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Tetraphenylethene–triphenylene oligomers with an aggregation-induced emission effect and discotic columnar mesophase†

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Tetraphenylethene derivatives not only exhibit ''aggregation-induced emission'' (AIE) effects, but also can form a mesophase with a turbine-like rigid core. Here we report the synthesis of three tetraphenylethene–triphenylene oligomers **7**, **8E** and **8Z** by a $CuSO_4$/sodium ascorbate catalyzed alkyne–azide cycloaddition reaction (CuAAC), and the successful separation of the *cis*- and *trans*-isomers by column chromatography. The structure and conformation of the oligomers were fully characterized. The photophysical properties were studied by using UV-vision and photoluminescent (PL) spectroscopy. The morphology of the aggregates was investigated by scanning electron microscopy (SEM), and the thermal stability and mesomorphic properties were investigated using thermal gravimetric analysis (TGA), polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD). The results revealed that the oligomers possess an AIE effect, but display no mesomorphism. However, **7** exhibits a hexagonal columnar mesophase when mixed with 2,4,7-trinitrofluorenone (TNF), forming a charge transfer complex.

1. Introduction

Discotic liquid crystals (DLCs) exhibit the property of self-organization into a highly ordered columnar mesophase as well as fast charge carrier mobility, and are emerging as a new kind of organic semiconductors.[1] In particular, a good solubility in organic solvents makes DLCs very useful materials for printed electronics, and they have been utilized in organic photovoltaic cells,[2] organic field effect transistors,[3] and organic light emitting diodes.[4] Triphenylene derivatives are one of the most important DLCs,[5] and have been commercially applied in optical compensation films for widening the view angle of liquid crystal displays.[6] In recent years, oligomers of triphenylenes have attracted considerable interest and much effort has been paid to the design and synthesis of new types of such oligomers. In order to get improved optical and electronic properties, these oligomers are usually designed by grafting triphenylene discotic unit onto various functional frameworks, such as perylene,[7] crown ether,[8] porphyrine,[9] calixarene,[10] fullerene C_{60}[11] *etc*. The polymeric materials can form a glass-state and exhibit fine mechanic properties, and low-molecular weight materials tend to show homeotropic alignment behavior to large size domains, and possess high charged carrier mobility. Triphenylene discotic oligomers usually possess both the properties of polymers and small molecules.[5b]

DLCs conventionally consist of a large aromatic core and several peripheral chains. However, molecules devoid of a flat core can also form mesophases by the micro-segregation of the polar cores from the lipophilic alkyl chains rather than the intra-columnar π–π stacking between the core regions, such as tetraphenylethene (TPE) derivatives,[12] triphenylamine derivatives,[13] octahedral metal complexes,[14] dendrimers and related compounds.[15] The propeller-shaped TPE derivatives consisting of four phenyl rotors and one olefinic stator display very interesting chemical and physical properties.

Tang *et al.*[16] in 2001 first reported the unusual photophysical phenomenon of ''aggregation-induced emission'' (AIE), for which the propeller-like molecular structure of silole derivatives was non-emissive in solution, but could turn ''on'' light emission by aggregate formation, due to the restricted intramolecular rotation (RIR) in the aggregates.[17] Like silole derivatives, TPE derivatives have also exhibited AIE effects. Molecules with an AIE effect provide a unique platform for exploitation as novel optical materials and sensors.[18] Luminescent LCs show both a light-emitting property and self-organization behavior, and have been attracting considerable interest over the past decade.[19] Recently, Tang *et al.*[20] reported a series of high solid-state efficiency luminescent LCs which consist of an AIE-active TPE core and four peripheral

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mesogenic substituents. XRD results have shown that the TPE cores are still capable of forming columnar mesophases.

Since Sharpless first introduced the new synthetic strategy of click chemistry,[21] copper catalyzed alkyne–azide cycloaddition reactions (CuAAC) have been widely used in the fields of biological, material, and medicinal chemistry, particularly as such a strategy has high selectivity and efficiency, functional group tolerance, and uses simple reaction conditions. In recent years, much attention has been paid to the synthesis of DLCs by using the CuAAC reaction,[22] and we also have been focusing on the synthesis of new triphenylene DLCs by using the click reaction.[23] Han *et al.*[24] have using the click reaction to synthesize novel fluorescent probes based on the TPE motif for biological studies. Herein, we report the synthesis of three TPE–triphenylene oligomers by the CuAAC click reaction and their AIE and liquid crystalline properties; Scheme 1 shows the structures and synthetic route.

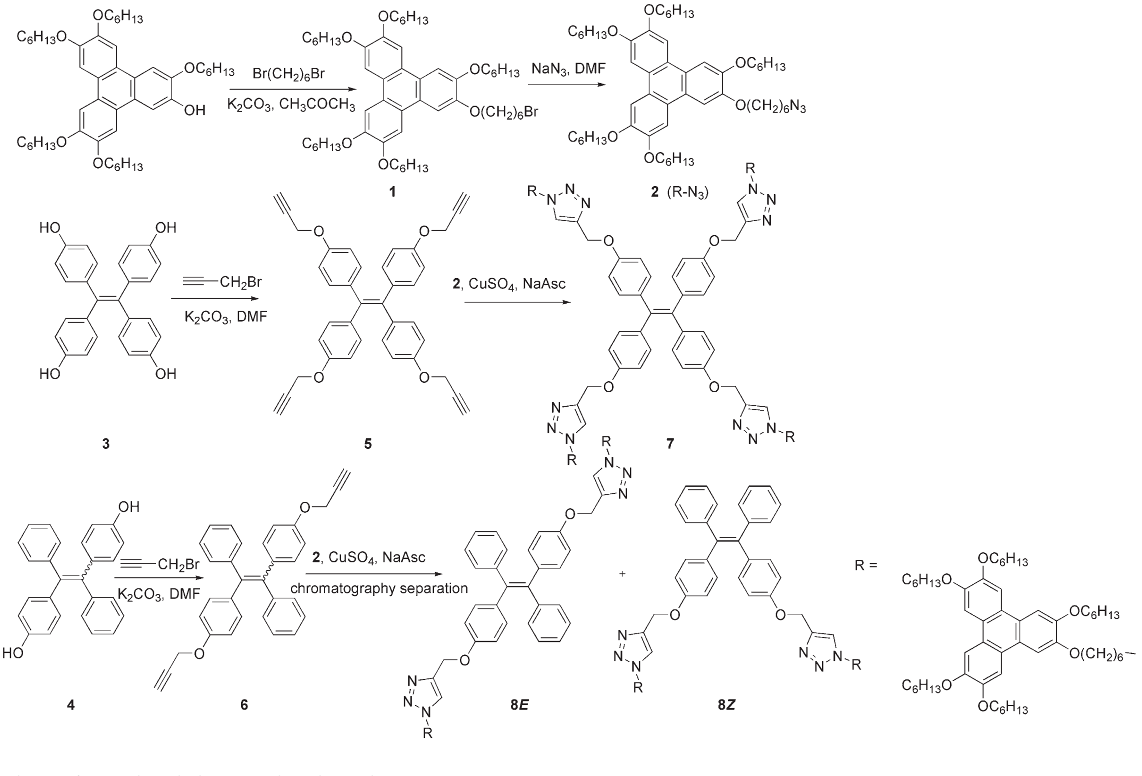
2. Results and discussion

2.1 Synthesis and characterization

2-Hydroxy-3,6,7,10,11-pentakis(hexyloxy)triphenylene as the starting material was prepared according to the reported method.[25] ω-Bromo-substituted triphenylene **1** was prepared in good yield by the reaction of monohydroxytriphenylene with excess 1,6-dibromohexane in the presence of K_2CO_3/acetone. Subsequently, **2** was prepared in a high yield through the nucleophilic substitution reaction of NaN_3 with bromotriphenylene **1**.[22a] Hydroxytetraphenylenes **3** and **4** were synthesized by the McMurry coupling reaction.[26] The etherification of **3** and **4** with 3-bromopropyne afforded the propargyl-attached TPE **5** and **6**, respectively. A Cu-catalyzed click reaction at room temperature between **5**/**6** and azido-functionalized triphenylene **2** then afforded three tetraphenylene-triphenylene oligomers **7**/**8** (see Scheme 1).

The characterization of the synthesized target molecules **7**, **8** was carried out using various spectroscopic methods (see the ESI†). For example, the formation of the triazole ring was confirmed by the single peak at δ 7.60 ppm in the ^1H NMR spectrum and the two peaks at δ 122.4 and 144.1 ppm in the ^{13}C NMR spectrum. The IR spectra of the oligomers displayed a weak band at 3081 cm^{-1} and an extreme sharp band at 1619 cm^{-1} due to the =C–H stretching and C=C, N=N stretching of the triazole ring. The three oligomers gave satisfactory mass data by high resolution mass spectrometry (EI, FAB, MALDI-TOF) and elemental content by elemental analysis.

The four phenyl rings of the TPE were twisted against the ethene-core and oriented in the same direction.[18c,27] **8** with one TPE core and two TP moieties would have *Z* and *E* stereoisomers. Disubstituted TPE derivatives had not been separated in most of the previous reports, and they have been simply studied for their chemical and physical properties as a mixture. In this report, we have successfully separated the isomers by using column chromatography and carefully selecting the elution conditions by using a mixed solvent of dichloromethane, petroleum ether, and ethyl acetate as the eluent, affording the pure *E* and *Z* isomers as pale white solids.



Scheme 1 Synthesis of tetraphenylethene–triphenylene oligomers.

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Very recently, Tang *et al.*[28] also successfully separated *E* and *Z* disubstituted TPE derivatives.

The polarity and melting point (m.p.) of a compound is related to its molecular symmetry: the higher the molecular symmetry, the lower the polarity and higher the m.p. In the present case, the *E* isomer should have lower polarity than the *Z* isomer, and with regard to the column chromatography, the first eluted compound is **8E** with lower polarity. Furthermore, we confirmed their m.p. by the use of DSC measurements, and the first eluted compound displayed a m.p. of 150 °C, whilst the second elutant had a m.p. of 92 °C. The first compound was relatively easy to crystallize and showed a thermal crystallization peak in the second heating run of DSC curves. We assigned the first eluted compound to be the *trans*-structure **8E** given its lower polarity and higher m.p.; the second eluted compound was the *cis*-structure **8Z**. The m.p. of **7**, **8E** and **8Z** measured by DSC were 112 °C, 150 °C and 92 °C, respectively.

Z and *E* isomers can be distinguished by NMR analysis.[18c,28] So we tested **8E**, **8Z** and a mixture consisting of an equal amount of the **8Z**/**8E** isomers. The full ^{1}H NMR spectra of the isomers are similar, but careful observation can find the differences. The most obvious spectral difference lies in the tetraphenylethene aromatic region at the chemical shift area of 6.65–7.15 ppm. The partially magnified spectra in the aromatic region is depicted in Fig. 1. It reveals that some of the resonance peaks of the **8Z** isomer are downfield-shifted from those of its **8E** counterpart and some of the resonance peaks are opposite. The **8Z** isomer resonates at $\delta \approx 6.73$ and 6.95 (Fig. 1A), where the **8E** isomer does not (Fig. 1C). On the other hand, the **8E** isomer exhibits a big resonance peak at $\delta \approx 6.68$ and 6.89. However, all of the resonance absorption peaks of the mixture **8Z**/**8E** are present (Fig. 1B). Obviously, these differences make it possible to monitor conformation changes of the isomers by NMR spectroscopy.

The thermal stability of the TPE–TP oligomers was measured by using TGA. Fig. S2, ESI† shows the TGA curves of **7**, **8E** and **8Z**. All three compounds displayed high thermal stability with 5% weight loss occurring above 300 °C.

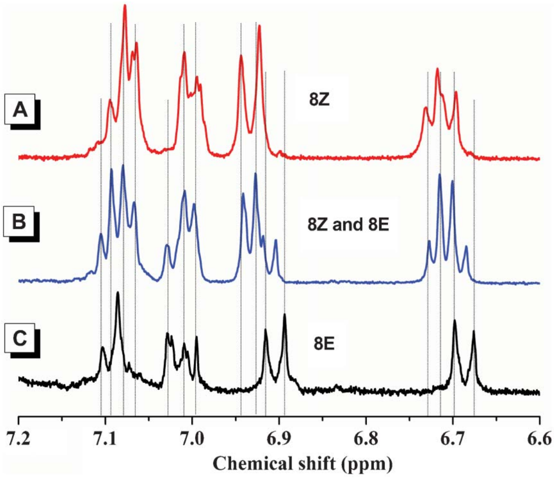

Fig. 1 ^{1}H NMR spectra of (A) **8E**, (B) mixture of **8E** and **8Z** (1 : 1), (C) **8Z** in chloroform-d.

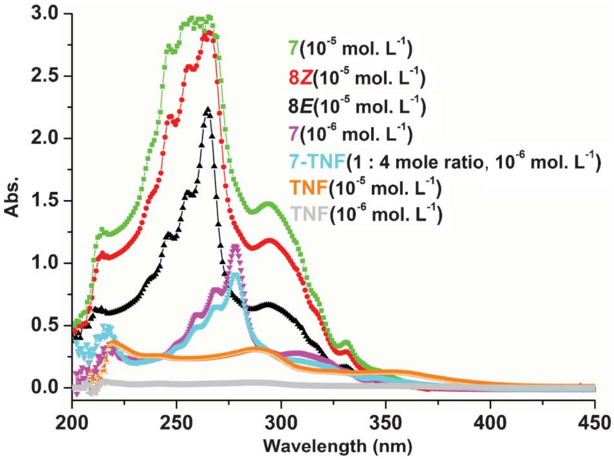

Fig. 2 UV-Vis absorption spectra of oligomers in THF.

2.2 Aggregation-induced emission behaviour

The UV-vis absorption spectra and fluorescent spectra of the oligomers **7**, **8E**, **8Z**, 2,4,7-trinitrofluoren-9-one (TNF) and **7**–TNF complex were measured. The oligomers in THF exhibited two absorption bands at 270 nm and 290 nm, as shown in Fig. 2. The stronger band at 270 nm was attributed to the π–π* transition of the aryl groups and the weaker band at 290 nm was due to the n–π* transition of the triazole ring. For the **7** and **7**–TNF complex, the lower concentrated solutions showed red-shifted absorption bands. The red shifts of UV-vis spectra might be attributed to the concentration-dependent micro-environment of the triphenylene cores of **7** and **7**–TNF, lead to the flat aromatic core effective stacking through π–π interactions. In a lower concentrated solution, the intermolecular π–π stacking of triphenylene resulted in the higher HOMO level, and the energy gap between the LUMO–HOMO is narrowed and the absorption peaks at the lower concentration showed a red shifted absorption band compared to that in the higher concentrated solution. TNF is well known to form solid-state charge-transfer complexes with various electron donors such as triphenylenes, and these complexes exhibit charge-transfer absorption bands in the visible spectral region. But the charge-transfer band of a **7**–TNF complex in diluted solution was not observed in its absorption spectrum in Fig. 2, due to the low molar absorption coefficients in solution.[29]

Fig. 3 shows the photoluminescent (PL) spectra of **7**. Oligomers **7**, **8E**, and **8Z** displayed good solubility in common organic solvents, such as CH_2Cl_2, $CHCl_3$, THF and DMF, but poor solubility in water. Almost no PL signals were detected for their dilute solutions in THF, revealing that the dyes were practically non-luminescent when dissolved in good solvents. As shown in Fig. 3A, the emission from the THF solution of **7** is so weak that its PL spectrum is virtually a flat line parallel to the abscissa. However, when the water fraction was increased (>40%) in the solution, the PL of **7** was switched on. When the water fraction was further increased, the light emission continuously intensified, and was accompanied by a blue-

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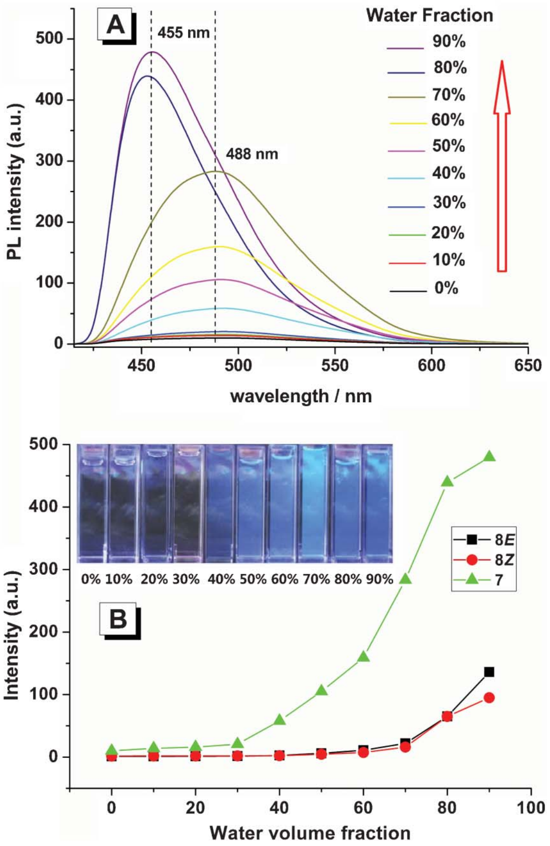

Fig. 3 (A) Fluorescent spectra of **7** in water–THF (10^{-5} mol L^{-1}) (percentages are volume fractions of water) and (B) peak intensities with the volume fractions of water; insets are the fluorescence emission images of **7** from 0% to 90% volume fractions of water under UV light, excitation wavelength: 365 nm.

shift from 488 nm to 455 nm for the PL peak. This was due to the aggregation morphology change of **7**.[18a,30] In a 90% aqueous mixture, the emission intensity was about 500-fold higher than that in pure THF solution (Fig. 3B). Similar effects were observed for the dyes **8E** and **8Z**, but their fluorescence was turned on when the water fraction increased to 70%. The fluorescent intensity only increased by about a 100-fold when the water fraction comprised 90% of the solvent (Fig. S3, ESI†). The differences of fluorescence excitation and fluorescent intensity of **7** and **8** is caused by the different degree of molecular size and rigidity which resulted in the rotation barrier. As water was a non-solvent for the TPE–TP dyes, the dye molecules thus must have aggregated in the water–THF mixtures with high water content. Apparently, the emissions of the TPE–TP dyes were induced by aggregate formation; in other words, they were AIE active. The RIR process is a plausible mechanism for the AIE activity of such TPE–TP oligomers.[17] That is, in dilute solution, the active rotations of the four phenyl rings against the ethylene core may have effectively non-radioactively deactivated the excited states. The enhanced light emission in the aggregate state is caused by the restricted motions of the aromatic rotors.

To prove that aggregates of the oligomers **7**, **8E** and **8Z** were formed when large amounts of water was present in their THF solutions, we investigated them by scanning electron microscopy (SEM). The samples were prepared by adding water into the THF solution of **7** and the aqueous mixtures were stood for 12 h to allow the molecules to be well self-assembled. Then, the aqueous mixture was dropped on a silica grid and the solvents were allowed to evaporate. As shown in Fig. 4, oligomer **7** aggregated into spherical particles in the aqueous mixtures. More interestingly, the aggregates of **7** were nanodimensional and their average diameters decreased from ∼1 μm, 620 nm, 500 nm and 310 nm when the water fraction in the mixture was increased from 40 to 90%. The molecules might agglomerate quickly to form small aggregates in mixtures with higher water contents, while the molecules of **7** might slowly assemble in an ordered fashion to form larger clusters at lower water content.[31]

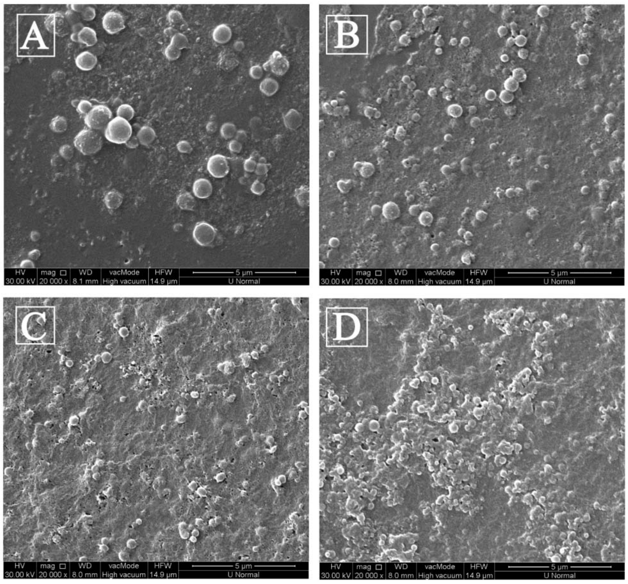

Fig. 4 SEM images of particles of **7** , prepared in a THF/water mixture with 40% (A), 70% (B), 80% (C) and 90% (D) water fraction.

2.3 Mesomorphic behavior

The liquid crystalline property of an organic compound is determined by its molecular shape and intermolecular interactions. Amongst the specific species available, charge-transfer complexes have opened up the prospect of new research. In order to increase intermolecular interactions and thus induce the mesophase, we have doped the electron-donating oligomers with electron-accepting TNF in different molar ratios. The results are summarized in Table 1 and are shown in Fig. 5.

From polarizing optical microscopy we observed that the **7**–TNF complex displayed a typical fan-shaped texture of the columnar mesophase. From optical textures given in Fig. S4, ESI,† it is clear that the average domain size decreases and becomes less defined on increasing the oligomer or TNF concentration in the binary mixture. The mesophase to isotropic transition temperature is affected remarkably by the TNF proportion in the binary mixture. Only when the TNF concentration is between 67% to 80%, can the complex obtain

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Table 1 Thermal and thermodynamic properties of the synthesized oligomers and their composites by DSC (10 °C min^{-1}) or POM

Compound/mixture [mole ratio]	Second heating scan Transition T (°C) and enthalpy change (ΔH, kJ mol^{-1})	First cooling scan Transition T (°C) and enthalpy change (ΔH, kJ mol^{-1})
7	Cr 112 (86.68) Iso^a	—
7 : TNF [2 : 1]	Col$_h$ 134 Iso^b	Iso 130 Col$_h$^{b}
7 : TNF [1 : 1]	Col$_h$ 174 Iso^b	Iso 172 Col$_h$^{b}
7 : TNF [1 : 2]	Col$_h$ 186 Iso^b	Iso 184 Col$_h$^{b}
7 : TNF [1 : 3]	Col$_h$ 186 Iso^b	Iso 184 Col$_h$^{b}
7 : TNF [1 : 4]	Col$_h$ 186 Iso^b	Iso 184 Col$_h$^{b}
7 : TNF [1 : 5]	Col$_h$ 120 Iso^b	Iso 118 Col$_h$^{b}
8E	Cr 150 (88.29) Iso^a	—
8Z	Cr 92 (65.41) Iso^a	—

^{a} From DSC and POM. ^{b} From POM. Cr: Crystal phase; Col$_h$: Hexagonal columnar phase; Iso: Isotropic phase.

the highest clearing point temperature, *i.e.* a suitable inducing action can be obtain a stable mesophase. When the molar ratio of donor to acceptor is 1 : 5, excess TNF will interfere with the formation of the mesophase; when less than 1 : 1, the complex cannot effectively form a mesophase (Fig. S4, ESI†). It is also notable that the disubstituted TPE–TP derivatives **8Z** and **8E** doped with TNF did not show any mesomorphic behavior. This may be associated with the anchor effect of the triphenylene discogen.[29,32] Oligomer **7** with four triphenylenes discogen can more easily self-assemble than **8** with two triphenylenes discogen when their formed charge-transfer complex is doped with TNF. As we know, TNF is known to be an efficient fluorescence quencher. So we tested the AIE effect of the charge-transfer complex **7**–TNF (mole ratio 1 : 4), and found that it did not show any AIE effect. Such molecules may be used as a fluorescent probe for detecting electron-deficient aromatic compounds.

We further used wide angle X-ray diffraction (XRD) to confirm the mesophase structure. The result of the XRD measurements of the charge-transfer complexes are shown in Fig. 6. In the small-angle region, we noted that the reflections at $2\theta = 2.27, 4.55, 5.95, 6.81$ and $10.29°$ are characteristic of the hexagonal columnar mesophase (Col$_h$) with a d-spacing ratio of $1, 1/\sqrt{4}, 1/\sqrt{7}, 1/\sqrt{9}, 1/\sqrt{21}$ corresponding to the Miller indices of 100, 200, 210, 300, 410 respectively. In the wide-angle region, a diffuse halo reflection at $2\theta = 15–24°$ was attributed to the molten state alkyl-chain distances in the columnar phase. At the 2θ value of 26.37°, there was a broad peak corresponding to ordered disc–disc stacking in the column. The lattice parameter of the Col$_h$ phase was calculated to be 4.52 nm.[1b] When the molecules most extended conformation was assumed, the molecular diameter is about 4.52 nm, which was calculated by the MM2 method. This value is consistent with the XRD result. Based on the XRD result and the MM2 calculation, we propose that the **7**–TNF complex possessed a hexagonal columnar phase, as schematically illustrated in Fig. 7.

3. Conclusions

In summary, we have synthesized tetraphenylethene–triphenylene oligomers **7**, **8E** and **8Z** by the CuAAC click reaction, and successful separated the *E* and *Z* isomers of **8** by using column chromatography. The oligomers displayed aggregation-induced emission (AIE) behavior, specifically the tetraphenylethylene derivatives in a mixed solvent of THF–water.

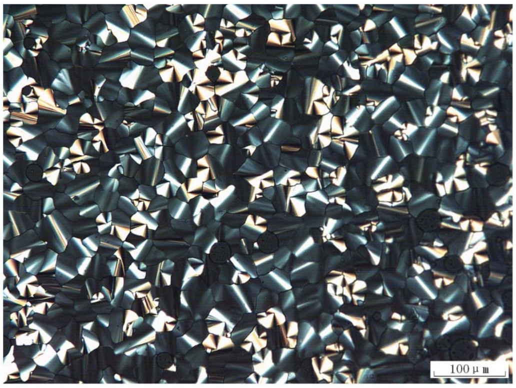

Fig. 5 Optical textures of the complex **7**–TNF (1 : 4 mole ratio) at 120 °C, crossed polarizers.

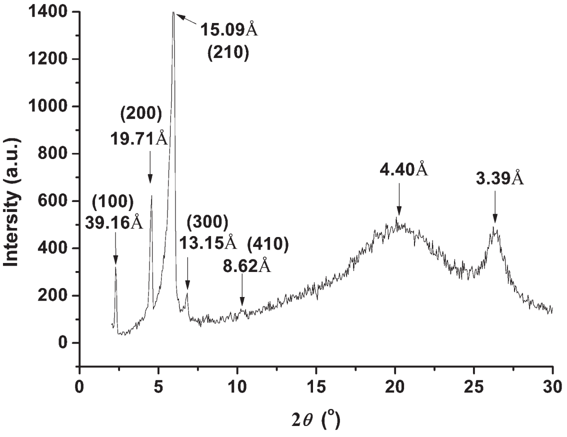

Fig. 6 X-Ray diffraction pattern of **7**–TNF (mole ratio 1 : 4) at 25 °C, sample slowly cooled from isotropic liquid.

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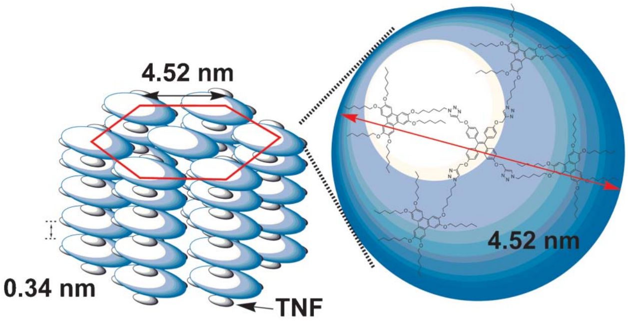

Fig. 7 Charge-transfer complex **7**–TNF (mole ratio 1 : 4) organized in an ordered hexagonal columnar mesophase.

Interestingly, the **7**–TNF complex exhibited a hexagonal columnar mesophase due to charge-transfer interactions in the binary mixture. These oligomers may be used as a fluorescent probe for detecting electron-deficient aromatic compounds. Tetraarylethenes provide useful building blocks which can be converted to the corresponding liquid crystalline 9,10-diarylphenanthrenes and dibenzo[*g*,*p*]chrysenes by oxidative cyclization.[33] The design and synthesis of new DLCs based on phenanthrenes or chrysenes as the mesogenic core is underway in our group.

Acknowledgements

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