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New polymorphs of Perylene:TCNQ charge transfer cocrystals

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Abstract. We report two hitherto unknown polymorphs of the charge transfer (CT) cocrystal perylene:tetracyanoquinodimethane (TCNQ) grown by physical vapour transport (PVT) in argon atmosphere. One of the polymorphs, named β, has stoichiometry 1:1 and adds to the three known structures with stoichiometry 1:1 (α), 2:1 and 3:1. Interestingly, below (280 ± 10) K the β structure undergoes a phase transition to what we refer to as the γ polymorph, with halving of the unit cell and reduction of symmetry from monoclinic to triclinic. Both new crystal structures present two alternating stacks with different intermolecular and intramolecular geometries. In stack S-I the perylene molecules show substantial deviations from planarity, with the angle between the naphthalene intramolecular moieties of 6.69°, and with the perylene and TCNQ molecular centroids shifted by 1.95 Å. In the second stack, S-II, the perylene is planar and the centroids almost coincident. Structural investigations on bond length complemented by vibrational IR spectroscopy indicate that in the new polymorphs the degree of charge transfer, ρ, can be 0 or 0.12. The higher value of ionicity to be due to donor-acceptor pairs in the S-II, while molecules in S-I are closer to neutrality. Thus the ionicity of the donor-acceptor pair depends on the stack and is comparable to that one of the α polymorph which we redetermined as $\rho = 0.15 \pm 0.05$.

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INTRODUCTION

Polymorphism in cocrystals is a rapidly growing and interesting aspect of crystal growth.[1-3] It is sometimes found that the polymorphism displayed by the cocrystal constituents can lead to a number of different cocrystal structures.[4] In addition, the presence of two or more components allows for different stoichiometries.[5, 6] The science of crystal growth has had to deal with such opportunities and challenges for long time,[7] but it is only recently that these concepts have started to be analysed focusing on cocrystals of π-conjugated molecules.[4, 8-10] The electrical conductive properties of conjugated molecules offer,[11] in addition, the functionality to operate in devices and recent efforts have demonstrated the possibility of controlling the electrical characteristics of organic transistors via structure and stoichiometry.[6, 12] Strictly speaking, crystals with different stoichiometry cannot be considered as polymorphs of the same cocrystal pair, but just compounds with different composition.[13]

The number of studies on cocrystals based on poly-aromatic hydrocarbons (PAH), such as anthracene, tetracene, perylene, coronene, picene, etc., combined with TCNQ derivatives has increased substantially.[4, 6, 11, 12, 14-17] This research effort involving many research groups around the world is motivated by the following aspects: (i) the cocrystals exhibit electrical or dielectric functionalities which are of possible use in devices; (ii) most PAH are planar with the π-electron system available to interact with acceptor molecules or chemical groups; (iii) in CT donor-acceptor crystals, the energetics of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the constituents are a crucial parameter, and these can be finely tuned in PAH via the topology of condensed aromatic rings and in TCNQ via halogenation;[16, 18] (iv) the unique intrinsic properties of PAH, either as pristine crystals or combined with other materials in cocrystals, can offer a wide range of exotic phenomena such as laser emission,[19] superconductivity,[20] and phase-transitions.[21, 22]

However, the intramolecular modifications necessary for tuning energy levels result in different intermolecular interactions and a large variety of CT cocrystal structures have been observed in recent years, both with two and three molecular components.[17] Perylene combined with TCNQ has emerged as one of the most studied donor-acceptor pairs, in part because of the variety of stoichiometries; 1:1,[23] 2:1,[6] and 3:1,[24] as well as with fluorinated TCNQ, 3:2.[4, 18, 25] We note that in perylene-TCNQ cocrystals polymorphism or structural transitions have not been reported, if we exclude indirect observations of a pressure driven neutral to ionic transition in peryelene:TCNQ-F4, the structure and stoichiometry of which has not been discussed or reported.[26]

In this communication, we report the first observation of polymorphism in the CT cocrystal perylene:TCNQ with stoichiometry 1:1. In contrast to the known monoclinic structure, which we indicate in this paper as α (CCDC: PERTCQ), the two new structures are: monoclinic (β) for temperatures above 280 K, and triclinic (γ) obtained from a reversible phase transition at (280 ± 10) K. Interestingly, both the new β and γ polymorphs show two different alternating stacks in the unit cell, S-I and S-II, differing in the donor-acceptor overlap, the intramolecular geometry of the perylene, and the charge transfer interaction. In S-I a projection along the stack reveals that the centroids of the donor and acceptor molecules do not coincide, which is instead the case for S-II. Concerning the intramolecular geometry we observe that in S-I the perylene has deviations from planarity, with the planes identified by the two naphthalene moieties forming an angle of up to 6.69°. The degree of charge transfer, ρ, is estimated from TCNQ infrared vibrations sensitive to the amount of charge transferred in the ground state and can be 0.0 or 0.12 *e* depending on the stack. While polymorphism has been recently reported in tetrathiafulvalene CT cocrystals,[27-29] and phenothiazine:TCNQ systems,[30, 31] the results reported here are the first observation of polymorphism in CT cocrystals of a PAH in combination with TCNQ.

EXPERIMENTAL

Perylene (>99% purity) was obtained from Sigma-Aldrich and TCNQ (>98% purity) was purchased from TCI-UK. Both materials were purified by sublimation in vacuum. The vacuum sublimation step was also used to prepare TCNQ crystals of maximum size 3x3x1 mm^3, to be used as starting materials for the growth of cocrystals in the PVT system. Cocrystals were grown using PVT in a horizontal quartz tube under argon stream.[32] Argon gas was obtained from BOC-UK with a purity of 6N. The tube with ~200 mg of each material placed at different positions as indicated in Figure 1 was placed in a Carbolite EHC 12/600B three zone furnace. To obtain large size cocrystals the starting materials were TCNQ and perylene crystals, since low surface area of the starting components leads to optimal sublimation conditions.[18] The exact position of the materials with respect to the temperature profile during growth is indicated in Figure 1. The tube was filled with quartz tubes of smaller diameter and 10 cm length, used to harvest the crystals at the end of the growth procedure. This glassware was cleaned by ultrasonication in deionized water, 2-propanol, and acetone. Before inserting the small tubes with the starting materials, the tube in the furnace was subjected to three gas/vacuum purge cycles then baked overnight to remove any residual moisture or other volatiles. This was performed to prevent the hydrolisation of the cyano-nitrile groups on TCNQ with residual moisture.

For the growth of pure perylene crystals, to be used as a starting component for the cocrystals, the sublimed perylene powder was placed 2 cm from the gas inlet (not shown and positioned at 15 cm in Figure 1b), with the hot zone at 490 K, the centre of the furnace at 420 K and the cold zone at 380 K. The cocrystal instead was grown using a temperature profile of 480/430/390 K. During growth the starting materials would then vaporise and be transported to the cooler end of the tube. Cocrystal growth occurred 30-40 cm from the position of the starting materials and formed thin needles with a maximum length of 15 mm after 48 hours at constant (±1 K) temperature settings. The growth resulted in crystals with different structures; typically α, β and 3:1 stoichiometry. The abundancy of each structure was not assessed and may change with temperature and gas flow settings.

Single crystal diffraction intensity data for all structures were collected 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 1.171.38.46, Rigaku Oxford Diffraction, 2015) and analysed using Mercury[33] and Diamond.[34] For all structures a symmetry-related (multi-scan) absorption correction was applied. Infrared spectra of the CT crystals were recorded with a Bruker ifs66 FTIR spectrometer, equipped with a liquid nitrogen cooled Mercury Cadmium Telluride (MCT) detector, and coupled to an Hyperion 1000 IR microscope. This instrument setup allows for both reflection and transmission measurements with polarized light. The parameter ρ was obtained from the shift in charge-sensitive modes of TCNQ specified in the results section and compared to both neutral TCNQ and a fully ionized potassium-TCNQ salt from our previous work.[4]

RESULTS and DISCUSSION

New polymorphic structures. Table 1 summarizes the crystallographic parameters for 1:1 perylene:TCNQ cocrystals. The α structure, that was previously reported by us (CCDC: PERTCQ02)[4] and many other groups,[5, 23, 24, 35] is monoclinic with space group $P2_1/c$ and two molecules per unit cell, CCDC: PERTCQ. The α polymorph is rarely obtained in our PVT system with stream of argon. Instead we have identified the optimal temperature growth conditions for such a structure when obtaining it in a vacuum-sealed ampoule.[4] The new polymorph β has a monoclinic symmetry with a unit cell in space group *C*2/*c*. The cell is substantially larger than α and it contains 8 molecular pairs (Z = 8). At about 280 K this new β polymorph undergoes a symmetry-breaking phase transition, losing the C-centring and transforming to its primitive reduced cell. We name the structure following this phase transition as polymorph γ. This shows a triclinic unit cell with $P\bar{1}$ symmetry and 4 molecular pairs per unit cell (Z = 4). Figures 2a,b show the projection of the new β and γ crystal unit cells on the *bc* planes, respectively. These projections clearly show that there are two geometrically different types of alternating stack, which we indicate as S-I and S-II, in both structures. To facilitate the discussion we have colored the perylene and TCNQ molecules of the β polymorph in purple and orange, and blue and red in the S-I and S-II stacks, respectively. In addition, we have indicated the pair belonging to either stacks with a dashed rectangle in Figure 2. For the γ structure we have used two additional colors, pink and yellow, to highlight the changes occurring in the phase transition, further discussed below.

We start by giving details on the structure of the β polymorph (Figure 2a), which is stable at room temperature, but it has poor mechanical properties and tends to shatter with little mechanical stress. When viewed along the *a* axis the S-I in the β polymorph has the centroids of TCNQ and perylene offset. The offset has been estimated to be approximately 1.95 Å by projecting the centroid of TCNQ perpendicularly to the mean plane of the perylene and then measuring the distance from this point to the perylene centroid. Such intrastack arrangement is in contrast to S-II, where the two molecules appear one on top of the other with almost coinciding centroids. There are other important differences between S-I and S-II. In S-II the adjacent stacks are staggered by one intermolecular distance, while there is no shift along the *a* axis among the stacks of S-I. This structural feature can be more clearly noticed in Figure 3a, where by looking down the *c* axis in S-I one observes overlapping perylene or TCNQ molecules in the crystal sites (brown on brown or orange on orange), while in S-II there is an alternation of perylene-TCNQ in each molecular site (red on blue or blue on red). In addition, the inclination of the molecular planes is different in the two types of stack. In S-I the angle between the mean molecular planes of perylene and TCNQ, excluding hydrogen atoms, is 0.15(3)° and becomes 2.15(4)° in S-II. Because of these small deviations from perfectly parallel molecular planes, intermolecular distances cannot be estimated using the mean molecular planes. Therefore, we have measured the smallest separation between the molecular centroid on TCNQ and the perylene plane, which is 3.409 Å in S-I and 3.383 Å in S-II. One of the most unusual observations concerns the deviation from planarity of perylene, a molecule that both in the gas phase and in its crystalline structures is highly planar.[36] In estimating deviations from planarity in S-I we record an angle of 6.13(6)° between planes passing through the two naphthalene moieties of the molecule, excluding hydrogen atoms again. This deviation is likely to impact on the donor-acceptor distance that is larger in S-I than in S-II by 0.026 Å and also ρ as discussed below.

At first sight the structure of the γ polymorph, derived from β by decreasing temperature below ~280 K, is very similar to its parent crystal structure, but closer inspection reveals many differences. The γ crystal still has the S-I and S-II stacks with the perylene molecules in S-I exhibiting deviation from planarity, with the angle between napthalenes 6.50° at 270 K. But the S-II in the γ structure is made of two stacks with slightly different interstack geometry. We have highlighted this difference by coloring the non-symmetrically equivalent perylenes in pink and TCNQs in yellow in Figure 2b and Figure 3b. In particular, in the *bc* plane projection one can notice a slightly different alignment of the TCNQ and perylene *long* molecular axes (C_2 symmetry) with respect to each other. In the dimers colored in blue/red the angle is 18.22(4)°, as measured between atoms C45 and C50 for perylene and C14 and C16 for TCNQ as projected along the *a* axis (see CIF for atom numbering). For the pink/yellow pair the angle increases to 21.88(5)°, measured using the same corresponding atoms. In addition, in comparing the relative arrangement of the stacks in S-I, we notice again differences between the γ and β structure. These can be seen in the relative position of the brown perylenes, which exhibit a small shift parallel to the *short* C_2 molecular symmetry axis. These crystallographic differences, notably the change in symmetry and dimension of the unit cell, are substantial and indicate the presence of a temperature-induced phase transition in a charge transfer cocrystal between a PAH and TCNQ. Looking at the intrastack arrangement of the donor-acceptor pair we have measured an interplanar spacing in S-II of 3.352 Å and 3.389 Å and angles between the molecular planes of 2.06(4)° and 2.31(5)° for the blue/red and pink/yellow pairs, respectively. These last two values of angles indicate that the misalignment of the *long* C_2 molecular axes is related primarily to deviations from perfect parallelism of the molecular planes. In S-I the spacing between the TCNQ centroid and the perylene plane has increased slightly to 3.410 Å and the angle between the molecular planes has increased to 0.53(4)°. The deviation from planarity of perylene has slightly increased to 6.14(6)°, as above measured from the naphthalene planes' inclination.

Experimental evidence supporting a phase transition is reported in Figure 4. To confirm the presence of a symmetry-breaking phase transition at 280 K, a crystal of β was subject to a variable temperature parametric study. The crystal was cooled in-situ on the diffractometer, with cooling paused at regular intervals to allow unit cell determinations at several temperatures either side of the transition. To enable direct comparison of the unit cell parameters across the phase transition, the data were indexed in the primitive unit cell setting (γ parameters) at all temperatures. The results in Figure 4 show remarkable changes at (280 ± 10) K. In particular, an abrupt change is noticeable in the *b* and *c* axis, Figure 4b,c, respectively. Further the α angle shows a different temperature dependence above and below the 280 K data point. We note that these changes are reversible upon temperature cycling and provide supporting evidence for a phase transition between the two polymorphs. In order to probe more precisely the phase transition temperature we have performed a differential scanning calorimetry study (DSC). However, Figure S2 reports a DSC scan between 255 and 300 K without any signature of a phase transition in the region close to 280 K. We have interpreted this considering that the DSC sample is heterogeneous and may contain only a small fraction of β crystals compared to α and 3:1 structures. Note that the latter two structures do not show phase transitions. In addition, the small changes in structure reported above may not correspond to appreciable variations in thermodynamic properties.

As evidence for the change in symmetry of the unit cell, and thus a phase transition, we have opted to work only on a β single crystal avoiding techniques requiring substantial amounts of material such as DSC. In Figure S3 of the Supporting Information we report reconstructed slices, or layers, through the complete diffraction data for the same [h, 0, l] layer, i.e. the slice through the single crystal for which the Miller index k = 0. The layer is very different at 280 K than at 300 K, which confirms that a symmetry-breaking phase change has taken place; there are many more diffraction reflections in the 280 K (Figure S3b) data than in the 300 K data (FigureS3a). For the 300 K data, we have a C-centred cell and thus expect *systematic absences* in the data, which means that only the reflections whose Miller indices satisfy the condition that $h + k = 2n$ are observed. This effectively means we expect to lose half the reflections that we would see in a P-cell. Observing double the number of reflections in the 280 K image, compared to the 300 K, confirms that we have changed crystal system from $C2/c$ to $P\bar{1}$.

Further cooling of the γ structure to 150 K does not result in any other significant structural changes, but only in small changes in the intermolecular distances. The unit cell parameters together with other relevant crystallographic data, such as cell volume, are reported in the last column of Table 1 and demonstrate an expected reduction of distances with decreasing temperature. As far as the intrastack geometry is concerned, we notice that the molecular centroid distances in S-II are now significantly different for the two stacks, namely 3.287 Å and 3.367 Å for the blue/red and pink/yellow, respectively. As expected both these values are smaller than those of the structure measured at 270 K and lead to larger angles between the molecular planes which are now 2.17(3)° and 2.56(4)° for blue/red and pink/yellow, respectively. In S-I the distance between the molecular centroids has decreased to 3.375 Å, the angle between the molecular planes has increased to 1.03(4)° and the perylene distortion has increased further to 6.24(5)°. Thus shorter donor-acceptor distances lead to deviations from parallelism. The angles between the *long* C_2 axes diverge further; in the dimers coloured in blue/red the angle shrinks to 15.71(4)° and for the pink/yellow dimers it increases to 23.01(5)°.

Besides the π-π interactions of donor-acceptor pairs and their mutual arrangement, it is also important to consider intermolecular distances close to the van der Waals (vdW) radii. In Figure S4 and S5 of the Supporting Information we highlight intermolecular atomic distances shorter than the sum of the vdW radii -0.1 Å. First, it appears that the interactions are in between S-I and S-II molecules and not intrastack. For molecules in S-II such intermolecular interactions involve only TCNQ (those colored in red and yellow), while in S-I they involve both TCNQ (orange) and perylene (purple). Interestingly, for the β polymorph it appears that the deviations from planarity of perylene might be caused by two C-H···N contacts between the perylene and two TCNQ molecules of different stacks in S-II. As the two TCNQ molecules in question are staggered, they favor the nonplanarity of perylene. Short C-H···N contacts are also seen between the aromatic C-H of TCNQ in S-II and cyano groups of TCNQ in S-I. This may compete with π-π interactions and shift the centroid of TCNQ in S-I with respect to the perylene centroid. The γ structure shows a slightly different pattern (Figure S4) where the perylene in S-I has short distance interactions with other perylenes within S-I and has weakened the interaction with one of the TCNQ in S-II. This last observation is in line with the augmented planarity in γ with respect to β. All together these observations suggest that both the deviation from planarity of perylene and the structural changes seem to be controlled by a delicate balance between π-π donor-acceptor interactions and interstack C-H···N intermolecular bonds involving aromatic CH groups and the cyano moiety on the TCNQ molecules.

Degree of charge transfer. One of the most important parameters in characterizing CT cocrystals is ρ, the amount of charge transferred from donor to acceptor.[37] This is relevant to understand the electronic structure of these materials which often exhibit remarkable electronic effects such as neutral-ionic transitions, ferroelectricity, Mott-insulator states and superconductivity.[37, 38] The value of ρ can be estimated from changes in the electronic structure of TCNQ, which are reflected in bond lengths and frequency of intramolecular vibrational modes.[17, 39]

With single crystal structures it is possible to estimate ρ from changes in the bond length between carbon atoms of TCNQ. This procedure involves the accurate measurement of four symmetrically inequivalent bonds as discussed by Kistenmacher.[40] It should be noted, however, that this method is notoriously inaccurate for low degrees of charge transfer (< 0.1), with the reported literature value of α perylene:TCNQ being 0.01±0.07.[6] We have therefore opted for the more accurate HOSE (Harmonic Oscillator Stabilization Energy) model,[17] that estimates the energy of deformation of the π-electron system of TCNQ, taking into account a reference structure with localized single and double bonds (Supporting Information). For the β polymorph, TCNQ molecules in S-I have a $\rho = 0.04$, while in S-II $\rho = 0.09$. However, the average excess charge on TCNQ for the molecule with $\rho = 0.04$ is actually positive. We are of the opinion that a positive charge density on the TCNQ is unlikely, considering that the HOMO and LUMO level alignment of perylene and TCNQ gives them the role of donor and acceptor, respectively.[41] This is probably another confirmation of the difficulties in determining the correct ionicity from structural parameters in almost neutral cocrystals. In the γ polymorph at 270 K the HOSE model gives $\rho = 0.05$ in S-I and $\rho = 0.19$ in S-II, whereas at 150 K $\rho = 0.04$ in S-I and $\rho = 0.02$ in S-II. While these values are all for a negative excess of charge and thus in line with the larger electronegativity of TCNQ with respect to perylene, they may still be affected by errors and more accurate estimates can be obtained from IR spectroscopy presented below. Nevertheless, the important message emerging from the structural analysis is that ρ may be different in S-I and S-II, with the TCNQ in S-II having a larger deviation from neutrality, at least at room temperature and at 270 K. From an intermolecular point of view, this is in accordance with the shorter interplanar distances found in S-II, the substantial offset between centroids in S-I and the deviations from planarity in perylene in S-I as well. It is known that larger charge transfer requires a short distance between donor and acceptor, together with a larger overlap of the π-orbitals between the pair.[17]

We and other groups have already employed IR spectroscopy to probe ρ in charge transfer cocrystals based on TCNQ.[4, 18, 39] The vibrational modes most sensitive to changes in ρ are the C=C and the C≡N stretching, which in the neutral molecule are at 1543 and 2226 cm^{-1}, respectively. As we will further discuss below the C≡N stretching does not provide a reliable estimate of ρ since the peripheral position of the group in the TCNQ molecules renders it influenced by crystal packing environments,[39] especially in this particular case where C-H···N intermolecular interactions are at work. In Figure 5 we report the IR spectra measured on the β phase of the perylene:TCNQ cocrystal (black curve) together with spectra of pure perylene (blue curve) and TCNQ (red curve) in the same spectral region. The IR spectrum on a larger frequency range is reported in Figure S6. At 1543 cm^{-1} the C=C stretching of neutral TCNQ can be clearly distinguished in the pure TCNQ crystal. In the β cocrystal it evolves into two closely spaced bands; one unshifted at 1543 and another shifted at lower energy, 1539 cm^{-1}. By knowing that in the TCNQ radical anion, $TCNQ^{\bullet -}$, this vibrational band is at 1509 cm^{-1},[4] we estimate values of $\rho \sim 0$ and $\rho = 0.12 \pm 0.03$ for the two bands. The spectral region of C≡N vibrations is shown in the inset of Figure 5 and shows how the band at ~2226 cm^{-1} shifts down to ~2219 cm^{-1} in the cocrystal. The shift in the C≡N corresponds to $\rho = 0.28$, larger than the value obtained from the shift in C=C stretching. While the C≡N is more prone to crystal effects and is probably overestimating ionicity here, the values of ρ from the C=C stretching are suggestive of a degree of charge transfer different from zero at least in one of the stacks.

These values of ρ appear to be in contrast to the α polymorph, for which previous IR studies indicated no charge transfer.[4, 6] However, a reanalysis of the IR spectra of the perylene-TCNQ crystals associated to a X-ray identification of each investigated crystallite has allowed us to unambiguously associate the IR spectrum reported in Figure S7 as the one of the α polymorph. Such spectrum is different from that originally reported by us in reference [4]. The C=C stretching frequency indicates $\rho = 0.15 \pm 0.05$ for α perylene-TCNQ. The 3:1 structure has $\rho = 0.2$ and this has been explained considering the larger availability of perylene donors for each TCNQ acceptor.[4] Thus the new β polymorph with stoichiometry 1:1 has the smallest ρ compared to all the other cocrystal structures of perylene and TCNQ. We have also recorded IR spectra below the transition temperature, but did not observe appreciable shifts in the 1539 cm^{-1} band. This observation together with the structural analysis above indicates that similar degrees of charge transfer are in the γ phase, at least at 270 K. The X-ray data analysis above indicates that TCNQ in S-I is more neutral than in S-II, an aspect that is clearly reflected in the two IR bands diagnostic for the ionicity of the TCNQ molecule. Another interesting aspect to mention is that the comparison of the thermal ellipsoids of the perylene in S-I of the β and γ phases, reported in Figure S8, suggests a substantial decrease in thermal motion. However, the IR data at different temperatures and the HOSE analysis on TCNQ in S-I, do not show evidence for a change in ρ in the two phases. All together this highlights π-orbital overlap rather than thermal motion as critical parameter in tuning the charge transfer degree because of the donor-acceptor centroid position, characteristic of S-I compared to S-II.

CONCLUSION

We report the observation of two new polymorphs, β and γ, of the CT cocrystal perylene:TCNQ with stoichiometry 1:1. The crystals have been obtained by PVT growth in a stream of hot argon and were not initially observed by us while growing crystals in a vacuum sealed ampoule. The γ structure is obtained by cooling the β crystals below 280 K and involves a phase transition with a change in the interstack C-H···N intermolecular interactions. Both crystal structures have a large unit cell which contains symmetrically inequivalent stacks, indicated S-I and S-II. We have estimated the ionicity of the new polymorphs which depends on the stack and in S-II it is higher than in S-I. The structures add to the rich variability of perylene cocrystals with TCNQ that already include structures with 3:1 and 2:1 ratios and constitute the first report of enantiotropic polymorphism in cocrystals between a PAH and TCNQ.

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Notes

The authors declare no competing financial interest.

SUPPORTING INFORMATION

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Estimation of ρ from HOSE theory, DSC data, change in cell symmetry at transition temperature, intermolecular distances close to vdW radii, IR spectra for β and α polymorphs.

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TABLES

Table 1. Crystallographic data for Perylene:TCNQ cocrystals obtained from single crystal X-ray diffraction at different temperatures. Z indicates the number of molecular pairs per unit cell. CCDC codes for the different structures are reported in the bottom line.

Perylene-TCNQ	α	β	γ	γ
Temperature (K)	290(2)	290(2)	270.01(10)	150.00(10)
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	7.2988(2)	6.8315(11)	6.8148(4)	6.7477(3)
b (Å)	10.8741(2)	30.944(5)	15.7910(12)	15.6571(9)
c (Å)	14.5519(3)	21.932(5)	21.9339(13)	21.8347(12)
α (°)	90	90	86.135(5)	84.268(4)
β (°)	90.254(2)	97.913(19)	82.172 (5)	82.234(4)
γ (°)	90	90	78.283(6)	79.390(4)
Cell volume (Å^3)	1154.94(4)	4592.1(15)	2287.7(3)	2239.9(2)
Z	2	8	4	4
Reflections collected	7288	13845	15633	13081
Independent reflections	2281	4556	8922	8149
R indices (I>2sigma(I))	R1 = 0.0423 wR2 = 0.1178	R1 = 0.0660 wR2 = 0.1457	R1 = 0.0614 wR2 = 0.1519	R1 = 0.0663 wR2 = 0.1583
R indices (all data)	R1 = 0.0476 wR2 = 0.1228	R1 = 0.1200 wR2 = 0.1853	R1 = 0.1011 wR2 = 0.1821	R1 = 0.1167 wR2 = 0.2078
GooF	1.033	1.024	1.017	1.025
CCDC no.	1576698	1576699	1576700	1576701

Figures

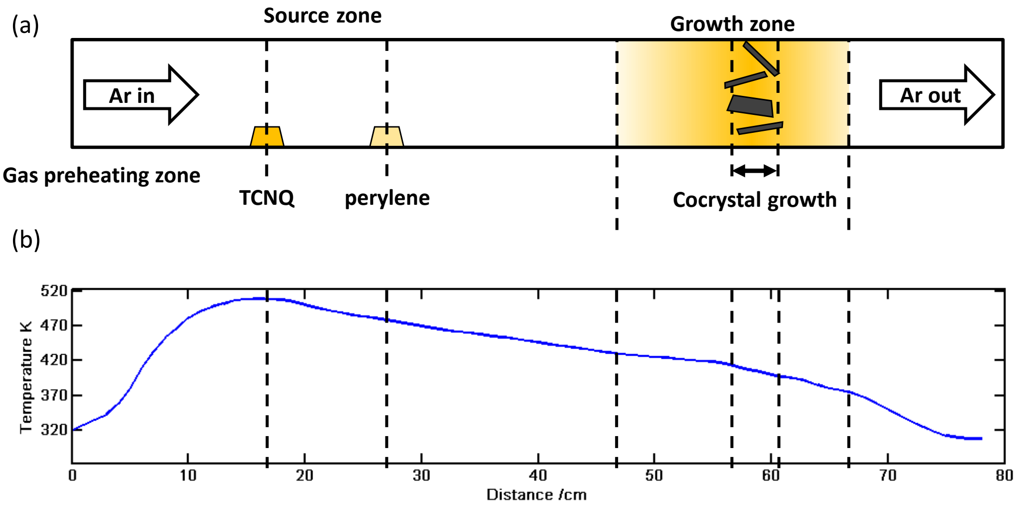

Figure 1. (a) Schematic of the furnace cross section. The source materials are placed in the hot part of the tube and the molecules in the gas phase are transported by the inert argon carrier to the growth region. (b) Furnace temperature profile. The dashed lines are a guide to the eye to identify the source zone, the growth zone and the zone where cocrystals are obtained.

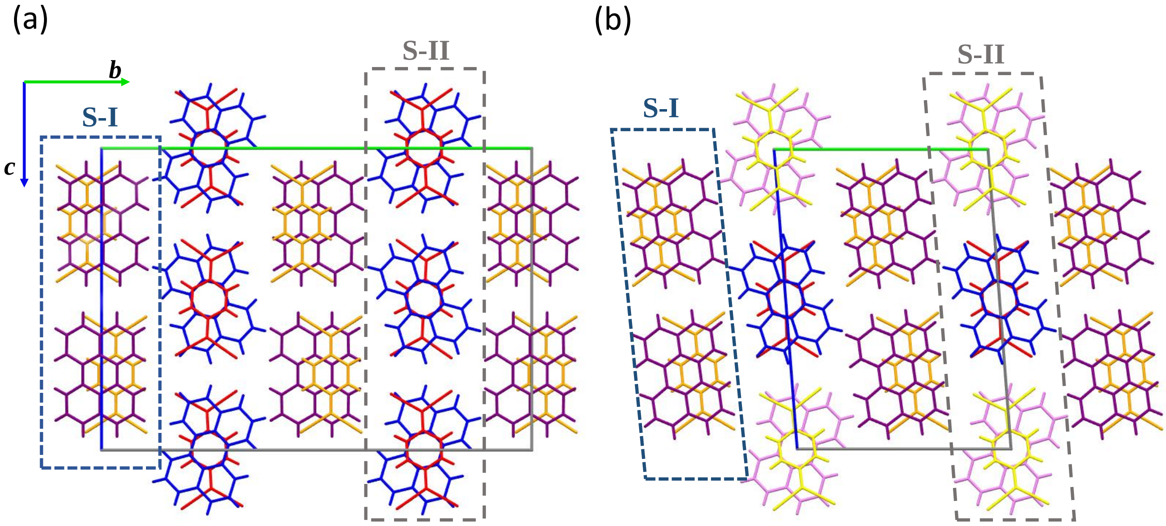

Figure 2. Crystal structures of the β (a) and γ (b) polymorphs of perylene:TCNQ projected in the *bc* plane of the respective unit cells. The identification of the two different stacks, S-I and S-II, is facilitated by the dashed rectangles and parallelograms. The unit cell is identified by the solid lines with the *b* and *c* axes in green and blue, respectively.

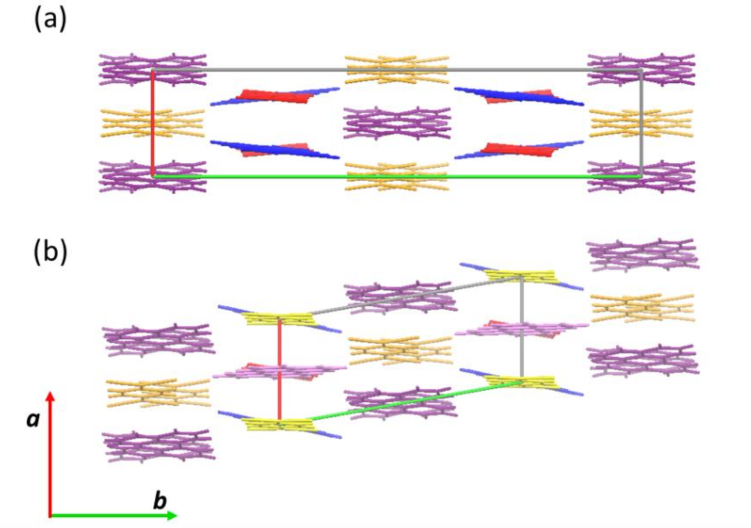

Figure 3. Crystal structures of the β (a) and γ (b) polymorphs of perylene:TCNQ projected in the *ab* plane of the respective unit cells. The unit cell is identified by the solid lines with the *a* and *b* axes in red and green, respectively.

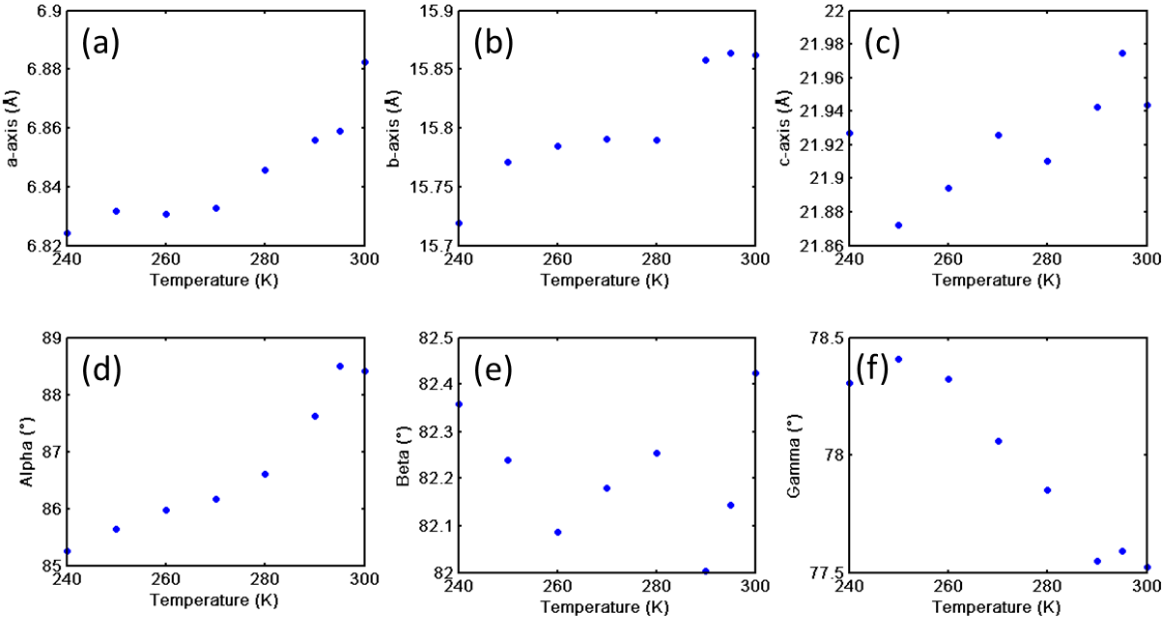

Figure 4. Unit cell parameters as a function of temperature for a γ single crystal; (a) *a* axis, (b) *b* axis, (c) *c* axis, (d) α angle, (e) β angle, (f) γ angle. The structure has been refined with a P-1 space group in the whole temperature range.

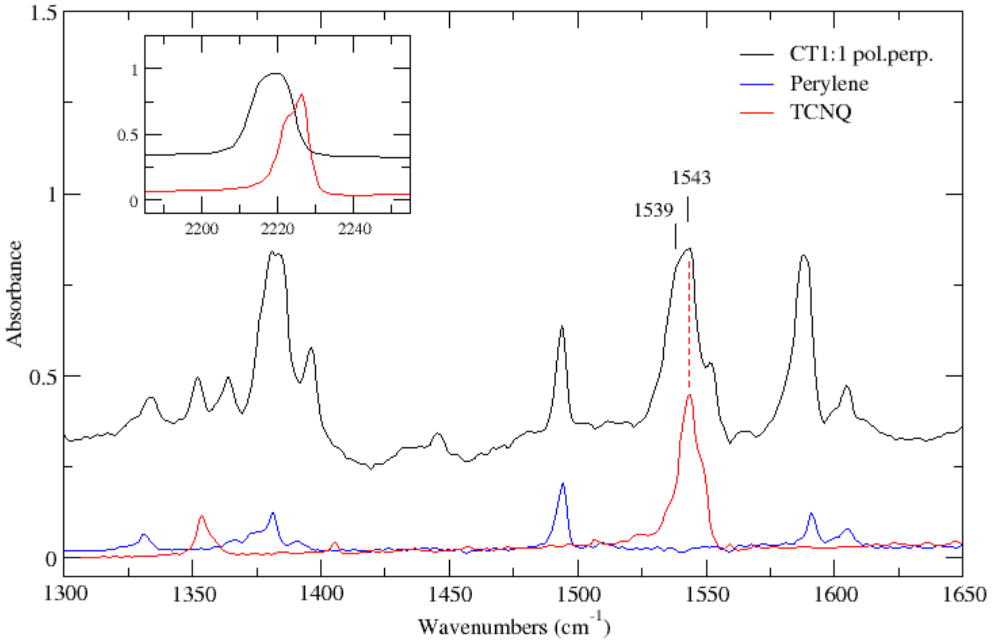

Figure 5. IR vibrational spectra of TCNQ (red curve), perylene (blue curve) and β phase perylene:TCNQ (black solid curve). The spectrum for the cocrystal has been recorded with polarization perpendicular to the long crystal axis. The vibration at 1543 cm^{-1} for the neutral TCNQ molecule is shifted to 1539 cm^{-1} in the cocrystal, although the original peak remains as well as still present unshifted indicating the presence of two different values of ρ. The inset shows the region of C≡N stretching vibrations.

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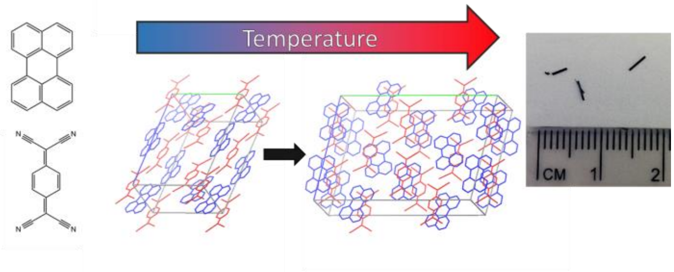
Table of Contents Graphic



We report two novel polymorphs of the charge transfer cocrystals perylene: tetracyanoquinodimethane (TCNQ). These have been investigated with x-ray crystallography and vibrational IR spectroscopy. The first structure is monoclinic and undergoes a phase transition below (280 ± 10) K, converting into the second, triclinic, form. This constitutes the first report of enantiomeric polymorphism in cocrystals between poly-aromatic hydrocarbons and TCNQ.