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Unique Reversible Crystal-to-Crystal Phase Transition – Structural and Functional Properties of Fused Ladder Thienoarenes

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Abstract

Donor-acceptor type molecules based on fused ladder thienoarenes, indacenodithiophene (IDT) and dithienocyclopenta-thienothiophene (DTCTT), coupled with benzothiadiazole, are prepared and their solid-state structures are investigated. They display a rich variety of solid phases ranging from amorphous glass states to crystalline states, upon changes in the central aromatic core and side group structures. Most notably, the DTCTT-based derivatives showed reversible crystal-to-crystal phase transitions in heating and cooling cycles. Unlike what has been seen in π -conjugated molecules variable temperature XRD revealed that structural change occurs continuously during the transition. A columnar self-assembled structure with slip-stacked π - π interaction is proposed to be involved in the solid-state. This research provides the evidence of unique structural behavior of the DTCTT-based molecules through the detailed structural analysis. This unique structural transition paves the way for these materials to have self-healing of crystal defects, leading to improved optoelectronic properties.

Introduction

Establishing structure/property relationships in organic semiconductors is crucial for optimal design of molecules for applications in optoelectronic devices such as organic photovoltaics (OPV). Decades of intensive research into materials development have established some useful design strategies which contributed to the development of high performance solar cells in recent years. One such example is the D₁-A-D₂-A-D₁ type of small molecular donors used in small molecular organic photovoltaic (sm-OPV) devices^{1,2}. This type of molecules has demonstrated impressive device results of up to 10% power conversion efficiency³⁻⁵. The active layer solid-state structures have also been investigated using both experimental and computational methods⁶⁻¹⁰. Controlling the solid-state structure and improving important properties such as charge transport properties could further improve the device performance. In conjugated organic materials, charge transport properties depend very heavily on the packing structure of the molecules as the packing structure determines the π -orbital overlap. However, the packing structure is mainly stabilized by weak van der Waals interactions and often has several crystalline packing states (polymorphs) and loosely bonded mesophases (liquid crystalline states). Depending on their packing, these states have various degrees of π -orbital overlap, and hence different electronic properties. Thus, they provide an interesting platform to investigate the intrinsic charge transport properties and the relationship between charge transport and packing structure¹¹⁻¹³. Various attempts were made to access the ideal packing structures for charge transport properties. Certain polymorphic structures have been induced by applying external stimuli^{14, 15}, controlling crystallization environment¹⁶, and utilizing intermolecular interaction with additives^{17, 18}. Liquid crystalline semiconductors¹⁹⁻²³ have also recently emerged as candidates for sm-OPV due to the possibility of utilizing their uniquely ordered solid-state structures.

Previously, we have reported a dithienocyclopenta-thieno[3,2-b]thiophene (DTCTT)-based molecular donor material for sm-OPV²⁴. Comparative studies between the DTCTT and the structurally analogous indacenodithiophene (IDT)-based molecular donor, which has a benzene core instead of the thienothiophene in DTCTT, demonstrated enhanced crystallinity of the DTCTT-based molecule induced by the S-S interactions from the thienothiophene unit. In this study, a series of novel IDT and DTCTT-based derivatives were synthesized (Fig. 1) to elucidate their packing structure in the solid state and how this affects their optoelectronic properties. Special focus was placed on the molecular rearrangement dynamics in the reversible phase transition behaviour seen in the DTCTT derivatives. This reversible phase transition, or enantiotropic phase transition, has been widely studied^{25, 26}. The structural reversibility and the associated properties of this transition are also interesting for optoelectronic²⁷⁻³¹, ferroelectric^{32, 33}, and energy^{34, 35} applications. Moreover, the thermally-induced structural reversibility demonstrated to have a self-healing function, reported recently³⁶. Structural investigation using X-ray

diffraction techniques revealed that the DTCTT molecules organized in one-dimensional columns with slip-stacked self-assembly and showed phase transitions similar to columnar liquid crystals, while retaining their three-dimensional order. Our investigation of the relationship between their molecular structures and unique self-assembled structures, together with preliminary p-type transistor properties, will provide an evidence of advanced crystal engineering of organic solids, which is a critical part for improving optoelectronic device performance.

Fig 1. Chemical structures of DTCTT and IDT-based small molecules

Experimental Methods

Sample Preparation: The DTCTT- and IDT-based small molecules in Fig. 1 were synthesized based on the synthetic scheme reported in our previous paper²⁴. The synthetic and characterization details are available in the supporting information.

Measurements: Differential scanning calorimetry (DSC) was performed using DSC Q10 (TA Instruments) under nitrogen flow (scanning rate of 10 or 2 °C/min). Optical microscope image was recorded using Eclipse E600 microscope (Nikon), equipped with Infinity-1 camera (Lumenera). Sample was placed on the hot plate Linkam THMS600 and heating rate and cooling rate was controlled by temperature controller Temmcon 102ST. Cross-polarization filter was applied in the case of taking polarized optical image. No color filters or computational treatment was applied to images. AFM images were obtained using Cypher S (Asylum Research) measured in tapping mode. Powder and thin-film X-ray diffraction pattern was measured using D8 advanced (Bruker) with copper X-ray source. X-ray crystallographic analysis was performed using the 4-circles goniometer Kappa geometry AXS D8 Venture (Bruker), equipped with a Photon 100 CMOS active pixel sensor detector with a copper monochromatized X-ray radiation. Simultaneous SAXS and WAXS experiments were performed on a Nano-inXider (SW-L model) from Xenocs, Sassenage, France using Cu K α radiation ($\lambda = 0.154189$ nm). The sample was placed between two Kapton films of 50 μm and in-situ measurements were run as function of temperature using the integrated temperature control stage Linkam HFX350. The thin-film

sample for GI-WAXS was prepared by dissolving molecules in a mixed solution of chloroform: *o*-dichlorobenzene = 9:1 (5 mg/ml) and spincoating the solution onto the substrates at 1000 rpm, resulting in ca. 200 nm thin film. The measurement was done at Stanford Synchrotron Radiation Lightsource (SSRL) beamline 11-3 in grazing incidence mode with a 2D MARCCD detector at a sample-detector distance of 250 mm. Beam energy was 12.735 keV and the incident angle used was 0.2 degrees.

Results

Molecular design: DTCTT and IDT-based molecules with different side groups were synthesized to investigate the effect of the backbone and the side group structure on their self-assembly behaviour. The side groups consist of benzo[2,1,3]thiadiazole (BT) and alkyl thiophenes. The molecules with one thiophene (Th) unit in the side groups ($R = R_1$) were expected to have less structural freedom compared to those with two Th units ($R = R_2$). In addition, extended dodecyl alkyl groups ($R = R_3$) were introduced in place of the hexyl chains in DTCTT to investigate their effect on the reversible phase transition behaviour. These IDT and DTCTT derivatives are interesting platforms to investigate the relationship between crystallinity and molecular structure as any slight change in chemical structures can result in the formation of different phases ranging from amorphous phase to crystalline phases with several crystalline polymorphs. Their phase transition behaviour will be discussed in the following sections.

Reversible phase transition behaviour: The difference in the backbone structure of both the IDT and DTCTT compounds is found to have a distinct impact on the thermal behaviour. The differential scanning calorimetry (DSC) graphs are shown in Fig. 2 and the thermodynamic properties are summarized in Table S2. In Fig. 2a, both the IDT derivatives showed glass transition temperatures of around 70 °C on cooling after their initial melting at around 110 °C. On the second cycle, melting and recrystallization are not observed, indicating they form a glass-supercooled liquid phase³⁷. On the other hand, the DTCTT derivatives have crystalline nature as recrystallization peaks can be observed after their initial melting (melting at 245, 235, 221 °C and crystallization at 226, 230, 203 °C for $R = R_1$, R_2 , and R_3 derivatives, respectively). In addition, cooling at 10 °C/min speed after the melting causes additional peaks for $R = R_2$ and R_3 derivatives. These transition peaks appeared reversibly even on the 3rd and 4th heating-and-cooling cycle (Fig. S2). Initially, this behaviour was thought to be a thermotropic liquid crystalline phase transition but the observation under polarized optical microscope (POM, Fig. 3 for $R = R_2$ and Fig. S3 for $R = R_3$) indicates this is a reversible crystal-to-crystal phase transition. From low to high temperature, each phase is assigned as L, H1, and H2 before melting into an isotropic liquid. These structure assignments are based on X-ray diffraction results presented in detail in the following discussion.

Fig. 2 Differential scanning calorimetry (DSC) of IDT derivatives (a) and DTCTT derivatives (b); black line is the first heating and cooling cycle and the dotted blue line is the second heating cycle, scanned at 10 °C/min rate.

Under cross polarization filters, a di(HTh2BT)DTCTT ($R = R_2$) film was placed on a hot plate (Fig. 3 at 30 °C) and heated to 270 °C which is above its melting temperature. No polarized light was observed at this temperature, indicating an isotropic liquid state. Upon cooling, crystallization took place, forming leaf-like crystals, and on further cooling, a subtle colour change was observed at around 130 °C under the cross polarizers, indicating a phase transition and reorganization of the molecules. On the second heating cycle, similar phase transition behaviour was observed at 130 °C and further heating up to 170 °C resulted in cracks in crystals. This observation matches well with the phase transition peaks observed in the DSC graphs (mixture of H2/H1/L transition at 145–125 °C on cooling, L/H1 transition at 128 °C and H1/H2 transition at 170 °C on second heating). It is worthwhile to note that a slower cooling rate did not change the shape of DSC curve but a faster cooling rate (higher than 30 °C/min) induced a “frozen” phase which did not show structural reversibility when observed under the POM and XRD (Fig. S4).

The di(C12Th2BT)DTCTT ($R = R_3$) also exhibits three phases as can be seen in the DSC graph (mixture of H2/H1/L transition at 108–100 °C on cooling, L/H1 transition at 113 °C and H1/H2 transition at 166 °C on heating) but no obvious morphological change was observed in the POM images. This implies that the structural reorganization takes place in a different manner from that of di(HTh2BT)DTCTT. It also showed scan rate-dependent DSC behaviour; a slower scanning rate (such as 2 °C/min) makes the crystal-to-crystal phase transition peaks sharper and peak splitting of the H2/H1/L transition on cooling and the H1/H2 transition on heating were observed (Fig. S5). This implies existence of additional polymorphic states at these temperatures. These phase assignments are corroborated by evidences presented in the

following discussion.

Fig. 3 Polarized optical microscope image of di(HTh2BT)DTCTT at 1st heating, cooling, and 2nd heating (thin film at 30 °C, isotropic liquid at 270 °C, cooling down to 60 °C, and 2nd heating up to 200 °C). Inset is the image under bright light.

Structural analysis of IDT derivatives: We will first focus on the structural analysis of IDT derivatives as these are good reference materials for the analysis of the solid-state behaviour of the DTCTT derivatives. Although both IDT derivatives showed amorphous nature (glass-supercooled liquid phase) in the thermal studies, they can be crystallized from a suitable mixed solvent system such as acetone/chloroform; their powder XRD data (Fig. S6) represent a typical peak pattern for crystalline samples. On the other hand, thin film XRD data had no peaks and post treatment such as thermal/solvent vapour annealing did not change these amorphous patterns. The difficulty for the IDT derivatives to form ordered structures in thin film originates from its molecular structure. The presence of four hexylphenyl groups on the sp³ carbon of the IDT moiety hinders strong π - π stacking. A poor solvent, such as acetone, is thus necessary to induce nucleation through solvent-solute interactions³⁸ and/or solvophobic effects³⁹.

A single crystal of di(HTh1BT)IDT ($R = R_1$) was grown and its self-assembled structure was studied using single crystal XRD (Fig. 4). Since the molecule has an inversion center on the central benzene ring,

half of the molecular structure was solved as an asymmetric unit. The crystal is monoclinic with space group $C2/c$ ($a = 23.73$, $b = 27.78$, $c = 38.16$ Å; $\beta = 100.1^\circ$; $Z = 8$). Three structural isomers are obtained, which have different rotation angles between the IDT, BT, and Th units (Fig. 4a). Coughlin and coworkers studied the rotational free energy of similar compounds and discussed its relationship with the structural factors^{6, 7}. Multiple nonbonding interactions such as π - π interactions, steric hindrance, and electrostatic forces compete with each other and when these interactions work together to stabilize the rotation angle, a “conformational lock” occurs. Three rotational isomers are formed in the di(HTh1BT)IDT crystal, implying that the intermolecular interactions are so weak that they allow more than one stable rotational isomer. The trimer structure shown in Fig. 4b indicates the lack of π - π stacking despite the elongated conjugation length. In fact, one of the rotational isomers has a high dihedral angle of 38.3° and the entire molecule is distorted along the long-axis (Fig. 4c). The calculated close atomic distances suggests that the S-S interactions between BT-BT, BT-IDT and Th-Th play a key role in stabilizing the trimer structure instead of the π - π or CH- π interactions. Incorporation of heteroatoms larger than carbon facilitates the overlap of π -orbitals; the S-S interaction is especially well known to enhance the hole mobility through this effect⁴¹⁻⁴³.

Fig. 4 Model structures solved using single crystal x-ray diffraction of di(HTh1BT)IDT: (a) ORTEP image of crystallographically independent molecular units with ellipsoids drawn at 50% probability, (b) trimer structure with sulfur atoms in ball-and-stick model c) molecular packing structure perpendicular to b-axis. C, N, S atoms are shown as black, blue, and yellow, respectively. Alkyl chains and protons are omitted for clarity.

Structural analysis of DTCTT derivatives in crystal: The DTCTT derivatives were also recrystallized from the acetone/chloroform solvent system. Although single crystals of suitable size for single crystal

XRD were not obtained, other X-ray diffraction techniques were used for structural analysis of the DTCTT derivatives. Powder XRD patterns were collected from the DTCTT samples prepared by grinding crystals (Fig. 5). Major peaks of di(HTh1BT)DTCTT ($R = R_1$) are seen at $2\theta = 4.97, 8.29, 9.82$, and 20.0° which correspond to d-spacing of 17.8, 10.7, 9.0, and 4.44 Å. As for di(HTh2BT)DTCTT ($R = R_2$), weak peaks at small angle regime indicate the lack of clear long-range order. However, subsequent annealing at 200°C induced structural reorganization, resulting in a different peak pattern at $2\theta = 4.25, 5.00$, and 5.68° which correspond to d-spacing of 20.8, 17.7, 15.6 Å. These results indicate that the packing structure of di(HTh2BT)DTCTT is sensitive to heating and mechanical deformation (grinding), and this sensitivity seems to be a factor in inducing the reversible phase transition that occurs in the crystal. The di(C12Th2BT)DTCTT ($R = R_3$) have strong peaks in both the small and wide angle regimes. The origin of peaks in the wide angle regime is not clear but the distance is close to the van der Waals radius of the sulfur atoms, and thus they may be due to the aromatic groups incorporated with sulfur atoms which have electron rich planes and result in strong diffraction. The longer alkyl chains and two thiophene rings seem to assist in stabilizing the ordered structure.

Fig. 5 Powder XRD patterns of DTCTT derivatives. Recrystallized samples were ground and used as powder samples. The same annealing condition of 200°C for 3 min was applied for all samples.

Fig. 6 X-ray scattering image of di(HTh2BT)DTCTT in the (a) small angle regime, and (b) wide angle regime in color map at different temperatures. Scattering patterns were recorded by changing temperatures in a cycle of heating from 25 °C to 230 °C (before the melting temperature) and cooling at 230 °C to 25 °C with a 5 °C step. Sample was prepared by melting before slow cooling at rate of 10 °C/min. The intensity is depicted with color bar in logarithmic scale on each regime. Note the small discontinuity in the peak positions at the L to H1 transition.

Fig. 7 X-ray scattering patterns of di(HTh2BT)DTCTT in the (a) small angle regime, and (b) wide angle regime when heating from 25 °C to 230 °C with a 5 °C step (blue, green, and red color correspond to L, H1 and H2 phase, respectively).

The temperature-variable small and wide angle X-ray scattering (SWAXS) was performed to investigate the reversible phase transition behaviour of di(HTh2BT)DTCTT ($R = R_2$). The sample was firstly melted at 270 °C on a hot plate and then cooled at a rate of 10 °C/min, the same conditions as in the DSC

measurements presented earlier. The diffracted X-rays were recorded using a 2D detector and the diffractogram was generated by integrating their intensities with respect to the scattering vector. The diffraction was recorded at varying temperatures (from 25 to 230 °C and back to 25 °C) at a 5 °C step. As shown in the colour map (Fig. 6), the three phases are clearly observed (L, H1, H2, and back to H1, L phases), corresponding well with the transitions seen in the DSC studies. For clarity, the diffraction patterns of only the heating up cycle, from 25 °C to 230 °C, are plotted in Fig. 7. At 25 °C, which corresponds to the L phase, two peaks ($q = 0.340$ and $0.342 \text{ \AA}^{-1}$) appear at low q (Fig. 7a). Upon heating, these peaks shift in a different manner; the peak that was originally at $0.342 \text{ \AA}^{-1}$ shifts to lower q while the peak at $0.340 \text{ \AA}^{-1}$ shows little shift. This peak position behaviour suggests anisotropic thermal expansion of the lattice parameters often seen in organic crystals⁴⁴⁻⁴⁶. Around 130 °C, the peaks at low q exhibit a continuous structural change but shift very sharply at 135 °C and both peaks separate out further ($q = 0.324$ and $0.345 \text{ \AA}^{-1}$) at 150 °C in the H1 phase. Above 175 °C, a drastic structural change takes place and new peaks appear ($q = 0.273$ and $0.389 \text{ \AA}^{-1}$), corresponding to the phase transition from H1 to H2. In this way, the different phases can be identified by XRD peak positions. However, since the phase transition from L to H1 occurs more gradually with ramping temperature, we have attempted to separate peak shift associated with phase transition from thermal expansion. The linear expansion of the two major peaks is plotted over the temperature range (Fig. S7). A slope of the relative change in d-spacing vs temperature line is proportional to the thermal expansion coefficient. The coefficients of the two peaks originally at 0.340 and $0.342 \text{ \AA}^{-1}$ are calculated to 5.3×10^{-5} and $2.1 \times 10^{-4} \text{ K}^{-1}$ in the temperature range of the L phase (25 – 95 °C); the similar value was reported in organic crystals⁴⁶⁻⁴⁸. At a high temperature range around 130 °C, steps of slope are seen and very large negative and positive discontinuities are observed which identify the phase transition from L to H1. Peaks in the wide angle regime ($q = 1.25 - 1.5 \text{ \AA}^{-1}$) (Fig. 7b), which will correspond $d = 4.19 - 5.03 \text{ \AA}$, also changed their patterns, indicating a change in the packing mode. The fact that the high q peaks are weak, together with the fact that L to H1 phase transition appears to take place gradually, suggest that this structural reorganization has very strong similarity to that of liquid crystalline materials. Attempts to assign each phase were made and are discussed in a later section. The same temperature-variable XRD measurement was performed for di(C12Th2BT)DTCTT ($R = R_3$). The sample was first melted at 250 °C and then cooled at a rate of 10 °C/min. The X-ray diffraction patterns were recorded during heating and cooling cycle (25 °C to 200 °C and then back to 25 °C again) (refer to Fig. S8 for the colour map and Fig. S9 for the diffraction patterns). Three major peaks ($q = 0.25$, 0.33 , and $0.41 \text{ \AA}^{-1}$) appear in the small angle regime at 30 °C, which gradually shifts to lower angle upon heating. At 125 °C, the phase transition from L to H1 takes place and the peak at $0.41 \text{ \AA}^{-1}$ shows discontinuity (with peaks at $q = 0.24$, 0.32 , and $0.39 \text{ \AA}^{-1}$ at 150 °C). Upon further heating, the phase transition of H1/H2 takes place and the middle peak disappears ($q = 0.24$ and $0.39 \text{ \AA}^{-1}$ at 200 °C). This

diffraction pattern of the H2 phase resembles that of di(HTh2BT)DTCTT at the high temperature. At this temperature, alkyl chains gain sufficient freedom to move and thus, intermolecular interactions between the backbone structures become dominant for stabilizing the structure. Less contribution from the alkyl chains is assumed to result in the similar packing structure. Upon cooling, however, the middle peak intensity remains weak and distinct reversibility was not observed. In this measurement, cooling rate of 10 °C/min was applied to the sample but di(C12Th2BT)DTCTT showed scan-rate dependence in the DSC measurement. It seems the packing structure of di(C12Th2BT)DTCTT reorganizes more slowly compared to that of the di(HTh2BT)DTCTT. Due to the complexity of this kinetical factor, we mainly focused on the structural assignment of di(HTh2BT)DTCTT in the following discussion.

GI-WAXS of di(HTh2BT)DTCTT in thin film: Grazing-incidence small and wide angle X-ray scattering (GI-WAXS) was performed on the thin film sample of di(HTh2BT)DTCTT using synchrotron X-ray source. The thin film was prepared by spin coating from solution on silicon substrates (as-spun sample) and subjected to thermal annealing at 200 °C for 5 min (annealed sample). Structural reorganization was detected upon the thermal annealing but the film structure did not return to the original phase, unlike its crystalline phases. The as-spun film (Fig. 8a) showed a strong diffraction peak at $d = 23.9 \text{ \AA}$ along Q_z , or the out-of-plane direction. Diffraction peaks at higher Q , corresponding to distances of $3.5\text{--}5 \text{ \AA}$, which are typical $\pi\text{--}\pi$ stacking distances for aromatic molecules, are observed off axis (have non-zero Q_{xy} and Q_z components). These results suggest that the molecules adopt an edge-on mode of packing structure: the out-of-plane peak corresponds to periodicity along the alkyl stack direction, and the off-axis higher Q peaks correspond to packing along the $\pi\text{--}\pi$ stacking direction in slip-stacked manner (see below for more discussion on the slip stacking). This general observation is true for both as-spun and annealed films. In the annealed film (Fig. 8b), molecular reorganization takes place and the two scattering patterns have distinct peak positions and intensities. The strong peak along the out-of-plane direction ($d = 23.9 \text{ \AA}$ in as-spun film) shifts to $d = 21.4 \text{ \AA}$ with multiple reflections along the Q_z direction, indicating the lamellar structure of (001), (002) and (003) reflections. Broad off-axis peaks ($d = 3.5\text{--}5 \text{ \AA}$ in as-spun film) become more intense with a certain degree of smearing. The annealed sample gives insight into the thermodynamically stable form of the molecule. Thermal energy allows molecules to reorient into an ordered packing structure, having both a long-range lamellar structure and a more ordered slip-stacked mode of $\pi\text{--}\pi$ stacking.

Fig. 8 2D GI-WAXS diffraction patterns of di(HTh2BT)DTCTT of: a) as spun film and b) annealed film. Spincoated film on silicon substrate was thermally annealed at 200 °C for 5 min.

Self-assembled structure of di(HTh2BT)DTCTT in the reversible phase transition states: Based on the above structural analysis, we attempted to assign the self-assembled structure of di(HTh2BT)DTCTT to its reversible phase transition states. The single molecular geometry was optimized using DFT method with a hybrid function of B3LYP/6-31G(d,p). As shown in Fig. 9a, the molecule has dimensions of 49 Å along the main axis of conjugation and 23 Å along the axis of the octyl phenyl groups. As revealed by X-ray crystallography, the structure of di(HTh1BT)IDT shows flexibility in the angles between the aromatic groups. Di(HTh2BT)DTCTT is also assumed to form such rotational isomers and the structure can be represented as a ellipsoid plane (Fig. 9a). Based on GI-WAXS measurement of the di(HTh2BT)DTCTT, we speculate a model of the molecular self-assembly as illustrated in Fig. 9b, having a one-dimensionally organized structure with slipped-stack manner of assembly so as to form a lamellar structure with a d-spacing of 21.4 Å. Sample prepared by the chloroform/acetone recrystallization process were found to crystalize in a fibre-like morphology, as revealed by atomic force microscopy (AFM) (Fig. S 10a and b). Those crystals can grow over 1 μm in length with a diameter ranging between 50–200 nm. Crystals of π -conjugated molecules tend to grow along the π -stacking direction⁴⁹. The crystal growth of di(HTh2BT)DTCTT is also assumed to be driven by the slip-stacked π - π stacking and they are speculated to form similar 1D organized structures in the crystal.

Fig. 9 Schematic illustration of the molecular self-assembly: a) optimized geometry of di(HTh2BT)DTCTT and b) plausible 1D organized molecular self-assembly of di(HTh2BT)DTCTT with a projected diameter of d.

In order to validate our assumption in Fig. 9b, the dimer structure determined from the geometry of the 1D organized molecular self-assembly was modelled using DFT calculation with the dispersion-corrected WB97XD function as a basis set. This function was selected for the calculation because it takes account of the effect of neighbouring segments, and so is suitable for modelling aromatic backbones⁵⁰. The initial coordination (Fig. S11) was taken from the geometry of the 1D organized structures in Fig. 9b with the diameter $d = 23.0$ Å. The diameter was extracted from the diffraction peak in the H2 phase. At high temperatures, alkyl chains show high flexibility and this structure is believed to be a more suitable initial coordination for the molecular simulation. A stable dimer structure was successfully obtained from the modelling, as shown in Fig. 10. In the stabilized structure, the distance between the two molecules is small near the centre of the dimer. The distortion of the aromatic backbone is observed, and this is especially pronounced in the peripheral thiophene groups. The combination of the strong interaction between the central cores and high flexibility of the end parts of the side groups could be the reason for sensitivity of the packing structure to temperature and grinding. The fact that the di(HTh1BT)DTCTT ($R = R_1$), unlike other the DTCTT-based derivatives ($R = R_2$ and R_3), did not show a reversibility in the solid-state indicates that an additional thiophene ring plays a key role in imparting structural flexibility, beneficial for the molecular reorganization.

Fig. 10 Slip-stacked dimer structure of di(HTTh2BT)DTCTT. The structure was optimized using DFT calculation with WB97XD/6-31(d,p) as a basis set.

Finally, the packing structures of the three phases (L, H1, and H2 phases) were analysed using structural data obtained in the temperature variable SWAXS measurement shown in Fig. 11. The gradual phase transition behaviour from L to H1 phase resembles the typical behaviour observed for columnar liquid crystals^{20, 23, 51-53}. In such systems, a hexagonal (100) peak gradually splits into tetragonal (110) and (200) peaks according to the temperature. Structural assignment of columnar liquid crystalline materials has been studied for a long time⁵⁴ and applying the 2D lattice symmetry into this system partially explained the phase transitions observed. The postulated packing structures of each phase are illustrated in Fig. 12. The L phase at 30 °C is assigned as “pseudo hexagonal” centred-rectangular phase (C2mm) with the lattice parameter $a = 36.6 \text{ \AA}$ and $b = 21.5 \text{ \AA}$ ⁵⁵. Upon heating, the shrinkage of the a -axis and the expansion of b -axis gradually transforms the material into the H1 phase with $a = 36.0 \text{ \AA}$ and $b = 23.0 \text{ \AA}$ at 150 °C. The diameter of the column is estimated to be around 21.5–23.0 Å, which is in good agreement with the slip-stacked geometry. The H1/H2 transition is a more dramatic transition and the H2 phase is assigned as the 2D rectangular shape (P4mm) with $a = 23.0 \text{ \AA}$ at 220 °C. In this case, clusters of columns re-align to accommodate the molecular reorganization during the phase transition. Such a drastic motion is assumed to induce mechanical stress and strain, and the cracks observed in the POM image can be attributed to this movement. It is worth noting that the diameter of the column does not change (23 Å)

but the peaks in the wide-angle regime shift to lower angles. This indicates that the slipped-stack mode of π - π stacking is reorganized in a different manner but still maintains a 1D organization. As a whole, the columnar liquid crystal-like phase transitions can explain the reorganization of the packing structure and it matches well with the other experimental results, but some experimental peaks remain unassigned. The three-dimensional packing structure and structural defects such as rotational isomers could be the reason for the observed deviation. The XRD patterns of di(C12Th2BT)DTCTT can be also assigned as the similar columnar phases (Fig. S12). This unique solid-state character of DTCTT derivatives arises from the molecular structure which provides the combination of attractive forces through the core-core interaction, repulsive forces from bulky phenyl side groups, and rotational freedom of the thiophene end groups.

Fig. 11 Intensity vs 2θ plot of SWAXS data of di(HTh2BT)DTCTT at different temperatures. The calculated peak positions with each space group are shown as black lines.

Fig. 12 Plausible explanation of the reversible phase transition behavior of di(HTH2BT)DTCTT in L, H1, and H2 phase. The blue and orange columns represent the slip-stacked form of the molecular self-assembly.

Conclusions

We have synthesized fused-ladder thienoarenes, the DTCTT and IDT, substituted with benzothiadiazole and alkyl thiophene side groups. DSC measurement revealed the rich solid-state phases of the system depending on the central core and end group structures. The crystal structure of di(HTH1BT)IDT solved by single crystal XRD explained why the IDT-based molecules remain amorphous; the bulkiness of the hexylphenyl side groups relative to the smaller size of the central core results in a distorted intramolecular conformation without strong backbone interactions, resulting in a lack of periodic π - π stacking. The S-S interactions seem to play an important role in stabilizing the structure of this molecular system. On the other hand, the crystallinity of the DTCTT derivatives was increased due to the incorporation of thienothiophene unit. In the presence of the flexible side groups ($R = R_2$ and R_3), an unusual thermally-induced reversible phase transition behavior was observed. The crystal-to-crystal phase transitions with continuous (L/H1) and discontinuous (H1/H2) phase transition were investigated in detail. Both experimental and computational results revealed that the DTCTT derivatives form a structure with a slip-stacked mode of π - π stacking and columnar 1D organization, and the structure of each phase was assigned with their 2D lattice symmetries. A combination of both the strong core-core interactions in the slip-stacked form and the flexibility of side groups was assumed to be the key factor for enhancing the

molecular reorganization. The 1D organization and π - π stacking manner is favorable to electronic applications. In fact, this assumption is evidenced by preliminary hole mobility measurement in OFET device (Fig. S13), resulting in the value of $1.9 \times 10^{-2} \text{ cm}^2/\text{V}\cdot\text{s}$ for the di(HTh2BT)DTCTT film which is two orders of magnitude higher than $3.0 \times 10^{-4} \text{ cm}^2/\text{V}\cdot\text{s}$ of amorphous di(HTh2BT)IDT film. Manipulating molecular reorganization using weak intermolecular interactions such as S-S interactions has been attempted to develop novel functionality in molecular crystals⁵⁶. This research provides an evidence of advanced crystal engineering which opens up an interesting possibility such as controlling semiconducting properties through reorganization of molecular alignment induced by post thermal treatment.

CCDC 1504077 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supporting Information

Details of synthesis and characterization of the DTCTT- and IDT-based molecules, UV-vis, DSC, POM, PXRD, SWAXS, Thermal expansion analysis, AFM, DFT calculation, structural assignment of di(C12Th2BT)DTCTT, and summary of X-ray crystallography of di(HTh1BT)IDT.

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55. There are some small peaks which are not assigned with the indicated symmetry. They comes from either symmetry violation (i.e. $2\theta = 4.1$ and 7.3 for L phase, 3.9 and 6.4 for H1 phase) or possible contaminated phases.

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