Laser spectroscopic study on (dibenzo-24-crown-8-ether) -water and -methanol complexes in supersonic jets

Satoshi Kokubu, Ryoji Kusaka, Yoshiya Inokuchi, Takeharu Haino,
and Takayuki Ebata*
Department of Chemistry, Graduate School of Science, Hiroshima University,
Higashi-Hiroshima 739-8526, Japan

Abstract

The conformation and complex formation with guest molecules have been investigated for jet-cooled dibenzo-24-crown-8-ether (DB24C8) by laser induced fluorescence (LIF), UV-UV hole-burning (UV-UV HB), and IR-UV double-resonance (IR-UV DR) spectroscopy. The results are compared with the results of dibenzo-18-crown-6-ether (DB18C6) and analyzed by density functional theory (DFT) calculations at the B3LYP/6-31+G* level. Five conformers are identified for DB24C8 under the jet-cooled condition, and the structure of the major isomer is determined to be a boat form, similar to the case of DB18C6. Two molecules (water and methanol) are investigated as the guest species for the encapsulation experiment. DB24C8 hardly encapsulates a water molecule, different from the case of DB18C6 in which a water molecule is efficiently captured. However, it is likely that larger (water)$_n$ clusters can be captured in the DB24C8 cavity. The different feature in the complex formation between DB24C8 and DB24C8 with the water molecules are attributed to a larger cavity size of DB24C8 than that of DB18C6. For methanol, two kinds of DB18C6-(methanol)$_1$ isomers are identified by IR-UV double resonance spectroscopy; one is the "OH---π"

H-bonded isomer, characteristic of methanol with one OH group, and the other is the "OH---O" H-bonded ones. These results indicate the multiple H-bond formation to the oxygen atoms of the ether ring may play an important role in the complexes of DB24C8 or DB18C6 with water.

1. Introduction

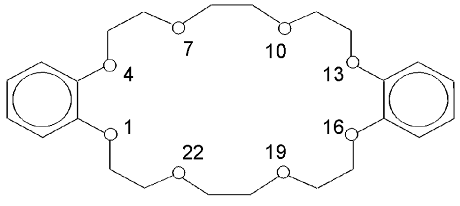
Crown ethers (CEs) are known as macrocyclic molecules consisting of oxyethylene (C–C–O) units. Depending on the size of the ether ring, CEs can form stable complexes with a variety of metal and organic cations, neutral molecules, and even anions.[1] Flexibility is another characteristic of CEs, and they adjust their ring structure to incorporate guest species with different shapes.[1,2] Because of their complex formation ability, CEs are used in many applications such as metal cation extraction,[3] fluoroionophore,[4] and phase transfer catalysis.[5] 18-crown-6-ether (18C6) forms an exceptionally stable 1:1 complex with K^+ with high symmetry (D_{3d}).[1,6,7] CEs also show other types of encapsulation, in which a guest species is enclosed by two CE molecules,[8,9] or two guests are held by one CE molecule.[10,11]

The preferential capture of K^+ by 18C6 was originally observed in condensed phase.[12,13] However, in condensed phase, it is difficult to distinguish the dominant intermolecular interaction that controls the encapsulation. In the gas phase measurement, 18C6 shows the largest intermolecular binding energy not with K^+ but with Li^+ among alkali-metal cations.[14,15] In addition, there are several studies suggesting the importance of the solvation effect on the stability of the complexes.[16-18] Thus, the stepwise study on the structure of CEs starting from isolated molecules to micro-solvated complexes is essential. It will be also important to specify the conformation of CEs exhibiting stable complexes, which is sometimes very difficult under the bulk condition because the structural information will be averaged over all possible conformers under the given temperature.

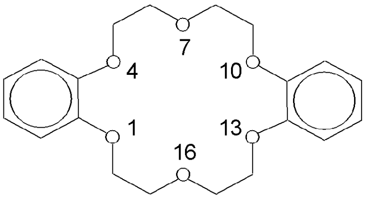
Very recently, we have started our study to elucidate the mechanism of the complex formation and recognition of guest species for dibenzo-18-crown-6-ether

(DB18C6) and benzo-18-crown-6-ether (B18C6) in supersonic jets.[19-21] The combination of cooling by the supersonic jet technique and laser spectroscopy enabled us to determine the conformation and the complex structures of DB18C6 and B18C6 unambiguously. For DB18C6, we found two isomers; one is a "boat" conformer, which is a major species, and the other is a “chair” type. In the boat conformer, the two benzene rings are more closely located than the chair form by bending the ether ring. The complex formation with water molecules predominantly occurs in the "boat" conformer. In B18C6, four conformers are identified in the bare form and the number of the conformer is reduced to one upon the complex formation with water molecules. Thus, we demonstrated that B18C6 adjusts its conformation to be fit to the shape of the guest molecules in the complex formation.

In this paper, we report the laser spectroscopic and theoretical study on the cavity-size and conformation effects in the complex formation. We investigate the conformation and complex formation of dibenzo-24-crown-8-ether (DB24C8) (Scheme 1a) with water and methanol, which is compared with those of DB18C6 (Scheme 1b). The size of the cavity of DB24C8 is larger than that of DB18C6, and DB24C8 is more flexible than DB18C6. We investigate how the difference of the cavity size and the flexibility of the host will be reflected in the complex formation with the guest species. We apply several laser spectroscopic techniques, such as laser induced fluorescence (LIF), mass-selected resonant two-photon ionization (R2PI), UV-UV hole-burning (UV-UV HB), and IR-UV double-resonance (IR-UV DR) spectroscopy, and the results will be analyzed with an aid of density functional theory (DFT) calculation.



Scheme 1(a) DB24C8



Scheme 1(b) DB18C6

Experimental

Details of the experiment were described in our previous papers.[19-21] In brief, we used a home-made pulsed nozzle to generate jet-cooled DB24C8.[22] We attached a sample housing made of poly-imido resin at the head of a commercial nozzle (General Valve series 9). DB24C8 powder (Tokyo Kasei Kogyo) was heated to ~400K. The mixture of DB24C8 and water or methanol vapor with He carrier gas (with a total pressure of 2 bar) was injected into a vacuum chamber through the nozzle for generating a supersonic jet of DB24C8. Partial pressure of water and methanol was controlled by regulating the temperature of a container connected to the gas line.

For LIF spectroscopy, an output of a tunable pulsed UV laser (Inrad, Autotracker (KDP)/Lambda Physik, Scanmate/Continuum, Surelite) was introduced to the vacuum chamber and crossed with the jet at 30 mm downstream of the nozzle. Fluorescence from the sample was collected by a series of lenses and detected by a photomultiplier tube (Hamamatsu Photonics, 1P28). For removing stray light, a glass filter (CVI, CG-WG-295) was placed in front of a photomultiplier tube. LIF spectra were obtained by plotting the fluorescence intensity as a function of UV frequency. For UV-UV HB spectroscopy, the UV laser in the LIF measurement was used for a probe light. The frequency of the probe UV laser was fixed to a vibronic band of a single species and the fluorescence signal was monitored. A pump UV laser (Inrad, Autotracker III /Continuum, ND6000/Continuum, Surelite II) was introduced to the jet at 10 mm upstream of the probe position. The time interval between the pump and the probe light was fixed to ~4 μs. When the pump laser frequency is resonant to a transition of the species monitored, the species is excited to the upper state. The excitation by the pump laser causes depletion of the fluorescence signal monitored by the probe light. Thus, an electronic spectrum of the monitored species was obtained as fluorescence dip spectra as a function of the pump UV frequency. The experimental scheme of IR-UV DR spectroscopy is similar to that of UV-UV HB spectroscopy. An output of a tunable IR laser (Laser Vision/Quanta-Ray, GCR250) was introduced coaxially with the UV probe laser 100 ns before the probe pulse. The frequency of the IR pump laser was scanned while monitoring the fluorescence signal. Depletion of the fluorescence occurs when IR frequency is resonant to a vibrational transition of the species monitored. IR spectra in the S_0 state were obtained as fluorescence dip spectra.

Quantum chemical calculations were carried out for DB24C8 and DB24C8-(methanol)$_1$. Geometry optimization and vibrational analysis were done at the B3LYP/6-31+G* level of theory by using GAUSSIAN 03.[23] To obtain the initial geometries of DB24C8 for DFT calculations, a conformational exploration was first performed by using the mixed torsional search with low-mode sampling[24] in MacroModel V.9.1[25] with MMFF94s force field.[26]

Results and discussion

1. Determination of conformation for DB24C8

1.1 LIF, UV-UV HB, and IR-UV DR spectra of DB24C8

Fig.1 (a) shows an LIF spectrum of jet-cooled DB24C8 in the origin band region. Figs.1 (b)-(f) show the UV-UV HB spectra obtained by monitoring bands A-E, respectively. Since these HB spectra are different from each other, bands A-E are due to the origin bands of different species. Almost all the other bands appearing in the LIF spectrum can be assigned to vibronic transitions of the five species. We then applied IR-UV DR spectroscopy to bands A-E in the OH stretching region, but did not obtain any bands assignable to the OH band. This result indicates that bands A-E can be assigned to conformers of the DB24C8 monomer. The UV-UV HB spectra in Fig.1 show quite different vibronic structures from each other. In the spectrum of band B, two bands with an interval of 9 cm^{-1} appear with equal intensity. This doublet can be assigned to the band origins which are split by the exciton coupling between the two benzene chromophores, from the analogy of the boat form of DB18C6 which exhibits a split with an interval of 5 cm^{-1}.

One possible experiment to investigate the conformation of CEs is to measure IR spectra in the CH stretching region. The left panel of Fig. 2 shows the IR-UV DR spectra for bands A-E. The IR bands appearing in the 2800-3000 cm^{-1} region are due to the CH stretch vibrations of methylene chain, and those in the 3000-3200 cm^{-1} region are to the CH stretch vibrations of the phenyl groups. Since the IR spectra are different from each other, the conformation of species A-E is different from each other.

1.2 Geometry and vibrational frequency calculations of DB24C8

Parallel to the experiments, we obtained stable conformers of DB24C8 by DFT calculations at the B3LYP/6-31+G* level. As was described in the experimental section, a conformational exploration was carried out to obtain the initial geometries by using the mixed torsional search with low-mode sampling[24] in MacroModel V.9.1[25] with

MMFF94s force field[26]. The 10000 initial geometries were generated, and following optimizations with PRCG algorithm gave more than one thousand conformers with a convergence threshold of 0.05 kJ mol^{-1} $Å^{-1}$. A collection of the conformers still contained many redundant structures due to the flexible nature of the molecule after elimination of them with the default setup for geometric considerations; thus, maximum distance threshold of 5.0 Å was set to eliminate redundant conformations from the collection.[25] This treatment gave rise to three unique conformations found within 13.0 kJ mol^{-1}, which were subjected to DFT calculations. In addition to the search by molecular mechanics calculation, we tried to find structures similar to those of DB18C6 obtained to the previous study[20] by adding two oxyethylene (-C-C-O-) units to the optimized structures of DB18C6. For the DFT calculation, we put a symmetry restriction for some of the conformers due to the reason described later. We obtained five conformers within 1000 cm^{-1} as shown in Fig. 3. Also shown are the two conformers of DB18C6 found in our previous study.[20] Conformer (a) is the most stable structure, and belongs to C_{2h} point group. The second stable conformer (b) has C_i symmetry. We call conformers (a) and (b) “chair form”, similar to the case of DB18C6. The conformers (c) to (e) have C_s, C_1, and C_1 symmetry, respectively. Conformer (d) can be called “boat form”, which is a similar form observed for DB18C6 as the most stable conformer. The calculated IR spectra of those conformers are shown in Fig. 2.

The calculated IR spectra are quite different from each other, indicating that IR spectroscopy in the CH stretching region is a useful technique to study the conformation of CEs. However, unfortunately, comparison of the calculated IR spectra with the observed ones does not show clear correspondence. Therefore, it is difficult to determine the conformation of DB24C8 from results of the IR spectra.

Though it is difficult to determine the conformation from the IR spectra, the electronic transition energies gave a useful information for the determination of conformer in the case of DB18C6.[20] Therefore, we applied a similar discussion to DB24C8, and tried to assign the band origins to either of the conformations in Fig. 3. There are two characteristic features in the electronic spectrum of DB24C8 in Fig. 1. First, band A is located at a position lower than the other bands by ~200 cm^{-1}. Second, band B has a doublet with an interval of 9 cm^{-1}. These features were also observed for DB18C6.[20] Fig. 4 shows the comparison of the LIF spectra of DB18C6 and DB24C8. For DB18C6, we assigned conformer **m1** to the C_i-chair form (Fig. 3).[21] Conformer **m2,** exhibiting 5 cm^{-1} splitting doublets, is assigned to the C_{2v}-boat form (Fig. 3). The splitting of conformer **m2** is due to the excition splitting caused by the interaction between the two benzene chromophores located at a distance of 8.8 Å.[21] This splitting is not observed for the chair form having the C_i symmetry, because one of the transitions is symmetry forbidden. By comparing the results of DB18C6, the species corresponding to band A can be assigned to a chair form having the inversion symmetry, that is either the C_{2h}-chair (Fig. 3(a)) or the C_i-chair (Fig. 3(b)). The species corresponding to band B, exhibiting 9 cm^{-1} splitting, is assignable to the C_1-boat form (Fig 3.(d)). The interval of 9 cm^{-1} is larger than that of **m2** of DB18C6 (5 cm^{-1}). The distance between the two benzene chromophores of the calculated C_1-boat form of DB24C8 (Fig. 3(d)) is 9.9 Å. Thus, in terms of the distance a smaller exciton splitting is expected for DB24C8 than that for DB18C6, which is opposite to the observation. However, the splitting is dependent also on the relative orientation of the transition moments of the two benzene rings, so the relative configuration of the benzene rings may be different between

DB24C8 and DB18C6. A further assignment of the conformers can be given by the S_1-S_0 transition energies calculated by DT-DFT calculation. The transition energy of the C_{2h}-chair, C_1-boat, and C_i-chair conformers are estimated as 39699, 40041, and 40420 cm^{-1}, respectively. In the LIF spectrum of DB24C8, band A is located at the lower frequency side of band B. As mentioned above, band B can be attributed to the C_1-boat conformer on the basis of the splitting of the origin band. From the calculated transition energies, therefore, band A can be safely assigned to the C_{2h}-chair conformer. For the remaining bands, C-E, it is difficult to determine their conformations definitely in the present stage.

2. Cavity size and conformation effects on the complexation of DB24C8 with guest species

The effect of the cavity size and the conformation in the complex formation was investigated with water and methanol as guest species. Fig. 5 shows LIF spectra of (a) DB24C8 and (b) DB24C8 with the water container in the gas line. We do not find any sharp bands attributed to the DB24C8-water complex in these spectra. This situation is quite different from DB18C6. The spectrum of DB18C6 in Fig. 4 shows many sharp bands assignable to DB18C6-(water)$_n$ complexes, even though the spectrum was observed only with residual water on the wall of the sample tubing. Thus, DB18C6 forms stable complexes with water molecules much more effectively than DB24C8. As was discussed in our previous paper,[20] the high ability of DB18C6 for the complex formation with water originates from the cavity size of DB18C6 suited to the size of water. In the DB18C6-(water)$_n$ complexes, the first water molecule is preferentially encapsulated inside the boat conformer (see Fig. 3) by forming the bidentate H-bonding to the middle of the O_1 and O_4 and that of O_{10} and O_{13}. In the case of DB24C8, on the other hand, the cavity size is too large for one or a few water molecule(s) to be encapsulated; the O_1-O_{13} inter atomic distance of the C_{2v}-boat DB18C6 conformer is 4.8 Å , while that of O_1-O_{16} of the C_1-boat DB24C8 form is 8.4 Å.

Though DB24C8 hardly encapsulates one or a few water molecules, it seems that it can encapsulate larger size water clusters, $(\mathrm{water})_n$. As seen in Fig. 5(b), the LIF spectrum exhibits a very broad feature in the 35500-35700cm^{-1} (hatched) region. This broad component is assignable to very large DB24C8-$(\mathrm{water})_n$ complexes, indicating that DB24C8 can hold large $(\mathrm{water})_n$ clusters. Therefore, it seems likely that a large $(\mathrm{water})_n$ cluster is bonded to a DB24C8 molecule by using several OH groups of the $(\mathrm{water})_n$ cluster cooperatively for the DB24C8---$(\mathrm{water})_n$ intermolecular bond. The large $(\mathrm{water})_n$ clusters can form the H-bond with a DB24C8 molecule simultaneously at both benzene ends of the ether ring, similar to the DB18C6-$(\mathrm{water})_1$ complex. These results suggest that the simultaneous H-bonding to the oxygen atoms next to the benzene rings is essential for the formation of the DB24C8-$(\mathrm{water})_n$ and DB18C6-$(\mathrm{water})_n$ complexes.

We then investigated the complex formation with methanol. Fig. 5 (c) shows the LIF spectrum of DB24C8 observed by adding methanol vapor to the sample gas. Five new bands (labeled by α - ε) attributed to DB24C8-$(\mathrm{methanol})_n$ complexes appear in the spectrum. To determine the size and the structure of the complexes, we measured IR-UV DR spectra for bands α - ε. Fig. 6 shows the IR-UV DR spectra in the CH and the OH stretching region obtained by monitoring bands α - ε in Fig. 5(c). All the spectra show a single band in the OH stretching region, indicating that bands α - ε can be assigned to DB24C8-$(\mathrm{methanol})_1$ complexes. Band α exhibits the OH stretch vibration at 3584 cm^{-1}, and for the other bands the OH stretch appears at 3504 cm^{-1}. The OH frequency of gas phase methanol is 3682 cm^{-1};[27] the red-shift for the species of band α and bands β- ε is 98 and 178 cm^{-1}, respectively. Thus, methanol acts as a proton donor in the DB24C8-(methanol)$_1$ complexes, and there are two types of the H-bond. From the magnitude of the red-shifts, the band at 3584cm^{-1} is assigned to the OH---π H-bond, and the other bands at 3504cm^{-1} to the OH---O H-bond. As a result, band α in the LIF spectrum (Fig. 5(c)) is attributed to the OH---π isomer, and bands β - ε to the OH---O isomers.

To determine the complex structure, we carried out the geometry optimization of the DB24C8-(methanol)$_1$ complex at the B3LYP/6-31+G* level. As seen in Fig. 5(c), bands α - ε are close to band B more than to band A. Band B is attributed to the C$_1$-boat conformer of DB24C8. Therefore, we employed the C$_1$-boat conformer for the structure of the DB24C8 part in the DB24C8-(methanol)$_1$ complex. The geometry optimization of the DB24C8-(methanol)$_1$ complex provides, three isomers: two OH---π H-bonded isomers and one OH---O H-bonding isomer (Fig. 7). In the OH---π isomers, the methanol molecule is H-bonded to a benzene ring from either outside or inside the boat form. In the OH---O isomer, the methanol OH group points to the middle of the two oxygen atoms (O$_1$ and O$_4$) nearby the benzene ring, and forms bifurcated H-bond. This bifurcated H-bonding is also found in DB18C6-(water)$_1$.[20] The calculated IR spectra are shown in the lower panel of Fig. 6. For comparison, the calculated frequencies are scaled with a factor of 0.954. A good agreement is seen between the observed and the calculated IR spectra in the OH stretching region, supporting the proposed H-bonding structure. Band α can assigned to the OH---π H-bonded isomer. This band is located in the middle of the doubly split bands of the C$_1$-boat conformer. When the methanol molecule is H-bonded to the π the electron cloud, the electronic transition of the benzene chromophore will be blue-shifted as is expected from the blue-shift of the S_1-S_0 electronic transition of the benzene-methanol OH---π complex.[28] Then the exciton splitting is removed and the transition of the benzene chromophore free from the OH-π H-bonding should appear in the middle of the doubly-split band B, that is band α. In the case of the DB18C6-(water)$_n$ complexes, no isomer is found with the OH---π H-bond. In addition, the DB24C8-(water)$_n$ complexes show broad absorption that is largely blue-shifted from band B (see Fig. 5(b)), implying that the (water)$_n$ cluster is bound not to the benzene π-electron but to the oxygen atoms of the ether ring. Therefore, the observation of the OH---π isomer for the DB24C8-(methanol)$_1$ complex indicates not only that the OH---π H-bond is characteristic of methanol, which has one OH group, but that the formation of the multiple H-bonds to the oxygen atoms of the ether ring is a predominant factor for the water complex of DB18C6 and DB24C8.

In conclusion, we investigated the conformation of dibenzo-24-crown-8-ether (DB24C8) and its complexes with two guest molecules, water and methanol. The results are compared with those of dibenzo-18-crown-6-ether (DB18C6). A cavity size difference was observed between DB24C8 and DB18C6 in the complex formation with water. DB18C6 easily forms encapsulation complex with water, while DB24C8 hardly forms the complex. The difference is explained by that the cavity size of DB18C6 just fit for the water molecule to form bidentate H-bonded complex. On the other hand, the cavity size of DB24C8 is too large to form the similar complex. In the case of methanol molecule as a guest, methanol can form the complex with DB24C8 either by forming OH-π H-bonding or birfurcated “OH---O” H-bonding.

Acknowledgment

This work is supported by Grant-in-Aid project (Grant Nos. 18205003 and 21350016) and MEXT for the Scientific Research on Priority Area “Molecular Science for Supra Functional Systems” (No. 477).

References

1. G. Gokel, *Crown Ethers and Cryptands*, Royal Society of Chemistry: Cambridge, U. K., 1991.

2. M. Dobler, *Ionophores and their Structures*, Wiley-Interscience: New York, USA, 1981.

3. G. G. Talanova, N. S. A. Elkarim, R. E. Hanes, Jr., H. Hwang, R. D. Rogers, R. A. Bartsch, *Anal. Chem*. 1999, **71**, 672–677.

4. J. S. Benco, H. A. Nienaber, K. Dennen, W. G. McGimpsey, *J. Photochem. Photobiol. A* 2002, **152**, 33–40.

5. A. M. Stuart, J. A. Vidal, *J. Org. Chem.* 2007, **72**, 3735–3740.

6. A. N. Chekholov, *Russ. J. Coord. Chem.* 2008, **34**, 434–437.

7. D. Li, M. Du, J. Dou, D. Wang, *Z. Anorg. Allg. Chem.* 2005, **631**, 178-181.

8. T. Akutagawa, T. Motokizawa, K. Matsuura, S. Nishihara, S. Noro, T. Nakamura, *J. Phys. Chem. B* 2006, **110**, 5897–5904.

9. V. W. Bhagwat, H. Manohar, N. S. Poonia, *Inorg. Nucl. Chem. Lett.* 1981, **17**, 207–210.

10. N. S. Poonia, M. R. Truter, *J. Chem. Soc., Dalton Trans.* 1973, 2062–2065.

11. B. T. Gallagher, M. J. Taylor, S. R. Ernst, M. L. Hackert, N. S. Poonia, *Acta Cryst.*

1991, **B47**, 362–368.

12. R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, J. J. Christensen, D. Sen, *Chem. Rev*., 1985, **85**, 271-339.

13. G. W. Gokel, W. M. Leevy, M. E. Weber, *Chem. Rev.*, 2004, **104**, 2723-2750 .

14. I. -H. Chu, H. Zuang, D. V. Dearden, *J. Am. Chem. Soc.*, 1993, **115**, 5736-5744.

15. S. Maleknica, J. Brodbelt, *J. Am. Chem. Soc.*, 1992, **114**, 4295-4298.

16. M. B. More, D. Ray, P. B. Armentrout, *J. Am. Chem. Soc.*, 1999, **121**, 417-423.

17. P. B. Armentrout, *Int. J. Mass Spectrom*. 1999, **193**, 227.

18. D. Feller, *J. Phys. Chem. A*, 1997, **101**, 2723-2731.

19. R. Kusaka, Y. Inokuchi, T. Ebata, *Phys. Chem. Chem. Phys.* 2007, **9**, 4452–4459.

20. R. Kusaka, Y. Inokuchi, T. Ebata, *Phys. Chem. Chem. Phys.* 2008, **10**, 6238–6244.

21. R. Kusaka, Y. Inokuchi, T. Ebata, *Phys. Chem. Chem. Phys.* 2009, **11**, 9132–9140.

22. T. Ebata, *Bull. Chem. Soc. Jpn.*, 2009, 82, 127-151.

23. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L.

Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussian 03*, Revision D.02,Gaussian, Inc., Wallingford CT, 2004.

24. I. Kolossváry, W. C. Guida, *J. Am. Chem. Soc.* 1996**, 118**, 5011.

25. MacroModel, version 9.1, Schrödinger, LLC, New York, NY, 2005.

26. T. A. Halgren, *J. Comput. Chem.* 1999**, 20**, 730-748.

27. G. Herzberg, "Molecular Spectra and Molecular Structure II", Van Nostrand Reinhold Co., New York, Cincinnati, Toronto, London, Melbourne, 1945.

28. P. N. Probble, F. C. Hagemeister, T. S. Zwier, *J. Chem. Phys.* 1997, **106**, 2145-2157

Table I. The positions of the S_1-S_0 origin band of DB24C8 and DB24C8-(methanol)$_1$ and their assignments.

Band	Position (cm^{-1})	Complex size	Assignment
A	35195	DB24C8	C_{2h}-chair
B	35408	DB24C8	C_1-boat
C	35435	DB24C8	
D	35438	DB24C8	
E	35525	DB24C8	
α	35413	DB24C8-(methanol)$_1$	C_1-boat OH- π
β	35502	DB24C8-(methanol)$_1$	C_1-boat OH- σ
γ	35676	DB24C8-(methanol)$_1$	
δ	35694	DB24C8-(methanol)$_1$	
ε	35705	DB24C8-(methanol)$_1$	

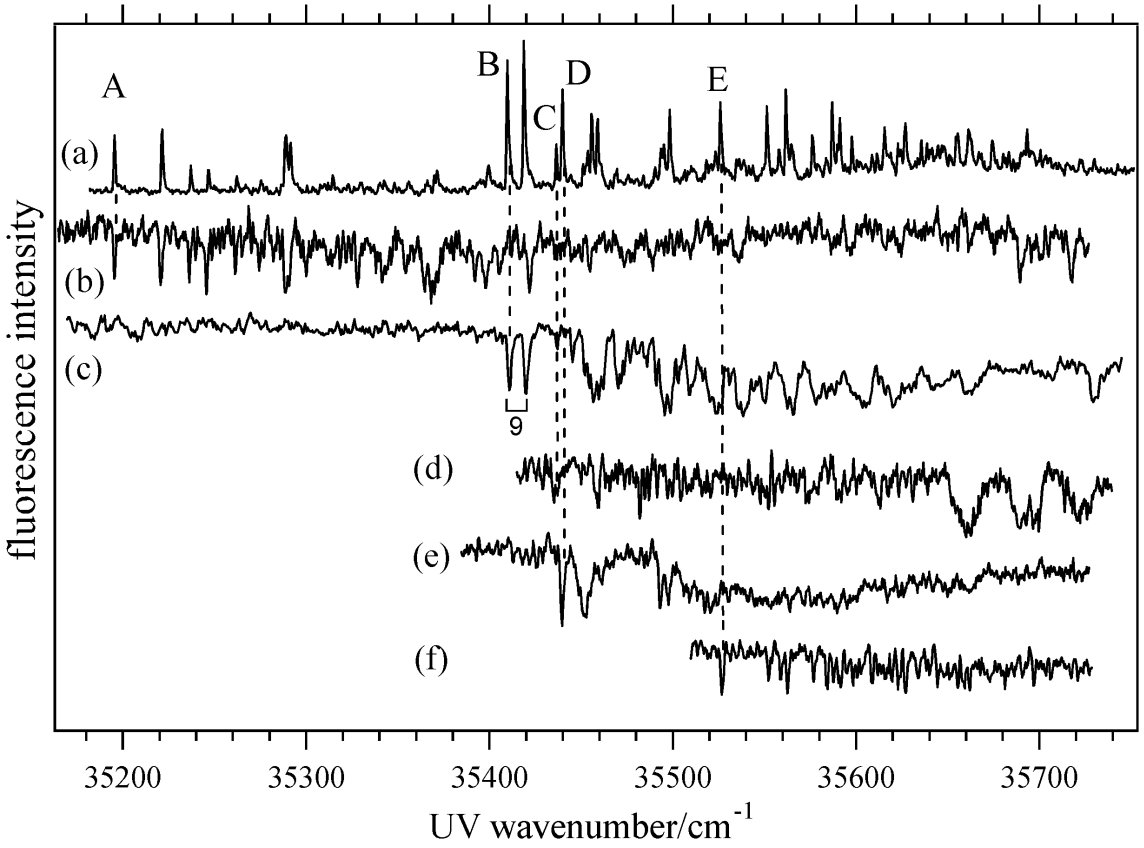


Fig. 1 (a) LIF spectrum of jet-cooled DB24C8. UV-UV HB spectra by monitoring (b) band A, (c) band B, (d) band C, (e) band D and (f) band E.

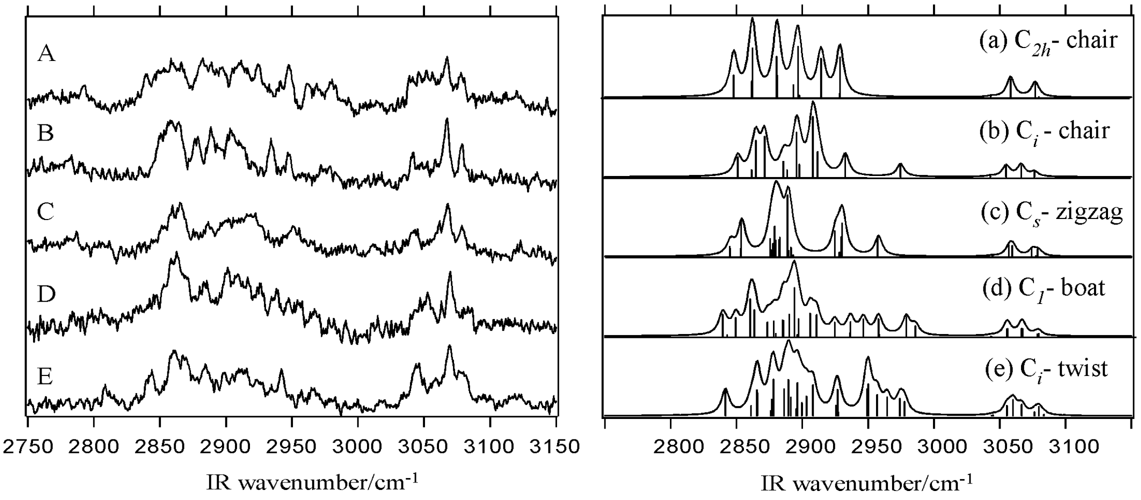
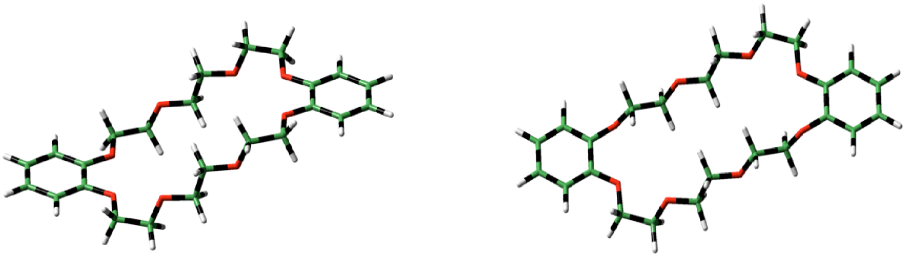
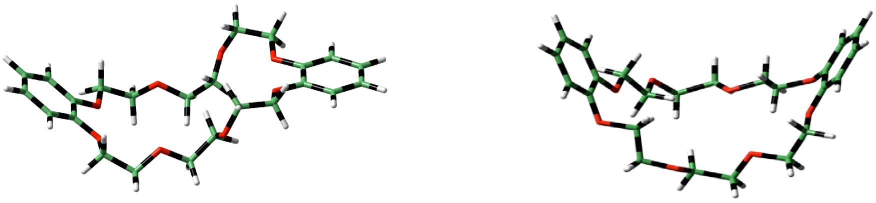


Fig.2 (Left) IR-UV double resonance spectra of DB24C8 obtained by monitoring bands A-E in the LIF spectrum of Fig. 1. (Right) IR spectra calculated for the five conformers of DB24C8.

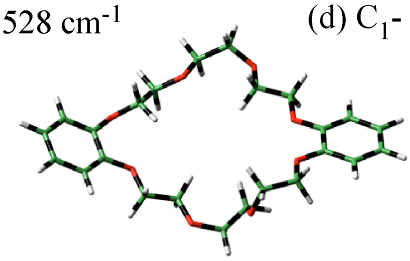
DB24C8



(a) C_{2h}- chair 0 cm^{-1} (b) C_i - chair 208 cm^{-1}

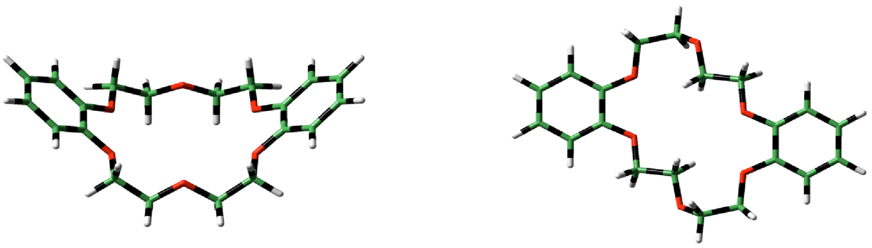


(c) C_s- zigzag 528 cm^{-1} (d) C_1- boat 790 cm^{-1}



(e) C_i- twist 813 cm^{-1}

DB18C6



C_{2v}- boat 0 cm^{-1} C_i - chair 542 cm^{-1}

Fig. 3 (Upper) Geometry optimized conformers of DB24C8. (Lower) Geometry optimized conformers of DB18C6. These structures are obtained at the B3LYP/6-31+G* level.

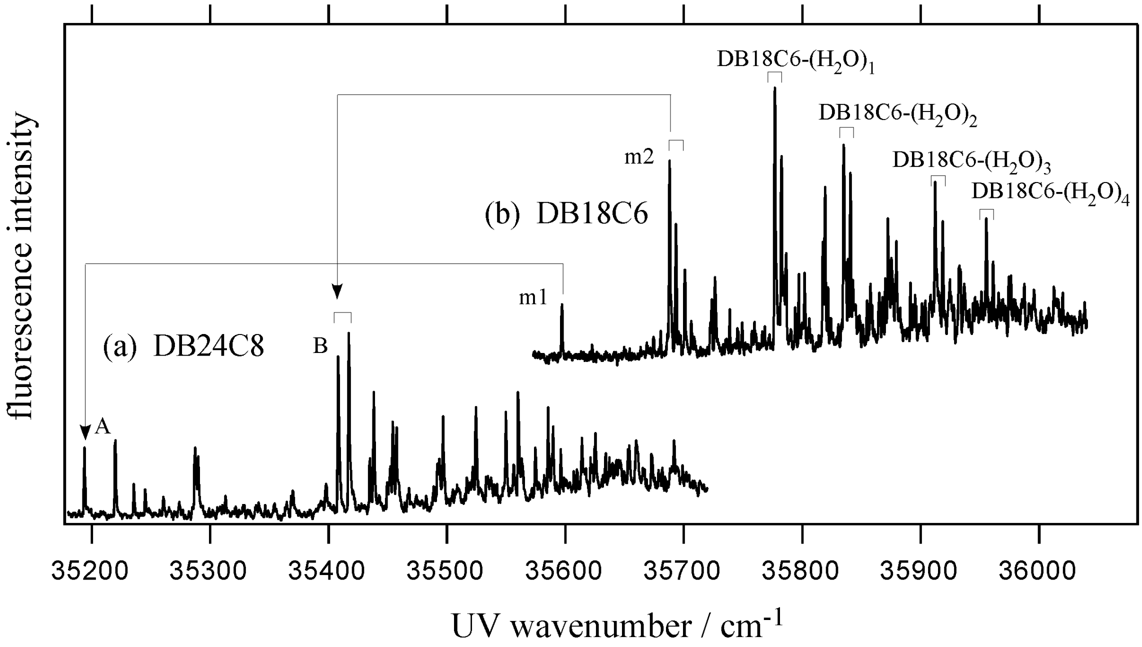


Fig. 4 (a) LIF spectrum of jet-cooled DB24C8. (b) LIF spectrum of jet-cooled DB18C6 and DB18C6-(water)$_n$ complexes.

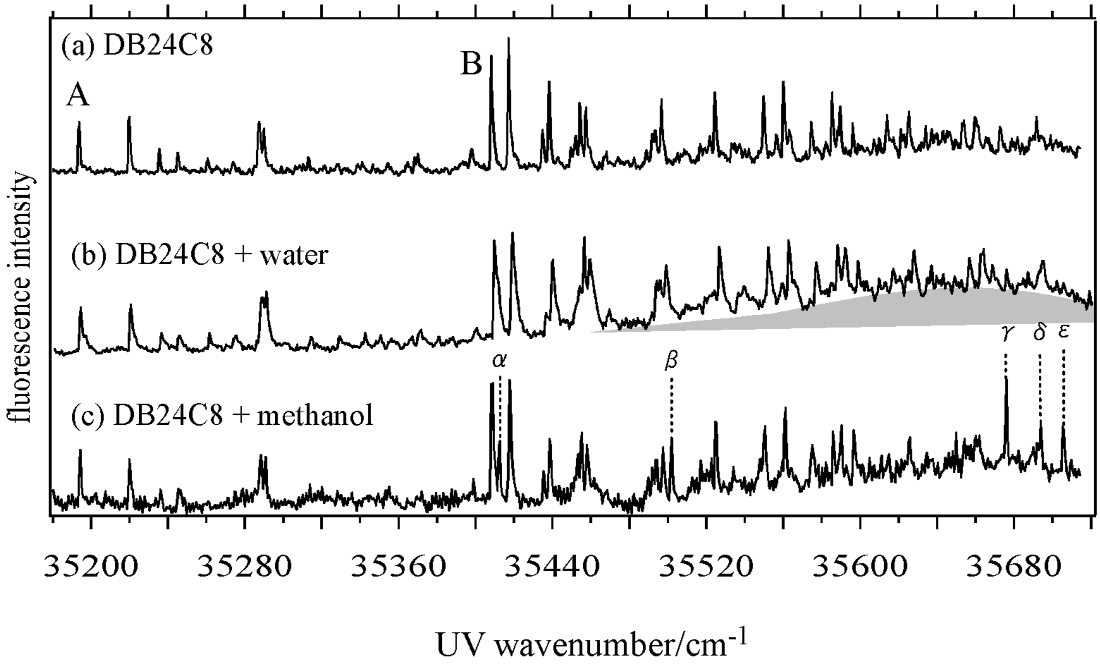


Fig. 5 (a) LIF spectrum of jet-cooled DB24C8. (b) LIF spectrum of jet-cooled DB24C8 observed by adding water vapor. (c) LIF spectrum of jet-cooled DB24C8 observed by adding metanol vapor.

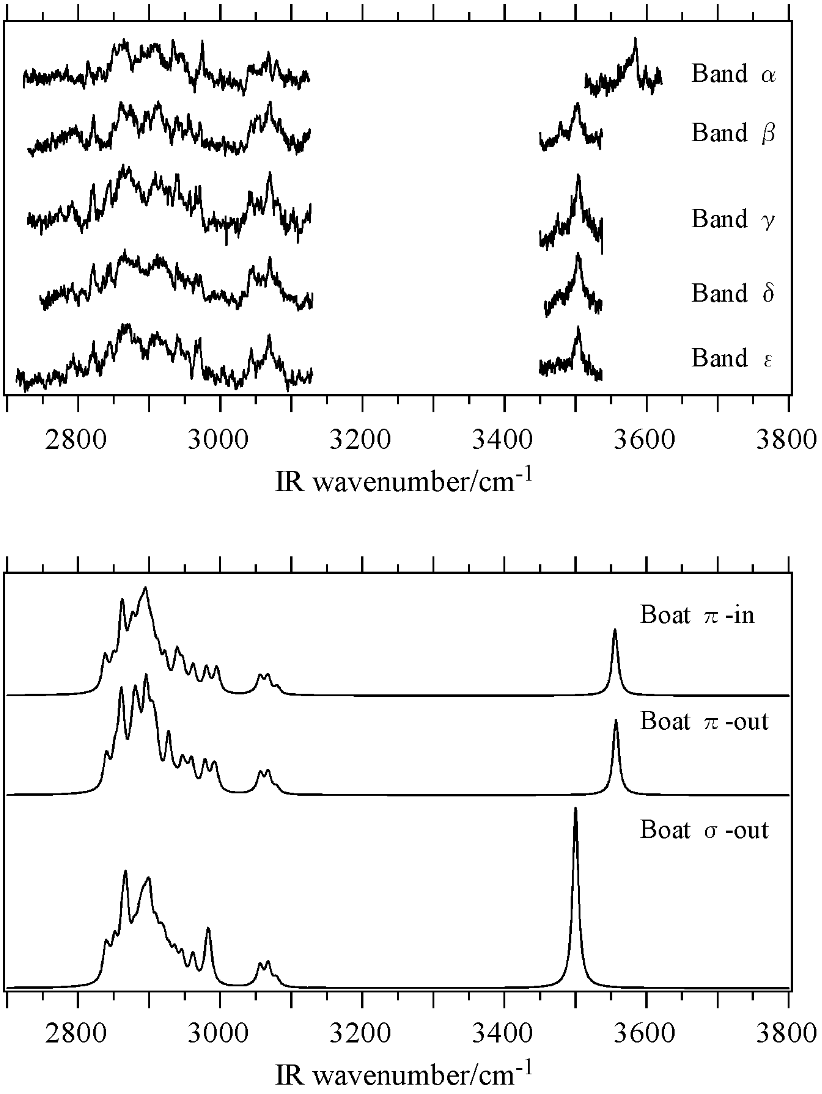
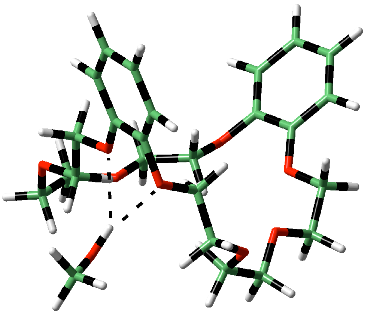


Fig. 6 (Upper) IR-UV DR spectra of DB24C8-methnaol observed by monitoring bands α–ε in the LIF spectrum of Fig. 5(c). (Lower) Calculated IR spectra for the isomers of "boat DB24C8"-(methanol)$_1$ complex in Fig. 7.

(a) Boat DB24C8-(methanol)$_1$ π-In

(b) Boat DB24C8-(methanol)$_1$ π-Out



(c) Boat DB24C8-(methanol)$_1$ σ-Out

Fig. 7 Energy optimized structures the “boat DB24C8”-(methanol)$_1$ complex obtained by DFT calculation at B3LYP/6-31+G* level.