

Controlling Polymorphic Transitions in n-Type Organic Semiconductor Single Crystals by Alkyl Chain Engineering

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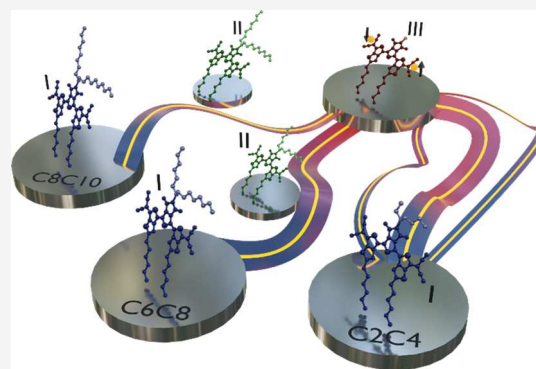


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ABSTRACT: Control of polymorphic behavior is crucial for designing functional organic semiconductor devices as even a slight structural difference may translate to dramatically different electronic properties. One route to controlling structure is through stimulus-induced polymorph transitions, which allows for switching those electronic properties. However, despite advances in predicting crystal structures, the molecular design characteristics governing the polymorphic transition mechanism remains unknown. Here, we systematically investigate a series of n-type organic semiconductor molecules based on 2-dimensional quinoial terthiophene with varying alkyl side chain lengths to modulate two distinct polymorph transitions, one cooperative martensitic transition and the other non-cooperative nucleation and growth transition. In the three molecular systems, we observe that shortening the alkyl chain past a critical length suppresses the cooperative polymorph transition by limiting the alkyl chain conformation change. On the other hand, the nucleation and growth transition temperature increases as the side chain length decreases, possibly driven by the increase in the melting point of the alkyl chains. We also found that tuning the alkyl chain length modulates the associated quinoial to aromatic biradical switching that drives the nucleation and growth transition, suggesting a synergy between the crystal structure and electronic structure. Ultimately depending on the exact mechanism of the polymorph transition, adjusting the alkyl chain length may lead to tuning of the polymorph transition temperature or suppression of the transition altogether. This offers a potential molecular design rule to target a particular transition mechanism based on the desired behavior for the system.



INTRODUCTION

The correlation between polymorph discovery and the time and effort spent researching a compound was famously proposed by McCrone in 1965.¹ Since then, the time and effort of countless researchers have been devoted to identifying an innumerable catalog of crystal structures (see CCDC²). While tremendous progress has been made in the prediction and access of various crystal structures, even today polymorphism is often found serendipitously. The importance of these structures is critical: polymorph selection in a crystal can dramatically modulate properties such as solubility of pharmaceuticals,³ electronic properties of semiconductors,^{4–6} and mechanical properties of metal alloys.^{7–9} Accessing polymorphic structures in a controlled and predictable way is necessary to realizing next-generation material properties. Polymorphic transition, induced by external stimuli (e.g., heat,^{10,11} light,^{12,13} and mechanical^{7,14}), is one method to control the crystal structure. Understanding how these transitions occur and how the molecular design impacts them offers the potential for developing molecular design rules

to encourage, tune, or even suppress a particular polymorphic behavior.

Polymorphic transitions also allow for incorporating various switching behaviors capable of controlling optoelectronic properties.^{4,6,15,16} These transitions may occur by two different mechanisms: either via a nucleation and growth transition,^{17,18} where the molecules move individually across a phase boundary, or by a cooperative transition,^{19–22} in which molecular motion is displacive and concerted. Typically, nucleation and growth transitions exhibit large changes in molecular packing and slow kinetics,¹⁴ making it promising for the kinetic stabilization of a particular metastable polymorph. Cooperativity, on the other hand, exhibits rapid transition kinetics^{9,23,24} and low energy barriers^{8,25} and is coupled with

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intriguing mechanical properties,^{7,11,23} offering pathways to novel, reversible switching devices. By controlling the presence of these transitions, we may provide a method of rationally designing new switching devices.

Previously, cooperative transition mechanisms have typically involved rotational^{7,11,21} or sliding motion within the crystal system.^{19,23,26} In organic molecules, this motion has been facilitated by the side chains of the molecules which have been shown to go through a rotational order–disorder^{11,27} transition or undergo a conformation change in the case of alkyl chains.²⁸ In our recent work,^{28,29} we observed that 2DQTT- C_8C_{10} undergoes two thermally accessible polymorph transitions: the I–II (cooperative) and II–III (nucleation and growth) transitions. The I–II cooperative transition was driven by a change in alkyl chain conformation, causing a change in the tilt of the molecules along the π -stacking direction in a domino-like effect. Although the II–III nucleation behavior was driven by biradical formation, a unique electronic ground state formed in quinoidal molecules^{30–32} and results in unique intermolecular interactions.^{33–36} This change in the core–core interactions was facilitated via disordering of the alkyl chains, which allowed increased mobility. In both cases, the alkyl chains played a key, yet distinct, role in the polymorph transition, suggesting a potential route to controlling the transition behavior via adjusting the structure of the alkyl chains.

In this work, we report the control of polymorphism in 2-dimensional quinoidal terthiophene (2DQTT) via tuning the chain length of the branched alkyl group. In the case of the I–II cooperative transition, when the side chains hit a critical length below C_6C_8 , the transition is no longer observed. Raman spectroscopy and single crystal X-ray diffraction (SCXRD) showed the C_2C_4 molecule packed in a polymorph II-like structure at room temperature, eliminating the driving force behind the transition. On the other hand, the II–III nucleation and growth transition temperature increases with reducing side chain length possibly due to a higher melting temperature for shorter tethered alkyl chains in the solid state.^{37–39} Finally, we observed a synergistic effect between the polymorph III crystal structure and biradical formation, which is mediated via the alkyl chain melting, providing a new way to modulate biradical stability.

RESULTS AND DISCUSSION

Polymorphic Transitions of 2DQTT Systems. Our previous work²⁹ on 2DQTT- C_8C_{10} (Figure 1a) showed two thermally induced polymorph transitions, occurring in single crystals at 164 and 223 °C, designated I–II and II–III, respectively. While the I–II exhibited a cooperative type mechanism and the II–III transition showed nucleation and growth behavior, both transitions are accompanied by key changes in the alkyl chains. The cooperative I–II transition was accompanied by a change in the alkyl chain packing, which we hypothesized was driving the cooperative behavior. The II–III transition showed a significant increase in the disorder of the alkyl chains, suspected to facilitate the formation of polymorph III. A series of 2DQTT molecules with different branched alkyl chain lengths were synthesized according to previous work^{40,41} to elucidate the molecular design criteria governing the polymorphic behavior observed in the C_8C_{10} system.

The branched side chains were systematically shortened from the original C_8C_{10} molecule to C_6C_8 and C_2C_4 ,

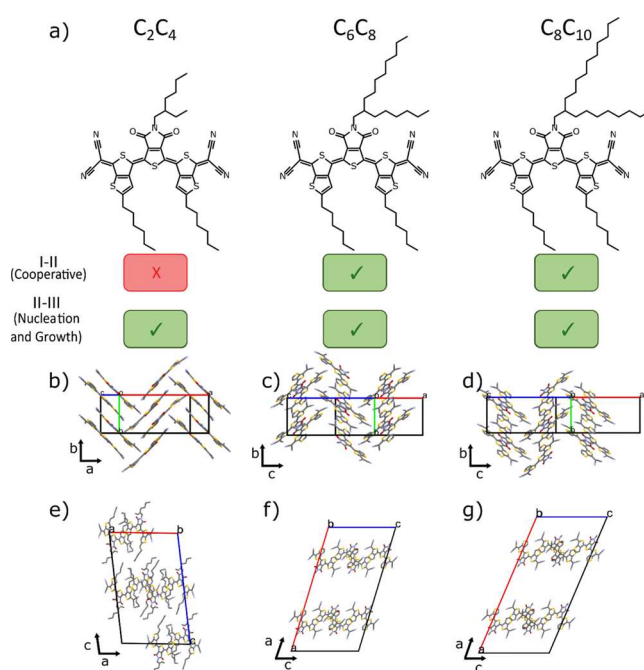


Figure 1. (a) Schematic showing the investigated 2DQTT systems, each of which was a racemic mixture based on the branched carbon stereocenter, and both isomers were observed through X-ray diffraction. (b–d) 1D π -stacks form along the b direction for all three systems. (e–g) Similar out of plane layering of the molecules, where the alkyl chains (omitted for clarity) fit in between the layers of 1D stacks.

decreasing the bulkiness and flexibility of the chains in the process. We note that each molecule contains a stereocenter at the branching carbon in the alkyl chains and is present as a racemic mixture in crystals. Single crystals of each molecule were crystallized into the stable polymorph at room temperature for all three systems. Crystals of the C_8C_{10} and C_6C_8 molecules were grown from a mixture of 1:1 dichloromethane and ethyl acetate by volume. However, in the C_2C_4 system, this method produced a metastable polymorph previously reported.⁴⁰ To access the stable form, slow growth from tetralin was used instead.

Both C_6C_8 and C_8C_{10} formed a $C2/c$ unit cell, with a glide plane perpendicular to the b direction (the π -stacking direction). While the C_2C_4 crystal packs in a $P2_1/c$ unit cell, a different symmetry compared to the other systems, crystals of each molecule showed similar packing motifs. In all three cases, the conjugated core forms 1D π -stacking along the b -direction of the unit cell (Figure 1b–d). This also results in a layered structure with layers of conjugated core separated by layers of greasy side chains, when viewed from the side down the b axis (Figure 1e–g). Based on the Bravais, Friedel, Dannay, and Harker (BFDH) morphology, we expect this layered stacking to occur out of plane relative to the substrate (Figure S1). Accordingly, the BFDH morphology suggests that the 1D π -stacks form along the longest axis in each of the crystals.

One key difference in molecular packing was in the tilt of the molecules in the 1D π -stacks (Figure S2). This becomes apparent in the top-down view seen in Figure 1b–d, where the C_2C_4 molecules appear to stand straight up from the ab plane. In fact, by measuring the angle between the average plane of the conjugated core and the (100) plane (or the (001) for C_2C_4) which is parallel to the substrate, we see that the C_6C_8

and C_8C_{10} molecules pack at tilts of 66° and 67° relative to the substrate, respectively, whereas the C_2C_4 molecule has a tilt of 88° , nearly perpendicular to the substrate (Figure S2a). This suggests that increasing the bulkiness of the alkyl chains forces the molecules to tilt more toward the substrate.

Crystals of each molecule were investigated under hot-stage polarized optical microscopy (POM). We observed both the I–II and II–III transitions in the C_6C_8 and C_8C_{10} crystals, but only a single transition was found in the C_2C_4 crystals, which was assigned to the I–III transition, as discussed later. The I–II transition occurred at similar temperatures in the C_6C_8 and C_8C_{10} crystals (169 and 163°C for C_6C_8 and C_8C_{10} , respectively) and showed the rapid kinetics as well as sharp phase boundaries that are hallmarks of the cooperative behavior (Figure 2a,b, Movies S1,2). However, crystals of

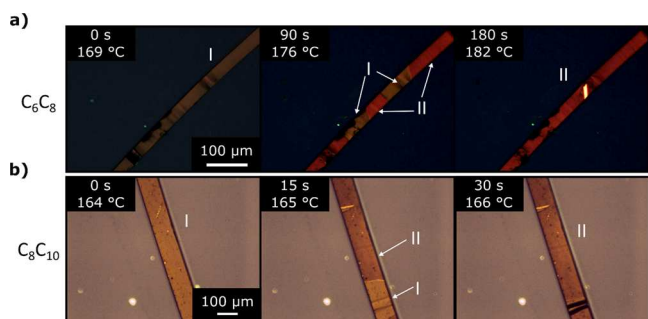


Figure 2. In situ POM images during the I–II transition in the (a) C_6C_8 and (b) C_8C_{10} crystals.

C_2C_4 showed no cooperative transition in the temperature region expected, suggesting that the shorter side chains suppressed the cooperative I–II transition altogether (Movie S3).

On the other hand, the transition to polymorph III persisted across all three molecular systems. The nucleation and growth behavior clearly showed under in situ POM by a diffusive phase boundary and formation of multiple phase boundaries (Figure 3a–c, Movies S4–6, respectively). This transition was followed by a characteristic increase in brightness of the crystals, which represents a significant change in the refractive index between the low-temperature and high-temperature polymorphs. Aside from similar transition, we note that the

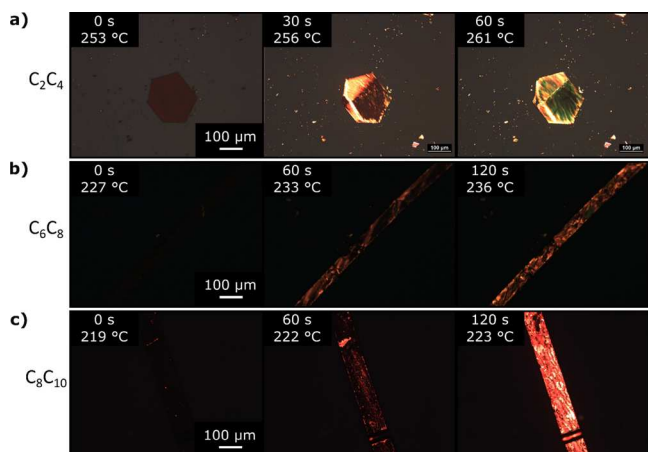


Figure 3. In situ POM images from the II–III transition observed in crystals of (a) C_2C_4 , (b) C_6C_8 , and (c) C_8C_{10} .

transition temperature is significantly higher in the C_2C_4 molecule ($\sim 20^\circ\text{C}$), relative to the molecules with longer side chains to be discussed later.

We also investigated these transitions via differential scanning calorimetry (DSC). For the C_6C_8 and C_8C_{10} systems, the DSC showed both the I–II and II–III transitions as expected from in situ POM (Figure S3a,b). Notably, the enthalpies were quite consistent among these transitions as well, suggesting similar transition mechanisms. To better characterize the I–II transition mechanism, we investigated the kinetics of the phase transitions via changing the heating ramp rate (Figure S4) using both the Starink and Vyazovkin methods as discussed by Joseph and Piedade et al.⁴² However, there was little if any dependence of the transition temperature on the ramp rate, suggesting an issue of applying these techniques to cooperative transitions. Indeed, similar issues with excessive activation energies have arisen in martensitic systems and required modeling an additional autocatalytic effect.^{43–45} Unfortunately, the proximity of the II–III phase transition to the degradation and sublimation temperatures prevented us from comparing these two transitions in terms of the ramping rate dependence.

The C_2C_4 system, on the other hand, exhibited a very complex DSC, featuring a rich set of phase transitions (Figure S3c). A full map of the known polymorphs is provided in Figure S5. This contrasting polymorphic behavior between the DSC and in situ POM results is due to a different starting polymorph. Specifically, DSC cycle 1 (Figure S3c) starts with a metastable polymorph designated here as I' rather than the stable polymorph I in the in situ POM study. Polymorph I' grows in a 2D brickwork structure as previously reported by Zhang and Zhu et al.⁴⁰ We were able to grow crystals of this metastable form and observed under in situ POM which confirmed the transition behavior of DSC cycle 1. However, these transitions were not single-crystal-to-single-crystal preventing us from reporting the structures. Despite this very different polymorphic behavior, a transition still occurred near 260°C starting from polymorph I', suggesting that polymorph III was obtainable regardless of the initial phase.

Unexpectedly, we note upon cooling from polymorph III under DSC, three additional phase transitions were observed. While initially missed in the in situ POM due to the lack of reflective index contrast and ease of kinetic trapping, indeed we observed at least two of these cooling transitions. This would initially suggest the reverse transitions of those observed upon heating; however, these transitions were observed in crystals of polymorph I as well, which showed no such heating transitions under in situ POM nor grazing incidence X-ray diffraction (GIXD). Moreover, upon heating through the second cycle of DSC (Figure S3d), the original polymorph transitions are no longer observable and are replaced with a transition at 171°C and the formation of polymorph III at 260°C . This appeared reversible as this same behavior, both the three transitions during cooling and two heating transitions were observed for the third cycle as well. Finally, we note a substantial difference in the transition enthalpy between the first (2.86 kJ/mol) and second (13.2 kJ/mol) cycles, suggesting on the second cycle we no longer observe the IV'–III transition, but rather a different polymorph transition altogether. We also deduce that polymorph VI is neither the 2D brickwork form I' nor polymorph I. This was confirmed via GIXD (Figure S6) and means cooling from polymorph III in the C_2C_4 system results in an entirely separate set of polymorphs not accessible via the

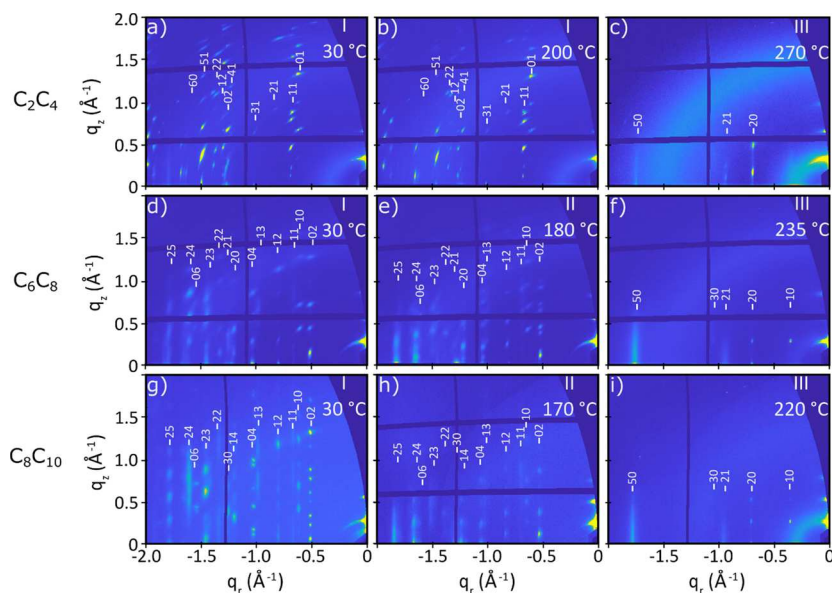


Figure 4. GIXD patterns of polymorphs I, I at 200 °C and III for C_2C_4 crystals (a–c), I, II, and III for C_6C_8 (d–f) and C_8C_{10} (g–i) crystals, respectively.

Table 1. Comparison of Unit Cells of All Polymorphs in Three Molecular Systems

	C_2C_4		C_6C_8			C_8C_{10}		
	I (SCXRD)	III (GIXD)	I (SCXRD)	II (GIXD)	III (GIXD)	I (SCXRD)	II (GIXD)	III (GIXD)
a (Å)	23.0	N/A	46.0	46.6	23	50.5	51.6	24.5
b (Å)	9.81		10.2	9.88	20.5	10.2	20.5	20.5
c (Å)	37.57		24.0	24.2	20.5	24.1	20.5	20.5
α (°)	90		90	90	120	90	90	120
β (°)	97.3		106.68	100.8	90	113	91.3	90
γ (°)	90		90	90	90	90	90	90

grown crystals. We suspect that the new polymorphs observed during cooling from polymorph III are related to persisting diradical states. But regardless of the initial starting polymorph in the DSC study, all roads lead to polymorph III at the same temperature, on which we will focus our discussion below.

Single crystal structures for polymorphs II and III were not obtainable due to bending and cracking in the I–II transition along with subsequent multiple domain formations in the II–III transition. However, we investigated the structural changes via GIXD. Using the structures from polymorph I of each molecule, we confirmed identical stable polymorphs in the thin films as in the corresponding single crystals (Figures 4a,d,g and S4). Upon heating, there is little change in the diffraction pattern for the C_2C_4 crystal (Figure 4a,b) except for thermal expansion prior to the II–III transition. In crystals of C_6C_8 and C_8C_{10} , there is a clear change in the number and position of diffraction peaks in the out-of-plane direction (q_z direction). Using the unit cell of the single crystal structure as a basis, we could fit a unit cell to the polymorph II and III diffraction patterns (Table 1). While this manifested as a doubling of the peaks in the C_6C_8 instead of the halving observed in C_8C_{10} , both cases reflect a decrease in the β -angle of the unit cell toward 90°.

After the high-temperature transition to polymorph III, we observed an uncanny similarity between the diffraction patterns of all three crystal systems (Figure 4c,f,i). In fact, the diffraction patterns for the C_6C_8 and C_8C_{10} crystals (Figure 4f,i, respectively) are identical. On the other hand, some of the

Bragg rods present in the longer alkyl chain crystal systems are not observed in the C_2C_4 diffraction pattern. Notably, the 01 and 03 Bragg rods are not present in the C_2C_4 crystals and the out-of-plane (q_z) positions of the observed peaks are shifted relative to those observed in the crystals from the longer alkyl chains. This indicates a different symmetry for polymorph III in the C_2C_4 crystals rather than the hexagonal symmetry observed in the C_6C_8 and C_8C_{10} systems, however, due to the reduced observable peaks a reliable unit cell was not obtainable in this case. While the q_z positions may be shifted, the visible Bragg rods are observed at the same q_r positions as the corresponding Bragg rods in the C_6C_8 and C_8C_{10} systems. Thus, despite a different symmetry, the packing motif may be similar in all three systems, which will be confirmed via Raman spectroscopy later.

Upon cooling of this polymorph III to room temperature (Figure S6a,b), we observe a different diffraction pattern. This pattern fits neither the 2D brickwork structure previously reported nor the 1D π -stack structure reported here. Interestingly, we found this diffraction pattern matched the pattern observed in films solution printed from chlorobenzene, though single crystals of this phase could not be obtained. During the heating, of this film, we see changes in the structure between 150 and 200 °C (Figure S6c), following the transitions observed starting from PVI. This structure then forms polymorph III at 275 °C. While it is still unclear where polymorphs IV and V correspond structurally, this is consistent

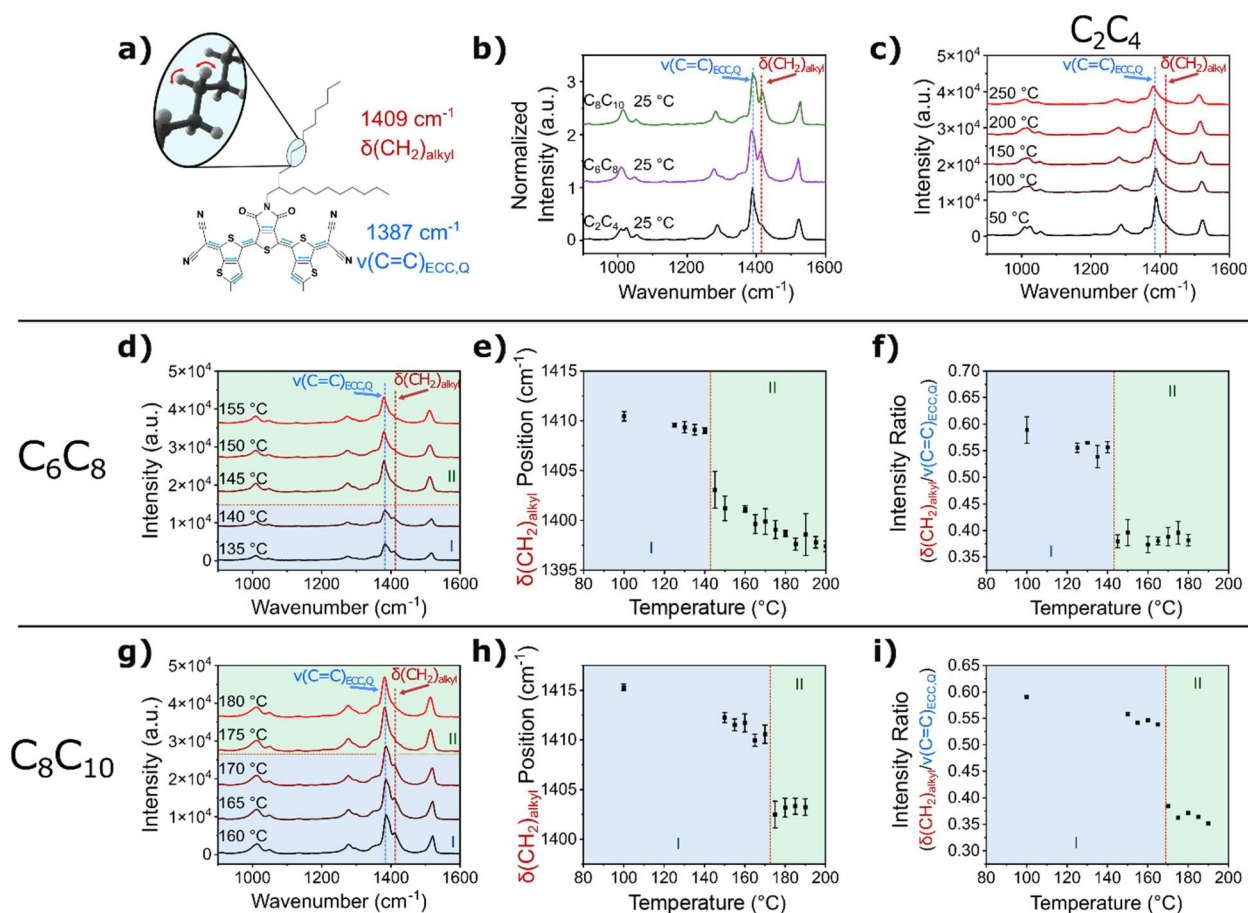


Figure 5. In situ Raman spectroscopy during the I–II transition. (a) Schematic showing the $\nu(\text{C}=\text{C})_{\text{ECC,Q}}$ and $\delta(\text{CH}_2)_{\text{alkyl}}$ vibrational modes associated with the 1387 (blue) and 1409 cm^{-1} (red), respectively. (b) Comparison of the Raman spectra for the C_2C_4 (black), C_6C_8 (purple), and C_8C_{10} (green) crystals. (c) Raman spectra of C_2C_4 crystals showing no significant change in the range 50–250 $^{\circ}\text{C}$ that would contain the I–II transition. Raman spectra of (d) C_6C_8 and (g) C_8C_{10} single crystals during the I–II transition. Change in the $\delta(\text{CH}_2)_{\text{alkyl}}$ (e,h) relative intensity and (f,i) peak position for the C_6C_8 and C_8C_{10} crystals, respectively. All Raman spectra were taken under 532 nm laser and with 30 s exposure.

with our DSC analysis and confirms the polymorphic pathways proposed in Figure S4.

Molecular Mechanism of I–II Transition. We next probe the alkyl chain conformation change during transitions to understand the molecular origin underpinning the difference in polymorph transition behaviors among three systems. Raman spectroscopy provides detailed information on the chemical environment of the molecules in the crystal structure and was performed on the crystals during heating. Our previous work²⁸ on the I–II transition showed significant changes in the peak at 1409 cm^{-1} , which was assigned to the CH_2 deformation vibrational mode ($\delta(\text{CH}_2)_{\text{alkyl}}$), located in the alkyl chains (Figure 5a,b, red). The peak at 1387 cm^{-1} , on the other hand, was assigned to the effective conjugation coordinate (ECC) mode of the quinoidal core, providing a consistent reference for comparison (Figure 5a,b, blue). With this assignment, we tracked the $\delta(\text{CH}_2)_{\text{alkyl}}$ in each system. Despite the similar packing motifs for each molecule, the room temperature spectra for the C_2C_4 crystal show a significantly reduced intensity of the $\delta(\text{CH}_2)_{\text{alkyl}}$ peak, as compared to the other systems (Figure 5b), suggesting a very different starting environment for the alkyl chains in the C_2C_4 structure. As expected from the lack of transitions observed during in situ POM experiments, no significant changes occurred to the C_2C_4 Raman spectra during heating up to 250 $^{\circ}\text{C}$ (Figure 5c).

In the C_6C_8 system, we see similar behavior to the C_8C_{10} crystals previously²⁸ studied (Figure 5d,g). In both cases, there is a sudden decrease in the intensity of the $\delta(\text{CH}_2)_{\text{alkyl}}$ peak during the transition. We note that the C_6C_8 crystal transitions at a temperature of 140 $^{\circ}\text{C}$, significantly lower than observed under in situ POM; we expect this is due to local heating from the laser combined with thicker slow evaporation grown crystals increasing the amount of energy absorbed. On the other hand, the transition temperature for the C_8C_{10} sample matched that from POM measurement closely because the crystal was formed via drop casting, resulting in a much smaller crystal and less laser absorption. We fit the $\delta(\text{CH}_2)_{\text{alkyl}}$ and $\nu(\text{C}=\text{C})_{\text{ECC,Q}}$ peaks to track the intensity ratio (based on peak area) during the transition. The $\nu(\text{C}=\text{C})_{\text{ECC,Q}}$ is expected to be relatively insulated from polymorph transitions and acts as a reference for investigating changes in the alkyl chain packing. Indeed, for the I–II transition, both the C_6C_8 and C_8C_{10} systems show a sudden drop in the intensity of the CH_2 deformation peak ($\delta(\text{CH}_2)_{\text{alkyl}}$), relative to the conjugated core stretching mode ($\nu(\text{C}=\text{C})_{\text{ECC,Q}}$) (Figure 5e,h). This is also coupled with a simultaneous redshift in the $\delta(\text{CH}_2)_{\text{alkyl}}$, indicative of the significantly different chemical environment of the alkyl chains in polymorph II. The decrease in intensity and redshift of the $\delta(\text{CH}_2)_{\text{alkyl}}$ peak indicate a reduction in the intermolecular interactions,^{39,45,46} potentially associated with reduced interdigitation of the alkyl side chains. This confirms

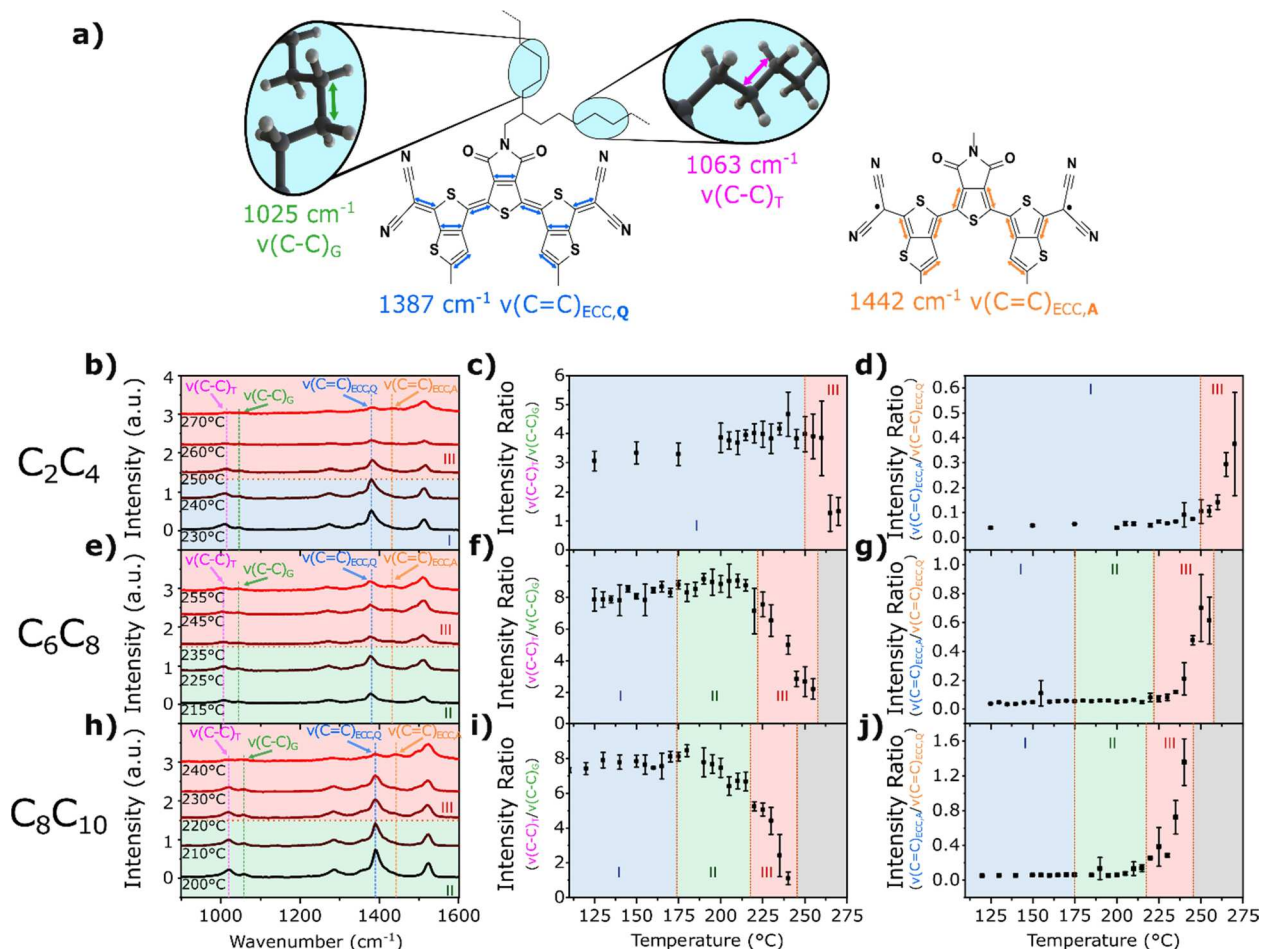


Figure 6. In situ Raman spectroscopy during the II–III transition. (a) Schematic showing the vibrational modes for the C–C stretching in the trans ($\nu(\text{C–C})_{\text{T}}$, 1063 cm^{-1}) and gauche ($\nu(\text{C–C})_{\text{G}}$, 1025 cm^{-1}) conformers as well as the C=C stretching of the quinoidal ($\nu(\text{C=C})_{\text{ECC,Q}}$, 1387 cm^{-1}) and aromatic ($\nu(\text{C=C})_{\text{ECC,A}}$, 1442 cm^{-1}) forms. In situ Raman spectra during the II–III transition (b,e,h), for each crystal system, showing the changes in the trans and gauche peaks as well as formation of the aromatic biradical peak. The trans to gauche intensity ratio approaches 1 for each system at the end of transition (c,f,i), showing the melting of the alkyl chains. The transition, and side chain disorder, is accompanied by the increase in the aromatic-to-quinoidal peak intensity ratio (d,g,j), indicating a synergy between the polymorph III structure and biradical formation.

that the cooperative behavior observed in both crystals undergoes an identical transition mechanism in both molecular systems.

Comparing this alkyl chain behavior to the C_2C_4 case, the Raman spectra collected from the C_2C_4 spectra for polymorph I at room temperature bear a remarkable resemblance to the C_6C_8 and C_8C_{10} polymorph II crystals. Particularly, the reduced intensity of the $\delta(\text{CH}_2)_{\text{alkyl}}$ signifies a similar packing environment of the alkyl chains between polymorph II in C_6C_8 and C_8C_{10} crystals and polymorph I in C_2C_4 crystals. This is coupled with the previous discussion of the single crystal structure showing a much larger tilt angle in polymorph I of the C_2C_4 crystals, another key feature of polymorph II in C_6C_8 and C_8C_{10} crystals. This suggests the increased bulkiness of the longer alkyl chains (C_6C_8 and C_8C_{10}) forces a lower tilt angle, preventing the molecules from standing up, like loading a spring. Then, once a high enough temperature is reached, that spring is released as the alkyl chains rearrange to become less interdigitated into the polymorph II conformation and the core is forced to tilt down further. This scenario is thus impossible in the shorter C_2C_4 side chain, which has less conformational freedom and causes less steric hindrance with neighboring chains within the crystal structure.

Modulation of Polymorph III Transition. Unlike the I–II transition, the II–III nucleation and growth transition was observed in all three systems. In analysis of the II–III transition mechanism in the C_8C_{10} crystals, four Raman peaks clearly described what was happening in the crystal.²⁸ The two peaks at 1025 and 1063 cm^{-1} were assigned to C–C stretching of the trans $\nu(\text{C–C})_{\text{T}}$ and gauche $\nu(\text{C–C})_{\text{G}}$ conformers in the alkyl chains (Figure 6a, pink and green). These peaks have been well studied in alkane molecules,^{45,47,48} and the intensity ratio between these peaks indicates dynamic disorder where a ratio of 1 represents freely moving and rotating chains in a disordered state. The II–III transition also exhibits a quinoidal-to-aromatic transition within the conjugated core, stabilizing a biradical ground state,²⁸ which is represented by the peaks at 1387 and 1442 cm^{-1} . The peak at 1387 cm^{-1} , as discussed previously represents the quinoidal ECC mode of the core C=C stretching ($\nu(\text{C=C})_{\text{ECC,Q}}$), whereas the 1442 cm^{-1} was shown to be the ECC mode for the aromatic core C=C stretching ($\nu(\text{C=C})_{\text{ECC,A}}$) (Figure 6a blue and orange). In our previous work,²⁸ this ratio was shown to correlate with an increase in concentration of spins observed under electron paramagnetic resonance spectroscopy and provides a ratio between the quinoidal and biradical species within the system.

Raman spectroscopy from the transitions in the C_2C_4 and C_6C_8 molecules follows similar changes to the vibrational modes observed in the C_8C_{10} molecule (Figure 6b,e,h), confirming our expectations from in situ POM. Indeed, in all three systems, the alkyl chains become increasingly disordered during the II–III transition, as the ratio of the trans (pink) to gauche (green) conformers approach 1 at the end of the transition (Figure 6c,f,i). A ratio of 1 indicates the alkyl chains are freely rotating around the C–C bonds, which is observed as melting in pure (untethered) alkanes. In the case of 2DQTT, this disordering of the alkyl chains couples with the quinoidal to aromatic transition to form polymorph III.²⁸ Intriguingly, despite the differing initial structure of the C_2C_4 crystal, this transition still follows an identical pathway as the II–III transition in the C_6C_8 and C_8C_{10} crystals. However, we note the temperature at which the alkyl chains become disordered decreases as we increase the alkyl chain length. This trend closely follows observations from in situ POM discussed previously (Figure 3) indicating a higher transition temperature in the C_2C_4 crystal. This increase in transition temperature as a result of the shorter alkyl chains is attributed to reduced steric hindrance that allows for stronger forces such as π – π interactions between the cores to dominate.^{37,38}

What was unexpected, however, was the biradical formation behavior. In our previous work,²⁸ we showed that the II–III transition is accompanied by an increase in the biradical nature of the molecule. This change in the electronic structure of the 2DQTT molecule results in new spin–spin interactions between radical centers, suspected to be the driving force for this transition. While the biradical form can be increased via heating,^{31,35} a key factor in stabilization is the extent of conjugation.^{30,49} The longer the conjugated core, the more stable the terminal radicals become and can further be tuned by adding various electron donating or withdrawing groups.^{30,35,36,49} We suspected the alkyl chain modification should not impede the biradical driving force and only affect the temperature at which the alkyl chains become disordered. Interestingly, however, in all three molecules, the increase in formation of the biradical state (orange in Figure 6a), relative to the quinoidal form (blue in Figure 6a), occurs simultaneously with the disordering of the side chains. This results in the temperature for stabilizing the biradical form, or in other words the II–III transition temperature, to increase to higher temperatures despite no changes to the conjugated core of the molecule (Figure 6d,g,j). To account for this, there must be a synergistic effect between the crystal structure and stabilization of the radicals. Stabilization of radicals in previous work has shown that spin–spin interactions may direct and control the crystal structure formation.^{50,51} Our results, on the other hand, suggest forming the right crystal structure can, in turn, stabilize radicals in a material that would otherwise exhibit a mostly quinoidal ground state.

CONCLUSIONS

Our work aimed to identify the molecular design rules controlling the behavior of two thermally induced polymorphic transitions in the 2DQTT system by systematically varying the length of the branched alkyl side chain. We found that the I–II and II–III transition behavior observed in the 2DQTT could be modified in distinct ways via tuning the branched alkyl chain length. Reducing the length of the alkyl chains effectively “turned off” the cooperative I–II transition by allowing a greater tilt in the molecule and reduced alkyl chain

conformational flexibility. Without the added bulkiness driving de-interdigitation, the C_2C_4 system eliminates the potential driving force of transition. On the other hand, regardless of both molecular and crystal structure, we observed the formation of a biradical state and analogous polymorph III crystal structure. Additionally, reducing the chain length increased the temperature at which the alkyl chains became disordered. This shifted the II–III transition temperature higher with a coupling between the polymorphic structure and stabilization of the biradical electronic structure. Such a synergy between structural transition and electronic transition provides novel modes of modulating the radical stabilization, beyond traditional tuning of conjugation length. Our results suggest that in the case of these branched chains, adjustments to the alkyl chain length can disrupt the observed cooperativity, while simultaneously tuning the nucleation and growth transition temperature, providing a route to design for these transition behaviors.

MATERIALS AND METHODS

Materials Synthesis. Synthesis of 2DQTT-o-B has been published in ref 41.

Single Crystal Fabrication. Single crystals of C_2C_4 were grown via slow evaporation from a 0.5 mg mL^{−1} tetralin solution to obtain hexagonal plates. Crystals of C_6C_8 and C_8C_{10} were grown via slow evaporation from a 1 mg mL^{−1} 1:1 mixture of dichloromethane and ethyl acetate. The solutions were then capped with parafilm, and 1–5 holes were created in the film using a needle. The vials were then placed in a glove bag under a nitrogen atmosphere for slow evaporation over a few weeks. The nitrogen in the glove bag was refilled every other day to prevent oxygen from reacting with the molecule and ensure that saturation of solvent vapors did not occur. Crystals were removed from the mother liquid prior to complete drying. Crystals of C_8C_{10} for Raman spectroscopy were grown via drop casting 5–15 μ L of 10–15 mg mL^{−1} of 2DQTT-o-B dissolved in a 1:1 mixture of dichlorobenzene and decane and heated to 100 °C. Drop casting was done onto phenyltrichlorosilane (PTS)-treated silicon wafers (SiO₂/Si) and allowed to dry overnight.

Polarized Optical Microscope. Single crystals grown under the slow evaporation procedure were placed under a Nikon H550S with a high-speed camera (Infinity 1) and heating stage (Linkam 402). The chamber was sealed with a magnetic lid and O-ring during heating. The temperature ramp was kept between 5 and 10 °C min^{−1}. Videos were recorded at framerates ranging from 1 to 7.5 fps.

Differential Scanning Calorimetry. DSC measurements were performed using a Discovery 2500 DSC. The powdered sample (3–5 mg) was loaded into a T0 aluminum pan. Heating rates varied between 5 and 10 °C min^{−1}. Enthalpies were extracted for the I–II and II–III transitions via peak integration.

Raman Spectroscopy. A Raman confocal imaging microscope with a 532 nm laser (Laser Quantum Ventus 532 with max power 50 mW) and 50 $\times$ long working distance objective lens (HORIBA LabRAM HR 3D) equipped with a HORIBA Synapse back-illuminated deep-depletion CCD camera was used to collect spectra. Using a 300 g mm^{−1} grating, we used a scan exposure time of between 20 and 60 s. An optical density filter of OD = 1 was used [OD = log(power transmission factor)], and no beam damage was observed except at only the highest temperatures after prolonged periods of laser exposure (>5 min). To eliminate this effect, each spectrum was recorded in a new position on the crystal to prevent overexposure of any area. For variable-temperature experiments, the samples were collected using a Linkam THMS600 heating stage with a closed chamber. The heating and cooling rate was kept at 10 °C min^{−1}. Each temperature was equilibrated until the temperature reading stabilized, and the Raman laser was refocused to account for substrate thermal expansion (approximately 5 min in total).

Single Crystal X-ray Diffraction. The single crystal structure for the C_6C_8 crystal was collected at NSF's ChemMatCARS (Sector 15) of the Advanced Photon Source, Argonne National Laboratory. Needle crystals grown via slow evaporation from 1:1 dichloromethane and ethyl acetate and measured at room temperature. The beam energy was 30 keV (0.41328 Å), and the beam size at the sample was $0.15 \times 0.15 \text{ mm}^2$. In total, 720 frames were taken using a Huber 3 circles diffractometer with a kappa angle offset of 60° and a Pilatus 1 M (CdTe) detector. The sample to detector distance was 130 mm and was collected at two θ -angles at 0° and ω -angles at -180° , followed by two different kappa angles, 0° and 15° , respectively. The φ -angle was scanned over the range of 360° using shutterless mode. The single crystal structure was analyzed using Mercury software to calculate the tilt of the conjugated core with respect to the (100) or (001) plane.

The single crystals of C_2C_4 were grown via slow evaporation from a $<1 \text{ mg/mL}$ solution of tetralin. Diffraction data were collected on a Bruker D8 Venture equipped with a four-circle kappa diffractometer and Photon II detector. The $I\mu\text{s}$ microfocus Mo ($\lambda = 0.71073 \text{ Å}$) source supplied the multi-mirror monochromated incident beam. The sample was mounted on a 0.3 mm loop with the minimal amount of Paratone-N oil. Data were collected as a series of φ and ω scans.

The cell refinement and integration of intensity data were carried out with the APEX3 software.⁵² Multi-scan absorption corrections were performed numerically with SADABS.⁵³ The initial structure solution was solved with the intrinsic phasing methods SHELXT⁵⁴ and refined with the full-matrix least-squares SHELXL program.⁵⁵

Grazing Incidence X-ray Diffraction and Unit Cell Determination. GIXD was performed at beamline 8-ID-E of the Advanced Photon Source at Argonne National Laboratory.⁵⁶ The data were collected at 10.91 keV on a 2D Pilatus 1M detector. Films of C_6C_8 and C_8C_{10} were solution coated at 0.3 mm s^{-1} from solution of 6 mg mL^{-1} chloroform onto PTS treated SiO_2 wafer. Films were annealed at 100°C to convert to the stable polymorph I. Films of C_2C_4 were drop-cast from tetralin at 100°C onto the PTS-treated substrate. The stable polymorph formed at the edge, where the solution was pinned at the edges of the wafer. In situ thermal annealing measurements were conducted in a He environment with the sample on a commercial thermal stage (Linkam HFSX350-GI), with the temperature ramped at 10°C/min and the exposure taken after equilibration at the target temperature for approximately 5 min. GIXSGUI software was used to correct for detector nonuniformity, beam polarization and to reshape the 2D data into the representation q_z vs q_x .⁵⁷ The incident angle was set at 0.14° to ensure total internal reflectance of the organic thin film. Each peak extracted for determining the unit cell was fit with a gaussian function to find the peak position. We then used a least square error fitting procedure to determine best-fit unit cells for each polymorph based on the experimental peak positions (see the Supporting Information). The fittings were then simulated using GIXSGUI to match the diffraction patterns with the unit cell.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.cgd.2c00724>.

Crystallographic data for 2DQTT-C6C8 and 2DQTT-C2C4 of polymorph I; BFDH morphology calculations for each crystal; comparison of the tilt in the conjugated core; corresponding DSC scans for each molecule; transition pathways for the 2DQTT-C2C4 crystals; GIXD matching the single crystal structures to the film structures; and GIXD images showing the reverse and second cycle of transitions in the 2DQTT-C2C4 system (PDF)

Movie for the 2DQTT-C6C8 I–II transition; movie for the 2DQTT-C8C10 I–II transition; movie of the 2DQTT-C2C4 II–III transition; Movie of the

2DQTT-C6C8 II–III transition; movie of the 2DQTT-C8C10 II–III transition (ZIP)

■ Accession Codes

CCDC 2182357–2182358 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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