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Full Paper

Crystal Structures of Two Calix[4]arene Isomers with Benzaldehyde Moiety and Their Photophysical Properties with Terbium(III) Ions

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Two calix[4]arene isomers with benzaldehyde moieties, *i.e.*, 5,11,17,23-tetra-*tert*-butyl-25,27-bis[2-(*o*-formylphenoxy)ethoxy]-26,28-dihydroxycalix[4]arene (**3**) and 5,11,17,23-tetra-*tert*-butyl-25,27-bis[2-(*p*-formylphenoxy)-ethoxy]-26,28-dihydroxycalix[4]arene (**4**), were synthesized according to a newly designed route in high yields, and their crystal structures have been determined by X-ray crystallographic study. The photophysical behavior on complexation of calix[4]arene derivatives **3** and **4** with terbium(III) nitrate was investigated in anhydrous acetonitrile at 25 ℃ by UV-Vis and fluorescence spectroscopies. The crystallographic structure of **3** indicated that the eight oxygen atoms formed a preorganized ionophoric cavity due to intramolecular π-π stacking, which could encapsulate lanthanide ions tightly. In sharp contrast, the compound **4** formed a linear array by intermolecular π-π stacking, hence the oxygen atoms of pendant arms could not coordinate with metal ions, giving a poor binding ability to Tb^{3+}. The absorption spectra of **3** with Tb^{3+} showed clearly a new broad intense absorption at 385 nm. Interestingly, the narrow emission line spectrum has also been observed for compound **3** with Tb^{3+}, and the results obtained were discussed from the viewpoint of energy transfer mechanism between host structures and the properties of lanthanide ions.

Keywords　calix[4]arene derivative, crystal structure, photophysical property, synthesis

Introduction

Calixarenes have been taken as a family of receptors to bind selectively the inorganic/organic ions or molecules forming the host-guest complexes, which have been applied successfully to separation science and technology.[1-5] Therefore, a great deal of effort has been devoted to design and synthesize novel calixarene receptors in order to exploit their application to the fields of recognition,[6] catalysis[7] and assembly.[8] One of the popular interests was focused on the sensitized luminescence with lanthanide ion complexes with the calixarene derivatives because of their potential application as probe and label to the sophisticated biological system.[9] Recently, we have reported the spectroscopic behavior on the resulting complex of calixarene derivatives with lanthanide nitrates in acetonitrile solution.[10] In order to further understand the relationship between structure and photophysical property, we herein report the crystal structures of two calix[4]arene isomers, and their photophysical behavior with lanthanides ions. It is our particular interest to investigate how the substituted difference on the modified side arms affects the conformational feature and assembly behavior of calixarene in the solid state and the luminescence behavior with Tb^{3+} in solution.

Experimental

Apparatus

The melting points were measured by an XT-4 apparatus without correction. ^1H NMR spectrum was recorded on a Varian INVOA 300 spectrometer in $CDCl_3$, using tetramethylsilane as an internal reference. Elemental analysis was performed on a Perkin-Elmer 2400C instrument. UV-Vis spectra were recorded in a conventional quartz cell (10 mm×10 mm×45 mm) at 25 ℃ on a Shimadzu UV-2401 PC spectrometer. The fluorescence spectrum was performed on a JASCO FP-750 spectrofluorimeter.

Materials

Starting materials were commercially available unless otherwise noted. The 5,11,17,23-tetra-*tert*-butyl-25,27-bis(2-bromoethoxy)-26,28-dihydroxycalix[4]arene (**2**) was synthesized according to the literature procedures.[11]

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General synthetic procedures

A sample of 5,11,17,23-tetra-*tert*-butyl-25,27-bis(2-bromoethoxy)-26,28-dihydroxycalix[4]arene (3 g, 3.48 mmol) was added to the corresponding aldehyde (1.5 g, 1.7 mmol) in the presence of anhydrous K_2CO_3 in CH_3CN solution with stirring for 30 h under N_2. After cooling, the precipitate was filtered. The filtrate was evaporated under reduced pressure to give light yellow solid, which was recrystallized from CH_2Cl_2/CH_3OH to afford pure product in high yield (Scheme 1).

5,11,17,23-Tetra-*tert*-butyl-25,27-bis[2-(*o*-formylphenoxy)ethoxy]-26,28-dihydroxycalix[4]arene (3): Yield: 87%. m.p. 278—280 ℃; ^{1}H NMR ($CDCl_3$) δ: 1.01 (s, 18H, CH_3), 1.25 (s, 18H, CH_3), 3.31 (d, J=12 Hz, 4H, $ArCH_2Ar$), 4.30 (d, J=12 Hz, 4H, $ArCH_2Ar$), 4.38 (t, J=6 Hz, 4H, OCH_2CH_2), 4.43 (t, J=6 Hz, 4H, OCH_2CH_2), 6.87 (s, 4H, ArH), 6.97—7.05 (m, 8H, ArH), 7.51 (s, 2H, OH), 7.56—7.58 (m, 2H, ArH), 7.83 (d, J=6 Hz, 2H, ArH), 10.50 (s, 2H, CHO).[12] Anal. calcd for $C_{62}H_{72}O_8$: C 78.78, H 7.68; found C 78.56, H 7.42.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis[2-(*p*-formylphenoxy)ethoxy]-26,28-dihydroxycalix[4]arene (4): Yield: 85%. m.p. 203—206 ℃; ^{1}H NMR ($CDCl_3$) δ: 1.04 (s, 18H, CH_3), 1.27 (s, 18H, CH_3), 3.32 (d, J=12 Hz, 4H, $ArCH_2Ar$), 4.32 (d, J=12 Hz, 4H, $ArCH_2Ar$), 4.37 (t, J=6 Hz, 4H, OCH_2CH_2), 4.46 (t, J=6 Hz, 4H, OCH_2CH_2), 6.90 (s, 4H, ArH), 7.00—7.06 (m, 8H, ArH), 7.47 (s, 2H, OH), 7.80—7.83 (m, 4H, ArH), 9.89 (s, 2H, CHO).[13] Anal. calcd for $C_{62}H_{72}O_8$: C 78.78, H 7.68; found C 78.66, H 7.47.

X-ray diffraction analysis

Crystals of **3** and **4** suitable for X-ray diffraction crystallography analysis were grown by slow diffusion between CH_3OH and CH_2Cl_2 mixture. X-ray crystallographic data were obtained on a Siemens SMART CCD area detector. Structures were solved with the SHELXS-97 software. Crystal data collection and refinement parameters are listed in Table 1.

Scheme 1

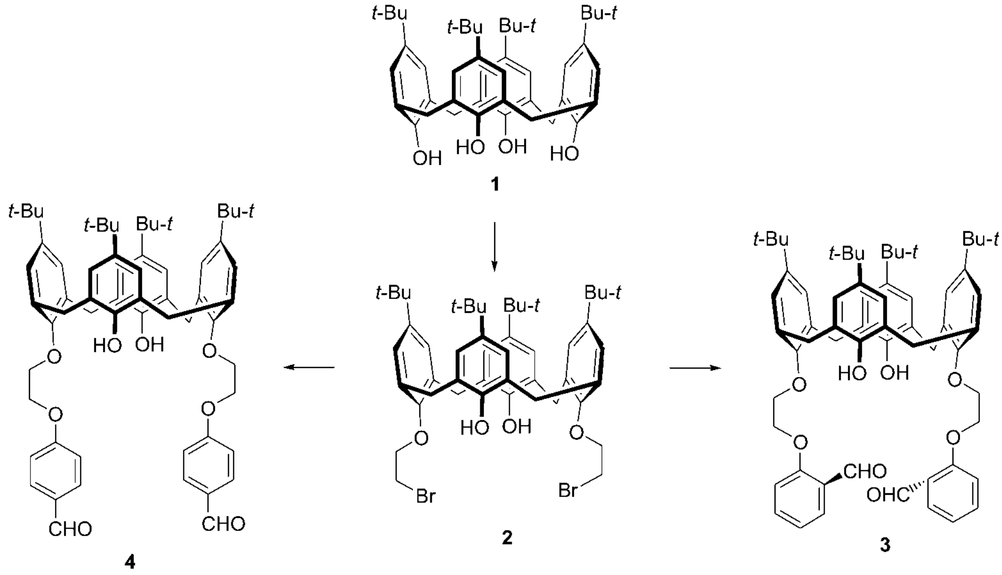

Table 1 Data collection and processing parameters for compounds **3** and **4**

	3	**4**
Empirical formula	$C_{62}H_{72}O_8$•CH_2Cl_2	$C_{62}H_{72}O_8$•CH_3OH
Formula weight	1028.11	977.24
Temperature/K	293(2)	293(2)
Wavelength/nm	0.071073	0.071073
Crystal system, space group	Monoclinic, *P*2(1)/*c*	Triclinic, *P*-1
Unit cell dimension	a=2.2491(9) nm	a=1.1561(5) nm
	b=2.0145(7) nm	b=1.2679(6) nm
	c=1.3541(5) nm	c=2.1317(9) nm
	α=90°	α=83.381(9)°
	β=98.647(8)°	β=85.846(8)°
	γ=90°	γ=69.361(8)°
Volume	6.066(4) nm^3	2.903(2) nm^3
Z, Calculated density	4, 1.126 Mg/m^3	2, 1.118 Mg/m^3
F(000)	2192	1052

Continued

	3	**4**
Crystal size	0.35 mm×0.30 mm×0.30 mm	0.35 mm×0.25 mm×0.15 mm
Reflections collected/unique	23851/10442 R(int)$=$0.1442	12081/10200 R(int)$=$0.0276
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	10442/2/701	10200/0/649
Final R indices [$I>2\sigma(I)$]	$R_1=0.1042$, $wR_2=0.2505$	$R_1=0.0698$, $wR_2=0.1766$
R indices (all data)	$R_1=0.2964$, $wR_2=0.3609$	$R_1=0.1784$, $wR_2=0.2293$

Results and discussion

The compounds **3**[12] and **4**[13] were synthesized according to a new route in high yield and characterized by melting point, ^{1}H NMR, elemental analysis and crystal structure analysis. Vicens and Tuntulani reported respectively the synthesis of the compounds **3** and **4** by the reactions of *p-tert*-butylcalix[4]arene with **2** or 4-(2-bromoethoxy)benzaldehyde in 32% final yields. Herein, different route was adopted to prepare the compounds **3** and **4** in 51% final yields. In previous method, the nucleophilic reaction between the hydroxyl in *p-tert*-butylcalix[4]arene and the bromoethoxyl in **2** or 4-(2-bromoethoxy)benzaldehyde should form different products with ratio from 1∶1 to 1∶4, while the present condition did only 1∶2 product, resulting in the enhancement of the final yields.

π-π Stacking interaction

The compound **3** adopts distorted cone conformation (Figure 1a). This is revealed clearly by the angles between the planes through the four CH_2 carbon atoms linking the aromatic rings and the planes of the individual benzene ring: 64.9°, 55.6°, 50.5° and 62.5°. The centroid distance and interplanar angle between two aromatic rings with substituted arms are 0.398 nm and 16.4°, respectively. The intramolecular π-π stacking interaction close to two substituted side arms resulted in a calixcrown-like 3D cavity, which will accommodate with lanthanide ions to form complex. Differing from the compound **3**, the compound **4** adopts a more flat cone conformation (Figure 1b), and the angles between the reference plane and individual benzene ring are 97.7°, 37.4°, 47.4° and 81.8°, respectively. Two substituted aromatic rings of calix[4]arene skeleton become more tilted, leading to the benzaldehyde moieties to extend to the outside of calixarene framework to form intermolecular π-π stacking to aggregate a linear array (Figure 2). The centroid distance and interplanar angle

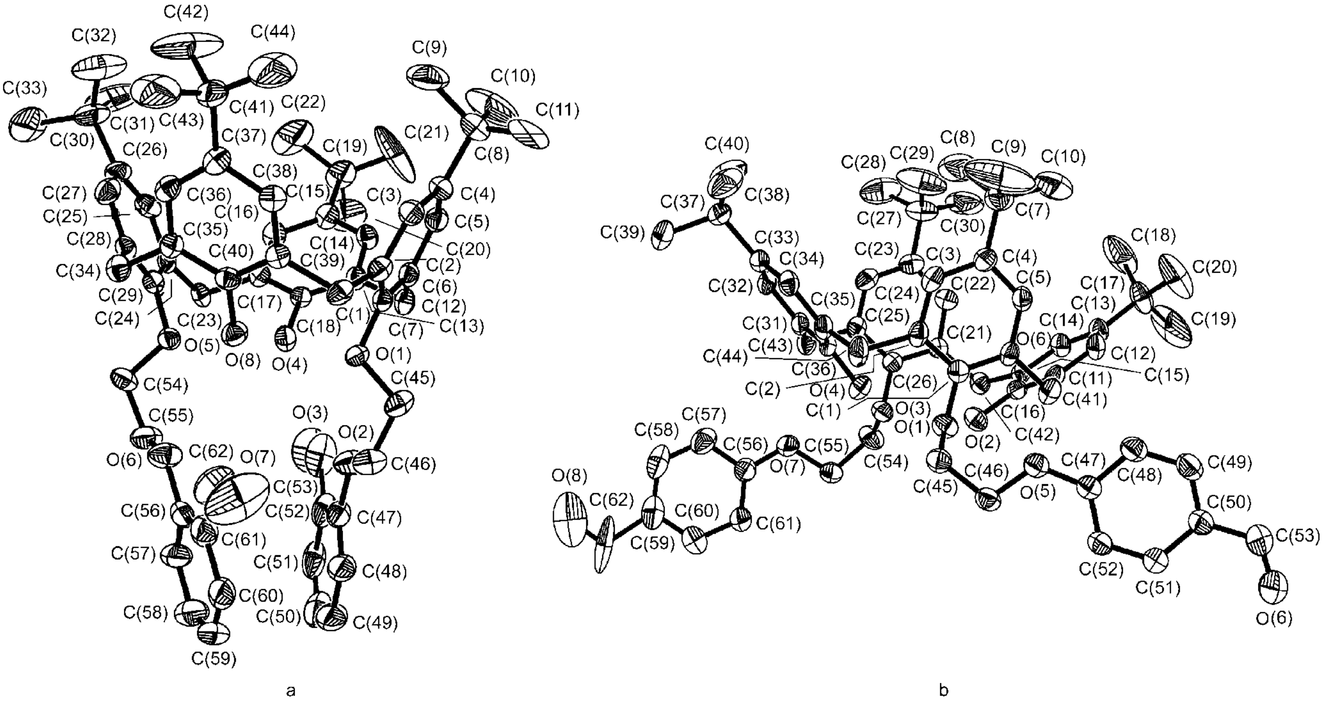

Figure 1 ORTEP representation of the molecular structures of **3** (a) and **4** (b). Hydrogen atoms and solvent molecules are omitted for clarity.

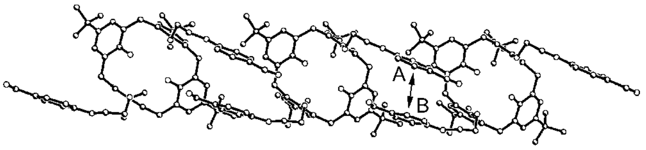

Figure 2 1D supramolecular architecture of **4** by intermolecular π-π stacking interactions.

between two benzaldehyde moieties A and B attributed to different molecules are 0.425 nm and 18.9°, respectively.

UV-Vis adsorption spectra

The adsorption spectrum of compound **3** shows two peaks at 286 and 315 nm, respectively. When terbium(III) nitrate was added into the compound **3** solution, not only the two maximum adsorption peaks of **3** were slightly red shifted and the corresponding adsorption intensity was decreased, but also a new adsorption peak appeared at 385 nm, as illustrated in Figure 3. The new adsorption band could be probably ascribed to the metal to ligand charge transfer (MLCT) between calixarenes and terbium(III) ions. However, with adding of Tb^{3+} to the compound **4** solution, no significant spectral change was observed, indicating that **4** could not form stable complex with the lanthanide ion.

Fluorescence spectra

As can been seen from Figure 4, the emission spectra for compound **3** with Tb^{3+} are composed of 490 ($^5D_4 \rightarrow {}^7F_6$), 546 ($^5D_4 \rightarrow {}^7F_5$), 582 ($^5D_4 \rightarrow {}^7F_4$) and 616 nm ($^5D_4 \rightarrow {}^7F_3$) at the maximum excitation of 280 nm. Taking the energy level of Tb^{3+} and phenol into account,[14,15] the triplet energy level of phenol units is high enough to transfer the energy to $^5D_4$ level of Tb^{3+}, making the emission of Tb^{3+} possible. For **3**, 3D pseudo cavity constructed by eight oxygen atoms could coordinate tightly with the Tb^{3+}, consequently prohibiting the photoinduced electron transfer (PET) between terbium(III) ions and solvent molecules, and thus making the narrow emission line spectrum be observed. For **4**, no significant sharp emission bands were observed, which could be ascribed to the poor coordination ability of **4** with Tb^{3+}.

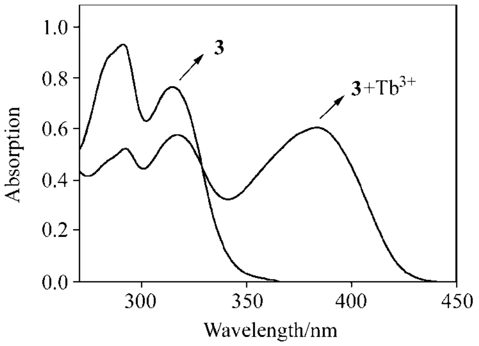

Figure 3 UV-Vis absorption of compound **3** and its complex with Tb^{3+}.

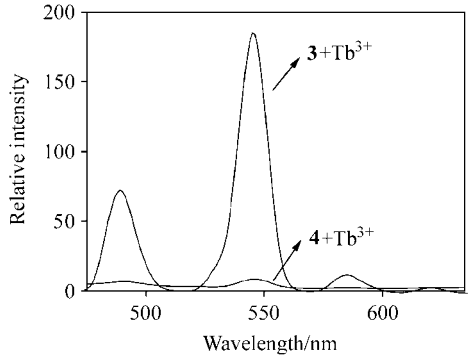

Figure 4 Fluorescence emission spectra of **3**-Tb^{3+} and **4**-Tb^{3+} in anhydrous acetonitrile solution, $\lambda_{ex}=280$ nm.

Conclusion

Two distinct crystal structures possessing monoclinic system $P2(1)/c$ for **3** and triclinic system P-1 for **4** have been obtained by two calix[4]arene isomers, respectively. The crystallographic studies show that the compounds **3** and **4**, possessing subtly different group substituted, revealed different stacking mode in solid state by intramolecular or intermolecular π-π interaction, and then displayed different ion binding ability and photophysical behaviors. The compound **3** with an induced pseudo cavity by intramolecular π-π stacking interaction could effectively coordinate with Tb^{3+}. The present results not only showed the coordination property of calixarene derivatives with rare earth ions but also were served to design and synthesize new calixarene derivatives possessing the stronger sensitizing ability toward rare earth ions.

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