Quadruple Anionic Buckybowls by Solid-State Chemistry of Corannulene and Cesium

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ABSTRACT: The buckybowl corannulene is known to be an excellent electron acceptor. UV photoelectron spectroscopy studies were performed with thin-film systems containing corannulene and cesium. Adsorption of submonolayer quantities of corannulene in ultrahigh vacuum onto thick Cs films, deposited at 100 K on a copper(111) substrate, induces a transfer of four electrons per molecule into the two lowest unoccupied orbitals. Annealing of thick corannulene layers on top of the cesium film leads to the formation of a stable film composed of \( C_{20}H_{10}^{-4} \) ions coordinated to four Cs\(^+\) ions. First-principles calculations reveal, as the most stable configuration, four Cs\(^+\) ions sandwiched between two corannulene bowls.

INTRODUCTION

Large efforts to identify organic superconductors with a high superconducting transition temperature (\( T_c \)) have been undertaken but with limited success so far. \(^1\) Graphite-intercalation superconductors, such as KC\(_{8}\), CaC\(_{6}\), and YbC\(_{6}\) with \( T_c \) typically in the range of 0.5–12 K were described early on.\(^2\)–\(^4\) With the advent of C\(_{60}\) in the 1990s came alkali-metal doping of fcc-C\(_{60}\) crystals which led to \( T_c \) as high as 38 K.\(^5\)–\(^6\) In this decade, the alkali-metal doped planar aromatic hydrocarbon (PAH) picene was found to become superconducting at 18 K,\(^7\) and very recently potassium doped “few-layer graphene” material showed a transition temperature of 4.5 K.\(^8\) A very promising candidate for alkali-doped organic superconductivity is corannulene (I, \( C_{20}H_{10} \), Figure 1), a bowl-shaped PAH fragment of C\(_{60}\). Transition temperatures of up to 66 K for the monoanion of I have been predicted by theoretical modeling of intermolecular electron–phonon coupling.\(^9\)

Motivated by the novel bowl-shape and five-fold symmetry of I, studies of corannulene-coated metal surfaces have revealed numerous surface stereochemical principles, such as optimal packing strategies of five-fold symmetric molecules in the plane,\(^10\)–\(^11\) effects of symmetry mismatch between substrate and molecules,\(^12\)–\(^14\) 2D phase transitions,\(^15\)–\(^16\) bicomponent packing,\(^17\) and surface-induced ball- and bowl-in-bowl complexation.\(^18\)–\(^19\) These primarily structural studies allow one to develop a molecular-based materials chemistry for I.

Having a \( \pi \)-electron surface area comparable to that of pyrene or perilene,\(^20\)–\(^21\) I should also display exceptional photophysical and electrochemical properties as a material,\(^22\) such as the intense blue-light electroluminescence reported for I;\(^23\) and the particularly intriguing, large electron-acceptor ability of I, which, if normalized per carbon atom, goes beyond that of C\(_{60}\).\(^24\) C\(_{60}\) with a triply degenerate lowest unoccupied molecular orbital (LUMO), can accommodate six extra electrons over 60 carbon atoms (0.1 e\(^-\)/C atom), whereas corannulene with a doubly degenerate LUMO can accommodate four extra electrons (0.5 e\(^-\)/C atom). Recent work characterized tetralithium-I complexes in solution,\(^25\) but it stays unresolved that I cannot form a \( C_{20}H_{10}^{-4} \) anion with larger ions, such as potassium.\(^26\) In particular, it has been suggested that alkali-I complexes of the type \( X_4C_{20}H_{10} \) (\( X \neq \text{Li} \)) will not form sandwich structures with four alkali ions located between two bowl molecules, as was the case for Li\(_4\)-I.\(^27\) Until recently,\(^28\) compounds containing anions of I were exclusively characterized in solution, and there only the tetraanionic Li-I aggregate has been identified.\(^29\) Such tetraanionic Li-I motif has
also been used to create supramolecular architectures with biconorannulenyl.

In refutation of the current hypothesis, this study shows that
codoposition of 1 and Cs metal onto a Cu(111) surface under
ultrahigh vacuum (UHV) conditions leads to a 1-Cs4
compound with a structure analogous to the Li4C20H10
complex. UV photoelectron spectra clearly reveal charge
transfer from Cs to 1 and the occupation of the two degenerate
LUMOs. Theoretical calculations suggest four Cs ions between
two distorted bowls of 1 are aligned in a square and a complete
occupation of the two lowest unoccupied orbitals, LUMO and
LUMO+1.

■ METHODS SECTION

Experimental Section. The experiments were performed in an
UHV chamber (p < 2 × 10−10 mbar), equipped with standard surface
science techniques like X-ray photoelectron spectroscopy (XPS), UV
photoelectron spectroscopy (UPS), low-energy electron diffraction
(LEED), and thermal desorption spectroscopy (TDS). After synthesis
and purification of 1,20 thermal evaporation (Temax = 384 K)
was performed from an effusion cell. Cesium was evaporated by using a
dispenser (SAES), which contained Cs2CrO4 embedded in Al and Zr,
acting as an oxygen getter. They are stable in air and easy to handle.
The copper(111) surface (Matek, Germany) was cleaned and
annealing at 800 K.31 The cleanliness and surface crystallinity was
checked by XPS and LEED. A monolayer of Cs is defined here for the
amount needed to create the (4 × 4) overlayer on Cu(111) at room
temperature,15 i.e., 9 × 1010 molecule/m2.

Theoretical. The conformational analyses of the molecular systems
were carried out using the B97D/Def2-TZVPP level of theory.32 The
semiepiphanically corrected functional, B97D, is in accord to the ansatz
proposed by Grimme (2006),33,34 using an ultrafine grid for evaluation
of integrals. The B97-D functional is a special reparameterization of the
original B97 hybrid functional of Becke,35 which is more neutral to
spurious dispersion contamination in the exchange part than the
original functional. The Def2-TZVPP basis set is that of Weigend and
Ahrlick.36 Full geometry optimizations were performed and uniquely
characterized via second derivatives (Hessian). From the fully
optimized structures of the alkali-metal-1 complexes, projected density
of states (PDOS) were determined using the Perdew–Burke–
Ernzerhof generalized gradient approximation (PBE-GGA),37 plane
wave basis sets, and Vanderbilt ultrasoft pseudopotentials,38
implemented in the Quantum-ESPRESSO package.39 The dimensions
of the unit cell are such that the distance among replicas are on the
order of 20 Å. Rydberg cut-offs of 25 and 250 are chosen for the wave
functions and the charge density, respectively. The calculations are
performed at the GAMMA point.

■ RESULTS AND DISCUSSION

Figure 2 displays a series of UP spectra of a thick film of
metallic Cs with increasing coverage of 1 at 100 K sample
temperature. The spectrum of the metallic Cs film (black
curve) features the characteristic S1/2 and S1/2 peaks of
cesium at 12 and 13.8 eV binding energy as well as the
characteristic valence Auger edge at 9.5 eV. The Cs film is thick
enough to extinct any Cu feature. The S1/2 peak is split into a
very sharp doublet, which occurs as the valence auger edge only in
metallic Cs films. The weak emission of electrons from the
Fermi edge is also clearly identified (Figure 2, inset). The Sp
peaks disappear upon gradual deposition of 1 and are
completely quenched in the 3 ML spectrum; an indication of
layer-by-layer growth, because otherwise features of the
underlying Cs film would be still observed. For initial coverages
of 1 (up to ~1 ML), two new features (A′ and A″) appear in
the molecular band gap at 0.8 and 2.6 eV binding energy,
respectively. These new peaks are associated with the
corannulene LUMOs becoming occupied by formation of a
charge-transfer complex with the underlying Cs. The work
function of 2.0 eV of metallic Cs, as determined from the
secondary electron cutoff here (not shown), is in good
agreement with previously reported values in the literature.40
The work function of the Cs doped film of 1 is even lower at
1.75 eV. The spectrum taken with 3 ML COR refers to the
undoped multilayer of corannulene, as can be seen in the
increased work function and the disappearance of the gap
states, again indicating a layer-by-layer growth of the molecular
film and no diffusion of the alkali metal. The bands of 1 (A–D)
are also observed for deposition on Cu(111) without Cs
involved.41

Multilayers of 1 desorb between 300 and 330 K and
multilayered metallic Cs desors also at 300 K.41 Heating a
thick (≈10 ML) film of 1 adsorbed on the thick Cs film, both
deposited at 100 K, does not result in such multilayer
desorption of components but rather in the formation of a
compound surface coating with thermal stability beyond those
of the single components.

Figure 3 shows the UP spectra with increasing temperatures.
The spectra at higher temperature show that the multilayer
bands of the single components (Figure 2) disappeared.
Furthermore, Cu bands are not observed, confirming that we
still deal with a thick film. Between 200 and 300 K, the spectra
change drastically. On one hand the molecular features (A–D)
decrease in intensity, broaden, and show initially a rigid shift to
higher binding energy. On the other hand the now-occupied
LUMOs (A′ and A″) and a second peak, associated with the
destabilized HOMO, appear. Upon heating to 420 K the Cs-
doped 1 A′ and A″ emissions are still very pronounced and
show no sign of decomposition. Starting from 275 K the
LUMOs are clearly visible around 1.0 and 2.5 eV. At increased
temperatures the Cs becomes mobile and diffuses into the film
resulting in a change in the local density of Cs atoms per
molecule.

Between 275 and 300 K, band A (presenting two degenerate
HOMOs) broadens and shifts to slightly lower binding energy,
whereas the gap states A′ and A″ shift to slightly higher binding
energy, thus decreasing the former HOMO–LUMO gap. This
observation and the growing intensity of the LUMOs must be
interpreted as the Cs increasingly dispersing in the film of 1
above and doping all the molecular layers that were undoped in

Figure 2. UP spectra of a clean Cs film (black) subsequently covered with one-half (red), 1.2 (blue), and three (green) monolayers of 1. The inset shows emergence of new occupied states (A′) near the Fermi edge. T = 100 K. Values of the work function of metallic Cs and work function change due to deposition of 1 are given.
the thick film before. Similar conclusions have been made for potassium doping of C_{60} multilayers.\textsuperscript{42,43} Moreover, there is no sign of increased intensity around the Cu d-band or the Fermi level indicating that desorption is not an issue and decomposition negligible, as indicated by the intact molecular structure. During this annealing procedure, the work function decreases from 3.4 eV at 100 K to 2.0 eV at 420 K, an indication that the diffusion of Cs and I still prevails. The gradual intensity increase of the two A′ and A″ photoelectron emission peaks supports this picture.

The appearance of two new gap states below the Fermi edge in the valence band UP spectra indicates that the two degenerate LUMOs become populated, but not if they are completely or only partially filled. As mentioned above, with Li, a tetraanion has been reported.\textsuperscript{24} Because Cs has a much lower ionization potential, such charge transfer can be expected from this point of view; however, the maximum reduction to −2 with potassium has been assigned to steric issues. Our XPS analysis of the film after thermal treatment (Figure 4), which is based on the intensity of the Cs 3d\textsuperscript{5/2} and C 1s peaks in the spectrum plus taking the corresponding sensitivity factors into account, reveals a carbon:cesium ratio of 5.1:1, i.e., basically four Cs atoms per one molecule of I. This supports the proposed tetraanionic coronannulene and the full occupation of the two degenerate LUMO and LUMO+1. A calculation of the PDOS and the symmetry structure of the highest occupied orbitals of the complex, which are identical to the LUMO of the free molecule, further supports the four-fold occupation of LUMO and LUMO+1 (Figure S1).

In order to evaluate the structure of complex of I and Cs in the film, we performed modeling at the B97D/Def2-TZVPP level of theory for different structures. Cs-corannulene complexes, including Cs\textsubscript{4}·I monomer structures and (Cs\textsubscript{4}·I)\textsubscript{2} dimer structures, have been fully optimized. Two monomer structures were optimized, one with two Cs atoms approaching the convex side and two Cs atoms approaching the concave side of I and one with all 4 Cs atoms approaching the convex side of I (Figure S2). The latter was calculated to be higher in energy (21 kcal/mol); however, a much more stable situation was found for the fully optimized dimer complex resulting in a stacked conformation, with four Cs atoms coordinated between the two stacked coronannulene molecules and two Cs atoms on the outer face of each bowl (Figures 5 and S2). An estimate of the complexation energy for the dimer, with reference to the lowest energy monomer structure, predicted a significant stabilization of the dimer by ∼156 kcal/mol. Such large stabilization energy may be in part due to the increased interaction capability of the Cs atoms between the two structures, which bind to both of the coronannulene surfaces (Figure 5).

**CONCLUSIONS**

The interaction of Cs leads to a quadruple anion of coronannulene in the solid state. In contrast to earlier claims, four Cs atoms are found to be located between two bowls in a sandwiched structure. Valence band spectra show population of two electronic levels that are assigned as the two degenerate LUMO orbitals of coronannulene. Up to 420 K, no decomposition was observed. Having a method for preparing films of X-1 at maximum alkali-metal doping level opens the door to study superconductivity and optoelectronic properties of these promising materials systems.
ASSOCIATED CONTENT

Supporting Information

DOS, PDOS, highest occupied orbitals of Cs-1 complex, and DFT-optimized complex structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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