

Computational Design of a Lantern Organic Framework

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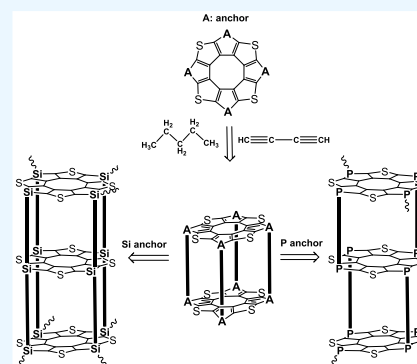
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ABSTRACT: This study employed a computational quantum chemistry approach to design lantern organic framework (LOF) materials. Using the density functional theory method with the B3LYP-D3/6-31+G(d) level theory, novel lantern molecules ranging from two to eight bridges made of sp^3 and sp carbon atoms to connect circulene bases that have phosphorous or silicon as anchor atoms were made. It was found that five- sp^3 -carbon and four- sp -carbon bridges are optimal candidates for constructing the lantern framework in the vertical direction. Although circulenes can be stacked vertically, their resulting HOMO–LUMO gaps remain relatively unchanged, indicating their potential applications as porous materials and for host–guest chemistry. The electrostatic potential surface maps reveal that LOF materials are relatively electrostatically neutral overall.



1. INTRODUCTION

One of the earliest structures having a “lantern-like” structure is paracyclophane, which was developed by Cram et al.¹ in the early 1950s. Building on this work, Boekelheide and Hop et al.^{2,3} successfully synthesized a new class of compounds called superphane, which has a cyclophane structure. The superphane structures have been extensively studied for decades and have been found to be well-suited for a number of areas of applications such as semiconductor materials, host–guest chemistry, drug delivery, ion extraction, biomolecular recognition, and cluster stabilization.^{4–10} Moreover, the term “lantern-like” structure or “lantern cage”^{5,11–14} has become increasingly common in the study of organic frameworks, which are often developed from materials such as metal–organic frameworks,^{15,16} covalent organic frameworks,^{17,18} and hydrogen-bonded organic frameworks.^{19–21}

Superphane-based structures are typically single molecules, which can pose challenges for adjusting pore size or connecting the lantern-like molecules together. Maintaining the desired lantern shape of a single molecule can also be difficult. To address the problem of connecting lantern structures, metal ions have been used, but the coordination bonding is known to be weak. Therefore, finding a solution to this issue is crucial for developing functionalized materials with stable, interconnected lantern structures. This study presents a computational design of a new class of paracyclophane that promises to offer more opportunities for applications. To achieve this, the benzene rings in paracyclophane are replaced by circulenes structures based on the sulflower molecule (octathia[8]circulene, $C_{16}S_8$), as shown in Figure 1. Such a molecule was already successfully synthesized by Nenajdenko et al.²² This larger size of the circulene ring compared to the benzene ring allows for better control of its cage size control and enables the exploration of electronic properties

unique to the π -conjugated system of circulene.²³ For example, Pittelkow et al.²⁴ have successfully created a [9]circulene structure, demonstrating that the core with eight rings can be expanded to a structure with 20 rings.²⁵ Moreover, in our recent study, we have shown the successful creation of larger fused ring structures, such as a [10]circulene, called oxisulflower.²⁶ Moreover, the sulflower circulene has exhibited good electron-donor properties and important thermal dynamics properties in thin film fabrication. The circulene structure can also be designed by inserting other heteroatoms, such as boron, nitrogen, silicon, selenium, and tellurium, in the position of sulfur atoms, as long as planarity is maintained, which is advantageous for organic synthesis.^{14,22,27–29}

In this study, we explore the use of phosphole and silole rings in the heterocirculene to form a circulene-based superphane. The advantage of the use of Si and P elements is the ability to construct a 3D structure via a vertical direction, whereas the borole and pyrrole rings are favored for 2D structure building. Thus, not only a single lantern-like molecule but also an organic framework, known as the lantern organic framework (LOF), is built. The development of a LOF material into a conjugated polymer structure also opens up new possibilities for its use. For porous applications, the use of circulene molecule can increase the gas affinity of the LOF structure, based on a computational study done by Pati et al.,³⁰ who demonstrated that the sulflower

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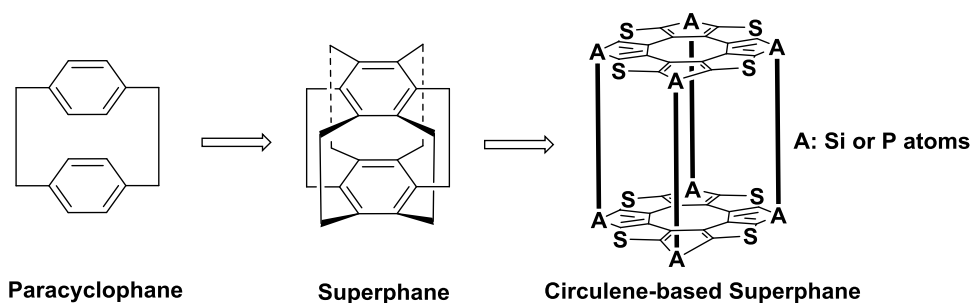


Figure 1. From paracyclophane to circulene-based superphane (lantern organic molecule).

molecule in the stacked aggregate can adsorb 10 H₂ molecules, or the LOF can have a potential structure as a COF structure demonstrated by Banerjee et al.³¹ in a study for the treatment of wastewater contaminated with toxic dyes and oil. Moreover, LOF can now be used to enhance the performance of photocatalytic hydrogen evolution and to make electrodes for lithium-ion batteries, among other electronic properties.^{32–35} With these improved properties and versatility, the LOF is expected to be a promising material as an organic framework structure for a wide range of applications in various industries, such as gas storage, catalysis, water treatment, and drug delivery.

2. COMPUTATIONAL DETAILS

2.1. Computational Methods. All 3D structures in this study are fully optimized at the level of theory B3LYP-D3/6-

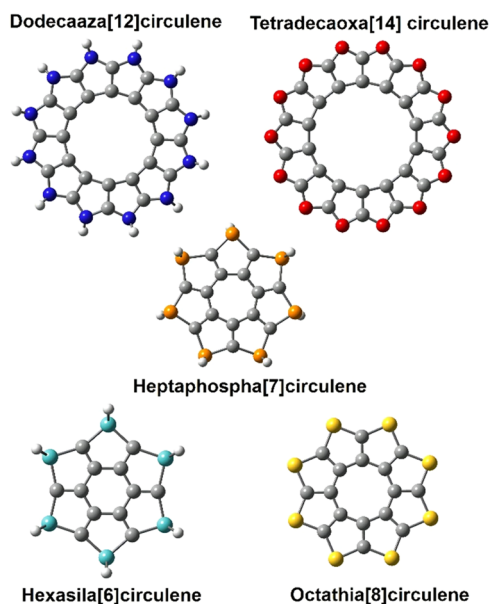


Figure 2. Template structures for building bases, where white represents hydrogen atoms, gray represents carbon atoms, blue represents nitrogen atoms, orange represents phosphorus atoms, red represents oxygen atoms, aqua-green represents the silicon atoms, and yellow represents sulfur atoms.

31+G(d) DFT by using the GAUSSIAN16 program.³⁶ The B3LYP method^{37,38} was chosen as it is known to provide accurate predictions of the HOMO–LUMO gap of heterocycles.^{39,40} Normally, the basis set 6-31G(d)^{27,41–45} is used for optimizing the circulene class and similar organic compounds. The addition of diffusion function in combination with Grimme's dispersion⁴⁶ has been recommended for more

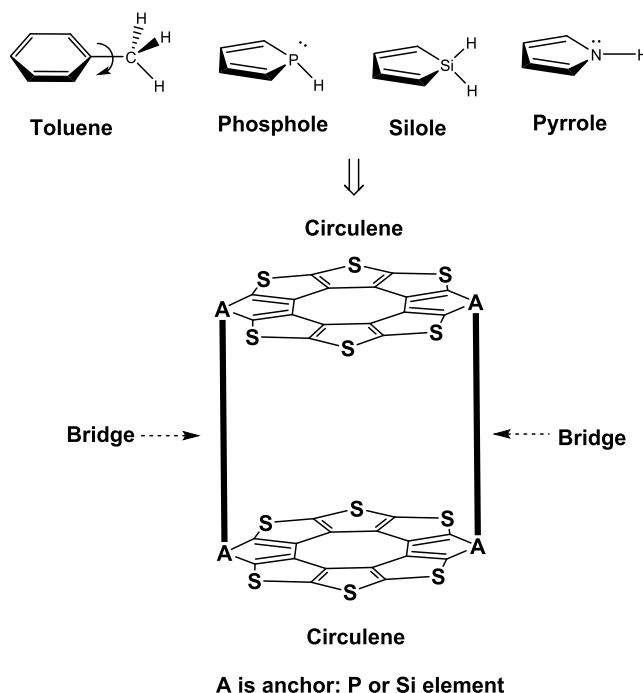


Figure 3. Dehydrogenation of phosphole and silole rings would form lantern molecules.

accurate accounting for the π – π stacking interaction between circulenes in the lantern structures.⁴⁷ Figure 2 shows five circulene molecules that were used as templates for building bases for lantern molecules in this study.

2.2. Structures of Lantern Organic Molecules. In Figure 3, we find that the phosphorous and silicon atoms within the circulene are stiffer compared to the benzylic carbon found in paracyclophane. Also, the hydrogen atoms on both P and Si atoms bend outside of the circulene basal plane, differing from a typical pyrrole ring. Thus, P and Si atoms can be used as anchor atoms for linking circulenes together in stacking arrangement using linear chains such as linear hydrocarbons. Furthermore, the phosphorous–carbon bond is reliably stable in cyclic structures.⁴⁸

A circulene-based superphane consists of two main parts: the base and the bridge. The base part consists of two circulene molecules, each containing at least two anchor atoms (phosphorous or silicon), while the bridge part contains at least two hydrocarbon chains connecting the anchor atom of one circulene to another. These bridged structures resemble a lantern commonly seen in Eastern Asian cultures and will be referred to as such in this study.

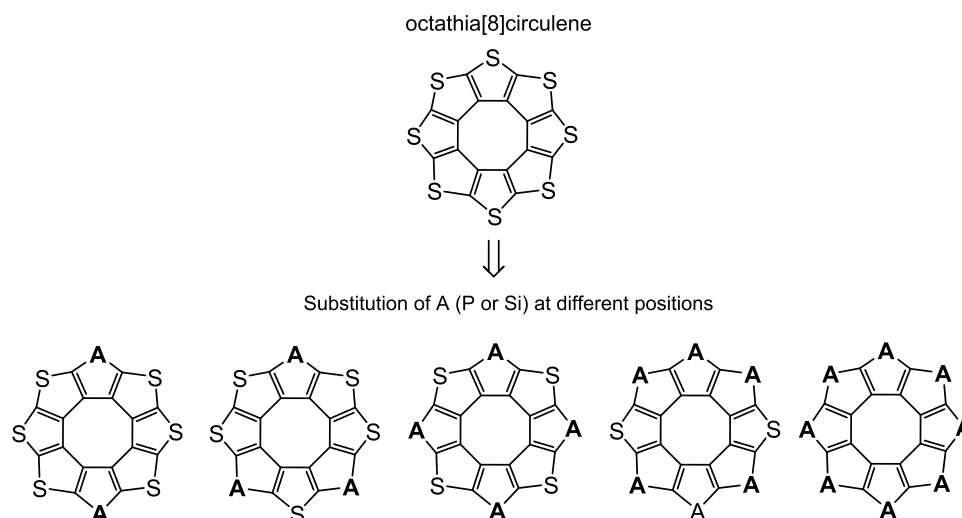


Figure 4. Possible circulenes based on sulflower (octathia[8]circulene). “A” can be either P or Si element.

3. RESULTS AND DISCUSSION

3.1. Lantern Organic Molecule Building. Figure 4 shows a number of possible bases for lantern molecules from two to

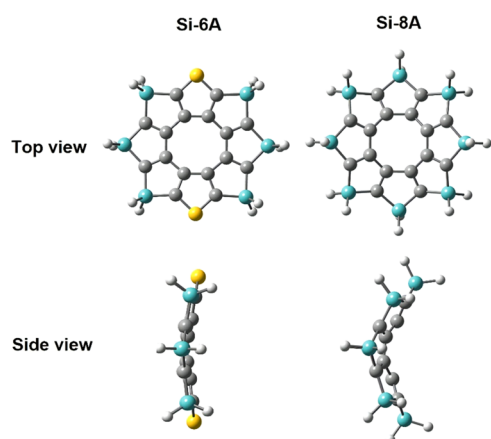


Figure 5. Nonplanar silicon-substituted circulenes.

eight P or Si substitutions on the sulflower (octathia[8]circulene molecule). The insertion of a Si atom(s) in the sulflower circulene results in three planar molecules: Si-2A, Si-3A, and Si-4A, whereas the Si-6A and Si-8A are nonplanar in Figure 5. In particular, Si-4A is also known as the tetrasilatetrathia[8]circulene, which was successfully synthesized by Miyake et al.²⁷ Interestingly, all phosphorous-substituted circulenes here have planar structures. All of their 3D structures are shown in Figure 6. It is worth noting that these circulenes are based on an experimentally available sulflower compound and thus possibly can be synthesized without much difficulty. Six additional highly symmetrical circulenes with 6–10 fused rings are shown in Figure S1.

To find optimal bridges for constructing lantern-shaped molecules, three types of carbon chains were explored: sp^3 (alkyl) chains, sp^2 (alkenyl) chains, and sp (alkynyl) chains with lengths from one to nine carbon atoms. Interestingly, the choice of a chain type with a two-anchor circulene results in many forms of the lantern molecule: parallel configurations (on-top, twisted, and slipped) and a nonparallel configuration (tilted) (Figure 7).

For all cases, we found that only the sp -bridge with one to four triple bonds and the sp^3 -bridge with an odd number of carbon atoms (ranging from one to nine) form different parallel

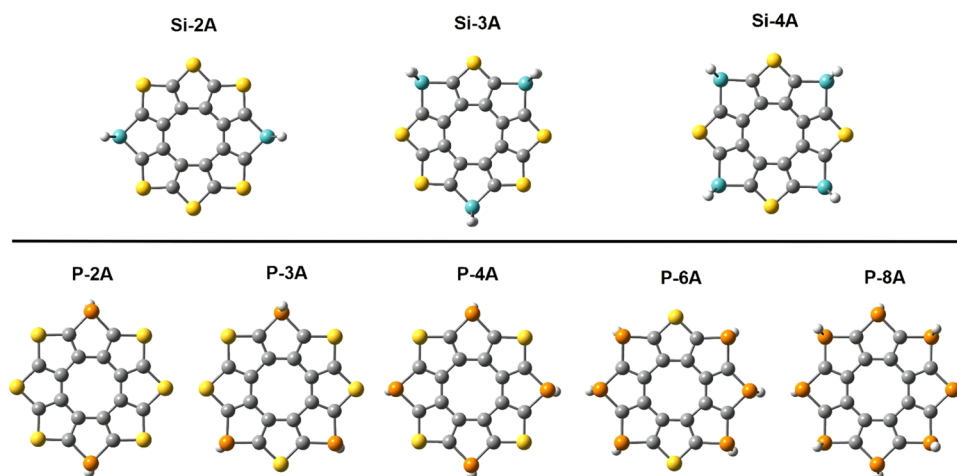


Figure 6. Planar circulenes used to build lantern structures, particularly Si-2A to Si-4A and P-2A to P-8A.

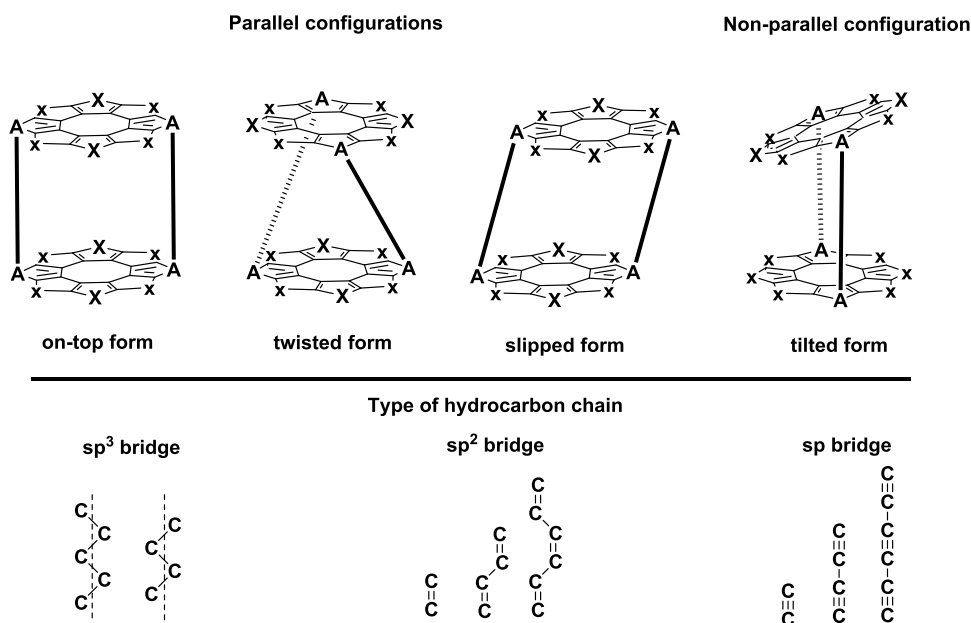


Figure 7. Three different types of hydrocarbon chains for finding optimal bridges for lantern-shaped molecules.

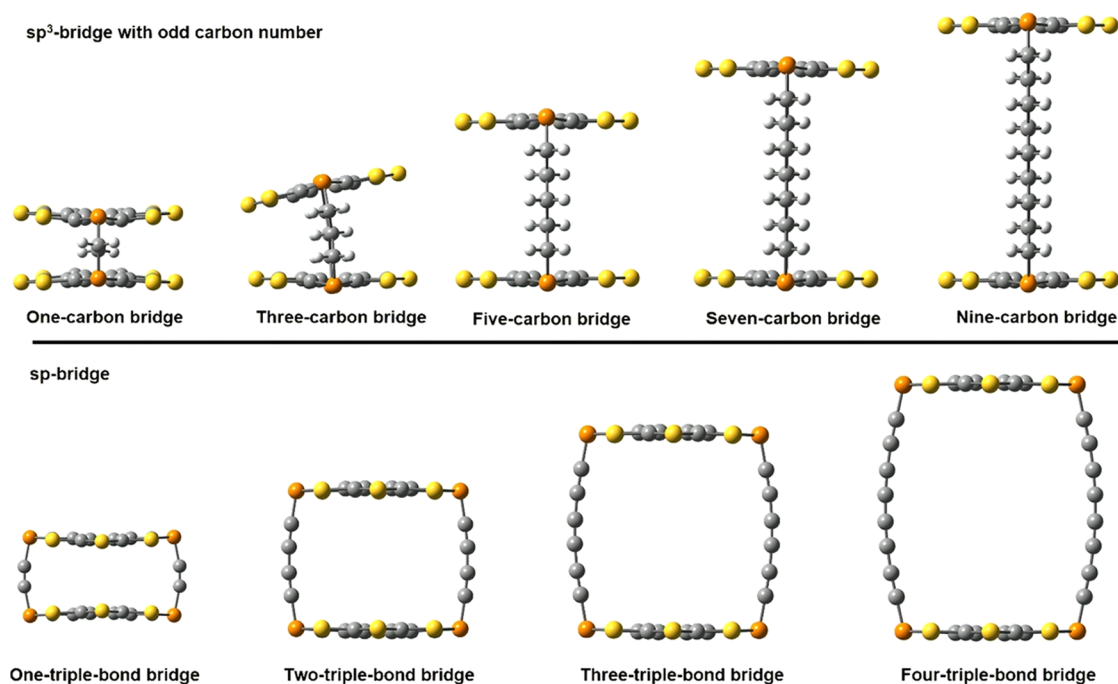


Figure 8. Structures of lantern molecules formed by sp^3 (alkyl) bridges with odd carbon numbers and sp (alkynyl) bridges.

configurations in general, as depicted in Figure 8. Moreover, in an experimental study conducted by Hegmann and Tykwinski et al.,⁴⁹ it was demonstrated that the sp -bridge chain can form up to 10 triple bonds in a series of triisopropylsilyl (TIPS) end-capped polyynes. On the other hand, the sp^2 -bridge with one or two double bonds retains two parallel lanterns in the slipped form, but two circulenes are not parallel when the bridge contains three double bonds, as shown in Figure 9. Also, the sp^3 -bridge with even carbon numbers results in twisted and nonparallel lanterns. With the goal of forming lantern-shaped molecules, we choose sp^3 - and sp -bridges that can form parallel bases, particularly the on-top configuration for further investigation. Specifically, the sp^3 -bridge with five carbon atoms and the sp -

bridge with four carbons (two triple bonds) are selected as representatives of these classes.

To name these lantern molecules, we propose a general notation: $(pX-Y-qZ)_n$. In particular, p is the number of anchor atoms, X is the anchor element, Y is the base class, q is the number of bridges, Z is bridge type, and n is the number of stacked bases starting from number 3. In this study, the anchor element can be P or Si, the base is the circulene class, and Z is the name of the bridge hydrocarbon.

For instance, the sp^3 -bridge with saturated carbons is named “pentane” for five sp^3 -carbon atoms; similarly, the sp -bridge with triple bonds is named “butadiyne” for four sp -carbon atoms. For example, $4P-[8]circulene-4-pentane$ denotes a lantern molecule

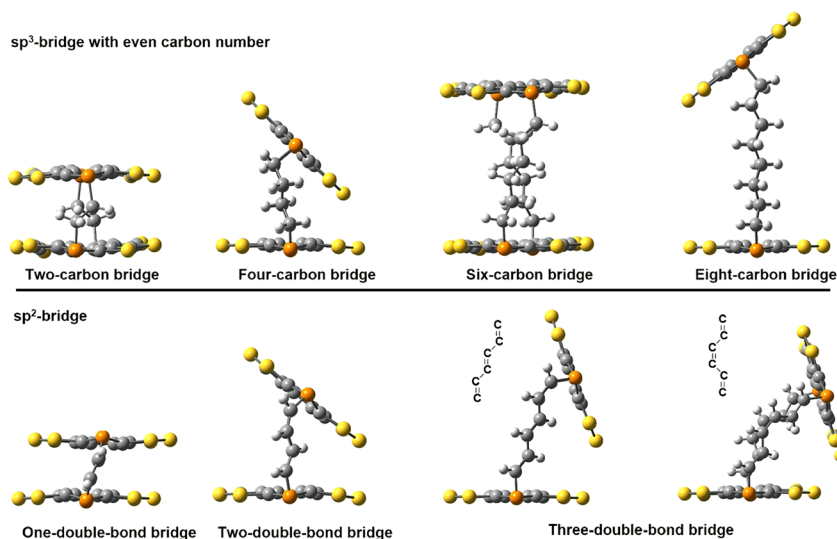


Figure 9. Structures of lantern molecules formed by sp^3 with even carbon numbers and sp^2 (alkenyl) bridges.

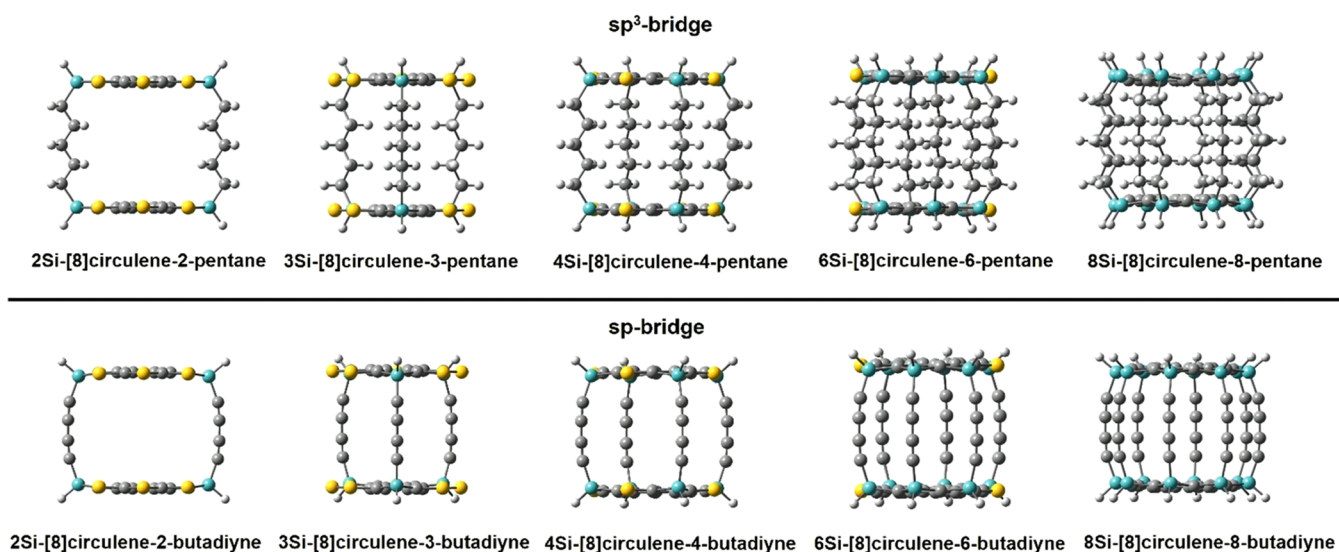


Figure 10. Lantern molecules composed of silicon anchors.

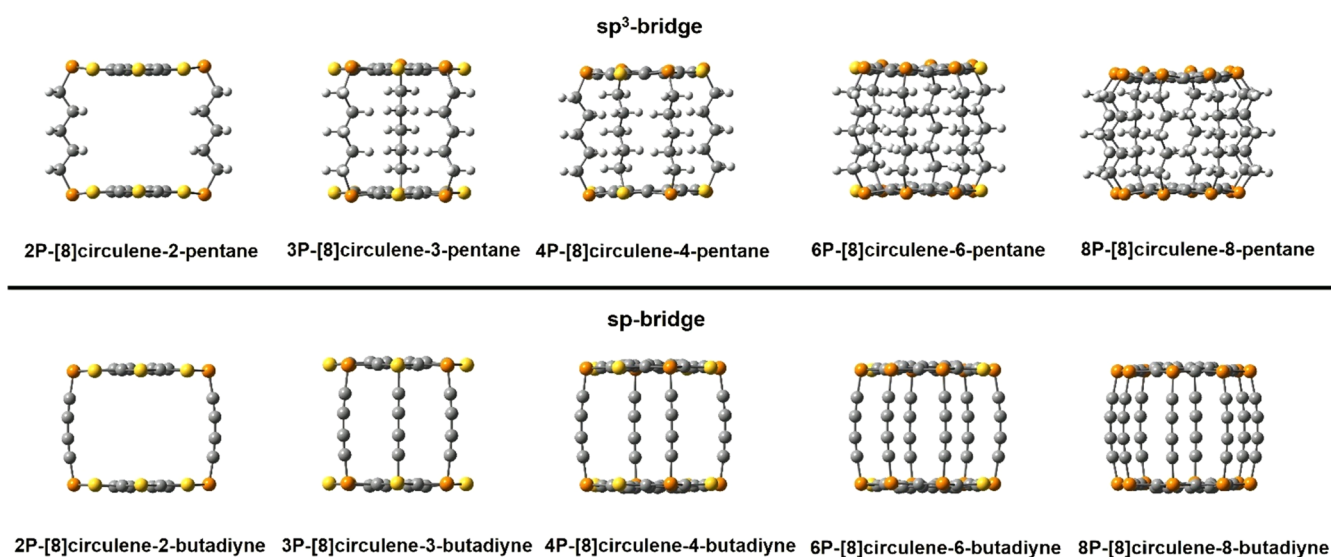


Figure 11. Lantern molecules composed of phosphorous anchors.

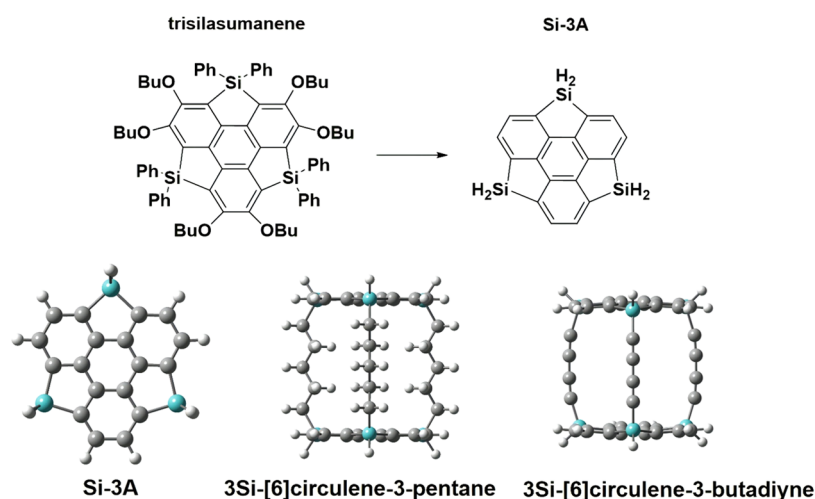


Figure 12. Potential Si-3A base was derived from a trisilasumanene: 3Si-[6]circulene-3-pentane and 3Si-[6]circulene-3-butadiyne.

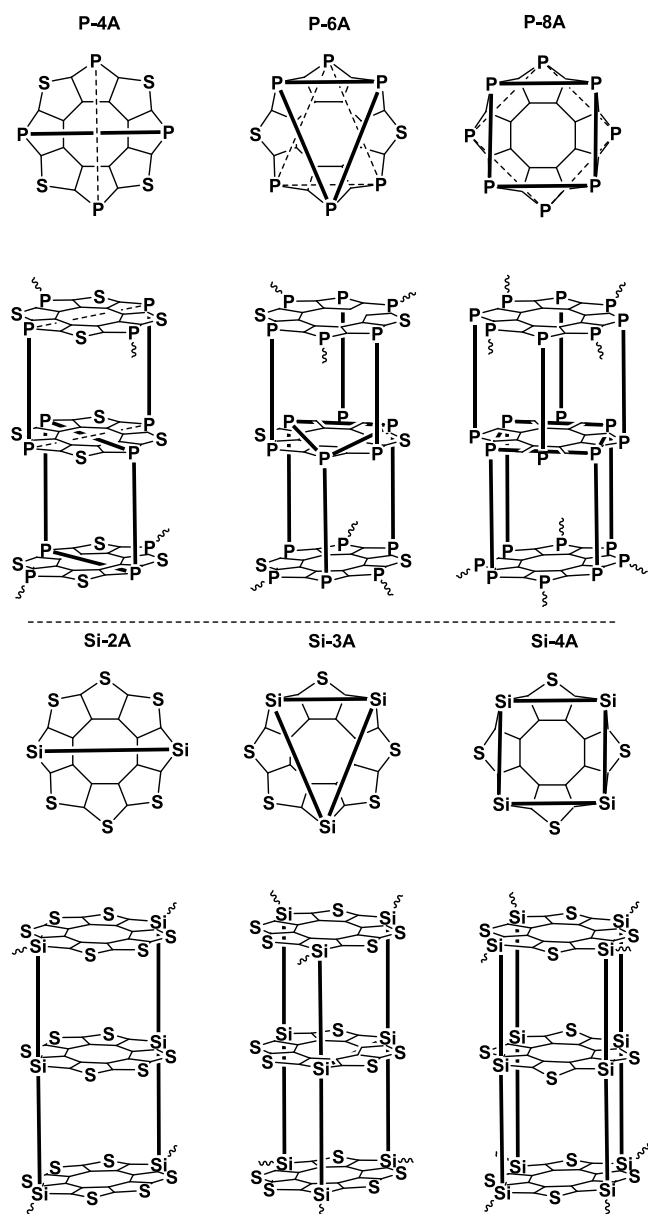


Figure 13. Forming LOF nanotubes by stacking LOF molecules.

Table 1. HOMO–LUMO Gap of Stacked Lantern Molecules (eV)^a

	P-4A (3.94)		Si-2A (3.68)	
circulene				
bridge type	sp ³	sp	sp ³	sp
single lantern	3.79	3.77	3.68	3.27
stack of three circulenes	3.79	3.72	3.60	3.09
stack of four circulenes	3.75	3.69	3.59	3.03

^aValues in parentheses are HOMO–LUMO gaps of the circulene bases. Note that the single-lantern-from P-4A has two bridges in order to be the same as its corresponding framework.

composed of two bases bound by four pentane bridges, and each base consists of a [8]circulene with four P anchor atoms. All lantern molecules in this study are shown in Figures 10 and 11. Interestingly, even though Si-6A and Si-8A (shown in Figure 5) are nonplanar, the bridges help to planarize these bases when forming the lantern molecule, as shown in Figure 10.

Next to the trisilapentathia[8]circulene (Si-3A in Figure 6) based on the suflower molecule, there is another potential Si-3A molecule that is derived from a trisilasumanene⁵⁰ (a [6]-circulene compound), as shown Figure 12. Also, Ge and Sn anchor elements can be inserted at the position of silicon in the sumanene molecules, as shown in a study by Bouit et al.⁵¹

3.2. Lantern Organic Framework Nanotube. Circulenes have the potential to not only form single-molecule lanterns but also create polymer-like nanotubes. By connecting the four, six, and eight phosphorus anchor bases, several lantern organic framework structures can be stacked vertically to create a tube. For example, to form the (4P-[8]circulene-2-pentane)₃ molecule in Figure 13, the central circulene uses two P atoms on the bolded line to bond with the paralleled phosphorous atoms of the below circulene. Similarly, connect the phosphorous atoms on the dashed line to its paralleled phosphorous atoms of the above circulene. This results in a structure where each of the two bases is bound by two bridges. The P-6A and P-8A bases can similarly be used to form the three-bridge-stacked structure and four-bridge-stacked structure, respectively, shown in Figure S2.

The use of silicon as an anchor also has the advantage of its four-valent property with a neutral charge, which allows one silicon atom to directly bind two bridges as shown in Figure 13. This enables the formation of multistacked structures with two bridges starting from Si-2A bases instead of P-4A bases. The 3D

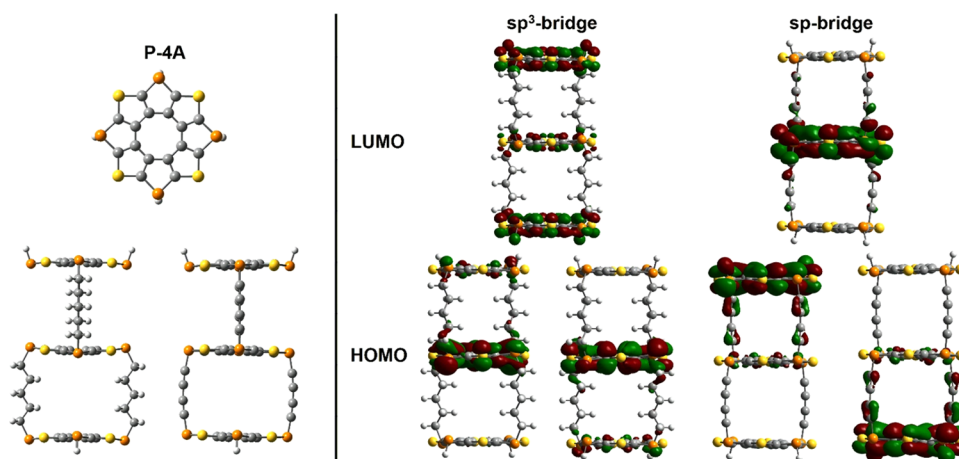


Figure 14. Plots of HOMO and LUMO orbitals of lantern organic framework nanotubes: $(4P\text{-}[8]\text{circulene-2-pentane})_3$, $(4P\text{-}[8]\text{circulene-2-butadiyne})_3$, and their frontier orbital plots (isovalue = 0.02).

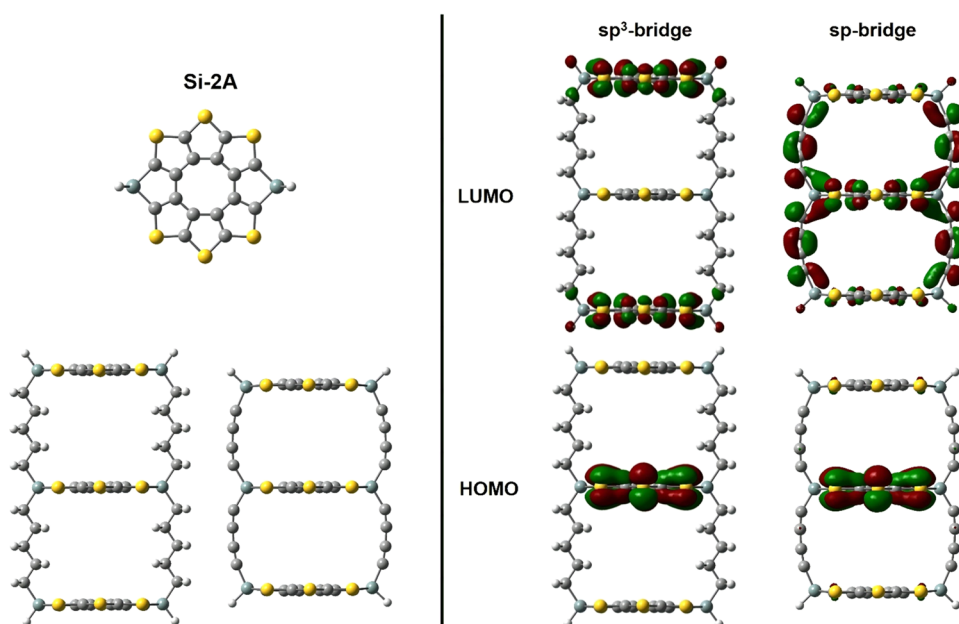


Figure 15. Plots of HOMO and LUMO orbitals of lantern organic framework nanotubes: $(2Si\text{-}[8]\text{circulene-2-pentane})_3$, $(2P\text{-}[8]\text{circulene-2-butadiyne})_3$, and their frontier orbital plots (isovalue = 0.02).

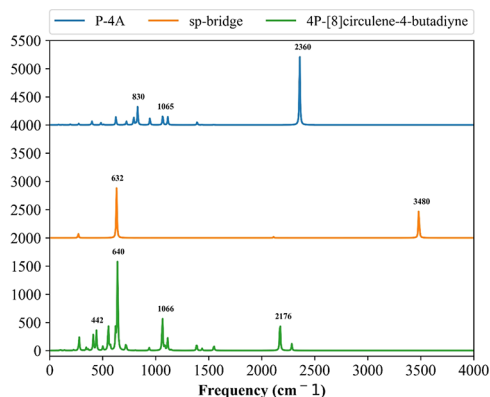


Figure 16. Predicted IR spectrum of $4P\text{-}[8]\text{circulene-4-butadiyne}$ and those of base and bridge components.

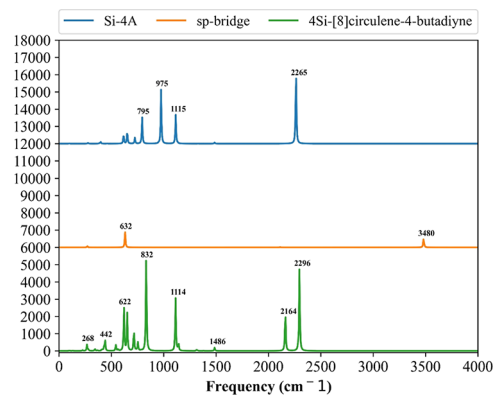


Figure 17. Predicted IR spectrum of $4Si\text{-}[8]\text{circulene-4-butadiyne}$ and those of base and bridge components.

structures of three- and four-stacked structures of Si circulenes are shown in Figure S3. Although theoretically, the phosphorous

element can form one additional bond to create a similar structure to silicon, the resulting P atom would be positively

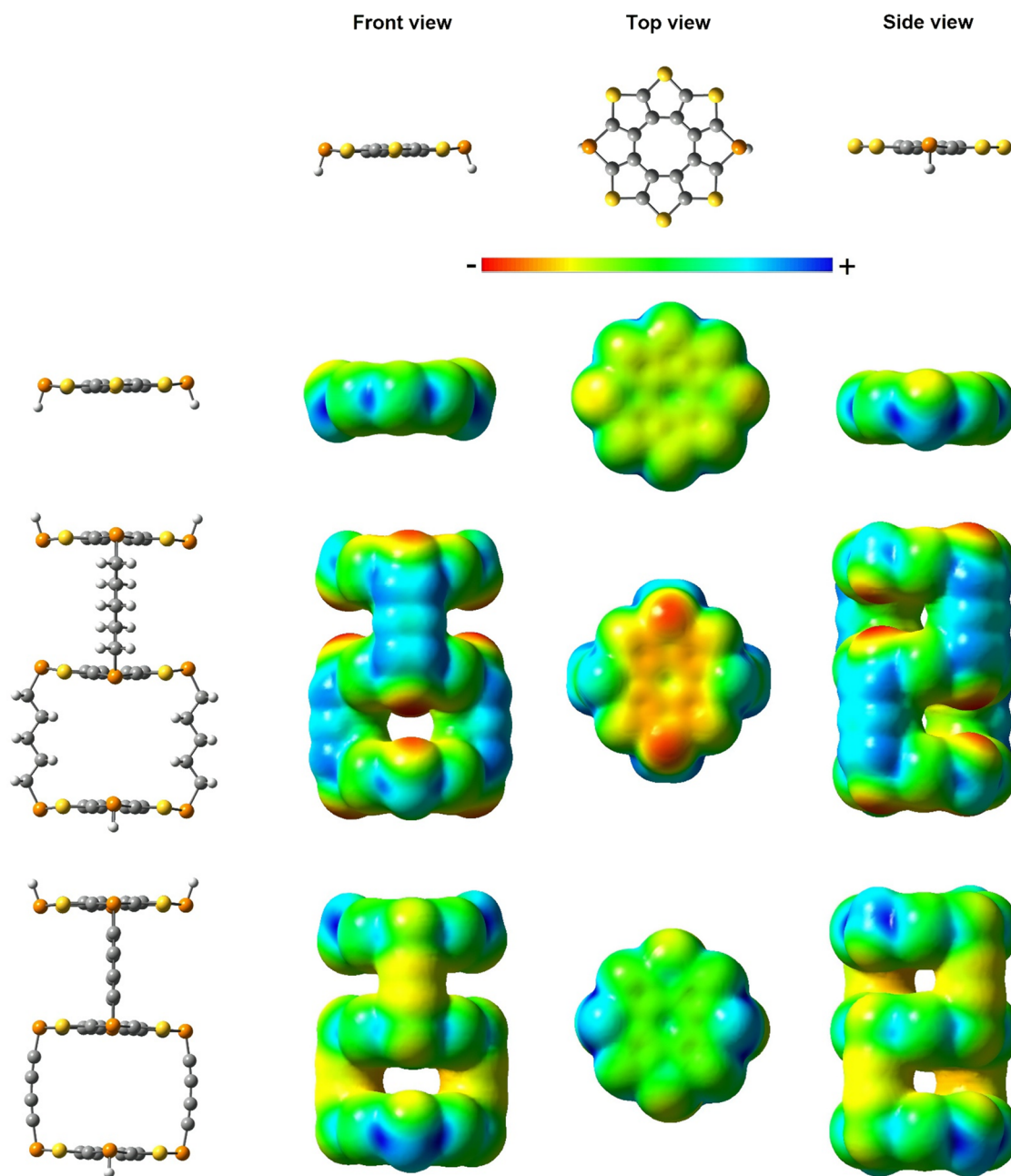


Figure 18. Visualization of the electrostatic potential surface of $(4P\text{-}[8]\text{circulene-2-pentane})_3$ and $(4P\text{-}[8]\text{circulene-2-butadiyne})_3$ (isovalue = 0.0001, ± 0.02 a.u.).

charged, which is beyond the scope of this study focused only on neutral structures.

In Table 1, the HOMO–LUMO gap of a single LOF molecule is relatively unchanged compared to its circulene base, except for a drop of about 0.40 eV in the case of the sp^3 -bridge of the Si-2A base. However, in the higher stacking numbers, the HOMO–LUMO gaps converge.

In Figure 14, we found that the three-stacked structure with an sp^3 -bridge of the P anchor circulene has the HOMO mainly located on the central circulene, while in the case of an sp -bridge, the HOMOs are shared by the two edge bases. On the other hand, in a three-stacked structure from the Si-2A base, the HOMO plot is still located on the central base in both sp^3 - and sp -bridges, but the LUMO is spread out from the central base to two sp -bridges (Figure 15). This is proposed to result in a

significant drop in single-lantern molecules when compared to the HOMO–LUMO gap of the Si-2A circulene base. The HOMOs and LUMOs plots of four-stack structures are given in Figures S4 and S5, respectively.

While vertical stacking of LOF units leads to the high symmetry and order of 3D materials, we found that horizontal stacking does not yield any ordered materials and thus we do not present any results here.

3.3. Infrared Spectra of Lantern Organic Structures. To assist with identifying and confirming the formation of such lantern structures, we provide additional IR analyses of the sample structures. In particular, $4P\text{-}[8]\text{circulene-4-butadiyne}$ and $4Si\text{-}[8]\text{circulene-4-butadiyne}$ were used.

In Figure 16, the P-4A circulene base has a bending (rocking) vibration of the P–H bond at $\nu = 830\text{ cm}^{-1}$ and a stretching

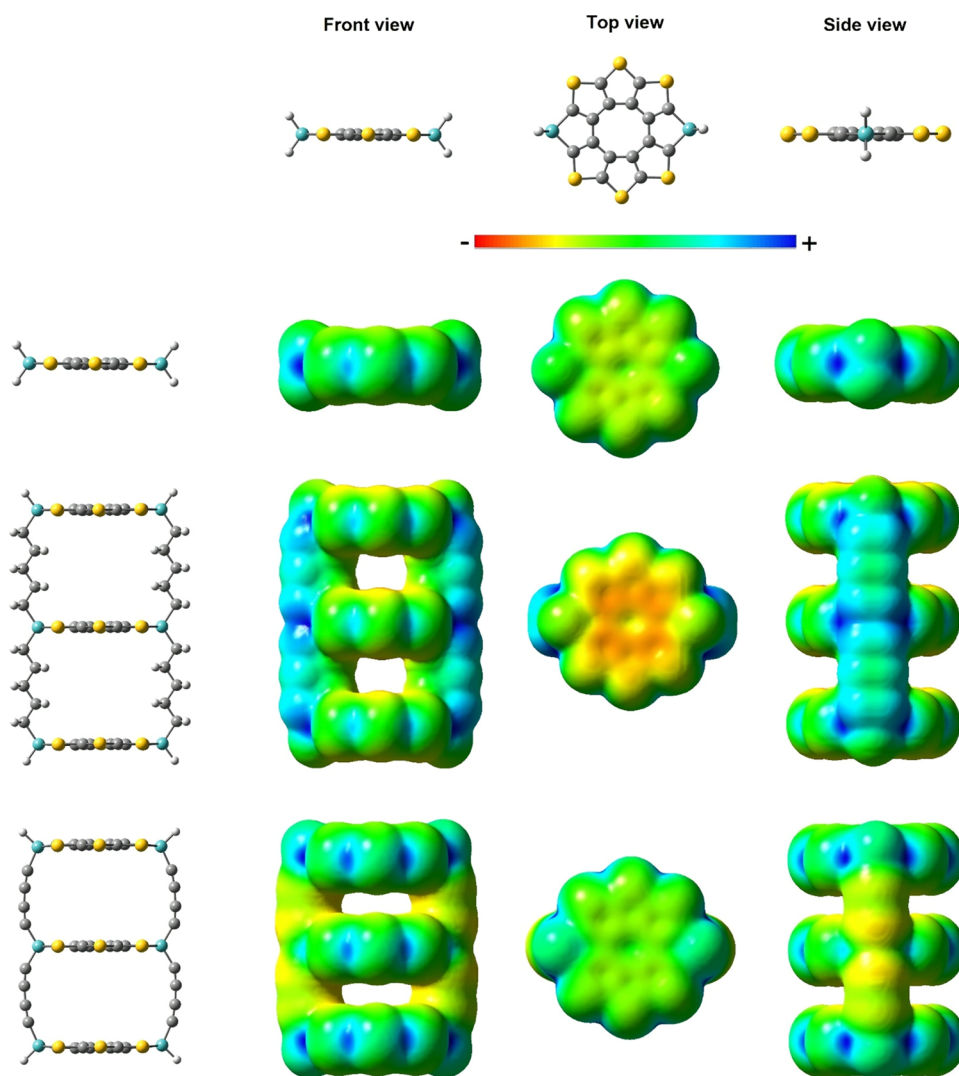


Figure 19. Visualization of the electrostatic potential surface of $(2\text{Si-[8]circulene-2-pentane})_3$ and $(2\text{Si-[8]circulene-2-butadiyne})_3$ (isovalue = 0.0001, ± 0.02 a.u.).

vibration of P–H at $\nu = 2360\text{ cm}^{-1}$, compared to the corresponding experimental signals: 991 and 2327–2421 cm^{-1} .⁵² However, the most potent signal that helps recognize the formation of the 4P-[8]circulene-4-butadiyne molecule is a strong band of the asymmetrical stretching vibration of the carbon–carbon triple bond in the lantern molecule, occurring at $\nu = 2176\text{ cm}^{-1}$. This value is approximately 35 times higher than the relative intensity of the stretching vibration in butadiyne. On the other hand, confirming the formation of the lantern molecule is challenging for experimentalists due to certain factors. The disappearance of the stretching vibration of the C–H bond in butadiyne at $\nu = 3480\text{ cm}^{-1}$ or the appearance of the strong P–C_{bridge} stretching signal at $\nu = 640\text{ cm}^{-1}$ can be difficult to discern. This difficulty arises because the C–H stretching vibration does not completely vanish, and its strong bending vibration ($\nu = 632\text{ cm}^{-1}$) can overlap with the signal of the P–C stretching signal in a mixture that contains an undesired product. In such cases, the bridge can only be bound with the base by one end. Similarly, in Figure 17, for the case for recognizing the formation of 4Si-[8]circulene-4-butadiyne molecule. There is also an increase in the relative intensity of the carbon–carbon triple bond stretching vibration at $\nu = 2164\text{ cm}^{-1}$. On one hand, the strong signal of the stretching vibration of the Si–H bond

from the base (at $\nu = 2265\text{ cm}^{-1}$, in the range of the experimental signal 2080–2280 cm^{-1})⁵³ still remains in the lantern with a higher frequency at $\nu = 2296\text{ cm}^{-1}$, since there is one hydrogen atom on each Si atom in the lantern. On the other hand, the strong scissoring vibration of two Si–H bonds at $\nu = 975\text{ cm}^{-1}$ in the Si-4A base is replaced by a rocking vibration of the Si–H bonds in the lantern at $\nu = 832\text{ cm}^{-1}$.

3.4. Electrostatic Potential Surface Map Analysis of Lantern Organic Structure. Figures 18 and 19 show electrostatic potential surface (EPS) maps of the entire lantern structures that are neutral (green), indicating that these molecules are not polar. Consequently, these molecules would not be expected to have noticeable solvent effects. In general, the charge distribution on bases bound by sp^3 -bridges is more electrostatic potential slightly negative than those of sp -bridges and the unbridged circulenes. Especially, there is a high electron density on phosphorous in the sp^3 -case, so the sp^3 -bridge class with a phosphorous anchor is promisingly applied not only for gas storage purposes but also in catalysis, since the lone pair of the phosphorous atoms can become active sites shown in the red zone for a variety of transition-metal coordinations.⁵⁴

While two pores from the phosphorous anchor are orthogonal, the pores from the silicon anchor are isometric.

The orthogonal-pore material such as zeolite material⁵⁵ generally has high thermal stability and enhances the surface area of porous material.⁵⁶ However, the LOF material can form more than two bridges, leading to the formation of many types of pores, and their undiscovered physical properties are suggested to be studied in the future.

4. CONCLUSIONS

This study proposes a fundamental theory-based computational approach for constructing the lantern organic framework (LOF) nanomaterial. A LOF single molecule consists of two circulenes stacked on top of each other and connected by at least two hydrocarbon bridges. By the B3LYP-D3/6-31+G(d) level theory, we propose that the optimal synthesis of the LOF material involves a vertical direction using five-sp³-carbon and four-sp-carbon bridges and Si/P anchor bases derived from the sulflower circulene molecule. Despite having stacked multilayers and being covalently connected with different types of bridges, the resulting LOF materials have relatively unchanged HOMO–LUMO gaps, exhibit small differences in their HOMO and LUMO characteristics, and have relatively neutral electrostatic potential surfaces. These LOF structures are designed with high surface area, tunable pore size, and stability, making them ideal for gas storage, catalysis, and drug delivery. This study suggests that developing LOF materials and their derivatives may lead to significant material advancements.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c03036>.

Includes Figures S1–S5 (PDF)

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Author Contributions

All calculations are conducted and written in this manuscript. Both authors read and approved the final manuscript.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

LOF, lantern organic framework; HOMO, highest occupied molecular orbital; LUMO, lowest occupied molecular orbital; EPS, electrostatic potential surface

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