Synthesis and characterization of novel mesogens based on a disc -shaped tripheylene core and multiple rod-shaped cyanobiphenyl tails

Chunxiu Zhang, ^{a,b} Zhiqun.He,^{a,*} Jialing Pu^b, Yongsheng Wang , ^a junjiewangand zhongxiao Li^b ^aInformation Recording Materials Lab, Beijing Institute of Graphic Communication Beijing102600, China,^bKey Laboratory of Luminescence and Optical Information, Ministry of Education, Institute of Optoelectronic Technology, Beijing Jiaotong University, Beijing 100044, PR China

Abstract

Two novel triphenylene-based molecules which combined one discotic-shaped mesogen and three rod-shaped mesogens through alkyl have been synthesized, one is of symmetric molecular structure and the other is of asymmetric molecular structure. Their chemical structures were determined by ¹H NMR, ¹³CNMR and Elemental analysis. The thermotropic liquid crystalline properties of them were characterized by polarizing optical microscopy and differential scanning calorimetry analysis revealed that two mesophases LC_1 and LC_2 exist in the molecule of symmetric molecular structure.

Introduction

Since their discovery of discotic liquid crystals by Chandrasekhar et al. in 1977 [1], Discotic liquid crystals have received widespread attention due to their remarkable one dimensional charge transport properties including conductivity, photoconductivity and photovoltaic properties[2]. Triphenylene nucleus are particularly attractive because its derivatives are relatively easy to synthesize, they are thermally and chemically stable, and they show a variety of mesophases having interesting electronic properties[3]. Recent efforts have been directed towards design novel triphenylene molecules with side chains bearing terminal groups such as azobenzene[4], cyanobiphenyl[5], carbazole[6], ferrocene[7], fullerene[8], sugars[9], crown ether[10] and mixed tails[11], which in some way combined the features of rod-shaped and disc-like shaped molecules. Most of previous attempts to bridge the gap between these differently shaped liquid crystals have result in nematic and soft-crystal phases [12]. Recently, a novel covalently linked disc-rod mesogen, containing a tripheylene moiety and three cyanobiphenyl-based rod-based moiety studied by Kouwer et al. show smectic phase. Another example of the combination of a triphenylene (disc-shaped mesogen) core and six peripheral azobenzene units (rod-shaped mesogen) shows kinetically controlled bimesomorphism with metastable smectic and stable hexagonal columnar phases.

Experimental section

1. Instrumentation



R: (CH₂)₉O-(CN)

Scheme1. Synthesis of triphenylene-based disc-shaped molecules Reagents and conditions: (i)Br(CH₂)₉Br,K₂CO₃,acetone,reflux,78%; (ii)Br(CH₂)₄CH₃,K₂CO₃/ethanol,reflux,91%;(iii)FeCl₃/CH₂Cl₂,MeOH ,64%;(iv)B-Bromocatecholboronane/CH₂Cl₂,6a:61%,6b:38%;(v)D MF,K₂CO₃,78°C,12h,7a:11.8%, 7b:12.4%. 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 using ¹H NMR and ¹³CNMR. ¹HNMR spectra were measured in CDCl₃ on a Brucker Avance (400MHz) spectrometer and ¹³C-NMR spectra were measured in CDCl₃ on a Brucker Avance (400MHz) spectrometer. Elemental analysis was carried out on an elementary analyzer (Elementar Analysensysteme GmbH Vario EL).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 DSC 2010) at a heating and cooling rate 10°Cmin⁻¹.

2. Synthesis

In the work described here, we have incorporated three rod-shaped cyanobiphenyl moieties into a triphenylene molecule and they linked together by alkyl chains (C11) using etherification, giving, two different triphenylene-based discotic liquid crystals 7a (C3 symmetry) and 7b (C3 asymmetry). The synthetic approach is outlined in Scheme1.Compound 2 (o-dipentylox ybenzene) was prepared by dialkylate catechol 1 with bromopentane in the present of potassium carbonate. 2, 3, 6, 7, 10, 11-Hexapentyloxytriphenylene 3 was prepared via an oxidative trimerisation of o-dipentyloxybenzene 2 using ferric chloride as a 2, 6, 10-trihydroxy-3, 7, 11 - tris catalyst [13]. (pentyloxy)triphenylene **6a** and 2, 7, 10-trihydroxy-3, 6, 11-tris(pentyloxy)triphenylene 6b was synthesized via cleavage of hexapentyloxytriphenylene with B-bromocatecholborane(Cat-B-Br)[14]. The flexible spacer was introduced by alkylation of cyanobiphenyl 4 with a 10-fold excess of 1.9-dibromononane in the present of potassium carbonate as base to give 4'-(11-bromononyloxy)-4-cyanobiphenyl 5. Finally, three rod-shaped 4'-(11-bromounnonyloxy)-4-cyanobiphenyl 5 were introduced into 2, 6, 10-trihydroxy- 3, 7, 11- tris(pentyloxy)triphenylene 6a and 2, 7, 10-trihydroxy-3, 6, 11-tris (pentyloxy)triphenylene 6b using etherification to give disc-like molecules 7a and 7b. The structures of the intermediates and the final compound were confirmed by ¹HNMR, ¹³CNMR, IR and elemental analysis.

2,6,10-tri[(9-(4'-cyano-biphenyl-4-loxy)nonyloxy)]-3,7,11-tris(p entyloxy)triphenylene7a:

The mixture of 4'-(9-bromononyloxy)-4-cyanobiphenyl **5** (0.94g, 2.2mmol), 2, 6, 10-trihydroxy-3, 7, 11-tris (pentyloxy) triphenylene **6a** (0.29g, 0.55mmol), potassium carbonate (3g, 21.7mmol), and DMF (30ml) was placed in a 100ml flask equipped with a condenser, N_2 inlet, and magnetic stirrer. The mixture was heated to 75°C and stirred overnight. The reaction mixture was removed from heat, filtered, and washed with CHCl₃. The excess solvent was evaporated under reduced pressure and the remaining liquid was poured in methanol to precipitate the product.

The solid was filtered, dissolved in CH₂Cl₂ and the mixture was transferred to a silica gel column (SiO2,eluent CH2Cl2 / EtOAc (10:1)) yielding a faint yellow powder 0.093g(11.8%). ¹HNMR (CDCl₃, 400MHz) δ7 84 (s,6H,triphenylene)7.61-7.69(m,6H,Ar-H),7.49-7.53(m,6H,Ar-H), 6.97-7.25(m,6H,Ar-H), 4.19-4.24 (t,12H, CH 2O), 3.98-4.00 (t,6H,CH₂O), 1.94-1.97 (t,12H,CH₂CH₂O) 1.81 (m,6H,CH₂CH₂O), 1.35-1.58 (m,54H,CH₂), 0.97(m,9H,CH₃); ¹³CNMR(CDCl₃,400MHz) : δ 160.0, 149.0, 145.2, 132.5, 131.2, 128.2, 127.0, 123.6, 119.1, 115.0, 109.9, 107.3, 76.6-77.4, 69.6, 68.1, 29.1-29.5, 28.3, 26.1-26.0, 22.5, 14.1ppm; Elemental analysis calcd for C₉₉H₁₁₇N₃O₁₂ :C,77.19;H:7.60; N:2.72. Found: C: 76.89; H: 7.54; N: 2.86%.

2. Phase Behaviors

The phase behavior of these molecules was investigated using differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The DSC results are summarized in Table 1. Despite the structure similarities between compound **7a** and **7b**, **7b** neither exhibit mesogenic behavior on either heating or cooling and melt at 10° C/min directly from crystalline solids to isotropic liquid at 54° C, the crystallization of **7b** take place at 31.45° C



Figure1. Optical polarizing microscopy photographs of 7b (a) at 56 $^{\circ}$ C (b, at 98 $^{\circ}$ C (c) at 102 $^{\circ}$ C (d) at 105 $^{\circ}$ C (×5).All Pictures taken with crossec polarizer (×120).

during cooling scan, no texture showed under POM. Compound 7a with symmetric structure showed two endothermic transitions prior to the isotropic transition at 109° C and with a shoulder at the lower temperature region. On cooling up to room temperature, only the crystallization peak rather than mesophse to mesophase transition was observed. 7a showed an optical texture of the fluid unknown LC_1 mesophase (Fig.1 (a)) in the temperature range 45-98°C and the transition from LC_1 mesophase to another mesophase LC₂ which is relatively narrow appeared in 98-107°C according to the POM observation (Fig.1(b),(c),(d)), when heating at 10° C/min and the isotropic temperature was 109° C, the transitions were reversible in these two temperature ranges, though no transition peak appear on DSC curve during cooling scanning. In the early stage of the formation of LC_1 mesophase was observed under crossed polarizing condition of a microscope as shown in fig.1(a), it was rather fluid, but, it change into highly viscous state when the temperature is above 98 °C and this phenomena is similar to the description in the work of Y. Shimizu et al.



Figure 2. DSC heating and cooling traces of compound 7a (10 $^{\circ}\mathrm{C}$ min $^{-1})$

Conclusion

In summary, a pair of disc-shaped molecules was prepared, based on one triphenylene mesogen and three cyanobiphenyl moieties linked through alkyl chain spacers. The optical textures and the DSC curves showed that the combination of rod and discotic units led to two kind of unknown mesophases and it needs extensively XRD studied to determine the exact nature of the two phases.

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Acknowledgements

This work was funded by the NSFC grants (20674004 and 10434030), the state key program for basic research of China (2003CB314707), the National Hi-Tech R&D Program of China (2006AA03Z412) and BJTU Science Fund (2006XM043).

Author Biography

Zhang chunxiu received the MS degree from Wuhan University, Wuhan, People's Republic of China in 1998. She is currently pursuing her PHD degree in Institute of Optoelectronic Technology at Beijing Jiaotong University. Her interests include optoelectronic materials and devices.

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