Electronic excitations of potassium intercalated manganese phthalocyanine investigated by electron energy-loss spectroscopy

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The electronic excitations of manganese phthalocyanine (MnPc) films were studied as a function of potassium doping using electron energy-loss spectroscopy in transmission. Our data reveal doping induced changes in the excitation spectrum, and they provide evidence for the existence of three doped phases: K₁MnPc, K₂MnPc, and K₄MnPc. Furthermore, the addition of electrons first leads to a filling of orbitals with strong Mn 3d character, a situation which also affects the magnetic moment of the molecule.

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I. INTRODUCTION

Molecular thin films consisting of metal phthalocyanines are well known due to their particular electronic properties, which are both of fundamental as well as of applied relevance. They, for instance, are successfully used in organic electronic or optoelectronic devices. In their pristine form, metal phthalocyanines are semiconductors. Moreover, due to their relatively open crystal structure their properties can be tuned by the incorporation of electron acceptors and donors, and, for example, electrical conduction can be induced by the incorporation of alkali metals. In addition, the incorporation of transition metal ions in the center of a phthalocyanine ring results in the formation of small, well defined molecules with a particular magnetic moment. Thus, transition metal phthalocyanines can be regarded as simple model compounds for the investigation of the fundamental electronic, and magnetic properties of many other transition metal containing molecules, among them molecular magnetic complexes or molecular magnets.

Manganese phthalocyanine (MnPc) is one of these interesting and fundamental compounds. For instance, MnPc is characterized by an unusual $S = 3/2$ spin state of the Mn$^{2+}$ ion, and MnPc has been referred to as a typical example of a molecular magnet. Also, in MnPc the Mn center has a formal $3d^5$ electronic configuration, and the Mn $3d$ orbitals are expected to lie close to the chemical potential. Recently, we demonstrated that the occupied electronic structure as well as the electronic excitation spectrum of MnPc is clearly different from all other transition metal phthalocyanines, which most likely is a direct consequence of the Mn $3d$ orbitals. In this context, it is also interesting to investigate the changes that are induced in MnPc by doping with e.g. alkali metals.

The physical properties of such doped molecular materials are closely related to the fact whether particular doped phases exist. The detailed microscopic understanding of the physical behavior of the material in question requires the knowledge of the underlying structure and stoichiometry. Recently, it was demonstrated that upon potassium doping of ZnPc, CuPc, and FePc two phases with $K_2MPc$ and $K_4MPc$ ($M = \text{Zn, Cu, Fe}$) stoichiometries are formed. This parallels the situation as it was found for other potassium doped molecular materials, e.g. alkali metal doped fullerenes. In addition, potassium doping of CoPc leads to a change of the Co spin and charge in the center of the molecule since the first electron transferred to a CoPc molecule will occupy a Co $3d$ orbital, i.e. charge...
transfer also might be used to access the magnetic degrees of freedom of such molecules.

In this contribution, we report on an investigation of the electronic properties of potassium doped MnPc films using electron energy-loss spectroscopy (EELS) in transmission. We discuss the changes that are induced in the electronic excitation spectrum as a function of doping, and we provide evidence for the formation of three doped phases with K\textsubscript{1}MnPc, K\textsubscript{2}MnPc, and K\textsubscript{4}MnPc composition. Moreover, our data also indicate filling of a metal 3\textit{d} orbital upon doping, which then must be accompanied by a change of the magnetic moment of the MnPc molecule in the charged state.

II. EXPERIMENTAL

For our investigations, thin free-standing films of MnPc were prepared under ultra high vacuum conditions (UHV) by thermal evaporation onto a KBr (100) substrate kept at room temperature. The deposition rate was about 0.5 nm/min as measured using a quartz microbalance, and the resulting film thickness was about 100 nm. Subsequently, the films were floated off in distilled water, mounted onto standard electron microscopy grids, and transferred into a purpose built spectrometer for EELS\textsuperscript{25}, where \textit{in situ} also the doping procedure was carried out. Prior to doping, the MnPc films were characterized using electron diffraction which showed that the films are essentially polycrystalline but well textured and mainly consist of the so called \textit{α}-polymorph.\textsuperscript{26,27} Potassium was added from a commercial SAES source (SAES GETTERS S.p.A., Italy). The doping took place at room temperature and under UHV conditions in several steps by evaporation of potassium from the getter source at a current of 6 A and a source-sample distance of about 30 mm. We note that this small distance might induce slight heating of the sample during potassium doping.

All EELS measurements were carried out in transmission and at room temperature using a dedicated 170 keV spectrometer described elsewhere.\textsuperscript{25} We note that at this high primary beam energy only singlet excitations are possible. EELS measures the so called loss function, \(\text{Im} \left( -1/\epsilon(q, \omega) \right) \) where \(\epsilon(q, \omega)\) is the dielectric function. It thus contains information on the dielectric response of the material under investigation and it can also probe the excitations as a function of momentum transfer \(q\) even far away from the optical limit.\textsuperscript{28–30} The loss function of our samples was measured for a momentum transfer of \(q=0.1 \text{ Å}^{-1}\), parallel to the film surface. In order to obtain a direction independent core level excitation information,
we have determined the core level data for three different momentum directions such that
the sum of these spectra represent a polycrystalline average also for the textured samples. The energy and momentum resolutions were 90 meV and 0.03 Å⁻¹ for the loss function and
diffraction measurements and 200 meV and 0.03 Å⁻¹ in the case of the measured core level
excitations. Furthermore, as molecular crystals often are damaged by fast electrons, we
repeatedly checked our samples for any sign of degradation and did not consider those with
changes in electronic or diffraction spectra. For further details of the sample preparation
and the experimental technique we refer the reader to previous publications.

III. RESULTS AND DISCUSSION

![Graph of electronic excitation spectra](image)

**FIG. 1:** Evolution of the loss function of MnPc upon potassium doping. The potassium
content increases from bottom to top. In the left panel, thicker lines with symbols indicate
particular doping stages, where the spectra indicate the formation of K doped MnPc
phases (see text). In the right panel, we only show the spectra of these K doped MnPc
phases. The various excitation features are labelled with capital letters (see discussion for
further details).

We start the presentation of our results with the evolution of the electronic excitation
spectra of MnPc upon potassium doping, which is shown in Fig. 1. These data were taken
with a momentum transfer of 0.1 Å⁻¹ and we note that for such a small momentum transfer
EELS probes dipole allowed excitations and the data are thus equivalent to those from
optical studies. The loss function of pristine MnPc (bottom curve in Fig. 1) consists of
several excitation features at 0.5, 0.8, 1.4, 1.8, 2.1, and 2.8 eV, which were already reported earlier. The electronic excitation features at 1.8 - 2 eV are associated with the well known Q band common to many phthalocyanines. This Q band in the solid state is broad and structured because of vibronic satellites and the impact of solid state effects. It has its origin in excitations from the occupied molecular orbital with a symmetry to an unoccupied molecular orbital with e symmetry. The exact origin of the excitations at lower energies is unclear to date. They have been discussed in terms of the contribution of Mn 3d states to the molecular orbitals close to the chemical potential in MnPc but there is no full, consistent understanding of what can be observed in Fig. 1 for pristine MnPc.

Upon potassium addition we observe significant changes in the excitation spectra. First, the two features A1 and A2 and the Q-band excitation (D) disappear while new spectral structures show up at 1.5 eV (C) and about 2.6 eV (E). Further doping leads to an energetic down-shift of feature E and the appearance of a further excitation at about 1.1 eV (B). The intensity of feature B reaches a maximum at intermediate doping and then decreases in intensity, while feature C grows slightly and feature E continues to shift to lower energies.

The data in Fig. 1 indicate the existence of distinct K-MnPc compositions (stages 1, 2 and 3) with particular stoichiometry and optical properties. Stage 1 is reached when the low energy structures A1 and A2 have vanished and features C and E have developed at 1.5 and 2.6 eV, respectively. The addition of more potassium induces the formation of stage 2, which is signalled by the appearance of feature B and the downshift of feature E. Finally, in stage 3 feature B disappears again, feature C increases in intensity and feature E reaches its final energy position at about 2.1 eV. In general, the formation of distinct potassium doped MnPc phases parallels the situation in other transition phthalocyanines upon addition of potassium, where it was reported that phases with compositions K2ZnPc, K4ZnPc, K2CuPc, K4CuPc, K2FePc, and K4FePc exist. However, we emphasize that the data in Fig. 1 indicate three potassium doped MnPc structures, one more than for the other phthalocyanines.

Our conclusion that stages 1, 2 and 3 as described above correspond to stable, potassium doped phases of MnPc requires that the spectra in-between can be described by a superposition of the spectra of the corresponding phases in the direct neighborhood, in analogy to what was observed for K doped CuPc. In Fig. 2 we show a comparison of corresponding data for potassium contents between undoped MnPc and stage 1 as well as stage 2 and 3,
FIG. 2: Comparison of the loss function of the observed K doped MnPc stages (see text) and data for samples with potassium content between pristine MnPc and stage 1 and between stage 2 and stage 3, respectively. The data for these intermediate compositions have been modelled by a weighted superposition of the corresponding intensities of neighboring stages. In the left panel the weights are 0.5 for both stages, while in the right panel they were 0.65 (stage 2) and 0.35 (stage 3).

respectively, with modelled data obtained by a weighted sum of the data for the respective phases. The agreement of measured and modelled data is very good, which corroborates our conclusion that these phases are formed.

Moreover, evidence that stable phases are formed can also be read off the evolution of the electron diffraction profiles of our samples. In Fig. 3 we show the doping induced changes around 1.1 Å\(^{-1}\) and 0.5 Å\(^{-1}\). The diffraction maximum at 1.12 Å\(^{-1}\) (left panel of Fig. 3) in the undoped MnPc samples is due to the (201) Bragg peak of the \(\alpha\)-polymorph of MnPc,\(^{26,27}\) and it vanishes upon potassium addition. Reaching doping stage 1, a new diffraction peak at 1.15 Å\(^{-1}\) is observed, which is further shifted going to the doped stages 2 and 3. The diffraction peak at 0.5 Å\(^{-1}\) in pristine MnPc (right panel of Fig. 3) corresponds to the (100) Bragg peak and shifts to lower values upon doping. For stage 1 it is found at about 0.48 Å\(^{-1}\), while for the two other stages it is at about 0.47 Å\(^{-1}\).

Further support for our conclusion, that stages 1, 2, and 3 are formed, can be obtained by a comparison of our data to the optical absorption taken for electrochemically charged MnPc molecules in solution.\(^{34,35}\) This is depicted in Fig. 4 which summarizes the excitation spectra obtained for the undoped MnPc and the three potassium doped stages and compares
FIG. 3: Doping dependence of the electron diffraction profiles around 1.1 and 0.48 Å⁻¹.

those to the excitation energies obtained for the MnPc⁻ monoion, MnPc²⁻ diion and MnPc⁴⁻
tetraion in solution. In consideration of the broadening upon going from single molecules
in solution to the solid state, and a possible different excitation energy due to different
screening effects, the data presented in Fig. 4 indicate the same trend for potassium doping
in the solid and negative charging in solution. We therefore assign our doped phases to
K₁MnPc (stage 1), K₂MnPc (stage 2) and K₄MnPc (stage 3).

Finally, the amount of potassium in the samples can be determined by EELS core level
excitation measurements at the C 1s and K 2p core levels. In Fig. 5 we show these core
excitations for undoped MnPc and the three identified doped phases. In general, the data in
Fig. 5 arise from excitations of carbon 1s electrons into unoccupied π* states at 285 - 291 eV,
those from the C 1s level into carbon derived σ* states with the so-called σ edge at 291 -
292 eV, and K 2p to K 3d excitations with maxima at 297.1 and 298.8 eV. The data
are normalized to the intensity of the first C 1s σ* feature at about 293 eV which represents
the amount of carbon in the sample. Fig. 5 clearly shows the increasing potassium content in
our samples. An analysis of the intensities of the K 2p excitation structures in comparison to
FIG. 4: Comparison of the loss function of $K_xMnPc$ phases with $x = 0, 1, 2, 4$. The bars indicate the excitation energies as seen in optical absorption for electrochemically reduced MnPc$^-$, MnPc$^{2-}$, and MnPc$^{4-}$ molecules in solution.\textsuperscript{34,35}

well characterized potassium doped fullerenes or highly oriented pyrolytic graphite (HOPG) yields a doping level $K_xMnPc$ of $x \sim 0.9, 2.1$ and $4$ for our samples. Details of this procedure can be found in previous publications.\textsuperscript{18,19,32,36–38} We estimate the error of this analysis to be $\Delta x \sim \pm 0.2$ ($K_xMnPc$). Thus, this core level analysis corroborates our assignment of the identified potassium doped MnPc phases to $K_1MnPc$, $K_2MnPc$ and $K_4MnPc$, respectively.

Consequently, in analogy to other transition metal phthalocyanines also K doping of MnPc results in particular doped phases, but MnPc is the only phthalocyanine reported so far that also forms a $K_1MnPc$ phase. This difference might be closely related to the occupancy and energy position of the $3d$ levels of the central transition metal. In the case of MnPc, data from photoemission spectroscopy, EELS and theory clearly indicate the presence of Mn $3d$ orbitals very close to the chemical potential, and actually at energies in-between the fully occupied $a_{1u}$ and the lowest unoccupied $e_g$ ligand molecular orbitals.\textsuperscript{13–16} Furthermore, these Mn $3d$ orbitals are also responsible for a significant change of the ionization potential and most likely also the electron affinity. Previous electrochemistry investigations have provided evidence that the first oxidation as well as the first reduction state of MnPc molecules have strong Mn $3d$ character.\textsuperscript{3,12} We therefore infer that the first electron that
FIG. 5: C 1\text{s} and K2 \text{p} core level excitations of pristine MnPc and the potassium doped MnPc phases.

is transferred by potassium addition to each MnPc molecule in the solid state will occupy a state with predominant Mn 3\text{d} character, which is in agreement with the disappearance of the low energy electronic excitations as seen in undoped MnPc and which might help to stabilize a phase with corresponding stoichiometry, K\textsubscript{1}MnPc. It is interesting to note, that also in potassium doped CoPc films the first electron occupies a metal (Co) 3\text{d} state before the ligand orbitals are filled\textsuperscript{[23]} Further electron transfer caused by further potassium addition then leads to the occupation of the ligand \(\epsilon_g\) orbitals with electrons and the formation of the other observed phases. The fact that for all transition metal phthalocyanines investigated so far the maximal potassium doping is \(x = 4\) is most likely a consequence of steric or geometrical reasons.

Finally, the observed filling of a Mn 3\text{d} orbital upon potassium addition demonstrates the formation of Mn(I) centers, which is directly accompanied by a change of the magnetic moment. This now evinces a way to deliberately change the magnetic properties of such molecules via charge transfer in thin films. It additionally might have consequences for the charge transport behavior of MnPc films, since electrons injected into a film might occupy metal 3\text{d} rather than ligand \(\pi\) orbitals with rather different wave function and hopping probabilities. The associated variation of the spin state of MnPc can also affect the spin
scattering mechanisms in spin-dependent transport.

IV. SUMMARY

To summarize, we studied the electronic properties of undoped and potassium doped manganese phthalocyanines using electron energy-loss spectroscopy. Our data allow the identification of three doped phases, \( K_1\text{MnPc} \), \( K_2\text{MnPc} \), and \( K_4\text{MnPc} \) and show the variations in the electronic excitation spectra upon doping. In addition, in \( K_1\text{MnPc} \) a MnPc orbital with predominant 3\textit{d} character is filled, i.e. doping can change the valence and spin state of the Mn center.

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