



# Article Deciphering the Color Origin of Pink Conch Pearl Using Nondestructive Spectroscopies and DFT Calculations

Chaoyang Chen <sup>1</sup>, Jing Yu <sup>1</sup>, Xu Ye <sup>2</sup> and Andy H. Shen <sup>1,\*</sup>

- <sup>1</sup> Gemmological Institute, China University of Geosciences, Wuhan 430074, China; chengic@foxmail.com (C.C.); jingyu@cug.edu.cn (J.Y.)
- <sup>2</sup> Institute of Jewelry and Jade Carving, Nanyang Normal University, Nanyang 473000, China; yexu5@mail2.sysu.edu.cn
- \* Correspondence: shenxt@cug.edu.cn

**Abstract:** Conch pearl is a calcareous concretion produced by the Queen conch mollusk and is of extremely high economic value. Its attractive pink color has remained a mystery for hundreds of years. This difficulty limits the development of cultivation and preservation technology of conch pearl. Due to its super-high value, it is generally impossible to use destructive chemical analysis methods. Here, various nondestructive spectroscopic analysis methods and theoretical calculations were used to reveal the color origin of pink conch pearl. The experimental Raman and UV-Vis spectroscopies were used to characterize the color and pigments. We further discuss the pigments in conch pearl by comparing the Raman spectral characteristics and pigments of the red coral. Based on the characteristics of the experimental spectra, we speculate that the carotenoids color the conch pearl. The theoretical Raman and UV-Vis spectra of all-trans polyene and carotenoids were simulated using DFT calculations. According to the results, we proposed that the pigments in pink conch pearl are polyenes containing 11 shortened C–C bonds with multiplicities > 1.5, which may be demethylated carotenoids.

Keywords: conch pearl; pigments; polyenes; Raman and UV-Vis spectroscopies; DFT calculations; color origin

## 1. Introduction

Conch pearls, calcareous concretions produced by the Queen conch mollusk, usually have an attractive pink color which may be enhanced by unique silky-looking flame structure [1]. The Queen conch mollusk was previously called *Strombus gigas*, however, this name has been changed to *Lobotus gigas* and then *Aliger gigas* in recent years. The beautiful pink color, mysterious and charming flame pattern structure, and extremely rare output make high-quality conch pearls very valuable and popular. In the jewelry market, high-quality conch pearl is in short supply. The distinctive pink color of conch pearl is completely different from other pearls and is hardly found in any other type of pearl. Unfortunately, the alluring pink color of conch pearl is unstable and will fade to light pink under long-term sunlight, which may be caused by the decomposition of the pigments exposed to ultraviolet light [1]. The pink color is the main characteristic of conch pearl, which plays an important role in the identification, quality assessment, and the development of cultivation technology and preservation technology.

Although the exact nature of pigment in conch pearl is not clear, it is preliminarily speculated that it is carotenoid based on the Raman spectral features [1]. Carotenoid is a common polyene pigment in nature. Carotenoid can be described chemically as a conjugated polyene chain molecule of finite length, with different substitutions at the ends of the polyene chain, and four characteristic methyl substitutions on the main chain of the polyene [2,3]. Pigments containing polyene chains are widely found in nature. For example, they exist in phytoplankton [4], vegetables [5], shells [6], pearls [7], red coral [8],



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). bird feathers [9], etc. Most of these polyene pigments belong to the carotenoid family. The structure of carotenoid changes under external influences, such as heating, ultraviolet radiation, and even during storage [10]. Conch pearl is a biomineral material in which inorganic minerals and various organic substances coexist. Due to the complexity of the composition, the instability of the polyene pigment, and high value of conch pearl, the pigments are difficult to analyze using destructive analytical chemistry methods such as High Performance Liquid Chromatography-Mass Spectrometry (HPLC-MS) after extracting the pigment. Raman spectroscopy is a powerful method to analyze carotenoids without damage and these pigments can be detected at very low concentrations even in complex systems such as biomineral materials [11]. Raman spectroscopy has been used to characterize the pigments contained in these biomineral materials such as seashells [6], red corals [12], snail shells [13], freshwater pearls [14], etc. Interestingly, the Raman spectral characteristics of red coral are quite similar to those of conch pearl. Considering that both biominerals may be very similar.

In this study, photographs taken under a D65 standard light source and UV-Vis spectroscopy were used to characterize the color of pink conch pearl. A nondestructive, efficient, and accurate method of Raman spectroscopy was used to characterize the pigments in pink conch pearl. Density Functional Theory (DFT) calculations were used to simulate the Raman spectra of polyene and carotenoids that may exist in pink conch pearl. The two results were compared and analyzed to identify the more reasonable pigment structures. Time-dependent Density Functional Theory (TDDFT) was used to calculate the electronic excitation in order to obtain the theoretical UV-visible spectra of these pigment structures, so that the color origin of pink conch pearl was interpreted using electron excitation analysis.

#### 2. Materials and Methods

#### 2.1. Materials

A pink conch pearl sample was purchased from a jewelry market. This sample weighs 0.22 g and has a size of 7.9 mm  $\times$  5.7 mm  $\times$  3.1 mm. The sample appears pink overall and has a distinct flame pattern structure. Before the experiment, the sample was thoroughly cleaned with alcohol and thoroughly washed with deionized water.

#### 2.2. Methods

In order to better show the color of the sample, a standard D65 light source was used to take photographs in the light box. Before photographing the conch pearl, we calibrated the camera using a grey plate under a standard D65 light source.

The UV-Vis spectrum of conch pearl was recorded using a Skyray Gem UV-100 ultraviolet visible spectrophotometer using reflection method. The spectral range was 350–800 nm, the integration time was 100 ms, and the average number of times was 8. Without considering the transmission of the sample, the reflection spectrum was converted to the absorption spectrum using the conversion formula: A (Absorbance) = 1 - R (Reflectance).

The Raman spectra were collected using a Raman spectrometer ThermoFisher DXR<sup>TM</sup>2xi. The incident laser excitation was provided by a YAG laser source operating at 532 nm and the power on the sample was 15 mW. The spectrum of conch pearl was taken with 4 cm<sup>-1</sup> resolution, at a collecting time of 30 s, and 1000 Scans were accumulated. The scanning range of the Raman shift was 600–1600 cm<sup>-1</sup>. In order to characterize the distribution of pigments in different areas of conch pearl, the Raman map was also collected, with excitations at 532 nm (Nd: YAG laser), a power on the sample of 15 mw, for 100 scans, and at a resolution of 4 cm<sup>-1</sup> used for analysis. A total of 26,208 Raman spectra were collected at different positions of conch pearl. All tests were carried out at 25 °C and the Raman spectra were corrected by baseline.

The quantum chemical program Gaussian 16 was used to perform all the DFT calculations, and the wave function analysis program Multiwfn was used to analyze the results [15,16]. The optimization on the structures of carotenoids and polyenes and the simulation on their Raman spectra were calculated at the B3LYP/6-31G (d) level [17]. Since the calculated harmonic vibrations overestimate the spectra, a scaling factor of 0.9614 was used for a better comparison of the calculated Raman shift with the experiment [18]. We calculated the electronic excitation of the possible pigment structure under different functional conditions (B3LYP [17], BHandHLYP [19], CAM-B3LYP [20], M06-2X [21], MN15 [22], PBE0 [23], TPSSH [24], and wB97XD [25]) based on TDDFT to obtain the theoretical UV-Vis spectra, which can be better compared with the experimental UV-Vis spectrum of conch pearl.

## 3. Results and Discussion

## 3.1. Color Characterization of Conch Pearl

We chose two methods to characterize the color of conch pearl, namely photographing under a D65 standard light source and UV-Vis spectroscopy. The results are shown in Figure 1a,b.



**Figure 1.** (a) Conch pearl sample in D65 light source. (b) The UV-Vis spectrum of the conch pearl sample.

To better show the appearance of the conch pearl, we place the sample in the light box and photograph it under the D65 standard light source. As shown in Figure 1a, the sample is irregular and flat, with a little white at both ends. Although the pink may be dark and light at different positions of the conch pearl, the distribution of attractive pink is relatively homogeneous. It can be seen that the surface of the sample has a distinctive flame structure, which greatly enhances the beauty and economic value of the conch pearl. As illustrated in Figure 1b, there is a broad absorption band centered at 516 nm in the UV-Vis spectrum of the conch pearl. It is this absorption band that selectively absorbs the visible light region, resulting in relatively more light passing through the red light region, forming the pink color in conch pearl.

#### 3.2. Raman Spectroscopic Characterization of Conch Pearl

Although the overall color distribution of the conch pearl is relatively uniform, color variation can still be seen. In addition to the structure of the inorganic minerals, this variation in color may be due to the uneven distribution of pigments. In order to study the pigments, we randomly collected three Raman spectra of three different locations on the conch pearl as shown in Figure 2. We found that the positions of the Raman spectral peaks of the three different locations were identical, with slight differences in the intensities of the spectral peaks, which may be due to the uneven distribution of the pigments.



Figure 2. Raman spectra of the conch pearl sample.

Similar to freshwater pearls, red corals, shells, and other such biominerals, there are Raman peaks of inorganic mineral (aragonite) and organic pigments (polyenes) in the Raman spectra of conch pearl. There are peaks at 1516, 1298, 1204, 1128, 1087, 1017, 707, and 704 cm<sup>-1</sup> in the Raman spectrum of conch pearl as shown in Figure 2. Among them, the peaks at 1087, 707, and 704  $\rm cm^{-1}$  are assigned to the inorganic mineral aragonite and the positions of these peaks are very stationary for pure aragonite [7,14]. The Raman peak at 1087 cm<sup>-1</sup> has the strongest peak intensity and stable position, thus we use this Raman peak as the base for normalization. All three Raman spectra in Figure 2 are normalized results. The peaks at 1516, 1298, 1204, 1128, and 1017  $\text{cm}^{-1}$  may belong to the polyene pigment [1]. It can be found that the peaks at 1516, 1298, 1204, 1128, and 1017 cm<sup>-1</sup> vary with the different intensities of the colors and the intensity of these peaks will be stronger at the locations where the pink color is relatively intense. Due to the very high intensity of C=C and C-C stretching vibrations (as the result of numerous conjugated double bonds), the corresponding Raman peaks at 1516  $\text{cm}^{-1}$  and 1128  $\text{cm}^{-1}$  are clearly visible [26,27]. Especially, there is a relatively direct relationship between the Raman shifts of the two peaks and the chain length of polyene [26]. At the same time, the areas on the conch pearl with color variations were selected for Raman mapping to obtain the distribution characteristics of Raman spectral peak intensities. The intensity distributions of peaks at 1516  $cm^{-1}$  and  $1128 \text{ cm}^{-1}$  on the surface of the conch pearl are shown in Figure 3.

The distribution of the pigment peak intensities could reflect the distribution of pigments on the surface of conch pearl. The Raman peak intensity of 1516 cm<sup>-1</sup> is similar to that of 1128 cm<sup>-1</sup>. The distribution rules of the two peaks are the same on the surface of the conch pearl. As the Raman spectrum of the conch pearl shows typical characteristics of polyene pigment, we employed the simple theoretical structures of polyenes containing only C and H and simulated their Raman spectra using DFT calculations. In this study, polyene containing N C=C double bonds is marked as CN polyene, as shown in Figure 4. Our simulation range is from the C4 polyene to C14 polyene. In fact, in the system of conjugated polyene, there are no C=C double bonds and C–C single bonds: there are alternating shorter and longer C–C bonds, all with multiplicities, intermediating between 1 and 2. For example, the polyene containing 11 C=C double bonds should be expressed as 11 shortened C–C bonds with multiplicities > 1.5. However, for the sake of description and comparison with similar published studies, we need to continue to use the terms "C=C double bond" and "C–C single bond" later.



Distribution of 1128 cm<sup>-1</sup> Raman peak intensity

Figure 3. Raman mapping of the conch pearl sample (from blue to red, the Raman intensity is increasing).



Figure 4. Schematic presentation of linear polyene chains with different C=C double bonds.

DFT calculation is a method to simulate molecular properties based on quantum mechanics theory, which can simulate various spectral properties of molecules. The accuracy of DFT theoretical simulation largely depends on the theoretical method used in the calculation (functional and basis set). The applicable theoretical methods may vary for different molecules. So, we selected the theoretical method in DFT calculation by referring to some previous research results on the simulation of Raman spectra of polyene and carotenoids [12,13]. Before calculating the spectral properties of molecules, it is necessary to optimize their structure. We optimized these structures of polyenes (C4 polyene to C14 polyene) and calculated their Raman spectra using functional B3LYP with basis set 6–31G (d). To ensure the accuracy of DFT calculations, we also used the functional B3LYP with a larger basis set 6-311G (d, p) to perform the same calculation. Generally speaking, DFT calculations often overestimate the Raman wavenumber. Thus, we corrected the Raman shifts calculated at B3LYP/6-31G (d) and B3LYP/6-311G (d, p) by 0.9614 and 0.9729, respectively, to obtain high-precision results [18,28]. Through DFT calculations, we obtained the theoretical Raman spectra of polyenes with different chain lengths. We identified the simulated Raman shift of C=C stretching for each polyene. The Raman shift

of C=C stretching is taken as the longitudinal axis and the number of C=C double bonds of polyenes is taken as the transverse axis. Two dot line plots can be drawn in Figure 5; the red dot line plot is the simulation result at B3LYP/6-31G (d) and the blue dot line plot is the simulation result at B3LYP/6-31G (d, p). It can be seen that under the condition of combining the appropriate frequency correction factor, the results obtained under the two calculation levels are very close.



**Figure 5.** Relationship between the number of C=C double bonds and simulated Raman.

Through the experimental Raman spectrum of conch pearl, we discovered that the position of the C=C double bond stretching vibration of the polyene pigment is at  $1516 \text{ cm}^{-1}$ . The polyene pigment, which directly determines the color of conch pearl, may be pink. Therefore, we mark a pink line horizontally at  $1516 \text{ cm}^{-1}$  of the ordinate in Figure 5. The position of the intersection of the pink line and the blue dotted line curve and the red dotted line curve in Figure 5 is very accurate. It is not between the points in the point-line curve, but directly intersects with the points in the point-line curve. The number of C=C double bonds corresponding to the abscissa of the intersection point is 11, which indicates that the pigment structure contained in conch pearl may contain 11 C=C double bonds. Therefore, we preliminarily judge that the pink color may be caused by polyene containing 11 C=C double bonds.

#### 3.3. Pigments in Conch Pearl: Comparative Analysis with Red Coral

Carotenoids are very common in some biominerals similar to conch pearl, such as freshwater pearl, shell, snail shell, red coral, etc. [4–9]. According to the previous studies on red coral [12,13,29], we found that the characteristics in the Raman spectrum of red coral are highly similar to those of conch pearl. At present, there is more convincing research progress in the extraction of pigment, combined with HPLC-MS and Raman spectroscopy [8,12,13,30–32]. Therefore, we could analyze the pigments in conch pearl by comparing them with the red coral. We selected a pink coral sample with similar color to conch pearl and collected its Raman spectrum as shown in Figure 6.



Figure 6. Raman spectra of red coral and conch pearl.

It can be seen from Figure 6 that the features in the Raman spectrum of red coral is highly similar to conch pearl. The inorganic minerals in red coral and conch pearl are mainly calcite and aragonite, respectively. The intensities of the Raman peaks of the two inorganic minerals are different. We mainly focus on the Raman peaks of polyene when discussing the pigment of conch pearl. The Raman peaks of pigment in red coral are mainly located at 1516, 1298, 1181, 1128, and 1017 cm<sup>-1</sup> and the Raman peaks of pigment in conch pearl are mainly located at 1516, 1298, 1204, 1128, and 1017 cm<sup>-1</sup>. Except for the peak at 1181 cm<sup>-1</sup> of red coral and peak at 1204 cm<sup>-1</sup> of conch pearl, the other peaks are completely consistent. According to their Raman spectra, we believe that the pink pigment of conch pearl is very similar to the red pigment of red coral and may even be the same pigment. The slight difference in peaks may be caused by the different environment of pigments in different biominerals. The Raman peaks of pigments in conch pearl and red coral and the assignments of these peaks are shown in Table 1.

**Table 1.** The Raman peaks of pigments in conch pearl and red coral and the assignments of these peaks.

Raman Peaks of Conch Pearl/cm <sup>-1</sup>	Raman Peaks of Red Coral/cm $^{-1}$	Assignments
1516	1516	$v_1$ (C=C stretching)
1298	1298	C–H bending
1204	1181	C–H bending
1128	1128	$v_2$ (C–C stretching)
1017	1017	CH <sub>3</sub> rocking

Many studies have discussed the pigment of red coral, but there are still some disputes at present. Some studies use Raman spectroscopy to study the pigment of red coral, and conjecture the pigment structure of red coral based on the characteristics of Raman spectroscopy [12,13,31,32]. However, Raman spectroscopy is not a method that can directly identify the exact structure of a pigment. Now, the research on the direct experimental evidence of the pigment composition in red coral is to extract the pigment from the red coral and identify the main pigment component (canthaxanthin) in red coral by using HPLC-MS [8]. Canthaxanthin is a common orange–red carotenoid that exists in various organisms, such as mushrooms, fish, algae, crustaceans, etc. [33]. The breakthrough research of the successful extraction and identification of canthaxanthin in red coral has aroused

widespread interest among scholars. However, there is still some controversy surrounding this theory due to the differences between the position of  $v_2$  (C–C single bond stretching vibration) of canthaxanthin and the position of  $v_2$  of red coral [31]. In carotenoids, the peak position of  $v_2$  is not only related to the stretching vibration of the C–C single bond but is also affected by the methyl group in polyene chain of the carotenoid structure. The peak position of  $v_2$  is generally at about 1150 cm<sup>-1</sup> in carotenoid, while in red coral the peak position of  $v_2$  is at 1128 cm<sup>-1</sup>. For red coral, it is also speculated that the color is caused by unmethylated polyene [12,13,31]. Similarly, there is also a slight difference between the  $v_2$ of conch pearl and the  $v_2$  of carotenoid. In the marine environment, demethylation occurs in some organisms [34]. We speculate that there may be demethylated carotenoids, which color the conch pearl. Therefore, we simulated the theoretical Raman spectra of different demethylated canthaxanthin derivatives using DFT calculations and the results are shown in Table 2.

It can be seen from Table 2 that with the continuous reduction in methyl groups in the polyene chain structure of canthaxanthin, the  $v_1$  at 1513 cm<sup>-1</sup> is very stable and remains unchanged and the  $v_2$  will be close to the  $v_2$  at 1128 cm<sup>-1</sup> of the conch pearl. The  $v_2$  at 1132 cm<sup>-1</sup> of 9,9',13,13'-demethyl-canthaxnthin is very close to the  $v_2$  at 1128 cm<sup>-1</sup> of the conch pearl. Based on this, we speculate that the pigments in conch pearl may be carotenoids without methyl in the polyene chain, which are probably the chromogenic substances in conch pearl. We hypothesize that carotenoid pigments in some biominerals (such as red coral and conch pearl) may undergo demethylation reactions during growth in the marine environment.

## 3.4. Color Origin of Conch Pearl

According to the comparative analysis of the experimental Raman spectrum characteristics of conch pearl and the theoretical Raman spectrum characteristics of C11 polyene and derivatives of canthaxanthin (9,9',13,13'-demethyl-canthaxanthin), we believe that the basic structure of the pigment in conch pearl is very likely to be C11 polyene and the specific molecular structure of the pigment is very similar to 9,9',13,13'-demethyl-canthaxanthin. Based on this, we calculated the electronic excitation of canthaxanthin, 9,9',13,13'-demethylcanthaxanthin, and C11 polyene using TDDFT to obtain their theoretical UV-Vis spectra. According to experience, the function of different HF exchanges has a relatively large influence on the calculated results of the theoretical UV-Vis spectrum. So, we calculated the first 10 excited states of the above substances using the functionals of different HF exchange with 6-311G (d, p) group. The results are shown in Table 3.

It can be found from Table 3 that, regardless of the difference between the position of the maximum absorption peak 516 nm in conch pearl's experimental UV-Vis spectrum, the positions of the theoretical maximum absorption peaks calculated under different functional functions of the three substances are located in the visible light region and their positions will blueshift with the increase in HF exchange, and redshift with the decrease in HF exchange. The position of the simulated maximum absorption peak depends on the HF exchange of the functional used. From the calculation results of canthaxanthin and 9,9',13,13'-demethyl-canthaxanthin, no matter which functional is calculated, the wavelength positions of them are almost the same; so, it can be considered that the existence of methyl on the polyene chain of canthaxanthin has little effect on the position of maximum absorption peak wavelength. Although not all of the C=C bonds are located on the polyene chain of canthaxanthin, there are some similarities with C11 polyene on the whole from the perspective of conjugated structure. No matter what functional calculation, it can be found that the maximum absorption peak positions of canthaxanthin and demethyl canthaxanthin derivatives are also close to C11 polyene. For polyene pigments, it is the conjugated chain that produces the color. In addition, from the simulation results, the calculated results under the functional MN15 are closest to the position of the experimental absorption peak in conch pearl.

Name	Molecular Structure	$\nu_1/cm^{-1}$	$\nu_2/cm^{-1}$
Canthaxanthin	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1513	1159
9-demethyl-canthaxnthin	X ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~	1513	1152
13-demethyl-canthaxnthin	X	1513	1145
9,13-demethyl-canthaxnthin	X	1513	1142
9,13'-demethyl-canthaxnthin	X A A A A A A A A A A A A A A A A A A A	1513	1142
9,9'-demethyl-canthaxnthin	X	1512	1146, 1138
13,13'-demethyl-canthaxnthin	X	1513	1139
9,13,9'-demethyl-canthaxnthin	× · · · · · · · · · · · · · · · · · · ·	1513	1141, 1132
9,13,13'-demethyl-canthaxnthin	X	1513	1136
9,9',13,13'-demethyl-canthaxnthin	× · · · · · · · · · · · · · · · · · · ·	1513	1132

Functional	HF Exchange	Canthaxanthin	9,9′,13,13′- Demethyl- Canthaxnthin	Polyene C11
TPSSh	10%	612	613	574
B3LYP	20%	585	586	555
PBE0	25%	565	566	539
MN15	25%	524	524	504
BHandHLYP	50%	496	496	481
M06-2X	54%	496	495	480
CAM-B3LYP	19%-65%	493	491	477
wB97XD	22.2%-100%	482	479	467

**Table 3.** The maximum absorption peak positions (nm) of theoretical UV-Vis spectra of canthaxanthin, 9,9',13,13'-demethyl-canthaxanthin, polyene C10 calculated under different functional conditions.

In order to more clearly discuss the origin of the absorption bands of canthaxanthin, canthaxanthin derivatives, and C11 polyene, we use the wave function analysis program Multiwfn to analyze and obtain the molecular orbital and electron–hole information involved in the electron excitation. According to the results, it could be found that the maximum absorption peaks of them are all dominated by HOMO–LUMO transition.

It can be seen from Figure 7 that the HOMO–LUMO orbitals of these three substances are on the polyene chain and the transition type is  $\pi$ - $\pi$ \* transition. Among them, HOMO–LUMO orbitals of canthaxanthin and 9,9',13,13'-demethyl-canthaxanthin are almost the same, which means that the presence or absence of methyl on the polyene chain has no effect on the HOMO–LUMO orbital shape and the methyl has no effect on the maximum absorption band generated by the electron excitation of the molecule. Electron excitation can be divided into local excitation and charge transfer excitation according to the space of the electron before and after excitation. If the space of the electron changes significantly before and after excitation, it belongs to charge transfer excitation, otherwise it belongs to local excitation. It is discovered that the electron excitation types of these three substances all belong to local excitation.

Electron-hole analysis is a useful method to reveal the nature of electron excitation and the theory can show the unique distribution of holes and electrons [35]. The former describes the space where the excited electrons leave and the latter describes the space where the excited electrons go. The hole and electric distribution are shown in Figure 8. It can be seen that the shapes of the hole isosurface and electron isosurface are the same as that of the HOMO isosurface the LUMO isosurface, respectively, which shows that the HOMO-LUMO transition can well describe the electron transition process. The electrons and holes of these three substances are all distributed on the polyene chain, revealing that these electron excitation processes are located on the conjugated polyene structure and belong to local excitation.

From the UV-Vis spectrum of conch pearl and the electronic excitation calculation of the canthaxanthin, 9,9',13,13'-demethyl-canthaxanthin, and C11 polyene, we believe that the color origin of conch pearl is the HOMO–LUMO transition on the conjugated polyene structure with 11 C=C double bonds. There is no obvious change in the position of electrons before and after excitation and the type of electronic excitation belongs to local excitation.



**Figure 7.** Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) of canthaxanthin, 9,9',13,13'-demethyl-canthaxnthin, and C11 polyene.



C11 polyene

## Hole and electron distribution

**Figure 8.** Hole and electron distribution and charge density difference of canthaxanthin, 9,9',13,13'demethyl-canthaxnthin, and C11 polyene. The blue isosurface represents a hole and the green isosurface represents an electron.

## 4. Conclusions

We analyzed the pigment in pink conch pearl through experimental spectroscopy technology and DFT calculations. The Raman spectrum of conch pearl shows the characteristics of polyene pigments. Furthermore, DFT calculation was carried out to simulate the Raman spectra of polyenes with different chain lengths. It is found that the polyene pigments in pink conch pearl contain 11 shortened C–C bonds with multiplicities > 1.5. It is also observed that the Raman spectra of pink conch pearl and red coral are very similar. By comparing the Raman peak characteristics of the red coral and performing DFT calculations on the possible pigment structures, we believe that the pigments of pink conch pearl are very similar with those of red coral and the color of conch pearl is probably caused by demethylated canthaxanthin. We collected the UV-Vis spectrum of pink conch pearl and calculated the electronic excitation of polyene and demethylated canthaxanthin based on TDDFT. It is discovered that the pink color is caused by the local electronic excitation of the conjugated polyene structure. Our research is meaningful for understanding the pigment structure and color origin of pink conch pearl.

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