The Stoichiometry of TCNQ-Based Organic Charge-Transfer Cocrystals

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Abstract: Organic charge-transfer cocrystals (CTCs) have attracted significant research attention due to their wide range of potential applications in organic optoelectronic devices, organic magnetic devices, organic energy devices, pharmaceutical industry, etc. The physical properties of organic charge transfer cocrystals can be tuned not only by changing the donor and acceptor molecules, but also by varying the stoichiometry between the donor and the acceptor. However, the importance of the stoichiometry on tuning the properties of CTCs has still been underestimated. In this review, single-crystal growth methods of organic CTCs with different stoichiometries are first introduced, and their physical properties, including the degree of charge transfer, electrical conductivity, and field-effect mobility, are then discussed. Finally, a perspective of this research direction is provided to give the readers a general understanding of the concept.

Keywords: single crystals; organic semiconductors; charge transfer cocrystals; the degree of charge transfer; conductivity; mobility

1. Introduction

Organic charge-transfer cocrystals (CTCs) is a new type of molecular crystal which is composed of organic donor and acceptor, in which electrons can transfer from the donor to the acceptor molecules [1–8]. Since quinhydrone as the first CTC was reported in 1844 [9], only the high conducting tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) began to attract considerable attention due to the wide range of applications in organic optoelectronics [10–14]. Furthermore, the balanced ambipolar charge transport properties of dibenzotetrathiafulvalene-tetracyano-quinodimethane (DBTTF-TCNQ) also opened a door for organic co-crystal electronics [15,16]. Recently, organic CTCs have received intensive attention due to their tunable physical properties, ranging from insulators to conductors, and some potential applications in various fields have also been reported, such as the pharmaceutical industry [17–19], bio-electrochemical energy transfer process [20], optoelectrical devices [21,22], surface chemistry [23], non-linear optical materials [24], multiferroicities [4,25] as well as energy and solar energy storage [21,26,27]. As a recently studied topic, organic CTCs can be applied as active semiconducting layers in field-effect transistors, in which n-type, p-type, and ambipolar (the charge carrier is both electrons and holes) charge transport properties are experimentally observed [28–30].

In general, the physical properties of organic CTCs can be tuned by three approaches. The first method involves the variation in the donor/acceptor molecular structures. Compared to inorganics, the changing of the donor/acceptor molecule is similar to the changing anions/cations in inorganics.
Crystals 2020, 10, x 2 of 19

For example, NaCl and KCl have different properties due to the difference of cations in inorganics. Organic CTCs, systems such as TTF-TCNQ and perylene-TCNQ exhibit different electrical conductivity properties due to the difference of the donor molecules [6,13]. The second alternative approach is to control the polymorphs. It indicates that the crystals have the same chemical formula but have different molecular crystal structures. For instance, CaTiO$_3$ has a cubic structure at high temperatures and orthorhombic symmetry at low temperatures [31]. The same feature can be observed in organic CTCs, for example, perylene-TCNQ exhibits two phases [32]: $\alpha$ phase with monoclinic symmetry (at room temperature) and $\gamma$ phase with triclinic symmetry (below 210 K). Finally, the stoichiometry between the donor and the acceptor is a particularly important factor in determining the physical properties of a given organic CTCs. In inorganics, the stoichiometry is determined by the oxidation state of elements. For example, owing to the different oxidation states of Hg, HgCl$_2$ and Hg$_2$Cl$_2$ have varied stoichiometries between Hg and Cl, which reveal quite different physical and chemical properties [33]. In organic CTCs, the stoichiometry between the donor and the acceptor can also play an important role in controlling the physical properties [34–36]. For example, perylene-TCNQ with the stoichiometry of 1:1 (P1T1) shows $n$-type semiconducting behavior with electron mobility of $10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, while perylene-TCNQ with the stoichiometry of 3:1 (P3T1) exhibits $p$-type semiconducting results with a hole mobility of $10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ [37]. It reveals that the charge transport type and performance can be tuned via the variation of the stoichiometry between the donor and the acceptor.

The degree of charge transfer (DCT) reveals the number of charges transferred from the donor to the acceptor [38–40]. The change of the stoichiometry can affect the DCT of organic CTCs. Thus, the DCT is introduced to evaluate the physical properties of CTCs. The DCT can be determined from the bond length variation in the charge transfer process by single X-ray diffraction (XRD) measurement or the wavenumber changes of certain vibration modes by infrared (IR) spectroscopy or Raman spectroscopy measurements [6,41,42].

There are many papers related to charge transfer cocrystals published in several special issues of the journal Crystals covering different aspects, including donor-acceptor packing type of cocrystals [43,44], hydrogen-bonded co-crystals [45,46], conducting and superconducting co-crystals [47,48], etc. However, it is still worth discussing the role of stoichiometry between donor and acceptor in co-crystals. Among the abovedescribed three methods, it is still difficult to precisely control the stoichiometry between the donor and the acceptor via the designed experiments, although a few related cases have been reported. Thus, this short review summarizes the change in the stoichiometry of organic CTCs, which is mainly based on the work of our group, in order to provide the readers with a comprehensive understanding of the concept. First, single-crystal growth methods for growing organic CTCs with different stoichiometries are discussed, and their physical properties, in particular, DCT and electronic properties, are then discussed in detail. TCNQ-based organic CTCs have been widely investigated in the last few decades; therefore, herein we limit ourselves to consider the TCNQ-based organic CTCs. The discussed organic donors and acceptors for the formation of organic CTCs are presented in Figure 1. Finally, a general perspective of this direction is provided.

![Figure 1](image_url)

**Figure 1.** Molecular structures of organic donors and acceptors for the formation of charge-transfer cocrystals discussed in this review.
2. Single-Crystal Growth of Organic Charge-Transfer Cocrystals with Different Stoichiometry

In general, controlling the molar proportion of the starting materials is a semi-empirical way to obtain organic CTCs with different stoichiometries, and in some cases, it works while it does not succeed in many other cases. In a practical scenario, it is actually difficult to know which experimental parameters will affect the stoichiometry of organic CTCs during the co-crystallization process. Therefore, it is necessary to analyze the single-crystal growth of organic CTCs, in order to analyze the function of the cocrystallization parameters in detail. Herein, three main cocrystallization methods are introduced: solid-state grinding method, solution-based method, and gas-phase method [49–52].

In the pharmaceutical industry, solid-state grinding is commonly employed as an efficient way to screen new organic CTCs. The solid-state grinding consists of two techniques: neat grinding and liquid assisted grinding. The difference between the two methods is that a small amount of an additional liquid is added to the grinding mixture for liquid assisted grinding. For example, Tothadi et al. [53] reported the synthesis of isonicotinamide and dicarboxylic acid CTCs (Figure 2a) by the liquid-assisted grinding method.

Figure 2. (a) Isonicotinamide and coformers (dicarboxylic acids) used for cocrystallization; (b) Powder X-ray diffraction (PXRD) of pimelic acid: isonicotinamide (red) (1:1) crystals and (black) (1:2) crystals; (c) PXRD of suberic acid: isonicotinamide (red) (1:1) crystals and (black) (1:2) crystals; (d) PXRD of azelaic acid: isonicotinamide (red) (1:1) crystals and (black) (1:2) crystals; (e) PXRD of sebacic acid: isonicotinamide (red) (1:1) crystals and (black) (1:2) crystals. Data are reproduced with permission from [53].
In the beginning, the donors and the acceptors were taken in the required stoichiometric ratio (1:1 or 2:1) and were ground after adding 2–3 drops of EtOH. Then, the ground powder was dissolved in a minimum amount of hot methanol (MeOH). After evaporation of the solvent for several days, the final CTCs with different stoichiometries were obtained. The powder XRD patterns show that the obtained CTCs with varied stoichiometries have a distinct phase for the four systems (Figure 2b–e). The alkali-TCNQ and some TTF-based CTCs can be synthesized by such methods, such as Cu-TCNQ [54], Rb$_2$-(TCNQ)$_3$I$_2$ [55], TTF-chloranil [56], etc.

Solid-state grinding is quite efficient in finding new CTCs with different stoichiometries by changing the starting ratio of the donors and the acceptors. However, it is not easy to obtain large crystals and it always needs post-treatment (such as solution-based method) to obtain single crystals.

The following four solution-based methods (Figure 3) can be employed to grow organic CTCs: slowing cooling method (Figure 3a), slow solvent evaporation method (Figure 3b), vapor diffusion method (Figure 3c) and liquid-liquid interface diffusion method (Figure 3d). For the first three methods, the donors and the acceptors are mixed together and then are dissolved in a certain solvent or mixed solvent. Once the charge transfer between the donor and the acceptor occurs, the CTCs can nucleate and then grow larger in size by decreasing the temperature or evaporating the solvent of the saturated CTCs solution. If the donors and the acceptors are dissolved separately in the two immiscible solvents, the CTCs single crystals can be achieved at the interfaces.

![Figure 3. Solution-based methods for the single-crystal growth of organic charge-transfer cocrystals (CTCs): (a) slowing cooling method; (b) slow solvent evaporation method; (c) vapor diffusion method; (d) liquid-liquid interface diffusion method.](image)

Organic CTCs can also be grown by simply mixing the donor and acceptor and simultaneously dissolving them in one or a mixed solvent. In the perylene-TCNQ system, the (perylene)$_1$-(TCNQ)$_1$ single crystals were prepared by slowly evaporating the chloroform solution with an equimolar ratio of perylene and TCNQ [57]. The (perylene)$_3$-(TCNQ)$_1$ single crystals were obtained by slowly evaporating the benzene solution with a different molar ratio of 3:1 between perylene and TCNQ [58].

However, in some special situations, the final stoichiometry of organic CTCs is not dependent on the molal proportion of the starting mixed donors and acceptors [59]. Our group previously found that the single-crystal growth of (perylene)$_1$-(TCNQ)$_1$ (P1T1) and (perylene)$_3$-(TCNQ)$_1$ (P3T1) by the slow cooling method exhibited solvent dependence on the stoichiometry (Figure 4a). Irrespective of the initial mixed molal proportion between perylene and TCNQ, the P1T1 single crystals are formed only from the toluene solvent, while the P3T1 single crystals are obtained solely from benzene solution. Single crystals of P1T1 are needle-like, while P3T1 crystals are cube-like. Thus they can be easily distinguished based on morphology (Figure 4b,c). The precipitation–dissolution equilibrium theory was employed to explain the phenomenon. The results indicate that the stoichiometry of the single-crystal growth is governed by the solubility of the CTCs. The solubility of P1T1 is larger than that of P3T1 in benzene and smaller than that of P3T1 in toluene (Figure 4d). Consequently, the P1T1 first precipitates in toluene, and P3T1 firstly precipitates in benzene. All the possible equilibria with regard to the single-crystal...
growth routes are shown in Figure 4e. In toluene, even if the P3T1 cocrystals are formed first, the P1T1 cocrystals are finally obtained due to their low solubilities. It is for the same reason that P3T1 cocrystals precipitate in benzene.

Figure 4. (a) Single-crystals growth of (perylene)$_3$-(TCNQ)$_1$ and (perylene)$_1$-(TCNQ)$_1$ by slow cooling method exhibits a solvent-dependent on the stoichiometry; (b) Optical images of (perylene)$_1$-(TCNQ)$_1$ single crystals from toluene; (c) Optical images of (perylene)$_2$-(TCNQ)$_1$ single crystals from benzene; (d) The solubilities of (perylene)$_3$-(TCNQ)$_1$ and (perylene)$_1$-(TCNQ)$_1$ in toluene and benzene at different temperatures (mol/L); (e) All possible equilibria in the perylene-TCNQ system. TCNQ: tetracyanoquinodimethane. Data are reproduced with permission from [59].

By using the solution method, it is easy to control the stoichiometry of the CTCs by controlling the ratio of starting materials, even though there are a few exceptions. Another advantage is that large, good quality crystals can be obtained. However, solvent molecules may get incorporated into the crystal structure, which prevents the preparation of the required CTCs [60].

Three gas-phase methods are used for the single-crystal growth of organic CTCs (Figure 5), depending on the sublimation temperatures of the starting materials. In one case, if the sublimation temperatures of organic donors and acceptors are nearly equal, the starting materials can be mixed together and put into a two-zone furnace with an argon gas flow for the single-crystal growth (Figure 5a). In another case, if the sublimation temperatures of organic donors and acceptors are dramatically different, the powders or single crystals of the starting materials with low sublimation temperatures can be placed at the left side of the furnace, and the powders or single crystals of the starting materials with high sublimation temperatures can be placed at the right side of the furnace. Then, under an argon gas flow, organic CTCs initially grow at the right end of the furnace (Figure 5b). Occasionally, if the sublimation temperatures of organic donors and acceptors are quite low, no time is allowed to nucleate organic CTCs in an open system. In this situation, a closed ampoule can be used for the single-crystal growth of organic CTCs. In detail, the sealed ampoule is placed into the two-zone furnace (Figure 5c). In the gas-phase growth process, the vapor pressure of the individual components is determined. In other words, the vapor pressure of the individual components determines the amount of donor/acceptor molecules sublimed to the single crystals zone, and further defines the stoichiometry of CTCs. Consequently, the stoichiometry of the final crystals is random.
In perylene-TCNQ systems, single crystals of both the monomolecular (perylene and TCNQ) and the three perylene–TCNQ CTCs [(perylene)$_1$–(TCNQ)$_1$, P1T1; (perylene)$_2$–(TCNQ)$_1$, P2T1; (perylene)$_3$–(TCNQ)$_1$, P3T1] are grown simultaneously by the gas-phase method (Figure 6).

Thus, they can be easily distinguished based on their color and morphology. Both perylene and TCNQ single crystals show a yellow color, while thin CTCs exhibit a green color, and thick CTCs display a dark-green or black color. Moreover, it was also possible to visually distinguish needle-like P1T1 crystals from platelet-shaped P2T1 and P3T1 crystals. However, only by single XRD or Raman spectroscopy, the P2T1 and P3T1 single crystals can be differentiated from each other. Obviously,
by using the gas-phase growth method, the contamination of the solvent can be easily avoided. Nevertheless, the stoichiometry of the final CTCs cannot be controlled.

Besides the perylene-TCNQ system, there are limited reports on the different stoichiometry CTCs with the same donor and acceptor for TCNQ-based systems, such as the TTT (tetrathiotetracene)-TCNQ system [61], and the coronene-TCNQ system [62]. The single-crystal growth parameters of different CTCs systems are summarized in Table 1.

Table 1. Single crystal growth parameters of different CTCs systems.

| Donor   | Acceptor | Stoichiometry | Method                  | Solvent ** | Ref. |
|---------|----------|---------------|-------------------------|------------|------|
| perylene| TCNQ     | 1:1           | slow cooling            | benzene:acetonitrile = 5:1 | [63] |
| perylene| TCNQ     | 1:1           | gas-phase open system   | N.A.       | [37,64] |
| perylene| TCNQ     | 1:1           | slow cooling            | toluene    | [59] |
| perylene| TCNQ     | 1:1           | slow solvent evaporation| acetonitrile | [65] |
| perylene| TCNQ     | 2:1           | gas-phase open system   | N.A.       | [37] |
| perylene| TCNQ     | 3:1           | vapor diffusion         | benzene    | [63,64] |
| perylene| TCNQ     | 3:1           | gas-phase open system   | N.A.       | [37] |
| perylene| TCNQ     | 3:1           | slow cooling            | benzene    | [59] |
| perylene| TCNQ     | 3:1           | slow evaporation        | acetonitrile | [65] |
| perylene| F1TCNQ   | 1:1           | gas-phase close system  | N.A.       | [66] |
| perylene| F1TCNQ   | 1:1           | gas-phase open system   | N.A.       | [67] |
| perylene| F1TCNQ   | 3:2           | gas-phase close system  | N.A.       | [66] |
| perylene| F2TCNQ   | 1:1           | slow cooling            | toluene:acetonitrile = 5:1 | [68] |
| perylene| F2TCNQ   | 3:2           | gas-phase open system   | N.A.       | [67] |
| perylene| F2TCNQ   | 3:2           | gas-phase close system  | N.A.       | [66] |
| perylene| F2TCNQ   | 1:1           | slow cooling            | toluene:acetonitrile = 5:1 | [68] |
| perylene| F2TCNQ   | 1:1           | gas-phase open system   | N.A.       | [67] |
| perylene| F2TCNQ   | 3:2           | gas-phase close system  | N.A.       | [66] |
| TTT     | TCNQ     | 1:1           | slow cooling            | methanol   | [61] |
| TTT *   | TCNQ     | 1:2           | slow cooling            | nitrobenzene | [61] |
| coronene| TCNQ     | 1:1           | slow solvent evaporation| dichloromethane | [62] |
| coronene| TCNQ     | 3:1           | slow cooling            | benzene    | [62] |
| coronene| MeTCNQ   | 1:1           | slow solvent evaporation| dichloromethane | [62] |
| coronene| MeTCNQ   | 2:1           | slow solvent evaporation| dichloromethane | [62] |
| coronene| F1TCNQ   | 1:1           | diffusion               | dichloromethane:pentane = 1:5 | [69] |
| coronene| F1TCNQ   | 2:1           | gas-phase close system  | N.A.       | [70,71] |

* TTT = tetrathiotetracene; ** N.A. = Not Applicable.

3. Electronic Properties of Charge-Transfer Cocrystals with Different Stoichiometry

3.1. The Degree of Charge Transfer

As mentioned in the Introduction section, DCT reveals the amount of charge transferred from the donor to the acceptor. The geometry of the donor or the acceptor may vary when the charge transferred [72]. Consequently, DCT can be estimated by calculating the variation in the bond length. In TCNQ or fluorinated TCNQ CTCs, the length of some bonds is especially sensitive to the negative charge on molecules [73–75]. It means that the bond lengths are changed when the acceptor shows an increasing negative charge. The population of electrons in TCNQ or fluorinated TCNQ leads to the increase in the length of two bonds (a and c), while decreasing the length of the other two bonds (b and d) (Figure 1) [76,77]. Therefore, DCT can be estimated by single-crystal XRD. The equations used for calculations are represented below [41,42,67]:

\[
DCT = \frac{a_{CT} - a_0}{a_{-1} - a_0}
\]

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, and charge transfer compound, respectively (Figure 1). The subscripts CT, −1, and 0 refer to the charge transfer compound, the anion, and the neutral molecular, respectively.
Furthermore, spectrophotometry is another convenient method to determine the DCT. When the charge has transferred from donor to acceptor, the intensities of molecular vibration bands get enhanced. Thus, the certain vibration mode of the CTCs in IR spectroscopy and Raman spectroscopy can be used to calculate the DCT. The corresponding equation is shown below [38,41,42,67,72]:

$$CT = 2\Delta v / v_0 \left(1 - v_1^2 / v_0^2\right)^{-1}$$

where $\Delta = v_0 - v_{CT}$. The $v_0$, $v_{CT}$ and $v_1$ represent certain stretching modes of pure TCNQ molecules, charge transfer compound, and TCNQ anion, respectively.

In TCNQ or fluorinated TCNQ CTCs, the C=C in-plane stretching mode ($A_g$ symmetry) [37,67,78] and the C≡N stretching mode ($b_{1u}$ symmetry) [67,79] are always used to determine the degree of charge transfer. The detection C=C in-plane stretching mode is convenient by Raman spectroscopy, and that of the C≡N stretching mode is convenient by IR spectroscopy. Figure 7 shows typical IR and Raman spectra of CTCs for calculating the DCT. For the pristine 2-fluoro-7,7,8,8-tetracyanoquinodimethane (F1 TCNQ), 2,5-difluoro-7,7,8,8-tetracyanoquinodimethane (F2 TCNQ), and 2,3,5,6-tetrafluoro-7,7,8,8-8-v-tetracyanoquinodimethane (F3 TCNQ), the peak for C=C in-plane stretching mode is observed at 1452 cm$^{-1}$. After the charge gets transferred from perylene to F1 TCNQ, F2 TCNQ, and F3 TCNQ, the peak downshifts by 11, 15, and 21 cm$^{-1}$ for perylene-F1 TCNQ, perylene-F2 TCNQ, and perylene-F3 TCNQ, respectively (Figure 7a,b). For the C≡N stretching mode, the peaks of pristine F1 TCNQ, F2 TCNQ, and F3 TCNQ are located at 2223, 2220, and 2230 cm$^{-1}$, respectively. After obtaining electrons from perylene, the peaks are redshifted to 2221, 2225, and 2221 cm$^{-1}$ for perylene-F1 TCNQ, perylene-F2 TCNQ, and perylene-F3 TCNQ, respectively (Figure 7c,e). Then, by using the equation mentioned above, the degree of charge transfer can be easily estimated.

Even though the absolute value of the DCT is different for the three methods, the existence of some trends between the stoichiometry and the DCT can still be concluded. Table 2 lists the DCT for some TCNQ and fluorinated TCNQ CTCs systems. In most cases, with the increase of donor numbers, the DCT increases. In other words, more than one donor contributes charges to one acceptor, which results in the increment of the DCT. For example, in the perylene-TCNQ system, the DCT increases from 0.01 to 0.23 attributed to the increase in the number of perylene molecules from 1 to 3 in the unit cell [37]. However, in perylene-F1 TCNQ, perylene-F2 TCNQ, and perylene-F3 TCNQ systems, the ratio between organic donors and acceptors is not an integer, which leads to nearly the same DCT [66,80]. For the 1:1 stoichiometry CTCs, the DCT increases dramatically with the increment of the number of F atoms. It is due to not only the strong electron affinity of fluorine atoms [67], but also the incorporation of strong C–H···N and C–H···F interaction [41]. For example, a strong C–H···F interaction results in a larger contributions to the DCT (0.46 ± 0.04) in naphtho[1,2-b:5,6-b’]dithiophene (NDT)-1,3,4,5,7,8-hexafluorotetracyanonaph-thoquinodimethane (F6TNAP) system [41].

**Table 2.** The degree of charge transfer in some TCNQ and fluorinated TCNQ CTCs systems.

| Donor     | Acceptor | Stoichiometry | Degree of Charge Transfer |
|-----------|----------|---------------|---------------------------|
|           |          |               | Bond Length | IR | Raman |
| perylene  | TCNQ     | 1:1           | 0.01 ± 0.07 [37] | -  | 0.04 ± 0.02 [37] |
| perylene  | TCNQ     | 2:1           | 0.12 ± 0.07 [37] | -  | 0.13 ± 0.02 [37] |
| perylene  | TCNQ     | 3:1           | 0.23 ± 0.06 [37] | -  | 0.17 ± 0.02 [37] |
| coronene  | F1 TCNQ  | 1:1           | -           | 0.1 [62] | - |
| coronene  | F2 TCNQ  | 2:1           | -           | 0.15 [71] | - |
| perylene  | F1 TCNQ  | 1:1           | 0.021 ± 0.061 [67] | 0.08 ± 0.05 [67] | - |
| perylene  | F1 TCNQ  | 3:2           | -           | 0.1 [66] | - |
| perylene  | F2 TCNQ  | 1:1           | -           | 0.13 [60] | - |
| perylene  | F2 TCNQ  | 3:2           | 0.17 ± 0.01 [67] | 0.15 [68] | - |
| perylene  | F3 TCNQ  | 1:1           | 0.30 ± 0.02 [67] | 0.25 ± 0.03 [67] | - |
| perylene  | F4 TCNQ  | 3:2           | -           | 0.29 [68] | - |
Even though the absolute value of the DCT is different for the three methods, the existence of some trends between the stoichiometry and the DCT can still be concluded. Table 2 lists the DCT for some TCNQ and fluorinated TCNQ based organic CTCs systems. In most cases, with the increase of donor numbers, the DCT increases. In other words, more than one donor contributes charges to one acceptor, which results in the increment of the DCT. For example, in the perylene-TCNQ system, the DCT increases from 0.01 to 0.23 attributed to the increase in the number of perylene molecules from 1 to 3 in the unit cell [37]. However, in perylene-F1TCNQ, perylene-F2TCNQ, and perylene-F4TCNQ systems, the ratio between organic donors and acceptors is not an integer, which leads to nearly the same DCT [66,80]. For the 1:1 stoichiometry CTCs, the DCT increases dramatically with the increment of the number of F atoms. It is due to not only the strong electron affinity of fluorine atoms [67], but also the incorporation of strong C–H···N and C–H···F interaction [41]. For example, a strong C–H···F interaction results in a larger contributions to the DCT (0.46 ± 0.04) in naphtho[1,2-b:5,6-b’]dithiophene (NDT)-1,3,4,5,7,8-hexafluorotetracyanonaphthoquinodimethane (F6TNAP) system [41].

### 3.2. The Electrical Conductivity and Field-Effect Mobility

Table 3 presents the conductivity of some TCNQ based organic CTCs with different stoichiometry. The analyzed data indicate that the conductivity has no relationship with the stoichiometry. In the perylene-TCNQ system, the CTCs with different stoichiometry show semiconducting properties with relatively low conductivity. However, the TTT-TCNQ CTCs exhibit quite high conductivity. Several reports indicate that the observed different conductivities are due to the different molecular packing in these organic CTCs systems [2,4,81,82].

| Donor    | Acceptor | Stoichiometry | Conductivity ($\sigma$)/S·cm$^{-1}$ | Ref. |
|----------|----------|---------------|--------------------------------------|------|
| perylene  | TCNQ     | 1:1           | $10^{-10}$–$10^{-8}$                  | [6,37]|
| perylene  | TCNQ     | 2:1           | $10^{-11}$–$10^{-9}$                  | [6,37]|
| perylene  | TCNQ     | 3:1           | $10^{-11}$–$10^{-9}$                  | [6,37]|
| TTT       | TCNQ     | 1:1           | 1                                    | [83]  |
| TTT       | TCNQ     | 1:2           | 100                                  | [83]  |
The schematic representation of organic CTCs with different molecular packing is shown in Figure 8a. In general, for 1:1 stoichiometry, there are two major molecular packings: mixed-stack and segregated-stack. In the mixed-stack systems, the donor and the acceptor molecules alternate (–D–A–D–A–) along the stacking direction and are parallel to each other. For example, in the anthracene-F_4TCNQ system, anthracene and F_4TCNQ molecules alternate not only along the b-direction, but also the c-direction (Figure 8b) [42]. However, in the segregated-stack systems, the donor and the acceptor molecules form adjacent separated (–A–A–A– and –D–D–D–) stacks, and the D and A columns are parallel to each other. TTF-TCNQ adopts this type of molecular stacking (Figure 8c) [6]. For 2:1 stoichiometry, three packing modes exist. First, more number of donors forms –D–D–A–D–D–A– packing along the stacking direction for mixed-stack system. Second, if existed in the segregated-stack systems, the donor and the acceptor molecules also form –A–A–A– and –D–D–D– stacks [84]. Finally, the donor and the acceptor molecules form –D–A–D–A– stacking along with the π-stacking orientations, and an additional donor molecule is inserted between the adjacent stacks. For example, in the P2T1 single crystals, one perylene molecule still undergoes face-to-face “π–π” stacking with nearby one TCNQ molecule and another perylene molecule undergoes “herringbone” packing between two –D–A–D–A– chains (Figure 8d) [37]. For 3:1 stoichiometry, the donor and the acceptor molecules form –D–D–A–D–A– stacking along the π-stacking orientations, and an additional donor molecule is inserted between adjacent stacks. In the P3T1 single crystals, two perylene molecules are located between each pair of TCNQ molecules, and a third perylene molecule is located between the perylene-TCNQ stacks (Figure 8e) [37]. In recent reports, the donor and acceptor can also form the 3:2 stoichiometry. There are two chains, and one chain adopts –D–A–D–A– stacking while another one takes –D–A–D–A–D– stacking (Figure 8f) [66]. It can be regarded as a mixed-stacking. In general, the mixed stacking system exhibits a lower conductivity, while the segregated stack normally generates a higher conductivity.

The mobility and carrier type are also dramatically affected by the stoichiometry. There are quite limited reports on the effect of stoichiometry on the field-effect mobility. Thus, the perylene-TCNQ system is still considered as an example [37,65]. The typical transfer curves of P1T1, P2T1, and P3T1 are shown in Figure 9. Single crystals of P1T1 show n-type property with maximum mobility of 10^{-3} cm^2 V^{-1} s^{-1}. The P3T1 cocrystals show p-type performance, and the maximum mobility is ~10^{-4} cm^2 V^{-1} s^{-1}. Comparative analysis indicates that the P2T1 cocrystals show ambipolar properties with a hole mobility of 3 \times 10^{-5} cm^2 V^{-1} s^{-1} and electron mobility of 7 \times 10^{-5} cm^2 V^{-1} s^{-1}. Noteworthy, when more perylene molecules contribute electrons to one TCNQ molecular, an n-type semiconductor becomes ambipolar and further becomes a p-type semiconductor. All the performances of the representative devices are presented in Table 4. The experimental results from the different research groups can get an agreement with the transport type, and the field-effect mobilities are higher or lower, depending on the different device fabrication techniques.

Table 4. Performance of single-crystal field-effect transistors based on (perylene)_1-(TCNQ)_1, (perylene)_2-(TCNQ)_1 and (perylene)_3-(TCNQ)_1.

| Donor       | Acceptor | Stoichiometry | Carrier Type | Mobility/cm^2 V^{-1} s^{-1} | Ref. |
|-------------|----------|---------------|--------------|------------------------------|------|
| perylene    | TCNQ     | 1:1           | n            | 10^{-3}                      | [37] |
|             |          |               |              | 0.05                         | [65] |
| perylene    | TCNQ     | 2:1           | ambipolar    | n                            | 7 \times 10^{-5} | [37] |
|             |          |               |              | P                            | 3 \times 10^{-5} | [37] |
| perylene    | TCNQ     | 3:1           |              | P                            | 10^{-4} | [37] |
|             |          |               |              |                              | 0.03  | [65] |
Hirshfeld surface analysis is a good way to investigate the intermolecular interactions in the molecular crystal [76,85–88]. The distance from the surface to the nearest nucleus in another molecule atom in the molecule itself is defined as distance internal to the surface (di) (Figure 11 b1 and d1). When the number of perylenes increased in the unit cell (perylene)2-(TCNQ)1; (f) Crystal packing of the (perylene)3-(TCNQ)1. (a) is reproduced with permission from [2]; (b) is reproduced with permission from [42]; (c) is reproduced with permission from [6]; (d,e) are reproduced with permission from [37]; (f) is reproduced with permission from [66].

**Figure 9.** Electrical characteristics of the perylene-TCNQ crystals. (a) (perylene)$_1$-(TCNQ)$_1$ with silver contacts (top contact); (b) (perylene)$_2$-(TCNQ)$_1$ with silver contacts (bottom contact); (c) (perylene)$_3$-(TCNQ)$_1$ with gold contacts (bottom contact). Data are reproduced with permission from [37].

Hirshfeld surface analysis is a good way to investigate the intermolecular interactions in the molecular crystal [76,85–88]. The distance from the surface to the nearest nucleus in another molecule is defined as distance external to the surface ($d_e$), while the distance from the surface to the nearest atom...
in the molecule itself is defined as distance internal to the surface ($d_i$). We take P1T1, P2T1, and P3T1 as examples to reveal the intermolecular interactions in the single crystals. The fingerprint plots visualizing $d_e$ and $d_i$ for C···C, C···H, C–H···N contacts (including reciprocal ones) generated for TCNQ in P1T1, P2T1, and P3T1 are shown in Figure 10. Meanwhile, the fingerprint plots visualizing $d_e$ and $d_i$ for C···C, C···H contacts (including reciprocal ones) generated for perylene in P1T1, P2T1, and P3T1 are shown in Figure 11. In all three charge transfer cocrystals, strong π-π stacking interaction between perylene and TCNQ molecules are illustrated by the green-yellow color around $d_e = d_i \approx 1.8 \text{ Å}$ (Figure 10a$_1$,b$_1$,c$_1$ and Figure 11a$_1$,c$_1$,e$_1$). In P2T1 and P3T1, the perylene contains two different positions. One is along the π-stacking orientations, and another is inserted between adjacent stacks (Figure 8d,e). Thus, the inserted perylene did not exhibit strong π-π stacking interaction with the TCNQ molecules (Figure 11b$_1$,d$_1$). When the number of perylenes increased in the unit cell from P1T1 to P3T1, the extra C···H interactions can be observed, which indicated that TCNQ acted as an acceptor as shown in Figure 10a$_2$,b$_2$,c$_2$). In P2T1 and P3T1, the perylene molecules contributed a strong C–H···π interactions. It is clearly seen that a “wings” in the fingerprint plots where $d_e > d_i$ (Figure 11c$_2$,e$_2$). Furthermore, in all P1T1, P2T1 and P3T1 charge transfer cocrystals, TCNQ acts only as C–H···N acceptor, as shown by the characteristic spike where $d_e < d_i$ (Figure 11a$_3$,b$_3$,c$_3$).

![Figure 10](image-url)
Conclusions

In summary, by presenting some representative organic charge-transfer co-crystal systems (CTCs), we have introduced the single-crystal growth methods and the physical properties of organic CTCs with different stoichiometries. The degree of charge transfer, conductivity, and field-effect mobility are discussed in detail. The stoichiometry of organic CTCs is a relatively new research topic, since there are still some experimental parameters that must be carefully controlled. The related research is still in its initial stage, which should be paid much attention to. The following key points should be developed in the future: (1) the single-crystal growth of organic CTCs with different stoichiometry should be developed. (2) Furthermore, in some special cases, the final stoichiometry of the CTCs is not dependent on the mixed molal ratio between the donor and the acceptor. Accordingly, the precise strategic design of the single-crystal growth of CTCs with different stoichiometry should be developed. (3) The conductivity is related to the molecular packing, and not affected by the increase of donor numbers, which is due to the fact that more than one donor contributes charges to the degree of charge transfer is dramatically affected by stoichiometry. The DCT increased with the one acceptor. (3) The conductivity is related to the molecular packing, and not affected by the increase of donor numbers, which is due to the fact that more than one donor contributes charges to the degree of charge transfer is dramatically affected by stoichiometry. The DCT increased with the one acceptor. (3) The conductivity is related to the molecular packing, and not affected by the increase of donor numbers, which is due to the fact that more than one donor contributes charges to the degree of charge transfer is dramatically affected by stoichiometry. 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Figure 11. Fingerprint plots visualizing $d_e$ and $d_i$ for C···C, C···H contacts (including reciprocal ones) generated for perylene in P1T1 (a1, a2, a3), P2T1 (b1, b2, b3), and P3T1 (c1, c2, c3, c4, c5, c6).
in some special cases, the final stoichiometry of the CTCs is not dependent on the mixed molal ratio between the donor and the acceptor. Accordingly, the precise strategic design of the single-crystal growth of CTCs with different stoichiometry should be developed. (2) Furthermore, the degree of charge transfer is dramatically affected by stoichiometry. The DCT increased with the increase of donor numbers, which is due to the fact that more than one donor contributes charges to one acceptor. (3) The conductivity is related to the molecular packing, and not affected by the stoichiometry for organic CTCs. However, the mobility can be modulated by the stoichiometry of the CTCs.

Despite some of the existing studies reviewed herein, the importance of the stoichiometry for organic CTCs is still underestimated. Thus, we hope this review would give some inspirations to look more into this topic and develop more systems to investigate the function of the stoichiometry in organic CTCs.

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