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Photoemission study of pristine and potassium intercalated benzylic amide [2]catenane films

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Abstract

In this paper we report a photoelectron spectroscopy (XPS and UPS) study of films of a benzylic amide [2]catenane on Au(111). We show that this molecule retains its molecular integrity during sublimation and that it chemisorbs on the metal surface. Potassium intercalation modifies the electronic structure of the films. We have observed a reduction of its amide functions and a modification of the charge density of the aromatic rings. The creation of polaron-like states in the gap of the neutral catenane and a decrease in the catenane work function of 0.8 eV have been demonstrated. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In recent years, new synthetic developments have made possible the preparation of molecules with non-trivial molecular-level architectures and

topologies [1–5]. Catenanes, supramolecular species composed of interlocked rings, by right belong to this arena and have been the focus of the concerted effort carried out by many important laboratories worldwide. The fundamental, and as yet unanswered question, arising from the newly acquired synthetic capabilities is whether these species, either as a class or individually, can have an impact in the real world as parts of devices whose design and construction would not be accomplished without their exploitation. Several of the interlocked structures prepared so far display the ability to change the relative positions of their component parts, i.e., macrocyclic rings (see Fig. 1) under the effect of an external stimulus. In particular, both solvents and temperature variations

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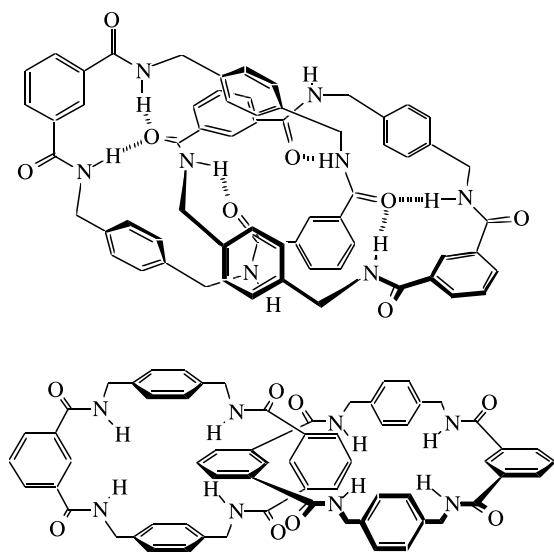


Fig. 1. Schematic drawing showing the X-ray crystal structure of the [2]catenane from Ref. [3]. Below, the idealised structure illustrating the interlocking of the macrocycles is presented.

affect the dynamics of the special degree of freedom unique to the catenanes, that is, the rotation of one ring inside the cavity of the other, also known as circumrotation. To date rather comprehensive work has been performed with the intent of characterising various types of catenanes [6–9]: in solution it was shown that the circumrotation rate of the macrocycles in benzylic amide catenanes can change over several orders of magnitude [10]. Control of this motion is of great importance if one wants to exploit the circumrotational activity in practical applications. Ceroni et al. [11] progressed in this direction by studying the original benzylic amide catenane electrochemically. Analysis of the kinetic data showed the existence of a reaction that was ascribed to the intra-molecular inter-ring soldering of the two macrocycles at the carbon atoms of two reduced carbonyls. Such process might provide a useful way of switching “on” and “off” the dynamics of circumrotation in devices and prompted us to try to understand the general effect of injecting charges into this system, which in the following will be called C1 or the original catenane. With possible future practical applications in mind, our work was carried out on films, where the circum-

rotational dynamics must be partly inhibited because of the hydrogen bonds between different catenanes. This is a novelty because, in its near totality, previous effort was performed in solution and only a very small fraction of the work was concerned with the solid state properties. The fundamental gap due to the lack of solid state characterisation, which is the first mandatory step towards real applications, is partially bridged in this paper. First, we studied the interface between the catenane and the Au(111) with X-ray photoelectron spectroscopy (XPS) to determine the adsorption mode of this molecule. Then we dosed potassium onto a catenane film and characterised the changes that occur in the electronic properties of the film. XPS and ultraviolet photoelectron spectroscopy (UPS) were used to investigate those changes.

2. Experimental

The catenane studied in this work is [2] (1,7,14,20-tetraaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzocyclohexacosane)–(1',7',14',20'-tetraaza-2',6',15',19'-tetraoxo-3',5',9',12',16',18',22',25'-tetrabenzocyclohexacosane) which was synthesised as described in Ref. [3]. The X-ray crystal structure of the [2]catenane and the idealised structure illustrating the interlocking of the macrocycles are shown in Fig. 1.

The photoemission experiments were performed in a two-chambers ultrahigh-vacuum system equipped with an ESCA SCIENTA-300 spectrometer and an Omicron VUV HIS 13 He discharge lamp. The base pressure in the analysis and preparation chambers was 1×10^{-10} and 8×10^{-11} Torr, respectively. The typical energy resolution in our experiments was 0.60 eV in XPS and 150 meV in UPS. All spectra presented in this paper were obtained using light from the monochromatised Al K α line (1486.6 eV). The UPS results were obtained using the HeI (21.21 eV) and HeII (40.8 eV) lines.

The substrate, an Au(111) single crystal, was cleaned by cycles of Ar $^{+}$ -ion sputtering and annealing until no more contaminants could be detected by XPS and a sharp LEED pattern with the characteristic $23 \times \sqrt{3}$ “herring bone” recon-

struction was observed. The catenane was sublimed at about 220°C from a Knudsen cell with a quartz crucible topped with a 2 mm stainless steel collimator. The cell was previously outgassed at about 150°C for 90 min then at 200°C for 15 min. The deposition rate was monitored by a quartz microbalance assuming a density of 1.3 g/cm³ [3] for the solid catenane, and amounted to about 1 Å/min. During the deposition, the substrate was held at 100°C. The potassium was sublimed from a well outgassed SAES getter source, the pressure rise to 2×10^{-10} Torr during K deposition was basically due to hydrogen developing from the getter source. Its coverage was calibrated by recording the photoelectron peak ratios of the K2p to the Au4d5/2 as a function of deposition time. A coverage corresponding to the first change in the slope of this ratio is defined as 1 monolayer (ML) for the purpose of this work.

3. Results and discussion

3.1. Clean catenane films

The catenane studied in this work decomposes when heated in air. It was therefore necessary to check that the sublimation described above does not damage the catenane. In order to do this, we have grown films of different thickness. In the general survey XPS spectra of these films, recorded in normal emission geometry (take-off angle (TOA) equal to 90°), the only detectable elements are carbon, oxygen, nitrogen and gold. We have measured the areas of the C1s, O1s and N1s core level peaks which, corrected by their relative sensitivity factors, enabled us to calculate the stoichiometry of these films. The results are summarised in Table 1. One can see that there is a very good agreement between the expected values and the measured ones. This gives strong support to the hypothesis that the catenane sublimes in UHV without degradation.

In Fig. 2 we show the photoemission spectra corresponding to the C1s, the O1s and the N1s core levels of a catenane film which is thick enough to obscure the interaction with the substrate (see below) but thin enough not to show any charging

Table 1

Calculated carbon, oxygen and nitrogen content of three films of different thickness (as measured by quartz microbalance) compared to the expected one

	Carbon (%)	Oxygen (%)	Nitrogen (%)
Expected stoichiometry	80	10	10
Film 1 (24 Å)	81	9	10
Film 2 (200 Å)	82	8	10
Film 3 (6 Å)	82	9	9

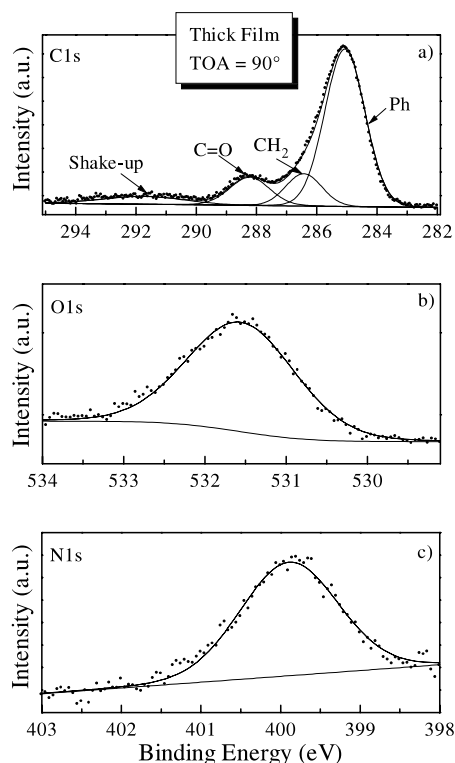


Fig. 2. XPS spectra of the (a) C1s, (b) O1s and (c) N1s levels recorded with a TOA of 90° on a thick film of catenane. The dots represent the experimental data and the lines are the results of the fitting procedure.

effect when exposed to the X-rays. We shall refer to such samples in the following as thick films. By applying a fitting procedure, which uses a linear combination of a Gaussian and a Lorentzian for each component, one can see that four components are needed to fit the C1s feature (full lines in Fig. 2a). The different peaks can be assigned as follows: the component at 285.1 eV corresponds to

aromatic carbons (indicated as Ph in Fig. 2a), the one at 286.4 eV to aliphatic carbons linked to the nitrogen of an amide function (indicated as CH₂ in Fig. 2a), the one at 288.2 eV to carbonyl functions (indicated as C=O in Fig. 2a) and the one at 291.7 eV is the shake-up feature associated to the aromatic rings. The ratio between all these components matches exactly the chemical structure of the catenane. Concerning the O1s and N1s levels (Fig. 2b and c), only one component, for each type of atom, positioned at 531.6 eV and 400.0 eV, respectively, is needed to fit the spectrum. Indeed, all the oxygen and the nitrogen atoms in the catenane are chemically identical. We thus conclude that the catenane is stable when sublimed at 220°C in UHV and adsorbs molecularly.

In order to establish the adsorption mode of the catenane molecule on the Au(111) surface a thin film has been grown and its XPS spectrum has been recorded with a TOA of 90°. The quartz microbalance for this evaporation indicated a thickness of 6 Å. However, if we estimate the thickness of this layer from the attenuation of the Au4f peaks, assuming a mean free path of 33 Å (deduced from the universal curve for the electron mean free path), we find 3 Å. We therefore conclude that this coverage is less than 1 ML. The C1s, O1s and N1s regions of the XPS spectra recorded on this thin film are presented in Fig. 3. The O1s and N1s photoelectron peaks have been fitted with two components each as shown in Fig. 3b and c. The intensity ratio between the two components in each spectrum results 73.5%/26.5%. The larger component is situated at 531.1 eV for oxygen and 399.4 eV for nitrogen, respectively, and corresponds to amide functions in the “bulk” (indicated as B in Fig. 3b and c). The binding energy for these components is lower than that measured for the thick film (Fig. 2) because the screening of the core hole by the gold image charge is more efficient in a thinner film [12].⁴ The new

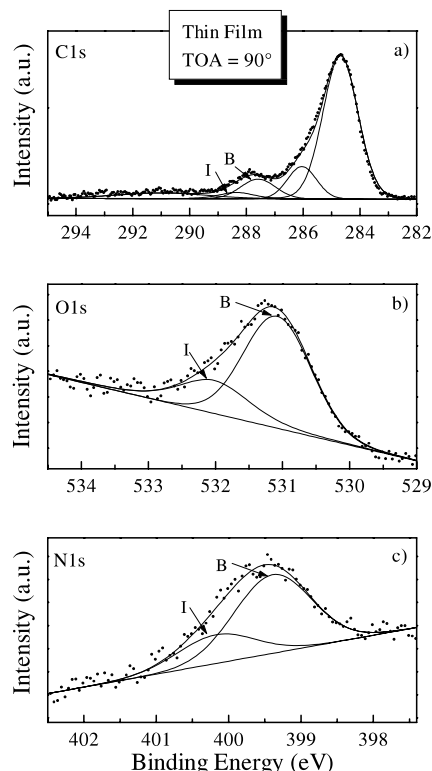


Fig. 3. XPS spectra of the (a) C1s, (b) O1s and (c) N1s levels recorded with a TOA of 90° on a thin film of catenane. The dots represent the experimental data and the lines are the results of the fitting procedure. The letter B indicates the bulk components and the letter I the interfacial components.

small component (indicated as I in Fig. 3b and c) is positioned at higher binding energy, at 532.0 eV for oxygen and at 400.2 eV for nitrogen. The appearance of a new component can be seen also in the C1s spectrum (Fig. 3a), where two peaks are needed to reconstruct the spectral features in the carbonyl region. We note that a good reconstruction of the spectrum is found when the intensity ratio of these two components is set to the same value as for the oxygen and the nitrogen peaks. The larger carbonyl C1s peak is situated at 287.7 eV and the smaller one at 288.5 eV. The total intensity of the two carbonyl components taken together amounts to the same proportion of the total C1s intensity as in the thick film, indicating that the chemical structure of the adsorbate is still that of the pristine catenane.

⁴ Final-state screening by the image charge is a well known phenomenon in photoemission and leads to the observation of distance-dependent shifts in the XPS line position as first shown by Kaindl et al. for adsorbed rare-gas atoms. G. Kaindl, T.-C. Chiang, D.E. Eastman and F.J. Himpsel, Phys. Rev. Lett. 45 (1980) 1808.

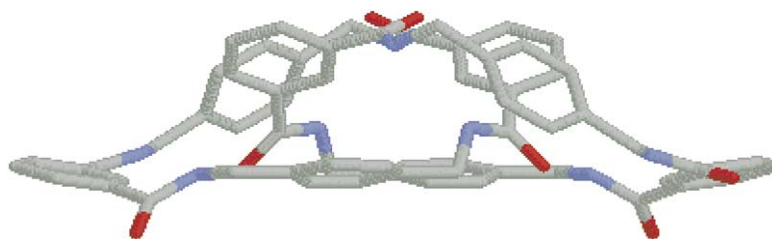


Fig. 4. Structure of a chemisorbed catenane on Au(111) as determined by MM3 calculations. The grey parts indicate carbon atoms, red parts correspond to oxygen atoms and blue parts represent nitrogen atoms, hydrogen atoms are not shown.

These new components in the C1s, N1s and O1s regions of the XPS spectrum are associated to interfacial amide functions that are chemisorbed on the Au(111) whose existence was already inferred on the basis of HREELS experiments [13]. An amide function can be adsorbed in many ways [14] and it is quite difficult to determine the adsorption geometry only on the basis of the XPS results. The higher binding energy of the components corresponding to adsorbed amide groups compared to that of “bulk” amides suggests a bond formation between catenane and gold in which electron transfer occurs from the amide to the metal surface. However, we cannot discriminate between a situation where only oxygen is linked to the surface and a situation where both the oxygen and nitrogen atoms of the amide groups are attached to gold atoms. In fact, in the first case the bonding involves probably the lone pairs of the oxygen and the empty orbital of the metallic surface as seen for the adsorption of acetone on Pt(111) [15]. We should thus observe a component at higher binding energy not only in the O1s spectrum because the oxygen has lost electrons but also in the C1s and N1s spectra because this loss of charge can be propagated through the whole amide group due to the conjugation. In the second case where both oxygen and nitrogen atoms are bound to gold, we should also observe new components situated at higher binding energy in the O1s, N1s and C1s spectra. In any event, when the oxygens and the nitrogens are attached to gold by their lone pairs, the loss of charge is felt by the entire amide group.

We performed molecular mechanics calculations using the MM3 method [16–18] to determine the most stable conformation of a chemisorbed

catenane on Au(111) [19]. A gold cluster of three layers for a total of 601 atoms was thought sufficient to account for the whole system. We made the hypothesis that the catenane was chemisorbed only by the oxygens of some amide groups. Calculations were performed with one, two and three Au–O linkages. The most stable structure proved to be the one presented in Fig. 4 with two oxygen atoms linked to the gold surface. There are thus two carbonyl groups out of eight that interact with the gold. This gives a ratio of 75/25 between the free C=O and the chemisorbed one. As mentioned above, with XPS we have determined a ratio of 73.5/26.5, which is in very good agreement with the ratio obtained by the calculations.

3.2. Intercalated catenane films

We have studied the evolution of the C1s, O1s and N1s photoemission peaks with increasing potassium coverage. Fig. 5 shows the C1s spectra of a thick film recorded with a TOA of 90°, the potassium coverage is expressed in ML units. One observes a shift of the spectra towards higher binding energies when the thickness of the potassium layer increases and the appearance of a new component. The shift occurs in steps and amounts to a total of about 1.6 eV as can be seen comparing the pristine film and the one with 0.9 ML of potassium. Since we could model the spectra collected after K deposition with the same peak shapes as those of the pristine film (except of course for the new component), we can assume that, in first approximation, the screening of the final state has not changed. Therefore the shift can be explained by the combined effect of the decrease

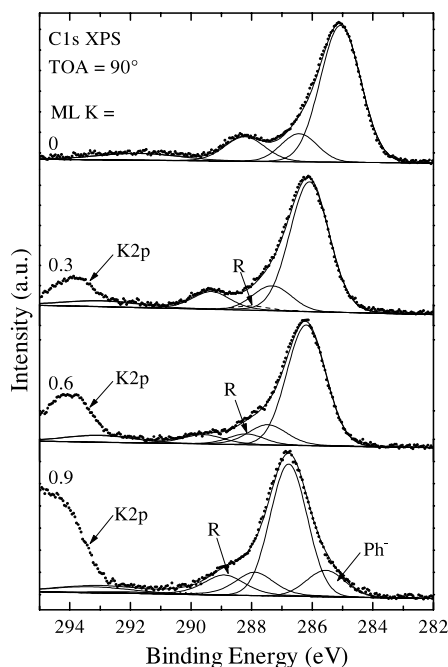


Fig. 5. Evolution of the XPS spectra of the C1s level with potassium deposition expressed in ML. The letter R indicates the reduced component of the amide functions and Ph⁻ shows the component associated to aromatic rings which have received electrons from the potassium. The dots represent the experimental data and the lines are the results of the fitting procedure.

in work function (discussed in connection with the UPS below) and the change in contact potential between the organic film and the metal substrate. Both changes are due to the electron transfer from the potassium to the catenane, but the change in contact potential will occur only if K diffuses throughout the whole film and reaches the organic/metal interface, as in our case (see below). This explanation is further confirmed by the fact that the shift is also observed for the spectra of the O1s and N1s levels (see Figs. 6 and 7) but not for the Au4f level. One should remark that we have assumed that the Fermi level of the catenane film and the one of Au(111) are aligned since we did not observe any charge effect and we could still see the Fermi level of the Au(111) on the UPS spectra of these samples.

A second consequence of potassium deposition on the C1s spectra (Fig. 5) is the appearance of a

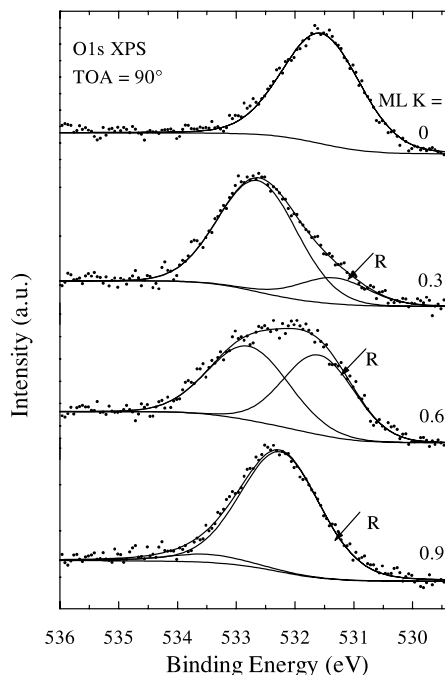


Fig. 6. Evolution of the XPS spectra of the O1s level with potassium deposition expressed in ML. The letter R indicates the reduced component of the amide functions. The dots represent the experimental data and the lines are the results of the fitting procedure.

new component (indicated as R in Fig. 5) at the low binding energy side of the carbonyl feature (288.2 eV), which can be assigned to amide functions reduced by potassium. The intensity of this component increases with the potassium coverage and dominates at 0.9 ML of potassium showing that almost all of the amide functions have been reduced. Finally, in the spectrum corresponding to 0.9 ML of potassium an additional shoulder (285.5 eV) becomes clearly visible at the right-hand side of the aromatic component. It can be attributed to aromatic rings which have become more electron rich as a consequence of the reduction of the amide functions linked to them. This interpretation is confirmed by EELS results obtained on similar samples where changes occurred in the $\pi-\pi^*$ on the benzene rings upon potassium doping [19]. We note that we did not include this new component in the modelling of the spectra for the lower potassium coverages because it was not necessary to

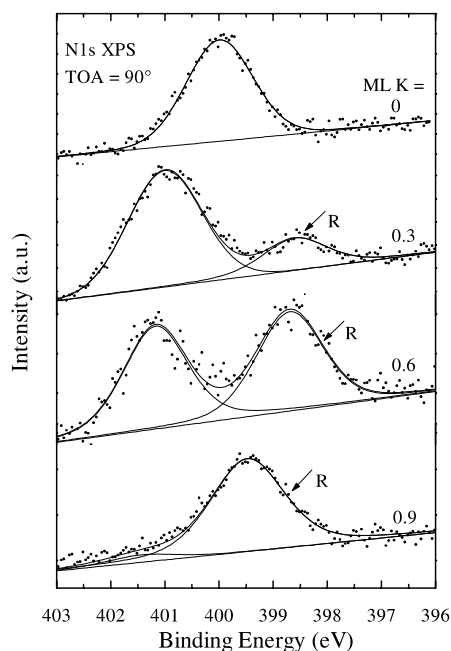


Fig. 7. Evolution of the XPS spectra of the N1s level with potassium deposition expressed in ML. The letter R indicates the reduced component of the amide functions. The dots represent the experimental data and the lines are the results of the fitting procedure.

reconstruct the spectra. However, this does not exclude that this component could already be present at low K coverages.

Similar results are obtained for the O1s and N1s photoelectron spectra shown in Figs. 6 and 7, respectively. Apart from the shift of 1.6 eV towards higher binding energies, a new component appears at low binding energy in each spectrum and becomes dominant for a potassium coverage of 0.9

ML. This shows clearly the reduction of the amide functions by the potassium.

From the areas of the photoelectron peaks of the C1s, O1s, N1s core levels (Figs. 5–7) and of the K2p core levels (not shown in this paper) we have calculated the number of potassium atoms per catenane in the different samples. By comparing the areas of the reduced and the non-altered components of the N1s spectra, we also deduced the percentage of reduced amide functions. We preferred the N1s level for this estimate since it presents more resolved components than the O1s or the C1s bands. The results are summarised in Table 2. These values are, of course, average values for the whole film since some catenanes will be totally reduced, others just partly, others still will not have interacted at all with potassium. One observes that after deposition of 0.9 MLs of potassium, almost all of the amide functions have been reduced. The total number of amide functions in this catenane is 8. The last two columns of Table 2 indicate how many of them are reduced per catenane, as observed for the two TOAs. If we compare the values at TOA = 90° with the number of potassium atoms per catenane, we see that the number of reduced amide functions is always larger than the number of potassium atoms. Moreover, we know from the XPS data (see above) and from EELS data [19] that the aromatic rings are also influenced by potassium. One way of rationalising this result, is to consider that one potassium atom influences, or effectively reduces, more than one amide group. The electron donated by potassium becomes delocalised over the conjugated part of the catenane, i.e. the isophthaloyl moiety, or, in other words, the phenyl ring with

Table 2

Average stoichiometry of the different samples calculated for a TOA of 90° and 15° on the basis of C1s, O1s, N1s and K2p levels compared to the percentage of reduced amide function and to the number of reduced amide function per catenane for different K depositions expressed in equivalent monolayers as deduced from the deposition time (see text)

Quantity of K (ML)	Average stoichiometry		Percentage of reduced amide		Number of reduced amide per catenane	
	TOA = 90°	TOA = 15°	TOA = 90°	TOA = 15°	TOA = 90°	TOA = 15°
0.3	K _{1.5} cat	K _{0.9} cat	22	11	1.8	0.9
0.6	K _{3.3} cat	K _{2.1} cat	49	35	3.9	2.8
0.9	K _{6.2} cat	K _{5.2} cat	93	89	7.4	7.1

two amide groups in meta position. As a consequence, only half of the phenyl rings are involved in the reduction, and the *p*-xylyl groups, which are isolated from the amide functions by two sp^3 carbons, are not influenced by potassium.

In Table 2 we also compare the percentages of reduced amide functions as calculated on the basis of spectra recorded with a TOA of 15° (not shown here) to those obtained for a TOA of 90° . The measurements collected with a TOA of 15° are more surface sensitive and therefore give information about the outermost layers while the data collected with a TOA of 90° contain information from the whole film. We can see that the number of potassium atoms per catenane is always larger for a TOA of 90° , indicating that the potassium diffuses into the film. The quantity of reduced amide groups is also larger in the bulk and this shows that potassium reacts not only at the surface but also after having diffused into the film. A similar phenomenon has been observed in the case of other organic materials on which alkaline earth metals were deposited and was explained by a breaking of weak bonds in the films due to energy of condensation given by the hot metal atoms impinging on the film [20].

A valence band study using UPS has also been performed. Figs. 8 and 9 present respectively the UPS HeI and HeII spectra recorded on the same samples used in the XPS study. When one starts dosing potassium on the catenane film, several changes occur. Firstly, there is a shift of all the spectra toward the high binding energies, both for HeI and HeII. It occurs in steps and amounts to a total of about 1.6 eV (1.3 eV then 0.3 eV). The origin of this shift is the same as for the shift observed in the core level spectra: a decrease in the work function of the catenane film and a change of the contact potential at the organic/metal interface. Secondly, a new spectral feature appears in the gap of the neutral catenane at around 2.9 eV in the HeI spectra. This peak is assigned to a polaron-like state created because of the electron transfer from the potassium to the catenane. If one compares the general shape of the spectra in Figs. 8 and 9, one observes that those recorded with HeI photons (Fig. 8) are quite strongly affected by potassium deposition while those recorded with

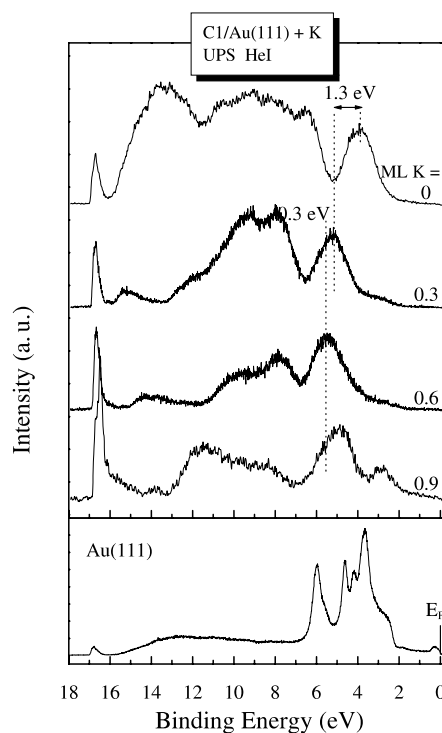


Fig. 8. Evolution of the UPS spectra recorded with HeI radiation with potassium deposition expressed in ML. The bottom panel shows the UPS spectrum of the clean Au(111). All the spectra are aligned with respect to the Fermi level of the Au(111). The dotted lines show the gradual shift of the spectra (1.3 eV then 0.3 eV).

HeII photons (Fig. 9) show only very minor changes. Since HeI probes mainly the p orbitals while HeII gives information on the s orbitals, this demonstrates that the π electronic structure of the catenane is strongly affected by the potassium but not the σ -electron structure. One should note that the peak situated near 2.7 eV in Fig. 9 is not a feature arising from the potassium doping but results from the 5d levels of the gold substrate as one can see by looking at the spectrum of clean Au(111) plotted at the bottom of Fig. 9.

Finally we measured the work function by recording UPS spectra with HeI photons on these same samples but with a bias voltage. We found values of work function of 4.5 eV for the pristine catenane film and of 3.7 eV for the intercalated films. This decrease in work function is another proof of the charge transfer from the potassium to

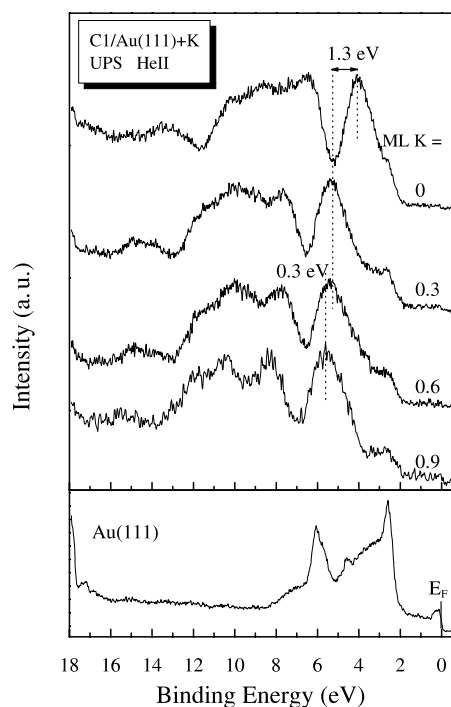


Fig. 9. Evolution of the UPS spectra recorded with HeII radiation with potassium deposition expressed in ML. The bottom panel shows the UPS spectrum of the clean Au(111). All the spectra are aligned with respect to the Fermi level of the Au(111). The dotted lines show the gradual shift of the spectra (1.3 eV then 0.3 eV).

the catenane. Furthermore, if we compare the work function change of 0.8 eV for the intercalated films with the binding energy shift of 1.6 eV observed in all photoemission spectra we can conclude that the contact potential at the organic/metal interface must have changed as well and this is a further proof of the diffusion of K through the whole film.

4. Conclusion

With the help of core level photoelectron spectroscopy, we have shown that it is possible to sublime a benzylic amide [2]catenane (C1) without decomposition and that the films prepared by this method were composed of intact catenanes. The XPS study of a very thin film of catenane supported by theoretical calculations indicated that

the catenane (C1) is chemisorbed on the Au(111) surface by two amide functions. The question whether this adsorption occurs only via the oxygen or via the oxygen and the nitrogen of these moieties remains still open.

The combined XPS and UPS study of the potassium intercalated films showed that the potassium is indeed able to reduce the amide functions. The intercalation induces a decrease of the work function of the catenane and the appearance of polaron-like states in the gap of the neutral catenane. We have also demonstrated that the reaction with potassium affects not only the amide functions but that the charge redistribution influences also the aromatic rings.

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