0025(4)	0.0025(8)	0.0030(2)	0.0032(9)	0.0046(4)	0.0025(4)
	P3T1	0.0014(1)	0.0016(6)	0.0017(6)	0.0021(1)	0.0026(4)	0.0014(1)

The following equilibria are assumed to occur:

In toluene, because P1T1 is less soluble than P3T1, the following equilibrium exist:

Consequently, P1T1 forms in toluene, in agreement with our experimental observations.

Similarly, in benzene, because P1T1 is more soluble than P3T1, the following

equilibrium exist:

Consequently, P3T1 crystals form in benzene.

All the possible equilibria were shown in Figure 4.21, indicating the crystal growth routes.

The K_{sp} values for P1T1 and P3T1 in toluene and benzene at various temperatures calculated from the solubility data according to Equations (8) and (9) are provided in Table 4.4 and 4.5.

These data show that the K_{sp} values for P1T1 in toluene are smaller than those in benzene for the temperature range 40 °C - 80 °C, while the opposite is true for the values corresponding to P3T1. The K_{sp} data indicate that P1T1 is more soluble than P3T1 in benzene and P3T1 is more soluble than P1T1 in toluene. The relationship between K_{sp} and solubility depends on the stoichiometry of the dissociation reaction⁴⁵. Accordingly, any direct comparison of K_{sp} values can only be made if the compounds have the same dissociation stoichiometry. To determine the thermodynamic data, the relationship between $\ln K_{sp}$ and $1/T$ was plotted in Figure 4.22.

In Toluene

In Benzene

Figure 4.21 All possible equilibria in the perylene-TCNQ system.

Table 4.4 Solubility product constant of P1T1 in toluene and benzene at different temperatures.

	40 °C	50 °C	60 °C	70 °C	80 °C
Toluene	1.12×10^{-7} ($\pm 0.11 \times 10^{-7}$)	1.73×10^{-7} ($\pm 0.11 \times 10^{-7}$)	1.87×10^{-7} ($\pm 0.11 \times 10^{-7}$)	2.12×10^{-7} ($\pm 0.11 \times 10^{-7}$)	2.54×10^{-7} ($\pm 0.11 \times 10^{-7}$)
Benzene	6.46×10^{-6} ($\pm 0.25 \times 10^{-6}$)	6.68×10^{-6} ($\pm 0.25 \times 10^{-6}$)	9.14×10^{-6} ($\pm 0.25 \times 10^{-6}$)	1.08×10^{-5} ($\pm 0.25 \times 10^{-6}$)	2.16×10^{-5} ($\pm 0.25 \times 10^{-6}$)

Table 4.5 Solubility product constant of P3T1 in toluene and benzene at different temperatures.

	40 °C	50 °C	60 °C	70 °C	80 °C
Toluene	2.08×10^{-9} ($\pm 0.17 \times 10^{-9}$)	2.74×10^{-9} ($\pm 0.17 \times 10^{-9}$)	5.31×10^{-9} ($\pm 0.17 \times 10^{-9}$)	1.48×10^{-8} ($\pm 0.17 \times 10^{-9}$)	2.79×10^{-8} ($\pm 0.17 \times 10^{-9}$)
Benzene	1.08×10^{-10} ($\pm 0.13 \times 10^{-10}$)	2.07×10^{-10} ($\pm 0.13 \times 10^{-10}$)	2.64×10^{-10} ($\pm 0.13 \times 10^{-10}$)	5.27×10^{-10} ($\pm 0.13 \times 10^{-10}$)	1.32×10^{-9} ($\pm 0.13 \times 10^{-10}$)

The slope and intercept were determined from the linear fit (see Equation 4-10). The enthalpy (ΔH) and entropy (ΔS) are presented in Table 4.6. The solubility product constants calculated for P1T1 and P3T1 in toluene and benzene at 25 °C are presented in Table 4.7.

Figure 4.22 Relationship between $\ln K_{sp}$ and $1/T$ (the black lines represent the fitting curves).

Table 4.6 Thermodynamic data for P3T1 and P1T1 in toluene and benzene.

	P1T1		P3T1	
	Toluene	Benzene	Toluene	Benzene
ΔH (kJ/mol)	17.06	26.23	62.78	54.17
ΔS (J/mol)	-77.75	-16.98	32.28	-18.47

Table 4.7 Solubility product constants of P3T1 and P1T1 in toluene and benzene at 25 °C.

	P1T1		P3T1	
	Toluene	Benzene	Toluene	Benzene
K_{sp}	8.88×10^{-8}	3.98×10^{-6}	4.83×10^{-10}	3.48×10^{-11}

From Equation (1), the precipitation constant, which indicates the ability to form the charge transfer compound from the donor and acceptor, is the reciprocal of K_{sp} . The Gibbs energy can be determined by using the K_{sp} values at different temperatures. The temperature dependence of the Gibbs energy to form P1T1 and P3T1 in the two selected solvents is shown in Figure 4.23. The Gibbs energy for P1T1 in toluene (~ -40 KJ/mol) is lower than that in benzene (~ -30 KJ/mol); the Gibbs energy of P3T1 in benzene (~ -60 KJ/mol) is lower than that in toluene (~ -52 KJ/mol). This is the reason why P1T1 is formed in toluene and P3T1 in benzene.

Figure 4.23 Temperature dependence of ΔG to form P1T1 and P3T1 in toluene and benzene.

The reaction quotient, Q , from reactions 6 and 7, can be calculated using concentrations of perylene in benzene or toluene and concentrations of TCNQ in benzene or toluene according to equations 15 and 16.

$$Q(P1T1) = [\text{perylene}][\text{TCNQ}] \quad (4-15)$$

$$Q(P3T1) = [\text{Perylene}]^3[\text{TCNQ}] \quad (4-16)$$

Then, we compared Q with the K_{sp} values. If $Q > K_{sp}$, precipitation will occur, but if $Q < K_{sp}$, no precipitates will form.

Figure 4.24 Solubility data of perylene and TCNQ in benzene and toluene.

From Figure 4.24, the solubilities of perylene and TCNQ (concentration in the saturation solution) in toluene are 5.1 mmol/L and 3.2 mmol/L at 25 °C, respectively. The Q values of P1T1 and P3T1 are 1.63×10^{-5} and 4.24×10^{-10} , respectively. Compared with the data in Table 6, the reaction quotient is larger than the solubility product constant for P1T1 ($1.63 \times 10^{-5} > 8.88 \times 10^{-8}$) and the reaction quotient is smaller than the solubility product constant for P3T1 ($4.24 \times 10^{-10} < 4.83 \times 10^{-10}$) at room temperature. This indicates that P1T1 will form and P3T1 will dissolve in toluene. In the same way, the solubility of perylene and TCNQ in benzene at 25 °C is 5.4 mmol/L and 0.7 mmol/L, respectively. At room temperature, the reaction quotient is larger than the solubility product constant for

P3T1 ($1.10 \times 10^{-10} > 3.48 \times 10^{-11}$) and the reaction quotient is smaller than the solubility product constant for P1T1 ($3.78 \times 10^{-6} < 3.98 \times 10^{-6}$), which indicate that P1T1 will dissolve and P3T1 will precipitate in benzene.

The higher solubility of TCNQ in toluene than in benzene causes the intensive steady-state absorption and fluorescence observed in the perylene – TCNQ solution in benzene, as discussed below.

Figure 4.25 Steady-state absorption and fluorescence spectra: (a) Perylene and TCNQ stock solutions in benzene and toluene; (b) Perylene + TCNQ 1:1 in benzene and toluene. (The spectrophotometers used to give correct results for the absorption only at values of $A < 2.5$ due to sensitivity limitations.)

The steady-state absorption and fluorescence spectra of perylene in benzene and toluene are identical (Figure 4.25a) since the perylene solubility in the two solvents is equal. The perylene fluorescence spectra in both solvents are in good agreement with the reported perylene monomer emission when the reabsorption effect is taken into consideration⁴⁶. The optical absorption of TCNQ in toluene, however, is over 10 times stronger than that in benzene due to the higher concentration.

Figure 4.26 Fluorescence decay kinetics of perylene + TCNQ 1:1 in benzene (blue) and toluene (red) at an emission wavelength of 472 nm.

At room temperature, the fluorescence of TCNQ is not detected in either solvent. As a control experiment, we performed the spectroscopic characterization of stock solutions (perylene + TCNQ 1:1) in benzene and toluene. Figure 4.25b presents the steady state spectra of both solutions. Figure 4.26 shows the fluorescence kinetics at $\lambda = 472 \text{ nm}$. It can be observed that the perylene fluorescence lifetime in the stock solution (perylene + TCNQ 1:1) in benzene is 4.2 ns, a value that is a little longer than the perylene radiative lifetime reported⁴⁶. This 10% lifetime lengthening is due to reabsorption⁴⁷. However, the perylene fluorescence lifetime in toluene is 1.6 times shorter than that in benzene, which indicates the perylene fluorescence is quenched by the highly-concentrated TCNQ in toluene (high solubility of TCNQ in toluene). It should be mentioned that the decay kinetics is independent of the emission wavelength both in benzene and in toluene. A

similar situation is observed in steady-state fluorescence (Figure 4.25b), but the intensity difference is much larger. Because of the high solubility of TCNQ in toluene, the absorption edge extends to 550 nm. Therefore the intensity of the steady-state fluorescence from perylene in toluene is much (4.4 times) weaker than in benzene.

4.3.5 Characterization of P1T1, P2T1 and P3T1

Due to P2T1 is occasionally grown and the quantity is very small, only nondestructive characterizations are done to P2T1 crystals. Therefore, some characterizations are only performed on P1T1 and P3T1.

Figure 4.27 Powder diffraction pattern of perylene, TCNQ, P1T1, P2T1 and P3T1. The index is according to the calculated data from single X-ray diffraction.

Figure 4.27 shows the powder diffraction pattern of P1T1, P2T1 and P3T1. The new charge transfer compound is differing from perylene and TCNQ monomer crystals. The index of the peak is well agreed with the calculation data from single crystal diffraction. It indicated that the P1T1, P2T1 and P3T1 are three different phases.

The TGA analysis of P1T1 and P3T1 are shown in Figure 4.28. The black line shows the weight change with temperature increasing and the red line shows the derivative of the black line. The peak of the derivative curve means materials are having the highest mass

loss at that temperature, which should be the sublimation temperature or decomposition temperature of the materials. P1T1 crystals started weight loss at 210 °C and finished at 270 °C, while P3T1 started at 220 °C and finished at 280 °C. It indicated that P3T1 is a little more stable than P1T1.

Figure 4.28 TGA analysis of P1T1 (a) and P3T1 (b).

Figure 4.29 IR spectra of perylene, TCNQ, PIT1 and P3T1 in the range of (a) 1620 cm⁻¹ to 1500 cm⁻¹ and (b) 2300 cm⁻¹ to 2140 cm⁻¹.

The IR spectra of PIT1 and P3T1 is different from perylene and TCNQ, which mean the new phase formed and charge transfer occurred (Figure 4.29). In the range of 1620 cm⁻¹ to 1500 cm⁻¹, perylene does not show significant vibrations. For pristine TCNQ, a C=C stretching mode was observed at 1542 cm⁻¹, which is not observed in perylene, PIT1 and P3T1. In PIT1, two C=C stretching modes were observed at 1539 cm⁻¹ and 1587 cm⁻¹, which came from the alternating stacking of perylene and TCNQ molecules. In P3T1,

three C=C stretching modes were observed at 1538 cm^{-1} , 1567 cm^{-1} and 1588 cm^{-1} , which came from the different packing of perylene molecules between TCNQ molecules (see Figure 4.19). In the range of 2300 cm^{-1} to 2140 cm^{-1} , perylene also does not show significant vibrations. The pristine TCNQ shows $\text{C}\equiv\text{N}$ stretching mode at 2226 cm^{-1} and 2222 cm^{-1} , which can be assigned to b_{1u} and b_{2u} mode⁴⁸. The same vibration peaks in P1T1 are 2221 cm^{-1} and 2217 cm^{-1} and in P3T1 is 2220 cm^{-1} and 2214 cm^{-1} . The shift of the peaks indicates charge transfer⁴⁹.

Figure 4.30 Raman spectra of perylene, TCNQ, P1T1 and P3T1 in low frequency range.

Several reports on P1T1 and P3T1 have been published^{50,51}, which were mainly discussing the high frequency Raman ($> 200\text{ cm}^{-1}$). In the low frequency range ($< 200\text{ cm}^{-1}$), the vibrations are predominantly intermolecular. Thus, the Raman spectra in low frequency range of perylene, TCNQ, P1T1, P2T1 and P3T1 were measured (Figure 4.30), which can be used to identify the three different charge transfer compounds. The first peak of P1T1, P2T1 and P3T1 is around 22 cm^{-1} , 15 cm^{-1} and 29 cm^{-1} . The Raman spectra of these three crystals are very different in the low frequency range, which can be used to identify the stoichiometry of the three compounds⁵².

4.3.6 Charge transfer degree calculation of P1T1, P2T1 and P3T1

Charge transfer degree, which reveals the fundamental physical property of materials, is the amount of charge transfer from donor to acceptor in the crystal formation. The geometry of intramolecular varies when there is a charge transfer between donor and acceptor⁵³. Thus, charge transfer degree can be estimated with the calculation of the bond length variation. In TCNQ, the length of bonds is especially sensitive to the negative charge on molecules⁵⁴⁻⁵⁶. The population of electrons in TCNQ is increasing the length of two bonds (a and c) while decrease the length of the other two bonds (b and d)²⁸. This method has been used to estimate many TCNQ related charge transfer compounds^{28,49,57,58}. The a, b, c, d bonds are shown in Figure 4.31.

Figure 4.31 Illustrated structure of TCNQ molecular (a,b,c,d represent the bond length).

The charge transfer degree can be estimated by using the $c/(b+d)$ value⁵⁸:

$$DCT = \frac{a_{CT} - a_0}{a_{-1} - a_0}$$

where: DCT is the degree of charge transfer, $a_x = c/(b + d)$, b, c and d are the bond lengths of TCNQ molecules in neutral TCNQ, TCNQ anion, P1T1, P2T1 and P3T1. The subscripts CT, -1 and 0 refer to charge transfer compound, the neutral molecular and the anion. Table 4.8 lists the bonds length, $c/(b+d)$ values and predicted charge transfer degree values of P1T1, P2T1 and P3T1.

The charge transfer degree can also be calculated by Raman spectrum. The charge transfer degree calculated from bond length method is well agreed with the data calculated from Raman spectra⁵². The compared data are shown in Table 4.9. Both calculations shown that the charge transfer degree is increase with perylene molecules increased in the unit cell. It may be due to more donor (perylene molecules) can give more electrons to acceptor (TCNQ molecules).

Table 4.8 Bond lengths and estimated charge transfer degree of TCNQ, TCNQ anion, P1T1, P2T1 and P3T1.

	a (Å)	b(Å)	c(Å)	d(Å)	c/(b+d)	CT
TCNQ ⁵⁹	1.346	1.448	1.374	1.441	0.476	0
TCNQ ⁵⁸	1.373	1.432	1.420	1.416	0.500	1
P1T1	1.338	1.441	1.368	1.428	0.477	0.04
P2T1	1.343	1.431	1.369	1.425	0.479	0.12
P3T1	1.346	1.429	1.375	1.429	0.481	0.21

Table 4.9 Comparison of charge transfer degree calculated from Raman spectrum and bond length derived from single X-ray diffraction.

Compound	Raman estimate ⁵²	bond length estimate
P1T1	0.04	0.04
P2T1	0.13	0.12
P3T1	0.19	0.21

4.3.7 Charge transport properties of P1T1, P2T1 and P3T1

Single crystal field-effect transistors based on P1T1 and P3T1 were fabricated to investigate the electronic properties. The device is using a top-contact, bottom-gate configuration, which is the same as shown in Figure 4.11. Typical output and transfer curves of P1T1 and P3T1 are shown in Figure 4.32 and 4.33. Single crystals of P1T1 showed n-type property. The maximum mobility of P1T1 was $0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. P3T1 showed p-type performance and the maximum mobility was $0.008 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Since P2T1 was sent to collaborators, the field effect performances were extract from the publication data shown in Figure 4.34. It shows ambipolar properties with hole mobility of $3 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and electron mobility of $7 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. All the performances of representative devices are presented in Table 4.10.

Figure 4.32 Transfer curve (a) and output curve (b) of P1T1 transistor.

Figure 4.33 Transfer curve (a) and output curve (b) of P3T1 transistor.

Figure 4.34 Transfer curve of P2T1 transistor (from collaboration work⁵²).

Table 4.10 Performance of single crystal field-effect transistors based on P1T1, P2T1, and P3T1.

Compound	Type	Mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)
P1T1	n	0.05
P2T1	n	7×10^{-5}
	p	3×10^{-5}
P3T1	p	0.008

TCNQ shows n-type semiconducting while perylene shows p-type semiconducting. From P1T1 to P3T1, the increase of perylene molecules in the unit cell may lead to the transformation of the single crystal from n-type to p-type. Therefore, only electron transport was found in P1T1 and only hole transport was found in P3T1. While ambipolar transport property was detected in P2T1. However, the on/off ratio of all three charge transfer compounds is 10^5 . It indicates that the different stoichiometry between donor and acceptor does not effect on on/off ratios.”

4.4 Conclusion

Perylene single crystals were grown by solution drop cast and physical vapor transport methods. The maximum mobility reached $0.05 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ in the linear region and $0.1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ in the saturated region. The on-off ratio and threshold voltage of the device is 3×10^4 and -31V, respectively. TCNQ single crystals were also grown by solution drop cast and physical vapor transport methods. The maximum mobility and the on-off ratio reached $0.02 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and 10^4 .

Crystal growth of binary compounds made from organic donors and acceptors is more complicated than that of monomolecular crystals. For studies of charge transfer degree, compounds with multiple stoichiometries are especially desired. However, systems with multiple stoichiometries are rare. Due to the different physical properties (solubilities, sublimation temperatures) of donors and acceptors, the stoichiometry of the synthesized compounds may differ from the stoichiometry of the starting materials. We observed an interesting phenomenon: the final stoichiometries of single crystal P1T1 (perylene1:TCNQ1) and P3T1 (perylene3:TCNQ1) are not affected by the stoichiometry of the starting materials, but by the solvent in which the perylene-TCNQ crystals were

grown. The P1T1 crystals were grown from toluene, whereas the P3T1 crystals were grown from benzene regardless of the acceptor/donor stoichiometry in the starting materials. The solubility data were employed to analyze the effect of solvent on the stoichiometry of the perylene-TCNQ charge transfer single crystals. The reason is that the crystals with lower solubility will precipitate first. Steady-state optical spectra and time-resolved fluorescence measured in a mixture of perylene and TCNQ in toluene and benzene, confirmed selective crystallization of P1T1 and P3T1 from toluene and benzene. In contrast to solution growth, when utilizing the PVT method, a mixture of monomolecular crystals, P1T1 (perylene1:TCNQ1), P2T1 (perylene2:TCNQ1) and P3T1 (perylene3:TCNQ1) is obtained. P2T1 is a new discovered structure. The charge transfer degrees of P1T1, P2T1 and P3T1 have been measured and calculated. Field-effect transistors on the single crystals' surfaces of P1T1, P2T1 and P3T1 have been made. The results reveal that P1T1 is typically an n-type semiconductor, P3T1 showed p-type behavior, whereas P2T1 showed ambipolar properties.

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Chapter 5

Perylene-F_xTCNQ charge transfer compound single crystals

In this chapter, the crystal growth and charge transport properties of F₄TCNQ single crystals are investigated. The methodologies of searching for novel organic charge transfer binary compounds and crystal growth in the case that only the two starting organic substances are known but the phase diagram is not known, the thermodynamic data of the binary compound are not known and even the existence of new binary compounds is not known were studied. We found that kinetically lowering the sublimation rate was the key factor for growing large-size charge transfer compound single crystals. By using this concept, crystals of novel perylene-F₁TCNQ, perylene-F₂TCNQ and perylene-F₄TCNQ charge transfer binary compounds were obtained by decreasing the evaporation area of the individual components. Field-effect behavior was not observed in perylene-F₄TCNQ FETs. However, we found that the strong acceptor F₄TCNQ transfers sufficient charge from perylene to cause room-temperature ferromagnetism. On the other hand, the weak acceptor, TCNQ, does not cause ferromagnetism in perylene-TCNQ because the degree of charge transfer is too low. These results explain previous observations of ferromagnetism in metal-free organics and enable the design of novel ferromagnetic compounds due to strong charge transfer. Such compounds may be vital components for room temperature spintronic devices.

5.1 Introduction

Organic semiconductors, made from polymers or small organic molecules, are fundamental components of emerging organic microelectronics. Printed, sprayed or even evaporated thin films are preferred for practical applications¹⁻³. However, for studies of fundamental processes in devices and intrinsic physical effects, it is convenient to study bulk single crystals at least a few micrometers large for structure determinations or a few millimeters large for transistors or optoelectronic devices prepared on crystal surfaces^{4,6}. There have been many reports on the preparation of single crystals made from one type of molecular building block⁷⁻⁹. Properties of such monomolecular solids are adjusted through the molecular formula, as well as the crystal structure. Especially, the design of organic molecules gives many possibilities in property control. Therefore, the charge mobility has systematically risen from the range of $10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ to a few tens of $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ during the last thirty years^{10,11}. However, some properties, such as superconductivity, are not achievable in substances made from one type of molecule. For example, to cause metallicity at room temperature¹² or even superconductivity at low temperature^{13,14}, an excess of charge needs to be provided to the molecules. Organic semiconductors based on a single molecular building block are equivalent to inorganic semiconductors made from a single chemical element, such as silicon or germanium. The combination of two or more elements in inorganic chemistry results in an immense amount of binary and multinary compounds with new optical and electrical properties not appearing in one-component solids. Usually, binary phase diagrams describe the presence of individual inorganic binary compounds. However, the binary phase diagrams between organics are rather rare, and the binary compounds in such phase diagrams are rarely known. Organic binary charge transfer compounds, which contain donor and acceptor molecules with mixed or segregated stacking⁹, show physical properties different from the individual properties of the donor and acceptor. The charge transfer compound may have high conductivity¹⁵, superconductivity^{16,17}, strong electron-phonon interactions¹⁸, ferromagnetism¹⁹, antiferromagnetism²⁰, and optical²¹ and photovoltaic properties²². Both the theoretical²³ and experimental results²⁴⁻²⁷ indicate that field effect transistors made from organic charge transfer compounds can display n-, p-, or ambipolar charge transport properties^{28,29}. Single crystals of charge transfer compounds provide the opportunity to

investigate the intrinsic properties⁶ and structure-property relationships due to the nearly perfect structures and minimum concentration of structure imperfections (i.e., grain boundaries) and impurities³⁰⁻³². The crystal growth of charge transfer compounds is more complex than that of monomolecular systems. Rather small crystals are required for X-ray or synchrotron crystal structure determination and, in this way, confirmation of compound existence. Larger crystals are required for electrical or optical property measurements. Even larger crystals are convenient for detailed studies of the anisotropy of the physical properties and the structure-property relationships. Generally, two methods are used to grow single crystals of charge transfer compounds: solution methods and vapor methods^{7,33}. The size of charge transfer compound single crystals varies from micrometers^{24,25,34-36} to millimeters^{37,38}. Solution growth methods, such as solvent evaporation, temperature lowering or antisolvent methods, use a third component, solvent, that complicates interpretation of the electrical or optical properties and can even form three-component charge transfer compounds in specific conditions. Therefore, gas phase transport in inert gas seems to be the method of choice for the crystallization of very pure, unknown compounds large enough for structure determination and properties measurements.

Ferromagnetism is present in some inorganic substances, such as iron based compounds. In organic compounds ferromagnetism may be observed when suitable metals are incorporated. In metal-free organics ferromagnetism has been reported at few degrees Kelvin^{19,39-42}, except for some recent observations of weak ferromagnetism at room temperature in Teflon⁴³, graphene⁴⁴ and a specific polymer blend⁴⁵. However, a general method for rational design of new high temperature ferromagnetic metal-free compounds has not been proposed. Ferromagnetism is not expected to be observed in organic crystals at room temperature. However, pure organic molecular based ferromagnet, TDAE-C₆₀¹⁹, shows π -electron ferromagnetism at comparatively high temperatures of 16 K. Ferromagnetism at room temperature, in an organic material, containing a metal, i.e. [V(TCNE)_x] $\cdot$ y(CH₂Cl₂) was reported in 1991⁴⁶ and another vanadium containing organic material in 1995⁴⁷. [V(TCNE)_x] $\cdot$ y(CH₂Cl₂) shows room temperature ferromagnetism which results from three-dimensional antiferromagnetic exchange of donor and acceptor spins. Furthermore, high-temperature metal-organic magnets were reported in 2007⁴⁸.

Room temperature weak ferromagnetism was sporadically reported in some metal-free organic molecules and polymers, such as P3HT and PCBM blend films⁴⁵, graphene⁴⁴ and modified-C₆₀⁴⁹. It was experimentally observed and calculated from first principles that strained Teflon displays weak ferromagnetism at room temperature due to unpaired electrons in dangling bonds⁶. After eliminating the presence of metals that may be responsible for this ferromagnetism, only the unpaired electrons localized in higher molecular orbitals can interact with each other, correlate their spins and show ferromagnetism. If the concentration of these unpaired electrons is large, ferromagnetism may be measurable. Control of dangling bonds is difficult and the concentration of unpaired electrons is rather low. Unpaired electrons forming dangling bonds are similar to unpaired electrons in molecular orbitals of charge transfer compounds. Both fill empty orbitals according to the Pauli Exclusion Principle. Charge transferred from donors to acceptors fills the molecular orbitals sequentially with unpaired electrons. We hypothesize that these transferred electrons may exhibit charge correlated phenomena from which ferromagnetism may be detectable.

Compared with TCNQ, F₄TCNQ has stronger electron affinity due to the four fluorine atoms. The molecular structure and the schematic of the electronic structure⁵⁰ are shown in Figure 5.1.

Figure 5.1 Molecular structure of F₄TCNQ (a) and schematic of electronic structure (b).

In this chapter, the crystal growth and charge transport properties of F₄TCNQ are

investigated. The methodologies of searching for novel organic charge transfer binary compounds and crystal growth in the case that only the two starting organic substances are known but the phase diagram is not known, the thermodynamic data of the binary compound are not known and even the existence of new binary compounds is not known were studied. We found that kinetically lowering the sublimation rate was the key factor for growing large-size charge transfer compound single crystals and finding new binary charge transfer compounds. By using this concept, crystals of novel perylene-F₁TCNQ perylene-F₂TCNQ and perylene-F₄TCNQ charge transfer binary compounds were obtained by decreasing the evaporation area of the individual components. Field-effect behavior was not observed in perylene-F₄TCNQ FETs, which may due to the surface is not good to detect the field-effect behavior. However, we found that the strong acceptor F₄TCNQ transfers sufficient charge from perylene to cause room-temperature ferromagnetism. On the other hand, the weak acceptor, TCNQ, does not cause ferromagnetism in perylene-TCNQ because the degree of charge transfer is too low. These results explain previous observations of ferromagnetism in metal-free organics and enable the design of novel ferromagnetic compounds due to strong charge transfer. Such compounds may be vital components for room temperature spintronic devices.

5.2 Experimental Methods

5.2.1 Chemicals and materials

Perylene (>99%) was purchased from Sigma-Aldrich. F₁TCNQ (>99%) and F₂TCNQ (>99%) were purchased from Tokyo Chemical Industry Co., Ltd. (Japan). F₄TCNQ (>99%) was purchased from Jilin OLED Material Tech Co. Ltd. (China). Perylene and fluorinated-TCNQ (F₁TCNQ, F₂TCNQ and F₄TCNQ) were purified at 180 °C and 220 °C via PVT⁷, respectively. The acetonitrile was used without further purification.

5.2.2 PVT growth of F₄TCNQ single crystals

The growth apparatus is shown in Chapter 3, Figure 3.5. F₄TCNQ was placed in Zone 1 with temperature 215 °C and the temperature of Zone 2 was set at 155 °C. Argon was fed as carrier gas with a flow rate at 60 sccm in the whole process. The crystal growth time is around 1 to 2 hours.

5.2.3 PVT growth of perylene-(fluorinated-TCNQ) single crystals

A two zone semi-transparent furnace was used for crystal growth. To grow single crystals, F₄TCNQ and perylene with mole ratios of 1:1 were weighed but not mixed. Perylene and F₄TCNQ were put in two separated zone of the furnace. The temperatures were set to 210 °C for the furnace zone where perylene was placed and 220 °C for the zone with F₄TCNQ. Argon was used as carrier gas with flow rate of 40 mL/min. The total growth procedure lasted ~8 hours. Small needle-like single crystals below 1 mm in length were grown when commercial, not purified powder was used. Larger needle-like crystals were grown from sublimed materials. The largest crystals, more than 1 cm long, were grown when only large crystals formed during purification of F₄TCNQ and large crystals formed during purification of perylene were used as starting materials. When pre-synthesized powder of compound Perylene-F₄TCNQ were used rather small crystal were formed.

To grow perylene-F₁TCNQ and perylene-F₂TCNQ single crystals, the same apparatus were used. The single crystals of F₁TCNQ, F₂TCNQ and perylene are used as starting materials to grow the large single crystals of the charge transfer compound. The growth apparatus of F₁TCNQ and F₂TCNQ single crystals is shown in Chapter 3, Figure 3.5. F₁TCNQ or F₂TCNQ was placed in Zone 1 with temperature 215 °C and the temperature of Zone 2 was set at 155 °C. Argon was fed as carrier gas with a flow rate at 40 mL/min in the whole process. The crystal growth time is around 1 to 2 hours.

5.2.4 Characterization

Sublimation rates were not measured during the crystal growth process but were measured as a function of time in a thermal gravimetric analyzer, TGA (TA Instruments, model Q500). Platinum TG pans were filled with commercial powders and single crystals of F₄TCNQ and perylene for TGA measurement. In TGA experiments, a purge gas of argon with 40 mL/min was used the same as crystal growth procedure. For F₄TCNQ powder and crystals, temperature was increased from room temperature to 220 °C with a rate of 20 °C/min and maintained at 220 °C for 60 minutes. For perylene powder and crystals, the ramping rate is the same, but the system maintained at 210 °C for 60 mins. The crystal structures of perylene-F₁TCNQ and perylene-F₂TCNQ and perylene-F₄TCNQ single crystals were obtained using a Bruker SMART APEX II single crystal

diffractometer (X-ray radiation, Mo K α , $\lambda = 0.71073$ Å). The copper grid with supporting carbon film was placed into the tube during the crystal growth procedure. Some small perylene-F₄TCNQ crystals were grown on the copper grid simultaneously. TEM and SAED measurements were carried out on an Energy Filtered Carl Zeiss TEM, LIBRA[®] 120. Infrared spectroscopy measurements were taken using a Perkin Elmer Spectrum GX spectrometer with a spectral resolution of 2 cm⁻¹ in a range of 400-4000 cm⁻¹. The single crystals mixed with KBr (Sigma-Aldrich) were completely grounded and then pressed into pellets for measurement. Magnetic measurements were carried out with a Physical Property Measuring System (PPMS: Quantum Design Inc., USA) equipped with a vibrating sample magnetometer (VSM) probe.

5.2.5 Density functional theory (DFT) calculation

Our calculations are based on the density functional theory (DFT)⁵¹ and the Perdew-Burke-Eznerhof generalized gradient approximation (PBE-GGA)⁵². The projector augmented wave (PAW) scheme^{53,54} as incorporated in the Vienna ab initio simulation package (VASP)⁵⁵ was used in the study. The Monkhorst and Pack scheme of k point sampling was used for integration over the first Brillouin zone⁵⁶. Van der Waals force was considered in our calculations^{57,58}. A 3×3×3 grid for k-point sampling for geometry optimization of unit cells, and an energy cut-off of 500 eV were consistently used in our calculations. Charge analysis was based on Bader scheme^{59,60}. Good convergence was obtained with these parameters and the total energy was converged to 2.0×10⁻⁵ eV/atom.

5.3 Results and discussion

5.3.1 F₄TCNQ single crystal growth and structure

Due to the strong electron affinity of F₄TCNQ, F₄TCNQ is very easy to interact with solvent. Therefore, no F₄TCNQ single crystals were obtained on the substrate by directly solution drop-casting methods and it is also difficult to get F₄TCNQ crystals from solvent by slow cooling. PVT method is used to grow large F₄TCNQ crystals and crystals on substrates.

F₄TCNQ single crystals are similar with TCNQ crystals shown in Figure 5.2. It shows needle-like with maximum length of 2 centimeters.

The F₄TCNQ single crystals also showed an orthorhombic symmetry, which belonged to the Pbca space group with $a = 9.300(8)$ Å, $b = 8.19(1)$ Å and $c = 14.628(6)$ Å. The selected crystal structure information is listed in Table 5.1. The molecular packing of F₄TCNQ along different direction is shown in Figure 5.3. Crystal structure indicates that the F₄TCNQ molecules are periodically packed to form single crystals and the intermolecular force between each molecular is Van der Waals force. Nearest F-F bond and the N-N bond distance are 4.436 Å and 3.300 Å, respectively.

Figure 5.2 Optical image of F₄TCNQ.

Table 5.1 Crystallographic data for F₄TCNQ derived from single crystal X-ray diffraction data

	F ₄ TCNQ
Formula	C ₁₂ F ₄ N ₄
Crystal system	Orthorhombic
Space group	P b c a
Lattice parameter a (Å)	9.300(8)
Lattice parameter b (Å)	8.19(1)
Lattice parameter c (Å)	14.628(6)
Lattice parameter (degree)	90
Lattice parameter (degree)	90
Lattice parameter (degree)	90
Cell volume (Å ³)	1114.4(48)
Formula units per cell Z	4
Temperature (K)	300K
R-factors	0.0459

Figure 5.3 Molecular packing of F₄TCNQ. (a) along (100) direction; (b) along (010) direction; (c) along (001) direction; (d) along (111) direction.

5.3.2 Charge transport properties F₄TCNQ single crystals

F₄TCNQ single crystal field effect transistor was fabricated with a top-contact, bottom-gate configuration, as shown in Figure 5.4. Gold is used as the source and drain electrodes.

Figure 5.4 Schematic device configuration (a) and the optical image of F₄TCNQ field effect transistor (b).

Figure 5.5 Transfer curve (a) and output curve (b) of F₄TCNQ transistor.

The transfer curve and output curve of F₄TCNQ transistor are shown in Figure 5.5. It shows n-type characteristic. The maximum mobility is reached $0.001 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and the on-off ratio is 10^3 . This value is much smaller than the reference⁶¹ ($0.2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). The possible reason is due to the dielectrics difference and the smoothness of surface of the single crystals. The reference used PDMS to fabricate an air-gap transistor^{31,62}, which is considered as the best device configuration and showed the best properties.

F₄TCNQ single crystals shows photo-response when the light is switched on or off at

$V_{SD}=10V$, as shown in Figure 5.6. When the light is switched on, I_{SD} is quick increased and when the light is turn of, I_{SD} is quick decreased. The photo-response time is lower than 500 ms.

Figure 5.6 Photo-response of single crystal F₄TCNQ at $V_{SD}=10V$.

5.3.3 Crystal growth of perylene-F₄TCNQ single crystals

To grow perylene- F₄TCNQ crystals, we used the PVT method, which was similar to the previously described method of growing one-component organic semiconductors. Perylene-F₄TCNQ system are employed to investigate the influence of the form of starting materials. The single crystals made from perylene-F₄TCNQ charge transfer compounds were grown using either commercial powder or crystals. The optical images of the starting materials and final crystals are shown in Figure 5.7. The optical images of the commercial powder of F₄TCNQ and perylene are shown in Figure 5.7 (d and e). The F₄TCNQ and perylene single crystals are shown in Figure 5.7 (g and h). The perylene-F₄TCNQ charge transfer compound single crystals had quite different sizes when using commercial powder or single crystals as the starting materials. The crystals showed a maximum length of 4 millimeters with an average length of 2 millimeters when powders were used. Crystals up to 1.5 centimeters long with an average length of 1 centimeter were grown when single crystals were used as the starting materials. It was noted that

only less than 1-mm-long perylene-F₄TCNQ crystals were obtained when perylene powder and grinded commercial F₄TCNQ powder were used. The optical images of the grinded powder and the final crystals are shown in Figure 5.7 (a and c).

TGA is widely used to determine the vaporization, thermal decomposition⁶³, sublimation pressures, diffusion coefficients⁶⁴ and sublimation rate of organics^{65,66}. Thus, the sublimation rate under the pressure of 1 atm of argon was determined by TGA. The TGA results of F₄TCNQ single crystals at 220 °C are shown in Figure 5.8. The derivative curve represents the sublimation rate. The climbing portion of the derivative curve was due to heating to the pre-set temperature of the TGA sample chamber. The sublimation rate was constant during the 60 minutes of heating in constant temperature under 1 atm of argon.

The sublimation rate of F₄TCNQ single crystals was compared with the sublimation rates of commercial F₄TCNQ powder and grinded commercial F₄TCNQ powder. The sublimation rate of perylene single crystals was compared with the sublimation rate of commercial perylene powder. The results are shown in Figure 5.9 and Figure 5.10. Perylene single crystals exhibited lower sublimation rate (~ 0.02 mg/min) than perylene powder (~ 0.05 mg/min). The powder form showed higher sublimation not only for perylene but also for F₄TCNQ. In addition, the sublimation rate of grinded commercial F₄TCNQ powder was much higher than that of commercial F₄TCNQ powder and single crystals, reaching sublimation rate of 0.1 mg/min. Both for perylene and F₄TCNQ, the sublimation rate of the powder was nearly twice that of the single crystals. The smaller particle size exhibited a higher sublimation rate due to larger surface area. After grinding, the commercial F₄TCNQ powder showed small particle size, which provided the highest sublimation rate.

The crystal growth can be divided into two steps⁶⁷: nuclei formation and the subsequent growth of the individual nuclei. In the nuclei formation process, stable nuclei are formed when the nuclei grow over a certain size⁶⁸. Then, the nucleation rate is determined by critical supersaturation^{69,70}.

Previous crystal growth experiments in an open system in an inert gas flow in 1 atm revealed that very low supersaturation was sufficient for spontaneous nucleation. The even placement of seeds along the entire length of the crystallization tube did not cause

seed growth but spontaneous nucleation on the seeds and on the glass tube. Increased crystallization temperature promoted surface diffusion of molecules and enhanced crystallization on the seeds. However, the higher growth temperature caused higher evaporation and therefore a higher sublimation rate, which caused higher supersaturation and spontaneous nucleation. Therefore, many small crystals were formed at low temperature due to low surface diffusion or at high temperature due to high sublimation rate. To obtain large crystals, the temperature needed to be elevated; however, the sublimation rate needed to be reduced. An inert gas atmosphere and reduced evaporation surface led to exactly such conditions.

Figure 5.7 Optical images of the starting materials and the final charge transfer compound single crystals. a: grinded commercial F₄TCNQ powder; b: commercial perylene powder; c: perylene-F₄TCNQ charge transfer compound single crystals; d: commercial F₄TCNQ powder; e: commercial perylene powder; f: perylene-F₄TCNQ charge transfer compound single crystals; g: F₄TCNQ single crystals; h: perylene single crystals; i: perylene-F₄TCNQ charge transfer compound single crystals.

Figure 5.8 Thermogravimetric measured weight loss and sublimation rate of F₄TCNQ single crystals at 1 atm of argon and 220 °C. During the first 10 minutes, the sample was heated from room temperature to 220 °C at a rate of 20 °C/min, and then the temperature was kept constant at 220 °C.

Figure 5.9 Sublimation rate vs time of perylene at 1 atm of argon and 210 °C.

Figure 5.10 Sublimation rate vs time of F_4 TCNQ at 1 atm of argon and 220 °C.

Figure 5.11 Optical images of perylene, F_1 TCNQ, F_2 TCNQ single crystals and the final charge transfer compound single crystals. a: F_1 TCNQ single crystals; b: perylene single crystals; c, perylene- F_1 TCNQ charge transfer compound single crystals; d: F_2 TCNQ single crystals; e: perylene single crystals; f: perylene- F_2 TCNQ charge transfer compound single crystals.

Therefore, powder with a large surface evaporates too fast, and many small crystals are formed. Decreasing the evaporation temperature decreases the transport of molecules to the growth zone; however, the temperature of the growth zone also decreases, and many

small crystals are formed. A two-component system is even trickier because the stoichiometry in the gas phase is difficult to control in an open system. Experimentally, crystals of individual components and crystals of binary compounds almost always form close to each other at the crystallization zone. In the case of perylene-F₄TCNQ, the band gap and the crystal symmetry of every component were different; therefore, it was possible to select binary compounds from F₄TCNQ or perylene crystals under optical microscopy.

By using single crystals as starting materials due to kinetically lowering the sublimation rate, unknown binary compounds can be obtained. Perylene-F₁TCNQ and perylene-F₂TCNQ charge transfer compound single crystals are also obtained by using this method.

F₁TCNQ and F₂TCNQ crystals are used to grow perylene-F₁TCNQ and perylene-F₂TCNQ charge transfer compound single crystals. The optical image of F₁TCNQ, F₂TCNQ, perylene and final charge transfer compound single crystals is shown in Figure 5.11. The perylene-F₁TCNQ and perylene-F₂TCNQ charge transfer compound single crystals exhibit also near 1 centimeter length. It indicates that such method is successfully applied to other systems. By using reflection mode of the optical microscope, all the three new charge transfer single crystals exhibit needle-like morphology with a dark color. However, by using transmission mode of the microscope, the three single crystals display different colors, as shown in Figure 5.12. Perylene-F₁TCNQ, perylene-F₂TCNQ and perylene-F₄TCNQ show green, dark yellow and red, respectively. It indicates that the new energy level was from in the charge transfer single crystals.

The single crystal X-ray diffraction data confirmed the existence of until now not known binary compounds. Both perylene-F₁TCNQ and perylene-F₄TCNQ show 1:1 stoichiometry of donor and acceptor, while perylene-F₂TCNQ shows 3:2 stoichiometries of perylene and F₂TCNQ. All the three perylene- fluorinated TCNQ crystals showed a mixed-stacking structure (shown in Figure 5.13, 5.14 and 5.15). In perylene-F₁TCNQ and perylene-F₄TCNQ, the ...D-A-D-A... stacking direction is along the a-axis (Figure 5.13b and 5.15b). However, in perylene-F₂TCNQ is a little bit complex. One ...D-A-D-A... stacking is along a-axis and the adjacent ...D-D-A-D-D-A... stacking is along b-

axis (Figure 5.14b). Perylene-F₁TCNQ has a monoclinic symmetry, which belonged to the P 21/c space group with $a = 7.1649(18)\text{\AA}$, $b = 10.894(3)\text{\AA}$, $c = 14.446(4)\text{\AA}$, and $\beta = 90.313(7)^\circ$. The Perylene-F₂TCNQ single crystals displayed a triclinic symmetry, which belonged to the P-1 space group with $a = 7.2167(12)\text{\AA}$, $b = 11.6944(19)\text{\AA}$, $c = 18.217(3)\text{\AA}$, $\alpha = 75.927(4)^\circ$, $\beta = 82.686(5)^\circ$, and $\gamma = 72.139(5)^\circ$. The perylene-F₄TCNQ single crystals also exhibited a triclinic symmetry, which belonged to the P-1 space group with $a = 6.9988(7)\text{\AA}$, $b = 7.2813(7)\text{\AA}$, $c = 11.2715(12)\text{\AA}$, $\alpha = 104.154(7)^\circ$, $\beta = 101.861(6)^\circ$, and $\gamma = 90.291(7)^\circ$. The selected crystal structure information is listed in Table 5.2.

Figure 5.12 Transmission optical images of perylene-F₁TCNQ (a), perylene-F₂TCNQ (b) and perylene-F₄TCNQ (c).

Figure 5.13 Molecular packing of perylene-F₁TCNQ. (a) along (100) direction; (b) along (010) direction; (c) along (001) direction; (d) along (111) direction.

Figure 5.14 Molecular packing of perylene- F_2 TCNQ. (a) along (100) direction; (b) along (010) direction; (c) along (001) direction; (d) along (111) direction.

Figure 5.15 Molecular packing of perylene- F_4 TCNQ. (a) along (100) direction; (b) along (010) direction; (c) along (001) direction; (d) along (111) direction.

Table 5.2 Crystallographic data for perylene-F₁TCNQ, perylene-F₂TCNQ and perylene-F₄TCNQ derived using single crystal X-ray diffraction.

	Perylene-F ₁ TCNQ	Perylene-F ₂ TCNQ	Perylene-F ₄ TCNQ
Formula	C ₃₂ H ₁₄ FN ₄	C ₈₄ H ₄₀ F ₄ N ₈	C ₃₂ H ₁₂ F ₄ N ₄
Formula weight	473.47	1237.24	528.5
Crystal system	monoclinic	triclinic	triclinic
Space group	P 1 2 _{1/c} 1	P -1	P -1
Lattice parameter <i>a</i> (Å)	7.1649(18)	7.2167(12)	6.9988(7)
Lattice parameter <i>b</i> (Å)	10.894(3)	11.6944(19)	7.2813(7)
Lattice parameter <i>c</i> (Å)	14.446(4)	18.217(3)	11.2715(12)
Lattice parameter α (degree)	90	75.927(4)	104.154(7)
Lattice parameter β (degree)	90.313(7)	82.686(5)	101.861(6)
Lattice parameter γ (degree)	90	72.139(5)	90.291(7)
Cell volume (Å ³)	1127.6(5)	1417.1(4)	544.14(10)
Calculated density (g/cm ³)	1.395	1.450	1.612
Formula units per cell Z	2	1	1
Temperature (K)	100	100	100
μ (Mo K α)/mm ⁻¹	0.090	0.096	0.121
<i>F</i> (000)	486	636	268
Reflections collected	14484	8624	7899
Independent reflections	2098	8624	2149
<i>R</i> _I (<i>I</i> > 2 σ (<i>I</i>))	0.0614	0.0637	0.0390
<i>wR</i> (<i>F</i> ²) (<i>I</i> > 2 σ (<i>I</i>))	0.1094	0.1479	0.1024
<i>R</i> _I (all data)	0.1854	0.1257	0.0533
<i>wR</i> (<i>F</i> ²) (all data)	0.1494	0.1669	0.1138
GOF	0.968	0.917	1.95

5.3.4 Characterization of perylene-F₄TCNQ

Figure 5.16 shows the powder diffraction pattern of perylene-F₄TCNQ. The new charge transfer compound is differing from perylene and F₄TCNQ monomer crystals. The pattern indicates the charge transfer process was happened and the new phase of perylene-F₄TCNQ charge transfer compound was formed. The index of the peak is well agreed with the calculation data from single crystal diffraction.

Charge transfer between perylene and F₄TCNQ was confirmed by infrared (IR) spectroscopy (Figure 5.17) using the measured position of the C≡N stretching modes. Perylene has no observable peaks in this region. For pure F₄TCNQ, two C≡N stretching peaks were observed, a strong one at 2227 cm⁻¹ and a weaker one at 2214 cm⁻¹, which can be assigned to vibrational modes with b_{1u} and b_{2u} symmetry, respectively⁷¹. For perylene-F₄TCNQ these two peaks are at 2220 cm⁻¹ and 2212 cm⁻¹, and are red shifted compared with pure F₄TCNQ, indicative of charge transfer. Furthermore, we identify a new peak near 2193 cm⁻¹ which also indicates charge transfer⁷².

Transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) indicated the crystal growth direction was [010] (Figure 5.18).

Figure 5.16 Powder diffraction patterns of perylene, F₄TCNQ and perylene-F₄TCNQ. The index is according to the calculated data from single X-ray diffraction.

Figure 5.17 IR spectrum of perylene, F₄TCNQ and perylene-F₄TCNQ to identify the charge transfer effect is occurred.

Figure 5.18 TEM and SAED image of perylene-F₄TCNQ.

5.3.5 Charge transfer degree and temperature dependence of perylene-F₄TCNQ

Charge transfer degree characterizes the amount of charges transferred from donor to acceptor in charge transfer compounds. It always varies with the geometry of intramolecular changes when charge transferred between donor and acceptor. Thus, charge transfer degree can be estimate with calculation of the bond length variation. This method this is widely conducted⁷³⁻⁷⁶ in TCNQ based charge transfer compound. Due to the structure similarity, this method was also successfully applied to several F₄TCNQ based charge transfer compounds^{72,77}. The Schematic drawings of F₄TCNQ were shown in Figure 5.19. Bond lengths a, b, c, and d directly correlate with the charge transfer degree between the donor and acceptor. Bond b, c and d are more sensitive to the charge transfer process. The c/(b+d) value was used to estimate the charge transfer degree⁷².

The c/(b+d) value was used to estimate the charge transfer degree:

$$DCT = \frac{a_{CT} - a_0}{a_{-1} - a_0}$$

where: DCT is the degree of charge transfer, $a_x = c/(b + d)$. The subscripts CT, -1 and 0 refer to charge transfer compound, the neutral molecular and the anion.

The bonds length, c/(b+d) values and predicted charge transfer degree values of perylene-F₄TCNQ and selected F₄TCNQ based charge transfer compound from literature are listed in Table 5.3. The pure F₄TCNQ crystal data was achieved from our measurement. The bond length of purely single ionized F₄TCNQ was take from M2P-F₄TCNQ⁷⁸ charge transfer compound.

Figure 5.19 Schematic drawings of F₄TCNQ (a, b, c and d represents bond length).

Charge transfer between perylene and F₄TCNQ was further confirmed by infrared (IR) spectroscopy, shown in Figure 5.16. This method is widely used to determine the charge

transfer degree in TCNQ^{79,80} and F₄TCNQ^{71,72} based charge transfer compound. The equation of charge transfer degree is shown below^{72,81}:

$$CT = 2\Delta\nu/\nu_0(1 - \nu_1^2/\nu_0^2)^{-1}$$

where $\Delta\nu = \nu_0 - \nu_{CT}$. The ν_0 , ν_{CT} and ν_1 are represent C $\equiv$ N stretching modes of pure F₄TCNQ, charge transfer compound and F₄TCNQ anion. The values of ν_0 , ν_{CT} and ν_1 ⁷¹ are 2227 cm⁻¹, 2220 cm⁻¹ and 2194 cm⁻¹, respectively.

The charge transfer degree, calculated from the IR spectra and the bond length variation for perylene-F₄TCNQ, is estimated to be 0.21 e and 0.153 e, respectively.

Table 5.3 Bond lengths and estimated charge transfer degree of F₄TCNQ, F₄TCNQ anion, perylene-F₄TCNQ at 300K

	a (Å)	b(Å)	c(Å)	d(Å)	c/(b+d)	CT
F ₄ TCNQ	1.333(2)	1.436(2)	1.371(8)	1.433(2)	0.4779	0
F ₄ TCNQ ⁻	1.356(4)	1.414(4)	1.415(4)	1.430(6)	0.4975	1
Perylene-F ₄ TCNQ	1.338(2)	1.434(2)	1.380(2)	1.438(3)	0.4805	0.15

Table 5.4 Bond lengths and estimated charge transfer degree of F₄TCNQ, F₄TCNQ anion, perylene-F₄TCNQ in different temperature.

	a (Å)	b(Å)	c(Å)	d(Å)	c/(b+d)	CT
F ₄ TCNQ	1.333(2)	1.436(2)	1.371(8)	1.433(2)	0.4779	0
F ₄ TCNQ ⁻	1.356(4)	1.414(4)	1.415(4)	1.430(6)	0.4975	1
Perylene-F ₄ TCNQ(300K)	1.338(2)	1.434(2)	1.380(2)	1.438(3)	0.4805	0.153± 0.012
Perylene-F ₄ TCNQ(200K)	1.337(2)	1.432(5)	1.382(0)	1.436(5)	0.4819	0.230± 0.01
Perylene-F ₄ TCNQ(100K)	1.344(3)	1.435(2)	1.387(2)	1.435(5)	0.4833	0.303± 0.005

The temperature dependence of the degree of charge transfer is shown in Table 5.4. Generally, in charge transfer compounds, lattice spacing decreases with decreasing temperature, the intermolecular distances between donor and acceptor are reduced

implying that interactions become stronger. Therefore, the charge transfer degree increased with temperature decreased in perylene-F₄TCNQ crystals.

5.3.6 Magnetic properties of perylene-F₄TCNQ

Transition metals always effect on the magnetic properties of pure organics. Therefore, inductively coupled plasma-mass spectrometry (ICP-MS) was used to determine the concentration of transition metals impurities in our sample.

The total amount of transition metal impurities (Fe, Co, Ni) was less than 1 ppm determined by inductively coupled plasma-mass spectrometry (ICP-MS). Generally, such metal concentration is too low for correlations between d electrons⁸². However, if all the metal atoms form a cluster, it will contribute to the ferromagnetic properties. If we assume that the 1 ppm impurity contributes to ferromagnetism the maximum moment should be 0.0002 emu/g for α -Fe cluster and 0.00014 emu/g for Fe₃O₄ cluster⁸², respectively. These values are at least ten times smaller than the numbers measured for our samples. This indicates that the ferromagnetic properties are from the perylene-F₄TCNQ crystals.

Figure 5.20 shows the field dependent magnetization ($M(H)$) at room temperature (RT = 300 K) for a field range of ± 1 kOe. To obtain the net magnetization of the sample, we subtract the magnetic contribution from the sample holder. The sample shows ferromagnetic properties. The inset of Figure 5.20 shows the $M(H)$ of perylene-F₄TCNQ for a field change of ± 500 Oe. The magnetization rises sharply at low magnetic fields (< 200 Oe) and saturates at 0.003 emu/g for fields > 500 Oe. A small hysteresis is observed at room temperature. The temperature variation of magnetization ($M(T)$) under 1 kOe field is shown in Figure 5.21. Critical temperatures (T_c values) were estimated to be above 300 K. The $M(H)$ isotherms at 100 K, 200 K, 300 K (Figure 5.22) show weak ferromagnetic behavior. The saturation magnetization values (M_s) increase at low temperature. For comparison we conducted similar measurements on perylene-TCNQ and didn't observe ferromagnetism (Figure 5.23).

Figure 5.20 Hysteresis $M(H)$ of perylene- F_4 TCNQ at room temperature for ± 1 kOe. (red circle: sample holder; black square: sample plus sample holder; blue triangle: net contribution due to the sample). The inset shows the hysteresis of perylene- F_4 TCNQ at room temperature in the field range of ± 500 Oe.

Figure 5.21 Field-cooling temperature dependence of magnetization from 100 K to 300 K (at 1000 Oe).

Figure 5.22 Magnetization versus field plots in the field range of ± 1.0 kOe at different temperatures (orange square: 300 K; green circle: 200 K; brown triangle: 100 K).

Figure 5.23 Magnetization versus magnetic field for perylene-TCNQ shown for comparison with perylene-F₄TCNQ. (red circle: sample holder; black square: sample plus sample holder; blue triangle: net contribution due to the sample).

The charge transfer degree, calculated from the IR spectra and the bond length variation for perylene-F₄TCNQ, is estimated to be 0.21 e and 0.153 e, respectively (see Chapter 5.3.5). For comparison, in perylene-TCNQ crystals, the charge transfer degree calculated from the Raman spectra and the bond length variation is 0.04 e and 0.01 e, respectively²⁸. In Figure 5.24, it is shown that both saturation magnetization (left scale) and the percentage of charge transfer degree (right scale) increase with decreasing temperature. The temperature dependence of the degree of charge transfer is shown in Table 5.4. Generally, in charge transfer compounds, lattice spacing decreases with decreasing temperature, the intermolecular distances between donor and acceptor are reduced implying that interactions become stronger. Thus, the increase in the degree of charge transfer causes an increase in the saturation magnetization (inset of Figure 5.24).

Figure 5.24 Temperature dependence of saturation magnetization (Ms) and charge transfer degree. Inset shows the relationship between Ms and charge transfer degree.

Figure 5.25 First-principles calculation based on density functional theory. a, Calculated TDOS of the perylene-F₄TCNQ molecule crystal. b, Calculated PDOS of the perylene-F₄TCNQ molecule crystal; c: Spin alignment in perylene-F₄TCNQ molecule crystal.

To determine the origin of the measured ferromagnetism, we investigated the magnetic properties of both crystals using a first-principles method based on density functional theory. Our calculations show that the magnetic state is more stable than the corresponding non-magnetic state for perylene-F₄TCNQ, even though the energy difference between the two states is small (8 meV per unit). On the other hand, the energy difference for perylene-TCNQ is essentially zero. The magnetic state of perylene-F₄TCNQ is further confirmed by the calculated total density of states (TDOS) (Figure 5.25a) which show asymmetric spin-up and spin-down densities, particularly at the Fermi level. The magnetic moment is estimated to be 0.15 μ_B /unit. The calculated partial density of states (PDOS) (Figure 5.25b) further reveal that the magnetic moment of perylene-F₄TCNQ is mainly due to N atoms (0.01 μ_B /N) and some C atoms (0.01~0.02 μ_B /C) (Figure 5.25c). Compared to perylene-TCNQ, more charges are transferred from the donor to the acceptor in perylene-F₄TCNQ. In perylene-F₄TCNQ, on an average, charges are transferred from H (0.043 e/H) to C (0.008 e/C), N (0.05 e/N) and F (0.01 e/F). In perylene-TCNQ, H loses 0.018 e while C gains 0.006 e and N gains 0.023 e. The total amount of charge transfer is estimated to be 0.43 e from perylene to F₄TCNQ and 0.17 e from perylene to TCNQ, respectively, which is in qualitative agreement with those obtained from IR spectrum. To confirm whether magnetism is due to changes in the molecular structure of the crystal compared to isolated molecules, or due to charge transfer, we calculated the magnetic properties of both molecules using structures optimized in the crystal environment. Both molecules are non-magnetic when they are

neutral. However, when they are charged at 1 e per molecule, both show magnetism. The magnetic moments of N and C atoms in charged perylene-F₄TCNQ are 0.04 and 0.08 μ_B , respectively, which are four times larger than those in the uncharged crystal. Hence, the observed magnetism is due to charge transfer. We note that a magnetic moment of 1 μ_B /unit should be observed in perylene-F₄TCNQ if the degree of charge transfer is 1. We anticipate that there are many metal-free organic ferromagnets based on a plethora of charge transfer compounds which remain to be discovered.

5.4 Conclusion

In summary, the crystal growth and charge transport properties of F₄TCNQ single crystals are investigated. F₄TCNQ single crystals showed an orthorhombic symmetry, which belonged to the Pbc_a space group with $a = 9.300(8)$ Å, $b = 8.19(1)$ Å and $c = 14.628(6)$ Å. It shows n-type characteristic. The maximum mobility is reached 0.001 cm²V⁻¹s⁻¹ and the on-off ratio is 10³. The methodologies of searching for novel organic charge transfer binary compounds and crystal growth in the case that only the two starting organic substances are known but the phase diagram is not known, the thermodynamic data of the binary compound are not known and even the existence of new binary compounds is not known were studied. We found that kinetically lowering the sublimation rate was the key factor for growing large-size charge transfer compound single crystals. By using this concept, crystals of novel perylene-F₁TCNQ perylene-F₂TCNQ and perylene-F₄TCNQ charge transfer binary compounds were obtained by decreasing the evaporation area of the individual components. Field-effect behavior was not observed in perylene-F₄TCNQ FETs. However, we found that the strong acceptor F₄TCNQ transfers sufficient charge from perylene to cause room-temperature ferromagnetism. On the other hand, the weak acceptor, TCNQ, does not cause ferromagnetism in perylene-TCNQ because the degree of charge transfer is too low. These results explain previous observations of ferromagnetism in metal-free organics and enable the design of novel ferromagnetic compounds due to strong charge transfer. Such compounds may be vital components for room temperature spintronic devices.

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Chapter 6

Charge transfer induced photoluminescence enhancement of WS₂/MoS₂-F₄TCNQ

In this chapter, charge transfer from the CVD-grown monolayer MoS₂ or WS₂ to F₄TCNQ was investigated. We found that the photoluminescence of this CVD-grown triangle monolayer of MoS₂ and WS₂ is enhanced by the deposition of F₄TCNQ on these monolayer surfaces. The intensity of the photoluminescence after deposition increases sharply. We concluded that charge transfer from the monolayer MoS₂ or WS₂ to F₄TCNQ is the key reason. Charge transfer increases the formation of neutral excitons at the expense of charged excitons.

6.1 Introduction

Two-dimensional (2D) materials such as graphene, hexagonal-BN, molybdenum disulfide (MoS₂) and tungsten disulfide (WS₂) have recently attracted broad interest because of their unique electronic, chemical and physical properties¹⁻⁵. Particularly great efforts have been made to apply the optical properties of the MoS₂ and WS₂ series for light-emitting^{6,7} and photo-transistor applications⁸.

The exciton plays an important role in the optical properties of 2D materials. The PL (photoluminescence) or absorption response of monolayer MoS₂ is dominated by neutral and charged excitons originating from the splitting of the valence band maximum at the K (K') point due to the large spin-orbital interactions^{9,10}. A previous report¹⁰ related that the densities of trions (many-body bound charged excitons) and excitons can drastically affect the photoluminescence. Therefore, the control of the excited carrier density is an effective method to modulate the optical properties of 2D materials. Switching the densities of trions and excitons via electrical gating and molecular adsorptions (e.g., H₂O, TCNQ) can dramatically enhance the photoluminescence of MoS₂¹¹⁻¹³.

The optical properties of MoS₂ and WS₂, especially the photoluminescence, are affected by the number of layers^{14,15}. Few-layered MoS₂ and WS₂ have an indirect band gap and show low photoluminescence, while monolayers of MoS₂ and WS₂ have a direct bandgap and strong photoluminescence^{15,16}.

The photoluminescence peak consists of two kinds of species, the trions (negatively or positively charged excitons) and neutral excitons^{9,10}. In quantum dots and wells, the concentration of two species can be modulated by laser excitation¹⁷, applying gate voltage¹⁸ and chemical doping¹⁹.

Mechanical exfoliation is the easiest and the fastest method to obtain monolayers of MoS₂ and WS₂. Recent publications related to the photoluminescence enhancement of MoS₂ and WS₂ reported this mechanical exfoliation method to obtain a monolayer^{9,12}. However, during exfoliation, only a small amount of MoS₂ and WS₂ crystals are monolayers, leaving a majority of samples as thicker flakes. By using exfoliation, it is difficult to produce large-scale monolayers of MoS₂ and WS₂. However, large-area, high-quality monolayers of MoS₂ and WS₂ can be grown by the CVD method used in this study.

To enhance the photoluminescence, a chemical doping method was used^{9,12}. In the doping process, acceptors were dissolved in a solvent, which may cause an interaction between the doping materials and the solvent²⁰.

In this study, we demonstrate the photoluminescence enhancement of large-area CVD-grown triangle monolayer MoS₂ and WS₂. The enhancement is due to the charge transfer between the monolayers of MoS₂ and WS₂ and the physical vapor-deposited thin layer of 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄TCNQ) molecules. It is found that the photoluminescence intensity is dramatically increased after deposition. The increment of the neutral exciton concentration by the dissociation of charged excitons is a consequence of the charge transferred from monolayer WS₂ and MoS₂ to the F₄TCNQ molecules. The weaker exciton–phonon scattering results in narrower PL peaks with larger amplitudes for WS₂ after F₄TCNQ deposition. No solvent is involved in the process, which prevents the interaction between solvent and monolayers and indicates that the increment in the excitons is only due to the charge transferred from the monolayer WS₂ and MoS₂ to the F₄TCNQ molecules.

6.2 Experimental Methods

6.2.1 Chemicals and materials

WO₃ (>99.5%), MoO₃ (>99.5%) and sulfur (>99.95%) powders were purchased from Sigma-Aldrich and used without any purification. F₄TCNQ (>99.5%) was purchased from Jilin OLED Materials Tech. Co. Ltd. and purified at 220 °C via physical vapor transport (PVT).

6.2.2 Preparation of MoS₂ and WS₂ monolayers

For both the triangular shaped MoS₂ and WS₂ monolayers, we used the same method of CVD. The growth process for the two materials is almost the same, with the only difference being the precursor. Commercially available SiO₂/Si substrates were used in this study. All the substrates were successively cleaned with acetone, methanol, H₂O₂/H₂SO₄ (1 volume / 4 volume) and distilled water in an ultrasonic bath for 5 min and then dried in ambient N₂. First, fine WO₃ or MoO₃ powder was spread on the bottom of the crucible. One piece of SiO₂/Si substrate (1×1 cm) was placed face-down on the crucible, and the crucible was put in the center of the growth furnace. Another small crucible with

approximately 50 mg sulfur powder was put in another part of the furnace near the gas input side at a temperature of 200 °C. The furnace was heated to 750 °C at 25 °C/min and then maintained at that temperature for 20 min before naturally being cooled down to room temperature. Argon gas was provided during the whole growth process at 60 sccm.

6.2.3 Preparation of F₄TCNQ layers on WS₂ and MoS₂ monolayers

2-nm F₄TCNQ was deposited on the WS₂ and MoS₂ monolayers by the evaporation of F₄TCNQ in a Tectra mini-coater (Germany) with a deposition rate of 0.1 angstrom per second. The system vacuum is 10⁻⁵ bar and the distance between sample and source is 20 cm.

6.2.4 Characterization

Photoluminescence was measured at the same area before and after F₄TCNQ deposition. Both the laser beams (solid-state laser, 473 nm and Nd:YAG solid-state laser, 532 nm) were collimated and focused through a ×100 objective onto the sample surface. All the spectra were collected using a confocal triple-grating spectrometer (Horiba-JY T64000). Raman spectra were recorded using a Renishaw Raman microscope configured with a charge-coupled device array detector with the excitation laser line of 532 nm. Atomic force microscopy was performed on a Digital Instruments 3100.

6.2.5 Density functional theory (DFT) calculation

The geometry of the F₄TCNQ on the surface of the MoS₂/WS₂ was optimized using the DMol³ ^{21,22} with the dispersion-corrected (OBS) PW91 (GGA) functional at the level of the DNP basis set. The geometry of the models is regarded as converged when the total energy difference is less than 1×10⁻⁵ Ha, the total force difference is less than 4×10⁻³Ha/Å, and the maximum displacement of atoms is less than 5×10⁻³Å during the optimization. The optimized geometries of the models were subsequently fed into the ORCA 3.0.3 package²³ to perform single-point energy calculations (with SCF convergence criteria set as 1×10⁻⁶ Ha) at the level of 6-31G(d,p) (with Mo and W atoms treated using SDD effective core potentials²⁴ using the B3LYP functional). To facilitate the charge transfer analysis, the MultiWFN 3.3.7 package²⁵ was used to calculate the charge transfer based on electron density difference.

6.3 Results and discussion

6.3.1 Monolayers WS₂ and MoS₂ fabrication

A triangle monolayer of WS₂ and MoS₂ was grown with the CVD method onto a Si/SiO₂ wafer. The monolayer growth apparatus is shown in Figure 6.1. Triangular WS₂ and MoS₂ were grown at random locations on the substrate.

Figure 6.1 Monolayer WS₂ and MoS₂ growth apparatus.

Figure 6.2 (a) Optical image of triangle monolayer WS₂. (b) AFM image of a monolayer WS₂ on a SiO₂/Si substrate and the corresponding section analysis. (c) Optical image of triangle monolayer MoS₂. (d) AFM image of a monolayer MoS₂ on a SiO₂/Si substrate and the corresponding section analysis.

6.3.2 Monolayers WS₂ and MoS₂ determination by AFM

Figures 6.2a and 6.2d show the optical images of the WS₂ and MoS₂, respectively. The thickness of the WS₂ and MoS₂ was determined by AFM, as shown in Figure 6.2c and 6.2e. The AFM images indicate that both the WS₂ and MoS₂ have a smooth surface. The cross section height of the WS₂ and MoS₂ is approximately 0.70 nm and 0.76 nm, respectively, which corresponds to the monolayers of WS₂^{9,26} and MoS₂^{6,27-29}.

6.3.3 Monolayers WS₂ and MoS₂ determination by Raman spectra

The monolayer structure of WS₂ and MoS₂ is further confirmed by the Raman spectrum shown in Figure 6.3. The E_{2g}¹ and A_{1g} modes of monolayer WS₂ are located at approximately 355 and 417 cm⁻¹, respectively^{30,31}. With the number of layers increased, the in-plane vibrational E_{2g}¹ is slightly red-shifted, and the out-of-plane A_{1g} mode is blue-shifted. The energy difference between the Raman E_{2g}¹ and A_{1g} modes increased with the layer number. Thus, the energy difference can be used to identify the number of layers of WS₂. The energy difference shown in Figure 6.3a is 62.5 cm⁻¹, which coincides with previous reports for monolayer WS₂^{30,32}. The same phenomenon is also observed in monolayer MoS₂. The in-plane vibrational E_{2g}¹ phonon mode is ~385 cm⁻¹, and the out-of-plane A_{1g} mode is ~404 cm⁻¹. The energy difference between the two modes is also dependent on the number of layers of MoS₂. The energy difference between the two modes is 18.2 cm⁻¹, as shown in Figure 6.3b, indicating that the MoS₂ is a monolayer^{12,28,33,34}.

6.3.4 The photoluminescence enhancement by charge transfer

Figure 6.4a shows that the photoluminescence (PL) intensity changed dramatically after F₄TCNQ was deposited onto monolayer WS₂. The PL intensity is approximately fifty times higher after the deposition. The position of the PL peak of monolayer WS₂ shifted to a slightly lower wavelength, while the shape did not change, as shown in Figure 6.4b. The PL intensity is also drastically increased by approximately ten times after the F₄TCNQ doping of monolayer MoS₂. The position of the peak is slightly changed, but the shape is not changed, as is shown in Figures 6.5a and 6.5b.

Figure 6.3 Raman spectra of a CVD-grown WS₂ monolayer (a) and MoS₂ monolayer (b). The inset shows the energy difference between the Raman E_{2g}¹ and A_{1g} modes.

Figure 6.4 PL spectra of monolayer WS₂ before and after F₄TCNQ doping (a) and PL peak shift of monolayer WS₂ before and after F₄TCNQ doping (b).

Figure 6.5 PL spectra of monolayer MoS₂ before and after F₄TCNQ doping (a) and PL peak shift of monolayer MoS₂ before and after F₄TCNQ doping (b).

The experimental results for PL enhancement for both MoS₂ and WS₂ are similar to the earlier reported photoluminescence of MoS₂ and WS₂ doped with F₄TCNQ from solution^{9,12}.

Figure 6.6 Fitted PL spectra of monolayer WS₂ (a) before and (b) after F₄TCNQ doping. Fitted PL spectra of monolayer MoS₂ (c) before and after F₄TCNQ doping (d). Lorentzian functions were used to fit the A and B peaks, with A peaks assumed to be composed of trions (X⁻) and excitons (X).

To understand the effects of charge transfer, the PL peaks have been analyzed by fitting them with photoluminescence from trions and photoluminescence from neutral excitons represented by two Lorentzian functions, as shown in Figure 6.6. For the all cases studied, the PL signal can be decomposed as A and B peaks, but the intensity of the B peak is negligible. The A peak can be further decomposed to trion (X^-) and exciton (X) components. Peak positions from the fitting can be found in Table 1. The values in brackets for peak positions were previously reported^{9,12}. The trion spectral weight was also calculated and is listed in Table 1.

Table 6.1 Peak position and width for Lorentzian functions used to fit PL peak A in Figure 6.6.

Sample	Peak name	Peak Position (eV)	FWHM (meV)	I_{X^-}/I_{total}
1 L WS ₂ as-prepared	X^- trion	1.972 (1.96)	35	0.63
	X exciton	1.985	35	
F ₄ TCNQ-doped 1 L WS ₂	X^- trion	1.973 (1.98)	42	0.25
	X exciton	1.991 (2.02)	33	
1 L MoS ₂ as-prepared	X^- trion	1.83 (1.84)	48	0.70
	X exciton	1.85 (1.88)	40	
F ₄ TCNQ-doped 1 L MoS ₂	X^- trion	1.83 (1.84)	70	0.20
	X exciton	1.865 (1.88)	60	

For both WS₂ and MoS₂, the trion spectral weight I_{X^-}/I_{total} decreases after charge transfer, as shown in Table 1. This indicates that the charge transfer significantly decreases the concentration of trions by transferring electrons from the trions into acceptors, thereby enhancing the photoluminescence.

To shed light into the charge transfer from MoS₂/WS₂ to F₄TCNQ, we also performed density functional (DFT) calculations³⁵ on the model systems shown in Figure 6.7. In both the F₄TCNQ-doped MoS₂ and WS₂ cases, charge density depletion (as indicated by the blue isosurfaces) were found in the interface regions where the nitrogen atoms in the F₄TCNQ molecules are closest to the surface sulfur atoms in MoS₂ and WS₂, as shown in Figures 6.7a and 6.7c, respectively. The charge density depletion in the MoS₂ layer is slightly greater than in the WS₂ layer according to the electron density difference plots. A

charge density increase (green isosurfaces) is observed on the F₄TCNQ molecules in both cases, as shown in Figures 6.7a and 6.7c. Charge transfer occurs around the interface regions in both cases. In addition, the barycenters of the holes (blue isosurfaces) shown in Figures 6.5b and 6.5d clearly suggest that the holes are close to the MoS₂ and WS₂ surfaces, indicating the charge transfer from MoS₂ or WS₂ to F₄TCNQ. The charge transfer distance (D_{CT}) between MoS₂ and F₄TCNQ (calculated $D_{CT} = 1.299 \text{ \AA}$) is shorter than that between WS₂ and F₄TCNQ (calculated $D_{CT} = 1.391 \text{ \AA}$). Additionally, the calculated charge transferred from MoS₂ and WS₂ to F₄TCNQ was 0.271 and 0.237, respectively. These data are in good agreement with the trion spectral weight data (Table 1). The shorter charge transfer distance associated with the larger amount of charge transferred causes more trions to be dissociated to excitons, thereby leading to a lower trion spectral weight.

Figure 6.7 (a) Electron density differences (with +/- isovalues of 0.005 a.u.) and (b) barycenters (with +/- isovalues of 0.0001 a.u.) of an F₄TCNQ-doped MoS₂ cluster model. Green and blue isosurfaces indicates positive and negative values. Electron density differences (with +/- isovalues of 0.005 a.u.) and barycenters (with +/- isovalues of 0.0001 a.u.) for F₄TCNQ-doped WS₂ cluster model are given in (c) and (d), respectively.

Upon the deposition of F₄TCNQ on the monolayers, the charge transfer reaches a maximum because the trion spectral weight reaches the saturation region at approximately 0.2, in agreement with those found in solution-based work¹². We observe that the peaks for the corresponding X⁻ and X of PL are sharper for WS₂ than for MoS₂. The wider peak width is associated with a stronger coupling strength or a larger Huang-Rhys factor *S* for a typical semiconductor^{36,37}, so that we may ascribe the narrower PL peaks for WS₂ samples compared to MoS₂ as indicative of slightly weaker exciton-phonon coupling³⁸. After charge transfer to the F₄TCNQ, the peak width change is almost the same. The weaker exciton-phonon scattering of WS₂ results in narrower PL peaks with a larger amplitude.

6.4 Conclusion

In summary, triangle monolayer WS₂ and MoS₂ were grown using the chemical vapor deposition (CVD) method. The formation of the monolayers was confirmed by both AFM and Raman spectra. The PL increased after a thin layer of F₄TCNQ was deposited on the surface of the WS₂ and MoS₂ monolayers. The reason for such an increase is the dissociation of trions. This means that charged excitons, trions, lose electrons during the charge transfer from monolayer WS₂ and MoS₂ to F₄TCNQ. Meanwhile, the weaker exciton-phonon interaction of WS₂ results in narrower PL peaks with larger amplitudes. Therefore, the charge transfer of electrons to the acceptor, such as F₄TCNQ, from CVD-grown monolayer WS₂ and MoS₂ enhances the PL, and materials with weaker exciton-phonon interactions show a stronger PL intensity. Charge transfer to or from MoS₂ and WS₂ provides an effective mechanism of tuning the optoelectrical properties of 2D materials and leads to the application of these materials in lasers or LEDs.

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Chapter 7

Conclusions and Recommendations

This chapter firstly summarized the results: 1. The LUMO-HOMO gaps of the charge transfer compound are lower compared with individual components; 2. The main reason for solvent-dependent stoichiometry of PIT1 and P3T1 is determined by the solubility of the charge transfer compound; 3. The stoichiometry of donor and acceptor in charge transfer compound affected on the charge transfer properties; 4. Kinetically lowering the sublimation rate is the key point for growing large organic charge transfer compounds; 5. Perylene-F₄TCNQ is a room-temperature metal-free organic ferromagnet; 6. Charge transfer induced photoluminescence enhancement of WS₂/MoS₂-F₄TCNQ. After summarizing the results, it suggests future research directions. The main findings are discussed with reflect in the original hypothesis, which is thus verified.

7.1 Result summary

7.1.1 The LUMO-HOMO gap lowering

The best ways to determine the filled and empty electronic states (LUMO and HOMO) of the organics are use ultraviolet photoelectron spectroscopy (UPS) and inverse photoemission spectroscopy (IPES) techniques. However, it is difficult to get the neat thin films and we do not have the possibility to find the equipment. Therefore, the color of the single crystals is used to determine the gap lowering qualitatively.

For perylene-TCNQ system, the donor and acceptor is yellow, while the charge transfer compounds shown the black color. It indicates that some new energy level formed, which show lower absorption edge.

The same for perylene- F_4 TCNQ, the color change from yellow to red. The color change from light to dark indicates the absorption changes.

Figure 7.1 Ultraviolet-visible spectra of perylene, F_x TCNQ and perylene- F_x TCNQ.

Further, ultraviolet-visible spectroscopy was used to analysis the absorption edge of perylene, F_4 TCNQ and the charge transfer compounds. The absorption of perylene and F_x TCNQ is in the range from 2.0 eV to 2.7 eV, respectively. The charge transfer compound has much lower absorption in the range from 0.7 eV to 1.2 eV. This is an

evidence of the LUMO-HOMO gap lowering.

7.1.2 Solvent-dependent stoichiometry of P1T1 and P3T1

It was also shown that the stoichiometry of a binary organic charge-transfer compound depends upon the stoichiometry of the starting materials^{1,2} However, by using solution method, we observed an interesting phenomenon: the final stoichiometries of single crystal P1T1 and P3T1 are not affected by the stoichiometry of the starting materials, but by the solvent which we choose for the growing of perylene-TCNQ crystals. The P1T1 crystals were grown from toluene, whereas the P3T1 crystals were grown from benzene regardless of the acceptor/donor stoichiometry in the starting materials.

The classical inorganic precipitation-dissolution theory is used to explain this phenomenon. The stoichiometry of the binary crystal is influenced by the type of solvent and not by the stoichiometry of the starting materials: the crystals with lower solubility will precipitate first. As a result, only P1T1 is formed from toluene because P1T1 is less soluble than P3T1 in this solvent. As P3T1 is less soluble than P1T1 in benzene, only P3T1 was crystallized from benzene. Moreover, steady-state and time-resolved fluorescence measurements indicate that the high solubility of TCNQ in toluene results in weak fluorescence of perylene from the toluene solution due to formation of P1T1 that utilizes the perylene from the solution.

7.1.3 Correlations between properties and stoichiometry of donor and acceptor

Most of the reported organic charge transfer compound single crystals are binary ones. Compared with the case of the inorganic binary compounds, where well-documented libraries of phase diagrams provide useful information on the stoichiometry control and phase co-existence, it is striking that such phase diagrams for *organic* binary compounds are rather rare. Nevertheless, the availability of this information is extremely crucial in controlling the properties of single crystals of charge-transfer binary compounds due to such properties are strongly linked to the crystal structures. One example is the charge transfer degree, which is coupled to the electrical properties³. That in turn is affected not only by the type of molecules of which the binary compound is built, but also by the molecular packing and the molecular stoichiometry^{3,4}. The easiest way is to change the

properties of donors and acceptors. There are several methods: 1) Design new structure which does not a modified known structure. For example, C_{60} is a new structure compared with aromatic structure. 2) Add side chains or groups to a known framework. Such as pentacene, 6,13-Bis(triisopropylsilylethynyl)pentacene. 3) Substitute the carbon atoms by sulphur, nitrogen, selenium and so on. Besides the changing the properties of donors and acceptors, varies of the stoichiometry between donors and acceptors still provide a method to tuning the properties.

In perylene-TCNQ system, there are three stoichiometries of perylene and TCNQ. The structure difference is shown in Figure 7.2. There is one perylene molecular in P1T1 unit cell, two perylene molecules in P2T1 unit cell and three perylene molecules in P3T1 unit cell. The charge transport properties were measured of the three charge transfer compound. We found that P1T1 is typically an n-type semiconductor, P3T1 showed p-type behavior, whereas P2T1 showed ambipolar properties. From P1T1 to P3T1, the increase of perylene molecules in the unit cell may lead to the transformation of the single crystal from n-type to p-type. It may due to the extra perylene molecular create a new path way for the carrier transport.

Figure 7.2 Molecular packing by stoichiometry of P1T1, P2T1 and P3T1.

7.1.4 Establishing a method to grow large organic charge transfer single crystals

Organic semiconductors based on a single molecular building block are equivalent to inorganic semiconductors made from a single chemical element, such as silicon or germanium. The combination of two or more elements in inorganic chemistry results in an immense amount of binary and multinary compounds with new optical and electrical properties not appearing in one-component solids. Usually, binary phase diagrams describe the presence of individual inorganic binary compounds. However, the binary

phase diagrams between organics are rather rare, and the binary compounds in such phase diagrams are rarely known. Organic binary charge transfer compounds, which contain donor and acceptor molecules with mixed or segregated stacking⁵, show physical properties different from the individual properties of the donor and acceptor. The charge transfer compound may have high conductivity¹, superconductivity, strong electron-phonon interactions, ferromagnetism, antiferromagnetism, and optical and photovoltaic properties. Both the theoretical⁶ and experimental results⁷⁻¹⁰ indicate that field effect transistors made from organic charge transfer compounds can display n-, p-, or ambipolar charge transport properties. Single crystals of charge transfer compounds provide the opportunity to investigate the intrinsic properties¹¹ and structure-property relationships due to the nearly perfect structures and minimum concentration of structure imperfections (i.e., grain boundaries) and impurities¹²⁻¹⁴. The crystal growth of charge transfer compounds is more complex than that of monomolecular systems. Rather small crystals are required for X-ray or synchrotron crystal structure determination and, in this way, confirmation of compound existence. Larger crystals are required for electrical or optical property measurements. Even larger crystals are convenient for detailed studies of the anisotropy of the physical properties and the structure-property relationships. Generally, two methods are used to grow single crystals of charge transfer compounds: solution methods and vapor methods^{15,16}. The size of charge transfer compound single crystals varies from micrometers^{7,8,17-19} to millimeters^{20,21}. Solution growth methods, such as solvent evaporation, temperature lowering or antisolvent methods, use a third component, solvent, that complicates interpretation of the electrical or optical properties and can even form three-component charge transfer compounds in specific conditions. Therefore, gas phase transport in inert gas seems to be the method of choice for the crystallization of very pure, unknown compounds large enough for structure determination and properties measurements.

We found that kinetically lowering the sublimation rate was the key factor for growing large-size charge transfer compound single crystals. By using this concept, crystals of novel perylene-F₁TCNQ perylene-F₂TCNQ and perylene-F₄TCNQ charge transfer binary compounds were obtained by decreasing the evaporation area of the individual components.

7.1.5 Room-temperature metal-free organic ferromagnet

Ferromagnetism is present in some inorganic substances, such as iron based compounds. In organic compounds ferromagnetism may be observed when suitable metals are incorporated. In metal-free organics ferromagnetism has been reported at few degrees Kelvin, except for some recent observations of weak ferromagnetism at room temperature in Teflon²², graphene²³ and a specific polymer blend²⁴. However, a general method for rational design of new high temperature ferromagnetic metal-free compounds has not been proposed. Ferromagnetism is not expected to be observed in organic crystals at room temperature. However, pure organic molecular based ferromagnet, TDAE-C₆₀²⁵, shows π -electron ferromagnetism at comparatively high temperatures of 16 K. Ferromagnetism at room temperature, in an organic material, containing a metal, i.e. [V(TCNE)_x] $\cdot$ y(CH₂Cl₂) was reported in 1991²⁶ and another vanadium containing organic material in 1995²⁷. [V(TCNE)_x] $\cdot$ y(CH₂Cl₂) shows room temperature ferromagnetism which results from three-dimensional antiferromagnetic exchange of donor and acceptor spins. Furthermore, high-temperature metal-organic magnets were reported in 2007²⁸. Room temperature weak ferromagnetism was sporadically reported in some metal-free organic molecules and polymers, such as P3HT and PCBM blend films, graphene and modified-C₆₀. It was experimentally observed and calculated from first principles that strained Teflon displays weak ferromagnetism at room temperature due to unpaired electrons in dangling bonds. Nevertheless, room-temperature metal-free organic ferromagnet is still undiscovered.

After eliminating the presence of metals that may be responsible for this ferromagnetism, only the unpaired electrons localized in higher molecular orbitals can interact with each other, correlate their spins and show ferromagnetism. If the concentration of these unpaired electrons is large, ferromagnetism may be measurable. Control of dangling bonds is difficult and the concentration of unpaired electrons is rather low. Unpaired electrons forming dangling bonds are similar to unpaired electrons in molecular orbitals of charge transfer compounds. Both fill empty orbitals according to the Pauli Exclusion Principle. Charge transferred from donors to acceptors fills the molecular orbitals sequentially with unpaired electrons. We found the charge transfer compound: perylene-F₄TCNQ shows weak ferromagnetism at room temperature. The moment of the material

is around 0.001 emu/g and it shows a small hysteresis.

7.1.6 Correlations between magnetic properties and charge transfer degree

Both IR spectra and bond length methods are used to calculate the charge transfer degree. We found both charge transfer degree and magnetic moment increasing with temperature decreasing. For comparison, perylene-TCNQ was used to measure the ferromagnetic properties at room temperature. However, the weak acceptor, TCNQ, does not cause ferromagnetism in perylene-TCNQ, which is due to the degree of charge transfer is too low. Therefore, we concluded that the magnetic moment will increase if the charge transfer degree is increased.

7.1.7 Charge transfer induced photoluminescence enhancement of WS₂/MoS₂-F₄TCNQ

Two-dimensional (2D) materials such as graphene, hexagonal-BN, molybdenum disulfide (MoS₂) and tungsten disulfide (WS₂) have recently attracted broad interest because of their unique electronic, chemical and physical properties. The photoluminescence of 2D materials is very important in optical-electrical devices.

The PL increased after a thin layer of F₄TCNQ was deposited on the surface of the WS₂ and MoS₂ monolayers. The reason for such an increase is the dissociation of trions. This means that charged excitons, trions, lose electrons during the charge transfer from monolayer WS₂ and MoS₂ to F₄TCNQ. Meanwhile, the weaker exciton-phonon interaction of WS₂ results in narrower PL peaks with larger amplitudes. Therefore, the charge transfer of electrons to the acceptor, such as F₄TCNQ, from CVD-grown monolayer WS₂ and MoS₂ enhances the PL, and materials with weaker exciton-phonon interactions show a stronger PL intensity. Charge transfer to or from MoS₂ and WS₂ provides an effective mechanism of tuning the optoelectrical properties of 2D materials and leads to the application of these materials in lasers or LEDs.

7.2 Conclusion

The presence of weak bonds in binary and multinary compounds allows using these bonds for engineering new physical properties. In the presented thesis following

examples have been explored:

- Method for large single crystal growth
- Formation of new crystal structures
- Formation of new electron structure
- Formation of new band structure
- Appearing of new optical properties as absorption
- Appearing of transport properties
- Unexpected magnetic properties

Many more properties should be expected in this emerging group of compounds.

7.3 Validation of hypothesis

For hypothesis 1 “*The LUMO-HOMO gap will decrease after charge transfer from donor to acceptor*”, the color of the charge transfer compounds and ultraviolet–visible spectroscopy indicated that new energy level was formed. Meanwhile, the new energy gap is smaller than the LUMO-HOMO gap of donor and acceptor.

The crystallographic data and field effect transistor data confirmed the hypothesis that “*The physical properties, especially the electrical properties of organic single crystal charge transfer compound can control by the stoichiometry of donors and acceptors.*”

P1T1 is typically an n-type semiconductor, P3T1 showed p-type behavior, whereas P2T1 showed ambipolar properties. From P1T1 to P3T1, the increase of perylene molecules in the unit cell may lead to the transformation of the single crystal from n-type to p-type.

The new organic charge transfer compound of perylene-F₄TCNQ, which is not containing metal, shows room-temperature ferromagnetism. It is a proven of the hypothesis “*The organic single crystal charge transfer compounds may express some new properties*”.

For hypothesis 4 “*The charge transfer between organic and inorganic will change some physical properties, such as electrical properties or optical properties*”, it is confirmed in every measured system. As an example the MoS₂/WS₂-F₄TCNQ system may be cited. The PL increased after a thin layer of F₄TCNQ was deposited on the surface of the WS₂ and MoS₂ monolayers. The reason for such an increase is the dissociation of trions. This means that charged excitons, trions, lose electrons during the charge transfer from monolayer WS₂ and MoS₂ to F₄TCNQ. Meanwhile, the weaker exciton-phonon

interaction of WS₂ results in narrower PL peaks with larger amplitudes.

7.4 Future work

7.4.1 Correlations between properties and charge transfer degree

Only the correlation between magnetic properties and charge transfer degree was investigated in this thesis. However, other correlations were not found. Due to the charge transfer degree is response with temperature, the temperature depended properties can correlated with it. The new system of the charge transfer degree change should be found. One possibility is to dramatically change the electron affinity of acceptor to change the charge transfer degree. Therefore, we use F_xTCNQ (x=0,1,2,4) with perylene to grow the charge transfer single crystals. The preliminary results are shown below:

By using the kinetically lowering the sublimation rate method, perylene-F₁TCNQ and perylene-F₂TCNQ were obtained. The single x-ray diffraction data are shown in Chapter 5. Also, the charge transfer degree is calculated by bond length method shown in Table 7.1.

Table 7.1 Bond lengths and estimated charge transfer degree of F₁TCNQ, F₁TCNQ anion, perylene-F₁TCNQ, F₂TCNQ, F₂TCNQ anion, perylene-F₂TCNQ at 100K.

	a (Å)	b(Å)	c(Å)	d(Å)	c/(b+d)	CT
F ₁ TCNQ ²⁹	1.336	1.433	1.370	1.430	0.4785	0
F ₁ TCNQ ⁻³⁰	1.358(4)	1.422(4)	1.412(5)	1.417(6)	0.4974	1
Perylene-F ₁ TCNQ	1.345(4)	1.441(5)	1.377(4)	1.434(5)	0.4789	0.021± 0.031
F ₂ TCNQ ³¹	1.328	1.443	1.376	1.437	0.4778	0
F ₂ TCNQ ⁻³²	1.332	1.424	1.412	1.425	0.4956	1
Perylene-F ₂ TCNQ	1.335(2)	1.437(2)	1.384(3)	1.441(3)	0.4809	0.174± 0.003
F ₄ TCNQ	1.333(2)	1.436(2)	1.371(8)	1.433(2)	0.4779	0
F ₄ TCNQ ⁻³³	1.356(4)	1.414(4)	1.415(4)	1.430(6)	0.4975	1
Perylene-F ₄ TCNQ	1.344(3)	1.435(2)	1.387(2)	1.435(5)	0.4833	0.303± 0.005

The charge transfer degree is increased with F atoms increased. This gives us a chance to find other properties correlated with charge transfer degree.

7.4.2 Print growth of charge transfer compound single crystals

Organic semiconductor devices will find use in wearable electronics, large-area chemical sensors and uncountable other applications. Printable electronics technology provides one way to manufacture low cost, flexible, large area electronic devices.

Thus, the following experiments are proposed: Firstly, a proper solvent should be found to dissolve the donor and acceptor as well as it also should be suitable for printing. Then, the source and drain electrodes are fabricated on SiO_2/Si wafers. A droplet of acceptor solution is printed between source and drain on the wafer. After that, donor solution droplet is printed on the same area. The charge transfer effect will occur during the solution droplet mix together. Temperature should be carefully controlled for charge transfer compound single crystals growth. The schematic diagram of the printing process is shown in Figure 7.3.

Figure 7.3 The schematic diagram of the printing process of growth charge transfer compound single crystals.

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