# Filling factor and electronic structure of Dy<sub>3</sub>N@C<sub>80</sub> filled single-wall carbon nanotubes studied by photoemission spectroscopy

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We report on a detailed study of the filling factor and electronic structure of the trimetal nitride fullerene  $Dy_3N@C_{80}(I)$  filled single-wall carbon nanotubes (SWCNTs), the so-called endohedral peapods ( $Dy_3N@C_{80}@SWCNTs$ ), using photoemission spectroscopy as a probe. The photoemission response close to the Fermi energy exhibits the manifestation of one-dimensional electronic structures, i.e., van Hove singularities and a power-law (Tomonaga-Luttinger liquid) behavior. Within the experimental accuracy the spectral shapes are the same as those of the pristine SWCNTs reference sample. From a comparison between the valence-band spectra of the peapods and the SWCNT measured with 400 eV photon energy, we determine the bulk filling of  $Dy_3N@C_{80}@SWCNTs$  to be  $74\pm10\%$ . In addition, from a detailed analysis of the resonant photoemission across the Dy 4d-4f edge, we show that the effective Dy valency of  $Dy_3N@C_{80}@SWCNTs$  is about 3.0 which is slightly larger than for  $Dy_3N@C_{80}$ .

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## I. INTRODUCTION

The endohedral peapods have a great potential to functionalize single-wall carbon nanotubes (SWCNTs) in a controlled manner because of a variety of the endohedral species in contrast to empty fullerenes. The first examples for the formation of the endohedral peapods are Gd@C<sub>82</sub>@SWCNTs and La<sub>2</sub>@C<sub>80</sub>@SWCNTs, which have been observed by high-resolution transmission electron microscopy (HRTEM).<sup>1,2</sup> The latter reported a freezing of the free rotation of the La atoms at room temperature by the encapsulation of the fullerenes into SWCNT.<sup>2</sup> The electric resistance of Gd@C<sub>82</sub>@SWCNTs exhibited a sharper increase with decreasing temperature down to 5 K compared with C<sub>60</sub>@SWCNTs,<sup>3</sup> which was attributed to the additional electron scattering due to the local electrostatic potential from the fullerenes. In addition, a band gap modulation of the SWCNT has been observed on Gd@C82@SWCNT having a chirality of (11,9) by scanning tunneling microscopy.<sup>4</sup> Raman spectroscopy of La2@C80@SWCNTs observed an up-shift of the G-band mode from the pristine SWCNTs, which was attributed to the charge transfer from the SWCNTs to the endohedrals.<sup>5</sup> This is the same tendency as a p-type semiconducting behavior at room temperature in  $Dy@C_{82}@SWCNTs.^{6}$  A study of  $La@C_{82}$ ,  $La_2@C_{80}$ , and Sc<sub>3</sub>N@C<sub>80</sub> by using the density functional theory (DFT) predicted downshifts of the endohedral fullerene-derived molecular orbitals which increase by increasing the tubefullerene distance.<sup>7</sup> This calculation also showed local radial deformations of the SWCNTs leading to shifts of the van Hove singularities (vHs). A broadening of the  $S_{11}$  optical transition peak of the SWCNTs upon La@C82 encapsulation can be understood as a consequence of the chiralitydependent energy shifts of vHs.8

Photoemission spectroscopy is a reliable tool to investigate the bulk electronic structures of such composite molecules because its element and site selectivity make it possible to extract the partial electronic structures of each of the constituents. In recent years photoemission studies contributed significantly to the understanding of the nature of endohedrals as well as fullerene peapods (e.g.,  $C_{60}$ @SWCNTs).<sup>9-21</sup>

In the present study, the recently synthesized trimetal nitride fullerene,<sup>23</sup> Dy<sub>3</sub>N@C<sub>80</sub> (isomer I), was successfully encapsulated into the SWCNTs. The bulk electronic structure of the endohedral peapods,  $Dy_3N@C_{80}@SWCNTs$ , were investigated by photoemission spectroscopy. In this paper, we show that the onedimensional electronic structure of the SWCNTs, i.e., vHs and a power-law (Tomonaga-Luttinger liquid) behavior, persists upon the formation of Dy<sub>3</sub>N@C<sub>80</sub>@SWCNTs. In addition, by taking advantage of the high atomic photoionization cross section of the Dy 4f states with 400 eV photon energy, we show that the effective valency of Dy is essentially trivalent. From the integrated intensity of the endohedral peapod spectrum relative to the SWCNT spectrum we determine quantitatively the bulk filling factor of Dy<sub>3</sub>N@C<sub>80</sub>@SWCNTs. For the given SWCNTs diameter distribution we observe a bulk filling factor of  $74 \pm 10$  %. In addition, a more quantitative analysis of the electronic configuration of Dy is performed by the resonant photoemission spectroscopy across the Dy 4d-4f edge. The Dy 4f multiplet profile extracted from the subtraction between on- and offresonant spectra is well reproduced with two sets of multiplets calculated for  $4f^9 \rightarrow \hat{4}f^8$  and  $4f^{10} \rightarrow 4f^9$  photoemission process, respectively. From the relative intensity of the two sets of multiplets, we estimate the bulk effective Dy valency of Dy<sub>3</sub>N@C<sub>80</sub>@SWCNTs to be 3.0, which is slightly larger than the previously reported value of 2.8 for a  $Dy_3N@C_{80}$  film.<sup>19</sup> The valence change observed is attributed to the additional charge transfer between the endohedral fullerene and SWCNT.

### **II. EXPERIMENTAL DETAIL**

The trimetal nitride fullerene Dy<sub>3</sub>N@C<sub>80</sub> (isomer I) was produced using the modified Krätschmer-Huffman dc-arc discharging method.<sup>22</sup> High performance liquid chromatography and laser desorption time-of-flight mass spectroscopy were used to isolate and identify Dy<sub>3</sub>N@C<sub>80</sub> fullerenes.<sup>23</sup> The SWCNTs were synthesized by the laser ablation method and purified by the H<sub>2</sub>O<sub>2</sub> treatment. A SWCNT film was prepared by drop coating from an acetone solution of SWCNTs and cleaned by annealing at 450 °C in ultrahigh vacuum (UHV) conditions as described previously.<sup>20</sup> After the measurements on the SWCNT film, a Dy<sub>3</sub>N@C<sub>80</sub> film with visible thickness was deposited onto the SWCNT film by the sublimation at a furnace temperature of up to 600 °C under UHV conditions using an evaporator specially designed for the purpose of subliming tiny amounts of molecules. The film was subsequently heated at 450 °C for more than 24 h to encapsulate  $Dy_3N@C_{80}$  into the SWCNTs: the temperature is slightly higher than the sublimation temperature of  $Dy_3N@C_{80} \sim 400$  °C, but lower than 500 °C which closes the SWCNT ends. After the encapsulation procedure, an additional heat treatment at 600 °C was performed in order to remove the excess Dy<sub>3</sub>N@C<sub>80</sub> which did not enter the SWCNTs. A complete removal of the excess  $Dy_3N@C_{80}$ on the SWCNT film surface was confirmed by observing the disappearance of the Dy3N@C80 film visually. TEM observations confirmed the SWCNTs to be filled.

The synthesized endohedral peapod film was transferred into the analysis chamber equipped with a helium cryostat without breaking UHV conditions. The photoemission experiment was performed at beamline UE 52 PGM, Bessy II, using a hemispherical photoelectron energy analyzer SCI-ENTA SES 200. The absorption spectrum was obtained by measuring the drain current of the sample. The experimental resolution and the Fermi energy ( $E_F$ ) were determined from the Fermi edge of a clean Au film. All spectra were recorded with an overall energy resolution better than 50 meV. The base pressure in the experimental setup was kept below  $3 \times 10^{-10}$  mbar.

#### **III. RESULTS AND DISCUSSION**

#### A. Filling factor

We first determine the bulk filling factor of  $Dy_3N@C_{80}@SWCNTs$  by comparing the integrated intensity of the valence-band photoemission spectrum of  $Dy_3N@C_{80}@SWCNTs$  with that of SWCNTs. For this purpose, we used the valence-band photoemission spectra of  $Dy_3N@C_{80}@SWCNTs$  and the SWCNTs measured with 400 eV photon energy which are plotted in Fig. 1 together with that of  $Dy_3N@C_{80}$ . The spectra were normalized so that the ratio between the elastic and inelastic signals of the difference spectrum  $Dy_3N@C_{80}@SWCNTs$  be-



FIG. 1. Photoemission spectra of SWCNTs,  $Dy_3N@C_{80}@SWCNTs$ , and  $Dy_3N@C_{80}$  collected with 400 eV photon energy. The difference spectrum between  $Dy_3N@C_{80}@SWCNTs$  and SWCNTs is also plotted.

comes the same as that of the pristine  $Dy_3N@C_{80}$  spectrum. While the SWCNT spectrum shows broad features, the  $Dy_3N@C_{80}@SWCNT$  spectrum exhibits two prominent peak structures at the binding energies around 7 and 10 eV, respectively. These peak structures are ascribed as the Dy 4*f* multiplets, which will be discussed in detail in Sec. III C. A large contribution of the Dy 4*f* states in the valence-band photoemission spectrum is due to the high atomic photoionization cross section of the Dy 4*f* state much larger than those of the valence states of C and N with 400 eV photon energy.

The integrated intensity of the valence-band photoemission from the  $Dy_3N@C_{80}@SWCNTs$  with a bulk filling factor of  $\nu$  is expressed as

$$I_{\mathrm{Dy}_{3}\mathrm{N}@\mathrm{C}_{80}@\mathrm{NT}} \propto N_{\mathrm{NT}}\beta_{\mathrm{NT}}\gamma_{\mathrm{NT}} + \nu \sum_{M=\mathrm{Dy}_{3},\mathrm{N},\mathrm{C}_{80}} N_{M}\beta_{M}\gamma_{M},$$
(1)

where  $N_M$  is the number of the atoms of the constituents  $M=Dy_3$ , N,  $C_{80}$ , SWCNT in a  $Dy_3N@C_{80}@SWCNT$  with 100% filling,  $\beta_M$  is the atomic photoionization cross section,  $\gamma_M$  is a factor to take into account the effect of a short photoelectron mean free path of  $0.80\pm0.20$  nm at 400 eV electron energy.<sup>21</sup> According to the previous photoemission work on  $C_{60}@SWCNTs$ ,<sup>21</sup> when  $\gamma_{NT}=1$ ,  $\gamma_{C_{80}}$  is calculated as  $0.75\pm0.10$  for a  $C_{80}@SWCNT$ , with a SWCNT diameter of 1.42 nm, which is the mean SWCNT diameter of the present sample and it will be obtained in the next paragraph. Also,  $\gamma_{Dy_3}$  and  $\gamma_N$  should be  $0.75\pm0.10$ . From the atomic

photoionization cross sections of 1.63 for Dy 4*f*, 0.032 for N 2*s*, 0.008 for N 2*p*, 0.020 for C 2*s*, and 0.002 for C 2*p* at 400 eV photon energy, we have  $\beta_{Dy_3}=1.63$ ,  $\beta_N=0.040$ , and  $\beta_{C_{60}}=\beta_{NT}=0.022$ .  $N_M$  in the unit length of the C<sub>80</sub> peas are  $N_{Dy_3}=3$ ,  $N_N=1$ ,  $N_{C_{80}}=80$ , and  $N_{NT}\sim185$  for a Dy<sub>3</sub>N@C<sub>80</sub>@SWCNT with a SWCNT diameter of 1.42 nm and C<sub>80</sub>-C<sub>80</sub> distance of 1.12 nm:<sup>24</sup> the latter is the sum of a C<sub>80</sub> (*I<sub>h</sub>*) diameter of 0.79 nm (Ref. 25) and the van der Waals distance in a graphite of 0.33 nm. By substituting the parameters into Eq. (1) and using the ratio between the integrated intensities of the Dy<sub>3</sub>N@C<sub>80</sub>@SWCNT and SWCNT spectra after the subtraction of inelastic backgrounds,  $I_{Dy_3N@C_{80}@SWCNTs}$  of  $\nu=74\pm10$  %.

Furthermore, by assuming a Gaussian distribution of the SWCNT diameter with a mean value of 1.42 nm and a standard deviation of 0.10 nm which will be obtained in the next paragraph, and the condition that only the SWCNT whose diameter is larger than a minimal value of  $d_{min}$  is completely filled,<sup>21</sup> the estimated bulk filling factor  $\nu$ =74±10% yields  $d_{min}$ =1.38±0.03 nm. This value is fully consistent with  $d_{min}$ ~1.36 nm predicted theoretically for Sc<sub>3</sub>N@C<sub>80</sub>@SWCNTs.<sup>7</sup>

We point out that this method opens a very reliable method to determine the filling factor on a bulk scale and is a much simpler and more straightforward analysis than the determination of the bulk filling factors in  $C_{60}$  peapods using electron energy-loss spectroscopy<sup>26</sup> or x-ray diffraction.<sup>27</sup>

#### **B.** One-dimensional electronic structures

As a second step we analyzed the electronic structure of Dy<sub>3</sub>N@C<sub>80</sub>@SWCNTs at low binding energies with special emphasis on the possible changes in the one-dimensional electronic properties, namely, vHs and Tomonaga-Luttinger liquid (TLL) behavior, in comparison with those of the SWCNTs. Figure 2 shows the valence-band photoemission spectra of Dy<sub>3</sub>N@C<sub>80</sub>@SWCNTs and the SWCNTs at binding energies below 1.5 eV collected with 125 eV photon energy. The sample temperature was kept at 17 K during measurements. Three peak structures are observed in both spectra whose shapes are similar to each other and to those of the spectra measured in the previous studies on SWCNTs and  $C_{60}$  peapods.<sup>20,21,28,29</sup> According to the procedure performed by Ishii et al.,28 the photoemission spectra were reproduced by the tight-binding calculation taking into account the Gaussian distribution of the SWCNT diameter and a shift of  $E_F$ . As plotted in Fig. 2, the calculated spectrum reproduces well the three peaks in both spectra with the same parameters: the mean and the standard deviation of the SWCNT diameter distribution are 1.42 and 0.10 nm, respectively, and  $E_F$  is shifted by 0.18 eV towards unoccupied states. The first two peaks at 0.5 and 0.8 eV binging energies correspond to the first and second vHs peaks of the semiconducting tubes, while the third peak located at 1.1 eV binding energy is assigned as the first vHs peak of the metallic tubes. The estimated mean diameter of 1.42 nm of the SWCNTs is similar to 1.44 nm of (14,7) SWCNT which has been reported to be the exothermic for encapsulation of  $La@C_{82}$ ,



FIG. 2. Photoemission spectra of  $Dy_3N@C_{80}@SWCNTs$  and SWCNTs below 1.5 eV binding energy recorded with 125 eV photon energy. The density of states (DOS) and photoemission spectrum reproduced by the tight-binding calculation are also plotted. The inset shows log-log plots of the photoemission spectra near the Fermi level.

La<sub>2</sub>@C<sub>80</sub>, and Sc<sub>3</sub>N@C<sub>80</sub> by the DFT calculation.<sup>7</sup> According to this calculation, the encapsulation of La@C<sub>82</sub>, La<sub>2</sub>@C<sub>80</sub>, and Sc<sub>3</sub>N@C<sub>80</sub> in (14,7) SWCNT gives rise to a deformation only of the SWCNT with about 1% local radial expansion leading to no appreciable shift (<0.01 eV) of the vHs peak positions. This is also confirmed by the present result where the vHs peak positions and widths exhibit no change by the formation of Dy<sub>3</sub>N@C<sub>80</sub>@SWCNTs.

As a next point regarding the one-dimensional electronic structure, the TLL behavior of Dy<sub>3</sub>N@C<sub>80</sub>@SWCNTs in comparison with that of the SWCNTs is investigated from the photoemission spectra near  $E_F$  which were plotted with a double logarithmic scale in the inset of Fig. 2. As seen in the figure, both spectra have no Fermi edge, instead, they exhibit TLL behavior, namely, a power-law dependence  $\varepsilon^{\alpha}$  on the binding energy  $\varepsilon$  with a power-law factor  $\alpha = 0.54 \pm 0.10$  for the  $Dy_3N@C_{80}@SWCNTs$  and  $0.57 \pm 0.10$  for the SWCNTs: the power-law factors were estimated by fitting the data in the binding energy region from 0.05 eV up to 0.25 eV to the power-law function. The estimated power-law factors are almost identical. Within experimental accuracy, this is in good agreement with the values reported in the previous works on SWCNTs and C<sub>60</sub>@SWCNTs.<sup>20,28,29</sup> In summarizing, the present results regarding vHs and TLL behavior show that the encapsulation of Dy3N@C80 fullerenes does not affect the low-energy excitation nature of SWCNTs and their onedimensional feature persists after the formation of  $Dy_3N@C_{80}@SWCNTs$ .

## C. Effective valency of Dy

We now turn to the valence-band electronic structure of the endohedral peapod with special emphasis on the response of the Dy ions which can be used to extract the effective Dy valency. The subtraction between the Dy<sub>3</sub>N@C<sub>80</sub>@SWCNTs and SWCNTs photoemission spectra taken with 400 eV photon energy can be used to extract the Dy 4f states. The obtained difference spectrum is, as a whole, similar to the pristine Dy<sub>3</sub>N@C<sub>80</sub> spectrum taken with the same photon energy as seen in Fig. 1, and essentially exhibits the trivalent Dy multiplets. As reported in the previous x-ray photoemission study of Dy<sub>3</sub>N@C<sub>80</sub> using Al  $K\alpha$  radiation,<sup>19</sup> the prominent structures corresponding to the divalent Dy were observed around 4 eV binding energy in the pristine Dy<sub>3</sub>N@C<sub>80</sub> spectrum. In contrast, the difference spectrum has less structures in this energy region.

Further details about the Dy valency are obtained from a resonance photoemission study in the Dy 4d-4f excitation region. The valence-band photoemission spectra of  $Dy_3N@C_{80}@SWCNTs$  measured in the Dy 4d-4f resonance region are plotted in Fig. 3. The photon energies were set to the energies at which the prominent structures appear on the Dy 4d-4f absorption spectrum plotted in the inset of Fig. 3. The absorption spectrum is similar to that of Dy metal in which Dy atoms are triply ionized.<sup>30</sup> As observed in Fig. 3, the photoemission spectra have narrow structures over the whole valence-band region which are the admixture between the 2s and 2p states of the carbon cages and the 4f states of the Dy ions. In the spectra taken with the photon energies around the giant peak in the Dy 4d-4f absorption spectrum, the three peak structures located at 6.7, 10.4, and 11.8 eV dominate. These peaks become most prominent in the spectrum taken with the photon energy 161 eV which is exactly the energy of the maximum of the giant peak in the Dy 4d-4f absorption spectrum. Therefore, these structures are assigned as the resonant-enhanced Dy 4f states. With a 149 eV photon energy which is just below the onset of the first structure in the Dy 4d-4f absorption spectrum, the Dy 4f structures are undetectable due to the Dy 4d-4f off-resonant condition, instead, the spectral features reflect predominantly the carbon molecular structures. Comparison with the pristine SWCNT spectrum collected with 149 eV photon energy (also plotted in Fig. 3) shows that the spectral shapes of Dy<sub>3</sub>N@C<sub>80</sub>@SWCNTs are almost the same as those of the SWCNTs. The peak structure around 18 eV becomes prominent with increasing photon energy. Since the atomic photoionization cross section of the C 2s state relative to that of the C 2p state increases with photon energy, this peak can be assigned as the C 2s state.

The subtraction between the Dy 4d-4f on-resonant spectrum (161 eV) and the off-resonant spectrum (149 eV) is used to accurately extract the Dy 4f multiplets. It should be taken into account upon the subtraction that the photoemission spectrum of SWCNTs also changes its shape slightly



FIG. 3. Valence-band photoemission spectra of  $Dy_3N@C_{80}@SWCNTs$  taken with the photon energies across the Dy 4*d*-4*f* edge. The inset shows the Dy 4*d*-4*f* absorption spectrum of  $Dy_3N@C_{80}@SWCNTs$ .

between the Dy 4d-4f on- and off-resonances. Thus in order to extract the Dy 4f multiplets we used the four spectra, namely, the on- and off-resonant spectra of Dy<sub>3</sub>N@C<sub>80</sub>@SWCNTs  $(I_{on}^{p}, I_{off}^{p})$  and those of SWCNTs  $(I_{on}^{s}, I_{off}^{s})$ . The subtraction was done between  $I_{on}^{p}-I_{on}^{s}$  and  $I_{off}^{p}-I_{off}^{s}$ . The obtained Dy 4f spectrum is plotted after the subtraction of the inelastic backgrounds in Fig. 4. The spectrum has the four prominent peak structures at the binding energies 6.7, 10.4, 11.8, and 15.0 eV, which is similar to the photoemission spectrum of Dy metal.<sup>31</sup> This indicates that the effective Dy valency of Dy<sub>3</sub>N@C<sub>80</sub>@SWCNTs is essentially trivalent. In addition to the trivalent Dy 4f multiplets, small lower binding-energy structures are observed around 4 eV. This is in good agreement with the 4f multiplets of Dy<sub>3</sub>N@C<sub>80</sub> reported recently,<sup>19</sup> and these structures can be safely identified as a contribution from the divalent Dy.

According to the procedure performed in the previous paper,<sup>19</sup> the experimental profile was reproduced from the atomic calculation for  $4f^9 \rightarrow 4f^8$  and  $4f^{10} \rightarrow 4f^9$  photoemission processes.<sup>32</sup> The photoemission multiplets are convoluted with Voigt function to take into account the experimental resolution of 50 meV and the lifetime broadening. For the latter, the different Lorentzian widths are used for two sets of



FIG. 4. Dy 4f spectrum (above) and calculated spectrum (below) together with the photoemission multiplets (vertical bars).

multiplets. The lowest-energy term  ${}^{7}F_{6}$  of  $4f^{9} \rightarrow 4f^{8}$  multiplets was reduced to 30% to take into account its weak resonance enhancement.<sup>33</sup> The result is shown in Fig. 4. The calculated photoemission profile reproduced well the experimental spectrum. The intensity ratio of 1:0.01 between the two sets of the photoemission multiplets,  $4f^{9} \rightarrow 4f^{8}$  and  $4f^{10} \rightarrow 4f^{9}$ , yields the effective Dy valency close to 3.0. This value is larger than 2.8 reported recently for pristine Dy<sub>3</sub>N@C<sub>80</sub> film,<sup>19</sup> which is the same tendency as observed with 400 eV photon energy. The Dy valence increase by the formation of the endohedral peapods can be attributed to the

additional charge transfer between the  $Dy_3N@C_{80}$  and SWCNTs.<sup>34</sup>

## **IV. CONCLUSIONS**

We have investigated the bulk filling factor and the electronic properties of the newly formed endohedral peapods,  $Dy_3N@C_{80}@SWCNTs$ , using photoemission spectroscopy as a probe. The valence-band photoemission responses show the electronic structure of pristine unfilled SWCNTs and that of pristine endohedrals. A comparison of the photoemission spectra taken with 400 eV photon energy between Dy<sub>3</sub>N@C<sub>80</sub>@SWCNTs and SWCNTs gives the filling factor of  $Dy_3N@C_{80}@SWCNTs$  of  $74 \pm 10$  %. Close to  $E_F$  we observed the manifestation of one-dimensional electronic properties, i.e., vHs and TLL behavior, which were within experimental accuracy identical to those of SWCNTs. The Dy 4fmultiplet profile extracted from the 4d-4f resonant photoemission spectroscopy of Dy<sub>3</sub>N@C<sub>80</sub>@SWCNTs and SWCNTs was well reproduced with the atomic photoemission multiplets,  $4f^9 \rightarrow 4f^8$  and  $4f^{10} \rightarrow 4f^9$ . From the relative intensity between two sets of the multiplets, we estimated the effective valency of the Dy ions to be about 3.0, which is larger than 2.8 reported previously for pristine  $Dy_3N@C_{80}$ .<sup>19</sup> This valence change observed might be due to the additional charge transfer between the Dy<sub>3</sub>N@C<sub>80</sub> and SWCNTs.

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- $^{24}$  The number of carbon atoms per C\_{80}-C\_{80} distance  $l_{\rm C_{80}-C_{80}}$  in a C\_{80} peapod  $N_{\rm NT}$  is given by

$$N_{\rm NT} = \frac{4\pi d_{\rm NT} l_{\rm C_{80}-C_{80}}}{3\sqrt{3}a_{\rm C-C}^2}$$

where  $d_{\text{NT}}$  is the SWCNT diameter and  $a_{\text{C-C}}$  is nearestneighbor distance between two carbon atoms. For  $d_{\text{NT}}$  =1.42 nm,  $l_{C_{80}-C_{80}}$ =1.12 nm and  $a_{C-C}$ =0.144 nm, we obtain  $N_{NT} \sim 185$ .

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- <sup>34</sup>Unfortunately the effect of the charge transfer between the  $Dy_3N @ C_{80}$  and SWCNTs is not observed as an energy shift of the vHs peaks. This can be easily explained by the fact that the number of SWCNT carbon atoms is about 85 times larger than the number of the Dy ions in the peapods with the filling of 74%. 0.2 electron doping per a Dy would correspond to a doping level of the SWCNT of 0.0024 hole per a carbon atom, which yields an energy shift below our detection limit expected from results on intercalated SWCNTs and C<sub>60</sub> peapods.