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Electronic structure of pristine and potassium-doped $Y@C_{82}$ metallofullerene

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Ultraviolet photoelectron spectra (UPS) of $Y@C_{82}$ have been measured with a synchrotron light source. UPS spectra reveal the photoelectron onset at 0.3 eV below the Fermi level, indicating the semiconducting nature of the metallofullerene, and contain low-binding-energy features associated with charge transfer from the encapsulated atom to molecular orbitals. As for empty fullerenes, when the incident photon energy is varied, the relative intensities of the valence-band features of $Y@C_{82}$ oscillate, showing that the endohedral atom does not significantly disturb the photoelectron interference effects of the fullerene cage. For $K_{2.3}Y@C_{82}$, which forms a fcc-like structure, core and valence states of $Y@C_{82}$ broaden and shift to higher binding energies but there is no evidence of density of states at the Fermi level. Finally, although core and valence states of $Y@C_{82}$ change considerably upon an intercalation of potassium, the encapsulated atom is well shielded from the outside chemical environment and its valency remains close to 3+.

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I. INTRODUCTION

Previous studies of alkali-doped C_{60} have shown the remarkable nature of its electronic structure, in which a full range of electronic properties from insulator to superconductor has been demonstrated.[1,2] Such properties are of vital importance when considering their use in nanoelectronic applications. When C_{60} is doped with potassium there is electron transfer from the metal to the molecule and occupation of the C_{60} lowest unoccupied molecular orbital (LUMO) is observed in photoemission experiments.[2,3] The electronic structure of *K*-doped fullerite compounds can be described by a charge transfer picture where the LUMO of C_{60} is gradually filled due to electrons donated by the alkali metal. While both the LUMO and (highest occupied molecular orbital) HOMO shift in a monotonic fashion toward higher binding energies with the doping, the HOMO-LUMO gap varies as a function of doping level.[4] Alkali doping of higher fullerenes such as C_{84} (Ref. 5) also shows a similar valence-band behavior, although the spectral features are less distinct than in C_{60} because of the decreased molecular symmetry. Although alkali-doped fullerenes have been studied to a large extent, to date there has just been one study, performed by Pichler *et al.*,[6] on the alkali intercalation of an endohedral metallofullerene. This group observed a new peak close to the Fermi level in photoemission spectra of *K*-doped $Tm@C_{82}$ and interpreted it as arising from the occupation of unoccupied states with potassium electrons.

The influence of the molecule-exohedral atoms interaction on the electronic structure and the chemical environment of an atom enclosed within a fullerene cage is the main motivation for our study of *K*-doped endofullerenes. Photoemission spectroscopy is an important technique in providing a direct measure of the occupied electronic structure of fullerenes and their behavior under alkali intercalation. Previous work on lanthanide endohedral fullerenes such as $La@C_{82}$ and $Ce@C_{82}$ has revealed a charge state close to 3+ for the metal atom encapsulated.[7–9] However, resonant photoemission measurements revealed a more detailed picture of the metal-cage interaction in endohedral fullerenes, which involves strong hybridization between the metal valence states and the molecular orbitals of the host fullerene in addition to the charge transfer.[10] This hybridization picture has been confirmed by recent density functional calculations on metallofullerenes, which show significant mixing between the metal valence states and the cage orbitals.[11,12] Up to now, yttrium endohedral fullerenes have received only a modest amount of attention, focused mainly on the molecular structure and the charge state of the yttrium atom. The endohedral nature of $Y@C_{82}$ was first proven using a combination of x-ray diffraction and the maximum entropy method,[13] which also found the yttrium ion strongly bound to the carbon cage. Very recently, Feng *et al.* have been able to determine the cage structure of $Y@C_{82}$, which was found to have C_{2V} symmetry.[14] In the endohedral form, $Y@C_{82}$ provides a unique way of studying single atoms of yttrium in controlled surroundings. Potassium is strongly electropositive, and one would expect an ionic bond between the fullerene carbon and the intercalated potassium. A key question of interest is whether the intercalant-cage ionic interaction has any effect on the electronic state of the yttrium, and the degree to which the endohedral atom is shielded from the outside chemical environment. We investigated this by taking a closer look at the electronic properties of the endohedral fullerene and its encapsulated atom, through a combined photoemission spectroscopy and a doping study of $Y@C_{82}$.

II. EXPERIMENTAL DETAILS

The experiments were performed on beam line 4.1 of the synchrotron radiation source at the Daresbury Laboratory, using a standard UHV chamber equipped with a Scienta SES200 hemispherical electron analyzer (angular acceptance of ±5°). The Ag(111) crystal was prepared by argon-ion sputtering and annealing cycles at approximately 420 °C, until no impurities could be detected by photoemission, and sharp, low-energy electron diffraction patterns of the clean surface were observed. $Y@C_{82}$ (purity >99.9%) was produced by the dc arc-discharge method and stored in a carbon disulphide (CS_2) solution. The production and purification of $Y@C_{82}$ have been described in detail elsewhere.[15,16] The CS_2 was allowed to evaporate in a tantalum crucible under ambient conditions before being transferred to the UHV system. Multilayer films were prepared by a sublimation of $Y@C_{82}$ at 550°C, while the Ag substrate was kept at 180 °C. During the endofullerene evaporation the pressure in the main chamber rose from 2×10^{-10} to 5×10^{-8} mbar. C_{84} (98% pure), purchased from Nano-C Inc., was deposited by sublimation in the same manner at 470 °C. Potassium was deposited from a well-degassed SAES getter source and doped samples were subsequently annealed at 220 °C for 5 min for equilibration. Photoemission spectra were acquired with the electron analyzer using synchrotron radiation for valence-band [ultraviolet photoemission spectroscopy (UPS)] spectra, and Mg $K\alpha$ x rays from a conventional x-ray gun for core-level [x-ray photoemission spectroscopy (XPS)] spectra. XPS survey of the film, before and after measurements, shows signals of C, Y, and K elements and no other impurities. To quantify the degree of K doping, we used the relative intensities of the C 1s and K 2p peaks, taking into account the appropriate photoemission cross sections of these states. All UPS spectra presented here were taken at normal emission and with the incoming light at 45° with respect to the surface normal.

III. RESULTS AND DISCUSSION

There are several reasons for growing a K-doped $Y@C_{82}$ film on Ag(111) in the manner described above. First, the Ag(111) surface is known to be relatively inert and prevented from oxidizing during growth of the endohedral fullerene film. Second, $Y@C_{82}$ in bulk is expected to have weak bonding between molecules, allowing us to measure the electronic properties of the pure endofullerene. And finally, analogous to alkali fullerides, C_{82}-based endofullerenes doped with an alkali metal can adopt a variety of intercalant-host-type structures.[6,17] For $K_xY@C_{82}$ films grown on heated substrates with $x\leq2.5$ a fcc-like molecular structure is expected, in which alkali ions occupy both octahedral and tetrahedral sites (the interstitial sites have a hard-sphere radii of 2.34 and 1.27 Å, respectively, based on a $Y@C_{82}$ radius of 5.65 Å, while the radius of a potassium atom is 1.33 Å). This film growth method permits us to probe the behavior of the endofullerene and the yttrium atom under potassium intercalation.

An interesting feature in the photoemission of fullerenes, which has not been observed for any other molecular systems, is that the intensities of the low-binding-energy states in the valence-band spectra show distinct oscillations as the incident photon energy is varied.[18] This phenomenon has been attributed to the interference of photoelectron waves emanating from each carbon atom in the near-spherical fullerene cage.[19] In this paper, we present a photoemission study of both pure and endohedrally doped fullerenes to further elucidate the photoelectron interference effect in fullerene systems. Doped fullerenes retain essentially their molecular structure, but the electronic states are modified by the encapsulated atom-cage interaction. It is proposed that if the intensity oscillation is only the molecular characteristic, similar photon-energy-dependent behaviors are observed for C_{84} and endohedral $Y@C_{82}$ as the cages of the two fullerenes are of comparable shape and radius. Figure 1 shows the valence-band spectra for $Y@C_{82}$ and C_{84} obtained with photon energies described to the right site of each spectrum. Broken lines indicate the approximate peak positions. The spectra in Fig. 1(a) display the characteristic features of higher metallofullerenes: the $C\pi$ derived states are organized in four distinct features B-E at 1.7, 2.0, 3.2, and 5.1 eV, respectively, and the $C\sigma$ orbitals are located above 6-eV binding energy, appearing in a clear peak F at 6.2 eV while other features are relatively weak. The small feature close to the Fermi level, located at 0.75 eV is similar to the onset seen previously on $La@C_{82}$ (Ref. 7) and $Ce@C_{82}$,[9] and was identified as a single occupied molecular orbital (SOMO) of $C\pi$ origin. The spectral features of the $Y@C_{82}$ valance band are particularly similar to those of $La@C_{82}$, i.e., metallofullerenes with a trivalent (or close to trivalent) encapsulated atom. It is known that the La ($5d^16s^2$) atom donates almost three valence electrons to the C_{82} cage to form the endohedral complex, which has the electronic structure of $La^{3+}@C_{82}^{3-}$. Two La 6*s* electrons are transferred to the C_{82} LUMO, while the unpaired 5*d* electron is strongly localized on the cage and gives rise to the SOMO peak. Compared to La, Y ($4d^15s^2$) has similar valence-band structure, however, density functional calculations found that the SOMO of $Y@C_{82}$ has little Y character.[20] This indicates that the *d*-derived electron is not as localized on the yttrium atom and that the Y atom is more strongly bound to the carbon cage compared to the lanthanum counterpart.[21]

The largest differences between the valence-band spectra of $Y@C_{82}$ and C_{84} are found in the highest occupied levels. The SOMO peak [labeled A in Fig. 1(a)] is completely absent from Fig. 1(b). The spectral features in the leading 4 eV of the C_{84} valence band are in good agreement with a previous study,[22] with peaks at binding energies of 2.1 and 3.7 eV, however, the peak observed at 5.2 eV is considerably broader and shifts downwards in binding energy by 0.2 eV. It is worth pointing out that there are structural (isomeric)

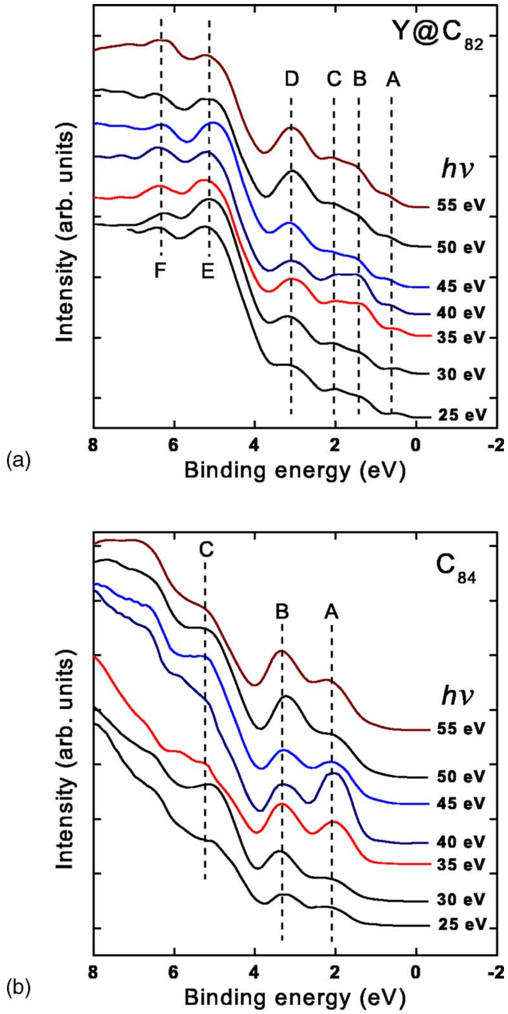

FIG. 1. (Color online) Valence-band spectra of (a) $Y@C_{82}$ and (b) C_{84} acquired at different photon excitation energies. There are six distinct features within the leading 8 eV range of the $Y@C_{82}$ spectra (labeled A–F) and three features in the C_{84} spectra (labeled A–C).

differences between the C_{84} samples in these studies. Comparison of the valence-band spectra for $Y@C_{82}$ and C_{84} shows that the metallofullerene displays broad structures at ~2 eV. This breadth reflects the splitting of electronic states due to the (generally) low symmetry of the carbon cage and the ionic interaction between the encapsulated metal and the host molecule. The spectral onsets of $Y@C_{82}$ and C_{84} are 0.3 and 1.1 eV below the Fermi level, respectively, suggesting that both are semiconductors. There are significant differences in the overall shape between the spectra of $Y@C_{82}$ and C_{84} throughout the leading 8 eV range of the valence band. This is because structural and isomeric differences between the $Y@C_{82}$ and C_{84} samples strongly affect the valence-band spectra. (C_{84} is a mixture in a 2:1 ratio with the D_2 majority and D_{2d} minority.[23])

The photoemission intensities of the lines in the photoemission spectra of both $Y@C_{82}$ and C_{84} oscillate as the incident photon energy is varied. The oscillations are particularly drastic for low-binding-energy features, below 4 eV. This phenomenon of photon-energy dependencies was attributed to the final-state photoelectron interference effects in fullerene systems.[19,24] It is worth pointing out that the original HOMO and near-HOMO (NHOMO) levels of the C_{82} cage in $Y@C_{82}$ (peaks C and D) show similar oscillating behavior with varied photon energies as the HOMO and NHOMO of C_{84} (peaks A and B). This apparently shows that the extra scattering center inside the cage does not significantly disturb the interference effects. The results further support the photoelectron interference model in the near-spherical structure of fullerenes[24] as the encapsulated atom has little effect on the shape of the molecules, with the bond lengths remaining similar to those of C_{82}.[7] Additionally, because of the strong photon-energy dependence of the valence-band spectra in the photoemission of fullerenes, determinations of the amount of charge transferred from the encapsulated atom to the carbon cage using the integrated intensities of the features near the valence-band edge,[25] are somewhat invalid.

Figure 2(a) shows valence-band spectra ($h\nu$=65 eV) of $Y@C_{82}$ and $K_{2.3}Y@C_{82}$, with the analogous spectrum of C_{84} also shown for comparison. The low-binding-energy features remain clearly visible in the $K_{2.3}Y@C_{82}$ spectrum, strongly suggesting that the molecule does not disintegrate upon potassium intercalation. We observe a shoulder formed at 0.45 eV below the Fermi level in the $K_{2.3}Y@C_{82}$, which has a direct counterpart in the valence band of *K*-doped $Tm@C_{82}$ and was explained as arising from the occupation of the states associated with the LUMO and LUMO+1 of the C_{82} cage by the *K*4*s* electrons.[6] There is no evidence of the density of states at the Fermi level for $K_{2.3}Y@C_{82}$, but the edge of the shoulder approaches the Fermi level. Peak A is not resolvable in the $K_{2.3}Y@C_{82}$ due to overlapping by the broadened *K*-derived shoulder. In comparison with $K_{2.3}Y@C_{82}$, the $C\pi$ derived states B, C, and D are all shifted to higher binding energies. Significant changes occur in the region above the 4-eV binding energy upon intercalation of potassium. Potassium is strongly electropositive and one would expect each intercalated potassium to donate one full electron to a neighboring fullerene molecule. These electrons, together with three electrons transferred from the encapsulated Y atom, results in, on average, 5.3 electrons residing on the C_{82} host molecule. The broad peak centred at ~6.1 eV is similar to a feature seen previously in heavily *K*-doped fullerenes and it was suggested that this is due to an interaction of potassium with contaminants in the UHV system.[26] This peak appears to coincide with the O 2*p* band which has a relatively large ionization cross section, although the level of oxygen incorporation into the film was below the detection limit of our XPS study.

Additional information can be extracted from the C 1*s* level spectra as depicted in Fig. 2(a). Both C_{84} and $Y@C_{82}$ display nearly symmetrical peaks, with a full width at half maximum (FWHM) measured at 0.96 and 1.20 eV, respectively. These peaks represent the envelope for the multitude of small differences in C 1*s* binding energies caused by the presence of the endohedral atom as well as inequivalent carbon sites in C_{82} and C_{84}. (There are at least three locally different carbon sites in C_{82} and higher fullerenes.[27]) $K_{2.3}Y@C_{82}$ possesses a higher degree of inequivalence for the carbon sites of the cage, resulting in a broad, asymmetri-

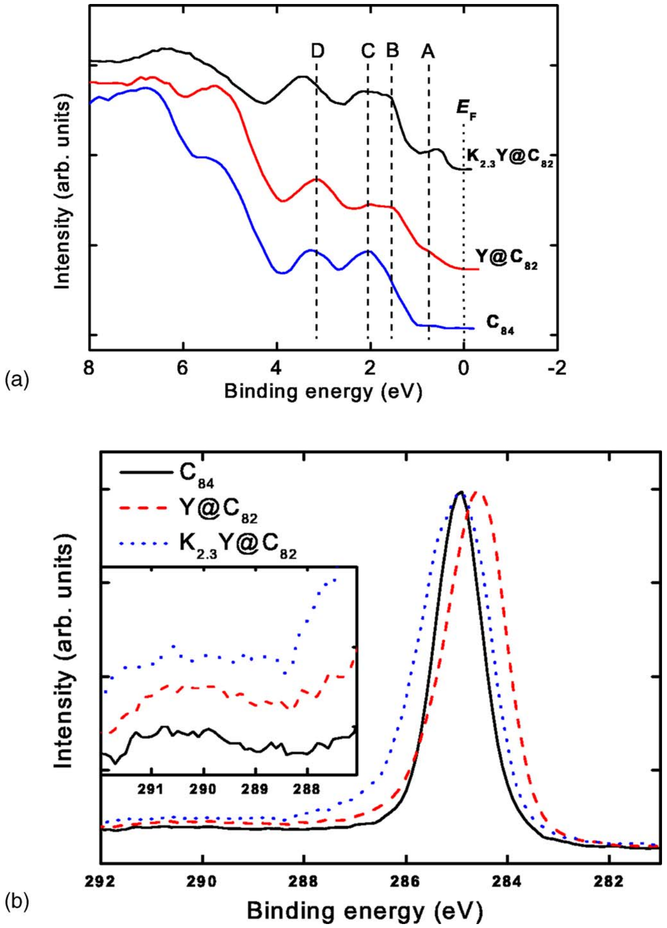

FIG. 2. (Color online) (a) Valence-band spectra of $Y@C_{82}$ and $K_{2.3}Y@C_8$, with the analogous spectrum of the empty fullerene C_{84} shown for comparison. The spectra were recorded using a photon energy $h\nu = 65$ eV. Broken lines indicate the peak positions of $Y@C_{82}$ and the Fermi level. (b) C 1*s* core-level spectra, taken using Mg $K\alpha$ x rays. Inset shows an enlarged view of the shake-up structures on the high-binding-energy side. The reduction in the intensity and broadening of the shake-up feature upon the potassium intercalation of $Y@C_{82}$ are apparent.

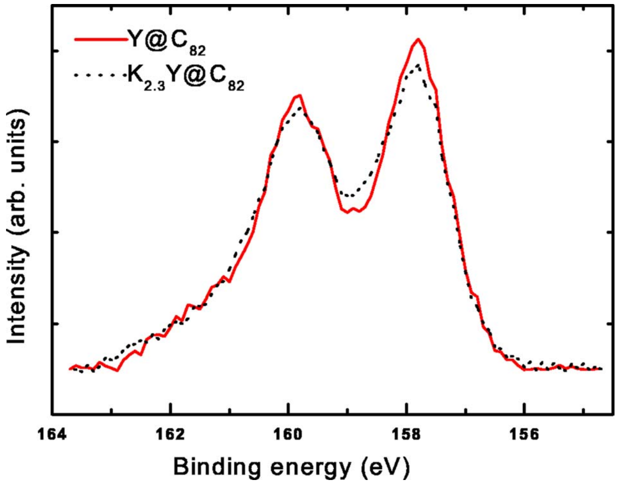

FIG. 3. (Color online) Core-level photoemission spectra of the Y 3*d* from $Y@C_{82}$ and $K_{2.3}Y@C_{82}$, acquired using Mg $K\alpha$ x rays. Both the spectra were normalized to the integrated intensities after the substraction of a linear background. No binding-energy shift associated with *K* doping is observed.

cal peak with a FWHM of 1.34 eV. Unlike potassium intercalated C_{60} and C_{70},[17] the C 1*s* peak position of $K_{2.3}Y@C_{82}$ shifts towards a higher binding energy by 0.41 eV compared to that of $Y@C_{82}$ (discussed below). As the symmetry of both C_{84} and $Y@C_{82}$ is considerably lower than that of C_{60}, photoemission from occupied states does not exhibit clear interband features and the only distinct peak that can be seen is the shake-up structures, centred at about 6 eV above the C 1*s* main line, normally associated with the creation of a collective π electron plasmon. Upon potassium intercalation of $Y@C_{82}$, the shake-up feature loses its intensity and broadens, indicating that there is screening of the collective electronic response of the molecule. As the shake-up feature reflects the final states in photoemission, i.e., the molecule left in an excited state, the widening of the shake-up feature also indicates a distortion of the carbon cage when the molecule is ionically bound to the potassium atoms. It, however, remains clearly visible in the $K_{2.3}Y@C_{82}$ spectrum, again suggesting that the molecule is still intact following the intercalation of potassium.

Having examined the effects of potassium intercalation on the electronic structure of the molecule, we continue to investigate the effect of the potassium-cage ionic bonding on the encapsulated atom. Monitoring Y 3*d* spectra is an excellent way of studying changes in the electronic state of the encapsulated atom since any sign of mixed electronic states will manifest itself on the Y 3*d* line shape. Furthermore, if there is any change in the valency of the yttrium atom (towards Y^{2+}), it will cause a clear shift in the 3*d* photoemission spectrum.[28] Figure 3 shows the Y 3*d* core-level spectra of the $Y@C_{82}$ film before and after the potassium intercalation. To allow for a better comparison, the spectra were subtracted by a linear background and normalized to the overall peak intensities. Both spectra comprise $3d_{3/2}$-$3d_{5/2}$ spin-orbit doublets. The overall Y 3*d* line shape is very similar to that of yttrium triiodide,[28] i.e., a yttrium atom of charge state close to 3+. A comparison of the two spectra clearly illustrates that there are only subtle differences following the potassium intercalation. The spectra are well aligned in the peak positions as well as the slope of the low-binding-energy side of each peak. Slight increases on the high-binding-energy side of the peaks may relate to an inelastic scattering of photoelectrons due to intercalated potassium atoms. Despite the formation of strong ionic bonds between the fullerene cage and potassium atoms and changes in the molecular chemical state as evidenced by the C 1*s* spectra, there is clearly no evidence of Y 3*d* binding energy shifts or spectral broadening. The results are consistent with a recent x-ray absorption study of $Ce@C_{82}$,[9] which found that the absorption spectrum of cerium remains unchanged when the molecule covalently bonds to a silicon surface. This is remarkable, since it demonstrates that the encapsulated atom remains impervious to dramatic changes to the molecular chemical environment. The results clearly highlight the high degree of shielding offered by the C_{82} cage to the yttrium atom and support the concept of a superatom character in endohedral metallofullerenes.

The shifts of the C 1*s* line as well as of the valence-band features to higher binding energies upon the intercalation of potassium have also been reported for *K*-doped $Sc_3N@C_{82}$ (Ref. 22) and carbon anions.[29] While the changes in the valence band of $Y@C_{82}$ upon the potassium intercalation are due to valence electron redistribution within the molecule and broken molecular symmetry, the shift of the C 1*s* line to a higher binding energy may appear anomalous if one considers that following potassium doping, carbon atoms should become more negatively charged. It is possible that this shift arises from final state effects, but this would seem unlikely if the molecular structure of the endofullerene is essentially unchanged. A more likely explanation is the proximity of carbon atoms to the potassium positive ions, resulting in an increase in binding energy from the Madelung potential.[30] For *K*-doped $Y@C_{82}$ the Madelung potential could be larger than the potential induced by the negative charge on carbon atoms because the charge is essentially spread over the fullerene cage, and on average rather distant from an individual carbon atom, while the potassium ions have a strongly localized positive charge and would be in close proximity to the cage surface. The absence of any shift in the Y 3*d* peak upon potassium intercalation clearly indicates that the Madelung potential does not influence the yttrium atom. This is because the atom is located inside the fullerene cage and therefore much further from the potassium ions.

In conclusion, we have performed a complete photoemission study of $Y@C_{82}$ and $K_{2.3}Y@C_{82}$. UPS reveals that $Y@C_{82}$ is semiconducting with a band gap of at least 0.3 eV and that its valence band contains features related to charge transfer from the yttrium atom to the cage. Upon intercalation with potassium, the valance states of $Y@C_{82}$ broaden and shift to higher binding energies. The C 1*s* photoemission further testifies to the ionic bonding to the potassium atoms and distortion of the fullerene cage. The valence state of the encapsulated yttrium has been probed by Y 3*d* XPS in both pristine and potassium-intercalated forms; the results show the atom remains “close to 3+” valence state and is well screened from the outside chemical environment of its hosting cage.

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