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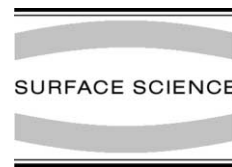
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# Effect of potassium intercalation on the electronic and vibrational properties of benzylic amide [2]catenane films

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## Abstract

The appearance of gap states in benzylic amide catenane thin films following potassium intercalation was investigated by electron energy loss spectroscopy and quantum chemical calculations. Both theory and experience find an excitation energy for transitions into these new states of  $\sim 2$  eV. The characteristics of these states are discussed.

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## 1. Introduction

Benzylic amide catenanes, BACs [1–3], are compounds with a topologically nontrivial structure made up by two interlocked macrocycles (see Fig. 1). Three fundamental reasons make BACs

appealing for experimental and theoretical investigation: (i) they can be produced in bulk quantities in a one-step self-assembly reaction [1–3], (ii) the lack of chemical bonding between the two rings enables circumrotation of one ring inside the cavity of the other [2,4], a degree of freedom unavailable in other less complicated systems, (iii) the threading can be seen as a very efficient means of bringing together a rather large number of chromophores (up to eight) in the same molecule and in a nearly globular form. Whilst other catenanes may fulfil one or more of the above [5], only BACs satisfy all three points.

Recent work has shown that the circumrotation rate of the macrocycles in BACs can vary over several orders of magnitude in solution [4]. Control of this motion is of great importance if the circumrotational action is to be exploited in

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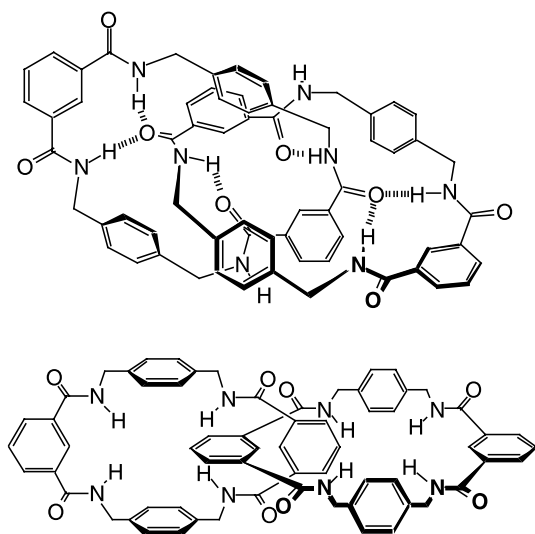


Fig. 1. Schematic drawing showing the X-ray crystal structure of the [2]catenane. Of particular interest are the bifurcated hydrogen bonds responsible for this particular molecular architecture. Below, the idealised structure illustrating the interlocking of the macrocycles is presented.

practical applications such as a solid state molecular switch. A step in this direction was the electrochemical study of the original BAC [6]. Ceroni et al. found an electrochemical behaviour peculiar to the catenane which is not observed in the parent macrocycle. The kinetic data were interpreted as evidence of an intramolecular interring reaction that soldered the two macrocycles at the carbon atoms of two reduced carbonyls. Such behaviour may provide a useful way of switching “on” and “off” the dynamics of circumrotation in devices where the movement of the mechanically interlocked components can selectively hide or reveal a particular functionality and prompted us to study the general effect of adding charges into the original isophthaloyl catenane. Understanding the anionic catenanes must, however, be considered as an initial step towards unravelling the complicated system of states born out of bringing together eight phenyl and eight carbonyl groups in the same molecule. These states are degenerate when the phenyl groups do not interact and form a band when the interaction is switched on, in this case, by the  $-\text{CH}_2-\text{NH}-$  bridges. A convenient

way to produce the anionic species in the solid state is to let the molecule interact with an alkali metal. While in a previous work [7] we established by photoemission spectroscopy that there is a chemical interaction between the catenane and potassium when the latter is dosed onto the catenane film, in this investigation, we focus on the changes in the vibrational properties and electronic transitions of the catenane film induced by the reaction with potassium. Electron energy loss spectroscopy (EELS) was used to investigate those changes and the results were compared to quantum chemical calculations.

## 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. [1]. Fig. 1 shows the X-ray structure as well as an idealised structure of this catenane.

The high resolution electron energy loss spectroscopy (HREELS) experiments were performed in a two-chamber ultrahigh-vacuum system equipped with a four grid low electron energy diffraction system which could also be used for Auger spectroscopy and a HREEL spectrometer (ISA-Riber). The latter consists of two hemispherical electrostatic selectors, one acting as monochromator, the other as analyser with an acceptance angle of  $1.2^\circ$  and allows for the energy of the incident electron beam to be varied from 0.5 eV up to 150 eV. The instrumental resolution was set at 12–15 meV for the vibrational spectra and at 0.03–0.05 eV for the study of the electronic structure. The base pressure in the analysis and preparation chambers was  $9 \times 10^{-11}$  and  $5 \times 10^{-10}$  Torr, respectively. All the spectra reported here are normalised to the total area of the spectrum. We verified that the electron beam of the HREELS did not damage the molecules: in fact, spectra taken right after deposition of the catenane film and after several hours of exposure to the electron beam are identical.

The substrate, a Au(111) single crystal, was cleaned by sputtering–annealing cycles until no contaminants were detected in the HREELS spectrum and a sharp low energy electron diffraction pattern was obtained. The catenane was sublimed in situ 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/cm<sup>3</sup> [1] for the solid catenane, and amounted to about 1 Å per minute. During the deposition, the substrate was held at 100 °C. The film thickness was estimated at about 30 Å. Previous XPS studies [7] have shown that the catenane remains intact when sublimed under these conditions. Potassium was sublimed from a well outgassed SAES getter source at a chamber pressure of  $8 \times 10^{-10}$  Torr and its coverage was calibrated by recording the Auger peak intensity ratio of the K 252 eV peak and the Au 69, 230 and 255 eV peaks as a function of deposition time on the clean Au substrate. A coverage corresponding to the first change in the slope of this ratio is defined as 1 ML for the purpose of this work.

### 3. Computational background

Calculation of electron energy loss spectra is a difficult task for any system, for a molecule of this complexity it becomes very hard indeed. Yet theory can offer a semiquantitative agreement and the possibility to provide some additional information. It was therefore decided to use a time-honoured semiempirical model, namely the CNDO/S model [8,9], to study the photon-allowed electronic transitions in the doubly charged and quadruply charged catenane. Simulation of the spectra is therefore relevant only to high-energy measurements.

The model is based on a self-consistent field calculation followed by configuration interaction in the space spanned by the  $\pi$ ,  $\pi^*$  and  $n$  orbitals. The model includes electron hole interactions explicitly in the form of Coulomb, exchange integrals [8,9]. The labels of the transitions in terms of HOMOs and LUMOs are therefore approximate,

since other excitations give partial contributions. The molecular structure of the catenane adsorbed on the Au surface was obtained by molecular mechanics calculations of the MM3 type [10–12]. The same model has been successful in the analysis of the structural information provided by temperature dependent NMR data of several BACs [13,14] and in the assignment of the inelastic neutron scattering of the present catenane [15].

## 4. Results and discussions

### 4.1. Experimental results

Fig. 2 shows the HREELS spectra (recorded in specular scattering geometry with a primary beam energy of 6 eV) of the catenane film dosed with increasing amounts of K. The potassium dose is expressed in equivalent ML coverage. One can see several losses at around 97, 135, 161, 177, 202 and 366 meV: the first four peaks correspond to deformations of the phenyl and CH<sub>2</sub> groups, the 202 meV shoulder is due to the C=O stretching mode and the 366 meV loss is ascribed to unresolved aromatic and aliphatic C–H stretchings [16–18]. We note that the NH stretching vibration around 415 meV manifests itself only as a reinforcement of

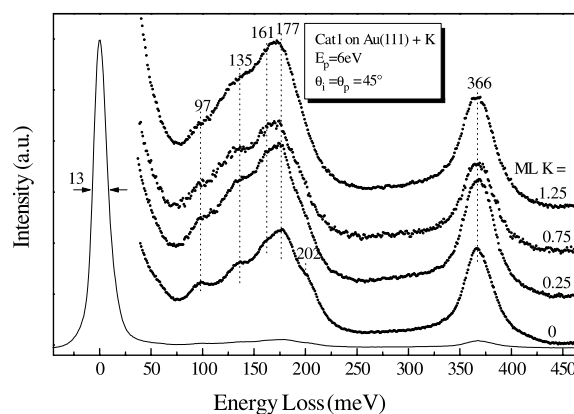


Fig. 2. HREELS spectra recorded in specular scattering geometry with a primary electron energy of 6 eV on a catenane film sublimed onto a Au(111) single crystal and exposed to increasing amounts of potassium. The potassium dose is expressed in monolayers (ML). Scaling factor = 14.

the tail of the 366 meV loss. In fact, the NH vibration is mainly excited by a dipolar scattering mechanism and therefore the intensity of the corresponding loss peak is strongly decreased by the disorder in the film [19,20]. As increasing amounts of potassium are deposited, the vibrational structure remains basically unchanged with the exception of the 202 meV band. The latter can no longer be observed. This is interpreted as signalling the reduction of the carbonyl(s) of the catenane, since formation of  $\text{CO}^-$  weakens the double bond causing a shift of the stretching peak to lower wavenumbers. Thus it becomes hidden under the broad loss structure of phenyl deformations. This interpretation agrees with a previous XPS investigation of the same system [7] which found that in a film of similar stoichiometry (0.9 ML K dosed onto a 24 Å catenane film, corresponding to about 6 K atoms per catenane) as the one with the highest potassium coverage measured here, approximately 90% of the amide functions are reduced.

Changes in the electronic transitions in the catenane film as a function of K doping have also been investigated. Fig. 3 presents the electron energy loss spectra for different K coverages recorded with an incident electron energy of 15 eV in specular scattering geometry. In the spectrum of the pure catenane four losses are observed corresponding to transitions from the highest occupied (HOMO, HOMO – 1) to the lowest unoccupied (LUMO, LUMO + 1) molecular orbitals at 3.7, 4.5, 5.6 and 6.5 eV. Interpretation of this spectrum has been discussed elsewhere [21]. In summary, the first two losses are dipole forbidden singlet–singlet transitions delocalised over the entire molecule (involving some  $n-\pi^*$  character from the  $\text{C}=\text{O}$  groups), the 5.6 eV structure corresponds to charge transfer states of the benzaldehyde type, and the 6.5 eV feature is a dipole allowed singlet–singlet transition centred on the phenyl rings ( $\pi-\pi^*$  transitions). The 2.6 eV spectral feature is the Au(111) interface plasmon which is still seen because of the long range character of the dipolar interaction and which occurs at nearly the same energy as the Au surface plasmon [22,23].

As the potassium coverage increases, important changes occur in the region of the  $n-\pi^*$  transitions

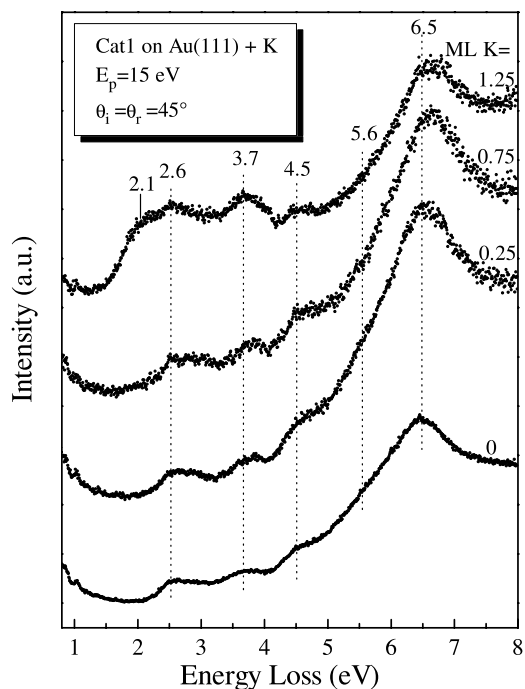


Fig. 3. EELS spectra recorded in specular scattering geometry with a primary electron energy of 15 eV on a catenane film sublimed onto a Au(111) single crystal and exposed to increasing amounts of potassium. The potassium dose is expressed in ML.

and for 1.25 ML K, one can also see a new loss at around 2.1 eV. In addition, the aromatic rings are affected by potassium as indicated by changes in the  $\pi-\pi^*$  transitions at 6.5 eV. This peak decreases in intensity and shifts to higher energy by 0.15 eV when the dose of potassium exceeds 0.25 ML.

The appearance of new low energy excitations as a consequence of doping is not unexpected, in fact, in the gas phase, doped molecules containing phenyl groups tend to have remarkably low excitations, for instance the phenoxyl radical has the first electronically excited state at 1.05 eV [24].

The HREELS observations are in good agreement with theoretical predictions obtained with the CNDO/S model [8,9] as shown in Fig. 4. In particular, to obtain a general trend, we decided to perform calculations on the bi- and tetra-anion of the title molecule, thereby avoiding the computational complexity of systems with an odd number of electrons. The rationale for this approach is that

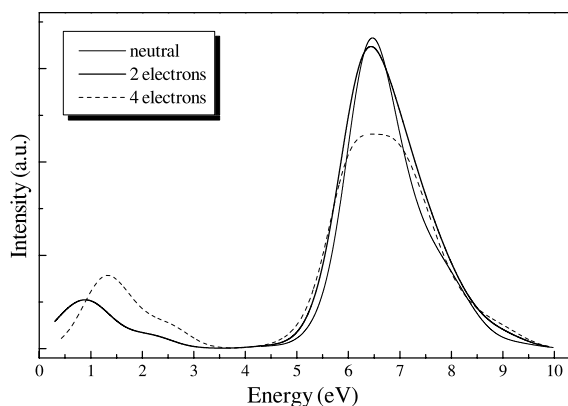


Fig. 4. Simulated CNDO/S spectrum of the photon-allowed electronic transitions in the neutral, doubly charged and the quadruply charged catenane. A gaussian broadening function was applied to simulate the experimental resolution.

the exact location of the K atoms in the doped catenane is not known and one may expect that a one-to-one distribution does not occur. Implicitly this will create some multiply charged catenanes and leave some of them in the neutral state. Such a scenario is also supported by X-ray photoemission studies on the same system [7]. The simulated spectra were obtained in the dipole moment approximation which holds exactly only for photons or high-energy electrons. Importantly, for both anions, a series of low-lying electronic states appear in the region between 1.0 and 2.6 eV. A list of the electronic state energies and their oscillator strengths is given in Table 1. These simulations are discussed further in Section 4.2 where the experimental data are compared to the calculations.

#### 4.2. The quantum chemical calculations

The spectral simulations reported in Fig. 4 qualitatively agree with experimental data. At  $\sim 2$  eV, a set of low-lying transitions appear in the gap of the neutral system in agreement with the loss observed at 2.1 eV in EELS (Fig. 3). In a qualitative picture, the states associated with them can be explained by examining the nature of the lowest unoccupied molecular orbitals of the neutral catenane that are, in turn, derived from the corresponding doubly degenerate ones of benzene: in

Table 1

Calculated electronic state energies, eV, and oscillator strengths,  $f_0$ , for the neutral, doubly charged, and quadruply charged catenane

Neutral cat.		Doubly charged cat.		Quadr. charged cat.	
Energy (eV)	$f_0$	Energy (eV)	$f_0$	Energy (eV)	$f_0$
6.232	0.82	0.485	0.72	1.197 <sup>a</sup>	2.05
6.268	0.32	1.051 <sup>a</sup>	1.43	1.256	0.26
6.282	1.04	1.714	0.25	1.516	0.64
6.305	0.59	2.293 <sup>a</sup>	0.27	1.866	0.51
6.330	1.19	5.948	1.19	2.564 <sup>a</sup>	0.53
6.338	0.69	6.005	0.71	5.177	0.44
6.365	0.66	6.144	0.34	5.812	1.04
6.372	0.36	6.185	0.68	5.868	0.33
6.401	1.00	6.207	0.68	5.885	0.31
6.490	0.36	6.236	0.30	5.933	0.60
6.580	0.64	6.269	0.45	5.988	0.55
6.728	0.40	6.288	0.38	6.045	0.36
6.761	0.37	6.342	0.55	6.202	0.83
6.786	0.35	6.393	0.71	6.276	0.31
6.865	0.47	6.402	0.32	6.706	0.52
6.988	0.49	6.513	0.33	6.708	0.52
		6.673	0.53	6.795	0.35
		6.744	0.42	6.798	0.50
		6.770	0.40	6.843	0.48
		6.860	0.33	7.094	0.31
		6.869	0.56	7.376	0.40
		7.138	0.58	7.394	0.32

Below 4.0 eV, only states with an oscillator strength larger than 0.15 are listed, above 4.0 eV only states with an oscillator strength larger than 0.30 are given.

<sup>a</sup>The transition electron density from the ground state is shown in Fig. 5.

BAC, two types of moieties with low-lying unoccupied orbitals are present: the first is the para substituted phenyl ring, the second is the isophthaloyl group which consists of a meta substituted phenyl ring conjugated to two carbonyl groups. An issue that arises concerns the effect of the presence of these eight rather similar groups on the anionic states of BAC. For instance, they can be either delocalised or localised within the molecule. Delocalisation, i.e., anionic states spread over the entire molecule, would facilitate electron transport in the solid, just as it does in conjugated polymers. According to our calculations, once the electrons are transferred from potassium, electron–electron repulsion transforms these orbitals in a rather broad band which spreads over  $\sim 2$  eV.

The higher-energy region centred at  $\sim 6$  eV is similar to that observed in the neutral system [21]. However, its structure is enriched by higher excitations of the “charging” electrons to the higher unoccupied  $\pi$  orbital of benzene. In agreement with this picture, the states of the doubly and quadruply charged catenane are calculated to be spread over a larger energy range (more interacting levels open a larger gap) and somewhat less intense (excitation between the doubly degenerate

LUMOs and the LUMO + 2 is symmetry forbidden in benzene).

The overall agreement between experimental and simulated spectra warrants further analysis of the calculations. Issues to be considered are the nature of the ground state of the anion(s) and the character of their excited states. In Fig. 5, the calculated electron density variation upon chemical reduction of two sets of charges is shown. In Fig. 5a and b the spread of charges over both

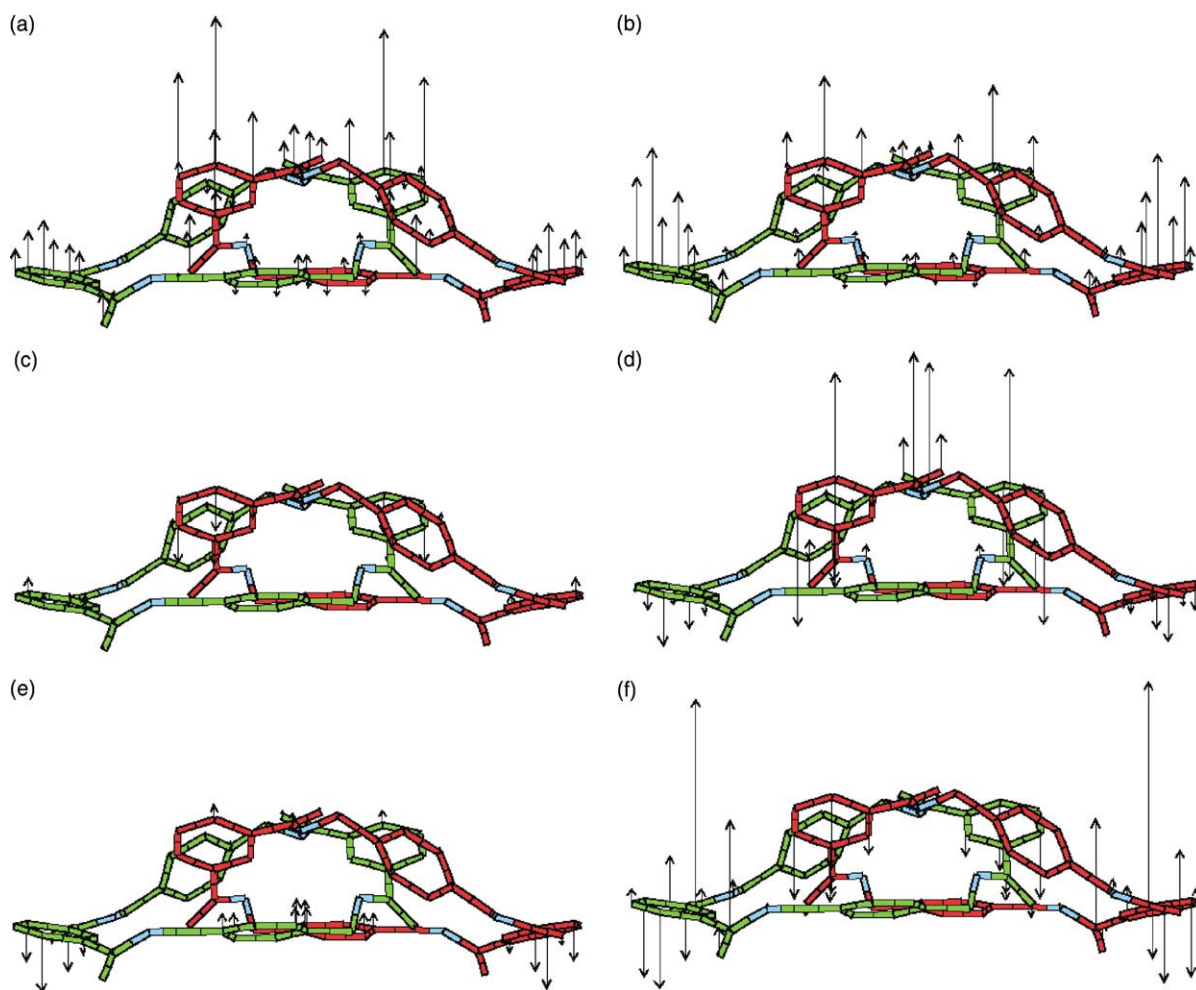


Fig. 5. Charge density variation in BAC: (a) upon injection of two electrons, (b) upon injection of four electrons, (c) upon excitation to the electronic state at 1.051 eV in the bi-anion, (d) upon excitation to the electronic state at 2.293 eV in the bi-anion, (e) upon excitation to the electronic state at 1.197 eV in the tetra-anion, (f) upon excitation to the electronic state at 2.564 eV in the bi-anion. Arrows pointing upwards represent an increase in electron density, conversely the arrows pointing downwards represent a decrease in electron density. Hydrogen atoms are not shown.

phenyl and carbonyl groups is readily identified. Lack of variation of intensity of the CO stretching band with increasing dosing of potassium supports the hypothesis that there is only partial involvement of the carbonyls. However, polarisation effects, that may be present on a surface or in the bulk, or solvent effects can effectively localise the charges on the carbonyl groups. In more detail, one can see that initially (Fig. 5a) the electrons tend to be localised on the top part of the catenane, that is in the region further away from the surface. Subsequently (Fig. 5b), the external phenyl groups that lie flat on the Au surface are reduced.

We note that BAC can adsorb on gold either through the phenyl or the carbonyl groups. The experimental adsorption energy for benzene on gold is 0.60 eV [25] while the calculated adsorption energy for the more reactive and therefore more strongly bonded HCO radical on gold is 0.58 eV [26]. These values imply that adsorption of BAC's moieties occurs via electrostatic, induction or dispersion forces which can at best polarise the molecular orbitals but hardly modify them strongly. Electronic excitation may promote charge redistribution. It is impossible to present pictures of all electronic states that contribute to the spectrum. Therefore, it was decided to provide a few case studies for states in the gap. In particular, two low-lying and two higher-energy electronic states are plotted here for each charge. At low energies, electron excitation shifts little or no charge (Fig. 5c and e). This effect can also be ascribed to the nature of the LUMO of benzene: once the electrons are added, they can freely access a band where every orbital has similar character and therefore no charge flow is observed. At higher energies, the states display (Fig. 5d and f) considerable charge flow centred on the phenyl groups. This can be taken as an indication of the breakdown of the molecular orbital picture, due to interaction between gap states and states of the neutral system.

## 5. Conclusions

We have dosed potassium onto a BAC film and studied changes that occur in the vibrational and

electronic properties of this molecule by EELS. The experimental results were compared to semi-empirical quantum chemical calculations. A consistent picture emerges in which electron transfer from potassium first populates anti-bonding molecular orbitals of benzene, with only partial occupancy of  $\pi^*$  states of the carbonyls. When the anions are excited to states that appear in the gap, the lower energy states do not modify the charge distribution of the ground state while higher excitations do. This behaviour may be of consequence for the photoconductivity of this material.

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