

# Effect of encapsulated atoms on the electronic structure of the fullerene cage: A case study on $\text{La}_2@C_{78}$ and $\text{Ti}_2C_2@C_{78}$ via ultraviolet photoelectron spectroscopy

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Ultraviolet photoelectron spectra (UPS) of metallofullerene,  $\text{La}_2@C_{78}$  were measured using a synchrotron-radiation light source. Its spectral onset energy was 0.70 eV below the Fermi level, indicating the semiconductive nature of this metallofullerene. The UPS consisted of numerous crests and troughs. Further, a change in intensity upon tuning the excitation energy was observed; however, the intensity of the change was not as large as those observed for other fullerenes. The UPS of  $\text{La}_2@C_{78}$  differ considerably from those of  $\text{Ti}_2C_2@C_{78}$ , although they are thought to have the same cage structure. Herein, this difference is explored using density-functional theory, and the origin of this difference was determined to be the hybridization of the  $\pi$ -electron wave functions.

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## INTRODUCTION

The synthesis and isolation of numerous metallofullerenes have been reported, and encapsulated metal atoms are known to donate electrons to the fullerene cage.<sup>1</sup> Encapsulation of multiple atoms, such as metal clusters,<sup>2,3</sup> metal nitrides,<sup>4,5</sup> and metal-carbon clusters<sup>6</sup> inside the cage has also been reported, which has attracted significant interest as a new class of endohedral fullerenes. The actual structure of metallofullerenes is an ongoing argument among researchers; namely, the position of the metal atom(s), the amounts of entrapped atom(s) and species, and so forth. The maximum entropy method (MEM) combined with Rietveld analysis of an x-ray-diffraction pattern is thought to be the best way to estimate the structure.<sup>7</sup> However, the results of these studies for  $\text{Sc}_2C_{84}$  ( $D_{2d}$ - $\text{Sc}_2@C_{82}$  was proposed)<sup>8</sup> were questioned based on a comparison of the ultraviolet photoelectron spectra (UPS) of  $\text{Sc}_2C_{84}$  (Ref. 9) and  $\text{Y}_2C_2@C_{82}$  (Ref. 10) as well as NMR spectroscopic analysis.<sup>11</sup> The actual structure of  $\text{Sc}_2C_{84}$  was determined to be  $C_{3v}$ - $\text{Sc}_2C_2@C_{82}$ . Similarly, analogous inconsistency was reported for  $\text{Ti}_2C_{80}$ . When  $\text{Ti}_2C_{80}$  was isolated and its NMR spectrum was taken, the compound was thought to be a mixture of two  $\text{Ti}_2@C_{80}$  isomers with  $D_{5h}$  and  $I_h$  symmetry.<sup>12</sup> However, this was questioned based on theoretical calculations,<sup>13,14</sup> and  $\text{Ti}_2C_{80}$  is currently reported to be  $\text{Ti}_2C_2@C_{78}$  with a  $D_{3h}$  structure [ $D_{3h}(78:5)$  based on the nomenclature reported by Fowler and Manolopoulos<sup>15</sup>].

Ultraviolet photoelectron spectroscopy is a powerful tool used to determine the electronic structure of numerous compounds, and is helpful in estimating the cage structure of fullerenes. Further, it has been established that the cage structure for monometal atom encapsulated metallofullerenes

is principally responsible for the electronic structure: metallofullerenes of the same cage symmetry with an incorporated metal atom of the same oxidation state<sup>16–18</sup> give essentially the same UPS. This empirical rule also holds for  $(\text{YC})_2@C_{82}$  (III) and  $\text{Y}_2@C_{82}$  (III), which both have  $C_{3v}(82:8)$  symmetry<sup>10</sup> and for trimetal nitride encapsulated  $I_h$ - $C_{80}$ .<sup>19</sup> Moreover, their electronic structures are almost identical, and entrapped carbon atoms do not cause serious distortion in the electronic structure of the cage.

Recently,  $\text{La}_2@C_{78}$  has been isolated, and its NMR spectrum and theoretical calculations indicate a  $D_{3h}(78:5)$  structure.<sup>20</sup> That is,  $\text{La}_2@C_{78}$  and  $\text{Ti}_2C_2@C_{78}$  have the same cage symmetry. Therefore, it is worthwhile to examine whether endohedral fullerenes that incorporate different elements in the  $C_{78}$  cage have analogous electronic structures.

In the current work, UPS of  $\text{La}_2@C_{78}$  are presented and compared with those of  $\text{Ti}_2C_2@C_{78}$ . The electronic structures are also examined in order to clarify the difference induced by encapsulation of different elements using density-functional-theory (DFT) calculations.

## EXPERIMENTAL AND CALCULATIONS

Soot containing  $\text{La}_2@C_{78}$  was produced by direct-current arc heating of an  $\text{La}_2\text{O}_3$ -graphite composite rod.  $\text{La}_2@C_{78}$  was separated with the aid of high-performance liquid chromatography. Details of the synthesis and isolation of  $\text{La}_2@C_{78}$  have been described elsewhere.<sup>20</sup> The sample for the photoelectron measurements was prepared by vacuum sublimation of  $\text{La}_2@C_{78}$  onto a gold-deposited molybdenum disk. Sublimation was conducted using a resistive heating quartz crucible in a preparation vacuum chamber directly

attached to a photoelectron measurement chamber.  $\text{La}_2@C_{78}$  sublimed at about 880 K, forming a thin film on the disk. The pressure of the chamber during the film deposition went up to  $1.0 \times 10^{-5}$  Pa (base pressure less than  $1.0 \times 10^{-7}$  Pa). The thickness of sublimed metallofullerenes deposited on the disk was measured using a quartz thickness monitor located beside the disk. This measured thickness did not reflect the actual thickness of the deposited film, because the crucible was collimated. Therefore, the reading from the thickness monitor was 0.4 nm, but the actual thickness of the film was thought to be greater than several nm, which was thick enough to prevent penetration of photoelectrons from the substrate. This was confirmed by the fact that no gold Fermi edge was observed in the photoelectron spectra of  $\text{La}_2@C_{78}$ .

The spectra were measured using a photoelectron spectrometer at BL8B2 of UVSOR (Ultraviolet Synchrotron Orbital Radiation Facility) at the Institute for Molecular Science. Energy calibration of the spectra was carried out using the Fermi edge of a gold-deposited sample disk prior to the measurement. The spectra were referenced against the Fermi level. The total energy resolution of the spectra was 110 meV, estimated from the width of the gold Fermi edge. The base pressure of the measurement chamber was  $\leq 3.0 \times 10^{-8}$  Pa, and the pressure during the measurement was about  $4 \times 10^{-8}$  Pa.

All calculations were performed using the local-density approximation (LDA) for density-functional theory.<sup>21,22</sup> A functional form fitted to the Monte Carlo results for a homogeneous electron gas<sup>23</sup> was used as the exchange-correlation energy among electrons.<sup>24</sup> Norm-conserving pseudopotentials were generated using the Troullier-Martins scheme, and were adopted to describe the electron-ion interaction.<sup>25,26</sup> The valence wave functions were expanded by the plane-wave basis set with a cutoff energy of 50 Ry. The conjugate-gradient minimization scheme was utilized both for the electronic-structure calculation and for the geometric optimization.<sup>27</sup> Structural optimization was performed until the a value of less than 5 mRy/Å was achieved for the remaining forces for each atom.

## RESULTS AND DISCUSSION

Figure 1 shows the valence band UPS of  $\text{La}_2@C_{78}$  obtained with a photon energy of  $h\nu=20\text{--}55$  eV. The spectral onset was 0.7 eV, which is close to that of  $\text{Ti}_2C_2@C_{78}$  (0.8 eV, published as  $\text{Ti}_2@C_{80}$ , and hereafter this metallofullerene is referred to as  $\text{Ti}_2C_2@C_{78}$ )<sup>17</sup> and  $\text{Y}_2C_2@C_{82}$  (III) (Ref. 10). Nine structures, labeled A–I, were observed in the UPS. The intensity of these structures was found to oscillate when the incident-photon energy was tuned. This oscillation has also been observed in the incident-photon-energy-dependent photoelectron spectra of other fullerenes.<sup>10,16–18,28</sup> However, the change in the first two structures was not as significant as that observed for other fullerenes. The intensity ratio of structure A to structure B was almost unity, and it varied merely from 7:9 ( $h\nu=25$  eV) to 7:6 ( $h\nu=40$  eV). The intensity ratio of structure A to structure C ranged from 2:3 ( $h\nu=25$  eV) to 4:5 ( $h\nu=40$  eV). The intensity oscillation

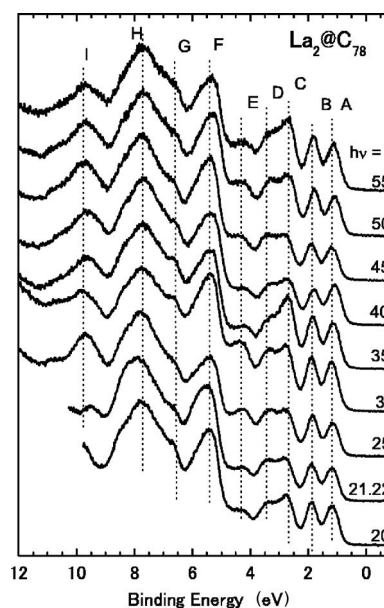


FIG. 1. Incident-photon-energy dependence of the ultraviolet photoelectron spectra of  $\text{La}_2@C_{78}$ . Nine structures labeled A–I are observed and their intensity changes upon the tuning of the incident-photon energy. Their peak position also shifts.

observed for empty fullerenes and other metallofullerenes was significantly larger; in  $C_{60}$ , the intensity ratio of the first band derived from the highest-occupied molecular orbital (HOMO) to the second ranged from 1:4 to 5:4,<sup>28</sup> and in  $\text{La}@C_{82}$  the ratio of the second to the third band ranged from 1:2 to slightly larger than unity.<sup>29</sup> The origin of the intensity oscillation is proposed by Hasegawa *et al.*<sup>30</sup> and Becker *et al.*<sup>31</sup> Hasegawa has attributed its origin to the interference of wave functions of photoelectrons ejected from fullerenes having a large radius and Becker has attributed its origin to photoelectron scattering at the fullerene cage. In both cases, the position of photoelectron generation is essentially crucial. Further, Hasegawa and his co-workers claim that the intensity oscillation can be expected in smaller molecules although its magnitude may be small. Present results on the magnitude of the intensity oscillation of  $\text{La}_2@C_{78}$  indicate that the molecular orbitals that contribute to the formation of structures A and B may have a slightly different character compared with corresponding structures of other fullerenes. Possibly the first few structures of the UPS of  $\text{La}_2@C_{78}$  may be derived from the molecular orbitals distributed in a much more confined area than the deeper ones.

The peak positions of structures A–I of the UPS were observed to deviate when the incident-photon energy was tuned. This deviation seems to correspond to the intensity oscillation. The observed peak positions and deviation ranges are summarized in Table I. The spectra primarily attributed to  $\sigma$  electrons (binding energy  $>5$  eV) are more or less analogous to those of other empty or endohedral fullerenes, which suggests that encapsulation of two La atoms does not have a significant effect on the electronic structure of the fullerene skeleton. On the other hand, the spectra for the  $\pi$  electrons (0–5 eV) are significantly different from those of other fullerenes. It is important to note that there is hardly

TABLE I. Position and range of structures in eV.

Structure	La <sub>2</sub> @C <sub>78</sub>	
	Peak top (nominal)	Peak range
A	1.17	1.07–1.22
B	1.86	1.78–2.01
C	2.68	2.61–2.82
D	3.44	3.27–3.45
E	4.30	4.20–4.37
F	5.42	5.30–5.57
G	6.53	6.50–6.71
H	7.74	7.54–8.02
I	9.75	9.50–9.87

any resemblance between the UPS of Ti<sub>2</sub>C<sub>2</sub>@C<sub>78</sub> (Ref. 17) and the present results.

Figure 2 shows the UPS of Ti<sub>2</sub>C<sub>2</sub>@C<sub>78</sub> and La<sub>2</sub>@C<sub>78</sub> obtained using 30 eV photons. The NMR spectra of Ti<sub>2</sub>C<sub>2</sub>@C<sub>78</sub> and La<sub>2</sub>@C<sub>78</sub> indicate *D*<sub>3h</sub> symmetry for both (Refs. 3 and 12). There are two *D*<sub>3h</sub> isolated-pentagon rule (IPR) satisfying isomers. Molecular-orbital calculations of

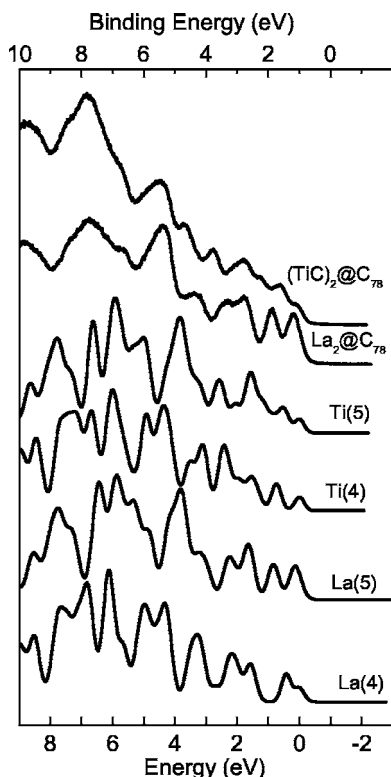


FIG. 2. The UPS of La<sub>2</sub>@C<sub>78</sub> and Ti<sub>2</sub>C<sub>2</sub>@C<sub>78</sub> obtained with 30 eV incident-photon energy indicated as their names. The scale for the UPS is shown in the upper frame. The bottom four lines are calculated density-of-state of La<sub>2</sub>@C<sub>78</sub> and Ti<sub>2</sub>C<sub>2</sub>@C<sub>78</sub> using two *D*<sub>3h</sub> geometry, namely, *D*<sub>3h</sub> (78:4) and *D*<sub>3h</sub> (78:5). La(4) and La(5) indicate the calculated results of La<sub>2</sub>@C<sub>78</sub> in *D*<sub>3h</sub> (78:4) and *D*<sub>3h</sub> (78:5) cages, respectively. Ti(4) and Ti(5) indicate the same.

Ti<sub>2</sub>C<sub>2</sub>@C<sub>78</sub> indicated that *D*<sub>3h</sub> (78:5) is more a plausible structure than *D*<sub>3h</sub> (78:4),<sup>13,14</sup> and MEM analysis of Ti<sub>2</sub>C<sub>2</sub>@C<sub>78</sub> indicated that it favors the same cage structure.<sup>32</sup> Further, molecular-orbital calculations<sup>20</sup> and MEM analysis of La<sub>2</sub>@C<sub>78</sub> (Ref. 32) also suggested that *D*<sub>3h</sub> (78:5) is more stable than *D*<sub>3h</sub> (78:4). These findings indicate that Ti<sub>2</sub>C<sub>2</sub>@C<sub>78</sub> and La<sub>2</sub>@C<sub>78</sub> have the same cage structure. Thus, analogous electronic structures are expected if the empirical rule that the cage structure is principally responsible for the electronic structure of metallofullerenes holds. In contrast, the UPS, which are a reflection of the electronic structure, differ significantly, as are shown in Fig. 2. In order to examine this contradiction, LDA calculation of the *D*<sub>3h</sub> caged Ti<sub>2</sub>C<sub>2</sub>@C<sub>78</sub> and La<sub>2</sub>@C<sub>78</sub> was performed. The results of density-of-state (DOS) calculations are also shown in Fig. 2. The simulated spectra differ from each other. It is plausible that spectra obtained with different cage structures give different electronic structures. Interestingly, even calculations using the same *D*<sub>3h</sub> cage structures gave quite different spectra. This suggests that encapsulated atoms seem to distort or make crucial changes to the electronic structures of the fullerene cage.

A simple inspection of the UPS and the calculated spectra indicates that the UPS of Ti<sub>2</sub>C<sub>2</sub>@C<sub>78</sub> is in good agreement with the calculated results for the (Ti<sub>2</sub>C<sub>2</sub>) encapsulated *D*<sub>3h</sub> (78:5) structure, and that for La<sub>2</sub>@C<sub>78</sub> is in good agreement with the calculated results for the (La<sub>2</sub>) encapsulated *D*<sub>3h</sub> (78:5). This agreement between the observed UPS and calculated spectra implies that the calculation is a good reflection of the electronic structure of the actual metallofullerenes. As described above, encapsulated atoms bring serious changes about on the electronic structure of the C<sub>78</sub> cage. These changes have not been observed in metallofullerenes in which the encapsulated metal atom(s) only donates electrons and does not provoke serious changes on the electronic structure of the cage. The Ti atom is particularly susceptible to forming carbide.<sup>33</sup> There may be a possibility that bonds are formed between encapsulated Ti atoms and the carbon atoms making up the cage. In an effort to examine this possibility, wave functions of these metallofullerenes were investigated.

Figure 3 depicts the wave functions of the HOMO and the second-highest-occupied molecular orbital (HOMO-1) of Ti<sub>2</sub>C<sub>2</sub>@C<sub>78</sub> and La<sub>2</sub>@C<sub>78</sub>. These two molecular orbitals consist primarily of  $\pi$ -electron character. The distribution of the HOMO wave functions for both metallofullerenes was analogous, and was located along the meridian of the fullerene cage (the positions of the two metal atoms are assumed to be in the plane of the equator). However, the distribution of the HOMO-1 wave functions was different from that of the HOMO. While the HOMO-1 wave function of La<sub>2</sub>@C<sub>78</sub> was distributed only along the carbon cage, the corresponding wave function for Ti<sub>2</sub>C<sub>2</sub>@C<sub>78</sub> was located not only on the cage, but also in the cage in the direction of the Ti atoms, suggesting there may be bonds between the cage C atoms and the encapsulated Ti atoms. Extension of the HOMO-1 wave function between the Ti and C atoms was derived from the hybridization between the Ti 3*d* orbitals and the C 2*p* orbitals. The electronic structure of occupied states for Ti<sub>2</sub>C<sub>2</sub>@C<sub>78</sub> was considerably different from that of the pure

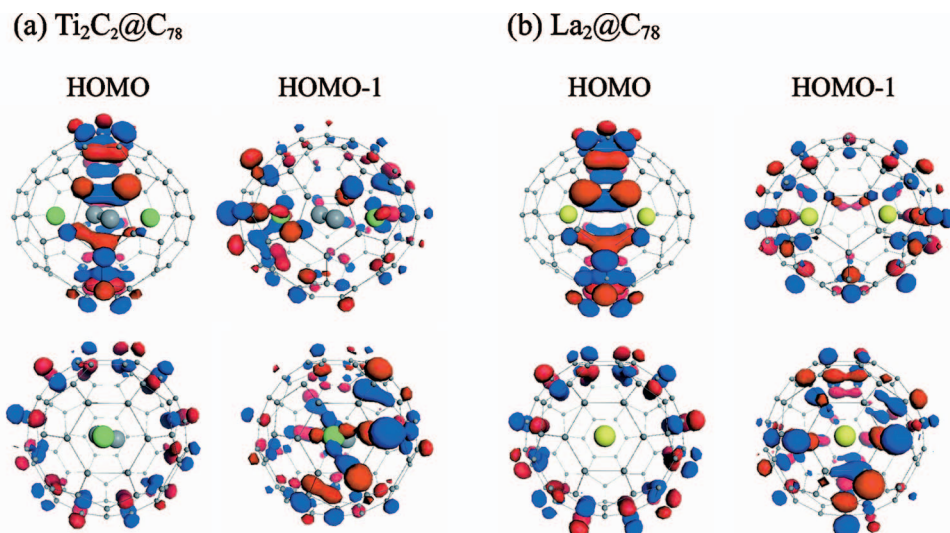


FIG. 3. (Color) Isosurfaces of the squared wave function of the HOMO and the HOMO-1 for  $\text{Ti}_2\text{C}_2@C_{78}$  (a) and  $\text{La}_2@C_{78}$  (b). Green and yellow balls indicate Ti atoms and La atoms, respectively. Gray balls indicate C atoms and encapsulated C atoms are depicted with large-size gray balls. Red and blue surfaces denote the positive and negative sign of the wave functions, respectively.

$C_{78}$  cage, namely,  $D_{3h}$  (78:5). This was thought to be due to hybridization in  $\text{Ti}_2\text{C}_2@C_{78}$ . On the other hand, the HOMO-1 wave function of  $\text{La}_2@C_{78}$  was localized along the carbon cage, and did not show any hybridized character between the La atoms and cage C atoms.

The HOMO and HOMO-1 were derived from electrons transferred from encapsulated-metal atoms to the fullerene cage. Therefore, the wave functions responsible for these orbitals might share the character of the encapsulated atoms. However, the  $\pi$ -electron wave function of  $\text{La}_2@C_{78}$  did not show any amplitude around La atoms. That is, almost all upper-valence electrons of the La atoms were transferred to the cage. This is further supported by calculations; DOS of  $\text{La}_2@C_{78}$  was almost identical to that of pure  $D_{3h}$ (78:5).<sup>5</sup> On the other hand, behavior of the  $\pi$ -electron wave function for  $\text{Ti}_2\text{C}_2@C_{78}$  was slightly different. The distribution of the  $\pi$ -electron wave function of the HOMO-1 of  $\text{Ti}_2\text{C}_2@C_{78}$  indicates that upper-valence electrons of Ti atoms are not completely transferred to the cage and possibly covalent bonds are formed between the  $\text{Ti}^{4+}$  cations and the  $C_{78}^{6-}$  cage (another two electrons are on encapsulated  $C_2$  acetylide).<sup>13</sup> Thus, the number of electrons transferred might be different for these two metallofullerenes.

When the electronic structure of metallofullerenes has been theoretically investigated, outer electrons of an entrapped metal atom were believed to be completely transferred to the cage.<sup>34</sup> However, resonance x-ray photoemission on  $\text{La}_2@C_{78}$  revealed that there is hybridization between the entrapped metal atom and the cage C atoms.<sup>35</sup> It also suggested that electrons derived from entrapped atoms retain the character of the mother atom even after the electron transfer, although it cannot be observed in ordinary ultraviolet photoelectron spectroscopy. The existence of hybridization is also pointed out in  $\text{Dy}_3\text{N}@C_{80}$ ; hybridization is brought by a large ionic radius of Dy.<sup>19</sup> Our present result on  $\text{Ti}_2\text{C}_2@C_{78}$  is an extension of these findings and brings a concept that there is a possibility of a drastic modification in

the electronic structure of endohedral fullerenes upon encapsulation of some specific atoms(s) having rather a small radius.

## CONCLUSIONS

The UPS of  $\text{La}_2@C_{78}$  show intensity oscillation upon tuning the incident-photon energy; however, the change in the first few structures (due to  $\pi$  electrons) is not significant compared with that of other fullerenes. This suggests that the nature of the first few structures in the UPS of  $\text{La}_2@C_{78}$  may differ slightly from that of other fullerenes; some of the electrons may be localized in a considerably more confined area than those in other fullerene cages. The UPS of  $\text{La}_2@C_{78}$  and  $\text{Ti}_2\text{C}_2@C_{78}$  agree very well with DOS calculated by LDA assuming  $D_{3h}$  (78:5) cage structure, which is an evidence that their cage structure is  $D_{3h}$  (78:5) and  $\text{Ti}_2\text{C}_{80}$  is actually  $\text{Ti}_2\text{C}_2@C_{78}$ . Although  $\text{La}_2@C_{78}$  and  $\text{Ti}_2\text{C}_2@C_{78}$  have the same structure, the UPS of  $\text{La}_2@C_{78}$  differs significantly from that of  $\text{Ti}_2\text{C}_2@C_{78}$ . LDA calculations on these metallofullerenes revealed that encapsulation of ( $\text{Ti}_2\text{C}_2$ ) and ( $\text{La}_2$ ) to the same  $D_{3h}$  (78:5) cage structure brought completely different electronic structures. This was attributed to the distribution of the  $\pi$ -wave functions of these two metallofullerenes. Hybridization of wave functions between Ti atoms and caged C atoms distorts the electronic structure of the  $C_{78}$  considerably, and bonds may form between the Ti atoms and the caged C atoms due to this distortion. Ti atoms have a high carbide-forming tendency. Thus hybridization or bond formation between encapsulated Ti atoms and the caged carbon atoms has been induced. The existence of hybridization between the encapsulated atom(s) and the fullerene cage has been observed in specific cases such as in  $\text{La}@C_{82}$  excited under resonance condition or in  $\text{Dy}_3\text{N}@C_{80}$  where the Dy ion has a large ionic radius. The  $\text{Ti}_2\text{C}_2@C_{78}$  case seems to be rather exceptional where hybridization is so large that comprehensive deformation of the electronic structure of the  $C_{78}$  cage takes place.

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