Interaction between the Non-Fullerene Acceptor ITIC and Potassium

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ABSTRACT: Using density functional theory calculations and photoemission measurements, we have studied the interaction between the non-fullerene small-molecule acceptor ITIC and K atoms (a representative of reactive metals). It is found that the acceptor–donor–acceptor-type geometric structure and the electronic structure of ITIC largely decide the interaction process. One ITIC molecule can combine with more than 20 K atoms. For stoichiometries Kx ≤ 6ITIC, the K atoms are attracted to the acceptor units of the molecule and donate their 4s electrons to the unoccupied molecular orbitals. K–ITIC organometallic complexes, characterized by the breaking of some S–C bonds in the donor unit of ITIC and the formation of K–S bonds, are formed for stoichiometries Kx ≥ 7ITIC. The complexes are still conjugated despite the breaking of some S–C bonds.

INTRODUCTION

Fullerene derivatives such as PC_{61}BM and PC_{71}BM have been the most popular electron acceptors used in organic solar cells (OSCs). However, fullerene derivatives have the drawback of very weak photoabsorption in the visible and near-infrared regions. Therefore, a high-performance non-fullerene (NF) acceptor is highly desirable. In the recent years, many NF small molecule acceptors (SMAs) have been developed,3−5 among which ITIC is the milestone molecule. The OSC based on ITIC exhibited a power conversion efficiency of 11.21%,7 and the existing more advanced NF-SMAs with higher efficiency up to 14.1% are the modifications of ITIC.8−11 One issue concerning OSCs and some other organic devices is the interaction between organic molecules and reactive metals (such as alkali and alkali earth metals). Reactive metal films have been extensively adopted as an electrode interlayer for optimizing contact property.12−15 Some metal salts such as LiF,16,17 CsF,17 NaI,18 and CsI18 have also been applied as an electrode interlayer. The metal atoms of the films or liberated from the salts interact with the organic molecules. The interaction can alter the electronic property of the organic molecules and even degrade the molecular structures as revealed by some published works. For example, K atoms donate electrons to CuPc.19 K and Ca atoms not only donate electrons to PC_{61}BM but also degrade the structure of this molecule.20−23 The molecular structures of P3HT and MEH-CN-PPV can also be degraded by some reactive metals.24−27

In a previous work,28 we slightly doped an ITIC film with Ca atoms to help to understand the X-ray absorption spectroscopy of ITIC. The electron transfer from Ca atoms to ITIC was observed. This observation indicates that the interaction between ITIC and reactive metals deserves careful research. In this work, we study the interaction between ITIC and K atoms with density functional theory (DFT) calculations and photoemission (PES) measurements. K was selected because it is a model-reactive metal. In addition, the diffusion of K atoms into an organic film is easy as compared with some other metal atoms such as the Ca atoms. We can thus prepare K-

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Figure 1. (a) Optimized molecular structure of ITIC (top and side views) and some orbital contours. The gray, white, red, blue, and yellow balls represent the C, H, O, N, and S atoms, respectively. (b) Energy-level diagram of ITIC.
intercalated ITIC bulk samples for a detailed experimental study of the interaction. The results reveal that the interaction is electron doping from K to intact ITIC molecule for stoichiometries K_{<6}ITIC. At higher stoichiometries, the molecular structure is degraded and organometallic complexes are formed.

■ RESULTS AND DISCUSSION

We first preset the representative DFT results to get an overview of the K–ITIC interaction. The optimized structure and some orbital contours of ITIC are shown in Figure 1a. One ITIC molecule has 186 atoms, including 94 C atoms, 4 S atoms, 4 N atoms, 2 O atoms, and the remaining H atoms. Four hexylphenyl side chains of the molecule are for the purpose of high solubility in organic solvents and have little relation to the electronic property. The conjugated main chain has a seven-ring fused indacenodithieno[3,2-b]thiophene (IT) core and two (3-oxo-2,3-dihydroinden-1-ylidene)malononitrile (INCN) end groups. The IT core is the electron donor (D) unit, and the INCN groups are the electron acceptor (A) units. The D, A units couple strongly as indicated by the contours of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO); these two orbitals are distributed both on the D unit and on the A units. As a whole, ITIC acts as an A–D–A-type electron acceptor.

The contours of the LUMO + 2 and LUMO + 3 are also shown in Figure 1a because the unoccupied molecular orbitals are much pertinent to the K–ITIC interaction. These two orbitals are delocalized on the INCN end groups. The LUMO + 1 is delocalized on the whole main chain as the case of the LUMO and thus not shown here. Some energy levels are shown in Figure 1b; the ground-state HOMO–LUMO gap is 1.193 eV.

Figure 2 shows some optimized structures of K_xITIC (x = 0, 6, 7, 10, and 16). For clarity, the side chains and the H atoms are hidden. The numbers 1, 1’, ..., 4, 4’ in the structure of ITIC label the eight S–C bonds. Some S–C bonds are broken at high stoichiometries.

![Figure 2. Optimized structures of some K–ITIC complexes. Both the top views and the side views are shown. The purple balls represent K atoms. The numbers 1, 1’, ..., 4, 4’ in the structure of ITIC label the eight S–C bonds. Some S–C bonds are broken at high stoichiometries.](image-url)
bonds are rather strong. In some other structures, especially those structures with stoichiometries higher than K$_{10}$ITIC, the Mulliken occupation of some K atoms is smaller than 0.5 e. For example, the Mulliken occupations for some K atoms in many K$_{20}$ITIC isomers are 0.2−0.5 e. The interaction between these K atoms and the ITIC molecule is weak but non-negligible. It seems that one ITIC molecule can combine with more than 20 K atoms.

Except the breaking of some S−C bonds, the remaining parts of ITIC are stable against the attack of the K atoms. The skeleton of the K$_{20}$ITIC complexes is still conjugated ( alternating C−C and C≡C bonds in the main chain) as examined for all the optimized structures including those not shown here.

To sum up, the DFT calculations afford five conclusions about the K−ITIC interaction. (1) The K atoms first combine with the end groups. (2) The molecular structure of ITIC remains intact at least until the stoichiometry of K$_{3}$ITIC. (3) Some S−C bonds break and K−ITIC complexes are formed above a certain stoichiometry. (4) S−C bonds 4 and 4' never break until K$_{20}$ITIC. (5) The mechanisms for the K−ITIC interaction are the electron transfer from K to ITIC and the formation of K−S ion bonds.

Generally, DFT results should be checked by basic physical and chemical considerations or experimental data. The first DFT conclusion can be easily understood by the A−D−A-type molecular structure: the INCN end groups are electron acceptor units. The second DFT conclusion can be easily understood by the electronic structure of ITIC. The LUMO and LUMO + 1 are delocalized on the entire main chain. The LUMO + 2 is not so extended as the LUMO and LUMO + 1 but still delocalized on the INCN end groups. Therefore, the electrons (transferred from the six K atoms) filling these orbitals are dispersed and cannot much affect a specific bond of ITIC. The third and fourth DFT conclusions, together with the formation of K−S bonds mentioned in conclusion (5), cannot be readily understood and need experimental verifications. The electron transfer, if observed directly, would solidly support other conclusions. In the following, we present and discuss the PES data. The density of state (DOS) curves calculated on the optimized structures shown in Figure 2 will be compared with the PES data.

Figure 3a shows the K 2p and C 1s PES. The spectra of the two core levels were measured simultaneously in the experiments, and the background region (from 289 to 292 eV) between them is hidden for clarity. We estimated the sample stoichiometries based on the intensity ratios between the K 2p and C 1s PES, taking the number (94) of C atoms of ITIC and the photoionization cross sections into consideration. The highest stoichiometry was determined to be K$_{20}$ITIC. Considering the previous DFT calculations, such a high stoichiometry is not a surprise, although there may be some extra K atoms on the sample surface. The variation from spectrum 11 to spectrum 12 is very small, indicating that the intercalation reaches saturation or at least is very near saturation in the detection depth of the core-level PES measurements. The detection depth is generally several nanometers for organic samples, although the definite value is unknown.

The K 2p PES is only for estimating the sample stoichiometries and will not be discussed further. The C 1s PES exhibits three notable characteristics: a long tail extending to ∼288 eV in the spectrum of the pristine ITIC (spectrum 1), the steady movements toward higher binding energy (BE) with more intercalation of K atoms, and a shoulder emerging at the lower BE side of the main peak for spectra 6−12 (indicated by the dashed line shown in Figure 3a). As seen below, these characteristics coincide with the DOS curves calculated on the structures shown in Figure 2 and thus support the DFT conclusions.

Figure 3b shows the C 1s DOS curves of ITIC, K$_{6}$ITIC, and K$_{10}$ITIC as representatives. The C 1s states of the main chain (the blue line) separate in energy from that of the side chains (the red line) with a minor overlap for ITIC. This is the reason why spectrum 1 shown in Figure 3a exhibits a long tail at ∼288 eV. The tail is mainly the PES from the main chain, while the main peak at 284.65 eV is mainly from the side chains. The signal from the main chain is rather weak although the number (46) of C atoms in the main chain is comparable with that (48) in the side chains. This may be due to that the delocalized π electrons of the main chain attenuate the C 1s signal.

In accord with the peak movement from spectrum 1 to spectrum 6 shown in Figure 3a, the DOS curves of K$_{6}$ITIC move distinctly to lower energy (higher BE) because of the Fermi-level shift caused by the electron transfer from K to ITIC. For K$_{6}$ITIC, the DOS curve of the states of the side chains (corresponding to the experimental main peak) moves slightly to still higher BE, coinciding with the movements of the main peaks of spectra 7−12 shown in Figure 3a.

With the electron transfer from K to ITIC, the C 1s states of the main chain exhibits chemical shifts to higher energy (lower BE), in addition to the movements to higher BE caused by the Fermi-level shift. The energy positions of the C 1s states of the side chains are less affected by the effect of chemical shift and mainly decided by the Fermi-level shift. For the DOS curves of K$_{6}$ITIC, nearly half of the C 1s states of the main chain move to the right side of the C 1s states of the side chains, which corresponds to the emergence of a shoulder at the lower BE side of the main peak observed for spectrum 6 shown in Figure 3a. With more K atoms combined with ITIC, more C 1s states of the main chain move to the right side of the C 1s states of the side chains, as can be seen from the DOS curves of...
Correspondingly, the C 1s PES exhibits an increasingly strong shoulder from spectrum 6 to spectrum 12 shown in Figure 3a. It seems that the PES from the main chain becomes stronger at high intercalation stages as compared with the case of the pristine ITIC, but the reason for this is unknown at present. According to the comparison between the DOS curves and the PES data, the sample of spectrum 6 shown in Figure 3a corresponds to a stoichiometry not far from K\(_{1.6}\)ITIC. The nominal stoichiometry of this sample is K\(_{7.2}\)ITIC. Therefore, our estimate of the stoichiometries for the experimental samples is generally reliable.

The S 2p PES shown in Figure 4a provides direct evidence of the breaking of some S–C bonds. The pristine ITIC exhibits the well-separated spin–orbit doublet 2p\(_{3/2}\) and 2p\(_{1/2}\) and the doublet is labeled I. There are two other sets of S 2p doublets in the figure, which are labeled II and III. Doublet I disappears completely in the top two spectra. Doublets II and III emerge at the intercalation stages of spectra 3 and 7, respectively, and persist until the intercalation saturation. The chemical shift from doublet I to doublet II is as large as −2.80 (−162.60–165.40) eV according to spectrum 7. The chemical shift from doublet II to doublet III is −1.95 (160.95–162.90) eV according to spectrum 12. The large and negative chemical shifts not only verify the breaking of some S–C bonds but also verify the formation of K–S bonds in which the S atoms gain electrons from the K atoms.

The three sets of S 2p doublets coincide with the structures shown in Figure 2. The S atoms in those structures can be classified into three types: the S atoms in intact thiophene rings (type I), the S atoms in the S–C bond of a broken thiophene ring (type II), and the S atoms detached from the main chain (type III). In the DFT calculations, we have found that bonds 4 and 4’ do not break up to the stoichiometry of K\(_{1.6}\)ITIC, giving identical numbers of type II and type III S atoms in some structures such as the K\(_{1.6}\)ITIC structure shown in Figure 2. The intensities of doublets II and III are near identical in the top two spectra shown in Figure 4a. The breaking of the thiophene rings starts at the stoichiometry of K\(_{1.6}\)ITIC according to the DFT calculations, while the experimental signal of type II S atoms can be observed on the sample of K\(_{1.7}\)ITIC (spectrum 3). This is because the experimental sample is not homogeneous. The nominal stoichiometries indicated in Figure 4a are averaged stoichiometries, and the concentration of K in a sample is not uniform. It is possible that a very small fraction of K\(_{1.6}\)ITIC is present in the sample of nominal K\(_{2.2}\)ITIC. Doublet II persists to the intercalation saturation because S–C bonds 4 and 4’ never break.

After six S–C bonds have been broken, there is no intact thiophene ring in the complexes (see, e.g., the K\(_{1.6}\)ITIC structure shown in Figure 2). Therefore, doublet I disappears in the top two spectra shown in Figure 4a. The breaking of the thiophene rings starts at the stoichiometry of K\(_{1.6}\)ITIC according to the DFT calculations, while the experimental signal of type II S atoms can be observed on the sample of K\(_{2.2}\)ITIC (spectrum 3). This is because the experimental sample is not homogeneous. The nominal stoichiometries indicated in Figure 4a are averaged stoichiometries, and the concentration of K in a sample is not uniform. It is possible that a very small fraction of K\(_{1.6}\)ITIC is present in the sample of nominal K\(_{2.2}\)ITIC. Doublet II persists to the intercalation saturation because S–C bonds 4 and 4’ never break.

The correspondence between the experimental doublets and the calculated three types of S atoms is more straightforward in comparison with the S 2p PES with the DOS curves. Figure 4b shows the S 2p DOS curves calculated on the optimized structures shown in Figure 2. The spin–orbit coupling has not been implemented in the DMol3 package, and thus each DOS peak corresponds to an experimental doublet. Fine structures or asymmetric shapes for some DOS peaks are due to different chemical environment of the S atoms belonging to the same type. The highest stoichiometry is K\(_{2.2}\)ITIC shown in Figure 4b, which is much smaller than the highest stoichiometry of the experimental samples. However, as mentioned previously, all the six S–C bonds that can be broken have been broken in this structure. Therefore, Figure 4b can be compared with the S 2p PES from the pristine ITIC to the intercalation saturation. The assignments (I, II, and III) of the DOS peaks to the three types of S atoms are based on local DOS (LDOS) analyses. It can be seen that Figure 4b shows a good correspondence compared with Figure 4a.

For quantitative comparison of the experimental and calculated chemical shifts, one can concentrate on one peak, either the 2p\(_{3/2}\) or the 2p\(_{1/2}\), of the experimental doublet. The chemical shift from type I to type II is rather large (~2.16 or ~1.90 eV), as shown in Figure 4b, although smaller than the experimental value of ~2.8 eV. The quantitative agreement is not bad considering the DFT calculations performed for specific stoichiometries of isolated complexes (as compared with the mixed phases and the solid state for an experimental sample). The chemical shift from type II to type III is ~2.07 eV, as shown in Figure 4b, comparable with the experimental value of ~1.95 eV.

N 1s and O 1s PES measured for a few intercalation stages (not shown here) also coincide with the DFT results. The O 1s PES exhibited a weak oxidation signal for the samples at high intercalation stages; the slight oxidation had no effect on the spectra shown in Figures 3 and 4.

For observing the electron transfer from K to ITIC, we measured (with hv = 21.2 eV) one valence state spectrum on the sample of K\(_{2.0}\)ITIC. More valence state spectra were measured on another K-intercalated ITIC film (the valence state samples). All these valence state spectra are shown in Figure 5. For the valence state samples, we measured the K 2p and C 1s core-level PES only after the last intercalation round, and the stoichiometry was estimated to be K\(_{2.2}\)ITIC. The stoichiometries for the samples of spectra 2–7 are unknown because we did not measure the corresponding K 2p and C 1s PES to avoid sample oxidation caused by too long experimental time (very slight oxidation could much affect the valence state spectra). Therefore, we indicate the electric
current through the K evaporation source and the deposition time for each intercalation round in the figure. We did not intercalate the valence state samples to saturation because the spectra shown in Figure 5 have been sufficient for observing the electron transfer.

Spectrum 1 of the pristine ITIC film exhibits four features, which are labeled A, B, C, and D. Feature A corresponds to the HOMO level of the pristine ITIC according to the valence state DOS curve (not shown here). Upon the intercalation of K, a new feature, which is labeled E, emerges between feature A and the Fermi level ($E_F$). For clarity, the signal near the Fermi level is magnified by 16 times (spectra 1–3) or 8 times (spectra 4–9) in the figure. Feature E is the direct evidence of the electron transfer.

The intensity of feature E increases monotonically from spectra 2–5, corresponding to more electrons filling the unoccupied molecular orbitals of intact ITIC. The intensity decreases slightly for spectrum 6, indicating the degradation of some molecules at this intercalation stage. After the degradation of the molecules, the intensity of feature E does not necessarily increase monotonically with more intercalation of K. Spectrum 9 has the characters (five features A–E and their energy positions) in line with the overall evolution trend shown in Figure 5, indicating that a conjugated skeleton exists until the intercalation saturation.

To sum up, the PES data shown in Figures 3–5 verify the DFT conclusions and make up for the deficiency of the DFT calculations performed only for $K_{x}ITIC$.

The results about the K–ITIC interaction have many implications to designing high-performance electrode interfaces for ITIC-based devices. For a metal salt interlayer (between ITIC and the electrode), the number of the released metal atoms from the salt may be not large enough to degrade the molecular structure, but the released metal atoms can alter the electronic property of ITIC through electron transfer. The altered electronic property needs further study. When reactive metal film is adopted as an electrode interlayer, one worries about the degradation of the molecular structure. Our results imply that the molecular skeleton of metal–ITIC complexes may be still conjugated and assure effective charge transport for some other reactive metals; these metals can then be adopted as interlayers. In this respect, further works are needed to study the detail of the interaction between ITIC and other reactive metals such as Ca, Ba, and Mg. Interfacial electronic states are crucial for the performance of the devices. The electronic states at the interface between ITIC and a metal film interlayer should be rather complicated because of the electron transfer and molecular degradation, and great efforts are desirable to obtain the detail of the electronic states.

### CONCLUSIONS

Six first arrived K atoms are dragged to the end groups (the acceptor units of ITIC) and donate their 4s electrons to the delocalized unoccupied molecular orbitals. The molecular structure is intact at least for the stoichiometries of $K_{x}ITIC$ and may keep intact until $K_{9}ITIC$. Then, the subsequently arrived K atoms interact with the IT core (the donor unit of ITIC) and break some S–C bonds. The two S–C bonds mostly near the molecular center (bonds 4 and 4'), however, never break. After the breaking of one or more S–C bonds, K–S ion bonds and the corresponding K–ITIC complexes are formed. The complexes are still conjugated.

### COMPUTATIONAL AND EXPERIMENTAL METHODS

**Computational Details.** DFT calculations were performed with the DMol3 package. We constructed and optimized many $K_{x}ITIC$ ($x = 0–20$) structures. The distances between a K atom and the atoms of ITIC were assured to be greater than the sum of the ionic radius of K and the atomic radius of the other atoms in the initial structures. The energy levels, orbital contours, Mulliken occupancy numbers, and DOSs were calculated for the optimized structures. We adopted the Perdew–Burke–Ernzerhof (PBE)-generalized gradient approximation functional and the double numerical basis sets plus polarization function (DNP) in the calculations. The PBE functional and the DNP basis set have been adopted in the study of K–PC$_{61}$BM interaction, which generated results coinciding excellently with PES spectra. The convergence criteria for the structural optimization are $10^{-6}$ Ha on the energy, $10^{-4}$ Ha/Å on the gradient, and $10^{-3}$ Å on the displacement. Self-consistent field procedures were carried out with a convergence criterion of $10^{-6}$ Ha on the energy and electron density.

**Experimental Details.** PES measurements were carried out at the Photoelectron Spectroscopy Endstation of the Beijing Synchrotron Radiation Facility. ITIC (purity > 99%, Solenne company) films were spin-coated on HF-etched Si/H(111) substrates in a N$_2$–H$_2$ ultrahigh vacuum environment ($2 \times 10^{-10}$ mbar) for more than 8 h. Before K intercalation, the samples were heated at $120 ^\circ$C for 30 min. No change of spectral shape could be observed, indicating the clean samples even before the heating.

K intercalation was performed in a stepwise manner with an SAES getter source located at 11 cm from the sample surface. During the deposition of the K atoms, the ITIC films were kept at room temperature. The concentration of K deep in the
samples may be smaller than that in the surface region because of the absence of annealing at elevated temperatures. However, such samples are competent for our research purpose. We intercalated two ITIC films, one for core-level measurements (with the photon energy of 700.0 eV) and the other for valence state measurements (with the photon energy of 21.2 eV). The core-level measurements were time-consuming. We measured the valence state PES on another film for worrying about sample oxidation caused by too long experimental time.

A Gammadata Scienta R4000 analyzer was used to collect the photoelectrons in a solid angle of ±19° with respect to sample normal. The 4f/2 core-level PES of a Au film (deposited on the sample holder just before the measurements) was frequently recorded for checking the photon energies. The overall energy resolution of the spectra was 0.7 eV for the core-level measurements and 0.05 eV for the valence state measurements. In the core-level measurements, K 2p, C 1s, and S 2p PES were measured for every stage of the sample preparation history. For reducing the experimental time and avoiding sample oxidation, we measured N 1s and O 1s PES only for a few intercalation stages.

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Notes
The authors declare no competing financial interest.

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