Photoluminescence in a glucose-coated sila-fullerane and its nanomedicine applications

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ABSTRACT

In this study, we introduce nano-baits that are formed based on the binding of glucose in a silicon nanoparticle. Sila-dodecahedrane has been selected among of four other famous nanostructures, due to its high stability, biocompatibility and its ability to engineer electronic features. Because of the glucose attached to nano-baits, they are attractive to cancer cells that consume high glucose. In this research, two nano-baits have been modeled with the chemical formulas of Si₂₀Η₁₉C₆Η₁₁Ο₆ and Si₂₀Η₁₉(C₆Η₁₁Ο₆)₇. Their optimal structures are obtained using density functional theory (DFT). For this, we use the B3LYP hybrid functional and 6-31+g(d,p) basis set. Vibration frequency calculations show that the glucose binding of a sila-dodecahedrane has a stable bond. These nano-baits with photoluminescence determine the location of cancer cells. By adjusting the number of glucoses attached to these nano-baits, the energy required for their excitation and light response can be adjusted. These nano-baits are a viable alternative to radioactive materials for locating cancer cells.

Keywords: Sila-dodecahedron, Photoluminescence, Nano-bait, Density functional theory, Cancer cells.

1. Introduction

Although surgery, chemotherapy, and radiotherapy are traditional and commonly used treatments for cancer, new methods such as antibodies, antigens, and photodynamic therapy have been proposed. Understanding the physiological characteristics and physiological roles of human cells will lead to an appropriate approach to solve biological problems. For example, the Photodynamic therapy method uses a photo sensitizer substance. By injection of Photo Sensitizer into the patient, this substance is accumulated in the cancerous tumor. To detect and treat illness, ultraviolet and red-light radiations are used, respectively. It can be said about the mechanism of photo sensitizer delivery to the tumor that they have Low-density lipoprotein (LDL) cholesterol receptors for example neoplastic materials, such as hydrophobic porphyrin. Since cancerous cells are associated with severe cell division, LDLs consume more than normal, so they need a lot of LDL and absorb it, therefore, by covering PS in the porphyrin, the chance of PS reaching the mass increases [1-4].
In this research, we focus on other characteristics of cancer cells. Cancer cells have higher glucose consumption than other cells in the body [5-6]. So this can give us a new idea at least for detecting the location of cancer cells, if we design nanoparticles that glucose molecules connected it, then these nanoparticles act as nano-baits. Now, if these nano-baits are injected into the patient's body, they accumulate in the tumor, and the cancer cells are detected by photoluminescence [7-8].

To identify the appropriate nanoparticles, first we investigate chemically and optically the fullerene, fullerene molecules and silicon analogues. Finally, we identified silicon structures as a good candidate for optical cancer detection, because in addition to its biodegradability and biodegradability [9-10], due to proper derivatization we expect the desired photoluminescence.

2. Computational Method

In this research, we use density functional theory method to investigate the structural features and stability of structures. We obtain the optimal structures and calculate the total energies with DFT. The B3LYP, the hybrid function that also includes the Hartree-Fock (HF) method, describes the interaction between atoms in our calculations, and for describing the orbitals shapes, we used split valence and polarized basis set that assembled in the form 6-31+g(d,p). Finally, our calculations are performed by using of Gaussian software [11-14].

3. Results

We first obtain the electrochemical properties of the structures introduced in the introduction, Buckminster fullerene, smallest fullerene, dodecahedrane, and sila-dodecahedrane. The schematic of these structures is shown in figure 1.

![Candidate structures to design nano-baits.](image)
For this, we obtain HOMO and LUMO energy levels with DFT calculations. Now, using the following equations, we can obtain electronic properties, such as HOMO-LUMO gap, chemical potential, chemical hardness, and the estimate of electron affinity [15-17]:

\[
E_{\text{Gap}} = E_{\text{LUMO}} - E_{\text{HOMO}}.
\]

\[
\mu = \frac{(E_{\text{HOMO}} + E_{\text{LUMO}})}{2}.
\]

\[
\eta = \frac{(E_{\text{HOMO}} - E_{\text{LUMO}})}{2}.
\]

\[
EA = -E_{\text{LUMO}}.
\]

The new index, electrophilicity, can be obtained using chemical potential and chemical hardness through equation 5. With regard to this index, the difference between the two structures can be seen better [18].

\[
\omega = \frac{\mu^2}{2\eta}.
\]

For the studied structures, we calculate the above electronic properties. The values are given in Table 1.

| Structures | HOMO | LUMO | \(E_{\text{Gap}}\) | \(\mu\) | \(\eta\) | \(EA\) | \(\omega\) |
|-----------|------|------|-----------------|------|------|------|------|
| C\(_{60}\) | -6.40 | -3.68 | 2.72 | -5.04 | 1.36 | 3.68 | 9.32 |
| C\(_{20}\) | -5.51 | -3.61 | 1.89 | -4.56 | 0.95 | 3.61 | 10.97 |
| C\(_{20}\)H\(_{20}\) | -7.24 | -0.19 | 7.04 | -3.71 | 3.52 | 0.19 | 1.96 |
| Si\(_{20}\)H\(_{20}\) | -6.83 | -2.36 | 4.48 | -4.60 | 2.24 | 2.36 | 4.72 |

Our first choice, to design a nano-bait was using C\(_{60}\), the fullerene molecule. Because a lot of research has suggested the fullerene molecule for tumor targeting, and the treatment of cancer [19-26]. However, the reported toxicity to fullerenes prevents work on this molecule, and this causes us to remove this molecule from our choices [27-29]. Its low chemical hardness and high electron affinity, confirms the toxicity of fullerene.

To increase the chemical hardness, we can consider the quantum confinement effect (QCE). As the size of the nanoparticles decreases, the energy gap increases due to the QCE, with the help of interpretation of the particle in the box [30-32]. For this reason, instead of C\(_{60}\) fullerene, we use the smallest fullerene, C\(_{20}\). But the smallest fullerene, the C\(_{20}\), has not stable structure [33-34]. Our results, such as low chemical hardness and high electrophilicity, confirm this. But with the saturation of its structure, everything changes.

When the C\(_{20}\) structure is saturated with hydrogen, the Dodecahedrane, with the chemical formula C\(_{20}\)H\(_{20}\), is formed. In 1982, Leo Paquette et al. succeeded in synthesizing this symmetric
molecule [35]. Dodecahedrane has the highest chemical hardness and the lowest electron affinity and electrophilicity, among the studied structures, according to our results given in Table 1. Since the selective structure is ultimately located in the biological environment, we are interested in examining the silicon analog of dodecahedrane as well as it is known as biocompatibility and biodegradability. We obtain interesting features for the sila-dodecahedrane. Sila-dodecahedrane has a stable structure so that even its chemical hardness is higher than C_{60} fullerene, but despite having a structure saturated with hydrogen, it also has high electron affinity and electrophilicity. It should be noted that in 2015, Wagner et al. synthesized silicon dodecahedrane as a sila-fullerane with an endohedral chloridelon [36]. Dodecahedrane and its silicon analogue are two candidate structures of the four introduced structures. But to determine which carbon or silicon structures can provide the desired optoelectronic properties, we dop their surfaces with functional groups containing oxygen. Since we want to attach the glucose molecule to the nanoparticle, we must choose a functional group that can be compared to glucose. To do this, we have chosen the hydroxel functional group, which in addition to its binding site is similar to the glucose molecule, also has a smaller number of atoms, which reduces the computational cost in DFT.

Now, we can calculate the optical absorption gap for pure and functionalized structures by subtracting the total energy of the optimized-ground state from the total energy of the excited state at the same geometry as the ground state, as shown in figure 2.

![Figure 2. The absorption and emission gaps of the system. Above schematic shows the cause of the absorption and emission gap differences in the nanoparticles.](image)

Because the number of electrons of the X_{20}Y_{20} is even, its spin state will be singlet, in the ground state. The lower-energy triplet excited-state is optically inactive, according to the ΔS=0 selection rule. Therefore, the lowest-energy allowed optical transition excites the system into the singlet excited state [37-39].

The energy of the singlet excited state is higher than the triplet state, due to larger repulsive coulomb interactions between antiparallel spins. Therefore, the excited system may relax from
the singlet state into the triplet one. Therefore, we calculate the emission bandgap from the relaxed exited triplet state to the ground state at the same energy, as shown in figure 2. Using equations 6 and 7, the absorption and emission gap can be obtained:

\[ Gap_{\text{Absorption}} = E_{\text{Triplet Excited}} - E_{\text{Singlet Ground}}. \] (6)

\[ Gap_{\text{Emission}} = E_{\text{Triplet Ground}} - E_{\text{Singlet Excited}}. \] (7)

Finally, the difference between the absorption and emission gaps shows the stoke shift:

\[ \Delta E_{\text{Stoke Shift}} = Gap_{\text{Absorption}} - Gap_{\text{Emission}} \] (8)

We present the calculated absorption and emission gaps of the desired structure in Table 2.

Table 2. A list of the electronic and optoelectronic gaps of the studied structures (in unit eV).

| Structures | HOMO  | LUMO  | H-L Gap | Absorption Gap | Emission Gap | Stoke Shift |
|------------|-------|-------|---------|----------------|--------------|-------------|
| C_{20}H_{20} | -7.24 | -0.19 | 7.04    | 6.34           | 5.83         | 0.51        |
| C_{20}(OH)_{20} | -7.41 | -2.14 | 5.27    | 4.48           | 3.99         | 0.49        |
| Si_{20}H_{20} | -6.83 | -2.36 | 4.48    | 3.71           | 3.32         | 0.39        |
| Si_{20}(OH)_{20} | -5.90 | -3.82 | 2.08    | 1.37           | 0.63         | 0.74        |

The data given in Table 2 clearly presents the two results. First, Optical gaps are smaller than HOMO-LUMO gaps, and second, silicon structures are more engineered electrical and electro-optical than carbon structures. These results are consistent with our previous researches [40-41]. More important than the above results, it is the emission gap of sila-dodecahedrane by suitable functionalized can be to reach the visible or even infrared range. While the dodecahedrane gives an ultraviolet response due to ultraviolet stimulating. Since silicon nanoparticles are known for their biocompatibility, their infrared response due to their ultraviolet stimulating can be used in thermotherapy [42]. The visible response can also be used to detect cancer cells, but to do, these particles must be attractive to cancer cells. Now we have to make sila-dodecahedrane functionalized in such a way that in addition to visible response to ultraviolet stimulating, it must also be an attractive bait for cancer cells. To do this, as mentioned earlier, we use the trick of attaching a glucose molecule to Sila-dodecahedrane. Since cancer cells consume a lot of glucose, our nanoparticles will act as nano-bait for them. In Figure 3, you can see a model of the desired nano-bait.
Figure 3. A labeled sila-dodecahedrane with glucose acts as a nano-bait.

It should be noted that the frequency calculations of introduced nano-bait do not have a negative frequency, i.e. the structure do not contain imaginary vibrations, so this structure is at the minimum level in the energy diagram and is stable [43]. Figure 4. Shows the infrared spectrum diagram for the introduced nano-bait.

Figure 4. The infrared spectrum of a labeled sila-dodecahedrane with glucose, that acts as a nano-bait.

Table 3. Contains the energies of the structure of pure and glucose-labeled sila-dodecahedrane in the ground and excited states. By calculating the energy required to transfer the structure from the ground state to the excited state, adiabatically, we obtain the absorption gap. Besides, calculating the difference of the excited structure energy in optimal geometry with the energy of
singlet state in the same geometry, we get the emission gap. Based on the data given in Table 3, we can conclude that our nano-bait is excited by UV-A rays and gives a visible response with indigo blue light.

Table 3. The absorption and emission gaps for the Si$_{20}$H$_{20}$ and its glucose-labeled structure (in unit eV).

| Nanoparticle & nano-bait | Singlet (Ground) | Triplet (Adiabatic) | Absorption gap | Singlet (Adiabatic) | Triplet (Ground) | Emission Gap | Stokes shift |
|--------------------------|------------------|---------------------|----------------|---------------------|------------------|--------------|--------------|
| Si$_{20}$H$_{20}$        | -157889.48       | -157885.77          | 3.71           | -157889.26          | -157885.94       | 3.32         | 0.39         |
| Si$_{20}$H$_{13}$C$_6$H$_{11}$O$_6$ | -176552.05       | -176548.81          | 3.24           | -176549.06          | -176551.74       | 2.68         | 0.56         |

The data in Table 2 show that we can conclude that by adding the number of glucoses attached to the sila-dodecahedrane, it is possible to excite the nano-bait even with less energetic light. Of course, with the same argument, we can conclude that it will respond with light with longer wavelengths too. In the following, another nano-bait with more glucose is introduced, you can see its model in Figure 5.

Figure 5. Dodecahedrane based silicon nano-bait surrounded by seven glucose molecules attached to it.

Figure 5. shows Si$_{20}$H$_{13}$(C$_6$H$_{11}$O$_6$)$_7$, a nano-bait formed by the binding of seven glucose molecules to a sila-dodecahedrane. Our calculations show that the absorption gap of this nano-bait is about
2.57 eV, and its emission gap is about 2.06 eV. As we expected, according to the procedure in Table 3, as the number of glucoses attached to the nanoparticles increases, the energy required for excitation also decreases, and the optical response shifts to longer wavelengths. Therefore, with proper functionalized, even the response of these nanoparticles reaches the infrared range, in which case, these nanoparticles can also be used for thermotherapy. The size of the nanoparticles shown in figure 5 are about 2 nanometers. Note that, it is not necessary for nano-baits to be sila-dodecahedrane based, because silicon nanoparticles with sizes of 1 to 2 nm, have similar chemical properties. This also reduces the production costs of these nanoparticles [44-45].

4. Conclusion

In this research, we introduced nano-baits that are formed based on the binding of glucose in sila-dodecahedrane. These nanoparticles, because of the glucose attached to them, are attractive to cancer cells that consume high glucose, and they can be used as bait. By adjusting the number of glucoses attached to these nanoparticles, the energy required for their excitation and light response can be adjusted. These nano-baitez can be a good alternative to methods of detecting cancer cell or even treating that have high costs and side risks.

DATA AVAILABILITY

All data generated for this study are included in the article.

AUTHOR CONTRIBUTIONS

M. Qasemnazhand carried out the simulations, analyzed the data and prepared the manuscript. F.K. supervised the project and revised the final manuscript. F. marsusi supported DFT calculations. All authors read and approved the final manuscript.

Competing interests: The authors declare no competing interests.

Acknowledgments
The authors gratefully acknowledge Ali Ghaemi, a hard-working physician, for his guidance on the idea of the work.
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