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RESEARCH ARTICLE

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Liquid crystalline behavior and fluorescent property of calix[4]arene containing azobenzene photochromic group

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Abstract The reaction of 4′-hydroxy-4-methyl azobenzene (**1**) and 1,6-dibromohexane afforded 6-bromo-1-((4- ((4-methylphenyl)azo)phenyl)oxy)hexane (**2**), which further reacted with *p-tert*-butylcalix[4]arene to give the calix[4]arene derivative (**3**) whose lower rim had been modified by the azobenzene photochromic group. The structure of **3** was characterized by ^{1}H-nuclear magnetic resonance (NMR) and electrospray ionization-mass spectrometry (ESI-MS). The fluorescence intensity of compound **3** was two to four times higher than that of compounds **1** and **2** as the azobenzene group concentration in the range of 1.6×10^{-5} to 8.0×10^{-4} mol/L, indicating that the fluorescence quantum yield of the azobenzene group had been improved through being attached to the calix[4]arene skeleton. The liquid crystalline behavior of compound **3** was studied by polarized microscopy (POM) and differential scan calorimeter (DSC). Compound **3** exhibited the enchased texture of a smectic liquid crystal from 209.4°C to 219.5°C on heating, while **2** exhibited a liquid crystalline phase from 87.4 to 83.2°C on cooling. It was found that the calix[4]arene skeleton was a good platform for conformation immobilization of azobenzene photochromic group and the formation of liquid crystalline.

Keywords azobenzene, calixarene, thermotropic liquid crystal, fluorescence

1 Introduction

Calix[n]arenes are cyclic oligomers of phenol moieties, which are linked via methylene units to provide unique cavity structures. Calixarenes offer an ideal platform due to the easy modification at their upper and lower rim. The new photoactive [1−3] and liquid crystal derivatives [4,5] based on calixarenes currently attract a lot of interest. Azo reagents have the advantage of high sensitivity and good selectivity to determine metal ion [6]. Azobenzene derivatives are used as molecular switch and data memory material because of the photoactive and reversible cis/trans isomers transformation properties [7]. Different azo group has been anchored to the upper rim of calixarene through diazotization [8,9]. The host molecule can selectively recognize and extract heavy metal ion due to soft coordination condition and special structure of calixarene [10,11]. Aobo et al. [12] synthesized calix[4]arene derivative with liquid crystal properties, of which initial phase-change temperature was low and phase-change temperature range was broad. The study on calix[4]arene with azobenzene group at lower rim is seldom reported. Rojanathanes et al. [13] synthesized calixcrown ethers modified by azobenzene group, which showed complexation of sodium and potassium ions presumably as the participation of the nitrogen atom of the diazo group in coordination with these ions. This complexation induced a thermal equilibrium shift between *cis*- and *trans*- isomers of the azobenzenes, which will led to the design and synthesis of new photo switchable ionophores. Matsuzawa et al. [14] fabricated molecular ultra-thin film of nematic liquid crystals, while calix[4]resorcinarene could incorporate liquid crystalline azobenzene in the hydrophobic cavity of long alkyl chain. The azobenzene molecule oriented perpendicular to a water surface for the hybrid molecule floating film.

In this paper, the reaction of 4′-hydroxy-4-methyl azobenzene (**1**) and 1,6-dibromohexane afforded 6-bromo-1-((4-((4-methylphenyl)azo)phenyl)oxy)hexane (**2**), which further reacted with *p*-tert-butylcalix[4]arene to give calix[4]arene derivative (**3**) of which lower rim had been modified by azobenzene photochromic group. The synthesis route is shown as follows (Scheme 1). The fluorescent properties and liquid crystalline behavior of the compounds were compared and studied by fluorescence spectrometer, polarized microscopy (POM), and differential scan calorimeter (DSC).

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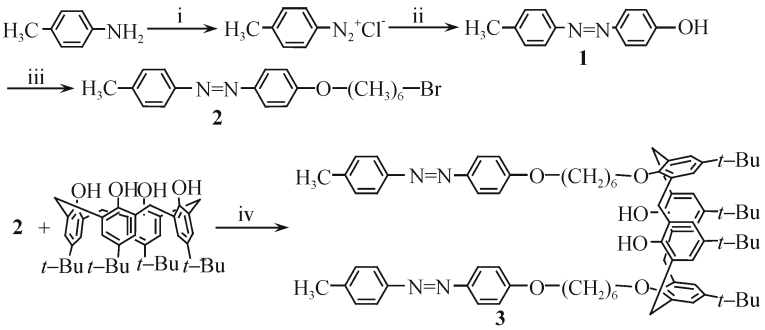

Reagents and conditions: (i) $NaNO_2$, 3 equiv.HCl, 0~5℃; (ii) C_6H_5OH,NaOH,0~5℃; (iii) $Br(CH_2)_6Br$, K_2CO_3,acetone, refux; (iv) K_2CO_3,acetone,reflux

Scheme 1 Route of the synthesis

2 Experimental

2.1 Instruments and reagents

^{1}H-NMR spectra were recorded at 298 K in $CDCl_3$ at 300 MHz on a Varian Mercury-VX300 spectrometer. The chemical shifts were recorded in parts per million (ppm) with tetramethyl silane (TMS) as the internal reference. Electrospray ionization (ESI) mass spectra (MS) were determined using Finnigan LCQ Advantage mass spectrometer (capillary column temperature 200°C, spray voltage 400V, anodic ionization mode). Fluorescence spectra were obtained on a Shimadzu RF-5301PC SHIMADZU spectrometer. DSC curves were carried out with a Perkin Elmer Diamond differential scan calorimeter (both the rates of heating and cooling course were 5°C/min). The liquid crystalline behavior was studied by OLYMPUS BX51. The melting points (uncorrected) were obtained from a Reichert 7905 microscopic melting point detector.

p-tert-Butylcalix[4]arene was prepared according to the literature [15] procedures. Solvents were dried and distilled before use. Other chemicals were analytical grade and used without further purification.

2.2 Synthesis

4′-hydroxy-4-methyl azobenzene (1) [16]. A solution of sodium nitrite (1.38 g, 0.02 mol) was added dropwise to *p*-methyl aniline (2.14 g, 0.02 mol) in 3 mol/L HCl, with the temperature kept at 0°C. After stirring for 15 min, sodium phenol (1.88 g, 0.02 mol) was added dropwise to the yellow solution. After stirring for another 15 min, the solvent was then removed by filtration and washed with water to weak acid. Recrystallization of the resulting crude product from ethanol/water (1:2) gave the title compound as a yellow solid (3.3 g, 78.1%).

6-bromo-1-((4-((4-methylphenyl)azo)phenyl)oxy)hexane (2) [15]. **1** (2.0 g, 4.38 mmol), 1.6-dibromohexylene (6.8 g, 0.028 mol) and K_2CO_3 (3.0 g, 0.01 mol) in acetone (50 mL) were heated at reflux for 24 h. The solvent was removed by evaporation. Then petroleum ether was added to gain the precipitate. The crude product was separated through column chromatography (chloroform as eluent solvent) to give the desired compound as a yellow solid (1.3 g, 78.9%).

Calix[4]arene derivative (3). *p-tert*-Butylcalix[4]arene (0.56 g, 0.75 mmol), compound **2** (0.80 g, 2.0 mmol) and K_2CO_3 (0.22 g, 1.6 mmol) in acetonitrile (50 mL) were reacted at refluxing temperature until raw material disappearance as detected by thin layer chromatography. After the evaporation of the solvent, the residue was extracted with CH_2Cl_2 (30 mL), washed with HCl (30 mL, 10%), H_2O (50 mL), and dried by anhydrous $MgSO_4$. The filtrate was concentrated to a light yellow powder. The resulting residue was subjected to column chromatography on silica gel to give **3** (0.67 g, 68.3%).

3 Results and discussion

3.1 Structure characterization and reaction study

The structures of three compounds were characterized by ^{1}H-NMR and ESI-MS. The analysis data gathered are shown in Table 1.

There was m/z = 1 238 $[M+1]^+$ peak in the mass spectrum of calixarene derivative **3**, which showed that compound **3** may be bisubstituted calixarene. The typical 1:1 singlets for *tert*-butyl and aromatic protons were both observed in ^{1}H-NMR spectrum, indicating that the structure of compound **3** was highly symmetrical. The cone conformation of compound **3** was deduced according to a pair of doublets for methylene and one singlet for hydroxyl in ^{1}H-NMR spectrum. All proved **3** was a 1,3-bisubstitute calixarene derivative.

The main product afforded by the reaction of *p-tert*-butylcalix[4]arene and 6-bromo-1-((4-((4-methylphenyl)azo) phenyl)oxy)hexane was still compound **3**, even four equiv. of **2** has been added.

3.2 Fluorescent properties

The solutions of compounds **1**, **2**, and **3** was confected at different concentrations using methanol and tetrahydrofuran

Table 1 ^{1}H-NMR, ESI-MS results of compound 1, 2, 3

Compound	Yield/%	mp/°C	^{1}H-NMR, ppm and ESI-MS
1	78.1	151–152	2.43 (s, CH_3, 3H), 6.95 (d, J = 8.7 Hz, ArH, 2H), 6.96 (overlapped, OH, 1H), 7.30 (d, J = 8.1 Hz, ArH, 2H), 7.80 (d, J = 8.4 Hz, ArH, 2H), 7.87 (d, J = 8.7 Hz, ArH, 2H).
2	78.9	100–101	1.86 (m, (CH_2)$_4$CH$_2$Br, 8H), 2.41 (s, CH_3, 3H), 3.43 (t, J = 6.6 Hz, CH_2Br, 2H), 4.04 (t, J = 5.8 Hz, OCH_2, 2H), 6.98 (d, J = 7.5 Hz, ArH, 2H), 7.28 (d, J = 7.5 Hz, ArH, 2H), 7.81 (d, J = 7.5 Hz, ArH, 2H), 7.93 (d, J = 7.5 Hz, ArH, 2H).
3	68.3	206–208	0.98 (s, C(CH_3), 18H), 1.28 (s, C(CH_3), 18H), 1.85 (m, (CH_2)$_4$, 16H), 2.42 (s, CH_3, 6H), 3.32 (d, J = 12.6 Hz, ArCH_2Ar, 4H), 3.99 (t, J = 7.5 Hz, CH_2O, 4H), 4.05 (t, J = 6.6 Hz, CH_2O, 4H), 4.29 (d, J = 12.6 Hz, ArCH_2Ar, 8H), 6.83 (s, ArH, 4H), 6.95 (d, J = 7.5 Hz, ArH, 4H), 7.05(s, ArH, 4H), 7.27 (d, J = 7.5 Hz, ArH, 4H), 7.74 (s, OH, 2H), 7.80 (d, J = 7.5 Hz, ArH, 4H), 7.86 (d, J = 7.5 Hz, ArH, 4H); ESI-MS: m/z = 1237.6[M + 1]$^+$.

(V:V = 15:1) as solvent. The fluorescence spectrum of compounds **1**, **2**, and **3** at different concentrations were obtained at the optimum excitation wavelength of 307 nm. Figure 1 is the plot of fluorescence intensity at different concentrations of the azobenzene photochromic group. When the azobenzene group concentration was in the range of 1.6×10^{-5} to 8.0×10^{-4} mol/L, the fluorescence intensities of compounds **1** and **2** were nearly the same at the same azobenzene group concentration. However, the fluorescence intensity of compound **3** was two to four times higher than that of compounds **1** and **2**, indicating that the fluorescence quantum yield of the azobenzene group had been improved through being attached to the calix[4]arene skeleton. The possible cause was that the molecular size of compound **3** was bigger than **1** and **2**, and the fluorescence intensity had been improved due to the decrease of the collision probability.

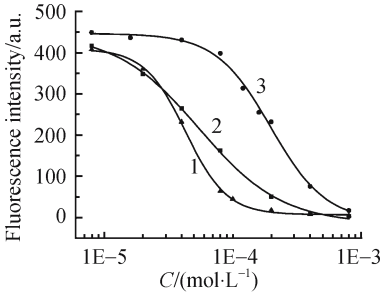

Fig. 1 Fluorescence intensity of compounds 1,2,3 at different concentration

The fluorescence intensities of the three compounds were low and approached zero when the azobenzene group concentration was higher than 8.0×10^{-4} mol/L. The molecule collision probability increased and the molecules showed strong fluorescence quenching at the high concentration. There was no distinct difference.

3.3 Liquid crystal behavior

Figure 2 was the DSC curve of compounds **1**, **2**, and **3**. The textile structure observed by POM is shown in Fig. 3. The heating and cooling curve of compound **1** both showed one peak, indicating no liquid crystal occurring in the heating and cooling courses. The phase of compound **1** transformed from solid to isotropy at 151.3°C in the heating course. The peak in the cooling course at 126.2°C was attributed to crystal peak. The melting peak at 101.6°C appeared in the heating DSC curve of compound **2**, as one bigger endothermic peak and one little shoulder peak at 87.4°C, 84.2°C appeared in the cooling curve. We observed the phase change by POM and found that the size of some regular spherocrystal grew bigger and bigger and finally assembled to cracked focal conic texture in the cooling course (see Fig. 3(a)). Compound **2** was the typical characteristic of smectic phase. Compound **3** had a high phase change temperature and heat stabilization, different from compound **2**. There was one bigger endothermic peak and one little peak at 209.4°C and 219.5°C, respectively, appearing in the heating DSC curve. We observed the mosaic structure in the temperature range by POM. Even the transconformation of the azobenzene group was mesomorphic, so the azobenzene of compound **3** was in the trans conformation. The two side-group of calixarene affected each other more strongly and the azobenzene unit arranged more orderly because the azobenzene group had been anchored to calixarene. Calixarene played an important role in fixing liquid crystal unit conformation and the formation of the high temperature liquid crystal phase. More attention would be drawn to the development of azobenzene optics devices with the application of azobenzene groups to modify calixarene.

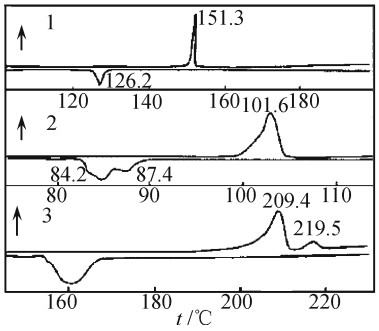

Fig. 2 The DSC curves of compounds **1**,**2**,**3**

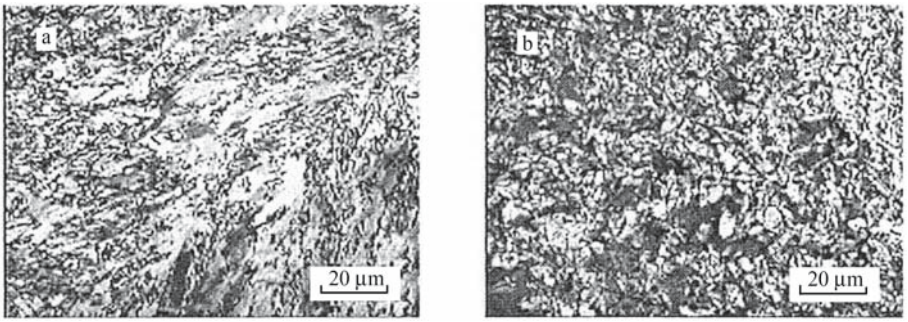

Fig. 3 The POM images of the liquid crystalline phase
(a) compound **2** at 84. 7°C in cooling process; (b) compound **3** at 215. 0°C in heating process

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