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On the Effect of Confinement on the Structure and Properties of Small-Molecular Organic Semiconductors

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Abstract

Many typical organic optoelectronic devices, such as light-emitting diodes, field-effect transistors and photovoltaic cells, use an ultra-thin active layer where the organic semiconductor is confined within nanoscale dimensions. However, the question of how this spatial constraint impacts the active material has rarely been addressed, even though it may have a drastic influence on the phase behavior and microstructure of the active layer and hence the final performance. Here we use the small-molecule semiconductor $p$-DTS(FBTTh$_2$)$_2$ as a model system to illustrate how sensitive this class of material can be to spatial confinement on device-relevant length scales. We also show that this effect can be exploited; we demonstrate, for instance, that spatial confinement is an efficient tool to direct the crystal orientation and overall texture of $p$-DTS(FBTTh$_2$)$_2$ structures in a controlled manner, allowing us to manipulate specific material’s properties including photoluminescence and charge transport characteristics. This insight should be widely applicable as we use temperature/confinement phase diagrams established via differential scanning calorimetry and grazing-incidence X-ray diffraction to identify specific processing routes that can be directly extrapolated to other functional organic materials, such as polymeric semiconductors, ferroelectrics or high-refractive-index polymers, to induce desired crystal textures or specific (potentially new) polymorphs.
1. Introduction

The promise of large-area, flexible and low-cost electronics has motivated intense research on solution processable $\pi$-conjugated organic semiconductors over the last two decades \[1\]. Typical devices manufactured from this class of semiconductors are organic field-effect transistors (OFETs), organic light emitting diodes (OLEDs) and organic photovoltaic (OPV) cells. These devices are based on architectures where the organic semiconductor is generally confined to small spatial volumes\[2\] of the same order of magnitude as the characteristic length scales of many dynamic and thermodynamic processes relevant for the material, such as crystallization, self-assembly and melting \[3\]. Frequently ignored is that the spatial restriction may cause these physical processes to develop differently relative to the same system in the bulk \[4\], often leading to altered solidification processes, changed phase behavior and thus different final solid-state structure formation. As a consequence, small modifications in confinement can affect the final material’s properties and hence device performance. Indeed, evidence of the effect of spatial constraints has been reported, including polymorphism \[5\], modification of the crystal lattice \[6\], difference in the material’s crystallinity \[7\], or the formation of special microstructural features such as extended-chain crystals\[8\] - often leading to an improvement of the material’s performance in devices\[6\]. Herein, we show how spatial restriction impacts the structural development of small-molecule semiconductors using $p$-DTS(FBTTl$_2$)$_2$ \[9\] as a model system (see Figure 1a for its for chemical structure) and controlling its degree of confinement using cylindrical nanopores of different diameters\[10\]. Nanoporous templates are ideal for this purpose as only the size/dimension of the active materials is varied. Therefore, the impact of other variables that can affect the structural behavior of materials during thin-film fabrication, e.g., non-equilibrium effects originating from processing, can be limited if not entirely hindered. Since $p$-
DTS(FBTTh2)2 can be processed from the molten state without degradation (see Supporting Information), “near-to-equilibrium phase transitions” can be expected to occur – in strong contrast to solution-deposition of thin films where the variation of the structure (and properties) with film thickness may not be solely related to the thickness but also to concentration, solvent evaporation rate, etc.

2. Results and Discussion

The phase behavior of $p$-DTS(FBTTh2)2 as a function of the degree of confinement is elucidated first in this paper. $p$-DTS(FBTTh2)2 is a good candidate for this purpose (as alluded to above) due to its easily accessible melting temperature, which allows cooling from the melt to establish its thermotropic behavior under confinement without significant thermooxidative degradation taking place (see Supporting Information for details). This material also has been shown to display a rich phase behavior\cite{11-14}, including and liquid crystalline mesophases \cite{14,15}, in addition to a thermodynamically favoured crystal phase\cite{11}. As confining media, we employed electrochemically grown nanoporous anodic aluminum oxide (AAO) \cite{15,16} comprising nanopores of 25, 40, 60, 180 and 400 nm in diameter, with a 100 µm pore length (Scanning electron microscopy (SEM) images of these AAO templates are presented in Figure S1a-f, Supporting Information).
Figure 1. (a) Chemical structure of p-DTS(FBTTh$_2$)$_2$. (b) Schematic of an AAO template containing p-DTS (FBTTh$_2$)$_2$ isolated in each nanopore. The AAO template is colored in white, while the p-DTS (FBTTh$_2$)$_2$ is shown in blue. (c) Representative differential scanning calorimetry (DSC) cooling thermograms of p-DTS (FBTTh$_2$)$_2$ confined in AAO pores of different diameters. A cooling rate of 20 °C/min was used. (d) Crystallization temperatures, $T_c$, deduced from the cooling thermograms in (c), plotted against the inverse of the pore diameter, used as an indicator of imposed lateral confinement (curved are scaled for clarity). Data for 400 nm and 180 nm include two points corresponding to the crystallizations via heterogeneous and heterogeneity-free nucleation. (e) Corresponding 2nd heating thermograms. (f) Peak melting temperatures, $T_m$, deduced from the heating scans in (e), and enthalpies of fusion ($\Delta H_f$) plotted as a function of the inverse of pore diameter.

Infiltration of p-DTS(FBTTh$_2$)$_2$ into the nanopores was achieved by wetting the AAO nanopores with molten p-DTS(FBTTh$_2$)$_2$[4c, 17]. Once p-DTS(FBTTh$_2$)$_2$ had infiltrated, the samples were quenched to room temperature. In a first set of experiments, the residual p-DTS(FBTTh$_2$)$_2$ remaining on top of the AAO templates was removed with a sharp blade. Then, samples were again molten at 240 °C for 5 min and cooled to room temperature at 20 °C/min. This procedure ensured that the nanopores were isolated nanodomains for the confined crystallization of the material, as depicted schematically in Figure 1b. As such, the entire crystallization process, namely nucleation and growth,
take place within a constrained geometry rendering it an optimal model system for elucidating the effect of two-dimensional confinement on small-molecule semiconductors’ crystallization – in contrast to the more complex thin-film fabrication process when solution-processing this small-molecular semiconductor.\[13\] SEM micrographs of exemplar p-DTS(FBTTh\(_2\))\(_2\) nanowires after being released from the porous template are also shown in Figure S1g,h, Supporting Information.

Clear signs of spatial confinement are observed in the differential scanning calorimetry (DSC) cooling scans (Figure 1c). The crystallization temperature, \(T_c\), strongly decreased with decreasing pore diameter (up to 50 °C difference in \(T_c\) is found for material confined in pores of 25 nm and the bulk, Figure 1d), demonstrating that a significant supercooling is needed to induce crystallization in the confined DTS(FBTTh\(_2\))\(_2\). This indicates that bulk p-DTS(FBTTh\(_2\))\(_2\), like most organic matter, crystallizes from heterogeneities (impurities) that are present in the melt. In contrast, the volume of the narrower pores (i.e. those below 60 nm in diameter) is significantly smaller than the average volume required for the presence of heterogeneities responsible for the heterogeneous nucleation. In this scenario, the p-DTS(FBTTh\(_2\))\(_2\) will crystallize via a heterogeneity-free nucleation mechanism, such as homogeneous nucleation. This nucleation mechanism needs to overcome high energetic barriers, meaning that it only sets in at very large supercoolings, i.e. low \(T_c\). In addition, it is important to note that heterogeneity-free nucleation mechanism depends strongly on the crystallizable material volume. This picture is in agreement with the observation of two exotherms for samples confined in 400 nm and 180 nm pores. Due to the relatively high volume of material that is present and a reduced confinement effect, it appears that both homogeneous and heterogeneous nucleation mechanisms can take place in these systems.
Further evidence for confinement effects occurring in some nanoporous templates is obtained from subsequent DSC heating runs, shown in Figure 1e, where we probed the melting of the crystalline moieties that developed during cooling from the melt in confined conditions, shown in Figure 1c. The peak melting temperatures, $T_m$, for samples confined in 400 nm, 180 nm, 60 nm, 40 nm and 25 nm pores are notably lower than that of the bulk material: we measure $T_{m,400} = 208 \, ^\circC$, $T_{m,180} = 203 \, ^\circC$, $T_{m,60} = 195 \, ^\circC$, $T_{m,40} = 190 \, ^\circC$, $T_{m,25} = 181 \, ^\circC$, respectively, compared to $T_{m,bulk} = 210 \, ^\circC$ (Figure 1f). We attribute this melting point depression in the confined samples to the reduced average size of the crystals that form within the pores. Plotting $T_m$ as function of $d^{-1}$ we find a linear dependence, as predicted by the Gibbs-Thomson equation\cite{18} (equation 1), which correlates the melting point depression to the crystal size.

$$\Delta T_m = T_0^0 - T_m(pore) = \frac{4T_0^0}{d \rho \Delta H_f^0} \gamma_{SL}$$  \hspace{1cm} \text{(Equation 1)}$$

$\rho$ in equation 1 represents the crystal density, $\Delta H_f^0$ is the heat of fusion per unit of mass, $d$ is the diameter of the crystal, $\gamma_{SL}$ is the surface energy of the crystal and $\Delta H_f^0$ and $T_m^0$ are the enthalpy of melting and the melting temperature of an infinite crystal. Accordingly, we can deduce the surface energy, $\gamma_{SL}$, of $p$-DTS(FBTTTh$_2$)$_2$ to be 19.7 mJ/m$^2$ (see Figure S4 Supporting Information for details).

It is also noteworthy that the melting endotherms become asymmetrical broadened towards the low temperature side for confined samples, indicative of both a pronounced heterogeneity in the crystalline moiety that develops under confinement and some reorganization of crystals occurring in these samples\cite{19}. When we deduce the overall degree of crystallinity from the enthalpy of fusion, $\Delta H_f$, we find that, as expected, it decreases strongly with decreasing pore diameter (Figure 1f): while $\Delta H_f \approx 48.3 \, J/g$ for
bulk $p$-DTS (FBTTh$_2$)$_2$, $\Delta H_f$ for 25-nm-samples is 11.3 J/g, which shows how effectively the material is confined within the AAO nanopores.

**Figure 2.** (a) Detailed DSC cooling (a) and heating (b) thermograms of $p$-DTS(FBTTh$_2$)$_2$ confined in pores of 25 nm, 40 nm and 60 nm allowing us to identify additional processes that occur in these samples compared to bulk $p$-DTS(FBTTh$_2$)$_2$. The arrows highlight the high-temperature thermal processes that are not discernable in Figure 1, which indicate the presence of additional phases. (c) Transition temperatures of the mesophase transitions observed upon heating, $T_{ms,h}$ (black circles) and upon cooling, $T_{ms,c}$ (blue squares) plotted against the inverse of the pore diameter. (d) GIWAXS intensity measured along the direction parallel to long axis of the pores (z-direction, Fig. 1b) collected upon cooling DTS(FBTTh$_2$)$_2$ confined in 40 nm pores.

Finally, we observe other features of low enthalpies in both the cooling and the heating DSC thermograms of strongly confined samples, i.e. in pores of 25, 40 and 60 nm (Figure 2a and 2b), indicating the presence of phase transitions that do not occur in the bulk. Interestingly, the transition temperatures (denoted here $T_{ms,c}$ for the exotherms during cooling and $T_{ms,h}$ for the endotherms detected in the heating thermograms) were found to be less sensitive to the diameter of pores than $T_m$ and the $T_c$ (Figure 2c).
In order to gain more information about the complex thermal behavior of confined p-DTS(FBTTh\textsubscript{2})\textsubscript{2}, we monitored as an example the structural evolution of p-DTS(FBTTh\textsubscript{2})\textsubscript{2} confined in 40 nm pores during cooling. Figure 2d shows the temperature-dependent diffraction intensity obtained from \textit{in situ} two-dimensional grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements. GIWAXS measurements were collected along the direction parallel to the long axis of the pores (z-direction, see Figure 1b) and integrated along the scattering vector, \(q_z\), at each temperature step to plot Figure 2d. Special care was taken to perform these measurements above the critical angles of p-DTS(FBTTh\textsubscript{2})\textsubscript{2} and alumina so as to probe the material confined in the nanopores below the sample surface, as a grazing incidence diffraction setup was employed for the analysis (see Experimental Section for more information). We found the first Bragg diffraction peaks to appear at \(\sim 185^\circ\text{C}\), the same temperature at which a the high-temperature exotherm is detected in the DSC cooling thermograms. Upon further cooling, an additional reflection, corresponding to the stack of (201) planes (see for details of the crystalline unit cell are provided in Figure S3, Supporting Information), develops at \(\sim 130^\circ\text{C}\), i.e. at the temperature of the prominent exotherm found by DSC. Since sharp Bragg reflections indicate long range molecular order, our data implies that confined p-DTS(FBTTh\textsubscript{2})\textsubscript{2} is molecularly ordered at temperatures above \(T_c\). We tentatively assign this to a mesomorphic lamellar phase (i.e. a phase that is composed of periodic alternation of layers), because the periodicity of the higher diffraction orders at increasing \(q\) is constant. Since the mesophase periodicity is equal to the \(d\)-spacing of (001) lattice planes in the crystal lattice (see Figure S5, Supporting Information), we suggest that this mesophase comprises periodic stacks of layers of the aromatic backbones and ethyl hexyl side moieties of the dithienosilole unit along the longitudinal direction of the nanopores (i.e. the z-direction). We note that no other features are detected in the GIWAXS pattern.
of this mesophase, which suggests the absence of molecular positional order within layers. As such, we conclude that the mesophase may be of smectic nature. In fact, positional order within layers starts to be observed when \( p\text{-DTS(FBTTh}_2\text{)}_2 \) crystallizes at \( \sim 130 \, ^\circ\text{C} \), as deduced from the appearance of the (201) reflection. The mesophase is also detected upon heating, as is shown in Figure S6, Supporting Information.

This raises the question why the mesophase only forms in pores smaller than 60 nm in diameter. Since \( p\text{-DTS(FBTTh}_2\text{)}_2 \) and other molecules with similar chemical structure were suggested to transiently form liquid-crystalline phases in the bulk \( p\text{-DTS(FBTTh}_2\text{)}_2 \) [14-15], we hypothesize that the presence of mesophases may be natural to this material but generally is challenging to be detected because the transition temperatures of the mesophase formation (\( T_{m,c} \)) and destruction (\( T_{m,h} \)) are too close to those of the crystalline phase (\( T_c \) and \( T_m \), respectively). In contrast, the crystallization and melting processes of strongly confined \( p\text{-DTS(FBTTh}_2\text{)}_2 \) (i.e. in pores with diameter <60 nm) are shifted to lower temperatures, allowing the mesomorphic phase to be clearly observed. In addition, the molecular anchoring on the rigid AAO pore walls may further promote the molecular orientation that can be propagated towards the center of the pores. This effect will be most pronounced for pores of small diameters.

Combining all our data and observations, we went on to establish a temperature/confinement phase diagram for \( p\text{-DTS(FBTTh}_2\text{)}_2 \), for both cooling and heating. They are displayed in Figure 3a) and summarize the rich phase behavior of the material as a function of both temperature and degree of spatial restriction (quantified in terms of inverse nanopore diameter). We also included the glass transition temperatures \( T_g \) determined according to the method shown in Figure S7, Supporting Information. According to the phase diagram, we selected three different scenarios to solidify \( p\text{-DTS(FBTTh}_2\text{)}_2 \), indicated as pathways I, II and III in Figure 3a. Pathway I corresponds
to the crystallization of bulk \( p \text{-DTS}(FBTTh_2)_2 \), pathway II to crystallization inside 400 nm diameter pores (i.e. weak confinement), and pathway III to crystallization inside 40 nm diameter pores (i.e. pronounced confinement). Interestingly, depending on the pathway selected, different crystal textures are induced. This can be deduced by following the structural evolution along these cooling pathways using GIWAXS (cooling rate \( \sim 40 \, ^\circ C/\text{min} \), \( q = q_z \)) (Figure 3b).

We start our discussion with pathway I: bulk solidification. As the bulk material was cooled from the melt, we observed the simultaneous appearance at \( T_c \sim 180 \, ^\circ C \) of multiple diffraction features (Figure 3b, left panel), which we attribute to the crystallization of the material. This leads to an isotropic polycrystalline structure, indicated by the ring-like signals in the room temperature GIWAXS pattern presented in the left panel of Figure 3c. Indexation of the GIWAXS diffraction patterns was performed using the crystal lattice shown in Figure S3, Supporting Information. In this lattice, \( \pi - \pi \) stacking can be describe by the (141) plane, whilst orthogonal to this, the molecules pack in alternating stacks of aromatic backbones and ethyl hexyl side chains of the dithienosilole unit describing the (001) planes. We note that this cell is fundamentally in accordance with that reported by Love et al. for \( p \text{-DTS}(FBTTh_2)_2 \) single crystals\(^{11}\).
Figure 3. (a) Temperature/confinement phase diagrams for \( p \)-DTS(FBTTh\(_2\))\(_2\) for cooling (left panel) and heating (right panel). The dark-grey shading corresponds to the T/confinement region where \( p \)-DTS(FBTTh\(_2\))\(_2\) is in either a glassy or crystalline state depending on the cooling rate applied. Light grey shading corresponds to the region where \( p \)-DTS(FBTTh\(_2\))\(_2\) is crystalline. Blue shading corresponds to conditions where the layered mesophase is formed, while the white region corresponds to the isotropic liquid. Cooling pathways I, II and III are indicated. (b) GIWAXS intensity measured along the \( z \)-direction upon cooling at 20 °C/min from 240 °C to room temperature for, respectively, bulk \( p \)-DTS(FBTTh\(_2\))\(_2\) (pathway I, left panel), \( p \)-DTS(FBTTh\(_2\))\(_2\) confined in 400 nm pores (pathway II, central panel) and \( p \)-DTS(FBTTh\(_2\))\(_2\) confined in 40 nm pores (pathway III, right panel). (c) Room temperature GIWAXS diffraction patterns of \( p \)-DTS(FBTTh\(_2\))\(_2\) samples crystallized through the pathways I (i.e. for bulk, left panel), pathway II (i.e. confinement in 400 nm pores, central panel) and pathway III (i.e. confinement in 40 nm pores, right panel) [Note: grey circles indicate crystallization temperatures; grey squares melting temperatures; blue down-pointing triangles mesophase formation; blue up-pointing triangles mesophase melting; dark grey pentagons glass transition temperatures].
Using pathway II, we detected the appearance at $T \approx 170$ °C of several diffraction maxima (Figure 3b, central panel), which we also attributed to the crystallization of the material, in agreement with our DSC data (Figure 1c). Clearly, $p$-DTS(FBTTh$_2$)$_2$ passes directly from an isotropic liquid to a crystalline phase when using this pathway, similar to bulk $p$-DTS(FBTTh$_2$)$_2$. However, in contrast to bulk solidification, a highly defined crystalline texture is induced in this confinement scenario with a large fraction of crystals orienting with their (201) lattice planes normal to the long axis of the pores (Figure 3c central panel). This preferred crystal orientation may result from a low crystal nucleation density of $p$-DTS(FBTTh$_2$)$_2$ crystals due to a reduced number of impurities present in the pores (note that number of impurities per pore must be low because our DSC data indicates that homogenous nucleation occurs in addition to heterogenous nucleation). A low nucleation density means that crystals within the pores can propagate over long distances. Following a “Bridgman-mechanism”\cite{20} for crystal propagation within capillaries, crystals can accordingly align along the crystallographic direction featuring the fastest growth rate with the long axis of the capillaries, which, in this case coincides with that in which (201) planes are normal to the long axis of the pores.

For pathway III, we also find a pronounced texture, yet the dominant crystal orientation in these samples is that where (001) planes lay normal to the long axis of pores (Figure 3c right panel). This finding suggests that during crystallization the crystals retain the molecular orientation of the mesophase. This may not be surprising. As discussed above, at $\sim 185$ °C a layered mesophase with the same periodicity as the crystalline (001) planes is formed, where layers are oriented perpendicularly to the pore’s longitudinal axis - despite further cooling to temperatures below $\sim 130$ °C, positional order within the aromatic layers is retained. Similar observations can be made for $p$-DTS(FBTTh$_2$)$_2$ confined in 25 nm and 60 nm pores (Figure S8, Supporting Information). The relative
population of (201) planes normal to pore axis decreases with the pore diameter (Figure S6, Supporting Information), suggesting that the ordering of the layered mesophase depends on the surface-to-volume ratio of the pores.

Having established that we can use confinement to induce mesophases and control the crystal texture of $p$-DTS(FBTTh$_2$)$_2$, we further scrutinized our approach, this time solidifying $p$-DTS(FBTTh$_2$)$_2$ confined in pores but in contact with a macroscoposcopic drop of molten $p$-DTS(FBTTh$_2$)$_2$, called the surface reservoir, located on the template surface as depicted in Figure 4a. Whilst following the same crystallization protocols as before, that is cooling the system from the melt at 20 °C/min through different regions of the temperature/confinement phase diagram, this represents a different scenario due to the presence of the surface reservoir, with each pore no longer an isolated entity. As such, the total volume of crystallizing material is considerably larger than the average volume required for the presence of a heterogeneity. Therefore, upon cooling, solidification via heterogeneous nucleation at crystallization temperatures similar to bulk $p$-DTS(FBTTh$_2$)$_2$ ($T_c \sim 180 ^\circ \text{C}$) can be expected to occur. Crystal nuclei will thus first develop in the reservoir (because the probability of finding heterogeneities in the surface reservoir is far higher than in the nanopores due to the large volume difference). These nuclei will develop isotropically into crystals that grow in the direction of the pores, and then propagate through the material contained within them. Accordingly, no further nucleation events take place inside the pores and crystallization of confined $p$-DTS(FBTTh$_2$)$_2$ is governed solely by crystal growth. Hence, a “Bridgman-mechanism” for propagation of the fast-growing crystallization modes will likely dictate the crystal orientation.
Figure 4. (a) Schematic of the samples where the confined $p$-DTS(FBTTh$_2$)$_2$ is attached to a macroscopic surface reservoir of the material. The AAO template is colored in white, while the $p$-DTS (FBTTh$_2$)$_2$ appears in blue. (b) Room temperature GIWAXS diffraction patterns of bulk $p$-DTS(FBTTh$_2$)$_2$ and $p$-DTS(FBTTh$_2$)$_2$ solidified with surface reservoir confined in 400 nm pores (c), 60 nm pores (d), 40 nm pores (e), and 25 nm pores (f). (g) Representative DSC heating thermograms of confined $p$-DTS(FBTTh$_2$)$_2$ solidified in this manner. (i) Peak melting temperatures, $T_m$, (black) and enthalpies of fusion ($\Delta H_f$, blue) plotted against the inverse of the pore diameter.

Figure 4c-f show that $p$-DTS(FBTTh$_2$)$_2$ nanostructures solidified in this matter exhibited either (201) or (141) planes oriented normal to pore long axis independent of the region of the phase diagram in which the processing was carried out. The clear majority of crystals within 400 nm (Figure 4c), 60 nm (Figure 4d) and 40 nm (Figure 4e) are oriented with the (201) planes normal to the long axis of the pores. Interestingly, the population of (141) planes normal to the long axis of the pores increases when the pore diameter decreases (see Figure S9, Supporting Information). Indeed, the (141) planes, associated with $\pi-\pi$ stacking stacking, dominates in samples confined within 25 nm pores (Fig 4f), providing an additional texture for $p$-DTS(FBTTh$_2$)$_2$. [Note that (201) or (141) planes
have also been observed normal to the longitudinal axis of the ribbon-like crystals of thin films processed from solutions.[13]

While additional crystal orientations can be realized in this solidification scenario, we highlight that the melting temperature depression in these solidified samples is significantly smaller than in samples crystallized without a surface reservoir (Figure 4h). Moreover, the degree of crystallinity (deduced from $\Delta H_f$) of these $p$-DTS(FBTTh$_2$)$_2$ nanostructures does not vary notably. This suggests that as expected, nanopore size does not conflict with the characteristic length scales of the $p$-DTS(FBTTh$_2$)$_2$ crystal growth process. The endotherm associated with the mesomorphic transition is nonetheless still clearly visible in the thermograms for the 25, 40 and 60 nm samples (Figure 4g), while it is absent in samples with less confinement.
Having characterized the effect of the spatial confinement on the microstructure of \( p\)-DTS(FBTTh\(_2\))\(_2\), we used our samples as model systems to probe how specific properties, namely photoluminescence spectral shape and charge transport characteristics, vary with pore size and the presence of a surface reservoir. We first assessed the impact of confinement on the optoelectronic properties of our samples by means of time-resolved microwave conductivity (TRMC) measurements. TRMC is a contactless spectroscopic probe, sensitive to both photo-induced charge carrier density and mobility. Full descriptions of this technique are available elsewhere.\(^{[21]}\) Briefly, we measure the transient microwave absorption of microwave energy (~9 GHz) by our confined \( p\)-DTS(FBTTh\(_2\))\(_2\) structures in response to a laser pulse (600 nm, 5 ns FWHM). Careful calibration of the instrument allows us to convert this transient microwave absorption to a quantitative value of the photoconductivity, expressed as the product of photo-induced charge carrier yield and the sum of the electron and hole mobilities, denoted \((\phi \Sigma \mu)\). TRMC transients of samples crystallized with surface reservoir and without surface reservoir are presented in Figure 5a and 5b, respectively.

Interestingly, TRMC measurements revealed that confinement increases the yield-mobility product, \((\phi \Sigma \mu)\), of \( p\)-DTS(FBTTh\(_2\))\(_2\). All spatially confined \( p\)-DTS(FBTTh\(_2\))\(_2\) samples showed higher \((\phi \Sigma \mu)\) values than bulk \( p\)-DTS(FBTTh\(_2\))\(_2\) (Figure 5c-f). Thereby, a correlation can be observed between the \((\phi \Sigma \mu)\) and the pore diameter (Figure 5c and 5e), independent of the crystalline texture of \( p\)-DTS(FBTTh\(_2\))\(_2\) nanostructures for the <201> and <001> orientations. This behavior may be related to the degree of crystallinity of the...
confined samples, as implied by the data presented in Figure 5d and 5f. For example, Figure 5d shows the relation of $\phi_{\Sigma \mu}$ of samples crystallized with surface reservoir plotted against the crystallinity, where a clear trend is observed for samples confined in pores larger than 25 nm, i.e. for samples with (201) and (001) planes oriented normal to nanopore length axis. Strikingly, the 25-nm-sample seems to deviate from the general behavior. We speculate that the special behavior of $p$-DTS(FBTTh$_2$)$_2$ confined in 25 nm pores might result from the fact that the $\pi-\pi$ stacking direction in this sample has a well-defined orientation – it is orthogonal – with respect to the microwave field, which is perpendicular to the pore’s long axis. Conversely, in the rest of samples, the $\pi-\pi$ stacking direction is isotropic with respect to the electric field vector. These results clearly illustrate that confinement has a major impact on the photoconductivity of small-molecule semiconductors. However, our results also demonstrate that the connection between the size of the material and its transport behavior is complex and further work is required in order to fully understand this relationship.
Figure 6. Photoluminescence (PL) spectra taken at 290 K and 10 K for confined \( p\)-DTS(FBTTh\(_2\))\(_2\) nanostructures crystallized with a surface reservoir (a, b) and without (c, d). The emission spectra from bulk material is shown shaded in grey for comparison.

PL spectra of the different \( p\)-DTS(FBTTh\(_2\))\(_2\) nanostructures and bulk samples (Figure 6a and 6c) showed relatively minor differences at room temperature (290K) (Figure S3; note that the Supporting Information shows the reference PL spectra for AAO templates in the wavelength range analyzed). Some variation in the underlying electronic structure can however be identified from the changing intensities at \( \sim 750 \) nm (i.e. vibronic 0-0 transition) and \( \sim 920 \) nm (0-2 transition) relative to bulk \( p\)-DTS(FBTTh\(_2\))\(_2\) when normalized to the 0-1 transition at 815 nm. The 0-0/0-1 ratio in molecular aggregates in a weak coupling limit, such as those investigated here is governed by a competition between long-range Coulombic coupling, which induces H-aggregate behavior (suppression of 0-0 PL intensity), and short-range charge-transfer-mediated coupling, which induces J-like behaviour\(^{[22]}\) (enhancement of 0-0 intensity). In contrast, variations in the 0-2 intensity (\( \sim 920 \) nm) relative to 0-1 maps changes in the Huang-Rhys parameter associated with the molecular vibronic progression, which indicates relative differences in nuclear rearrangement between ground and excited states.

To better resolve these spectral differences, PL was recorded at 10K (Fig 6b and 6d), as the low temperature limits the effects of inhomogeneous broadening. We note that the relative 0-0 intensity is highest in the 180 nm pore film (attributed to an orientation where (201) planes are normal to pore axis), indicating enhanced J-like character. In all films, except that with 400 nm pores, the 0-2/0-1 ratio is higher than in bulk \( p\)-DTS(FBTTh\(_2\))\(_2\), indicating a lower reorganization energy, perhaps indicative of a more rigid conformation compared to the bulk. Interestingly, we note a substantial change in spectral shape and location of the emission from the 25 nm pore film (with surface film), attributed to a
crystal oriented with (114) planes normal to pore axis. This softening of the effective mode in conjunction with the change in relative peak intensities (0-2 becomes most pronounced), relative to the same sample at 290 K, suggests a temperature dependent change in crystal structure (phase transition) and thus the $p$-DTS(FBTTh$_2$)$_2$ chromophores’ environment, which only occurs under very strong confinement.

3. Conclusions

We have demonstrated strong spatial confinement effects on the structural behavior of $p$-DTS(FBTTh$_2$)$_2$. Isotropically oriented crystals are induced in bulk $p$-DTS(FBTTh$_2$)$_2$; samples with clear texture having the (201) lattice planes oriented normal to the long axis of the nanopores were produced when $p$-DTS(FBTTh$_2$)$_2$ was crystallized under weak confinement conditions. In contrast, crystal with the (001) planes normal to nanopore axis are obtained in highly confined $p$-DTS(FBTTh$_2$)$_2$. In the case solidification is performed in the presence of the surface reservoir, crystals with (201) planes normal to nanopore axis were detected in pores larger than 60 nm, while a (114) crystals were dominant in 25 nm pores. This allowed us to compare how specific properties – photoconductivity and photoluminescence – depend on the size of the $p$-DTS(FBTTh$_2$)$_2$ nanodomain. As importantly, the formation of a mesophase was detected in DTS(FBTTh$_2$)$_2$ at high degrees of confinement, which supports previous reports that confinement may be important in thin-film formation for device fabrication.

Unambiguously, our work shows that confinement effects cannot be neglected when processing organic semiconductors. Many of our observations are in agreement with findings made on thin-film structures: In thin-film confinement, $p$-DTS(FBTTh2)$_2$ crystals were reported to form wire-like structures that propagate throughout the films with characteristic widths of 30–50 nm and lengths of hundreds of nanometers.$^{[11]}$ These
wire-like structures are remarkably similar to the ones that we observe within the nanopores of AAO templates. Therefore, from the point of view of microstructure development, AAO pore confinement seems to be very similar to the one of thin films; in both p-DTS(FBTTh2)2 has the tendency to aggregate into one-dimensional nanostructures. Our observations also concur with those made by Abdelsamie *et al.* [13] who have recently shown that p-DTS(FBTTh2)2 develops liquid mesophases in thin-film architectures, similar to what we observe in nanopores. This implies that in devices such as OLEDs, OPVs and OFETs confinement effects need to be considered otherwise small variations in the processing conditions will lead to different confinement scenarios, and hence different properties, as we show here.

4. Experimental Section

**Materials.** p-DTS (FBTTh₂)₂ was purchased from 1Materials, Canada. Self-ordered anodic aluminum oxide (AAO) templates with pore diameters of 25 nm, 40 nm, 60 nm, 180 nm and 400 nm, and a pore depth of 100 µm were obtained from SmartMembranes GmH (Germany).

**Sample preparation.** p-DTS (FBTTh₂)₂ was infiltrated inside the AAO nanopores by melt wetting [5c, 18]. First, the AAO templates were sonicated in solvents of different polarity (hexane, acetone, isopropanol and water) to remove organic molecules attached to the pore walls, which decrease the surface energy of the walls. p-DTS (FBTTh₂)₂ chunks were then placed on the surface of the AAO templates and melted at 240 °C under nitrogen atmosphere. Molten p-DTS (FBTTh₂)₂ is a low surface energy liquid that spontaneously enters in the AAO nanopores in order to wet the pore walls, which are of high surface energy. After 10 min, pores are filled with p-DTS (FBTTh₂)₂ and the samples
were cooled down to room temperature at 20 °C/min. Finally, the residual $p$-DTS (FBTTh$_2$)$_2$ located on top of the AAO templates was removed with a sharp blade so that the $p$-DTS (FBTTh$_2$)$_2$ within the AAO were isolated entities separated from each other. We scrutinize that $p$-DTS (FBTTh$_2$)$_2$ does not degrade via differential scanning calorimetry using the same conditions as during the infiltration experiments. Subsequent heating scans were identical, illustrating the material did not degrade under these conditions (heating to 240 °C/N$_2$ environment; see Supporting Information S9).

**Characterization.** The morphological characterization of the samples was conducted by scanning electron microscopy (SEM, Hitachi SU8000) with 0.5 kV accelerating voltage. For the exploration of the $p$-DTS (FBTTh$_2$)$_2$ nanostructures, these were from the template with NaOH (10 wt.%). A Mettler–Toledo DSC1 Star differential scanning calorimeter (DSC) was used for the thermal characterization of the samples. Heating and cooling runs at 20 °C/min were carried out under a constant flow of nitrogen. For the DSC study, the aluminum substrates attached to the AAO templates were selectively etched employing a mixture of 1.7 g CuCl$_2$•H$_2$O, 50 ml concentrated HCl and 50 ml deionized water. The glass transition temperatures ($T_g$) of the nanoconfined $p$-DTS(FBTTh$_2$)$_2$ samples were measured at 100 °C/s employing a fast scanning calorimeter (Flash DSC 1, Mettler Toledo). Prior to these measurements, samples were rapidly quenched into the glassy state from 240 °C to -50 °C at 5000 °C/s. AAO- $p$-DTS (FBTTh$_2$)$_2$ ensembles were powdered in an agate mortar and then placed on the chip sensor, which contained a fluorinated oil to enhance the thermal transport between the sample and the sensor surface. Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS) experiments were conducted at D-line, Cornell High Energy Synchrotron Source (CHESS) at Cornell University. Special care was taken to perform these measurements above the critical
angles of p-DTS(FBTTh₂)₂ and alumina so as to probe the material confined in the nanopores buried below the surface (see Experimental Section for more information). A wide band-pass (1.47%) X-ray beam with a wavelength of 1.155Å was shone on the samples with incidence angles between 0.5° and 1°. A Pilatus 200k detector with a pixel size of 172μm was placed at a distance of 16.5 cm from the samples. A 1.5 mm wide molybdenum rod was used to block the intense scattering in the small-angle area. The exposure time for room temperature measurements was 1s. The nanowire arrays were placed in the set up so that the p-DTS (FBTTh₂)₂ nanowires (i.e. the longitudinal axis of the nanopores) were aligned with the vertical z-direction (Fig 1b). For the temperature resolved WAXS measurements, a hot stage with a water-cooled base was employed and a cooling rate of approx. 40 °C/min was applied. Microwave conductivity Transient microwave-frequency absorption (TRMC) of nanostructures were measured in response to 600 nm, 5-ns laser pulse, (Spectra Physics Quanta-Ray Pro 230/30 & GWU PremiScan OPO). Samples were mounted near the electric-field maximum of an X-band TE₁₀₂ microwave resonance cavity tuned to ~9 GHz. The samples were sandwiched between a pair of fused quartz slides to provide mechanical support, and inserted in a specially machined waveguide cavity, which was loaded and sealed in a nitrogen glovebox. The sensitivity factor of this arrangement, necessary for converting microwave power loss into a quantitative transient photoconductivity, was calculated through finite element simulations of the field distribution in the cavity, as described elsewhere.[22b]

Photoluminescence (PL). PL measurements were performed on the p-DTS(FBTTh₂)₂-AAO ensembles at room temperature and 10 K following excitation at 620 nm. Empty AAO templates showed flat emission as shown in the Fig. S7 Supporting Information. The samples were inside a helium filled gas cooled closed-cycle cryostat, with emitted light collected perpendicular to excitation and focused into an optical fibre after passing
through a 650 nm low-pass filter to attenuate incident beam reflections. An Andor SR-163 spectrometer was then used to disperse the emitted light onto a CCD (Andor i-Dus). Spectra had a constant background subtracted (due to experimental background drift), before correcting with a calibration file derived from a known light source to account for detector response. Finally, the presented spectra were peak normalised. No changes aside from temperature were made to the optical configuration between measurements.

Supporting Information.

Supporting Information is available from the Wiley Online Library or from the author.

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We demonstrate strong spatial confinement effects on the structural behavior of the small-molecule semiconductor $p$-DTS(FBTTh)$_2$. We show that spatial confinement is an efficient tool to direct the crystal texture of $p$-DTS(FBTTh)$_2$ structures in a controlled manner, allowing us to manipulate specific material’s properties including photoluminescence and charge transport characteristics.