

Homeotropic alignment through charge-transfer-induced columnar mesophase formation in an unsymmetrically substituted triphenylene derivative*

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Abstract: An unsymmetrically substituted triphenylene, with two adjacent chloroethoxyethyl lateral flexible chains, was synthesized and characterized. Although this compound showed no mesomorphic behavior, it formed a donor–acceptor charge-transfer complex with 2,4,7-trinitrofluorenone (TNF). The resulting 1:1 complex has been investigated using UV–vis and IR spectroscopy, optical microscopy, thermal analysis, and X-ray diffraction. A columnar mesophase with hexagonal symmetry was found. More interestingly, this charge-transfer complex can be easily aligned on a glass surface in a homeotropic orientation, which is stable at room temperature (RT) and over a wide temperature range.

Keywords: charge-transfer complex; columnar mesophase; homeotropic alignment; triphenylene.

INTRODUCTION

The first report of liquid-crystal phases as a fourth state of matter is credited to F. Reinitzer in 1888 from his observations of cholesterol esters [1]. It was soon identified that a general structural template for liquid-crystal-phase formation was rod-shaped (calamitic) molecules containing rigid and flexible parts. It was not until 1977 that liquid-crystal phases from disk-like molecules were first identified by Chandrasekhar [2]. These so-called discotic materials generally consist of a planar, disc-shaped core surrounded by a number of relatively long flexible chains around the periphery. They most commonly form columnar liquid-crystal phases in which the molecular cores stack in columns. Discotic nematic phases are also known but are observed less frequently.

Discotic liquid crystals (DLCs) can now be formed from a large variety of aromatic cores, and a number of review papers have appeared in recent years [3–10]. The most extensively studied discotic molecules are based on the cores of phthalocyanines and porphyrins [11], triphenylenes [12–14], hexa-

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peri-hexabenzocoronenes (HBCs), and the larger graphenes [15]. Interest in the structures stems in part from the discovery of low-dimensional charge transport (with mobility along the columns favored) and potential application in optoelectronic devices [4,16].

Central cores other than hard aromatic disks can also be designed to organize via self-assembly and form columnar mesophases. These include dendritic structures [17,18], calixarene [19], and crown-ether [20] cores. Indeed, we recently reported crown-ether-linked triphenylenes which show columnar mesophase behavior [21]. It has also been demonstrated that columnar mesophases may be induced [22] or manipulated [23,24] by self-assembly of non-disk-like molecules via intramolecular interactions, such as hydrogen bonds [25,26], dipole–dipole, or charge-transfer effects [27].

Contributions of charge-transfer interactions to the formation of the supramolecular structures has attracted a great deal of interest from scientists and engineers [28–30]. Many potential mesogenic DLC species have extended aromatic cores and are electron-rich. They are, therefore, excellent candidates for forming charge-transfer complexes with flat electron-deficient molecules, such as non-liquid-crystalline electron acceptor 2,4,7-trinitrofluorenone (TNF) [31]. It has been found that charge-transfer interaction has a profound effect on the induction and stabilization of mesophases [32]. An interesting example is the creation of a columnar nematic and columnar hexagonal phase by mixing non-liquid-crystalline multiynes with TNF [33]. Trifluoroacetic acid (TFA) is another candidate, its ability to broaden a mesophase transition temperature range and even induce mesomorphism when used as a dopant was found accidentally in systems containing alkyloxy discotic compounds. It was suggested that the induction of the mesomorphic properties in these systems is due to even stronger interaction in a charge-transfer complex, the oxonium ion complex [34]. In many such examples of charge-transfer complexes forming mesophases, it is impossible to determine whether mesophase formation results from the charge-transfer interaction itself or rather from the more subtle shape and packing changes resulting from face-to-face complex formation. Bushby and co-workers have examined a series of electron-rich and -poor discotic structures and explained the mesophase formation in mixtures based on complementary polytopic interactions (CPIs) [35–37].

One of the key factors in determining the utility of discotic materials in devices is being able to control their stable molecular assembly and orientation. Structures with substantial orientation (alignment) have optimized materials properties. To use discotic materials in organic optoelectronic device applications, the control of macroscopic orientations of columnar superstructures on surfaces remains a challenging issue. According to the application, discotic columns need to be assembled in two ways: a homogenous (planar or edge-on) alignment has edge-on orientation of the molecules with columns parallel to the substrate, or a homeotropic (face-on) alignment has the columnar axes perpendicular to the substrate. The former can be used to construct field-effect transistors [38], and the latter is expected to be beneficial for the performance in photovoltaic cells [39] or light-emitting diodes [40]. Alignment of columnar mesophases has proved more challenging than for the typical calamitic nematic materials used in traditional display devices. It was found that molecular alignment on the substrates is governed by a numbers of factors including the selection of substrate surface and treatments [41,42], chemical structure of the molecules [43–45], and thermal history [46].

Orientation of triphenylene derivatives on different surfaces has been investigated by many researchers [47,48]. A successful homeotropic alignment of a hexapentyloxytriphenylene (HPT) in-between a quartz and an Al-coated surface was reported by Adam [49] along with their first photoconductivity measurement in discotic liquid-crystal phases. Gearba et al. reported a homeotropic alignment of phthalocyanines on nanopatterned surfaces fabricated by means of friction transfer of polytetrafluoroethylene (PTFE) [50]. It was found that the type of columnar phase is crucial for the homeotropic orientation on PTFE-rubbed substrates, with thermal cycling through the hexagonal phase giving the best results. Another way to create homeotropic alignment is the use of a template (e.g., nanoporous alumina) to guide the alignment of 2-adamantanoyl-3,6,7,10,11-penta(1-butoxy)triphenylene [51]. However, this procedure is rather laborious, and it is impossible to fill the nanometer-size pores efficiently.

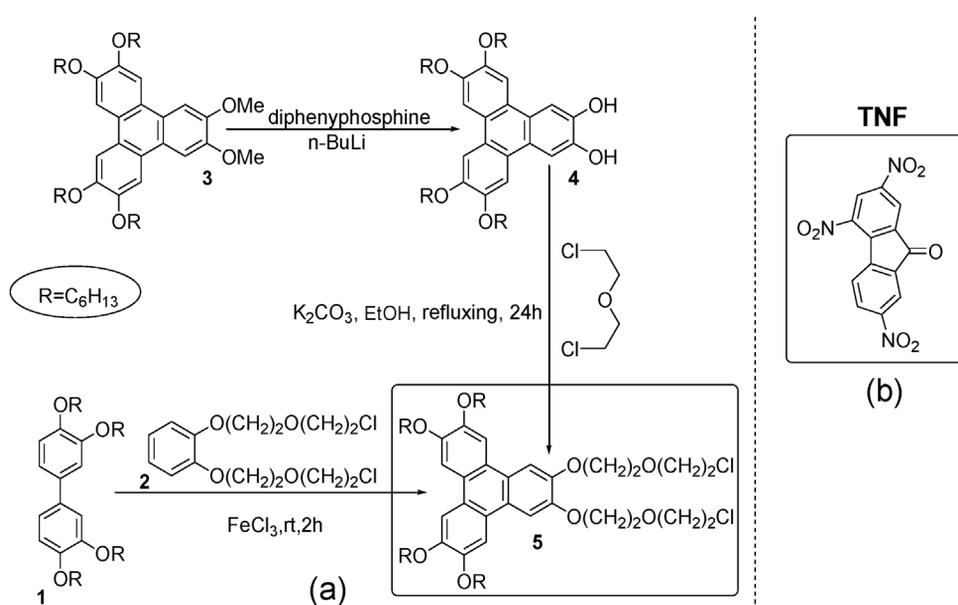
Other techniques have also been developed to produce homeotropic alignment, such as alignment in a magnetic field [52,53]. For example, Shklyarevskiy reported a 10-times enhancement in a field-effect transistor measured carrier mobility in magnetic field aligned hexa(4-dodecylphenyl)hexa-*peri*-hexabenzocoronene specimen [53]. Photoaligning of an azobenzene-containing polymer was also reported to align and micropattern discotic liquid-crystal films [54]. More recently, a free electron laser (FEL) with a highly tuned pulsed laser beam of a variety of wavelengths from UV to far-infrared (0.3–20 μm), including mid-infrared light, has been developed. Tuning the wavelength of the laser pulse for various infrared absorption bands of the mesogens in FEL, a chemical bond can be selectively excited to photoinduce alignment change in liquid-crystalline domains. A completely homogeneous alignment from a homeotropically aligned hexagonal columnar phase of 2,3,6,7,10,11-hexakisheptyloxytriphenylene [55], or homeotropic alignment from the plastic mesophase of 2,3,6,7,10,11-hexabutyloxytriphenylene [56] can be achieved.

In order to allow the use of DLCs in device fabrication, thin films ideally should be built in a layer-by-layer manner. Homeotropic alignment of discotic materials between two solid substrates does not guarantee a homeotropic alignment in an open film on a single substrate with the other side free-standing in contact with air. A number of recent efforts have been dedicated to addressing this particular issue. Gearba et al. achieved spontaneous formation of macroscopic homeotropically aligned liquid-crystal monodomains on nanopatterned surfaces fabricated by means of friction transfer of PTFE where the a^* vector of the hexagonal liquid-crystal lattice is parallel to the rubbing direction [50]. In 2008, Charlet et al. achieved a homeotropic alignment of an ultrathin film of benzo- $[g,h,i]$ -perylene-1,2,4,5,10,11-hexacarboxylic-1,2-di-(2-ethyl-hexyl)-ester-4:5,10:11-di-(4-heptyl)-imide on indium tin oxide (ITO) surface after UV ozone or nitrogen plasma treatments [57]. More recently, homeotropic alignments of 2,7-biscarbethoxy-3,6,10,11-tetrapentyloxytriphenylene on a variety of substrates with a wide range of thickness were also obtained by cooling from the columnar mesophase or annealing [58]. Schweicher et al. made an interesting comparison and concluded that the existence of a hexagonal columnar mesophase (Col_h) is a necessary condition for observing homeotropic alignment [59], supporting previous observations.

In this work, we demonstrate a preliminary but interesting study on homeotropic alignment via a charge-transfer-complex-induced mesophase. An unsymmetrically substituted triphenylene derivative **5** was synthesized. Although **5** is non-mesomorphic in nature, it is found that a stable columnar liquid-crystalline phase can be induced via complexation with TNF. The identification of the complex and the induction of the liquid-crystalline phase are also discussed. Although the stabilization or induction of mesophase by charge-transfer effects have been reported extensively and the list of dopants has also been extended to several families, there is no report on the alignment behavior for such induced liquid-crystalline systems and the stability of such alignment.

RESULTS AND DISCUSSION

2,3-Bis(chloroethoxy)ethoxy triphenylene **5** was synthesized following the procedures as shown in Scheme 1 [21]: 2,3-dimethoxy-6,7,10,11-tetrakisheptyloxytriphenylene (**3**) was prepared as previously described [60]. It was demethylated using *n*-butyllithium and diphenylphosphine at -78°C to obtain dihydroxytriphenylene (**4**) [61]. Alkylation of **4** with an excess of bis(2-chloroethyl) ether gave the target material 2,3-bis(chloroethoxy)ethoxy triphenylene (**5**). The crude product was purified by column chromatography (eluting with ethyl acetate/petroleum ether 1:4) to give pure compound **5** as a white solid (yield 0.13 g, 20 %). A different route was also used to synthesize **5** via FeCl_3 -mediated oxidative coupling between biphenyl (**1**) and 1,2-bis(chloroethoxy)ethoxybenzene (**2**) [5,12,44]. A higher yield (36 %) was obtained via this route, but it was overall equally efficient by either synthesis. Triphenylene **5** was characterized [62] by ^1H NMR, ^{13}C NMR, elemental analysis, and mass spectrometry [21].



Scheme 1 (a) Two synthetic routes were used to prepare target unsymmetrical chloroethoxy triphenylene **5**; (b) the molecular structure of TNF.

Both TNF and TFA were selected as acceptors to prepare complexes by mixing with 2,3-bis(chloroethoxy)ethoxy triphenylene (**5**) as donor. The preparation procedures involved mixing dichloromethane solutions of **5** and an equal molar ratio, i.e., $n_{\mathbf{5}}:n_{\text{TNF}}$ (or n_{TFA}) = 1:1, with one of the acceptors (either TNF or TFA). We denoted such specimens prepared by mixing as [**5**:TNF] or [**5**:TFA] after solvents were removed at a reduced pressure at room temperature (RT). Charge-transfer complex formation following these mixing processes caused a distinct change in color from colorless **5** or lightly colored TNF to dark brown color in [**5**:TNF]. TFA was also colorless while [**5**:TFA] is lightly colored.

Initial evidence to support the formation of a charge-transfer complex was therefore their changes in colors and hence in absorption spectra. UV-vis absorption was measured (Perkin Elmer Lambda 35) by drop-casting films on quartz from a dichloromethane solution and then dried. Neat compound **5** and TNF have almost no absorption in the visible spectral range, while a broad absorption at longer wavelength was developed in [**5**:TNF] (see Fig. 1). This low energy absorption indicates the formation of the charge-transfer complex in the mixture. In order to find further structural identification in the complexes, Fourier transform infrared (FT-IR) absorption spectra of **5**, TNF and [**5**:TNF] were measured (on Bruker IR spectrometer ECTOR22) in an attempt to characterize structures. It was found from Fig. 2 that the IR spectra from [**5**:TNF] show the character of both components, but with their major absorption at 1629 cm⁻¹ from **5** (responsible for C-C aromatic stretching vibration [63]) and 1533 cm⁻¹ from TNF (the character absorption of NO₂) was slightly altered. This may relate to the interaction between the core of triphenylene and polar NO₂ group of TNF.

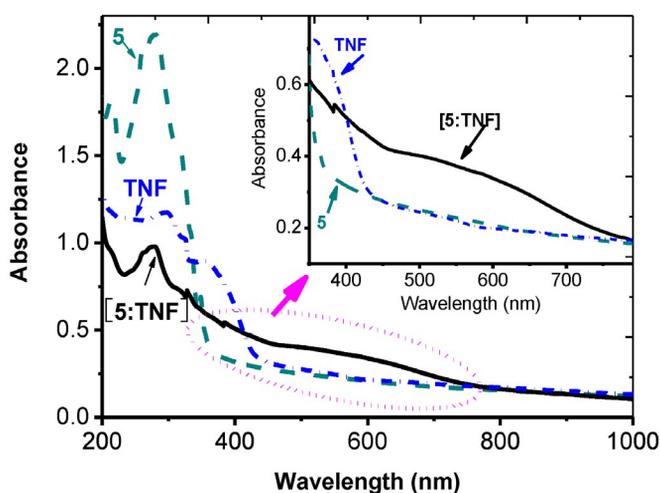


Fig. 1 UV-vis absorption spectra obtained from films of [5:TNF] (solid line), **5** (dashed line), and TNF (dash-dotted line).

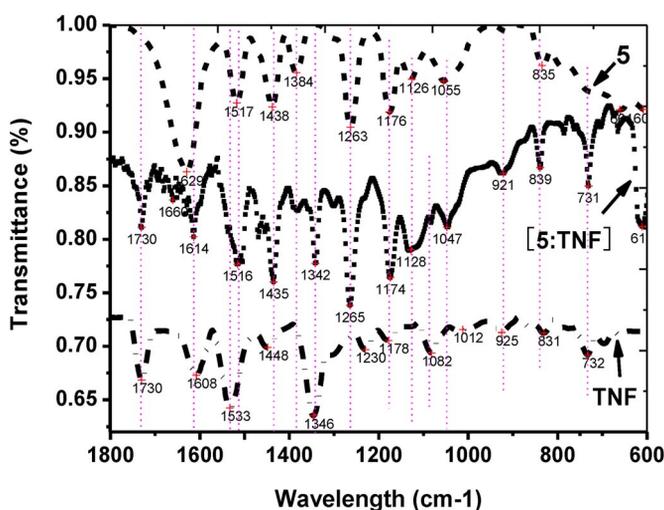


Fig. 2 FT-IR spectra of [5:TNF] (scattered), **5** (dashed line), and TNF (dashed-dotted line).

The most dramatic change in properties on charge-transfer complex formation was on thermal behavior. Chloroethoxy triphenylene derivative **5** is a crystalline compound, and it melts directly to an isotropic liquid at 78 °C (polarizing optical microscopy, Leica DMRX/Linkam THMSE 600) upon heating and recrystallizes without forming an intermediate mesophase at 66 °C. The transition temperatures were consistent with results measured by differential scanning calorimetry (DSC) (Thermal Analysis Q100) at a scanning rate of 20 °C/min (Fig. 3a), where a peak melting temperature of **5**, $T_{M,5} = 80.6$ °C (change of enthalpy, $\Delta H = 54.82$ J/g) on heating and a crystallizing temperature $T_{C,5} = 63.1$ °C ($\Delta H = 56.50$ J/g) on cooling were obtained. Two additional weak peaks were repeatedly detected in DSC scans, with $T_1 = 27.7$ °C and $T_2 = 36.0$ °C during heating and $T_1' = 13.6$ °C and $T_2' = 25.9$ °C during cooling.

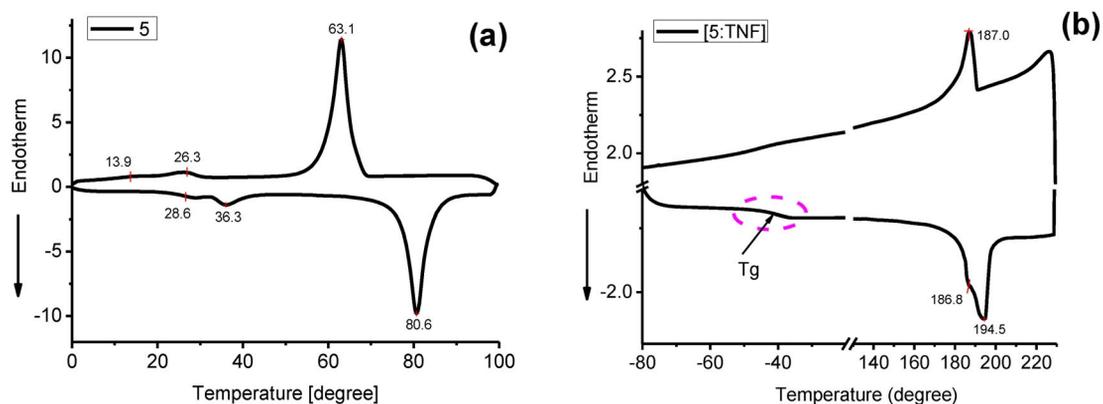


Fig. 3 DSC heating and cooling runs from **5** (a) and **[5:TNF]** (b) at a scanning rate of 20 °C/min.

TNF is also a crystalline material with a melting temperature as measured to be 176–177 °C (reported 175.2–177.0 °C [64]). The complex **[5:TNF]** showed completely different phase transitions, measured using both polarized optical microscopy and DSC. At RT, specimen **[5:TNF]** was a soft, sticky, and birefringent (when sheared) material as shown in Fig. 4a. When slowly heated at 1 °C/min, a distinct texture change can be observed around 186 °C (in Fig. 4b), and it cleared at around 201 °C. During cooling at the same rate from the isotropic liquid, a texture characteristic of columnar hexagonal mesophase formation appeared at 196 °C. These transition temperatures are substantially higher than the melting temperatures of both pure compounds (80.6 °C for **5** and 177 °C for TNF). In the DSC, it can be seen that the mesophase persists with no evidence of recrystallization. In DSC heating scans at a rate of 20 °C/min from RT, a transition peaked at 194.5 °C with a shoulder at 186.8 °C (total $\Delta H = 4.57$ J/g) can be observed. During the cooling scan a transition at 187.0 °C ($\Delta H = 4.298$ J/g) can be defined (Fig. 3b). However, the small heat of fusion suggests that the structure below clearing temperature could have a low degree of order, i.e., a mesophase. After the specimen was quenched from the melt and reheated from low temperature of –80 °C, a glass transition, T_g , can be observed at about –40 °C. The lack of further transition temperatures suggests that the mesophase can be preserved for a very wide temperature range, including RT. Such a substantial change in thermal properties with this extremely low T_g is surprising. However, a number of related reports do mention that mesophases induced from charge-transfer complex formation can extend to below RT, though without a defined glass transition [37,65].

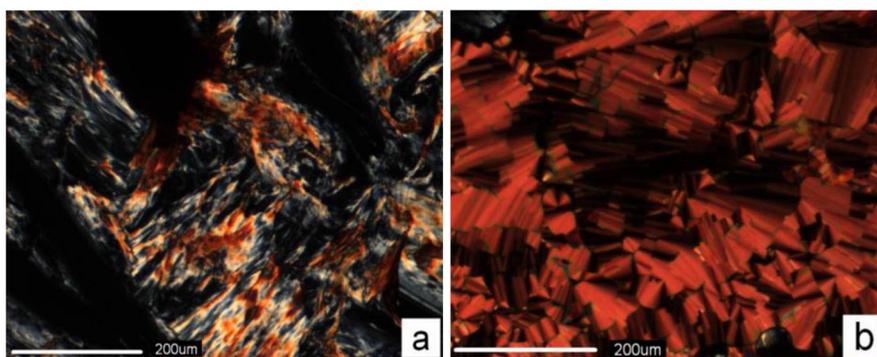


Fig. 4 Photographs of cross-polarized optical microscope from specimen **[5:TNF]** (a) at RT before heating; (b) at 186 °C.

TFA was also selected as another candidate to prepare charge-transfer complex with compound **5**. A 1:1 mixture showed evidence for complex formation. Under a polarized optical microscope at about 78 °C, the initial [**5**:TFA] specimen began to flow with strong birefringence. This was cleared out at 96 °C. During the cooling cycle, birefringence re-covered at 81 °C. It was then solidified at 68 °C. These transitions are higher than that for neat compound **5**, but no evidence of hexagonal or orthorhombic texture built up. The transitions were similarly verified by DSC. However, a slow evaporation of TFA from the mixture was observed. The instability of the complex indicated that the material did not warrant further investigation.

Wide-angle X-ray diffractions of both **5** and [**5**:TNF] were measured using a Rigaku D/Max 2400 X-ray powder diffractometer with Cu K α radiation. Specimens for these measurements were drop-casted onto a thin glass cover slide. X-ray diffractions were all taken at RT. It can be seen from Fig. 5a that the chloroethoxy triphenylene derivative **5** crystallized at RT showing a series of sharp diffractions at relatively low angles, $2\theta = 3.7^\circ, 4.6^\circ, 5.5^\circ, 6.9^\circ, 7.3^\circ, 8.3^\circ$, and up to over 20° which corresponds to d -spacing = 23.8, 19.3, 16.0, 12.9, 12.1 Å and a diffused high-angle peak centered around 21.4° ($d = \sim 4.1$ Å). From data analysis and simulation (Jade software), it is suggested that this crystallized structure is monoclinic and its major diffractions can be indexed as [001], [100], [-101], [011], [110], [111].

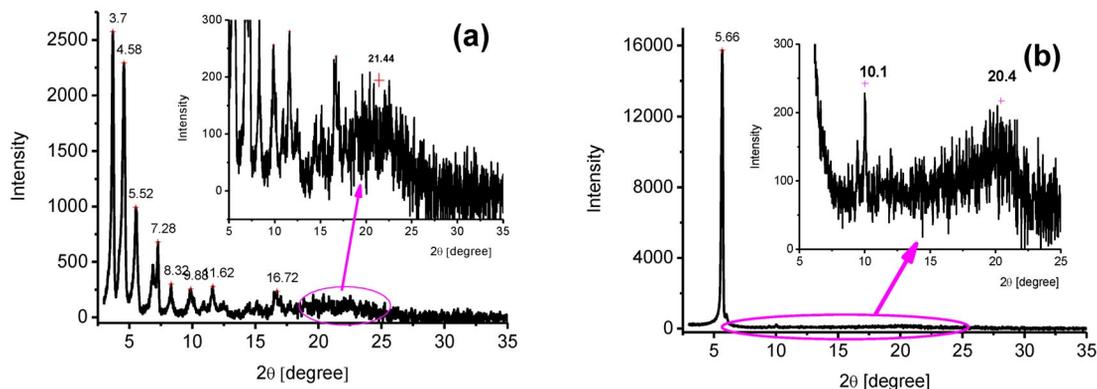


Fig. 5 Wide-angle X-ray diffraction patterns from compound **5** (a) and specimen [**5**:TNF] (b) at ambient condition.

In contrast, X-ray diffraction from specimen [**5**:TNF] shows an intensive diffraction peak at a relatively low angle $2\theta = 5.7^\circ$ ($d = 15.6$ Å) in addition to a few very weak diffractions at $2\theta = 6.0^\circ, 10.1^\circ$ ($d = 14.7, 8.8$ Å) and a diffused peak in the range of 17 – 22° ($d = 4.0$ – 5.2 Å) centered at $2\theta = 20.4^\circ$ ($d = 4.3$ Å) (Fig. 5b). The sharp low-angle diffraction represents a highly ordered structure related to this d -spacing which could extend to micrometer scale from its line width. Further analysis and simulation suggested that this structure is close to a hexagonal symmetry, which agrees with our microscopic observation. Such a diffraction pattern is distinctive for a columnar mesophase and related to the column spacing [6,66]. In this case, the distance between the columns is 18 Å. However, the diffused diffractions at relatively high angle $\sim 20.4^\circ$ indicates that the degrees of order other than packing of columns are low. There is no evidence of order for face-to-face packing within the column. A structure with a high degree of ordering in one dimension and disordered in the other dimension is the character for a liquid-crystalline phase. It agrees with thermal properties measured and forms a mesophase at RT. It therefore appears that simple solution drop-casting produces a columnar hexagonal mesophase of [**5**:TNF], itself an interesting observation.

So far it has been demonstrated that TNF successfully forms a charge-transfer complex with **5** and induces a columnar hexagonal mesophase. The formation of charge-transfer complex [**5**:TNF] both on

cooling and directly from cast solution makes such materials interesting from an organic materials perspective. However, in order for such materials to be even more useful, control over organization and alignment of this film is important and a recognized challenge. Alignment of thin films of complex [5:TNF] was investigated and observed using polarized optical microscopy. It was found that slow cooling from its melt yielded near perfect homeotropically aligned samples. This is clearly seen from the growing hexagonal domains (polarizers uncrossed) that are optically extinct when viewed between crossed polarizers (Fig. 6). The molecular orientation remained unchanged down to RT, supporting the

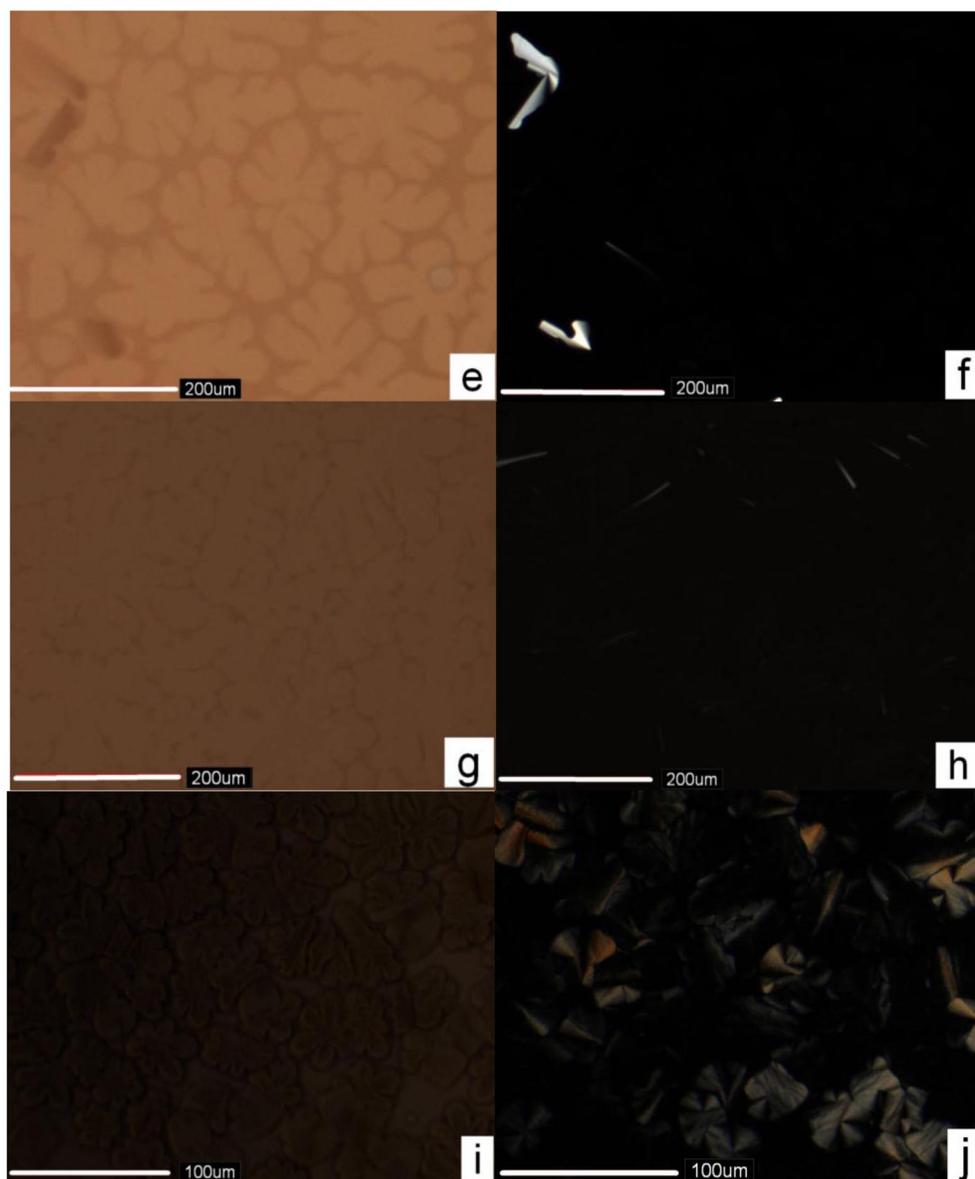


Fig. 6 Photographs of optical microscopy from complex [5:TNF] (e) at 188 °C at a cooling rate of 1 °C/min (natural light); (f) at 188 °C at a cooling rate of 1 °C/min; (g) down to RT at a cooling rate of 5 °C/min (natural light); (h) down to RT at a cooling rate of 5 °C/min; (i) down to RT at a cooling rate of 20 °C/min (natural light); (j) down to RT at a cooling rate of 30 °C/min (with cross-polarizers if not specified).

X-ray evidence for formation of a columnar hexagonal glass. Our investigation revealed that homeotropic alignment in this system was particularly easy to achieve with cooling rates between 1 and 30 °C/min. This is an unexpected but exciting result, which is critically important for application of such materials in optoelectronic devices.

CONCLUSIONS

An unsymmetrically substituted, non-mesogenic chloroethoxyethyl triphenylene has been synthesized and characterized. When mixed with TNF in an equimolar ratio it forms a stable donor–acceptor charge-transfer complex that exhibits columnar mesophase formation over a wide temperature range. The mesophase was identified as a hexagonal columnar mesophase by its characteristic texture, and X-ray diffraction indicates that the columnar order remains at RT and is equally accessible by solution casting. More importantly, it was discovered that with this complex, a homeotropic molecular orientation can be easily achieved on glass substrates. These alignments appear to be stable at RT, with DSC and optical microscopy evidence supporting formation of a liquid-crystalline glass. This approach to achieve molecular orientation without crystallization via a charge-transfer complex process involving an unsymmetrically substituted triphenylene could prove particularly useful and versatile in organic optoelectronic device applications.

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62. ¹H NMR (CDCl₃, TMS, 400 MHz): δ_H 7.91(2H, s, ArH-5,12), 7.83 (4H, d, J = 3.1 Hz, ArH-1,4,8,9), 4.42 (4H, t, J = 4.5 Hz, ArOCH₂CH₂OCH₂CH₂Cl), 4.21–4.25 (12H, m, OCH₂(CH₂)₄CH₃), 4.02 (4H, t, J = 4.7 Hz, ArOCH₂CH₂OCH₂CH₂Cl), 3.92 (4H, t, J = 5.8 Hz, ArO(CH₂)₂OCH₂CH₂Cl), 3.71 (4H, t, J = 5.8 Hz, ArOCH₂CH₂OCH₂CH₂Cl), 1.98–1.91 (8H, m, OCH₂CH₂), 1.39–1.59 (24H, m, O(CH₂)₂(CH₂)₃CH₃), 0.94 (12H, t, J = 7.1 Hz, CH₃); ¹³C NMR (CDCl₃; 75.45 MHz): δ_C 149.3, 148.6, 124.4, 123.8, 123.6, 108.7, 107.5, 107.3, 70.5, 71.8, 70.2, 69.9, 69.8, 69.5, 43.1, 31.9, 29.6, 26.0, 22.9, 14.3; elemental analysis for C₅₀H₇₄O₈Cl: required C 68.71, H 8.53; found C 68.45, H 8.49; mass spectrum (*m/z*, ES) measured 895.5 ([M + Na]⁺, 100 %).
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