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Impact of potassium doping on the electronic structure of tetracene and pentacene: An electron energy-loss study

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We report the doping induced changes of the electronic structure of tetracene and pentacene probed by electron energy-loss spectroscopy in transmission. A comparison between the dynamic response of undoped and potassium-intercalated tetracene and pentacene emphasizes the appearance of a new excitation feature in the former gap upon potassium addition. Interestingly, the momentum dependency of this new excitation shows a negative dispersion. Moreover, the analysis of the C 1*s* and K 2*p* core-level excitation results in a significantly lower doping level compared to potassium doped picene, a recently discovered superconductor. Therefore, the present electronic structure investigations open a new pathway to better understand the exceptional differences between acenes and phenacene and their divergent behavior upon alkali doping. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4934263]

I. INTRODUCTION

The capability to incorporate electron acceptors and donors into molecular crystals enables to control their electronic properties by introducing charge carriers. This special ability represents a promising way for new technology as well as to study the fundamental properties of molecular crystals. It is generally assumed that the electronic properties of molecular solids are to a large extent determined by those of the individual molecular building blocks, which are only slightly modified in the solid by the weak intermolecular interactions. Nevertheless, detailed information about their electronic structure is of vital importance for both understanding of the underlying physics and numerous applications.

Especially, in recent years, the investigation of the physical properties of organic solids has attained greatly increased interest. The wide variety of these compounds, the advantages of the relatively low cost, and the possibility to modify them using the methods of synthetic organic chemistry in a practically unlimited fashion have aroused high expectations for the development of new materials. In this context, organic semiconductors have attracted considerable interest as promising materials for optoelectronic devices. These have, for instance, been exploited in organic field effect transistors, organic photovoltaic cells, or organic light emitting diode.[1–6]

In particular, pentacene showed encouraging behavior in the field of flexible electronics.[7,8] Single crystals of this material can be grown in a very high quality, and thus, very high charge carrier mobilities could be achieved.[9] The optical properties of pentacene and related oligoacenes have been studied previously with the aim to microscopically understand their behavior and gain fundamental insight into

the materials itself but also into the entire class of organic semiconductors.[10,11] In addition, because of the relatively open crystal structure of the molecular solids, intercalation with additional charges directly influences the electronic structure as well as the physical properties. One of the remarkable examples is the doped fullerene compounds, whereby their properties range from insulators to metallic and even superconducting behaviors as a function of doping level.[12]

More recently, superconductivity, with rather high transition temperatures, was observed in several metal doped, hydrocarbon based molecular materials, e.g., picene.[13] Interestingly, picene is also made of five benzene rings, joined in a zigzag manner, instead of a linear arrangement as in pentacene (cf. Fig. 1). Also, in 2009, Craciun *et al.* reported transport measurements revealing a metal-to-insulator transition in potassium-intercalated pentacene films depending on the amount of intercalated K atoms.[14] Conductivity first increases with increasing potassium amount and then suffers a sudden drop at a K concentration of exactly one K atom per pentacene molecule. According to their interpretation, for this particular composition, half filling is achieved and the system is driven into a Mott-insulating state. This observation was confirmed by first photoemission measurements on K doped pentacene.[15]

In this contribution, we report experimental studies of the influence of potassium addition on the electronic excitation spectrum of tetracene as well as pentacene using electron energy-loss spectroscopy (EELS). EELS studies of other undoped as well as intercalated molecular materials in the past have provided useful insight into their electronic properties and the change occurring upon addition of charge carriers. The aim of this paper is to shine more light on the doping introduced changes of the electronic structure and the different behaviors upon intercalation between acenes and phenacenes.

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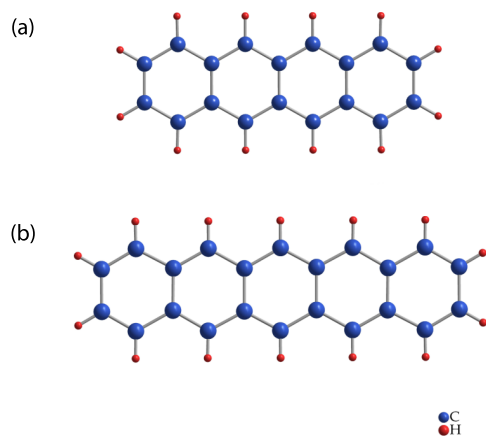b)Electronic mail: M.Knupfer@ifw-dresden.de

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FIG. 1. Schematic representation of the molecular structure of the investigated hydrocarbons. (a) Tetracene and (b) pentacene.

II. EXPERIMENTAL

For the present work, thin, freestanding films of tetracene and pentacene with a thickness of ~100 nm have been produced by thermal evaporation under high vacuum conditions onto KBr single crystals kept at room temperature in a separate vacuum chamber. Subsequently, the films were floated off in distilled water, mounted onto standard electron microscopy grids, and transferred into the spectrometer.

In several steps, the samples were exposed to potassium that was evaporated from a commercial getter source (SAES GETTERS S.p.A., Italy). The doping took place at room temperature under ultrahigh vacuum conditions (base pressure lower than 10^{-10} mbar), a current through the getter source of 6 A, and a source-sample distance of about 30 mm were applied. This has been carried out for several times until saturation, i.e., until no further stoichiometry change could be observed in the spectra. Since post-annealing of the films did not change the doping level or structure, one can assume that doping under these conditions leads to a homogeneous distribution in the films and no alkali metal atoms are accumulated on the surface of the sample.

All electron diffraction studies and loss function measurements were carried out using a dedicated 172 keV spectrometer described in detail elsewhere.[16,17] The energy and momentum resolution were chosen to be 85 meV and 0.03 Å^{-1} for valence band excitation and 200 meV and 0.03 Å^{-1} for core-level excitations, respectively. We have measured the loss function Im$[-1/\epsilon(\mathbf{q},\omega)]$, which is proportional to the dynamic structure factor $S(\mathbf{q},\omega)$, for a momentum transfer $\mathbf{q}$ parallel to the film surface [$\epsilon(\mathbf{q},\omega)$ is the dielectric function].

III. RESULTS AND DISCUSSION

We start our discussion of the changes, which occur upon potassium addition, with an analysis of the C 1s and K 2p core excitation edges in order to determine the amount of potassium in our doped samples. In Fig. 2, we show the core level spectra, both for undoped/doped tetracene and pentacene, respectively. Due to dipole selection rules, these data represent transitions into empty C 2p-derived levels. In other words, core level EELS is able to probe the projected
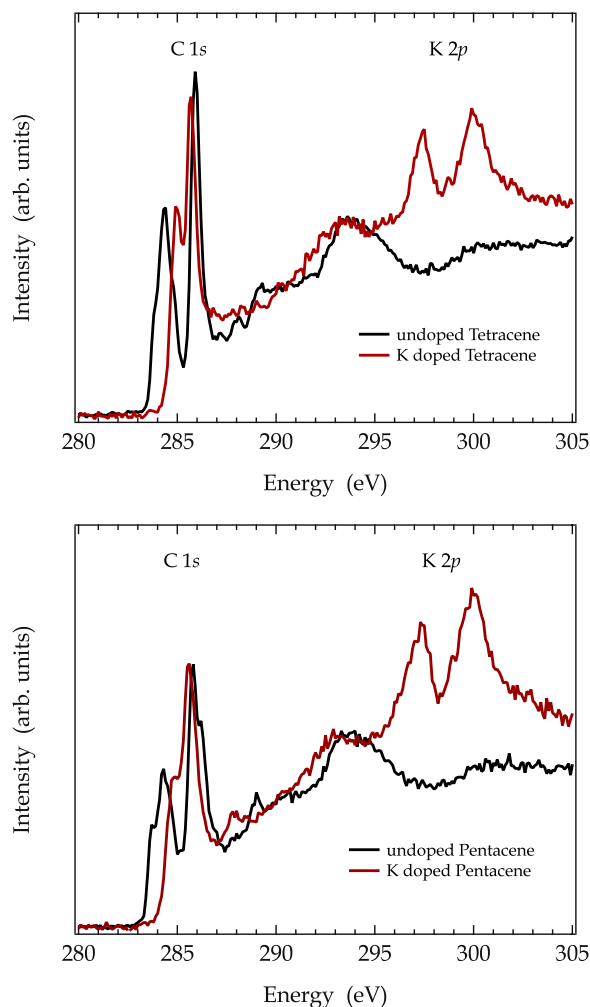

FIG. 2. C 1s and K 2p core level excitations of undoped and potassium doped tetracene (upper panel) and pentacene (lower panel).

unoccupied electronic DOS of carbon-based materials.[18] All spectra were normalized at the step-like structure in the region between 291 eV and 293 eV, i.e., to the σ^* derived intensity, which is proportional to the number of carbon atoms in the system under investigation. For the undoped samples, the spectra are dominated by a well defined two peak feature with maxima at 284.3 and 285.9 eV for tetracene and pentacene. Moreover, in case of pentacene, one can identify two shoulders at 283.7 and 286.2 eV, whereas in case of tetracene, one can observe a weak shoulder around 284 eV. Below ~291 eV, the structures can be assigned to transitions into π^* states representing the unoccupied electronic states. The sharpness of the π^* resonances can be seen as a clear indication of strong localization of the excitation (excitonic effect — excitonic interactions with the core hole).[19,20] Furthermore, our results are in a very good agreement with previous x-ray absorption measurements, where the two main π resonances were attributed to electronic core excitations at different C atoms to the two lowest unoccupied molecular orbitals LUMO and LUMO+1.[21–23]

Upon K doping, changes in the core level spectrum are obvious. First of all, the successful K doping can be seen by the appearance of the K 2p core level excitation at 297.5 and 299.9 eV. To determine the amount of potassium in

our samples, we compare the ratio of C $1s$ and K $2p$ core excitation intensities with other doped molecular films with well known stoichiometry, e.g., K doped C_{60}[24] or potassium doped picene.[25] For a detailed description, we refer the reader to a previous publication.[26] The results shown in Fig. 2 indicate a saturation doping level of about x = 2 for both tetracene and pentacene.

Moreover, the energy position of the K $2p$ core level excitations as seen in Fig. 2 exactly matches those in doped fullerenes,[26,27] where the charge transfer from potassium to the molecules is complete. Also the energies are very similar to the respective excitation spectra of ionic potassium compounds.[28,29] This represents clear evidence that upon the addition of potassium to pentacene and tetracene, there is full charge transfer of one electron per potassium to the hydrocarbon molecules.

Further on, upon potassium doping, we can observe significant changes in the C $1s$ derived features for both compounds. For tetracene, we can identify two maxima at 284.9 and 285.6 eV. These represent excitations into the LUMO+1 and probably energetically higher orbitals. Since there are symmetrically inequivalent C atoms in the two molecules, the two maxima might also arise from excitations into the LUMO+1 only. A detailed analysis would require theoretical work which is beyond the scope of this publication. In case of pentacene, the situation is nearly the same. For both molecules, the substantial changes of the C $1s$ excitation spectra clearly evidence a successful doping.

Interestingly, the achieved maximal doping level in tetracene and pentacene is different compared to doped phenacenes, e.g., chrysene or picene.[25,30] In the latter case, a doped phase with a stoichiometry close to K_3 chrysene or K_3 picene was reached, which, in case of intercalated picene, is supposed to show superconductivity up to 18 K.[13] However, for the two compounds investigated here, the maximum doping level of about K_2 tetracene and K_2 pentacene is lower. We attribute this difference to the underlying electronic structure

of these two material classes. For chrysene and picene, calculations have shown that there are several unoccupied electronic levels very close in energy,[31–34] while for tetracene and pentacene, the splitting of the two individual lowest unoccupied levels is much larger.[35,36] Consequently, the addition of more than two electrons to the latter requires substantially more energy, which renders higher doping levels unfavorable.

Potassium addition to the two materials under investigation here causes also major changes in the electronic excitation spectrum as revealed in Fig. 3, where we show a comparison of the loss spectrum in an energy range of 0–10 eV for the undoped as well as the doped cases. These data are taken with a small momentum transfer q of 0.1 Å^{-1}, which represents the optical limit. The undoped spectra are dominated by a strong excitation feature followed by further sharp maxima right after the excitation onset of 2.2 eV for tetracene and 1.75 eV for pentacene, respectively. These structures can be clearly attributed to excitons followed by vibronic satellites in the two compounds, whereby recent studies show that they can only be understood when an admixture of charge transfer excitations to the molecular (Frenkel)-excitons is taken into account.[37–39] A detailed analysis and discussion of the loss spectra of undoped pentacene and tetracene can be found in Refs. 10, 40, and 41.

Upon doping, there is first a spectral broadening and a downshift of the major excitation observable. The broadening indicates a lower lifetime of the excitations, which might be a result of the larger screening ability of the larger number of electrons after the doping process. The energetic downshift is typical for doped π-conjugated materials and arises from a relaxation of the molecular structure upon filling the anti-bonding LUMO.[24,25,30] Second, the lowest excitons, a characteristic of the undoped materials, disappear while new features show up at somewhat smaller energies. In the case of pentacene, an additional shoulder-like structure is visible around 1 eV. We note that, apart from this low energy shoulder,
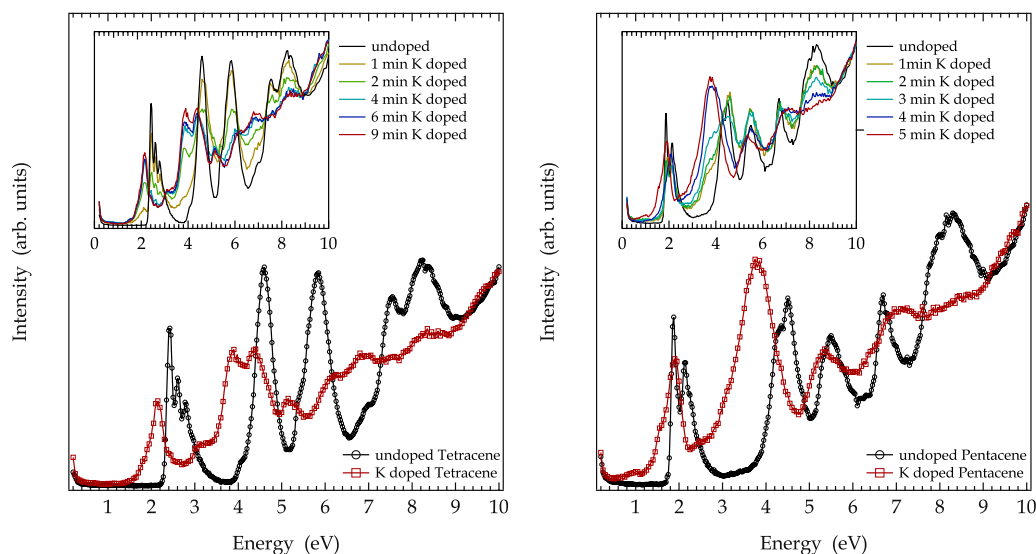

FIG. 3. Comparison of the electronic excitation spectra of solid tetracene (left panel) as well as pentacene (right panel) between the undoped (black curve) and fully potassium doped (red curve) case. The inset shows the evolution of the loss function for both materials in the range of 0–10 eV upon potassium intercalation.

the lowest main absorption maxima in K_2 tetracene and K_2 pentacene at about 2.1 eV and 1.8 eV, respectively, agree very well with those observed for the respective dianions in solution associated with potassium ions,[42] which is fully consistent with our doping level analysis from the core levels above.

As also mentioned above, the LUMO levels of tetracene and pentacene are energetically well separated from the respective LUMO+1 level. This energy splitting has been reported to be about 1.7 eV and 1.4 eV for tetracene and pentacene, respectively.[35,36,43–46] Taking into consideration a relaxation of the unoccupied levels upon charging the molecules, which is somewhat larger for the LUMO and LUMO+1 levels, there is very good agreement of these energies to the excitation energies in our spectra for the doped compounds. Consequently, it is reasonable to ascribe the lowest excitations both in the solid state and in solution to transition from the now occupied former LUMO to the former LUMO+1 level.

For both systems under investigation, a clear energy gap can be identified in the electronic excitation spectrum in Fig. 3, i.e., both K_2 tetracene and K_2 pentacene are insulators or semiconductors, respectively. Since the former LUMO level of tetracene and pentacene becomes completely filled upon the addition of two potassium per molecule and the related charge transfer, it is reasonable to describe K_2 tetracene and K_2 pentacene as band insulators. The question however arises whether at lower doping levels metallic phases might be formed. We emphasize that also at lower potassium doping levels, none of our samples showed a closure of the energy gap or any other evidence for a metallic ground state. This is illustrated in the inset of Fig. 3, where we show the evolution of the excitation spectra upon increasing potassium doping. Interestingly, electrical transport studies of potassium doped pentacene films[14] provided evidence for the formation of a Mott insulator for a doping level of K_1 pentacene, whereas at lower doping levels, indications for metallic conductivity have been observed. This formation of a Mott state for K_1 pentacene was also concluded from recent photoemission studies.[15] However, these photoemission data did not signal the existence of a conducting, metallic phase for lower doping levels. Equivalent data for doped tetracene films are not available, unfortunately.

The formation of an insulating Mott state for K_1 pentacene and its coexistence with a band insulating phase for K_2 pentacene at doping levels larger than x = 1 (K_x pentacene) could well explain our spectra and the lack of low energy excitation or a gap closure therein. This is also be corroborated by photoemission investigations of Cs doped pentacene films which also did not find evidence for emission from the Fermi level as a signature for metallicity.[47] We note, however, that the phase diagram of the system K-pentacene is unknown yet, and further studies should be carried out in order to clarify the issue of stable phases and their electronic ground state finally. Recently, Kim *et al.* pointed out that apart from the correlation energy U, the ground state of doped hydrocarbons depends on the energy splitting of the lowest unoccupied molecular orbitals.[48] This places pentacene^{3-} solids close to a Mott insulating state whereas, e.g., picene^{3-} materials fall into the metallic regime. A Mott insulating ground state for lower charging/doping levels would be in good agreement with this scenario.

For pristine pentacene and tetracene, the lowest electronic excitations are bound excitons, which are characterized by an anisotropic exciton band structure which has been discussed in terms of the admixture of Frenkel and charge transfer excitons.[10,37–41] To shine more light on the nature of the new low energy excitations of fully doped pentacene and tetracene, situated at 1.93 eV and 2.15 eV, respectively, we have also studied the momentum dependence of the electronic excitation spectra using EELS. In Fig. 4, we show the evolution of these spectra of our potassium doped polycrystalline samples as a function of momentum transfer up to 0.6 Å^{-1}. Interestingly, the first feature shows a clear negative dispersion with a bandwidth of ≈250 meV for tetracene and ≈320 meV in case of pentacene (cf. Fig. 5). Moreover, even the next excitation features around 4 eV show a clear negative shift to lower energies by increasing the momentum transfer. A negative dispersion of excitons has important consequences for the luminescence behavior of the respective material. An exciton which, after its primary excitation, can relax to lower energy levels at finite momentum cannot directly recombine any more due to momentum conservation law. As a consequence, we would expect luminescence of K_2 tetracene and K_2 pentacene to be substantially suppressed.
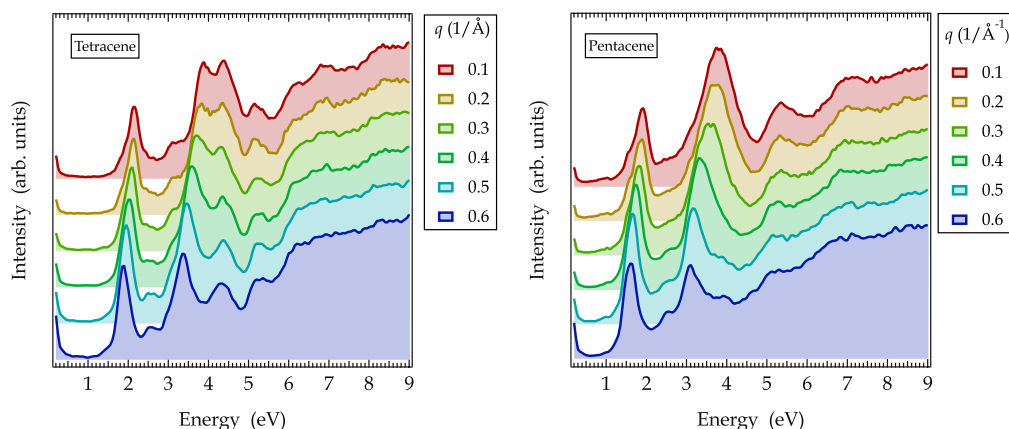

FIG. 4. Momentum dependency of the loss function of potassium intercalated tetracene (left panel) and pentacene (right panel) in a momentum range between $q = 0.1$ and 0.6 Å^{-1}. (q increases from top to bottom.).
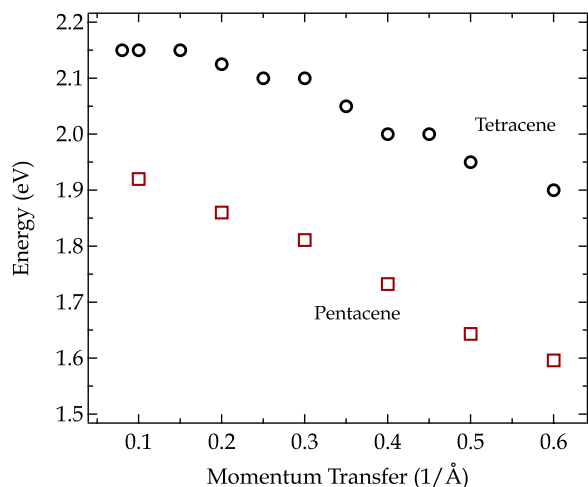
FIG. 5. Energy position of the first excitation feature in K doped tetracene (black circles) and pentacene (red squares) in the considered momentum range between 0.1 and 0.6 Å^{-1}. The resulting bandwidth is ≈250 meV for tetracene and ≈320 meV for pentacene, respectively.

IV. SUMMARY

To summarize, we have successfully prepared potassium doped films of tetracene and pentacene, respectively. Our investigation using elastic and inelastic electron scattering demonstrates that the films are polycrystalline and that in both cases, a stoichiometry of two potassium per hydrocarbon molecule has been reached. Furthermore, the changes in the C 1s core level and valence band excitation spectra show the charge transfer from potassium to the molecules. Within our investigations, all prepared samples are characterized by a finite energy gap in the excitation spectrum, i.e., none of the samples became metallic. This might be related to the yet unknown phase diagram for the systems K-tetracene and K-pentacene, in particular to the existence of a Mott insulating phase at a doping level of one potassium per molecule as discussed in the literature. Further investigations are required in order to finally rationalize all details.

ACKNOWLEDGMENTS

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