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Chemical Control and Spectral Fingerprints of Electronic Coupling in Carbon Nanostructures

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Abstract

The optical and electronic properties of atomically thin materials such as single-walled carbon nanotubes and graphene are sensitively influenced by substrates, the degree of aggregation, and the chemical environment. However, it has been experimentally challenging to determine the origin and quantify these effects. Here we use time-dependent density-functional-theory calculations to simulate these properties for well-defined molecular systems. We investigate a series of core-shell structures containing C₆₀ enclosed in progressively larger carbon shells and their perhydrogenated or perfluorinated derivatives. Our calculations reveal strong electronic coupling effects that depend sensitively on the interparticle distance and on the surface chemistry. In many of these systems we predict considerable orbital mixing and charge transfer between the C₆₀ core and the enclosing shell. We predict that chemical functionalization of the shell can modulate the electronic coupling to the point where the core and shell are completely decoupled into two electronically independent chemical systems. Additionally, we predict that the C₆₀ core will oscillate within the confining shell, at a frequency directly related to the strength of the electronic coupling. This low-frequency motion should be experimentally detectable in the IR region.

Graphical abstract

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ASSOCIATED CONTENT

Supporting Information

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Supplementary computational methodology, frontier orbitals, density of states, Mulliken charge distribution, UV-visible, IR, and spectra of the core-shell complexes (PDF)

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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INTRODUCTION

The electronic and optical properties of atom-thick materials such as single-walled carbon nanotubes (SWCNTs) and graphene are extremely sensitive to substrates,^{1–3} aggregation states,^{4–6} and the chemical environment.⁷ The collective electrical and mechanical properties of these materials also depend strongly on electronic coupling at the interparticle contacts. Strong noncovalent intermolecular coupling can control the electronic structure,^{2,4} stability,⁸ and the ease of charge transfer,⁶ all of which affect carrier mobility at heterojunctions. On the other hand, chemical modification is an efficient method to tailor electronic structures by the introduction of covalent quantum defects.⁹ In particular, introducing sp^3 defects disturbs the structural and electronic symmetries of electronically coupled nanostructures, resulting in creation of optically allowed new states,^{9,10} promoting the spatial localization of electron density,^{10,11} or modification of electrical transport properties.^{12,13} It still remains unclear how multifunctional structural modification quantitatively influences intermolecular electronic coupling.

To exploit the consequences of these intriguing effects, it is essential to investigate how one can achieve simultaneous control of the molecular interaction and the electronic structure. For example, in a sensing application, it is important to enhance the free-molecule properties with a contact to a substrate where charge transport and luminescence can be improved by localized electronic states.¹⁴ Conversely, an efficient energy harvesting device requires strong electronic coupling to maximize the effective charge transfer and carrier transport.^{3,6} At this point in time we lack sufficient understanding of the interplay between electronic coupling and surface properties to design advanced molecular hybrids in a systematic and controlled fashion.

Here, we seek to acquire a quantitative understanding of electronic coupling in carbon nanostructures by quantum chemical simulations of a series of C_{60} core–carbon shell complexes with tailored surface chemistry. These model complexes feature atomically defined structures and are free of edge effects, making it possible to perform high-precision time-dependent density functional theory (TD-DFT) calculations on the effects of electronic coupling for incommensurate nanostructures⁵ where periodic boundary conditions cannot be applied. The electronic coupling between the quantum state of the core (indexed by i in eq 1 below) and the quantum state of the outer layer (indexed by o) can be expressed as a transition matrix element of the interaction Hamiltonian between the two carbon layers:

$$V_{io} = \langle \psi_i | \hat{H}_e | \psi_o \rangle \quad (1)$$

The interaction Hamiltonian in eq 1 makes the V_{io} electronic coupling distance and orientation dependent. We find that the minimum-energy geometry, electronic structure, and the strength of electronic coupling are controlled by both the interparticle separation within the core-shell complex and the surface chemistry of the carbon shell. For strongly coupled systems such as $C_{60}@C_{180}$, the frontier orbital of the C_{60} core spatially extends beyond the shell. Consistently, core-shell charge transfer transitions give rise to intense absorption peaks in the UV-visible spectrum. This electronic coupling can be tailored systematically by tuning the interparticle spacing (control through $\hat{H}_e$) and covalent surface chemistry (control through $|\psi_o\rangle$). This latter modifies the confining potential for the C_{60} core. As the interparticle spacing increases, the coupling is weakened progressively until the C_{60} core behaves as an isolated molecule.

Finally, we develop, based on our DFT calculations, a double-well potential to describe the oscillatory motion of the C_{60} core within the encapsulating carbon shell. The frequency of this motion is directly correlated with the electronic coupling strength. This suggests an avenue to use spectroscopy to measure this coupling strength.

COMPUTATIONAL METHODOLOGY

Geometry Optimization

Structures were optimized at the BLYP-D3 level of theory with a double- ζ (DZ) basis set. Here Becke-Lee-Yang-Parr (BLYP) designates the density functional used and D3 denotes inclusion of the improved dispersion corrections of Grimme et al.¹⁵ We use the Amsterdam Density Functional 2014 (ADF) suite of codes.¹⁶ The basis sets implemented in the ADF suite are based on Slater-type atomic orbitals (STOs), which better describe the electronic wave function near the nuclear or electronic cusp regions than Gaussian-type orbitals (GTOs). The energy and gradient thresholds used in the geometry optimizations were 5×10^{-5} and 5×10^{-4} au, respectively. For the structures with larger shells, such as $C_{60}@C_{320}$ and $C_{60}@C_{240}F_{240}$, the existence of deep local potential minima rendered geometry optimization more difficult. To reduce the computational cost, we increased the convergence thresholds by a factor of 10. The geometry optimization was continued until the predicted spectral features changed little over six consecutive iterations (Figure S1).

For the geometry optimization of $C_{60}@C_{320}H_{320}$ and $C_{60}@C_{320}F_{320}$, the outer shells were preoptimized with the static variant of the Merck molecular force field 94 (MMFF94s)¹⁷ as implemented in the Avogadro¹⁸ program. These coordinates were then used to construct a first estimate of the structure of the core-shell complexes. The MMFF94s model describes relatively well conformational, intramolecular, and intermolecular interactions at lower computational cost. To reduce the computational cost to a reasonable level, these two core-large-shell complexes were optimized at fixed encapsulating-shell geometries using the same method and basis set as the other complexes. The optimized structural parameters and

interparticle separations for all modeled structures are given in the Supporting Information (Tables S1 and S2).

Interparticle Electronic Transitions

We used the time-dependent density-functional tight-binding (TD-DFTB) method¹⁹ to simulate the UV–visible absorption spectra corresponding to singlet–singlet electronic transitions of the isolated cores and shells and core–shell complexes. These calculations were based on the Quasinano2013.1 parameter set²⁰ as implemented in the ADF package. The tight-binding approximations in the TD-DFTB approach use only two-center integrals, which allow excited states to be calculated at high speed while retaining the major spectral features.²¹ We note that the TD-DFTB method without long-range correction can decrease the accuracy of the calculated UV–vis spectra. However, previous studies have shown that the TD-DFTB method on conjugated systems such as C₆₀ produces reasonably good agreement with the experimental values.^{22,23}

The Quasinano2013.1 parameter set is optimized to include the C, H, and F atoms, which are involved in the present study.²⁰ In our spectral calculations we include all 9000 singlet–singlet transitions with an excitation energy less than 21.8 eV (0.8 hartree). The suitability of our methodology is confirmed by the good agreement between calculated and experimental²⁴ UV–vis spectra of C₆₀ (Figure S2). We have also explored the dependence on basis sets of the geometry optimization. Both DZ and larger basis set of triple- ζ quality (TZP) give practically the same results for the spectral calculations of C₆₀@C₂₄₀ (Figure S4). Consequently, all our additional studies were based on the BLYP-D3/DZ calculations.

Oscillatory Motion of C₆₀ within an Encapsulating Shell

This motion is investigated by two different approaches. First, we use the ORCA 3.0.3 program²⁵ with the BLYP-D3/TZVP choice of DFT functional and orbital basis, to determine the coordinate dependence of the core–shell potential energy as a function of the displacement x of the core from the center of the complex along the x -axis. Similarly, we determined such potential energy curves for y and z displacements along the y - and z -axes, respectively. We then use the discrete variable representation (DVR) method²⁶ to solve the resulting one-dimensional nuclear Schrödinger equation with the reduced mass of a complex defined as $1/\mu = 1/m_{\text{core}} + 1/m_{\text{shell}}$. In the second approach, the Gaussian 09 program²⁷ and the semiempirical AM1 method²⁸ are used to determine the harmonic normal modes for the motion of the C₆₀ around its minimum. In contrast to the DVR calculations, which are performed only along the coordinate, the AM1 calculations assess all three normal modes for the radial oscillatory motion. The similarities between the zero-point vibrational frequencies suggest rather high symmetry of this motion in all three dimensions (x , y , z).

Interaction Energy between Constituent Particles

Here we define the interaction energy as the energy difference between a core–shell complex and its individual constituents; namely $E = E_{\text{cplx}} - E_{\text{free core}} - E_{\text{free shell}}$. These energies are calculated with the ORCA 3.0.3 software at the BLYP-D3/DZ and the BLYP-D3/TZVP levels.²⁵ A valence triple- ζ plus polarization (TZVP) basis set gives a larger contribution to exchange energies (Heitler–London electron repulsion) for C₆₀@C₁₈₀ (the shortest

interlayer separation), leading to more repulsive interaction energy in this case. For the other complexes, with increased interlayer separation, the interaction energy is lowered as expected due to better description of dispersion component of the interaction energy.

RESULTS AND DISCUSSION

Electronic coupling is directly visualized by mapping the spatial distribution of the highest occupied molecular orbitals (HOMOs) of C_{60} within the core-shell model complexes (Figure 1). For free C_{60} with icosahedral symmetry (I_h) the HOMOs are fivefold degenerate while the lowest unoccupied molecular orbitals (LUMOs) are threefold degenerate.²⁹ When C_{60} is encapsulated within the larger complexes considered here, this high structural symmetry is lifted and the frontier orbitals of C_{60} lose their degeneracy (Figures S5 and S6). In the core-shell species $C_{60}@C_{180}$, $C_{60}@C_{240}$, and $C_{60}@C_{180}H_{180}$, the HOMO spreads across both constituent components. In the remaining examples in Figure 1, the core and shell are electronically decoupled, with the result that the HOMO is localized within the constituent particle, C_{60} in particular.

As the number of atoms in the encapsulating shell increases from 180 to 320, the core-shell spacing increases and the electronic coupling becomes weaker. The degree of electronic coupling depends strongly on two factors: core-shell spacing and surface functionality. The strongest interaction is observed for the smallest outer shell, C_{180} . Here electron density from C_{60} leaks out and spreads over the shell. As the diameter of the encapsulating shell increases, the frontier orbitals of C_{60} extend spatially over the shell, as in C_{240} , and then, in the case of $C_{60}@C_{320}$, become completely localized within the core, comparable to the free C_{320} and free C_{60} , where the shell has, effectively, an infinite diameter. Also, when the encapsulating shell is covalently substituted, the HOMO of C_{60} is spatially confined by the shell. In particular, perfluorination leads to stronger decoupling than perhydrogenation. This suggests that the strength of the electronic coupling can be finely tailored by judicious choice of the surface functional groups.

Consistently, the relative energy gaps (E_g) of these model complexes (Figure 2) depend strongly on the interparticle distance and the surface chemistry of the confining shell. The energy gap of $C_{60}@C_{180}$ is lower than those of free C_{60} and C_{180} by 0.993 and 0.446 eV, respectively. This can be attributed to strong interparticle, electron hybridization at a coupling distance that is smaller than the interlayer distance in graphite (3.35 Å). At this small interparticle distance, the frontier orbital energies of C_{60} reveal considerable destabilization effects (see Figure S6 and Table S3). Compared with free C_{60} , the HOMO and LUMO levels of the C_{180} encapsulated C_{60} are higher by 400 and 593 meV, respectively. As the size of the confining shell increases, in $C_{60}@C_{240}$ or $C_{60}@C_{320}$, the HOMO energy level of the C_{60} becomes comparable to that of free C_{60} while the LUMO level is ~100 meV lower.

Independent of the size, chemical functionalization of the encapsulating shell gives rise to consistent trends in E_g and the density of states distribution (see Figures S6 and S7). The covalent functionalization pushes the energy level of the LUMOs down to the level of free C_{60} . For a decoupled complex one would anticipate that the HOMO-LUMO gap will

approach that of isolated C_{60} . Especially for the C_{320} species, both perhydrogenation and perfluorination give an E_g that is nearly identical to that of free C_{60} .

To quantify further the influence of the interparticle distance and surface functionalization on the electronic coupling, we simulated the UV–visible absorption spectra of these model complexes in direct comparison with free C_{60} (Figure 3). The spectrum of free C_{60} is characterized by three distinct peaks located at approximately 220, 270, and 350 nm and a very weak fourth band at around 420 nm. When the C_{60} is encapsulated in C_{180} , “inner-to-outer” and “outer-to-inner” charge-transfer transitions occur giving rise to a number of new peaks: two (201 and 220 nm) below the first C_{60} transition band at 220 nm, two (230 and 270 nm) between the first and second (240 nm) transitions, seven (270, 290, 320, 333, 361, 375, and 414 nm) between the third and fourth (420 nm) transitions of free C_{60} , and three (455, 494, and 555 nm) above the fourth band. Upon perhydrogenation, the number of core–shell transitions diminishes while inner–outer hybrids to the inner charge transfer peaks develop at 225, 241, and 272 nm.

Within the considered spectral range, only inner-to-inner transitions are present in the perfluorinated species. When C_{60} is encapsulated by the larger diameter C_{240} , some “outer-to-inner” transitions are allowed, including peaks at 235, 262, 296, 343, 356, 402, and 510 nm, but these interparticle transitions are completely eliminated by either perhydrogenation or perfluorination. This behavior confirms that both interparticle distance and surface chemistry are the key factors for electronic coupling and decoupling. The spectral shape also reflects significant reduction of electronic coupling upon the chemical modification of the outer layer. Due to the reduced coupling, the UV–visible spectra of functionalized $C_{60}@C_{180}$, $C_{60}@C_{240}$, and $C_{60}@C_{320}$ are similar in shape to that of an isolated C_{60} (Figures S8–S10).

To identify how specific molecular interactions affect the trends of coupling and decoupling, we studied the internal motion of the encapsulated C_{60} (Figure 4). This can be a back-and-forth motion of the C_{60} in its cage, or vibrational motion around a fixed point. Potential curves for the former, as a function of x , the displacement from the center of the cage, are shown in Figure 4b. As shown in Figure 4c, the calculated potential curves are almost symmetric harmonic oscillators, centered at $x = 0$, for C_{180} , C_{240} , and C_{260} complexes. Thus, for these complexes, the core C_{60} oscillates around the center of the core–shell, which is the equilibrium position. The vibrational frequency changes with the shell radius: As the diameter of the confining cage increases, the potential curve broadens because the core–shell repulsion decreases.

For $C_{60}@C_{320}$ the confining cage is so large, the minimum energy occurs when the C_{60} is off-center, closer to one inner wall. The potential curve becomes a Mexican hat potential along the C_{60} displacement coordinate. The potential minimum of $C_{60}@C_{320}$ occurs at $x = 1.36 \text{ \AA}$, and the center of the complex ($x = 0$) is a local maximum, lying $\sim 6700 \text{ cm}^{-1}$ above the minimum. Therefore, electronic coupling is stronger when the C_{60} is located at $|x| \sim 1.36 \text{ \AA}$, where the attractive van der Waals interaction between core and shell is the strongest. However, if the C_{60} approaches closer to the shell, the repulsive forces become dominant, resulting in the drastic increased potential at $|x| > 1.36 \text{ \AA}$. Because of this

Mexican hat potential, geometry optimization is difficult for the complex where C_{320} (or its derivative) is the encapsulating shell.

Table 1 provides a quantitative perspective on the character of the interactions and their impact. We determine zero-point energies ($E_{v=0}$) of the C_{60} oscillatory motion inside the encapsulating shell by the DVR (treating the motion shown in Figure 4 as one-dimensional, see Computational Methodology) and AM1 (full three-dimensional (3-D) approach) methods. For a harmonic potential with force constant k , the vibrational frequency is $\omega = (k/\mu)^{1/2}$, where μ is the core-shell reduced mass. Both methods predict comparable vibrational frequencies. A lower $E_{v=0}$ for a larger confining shell is indicative of a smaller force for the oscillatory motion. The AM1 calculations assess all three dimensions (x, y, z) of normal modes for the oscillatory motions. The normal modes of studied systems are spherically symmetric except for slight difference in $E_{v=0}$ in $C_{60}@C_{180}$ due to the broken spherical symmetry.

We note that it is computationally challenging to calculate the zero-point energy of $C_{60}@C_{320}$ since the energy minima are not located at $x = 0$ due to the Mexican hat potential geometry. Covalent functionalization-induced electronic decoupling also lowers the force constants and, hence, the vibrational energy. This oscillatory motion is IR active and lies in the low-frequency range ($E/hc < 200 \text{ cm}^{-1}$). The predicted infrared spectra (Figure 5, Figure S11) reveal the detailed influence of the local chemical environment and the oscillatory motion of C_{60} within its cage. As a core-shell structure becomes decoupled by chemical functionalization of a shell (left column in Figure 5) or by increasing intermolecular distance (right column in Figure 5), the C_{60} 's oscillation frequency within a shell is lower. Additionally, the Raman shifts for the radial breathing mode (RBM) and twisting mode of C_{60} rotations are dependent on the interparticle coupling: The Stokes shifts of RBM (on the order of 100 cm^{-1}) can be observed in the decoupled structures (see Figure S12). Our calculations suggest that the electronic coupling strength can be experimentally measured by vibrational spectroscopy. In fact, such phenomena have been experimentally observed in the case of double-walled carbon nanotubes and outer wall-selectively functionalized DWCNTs using Raman scattering.^{30,31} Our theoretical predictions are generally consistent.

To clarify the dominant noncovalent coupling in the complexes, the geometrical parameters are analyzed (Figure 6, Tables S1 and S2). Here we consider the hybridization of shell carbons and the inductive effects. The radii of core and shell depend on the size and chemical functionality of the shell. The average interparticle separation, ξ , is defined as the difference between the average radii of the inner and outer shells. The average radius is calculated as an arithmetic average of distances between the carbons of the shell and the origin of system of coordinates. In the nonfunctionalized shells, the intermolecular hybridization between the sp^2 orbitals of core and shell is the determining factor of the noncovalent interactions. We compare ξ of each complex to the interlayer separation of bilayer graphene ($3.4 \text{ \AA}$). The ξ of $C_{60}@C_{180}$ is $0.64 \text{ \AA}$ shorter than $3.4 \text{ \AA}$, which is ascribed to the strong intermolecular repulsion as well as the destabilized frontier orbitals with respect to those of free C_{60} . The ξ in $C_{60}@C_{240}$ is comparable to that of bilayer graphene, where the hybridization between sp^2 layers is stable. The $C_{60}@C_{320}$ complexes possess the

largest interparticle separation of 4.61 Å. Note that ξ values obtained in this work for the $C_{60}@C_{180}$ and $C_{60}@C_{240}$ are consistent with the results of Casella et al.³² At fixed outer shell dimension (fixed number of outer shell carbons), ξ increases as the outer layer is perhydrogenated or perfluorinated. Structurally, the carbon–carbon bond length of the covalently modified shell increases from 1.41 Å (double bonds between two hexagons) to 1.69 Å (perfluorinated), and the complex becomes inflated up to 18%. This structural change is affected by the electronegativity of the functional groups. The perfluorinated structures exhibit larger ξ values than the perhydrogenated ones, indicating more effective quantum decoupling within the perfluorinated complex.

More importantly, the relative radius changes (Δr) of inner and outer shells highlight how the chemical environment affects the structure and electronic properties of a carbon nanostructure, C_{60} in particular. When C_{60} is encapsulated by C_{180} , C_{60} contracts slightly, by 0.85%. This radius change is correlated with the increased exchange–repulsion energy due to the fairly short interparticle separation in $C_{60}@C_{180}$. Both perhydrogenation and perfluorination expand the complex, by 1.21 and 2.23%, respectively. Conversely, within the complex, C_{180} expands to reduce the repulsive interaction with the inner C_{60} . As it is functionalized, the radius of C_{180} decreases due to the reduced repulsive interactions. For larger complexes, $C_{60}@C_{240}$ or $C_{60}@C_{240}H_{240}$, C_{60} expands by 1.47 and 1.35% due to the attractive forces from the outer layer. However, perfluorination of the outer C_{240} results in considerable contraction of the C_{60} by 2.03%. $C_{60}@C_{240}F_{240}$ is stabilized by attractive forces between the electron-deficient shell carbons and the electron-rich core, resulting in shrinking of the shell in comparison with a free $C_{240}F_{240}$. These structural characteristics are consistent with Mulliken analysis of the charge distribution³³ (Figure S13). In contrast to a free C_{60} , the core C_{60} exhibits nonzero charge. The net charge of the core C_{60} is slightly negative when it is encapsulated by a sp^2 hybridized shell. As the size of the outer shell (as well as the interparticle coupling distance) increases, the C_{60} charge approaches zero, indicating that the molecular orbital of core C_{60} decouples from that of the core–shell complex. On the other hand, covalent functionalization of the outer shell of $C_{60}@C_{180}$ leads to the positive net charge of core C_{60} by the influences of strong electron-withdrawing fluorine groups and electronegative perhydrogenated carbon shell.

Lastly, we discuss how the electronic coupling influences the structural stabilization and interaction energy (E) of selected model structures (Table 2). From the perspective of structural stabilization, a positive interaction energy indicates the complex is not energetically favorable in comparison with isolated constituents. For example, $C_{60}@C_{180}$ interaction energy calculated with the BLYP-D3/DZ method is +80.1 kcal/mol, consistent with the substantial destabilization of C_{60} within $C_{60}@C_{180}$ (Figure 2a). Note that E is +51.2 kcal/mol higher in BLYP-D3/TZVP because the TZVP basis set accounts for larger contribution to exchange energies (Heitler–London electron repulsion), leading to larger repulsive interaction energy in smaller interlayer separation. The large interparticle distance, including both C_{240} and C_{320} series, contributes to the energetically stable complexes. One of the stabilization factors is the reduced angle strain within the sp^2 hybridized large diameter shell. If the angle strain of outer shell sp^2 carbons is considered, the C_{320} complex has the largest interaction because the sp^2 hybridized outer shell becomes closer to a planar structure. Interestingly, the largest stabilization is observed for C_{240} complexes, presumably

because of the effective intermolecular orbital hybridization within $C_{60}@C_{240}$. The interaction energy of $C_{60}@C_{320}$ becomes negligible since the interparticle distance of $C_{60}@C_{320}$ is sufficiently large that the noncovalent interactions are weakened and electronic coupling due to overlap effect practically vanishes. This is shown as no substantial geometrical change upon surface functionalization in Figure 6c. All perhydrogenated complexes are energetically stable with respect to their nonfunctionalized parent core-shell structures. This clearly suggests that the covalent functionalization and corresponding inductive effects play a significant role in long-range noncovalent interactions.

CONCLUSIONS

To understand the fundamentals of electronic coupling in carbon nanostructures, we have performed dispersion-corrected density-functional and time-dependent density-functional tight-binding calculations of model core-shell carbon complexes. We found that the electronic coupling is a function of the interparticle distance and surface functionality. Our work also provides new theoretical insights on investigating electronic structure and optical properties in electronically coupled systems. Close interparticle distances and interlayer hybridization lead to strong electronic coupling. As an example, in the $C_{60}@C_{180}$ core-shell species the frontier orbital of the core is mixed with that of the shell. The consequent electron density spillover alters the electronic structure of core-shell complexes, facilitating charge transfer between the layers. The coupling is diminished when the encapsulating shell increases in size or if it is covalently functionalized. The C_{60} core can oscillate inside the encapsulating shell, governed by a potential which reflects the molecular interactions that affect the electronic coupling and structural stability. We predict low-frequency IR active radial motion and Raman active twisting motion of the core within the confining potential defined by the (functionalized) carbon shell. We propose that vibrational energy shifts can be used as an experimental probe for quantitative measurement of the interactions between carbon nanostructures.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

HOMOs of C_{60} within a functional carbon shell of controlled dimension and surface functionality.

Figure 2.

Total density of states for the modeled carbon complexes: (a) $C_{60}@C_{180}$ series, (b) $C_{60}@C_{240}$ series, and (c) $C_{60}@C_{320}$ series, calculated by the TD-DFTB method with the Quasinano2013.1 parameter set. Color codes: free C_{60} (gray), nonfunctionalized core-shell structure (black), and its perhydrogenated (blue) and perfluorinated derivatives (red). The Fermi level defines the zero of energy, depicted as a horizontal solid line. The arrows indicate the LUMO levels.

Figure 3.

Calculated UV–visible spectra of $C_{60}@C_{180}$ (left), $C_{60}@C_{240}$ (middle), $C_{60}@C_{320}$ (right), and some of their derivatives. These excitation spectra are calculated by the TD-DFTB method with the Quasinano2013.1 parameter set and by further convolution over a Gaussian with 10 nm full width at half-maximum (fwhm). The gray lines represent the spectrum of isolated C_{60} , whose intensity is shown at 1/10 of the calculated intensity for clarity. Pink and green indicate inner $\rightarrow$ outer and outer $\rightarrow$ inner charge transfer transitions, respectively. Some of these transitions involve an orbital that extends over both moieties.

Figure 4.

Oscillatory motion of C₆₀ in a confining shell. (a) Oscillatory motion of core C₆₀ inside a larger shell, C₁₈₀, C₂₄₀, and C₃₂₀. (b) Schematics of the C₆₀ radial oscillatory motion along one of the Cartesian coordinates (x) (interior rings) intercalated inside a carbon shell. x is a deviation from the center of the carbon complex. (c) Potential energy curves as a function of C₆₀ position shift (Å): C₆₀@C₁₈₀ (red), C₆₀@C₂₄₀ (blue), C₆₀@C₂₆₀ (black), and C₆₀@C₃₂₀ (green).

Figure 5.

Calculated IR spectra of core-shell complexes using semiempirical AM1 method: (a) $\text{C}_{60}@\text{C}_{180}$; (b) $\text{C}_{60}@\text{C}_{180}\text{H}_{180}$; (c) $\text{C}_{60}@\text{C}_{180}\text{F}_{180}$; (d) $\text{C}_{60}@\text{C}_{240}$; (e) $\text{C}_{60}@\text{C}_{260}$; (f) $\text{C}_{60}@\text{C}_{320}$. The spectra were further convoluted using a Gaussian line shape with fwhm of 2 cm^{-1} to mimic various broadening effects in experimental measurements. The peaks corresponding to the C_{60} oscillatory motion are indicated with asterisks (*).

Figure 6.

Interlayer separation (ξ) and radii for (a) $C_{60}@C_{180}$, (b) $C_{60}@C_{240}$, and (c) $C_{60}@C_{320}$ derivatives. The structures are optimized at the BLYP-D3/DZ level with dispersion corrections. The radius is defined as the average distance of carbon atoms from the center of the system. The changes are plotted with respect to the isolated carbon complex. The dashed blue line indicates the distance between two adjacent layers in graphite (3.35 Å).

Table 1Oscillatory Motion of C₆₀ in a Confining Shell^a

system	E_0 [BLYP-D3] (cm ⁻¹)	E_0 [AM1] (cm ⁻¹)	k [BLYP-D3] ^b (kg/s ²)	k [AM1] ^b (kg/s ²)
C ₆₀ @C ₁₈₀	86	(71,71,70)	941.6	641.8
C ₆₀ @C ₁₈₀ H ₁₈₀	–	(37,37,37)	–	177.7
C ₆₀ @C ₁₈₀ F ₁₈₀	–	(24,24,24)	–	86.6
C ₆₀ @C ₂₄₀	23	(28,28,28)	71.9	106.5
C ₆₀ @C ₂₄₀ H ₂₄₀	–	(16,16,16)	–	35.3
C ₆₀ @C ₂₆₀	9	(22,22,22)	11.2	66.8
C ₆₀ @C ₃₂₀	25	–	32.2	–

^aForce constants, k , and zero-point energies, E_0 , as calculated by the DFT (BLYP-D3/TZVP) and AM1 methods. The entries for E_0 [AM1] denote frequencies along the x , y , and z directions (ν_x , ν_y , ν_z).

^bThe force constant (k) is calculated using the reduced mass of the complex μ .

Table 2Interlayer Interaction Energies^a

	interaction energy, E (kcal/mol)	
	DZ basis	TZVP basis
$C_{60}@C_{180}$	80.1	131.3
$C_{60}@C_{180}H_{180}$	-163.2	-168.2
$C_{60}@C_{240}$	-185.0	-189.7
$C_{60}@C_{240}H_{240}$	-308.3	-279.8
$C_{60}@C_{320}$	-78.9	-92.8
$C_{60}@C_{320}H_{320}$	-45.5	-40.8

^aThe energy is derived from the energy difference between a double layer complex and its individual constituents: interaction energy = $E(\text{core-shell complex}, C_{60}@C_{\text{shell}}) - E(\text{free } C_{60}) - E(\text{free } C_{\text{shell}})$.