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RESEARCH ARTICLE

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Synthesis of arylenealkyne conjugated macrocycles containing a long alkylene bridge

Abstract The synthesis of the first two arylenealkyne conjugated macrocycles containing a long alkylene bridge *via* Glaser coupling of template-directed tetraacetylenes was reported. Tetraacetylene intermediates with complex structures were constructed rapidly *via* quadruple Hagihara coupling of monoprotected bisacetylenes to appropriate tetraiodides and subsequent desilylation. The characterization of such compounds was carried out by NMR, GPC and UV-Vis spectra. Unfortunately, the two compounds were not liquid crystals and had no biaxial nematic mesophase character as expected.

Keywords macrocycles, arylenealkyne, template, biaxial nematic phase, liquid crystal

1 Introduction

Since the existence of Freiser's prediction [1], its potentially wide application in optical, electronic and magnetic materials, biaxial nematic phase (Nb) has attracted considerable interest. However, despite researchers trying to make this prediction real, the discovery of a Nb phase in thermotropic liquid crystals has remained elusive [2]. Functional shape persistent macrocycles with defined structures play a special role in supramolecular chemistry [3]. Recently, a new design principle for discotic liquid crystals with shape persistent arylenealkyne macrocycles containing intraannular long alkylchains have been reported. Such compounds composed of a rigid periphery and flexible side groups pointing to the inside can present nematic mesophases with inverted topology compared to the classic discotic liquid crystals [4]. For the synthesis of such macrocycles, four strategies are categorized: (i) Staab's one-step oligomerization/cyclization; (ii) Moore's intramolecular ring-closure of bisfunctionalized oligomers; (iii) intermolecular oxidative Glaser coupling of the rigid bisacetylenes (''halfrings'') under pseudo high-dilution conditions; (iv) and a template-directed strategy reported by Hoeger etc. The first three strategies have many disadvantages such as low yield, time-consuming multisteps, and difficult purification operation. A template-directed strategy can prepare functional phenylethynyl macrocycles in very high to nearly quantitative yields by the covalent attachment of bisactylenic precursors to an appropriate template or by preparing the tetraacetylenes at the template prior to the cyclization step. Motivated by the facts that shape persistent macrocycles with intraannular alkylchains can represent nematic liquid mesophases and the advantage of the template-directed synthesis method, we decided to design shape biaxial arylenealkyne conjugated macromolecules with intraanular alkyl chains and long alkylene bridge *via* Glaser coupling of the template-directed tetraacetylenes, hoping that a biaxial nematic phase which has positional order and at least two perpendicular axes of molecules could be realized. The syntheses of such compounds are shown in Scheme 1.

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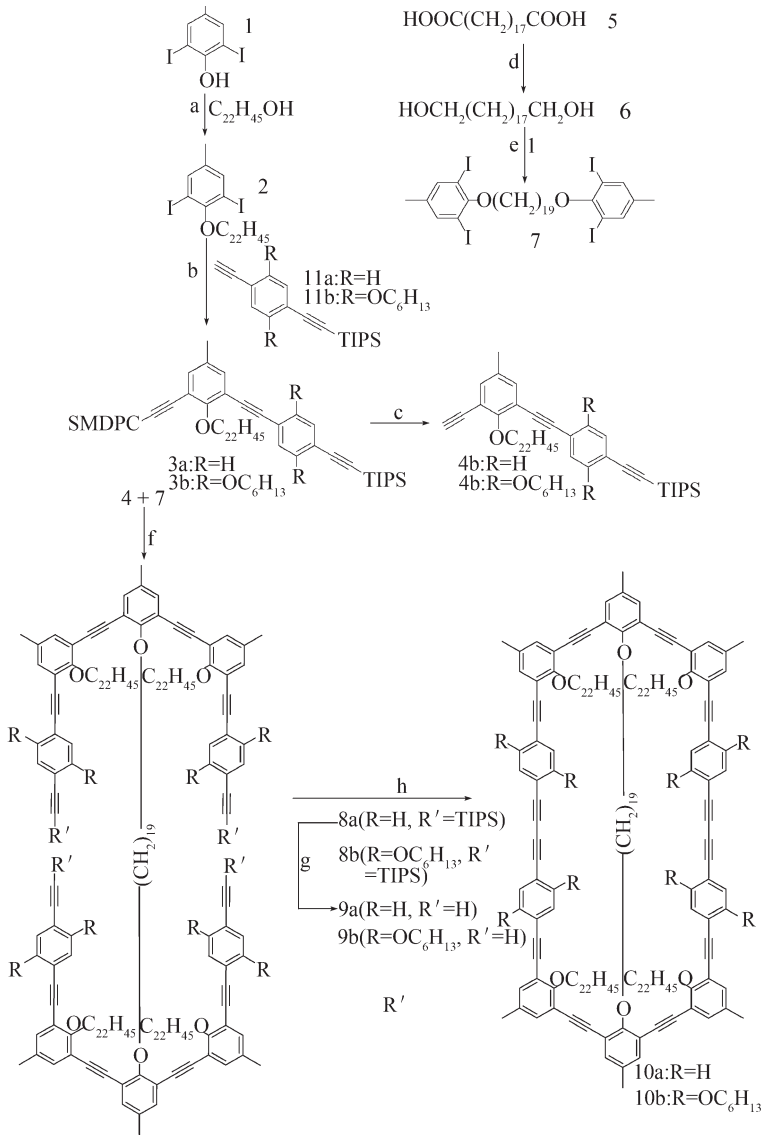
2 Experimental

2.1 Apparatuses and materials

^{1}H-NMR and ^{13}C-NMR spectra were obtained using Bruker-WH-250, Bruker-AM-400 or Bruker-DRX-500 spectrometers. High resolution MS (HR-MS) was recorded using a Finnigan MAT 90 spectrometer at an ionization potential of 70 eV. Field-desorption (FD)



Scheme 1 Synthesis of oval-form macrocycle **10a** and **10b**

a: PPh_3, DIAD, THF (88.4%); b: (1) Tipsphenylacetylene (**11a**, **11b** respectively) $PdCl_2(PPh_3)_2$, CuI, Piperidine, (2) (CPDMS) acetylene, $PdCl_2(PPh_3)_2$, CuI, Piperidine (**3a** 29.9 %; **3b** 27.1 %); c: K_2CO_3, MeOH, THF (**4a** 91.6 %; **4b** 73.1%); d: BF_3.THF (84.5%); e: PPh_3, DIAD, THF (91.1 %); f: $PdCl_2(PPh_3)_2$, CuI, piperidine (**8a** 87.3 %; **8b** 36.7%); g: Bu_4NF, THF (**9a** 89.2 %; **9b** 72.8 %); h: CuCl/$CuCl_2$ (**10a** 84.1 %; **10b** 93.5 %).

mass spectra were obtained using a VG ZAB 2-SE-FPD. Thin-layer chromatography was carried out on aluminum plates precoated with 5735 silica gel 60 PF_{254} (Merck). Column chromatography was carried out on Merck silica gel 60 (230–400 mesh). Radial chromatography was conducted on a Chromatotron (Harrison Research Europe, Muttenz) with glass plates coated with 4 mm silica gel 60 PF_{254} containing gypsum (Merck). 4-Methyl-phenol, nonadecanedioic acid, diisopropyl azodicarboxylate (DIAD), piperidine, *n*-docosanol, ethylmagnesium bromide solution (1.0 mol/L in tert-butylmethyl ether), ethynylmagnesium bromide (0.5 mol/L in THF), (3-cyanopropyl) dimethylsilyl chloride, BF_3.THF, and (4-ethynyl-phenylethynyl)-triisopropyl-silane (**11a**) were bought from Aldrich. $(Ph_3P)_2PdCl_2$ was self-made, tetrahydrofuran (THF) distilled from sodium prior to use. Pyridine and piperidine were distilled from CaH_2 prior to use. Commercially available chemicals were used as received. Reactions requiring an inert gas atmosphere were conducted under argon and the glassware was oven-dried (140°C). 2,6-Diiodo-4-methyl-phenol (**1**) was prepared according to Ref. [5]; yield 80.2%, m. p. 59–61°C (lit [5]: 55–58°C). ω–Nonadecane-diol (**6**) was prepared according to Ref. [6]; yield 84.5 %; mp 100–101°C (lit [6]: 99–100°C).

2.2 Synthesis of arylenealkyne conjugated macrocycles containing long alkylene bridge (**10a** and **10b**)

2.2.1 1,19-Di-(2,6-diiodo-4-methyl-phenyloxyl) nonadecane (**7**)

To a solution of **1** (997.7 mg, 2.77 mmol), **6** (380 mg, 1.26 mmol) and PPh_3 (990.36 mg, 3.78 mmol) in THF (10 mL), DIAD (763.6 mg, 3.7 mmol) was added dropwise. The mixture was stirred overnight under RT. Et_2O (150 mL) and H_2O (50 mL) were added for extraction. The organic phase was separated, washed with H_2O (3 × 40 mL) and brine (3 × 20 mL), and dried over $MgSO_4$. The solvent was then removed *in vacuo*, and the residue was purified by columnar chromatography (petroleum ether /CH_2Cl_2 4:1, $R_f = 0.44$). Yield 1.13 g (91.1 %), colorless solid, m. p. 77–79°C; $C_{33}H_{48}I_4O_2$ (Cal. 984.35); FAB $m/z = 984.9$ (M^+, 100 %); HRMS (FAB) Calcd for: $C_{33}H_{48}I_4O_2$ (M^+) 984.9867, Found: 984.9915; ^{1}H-NMR (250 MHz, CD_2Cl_2) δ : 7.55 (s, 4 H, Ar-H), 3.89-3.84 (t, $J_{(H, H)} = 6.7$ Hz, 4 H, 2 OCH_2), 2.18 (s, 6 H, 2 CH_3), 1.89–1.76 (m, 4 H, 2 CH_2), 1.54–1.41 (m, 4 H, 2 CH_2), 1.34–1.16 (m, 26 H, 13 CH_2); ^{13}C-NMR (100 MHz; CD_2Cl_2) δ : 155.05, 139.54, 136.95, 89.60, 72.67, 29.24, 28.94, 28.92, 28.88, 28.84, 28.75, 25.19, 18.60.

2.2.2 2-Docosyloxy-1,3-diiodo-5-methyl-benzene (**2**)

Prepared as the procedure described for **7**. Yield 88.4 %, colorless crystal, m. p. 71-72°C; $C_{29}H_{50}I_2O$ (Cal. 668.52); EI-MS $m/z = 668.2$ (M^+, 100 %); HRMS (EI) Calcd for $C_{29}H_{50}I_2O$ (M^+) 668.1951, Found 668.1956; ^{1}H-NMR (250 MHz, CD_2Cl_2) δ : 7.57 (s, 2 H, Ar-H), 3.95-3.90 (t, $J_{(H, H)} = 6.7$ Hz , 2 H, OCH_2), 2.23 (s, 3 H, CH_3), 1.91-1.83 (m, 2 H, CH_2), 1.57-1.50 (m, 4 H, 2 CH_2), 1.32-1.19 (m, 34 H, 17 CH_2) 0.90-0.85 (m, 3 H, CH_3); ^{13}C-NMR (100 MHz; CD_2Cl_2) δ : 156.21, 140.70, 138.09, 90.74, 73.82, 32.33, 30.39, 30.09, 30.04, 29.99, 29.91, 29.76, 26.34, 23.09, 19.75, 14.28.

2.2.3 4-[(2-Docosyloxy-5-methyl-3-{4-[(triisopropylsilanyl)-ethynyl]-phenylethynyl}-Phenylethy-nyl)-dimethyl-silanyl]-butyronitrile (**3a**)

To a solution of **2** (2 g, 2.99 mmol) and **11a** (845 mg, 2.99 mmol) in THF (15 mL) and piperidine (7 mL), PPh_3 (30 mg), CuI (15 mg) and $(Ph_3P)_2PdCl_2$ (30 mg) were added. The mixture was stirred at 40°C for 12 h, then [(3-cyanopropyl)dimethylsilyl] acetylene {prepared according to Ref. [9] (1.36 g, 8.97 mmol)} was added. The mixture was further stirred at 40°C for 24 h, cooled to RT, then poured into a mixture of CH_2Cl_2 (150 mL) and H_2O (50 mL) for extraction. The organic phase was separated; washed with 10% acetic acid (3 × 40 mL), H_2O (3 × 40 mL), aqueous NaOH (3 × 40 mL), H_2O (3 × 40 mL) and brine (3 × 40 mL); dried over $MgSO_4$; the solvent was then removed *in vacuo.* Purification of the product was done by radial chromatography (petroleum ether: dichloromethane 2/1, $R_f = 0.34$). Yield 758 mg (30.0%), yellow oil; $C_{56}H_{87}NOSi_2$ (Cal. 846.47); HRMS (EI) Calcd for $C_{56}H_{87}NOSi_2$ (M^+) 846.6360, Found 846.6398; ^{1}H-NMR (250 MHz, CD_2Cl_2) δ : 7.42(s, 4 H, Ar-H), 7.25–7.24 (d, $J_{(H, H)} = 2.1$ Hz, 1 H, Ar-H), 7.19–7.18 (d, $J_{(H, H)} = 2.2$ Hz, 1 H, Ar-H), 4.17–4.12 (t, $J_{(H, H)} = 6.7$ Hz, 2 H, OCH_2), 2.38–2.36 (t, $J_{(H, H)} = 7.0$ Hz, 2 H, CH_2CN), 2.23 (s, 3 H, CH_3), 1.84–1.71 (m, 4 H, 2 CH_2), 1.51–1.44 (m, 2 H, CH_2), 1.26–1.16 (m, 36 H, 18 CH_2), 1.09–1.07 (m, 21 H, 6 CH_3, 3 CH), 0.86–0.77 (m, 5 H, CH_2, CH_3), 0.25 (s, 6 H, 2 CH_3); ^{13}C-NMR (100.6 MHz, CD_2Cl_2) δ : 161.82, 136.85, 136.58, 135.29, 134.11, 133.49, 125.64, 125.38, 121.89, 119.39, 119.22, 108.73, 104.43, 98.87, 95.15, 94.98, 89.64, 76.75, 34.14, 32.73, 31.92, 31.89, 31.85, 31.58, 28.48, 24.91, 22.89, 22.62, 22.26, 20.62, 17.82, 16.10, 13.52.

2.2.4 4-[(3-{2,5-Bis-hexyloxy-4-[(triisopropylsilanyl)-ethynyl]-phenylethynyl}-2- docosyloxy-5-methyl-phenylethynyl)-dimethyl-silanyl]-butyronitrile (**3b**)

Prepared according to the procedure as described for **3a**. **11**b was prepared according to Ref. [8]. Yield of **3a**: 28.0 %, yellow oil; $C_{68}H_{111}NO_3Si_2$ (Cal. 1046.76). ^{1}H-NMR (250 MHz, CD_2Cl_2) δ : 7.24–7.23 (d, $J_{(H, H)} = 2.1$ Hz, 1 H, Ar-H), 7.19–7.18 (d, $J_{(H, H)} = 2.0$ Hz, 1 H, Ar-H), 6.92 (s, 2 H, Ar-H), 4.22–4.17 (t, $J_{(H, H)} = 6.6$ Hz, 2 H, OCH_2), 4.00–3.90 (m, 4 H, 2 OCH_2), 2.42–2.37 (t, $J_{(H, H)} = 7.1$ Hz, 2 H, CH_2CN), 2.23 (s, 3 H, CH_3), 1.83–1.73 (m, 6 H, 3 CH_2), 1.53–1.33 (m, 6 H, 3 CH_2), 1.31–1.10 (m, 65 H, 22 CH_2,, 18 CH_3, 3 CH) , 0.90–0.79 (m, 9 H, 3 CH_3), 0.25 (s, 6 H, 2 CH_3). ^{13}C-NMR (100 MHz, CD_2Cl_2) δ: 161.61, 156.41, 155.51, 136.69, 136.61, 135.12, 121.86, 119.63, 118.56, 116.21, 116.07, 105.17, 104.56, 98.74, 96.42, 92.92, 90.28, 76.69, 71.83, 71.54, 34.12, 33.90, 32.72, 31.90, 31.85, 31.64, 31.55, 31.53, 28.39, 28.07, 27.89, 24.88, 24.85, 22.87, 22.66, 22.60, 22.53, 22.21.1.

2.2.5 [4-(2-Docosyloxy-3-ethynyl-5-methyl-phenylethynyl)-phenylethynyl]-triisopropyl-silane (**4a**)

To a mixture of **3a** (651 mg, 0.77 mmol) in (8 mL) and MeOH (4 mL), K_2CO_3 (638 mg, 4.62 mmol) was added. The mixture was stirred at RT for 24 h, then poured into a mixture of CH_2Cl_2 (200 mL) and H_2O (50 mL). After extraction, the organic phase was separated, washed with H_2O (3 × 40 mL) and brine (3 × 40 mL), dried over $MgSO_4$, and the solvent removed *in vacuo.* Purification of the product was done by column chromatography (petroleum ether: dichloromethane 2/1, $R_f = 0.34$). After evaporation of the solvent to 30–40 mL, methanol was added to the solution, and the product was precipitated by adding

100 mL of methanol and collected by filtration. Yield: 510 mg (91.6 %), high viscous yellow gel; $C_{50}H_{76}OSi$ (Cal. 721.22); HRMS (EI) Calcd for $C_{50}H_{76}OSi$ (M^{+2}) 722.5733, Found 722.5812; ^{1}H-NMR (250 MHz, CD_2Cl_2) δ: 7.42 (s, 4 H, Ar-H), 7.27–7.26 (d, $J_{(H,\ H)} = 2.1$ Hz, 1 H, Ar-H), 7.22–7.21 (d, $J_{(H,\ H)} = 2.2$ Hz, 1 H, Ar-H), 4.18–4.15 (t, $J_{(H,\ H)} = 6.6$ Hz, 2 H, OCH_2), 3.22 (s, 1 H, CH), 2.23 (s, 3 H, CH_3), 1.80–1.75 (m, 2 H, CH_2), 1.52–1.45 (m, 2 H, CH_2), 1.24–1.20 (m, 36 H, 18 CH_2), 1.13–1.10 (m, 21 H, 6 CH_3, 3 CH), 0.86–0.84 (m, 3 H, CH_3); ^{13}C-NMR (100 MHz, CD_2Cl_2) δ: 159.03, 134.09, 133.73, 132.37, 131.14, 130.51, 122.67, 122.36, 116.44, 115.56, 105.73, 92.17, 92.07, 86.62, 80.37, 78.91, 73.87, 31.17, 29.64, 29.30, 28.95, 28.89, 28.78, 28.61, 25.38, 21.94, 19.30, 17.65, 13.13, 10.81, 10.53, 10.25.

2.2.6 [4-(2-Docosyloxy-3-ethynyl-5-methyl-phenylethynyl)-2,5-bis-hexyloxy-phenyl ethynyl]-triisopropyl-silane (**4**b)

Prepared according to the procedure described for **4a.** Yield 73.1%, light yellow high viscous gel; $C_{62}H_{100}O_3Si$ (Cal.921.54); HRMS (EI) Calcd for $C_{62}H_{100}O_3Si$ (M^+) 920.74, Found 920.7434. ^{1}H-NMR (250 MHz, CD_2Cl_2) δ: 7.24–7.23 (d, $J_{(H,\ H)} = 1.9$ Hz, 1 H, Ar-H), 7.21–7.20 (d, $J_{(H,\ H)} = 1.5$ Hz, 1 H, Ar-H), 6.91 (s, 2 H, Ar-H), 4.22–4.17 (t, $J_{(H,\ H)} = 6.6$ Hz, 2 H, OCH_2), 3.99–3.89 (m, 4 H, 2 OCH_2), 3.25 (s, 1 H, CH), 2.23 (s, 3 H, CH_3), 1.81–1.71 (m, 6 H, 3 CH_2), 1.49–1.35 (m, 6 H, 3 CH_2), 1.41–1.08 (m, 44 H, 22 CH_2), 0.82–0.90 (m, 9 H, 3 CH_3); ^{13}C-NMR (100 MHz, CD_2Cl_2) δ: 160.03, 154.63, 153.74, 135.55, 135.01, 133.34, 117.73, 116.72, 114.46, 114.27, 103.40, 96.94, 91.11, 90.57, 81.56, 81.37, 80.22, 74.95, 70.03, 69.74, 34.54, 32.35, 32.12, 32.06, 30.83, 30.13, 30.09, 30.03, 29.87, 29.75, 29.44, 26.50, 26.12, 23.11, 23.07, 22.75.

2.2.7 Tetraacetylene derivative (**8a** and **8b**)

8a: To a solution of **7** (113.6 mg, 0.115 mmol) and **4a** (499.2 mg, 0.692 mmol) in THF (10 mL) and piperidine (5 mL), PPh_3 (5 mg), CuI (2.5 mg) and $(Ph_3P)_2PdCl_2$ (10 mg) were added. The mixture was stirred at 40°C for 24 h, cooled to RT, and poured into a mixture of CH_2Cl_2 (150 mL) and H_2O (50 mL). After extraction, the organic phase was separated; washed with 10% acetic acid (3 × 40 mL), H_2O (3 × 40 mL), aqueous NaOH (3 × 40 mL), H_2O (3 × 40 mL) and brine (3 × 40 mL); dried over $MgSO_4$; and the solvent removed *in vacuo.* Purification of the product was done by radial chromatography (petroleum ether: dichloromethane 4/1 $R_f = 0.23$). Yield: 335.6 mg (87.3 %), light yellow liquid; $C_{233}H_{348}O_6Si_4$ (Cal. 3357.59); ^{1}H-NMR (250 MHz, CD_2Cl_2) δ : 7.42 (s, 16 H, Ar-H), 7.26 (s, 12 H, Ar-H), 4.27–4.21 (m, 12 H, 6 OCH_2), 2.26 (s, 18 H, 6 CH_3), 1.78–1.56 (m, 12 H, 6 CH_2), 1.54–1.49 (m, 12 H, 6 CH_2), 1.20–1.16 (m, 170 H, 85 CH_2), 1.13–1.17 (m, 84 H, 24 CH_3, 12 CH), 0.85–0.78 (m, 12 H, 4 CH_3); ^{13}C-NMR (100 MHz, CD_2Cl_2) δ : 158.40, 158.32, 133.49, 133.37, 133.29, 132.27, 131.13, 130.52, 122.63, 122.50, 116.71, 116.67, 116.42, 105.79, 92.13, 92.01, 88.99, 86.92, 73.96, 31.18, 29.85, 29.05, 28.96, 28.91, 28.62, 25.63, 21.94, 19.39, 17.66, 13.13, 10.55.

8b was prepared according to the procedure as described for **8a**. Yield 36.7 %, light yellow liquid; $C_{281}H_{444}O_{14}Si_4$ (Cal. 4158.87); ^{1}H-NMR (250 MHz, CD_2Cl_2) δ : 7.27–7.25 (m, 12 H, Ar-H), 6.93–6.92 (m, 8 H, Ar-H), 4.30–4.25 (m, 12 H, 6 OCH_2), 3.99–3.90 (m, 16 H, 8 OCH_2), 2.30–2.26 (m, 18 H, 6 CH_3), 1.85–1.71 (m, 12 H, 6 CH_2), 1.60–1.49 (m, 12 H, 6 CH_2), 1.48–1.11 (m, 278 H, 97 CH_2, 24 CH_3, 12CH), 0.86–0.80 (m, 36 H, 12 CH_3); ^{13}C-NMR (100 MHz, CD_2Cl_2) δ : 158.29, 158.20, 153.47, 152.58, 133.41, 133.33, 133.23, 132.12, 116.71, 116.58, 115.61, 113.22, 102.25, 95.73, 90.20, 89.31, 88.94, 88.87, 73.89, 68.88, 68.57, 31.18, 30.96, 30.90, 29.86, 29.09, 28.98, 28.91, 28.71, 28.61, 28.60, 25.67, 25.58, 25.13, 24.96, 21.93, 21.91, 19.36.

2.2.8 Tetraacetylene derivative **(9a** and **9b)**

9a: Tetra-*n*-butyl ammonium fluoride (1 mol/L in THF) (1.19 mL, 1.19 mmol) was added to a solution of **8a** (326 mg, 0.099 mmol) in THF (15 mL); the mixture was stirred at RT for 24 h. CH_2Cl_2 (150 mL) and water (20 mL) were added; the organic phase was separated; washed with H_2O ((3 × 25 mL) and brine (2 × 25 mL); dried over $MgSO_4$ and the solvent removed *in vacuo*. The product was purified by column chromatography (petroleum ether: dichloromethane 4/1, $R_f = 0.19$). Yield 240 mg (89.2%), yellow high viscous gel; $C_{197}H_{268}O_6$ (2732.32); GPC: single peak at Mw: 3600.57; ^{1}H-NMR (250 MHz, CD_2Cl_2) δ : 7.44 (s, 16 H, Ar-H), 7.26 (s, 12 H, Ar-H), 4.29–4.21 (m, 12 H, 6 OCH_2), 3.19 (s, 4H, 4 CH), 2.26 (s, 18 H, 6 CH_3), 1.84–1.77 (m, 12 H, 6 CH_2), 1.55–1.47 (m, 12 H, 6 CH_2), 1.28–1.10 (m, 170 H, 85 CH_2), 0.85–0.80 (m, 12 H, 4 CH_3); ^{13}C-NMR (100 MHz, CD_2Cl_2) δ : 159.57, 134.72, 134.53, 133.44, 133.34, 132.46, 131.76, 124.25, 122.35, 117.87, 117.82, 117.49, 92.91, 90.16, 89.94, 88.21, 83.42, 79.27, 75.13, 32.33, 31.00, 30.20, 30.12, 30.06, 29.77, 26.78, 23.09, 20.54, 17.96, 14.28, 13.02, 12.70.

9b: Prepared according to the procedure as described for **9a**. Yield 72.8 %, yellow high viscous gel, m. p. 68–70°C; $C_{245}H_{364}O_{14}$ (3533.50); GPC: single peak at Mw: 4263.46; ^{1}H-NMR (250 MHz, CD_2Cl_2) δ : 7.27–7.25 (m, 12 H, Ar-H), 6.95–6.94 (m, 8 H, Ar-H), 4.30–4.24 (m, 12 H, 6 OCH_2), 3.98–3.91 (m, 16 H, 8 OCH_2), 3.33 (s, 2 H, CH), 2.27–2.26 (m, 18 H, 6 CH_3), 1.85–1.71 (m, 12 H, 6 CH_2), 1.73–1.33 (m, 12 H, 6 CH_2), 1.32–1.15 (m, 194 H, 97 CH_2), 0.89–0.80 (m, 36 H, 12 CH_3); ^{13}C-NMR (100 MHz, CD_2Cl_2) δ : 159.46, 159.38, 154.50, 153.79, 134.60, 134.48, 133.30, 117.99, 117.89, 117.87, 117.76, 117.19, 114.93, 112.97, 91.53, 90.16, 90.07, 90.05, 82.59, 80.35, 75.11, 75.06, 69.99, 69.97, 68.14, 32.33, 32.05,

31.97, 31.04, 31.01, 30.24, 30.15, 30.12, 30.07, 29.77, 29.70, 29.59, 26.83, 26.74, 26.11, 26.03, 23.10, 23.07.

2.2.9 Arylenealkyne conjugated macrocycles containing long alkylene bridge (**10a** and **10b**)

10a : **9a** (111.9 mg, 0.0421 mmol) in 15 mL dry pyridine was added to a suspension of CuCl (854.3 mg) and $CuCl_2$ (169 mg) in 50 mL dry pyridine over 95 h at RT. The mixture was poured into CH_2Cl_2 (400 mL) and water (200 mL); the organic phase was separated and washed with 25% NH_3 solution, water, 10% acetic acid, water, 10% aqueous NaOH, water and brine and dried over $MgSO_4$. After evaporation of the solvent to 30–40 mL, the coupling rough product was precipitated by adding 100 mL MeOH and collected by filtration. The rough product was dissolved in toluene again, filtered over silica gel and washed with hot toluene. After evaporation of the solvent to 30–40 mL, the coupling product was precipitated by adding 100 mL MeOH and collected by filtration, and followed by recrystallization from $CHCl_3$. Yield: 94.4 mg (84.1 %), light yellow solid, m. p. 174–175°C; $C_{192}H_{262}O_6$ (Cal. 2666.13); GPC: single peak at Mw:2657.22; ^{1}H-NMR (250 MHz, THF-d_8) δ : 7.52 (s, 16 H, Ar-H), 7.34–7.30 (m, 12 H, Ar-H), 4.31–4.30 (m, 12 H, 6 OCH_2), 2.33 (s, 18 H, 6 CH_3), 1.85–1.75 (m, 12 H, 6 CH_2), 1.59-1.52 (m, 12 H, 6 CH_2), 1.32–1.07 (m, 170 H, 85 CH_2), 0.89–0.86 (m, 12 H, 4 CH_3).

10b was prepared according to the procedure as described for **10a**. Yield 93.5 %, light yellow solid, m. p. 126–128°C; $C_{240}H_{358}O_{14}$ (Cal. 3467.40); GPC: single peak at Mw:3243.63; ^{1}H-NMR (250 MHz, $CDCl_3$) δ : 7.21–7.19 (m, 12 H, Ar-H), 6.89–6.88 (m, 8 H, Ar-H), 4.27–4.19 (m, 12 H, 6 OCH_2), 3.93–3.88 (m, 16 H, 8 OCH_2), 2.23–2.22 (m, 18 H, 6 CH_3), 1.79–0.89 (m, 218 H, 109 CH_2), 0.89–0.80 (m, 36 H, 12 CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$) δ : 158.60, 158.29, 153.95, 152.27, 133.20, 132.55, 131.42, 131.32, 124.50, 116.55, 116.50, 116.28, 115.91, 114.23, 111.58, 90.85, 89.09. 88.84, 88.70, 68.61, 68.59, 66.96, 52.40, 30.92, 30.61, 30.59, 30.45, 30.35, 30.30, 30.17, 30.14, 29.44, 29.30, 28.82, 28.79, 28.76, 28.74, 28.72, 28.67, 28.36, 28.25, 28.16.

3 Results and discussion

The synthesis of oval-biaxial arylenealkyne conjugated shape persistent macrocycles with two C_{22} intraannular long alkyl chains and a long alkylene bridge is shown in Scheme 1. Key compounds are the mono-protected bisacetylene **4** and asymmetric templated tetraiodide **7**. **4** was prepared from diiodide aromatic phenol **1**, which was first etherified with $C_{22}H_{25}OH$ under the Mitsunobu conditions to offer **2**. Then **2** was treated with 1 equivalent of TIPS acetylene **11** [8], and then with 3 equivalent of [(3-cyanopropyl) dimethylsilyl (CPDMS)] acetylene [7] to give the CPDMS-TIPS-protected bisacetylene **3**. The reason for using excess (CPDMS)acetylene is that mono-protected **2** by phenyl acetylene (**11**) and unreacted **2** can be both coupled with (CPDMS) acetylene, yielding product (**3**) and by-products. The CPDMS protecting group has a rather high polarity. This makes the product and all by-products have significantly different R_f values, enabling the easy separation of **3** [7]. Potassium carbonate-induced deprotection of the CPDMS group gives the mono-TIPS-protected bisacetylene **4** in nearly quantitative yield.

7 was synthesized by the etherified reaction between diiodide aromatic phenol **1** [5] and nondecane diol **6**, which acts as an asymmetric template and was obtained from the reduction of the commercially available ω-nondecane dicoboxyacid **5** with BF_3 in THF solvent. The templated tetraacetylene **9** needed for the cyclization was then prepared from the quadruple palladium-catalyzed Hagihara coupling of monoprotected bisacetylene **4** to tetraiodide **7**, providing the templated symmetrical tetraacetylene (TSTA) with intraannular C_{22} alkyl chains in its TIPS-protected form **8**. Subsequent desilylation of **8** using tetrabutylammonium fluoride gave the templated symmetrical tetraacetylene **9** (TSTA-**9**). The cyclization of **9** under pseudo-high-dilution condition [9] was carried out by slow addition of a solution of **9** in pyridine to a slurry of $CuCl/CuCl_2$ in the same solvent at room temperature. After complete addition, the mixture was stirred for an additional two days at room temperature. The GPC data of **9** and of the crude cyclization product indicate that the latter contained more than 95% of **10**. Chromatographic purification afforded pure **10a** (yield 84%) and **10b** (yield 93%).

The purity of tetraacetylene derivatives of **9** (half ring) and corresponding macrocycles **10** are measured by GPC; all represent single peaks. The UV-Vis spectra of the tetraacetylene derivatives of **9** and the corresponding macrocycles **10** show a significant difference (Fig. 1).

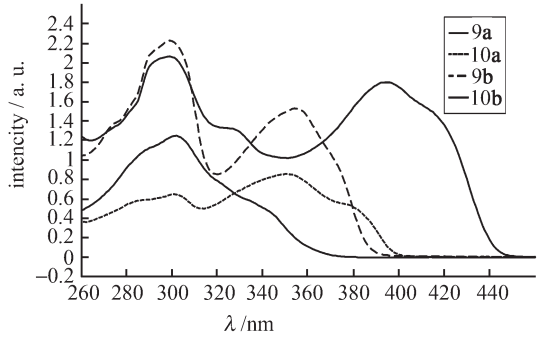


Fig. 1 UV-Vis Absorption spectra of **9a** (λ_{max}: 301 nm) , 10a (solid line, λ_{max}: 352 nm; shoulder at 301 nm), **9b** (λ_{max}: 298 nm; shoulder at 353 nm) and **10b** (λ_{max}: 298 nm; shoulder at 396 nm) in THF

Compounds **10a** and **10b** have a persistent oval form containing two intraannular C_{22} alkyl chains and a long alkylene bridge. According to the new design principle for the inverted-topology of discotic liquid crystals [4], liquid crystalline character was expected from these compounds. Unfortunately, compounds **10a** and **10b** showed no mesophase under polarized light optical microscopy (OM). **10a** represents only a melting point between 174–175°C, while **10b** represents a melting point between 126–128°C. **10b** has four more hexyloxy chains compared with **10a**, but only caused a lower melting point and had no mesophase behavior. The possible reason may be that the template makes the internal cavity rigid or twist, so that the macrocycles no longer have a flexible core and do not reach the requirement of the new design principle for discotic liquid crystals with inverted topology (flexible core and rigid periphery).

In conclusion, arylenealkyne conjugated macrocycles containing a long alkylene bridge were synthesized with high yields. The precursors for cyclization can be obtained only through a few steps. By applying such a template-directed intramolecular cyclization, the product is easily purified and the yield is high. The two macrocycles synthesized here are not mesogens without Nb mesophases as expected.

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