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Novel supramolecular liquid crystals: cyclodextrin-triphenylene column liquid crystals based on click chemistry†

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Three new cyclodextrin-triphenylene derivatives 6, 7a and 7b were designed and synthesized by introducing a triphenylene unit into cyclodextrin based on click chemistry and further acylation of hydroxyl groups of the cyclodextrin unit. The column liquid crystal behaviour of cyclodextrin-triphenylene 7a was observed for the first time.

The self-assembly of relatively simple building blocks into complex ordered structures is a subject of increasing research interest for the fundamental understanding of soft-matter self-organization.[1–3] Liquid crystals are typical soft matter with a mesophase between a crystalline solid and an isotropic liquid state of matter. Triphenylene is one of the most widely studied discotic liquid crystals with various possible applications in organic light-emitting diodes, organic photovoltaic cells, organic field-effect transistors, gas sensors, photocopying machines, *etc.*[4–9] All kinds of triphenylene derivatives with unique structures and interesting mesomorphic properties, such as hydrogen-bond stabilized triphenylene columns, polymers or oligomers of triphenylene, dendrimers of triphenylene, nanoparticles of triphenylene, have been investigated.[7–13] Recently, much attention was focused on the supramolecular macrocycle-triphenylene derivatives. Cammidge *et al.* first reported the triphenylene dimers linked by a shape-persistent conjugated macrocycle and a crown ether macrocycle with interesting mesomorphic properties in 2010.[14,15] Also, the syntheses and mesomorphic properties of a series of crown ether-based triphenylene dimers were described by Laschat and Peng at the same time, respectively.[16–19] Recently, we reported a series of calixarene-triphenylene liquid crystals for the first time.[20–22] All these literature studies suggested that the supramolecular macrocycle-triphenylene derivatives possessed the guest-recognition abilities based on macrocyclic units and the liquid crystal behaviors based on triphenylene units. Moreover, the mesomorphic properties were induced or changed by the guest-recognition of macrocyclic units, which led to potential applications such as ion-sensors, ion-selective supramolecular liquid crystals, ion-switch of liquid crystals, *etc.* However, besides these few examples of supramolecular crown ether-triphenylene and calixarene-triphenylene derivatives, no other macrocycle-triphenylene derivatives, such as cyclodextrin-triphenylene liquid crystals, are known.

Cyclodextrins (CDs) are cyclic oligosaccharide molecules comprising six, seven or eight glucose units which are bonded through the α-(1,4)-linkages, assigned as α-, β-, γ-CD, respectively.[23] They were used as excellent platforms to construct the supramolecular cyclodextrin derivatives with potential applications in molecular recognition, molecular self-assembly, bioenzyme mimics, *etc.* However, due to their big irregular shapes and strong hydrogen bonds, it was difficult to construct the cyclodextrin liquid crystals. Until now, only two examples of cyclodextrin-biphenyl thermotropic liquid crystals and amphiphilic thio-β-cyclodextrin liquid crystals have been reported.[24,25] On the other hand, the click reaction was used as a good method to prepare liquid crystals recently, such as liquid-crystalline gold nanoparticles and liquid-crystalline pillar(arenes).[26,27] In this paper, we wish to describe the design and syntheses of the first examples of cyclodextrin-triphenylene derivatives based on click chemistry. Moreover, after the acetylation of hydroxyl groups of the cyclodextrin unit, the cyclodextrin column liquid crystals were observed for the first time.

Scheme 1 shows the synthetic routes towards cyclodextrin-triphenylene derivatives **6**, **7a** and **7b**. The mono-6-azido-β-CD **3** was obtained from the readily available mono-6-tosyl-β-CD.[28–30] On the other hand, triphenylene derivative **5** with the alkynyl group was prepared in high yield according to the literature.[31]

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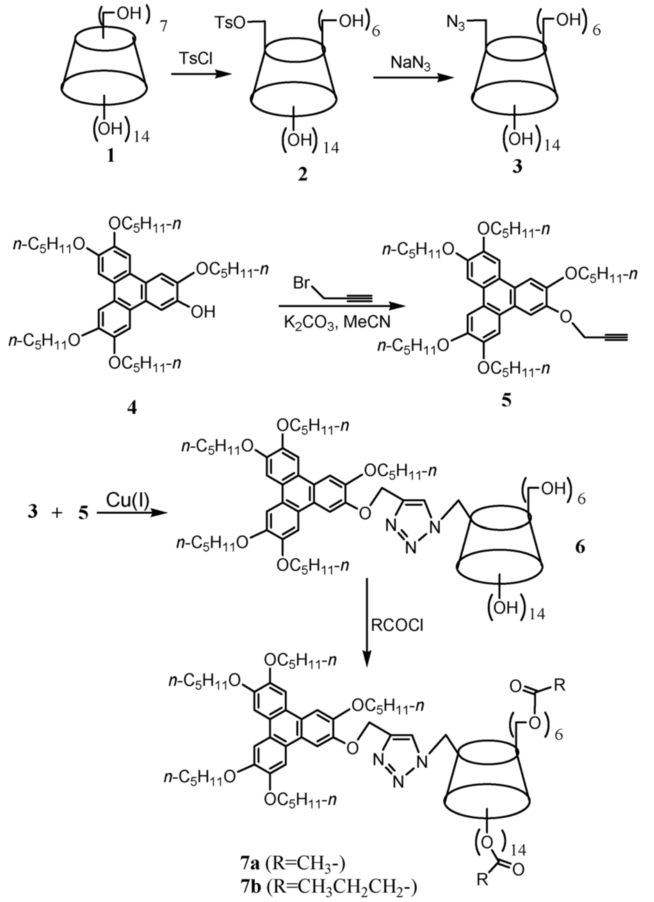

Scheme 1 The synthetic routes towards cyclodextrin-triphenylene **6**, **7a** and **7b**.

Subsequently, the coupling of triphenylene derivative **3** and β-CD derivative **5** was accomplished *via* click reaction using Cu(I) as a catalyst, and the first triphenylene-cyclodextrin derivative **6** was obtained in a high yield of 80%. After acylation of compound **6** with acetic anhydride or butyric anhydride, the triphenylene-cyclodextrin derivatives **7a** and **7b** were prepared in yields of 72% and 65%, respectively. The novel compounds **6**, **7a** and **7b** were characterized by elemental analysis, FT-IR, ESI-MS and ^{1}H NMR spectra. Their ESI-MS spectra showed the corresponding molecular ion peaks. In their ^{1}H NMR spectra, the signals of protons were assigned well for the structures of compounds **6**, **7a** and **7b** as shown in Scheme 1.

The phase transition behaviours of compounds **6**, **7a** and **7b** were first observed using polarized optical microscopy upon heating and cooling. Results showed that compounds **6** and **7b** undergo the transition from the solid state to the isotropic phase directly upon melting, and no mesophase could be observed. However, compound **7a** showed two phase transitions of solid state–mesophase and mesophase–isotropic phase upon heating and cooling. The clear columnar fan-shaped texture was formed as shown in Fig. 1. This texture was similar to the known textures for columnar phases of triphenylene derivatives.[32–37]

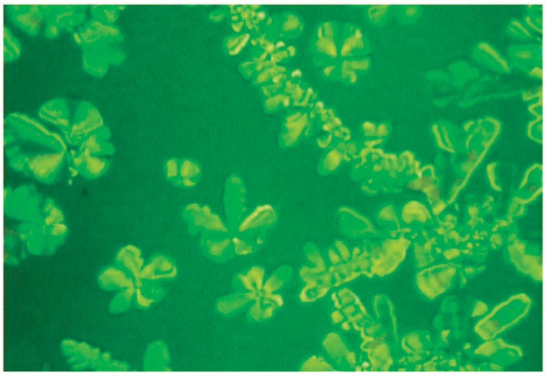

Fig. 1 The texture of **7a** under a POM upon cooling at 120 °C (×400).

Further, the thermal behaviours of compounds **6**, **7a** and **7b** were studied by differential scanning calorimetry (DSC) as shown in Fig. 2. Compound **6** exhibited no clear peak, which indicated that it underwent no obvious phase transition upon heating and cooling. The melting point determination also showed that it had no clear melting point below 200 °C and decomposed gradually above 200 °C. These results might suggest that compound **6** is an amorphous solid. Compound **7b** showed one peak upon second heating and cooling, which implied that it underwent one phase transition upon melting. However, compound **7a** exhibited two phase transitions upon second heating and cooling as shown in Fig. 2 and Table 1. Combining the experimental results of polarized optical microscopy and differential scanning calorimetry, it could be deduced that compound **7a** exhibited the liquid crystal behaviour of solid state–mesophase and mesophase–isotropic phase upon melting, but compounds **6** and **7b** possessed no mesophase upon melting.

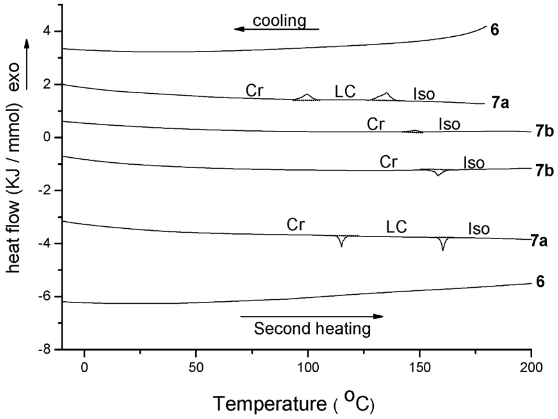

Fig. 2 The DSC traces of compounds **6**, **7a** and **7b** upon second heating and cooling (scan rate 10 °C min^{-1}).

Table 1 Transition temperatures (°C) and enthalpy changes (kJ mol^{-1}) of **6**, **7a** and **7b**

Compound	Phase transition[a]	Heating scan $T(\Delta H)$	Cooling scan $T(\Delta H)$
6	None	None	None
7a	Cr-Col	115.2(8.68)	100.1(8.14)
	Col-Iso	160.4(10.46)	135.3(10.86)
7b	Cr-Iso	158.2(7.72)	147.2(3.21)

[a] Cr = crystalline, Col = column liquid crystal, Iso = isotropic.

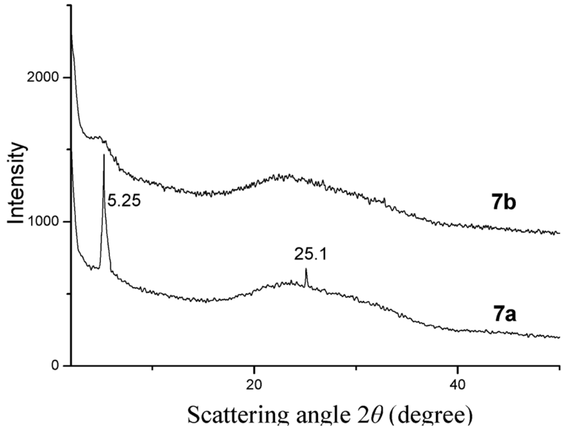

Fig. 3 XRD traces of compounds **7a** and **7b** at 120 °C.

In order to investigate the mesomorphic stacking behaviour deeply, compounds **7a** and **7b** were studied by X-ray powder diffraction as shown in Fig. 3. A survey of the literatures indicated that triphenylene liquid crystals with a hexagonal columnar phase exhibited a low angle peak ($2\theta = 5^\circ$ approximately) for the diameter of the triphenylene groups and a broad region feature at a high angle ($2\theta = 18$–22°) for the average distance of the molten alkyl chains and high angle ($2\theta = 25^\circ$ approximately) for the intracolumnar order.[32–37] As shown in Fig. 3, compound **7b** only exhibited the strong reflection of the average distance of the molten alkyl chains ($2\theta = 18$–24°) and no obvious reflection for the triphenylene column. This result suggested that the triphenylene units of compound **7b** could not stack orderly in the column phase upon melting. However, it could be seen that compound **7a** exhibited the reflections at $2\theta = 5.25^\circ$, 18–24° and 25.1°, respectively, which were the typical peaks of the hexagonal columnar phase of triphenylene liquid crystals and agreed with the diameter of the triphenylene groups (16.8 Å), the average distance of the molten alkyl chains (4.9–3.7 Å) and the intracolumnar order (3.6 Å), respectively.[32–37] On the other hand, no obvious reflection for the cyclodextrin unit was observed.[24,25] From these XRD results, it could be deduced that compound **7b** possessed no triphenylene column but compound **7a** had a triphenylene column as a core with cyclodextrin units on ancillary lateral sides, which exhibited the XRD peaks for the triphenylene column unit but no XRD peak for the cyclodextrin unit due to the disordered tropism of cyclodextrin units on ancillary lateral sides. Comparing the structures of compounds **7a** and **7b**, it could be deduced that the long butyryl chains of cyclodextrin units in compound **7b** were not favourable for the mesophase. A possible reason was that the strong disordered intermolecular forces of twenty long butyryl chains on lateral cyclodextrin units damaged the ordered π–π stacking of the triphenylene column.

Based on the analysis of structures and liquid crystal properties of compounds **6**, **7a** and **7b**, it could be concluded that the hydroxyl groups in cyclodextrin units were the obstacle for the liquid crystal behaviors. Moreover, although the influences of hydroxyl groups of the cyclodextrin unit were eliminated by acylation of hydroxyl groups, compound **7a** with acetyl groups exhibited the mesophase but compound **7b** with butyryl groups possessed no mesophase. These results suggested that the structures of alkyl chains of acyl groups also played important roles in mesomorphic properties. The long alkyl chain might be not favorable for the liquid crystals. In other words, the mesomorphic properties of cyclodextrin-triphenylene derivatives were decided by both the hydroxyl groups and the structures of acyl groups of cyclodextrin units.

In conclusion, the design and synthesis of the first examples of cyclodextrin-triphenylenes **6**, **7a** and **7b** were accomplished in high yields. Compounds **6** and **7b** with butyryl groups showed no mesophase. Compound **7a** with acetyl groups exhibited the column liquid crystals, which was confirmed by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray diffraction (XRD). These results suggested that the mesomorphic properties of cyclodextrin-triphenylene derivatives were dependent on both the hydroxyl groups and the structures of acyl groups of cyclodextrin units. The studies on inclusion properties for guests based on cyclodextrin units and their influences on mesomorphic properties will be further investigated in the following work.

Experimental

General

All chemical reagents were obtained from commercial suppliers and used without further purification. The other organic solvents and inorganic reagents were purified according to standard anhydrous methods before use. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200–300 mesh). NMR spectra were recorded in $CDCl_3$ on a Bruker-ARX 400 instrument at 30 °C. Chemical shifts are reported in ppm, using tetramethylsilane (TMS) as internal standard. ESI-MS spectra were obtained using a DECAX-30000 LCQ Deca XP mass spectrometer. Elemental analyses were performed using a Vario EL III Elemental Analyzer. A polarized optical microscope (Leica DMRX) was used along with a hot stage (Linkam THMSE 600) to examine phase transitions. Thermal analysis of the materials was carried out using a differential scanning calorimeter (DSC) (Thermal Analysis Q100) at a scan rate of 10 °C min^{-1} under a N_2 atmosphere. X-ray diffraction (XRD) experiments were performed on a SEIFERT-FPM (XRD7), using Cu Kα 1.5406 Å as the radiation source with 40 kV, 30 mA power.

Synthetic procedure of β-cyclodextrin-triphenylene 6

Reaction of compound **3** (0.31 g, 0.43 mmol) with compound **5** (0.5 g, 0.43 mmol) was carried out in DMF (20 mL) in the presence of Cu(I) generated by the reduction of copper sulfate (0.011 g, 0.043 mmol) with sodium ascorbate (0.043 g, 0.22 mmol). The mixture was stirred at 60 °C for 8 h and then cooled to room temperature. TLC detection indicated the disappearance of materials. Then 20 mL of distilled water and 30 mL of $CHCl_3$ were added into the solution with vigorous stirring at room temperature. Then the solutions were formed with three layers: upper layer (DMF and water), middle layer (solid), and lower layer ($CHCl_3$). The middle layer was separated out and was further purified by flash column chromatography on silica gel using a mixture of *n*-butanol : ethanol : water = 5 : 4 : 3 as an eluent. Compound **6** was obtained as a gray solid in a yield of 80%. Compound **6**: ^1H NMR (400 MHz, DMSO) δ (ppm): 0.93 (t, 15H, J = 6.6 Hz, CH_3), 1.41–1.85 (m, 30H, CH_2), 3.44–3.65 (m, 40H, H2–H6), 4.24 (bs, 12H, $TpOCH_2$ and NCH_2), 4.50–5.88 (m, 29H, CH_2, CH and OH), 7.90–8.29 (m, 7H, TpH and CH); IR/cm^{-1}: 3395, 2930, 2869, 1690, 1616, 1508, 1432, 1366, 1261, 1156, 1035, 583; MS m/z (%): 1896.0 (MNa^+, 100). Anal. calcd for $C_{88}H_{133}N_3O_{40}$: C, 56.43; H, 7.16; N, 2.24%; found: C, 56.39; H, 7.21; N, 2.22%.

Synthetic procedure of β-cyclodextrin-triphenylene 7a

Compound **6** (0.3 g, 0.16 mmol) and I_2 (0.05 g, 0.2 mmol) were stirred in acetic anhydride (6 mL) overnight under a N_2 atmosphere. Then the mixture was stirred at 40 °C and cooled to room temperature. TLC detection indicated the disappearance of materials. Then 20 mL of distilled water and sodium thiosulphate (0.05 g, 0.2 mmol) were added into the solution with vigorous stirring, and the pH was adjusted to 7 with $NaHCO_3$. The organic layer was separated with 30 mL of CH_2Cl_2, dried over anhydrous $MgSO_4$, and then filtered, concentrated and recrystallized in MeOH–CH_2Cl_2. Compound **7a** was obtained as a beige solid in a yield of 72%. Compound **7a**: ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.97 (bs, 15H, CH_3), 1.47–1.96 (m, 30H, CH_2), 2.10 (s, 60H, $COCH_3$), 3.53–5.52 (m, 61H, CH1-5, NCH_2 and OCH_2), 7.84 (s, 6H, TpH), 8.11 (s, 1H, H7); IR/cm^{-1}: 2929, 2867, 1747, 1616, 1509, 1433, 1372, 1238, 1166, 1042, 699, 603; MS m/z (%): 2735.4 (MNa^+, 100). Anal. calcd for $C_{128}H_{173}N_3O_{60}$: C, 56.65; H, 6.43; N, 1.55%; found: C, 56.61; H, 6.491; N, 1.49%.

Synthetic procedure of β-cyclodextrin-triphenylene 7b

Compound **6** (0.3 g, 0.16 mmol) and I_2 (0.05 g, 0.2 mmol) were stirred in *n*-butyric anhydride (6 mL) overnight under a N_2 atmosphere. Then the mixture was stirred at 40 °C and cooled to room temperature. TLC detection indicated the disappearance of materials. Then 20 mL of distilled water and sodium thiosulphate (0.05 g, 0.2 mmol) were added into the solution with vigorous stirring, and the pH was adjusted to 7 with $NaHCO_3$. The organic layer was separated with 30 mL of CH_2Cl_2, dried over anhydrous $MgSO_4$, and then filtered and concentrated. Purification was performed by column chromatography on silica gel (100–200 mesh), and the column was eluted initially with petroleum ether and then with methanol as an eluent. Compound **7b** was obtained in the yield of 65%. Compound **7b**: ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.89–0.99 (t, 75H, CH_3), 1.43–2.27 (m, 110H, CH_2 and CH_2CO), 3.62–5.47 (m, 61H, CH2-5, NCH_2 and $TpOCH_2$), 7.52–7.84 (m, 6H, TpH), 7.89 (s, 1H, H7); IR/cm^{-1}: 2962, 2874, 1744, 1614, 1510, 1433, 1262, 1170, 1043, 959, 749; MS m/z (%): 3295.5 (MNa^+, 100). Anal. calcd for $C_{168}H_{253}N_3O_{60}$: C, 61.61; H, 7.79; N, 1.28%; found: C, 61.66; H, 7.89; N, 1.26%.

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