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COMMUNICATION

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Charge-transfer (CT) crystals bearing segregated domains between the electron donor and acceptor molecules are a promising platform for developing new organic functional solid-state materials. However, there is limited diversity in the segregated structures of CT crystals. Herein, we report a novel structure of a CT crystal using hexaarylbenzene (HAB) and tetracyanoquinodimethane (TCNQ) as the electron donors and acceptors, respectively. Single-crystal X-ray diffraction (XRD) studies revealed that hexapyridyl benzene and TCNQ form a segregated layer in crystalline media, and the CT feature of TCNQ was observed in terms of the observed chemical bond lengths in the crystal.

Organic charge-transfer crystals (CT crystals) are constructed by assembling electron donor and acceptor reagents in the solid state. Generally, charge-transfer events can occur between the donor and acceptor molecules in densely packed media, and the CT characteristics can be used to develop a novel material with electrical[1] or optical properties[2] originating from the CT character in the solid state.[3-5]

Two major molecular packing motifs for CT crystals have been reported. A typical CT structure is a mixed stack in which the donor and acceptor molecules are alternately stacked, while another structure type is a segregated stack, in which the donor and acceptor assemble separately (Figure 1a). These two types of crystal structures usually exhibit distinct charge-transfer features, which can be evaluated by the charge-transfer parameter ρ, defined as the amount of transferred charge from donor to acceptor.[6] The variety of segregated stack CT crystals is relatively smaller than that of mixed stack crystals.[7,8] This is probably because the mixed stack structure can form a thermodynamically stable packing structure through the relatively strong intermolecular interactions between the alternately nested donor and acceptor molecules. In contrast, for segregated CT crystals, donor or acceptor molecules constitute a column or layered structure and exhibit electrostatic repulsion between donor-donor or acceptor-acceptor pairs, thus making crystal formation more difficult.

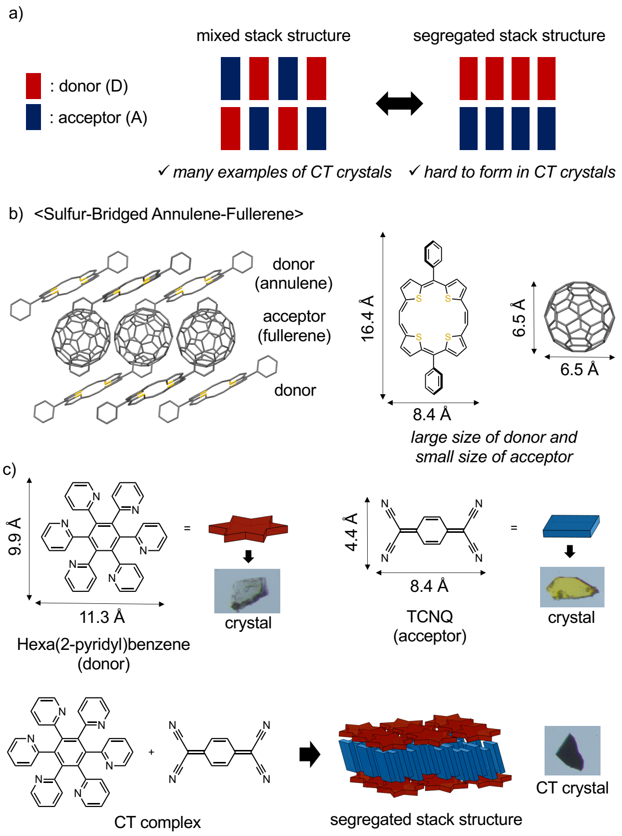

Figure 1. a) Two major packing types for CT crystals. b) Example for the segregated packing structure of CT crystal and the size difference between the donor and acceptor molecules. c) Structural representation for hexa(2-pyridyl)benzene (red star), TCNQ (blue block), the observed CT complex, and

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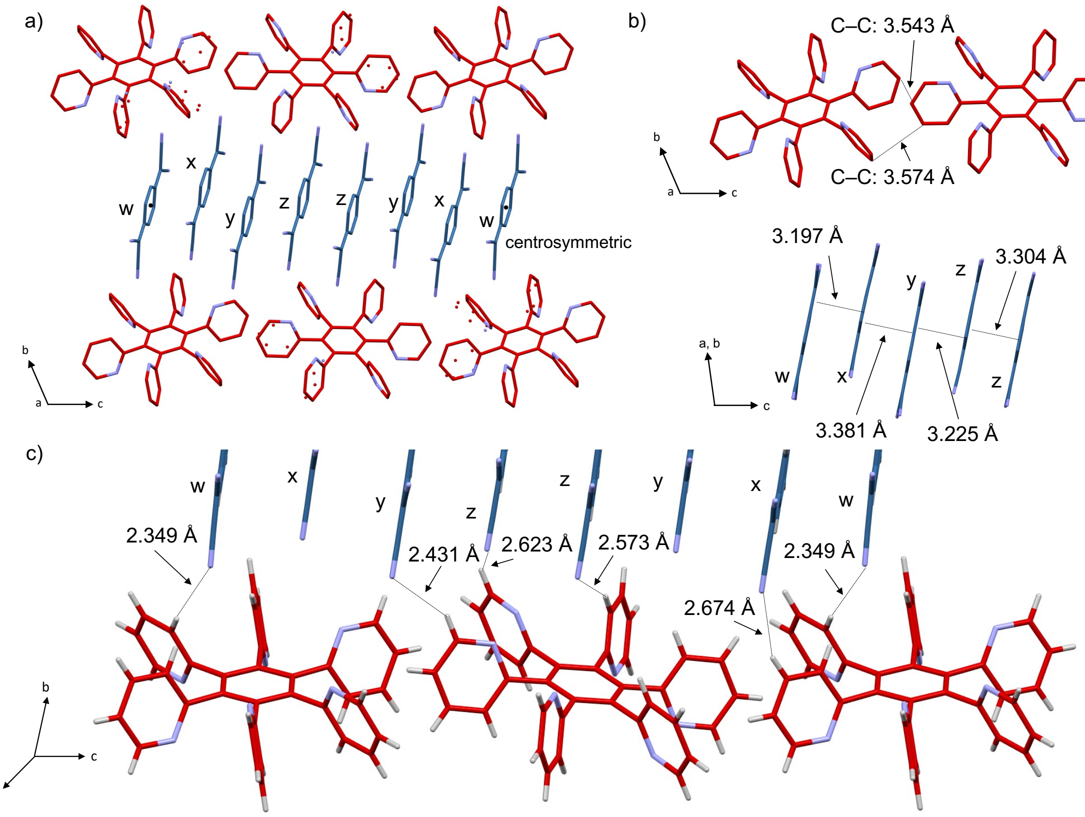

Figure 2. Crystal packing structure of CT crystal. a) View from *a*-axis and black dot indicating inversion center. b) Intermolecular distances between each of the HPyBs (above) and TCNQs (below). c) Intermolecular distances between HPyB and TCNQ.

photographs of crystals of hexa(2-pyridyl)benzene (colourless), TCNQ (yellow), and CT complex (dark blue) taken under room light.

A combination of fullerene as an acceptor and large π-conjugated reagents, such as annulene derivatives, as donors have been reported as a type of segregated stack CT crystals (Figure 1b).[9,10] In the crystal, there was a large gap and shape difference between the donor and acceptor molecules. The size of the donor was 16.4 Å for the long side and 8.4 Å for the short side, which is larger than the size of the acceptor (6.5 Å) (Figure 1b). Inspired by these structures, we hypothesised that a combination of different sizes and shapes between the donor and acceptor molecules may aid in the formation of a segregated stack structure. Based on this idea, we focused on hexaarylbenzene(HAB) as the donor[11,12] and TCNQ as the acceptor molecule. The size of HAB (11.3 and 9.9 Å) is larger than the TCNQ molecule (8.4 and 4.4 Å) (Figure 1c). Indeed, their molecular geometry would prevent intermolecular π–π interactions and favour a segregated stack structure.[13,14]

Herein, we report the formation of a segregated CT crystal using HAB as the donor and TCNQ as the acceptor. We investigated hexa(phenyl)benzene and hexa(2-pyrdyl)benzene(HPyB) as HAB donor molecules. Consequently, we confirmed the segregated stack structure of the co-crystal of HPyB (red star shape) and TCNQ (blue block shape) by single-crystal X-ray crystallography (Figure 1c; for more details, see ESI). The degree of charge transfer, *ρ,* was estimated from the TCNQ bond length obtained by single-crystal XRD. Its value was comparable to that of the previously reported segregated stack CT crystals.

HPyB was synthesised and purified using a previously reported procedure.[15] Dark blue mixed crystals, including one equivalent HPyB and two TCNQs, were obtained by mixing an equimolar amount in chloroform solutions, followed by slow evaporation. The clear colour difference between the mixed crystal and colourless HPyB and TCNQ crystals establish the CT character of the mixed crystals (Figure 1c).

Single-crystal X-ray diffraction analysis of the obtained CT crystals was performed (Figure 2), where the crystals were found to crystallise in the space group *P*-1. The composition of the crystal was two HPyBs and seven TCNQs. Four independent TCNQ were denoted as w–z, and one of the TCNQ, indicated as w, was found to be located on inversion center (Figure 2a and S3). Moreover, it was found that all the 2-pyridyl groups of HPyB were disordered. In the crystal packing structure, each donor and acceptor molecule were segregated and formed a layer-like arrangement along the a–c plane (Figure 2a). HPyBs were packed with intertwined pyridine blades between adjacent HPyBs, whereas TCNQs were stacked in a face-to-face manner with each other in the segregated domain (Figure 2b). In the TCNQ domain, the distances between each TCNQ were approximately 3.197 Å to 3.389 Å, indicating that π-stacking was the driving force for TCNQ molecules in the columnar structure (Figure 2b). In HPyBs, they were stacked as a gear-mesh, where one pyridyl group was sandwiched between two pyridyl groups of the adjacent HPyBs (Figure 2b). The distances between the sandwiched pyridyl groups were 3.543 and 3.574 Å, which are slightly larger than the sum of the van der Waals radii of the two carbon atoms.

We also focused on the stacking structure of HPyBs in the a-axis direction (Figure S3). Along this crystallographic axis, the HPyBs were stacked on top of each other with shifts. The closest intermolecular distance between the nitrogen atoms of the pyridyl groups in the HPyB molecules was 2.991 Å. In TCNQ, the closest intermolecular distance was 3.278–3.428 Å between the nitrogen atom of the nitrile group and the carbon atom of the quinone moiety. It was expected that there would be a small π orbital overlap in HPyB and TCNQ, suggesting a low electronic interaction in the a-axis. The interactions between HPyB and TCNQ were mainly attributed to the nitrogen atom of the nitrile groups in TCNQ and the carbon atoms in HPyB (Figure 2c). Their distances were in the range of 2.349 Å to 2.674 Å, suggesting that a large number of CH–N interactions might support the construction of the segregated stack in the crystal.

To confirm the CT character of the HPyB-TCNQ crystal, we evaluated the value that shows the degree of charge transfer, ρ. In numerous CT crystals, the value of ρ is highly correlated with the electronic properties[16,17] as well as the crystal structures. In particular, CT crystals with segregated stack structures usually exhibit higher ρ values than mixed stack structures.[18,19] In several examples of CT crystals containing TCNQ, the bond length change of TCNQ is known to be sensitive to the electronic environment. When the ρ value increases, the geometry of TCNQ becomes rather benzenoid; therefore, the bond lengths of a and c are elongated, and b and d are shortened (Figure 3a). ρ can be estimated from the equation proposed by Kistenmacher et al.[20]

$$\rho = \frac{\alpha_{CT} - \alpha_0}{\alpha_{-1} - \alpha_0}$$

where $\alpha_x = c / (b + d)$, and CT, 0 and -1 refer to the CT, neutral, and anionic states of TCNQ, respectively.

From the XRD results of the CT crystal, there were four independent TCNQs in a unit cell, denoted as w, x, y, and z (Figure 3b). Because some TCNQs were not C2 symmetric, the average of the bond lengths was used to calculate ρ. As shown in Table 1, the ρ values of x (ρ = 0.67) and z (ρ = 0.86) were higher than those of w (ρ = 0.46) and y (ρ = 0.35). The high ρ value indicates that the molecule exhibits ionic character, while the low ρ value indicates a neutral state. The ρ values at 293 K were evaluated as smaller than those in 123 K, but still around 0.50 (Table S3). We also evaluated the ρ by using different equations, and no significant differences among the ρ values were observed (Table S4).[21,22]

The ρ of TCNQs indicated that the HPyB worked as the donor and had ca. +1.63 of the oxidation value with respect to of the CT crystal composition (seven TCNQs per two HPyB). The CV measurements revealed that the HPyB exhibited two irreversible oxidation potentials at 1.36 and 1.79 V vs Ag/Ag$^+$. The estimated HOMO energies from the CV measurement were –6.00 and –6.43 eV, which are calibrated bythe HOMO energy and CV values of ferrocene (Table S5). The calculated HOMO level of HPyB was similar to that of naphthalene, which could also form CT crystal with TCNQ and work as donor molecules.[23] These results suggested that the HPyB functioned as the donor and could have over +1.0 of oxidation value per one molecule.

We compared the ρ value with those of previously reported donor–TCNQ CT crystals, including mixed stack crystals[23] and segregated stack crystals.[24] The average value of ρ for all four TCNQs was used (ρ = 0.59). Comparing the ρ value of naphthalene-TCNQ (ρ = 0.07), which has a mixed stack crystal structure, the ρ value of HPyB-TCNQ (ρ = 0.59) is considerably larger than that of naphthalene-TNCQ. Furthermore, the ρ value of HPyB-TCNQ is comparable to that of TTF-TCNQ (ρ = 0.62) which has a segregated stack structure.

The high ρ value observed in the CT crystal would be attributed to the specific stoichiometry of the donor (HPyB) and acceptor (TCNQ) molecules (1:3.5). The electrons of one HPyB molecule could be strongly extracted by 3.5 of TCNQs and enhanced the degree of charge-transfer. In fact, the stoichiometry effect was reported in other CT crystals that the donor exceeded to the acceptor.[25] In addition, the molecular geometry of CT crystal can largely alter its ρ value.[8,20,26] Most CT crystals showed higher ρ value in segregated stack manner than in a mixed manner, suggesting that the segregated stacking structure of TCNQs in the CT crystals with HPyB would also induce the high ρ value. Furthermore, the ability to become dication of HPyB was expected to be essential for realizing the high ρ value with the high ratio of TCNQ composition.

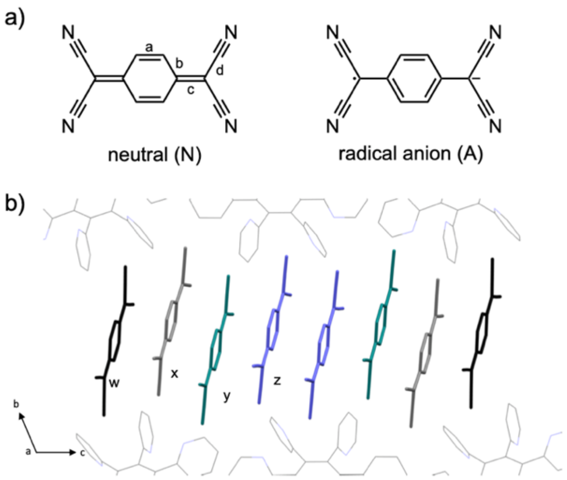

Figure 3. a) Neutral structure and anion structure of TCNQ. b) Four independent TCNQs in a unit cell.

Table 1. Bond length of TCNQ and the calculated ρ values

	a (Å)	b (Å)	c (Å)	d (Å)	ρ
w	1.353(3)	1.437(4)	1.393(3)	1.417(4)	0.46
x	1.354(3)	1.429(4)	1.438(3)	1.424(4)	0.67
y	1.348(3)	1.438(4)	1.387(3)	1.427(4)	0.35
z	1.361(3)	1.424(4)	1.413(3)	1.420(4)	0.86
Avg	1.354(3)	1.432(4)	1.408(3)	1.422(4)	**0.59**
Naphthalene -TCNQ[19]	1.343	1.444	1.374	1.434	0.07
TTF-TCNQ[20]	1.356	1.433	1.402	1.423	**0.62**

w–z denotes each TCNQ in the unit cell. Ave is the average of the four TCNQs. TTF-TCNQ is an example of a segregated stack structure of a CT crystal, and naphthalene-TCNQ is a mixed stack. The crystal structures obtained at 123 K or 100 K.

In summary, we designed and synthesised CT crystals based on a segregated stack structure using HPyB and TCNQ. The formation of the CT crystal was clearly identified by its crystal colour, which is different for HPyB and TCNQ. It was confirmed from single-crystal XRD that CT crystals were constructed from two HPyBs and seven TCNQs and arranged in a segregated stacked layer. The HPyBs were stacked in a gear-mesh-like arrangement, which enabled columnar stacking. Furthermore, we estimated the degree of charge transfer from the TCNQ bond length. All four independent TCNQs exhibited a moderate degree of *ρ* (0.59), suggesting that partial charge transfer would occur. The novel segregated CT crystal motif presented herein can also potentially inspire the fabrication of new electron-conducting materials.[27] Further exploration of the structure of HAB will lead to the development of a new platform for CT crystals with a segregated stack structure.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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27 Because of the small crystal size of the CT crystal, we could not measure its electron conductivity.

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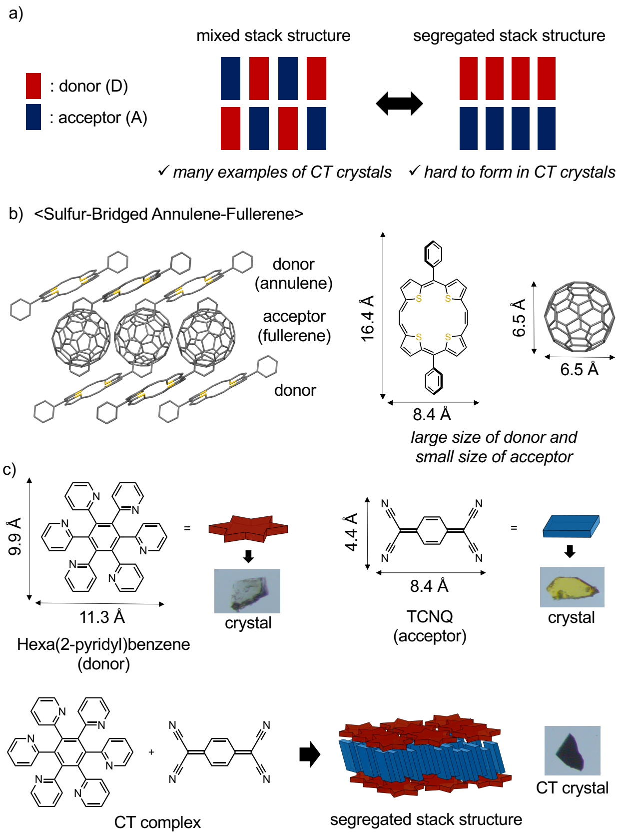

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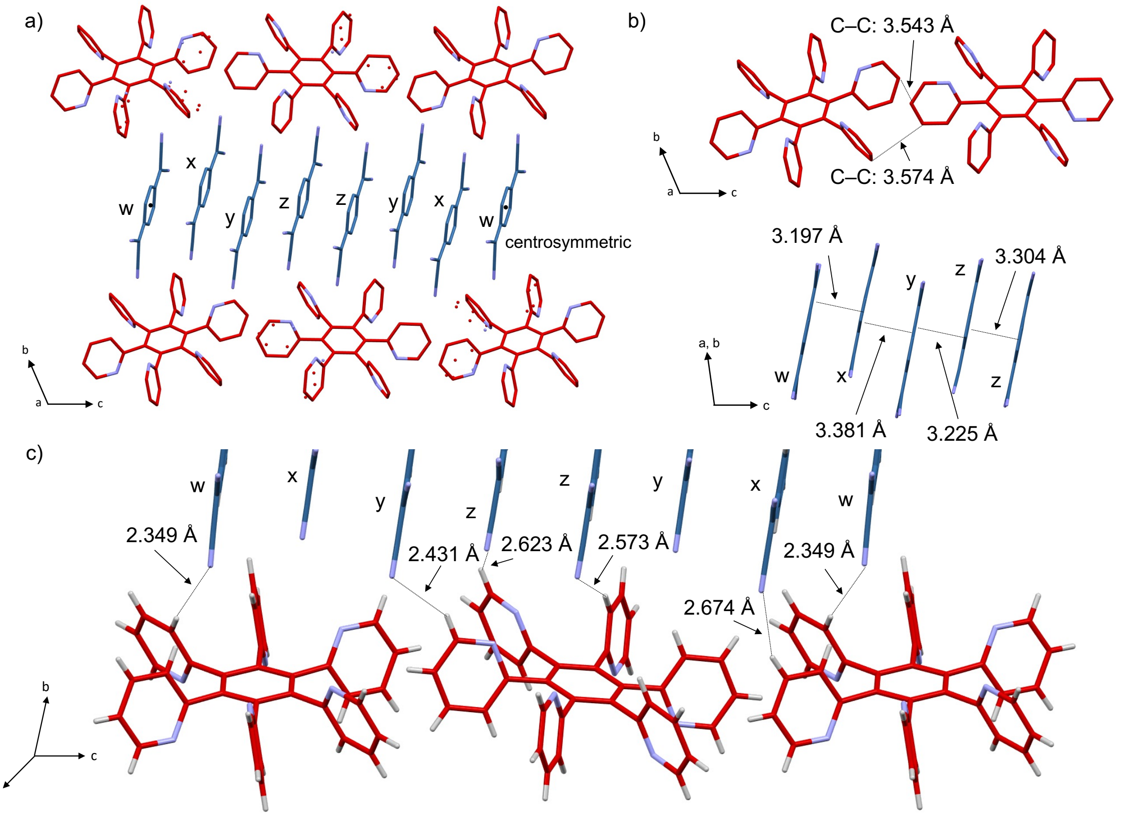

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$$\rho = \frac{\alpha_{CT} - \alpha_0}{\alpha_{-1} - \alpha_0}$$

where $\alpha_x = c / (b + d)$, and CT, 0 and -1 refer to the CT, neutral, and anionic states of TCNQ, respectively.

From the XRD results of the CT crystal, there were four independent TCNQs in a unit cell, denoted as w, x, y, and z (Figure 3b). Because some TCNQs were not C2 symmetric, the average of the bond lengths was used to calculate ρ. As shown in Table 1, the ρ values of x (ρ = 0.67) and z (ρ = 0.86) were higher than those of w (ρ = 0.46) and y (ρ = 0.35). The high ρ value indicates that the molecule exhibits ionic character, while the low ρ value indicates a neutral state. The ρ values at 293 K were evaluated as smaller than those in 123 K, but still around 0.50 (Table S3). We also evaluated the ρ by using different equations, and no significant differences among the ρ values were observed (Table S4).[21,22]

The ρ of TCNQs indicated that the HPyB worked as the donor and had ca. +1.63 of the oxidation value with respect to of the CT crystal composition (seven TCNQs per two HPyB). The CV measurements revealed that the HPyB exhibited two irreversible oxidation potentials at 1.36 and 1.79 V vs Ag/Ag$^+$. The estimated HOMO energies from the CV measurement were –6.00 and –6.43 eV, which are calibrated bythe HOMO energy and CV values of ferrocene (Table S5). The calculated HOMO level of HPyB was similar to that of naphthalene, which could also form CT crystal with TCNQ and work as donor molecules.[23] These results suggested that the HPyB functioned as the donor and could have over +1.0 of oxidation value per one molecule.

We compared the ρ value with those of previously reported donor–TCNQ CT crystals, including mixed stack crystals[23] and segregated stack crystals.[24] The average value of ρ for all four TCNQs was used (ρ = 0.59). Comparing the ρ value of naphthalene-TCNQ (ρ = 0.07), which has a mixed stack crystal structure, the ρ value of HPyB-TCNQ (ρ = 0.59) is considerably larger than that of naphthalene-TNCQ. Furthermore, the ρ value of HPyB-TCNQ is comparable to that of TTF-TCNQ (ρ = 0.62) which has a segregated stack structure.

The high ρ value observed in the CT crystal would be attributed to the specific stoichiometry of the donor (HPyB) and acceptor (TCNQ) molecules (1:3.5). The electrons of one HPyB molecule could be strongly extracted by 3.5 of TCNQs and enhanced the degree of charge-transfer. In fact, the stoichiometry effect was reported in other CT crystals that the donor exceeded to the acceptor.[25] In addition, the molecular geometry of CT crystal can largely alter its ρ value.[8,20,26] Most CT crystals showed higher ρ value in segregated stack manner than in a mixed manner, suggesting that the segregated stacking structure of TCNQs in the CT crystals with HPyB would also induce the high ρ value. Furthermore, the ability to become dication of HPyB was expected to be essential for realizing the high ρ value with the high ratio of TCNQ composition.

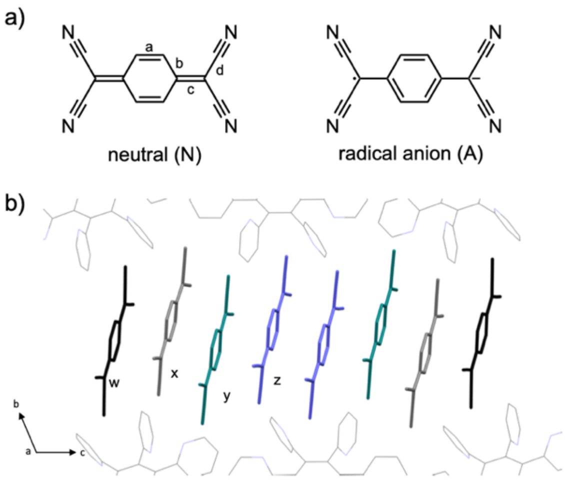

Figure 3. a) Neutral structure and anion structure of TCNQ. b) Four independent TCNQs in a unit cell.

Table 1. Bond length of TCNQ and the calculated ρ values

	a (Å)	b (Å)	c (Å)	d (Å)	ρ
w	1.353(3)	1.437(4)	1.393(3)	1.417(4)	0.46
x	1.354(3)	1.429(4)	1.438(3)	1.424(4)	0.67
y	1.348(3)	1.438(4)	1.387(3)	1.427(4)	0.35
z	1.361(3)	1.424(4)	1.413(3)	1.420(4)	0.86
Avg	1.354(3)	1.432(4)	1.408(3)	1.422(4)	**0.59**
Naphthalene -TCNQ[19]	1.343	1.444	1.374	1.434	0.07
TTF-TCNQ[20]	1.356	1.433	1.402	1.423	**0.62**

w–z denotes each TCNQ in the unit cell. Ave is the average of the four TCNQs. TTF-TCNQ is an example of a segregated stack structure of a CT crystal, and naphthalene-TCNQ is a mixed stack. The crystal structures obtained at 123 K or 100 K.

In summary, we designed and synthesised CT crystals based on a segregated stack structure using HPyB and TCNQ. The formation of the CT crystal was clearly identified by its crystal colour, which is different for HPyB and TCNQ. It was confirmed from single-crystal XRD that CT crystals were constructed from two HPyBs and seven TCNQs and arranged in a segregated stacked layer. The HPyBs were stacked in a gear-mesh-like arrangement, which enabled columnar stacking. Furthermore, we estimated the degree of charge transfer from the TCNQ bond length. All four independent TCNQs exhibited a moderate degree of ρ (0.59), suggesting that partial charge transfer would occur. The novel segregated CT crystal motif presented herein can also potentially inspire the fabrication of new electron-conducting materials.[27] Further exploration of the structure of HAB will lead to the development of a new platform for CT crystals with a segregated stack structure.

Conflicts of interest

There are no conflicts to declare.

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27 Because of the small crystal size of the CT crystal, we could not measure its electron conductivity.