Journal of Inclusion Phenomena and Macrocyclic Chemistry (2007) 58:63–69
DOI 10.1007/s10847-006-9120-3

Interaction of Cucurbit[n = 6∼8]urils and Benzimidazole Derivatives

JUN-YING GE[1], SAI-FENG XUE[2,*], QIAN-JIANG ZHU[2], ZHU TAO[2] and JIAN-XIN ZHANG[3]

[1]*Department of Chemistry and Engineering, Weifang Education College QingZhou, Shandong, 262500, Peoples Republic of China;* [2]*Institute of Applied Chemistry, Guizhou University, Guiyang, 550025, Peoples Republic of China;* [3]*Key Laboratory of Chemistry for Natural Products of Guizhou Province, Guiyang, 550002, Peoples Republic of China*

(Received: 23 February 2006; in final form: 2 May 2006)

Key words: cucurbit[n = 6∼8]urils, benzimidazole derivatives, host–guest, ^{1}H NMR spectroscopy, electronic absorption spectroscopy, fluorescence spectroscopy

Abstract

The structures and optical properties of host–guest complexes produced from cucurbit[n = 6–8]urils and some benzimidazole derivatives have been investigated by ^{1}H NMR spectroscopy, electronic absorption spectroscopy and fluorescence spectroscopy. The experimental results reveal that calculations of $A\sim N_{Q[n]}/N_{guest}$ and $I_f\sim N_{Q[n]}/N_{guest}$ for the same association complex both support a good fit to an identical binding model. In particular, the $A\sim N_{Q[n]}/N_{guest}$, $I_f\sim N_{Q[n]}/N_{guest}$ calculations and the ^{1}H NMR determinations for three Q[6]–ge(1∼3) complexes and three Q[8]–ge(1∼3) complexes all support a binding model of 1:1 and 1:2 respectively.

Introduction

Similar to the well known macrocyclic host compounds, such as crown ethers, cyclodextrins and so on, the cucurbit[n]urils homologues display remarkable affinity and selectivity due to the rigid macrocyclic structure with a unique cavity, rimmed by carbonyl oxygens. Cucurbit[6]uril (Q[6]), the first member of cucurbit[n]-urils family was reported by Behrend in 1905 [1] and its structure was determinated by Mock and co-workers in 1981 [2], and a series of cucurbit[n]urils homologues, such as Cucurbit[5]uril (Q[5]), Cucurbit[7]uril (Q[7]), Cucurbit[8]uril (Q[8]) and Cucurbit[10]uril (Q[10]) as its CB[10]@CB[5] inclusion complex was reported two decades later by Day and Kim respectively [3–5]. These new members of the Qs family display a range of novel properties and applications [6], including gas encapsulation of Q[5] [7], interaction of Q[7] with some small cage compounds [8], viologen and its derivatives [9], and of particular interest the ability of Q[8] to simultaneously bind two aromatic guests [10].

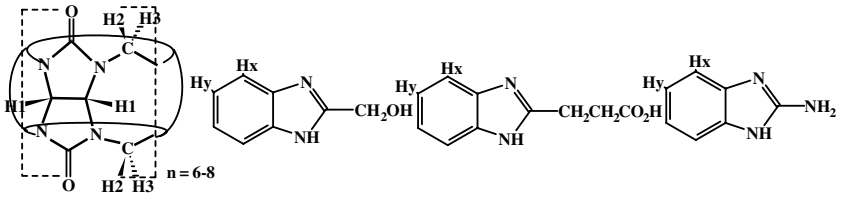
Recently, we studied the interaction between Cucurbit[n = 6∼8]urils with some guests with two moietis, a moiety could be five member ring, such as thiophen, pyrrole and furan ring, or six member ring, such as pyridine or benzyl, another moiety is adamantine, ingress and egress of the moiety of the guests is controlled by the size of the carbonyl portal of the different Qs, for example, Q[6] include selectively the aromatic ring moiety, and Q[7] or Q[8] include selectively the adamantine moiety [11]. Kaifer and co-workers studied the interaction between Q[7] and Viologen derivatives with the aliphatic substituents, their experimental results reveal that Q[7] include selectively the viologen nucleus of the viologen derivative having identical aliphatic substituents with chains shorter than three carbon atoms, while Q[7] includes selectively the aliphatic substituents with chains longer than four carbon atoms [9].

In this paper, we report the interaction and formation of host–guest complexes between Q[6∼8] with some HCl salt of benzimidazole derivatives, which are 2-benzimidazolemethanol·HCl (ge1), 2-benzimidazolepropionic acid·HCl (ge2) and 2-aminobenzimidazole·HCl (ge3) (Figure 1). It demonstrates not only 1:1 interaction model, such as the interaction of Q[6] or Q[7] and the guests, but also 1:2 interaction model, such as the interaction of Q[8] and the guests. Nevertheless, the interaction between Q[6] with ge2 or ge3 extends the binding model examples in which the binding site could be the phenyl moiety or the aliphatic chains shorter than three carbon atoms of ge2 or ge3.

Experimental

2-benzimidazolemethanol (ge1'), 2-benzimidazolepropionic acid (ge2') and 2-aminobenzimidazole (ge3') were obtained from Aldrich and used without further purification. Cucurbit [n = 6∼8]urils were prepared and purified according to the method developed in our laboratories [12].

* Author for correspondence. E-mail: gzutao@263.net



Q[n] ge1' ge2' ge3'

Figure 1. Structures of cucurbiturils and the related guests.

The corresponding HCl salts ge1, ge2 and ge3 were prepared by dissolving the benzimidazole derivatives in 5 M HCl followed by crystallization with ethanol or acetone, collecting them by filtration and drying.

For the study of host–guest complexation of Q[*n*] and the title guests respectively, $2.0\sim2.5 \times 10^{-3}$ mmol samples of Q[*n*] in 0.5∼0.7 g D_2O with [guest]/[Q[*n*]] ranging between 1 and 100 were prepared. The ^{1}H NMR spectra were recorded at 20 °C on a VARIAN INOVA-400 spectrometer.

Absorption spectra of the host-guest complexes were recorded on a Aglient 8453 Photospectrameter and flurorescence spectra of the host-guest complexes were recorded on a RF-540 Photofluorescent spectrometer (Hitachi Japan) at room temperature. Experimental method: The aqueous solutions of the HCl salts of the title benzimidazole derivatives were prepared with a concentrations of 4.0×10^{-4} mol L^{-1} (for absorption spectra), 2.00×10^{-5} mol L^{-1}(for flurorescence spectra). Samples of these solutions were combined with Q[8] to give solutions with a guest:Q[8] ratio of 0, 8:1, 4:1, 2:1, 1:1 and 1:2 and so on.

Results and discussion

It is common that each member in the Qs family has a cavity and two carbonylfringed portals, the cavity comprises a deshielding region, in which protons of a bound guest experience an upfield shift; the portals comprise a deshielding region, where protons of a bound guest could experience an downfield shift [6, 13]. Thus, ^{1}H NMR technique can be used to investigate the interaction between Qs and guest base on the change of chemical shift of the relative components. In addition, the bonding in the cavity or at the portals of a Q, electronic absorption or fluorescent response of a guest could be dramatically changed, so that we can demonstrate that the benzimidazole derivatives engage in both cavity and portal binding which was detected by both electronic absorption spectroscopy and fluorescence spectroscopy.

^{1}H NMR spectra analysis on the interaction between Q[6] with ge1, ge2, ge3 respectively

A obvious binding interaction between Q[6] and the guests of ge1, ge2 or ge3 are shown in the corresponding ^{1}H NMR spectra (Figure 2).

Comparing to the free guest, one set of the phenyl moiety of each bound guest in three host–guest systems Q[6]–ge1, Q[6]–ge2 and Q[6]–ge3 entries a shielding region, and the protons (Hx and Hy) on the phenyl experience an upfield shift by 0.6 ∼ 0.8 ppm, it indicates that these protons are in the cavity of Q[6]. A downfield shifts by 0.1 ∼ 0.35 ppm for the methylene protons of ge1 or ge2 is also observed. This indicates that these protons are at the portal in the deshielding zone of the carbonyls. It suggests that the phenyl moiety of the bound guest in each of interaction systems is contained within the cavity and that the substitute group, such as –CH_2OH, –$CH_2CHCOOH$ and –NH_2 is contained within the portal of Q[6]. Additional supporting evidence for this asymmetric structure is the two sets of equally intense doublets for the correlated methylene protons, and one singlet for the methine protons of Q[6]. This indicates that the guest affects each of the portals differently, with the guest HCl salt protruding from only one portal. A comparison of the integrals of the protons of the bound ge1 with the protons of Q[6] revealed the complex to be an asymmetric model with a ratio of 1:1 Q[6]:ge1(referring to the model-a in Figure 2).

On the other hand, another set of the phenyl moiety in the ^{1}H NMR spectra of Q[6]–ge2 and Q[6]–ge3 seems to stay at the portal in the deshielding zone of the carbonyls, the protons (Hx and Hy) on the phenyl experience an downfield shift by 0.1 ∼ 0.2 ppm, it indicates that these protons in are the cavity of Q[6], however, the methylene protons of ge2 experience an upfield shift by 0.2 ∼ 1.2 ppm, a significant shift of the –CH_2CH_2COOH group indicates deep cavity binding. Thus, the substitute group of ge2 or ge3 is contained within the cavity and the phenyl moiety of the bound guest is contained within the portal of Q[6] (referring to the model-b in Figure 2).

Above experimental results indicate that two inclusion complex isomers form in the Q[6]–ge2 and Q[6]–ge3 systems, all models in slow exchange give distinct set of peaks. According to the integrals of the bound guest protons, the two isomers are formed in a ratio of 2:1 for Q[6]–ge2 system and 1:1 for Q[6]–ge3 system.

^{1}H NMR spectra analysis on the interaction between Q[7] with ge1, ge2, ge3 respectively

It is common that only one set of signals of the guest is observed in the ^{1}H NMR spectra of the Q[7]–guest systems in this work, it implies that the exchange between the bound guest and the free guest is fast on the NMR time scale. Thus, ^{1}H NMR titration method is

used to obtain information of interaction between Q[7] and the title guests. Figure 3 shows the selective ^{1}H NMR titration spectra of ge2 in D_2O recorded with increasing equiv of Q[7] (from top to bottom), a graduate upfield displacement of the aromatic protons of the guest, while a graduate downfield displacement of the aliphatic protons of the ge2 were observed upon Q[7] addition. Comparing to the Hx and Hy protons of the free ge2, the Hx and Hy protons of the bound ge2 shift to chemical shift values overlapping each other upon addition of 0.7 equiv of Q[7], and then the Hx and Hy protons swap the resonance position with the further Q[7] addition. On the other hand, the protons of aliphatic group $-CH_2CH_2COOH$ shift $0.25 \sim 0.35$ ppm downfield.

The insert in Figure 3 shows the curves of $\delta_{Hx} \sim N_{ge(1\sim3)}/N_{Q[7]}$ for the three host–guest systems. The chemical shift of the Hx aromatic proton for the three bound guests vs. ratios of $N_{ge(1\sim3)}/N_{Q[7]}$ data can be fitted close to a 1:1 binding model. Herein: δ_{Hx} presents the chmical shift of the corresponding proton, $N_{ge(1\sim3)}/N_{Q[7]}$ presents the mole ratio of the guest vs. the host Q[7].

^{1}H NMR spectra analysis on the interaction between Q[8] with ge1, ge2, ge3 respectively

Figure 4 shows the ^{1}H NMR spectra of ge2 in the absence (top) and in the presence (bottom) of 2 equiv of Q[8]. The most noticeable effect observed upon Q[8] addition is the significant upfield displacement of the Hx and Hy aromatic protons of the guest. The resonances of the Hx and Hy protons of the bound ge2 shifts to chemical shift values overlapping each other with a 1.4 and 1.2 ppm upfield shift respectively upon addition of 2 equiv of Q[8], while the protons of aliphatic group $-CH_2CH_2COOH$ shifted $0.1 \sim 0.2$ ppm downfield. A comparison of the integrals of the protons of the bound ge2 with the protons of Q[8] shows a ratio of 1:2, that is to say a Q[8] can includes two ge2 and form a complex with 1:2 of Q[8]:ge2. The consequence of a 1:2 complex could be a symmetric structure with part of the guest protruding from two portals respectively, hence the two sets of equally intense doublets for the methylene protons, and one singlet for the methine protons of Q[8] are observed (referring to the insert in Figure 4). Additional supporting evidence for the symmetric structure is the significant upfield shifts of the Hx and Hy aromatic protons comparing to the above Q[6]–guest systems, there is about 0.6 ppm gap which could be caused by the π–π stacking of the two aromatic rings included in the cavity of Q[8].

We also attempted to investigate interaction between Q[8] and the guest ge1 or ge3 by ^{1}H NMR technique, only resonance of free ge1 or ge3 was observed. To understand the poor solubility of the interacted product of Q[8] and the guest or no interaction between Q[8]

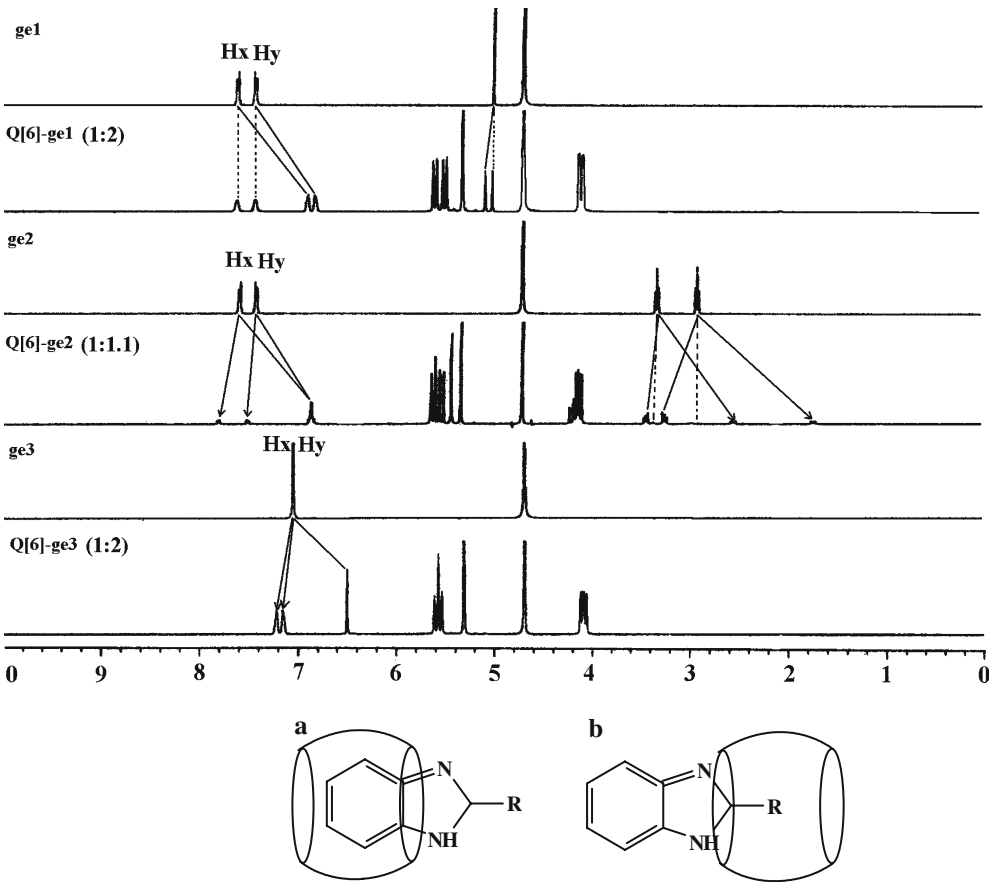


Figure 2. ^{1}H NMR spectra of Q[6]-ge(1∼3) system and possible interaction models.

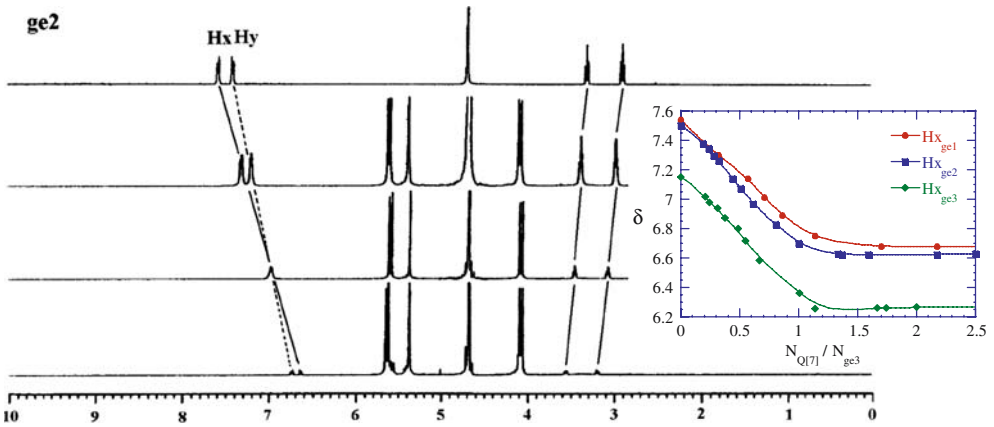


Figure 3. ^{1}H NMR spectra of titration expriment of [7]-ge2 system and δ_{Hx}–$N_{[7]}/N_{ge(1-3)}$ curves of the related protons in Q[7]-ge(1–3) systems.

with the guest at all, such an experiment was performed by gradually adding a solution of ge1 or ge3 in D_2O to a water soluble Q[8]–guest system, where the stability of the bound guest with Q[8] is not larger than that of Q[8]–ge1 or Q[8]–ge3, some useful details of the Q[8]–ge1 or Q[8]–ge3 systems could be concluded from the competitive interaction of Q[8] with the referred guest. In this work we selected Q[8]–N,N′-dimethyl-4,4′ (MV^{2+})/D_2O system as the water soluble Q[8]–guest system, the mixed solution become cloudy and large amount of precipitation was observed with increasing of ge1 or ge3. Figure 5, for example, shows the ^{1}H NMR titration spectra of Q[8]–MV^{2+} in D_2O recorded by adding ge1 gradually. It is noticeable that the resonances of Q[8] eliminate with increasing of ge1, while the ratios of Q[8]:MV^{2+} decrease from top to bottom, and a downfield displacement of the aromatic protons of the MV^{2+} is observed upon ge1 addition. However, the added ge1 is not observed until the signals of Q[8] disappear, and some excess ge1 shows up in the ^{1}H NMR spectrum (the bottom spectrum in Figure 5). It suggests that the guest ge1 or ge3 is bound by the host Q[8], and the formed complexes have a poor solubility.

The ^{1}H NMR spectroscopy revealed that Q[8] could bind ge1 or ge3, and formed a limited soluble complex, but it was hard to conclude the ratio of host and guest in the complex. To obtain information of interaction between Q[*n*] and the guest(s) electronic absorption and fluorescence spectra were recorded. Both of these techniques are applicable to low concentrations of Q[*n*] and guest complexes. (The information of interaction between Q[*n*] with the guest(s) could also be accomplished by absorption or fluorescence spectrophotometric measurements.)

In this work, it is common that the absorption bands of the guests in different systems exhibits progressively lower absorbance with a slight red shift as the ratio of $N_{Q[8]}/N_{MV^{2+}}$ is increased, and the hosts show no absorbance within the range of >210 nm. Figure 6a, b and c, for example, shows the UV spectra obtained with aqueous solutions containing a fixed concentration of the ge2 (24 mM) and variable concentrations of Q[6], Q[7] and Q[8] respectively. The absorbance (A) vs. ratios of mole of the host Q[6 or 8] and the gust ge2 ($N_{Q[n]}/N_{ge2}$) data can be fitted to a 1:1 binding model for the Q[6]–ge2 system at λ_{max} = 275 nm, 1:2 binding model for the Q[8]–ge2 system at λ_{max} = 275 nm, they are consistent with the experiment results from ^{1}H NMR technique (Figure 6d). However, The absorbance (A) vs. ratios of mole of the host Q[7] and the gust ge2 ($N_{Q[7]}/N_{ge2}$) data can be fitted to a ratio of 1.5:1 for the Q[7] with ge2 at λ_{max} = 275 nm, while the experiment results from ^{1}H NMR technique show a 1:1 binding model. A similar change of absorption bands and curve fit for the Q[*n*]–ge1 or Q[*n*]–ge3 series systems were oberseved (see the supporting information).

Comparing to the electronic absorption spectra, the fluorescence emission spectra of the guests are varied. The fluorescence spectra of ge1 and ge2 exhibited progressively higher spectra in intensity with a significant

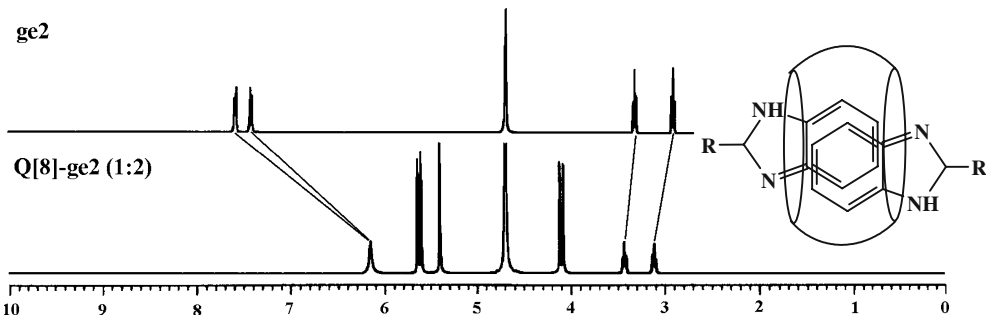


Figure 4. The ^{1}H NMR spectra of ge2 in the absence (top) and in the presence (bottom) of 2 equiv of Q[8], and the possible interaction model.

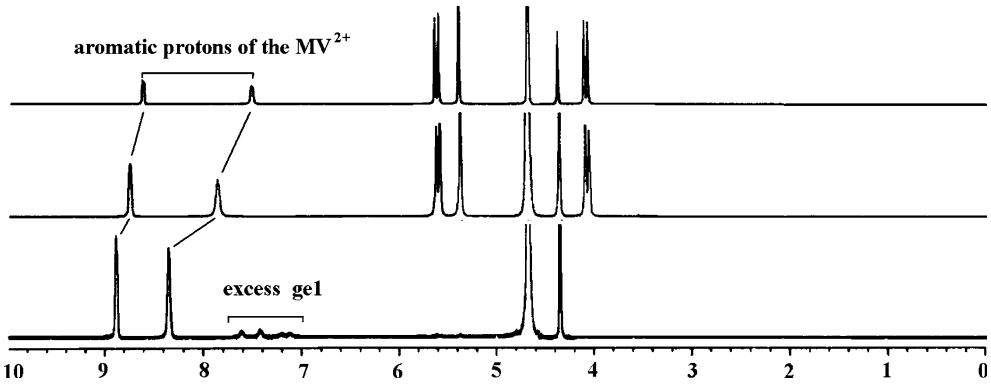


Figure 5. ^{1}H NMR spectra of titration experiments of [8]-dm44 and ge1 system, absorption spectrophotometric and fluorescence spectroscopy analysis on the interaction between Q[8] with ge1, ge2, ge3 respectively.

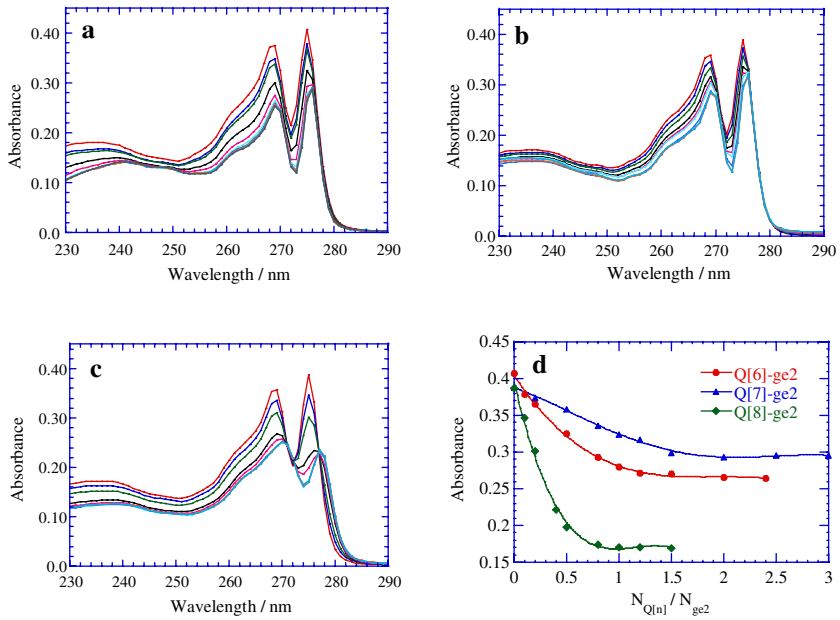


Figure 6. Electronic absorption spectrum of ge2 in the presence of increasing concentrations of Q[6], Q[7] or Q[8] respectively and corresponding $A \sim N_{Q[n]}/N_{ge2}$ curves at $\lambda_{max} = 275$ nm.

violet shift upon addition of Q[6] or Q[7] to the solution respectively, and one can see the sharp isosbestic point, which imply some formation of host–guest complex of ge1 or ge2 and Q[6] or Q[7]. However, the intense fluorescence spectra of ge1 and ge2 was depressed in the presence of Q[8], and the peak wavelengths of ge1 and ge2 were slightly violetshift. Moreover, the fluorescence of ge3 exhibited simply enhanced or quenched, and the peak wavelengths for ge3 were nearly invariable upon Q[*n*] addtion. For example, a significant fluorescence

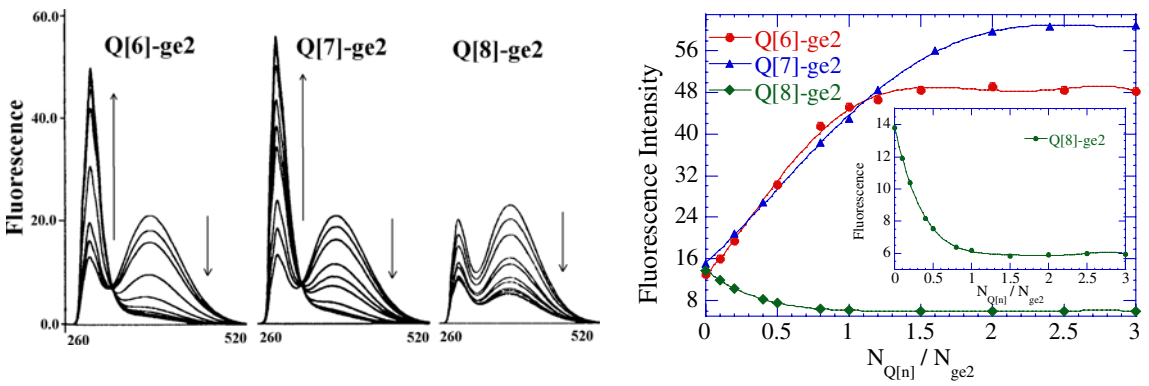


Figure 7. Fluorescence emission spectra and corresponding I_f–$N_{Q[n]}/N_{ge2}$ curves for the Q[6–8]-ge2 systems.

enhancement of ge3 was observed upon Q[6] addition, while a obviously fluorescence quenching of ge3 was observed upon Q[8] addition. It was noticeable that the fluorescence spectrum of ge3 was found to increase in intensity upon Q[7] addition, and then to decrease upon until addition of 1.5 equiv. of Q7 to the solution.

The fluorescence in intensity (I_f) vs. ratio of mole of the host and the guest ($N_{Q[n]}/N_{guest}$) data of the related host–guest systems was drawn at 299 nm for ge1, 292 nm for ge2 and 303 nm for ge3 respectively. The data can be best fitted to a 1:1 binding model for the three Q[6]–guest systems, and 1:2 binding model for the three Q[8]–guest systems, the results were consistent with those from the ^{1}H NMR and UV spectroscopy. it was noticeable that the data for the three Q[7]–guest systems can be also fitted to a 1.5:1 binding model as observed in Absorption spectrophotometric analysis, moreover, the fluorescence in intensity vs. ratio of $N_{Q[7]}/N_{ge3}$ data were linearly increased upon Q[7] addition until the ratio of $N_{Q[7]}/N_{ge3}$ was upto 1.5, then the data were decreased upon further Q[7] addition. Figure 7, for example, shows fluorescence emission spectra of 1.2 mM ge2 in the presence of increasing concentrations of Q[n = 6, 7 or 8] and the corresponding fluorescence intensity $\sim N_{Q[n]}/N_{ge2}$ curves for the Q[6$\sim$8]–ge2 systems at Ex/Em = 270/292 nm, the insert represents the curve of $N_{Q[8]}/N_{ge2}$ system for charity. The other spectra and curves are in supporting information.

Inclusion constants of the inclusion complexes in the title host–guest systems

In previous literature references [14], a series of methods have been introduced to measure binding constants for the inclusion complexes involving with Q[n]s, such as NMR technique, electronic absorption spectroscopy and fluorescence spectroscopy and so on. As mentioned above, the absorbance (Figure 6d and supporting information) and fluorescence intensity (Figure 7 and supporting information) vs. the ratio of $N_{Q[6\ or\ 8]}/N_{guest}$ are well fitted to 1:1or 1:2 binding models for the Q[6]–guest or Q[8]–guest systems respectively. Thus, the electronic absorption spectroscopy and fluorescence spectroscopy have been used to determine the binding constants of Q[6]–guest and Q[8]–guest systems; while the ^{1}H NMR technique has been used to measure the binding constants of Q[7]–guest systems due to the unusual curve fittings of the Q[7]–guest data from the electronic absorption spectroscopy and fluorescence spectroscopy, the origin of this experimental results is not really understood at this time. A suggestion is that there are multiple interaction models with different ratio of the host and guest. Table 1 shows the corresponding binding constants of the host–guest complexes in the title systems.

Comparing K^a and K^b for a host–guest system in this work, there is no significant difference from each other, the trend is systematically K(Q[6 or 8]–ge2) > K(Q[6 or 8]–ge1) > K(Q[6 or 8]–ge3), but the constant differences are relatively small, it is convincible that three guests have a similar structure. However, the order of the constant for the Q[7]–guest systems is K(Q[7]–ge3) > K(Q[7]–ge2) > K(Q[7]–ge1). As for the Q[6]–guest and Q[7]–guest systems, except the Q[7]–ge1 system which has the lowest binding constant, one could hardly justify the apparent correlation with the data analysis.

Table 1. Inclusion constants for the host-guest complexes of Q[6], Q[8] with ge1, ge2or ge3 by using electronic absorption spectroscopy and fluorescence spectroscopy

Host–guest	Q[6]-ge1	Q[6]-ge2	Q[6]-ge3
K^a, M	3.66×10^4	4.78×10^4	5.95×10^3
K^b, M	1.84×10^4	2.68×10^4	7.80×10^3
	Q[7]-ge1	Q[7]-ge2	Q[7]-ge3
K^c, M	9.22×10^2	1.03×10^4	1.64×10^4
	Q[8]-ge1	Q[8]-ge2	Q[8]-ge3
K^a, M^2	5.18×10^{11}	5.44×10^{11}	1.12×10^{12}
K^b, M^2	4.72×10^{11}	9.5×10^{11}	2.46×10^{12}

[a]absorption spectroscopy.
[b]fluorescence spectroscopy.
[c]^{1}H NMR spectroscopy.

Conclusion

We have been able to investigate, using ^{1}H NMR spectroscopy, electronic absorption spectroscopy and fluorescence Spectroscopy, the structures of host–guest of cucurbit[n = 6–8]urils with three benzimidazole derivatives. The experimental results reveal that although absorption spectra and fluorescence spectra for the title host–guest systems are quite different, $A\sim N_{Q[n]}/N_{guest}$ data and $I_f\sim N_{Q[n]}/N_{guest}$ data for the same system can be well fitted to the same binding model. Such as $A\sim N_{Q[6]}/N_{guest}$ data and $I_f\sim N_{Q[6]}/N_{guest}$ for the three Q[6]–ge(1$\sim$3) systems are all fitted to a 1:1 binding model, for the three Q[8]–ge(1$\sim$3) systems to a 1:2 binding model. These conclusions are supported by the ^{1}H NMR determination, and the possible binding models are shown Figure 2 and 4. It noticeable that $A\sim N_{Q[7]}/N_{guest}$ data and $I_f\sim N_{Q[7]}/N_{guest}$ data for the three Q[7]$\sim$ge(1$\sim$3) systems are all fitted to a 1.5:1 binding model, while the $\delta_{Hx}\sim N_{Q[7]}/N_{ge(1\sim3)}$ curves are clearly fitted to a 1:1 binding model. This difference in spectral behaviors between different methods is not understood at this time.

Acknowledgements

We acknowledge the support of the National Natural Science Foundation of China (Grant No. 20261002), the International Collaborative Project of the Ministry of Science and Technology (Grant No. 2003DF000030), and the International Collaborative Project of Guizhou Province.

References

1. R. Behrend, E. Meyer, and F Rusche: *Liebigs Ann. Chem.* **339**, 1 (1905).
2. W.A. Freeman, W.L. Mock, and N.Y. Shih: *J. Am. Chem. Soc.* **103**, 7367 (1981).
3. (a) J. Kim, I.-S. Jung, S.-Y. Kim, E. Lee, J.-K. Kang, S. Sakamoto, K. Yamaguchi, and K. Kim: *J. Am. Chem. Soc.* **122**, 540 (2000); (b) K. Jansen, H.-J. Buschmann, A. Wego, D. Dopp, C. Mayer, H.-J. Drexler, H.-J. Holdt, and E. Schollmeyer: *J. Incl. Phenom. Macrocycl. Chem.* **39**, 357 (2001).
4. A. Day, A.P. Arnold, R.J. Blanch, and B. Snushall: *J. Org. Chem.* **66**, 8094 (2001).
5. A.I. Day, R.J. Blanch, A.P. Arnold, S. Lorenzo, G.R. Lewis, and I. Dance: *Angew. Chem. Int. Ed. Engl.* **41**, 275 (2002).
6. Reviews (a) J. Lagona, P. Mukhopadhyay, S. Chakrabarti, and L. Isaacs: *Angew. Chem. Int. Ed.* **44**, 4844 (2005); (b) J.W. Lee, S. Samal, N. Selvapalam, H.J. Kim, and K. Kim: *Accounts Chem. Res.* **36**, 621 (2003); (c) O.A. Gerasko, D.G. Samsonenko, and V.P. Fedin: *Russian Chem. Rev.* **71**, 741 (2002); (d) J.A.A.W. Elemans, A.E. Rowan, and R.J.M. Nolte: *Ind. Eng. Chem. Res.***39**, 3419 (2000); (e) T.J. Hubin, A.G. Kolchinski, A.L. Vance, and D.H. Busch: *Adv. Supramol. Chem.* **5**, 237 (1999); (f) P. Cintas: *J. Incl. Phenom. Molec. Reco. Chem.* **17**, 205 (1994).
7. (a) Y. Miyahara, K. Abe, and T. Inazu: *Angew. Chem. Int. Ed.*, **41**, 3020 (2002). (b) A.K. Kellersberger, J.D. Anderson, S.M. Ward, K.E. Krakowiak, and D.V. Dearden: *J. Am. Chem. Soc.* **123**, 11316 (2001).
8. (a) R.J. Blanch, A.J. Sleeman, T.J. White, A.P. Arnold, and A.I. Day: *Nano. Lett.* **2**, 147 (2002); (b) S. Liu, C. Ruspic, P. Mukhopadhyay, S. Chakrabarti, P.Y. Zavalij, and L. Isaacs: *J. Am. Chem. Soc.* Online (2006).
9. (a) V. Sindelar, M.A. Cejas, F.M. Raymo, and A.E. Kaifer: *New J. Chem.* **29**, 280 (2005); (b) V. Sindelar, K. Moon, and A.E. Kaifer: *Org. Lett.* **6**, 2665 (2004); (c) W. Ong and A.E. Kaifer: *J. Org. Chem.* **69**, 1383 (2004); (d) K. Moon and A.E. Kaifer: *Org. Lett.* **6**, 185 (2004).
10. (a) Y. H. Ko, K. Kim, J.-K. Kang, H. Chun, J.W. Lee, S. Sakamoto, K. Yamaguchi, J.C. Fettinger, and K. Kim: *J. Am. Chem. Soc.* **126**, 1932 (2004); (b) K. Moon, J. Grindstaff, D. Sobransingh, and A.E. Kaifer: *Angew. Chem. Int. Ed.* **43**, 5496 (2004); (c) H. Fu, S. Xue, L. Mu, Y. Du, Q. Zhu, Z. Tao, and J. Zhang: *Sci. in Chin. Ser. B: Chemistry* **48**, 305 (2005); (d) W.S. Jeon, H.-J. Kim, C. Lee, and K. Kim: *Chem. Comm.* (17), 1828 (2002).
11. P.-H. Ma, J. Dong, S.-C. Xiang, S.-F. Xue, Q.-J. Zhu, Z Tao, J.-X. Zhang, and X Zhou: *Sci. Chin. Seri. B: Chem.* **47**, 301 (2004).
12. G.L. Zhang, Z.Q. Xu, S.F. Xue, Q.J. Zhu, and Z. Tao: *Chin. J. Inorg. Chem.* **19**, 655 (2003).
13. (a) W.L. Mock: *Top. Curr. Chem.* **175**, 1 (1995); (b) C. Marquez, R.R. Hudgins, and W.M. Nau: *J. Am. Chem. Soc.* **126**, 5806 (2004); (c) H.-Y. Fu, S.-F. Xue, Q.-J. Zhu, Z. Tao, J.-X. Zhang, and A.I. Day: *Sci. Chin. Ser.: B Chem.* **52**, 101 (2005).
14. (a) A. Flinn, G.C. Hough, J.F. Stoddart, and D.J. Williams: *Angew. Chem.* **104**, 1550 (1992); (b) H.J. Buschmann, E. Cleve, and E. Schollmeyer: *Inorg. Chim. Acta.* **193**, 93 (1992); (d) W.L. Mock and N.Y. Shih: *J. Am. Chem. Soc.* **110**, 4706 (1988); (e) W.L. Mock and N.Y. Shih: *J. Org. Chem.* **51**, 4440 (1986); (f) W.L. Mock and N.Y. Shih: *J. Org. Chem.* **48**, 3618 (1983).