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Tracing a Common "Origin" of Phase Transformation, Polymorphism, Disorder, Isosterism, and Isostructuralism in Fluorobenzoylcarvacryl Thiourea

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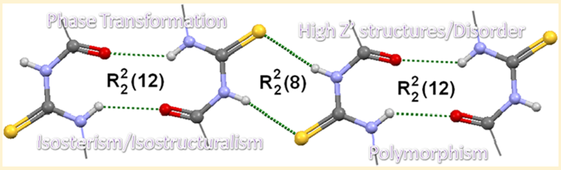
Supporting Information

ABSTRACT: The terms phase transformation, polymorphism, disorder, isosterism, and isostructuralism are often the keywords used in the design and engineering of molecular crystals. Three benzoylcarvacryl thiourea derivatives with [-NH−C(S)−NH−C(O)-] cores generate molecular crystals, which provide the basis for exploring a common link between the structures related by aforementioned terms. The apparent "origin" of all these structural modifications has been traced to the formation of a planar molecular dimeric chain built with homomeric $R_2^2(12)$ and $R_2^2(8)$ synthons occurring in tandem, one formed with N−H···O and the other with N−H···S hydrogen bonds.



■ INTRODUCTION

Growth of a molecular crystal depends on a delicate balance between a variety of thermodynamic and kinetic factors.[1] The strength and directionality of intermolecular interactions in molecular crystals control these factors in terms of the formation of "supramolecular synthons".[2] It is obvious from the wealth of crystal structure data available that the formation of high Z' structures, occurrence of phase transitions with temperature or pressure, formation of polymorphic modifications, and disorder in crystal structures are indeed dictated by the variability offered by synthons. Further, the robustness associated with synthons can provide a landscape for isostructurality and isosterism.[3] Recently, it has been demonstrated that synthons can also serve as potential fragments for the transferability of charge density distributions in molecular crystals (SBFA methodology).[4] However, so far in the literature, the potency of a synthon to serve as a "common linker" between polymorphism, disorder, phase transformation, isostructurality, and isosterism has not been explored. In this paper, we examine the credibility of a robust synthon to serve as a common link to generate such a structural diversity in single molecular species[5] (parent molecule and F-substituted derivatives).

Supramolecular synthons in high Z' structures appear to be in their primitive stages and hence provide clues about possible nucleation pathways.[6] In several recent articles, it has been discussed that high Z' structures would indeed allow for alterations in the packing motifs assisting the prediction of new polymorphic modifications of lower Z' (preferably $Z' = 1$).[7] Systematic studies of high Z' structures exhibiting pseudosymmetry elements bring out their susceptibility for temperature or pressure induced phase transformations.[8] Although, in many cases, the lowering of crystal symmetry is observed upon lowering the temperature, there are examples resulting in higher symmetry with lowering of temperature.[8,9] More interestingly, it has been reported that two polymorphs, both stable under ambient conditions, can reversibly be interconverted into one another under the given set of temperature conditions.[10] In all these cases, the very existence of a robust synthon in the lower Z' form has been well associated with synthons in their evolutionary stages in the corresponding polymorphs with higher Z'.[11]

In the context of crystallography, the atoms or ions with comparable atomic or ionic volumes are referred to as being isosteric. Molecules differing only in the substitution of isosteres at specific positions, in general, result in the formation of similar crystal structures due to isosterism among the substituents. A fluorinated analog is geometrically very similar to its parent molecule and hence satisfies isosteric requirements in the ensuing crystal structures.[12] As a result, compounds with monofluorophenyl rings, in particular, *ortho*-fluoro- and *meta*-fluorophenyl compounds are commonly found to be orientationally disordered in the crystal structures.[13] However, it is interesting to note that, in general, if the fluorine atom is involved in hydrogen bonding (C−H···F, N−H···F; for example), this orientational disorder is reduced. Isostructurality with its parent nonfluoro compounds, mainly controlled by a size factor, is yet another feature observed in fluorinated analogs. Even though in general isostructurality prevails,[3] there are examples that display significant structural deviations on

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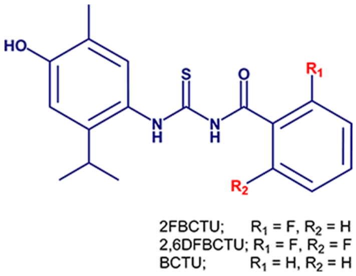
substitution of fluorine at the hydrogen positions.[14] Indeed, several recent articles,[15] draw attention toward the structure-directing role of "organic" fluorine in this regard.

Benzoylcarvacryl thiourea [BCTU] derivatives belong to a class of insect growth regulators with *N*-acyl thiourea [-NH−C(S)−NH−C(O)-] functionality and are widely used in the agricultural industry.[16] Three compounds, namely, 2-fluoro benzoylcarvacryl thiourea [2FBCTU], 2,6-difluoro benzoylcarvacryl thiourea [26DFBCTU], and benzoylcarvacryl thiourea [BCTU] (Scheme 1), have been identified for the evaluation of important structural features associated with interchangeability of a hydrogen atom and a fluorine atom in the presence of strong H-bond donors (N−H) and acceptors (C═O and C═S).

Scheme 1. Chemical Structures of the Compounds 2FBCTU, 26DFBCTU, and BCTU



■ EXPERIMENTAL SECTION

The compounds 2FBCTU, 26DFBCTU, and BCTU were synthesized by the reaction of the corresponding benzoyl chlorides with 4-amino-5-isopropyl-2-methylphenol and ammonium thiocyanate in acetone (see Supporting Information for detailed synthetic procedures). X-ray diffraction data were collected on an Oxford Mova diffractometer,[17] equipped with an EoS detector, utilizing Mo Kα radiation (λ = 0.71073 Å). All structures were solved by direct methods using SHELXS-97 and refined against F^2 using SHELXL-97.[18] H-atoms except for the ones on nitrogen (N−H) were fixed geometrically and refined isotropically. The hydrogens of the amino group were located from difference Fourier maps and refined isotropically. WinGX[19] and OLEX2[20] were used for structure refinement and production of data tables, and ORTEP-3[21] was used for structure visualization. Analysis of the H-bonded and π interactions was carried out using PLATON.[22] Packing diagrams were generated with MERCURY.[23]

■ RESULTS AND DISCUSSION

The compound 2-fluoro benzoylcarvacryl thiourea, 2FBCTU, was crystallized from its saturated solution in ethyl acetate/hexane (7:3) under ambient conditions. Room-temperature X-ray diffraction data acquired on a plate-shaped colorless crystal revealed that the structure belongs to a noncentrosymmetric space group *P*1 with four molecules in the asymmetric unit

Table 1. Crystallographic Details of Compounds 2FBCTU, 26DFBCTU, and BCTU

	2FBCTU				
	form IA	form IB	form II	26DFBCTU	BCTU
formula	$C_{18}H_{19}O_2\ F_1S_1N_2$	$C_{18}H_{19}O_2\ F_1S_1N_2$	$C_{18}H_{19}O_2\ F_1S_1N_2$	$C_{18}H_{18}O_2\ F_2S_1N_2$	$C_{18}H_{20}O_2S_1N_2$
formula wt	346.4	346.4	345.4	364.4	328.4
color	colorless	colorless	colorless	colorless	colorless
cryst morphology	plate	plate	block	block	block
cryst size (mm^3)	0.09 × 0.25 × 0.30	0.09 × 0.25 × 0.30	0.25 × 0.30 × 0.30	0.20 × 0.30 × 0.30	0.20 × 0.30 × 0.30
temp (K)	295(2)	90(1)	100(1)	100(1)	110(1)
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	*P*1	$P2_1$	*C*2/*c*	*C*2/*c*	*C*2/*c*
a (Å)	10.0715(4)	10.0148(18)	23.5271(12)	23.4200(19)	23.4872(11)
b (Å)	14.8192(7)	14.7799(27)	10.7467(6)	10.7880(9)	10.7385(5)
c (Å)	11.8886(6)	11.6010(21)	13.5653(9)	13.5978(12)	13.6376(8)
α (deg)	87.715(4)	90	90	90	90
β (deg)	90.239(3)	90.796(3)	97.631(5)	95.991(3)	98.421(5)
γ (deg)	89.911(3)	90	90	90	90
vol (Å^3)	1772.96(14)	1716.99(5)	3399.46(24)	3416.8(5)	3402.54(27)
Z	4	4	8	8	8
density (g/mL)	1.30	1.34	1.35	1.42	1.28
μ (1/mm)	0.205	0.211	0.213	0.224	0.201
F (000)	727.9	727.9	1447.8	1519.8	1391.8
θ (min, max)	2.4, 25.0	2.0, 25.0	2.5, 25.0	1.8, 25.0	2.5, 25.0
no. unique reflns	11871	6040	2994	3005	2963
no. of params	881	450	239	238	214
$h_{\min,\max}$	−11, 11	−11, 11	−27, 27	−27, 26	−27, 18
$k_{\min,\max}$	−17, 17	−17, 17	−12, 12	−8, 12	−12, 11
$l_{\min,\max}$	−14, 14	−13, 13	−16, 16	−16, 15	−16, 15
$R_{\_all}$, $wR2_{\_all}$	0.084, 0.085	0.072, 0.084	0.042, 0.090	0.047, 0.112	0.067, 0.103
$R_{\_obs}$, $wR2_{\_obs}$	0.047, 0.078	0.046, 0.075	0.033, 0.086	0.042, 0.109	0.045, 0.093
$\Delta\rho_{\min}$, $\Delta\rho_{\max}$ (e Å^{-3})	−0.180, 0.221	−0.269, 0.293	−0.233, 0.271	−0.249, 0.648	−0.298, 0.334
GOF	0.85	0.99	1.06	1.04	1.01

[2FBCTU, form IA; Table 1]. These molecules are held in pairs as two independent dimers with the connecting N−H···O hydrogen bonds of dissimilar lengths forming an $R_2^2(12)$ motif (Supporting Information; Figure S1, Table S1). Figure 1 shows a view of one of the dimers formed with N−H···O hydrogen bonds. The individual dimers are held together by two N−H···S hydrogen bonds (forming an $R_2^2(8)$ motif) generating a distorted molecular dimeric chain along the *a*-axis. Figure 2a shows a packing diagram of the structure wherein four symmetry-independent molecules are color coded. The dimers (formed between red−yellow and blue−green molecules) are further related by a pseudo-2_1-screw axis along the *b*-direction, which is not operative mainly because of the subtle conformational differences among the four molecules and hence among the two dimers (see Supporting Information; Figure S1, Table S2). Notably, the molecules in the adjacent dimers are interlinked through their hydroxy ends via O−H···O hydrogen bonds (Supporting Information, Figure S2), a feature commonly observed in high Z' structures of hydroxy-containing compounds with the occurrence pseudosymmetry.[8] A supportive C−H···π contact is an important factor stabilizing a nonplanar conformation of these dimers (Figure 1).

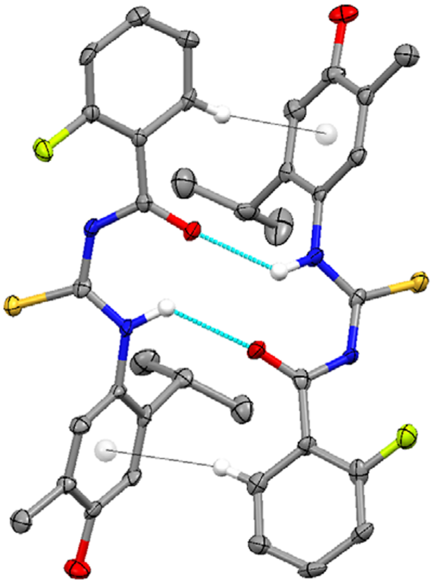
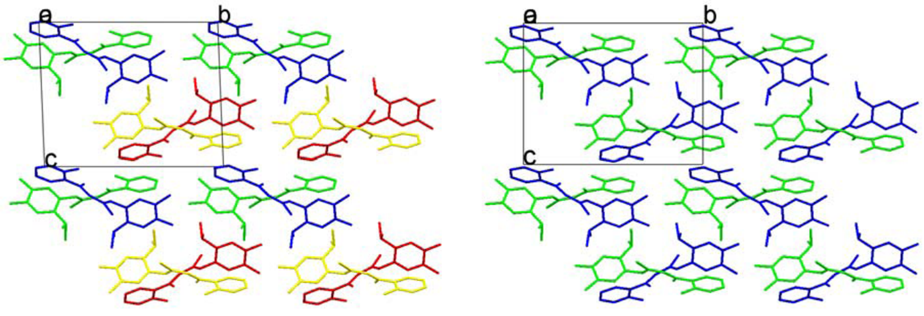


Figure 1. View of a noncentric dimer of 2FBCTU (form IA and form IB) built with N−H···O hydrogen bonds and C−H···π interactions.

Single Crystal to Single Crystal Transformation (SST) in 2FBCTU. In order to precisely determine the wide range of intermolecular interactions offered by four symmetry-independent molecules, data were collected at 90 K on the same crystal. Interestingly, crystal structure at this temperature was solved in the monoclinic space group $P2_1$, now with two symmetry-independent molecules [2FBCTU, form IB; Table 1]. A slight rearrangement of the four symmetry-independent molecules in form IA upon cooling of the crystal is clearly reflected by the small, yet significant, changes in the representative torsion angles [given in Supporting Information, Table S2]. Upon cooling, the N−H···O and N−H···S hydrogen bonds reorganize slightly such that the dimeric $R_2^2(12)$ and $R_2^2(8)$ motifs attain a little more planarity. Although slender, the concomitant conformational changes in all four independent molecules in $P1$ manifest in such a way that the molecular conformation and the dimeric conformation in both dimers becomes identical, and as a result, a pseudo-2_1-screw in form IA actually becomes operational forcing the structure into the space group $P2_1$ (form IB), obviously without much significant changes in the cell parameters (Table 1). Figure 2a,b provides a comparison between the packing arrangements of form IA and form IB. In order to determine the temperature at which the phase transformation (SST) occurs, complete sets of data were collected on the same crystal every 20 K from room temperature, and the phase change from $P1$ to $P2_1$ was observed at 190(1) K with the transformation being reversible. Details of variable-temperature single-crystal XRD experiments along with CIFs have been provided in the Supporting Information. It is important to note that, although the molecule does not contain any chiral center, it prefers to pack in a noncentrosymmetric space group, $P1$, and reversibly transforms to a space group $P2_1$ mainly because of adoption of a conformationally chiral dimeric unit owing to the molecular flexibility of 2FBCTU.

Polymorphism in 2FBCTU. A detailed Cambridge Structural Database[24] [ConQuest 1.14; Feb 2012 update] analysis (provided in Supporting Information) revealed that the commonly adopted packing motif for molecules with *N*-acyl thiourea [-NH−C(S)−NH−C(O)-] linkage is a planar molecular dimeric chain formed through centrosymmetric $R_2^2(12)$ and $R_2^2(8)$ packing motifs built with N−H···O and N−H···S hydrogen bonds as shown in Figure 3.



(a) (b)

Figure 2. Packing diagram of (a) form IA, space group $P1$, $Z' = 4$, and (b) form IB, space group $P2_1$, $Z' = 2$, of 2FBCTU. Symmetry-independent molecules are color coded. Molecular dimeric chains running along the *a*-axis (perpendicular to plane of the paper) are formed via N−H···O/N−H···S hydrogen bonds: red with yellow molecules and green with blue molecules.

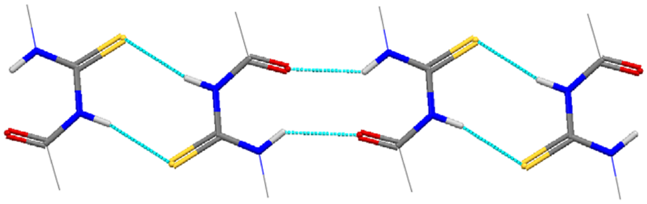


Figure 3. Planar molecular dimeric chain formed with N−H···S and N−H···O dimers from the [-NH−C(S)−NH−C(O)-] units, both across the center of inversion. Color codes: sulfur, yellow; oxygen, red; nitrogen, blue; carbon, gray; hydrogen, white.

In order to probe a structure with lower Z' value (preferably $Z' = 1$) following the most preferred packing pattern (Figure 3), crystallization of 2FBCTU was attempted under different experimental conditions. Indeed, an anticipated centrosymmetric structure with $Z' = 1$ was obtained for a block-shaped crystal grown from a relatively polar solvent, acetonitrile, at room temperature. It is of interest to note that though the crystals belong to the monoclinic space group $C2/c$ ($Z' = 1$), the *ortho*-fluorine atom is rendered disordered! Figure 4 shows an ORTEP view of the structure [form II, 2FBCTU; Table 1] with partial occupancies of the disordered fluorine atom.

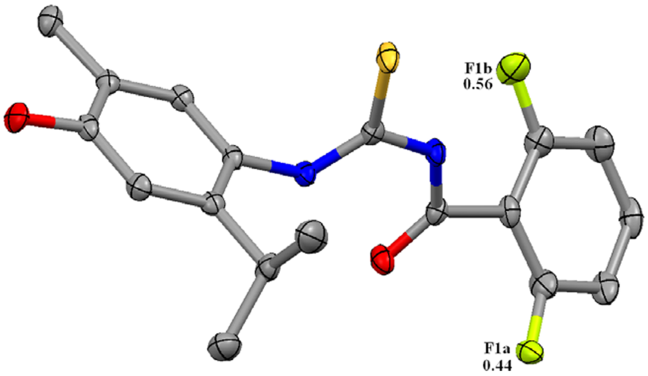
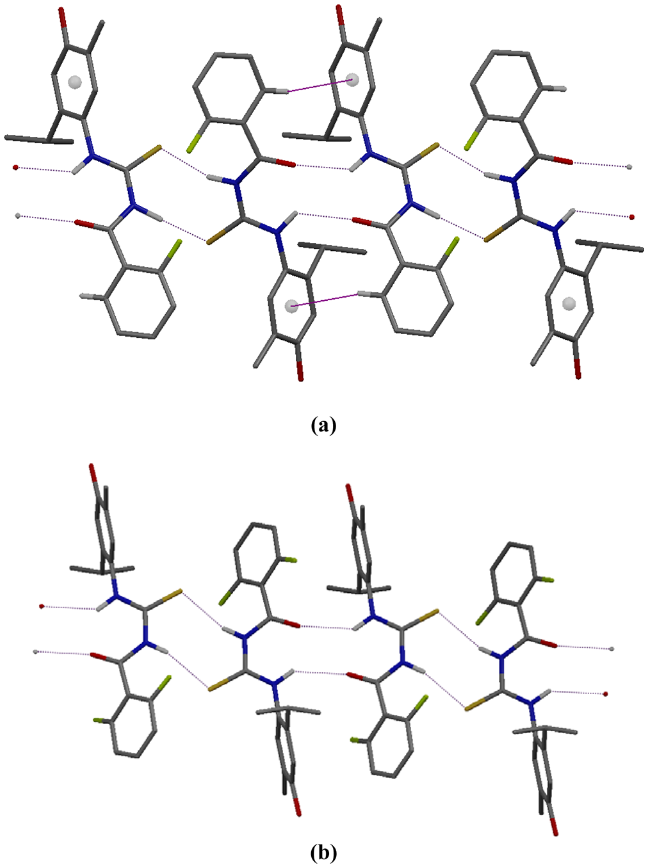


Figure 4. ORTEP diagram of form II of 2FBCTU ($C2/c$; $Z' = 1$) at 50% ellipsoidal probability. Notice the disorder of F-atom over two *ortho*-positions with partial occupancies of 44% and 56%.

The molecular conformation in this structure is slightly different from that of forms IA and IB (Supporting Information, Table S2). The molecules form similar N−H···O and N−H···S mediated dimers but now with the $R_2^2(12)$ and $R_2^2(8)$ motifs being exactly planar and devoid of any C−H···π interactions. Figure 5a,b gives a clear picture for the comparison of molecular and supramolecular features of form I (A and B) and form II structures, respectively.

Clearly, a driving force for both the phase transformation and the polymorphism in 2FBCTU is the formation of a planar molecular dimeric chain built with a pair of homomeric $R_2^2(12)$ and $R_2^2(8)$ synthons occurring in tandem, one formed with N−H···O and the other with N−H···S hydrogen bonds. The concomitant conformational changes on lowering of the temperature transform the distorted dimeric chain in form IA toward a slightly better planar one in form IB. Whereas, the requirement of this feature demands the molecule to disorder the ortho-positioned fluorine atom in form II, 2FBCTU.

Isostructuralism through Isosterism. The compounds 26DFBCTU and BCTU were specially designed as a difluoro and a nonfluoro analog of 2FBCTU, respectively (Scheme 1).



(a)

(b)

Figure 5. Molecular dimeric chains in (a) form IA, form IB, and (b) form II of 2FBCTU. Compare these figures in terms of the N−H···O and N−H···S dimers; notice the change in molecular orientations from panel a to b and positional disorder of F-atom in panel b.

These are the best candidates to verify the isosterism of F and H in the presence of strong H-bond partners and to examine the influence of asymmetric monofluoro substitution (at *o*-position) in the formation of high Z' structure (form IA), associated phase transition (form IB), and disorder-mediated polymorphism (form II) in 2FBCTU.

An orientational disorder of fluorine over the two ortho positions and its noninvolvement in any significant structure-guiding interactions in form II of 2FBCTU implies the isostructural models for compounds 26DFBCTU and BCTU keeping in view the intact nature of strong N−H···O and N−H···S driven $R_2^2(12)$ and $R_2^2(8)$ synthons in 2FBCTU. Indeed, the compounds 26DFBCTU and BCTU adopt the same space group $C2/c$ with comparable cell parameters (Table 1). Figure 6 shows a packing overlay diagram depicting the isostructural features of 2FBCTU (form II), 26DFBCTU, and BCTU. Interestingly, the intermolecular interactions in all the three structures are notably similar with the C−H···π in BCTU replaced by C−F···π in 2FBCTU (form II) and 26DFBCTU (Supporting Information, Table S1). Further, a short F···F [F2···F2, 2.42 Å] contact appears in 26DFBCTU as a consequence of preserving the isostructural features with a disordered monofluoro and a nonfluoro compound. Notably, the probability ellipsoid of F2 appears to be slightly elongated indicating its disorder, and hence this rather short F···F contact between the symmetrically equivalent F-atoms suggests that the F2 atoms in the adjacent molecules are disordered in a counter phase fashion.

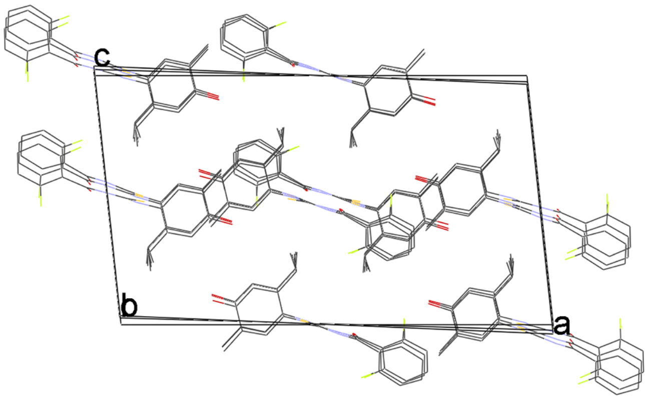


Figure 6. A packing overlay diagram of the three isostructural ($C2/c$; $Z = 8$) compounds: 2FBCTU (form II), 26DFBCTU, and BCTU. The hydrogen atoms have been omitted for clarity. Molecular dimeric chains (shown in Figure 3) formed via N−H···S/N−H···O hydrogen bonds are along the *b*-axis, that is, running out of plane of the paper.

■ CONCLUSION

It has been shown that the propensity to form a planar molecular dimeric chain through centrosymmetric $R_2^2(12)$ and $R_2^2(8)$ synthons built with well-defined N−H···O and N−H···S hydrogen bonds dictates the phase transformation, polymorphism, and disorder in compound 2FBCTU. Indeed the same "symmetry-driven, geometry-controlled" requirement brings in isosterism and isostructuralism in the crystals of 2FBCTU (form II), BCTU, and 26DFBCTU. The potential of a conserved synthon to serve as a common "origin" for polymorphism, disorder, phase transformation, isostructuralism, and isosterism in a single molecular species (parent molecule and F-substituted derivatives) has been illustrated.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed procedure for the synthesis of compounds 2FBCTU, BCTU, and 26DFBCTU with spectroscopic data, CSD search details with REFCODES, crystallographic information files (CCDC 805403, 870457-60) of 2FBCTU (form IA, form IB, and form II), BCTU, and 26DFBCTU, and details of variable-temperature single-crystal XRD experiments with CIFs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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