Mixed Stack Organic Semiconductors: The Anomalous Case of the BTBT- TCNQF_x Series

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Synopsis

We report on a series of charge-transfer (CT) crystals where BTBT electron donor is associated with TCNQF_x ($x = 0, 2, 4$). At variance with Perylene-TCNQF_x series, the degree of CT ρ does not increase with TCNQF_x electron affinity. The anomaly is explained by the involvement of BTBT HOMO and HOMO-1 in the CT mechanism and by the Madelung energy behavior.

Abstract

We present a detailed characterization of three mixed stack organic semiconductors, where benzothieno-benzothiophene electron donor is associated with fluorine-substituted TCNQ of increasing electron affinity. BTBT-TCNQ and BTBT-TCNQF₂ are isomorphous, whereas the three-dimensional packing of BTBT-TCNQF₄ is different. Rather surprisingly, we found that the degree of charge transfer is almost constant along the series, at variance with what has been found in analogous cocrystal

series in which TCNQF_x are involved. We explain this finding in terms of the Madelung energy resulting from interstack packing of the cocrystals, and of the fact that both the HOMO and HOMO–1 of BTBT are involved in the charge transfer mechanism. We also propose that the difference in interstack packing resulting from increasing F substitution is a consequence of electrostatic interactions.

Introduction

In the quest for new and more efficient organic semiconductors for low-cost, eco-friendly electronic devices, considerable attention has been recently devoted to two-component, mixed stack charge transfer (CT) crystals, due to the suggestion of possible ambipolar transport⁽¹⁾ and of facile tuning of the band gap by changing one of the two components, generally the electron acceptor, applying the so-called molecular electrical doping.^(2–5) Benzothieno-benzothiophene (BTBT) alkylated derivatives that shown outstanding *p*-channel semiconducting properties^(6, 7) have recently been combined with TCNQF_x acceptors to explore the possibilities of the two-component approach.^(8, 9) Surprisingly enough, the obtained transistors are of *n*-type,^(9, 10) and the degree of charge transfer do not correlate with the TCNQF_x acceptor strength, as happens for instance with other mixed stack CT crystals, e.g., the perylene-TCNQF_x series.^(3, 4) In order to disentangle the possible effects of the alkyl side-chains on this behavior, we decided to investigate the physical properties of the charge transfer crystals of the TCNQF_x series of acceptors (*x* = 0, 2, 4) with unsubstituted BTBT. Independently from us, the same crystals were prepared by Sato et al.,⁽¹¹⁾ and studied in OTFT devices. Here we shall report a more detailed characterization, accompanied by a theoretical analysis aimed at understanding the peculiar properties of this series of crystals.

Experimental Section

Sample Preparation

TCNQ, TCNQF₂, and TCNQF₄ (purity ≥98%) were purchased from TCI. BTBT (purity ≥99.99%) was purchased from the Laboratoire de Chimie des Polymers (Université Libre de Bruxelles). Each material was utilized as received. For the growth of single crystals, 2 mg of BTBT were dissolved in dichlorobenzene (DCB) with the proper amount of TCNQF_x to form an equimolar solution. The solutions were heated up to 90 °C and the total volume of DCB was determined to have saturated starting solutions. Each solution was then inserted in a programmable oven that was set up to decrease the temperature from 90 to 24 °C in 48 h. The slow and controlled cooling process provided a way to reach the supersaturation conditions in a less dramatic way than the simple spontaneous cooling of the solution at room temperature, thus enabling the formation of diffraction quality single crystals. Finally the so obtained crystals were carefully extracted and dried on filter paper.

X-ray Diffraction Measurements

Single crystals of the three complexes were mounted on a Bruker SMART 1000 CCD diffractometer equipped with graphite monochromated Mo K α radiation (λ = 0.71073 Å) fine-focus sealed tube. The intensity data were collected using ω scan at 294(2) K.

Cell refinements and data reductions were performed using the Bruker SAINT software.⁽¹²⁾ Multiscan absorption corrections were applied empirically to the intensity values ($T_{\min}$ and $T_{\max}$ = 0.954, 0.992 for BTBT-TCNQ; 0.965, 0.994 for BTBT-TCNQF₂; 0.918, 0.982 for BTBT-TCNQF₄) using SADABS.⁽¹²⁾ The structures were solved by direct methods using the program SHELXT⁽¹³⁾ and refined with full-matrix least-squares based on F^2 using the program SHELXL2014/7.⁽¹⁴⁾ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically and refined using a riding model approximation, with C–H = 0.93 Å and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$. The molecular graphics were prepared using the ORTEP,⁽¹⁵⁾ SCHAKAL99,⁽¹⁶⁾ and Jmol⁽¹⁷⁾ programs.

Spectroscopic Measurements

Infrared (IR) spectra of the crystals were recorded with a Bruker IFS66 Fourier transform IR (FT-IR) spectrometer coupled to an IR microscope Hyperion 1000. Spectral resolution: 2 cm⁻¹. The Raman spectra were recorded with a Renishaw 1000 Raman spectrometer equipped with the appropriate edge filter, and coupled to a Leica M microscope. A Lexel Kr laser was used as light source. Exciting line: 532 nm.

Theoretical Calculations

We have followed a recently proposed approach.^(18, 19) The method uses ground-state density functional (DFT) calculations (Gaussian09 package⁽²⁰⁾) for individual molecules and donor–acceptor (DA) dimers, and on the atomistic modeling of intermolecular electrostatic interactions. All calculations have been performed in vacuum using the unrestricted ω B97XD hybrid functional together with the 6-31+G* basis set. The average charge residing on BTBT and TCNQF_x molecules is estimated on the basis of the computed Hirshfeld atomic charges. Intermolecular charge transfer integrals have been calculated by using ADF⁽²¹⁾ with TZP basis and GGA:PBE functional. The electrostatic interaction V within a DA pair and the Madelung energy M are computed by adopting the point-charge approximation of the molecular charge density based on ESP atomic charges computed for neutral and charged molecules and lattices. The crystal electrostatic sums have been obtained for finite clusters of increasing size using the MESCAL code.⁽²²⁾

Results

All compounds crystallize as alternating D–A stacks. The structures essentially coincide with those independently reported by Sato et al.⁽¹¹⁾ Detailed crystallographic information is given in Table S1 of the [Supporting Information](#) and in the deposited CIF files (CCDC: [1556355](#), [1556356](#), [1556357](#)).

BTBT-TCNQ and BTBT-TCNQF₂ are isomorphous, both belonging to the triclinic $P\bar{1}$ space group. The molecules are stacked along the a crystal axis, and there is one DA pair per unit cell. Notice that the β angle is almost 90°. BTBT-TCNQF₄ instead crystallizes in the monoclinic $P2_1/c$ group, with two DA pairs per unit cell, stacked along the b crystal axis. In BTBT-TCNQF₄ the volume per DA pair is appreciably larger (531.5 Å³) than in the other two CT crystals. [Figure 1](#) puts in evidence the similarity in the stack structure of the isomorphous BTBT-TCNQ and BTBT-TCNQF₂, and of BTBT-TCNQF₄. In all cases the molecules are tilted by approximately the same angle (about 20°) with respect to the stacking axis. However, the reciprocal arrangement of the stacks is different: The layers perpendicular to the stacking axis are made up of equal molecules in BTBT-TCNQ and BTBT-TCNQF₂ ([Figures 1](#) and [S4, S5](#)), whereas they are arranged in a chessboard layout in BTBT-TCNQF₄ ([Figures 1](#) and [S6](#)).

Figure 1. (Top) Crystal structure of BTBT-TCNQF₂ viewed from the *b* axis. (Bottom) Crystal structure of BTBT-TCNQF₄ viewed from *a* axis. The chosen view puts in evidence the stack structure and the three-dimensional stack arrangement.

The average planes of BTBT and TCNQF_{*x*} are slightly inclined each other, and the inclination decreases in going from TCNQ to TCNQF₄, as the interplanar distance does, changing from 3.386 to 3.300 Å ([Table S1](#)). The same trend, albeit less pronounced, is found in the analogous series of 2,7-dioctyl[1]benzenothieno[3,2-*b*][1]benzothiophene with TCNQF_{*x*} (8BTBT-TCNQF_{*x*}).⁽⁹⁾ Of course, the reciprocal arrangement of D and A molecules is such to give the optimum CT overlap. However, in the case of BTBT complexes the overlap is not only between the HOMO and LUMO of the DA pair, but also involves the HOMO–1 orbital of BTBT.^(8, 9) This is pictorially shown in [Figure 2](#), where the HOMO, HOMO–1 of BTBT and the LUMO of TCNQ are drawn together with the projection of BTBT molecule over TCNQF₂ (the projection over TCNQ and TCNQF₄ is similar). This peculiar overlap was already pointed out in the 8BTBT-TCNQF_{*x*} series:⁽⁹⁾ Thus, the lateral chains have negligible effects on the one-dimensional packing, as we shall also discuss below. We also notice that, at variance with other complexes of TCNQF₂, for instance with perylene,⁽⁴⁾ in BTBT-TCNQF₂ there is no disorder in the F atom position resulting from rotational disorder, due to the asymmetrical superposition of BTBT and TCNQF₂ along the stack (bottom left side of [Figure 2](#)).

Figure 2. Pictorial representation of the HOMO, HOMO–1 of BTBT and of LUMO of TCNQF₂, and projection of TCNQF₂ on BTBT plane along the stacking axis.

We now turn our attention to the determination of the degree of CT or ionicity, ρ , one of the basic parameters characterizing CT crystals.^(3-5, 19) Sato et al.⁽¹¹⁾ used the TCNQF_{*x*} bond lengths and the IR CN stretching frequency, obtaining somewhat inconsistent results, as shown in [Table S1](#) of the paper [Supporting Information](#).⁽¹¹⁾ Both methods suffer from some drawback: The bond lengths method depends on the adopted calibration, and the CN stretching frequency is known to give unreliable, generally overestimated, ρ values.⁽²³⁾ As in the case of perylene-TCNQF_{*x*} series,⁽⁴⁾ we have obtained ρ from the frequencies of other, well tested, IR active charge sensitive modes of TCNQF_{*x*}.^(4, 23, 24)

[Figure 3](#) reports the single crystal IR absorption spectra of BTBT-TCNQ, BTBT-TCNQF₂, and BTBT-TCNQF₄, collected with the electric field of the incident radiation perpendicular to the stack axis, so that the in-plane vibrational modes can be selectively observed. Only the spectral range 1280–1680 cm^{–1} is shown, since all the charge sensitive bands lie in this region. In [Figure 3](#) we also report the spectra of BTBT powders, to show that bands originated by this molecule do not interfere with the

identification of the charge sensitive bands of TCNQF_x in the three cocrystals. Their frequency is reported directly in the figure.

Figure 3. IR absorption spectra of BTBT-TCNQ, BTBT-TCNQF₂, and BTBT-TCNQF₄ single crystals, with polarization perpendicular to the stack axis. The spectra are offset by one absorbance unit for clarity. The top blue line is the spectrum of neutral BTBT powder. The frequencies of the charge sensitive bands are reported.

In the case of BTBT-TCNQ the ionicity is estimated through the position of the TCNQ $b_{1u}v_{20}$ C=C antisymmetric stretching. The frequency is shifted by 4 cm⁻¹ with respect to the neutral TCNQ. Since the ionization frequency shift of this mode is 47 cm⁻¹,⁽²⁴⁾ we obtain a ρ value of 0.10 ± 0.02 . In case of TCNQF₂ and TCNQF₄ we have three IR active charge sensitive vibrations in this spectral region. For neutral TCNQF₂ they are located at 1575, 1550, and 1393 cm⁻¹, with a ionization frequency shift of 50, 63, and 44 cm⁻¹, respectively,⁽⁴⁾ and for neutral TCNQF₄ they are found at 1599, 1550, and 1396 cm⁻¹, with a ionization frequency shift of 59, 49, and 43 cm⁻¹.⁽²³⁾ From the frequencies reported in [Figure 3](#) we then derive $\rho = 0.09 \pm 0.05$ and $\rho = 0.12 \pm 0.05$ for BTBT-TCNQF₂ and BTBT-TCNQF₄, respectively. The averages values we report are weighted by ionization frequency shifts, and the larger uncertainties given for BTBT-TCNQF₂ and BTBT-TCNQF₄ are due to the fact that some of the charge sensitive bands are split ([Figure 3](#)), probably as a consequence of Fermi resonance with other vibrational modes.

The Raman spectra (see [Figures S7–S9](#)) confirm that the degree of charge transfer remains more or less the same in the series, around 0.1. This is a somewhat surprising result, since by combining the same donor with molecules of increasing electron affinity, one would expect an increasing value of ρ , as in the case for the series of perylene with TCNQF_x or for the one involving 3,3',5,5'-tetramethylbenzidine with a wider series of electron acceptor molecules.⁽²⁵⁾

Discussion

Although infrequent, the relative insensitivity of the degree of CT to the difference between the ionization potential of the donor and the electron affinity of the acceptor has already been encountered. Besides the obviously similar case of the cocrystals TCNQF_x with alkylated BTBT,^(8, 9) this unusual effect has already been explicitly noticed in the CT crystals formed from TCNQ and TCNQF₄ with dithieno[2,3-d;2',3'-d']benzo[1,2-b;4,5-b']dithiophene (DTBDT),⁽²⁶⁾ a molecule which presents some similarity to BTBT, being characterized by the same motif of two fused thiophene rings, separated by a benzene ring. In that case the authors used extensive DFT calculations to try to explain the phenomenon, ascribing it to a difference in the CT mechanism due to the presence of fluorine ligands.⁽²⁶⁾ We feel that such a fully computational approach may be missing some relevant aspect, and in any case the proposed mechanism of the

anomaly cannot be extended to the present case, where the overlap between donor and acceptor molecules is the same (Figure 2) in the three studied crystals, and where the BTBT-TCNQ and BTBT-TCNQF₂ crystals are isomorphous.

We have then decided to follow a different approach, where DFT calculations are only used to estimate the basic parameters entering a simplified Hamiltonian able to catch the essential physical chemistry of mixed stack CT crystals. The method has been recently applied successfully to model a series of different CT crystals.⁽¹⁹⁾ Since we are making a relative comparison in a series of similar molecules, we can safely assume that some of the relevant parameters, like the intramolecular relaxation energy, are constant, so that we can limit the calculation to the following parameters: t , the hopping or CT integral between D and A; V , the DA intermolecular Coulomb potential; $z = (I_d - A_A) - (1/2) V$, half the energy required to form an ionic pair⁽¹⁹⁾ (I_d is the D ionization potential and A_A the A electron affinity); and M , the Madelung energy.

Delchiaro et al.⁽¹⁹⁾ used a CT dimer model to estimate t and z . However, this two-state model does not consider the possibility of having more than one CT integral, as is known to occur in BTBT cocrystals: BTBT HOMO and HOMO-1 are close in energy (about 0.5 eV), so we have two CT integrals and two CT transitions.^(8, 9)

In the present case we have therefore decided to directly calculate z and t . The latter corresponds to the Fock matrix elements between the involved D and A orthogonalized molecular orbitals.⁽²¹⁾ The intermolecular Coulomb potential V and Madelung energy M are calculated in the point-charge approximation of the molecular charge density based on the computed atomic ESP charges. Finally, I_d and A_A energies entering (with V) in the definition of z are taken as the HOMO and LUMO DFT energies. The results of the calculations are summarized in Table 1.

Table 1. Basic Electronic Parameters (eV) of the Studied Compounds

system	z	ρ_{dim}	ρ_{exp}	t^a	V	M	$V - 2M$
BTBT-TCNQ	0.51	0.07	0.10	0.12, 0.23	— 2.12	— 0.96	−0.20
BTBT-TCNQF ₂	0.25	0.08	0.09	0.09, 0.22	— 2.06	— 0.93	−0.20
BTBT-TCNQF ₄	0.06	0.09	0.12	0.10, 0.22	— 1.99	— 1.31	0.63
10BTBT-TCNQ	0.36 dimer:	0.76	0.05 --	0.11, 0.21 dimer: 0.25	— 2.00	— 1.00	0.00
10BTBT-TCNQF ₄	−0.10 dimer: 0.57	0.06 --	0.12, 0.21 dimer: 0.23	— 1.89	— 0.95	0.02	

The two reported values of t correspond to the HOMO-LUMO and (HOMO-1)-LUMO integrals, in this order. In the case of 10BTBT-TCNQ and 10BTBT-TCNQF₄ the values obtained by the dimer model (ref ¹⁹) are reported for comparison.

Although only the *relative* value of the computed parameters is important here, we have nonetheless verified the effect of different choices in the DFT functional and basis set, taking as reference either the experimental values or the results from the dimer model.⁽¹⁹⁾ The basis set choice has in general little influence, provided one uses an extended basis with diffuse contribution, as the 6-31G* of Gaussian⁽²⁰⁾ or the TZP of

ADF.(21) The choice of functional instead affects considerably the orbital energies. In reporting z in [Table 1](#), we use the ω B97XD MO energy values, shifting the zero of the energy in such a way that $(I_d - A_A)$ reproduces the experimental difference (1.57 eV) between the ionization potential of BTBT(27) and the TCNQ electron affinity.(28) In any case the difference between the two extremes, BTBT-TCNQ and BTBT-TCNQF₄ (about 0.5 eV), is essentially the same whatever DFT functional is adopted, and is always somewhat less than the difference between experimentally determined electron affinities of TCNQ and TCNQF₄.(28) In the calculation of t we can divide the effects of the functional in two categories: use of Generalized Gradient Approximations (GGA) always underestimates the t value, whereas hybrid methods such as B3LYP or ω B97XD overestimate it. In [Table 1](#) we report the values obtained by GGA-PBE functional and TZP basis set, which compare well with those obtained with similar methods in ref 9, and which are underestimated by a constant factor of 1.25 with respect to the experiment and to the dimer model.(19) Finally, the V and M values estimated from ESP charges do not depend significantly on the adopted functional and basis set. In [Table 1](#) we have added for comparison the electronic parameters of 2,7-didecyl[1]benzenothieno[3,2-*b*][1]benzothiophene (10BTBT) as calculated with the dimer model(19) and by the present method. First of all, we remark that the CT integrals of 10BTBT-TCNQF_x cocrystals are essentially the same as those of the unsubstituted BTBT, confirming that the side chains have little effect on the one-dimensional arrangement of donor and acceptor molecules. From [Table 1](#) it is also seen that by increasing the TCNQ electron acceptor strength z , the energy required to form a DA pair (first column) decreases, i.e., the system tends to become more ionic, as expected. The trend is confirmed by the computed degree of CT for the isolated DA pair in gas phase, ρ_{dim} .(19) As shown in the second column of [Table 1](#), ρ_{dim} increases monotonically in going from TCNQ to TCNQF₄, whereas the experimental ρ_{exp} shows a non-monotonic trend (third column). It is indeed the Madelung energy M which makes the difference when the DA pair is embedded in the crystal.(19) As shown in the sixth column of [Table 1](#), M slightly decreases in going from BTBT-TCNQ to the isomorphous BTBT-TCNQF₂, then it increases in BTBT-TCNQF₄, despite the fact that in this case we have an increase of the volume per DA pair ([Table S1](#)). This nonlinear trend accounts for the experimental ρ_{exp} values found in the three cocrystals: There is practically no change by replacing TCNQ with TCNQF₂, as the decrease of z is compensated by the decrease of M . In BTBT-TCNQF₄; on the other hand, both the decrease of z and the increase of M correlate with the very small increase of ionicity. Even if both z and M contribute to increase the degree of CT in BTBT-TCNQF₄ with respect to BTBT-TCNQ, the increase is almost nil, at variance with other cases.(4) This is due to the effect of CT integral: The larger t is, the larger the electron delocalization along the stack, and the smaller the effect of z and M .(19) In the case of BTBT we have two CT integrals, whose combined effect is at the origin of the insensitivity of ρ to the increased electron affinity of the TCNQF_x. Notice incidentally that the (HOMO–1)–LUMO CT integral is about twice the HOMO–LUMO one. This has to be ascribed to a better overlap, as can be appreciated from [Figure 2](#). The fact that in BTBT the two frontier HOMOs are close in energy has been already remarked in the context of cocrystals involving BTBT and BTBT derivatives,(8,9) but as far as we know, the consequences on the physical properties of the various systems have not been extensively addressed. For instance, we believe that the small energy difference (~ 0.5 eV) between HOMO and HOMO–1 has the likely consequence of the lack of symmetry between the conduction and valence band, a requirement for ambipolar transport in CT crystals,(1) and indeed, BTBT-TCNQF_x cocrystals exhibit n -

channel transport only.⁽¹¹⁾ On the other hand, this proximity might well explain the very good *p*-channel semiconducting properties of pristine BTBT derivatives.⁽⁷⁾ A more detailed discussion of the above points goes beyond the aim of the present paper, and now we address the question of why the Madelung energy slightly decreases in going from BTBT-TCNQ to the isomorphous BTBT-TCNQF₂, although the unit cell volume is decreasing (Table S1). As a matter of fact, the three-dimensional packing of the DA stacks reflects the effect of the Madelung energy, which is indeed a geometric parameter.⁽²⁹⁾ This is clearly seen in Figure 4, which shows the layers of BTBT and TCNQF_x perpendicular to the stacking axis of BTBT-TCNQ and BTBT-TCNQF₂. Since the structures have a DA pair per unit cell, the layers perpendicular to the stacks contains molecules of the same kind. Figure 4 reports the shortest distances between H, F, and N atoms in nearby molecules. Since the (negative) molecular charge in TCNQF_x is concentrated on the N, but also in F atoms when present, the repulsion between the stacks is increased in BTBT-TCNQF₂ with respect to BTBT-TCNQ, hence the decrease of the Madelung energy. This electrostatic effect can also explain why the BTBT-TCNQF₄ structure is not isomorphous with the other two. The presence of two more F atoms would make the triclinic structure less stable, with a further decrease of the electrostatic energy. Therefore, BTBT-TCNQF₄ prefers to adopt the monoclinic structure, with two DA pairs per the unit cell, so that in the layers perpendicular to the stack we have the same kind of molecules along the *c* axis, but BTBT and TCNQF₄ alternate along the *a* axis (Figure S6).

Figure 4. View of the isomorphous BTBT-TCNQ and BTBT-TCNQF₂ structures perpendicular to the stacking axis, showing the H–H, N–N, and F–F shortest distances.

In order to give a more quantitative basis to the above discussion, we report in the rightmost column of Table 1 the difference between V and $2M$ (the 2 factor is due to the definition of V and M ⁽¹⁹⁾). V represents the attractions between nearby oppositely charged molecules, and essentially represents the intrastack Coulomb potential. The Madelung energy M is instead the three-dimensional Coulomb potential, extended to the whole crystal so that $V - 2M$ is representative of interstack interactions. Negative values, as in the case of BTBT-TCNQ and BTBT-TCNQF₂, point to the presence of dominant repulsive interstack interactions, larger than the attractive intrastack interaction. To test the idea that the change of structure of BTBT-TCNQF₄ is due to unfavorable electrostatic interactions, we have calculated $V - 2M$ for a hypothetical triclinic structure of BTBT-TCNQF₄, isomorphous with the other two structures in the series, and we have indeed found a very large negative value, -0.59 eV, which indicates an unstable structure. On the other hand, in systems with small or positive $V - 2M$, intra- and interstack interactions compensate each other. As shown in Table 1, this is the case of BTBT-TCNQF₄, but also of 10BTBT-TCNQ and 10BTBT-TCNQF₄. The structure of the two latter systems is similar to that of BTBT-TCNQ, triclinic centrosymmetric with one DA pair per unit cell, but in this case nearby equal molecules in the layer perpendicular to the stack are kept apart by the lateral alkyl chains, giving another indirect indication of the importance of electrostatic interactions in establishing the three-dimensional packing of the cocrystals.

Conclusions

In this paper we have presented a combined structural and spectroscopic characterization of the series of CT crystals BTBT-TCNQF_x. Through an accurate determination of the degree of CT by polarized IR spectra we have detected a rather anomalous behavior: At variance with other series involving different donors, like perylene,⁽⁴⁾ we have found that ρ increases very little, and in a nonlinear manner, on increasing the TCNQF_x electron accepting strength from TCNQ to TCNQF₄. Extensive calculations have allowed us to explain this anomaly as being due to the combination of the CT mechanism involving both HOMO and HOMO–1, and three-dimensional Madelung energy. Focusing attention on the latter, we have discovered that the difference in the crystal packing between BTBT-TCNQ and BTBT-TCNQF₂, on one side, and BTBT-TCNQF₄ on the other, is due to the differences in the interstack electrostatic interactions, as measured by $V - 2M$. From this point of view, the comparison with alkylated BTBT-TCNQF_x cocrystals⁽⁹⁾ shows that the role of the alkyl chains is just that of keeping apart the DA stacks, reducing the effect of three-dimensional electrostatic interactions. We believe the above is an important clue in the endeavor to understand the role of intermolecular interactions in the crystal packing of CT crystals, and further studies in this direction are in progress in our laboratory.

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