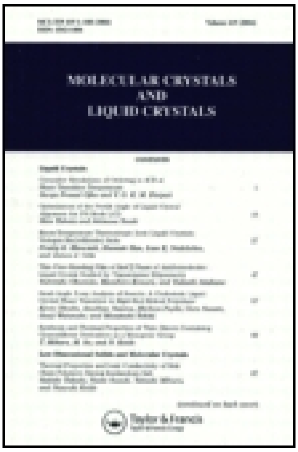

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The Synthesis and Mesophases Studies of a Novel Discotic Compound Containing Two Triphenylene Cores Linked by Crown Ether

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In this study, a novel discotic compound based on triphenylene core were synthesized. 6,7,10,11-tetrapentyloxy-2-hydroxy-3-methoxy triphenylene was synthesized via the common synthisis route including the Williamson Etherification of catechol, the iodination of 1,2-dipentyloxybenzene, the Ullman Coupling and the coupling of 3,3′-4,4′-tetrapentyloxy diphenyl and methoxy-phenol;Bis-(8-bromooctanoyl)-dibenzo-18-crown-6 was obtained from 8-bromooctanoic acid and dibenzo-18-crown-6 in polyphosphoric acid and then reacted in Et_3SiH *with trifluoroacetic acid as catalyst to obtain bis-(8-bromooctyl)-dibenzo-18-crown-6. Bis-(8-bromooctyl)-dibenzo-18-crown-6 reacted with 6,7,10,11-tetrapentyloxy-2-hydroxy-3-methoxy triphenylene via Williamson reaction to produce the goal product. The chemical structures of the compounds were identified by using fourier transform infrared spectroscopy, nuclear magnetic resonance and the thermal properties were characterized by optical polarizing microscope and differential scanning calorimeter.*

Keywords DSC calorimetry; mesophases; POM picture; triphenylene

1. Introduction

The molecular self-organization and self-assembly at nanometer or micrometer scale are useful strategies in development of novel function materials and are currently exciting areas of intense research [1]. Liquid crystalline materials are self-assembling by nature and can offer a very elegant and effective way of controlling and tuning the physical properties that ultimately defined the self-organizing and self-assembly process. Investigation of the structures and properties of liquid crystalline materials may

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lead to further understanding the self-organizing and self-assembling processes and the control through the mesophase [2–6]. Since it was first reported by Pedersen C. J. in 1967, the ability of selective coordination crown ether with metal salts made it received great research interests in molecular recognition and supermolecular self-organization. Crown ethers has also been reported that can form smectic and columnar liquid crystal phase which can be stabilized via complexation with KI [7]. Much evidences proved that crown ethers can be used as mesomorphic modifiers. Molecule having different type mesogenic units bonded within one entity may have interesting phase behaviour and property and always be used as self-assembly materials. Such structure has been synthesised with two or more of different mesogenic units tied together to give "heterogeneous" dimer, "heterogeneous" trimer, or even oligmer and dendrimer via covalent or non-covalent bond. Our goal in this study is to synthesize new molecule based on crown ether and the famous discotic precusor-triphenylene and study the thermal properties of the new compound.

2. Experimental Methods

2.1. *Materials and Instrumentation*

All solvents used in the synthesis if not specified were all analytic reagents (Beijing Chemical Reagents Co.) and reagents were purchased from Aldrich Chemical used as received (without further purification). Dry CH_2Cl_2 was prepared by distillation over CaH_2 under a N_2 atmosphere. The characterization of these compounds synthesized was verified by using ^1H NMR. ^1H NMR spectra were measured in $CDCl_3$ on a Brucker Avance (400 MHz) spectrometer. The phase transition behavior of these compounds was observed by using a Leica polarizing optical microscope equipped with a Linkam LC600 hot stage and differential scanning calorimeter (DSC) (Thermal Analysis DSC2010) at a heating rate 10°C/min.

2.1. *Synthesis*

1,2-Dipentyloxybenzene, 1. A mixture of catechol (44 g, 0.4 mol), 1-bromopentane (145 g, 0.96 mol) and anhydrous 110 g potassium carbonate in 400 ml ethanol was stirred under nitrogen and reflux for 24 h. The mixture was filtered and removed the solvent; the filtrate was evaporated under vacuum (5mmHg, 144–162°C) to produce 1,2-dipentyloxybenzene as a pale yellow oil (95 g, 0.38 mol), yielding: 95%.

^1H NMR ($CDCl_3$): $\delta = 6.88$ (s, 4H, ArH), 3.99 (t, 4H, OCH_2), 1.82 (m, 4H, OCH_2CH_2), 1.33–1.50 (m, 8H, $OCH_2(CH_2)_2CH_3$), 0.93(t, 6H, CH_3).

3,3′,4,4′-Tetrakispentyloxy biphenyl, 3. A mixture of 1,2-dipentyloxybenzene (10 g, 40 mmol) and iodine monochloride (8.8 g, 54 mmol) in $CHCl_3$ was stirred at room temperature for 2.5 h. The mixture was washed twice with 150 ml of 1 M sodium metabisulphite solution followed by washing with 100 ml of water. The organic phase was dried over anhydrous Na_2SO_4. The solvent was evaporated and the crude product (1,2-dipentaloxy-4-iodobenzene **2**) (13 g, 34.5 mmol) was obtained, yielding: 89%) as an intermediate for the synthesis of 3,3′,4,4′-tetrakispentyloxy biphenyl. The crude compound was used in the next reaction without further purification. For the coupling reaction a mixture of 1,2-dipentaloxy-4-iodobenzene (9.0 g, 24 mmol) and 6.3 g copper powder were heated at 270°C for 1 h, while the reaction mixture was vigorously stirred. After cooling the mixture to room temperature, 250 ml of CH_2Cl_2 was added and the reaction mixture was filtered. The crude compound was recrystallized from ethanol to obtain the 3,3′,4,4′-tetrakispentyloxy biphenyl **3** (2.53 g, 6.7 mmol), yielding: 42.3%.

^{1}H NMR ($CDCl_3$): $\delta = 6.62$–7.28 (m, 3H, ArH), 3.97 (t, 4H, OCH_2), 1.84 (m, 4H, OCH_2CH_2), 1.34–1.61 (m, 8H, $O(CH_2)_2(CH_2)_2CH_3$), 0.95 (t, 6H, CH_3).

2-Hydroxy-3-methoxy-6,7,10,11-tetrapentyloxytriphenylene, 4. 3,3′,4,4′-tetrakispentyloxy biphenyl (6.0 g, 0.012 mol) and Guaiacol (3.0 g, 0.012 mol) were added into a stirred mixture of 60 ml $CHCl_2$ and 7.5 g $FeCl_3$ in a three neck flask and stirred for 1 h. Then the react mixture was poured into 400 ml cool methanol; the precipitate was recrystallized from ethanol to give the ultimate product (3.52 g,yield: 48%).

^{1}H NMR ($CDCl_3$): $\delta = 7.79$–7.96 (m, 6H, ArH), 5.59 (S, 1H, OH), 4.2–4.25 (t, 8H, OCH_2), 4.14 (S, 3H, OCH_3), 1.94–1.97 (m, 8H, CH_2), 1.5–1.54 (m, 8H, CH_2), 1.42–1.45 (m, 8H, CH_2), 1.26 (s, 8H, CH_2), 0.86–1.0 (m, 12H, CH_3).

(8-Bromooctanoyl) dibenzo-18-crown-6, 5. 8-bromooctanoyl acid (11.4 g, 51 mmol) and dibenzo-18-crown-6 (8.0 g, 22.2 mmol) were added into a 250 ml three neck flask equipped with a thermometer and condenser, and then added 80 g poly-phosphoric acid into the flask. The mixture was heated up to 90°C and stirred mechanically at the temperature for 1 h. Then the mixture was poured into a mixture of ice and cold water and stirred for 2 h. The precipitate was recrysctallized from EtOH to yield 15.2 g, 89%.

^{1}H NMR ($CDCl_3$): $\delta = 1.20$–2.00 (m, 20H, CH_2, C=O,), 2.83 (t, 4H, CH_2CO), 3.34 (t, 4H, CH_2Br), 3.96 (s, 8H, CH_2O-crown ring,), 4.14 (8H, CH_2O-Ph), 6.76 (d, 2H, Ph), 7.41–7.63 (d, 4H, Ph).

(8-Bromooctyl) dibenzo-18-crown-6, 6. (8-bromooctanoyl) dibenzo-18-crown-6 (3.8 g, 4.9 mmol) was resolved with 50 ml trifluoroactic acid in a single neck flask. Et_3SiH (4 ml, 25 mmol) was added into the stirred solution and the mixture was stirred at room temperature for 2 h. The reaction mixture was diluted by $CHCl_3$ and then the solution of $NaHCO_3$ and water was added slowly, then the organic layer was separated and dried with Na_2SO_4. The $CHCl_3$ was removed under vacuum to produce 2.4 g (8-bromooctyl) dibenzo-18-crown-6,.yield 65%.

^{1}H NMR (CDCl, TMS, δ, ppm) 1.30–1.90 (24H, CH_2, m), 2.51 (4H, CH_2Ph, t), 3.40 (4H, CH_2Br, t), 4.03 (8H, CH_2O-crown ring, s), 4.14 (8H, CH_2OPh, s), 6.69–6.80 (6H, Ph, m).

Bis (8-(3-methoxy 6,7,10,11-tetrapentyloxy triphenylen-2-yloxy)-octyloxy-) dibenzo-18-crown-6,7. (8-bromooctyl) dibenzo-18-crown-6 (0.12 g, 0.22 mmol) and 2-hydroxy-3-methoxy-6,7,10,11-tetrapentyloxyl (0.26 g, 0.42 mmol) were added into the mixture of 4 g anhydrous potassium carbonate and 40 ml anhydrous acetone in a 100 ml three neck flask equipped with condenser. The react mixture was stirred mechanically and refluxed for 12 h and then was filtered. Then acetone was removed under vacuum, the solid product was further purified by chromatography to give the ultimate product.

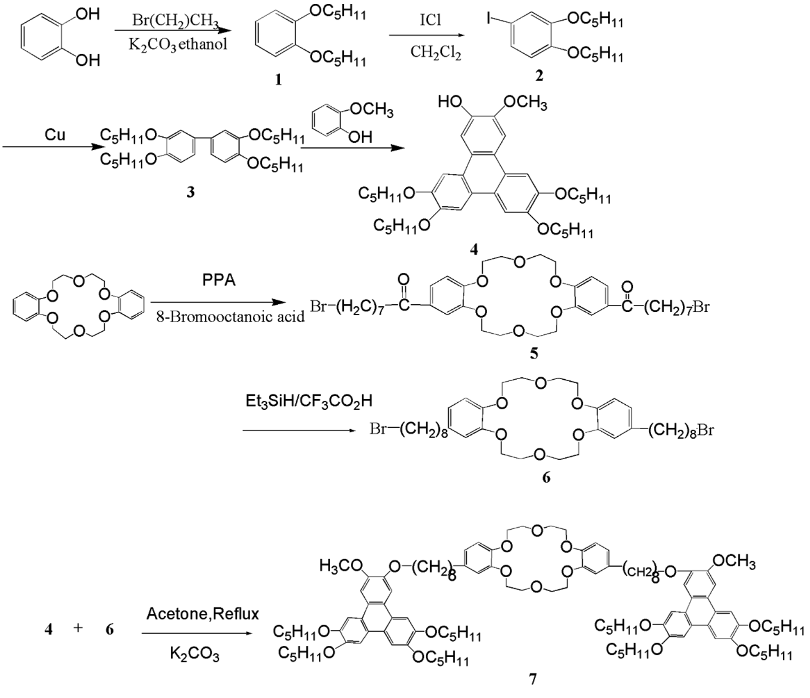
^{1}H NMR ($CDCl_3$): $\delta = 7.07$ (S, 12H, ArH), 6.90–6.94 (m, 6H, ArH), 4.1–4.3 (m, 8H, $PhOCH_2$), 3.98 (S, 20H, $PhOCH_2$), 3.90–3.98 (m, 20H, $PhOCH_2CH_2$), 3.87–3.89 (t, 22H, OCH_3, OCH_2), 2.06–2.11 (m, 12H, CH_2), 2.49–2.54 (m, 4H, CH_2), 2.26–2.30

(m, 4H, CH_2), 1.61 (S, 32H, CH_2), 1.21–1.34 (m, 24H, CH_2), 0.877–0.91 (m, 24H, CH_3).

3. Results and Discussion

3.1. *Synthesis*

The synthesis route of the triphenylene-crown ether is shown in Scheme 1. The synthesis (8-bromooctyl) dibenzo-18-crown-6 involved two step reactions. Firstly, dibenzo-18-crown-6 was acylated with 8-bromooctanoic acid by using the viscous poly-phosphoric acid as solvent as well as catalyst to produce (8-bromooctanoyl) dibenzo-18-crown-6. No side product exist in this reaction and a fairly good yield of about 90% was obtained. This result just proved the V. Percec's report on the synthesis of (8-bromooctyl) dibenzo-18-crown-6 [2]. During the second step, (8-bromooctyl) dibenzo-18-crown-6 was reduced with triethylsilane in trifluoroactic acid to give (8-bromooctyl) dibenzo-18-crown-6. It was a relatively easy and simple process. The synthesis of triphenylene route was a traditional one and included four steps. The first step was the etherization of catechol via Williamson reaction to give 1,2-di-pentyloxybenzene and of high yield 96%. 1,2-dipentyloxybenzene was iodinated by iodine monochloride to give 1,2-dipentaloxy-4-iodobenzene and the coupling of 1,2-dipentaloxy-4-iodobenzene was catalysed by copper and react at a higher temperature 270°C. The last step was the trimerization of 3,3′,4,4′-tetrakispentyloxy biphenyl and o-methoxyphenol using $FeCl_3$ as catalyst to give 2-hydroxy-3-methoxy-6,7,10,11-tetrapentyloxytriphenylene. The last two steps have only a



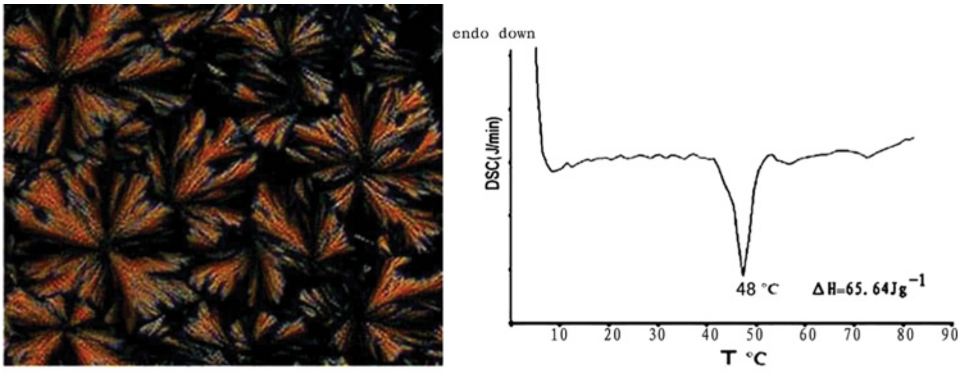
Scheme 1. The synthesis route of the triphenylene-crown ether compound 7.

medium yield about 50–60%. Ultimately, the (8-bromooctyl) dibenzo-18-crown-6 and 2-hydroxy-3-methoxy-6,7,10,11-tetrapentyloxytriphenylene react in acetone at the presence of K_2CO_3 and refluxed for 12 h to give the ultimate goal compound Bis(8-(3-methoxy 6,7,10,11-tetrapentyloxy triphenylen-2-yloxy)-octyloxy-)dibenzo-18-crown-6.

3.2. *Mesophases*

The thermal properties of the new compound Bis(8-(3-Methoxy 6,7,10,11-tetrapentyloxy triphenylen-2-yloxy)-octyloxy-)dibenzo-18-crown-6 (compound 7) was characterized by using DSC and POM at the heating rate equal to 10°C/min. The DSC curve and POM picture was showed in Figure 1. The DSC results showed that the pure compound-two triphenylene ring using di-benzo-18- crown-6 as linkage melted into liquid at 48°C when heating. The POM observation showed that the compound melted sharply at 54°C when heating and crystallized at 42°C when cooling. The POM picture in Figure 1 showed the spherulite texture and showed cross-extinction under polarizer.

In order to display the effect of molecular structures on mesophases and recognition, the miscibility measurement between compound 7 and 2,3,6,7,10,11-hexapentaloxytriphenylene (Cr 66°C $\mathrm{Col_h}$ 122°C) was carried out. We put these two kinds of materials on glass plate under POM and observed and they are adjacent to each other when heating. It was found that when crown ether has melted into anisotropic liquid, the HAT5 has not go into liquid crystal phase (see Figure 2(a)). Continue to heating, the interface between these two area became slurry with the increasing of temperature. Both these two area go into dark at 130°C. During cooling the mixture showed columnar phase in mixed area (see Figure 2(b)). At second heating run, the mixture showed columnar phase texture at 66°C and became isotropic liquid at 125°C. During the second cooling run, the mixture area showed columnar texture at 125°C and became a crystal at 53°C. The DSC result also can proved that these two materials were miscible (see Figure 2(c)). The DSC curve presented was obtained from the second heating run. On DSC curve, there was an endothermic peak at 65°C and another at 118°C. The LC temperature range was comparable with that of HAT5. The compound 7



(a) (b)

Figure 1. The POM picture and DSC curve of the triphenylene-crown ether compound 7, heating at 10°C/min. (Figure appears in color online.)

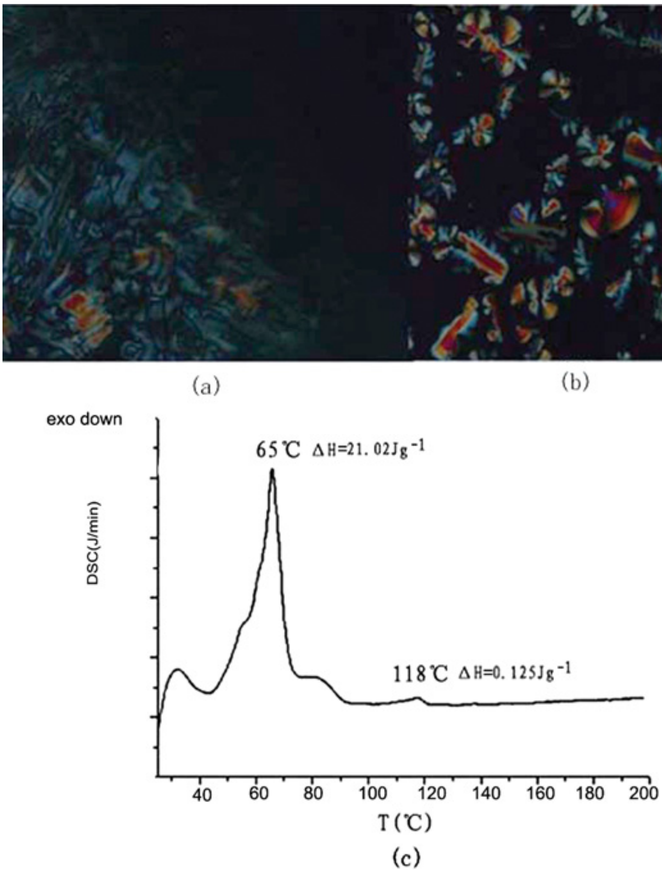


Figure 2. The POM picture and DSC curve of the 1:1 mixture of compound 7 and 2,3,6,7,10,11-hexapentaloxytriphenylene (HAT5), heating at 10°C/min. (Figure appears in color online.)

did not showed LC phase bacuse the benzene ring of the crown ether linkage have an negative effect on the stacking of triphenylene cores. These can also proved by other examples [2]. S. Lashat group has reported that some triphenylene substituted 18-crown-6 ethers showed columnar phases. In those examples, two benzene rings of 18-crown-6 served as parts of the two triphenylene rings and 18-crown-6 became two flexible linkages between two triphenylene rings. So, those compounds showed columnar phase without the disturbance of the two benzene rings of dibenzene-18--crown-6. The miscibility of these two materials proved that the new compound of two triphenylene rings and HAT5 can recognize each other. Although compound 6 did not show LC phase, but when doped with HAT5, the stacking of triphenylene rings of compound 7 can be strengthened via HAT5 molecules.

4. Conclusions

A new crown-ether-triphenylene compound was synthesized. The chemical structure was defined by using ^{1}H NMR spectrum. The thermal properties were carried out by using DSC and POM methods. The new compound do not show LC phase and the benzene ring of the crown ether linkage have an negative effect on the stacking of triphenylene cores. The miscibility between the new compound and HAT5 was carried out by using DSC and POM methods. The results showed that the two materials are miscible and the mixture of these two materials showed columnar LC phase between 65°C and 118°C. The miscibility of the materials proved that these two kinds of materials with a similar triphenylene structure can recognize each other. The stacking of triphenylene rings of compound 7 can be strengthened via HAT5 molecules.

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