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Novel symmetrical triads of triphenylene-calix[4]arene-triphenylene: synthesis and mesomorphism

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ABSTRACT

Two novel symmetrical triads of triphenylene-calix[4]arene-triphenylene bridged by aromatic amido or hydrazone spacers were synthesized with stepwise procedures in yields of 67% and 68%, respectively. They exhibited interesting mesomorphic behavior of triphenylene column with calix[4]arene units on ancillary lateral sides.

Discotic and columnar liquid crystals have been extensively studied due to their various applications, such as organic light-emitting diodes, organic photovoltaic cells, organic field-effect transistors, gas sensors, photocopying machines.[1–4] Triphenylenes are one of the most widely studied discotic liquid crystals.[1–8] To improve their processability and functionality, twinned structures of triphenylene have received much attention recently.[9–12] The studies indicated the mesomorphic properties and molecular stacking behaviors of twinned triphenylene derivatives were greatly influenced by the functional group, length, and flexibility of linking spacer.[13,14] Recently, the macrocycle-linked triphenylene dimers attracted much attention. In 2010, Cammidge reported the triphenylene dimers are linked by shape-persistent conjugated macrocycle or crown ether macrocycle with interesting mesomorphic properties.[15,16] Peng and Laschat, respectively, also described the syntheses and mesomorphic properties of similar macrocycle-linked triphenylene dimers.[17,18] Lately, Wang synthesized triphenylene-fused porphyrins with interesting UV–vis absorptions.[19] These researches suggested that macrocycle-linked triphenylene dimers showed interesting properties due to their unique structures and the mesomorphic properties were controlled by the complexation behaviors of macrocycle units in some cases.[18] Obviously, the mesomorphic properties tuned by the complexation capabilities of macrocycle units exhibit application prospects on molecular switch of liquid crystal, which deserve to be studied extensively. However, apart from these several examples, the macrocycle-linked triphenylene dimers were almost unknown until now.

Calixarenes are the third generation supramolecular platforms after crown ether and cyclodextrin.[20,21] Many researches were focused on syntheses and complexation properties of various calixarene derivatives. Some of calixarene-based liquid crystals were also studied by introducing the long alkyl chain on the upper or lower rim of calixarene skeleton.[22–27] Most recently, we reported the first example of calixarene-linked triphenylene dimers bridged by long alkyl chain.[28] It exhibited interesting mesomorphic stacking behavior of the calixarenes bowlic column with two triphenylene units as ancillary lateral columns (as shown in Fig. 4(a)). Has there any other molecular stacking behavior for this kind of triads?

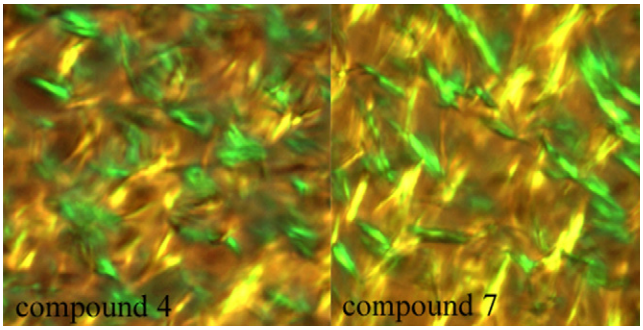

Figure 1. The textures of triads **4** and **7** under POM on cooling at 45 °C (×400).

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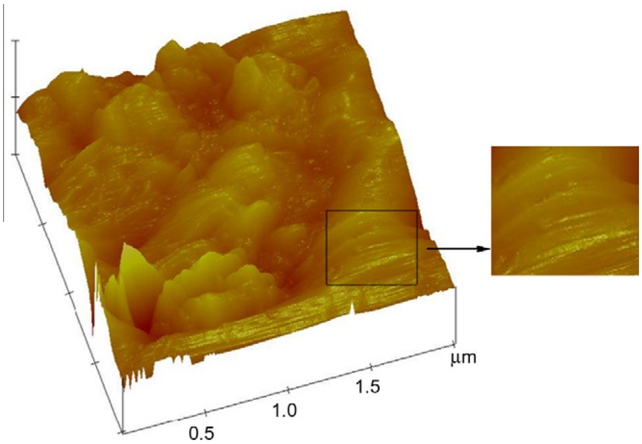


Figure 2. AFM image of triad **4** with columnar structure.

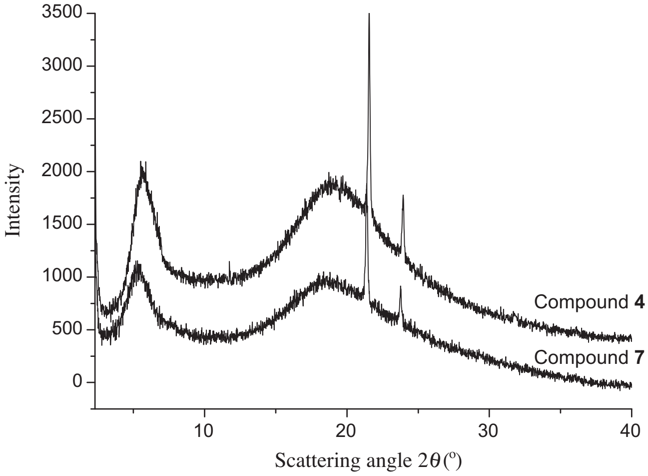


Figure 3. XRD traces of triads **4** and **7** at 45°C.

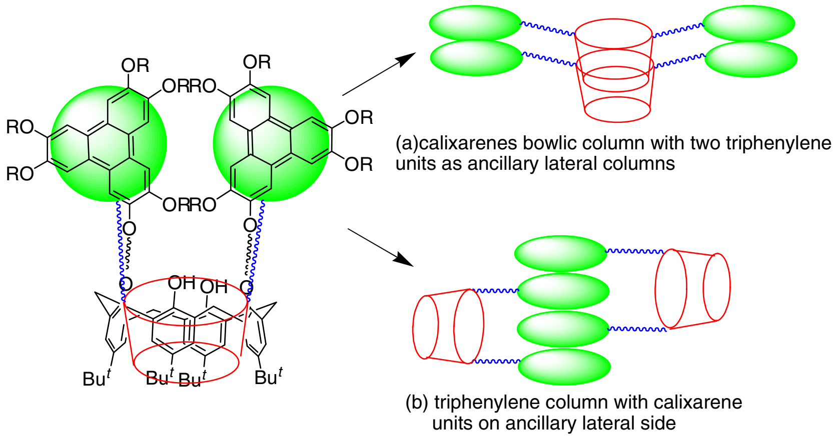
Considering the fact that mesomorphic properties were greatly influenced by the structures of linking spacers, we are interested in studying the relationship between structures and mesomorphic stacking behaviors for this kind of triads. In this Letter, we wish to report the design and syntheses of novel symmetrical triads of triphenylene-calix[4]arene-triphenylene bridging by aromatic amido or hydrazone spacers, which were utterly different from alkyl chains. Moreover, the mesomorphic experiments indicated that they possessed novel interesting mesomorphic properties of triphenylene column with calixarene units on ancillary lateral sides, which were observed for the first time.

The synthetic route of symmetrical triad of triphenylene-calix[4]arene-triphenylene bridged by aromatic amido spacers **4** was shown in Scheme 1. According to the literature methods,[8] ω-bromo-substituted triphenylenes **1** was prepared by reacting monohydroxytriphenylene with excess 1, 6-dibromohexane under K_2CO_3/MeCN system in a good yield. Subsequently, by reacting compound **1** with Boc-protected aminophenol and then deprotection by trifluoroacetic acid, compound **2** was obtained in a high yield. After the acylation of compound **2** with chloroacetyl chloride, triphenylene derivative **3** with terminal-chloromethyl group was prepared in a yield of 94%. Then refluxing compound **3** with *p-tert*-butyl calix[4]arene under K_2CO_3/MeCN system for 48 h by using KI as the catalyst, target triad **4** was separated successfully after column chromatography in a yield of 67%.[29] No matter what the ratios of starting materials were, compound **4** was still the main product and no tetra-substituted calix[4]arene derivative was obtained due to the influence of steric hindrance.

Also, another similar triad of triphenylene-calix[4]arene-triphenylene bridged by hydrazone spacers **7** was designed and synthesized as shown in Scheme 2. By the etherization of compound **1** with methyl 6-bromohexanoate and then ammonolysis with hydrazine hydrate, compound **5** was obtained in an 82% yield. Then, compound **5** was treated with calix[4]arene di-benzaldehyde derivative **6**[30] to afford novel triad of triphenylene-calix[4]arene-triphenylene **7** in a 68% yield after column chromatography.[31]

New compounds were characterized by element analyses, UV, IR, ESI-MS, and NMR spectra. The ESI-MS spectra of them showed corresponding molecular ion peaks. All the protons were assigned well in their ^{1}H NMR spectra. Especially, compounds **4** and **7** exhibited two singlets (1:1) for the *tert*-butyl groups and one pair of doublets (1:1) for the methylene bridges, which indicated that calix[4]arene unit adopts cone conformation.

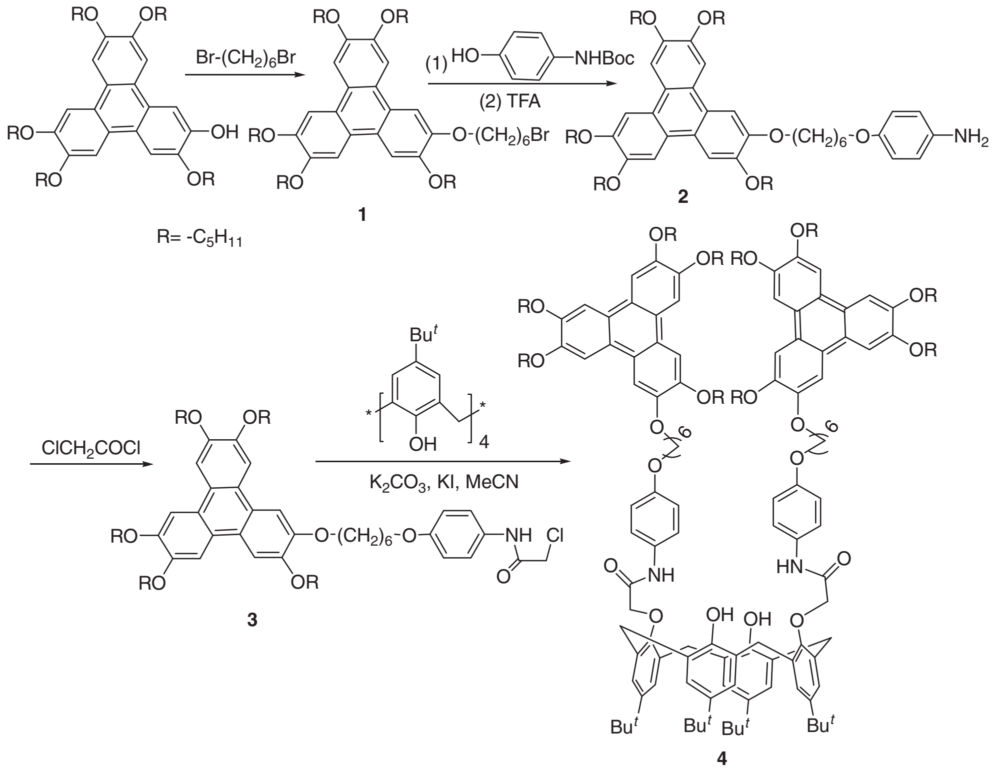
The mesomorphic behaviors of compounds **4** and **7** were preliminarily studied by differential scanning calorimetry. The results were shown in Table 1. It can be seen that both compounds possessed multiple phase transitions upon heating and cooling. Compound **4** showed three phase transfer temperatures at 39.47 °C, 48.64 °C, and 72.96 °C upon second heating process and three reverse processes at 65.60 °C, 51.60 °C, and 37.26 °C upon cooling process. Similarly, compound **7** exhibited three phase transfer temperatures at 34.13 °C, 46.64 °C, and 66.80 °C upon second heating scan and three reverse processes 51.93 °C, 35.18 °C, and 30.0 °C upon cooling. Judging from these DSC data, it could be deduced



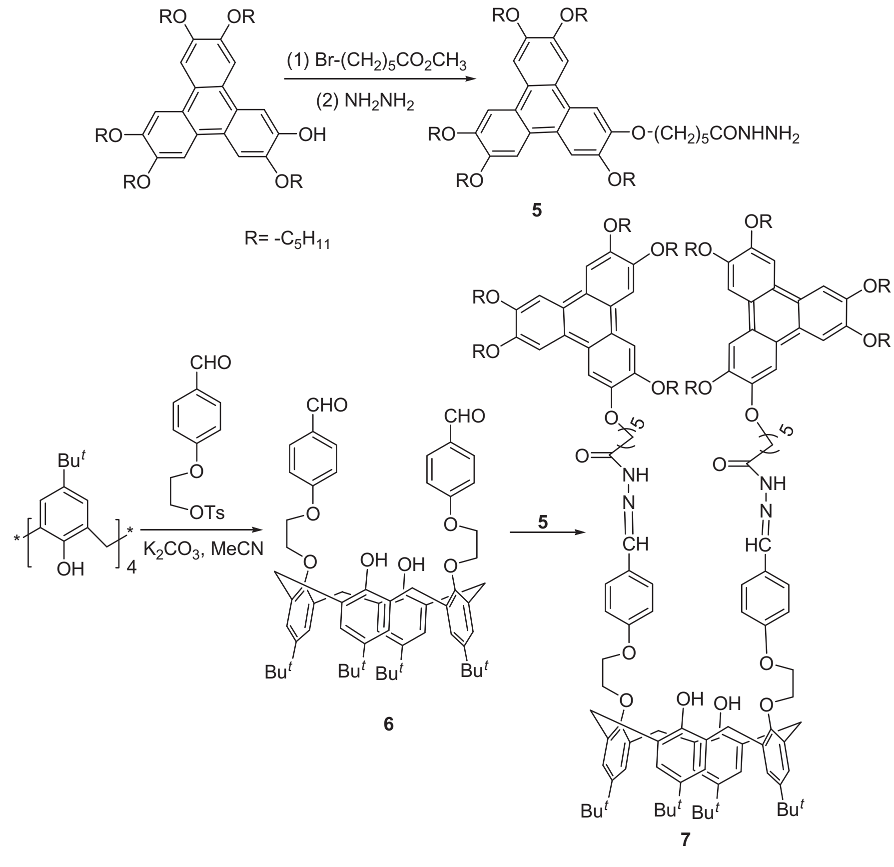
(a)calixarenes bowlic column with two triphenylene units as ancillary lateral columns

(b) triphenylene column with calixarene units on ancillary lateral side

Figure 4. Two kinds of schematic representation of the columnar layered molecular arrangement for triads of triphenylene-calixarene-triphenylene.



Scheme 1. The synthetic route of triad of triphenylene-calix[4]arene-triphenylene bridged by aromatic amido spacers **4**.



Scheme 2. The synthetic route of triad of triphenylene-calix[4]arene-triphenylene bridged by hydrazone spacers **7**.

Table 1
Transition temperatures (peak temperature/°C) and associated enthalpy changes (kJ/mol in parentheses) of **4** and **7**

Triads	Phase transition[a]	$T(\Delta H)$ Heating scan	$T(\Delta H)$ Cooling scan
4	Cr–Col_1	39.47(14.4)	37.26(3.84)
	Col_1–Col_2	48.64(0.49)	51.60(1.67)
	Col_2–Iso	72.96(2.14)	65.60(0.89)
7	Cr–Col_1	34.13(41.0)	30.0(2.46)
	Col_1–Col_2	46.64(0.40)	35.18(10.1)
	Col_2–Iso	66.80(2.24)	51.93(19.5)

[a] Cr = crystalline, Col = columnar, Iso = isotropic.

that mesophase existed on melting process with state-mesophase(Col_1 and Col_2 phase)-isotropic phase on heating. Further, based on the DSC results, the phase textures of mesophase of compounds **4** and **7** were investigated under polarized optical microscopy as shown in Figure 1. The clear columnar-shaped textures were observed. These textures were similar to the known textures for columnar phase of triphenylene derivatives.[32–36]

The molecular stacking behavior of compound **4** was also studied by AFM in tapping mode as shown in Figure 2. The plump stripes in the image represented the columnar structure. This result demonstrated that triad **4** possessed highly ordered columnar phase, which was in accordance with the previous reports of triphenylene columnar phases.[32–37]

In order to investigate the mesomorphic stacking behavior further, triads **4** and **7** were studied by the XRD. The results were shown in Figure 3. It can be seen that the peaks ($2\theta = 5$ °C, 21 °C and 24 °C approximately) were observed for compounds **4** and **7**, which were the typical peaks of columnar phase of triphenylene liquid crystal.[32–37] The reflections at about $2\theta = 5.2$–5.8 °C corresponded to distances of 15–17 Å, which agreed approximately with the diameter of the triphenylene groups. The reflection at about $2\theta = 17$–21 °C (4.2–5.2 Å broad halo) and 24 °C (3.7 Å) was assigned to the average distance of the molten alkyl chains and the intracolumnar order, respectively. Moreover, it was interesting that no peak of calixarene liquid crystal was observed.[38–41] These XRD results were utterly different from our previous report of the first calix[4]arene-linked triphenylene dimers with alkyl spacers.[28] These results indicated compounds **4** and **7** possessed the novel mesomorphic molecular stacking behaviors. In theory, there are two possible mesoporphic staking behaviors for liquid crystal of calix[4]arene-linked triphenylene dimers as shown in Figure 4. One way was calixarene as cores, that is, calixarene bowlic column with two triphenylene units as ancillary lateral columns, which should show the XRD peaks for both calixarene and triphenylene just like our previous report (as shown in Fig. 4(a)).[28] Another way was triphenylene as cores, that is, triphenylene column with calixarene units on ancillary lateral sides, which should exhibit XRD peaks for triphenylene and might have some peaks for calixarene controlled by the tropism of calixarene units. Based on the XRD results of triads **4** and **7** without visible peaks for calixarene units, it could be deduced that they possessed the triphenylene column with calixarene units on ancillary lateral sides as shown in Figure 4(b), which were observed for the first time. Combining these results with our previous report,[28] it could be concluded that the structural feature of spacers between calixarene unit and triphenylene unit played crucial roles on the mesomorphic stacking behaviors of triads of triphenylene-calixarene-triphenylene.

In conclusion, the design and synthesis of novel symmetrical triads of triphenylene-calix[4]arene-triphenylene bridging by aromatic amido or hydrazone spacers were described. Their mesophase behaviors were studied by differential scanning calorimetry, polarizing optical microscopy, atomic force microscopy, and X-ray diffraction. They exhibited novel mesoporphic behavior of the triphenylene column with calixarene units on ancillary lateral sides for the first time. The studies on complexation property and its influences on mesomorphic property will be studied and reported in due course.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2012.01.067.

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29. *Compound **4***: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 0.97 (t, 30H, $J = 7.2$ Hz, CH_3), 1.07 (s, 18H, $C(CH_3)_3$), 1.28 (s, 18H, $C(CH_3)_3$),1.42–1.96 (m, 76H, CH_2), 3.49 (d, 4H, $J = 13.6$ Hz, $ArCH_2Ar$), 3.96 (t, 4H, $J = 6.4$ Hz, OCH_2), 4.23 (m, 28H, $TpOCH_2$ and $ArCH_2Ar$), 4.60 (s, 4H, OCH_2), 6.74 (d, 4H, $J = 9.2$ Hz, ArH), 6.98 (s, 4H, ArH), 7.12 (s, 4H, ArH), 7.33 (d, 4H, $J = 9.2$ Hz, ArH), 7.83 (s, 12H, ArH), 8.05 (s, 2H, NH), 10.13 (s, 2H, OH); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm: 14.149, 22.601, 23.646, 26.558, 28.435, 29.175, 29.726, 31.093, 31.254, 31.535, 31.725, 31.952, 33.865, 34.037, 66.610, 68.843, 68.910, 69.010, 69.289, 69.559, 69.879, 73.688, 107.008, 107.108, 107.390, 107.471, 107.671, 107.740, 108.414, 114.924, 122.996, 123.115, 125.735, 127.810, 129.543, 132.888, 141.490, 146.227, 147.189, 148.096, 148.747, 148.908, 149.035, 149.116, 149.256, 149.320, 149.439, 149.511, 149.649, 150.641, 160.765; IR/cm^{-1}: 3436, 2955, 2926, 1682, 1615, 1510, 1433, 1262, 1169, 1040, 832; UV–vis: 278 nm. MS m/z (%):

2460.34 (M^+, 100). Anal. calcd for $C_{158}H_{214}N_2O_{20}$: C77.10, H 8.76, N 1.14; found C 77.14, H 8.72, N 1.18%.

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31. *Compound* **7**: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 0.97 (m, 48H, CH_3 and $C(CH_3)_3$), 1.32 (s, 18H, $C(CH_3)_3$),1.42–1.95 (m, 72H, CH_2), 2.80 (t, 4H, $J = 5.6$ Hz, CH_2CO), 3.28 (d, 4H, $J = 12.8$ Hz, $ArCH_2Ar$), 4.232 (bs, 32H, $TpOCH_2$ and OCH_2), 4.33 (d, 4H, $J = 12.8$ Hz, $ArCH_2Ar$), 6.80~7.74 (m, 20H, ArH, OH and CH), 7.82 (s, 12H, ArH), 7.91 (s, 2H, NH); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm: 14.341, 22.802, 23.667, 26.257, 26.319, 26.608, 28.606, 29.374, 29.531, 29.744, 31.155, 31.268, 31.506, 31.813, 31.897, 32.242, 32.446, 34.220, 34.408, 68.096, 69.903, 69.923, 74.676, 107.536, 107.590, 107.669, 114.795, 123.805, 123.854, 123.875, 123.901, 125.261, 125.916, 125.996, 126.595, 127.659, 129.937, 132.273, 135.427, 144.085, 148.403, 149.141, 149.188, 149.218, 149.238, 149.507, 150.113, 161.543, 163.479; IR/cm^{-1}: 3440, 2924, 2855,1670, 1611, 1510, 1461, 1435, 1261, 1168, 1046, 833 UV–vis: 278 nm. MS *m*/*z* (%): 2514.13 (M^+, 100). Anal. calcd for $C_{160}H_{216}N_4O_{20}$: C76.40, H 8.66, N 2.23; found C 76.44; H 8.58, N 2.28%.
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