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Ion complexation-induced mesomorphic conversion between two columnar phases of novel symmetrical triads of triphenylene-calix[4]arene-triphenylenes

Fafu Yang [a,b,*], Xiaoyan Bai [a], Hongyu Guo [a], Congcong Li [a]

[a] College of Chemistry and Chemical Engineering, Fujian Normal University, Fuzhou 350007, PR China
[b] Fujian Key Laboratory of Polymer Materials, Fuzhou 350007, PR China

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ABSTRACT

Two novel symmetrical triads of triphenylene-calix[4]arene-triphenylenes **6a** and **6b** bridged by hydrazone spacers were synthesized in high yields. They possessed interesting ion complexation-induced mesomorphic conversion between two columnar phases. The neat compounds **6a** and **6b** showed mesophase with calixarene's bowlic column as cores. The Ag^+-complexes of **6a** and **6b** exhibited mesophase with triphenylene column as cores.

Triphenylene derivatives with aliphatic chains are the most widely studied discotic liquid crystals with possible various applications in organic light-emitting diodes, organic photovoltaic cells, organic field-effect transistors, gas sensors, photocopying machines, etc.,[1–4] All kinds of triphenylene derivatives were synthesized and exhibited excellent mesomorphic properties in the past decades.[1–8] Recently, much attention was paid to the macrocycle-modified triphenylenes. The mesomorphic properties of this kind of compounds could be changed by the guest recognition of macrocycle units. In 2010, Cammidge reported the triphenylene dimers linked by shape-persistent conjugated macrocycle and crown ether macrocycle with interesting mesomorphic properties.[9,10] Laschat and Peng also described the syntheses and mesomorphic properties of a series of crown ether-based triphenylene dimers at the same time, respectively.[11–14] Lately, Wang synthesized triphenylene-fused porphyrins with good UV–vis absorptions.[15] All these literatures indicated that the mesomorphic properties were induced or influenced by the ion complexation behaviors of crown ether units. Obviously, the mesomorphic properties tuned by the complexation capabilities exhibited application prospects such as ion-sensors, ion-selective supramolecular liquid crystals, and ion-switch of liquid crystal. However, besides these few examples of crown ether-modified triphenylenes, the other macrocycle-based triphenylenes were almost unknown so far.

Calixarenes possess tuneable 3D-shaped cavities and are easily modified to prepare various calixarene derivatives with unique complexation properties.[16,17] Some of the calixarene-based liquid crystals were also synthesized by introducing the long alkyl chain on the upper or lower rim of calixarene skeleton.[18–23] Lately, we reported the first examples of calixarene-linked triphenylene dimers.[24,25] They exhibited interesting mesomorphic stacking behavior with calixarene's bowlic column as cores or triphenylene column as cores. However, the influences of complexation behaviors on mesomorphic properties of these novel calixarene-linked triphenylene were not investigated up to now. In this Letter, we wish to describe the design and syntheses of two novel symmetrical triads of triphenylene-calix[4]arene-triphenylenes **6a** and **6b** bridged by aromatic hydrazone spacers. Moreover, the studies on relationship between complexation and mesomorphic properties indicated that they possessed an interesting ion complexation-induced mesomorphic conversion between two columnar phases, which was observed for the first time.

Scheme 1 showed the synthetic route of novel symmetrical triads of triphenylene-calix[4]arene-triphenylenes **6a** and **6b** bridged by aromatic hydrazone spacers. ω-Bromo-substituted triphenylenes **2a**, **2b**, and calix[4]arene 1,3-bis-hydrazide derivative **5** were synthesized by literature methods, respectively.[26,27] By reacting compounds **2a** or **2b** with 4-hydroxy benzaldehyde, triphenylene derivatives with aldehyde group **3a** and **3b** were obtained in yields of 85% and 86%, respectively. Then by '1+2' Schiff-base condensation of compounds **3a** and **3b** with compound **5** under $CHCl_3$/

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* Corresponding author. Tel./fax: +86 591 83465225.
E-mail address: yangfafu@fjnu.edu.cn (F. Yang).

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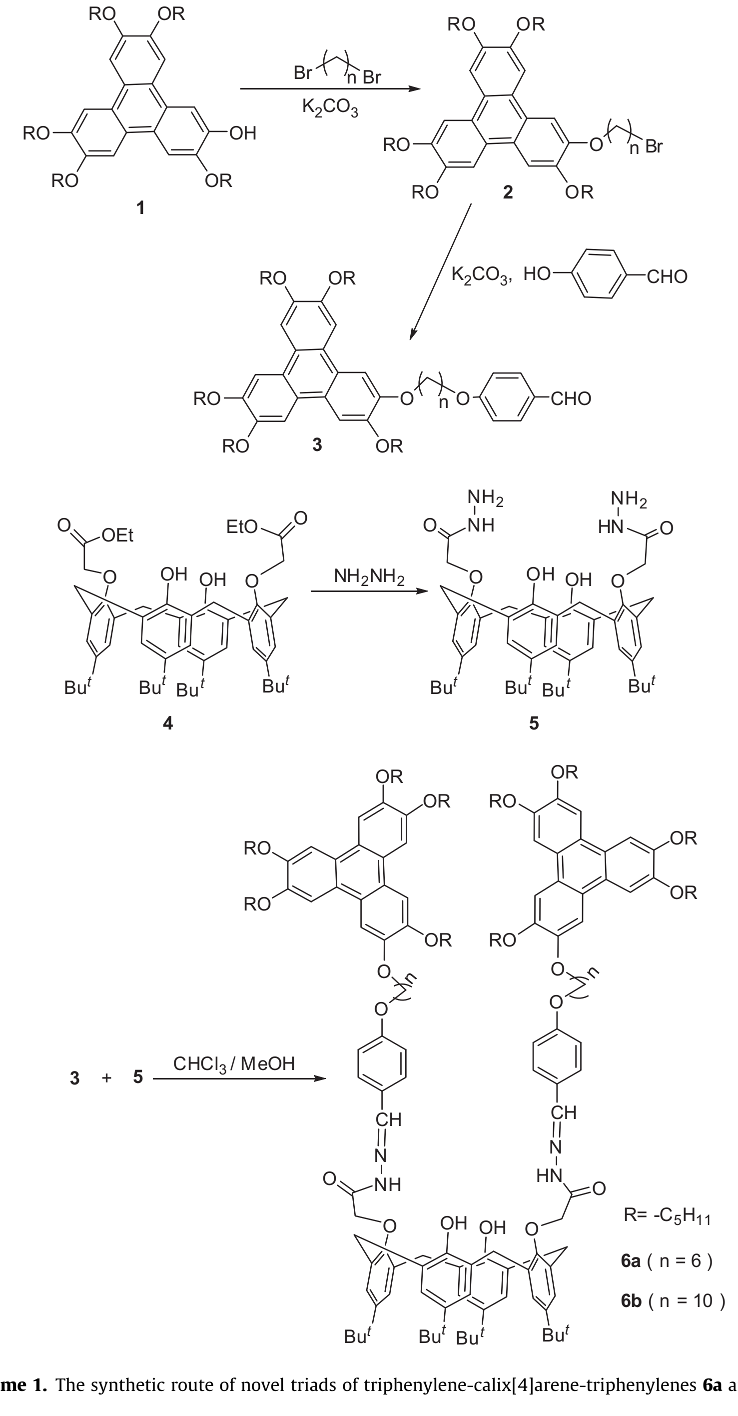

Scheme 1. The synthetic route of novel triads of triphenylene-calix[4]arene-triphenylenes **6a** and **6b.**

MeOH system for 12 h, target triads **6a** and **6b** was successfully obtained in yields of 88% and 86% with recrystallization, respectively. Although compounds **6a** and **6b** were prepared by the stepwise procedures, the separation of each step was simple with recrystallization and the total yields were as high as 58%.

New compounds were characterized by elemental analyses, FT-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 ^1H NMR spectra. Two singlets (1:1) for the *tert*-butyl groups and one pair of doublets (1:1) for the methylene bridges in the calixarene skeleton of compounds **6a** and **6b** indicated that the calix[4]arene units adopt a stable cone conformation.

The ion complexation abilities of compounds **6a** and **6b** were preliminarily studied by liquid–liquid extraction experiments for metallic ions ($CHCl_3/H_2O$, 1×10^{-3} M for both guest and host solutions).[28] The extraction percentages of **6a** for Li^+, Na^+, K^+, Ag^+, Hg^{2+}, and Cu^{2+} were 65.6%, 72.4%, 68.8%, 81.5%, 67.7%, and 57.5%, respectively. The extraction percentages of **6b** for these cations were 60.4%, 73.6%, 61.3%, 80.8%, 64.2%, and 60.1%, respectively. These results indicated compounds **6a** and **6b** were excellent hosts for cations, especially, for Ag^+. In order to investigate deeply the complexation behaviors, the 1:1 complexes of triads **6a**(**6b**) with $AgClO_4$ were prepared in DMSO solutions. Their ^1H NMR spectra were recorded as shown in Figure 1. The peaks of NH and OH of triads **6a** and **6b** shifted from high field to low field obviously. These results suggested the NH and OH groups were involved in the coordination and the ions were bound in the cavities composed of N-containing chains and calixarene skeletons in complexation systems.

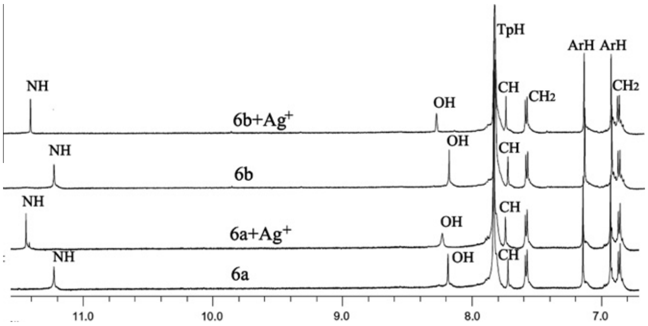

Figure 1. The ^{1}H NMR spectra of triads **6a**, **6b**, and their 1:1 complexes with $AgClO_4$.

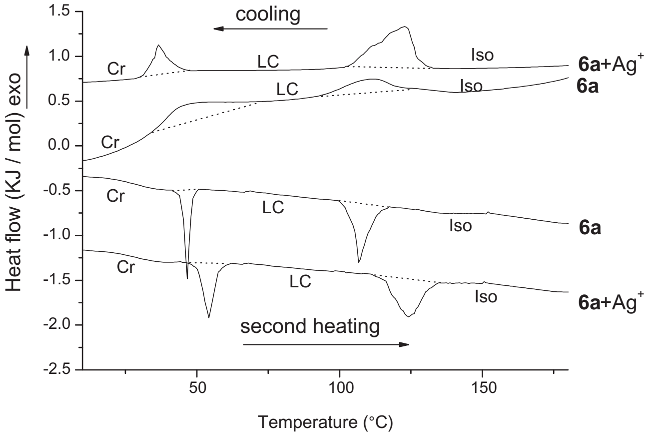

Figure 2. The DSC traces of **6a** and complex **6a+**Ag$^+$ on second heating and cooling (scan rate 10 °C min^{-1}).

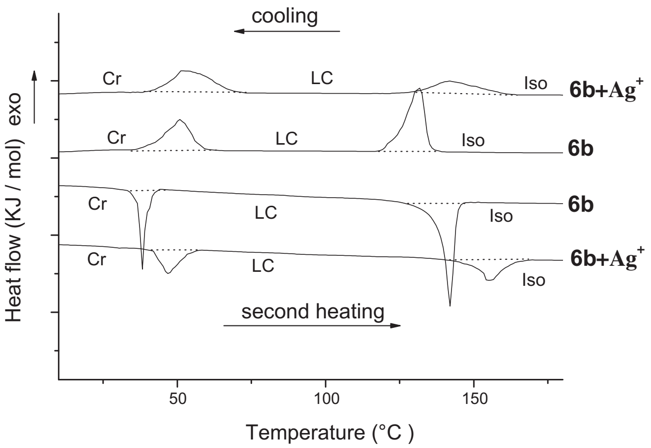

Figure 3. The DSC traces of **6b** and complex **6a**+Ag$^+$ on second heating and cooling (scan rate 10 °C min^{-1}).

Table 1
Phase transfer temperatures (°C) and associated enthalpy changes (kJ/mol in parentheses) of **6a**, **6b**, and their complexes

Triads	Phase transition[a]	T(ΔH) Heating scan	T(ΔH) Cooling scan
6a	Cr–Col	42.1(8.68)	32.6(7.88)
	Col–Iso	100.3(10.93)	93.9(7.53)
6b	Cr–Col	34.6(24.46)	34.1(28.54)
	Col–Iso	128.1(40.17)	118.7(41.17)
6a+Ag$^+$	Cr–Col	46.0(6.78)	31.1(6.89)
	Col–Iso	113.7(9.97)	103.3(12.24)
6b+Ag$^+$	Cr–Col	42.1(9.29)	41.0(19.79)
	Col–Iso	142.4(12.66)	129.5(11.88)

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

Moreover, the mesomorphic behaviors of **6a**, **6b**, and their complexes were studied. The complexes **6a** and **6b** with $AgClO_4$ were obtained by evaporating the solvent of the corresponding 1:1 complexation DMSO solutions. Their DSC results were exhibited in Figure 2, Figure 3 and Table 1. All of them exhibited two phase transitions upon second heating and cooling. For example, compound **6a** showed two phase transfer temperatures at 42.1 °C and 100.3 °C upon second heating process and two reverse processes at 32.6 °C and 93.9 °C on cooling. However, the phase transfer temperatures of neat compounds **6a** and **6b** were different from those of their complexes. Also, the mesomorphic ranges of complexes became wider from 60 °C to 70 °C for **6a** and from 94 °C to 109 °C for **6b**, respectively. These DSC results strongly implied that mesophases existed on the melting process with state-mesophase-isotropic phase for **6a**, **6b**, and their complexes. The different phase transfer temperatures indicated the complexation influenced the mesomorphic properties greatly. These results were also in accordance with the DSC results of complexes of crown ether-based triphenylene with ions. [11–14]

Further, based on the DSC results, the phase textures of mesophase of compounds **6a**, **6b**, and their complexes with $AgClO_4$ were investigated by polarized optical microscopy. Two phase transitions of solid state-mesophase and mesophase-isotropic phase on heating and cooling were observed. Their mesophases were shown in Figures 4 and 5. It could be seen that the clear columnar fan-shaped textures were formed. These textures were similar to the known textures for columnar phases of triphenylene derivatives.[29–34] These results of POM experiments were in accordance with the results of DSC experiments.

In order to investigate the mesomorphic stacking behavior further, triads **6a**, **6b**, and their complexes were studied by the XRD. The results were shown in Figures 6 and 7. It was interesting that neat compounds and complexes exhibited utterly different reflection peaks, which might suggest the different molecular stacking behaviors for neat compounds and complexes.

As we reported previously,[24,25] there had been two possible mesomorphic staking behaviors for liquid crystal of calix[4]arene-linked triphenylene dimers as shown in Figure 8. One way was calixarene column as cores, that is the calixarene's bowlic column with two triphenylene units as ancillary lateral columns, which should show the XRD peaks for both calixarene columns and triphenylene columns (Fig. 8 (a)).[24] Another way was triphenylene column as cores, that is, triphenylene column with calixarene units on ancillary lateral sides (Fig. 8 (b)), which should exhibit XRD peaks for triphenylene and might had some peaks for calixarene column decided by the tropism of calixarene units.[25] A survey of literatures indicated a low angle peak (2θ = 2–4 and/or 5–6), a mid angle peak (2θ = 8–9), and a broad region feature at high angle (2θ = 18–22) for calixarene liquid crystal with bowlic columnar phase.[35–39] On the other hand, literatures suggested a low angle peak (2θ = 5 approximately), a broad region feature at high angle (2θ = 18–22), and a high angle (2θ = 25 approximately) for triphenylene liquid crystal with columnar phase.[29–34] From the XRD traces of neat **6a** and **6b** in Figures 6 and 7, the d-spacings of the reflections observed for **6a** and **6b** at 2θ = 3.4 (25.9 Å), 5.1 (17.3 Å), and 18.6 (4.8 Å) were associated with the first, second, and third reflections of the calixarene bowlic columnar phase,[35–39] and 2θ = 6.0 (14.7 Å), 18–22 (4.04–4.92 Å), and 24.1 (3.7 Å) were agreed with the diameter of the triphenylene groups, the average distance of the molten alkyl chains and the intracolumnar order

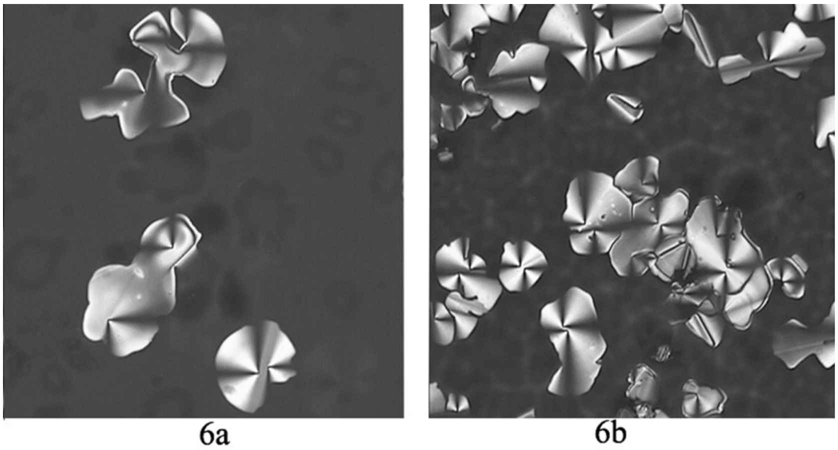
6a 6b

Figure 4. The textures of **6a** and **6b** under POM on cooling at 70 °C (×400).

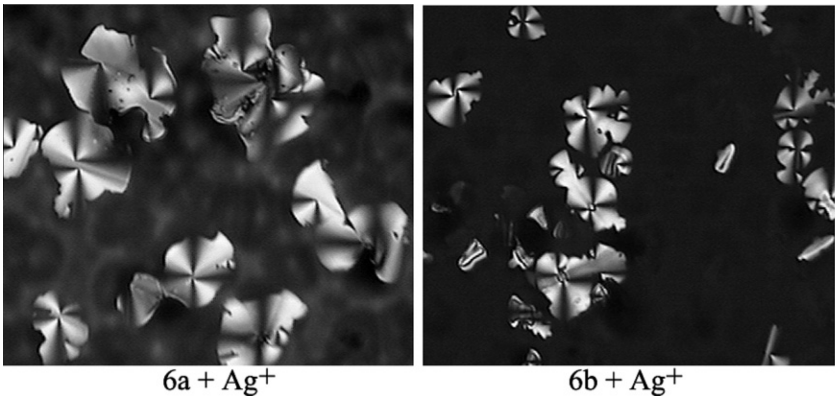
6a + Ag+ 6b + Ag+

Figure 5. The textures of complexes **6a** and **6b** with $AgClO_4$ under POM on cooling at 70 °C (×400).

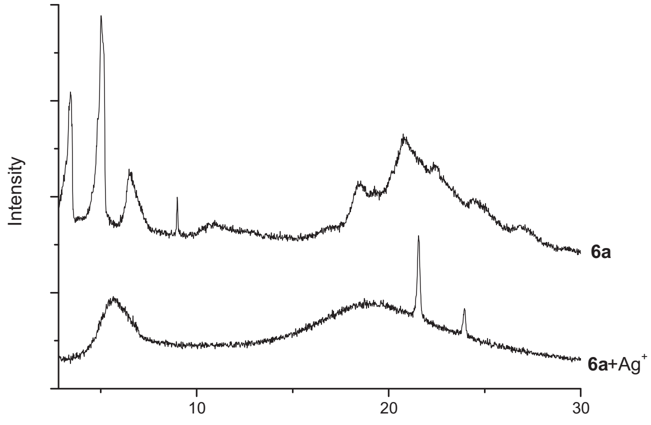

Figure 6. XRD traces of neat triad **6a** and its complex at 70 °C.

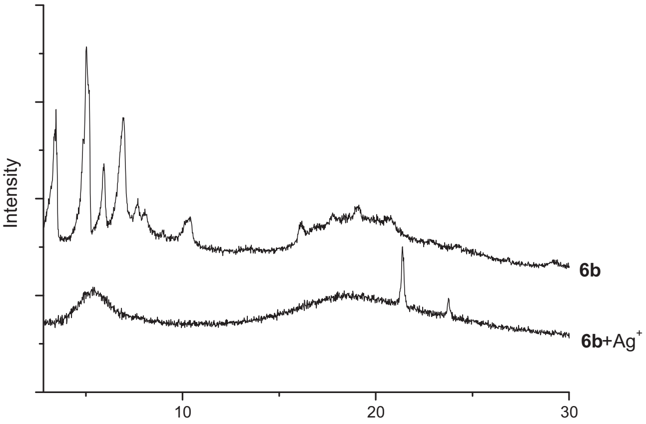

Figure 7. XRD traces of neat triad **6b** and its complex at 70 °C.

of the two ancillary lateral triphenylene columns, respectively.[29–34] These XRD results indicated that neat **6a** and **6b** had mesomorphic properties of calixarene's bowlic column with two triphenylene units as ancillary lateral columns (Figure 8 (a)). On the other hand, the XRD results of their complexes showed peaks at $2\theta = 5.0$ (17.6 Å), 18–22 (4.04–4.92 Å), and 24.0 (3.7 Å), which were the typical peaks of the columnar phase of triphenylene liquid crystal and agreed with the diameter of the triphenylene groups, the average distance of the molten alkyl chains, and the intracolumnar order, respectively.[29–34] However, no obvious peak of calixarene liquid crystal was observed for complexes in Figures 6 and 7. These XRD results of complexes indicated the complexes possessed novel mesomorphic molecular stacking behaviors of the triphenylene column with calixarene units on ancillary lateral sides (Fig. 8 (b)), which were in accordance with previous report.[25]

These interesting XRD changes of mesomorphic molecular stacking behaviors before and after complexation could be explained by that the cavity of calixarene was occupied by ions after complexation, which was an obstacle for the stacking of calixarene

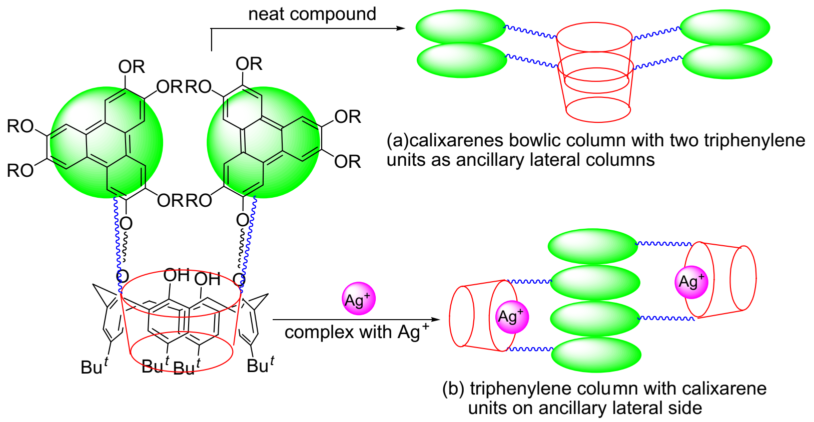

Figure 8. Two kinds of schematic representation of the columnar layered molecular arrangement for triads of triphenylene-calixarene-triphenylenes **6a** and **6b** before and after complexation.

bowlic columnar phase. As a result, the complexes adopt novel molecular stacking behaviors of triphenylene column with calixarene units on ancillary lateral sides to avoid the steric hindrance. These interesting ion complexation-induced mesomorphic conversions between two columnar phases were observed for the first time in supramolecular chemistry and might be applied in ion-selective supramolecular liquid crystals, ion-induced switch of liquid crystal, etc.

In conclusion, the design and synthesis of novel symmetrical triads of triphenylene-calix[4]arene-triphenylenes **6a** and **6b** bridged by hydrazone spacers were described in good yields. Their mesophase behaviors were studied by differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction. They exhibited interesting ion complexation-induced mesomorphic conversion between two columnar phases. The neat compounds **6a** and **6b** showed mesophase with calixarene's bowlic column as cores. But their Ag^+-complexes exhibited mesophase with triphenylene column as cores. The influences on mesomorphic properties by complexation with other ions will be further investigated deeply in following works.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.11.029.

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