

Investigation of Optical Properties for N and F Doped Triangular Shaped Carbon Molecules

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Abstract

Optical properties of N and F doping triangular shaped carbon molecules have been investigated in theory and experiment. The theoretical results showed that carbon molecules with impurity F and Cl have the same characters with pure carbon. Doping N into pure carbon molecule would change the optical rotation at 589nm. For doping N replacing hydrogen atom structures (N-doping 1 and N-doping 2 molecules), the absorption spectra of them are similar to pure carbon molecule. However, for molecules with impurity N atom in benzene ring (N-doping 3 and N-doping 4 molecules), the peaks of wavelength of absorption spectra shift to long wavelength compared to that of pure carbon molecule. Moreover, the delocalization of molecular orbital (MO) is different from pure carbon molecule, which is caused by the impurity N changing the electrons distribution of benzene ring. We have calculated 3 without H and 4 without H molecules which are removing hydrogen atom in nitrogen atom from N-doping 3 and 4. 3 without H and 4 without H molecules have similar optical properties with pure carbon molecule. The results testified that the impurity N and F would not change the optical properties of carbon molecule if impurity did not change the delocalization of all benzene rings.

1. Introduction

Carbon dots (CDs) have potential application in nano-probes, opto-electronic devices, catalysis, biomedicine for their good optical properties, small size, low cost and biocompatibility¹⁻¹⁵. Photoluminescence (PL) of CDs is most in the blue and green spectral regions with most high quantum yield (QY) close to 100%¹⁶⁻¹⁸. However, CDs with long wavelength emission, such as deep red/NIR emission have lower QY. Different solvent and synthetic raw materials would lead to the long wavelength emission and high QY of CDs¹⁹⁻²¹. Hetero-atom doping is another method to control the PL of CDs. Among the different hetero-atoms, nitrogen impurity can improve the QY of CDs for doping nitrogen atoms would stabilize the surface defect of CDs and improve the PL²²⁻²⁴. Besides, nitrogen doped CDs have different PL range compared to pure CDs. Lin et al used phenylenediamines (three isomers: *o*-phenylenediamine, *m*-phenylenediamine and *p*-phenylenediamine) as precursors to synthesis CDs with different emission²⁵. In 2016, Xu et al provided an overview of heteroatom doped CDs and a detailed description of the influence of single or co-doping heteroatoms on emission behavior of CDs.²⁶ Halogen (F, Cl and I) doped CDs is different from nitrogen doped structures. Impurity F in the surface of CDs maybe form hydrogen-bonding²¹. Lu et al. reported a novel kind of N and F co-doped CDs with D- π -A conjugated N-CDs-F, which have very bright deep-red emission and can be used for efficient in vivo NIR imaging²⁷. To get a better insight about the underlying mechanism and stability of these CDs, chemical reactivity descriptors have been analyzed²⁸⁻³⁴.

In theory, time-dependent DFT (TDDFT) have been wide used to predict the optical properties of CDs³⁵⁻³⁸. In 2018, Fan et al. reported a kind of narrow bandwidth emission CDs (full width at half maximum of 30nm)¹³. Simultaneously, in theory they confirmed that the unique highly crystalline triangular structure functionalized with pure electron-donating hydroxyl groups at the edge sites show highly delocalized

charges, outstanding structural stability, and thus dramatically reduced electron–phonon coupling, which are responsible for the high color-purity excitonic emission of the CDs with TDDFT. Recently, many references researched optical properties in theory. The main oscillation strength and major contribution to electronic transitions could be determined³⁹⁻⁴⁰.

This paper would study optical properties of nitrogen and fluorine doped sp^2 hybrid carbon molecules in experiment and in theory with TDDFT. Nitrogen atoms have two position in CDs: replacing the hydrogen atom and replacing the carbon atom in benzene ring. For fluorine doped CDs, fluorine atom only replaces hydrogen atom. Besides, we also investigated the characters of nitrogen and fluorine co-doped CDs in experiment and in theory.

2. Syntheses Of N And F Doping Cds

Materials: The urea ($CO(NH_2)_2$, AR, 99.5%) was purchased from Aladdin. The citric acid (AR, 99.5%) was obtained from Macklin Biochemical Co., Ltd. The ammonium fluoride (AR) was acquired from Shanghai Shenbo Chemical CO., LTD. The N, N-dimethylformamide (DMF) was brought from Sinopharm Chemical Reagent Co., Ltd (China).

Syntheses of N doping CDs: In a typical synthesis, citric acid (2 g) and urea (4 g) were first dissolved in 20 mL of DMF or deionized (DI) water thoroughly. Then, the above solution was sonicated for 10 min. The solution was transferred to a Teflon-lined stainless-steel autoclave, reacted at 180 °C for 4 h, and cooled down to room temperature naturally and filtered through a 0.22 μm filter membrane to remove the large particles. As a result, the dark brown solution was obtained. To remove the excess precursor and byproducts, the solutions were further dialyzed against DI water through a dialysis membrane with a molecular weight cut-off of 1000 for 24 h. After removing solvent and freeze-drying further, a black powder was obtained.

Syntheses of F doping CDs: citric acid (2 g) and NH_4F (0.2g) were dissolved in 20 mL of DMF thoroughly. After 10 min ultra-sonic, the precursor was transferred to the Teflon-lined stainless-steel autoclave, reacted at 180 °C for 4 h, and cooled down to room temperature naturally. Then the purification method is the same as above.

Syntheses of N and F co-doping CDs: citric acid (2 g), urea (4 g) and NH_4F (0.2g) were first dissolved in 20 mL of DMF thoroughly. Then, through 10 min of ultrasonic and 180 °C, 4 hours reaction in the Teflon-lined stainless-steel autoclave, cooling to obtain the corresponding products. The purification method is the same as above.

Calculation method

For DFT calculation, we adopted Becke's three-parameter hybrid exchange functional with the correlation functional by Lee et al. B3LYP/6-31G (d, p) basis set as it was implemented in Gaussian 03 program⁴¹. Figures of geometric structures were generated using GaussView program⁴². Absorption spectra of these

molecules were obtained with TDDFT. Bonds characters and aromaticity calculating using *natural bond orbital* (NBO) and nuclear magnetic resonance (NMR) = GIAO in (nucleus independent chemical shift) NICS (0). Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) was calculated using B3LYP/6-31G (d, p) and CAM-B3LYP/6-31G (d, p), showed with GaussView⁴².

3. Results And Discussion

3.1 Optical properties of nitrogen and fluorine doped CDs

Using citric acid as carbon source, water or DMF as solvent, we have synthesized CDs. Ammonium fluoride and urea is added as F and N source for F and N doped CDs. The absorption and PL spectra of pure and doping CDs are showed in Figure 1. In water and DMF, the absorption and PL spectra of CDs have a little difference, which may be caused by solvent effect. The wavelength of the absorption and PL for F doping CDs are similar to those of pure CDs. However, N doping CDs have different optical properties with pure CDs. The absorption spectra of N doping CDs have multiple peaks. The wavelength of PL is shifting to red. N and F co-doping CDs have similar optical properties with N doping CDs. Obviously, impurity of F would not change optical properties of CDs. The absorption spectra of CDs with impurity of N have many peaks. The wavelength of PL spectra for N doping CDs shift to long wavelength. Therefore, using citric acid as carbon source, the wavelength of PL spectra of CDs would be controlled through doping N impurity.

3.2 The influence of location of doping N

CDs have more atoms, which results in the whole CDs being difficult to calculate with Gaussian. In this paper, small molecules have been chosen as unit to obtain the characters of CDs and N or F doping CDs. Configures and electronic density differences maps (EDDM) of pure and N doping molecules are listing in Figure 2. All molecules are stable structures for the positive frequency (Table 1). The cohesive energy per atom (E_p) in Table 1 is calculated using the following formula⁴³:

$$E_p = \frac{E_T - N_C * E_C - N_H * E_H - N_N * E_N}{N_C + N_H + N_N}$$

where E_p , E_T , E_C , E_H and E_N is cohesive energy per atom, the total energy of CDs, the energies of C, H and N atoms. N_C , N_H and N_N are the numbers of C, H and N atoms.

Molecule without N doping (pure carbon 0) is planar with dipole moment (DM) 0.0018 Debye and D_{3h} symmetry. For N doping molecules, there are two kind of doping types. The first one is doping nitrogen replacing one hydrogen atom of surface. The other one is doping nitrogen atom in the ring of benzene,

whose nitrogen atom replaces one carbon atom of benzene ring. N-doping carbon molecules are showed in Figure 2. Nitrogen atoms in N-doping 1 and N-doping 2 molecules take the place of hydrogen atoms. Those in N-doping 3 and N-doping 4 molecules take the place of carbon atoms of benzene ring. In N-doping carbon 1 molecule, except two hydrogen atoms linking to doping N atom, all atoms are in the same plane. This structure has low symmetry C_1 and high DM 2.1784 Debye. Benzene rings in N-doping 2 molecule are not in the same plane, which is different from N-doping 1 molecule. It is owing to the change of location of doping N atom, which makes the whole molecule be distorted for large steric resistance. DM of N-doping 2 molecule is 1.5719 Debye. The cohesive energy per atom for N-doping 1 and N-doping 2 is -6.470 and -6.463 eV, respectively. Obviously, N-doping 1 has lower energy and better stability. For N-doping 3 and 4 molecules, doping N atoms are in the ring of benzene. The difference between them is the location of doping N atoms. N-doping 3 is not a planar structure for the hydrogen in nitrogen atom is out of the plane. N-doping 4 is planar. These two molecules have worse symmetry and high DM. The cohesive energy per atom of N-doping 3 (-6.466 eV) is lower than N-doping carbon 4 (-6.057 eV). N-doping 3 molecule has better stability. From the above data, it is confirmed that for two doping types, the steric hindrance would influence the stability molecules.

The aromaticity, optical rotation at 589nm, molecular orbital, and UV-Vis spectra of pure and N-doping molecules have been investigated. Aromaticity is judged with NICS data calculated with NMR. The negative NICS value shows that the molecule is aromatic. And the positive NICS value shows the molecule is anti-aromatic. Investigation of NMR illustrates that NICS(0) value in center benzene is lower (-6ppm) than those in other three benzene rings (-13ppm) for pure carbon 0. Namely, outside benzene rings have better aromaticity, which is because the six delocalized electrons in center benzene ring being share with the outside three benzene rings. Electrons would run to the outside benzene. For N-doping 1 and 2 molecules, NICS(0) value has the same rule with that of pure carbon 0 molecule. NICS(0) value in center benzene is -9ppm and -6ppm for N-doping 1 and 2 molecules. NICS(0) values in three outside benzene rings are -14ppm. Aromaticity of N-doping 1 and 2 molecules is similar to pure carbon 0 molecule. Namely, doping nitrogen atom in surface of pure carbon 0 molecule has little influence on the delocalization of benzene rings. However, for N-doping 3 and N-doping 4 molecules whose nitrogen atoms replace one carbon atom of benzene ring, the NICS values have different rule with pure carbon molecule. NICS(0) value in center benzene is -7ppm and those in other two benzene ring is -13ppm for N-doping carbon 3 molecule. The third benzene ring whose one carbon atom is replaced by nitrogen has NICS(0) value +8, showing that this benzene ring is anti-aromatic. N-doping carbon 4 molecule has similar characters as N-doping 3. NICS(0) value in center benzene is -2ppm and those in other two benzene ring is -13ppm for N-doping 4 molecule. NICS(0) value of the rest benzene ring is +10. In a word, doping nitrogen replacing hydrogen atom has little influence on the delocalization and aromaticity of benzene rings. However, doping nitrogen atom in the ring of benzene would change the delocalization and aromaticity. EDDM (Figure 2b) showed that nitrogen atom has changed the electron distribution.

Table 1 characters of carbon molecule and N-doping carbon molecules.

characters structure	cohesive energy per atom (eV)	Dipole Moment (Debye)	symmetry	Frequency (Hz)	589nm (deg)	Band gap (eV)
pure carbon 0	-6.557	0.0018	D _{3h}	55	-2	4.91
N-doping 1	-6.470	2.1784	C ₁	47	25	4.37
N-doping 2	-6.463	1.5719	C ₁	45	-51	4.39
N-doping 3	-6.466	1.5596	C ₁	62	-208	2.20
N-doping 4	-6.057	3.6723	C _s	29	73	2.20
3 without H	-6.632	1.7562	C ₁	59	0	4.74
4 without H	-6.626	2.8033	C ₁	52	2	4.74

Optical rotation at 589nm for pure carbon 0 and N-doping carbon molecules have been investigated (Table 1). Seen from table, the value of pure carbon 0 is smaller than those of N-doping carbon molecules. Moreover, N-doping 1 and N-doping 4 structures, whose doping N atoms locate in interposition, are right-hand circular. And N-doping 2 and N-doping 3 structures, doping N atoms locating in adjacency, are left-hand circular. Clearly, nitrogen atoms doped into pure carbon structure, the optical rotation would be changed. And the location of doping nitrogen atoms would influence the optical rotation. Therefore, we can use doping nitrogen to change the optical rotation of CDs.

As showing in Figure 3, HOMO and LUMO orbitals of pure carbon and N-doping molecules are different. HOMO and LUMO orbitals have been repeated using B3LYP/6-31G (d, p) and long range corrected exchange correlation functional CAM-B3LYP/6-31G (d, p). The calculating results are the same. The band gap from HOMO to LUMO for pure carbon 0 molecule is 4.91eV, which is in the range of insulator. In fact, carbon dots are semiconductor materials. The band gap of pure carbon 0 is broadening, compared with CDs, which is caused by quantum size effect. Namely, the size of pure carbon 0 structure is smaller than that of CDs. Therefore, the absorption spectra of pure carbon 0 structure shift to short wavelength. Besides, HOMO and LUMO orbitals are calculated with For N doping molecules, the band gap becomes smaller, which results in the wavelength of absorption spectra shifting to red. Moreover, the band gap data of N-doping 3 and 4 molecules with doping nitrogen replacing one carbon atom of benzene ring are 2.20eV, which is in the range of semiconductor. Clearly, doping nitrogen atoms into pure carbon would decrease the band gap, leading to the wavelength of absorption spectra shifting to red, particularly for doping nitrogen replacing one carbon atom of benzene ring structures. Therefore, we can use doping nitrogen to control the luminous wavelength of CDs. This conclusion is similar to the above experimental results. Calculated UV-Vis spectra have been shown in Figure 4. Pure carbon 0, N-doping 1 and 2

molecules have similar absorption spectra. The difference is that the peaks of wavelength of absorption spectra for N-doping 1 and 2 shift to red comparing to pure carbon 0, which is agreement with the above experimental results. It is consistent with the band gap results. Absorption spectra of N-doping 3 and 4 have three absorption peaks, which are assigned to the π - π^* transition of the conjugated olefin, and n - π^* transitions of a class of unsaturated double bonds containing heteroatoms⁴⁴. Besides, absorption spectrum of pure carbon 0 has been calculated with ZINDO/S⁴³, with the peak position 267nm. That with b3lyp/6-31g(d,p) is about 250nm which is shorter than that with ZINDO/S, which is similar to reference⁴⁵.

3.3 Halogen doping and halogen-nitrogen co-doping molecules

For halogen doping molecules, doping halogen atom only can replace the location of hydrogen atom in benzene ring. We have investigated fluorine or chlorine single doping structures and fluorine-nitrogen co-doping structures. Configurations of fluorine and chlorine single doping carbon structures are showing in Figure 5a. Except Cl-doping 1 molecules, other structures are planar. Seen from UV-Vis spectra (Figure 4b), F doping molecules have shorter wavelength than those of Cl doping molecules. F and Cl doping molecules have similar absorption intensity and absorption wavelength with pure carbon molecules, which shows that F and Cl doping have little influence on the optical characters of CDs, which is similar to the above experimental results.

We have investigated two types of F and N co-doping molecules: nitrogen atom in benzene ring and nitrogen atom as amino. There are many isomers for different position of F atoms. All isomers have been optimized. Estimated with the total energy, we have obtained the most stable structures (Figure 6). Absorption spectra of three molecules are different. Structure 1 and 3 have the same absorption spectra, which is similar to pure carbon structure. Structure 2 has different absorption spectra with other molecules. Nitrogen atom in structure 2 can not form delocalized π bonding with the carbon atoms in the ring. Structure 2 have C-N bonding, which is similar to the above N-doping 3 and 4 molecules. Besides, we have calculated molecules similar to N-doping 3 and 4 molecules. The difference is that there is no hydrogen atom in nitrogen atom (Figure 4c). Seen from the data, it is confirmed that without hydrogen atom, 3 and 4 without hydrogen molecules have the same optical properties with pure carbon molecule (Figure 4d). Optical rotation at 589nm and band gap are close to pure carbon 0 molecule. Obviously, the position of nitrogen atom has little influence on the optical properties if the doping nitrogen atom does not destroy the delocalization of benzene ring.

Besides, we have investigated influence of solvent on optical properties of nitrogen doped carbon molecules. We have calculated N doped carbon molecules with water and DMF as solvent^{32, 34, 46-48}. The data are listing in table 2. Obviously, peaks location of UV-Vis spectra in water and DMF are similar, which is shift to longer wavelength than those without solvent. However, theoretical UV-Vis spectra in water and DMF are shift to shorter wavelength than those of experiment, which is maybe caused by quantum size effect. The size of carbon molecules in theory is smaller than prepared CDs in experiment.

Table 2 Peaks location of UV-Vis spectra in water, DMF and without solvent (nm)

	pure carbon 0	N-doping 1	N-doping 2	N-doping 3	N-doping 4
in water	256	263	259	334/428	325/472
in DMF	256	263	259	334/428	320/465
no solvent	250	256	255	337/416	348/449

Conclusion

In a word, F and Cl doping have little influence on the optical properties of pure carbon molecules. The position of N atom has no influence on the optical properties. When doping N atom destroyed the delocalization of benzene ring, optical properties of pure carbon molecules would be changed. Experimental and theoretical results are almost agreement. Besides, theoretical data show that impurity N has changed the optical rotation at 589nm. Therefore, we can change the optical rotation by doping N into CDs.

Declarations

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There is no conflict of interest

Ethics approval: approvals

Consent to participate

Consent for publication

Data and material are Availability for Journal of Molecular Modeling

Code availability: software is available

Authors' contributions: All authors contributed to the study conception and design. Material preparation and data collection were performed by [Shuhong Xu], [Linfeng Tan] and [Fan Liu]. Analysis were performed by [Yiping Cui], [Chunlei Wang] and [Rong Zhang]. The first draft of the manuscript was written

by [Shuhong Xu], [Yiping Cui], [Chunlei Wang], [Rong Zhang] and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Figures

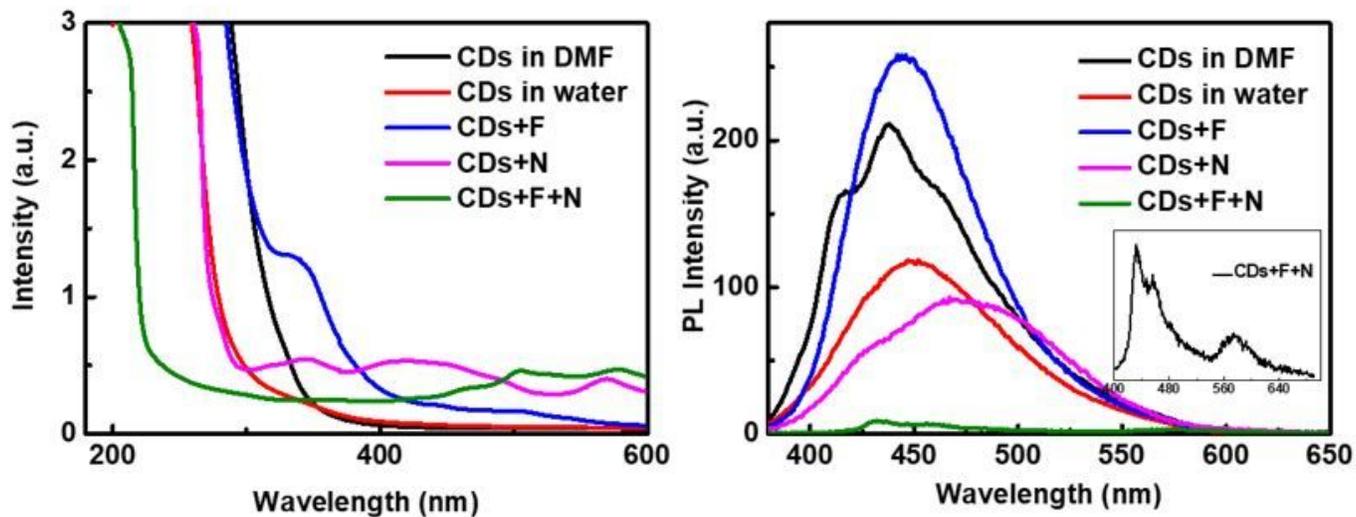


Figure 1

The absorption and PL spectra for CDs. (left) absorption spectra of CDs in DMF and water, and N, F doping CDs; (right) PL spectra of CDs in DMF and water, and N, F doping CDs.

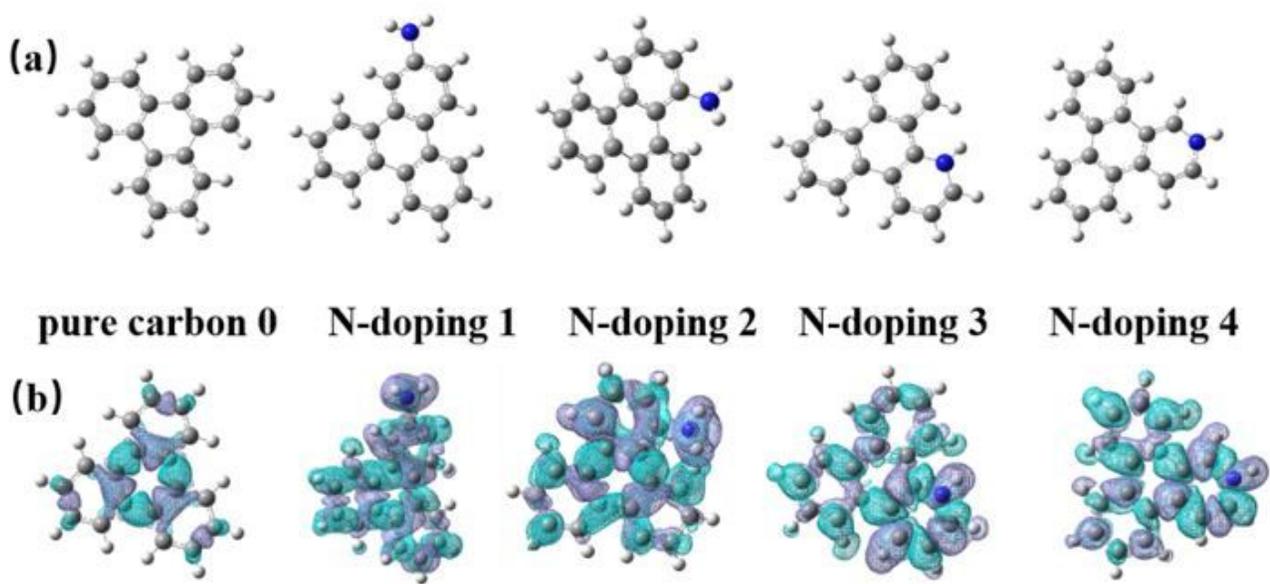


Figure 2

(a) Configures of pure carbon molecule and N-doping carbon molecules. (b) And electronic density differences maps (EDDM).

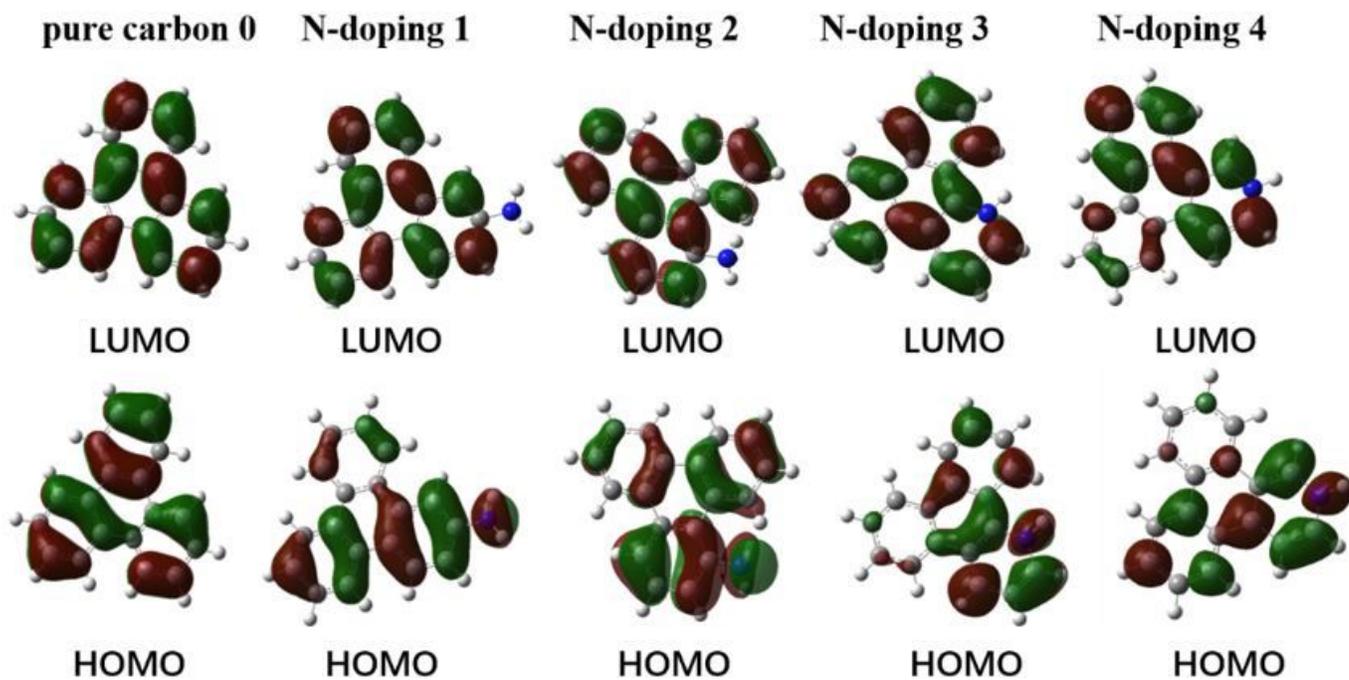


Figure 3

Molecular orbital for pure carbon molecule and N-doping carbon molecules.

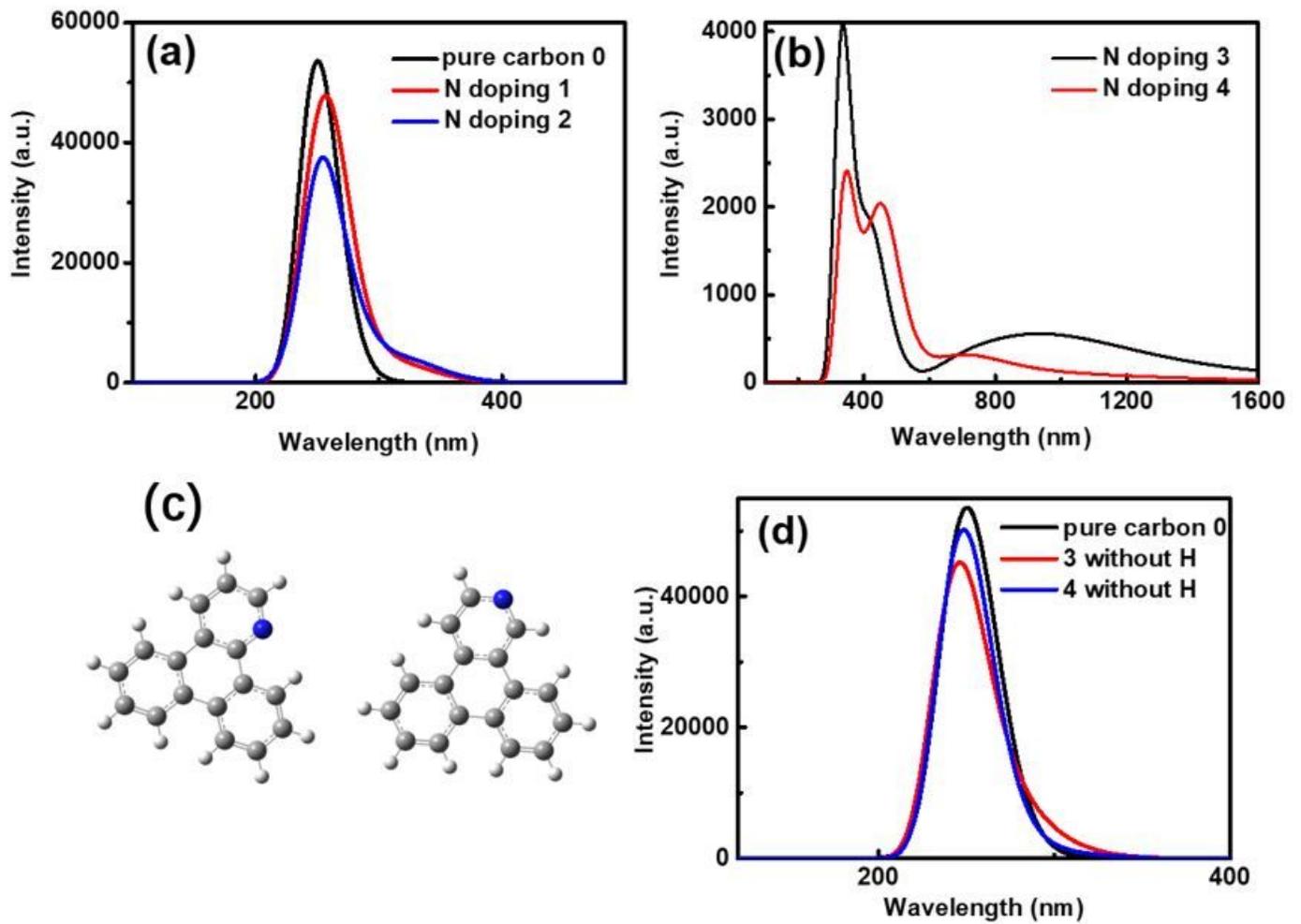


Figure 4

UV-Vis spectra for pure carbon molecule and N-doping carbon molecules UV-Vis spectra of pure carbon molecule, N doping 1 and 2 (a); UV-Vis spectra of N doping 3 and 4 (b); configures and UV-Vis spectra of 3 and 4 without hydrogen molecules (c-d).

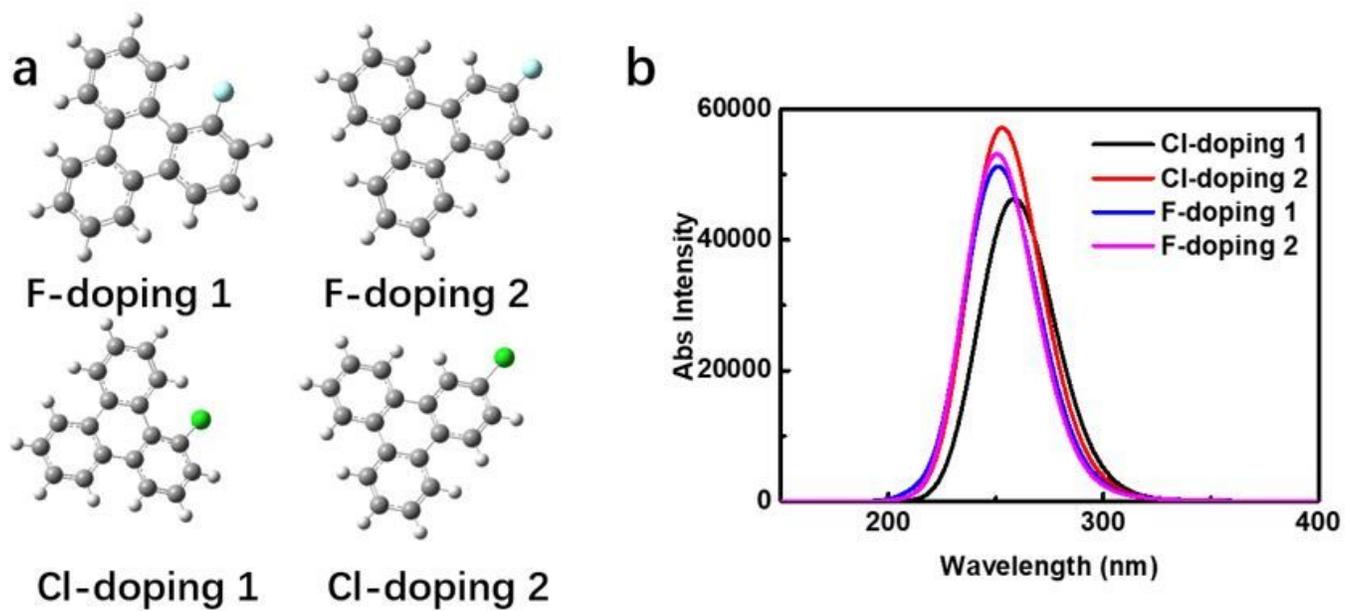


Figure 5

Configurations of fluorine and chlorine single doping carbon molecules (a); UV-Vis spectra of fluorine and chlorine single doping carbon molecules (b).

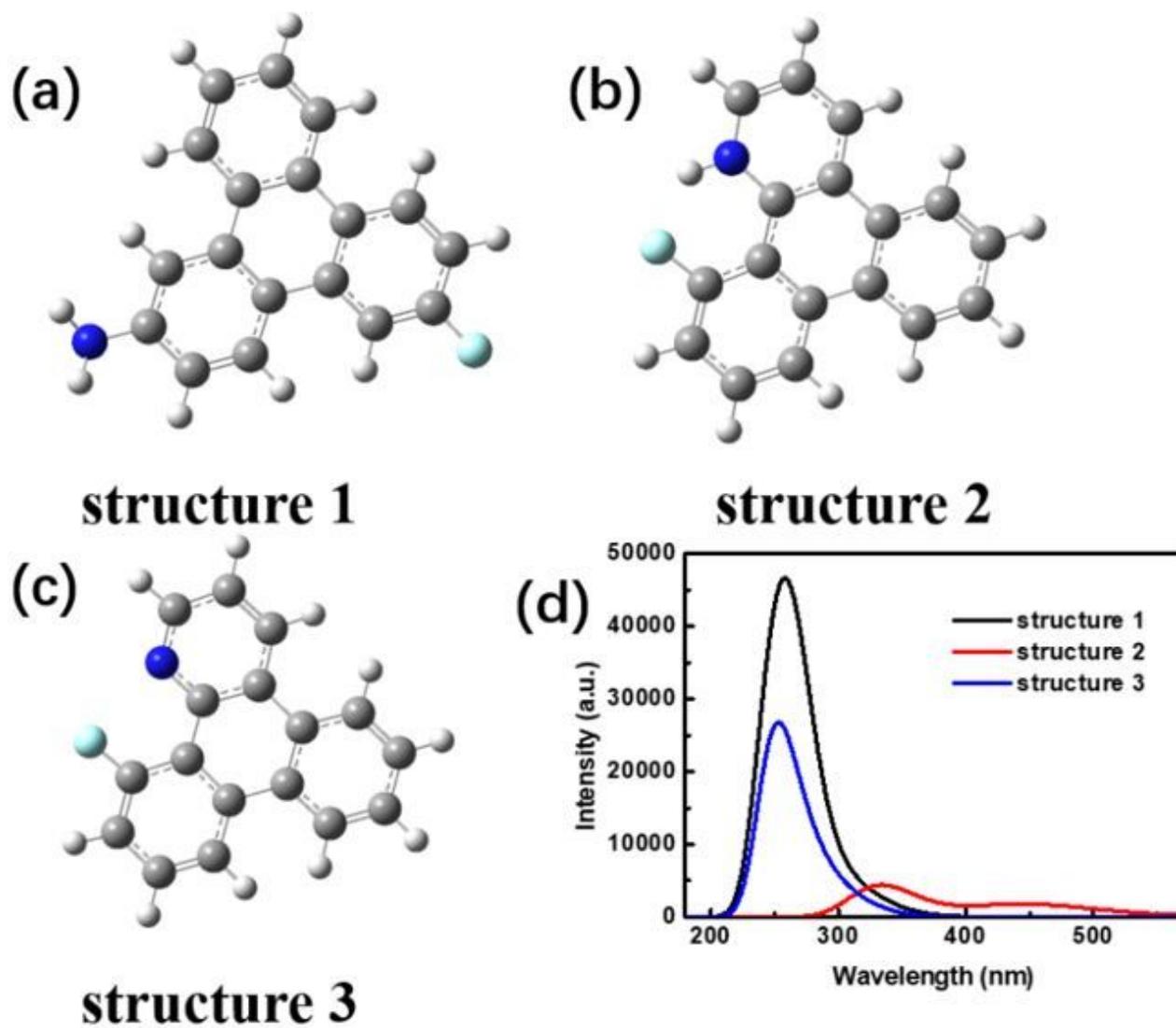


Figure 6

Configurations of nitrogen and fluorine co-doping carbon molecules (a-c); the absorption spectra of nitrogen and fluorine co-doping carbon molecules (d).