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Abstract. Semiconductor charge transfer (CT) cocrystals are an emerging class of molecular materials which combines the characteristics of the constituent molecules in order to tune physical properties. Cocrystals can exhibit polymorphism, but different stoichiometries of the donor-acceptor (DA) pair can also give different structures. In addition, the structures of the donor and acceptor as pristine compounds can influence the resulting cocrystal forms. We report a structural study on several CT cocrystals obtained by combining the polyaromatic hydrocarbon perylene with 7,7,8,8-tetracyanoquinodimethane (TCNQ) and its fluorinated derivatives having increasing electronegativity. This is achieved by varying the amount of fluorine substitution on the aromatic ring, with TCNQ-F_2 and TCNQ-F_4. We find structures with different stoichiometries. Namely, the system perylene:TCNQ-F_0 is found with ratios 1:1 and 3:1, while the systems perylene:TCNQ-F_x (x=2,4) are found with ratios 1:1 and 3:2. We discuss the structures on the basis of the polymorphism of perylene as pure compound, and show that by a judicious choice of growth temperature the crystal structure can be in principle designed a priori. We also analyse the structural motifs taking into account the degree of charge transfer between the perylene donor and the TCNQ-F_x acceptors and the optical gap determined from infrared (IR) spectroscopy. This family of materials exhibits tuneable optical gaps in the near-IR (NIR), promising applications in organic optoelectronics.

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INTRODUCTION

Organic molecular materials for electronic applications are typically based on pi-conjugated systems. The extension of the pi-conjugation and the presence of heteroatoms determines the electronic structure and many of the resulting properties, although the molecular packing in the solid state plays a crucial role when transport of excitons or charges are of interest.[1, 2] A more drastic approach in changing the properties of what are known as organic semiconductors is to combine materials in blends or cocrystals.[3] Recently, donor-acceptor (DA) CT crystals attracted substantial attention as candidates for ambipolar charge carrier mobility organic semiconductor materials.[4] This prediction, however, heavily relies on their crystal structure, because the supramolecular arrangement determines the bandwidth of the valence and conduction bands involved in the charge carrier transfer. Ideally, the bandgap, the bandwidth, and as a consequence the carrier transport characteristics could be tuned by performing small modifications to the donor or acceptor molecules in order to change their electronegativity. The issues in pursuing such an approach are intrinsically related to the crystal structure, since small variations in the chemical structure could promote novel unforeseen crystalline arrangements and polymorphs. In addition, if the DA pair of choice exhibits already polymorphism as pure compounds, i.e. exhibits different crystal structures, it is not immediately clear if polymorphism will be also encountered in the mixed crystal. In recent years the combination of aromatic hydrocarbons and halogenated acceptors attracted considerable attention for functional materials in electronics and photonics.[4-7] It is also well known that some aromatic hydrocarbons exhibit polymorphism[8, 9] and that the structure of halogenated compounds shows remarkable structural changes when more halogen atoms are inserted in the acceptor chemical skeleton. This is also one of the important aspects within the research focus of halogen bonding.[10]

Polymorphism developed as a massive research field, due to the opportunities that it offers for crystal engineering,[11] but also the challenges for structural purity in organic electronics applications.[12-14] The study of polymorphs, that was initially concentrated on pharmaceuticals, dyes and pigments, has nowadays expanded towards other types of molecular materials such as semiconductors,[15] superconductors,[16] and also conjugated polymers.[17, 18] The nature of polymorphism is intrinsically linked to the intermolecular interactions which hold together the molecules in the solid and their directionality.[19] Polymorphism becomes more complex when

the molecules constituting the crystal have different chemical identities and, together with the dispersive intermolecular interactions, other forces are at play. Two interesting examples are CT or mixed-valence crystals and solvates,[20] where orbital hybridization may occur.

Strictly speaking, the term polymorphism is historically linked to different crystalline structures of the same single component material. However, polymorphism in cocrystals exists and has been found in several CT crystals.[3, 21, 22] When studying cocrystals, different structures may arise just as a consequence of different stoichiometry of the two compounds, therefore, we name the phenomenon of different structures from different stoichiometry, *stoichiomorphism*. This name is also used in the science studying networks for a different purpose, which is network mapping.[23]

In this paper we have chosen to work with DA couples based on perylene and TCNQ-F_x, where x= 0 (TCNQ), 2, 4. We performed single crystal growth from solution and by physical vapour transport (PVT). The mixed crystals obtained combining perylene and TCNQ have already demonstrated promising semiconductor characteristics in single crystal field effect transistors (FET) and their ambipolar behaviour opens interesting possibilities for optoelectronic devices.[24, 25] Besides reviewing the crystal structures of perylene:TCNQ, we also present three new crystals forms obtained by combining perylene with TCNQ-F_2 and TCNQ-F_4. These three crystal structures are classified by stoichiometry exhibiting a 1:1 or 3:2 perylene:TCNQ-F_x ratio. Interestingly, while the 1:1 structures exhibit a typical alternating DA stack, the 3:1 and 3:2 stoichiomorphs are different and exhibit a common structural motif, i.e. two perylene molecules in a sandwich configuration with the TCNQ based acceptor in between. This quasi-1D trimeric arrangements are also accompanied by orthogonally oriented molecular units. In 3:1 perylene:TCNQ these orthogonal units are just perylene molecules, whereas in the 3:2 structures of perylene:TCNQ-F_2 and :TCNQ-F_4 the units are alternating DA stacks. By performing a series of optical spectroscopy experiments in the middle IR and NIR we determine: i) the degree of ionicity, ρ, between donor and acceptor analysing the charge sensitive vibrations of TCNQ-F_x and ii) the optical bandgap from the onset of CT exciton absorption band. The room temperature degree of charge transfer varies from a minimum of almost 0 for perylene:TCNQ (1:1) to a maximum of ~0.3 for perylene:TCNQ-F_4 cocrystals. For the same compounds the optical gap, from the absorption onset, varies from ~1.06 to 0.68 eV, respectively. We discuss the structures of cocrystals on the basis of ρ and the polymorphism in pure perylene. The possibility that the polymorphism of perylene could

influence cocrystal structures is suggested by the different growth temperatures of the stoichiomorphs above and below the phase transition temperature of perylene phases.

EXPERIMENTAL SECTION

Perylene (purity 99%) and TCNQ (98%) were purchased from Aldrich, whereas TCNQ-F_2 (98%) and TCNQ-F_4 were obtained from TCI (98%). The materials were used as received. Solvents of spectroscopic grade were purchased from Aldrich. For PVT growth, the materials were mixed in a glass ampoule which was sealed after 3 cycles of vacuum and nitrogen purging, with the last step of vacuum pumping overnight. The ampoule was then placed horizontally in a two zone furnace with some of the typical temperature profiles used for growth illustrated in Figure 1. Single co-crystals of perylene with TCNQ-F2 and with TCNQ-F4 were also obtained from solution growth. Equimolar solutions of perylene and TCNQ-F2 or –F4 were dissolved in a solvent mixture of toluene/acetonitrile (5/1) heated at 324 K. The solutions were left to cool at room temperature in sealed bottles in the laboratory environment. The single crystals were gathered from the solutions.

Single crystal diffraction intensity data for all structures were collected at 150 K on an Agilent SuperNova-E Dual diffractometer equipped with an Oxford Cryosystem, using CuKα radiation (λ= 1.5418 Å). Data were processed using the CrysAlisPro software (CrysAlisPro, Agilent Technologies, Version 1.171.37.35, release 13-08-2014 CrysAlis171.NET). For all structures a symmetry-related (multi-scan) absorption correction was applied. Crystal parameters are provided in Table S1. Structure solution, followed by full-matrix least squares refinement was performed using the WINGX-v2014.1 suite of programs throughout.[26]

Infrared spectra of the CT crystals were recorded with a Bruker ifs66 Fourier transform IR (FT-IR) spectrometer coupled to an IR microscope Hyperion 1000. The spectrometer is equipped with a liquid nitrogen cooled Mercury Cadmium Telluride (MCT) detector. The instrument setup allows for reflection and transmission measurements with polarized light. The parameter ρ was obtained from the shift of charge sensitive modes of TCNQ-F_x specified below and by benchmarking with respect to the neutral acceptor and fully ionized salts of TCNQ-F_x with potassium.[27] We have preferred to use this method in contrast to TCNQ-F_x bond lengths from X-ray measurements, since the vibrational frequencies will provide the ionicity of the cocrystals at room temperature and thus are more relevant for optoelectronic device applications.

RESULTS

We start the presentation of our results by reviewing the crystal structure of the pure compounds perylene and TCNQ-F_x. This will help in discussing the stoichiomorphism in the mixed cocrystals.

***Perylene*.** The donor, perylene, shows enantiotropic polymorphism, i.e. the Gibbs free energy of the two polymorphs, α and β, plotted as a function of temperature shows a crossing point before the respective melting points have been reached.[28] This is an important aspect, since above a certain temperature, 420 K for perylene, only the α phase is stable. Figure 2 (a,b) shows the molecular packing of the two known polymorphs of perylene. The β polymorph in Fig.2(a) exhibits a herringbone arrangement, also known as γ structure according to the classification of polyaromatic hydrocarbons (PAH) by Desiraju and Gavezzotti,[29] while the α is a sandwich herringbone. This different packing most remarkably results in different number of molecules per unit cell, Z, which is 2 and 4 for β and α, respectively. The symmetry space group and crystal system are instead the same, $P2_1/c$ and monoclinic. The polymorph α can be obtained through a phase transition by heating the β phase above 420 K,[9] but can also be prepared as pure phase by different methods and is stable at room temperature.[30, 31] The α polymorph melts at about 551 K. From a molecular point of view in the α-phase perylene molecules are not exactly planar and an angle of 1.6° can be measured between planes identified by the two condensed biphenyls. In α the intermolecular interactions are due to π–π dimer interactions in the sandwich, which accounts for 21% of the total contribution, the other main contribution is from molecules constituting a nonparallel dimer within the same sandwich herringbone plane.[32]

***TCNQ-F*$_x$.** Acceptors based on TCNQ are well known in the literature and as pure materials form different crystalline structures depending on the number of fluorine atoms substituting the hydrogens on the aromatic core. To the best of our knowledge, we could not find any report of polymorphism for these compounds.[33] We have re-determined the crystalline structures of TCNQ and TCNQ-F_4 and examined them all, the one of TCNQ is shown in Figure S1(a). It has a monoclinic crystal packing with space group *C2/c* and four molecules in the unit cell and confirms the structure by Long et al.[34] and Krupskaya et al.[35], CCDC: TCYQME and TCYQME03, respectively. The molecules are arranged in herringbone fashion and it is possible to identify four different π-stacking directions. Figure S1(b) shows the crystal structure of TCNQ-F_2, characterized by two molecules per unit cell (BERZON02).[35] The space group is *C2/m* and the unit cell is monoclinic. TCNQ-F_4 has four molecules in an orthorhombic

unit cell with space group *Pcab* and its structure is reported in Figure S1(c) and confirms the structures obtained by Emge et al.[36] (BAKPAE) and Krupskaya et al.[35] (BAKPAE01).

Perylene:TCNQ cocrystals. The structures of the two stoichiomorphs of perylene:TCNQ are reported in Figure 3a,b. These are two of the three structures reported thus far, since Kloc and coworkers recently reported a 2:1 stoichiomorph, that we could not observe in our growth experiments.[25] In the 1:1 stoichiomorph, the unit cell is monoclinic with space group $P2_1/c$ and two inequivalent molecular pairs per cell as already presented in previous investigations (CCDC: PERCTQ).[37] The molecules are arranged in two alternating stacks with a tilt angle between the long axis of perylene molecules belonging to different stacks, see projection on *bc* plane in side figure. There is also a tilt angle of 21.19° between the planes of perylenes from different stacks. Interestingly, the molecular planes of perylene and TCNQ in both the DA stacks are not parallel, but exhibit an inclination angle of 4.34°. This aspect together with a DA distance of 3.3 Å (plane to centroid), has important implications for charge transfer and likely also transport. The inclinations in these stacking planes could be linked the structure of pure TCNQ, where the inclination of planes passing through the inequivalent TCNQ molecules is 47.23° and the C_2 molecular symmetry axes are not aligned, c.f. Fig.S1(a).

Largely different is the arrangement of perylene in the 3:1 stoichiomorph first reported by Hanson (CCDC: TCQPER)[38] and then by Truong et al.[39] Here, each perylene molecule in the stack with TCNQ is paired with a second perylene and further there are perylene molecules with their planes parallel to the *a* axis, thus not directly involved in CT with TCNQ.[40] The unit cell structure is triclinic with *P-1* symmetry, with one *molecular trimer* per cell and the TCNQ molecule on the inversion centre in accordance to previous reports. It is important to underline here the similarity in the arrangement of the perylene molecules in the 3:1 complex with respect to the polymorph α of pure perylene (Fig. 2b). In comparing the two figures it appears as if TCNQ molecules are inserting in between the perylene dimers in the sandwich structure. The molecular planes of perylene and TCNQ are not parallel in the DAD stack, but form an angle of 2.99°. Therefore, it is not possible to quote a distance between the molecular planes, but we have calculated the distance between the perylene plane and the centroid on TCNQ, which is 3.249 Å. Further, perylene molecules in the DAD stack are not exactly planar with an angle of 0.86° between the biphenyls, in contrast to the perylenes parallel to the *a* axis, which are fully planar. An important aspect that will be further discussed below concerns the *growth temperatures* for the two polymorphs. In order to effectively guide the stoichiomorphic

product, the 1:1 structure was obtained only by setting the high temperature side of the two zone furnace at 413 K while the cold at 373 K, thus both below the transition temperature for the pristine perylene phases of 420 K. For the 3:1 stoichiomorph the settings were instead 443 K and 383 K, respectively.

In terms of optical gap and charge transfer, the 1:1 cocrystal is already rather well characterized. In early optical reflectance studies the CT transition has been located around 10800 cm^{-1} (1.34 eV) and 12000 cm^{-1} (1.5 eV), with an onset at 8500 cm^{-1} (~1.05 eV) ref.[41, 42]. From the frequency and the oscillator strength of this transition, Ida et al.[41] estimated the degree of charge transfer (or ionicity) ρ to be around 0.1, and the hopping integral, t_{DA}, about 0.25 eV. Recent estimates of ρ by Raman spectra and the X-ray bond length of TCNQ give ρ = 0.01 and t_{DA} = 0.375 eV by DFT calculations.[25] It is known since long time that Raman frequencies do not provide a reliable estimate of the ionicity in mixed stack CT crystals due to perturbing effect of electron-molecular vibration coupling.[43] Therefore, in our work we are using IR spectra, by looking at selected charge sensitive modes. The IR spectra of perylene:TCNQ 1:1 in Figure 4a are shown together with those of pristine perylene and TCNQ. In Figure S2 we also compare the IR spectra of TCNQ and of the ionic compound K:TCNQ, the latter representative of $(TCNQ^{\bullet})^{-}$ molecular vibrations. From this last comparison we identify the unique asymmetric C=C stretching at 1543 cm^{-1} which shifts to 1509 cm^{-1} in charged $(TCNQ^{\bullet})^{-}$, as giving a reliable estimate of ρ. We have opted for this genuine reporter of ρ, in contrast to the quite often used frequencies of CN stretching modes above 2200 cm^{-1} which are subjected to extrinsic effects such as the crystal environment.[44] As shown in Fig. 4a, for both light polarizations, parallel to the *a* axis (red curve) and parallel to *b* (blue curve) the C=C stretching coincides with the same mode measured in pristine TCNQ. The spectra of the 1:1 cocrystal is indeed the superposition of the spectra of neutral perylene and TCNQ, and we conclude that in this complex $0 \leq \rho < 0.1$. The agreement with the Raman estimations in reference [25] is not surprising in this case, as the perturbing effect of the electron-molecular vibration becomes evident at intermediate ionicities.[43]

The optical reflectivity spectra of the 3:1 cocrystal from literature shows a band at 10500 cm^{-1} (1.3 eV) with onset at 9000 cm^{-1} (1.12 eV), ascribed to a charge transfer exciton, with a shoulder at 12000 cm^{-1} (1.5 eV), whose origin is not clear.[40] Figure 4b shows the IR spectrum of the 3:1 cocrystal recorded with light impinging perpendicularly to the *ab* crystal plane and polarized parallel and perpendicular to the *b* axis. For such polarizations the TCNQ

antisymmetric C=C stretching has components in both polarizations. The charge sensitive mode is at 1535 cm^{-1}, yielding a value of ρ of about 0.2. With the help of earlier calculations[45] of the frequency of the CT transition as a function of the above estimate of ρ and the transition energy of the CT transition[40] yield an estimate of t_{DA} = 0.4 eV. This value can be compared with the above reported estimate t_{DA} = 0.2 eV for the 1:1 co-crystal,[41] obtained from an analogous combination of experiment and calculations. We conclude that the mixing between D and A states is indeed larger in the DAD trimer of the 3:1 cocrystal than in the regular stack of the 1:1 co-crystal, as it can be expected from the shorter D-A distances by 0.051 Å.

Perylene:TCNQ-F_2 cocrystals. We report two new structures from perylene combined with TCNQ-F_2, whose unit cells are shown in Figure 3c,d. The structure of the 1:1 cocrystal exhibits two alternating stacks along the *a* axis. The unit cell is monoclinic with symmetry $P2_1/n$ and two inequivalent pairs of molecules. In comparing this 1:1 structure with the one formed by perylene and TCNQ (Fig.3a) it can be noticed that the stacks with TCNQ-F_2 are slipped one respect to the other by one molecular unit. In addition, the relative orientation of the perylene in the two stacks is different from the one observed for perylene:TCNQ shown above. This can be clearly noticed in the two projections on the side of Fig.3a and c. The stack is regular (molecules on inversion centers), with 3.28 Å distance between D and A. The F atoms are disordered as a result of the rotational disorder and the average occupation of the position pairs (2,5) and (3,6) is 70:30. The molecular planes of perylene and TCNQ-F_2 form an angle of 2.37° in both stacks. The perylene molecule is planar.

Figure 3d shows the structure of the 3:2 stoichiomorph which is isostructural to the one of perylene:TCNQ-F_4 presented below. The crystal structure is triclinic, with *P-1* symmetry and two pairs of inequivalent molecules in the unit cell. The structure is characterized by DAD trimers arranged in a quasi-one dimensional stack parallel to the *c* axis. There are two types of trimers characterized by different inclination angles between perylenes and TCNQ-F_2 of 1.75° and 1.89°. In addition, the two types of trimers are tilted by about 48°, a value measured for the planes passing through the TCNQ-F_2 of the two trimers. This latter inclination angle is reminiscent of the herringbone angle between sandwiches in α perylene. A slightly dimerized perylene-TCNQ-F_2 stack (distance between D and A is d = 3.28(1) Å) is found along the *a* axis, approximately perpendicular to the trimers' layer. In this dimerized DA stack the molecules are almost parallel with an angle of 0.52°. There are two equivalent DA stacks in the unit cell, slipped with respect to the other. This slipping is reminiscent of the 1:1

stoichiomorph from the same DA pair. In terms of intramolecular planarity the perylene molecules are planar in the DA stacks, while they exhibit an angle of ~1.2° between the byphenyls in the DAD stacks. Like the 1:1 stoichiomorph, the 3:2 shows orientational disorder in the position of the fluorines. We notice that a good yield of the 1:1 structure was reached by performing the growth with the cold end of the ampoule at 387 K, while for the 3:2 stoichiomorph the temperature was increased to 413 K.

In the 1:1 stoichiomorph we are able to observe the onset of the CT absorption band at 7000 cm^{-1} (0.88 eV) from IR spectroscopy (Figure S3(a)). Although we are not able to measure the frequency of the peak, it is clear that the CT frequency is well below the CT excitons of both perylene:TCNQ cocrystals presented above. The polarized IR spectra of the *ab* plane are compared in Figure 5a with those of neutral perylene and TCNQ-F_2. The IR spectra of TCNQ-F_2 and K:TCNQ-F_2 are reported in Fig. S4, where we can identify three charge sensitive modes at 1575, 1550 and 1395 cm^{-1}, with ionization frequency shifts of 50, 63 and 44 cm^{-1}, respectively. The frequencies of these three bands in the 1:1 cocrystal yield an estimation of ρ of 0.13, 0.15 and 0.1, respectively. The two polarizations explored give very similar results and show mainly a difference in intensity correlated to the orientation of the TCNQ-F_2 molecules in the unit cell. On the basis of these results we estimate that ρ is ~0.14, considerably higher than in the 1:1 cocrystal of perylene:TCNQ.

For the 3:2 cocrystal, similarly to the 1:1, the onset of CT transition is about 7000 cm^{-1} (Figure S3(b)), but, at variance with the 1:1, does not show a detectable dichroism in our measurements, which are performed with light polarized along the *a* or *c* axis. From the structural data of Fig. 3d, we associate the band polarized along *a* to the CT exciton along the DA stack, and the band polarized along *c* to a CT exciton in the DAD trimer. In order to estimate the degree of charge transfer we have focused on the same spectral region as for the 1:1 cocrystal. However, the more complex structure of the unit cell requires a more detailed spectral analysis. Figure 5b compares the polarized IR spectra of the *ac* plane with the spectra of neutral TCNQ-F_2, evidencing the frequency shifts of the three charge sensitive bands. The vibrational bands at 1541 and 1383 cm^{-1}, are sensitive to polarization, while the band at 1570 cm^{-1} exhibits weak dichroism. A more detailed analysis of the 1570 cm^{-1} band and comparison with the Raman spectra (Figure S5) reveals the presence of a vibronic band[46] superimposed to the charge sensitive mode in the spectrum polarized along the *c* axis. We note also that the bands at 1570 and 1541 cm^{-1} have a doublet structure. While it is difficult to interpret this last

observation without calculations of vibrational modes, we suggest that this is due to a slightly different ionicity of TCNQ-F_2 in the DA stack and in the DAD trimer. The spectral shifts of these modes result in an estimated ionicity, dependent on which peak of the doublet is considered, ranging from 0.10 to 0.22. However, on the basis of the data collected so far it is not possible to clearly distinguish between the ionicity of TCNQ-F_2 in the DAD trimers from the one in DA stacks.

Perylene:TCNQ-F_4 cocrystals. Figure 3e,f shows the two stoichiomorphs that we have obtained. While the 1:1 stoichiomorph shown here is not reported thus far, the 3:2 structure in Fig3f confirms the structural data by Tsutsumi and coworkers (CCDC: NUSZUY).[47] The 1:1 structure was obtained only from solution growth and is characterized by a row of molecules with DA stacking. Initially we characterized a 1:1:1 solvated structure where the third component was a toluene molecule from the solvent, as reported in Figure S6 and Table S1. Note that the toluene molecule in the unit cell shows orientational disorder. A full desolvation of this system could be obtained after a few days in the atmosphere, resulting in the structure shown in Fig.3e. Several attempts to grow the perylene:TCNQ-F_4 by vapour transport did not produce crystals large enough for a detailed crystallographic analysis. In fact, the growth by vapour transport with the cold end of the ampoule held at 403 K leads to the formation of the 3:2 stoichiomorph or very small crystals with undetermined structure.

The 1:1 Perylene:TCNQ-F_4 crystal has a triclinic unit cell with *P-1* symmetry and one pair of molecules per unit cell. The DA regular stack is along the *a* axis with the perylene and TCNQ-F_4 molecular planes tilted by 1.68°. The perylene molecule is planar and the DA distance between the perylene molecular plane and the TCNQ-F_4 centroid is one of the shortest among all compounds, 3.235 Å.

The 3:2 stoichiomorph is shown in Fig.3f and exhibits a structure similar to the one reported in Fig.3d for the 3:2 co-crystal with TCNQ-F_2, as the two crystals are isostructural. The unit cell is triclinic with space group *P-1* and two pairs of inequivalent molecules. A detailed analysis of the inclination between the perylene and TCNQ-F_4 molecular planes reveals that in the two DAD trimer stacks there are angles of 2.17° and 1.95°, respectively. In the perpendicularly oriented DA stacks the molecular planes are instead parallel. The distances between perylene and TCNQ-F_4 are 3.269 and 3.210 Å in the two DAD trimers, respectively, and 3.284 Å in the DA stack. The perylene in the DA stack is not planar with an angle of 0.72° between the biphenyls.

The lowest electronic transition in the 1:1 structure has an onset at 5700 cm^{-1} (0.71 eV) which is mainly polarized parallel to the crystal growth direction, likely the *a* axis of the unit cell (Fig. S7(a)). This is the lowest optical gap among the materials presented in this study and corresponds to an onset for light absorption of wavelength close to 1.82 μm. In Figure 6a we report the vibrational spectra for polarizations parallel to the *a* (red curve) and *b* (blue curve) axes. Those are compared with the spectrum of neutral perylene and TCNQ-F_4. The spectra of neutral and fully ionized TCNQ-F_4 are reported in Fig. S8, have been extensively described in the literature and we focus here on the charge sensitive modes at 1396, 1550, and 1599 cm^{-1} (ref. [27]). In the cocrystal the mode at 1599 cm^{-1} shifts down to 1581 cm^{-1} showing a weak dependence on polarization, which is mainly due to the orientation of its transition dipole moment, not perfectly aligned with the *a* crystallographic axis (Figure 3e). The ionicity ρ from the three modes is 0.30, 0.25, and 0.32, respectively, suggesting a substantial transfer of charge from the perylene to TCNQ-F_4.

In the 3:2 stoichiomorph the optical absorption from charge transfer excitons shows an onset at 5500 cm^{-1} (0.68 eV) when the light is polarized along the main direction of crystal growth. This onset is shifted to 6200 cm^{-1} (0.77 eV) when the light polarization is turned by 90º (Fig. S7(b)). From these observations, we can extrapolate that the long axis of the crystal corresponds to the *a* axis of the unit cell, where the coupling with the transition dipole moment of CT excitons in the DA stack is optimal. When the light polarization is rotated we are instead probing in a direction almost parallel to the crystallographyc axis *c*, and therefore this band is associated to the CT excitons within the trimer. This assignment allows us to clearly distinguish the degree of charge transfer from the dichroism of the charge sensitive vibrations of TCNQ-F_4. Figure 6b shows the spectra for the two polarizations in the range 1300 to 1650 cm^{-1}. The investigated modes are the same as for the 1:1 cocrystal and small shifts can be noticed for the two polarizations, with the exception of the 1580 cm^{-1} band, in which the polarization parallel to *a* results in a weak intensity signal at the noise level. From the peaks and their polarizations, values of ρ of 0.29, 0.22 and 0.28 are found in the DA stack, whereas the values in the DAD trimers are 0.30 and 0.28. These are on average larger when compared to the interval of ρ (0.1-0.22) estimated for the isostructural stoichiomorph perylene:TCNQ-F_2. Considering that the structural differences between these 3:2 stoichiomorphs are minimal, the larger ρ and low optical bandgap for the TCNQ-F_4 based cocrystals arise from the larger electronegativity of this acceptor molecule.[48]

DISCUSSION

There is a similarity between the polymorphs of perylene and the stoichiomorphs that we have observed combining perylene with TCNQ-F_x in cocrystals. The sandwich structural motif of α perylene seems to be maintained with the insertion of a TCNQ acceptor in between the perylenes in all the stoichiomorphs with imbalanced ratios, i.e. 3:1 and 3:2. These structures are all characterized by perylene molecules deviating from perfect planarity, in a way similar to α perylene. In addition, both 3:2 structures have trimers with a herringbone arrangement. These structural similarities, together with the evidence that 3:1 and 3:2 stoichiomorphs are observed predominantly when the temperatures in the furnace are set above the phase transition temperature of β to α perylene (~420 K), indicate that the polymorphism of perylene could guide the stoichiomorphism in cocrystals. This rationale is also supported by the observation that 1:1 stoichiomorphs can be obtained only by setting below 420 K the low temperature part of the ampoule, where nucleation and growth occur, or by growing the crystals from solution at room temperature (perylene:TCNQ-F_4). However, the recent preparation of DA stoichiomorphs from other compounds, coronene:TCNQ,[49] where pure coronene is not known to have room temperature stable polymorphs, indicates that stoichiomorphism in cocrystals can be encountered independently of the D aromatic hydrocarbon structures. Therefore, this guiding effect cannot be generalized and a more in depth analysis of the intermolecular interactions is required to understand the structural motifs guiding cocrystal formation. In the 1:1 stoichiomorphs there seems to be a more pronounced role of TCNQ-F_x in driving the details of the molecular arrangement in the cocrystals. For example, the increasing fluorine substitution leads to slipped stacks in perylene:TCNQ-F_2 and perylene:TCNQ-F_4. These slipped stacks are also encountered when looking along the *a* axis of the dimerized DA rows in the two almost identical 3:2 stoichiomorphs.

In general, the ionicity ρ reported in Table 1 for all compounds, shows an increasing trend with the electronegativity of TCNQ-F_x in 1:1 cocrystals, but not a monotonic trend in the other stoichiomorphs and it is strongly correlated with the structure of the cocrystals. A common aspect that we want to discuss here is how the ionicity changes from the DAD trimers to the DA dimer structures. We observe that, when considering the same starting perylene:TCNQ-Fx couple, trimers, ie DAD, exhibit larger values of ρ in all the cocrystals. This could have a simple explanation connected to the availability of nearest neighbor perylene donors in the structure. In other words, in a simple picture a TCNQ-F_x molecule in a dimer stack has only

one perylene molecule with which can undergo a charge transfer interaction, whereas in a trimer more perylene donors can transfer charge density.

We now shortly comment on the perspective of charge transport and optoelectronic applications for the cocrystals reported here. Transport and optoelectronic properties of perylene-TCNQ 1:1 and 3:1 have been already characterized, [24, 25] whereas the generation of photocarrier has been investigated in perylene:TCNQ-F_4 3:2. [47] The transport properties along the mixed stack chain are connected to the superexchange or effective integral t^{eff} (t_{DAD} for holes and t_{ADA} for electrons), which in 1:1 perylene:TCNQ has been calculated in the range 50-70 meV for both holes and electrons.[24, 25] In perturbation theory the superexchange integral is connected to the direct CT integral t_{DA} and to Δ, the gap energy between DA and D^+A^- states in a DA pair:[4]

$$t^{eff} = \frac{t_{DA}^2}{\Delta}$$

For perylene-TCNQ 1:1 t_{DA} ~ 0.3 eV (see above), and from the optical gap we estimate Δ ~ 1 eV, so that the above equation gives t^{eff} ~ 90 meV, against the calculated 50-70 meV. We can then use perturbation theory to predict that the 1:1 co-crystal of perylene:TCNQ-F_2 should have a greater t^{eff} , since preliminary calculations show that t_{DA} is more or less the same, whereas Δ is certainly lower than the perylene:TCNQ homologue. According to the experiments by Tsutsumi et al.[47], the TCNQ-F_2 should exhibit good photocarrier generation and transport. We finally remark that for the three 1:1 co-crystals of perylene with TCNQ-F_x the optical gap, i.e. the energy of the CT transition, follows the well know linear relationship with ΔE_{REDOX}, ie the difference between the oxidation potential of D and the reduction potential of A.[50] Indeed, the reduction potential of TCNQ-F_2 (0.41 V vs. SCE) is about half-way between that of TCNQ (0.22 V) and TCNQ-F_4 (0.60 V),[51] as does the optical gap (Table 1).

The 1:1 cocrystal with TCNQ-F_4 is the closest to the Neutral-Ionic transition boundary, like for the CT cocrystal Tetrathiafulvalene-Chloranil, and indeed it exhibits the Neutral-Ionic transition under pressure[50]. This characteristic may lead to interesting ferroelectric and ferromagnetic phenomena. Since crystals of this compound have been obtained from solution, it would be interesting to explore the possibility to finely control their yield by using different solvents as it was recently done for perylene:TCNQ.[52] The structure of 3:2 stoichiomorphs is particularly interesting, since they could show anisotropic exciton and charge carrier transport in two orthogonal directions. In addition, we note that very similar CT cocrystals are known to

have a large third order optical nonlinearity and could be exploited in photonic applications for frequency conversion or light modulation.[53] Future work will be focusing on the nature of CT excitons and charge carrier photogeneration phenomena as well as nonlinear optical processes by time resolved spectroscopy in the NIR.[54]

CONCLUSION

We have reported the growth and design of some novel crystal structures based on perylene and TCNQ-F_x DA compounds. Interestingly, we have found that the cocrystals differ in stoichiometry and crystal structure, giving rise to the phenomenon of stoichiomorphism, can be guided by choosing growth temperatures above and below the phase transition temperature between perylene polymorphs. We notice a correlation between electronegativity and degree of charge transfer in the DA couples, but also an important role of structure in which trimeric assemblies result in a higher ionicity of the TCNQ-F_x molecules. The 3:2 stoichiomorphs of perylene with TCNQ-F_2 and TCNQ-F_4 exhibit optical gaps in the NIR part of the spectrum and a structure that is ideal for transport of charge and excitations in two perpendicular directions. This unique features promise a great potential for applications in organic optoelectronics. The results are also of importance for understanding CT interfaces between laminated pairs of single crystals.[55-57]

ASSOCIATED CONTENT

Supporting information. CIF file and checkCIF reports for perylene:TCNQ (3:1) CCDC-1439130, perylene:TCNQ (1:1) CCDC-1439129, perylene:TCNQ-F_2 (1:1) CCDC-1439123, perylene:TCNQ-F_2 (3:2) CCDC-1439126, perylene:TCNQ-F_4 (1:1) CCDC-1472427, perylene:TCNQ-F_4:toluene (1:1:1) CCDC-1439127, perylene:TCNQ-F_4 (3:2) CCDC-1439128, TCNQ CCDC-1439125, and TCNQ-F_4 CCDC-1439124. Infrared spectra of TCNQ, K:TCNQ, TCNQ-F_2, K: TCNQ-F_2, TCNQ-F_4, K:TCNQ-F_4. NIR spectra of all cocrystals and table with structural parameters. This material is available free of charge on the ACS Publications website at DOI:

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Figures

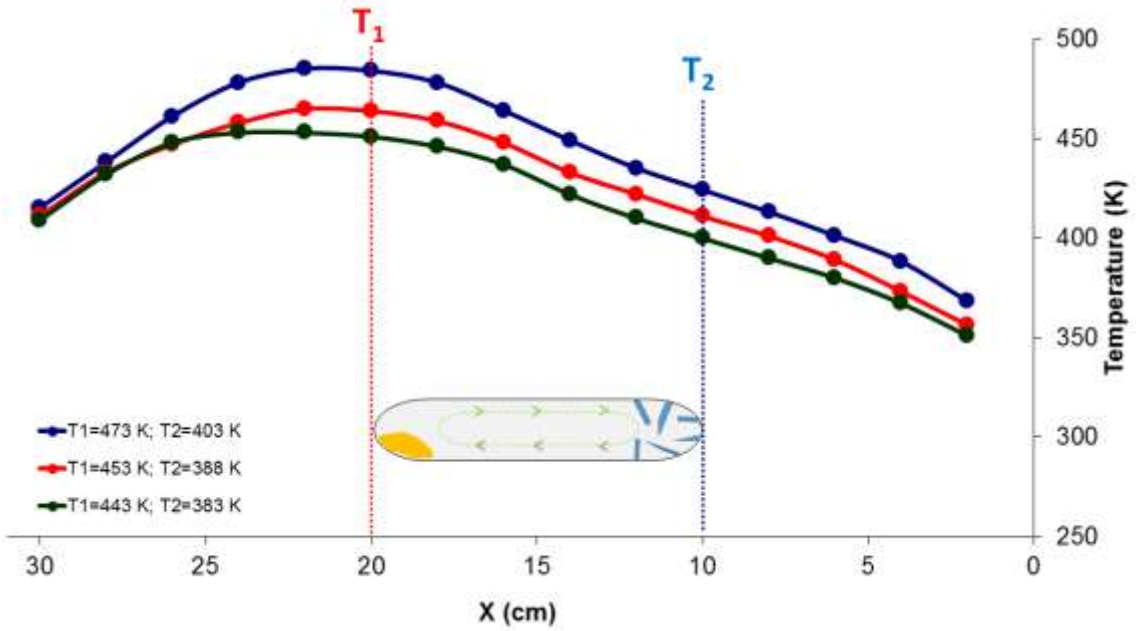

Figure 1. Scheme of the PVT crystal growth technique. The position of the quartz ampoule with respect to the two heating zones of the furnace is shown together with some of the temperature profiles used for the crystal growth reported in this work.

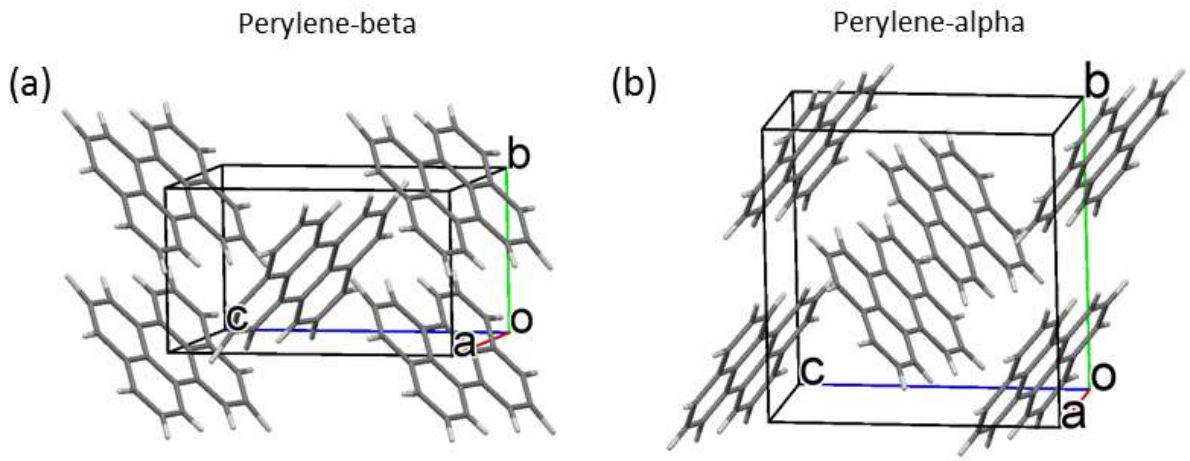

Figure 2. The two known polymorphs of perylene. (a) β perylene unit cell with two inequivalent molecules per cell. (b) α perylene with four molecules per unit cell.

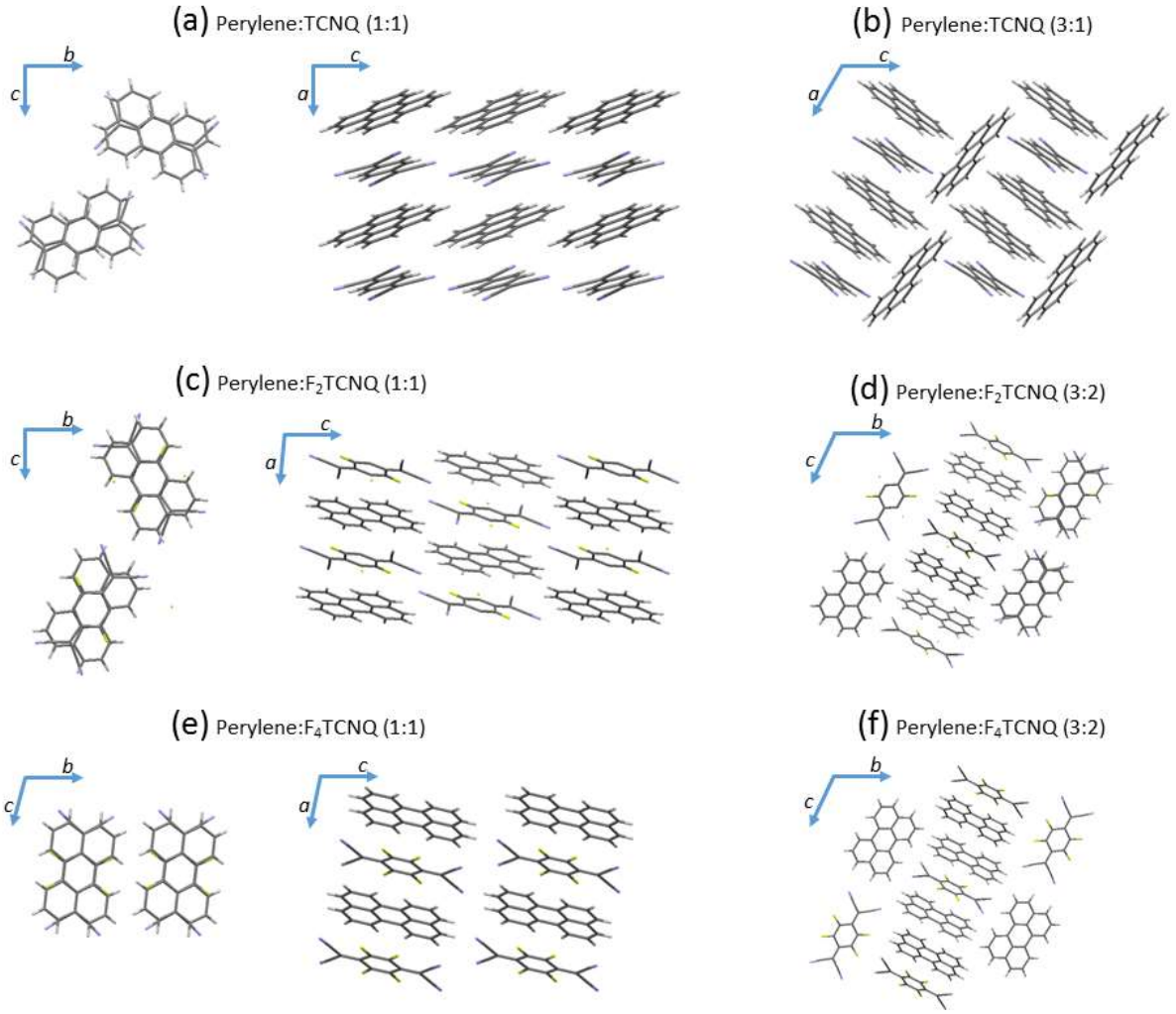

Figure 3. Crystal structures of (a) perylene:TCNQ 1:1, (b) perylene:TCNQ 3:1, (c) perylene:TCNQ-F_2 1:1, (d) perylene:TCNQ-F_2 3:2, (e) perylene:TCNQ-F_4 1:1, and (f) perylene:TCNQ-F_4 3:2.

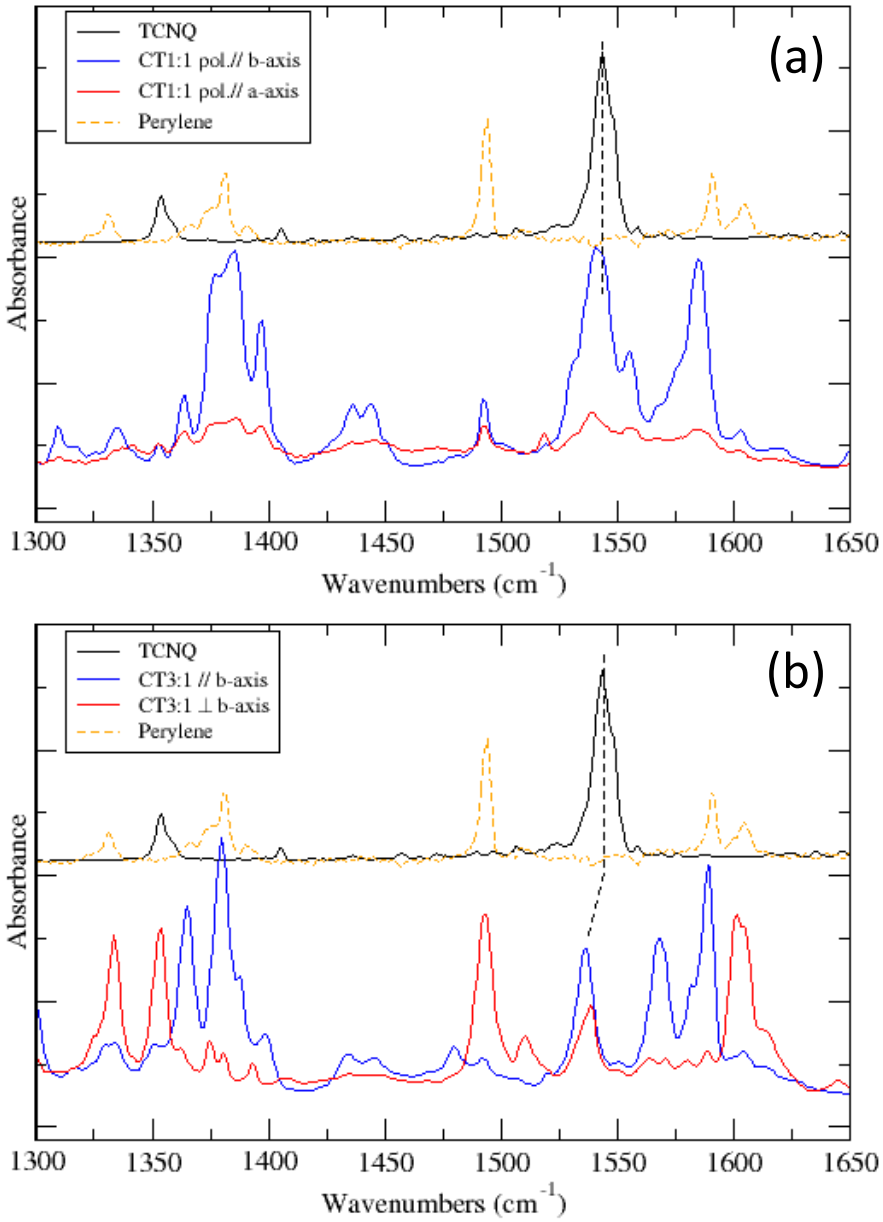

Figure 4. (a) Vibrational spectra of TCNQ (black solid line) and perylene (orange dashed line). The vibration at 1543 cm^{-1} for the neutral molecule is shifted to 1509 cm^{-1} when it is negatively charged in K:TCNQ (Fig. S2). Perylene:TCNQ (1:1) for polarizations parallel to the *b* axis (blue) and parallel to the *a* axis (red). (b) Vibrational spectra of perylene:TCNQ 3:1 for polarizations parallel (blue) and perpendicular (red) to the *b* axis.

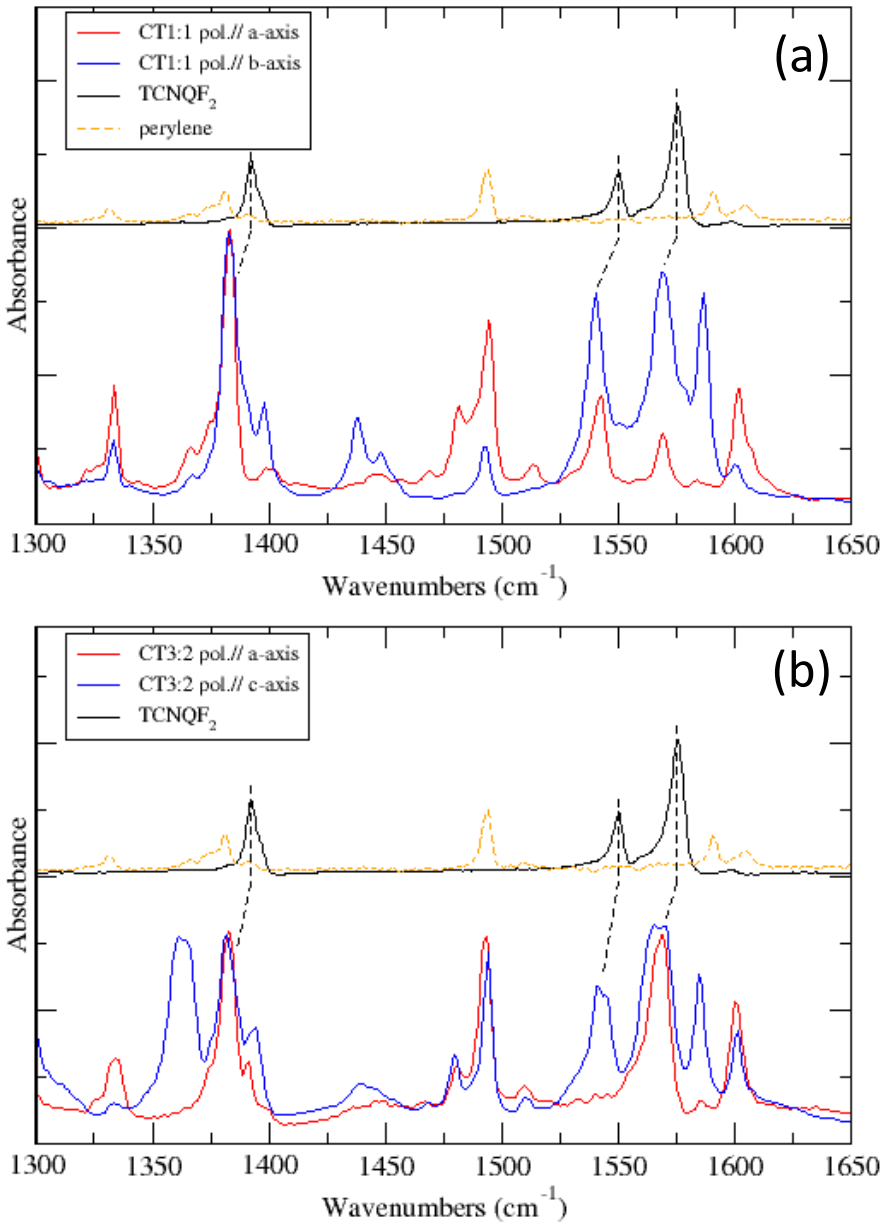

Figure 5. (a) Vibrational spectra of TCNQ-F_2 (black solid line) and perylene (orange dashed line) together with perylene:TCNQ-F_2 1:1 for polarizations parallel to the *a* axis (red) and parallel to the *b* axis (blue). The spectrum of K:TCNQ-F_2 is reported in (Fig. S4) (b) Vibrational spectra for perylene:TCNQ-F_2 3:2 for polarizations parallel to the *a* axis (red) and to the *c* axis (blue).

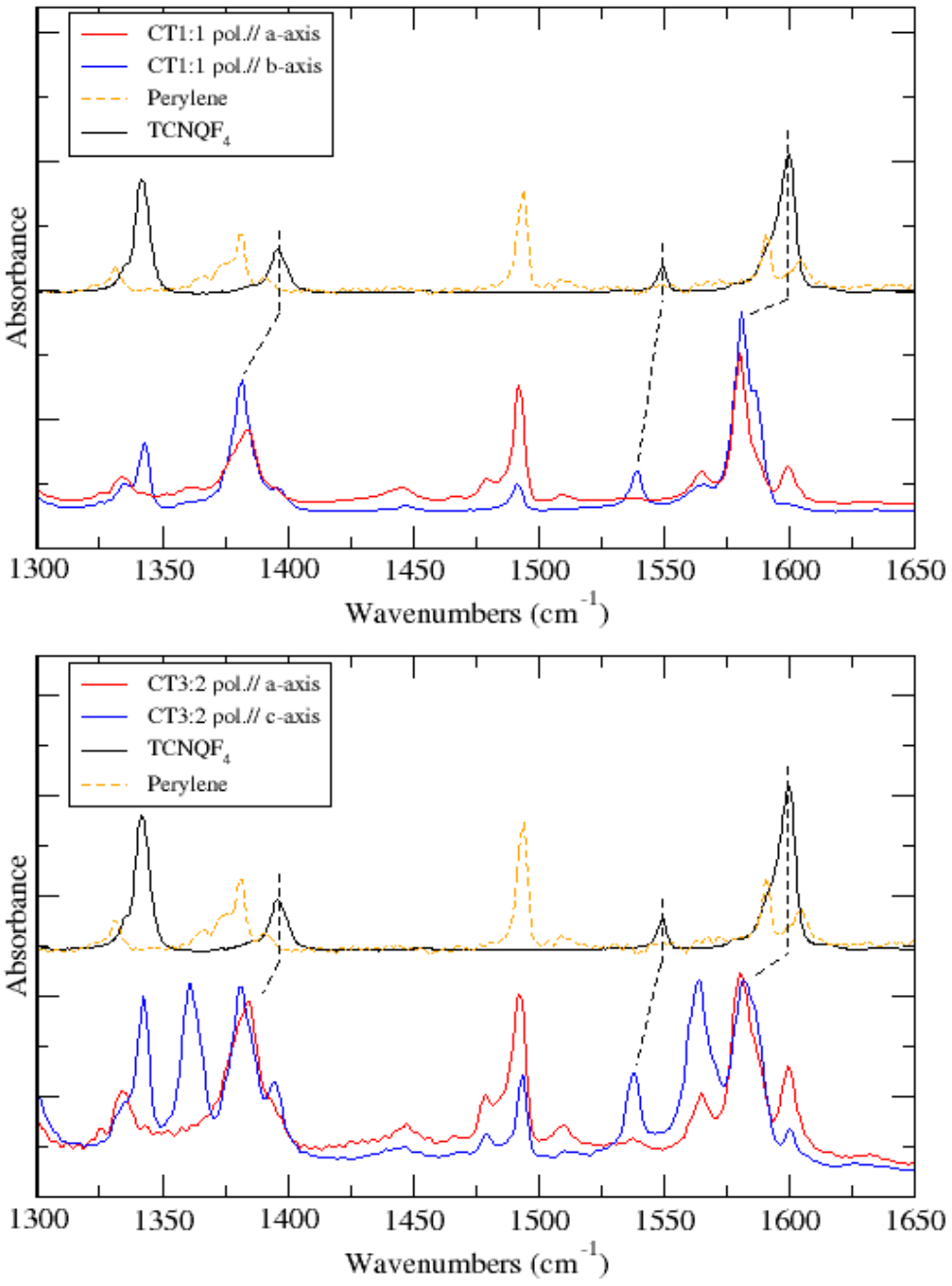

Figure 6. (a) Vibrational spectra of TCNQ-F_4 (black solid line) and perylene (orange dashed line) together with perylene:TCNQ-F_4 1:1 for polarizations parallel to the *a* axis (red) and parallel to the *b* axis (blue). (b) Vibrational spectra of perylene:TCNQ-F_4 3:2 for polarizations parallel to the a axis (red) and to the *c* axis (blue).

Compound	**ρ**	**ω_{CT} (eV)**
Perylene:TCNQ (1:1)	~ 0.0	1.34[a] onset 1.05 eV[a]
Perylene:TCNQ-F_2 (1:1)	0.13	onset 0.88
Perylene:TCNQ-F_4 (1:1)	0.29	1 eV[b] onset 0.71
Perylene:TCNQ (3:1)	0.20	1.3[c] onset 1.12 eV[c]
Perylene:TCNQ-F_2 (3:2)	0.13/0.15	onset 0.88
Perylene:TCNQ-F_4 (3:2)	0.26 (dimer) 0.29 (trimer)	onset 0.68

[a]from ref. [40]; [b]from Ref. [50]; [c]from Ref. [40]

Table 1. Degree of CT ρ and peak/onset of CT exciton absorption in perylene:TCNQ-Fx cocrystals.

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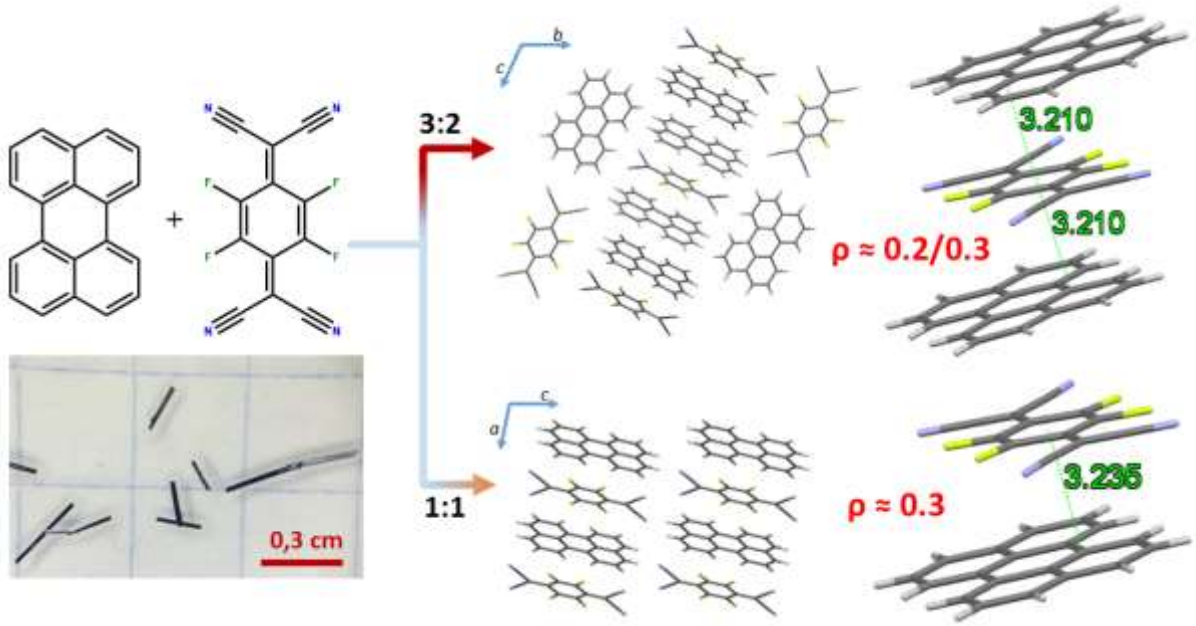
TABLE OF CONTENT

The stoichiometry and structure of perylene:TCNQ-Fx cocrystals determines their properties in terms of charge transfer and optical bandgap. We present a structural study with an accurate determination of ionicity, r, based on infrared spectroscopy. r depends both on electronegativity of TCNQ-Fx and crystal structure. The stoichiometry of the compounds can be controlled by fine tuning the temperatures of growth in vacuum physical vapor deposition.



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Structure, Stoichiometry, and Charge Transfer in Cocrystals of Perylene with TCNQ-Fx

T. Salzillo, M. Masino, G. Kociok-Köhn, D. Di Nuzzo, E. Venuti, R.G. Della Valle, D. Vanossi, C. Fontanesi, A. Girlando, A. Brillante, E. Da Como