

**Experiment title:**

Conformational transitions and permanent dipole moment of organic macrocycles

**Experiment number:**

SI-1889

**Beamline:**

ID 32

**Date of experiment:**

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to:

30/06/2009

**Date of report:**

12/01/2010

**Shifts:**

18

**Local contact(s):**

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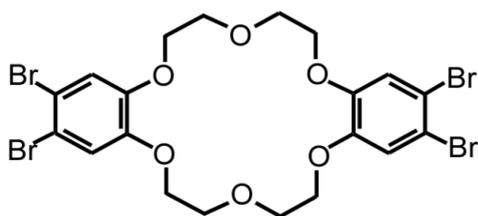
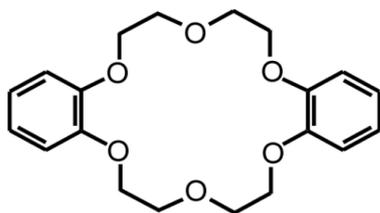
*Chiba University, Graduate School of Advanced Integration Science, Japan***Report:****1. Introduction**

Figure 1: Chemical structure of (from top to bottom) dibenzo-18-crown-6 (DB18C6) and tetrabromide DB18C6 (Br4DB18C6).

As described in the proposal, the purpose of the experiments at ID32 was to measure the bonding distances and possible conformations of dibenzo-18-crown-6 (DB18C6) and tetrabromide DB18C6 (Br4DB18C6) on Cu(111). The X-ray standing wave (XSW) measurements were performed to complement existing experimental and theoretical studies on the electronic structure of these large macrocyclics and to establish a fundamental understanding of the molecular conformation of flexible macrocyclic molecules on Cu(111). In particular, we were interested in how the flexible ether ring, the rigid benzene ring, and the halogen substituent (Br) influence the adsorption geometry of the molecules.

After controlled preparation of the organic films in the UHV chamber at ID32 we were able to take high quality XSW data on Cu(111). Below we give a short summary of results from our beamtime SI-1889.

## 2. XPS measurements on monolayers of DB18C6 and Br4DB18C6 on Cu(111)

Several films of DB18C6 and Br4DB18C6 with coverages between a sub-monolayer and a monolayer were prepared and characterized in detail by XPS and XSW. For both adsorbate systems we measured the carbon C(1s) and the oxygen O(1s) core-level signals; for Br4DB18C6/Cu(111) we also used the Br(3s) or Br Auger(LMM) signal. To characterize our samples before the XSW measurements high-resolution XPS spectra were taken, see Fig. 2. Unexpectedly, we found that the O(1s) – and to a smaller extent also the C(1s) spectra – of DB18C6 exhibit characteristic X-ray induced changes, while the Br4DB18C6 spectra do not alter significantly under the same conditions. This finding suggests that the adsorption geometry of DB18C6 may change due to irradiation with X-rays and that the adsorbate may be stabilized by introducing Br atoms.

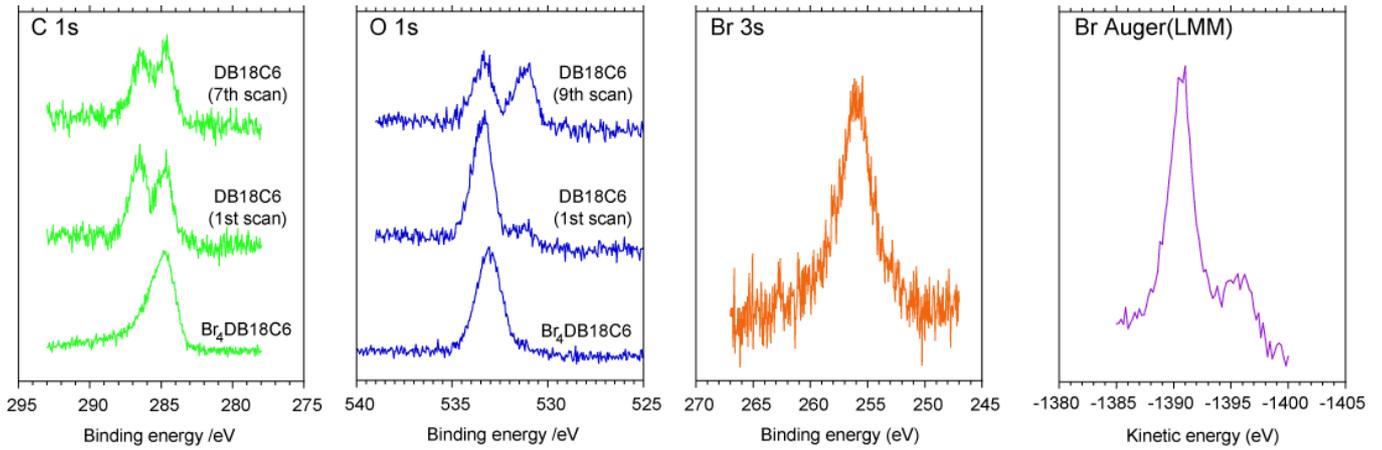


Figure 2: High-resolution XPS spectra measured on a sub-monolayer of DB18C6 and Br4DB18C6 on Cu(111). All depositions were done at a constant substrate temperature of  $T=40$  °C. For DB18C6 molecules we found major (minor) characteristic changes in the O(1s) (C(1s)) spectra due to the exposure to the X-ray beam, whereas for Br4DB18C6 molecules no such effect was observed..

## 3. XSW measurements on monolayers of DB18C6 and Br4DB18C6 on Cu(111)

After several sputtering and annealing cycles the Cu(111) crystal used in the experiment showed a suitable reflectivity curve (FWHM 0.9 – 1.1 eV in back-reflection geometry) [1,2]. The variation of the photo electron yield  $Y_p$  around the Bragg peak at  $E_{\text{Bragg}}=2.97$  keV was measured to derive the coherent positions  $P_H$  and coherent fractions  $f_H$ , see Fig. 3. The corresponding parameters for DB18C6 and Br4DB18C6 on Cu(111) collected in Tab. 1 were used to calculate the average bonding distances  $d_H$  of the molecules.

	DB18C6		Br4DB18C6		
	C(1s)	O(1s)	C(1s)	O(1s)	Br(3s) and LMM
$f_H$	$0.20 \pm 0.06$	$0.27 \pm 0.04$	$0.08 \pm 0.03$	$0.21 \pm 0.03$	$0.86 \pm 0.08$
$P_H$	$0.17 \pm 0.08$	$0.68 \pm 0.08$	$0.54 \pm 0.04$	$0.46 \pm 0.05$	$0.94 \pm 0.03$
$d_H$	2.55 or 4.63 Å	3.49 Å	3.21 Å	3.05 Å	1.95 Å

Table 1: Summary of X-ray standing wave results for DB18C6 and Br4DB18C6 on Cu(111). For DB18C6 the XSW results of the fresh spot shown in Fig 3. are excluded for this summary.

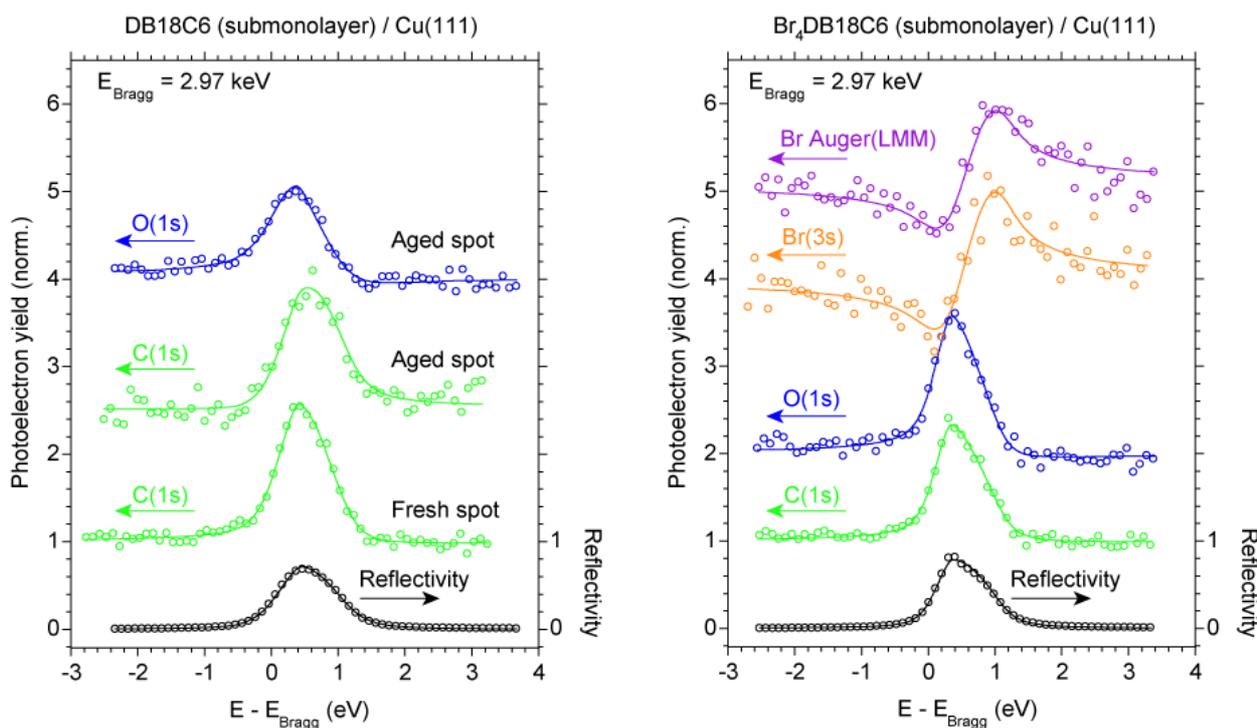


Figure 3: X-ray standing wave scans obtained on DB18C6 (left) and Br<sub>4</sub>DB18C6 (right) on Cu(111). The black and the coloured open circles represent the reflectivity data and the photo electron yield, respectively. XSW of DB18C6 was measured several times on the same spot since we found a time dependence of XPS spectra of C1s and O1s as shown in Fig. 2, while Br<sub>4</sub>DB18C6 films were stable.

Because of the complex spectral changes described above a final interpretation of the XSW data taken on DB18C6 films is not yet available. However, the XSW data of Br<sub>4</sub>DB18C6 films are easier to understand and show themselves some interesting features. For example, the coherent fractions  $f$  of the atoms in the molecule differ significantly: While for bromine we find  $f \approx 0.9$ , the corresponding parameters for oxygen and especially carbon are much smaller. This finding can be reasonably understood by taking into account the zigzag conformation of the ether ring in the free Br<sub>4</sub>DB18C6. The Br bonding distance of 1.95 Å, which is similar to the value reported for Br adsorption on Cu(111) [3], indicates a strong (local) interaction with the substrate. Possibly the strong bonding between the Br and the substrate atoms increases the stability of Br<sub>4</sub>DB18C6 films compared to DB18C6 molecules on Cu(111). In this case bromine substitution seems to promote stable adsorption of the macrocyclic molecules.

A manuscript with these results for DB18C6 and Br<sub>4</sub>DB18C6 on Cu(111) is in preparation. We wish to thank our local contact for the excellent support on ID32.

#### 4. References

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