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Tuning spectral properties of fullerenes by substitutional doping

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We propose a substitutional doping approach to achieve tunable optical properties from fullerenes. Taking C_{60} as an example and using time-dependent density functional theory, we compute the absorption spectra of heterofullerenes $C_{60-n-m}N_nB_m$, and demonstrate that their optical gaps and first triplet energies can be tuned from the near-infrared up to the ultraviolet by tailoring the dopant numbers n and m. This is supported by experiment and suggests heterofullerenes as single-molecule fluorescent probes and as building blocks for the bottom-up assembly of tunable luminescent devices. For the example of $C_{59}HN$, we discuss the effect of organic functionalization, which is needed for device fabrication, on optical properties.

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Over the past decade, clusters, quantum dots, nanocrystals and nanocomposites have attracted much attention due to their tunable optical properties (TOPs).[1–6] Usually, those TOPs are realized by tailoring the size, shape, chemical surroundings, pressure or temperature of the materials.[1–6] For example, the optical gap of a Au/SiO_2 nanocomposite can be tuned from 560 to 1130 nm by varying the temperature;[2] the emission spectra of InP, InAs and CdSe nanocrystals can be tuned from 400 to 2000 nm by tailoring their sizes;[1] Au nanorings exhibit TOPs in a wide wavelength range by varying the ratio of the ring thickness to radius.[3] The TOPs of these systems can be used to design tunable optical devices for a wide range of applications,[1–5] for example, in information displays, nanoscale electronics, laser technology, optical filters, optical storage, scintillators, medical imaging detectors, optical sensors, optical switches, solar cells, biological fluorescent labeling, and even children's "glow-in-the-dark" toys. The prospect of realizing these devices has been a driving force for the search for new materials with TOPs.

The electronic and optical properties of fullerenes have been studied intensively.[7] Doping should alter the charge distributions, electronic structures, and energy gaps Δ between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the parent fullerenes.[7,8] Because of the cage structure of fullerenes, doping can be exohedral, endohedral or substitutional.[7] Hence, a wide range of schemes for obtaining TOPs from fullerenes should be available with these doping approaches. In this communication, we show how substitutional doping can achieve this goal. Taking C_{60} as an example and using time-dependent density functional theory (TD-DFT),[9] we demonstrate that the optical gaps E_{og} and the first triplet energies ${}^{(3)}E_1$ (two key quantities in fluorescence and phosphorescence[10]) of heterofullerenes $C_{60-n-m}N_nB_m$ can be tuned from the near-infrared up to the ultraviolet (UV) by varying the dopant numbers m and n. Available experiments support our theoretical demonstration. Over the past decade, $C_{59}N^+$,[11,12] $C_{59}HN$,[13] $C_{60-m}B_m$ $(1 \leqslant m \leqslant 6)$,[14] $C_{60-n}N_n$ $(1 \leqslant n \leqslant 4)$,[15] and $C_{58}BN$[16] have been synthesized. Two recent experiments suggested the existence of $C_{48}N_{12}$ (Ref. 17) and $C_{p-n}N_n$ $(40 \leqslant p \leqslant 50,\ 1 \leqslant n \leqslant 9)$.[18] Thus, the heterofullerene TOPs and chemical flexibility should make them ideal for use as single-molecule fluorescent probes in polymer science, biology[5] and medicine[19,20] (for example, labeling DNA and RNA, lighting up polymers, photodynamic therapy, de-

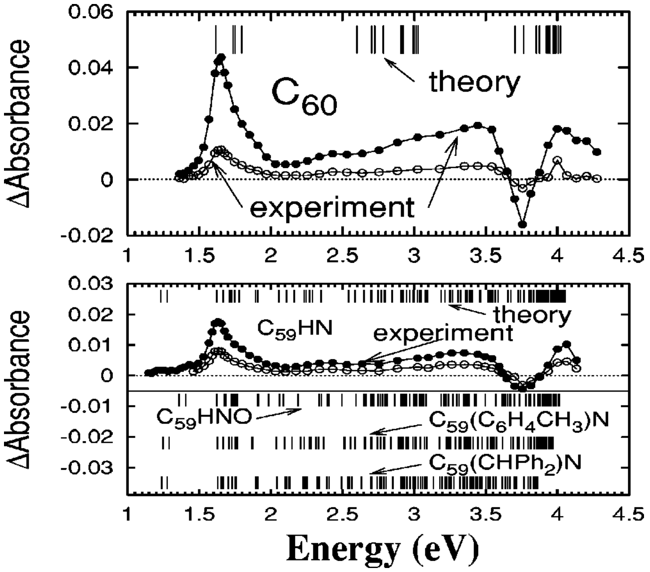

FIG. 1. Transient triplet–triplet absorption spectra of C_{60} and $C_{59}HN$ in toluene measured with 355 nm excitation, where closed and open circles are spectra 5 and 50 μs after a ns-laser pulse, respectively. Vertical lines are the calculated ${}^{(3)}E_i$ for C_{60}, $C_{59}HN$, $C_{59}HNO$, $C_{59}(C_6H_4CH_3)N$ and $C_{59}(CHPh_2)N$.

TABLE I. Calculated Δ (eV), E_{og} (eV) (also $\tilde{f}=10^2 f_{osc}$), ${}^{(3)}E_1$ (eV) and ${}^{(1)}E_1$ (eV) of (hetero)fullerenes. E_{og}^{exp} is from experiment. $X_1=C_6H_4OCH_3$, $X_2=C_6H_4CH_3$, and $X_3=CHPh_2$.

Fullerenes	Δ	${}^{(3)}E_1$	${}^{(1)}E_1$	E_{og}	$\tilde{f}$	E_{og}^{exp}
$C_{20}(BN)_{20}$	2.54	2.33	2.62	3.05	1.00	
$C_{22}(BN)_{19}$	2.38	2.21	2.50	2.50	0.27	
$C_{26}(BN)_{17}$	2.16	2.01	2.25	2.25	0.25	
$C_{30}(BN)_{15}$	1.97	1.85	2.08	2.08	1.25	
C_{60}	1.81	1.62	1.83	2.92	0.19	3.04[a]
$C_{40}(BN)_{10}$	1.80	1.67	1.91	1.91	0.32	
$C_{54}(BN)_3$	1.72	1.58	1.78	1.82	0.04	
$C_{48}N_{12}$	1.63	1.55	1.70	1.70	0.03	
$C_{58}(BN)_1$	1.62	1.50	1.67	1.67	0.12	
$C_{59}HNO$	1.46	1.36	1.53	1.53	0.28	1.63[b]
$C_{59}N^+$	1.43	1.35	1.49	1.49	0.01	1.60[c]
$C_{59}X_1N$	1.35	1.25	1.42	1.42	0.37	1.57[d]
$C_{59}X_2N$	1.34	1.25	1.42	1.42	0.37	1.57[d]
$C_{59}HN$	1.33	1.23	1.41	1.41	0.40	1.52[b,e]
$C_{59}X_3N$	1.33	1.24	1.40	1.40	0.38	1.53[f]
$C_{54}N_6$	1.18	1.10	1.28	1.28	0.32	
$C_{59}B^-$	1.09	1.04	1.17	1.17	0.03	
$C_{52}B_8$	1.03	0.92	1.06	1.06	0.02	
$C_{58}B_2$	1.02	0.91	1.10	1.10	0.04	
$C_{54}B_6$	0.97	0.82	1.04	1.04	0.01	
$C_{56}B_4$	0.81	0.71	0.93	0.93	0.10	
$C_{52}N_8$	0.75	0.67	0.83	0.83	0.08	
$C_{56}N_4$	0.74	0.68	0.83	0.83	0.12	
$C_{58}N_2$	0.73	0.64	0.80	0.91	0.37	
$C_{48}B_{12}$	0.59	0.53	0.64	0.64	0.02	

[a] Reference 27.
[b] Reference 26.
[c] This work.
[d] Reference 34.
[e] Reference 13.
[f] Reference 33.

tection of cancer), as single-molecule fluorescence-based sensors and switches,[5] and as building blocks for the bottom-up assembly of tunable fluorescent/phosphorescent devices.[1,4]

Our computational technique is based on the TD-DFT[9] implemented in the GAUSSIAN 98 program.[21] The exchange-correlation potential v_{xc} in the TD-DFT is given as the functional derivative of the time-dependent exchange-correlational action A_{xc},[9] an unknown functional of the charge density over both space and time. In practical applications,[9,21] this unknown A_{xc} is approximated by using the same exchange-correlation functional E_{xc} as in the time-independent Kohn–Sham theory[22] but evaluated using the charge density at the time t (this local approximation in time is commonly referred to as the adiabatic approximation[9]). Detailed TD-DFT implementation is illustrated in the GAUSSIAN 98 package[21] and the work of Stratmann *et al.*[9] The ground-state structures of the molecules studied here were optimized by using DFT[22] with the hybrid B3LYP functional[23] and a 6-31G(d) basis set.[21] Then, using a 3-21G basis set[21] (this basis set is sufficient for the present work, see our support material[24]), we compute the energies ${}^{(1)}E_i$ and ${}^{(3)}E_i$ of the ith singlet and triplet excited states, respectively, and the absorption spectra, the energy E_{og} (Ref. 6) of the first dipole-allowed transition (DAT) in the absorption spectra and the oscillator strengths f_{osc} of the DATs. We calculate the percentage, P_n^v, that shows the excitation participation contribution of an electron-hole (e-h) pair (v,n) to a specified singlet or triplet state, where v and n represent the $(\mathrm{LUMO}+v)$th unoccupied and $(\mathrm{HOMO}\text{-}n)$th occupied single-electron states of a molecule in its ground state. Details of experimental procedures and facilities for measuring UV/visible and transient absorptions reported here can be found in Refs. 25,26.

We ensure the accuracy of the calculations for heterofullerenes by choosing suitable exchange and correlation functionals (see our supplemental material[24]). Because accurate UV/visible absorption spectra of C_{60} in the gas phase and solution are available, we choose C_{60} as a benchmark.[24] We found that TD-DFT with a local spin density approximation and various non-hybrid functionals leads to similar results[24] for E_{og}, ${}^{(3)}E_1$, ${}^{(1)}E_1$, and f_{osc}, which agree with experiment.[27] However, TD-DFT with hybrid functionals leads to unsatisfactory results.[24] Based on this test, we choose Becke's B88 exchange[28] and Perdew's P86 correlation[29] functionals. Our calculated absorption spectrum[24] of C_{60} shows that the first three DATs are at 2.92, 3.62, 4.62 eV with $f_{osc}=0.0019$, 0.1197, 0.3470, respectively,[30] which agree well with experiment (3.04, 3.73, 4.60 eV with $f_{osc}=0.003$, 0.09, 0.46).[27] The calculated triplets of C_{60}, reported in Fig. 1, characterize well our measured transient absorption peaks and the bleaching maximum[31] at 3.76 eV, which coincides with the UV absorption at 3.73 eV.

Our calculated results for the most stable isomers[32] of $C_{60-n-m}N_nB_m$ are summarized in Table I, and the absorption spectra for single N-doped cases are presented in Fig. 1 and Fig. 2. The first singlets of heterofullerenes come mainly from the (0,0) e-h pair (e.g., P_0^0 is 42% for $C_{20}B_{20}N_{20}$). Accordingly, ${}^{(1)}E_1$ of $C_{60-n-m}N_nB_m$ follows the ordering of Δ. Comparing ${}^{(1)}E_1$ with E_{og} shows that the first singlets of C_{60}, $C_{20}(BN)_{20}$, $C_{54}(BN)_3$, and $C_{58}N_2$ are dipole-forbidden and $E_{og}>{}^{(1)}E_1$. For the other heterofullerenes, the first singlet is dipole-allowed and $E_{og}={}^{(1)}E_1$. This is due to the heterofullerene symmetry which determines the optical activity. Substitutional doping of C_{60} lowers the I_h symmetry of C_{60}.[7,8] Correspondingly, the LUMO and HOMO symmetries can change,[7,8] and influence the optical activity of the lowest singlets. For example, although it is an isoelectronic analogue to C_{60}, $C_{20}(BN)_{20}$ has S_{10} symmetry.

$C_{60-k}N_k$ ($C_{60-k}B_k$) is isoelectronic with ${C_{60}}^{-k}$ (${C_{60}}^{+k}$). Replacing k C atoms by k N (B) atoms results in a complete filling (removing) of k electrons into (from) the lowest LUMOs (highest HOMOs) of C_{60}[8] with Δ determined by the smaller intraband spacing between LUMOs (HOMOs) rather than the full LUMO-HOMO gap of C_{60}. Moreover, substitutional doping lowers the symmetry of C_{60} and thus removes the degeneracy of its original levels[7,8] providing even smaller Δ. As indicated in Table I, $C_{60-n}N_n$ and $C_{60-m}B_m$ have smaller Δ than C_{60}, and the corresponding E_{og} are

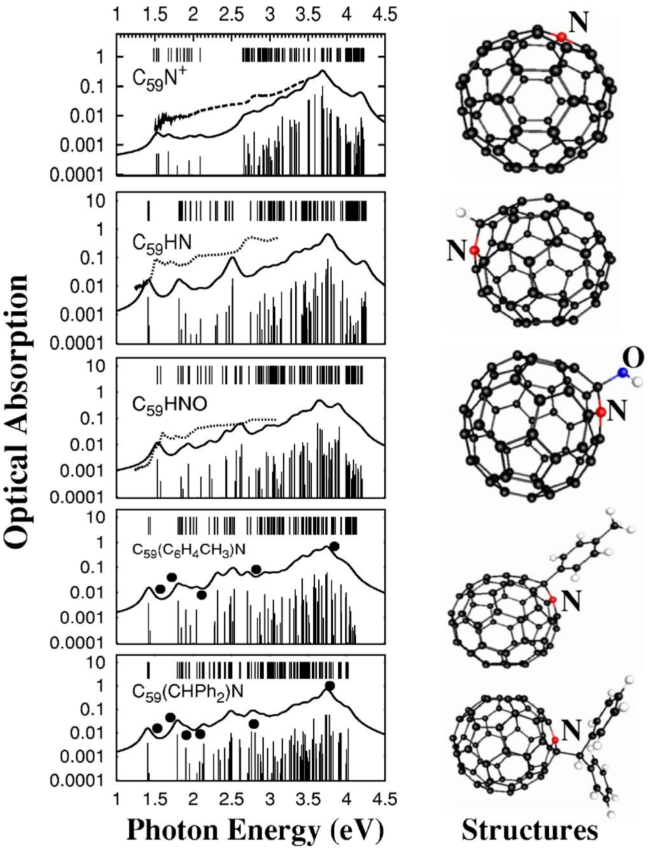

FIG. 2. (Color online) Calculated absorption spectra for single N-doped cases ($Ph=C_6H_5$). A Lorentzian function with a width of 0.06 eV has been used to simulate a finite broadening. Vertical lines are the calculated f_{osc} (bottom) and ${}^{(1)}E_i$ (top). Dotted (dashed) lines are spectra from previous—Refs. 26 and 27 (present) experiments, and closed circles mark the energies of the most intensive absorptions from previous experiments (Refs. 33 and 34). Structures: C (black ball), H (white ball), N and O are specified.

redshifted by 1.2 to 2.3 eV relative to that of C_{60}. For cases of single N-doping, the predicted E_{og} and redshift are in good agreement with previous[13,26,27,33,34] and present experiments. For high BN-doping, the HOMO occupies mainly the BN sites and is little changed, but the LUMO is increasing more antibonding with higher energy.[32] Thus, the Δ for high BN-doping can be larger than that for C_{60}. Table I shows that $C_{60-2n}(BN)_n$ ($10<n\leqslant 20$) has a larger Δ than C_{60}, and the corresponding E_{og} is blueshifted by 0.2 to 2.5 eV relative to that of $C_{60-n}N_n$ or $C_{60-m}B_m$. Consequently, high optical gaps can be tailored with high BN doping, while low optical gaps can be tailored by B or N doping, with the E_{og} of $C_{60-n-m}N_nB_m$ tuned from 3.05 eV (407 nm) to 0.64 eV (1937 nm) by tailoring the dopant numbers n and m. This TOP suggests the application of heterofullerenes in tunable fluorescent devices.

The first triplets of heterofullerenes are found mainly from the (0,0), (1,0) or (0,1) e-h pair with, for example, a P_n^v of 57_0^0 (56_1^0, 48_0^1) for $C_{58}N_2$ ($C_{58}B_2$, $C_{58}BN$). As a result, ${}^{(3)}E_1$ of $C_{60-n-m}N_nB_m$ generally follows the ordering of Δ and can be tuned from 0.53 to 2.33 eV. Our measured ${}^{(3)}E_1$ for C_{60}, $C_{59}N^+$ and $C_{59}HN$ are 1.60, 1.32, 1.21 eV, respectively, in good agreement with the calculations. Since ${}^{(3)}E_1 < {}^{(1)}E_1$, the lowest triplet is a metastable state. This suggests the application of heterofullerenes in tunable phosphorescent devices.[4,10]

(Hetero)fullerenes are difficult to process due to their poor solubility in most organic solvents.[19,20,35] However, this difficulty can be surmounted with the aid of organic functionalizations.[35] Moreover, functionalized complexes such as arylated azafullerenes are more stable and producible with high yield.[35] Therefore, for luminescent applications,[4,5,10] organic functionalization of heterofullerenes will be useful and it is important to examine the effect of functionalization on their optical properties. We choose $C_{59}HN$[13] as an example to discuss this effect since several functionalized complexes[26,33,34] of $C_{59}HN$ have been synthesized.

First we discuss the calculated results for $C_{59}HN$ and then compare them with those of functionalized complexes to see the effect of functionalization. The energy levels of $C_{59}HN$ in its ground state are computed and presented in our supporting material,[24] and the calculated absorption spectra are shown in Fig. 2. In the visible region, absorption maxima appear at 1.41, 1.81, 2.09, 2.52 eV, which agree with experiment (1.52, 1.68, 2.07, 2.76 eV).[13,26] The main contributions to the four dipole-allowed singlets are from (0,0), (2,0), (0,4) and (3,0) e-h pairs.[24] The calculated triplets of $C_{59}HN$, presented in Fig. 1, show that the lowest triplet–triplet absorption occurs in the first triplet band (1.20–1.30 eV) which contains ${}^{(3)}E_1$ and ${}^{(3)}E_2$. The maximum triplet–triplet absorption at 1.65 eV appears in the second triplet band (1.60–1.80 eV)[24] which includes ${}^{(3)}E_{i=3,\ldots,9}$. The bleaching maximum at 3.76 eV coincides with the calculated maximum UV absorption at 3.76 eV shown in Fig. 2.

To study the effect of functionalization, we synthesized and isolated $C_{59}HN$ in its pure form, and oxidized $C_{59}HN$ to form $C_{59}HNO$.[26] In Fig. 1 and Fig. 2 are presented the calculated results for $C_{59}HNO$, which are similar to those of $C_{59}HN$. In the visible region, absorption maxima of $C_{59}HNO$ appear at 1.53, 1.94, 2.21, 2.63 eV, which agree with our experiment (1.63, 1.78, 2.08, 2.78 eV).[26] The calculated E_{og} and ${}^{(3)}E_1$ of $C_{59}HNO$, due to the functionalization, are blueshifted by only 0.11 and 0.13 eV, respectively. The E_{og}-blueshift agrees with the measured blueshift.

To understand the small effect of functionalization, we also compute the energy levels of $C_{59}HNO$ in its ground state (see Ref. 24). We find that the O-H interaction shifts the $C_{59}HN$ orbitals to lower energy by 0.01 to 0.1 eV without changing the orbital symmetries.[24] The first new orbital is HOMO-5, the p orbital of O atom.[24] However, this new orbital makes little contribution to the lowest transition. Thus, $C_{59}HNO$ and $C_{59}HN$ have similar optical gaps. Because the O-H interaction increases the LUMO-HOMO gap by 0.13 eV,[24] the E_{og} and ${}^{(3)}E_1$ of $C_{59}HNO$ are blueshifted by about 0.13 eV. Similar results (see Fig. 1, Fig. 2 and Table I) are obtained for the arylated complexes of $C_{59}HN$, such as $C_{59}(CHPh_2)N$,[33] $C_{59}(C_6H_4CH_3)N$,[34] and $C_{59}(C_6H_4OCH_3)N$.[34] All of the above results show that functionalization has a small effect on the optical properties of $C_{59}HN$.

In conclusion, we have demonstrated the substitutional doping approach to achieve TOPs from fullerenes. The optical gaps and the first triplet energies of heterofullerenes can be tuned from the near-infrared up to the ultraviolet, making heterofullerenes ideal for use as single-molecule fluorescent probes and as building blocks for tunable luminescent devices.

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