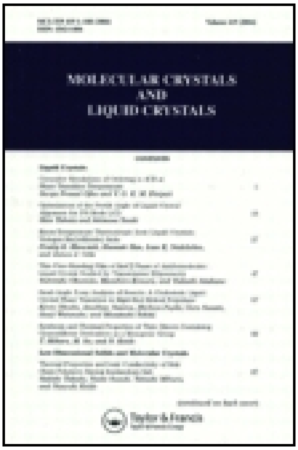

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Synthesis of Triphenylene Discotic Liquid Crystal Dimers: Click Chemistry As an Efficient Tool

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Synthesis of Triphenylene Discotic Liquid Crystal Dimers: Click Chemistry As an Efficient Tool

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Click chemistry between alkynes and azides high efficiently produces triazoles and would be a convenient tool for synthesis of discotic liquid crystal dimers, oligomers and polymers. In this report, triphenylenes containing terminal alkynes and azides were prepared, and the cycloaddition reaction (click chemistry) between them catalyzed by CuI-Et_3N in toluene produced discotic liquid crystal dimers in high yield and good selectivity. The dimers and intermediates have been fully characterized by ^1H NMR and high resolution MS. Polarized optical microscopy (POM) and differential scanning calorimetry (DSC) results show the dimers possess columnar mesophase in wide temperature range from very low temperature. The triazole moiety in the dimer can act as electron and hydrogen bond acceptor, and ionic forming part, rich chemical and physical properties can be expected from these new structure discotic dimers.

Keywords: click chemistry; discotic liquid crystal; huisgen cycloadditon reaction; liquid crystal dimer; triphenylene

1. INTRODUCTION

Discotic liquid crystals (DLC) such as triphenylene derivatives have attracted much attention for their remarkable electro-optical properties [1–4], and it offers potential applications as organic charge

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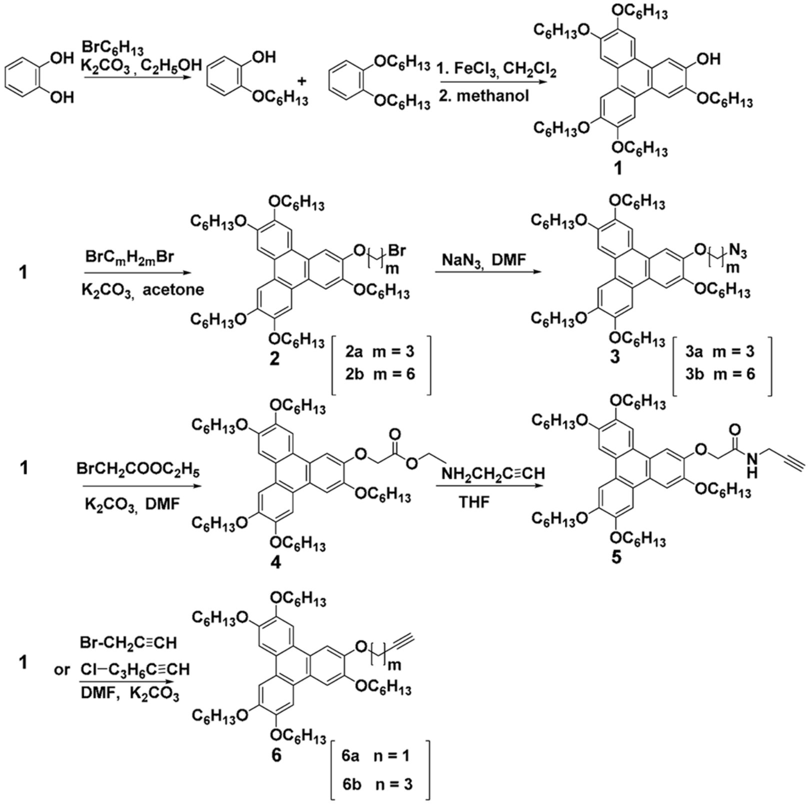
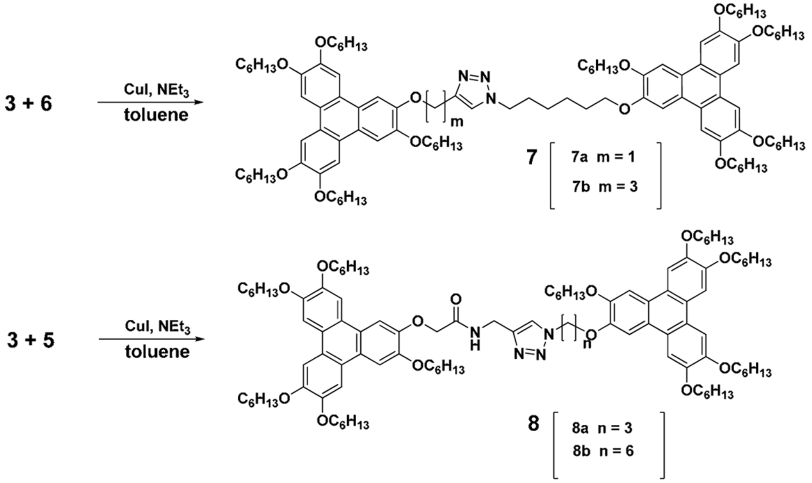


SCHEME 1 Synthesis of functional group containing triphenylenes.

transport materials in a variety of devices such as one-dimensional conductors, photoconductors, field effect transistors, photovoltaic solar cells, etc. [5–8]. So in the last decades lots of efforts have been made to design, synthesis, and characterize various DLC.

It is well known that connecting two discotic mesogens (DLC dimers) together via a flexible spacer or through a rigid spacer stabilizes the columnar mesophase significantly [9], and triphenylene as electron donor when doped with electron acceptor can form charge-transfer (C-T) complex. C-T interaction also can stabilize the columnar mesophase and increase the charge transport [10,11].

Huisgen $3+2$ cycloaddition reaction (“click chemistry” CC), which take place between terminal alkynes and high-energy azides under thermal condition, get two isomer products, the 1,4- and 1,5-disubstituted 1,2,3-triazoles [12,13]. In 2001, Kolb, Finn, and Sharpless



SCHEME 2 Synthesis of triphenylene dimers by click chemistry.

published a landmark review describing a new strategy for CC. They have used Cu(I) salt as the catalyst, and just got the 1,5-disubstituted 1,2,3-triazoles selectively [14]. Since then the CC has been broadly used in the areas of biological, materials, and medicinal chemistry as for the high yield, many functional groups tolerance, and the simple reaction condition and so on.

We have been focusing on the synthesis of triphenylene discotic liquid crystals materials, and hope to enhance their charged carrier mobility and electro-optical properties, and broaden the mesophase range by simple syntheses way under mild condition. We believe that new chemistry can synthesize new structure compounds and would expect novel chemical and physical properties, and potential applications would be found. To our knowledge, there are few examples using CC in liquid crystalline molecular designing and synthesis [15,16]. Here we design and synthesis triphenylene discotic dimers **7** and **8** (Schemes 1 and 2), in their structure heterocycle 1,2,3-triazole acts as the linking bridge which formed by Huisgen $3 + 2$ cycloaddition reaction.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization

2-Hydroxy-3,6,7,10,11-penta(hexyloxy)triphenylene, **1**, was used as the starting material, which has been synthesized and purified as described [17]. Etherification **1** with 3-bromo-1-propyne, 5-chloro-1-pentyne, and ethyl 2-bromoacetate produced **6a, 6b** and **4** respectively. **4** underwent ammonolysis in presence of mono-propargylamine formed **5**, which has a terminal alkynyl group. **3** was prepared in high yield through nucleophilic substitution reaction of NaN_3 with alkyl bromide **2**, which synthesized from etherification of **1** with 1,6-dibromohexane or 1,3-dibromopropane. In the mono etherification reaction of α,ω-dibromoalkane, solvent is very important for its success. In acetone, mono etherification is the main product. However, reaction in DMF led to the byproduct of di-etherification. Finally, **3** clicked with **5,** or **6** in toluene, and catalyzed by CuI-NEt_3, produced successfully the discotic dimer **7** and **8.** The click chemistry took place in room temperature in less than 12 hours. The dimer **7** and **8** were purified by column chromatography and fully characterized by ^1H NMR, and high resolution Mass.

The Figure 1 shows the ^1H NMR spectra of **8b** and alkynes **6** in chloroform-d. Figure 1A shows the alkyne proton resonance at $\delta = 2.26$, and the methylene proton resonance between amide and alkynes around $\delta = 4.2$. After click reaction, the alkyne proton resonance transform to $\delta = 7.8$, and the methylene proton resonance transform to $\delta = 4.77$. The differences have been shown in Figure 1B. Bertrand [18], Stoddart [19], and others [20] have reported that the proton resonance in 1,5-disubstituted 1,3,5-triazoles at $\delta = 7.8$–8.6. Thus the two ^1H NMR spectra confirm that **8b** is our desired molecular. All the discotic dimers have been further characterized by high resolution mass spectra, and the results support our conclusion.

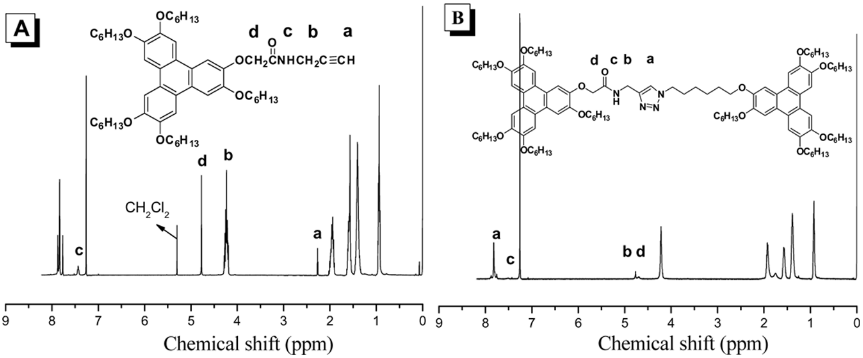


FIGURE 1 ^1H NMR spectra of **5** and discotic dimer **8b.**

2.2. Mesomorphism

The liquid crystalline behaviors of the triphenylene derivatives and discotic dimers were investigated by differential scanning calorimetry (DSC), the results are summarized in Table 1, and the DSC traces of intermediates and dimers are drawn in Figures 2 and 3. The textures of the mesophases were observed and recorded by polarized optical microscopy (POM) and typical photomicrographs are shown in Figure 4.

As showed in Table 1 and Figure 2, all triphenylene intermediates exhibits mesophases. When heating the sample powder among two plate untreated glasses to isotropic liquid, and slowly cooling, typical fan shaped textures, the feature of hexagonal columnar mesophases, were observed from the POM.

Figure 3 draws the DSC traces of triphenylene dimers, the click chemistry products. Figure 3a is the first heating traces, and Figure 3b is the second heating traces. There are two peaks for **7b, 8a**, and **8b** on the first heating traces. The first peak is the transition of crystal phase to mesophase, and the second one, mesophase to isotropic liquid. The crystallization can not be observed on the cooling run until −50°C. 7a showed different behavior from other dimmers, that it appeared three peaks on the first heating trace. The second peak is the transition between different mesophases, which can not

TABLE 1 Thermal and Thermodynamic Property of Triphenylene Derivatives by DSC (10°C min^{-1}) (Cr: Crystal; Col_h: Hexagonal Columnar Phase; I: Isotropic liquid)

	Mesophases, transition temperature and enthalpy changes	
Compd.	Heating/°C (ΔH, kJ mol^{-1})	Cooling/°C (ΔH, kJ mol^{-1})
2a	Cr 56 (32.07) Col_h 100 (4.79) I	I 98 (4.55) Col_h 28 (32.12) Cr
2b	Cr 60 (41.22) I	I 51 (1.56) Col_h 47 (38.22) Cr
3a	Cr 62 (37.20) Col_h 92 (3.76) I	I 92 (3.65) Col_h 43 (33.60) Cr
3b	Cr 54 (40.33) I	I 49 (1.48) Col_h 44 (38.69) Cr
4	Cr 48 (40.22) Col_h 118 (7.65) I	I 118 (7.59) Col_h 7 (29.98) Cr
5	Cr 67 (33.80) Col_h 134 (5.01) I	I 133 (4.95) Col_h 47 (33.03) Cr
6a	Cr 66 (39.96) Col_h 100 (4.48) I	I 100 (4.67) Col_h 27 (30.44) Cr
6b	Cr 52 (30.79) Col_h 98 (4.97) I	I 97 (4.97) Col_h 24 (25.56) Cr
7a	Cr 48 (39.33) Col_1 75 (2.44) Col_2 88 (12.31) I	I 86 (11.10) Col_2 74 (2.60) Col_1
7b	Cr 18 (65.89) Col_h 95 (60.21) I	I 67 (4.95) Col_h
8a	Cr 71 (29.04) Col_h 97 (9.54) I	I 93 (9.42) Col_h
8b	Cr 81 (51.47) Col_h 104 (10.47) I	I 103 (10.10) Col_h

7 and **8** measured in the first heating and cooling run; others, the second heating and cooling circle.

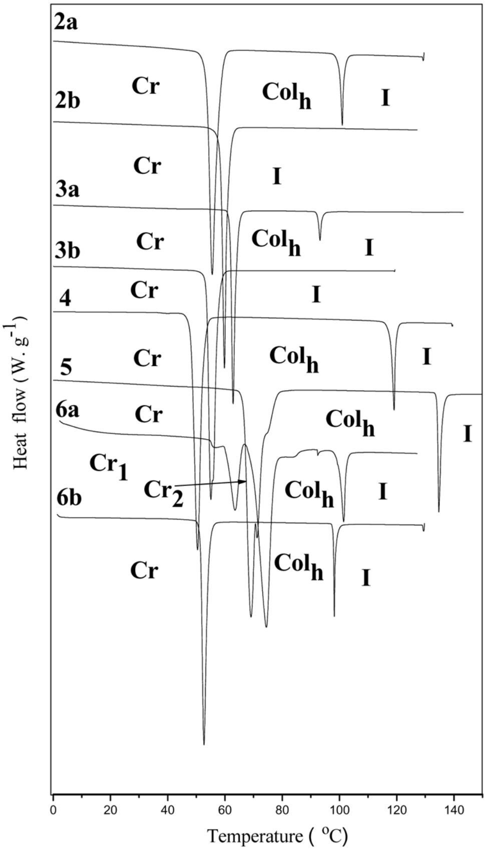


FIGURE 2 DSC traces of the triphenylene intermediates.

been observed from POM textures. So we can say that all the discotic triphenylene dimmers are room temperature liquid crystals after the first heating to isotropic.

We have put lots of efforts on learning the effects of hydrogen bonding among intermolecular amide functional groups on discotic liquid crystalline properties [21–23]. **8a** and **8b** are amide containing discotic dimers, the DSC data showed that they have higher clearing points than **7a, 7b**. This result may be caused by the intermolecular hydrogen bonding of dimer **8**.

Figure 4, the photomicrographs of **7** and **8**, showed the same optical textures of well-characterized discotic columnar mesophase [24]. The detail information of molecular packing in the columnar organization should be further studied with XRD. However, the dimers prepared by

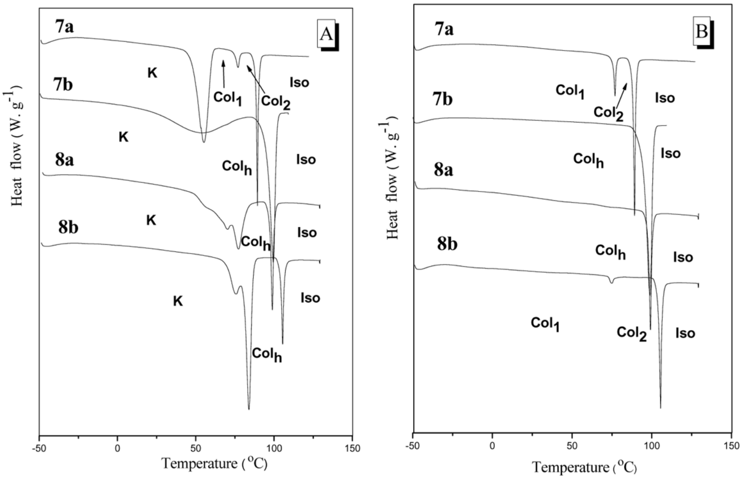


FIGURE 3 DSC traces of triphenylene discotic dimmers (A) first heating run; (B) second heating run; heating and cooling rate 10°C/min.

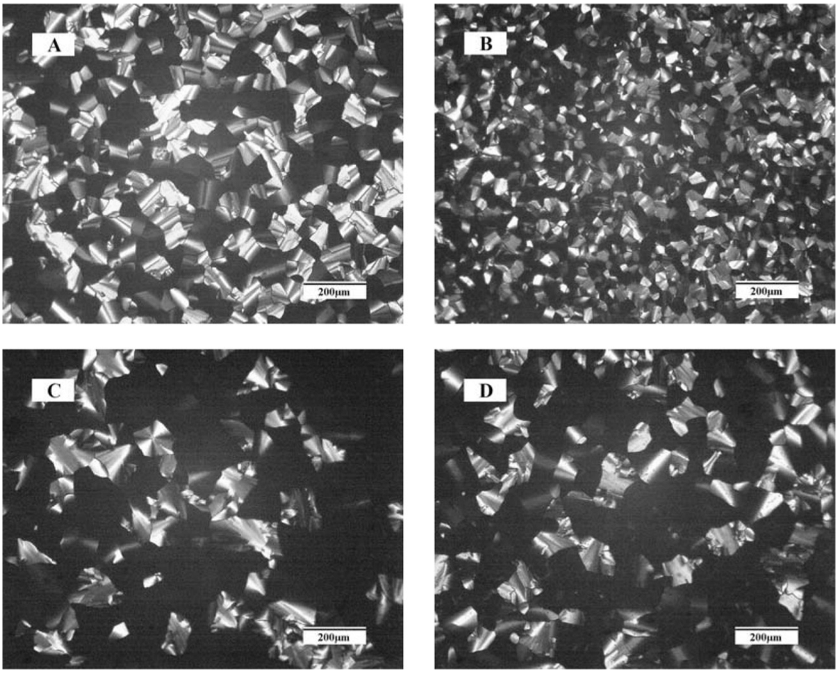


FIGURE 4 POM photographs of triphenylene dimers, obtained on slowly cooling from the isotropic liquid, (A) **8b**, 81°C; (B) **8a**, 89°C; (C) **7a**, 68°C; (D) **7b**, 69°C.

click chemistry have different thermotropic properties, such as wide mesophase ranges and high viscosity, compared with triphenylene dimers connected with alkyl chain [25].

The novel chemistry of click reaction produced new triphenylene discotic dimers in chemical structure. New structure would result in new physical properties. triphenylene is an electron-rich molecule and it can form charge-transfer (C-T) complex with electron acceptor, such as trinitrofluorenone (TNF), and stabilize the columnar assembly. Although nitrogen-containing heteroaromatic rings such as pyridine [26–28], pyrazine [29, 30], pyrimidine [31] and pyridazine [11] and others such as 2,4,7-trinitrofluorenone (TNF) [32–35] and so on [12,36] have been employed as electron acceptors, the heterocycle 1,2,3-triazole as an electron acceptor in the discotic dimer system has not been reported. As the triphenylene moiety is electron-rich and triazole moiety electron-poor, the C-T complex formed or not in the columnar assembly should be further verified. Further more, triazole moiety can be acted as hydrogen bond acceptor and forming ionic liquid crystals after reacted with alkyl halide. The click chemistry formed triazole discotic liquid crystalline dimers reported here would expect rich chemical and physical properties.

3. CONCLUSION

Novel triphenylene discotic liquid crystalline dimers composed of two triphenylene discogens and a triazole moiety have been prepared. The click chemistry reaction catalyzed by CuI-NEt$_3$ in toluene at room temperature produced the discotic liquid crystal dimers in high yield and good selectivity. The discotic dimers show mesophase in wide mesophase range from very low temperature. This research work has demonstrated that the click chemistry, combined with the easy available of alkynes and azides, would be an efficient tool for synthesis of novel liquid crystal dimers, oligomers and polymers.

4. EXPERIMENTAL

Instrumentation and Chemicals

^{1}H NMR (600 MHz) spectra were recorded by Bruker-Avance-600, ^{1}H NMR (400 MHz) Varian UNITY INOVA-400, using CDCl$_3$ as a solvent and Me$_4$Si as an internal standard. The high resolution Mass was recorded on Varian 7.0 T FTICR-MS (ESI, or MALDI mode). Melting points, phase transition temperatures and enthalpy changes were measured using differential scanning calorimetry (DSC) on TA-DSC

Q100 system, and heating and cooling scan rate of 10°C min^{-1}. Transition enthalpies ΔH were changed into kJ mol^{-1}. The texture of the mesophases was observed using polarizing optical microscopy (POM) XP-201, with a hot stage XP-201.

Commercial Chemicals and solvents were used without further purification if no special notification. 2-Hydroxy-3,6,7,10,11-pentakishexyloxytriphenylene was prepared according to reported method [17].

$C_{18}H_6(OC_6H_{13})_5(OC_6H_{12}Br)$, **2b***.* 2-hydroxyl-3,6,7,10,11-pentakishexyloxytriphenylene **1** (1.414 g, 1.9 mmol) and potassium carbonate (1.04 g, 7.6 mmol) was added to acetone (20 mL). Then 1,6-dibromohexane (1.113 g, 4.5 mmol) was added, and the solution was refluxed 12 h. the mixture was poured into water and extracted with dichloromethane. The organic layer was dried with magnesium sulfate, and the organic solvent was removed under vacuum. The crude compound was purified by column chromatography with silica gel afforded **2b** white solid (1.3986 g, 81%, mp: 60°C). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ: 7.83 (s, 6 H), 4.23 (t, $J = 6.4$ Hz, 12 H), 3.45 (t, $J = 6.8$ Hz, 2 H), 1.90–1.97 (m, 14 H), 1.56–1.60 (m, 14 H), 1.36–1.40 (m, 20 H), 0.93 (t, $J = 7.2$ Hz, 15 H).

$C_{18}H_6(OC_6H_{13})_5(OC_3H_6Br)$, **2a***.* **2a** was synthesized as **2b** (79%, Cr 56°C Col_h 100°C Iso). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ: 7.89 (s, 1 H), 7.84 (s, 5 H), 4.39 (t, $J = 5.6$ Hz, 2 H), 4.23 (t, $J = 6.4$ Hz, 10 H), 3.74 (t, $J = 6.4$ Hz, 2 H), 2.44–2.50 (m, 2 H), 1.91–1.98 (m, 10 H), 1.54–1.60 (m, 10 H), 1.36–1.41 (m, 20 H), 0.93 (t, $J = 7.2$ Hz, 15 H).

$C_{18}H_6(OC_6H_{13})_5(OC_6H_{12}N_3)$, **3b***.* A mixture of compound **2b** (907 mg, 1 mmol) and NaN_3 (845 mg, 13 mmol) in DMF was stirred at room temperature for 12 h. After added 20 mL water, the reaction mixture was 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 product as white solid (824 mg, 95%, mp: 54°C). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ: 7.84 (s, 6 H), 4.24 (t, $J = 6.4$ Hz, 12 H), 3.31 (t, $J = 6.8$ Hz, Hz, 2 H) 1.91–1.98 (m, 12 H), 1.50–1.72 (m, 16 H), 1.34–1.36 (m, 20H), 0.94 (t, $J = 6.8$ Hz, 15 H).

$C_{18}H_6(OC_6H_{13})_5(OC_3H_6N_3)$, **3a***.* The synthetic procedure is the same as **3b**, except that the crude product was purified by column chromatography with silica gel. (83%, Cr 62°C Col_h 92°C Iso). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ: 7.87 (s, 1 H), 7.84 (s, 5 H), 4.33 (t, $J = 6$ Hz, Hz, 2 H), 4.23 (t, $J = 6.4$ Hz, 10 H), 3.66 (t, $J = 6.8$ Hz, 2 H), 2.20 (t, $J = 6$ Hz, 2 H), 1.90–1.98 (m, 10 H), 1.58–1.62 (m, 10 H), 1.36–1.46 (m, 20 H), 0.92–0.96 (m, 15 H).

$C_{18}H_6(OC_6H_{13})_5(OCH_2COOC_2H_5)$, **4**. $BrCH_2COOC_2H_5$ (652 mg, 3.9 mmol), 2-hydroxyl-3,6,7,10,11-pentakishexyloxy-triphenylene (858 mg, 1.3 mmol) were added to the suspension of potassium carbonate and DMF. The mixture was refluxed 12 h, poured into the water with ice, 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%, Cr 48°C Col_h 118°C Iso). ^1H NMR ($CDCl_3$, 600 MHz) δ: 7.94 (s, 1 H), 7.83 (t, $J = 5.4$ Hz, 4 H), 7.79 (s, 1 H), 4.87 (s, 2 H), 4.29–4.33 (q, 2 H), 4.20–4.23 (m, 10 H), 1.94–1.99 (m, 10 H),1.56 – 1.60 (m, 10 H), 1.30–1.40 (m, 20 H), 1.29 (t, $J = 3.78$ Hz, 3 H), 0.93 (t, $J = 6.60$ Hz, 15 H).

$C_{18}H_6(OC_6H_{13})_5(OCH_2CONHCH_2C{\equiv}CH)$, **5**. A solution of **4** (166 mg, 0.2 mmol), and $CH{\equiv}CCH_2NH_2$ (66 mg, 1.2 mmol) in THF (10 mL) was refluxed 72 h. Then the mixture was poured into the water with ice, and extracted with dichloromethane. The organic layer was dried with magnesium sulfate, and the organic solvent was removed under vacuum. The crude product was purified by column chromatography with silica gel afforded product as white solid (167.8 mg, 77%, Cr 67°C Col_h 134°C Iso). ^1H NMR ($CDCl_3$, TMS, 400 MHz) δ: 7.87 (s, 1 H), 7.83 (s, 4 H), 7.77 (s, 1 H), 7.43 (t, $J = 4.8$ Hz, 1 H), 4.77 (s, 2 H), 4.19–4.28 (m, 12 H), 2.27 (t, $J = 2.4$ Hz, 1 H) 1.92–1.98 (m, 10 H), 1.57–1.62 (m, 10 H), 1.40–1.46 (m, 20 H), 0.92–0.96 (m, 15 H).

$C_{18}H_6(OC_6H_{13})_5(OC_3H_6C{\equiv}CH)$, **6b**. 2-hydroxyl-3,6,7,10,11-pentakishexyloxytriphenylene (201 mg, 0.27 mmol) and potassium carbonate (147 mg, 1.08 mmol) was added to DMF (3 mL). Then the 5-chloropentyne (1.113 g, 4.5 mmol) was added, and the solution was stirred over 12 h. After removing the solvent, the residue was washed with water and extracted with dichloromethane. The organic layer was dried with magnesium sulfate, and the organic solvent was removed under vacuum. The crude compound was purified by column chromatography with silica gel afforded the product as white solid (218.7 mg, 87%, Cr 52°C Col_h 98°C Iso). ^1H NMR ($CDCl_3$, 600 MHz) δ: 7.87 (s, 1 H), 7.84 (d, $J = 4.0$ Hz, 5 H), 4.34 (t, $J = 6.1$ Hz, 2 H), 4.23 (t, $J = 6.5$ Hz, 10 H), 2.52–2.55 (m, 2 H), 2.13–2.17 (m, 2H), 2.00 (t, $J = 2.8$ Hz, H), 1.91–1.96 (m, 10H), 1.57–1.60 (m, 10 H), 0.94 (t, $J = 7.1$ Hz,15 H).

$C_{18}H_6(OC_6H_{13})_5(OCH_2C{\equiv}CH)$, **6a**. **6a** was prepared as **6b** (260.3 mg, 83%, Cr 66°C Col_h 100°C Iso). ^1H NMR ($CDCl_3$, 600 MHz) δ: 8.08 (s, 1 H), 7.84 (d, $J = 7.5$ Hz, 5H), 4.96 (d, $J = 2.3$ Hz, 2H), 4.22–4.26 (m, 10H), 2.56 (t, $J = 2.3$ Hz, 1 H), 1.91–1.97 (m, 10H), 1.54–1.59 (m, 10H), 1.37–1.40 (m, 20H), 0.93 (t, $J = 7.0$ Hz,15H).

$C_{18}H_6(OC_6H_{13})_5[OC_3H_6CCHN_3C_6H_{12}O]C_{18}H_6(OC_6H_{13})_5$, **7b**. **3b** (40.5 mg, 0.05 mmol) and **6b** (43.45 mg, 0.05 mmol) were dissolved in toluene (2 ml), then CuI (13 mg) and NEt_3 (1.5 ml) were added. The solution was stirred 12 h at room temperature. The toluene was removed in vacuum, and the residue solid was purified by column chromatography with silica gel afforded the product as white solid (75.6 mg, 90%, Cr 18°C Col_h 94°C Iso). ^1H NMR ($CDCl_3$, TMS, 400 MHz) δ: 7.82 (t, $J = 4.8$ Hz, 13 H), 4.16–4.41 (m, 26 H), 3.06–3.18 (m, 2 H), 2.32–2.41 (m, 2 H), 1.87–1.96 (m, 24 H), 1.53–1.79 (m, 24 H), 1.38–1.44 (m, 40 H), 0.89–0.95 (m, 30 H). Exact mass: calculated ($C_{105}H_{157}O_{12}N_3Na^+$), 1675.1659; found, 1675.1665.

$C_{18}H_6(OC_6H_{13})_5[OCH_2CCHN_3C_6H_{12}O]C_{18}H_6(OC_6H_{13})_5$, **7a**. **7a** prepared as **7b** (93.5 mg, 81%, Cr 48°C Col_1 75°C Col_2 88°C Iso). ^1H NMR ($CDCl_3$, TMS, 600 MHz) δ: 8.08 (s, 1 H), 7.81 (d, $J = 2.22$ Hz, 12 H), 5.44–5.52 (m, 2 H), 4.40–4.43 (m, 2 H), 4.17–4.29 (m, 22 H), 1.88–1.95 (m, 24 H), 1.57–1.70 (m, 24 H), 1.32–1.48 (m, 40 H), 0.90–0.94 (m, 30 H). Exact mass: calculated ($C_{107}H_{162}O_{12}N_3^+$), 1681.2153; found, 1681.2163.

$C_{18}H_6(OC_6H_{13})_5[OCH_2CONHCH_2CCHN_3C_3H_6O]C_{18}H_6(OC_6H_{13})_5$, **8a**. **8a** synthesized as **7b** (84%, Cr 71°C Col_h 97°C Iso). ^1H NMR ($CDCl_3$, TMS, 600 MHz) δ: 7.70–7.84 (m, 13 H), 7.43 (s, 1 H), 4.64–4.73 (m, 4 H), 4.13–4.26 (m, 24 H), 2.42–2.52 (m, 2 H), 1.91–1.93 (m, 20 H), 1.54–1.60 (m, 20 H), 1.38–1.40 (m, 40 H), 0.92–0.94 (m, 30 H). Exact mass: calculated ($C_{104}H_{154}O_{13}N_4Na^+$), 1690.1404; found, 1690.1412.

$C_{18}H_6(OC_6H_{13})_5[OCH_2CONHCH_2CCHN_3C_6H_{12}O]C_{18}H_6(OC_6H_{13})_5$, **8b**. **8b** synthesized as **7b** (75 mg, 88%, Cr 81°C Col_h 104°C Iso). ^1H NMR ($CDCl_3$, TMS, 600 MHz) δ: 7.76 – 7.88 (m, 13 H), 7.52 (s, 1 H), 4.77 (s, 2 H), 4.68 – 4.71 (m, 2 H), 4.19 – 4.26 (m, 24 H), 1.74–1.87 (m, 28 H), 1.52 – 1.58 (m, 20 H), 1.34 – 1.43 (m, 40 H), 0.90 – 0.93 (m, 30 H). Exact mass: calculated, ($C_{107}H_{161}O_{13}N_4^+$) 1710.2055; found, 1711.2091.

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