

## NOTE

### Investigation on Host-Guest Interaction of Cucurbit[8]uril with 1,6-Bis(2-amino-pyridyl)hexane Bromide

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(Received: 20 January 2011;

Accepted: 31 May 2011)

AJC-10017

The host-guest interaction between a designed guest, 1,6-bis(2-amino-pyridyl)hexane bromide ( $\text{BAPH}^{2+}$ ) and cucurbit[8]uril (**Q[8]**, host) has been investigated with electronic absorption spectroscopy and  $^1\text{H}$  NMR. UV-VIS spectra titration has been employed and a moderate association constants of  $1.6 \times 10^4$  L/mol has been obtained in a ratio of 1:1. The model of inclusion complex has been confirmed by using  $^1\text{H}$  NMR.

**Key Words:** Cucurbit[8]uril, Host-guest interaction, Inclusion complex, Supramolecular chemistry.

Cucurbit[n]urils ( $\text{Q}[n]$ ,  $n = 5-8, 10$ , Fig. 1) are kinds of relatively novel macrocyclic cage compounds rimmed by a number of carbonyl oxygens<sup>1</sup>. The members in the  $\text{Q}[n]$  family have common characteristic features, *i.e.*, a hydrophobic cavity and two opening hydrophilic portals<sup>2</sup>. The novel structure and a capability for forming host-guest complexes with molecules and ions make the  $\text{Q}[n]$  lots of attraction as a synthetic receptor for supramolecular assemblies<sup>3,4</sup>. The varying cavity and portal sizes lead to the ability of the  $\text{Q}[n]$ s to form inclusion or exclusion complexes with different organic or inorganic species through a combination of dipole-ion, hydrogen bonding and hydrophobic interactions and these achievements have been summarized in different reviews in different period of development of  $\text{Q}[n]$ s chemistry<sup>5,6</sup>.

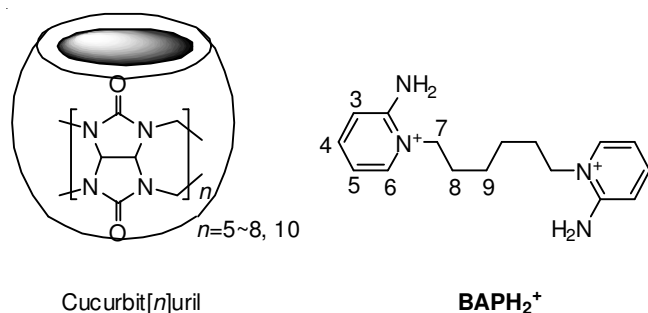


Fig. 1. Structures of cucurbiturils and 1,6-bis(2-amino-pyridyl)hexane bromide ( $\text{BAPH}^{2+}$ ) guest

The cavity size of  $\text{Q}[n]$ s has been determined by the unit count of glycoluril.  $\text{Q}[8]$ , which has a larger cavity than  $\text{Q}[6]$  and  $\text{Q}[7]$ , can include stoichiometric guests to form 1:2 or 1:1:1 ternary complexes with charge-transfer interaction between the electron-rich and the electron-poor guests<sup>7</sup>. The unique properties of  $\text{Q}[8]$ -controlled stoichiometry and charge-transfer in host-guest interactions have been used extensively to design, construct and functionalize novel supramolecular building blocks and to drive supramolecular machines and command devices confined within the  $\text{Q}[8]$  cavity<sup>8</sup>. In this work, we report  $\text{Q}[8]$ -induced a U-shaped conformation of 1,6-bis(2-amino-pyridyl)hexane bromide ( $\text{BAPH}^{2+}$ , Fig. 1) with  $^1\text{H}$  NMR spectra and UV-VIS spectra.

Chemicals, such as 2-aminopyridine and 1,6-dibromohexane were obtained commercially from Shanghai Jingchun Industry Co. Ltd. and used without further purification. Cucurbit[8]uril ( $\text{Q}[8]$ ) was prepared and purified according to the published procedures developed in our laboratory. The guest 1,6-bis(2-amino-pyridyl)hexane bromide ( $\text{BAPH}^{2+}$ ) has been synthesized from 2-aminopyridine and 1,6-dibromohexane with a 1:1 ratio in refluxing toluene for 8 h.

$^1\text{H}$  NMR spectra were recorded at 293 K on a VARIAN INOVA-400 spectrometer in  $\text{D}_2\text{O}$ . UV-VIS spectra were measured on a Unico UV-2102 instrument at 25 °C.

Absorption spectrophotometric analysis has been employed to quantitatively define the interaction between  $\text{Q}[8]$  and the 1,6-bis(2-amino-pyridyl)hexane bromide ( $\text{BAPH}^{2+}$ )

and the results are exhibited in Fig. 2. The concentration of the guests is fixed as  $C_{\text{BAPH}^{2+}} = 5.0 \times 10^{-5} \text{ mol L}^{-1}$  and the spectra are recorded with the increasing concentrations of Q[8] along with the arrow in the Fig. 2. Generally, Q[8] shows no absorbance above  $\sim 210 \text{ nm}$ , but the maximum absorbance of  $\text{BAPH}^{2+}$  at  $\lambda = 301 \text{ nm}$  become progressively lower with increasing concentration of host from  $5.0 \times 10^{-5}$ – $1.0 \times 10^{-4} \text{ mol L}^{-1}$ . The sharp isosbestic points at  $\lambda = 220 \text{ nm}$ ,  $\lambda = 238 \text{ nm}$ ,  $\lambda = 262 \text{ nm}$  and  $\lambda = 320 \text{ nm}$  are consistent with a host-guest interaction between Q[8] and  $\text{BAPH}^{2+}$ . The absorbance *versus* ratios of mole of the host Q[8] and the guest  $\text{BAPH}^{2+}$  ( $C_{\text{Q[8]}}/C_{\text{guest}}$ ) data can be fitted to a 1:1 binding model for the Q[8]- $\text{BAPH}^{2+}$  system at  $\lambda = 301 \text{ nm}$  (Fig. 2) and the corresponding binding constant ( $K_{\text{Q[8]-BAPH}^{2+}}$ ) was found to be  $1.6 \times 10^4 \text{ L mol}^{-1}$  by non-linear least square fitting.

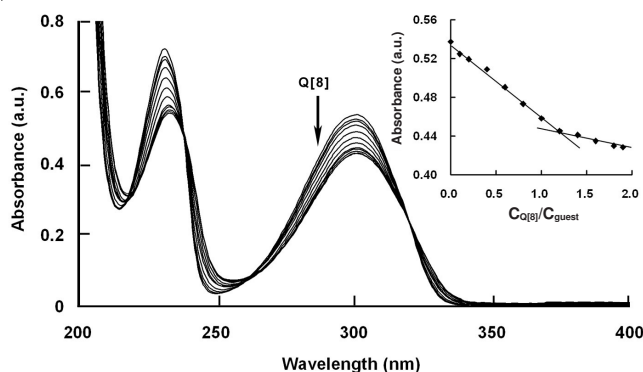


Fig. 2. Absorption spectra changes of the mixtures of host-guest and curve-fitting analysis for the inclusion complex. Inset: related absorbance *versus*  $C_{\text{Q[8]}}/C_{\text{BAPH}^{2+}}$  curve at 301 nm

The host-guest interaction model in aqueous solution, in a general way, can be revealed by comparing the  $^1\text{H}$  NMR spectrum of cucurbit[n]urils bound guest with free guest the upfield shifts of the resonances from guest protons represent insertion of cucurbituril into the cavity, while the downfield shifts of the resonances from guest protons represent the proximity of cucurbituril to the outside of the portal. The two  $^1\text{H}$  NMR spectra (Fig. 3a,b) of the free  $\text{BAPH}^{2+}$  guest and Q[8] with guest  $\text{BAPH}^{2+}$  show the difference of bound and unbound guest. It is clearly evident in Fig. 3b that the two sets of  $\text{BAPH}^{2+}$  lie in different magnetic environments. The proton resonances of bound guest at 7.20, 6.28, 6.18, 3.68, 1.21 and 1.06 ppm move upfield of the unbound guest proton resonances at 7.66 (overlapped doublet and triplet, H6 and H4), 6.88 (doublet, H3), 6.73 (triplet, H5), 3.98 (triplet, H7) 1.67 (doublet, H8) and 1.21 (doublet, H9) ppm, respectively. These observations indicate that the whole  $\text{BAPH}^{2+}$  guest is contained within the cavity of Q[8]. Combining with the results of

electron absorption that the host-guest inclusion complex is formed with a ratio of 1:1, the  $^1\text{H}$  NMR investigation suggest that the bent  $\text{BAPH}^{2+}$  guest with a U-shaped conformation resides in the cavity of Q[8] (Fig. 3b). In addition, the interactions between  $\text{BAPH}^{2+}$  and Q[8] lead to broadened resonance signals of the guest and the broadness indicates a relatively fast exchange between guest and Q[8] on the NMR time scale.

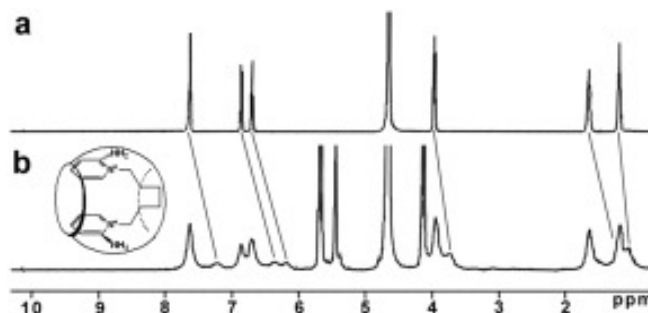


Fig. 3.  $^1\text{H}$  NMR spectra of (a)  $\text{BAPH}^{2+}$  guest and (b) inclusion complex of Q[8]-guest

## Conclusion

In summary, the host-guest interaction of  $\text{BAPH}^{2+}$  and Q[8] is investigated by UV-VIS and spectroscopy. The electron absorption titration reveals that the host-guest inclusion complex is formed in a ratio of 1:1 and a moderate association constant of  $1.6 \times 10^4 \text{ L mol}^{-1}$  is found. The  $^1\text{H}$  NMR illuminates that the  $\text{BAPH}^{2+}$  guest can be included in whole in Q[8]'s cavity. The above evidences suggest the formation of Q[8]-induced U-shaped confirmation of  $\text{BAPH}^{2+}$  guest.

## ACKNOWLEDGEMENTS

The authors acknowledged the financial support of the Natural Science Foundation of Guizhou Province (No. [2009]2073, [2010]2126).

## REFERENCES

1. A. Day, A.P. Arnold, R.J. Blanch and B. Snushall, *J. Org. Chem.*, **66**, 8094 (2001).
2. J.W. Lee, S. Samal, N. Selvapalam, H.J. Kim and K. Kim, *Acc. Chem. Res.*, **36**, 621 (2003).
3. L. Isaacs, *Chem. Commun.*, 619 (2009).
4. P. Mukhopadhyay, A. Wu and L. Isaacs, *J. Org. Chem.*, **69**, 6157 (2004).
5. K. Kim, N. Selvapalam, Y.H. Ko, K.M. Park, D. Kim and J. Kim, *Chem. Soc. Rev.*, **36**, 267 (2007).
6. O.A. Gerasko, D.G. Samsonenko and V.P. Fedin, *Russ. Chem. Rev.*, **71**, 741 (2002).
7. J.W. Lee, I. Hwang, W.S. Jeon, Y.H. Ko, S. Sakamoto, K. Yamaguchi and K. Kim, *Chem. Asian J.*, **3**, 1277 (2008).
8. Y.H. Ko, E. Kim, I. Hwang and K. Kim, *Chem. Commun.*, 1305 (2007).