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Synthesis of Amide Group Containing Triphenylene Derivatives as Discotic Liquid Crystals and Organic Gelators

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Intermolecular hydrogen bond is an efficient way to anchor columnar assembly of discotic liquid crystals, and would result in more ordered columnar mesphase and faster charged carrier mobility. In this report, a series of peripheral functionalized triphenylene derivatives, $C_{18}H_6(OC_6H_{13})_4(OCH_2CONHR)_2$, which contains amide groups at the 2,7-positions, have been synthesized. The polarized optical microscopy (POM) and differential scanning calorimetry (DSC) results showed that these compounds exhibit hexagonal columnar mesophases. The triphenylene derivatives gelate in the solution of octane, petroleum ether, cyclohexane and p-xylene and form stable organic gels. The xerogels formed from organic solvents were analyzed by scanning electron microscope (SEM) and showed fiber-like or sponge-like morphology. It is demonstrated that intermolecular hydrogen bonds stabilize the columnar molecular organization and assembly in mesomorphic state and organic gel.

Keywords: discotic liquid crystal; hydrogen bond; self-assembly; small molecular mass organic gelator; supramolecular organic gel; triphenylene

1. INTRODUCTION

The supramoleculer organization of discotic liquid crystals (DLCs), such as triphenylene and hexabenzocoronene derivatives, have been

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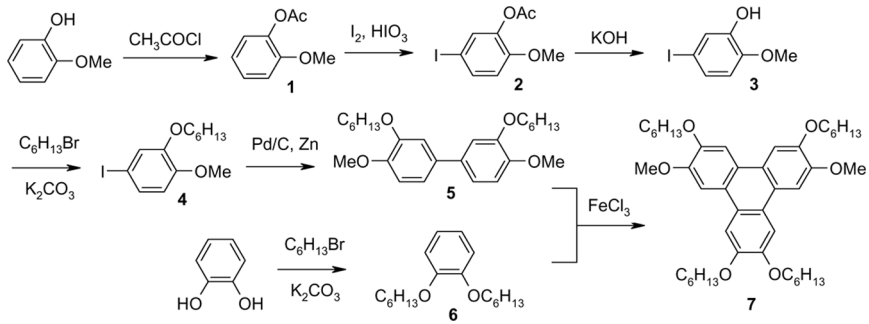
attracting considerable interests since 1977 [1–5], as they can self assemble to highly ordered hexagonal columnar mesophases promoted by the π-π interactions between the polyaromatic cores [6], and this leads to the formation of one-dimensional pathway for transport of charged carriers along the columns. The charged carries mobility rate in DLCs arrives at $0.12\,cm^2\,V^{-1}\,s^{-1}$, this value is comparable to the commercially used silicon semiconductors [7]. Therefore DLC materials are potential candidate materials as photovoltaic devices, field effect transistors and organic light emitting diodes, gas sensors and other molecular electronics [8–12].

In the columnar assemblies, the DLC molecules can fluctuate in the column, slide out of the column, or rotate around the columnar axis, it therefore significantly disturbs the charged carrier mobility [13]. Thus restricting and controlling the molecular movements in the columnar mesophase are desired. Usually some approaches such as using β-oxygen effect [14–16], fluorophobic-fluorophilic effect [17–19], hydrophilic-hydrophobic effect [20,21], donor-acceptor interaction [22,23], and ionic interaction [24,25] have been used to provide such kind of controlling. Hydrogen-bonding is an important self-assembling tool as its moderate bonding energy, directionality, selectivity, and reversibility. H-bondings make the adjacent polyaromatic cores approach each other more closely, the HOMO-LUMO splitting increase, and a high charge carrier mobility ensure.

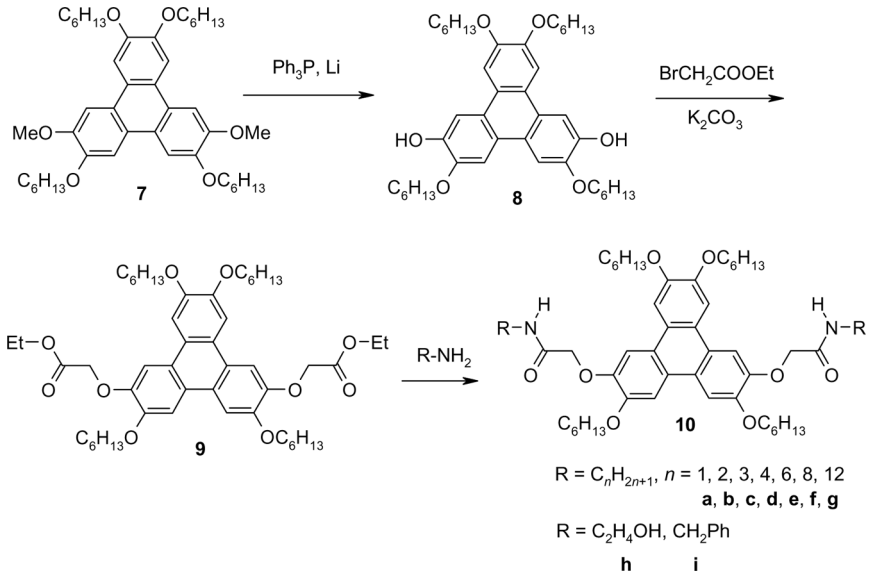
H-bonding interactions provide a promise way for the stabilization of columnar organization, and different approaches have been developed for H-bonding stabilization of triphenylene derivatives. However, not all H-bonding system results in stable columnar mesophase. For example, Shimizu's group synthesized a series of triphenylene derivatives, $C_{18}H_6(OC_6H_{13})_4(OC_nH_{2n}COOH)_2$, with carboxylic groups at the terminal of 2,3-position [26,27]. The spacer length between carboxylic group and triphenylene core was changed, only few triphenylenes exhibited narrow monotropic mesophases. Kumar prepared series of mono-, di-, and tri-acetylamino hexabutyloxytriphenylenes, $C_{18}H_6(OC_4H_9)_6(NHAc)_n$, $n = 1$–3, only 1-acetylamine-2,3,6,7,10,11-hexabutyloxy- triphenylene showed monotropic mesophase [28]. Shinkai reported six-fold H-bonding triphenylenes, $C_{18}H_6(OCH_2CONHR)_6$, $R = C_4H_9$ and $C_{12}H_{15}$, no thermotropic liquid crystalline properties was reported [29]. Marcelis synthesized several triphenylene derivatives with amide, urea or thiourea group in one of peripheral chains, and the amide-containing triphenylenes did not show mesomorphism [30]. Some H-bonding triphenylenes indeed show stabilized Col_{ho} phase and higher charge mobility. For example, Zhao has prepared series of amide-containing triphenylene, $C_{18}H_6(OC_nH_{2n+1})_{6\text{-}x}(OCH_2$



SCHEME 1 Synthesis of triphenylene discotic intermediate.

CONHR)$_x$, x = 1, 3, n = 4–9, and wider columnar mesophase ranges were found [31–33]. Marcelis and Zuihof synthesized a H-bond triphenylene and displayed the highest charge carrier mobility value. The above examples tell us that rational molecular design is important for the success of stable Col$_{ho}$ phase and high charge mobility.

Small molecular mass organic gels are attracting lot of attentions for the academic interests and potential industrial application in membrane and separation technology, catalysis or drug delivery [34–36]. The investigation showed that aromatic π-π interactions,



SCHEME 2 Synthesis of amide group containing triphenylene discogens.

H-bondings, and van de Waals interactions are the mechanism for stable organic gels. From these points of views, H-bonding discotic liquid crystals and organic gels have similarity, and it has demonstrated that organic gelation improved the light emitting properties and charge carrier mobility of discotic triphenylene derivatives [29,37].

In this paper, we synthesize a series of triphenylene derivatives, $C_{18}H_6(OC_6H_{13})_4(OCH_2CONHR)_2$, which contain amide functional group at 2,7-positions. The polarity, size and length of the peripheral chains have been modified, and these compounds showed stable hexagonal columnar mesophases. Further more, these discogens formed stable organic gel in some hydrocarbon organic solvents, and these behaviors are explained with the intermolecular hydrogen bonding among the discotic molecules. The synthetic route of target molecules is shown in Schemes 1 and 2.

2. RESULTS AND DISCUSSION

2.1. Synthesis

Triphenylene derivatives are well known discotic liquid crystals, and its synthetic methodology has been well developed. In most case, these synthetic methods can be divided into three categories [38]: (1) terphenyl route; (2) benzene and biphenyl route; (3) statistic route. The benzene and biphenyl route is longer than others, however it has better selectivity, therefore it is favorite to synthesis triphenylene derivatives with multiple functional groups. In this report, we use benzene and biphenyl route preparing the target molecules. See Schemes 1 and 2.

In this report, the key triphenylene intermediate, **7** synthesized by oxidative coupling of 1,2-bis(hexyloxy)benzene (**6**) and 3,3′-Bis (hexyloxy)-4,4′-dimethoxy-biphenyl (**5**). The tetraalkoxybiaryls usually synthesized from homo-coupling of aryl halides in presence of a stoichiometric amount of copper, called Ullmann reaction. High temperature and more active copper of Ullmann coupling often resulted in low yield. In this synthesis, copper has been replaced by palladium, zinc and aqueous solution of KOH, and this modification makes the reaction very simple and reduces the reaction time to only 7–10 h and the palladium catalyst can be recycled. It is noted that in this synthetic route, compound **2** was prepared in low yield (34%), as compound **1** is not electron-rich enough in the iodization reaction, and the electron-donating ability of methoxy group in **1** is weaker than that of other alkoxyl group, such as hexyloxy.

All the synthesized compounds were characterized with 600 MHz ^{1}H NMR, elemental analysis, high resolution Mass and the analytical data are concordant with their chemical structures.

In order to obtain information about hydrogen bonding and self-assembled structures of triphenylene derivatives, FT-IR spectra were measured. IR spectra of compound **9**, **10d**, **10h**, **10i** were recorded at room temperature using dry powder samples in KBr. For **10d**, ν(N-H) is 3315 cm^{-1} and ν(C=O) is 1660 cm^{-1}; for **10h** ν(N-H) is 3315 cm^{-1} and ν(C=O) is 1651 cm^{-1}; for **10i** ν(N-H) is 3408 cm^{-1} and ν(C=O) is 1663 cm^{-1}; for **9** ν(C=O) is 1768 cm^{-1}. Compared with the literature reported value [7,31], weak to medium strength intermolecular H-bonds exist in the amide containing triphenylenes.

2.2. Mesomorphism

The phase transition temperatures and enthalpy changes of the synthesized triphenylene derivatives were studied with differential scanning calorimetry (DSC), and the results are drawn in Figure 2 and summarized in Table 1. The optical textures of the mesophases were observed and recorded with a heating plate polarized optical microscopy (POM) and typical photomicrographs showed in Figure 1.

POM studies has revealed that, when powder sample in thin untreated glasses was first heated to isotropic liquid and then cooled slowly, compound **9**, **10b – 10f** formed the typical fan shaped texture of hexagonal columnar mesophases, compound **10h** and **10i** formed the same texture just in cooling run, and for compound **10a** and **10g**, no mesophase optic texture was observe. These compounds showed very big domains or homeotropic alignment behaviors, and are suitable for charge carrier mobility measurement and electronic devices manufacture.

DSC analysis showed that these triphenylene derivatives have only one mesophase (Col_h phase). The melting points of compound **10a** to **10g** gradually decreased with the amide tail lengthening at first, and increased after $n > 4$. The clearing points showed the reverse trend. **10d** displayed the widest mesophase range, about 88°C, among these compounds. **10h** and **10i** had monotropic mesomorphism, and the mesophase rang only about 27°C. The phase diagram of **10a – 10g** are drawn in Figure 3.

The chemical structure of **10h** has polar hydroxyl group at the end of amide chain, and **10i** possesses bulk benzyl group at the terminal of amide group, it is obvious that the large size and polar substituents destabilize and disturb the columnar organization of triphenylene derivatives. It should be the same reason that **10a** and **10g** did not

TABLE 1 Phase Transition Temperatures and Transition Enthalpies of Triphenylene Derivatives **9**, and **10a – 10i**, 2,7-$C_{18}H_6(OC_6H_{13})_4(OCH_2CONHR)_2$, $R = C_nH_{2n+1}$

	Mesophases, transition temperature and enthalpy changes	
Compd. (R)	Second heating/°C (ΔH, kJ mol^{-1}, ΔS, J mol^{-1} k^{-1})	First cooling/°C (ΔH, kJ mol^{-1}, ΔS, J mol^{-1} k^{-1})
9	K 56 (32.2, 92.3) Col_h126 (8.4, 21.0) I	I 129 (9.4, 23.3) Col_h21 (24.8, 84.5) K
10a (CH_3)	$K_2$125 (26.9, 67.7) $K_1$173 (53.9, 121.0) I	I 147 (48.4, 115.1) $K_1$18 (15.8, 54.1) K_2
10b(C_2H_5)	K 144 (44.9, 107.7) Col_h159 (7.3, 16.9) I	I 159 (7.3, 16.9) Col_h120 (40.5, 103.2) K
10c(C_3H_7)	K 100 (38.5, 103.2) Col_h163 (8.5, 19.4) I	I 163 (8.2, 18.7) Col_h78 (20.0, 57.1) K
10d(C_4H_9)	K 77 (18.4, 52.6) Col_h165 (8.4, 19.2) I	I 165 (8.3, 18.9) Col_h74(16.3, 47.0) K
10e(C_6H_{13})	K 85 (24, 67) Col_h151 (8.4, 19.9) I	I 150 (8.2, 19.3) Col_h79 (21.5, 61.1) K
10f (C_8H_{17})	$K_2$83 (3.8, 10.6) $K_1$100 (36.3, 97.4) Col_h128 (6.5, 16.3) I	I 127 (6.7, 16.8) Col_h79 (21.6, 61.4) K
10g($C_{12}H_{25}$)	$K_2$44 (26.0, 82.1) $K_1$102 (49.5, 132.1) I	I 80 (3.8, 10.9) $K_1$62 (15.5, 46.3) K_2
10h(CH_2CH_2OH)	K 192 (61.0, 131.1) I	I 182 (12.9, 28.4) Col_h156 (39.1, 91.3) $K_2$46 (19.3, 60.6) K_1
10i(CH_2Ph)	K 135 (77.6, 190.1) I	I 114 (6.0,15.5) Col_h87 (30.4, 84.4) K

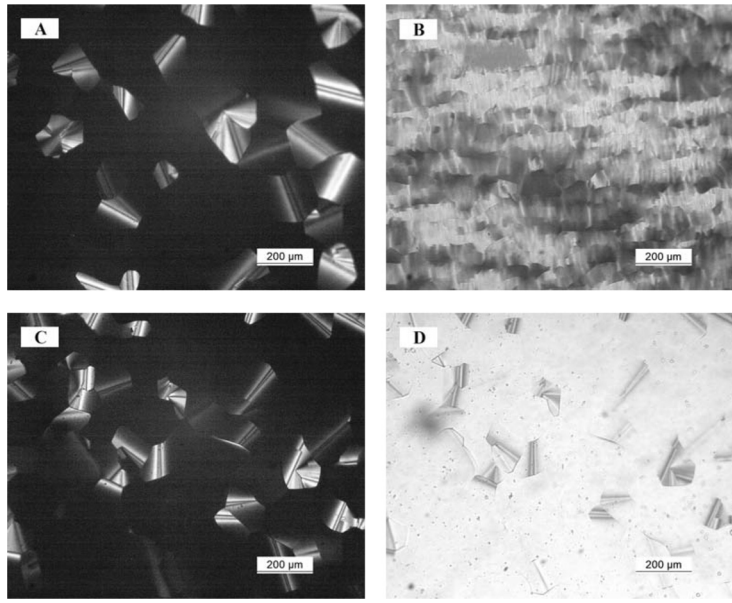


FIGURE 1 POM photographs of triphenylene derivatives. All photos taken in the slowly cooling run from isotropic liquid: (A) **9**, 105°C, Col_h phase; (B) **10d**, 119°C, with shearing; (C) **10d**, 132°C, Col_h phase; (D) same with (c), two parallel polarizers.

show mesomorphism, as the amide chain is too short to **10a** (methyl group), and too long to **10g** (dodecyl group). These two compounds showed polymorphism, they have two crystal phases but obviously not liquid crystal phase under POM. In contrast, the melting points of all amide containing triphenylene derivatives **10**, are higher than that of **9**, which contains ester functional groups. It has reported that the melting and clearing points increased with the number of amide containing tail increasing [31,32]. To the triphenylenes, $C_{18}H_6(OC_6H_{13})_x(OCH_2CO\ NHBu)_{6-x}$, melting points increasing is more obvious than that of clearing points.

2.4. Gelation Test

The gelation tests have been done (see Fig. 4) and results summarized in Table 2. **10d** can form gels in octane, petroleum ether, cyclohexane and p-xylene, but can not form gels in the solvents such as toluene, acetone, $CHCl_3$. **10h** and **10i** with polar and bulky peripheral groups respectively did not form organogel. This demonstrates that weak to

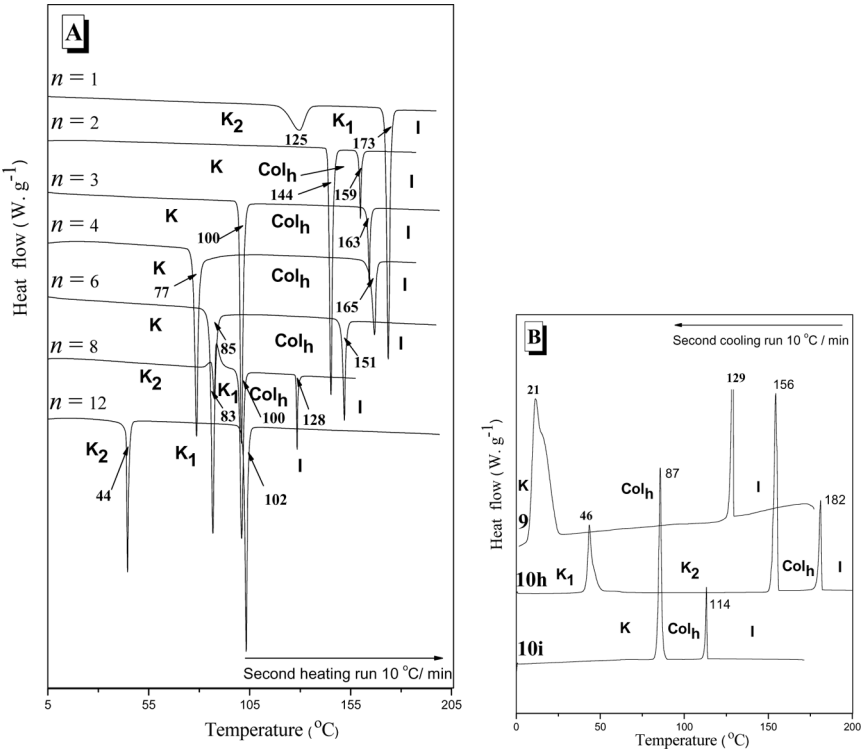


FIGURE 2 DSC traces of triphenylene derivatives. (A) heating run of **10a – 10 g**, 2,7-$C_{18}H_6(OC_6H_{13})_4(OCH_2CONHR)_2$, $R = C_nH_{2n+1}$; (B) cooling run of **9**, **10h**, **10i**.

medium, not strong H-bonding in the amide group containing triphenylene derivatives. The IR and gelling test arrives the same conclusion.

The organogel aggregate structure of **10d** can be visualized by SEM observations. The SEM images of the xerogels obtained from **10d** in cyclohexane and petroleum ether showed very long fibrous ribbons with 10–20 μm in diameters or sponge-like plates (Fig. 5). The primary experiments show that the morphology of the supramolecular assembly can be controlled by organic solvent selection or evaporation rate of organic solvents.

The supramolecular assembly to discotic columns or organic gel by intra-columnar intermolecular hydrogen bonds of amide groups has been demonstrated in Figure 6.

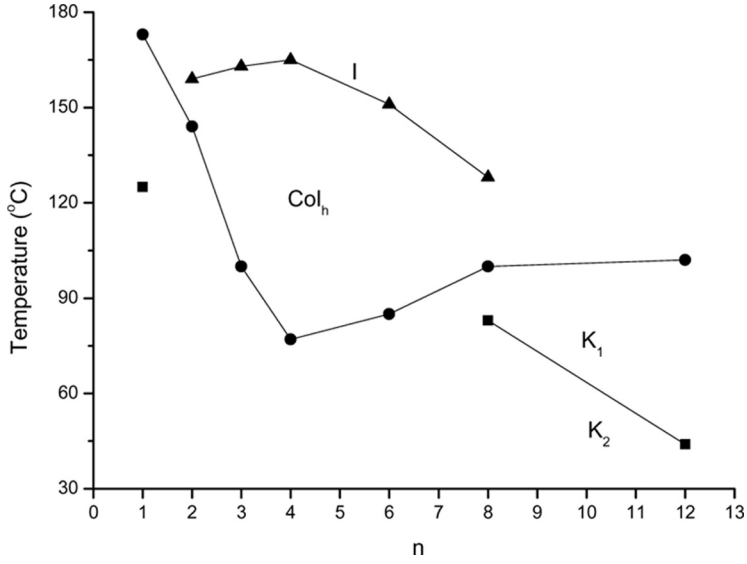


FIGURE 3 Phase diagraph of triphenylene discogens **10a – 10g**, 2,7-$C_{18}H_6(OC_6H_{13})_4(OCH_2CONHR)_2$, $R = C_nH_{2n+1}$.

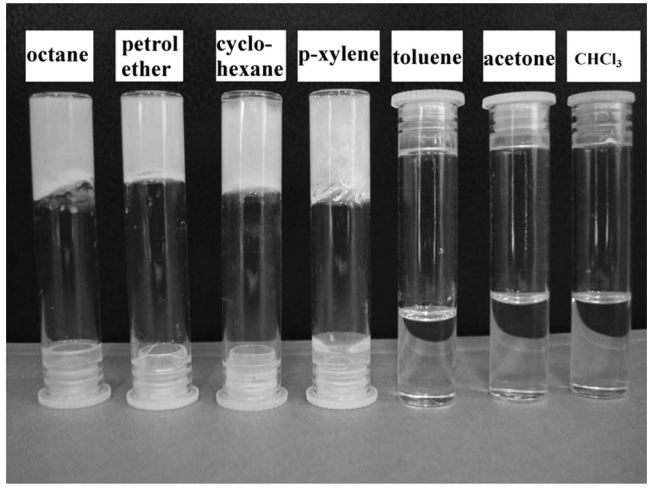


FIGURE 4 The photograph of organic gels formed by **10d**, 2,7-$C_{18}H_6(OC_6H_{13})_4(OCH_2CONHC_4H_9)_2$ in different organic solvents.

TABLE 2 Organic Solvents Tested for Gelation by **10d**, **10g**, **10h**, and **10i** (4×10^{-3} mol/L)

	hexane	petroleum ether	cyclo-hexane	p-xylene	toluene	acetone	Chloroform
10d	G	G	G	PG	S	S	S
10g	G	G	PS	PS	S	S	S
10h	I	I	I	I	S	S	S
10i	I	I	I	I	S	S	S

PS, poor solution; I, insoluble; S, soluble; G, gelation; PG, partial gelation.

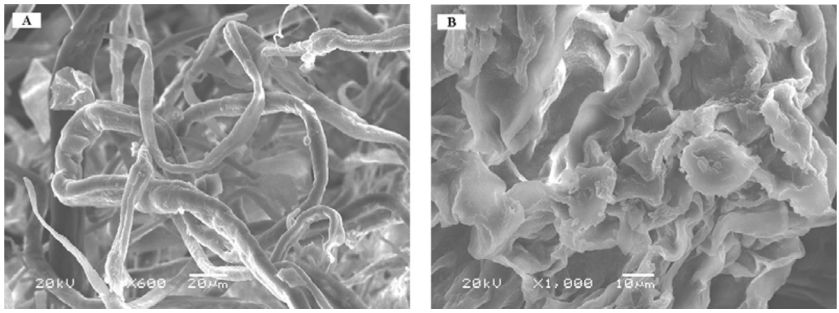


FIGURE 5 Scanning electron micrographs of the xerogel. (A), **10d** from cyclohexane; (B), **10d** from petroleum ether.

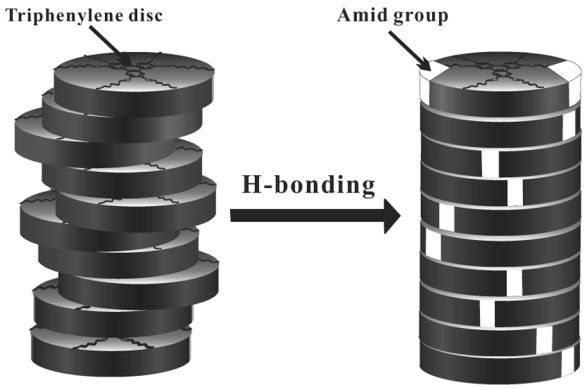


FIGURE 6 Hydrogen bonds anchor the columnar organization resulted in more ordered Col_h mesophase and organic gel.

3. CONCLUSION

A series of triphenylene derivatives which containing amide groups at 2,7-position has been synthesized. **10a** and **10g** did not show any mesomorphism as their two amide peripheral chains too short or too long, Most of the compounds with alkyl chain exhibit enantiotropic hexagonal columnar mesophase, and the compound with $-C_2H_4OH$ and $-CH_2Ph$ just exhibit monotropic mesophase. The melting points of compound **10a** – **10g** gradually decrease accompany with the length of tail group at first, and increase after butyl. The clearing points showed the reverse trend. As **10d** has six almost equal length peripheral chains, and therefore better molecular symmetry, it exhibits the widest mesophase temperature rang among all the compounds, about 88°C. IR spectra, gelation tests have demonstrated the intermolecular hydrogen bond exists among the triphenylene derivatives. The investigation for the influence of hydrogen bond interactions on the charged carrier mobility of functionalized triphenylene discogens is underway.

4. EXPERIMENTAL

Instrumentation

^{1}H NMR (600 MHz) spectra were recorded with Bruker-Avance-600, using $CDCl_3$ as solvent and Me_4Si as internal standard. IR spectra were obtained with KBr pellets using NICOLETMX-IE FT-IR. The elemental analysis was performed with Carlo Erba 1106. The high resolution Mass were recorded on Varian 7.0 T FTICR-MS (MALDI mode). Melting points, clearing points, phase transition enthalpies were measured using differential scanning calorimetry (DSC) on TA-DSC Q100 system, with heating and cooling rate of $10°C\,min^{-1}$. Phase transition enthalpies were transferred into $kJ\,mol^{-1}$, entropy changes transferred into $J\,mol^{-1}\,K^{-1}$. The mesophase textures were observed and recorded using polarizing optical microscopy (POM) XP-201, with a hot stage XP-201.

Chemicals and Synthesis

All chemicals are commercial products and used without further purification.

2-Methyloxyphenyl Acetate, 1

Acetyl chloride (49 g, 0.62 mol) was slowly added to the guaiacol (59.5 g, 0.48 mol) in 30 min, and the mixture was stirred for further 24 h at room temperature. Dichloromethane was added and the

solution was washed with aqueous potassium carbonate until the aqueous layer was basic. The organic layer was dried with anhydrous magnesium sulfate, and the organic solution was removed under vacuum. Distillation of the residue at 110–120°C at 7.6 mmHg afforded product as light yellow oil (68.5 g, 86%).

2-Methyloxy-5-iodophenyl Acetate, 2

The compound **1** (28.5 g, 171.87 mmol) was added to the mixture of iodine (17.46 g, 68.75 mmol), HIO_3 (7.18 g, 40.8 mmol), glacial acid (190 ml), chloroform (50 ml), water (65 ml) and concentrated sulfuric acid (2 ml), the mixture was stirred for 24 h at 40°C. Then 50 mL chloroform and 30 mL water was added. The mixture was washed with dilute $NaHSO_3$ solution three times, then by water one time. The organic layer was dried with magnesium sulfate, and the organic solvent was removed under vacuum. Recrystallization from ethanol afforded the product as white crystal (17.06 g, 34%).

2-Methyloxy-5-iodophenol, 3

The compound **2** (15.7 g, 53.77 mmol) was dissolved in the solution of potassium hydroxide (18.14 g, 0.324 mol) in the mixture of ethanol (80 mL) and water (60 mL). The mixture was refluxed for 2 h, then cooled to room temperature, acidified with 10% (V/V) hydrochloric acid. The mixture was extracted with dichloromethane three times, and the organic layer was dried with magnesium sulfate, then solvent was removed under vacuum. Recrystallization from light petroleum afforded product as white crystal (10.5 g, 78%).

2-Hexyloxy-4-iodoanisole, 4

BrC_6H_{13} (10.3 g, 62.4 mmol) and the compound **3** (13 g, 52 mmol) were added to the mixture of potassium carbonate (10.76 g, 78 mmol) in ethane (100 mL), the mixture was refluxed 12 h, then cooled to room temperature. Dichloromethane (50 mL) was added to the mixture and solid was filtered off. The filtrate was concentrated under vacuum. Recrystallization from ethanol afforded product as white crystal (15.7 g, 90%).

3,3′-Bis(hexyloxy)-4,4′-dimethoxybiphenyl, 5

10% Pd/C (3.96 g), Zn dust (9.1 g, 140 mmol), the solution of KOH in water (6 ml, 2 mol L^{-1}) were added to the mixture of acetone (150 mL) and water (60 mL), and the suspension was stirred 0.5 h, then the compound **4** (15.6 g, 46.7 mmol) was added. The mixture was refluxed 10 h, and cooled to room temperature. The solid was filtered and the filtrate was extracted with dichloromethane. The organic layer was dried with

magnesium sulfate, the solvent was removed under vacuum. Recrystallization from light petroleum afforded product as white crystal (6.24 g, 64.5%).

1,2-Bis(hexyloxy)benzene, 6

Bromohexane (36.3 g, 0.22 mol), catechol (11 g, 0.1 mol) were added to the suspension of potassium carbonate (41.4 g, 0.3 mol) and ethanol (150 mL), and the mixture was refluxed 24 h. The solid was filtered and the solvent was removed under vacuum. Distillation of the residue at 152–160°C at 7.6 mmHg afforded the product as yellow liquid (22.38 g, 80.5%).

2,7-Dimethoxy-3,6,10,11-tetrakis(hexyloxy)triphenylene, 7

The compound **5** (6.21 g, 15 mmol), **6** (16.68 g, 60 mmol), anhydrous iron (III) chloride (24.38 g, 150 mmol) and concentrated sulfuric acid (10 drops) were added to dichloromethane (100 mL), and the mixture was stirred 2 h at 30°C. The reaction mixture was carefully poured into the methanol (300 mL), and kept it in ice over 2 h. The resulting solid was filtered off and washed with cold methanol. Separation from columnar chromatography on silica afforded the triphenylene as white crystal (7.12 g, 69%, mp: 98°C).

2,7-Dihydroxy-3,6,10,11-tetrakis(hexyloxy)triphenylene, 8

Metal Li (1.07 g, 0.153 mol) was added to the solution of PPh_3 (16 g, 0.0612 mol) in dry THF (150 mL), after the mixture was stirred over 1 h, t-BuCl (5.66 g, 0.0612 mol) was added by three times and refluxed 1 h. Compound **7** (7 g, 0.0102 mol) was added under the nitrogen atmosphere, and stirred 2 h at room temperature. Then the reaction mixture was poured carefully into the ice water, and acidified with 10% HCl solution (100 mL), and extracted with dichloromethane. The organic layer was dried with magnesium sulfate, and the organic solvent was removed under vacuum. Purification through columnar chromatography on silica afforded the product as white crystal (5.83 g, 92%, mp: 186°C).

Compound 9, 2,7-$C_{18}H_6(OC_6H_{13})_4(OCH_2COOC_2H_5)_2$

2,7-di(ethyloxycarbonylmethyloxy)-3,6,10,11-tetrakis(hexyloxy)triphenylene. $BrCH_2COOC_2H_5$ (652 mg, 3.9 mmol), compound **8** (858 mg, 1.3 mmol) were added to the suspension of potassium carbonate and DMF. The mixture was heated at 120°C with stirring for 12 h, poured onto the ice water, and extracted with dichloromethane. The organic layer was dried with magnesium sulfate, and the organic solvent was

removed under vacuum. The residue recrystallization from ethanol afforded the product as white solid (1.08 g, 89%, mp: 56°C).

Compound 10d: 2, 7-$C_{18}H_6(OC_6H_{13})_4(OCH_2CONHC_4H_9)_2$

2,7-di(butylaminocarbonylmethyloxy)3,6,10,11-tetrakis(hexyloxy) triphenylene. The compound **9** (83.2 mg, 0.1 mmol) was added to *n*-butylamine (1.46 g, 20 mmol), and the mixture was refluxed 12 h. The excessive *n*-butylamine was removed by distillation. The residue recrystallization from ethanol and further purified by column chromatography afforded the product as white solid (73 mg, 82%, mp: 77°C). ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ: 7.85 (s, 2 H), 7.83 (s, 2 H), 7.76 (s, 2 H), 7.09 (s, 2 H), 4.74 (s, 4 H), 4.26 (t, $J = 6.48$ Hz, 4 H), 4.23 (t, $J = 6.42$ Hz, 4 H), 3.39–3.42 (m, 4 H), 1.93–1.98 (m, 8 H), 1.57–1.62 (m, 8 H), 1.54–1.56 (m, 4 H), 1.38–1.44 (m, 20 H), 0.93–0.96 (m, 18 H). Anal. Calcd for $C_{54}H_{82}O_8N_2$: C 73.10 H 9.32 N 3.16; found C 72.97 H 9.38 N 3.18. MALDI-MS: calculated $[M]^+$ ($C_{54}H_{82}N_2O_8^+$), 886.6066; found 886.6075.

Compound 10a: 2, 7-$C_{18}H_6(OC_6H_{13})_4(OCH_2CONHCH_3)_2$

2,7-di(methylaminocarbonylmethyloxy)-3,6,10,11-tetrakis(hexyloxy)triphenylene. This compound was prepared as the method described above (83%, mp: 173°C). ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ: 7.86 (s, 2 H), 7.82 (s, 2 H), 7.76 (s, 2 H), 7.14 (s, 2 H), 4.75 (s, 4 H), 4.26 (t, $J = 6.42$ Hz, 4 H), 4.23 (t, $J = 6.48$ Hz, 4H), 2.97 (d, $J = 5.1$ Hz, 6 H), 1.93–1.99 (m, 8 H), 1.57–1.62 (m, 8 H), 1.40–1.46 (m, 16 H), 0.93–0.96 (m, 12 H). Anal. Calcd for $C_{48}H_{70}O_8N_2$: C 71.79 H 8.79 N 3.49; found C 71.41 H 8.88 N 3.45. MALDI-MS: calculated $[M]^+$ ($C_{48}H_{70}N_2O_8^+$), 802.5127; found 802.5129.

Compound 10b: 2, 7-$C_{18}H_6(OC_6H_{13})_4(OCH_2CONHC_2H_5)_2$

2,7-di(ethylaminocarbonylmethyloxy)-3,6,10,11-tetrakis(hexyloxy) triphenylene. This compound was prepared as the method described above (86%, mp: 144°C). ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ: 7.86 (s, 2 H), 7.83 (s, 2 H), 7.77 (s, 2 H), 7.09 (s, 2 H), 4.74 (s, 4 H), 4.26 (t, $J = 6.36$ Hz, 4 H), 4.23 (t, $J = 6.6$ Hz, 4 H), 3.43–3.47 (m, 4 H), 1.93–1.98 (m, 8 H), 1.59–1.60 (m, 8 H), 1.38–1.46 (m, 16 H), 1.23–1.26 (t, $J = 7.20$ Hz, 6 H), 0.93–0.96 (m, 12H). Anal. Calcd for $C_{50}H_{74}$ O_8N_2: C 72.26 H 8.07 N 3.37; found C 72.36 H 9.02 N 3.38. MALDI-MS: calculated $[M]^+$ ($C_{50}H_{74}N_2O_8^+$), 830.5440; found 830.5444.

Compound 10c: 2, 7-$C_{18}H_6(OC_6H_{13})_4(OCH_2CONHC_3H_7)_2$

2,7-di(propylaminocarbonylmethyloxy)-3,6,10,11-tetrakis(hexyloxy) triphenylene. This compound was prepared as the method described above (86%, mp: 100°C). ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ: 7.85 (s, 2 H), 7.83 (s, 2 H), 7.76 (s, 2 H), 7.13 (s, 2 H), 4.75 (s, 4 H), 4.26 (t, $J = 6.54$ Hz, 4 H), 4.23 (t, $J = 6.48$ Hz, 4 H), 3.36–3.39 (m, 4 H), 1.93–1.98 (m, 8 H), 1.57–1.66 (m, 12 H), 1.37–1.41 (m, 16 H), 0.97–0.99 (t, $J = 7.5$ Hz, 6 H), 0.93–0.96 (m, 12 H). Anal. Calcd for $C_{52}H_{78}O_8N_2$: C 72.69 H 9.15 N 3.26; found C 72.25 H 9.19 N 3.28. MALDI-MS: calculated $[M]^+$ ($C_{52}H_{78}N_2O_8^+$), 858.5752; found 858.5759.

Compound 10e: 2,7-$C_{18}H_6(OC_6H_{13})_4(OCH_2CONHC_6H_{13})_2$

2,7-di(hexylaminocarbonylmethyloxy)-3,6,10,11-tetrakis(hexyloxy) triphenylene. This compound was prepared as the method described above (90%, mp: 85°C). ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ: 7.85 (s, 2 H), 7.83 (s, 2 H), 7.77 (s, 2 H), 7.10 (s, 2 H), 4.75 (s, 4 H), 4.26 (t, $J = 6.48$ Hz, 4 H), 4.23 (t, $J = 6.66$ Hz, 4 H), 3.37–3.41 (m, 4 H), 1.93–1.99 (m, 8 H), 1.56–1.61 (m, 12 H), 1.36–1.42 (m, 20 H), 1.28–1.29 (m, 8 H), 0.93–0.96 (m, 12 H), 0.85–0.88 (t, $J = 6.84$ Hz, 6 H). Anal. Calcd for $C_{58}H_{90}O_8N_2$: C 73.58 H 9.62 N 2.97; found C 73.55 H 9.65 N 2.97. MALDI-MS: calculated $[M]^+$ ($C_{58}H_{90}N_2O_8^+$), 942.6692; found 942.6697.

Compound 10f: 2,7-$C_{18}H_6(OC_6H_{13})_4(OCH_2CONHC_8H_{17})_2$

2,7-di(octylaminocarbonylmethyloxy)-3,6,10,11-tetrakis(hexyloxy) triphenylene. This compound was prepared as the method described above (90%, mp: 100°C). ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ: 7.85 (s, 2 H), 7.83 (s, 2 H), 7.76 (s, 2 H), 7.09 (s, 2 H), 4.75 (s, 4 H), 4.26 (t, $J = 6.42$ Hz, 4 H), 4.23 (t, $J = 6.42$ Hz, 4 H), 3.37–3.40 (m, 4 H), 1.93–1.98 (m, 8 H), 1.56–1.61 (m, 12 H), 1.39–1.42 (m, 16 H), 1.23–1.36 (m, 20 H), 0.93–0.96 (m, 12 H), 0.85–0.87 (t, $J = 6.78$ Hz, 6 H). Anal. Calcd for $C_{62}H_{98}O_8N_2$: C 74.51 H 9.88 N 2.80; found C 74.67 H 9.96 N 2.78. MALDI-MS: calculated $[M]^+$ ($C_{62}H_{98}N_2O_8^+$), 998.7318; found 998.7316.

Compound 10g: 2,7-$C_{18}H_6(OC_6H_{13})_4(OCH_2CONHC_{12}H_{25})_2$

2,7-di(dodecylaminocarbonylmethyloxy)-3,6,10,11-tetrakis(hexyloxy) triphenylene. This compound was prepared as the method described above (72%, mp: 102°C). ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ: 7.85 (s, 2 H), 7.83 (s, 2 H), 7.76 (s, 2 H), 7.09 (s, 2 H), 4.75 (s, 4 H), 4.26 (t, $J = 6.36$ Hz, 4 H), 4.23 (t, $J = 6.60$ Hz, 4 H), 3.37–3.40 (m, 4 H),

1.93–1.99 (m, 8 H), 1.56–1.61 (m, 12 H), 1.39–1.45 (m, 16 H), 1.35–1.37 (m, 4 H), 1.32–1.33 (m, 8 H), 1.28–1.29 (m, 24 H), 0.93–0.96 (m, 12 H), 0.86–0.88 (t, $J = 6.96$ Hz, 6 H). Anal. Calcd for $C_{70}H_{114}O_8N_2$: C 75.63 H 10.34 N 2.52; found C 75.54 H 10.40 N 2.50. MALDI-MS: calculated $[M]^+$ ($C_{70}H_{114}N_2O_8^+$), 1110.8570; found 1110.8574.

Compound 10h: 2,7-$C_{18}H_6(OC_6H_{13})_4(OCH_2CONHC_2H_4OH)_2$

2,7-di(hydroxyethylaminocarbonylmethyloxy)-3,6,10,11-tetrakis(hexyloxy)-triphenylene. This compound was prepared as the method described above (88%, mp: 192°C). ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ: 7.75 (s, 2 H), 7.69 (s, 2 H), 7.64 (s, 2 H), 7.75 (s, 2 H), 4.73 (s, 4 H), 4.18–4.22 (m, 8 H), 3.81–3.84 (m, 4 H), 3.57–3.60 (m, 4 H), 2.66 (s, 2 H), 1.93–1.98 (m, 8 H), 1.57–1.63 (m, 8 H), 1.37–1.44 (m, 16 H), 0.94–0.96 (t, $J = 7.02$ Hz, 12 H). Anal. Calcd for $C_{50}H_{74}O_{10}N_2$: C 69.58 H 8.64 N 3.25; found C 69.11 H 8.72 N 3.22. MALDI-MS: calculated $[M]^+$ ($C_{50}H_{74}N_2O_{10}^+$), 862.5337; found 862.5344.

Compound 10i: 2,7-$C_{18}H_6(OC_6H_{13})_4(OCH_2CONHCH_2Ph)_2$

2,7-di(benzylaminocarbonylmethyloxy)-3,6,10,11-tetrakis(hexyloxy)-triphenylene. This compound was prepared as the method described above (83%, mp: 135°C). ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ: 7.88 (s, 2 H), 7.76 (s, 4 H), 7.46 (s, 2 H), 7.26–7.31 (m, 10 H), 4.83 (s, 4 H), 4.59 (d, $J = 6.06$ Hz, 4 H), 4.22 (t, $J = 6.48$ Hz, 4 H), 4.12 (t, $J = 6.42$ Hz, Hz, 4 H), 1.93–1.98 (m, 4 H), 1.75–1.80 (m, 4 H), 1.57–1.62 (m, 4 H), 1.38–1.46 (m, 12 H), 1.30–1.32 (m, 8 H), 0.90–0.95 (m, 12 H). Anal. Calcd for $C_{60}H_{78}O_8N_2$: C 75.44 H 8.23 N 2.93; found C 75.14 H 8.31 N 2.95. MALDI-MS: calculated $[M]^+$ ($C_{60}H_{78}N_2O_8^+$), 954.5752; found 954.5749.

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