

Origins of dihydrogen binding to metal-inserted porphyrins: Electric polarization and Kubas interaction

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Using density functional theory calculations, we have investigated the interactions between hydrogen molecules and metalloporphyrins. A metal atom, such as Ca or Ti, is introduced for incorporation in the central N_4 cavity. Within local density approximation (generalized gradient approximation), we find that the average binding energy of H_2 to the Ca atom is about 0.25 (0.1) eV/ H_2 up to four H_2 molecules, whereas that to the Ti atom is about 0.6 (0.3) eV per H_2 up to two H_2 molecules. Our analysis of orbital hybridization between the inserted metal atom and molecular hydrogen shows that H_2 binds weakly to Ca-porphyrin through a weak electric polarization in dihydrogen, but is strongly hybridized with Ti-porphyrin through the Kubas interaction. The presence of d orbitals in Ti may explain the difference in the interaction types. © 2011 American Institute of Physics. [doi:10.1063/1.3583813]

I. INTRODUCTION

Since hydrogen is a clean and recyclable energy carrier producing no pollution, there has been a great deal of effort to find good hydrogen storage materials. So far, much attention has been paid to low-dimensional nanostructures, since compact and light-element storage materials are required for mobile applications. In particular, carbon-based nanostructures such as carbon nanotubes, fullerenes, and polymers were expected to be good candidates for hydrogen storage because of their large surface areas to adsorb hydrogen.^{1–8} However, pure carbon-based structures have a drawback of insufficient binding energy^{6,8} near room temperature: their binding energies are lower than that for good hydrogen storage which should be 0.2–0.3 eV to operate at ambient conditions.^{9–11} On the other hand, carbon-based nanostructures have been studied as promising catalysts for hydrogen release.^{12–14} Berseth *et al.*¹² showed that carbon nanostructures may be used as catalysts for hydrogenation/dehydrogenation of sodium aluminum hydride (sodium alanate; $NaAlH_2$).

As candidates having aforementioned optimal binding energies among nanostructures, metal-decorated materials such as metal-carbon based materials,^{8,15–22} metal-organic frameworks,^{23–27} and metal-decorated polymers^{9,28,29} were suggested to increase the potential for hydrogen storage. For *cis*- and *trans*-polyacetylene decorated with Ti atoms,²⁸ up to five and four hydrogen molecules bind to a Ti atom, respectively, and the optimal binding energy of H_2 molecules is around 0.2–0.3 eV. Because of their high cohesive energy (>4 eV), however, transition metals (TMs) such as Ti and V have a strong tendency of clustering. Besides, they can act as catalysts to destroy the carbon-based frameworks or to dissociate H_2 . Consequently, the hydrogen storage capability is significantly reduced. To prevent clustering of

metal atoms, researchers have considered alkali-earth metals (AEMs) with lower cohesive energy (1–2 eV). Recently, Yoon *et al.*²⁰ showed that a coating of C_{60} fullerenes with Ca could be a non-dissociative hydrogen storage material, using *ab initio* calculations within generalized gradient approximation (GGA). On the other hand, it is known that alkali metal (AM) elements have relatively low cohesive energies (<1.7 eV), which can also avoid clustering effectively.²⁵ Li-covered graphene were investigated to show that each adsorbed Li on graphene adsorbs up to four H_2 molecules amounting to 12.8 wt%.²² For alkali-metal-decorated organic molecules, Huang *et al.* found that Li-doped cases exhibit a higher storage capacity (>10 wt%) than Na- and K-doped cases with the adsorption energy of ~0.1–0.3 eV/ H_2 .²⁵ Here, it is noted that AM elements are more reactive than AEM elements in ambient conditions.

As a famous group in organic chemistry, porphyrin consists of four pyrrole-like subunits joined together by four methine (=CH–) groups. Four nitrogen atoms in a porphyrin molecule can be saturated by a single metal ion instead of two H atoms. In nature, a heme contains a porphyrin coordinated to Fe, and a chlorophyll contains a porphyrin coordinated to Mg. Porphyrins are easy to synthesize and become important molecular building blocks that can be used to make several structures in materials chemistry.^{30–32} Recently, many studies focus on the application of various properties of porphyrin.^{33,34} Previously, we also studied energetics of Ca-porphyrin where Ca is incorporated into the central N_4 cavity of porphyrin.³⁵

In this paper, we present the different origins of dihydrogen binding to AEM- and TM-inserted porphyrin molecules on the basis of first-principles electronic structure calculations. Ca and Ti were chosen as metal atoms inserted in the central N_4 cavity of porphyrin ($C_{20}H_{12}N_4$). First, we compared energetics of both Ca- and Ti-porphyrins. Then we investigated interaction between dihydrogen and an AEM (Ca) or a TM (Ti) atom incorporated to porphyrin. As a result, we

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TABLE I. The binding energies (eV per H₂ molecule) of $n\text{H}_2$ on metalloporphyrin.

$n\text{H}_2/\text{M-porphyrin}$	Ca-porphyrin						Ti-porphyrin	
	1H ₂	2H ₂	3H ₂	4H ₂	5H ₂	6H ₂	1H ₂	2H ₂
LDA (eV/H ₂)	0.26	0.26	0.26	0.25	0.21	0.19	0.76	0.63
GGA (eV/H ₂)	0.13	0.12	0.10	0.09	0.07	0.07	0.43	0.32

found that dihydrogen binds weakly to the Ca atom through a weak polarization of dihydrogen, but interacts strongly with the Ti atom with the so-called Kubas interaction. Finally, we discussed a possibility of porphyrin-based superstructures as hydrogen storage materials.

II. CALCULATION METHODS

We carried out first-principles calculations within local density approximation (LDA) and generalized gradient approximation (GGA), using ultrasoft pseudopotentials implemented in the Vienna *ab initio* simulation package (VASP).^{36,37} The cutoff energies for a plane wave basis set were 400 eV (Ca-porphyrin) and 275 eV (Ti-porphyrin), and the atomic positions were relaxed with residual forces smaller than 0.01 eV/Å. The vacuum region was about 10 Å between porphyrin molecules, which was enough to avoid the image-image interaction. First, we optimized the structure of metalloporphyrin such as Ca- and Ti-porphyrin molecules. The inserted metal (Ca or Ti) atom is located at the center of the cavity surrounded by four N atoms. The Ca atom is placed above the porphyrin plane while the Ti atom is located at the same plane to the z -axis in the metalloporphyrin. For the Löwdin charge analyses and the wave function plots, we employed the Quantum Espresso package.³⁸

III. RESULTS AND DISCUSSION

In a previous paper,³⁵ we briefly studied H₂ adsorption on Ca-porphyrin to find that binding energy of H₂ is about 0.25 eV per H₂, using LDA up to four adsorbed hydrogen molecules. Here, we present the detailed results of binding energies and configurations for $n\text{H}_2$ ($n = 1, 2, \dots, 6$) on Ca-porphyrin along with the case of Ti-porphyrin. The binding

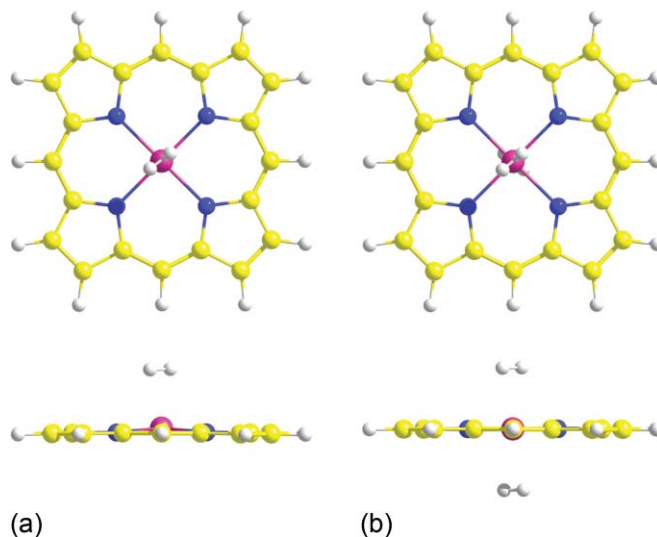


FIG. 2. Optimized configurations of H₂ molecules adsorbed on Ti-porphyrin. The upper and lower panels show top and side views of optimized structures, respectively. Yellow, blue, red-violet, and white balls represent carbon, nitrogen, titanium, and hydrogen atoms, respectively.

energy E_b per H₂ for n hydrogen molecules adsorbed on metalloporphyrin (M-porphyrin) is defined by

$$E_b = (1/n)[E(\text{M-porphyrin}) + nE(\text{H}_2) - E(n\text{H}_2/\text{M-porphyrin})],$$

where $E(\text{M-porphyrin})$, $E(\text{H}_2)$, and $E(n\text{H}_2/\text{M-porphyrin})$ are the total energies of M-porphyrin, H₂, and $n\text{H}_2/\text{M-porphyrin}$, respectively. The binding energies for Ca-porphyrin as well as Ti-porphyrin using both LDA and GGA are listed in Table I, while the respective optimized geometries are shown in Figs. 1 and 2.

For Ca-porphyrin, tilted configurations of H₂ molecules are the most stable up to four adsorbed hydrogen molecules. The GGA binding energies are quite small (about 0.1 eV/H₂) compared to the LDA values (about 0.25 eV/H₂ up to four H₂ molecules). Note that CaC₆₀ attracts up to 5H₂ molecules with a uniform binding energy of ~ 0.2 eV/H₂ for GGA and ~ 0.4 eV/H₂ for LDA.²⁰ Since the binding energies for the fifth and sixth molecules are relatively small, the H₂ molecules are considered to be physisorbed on porphyrin.

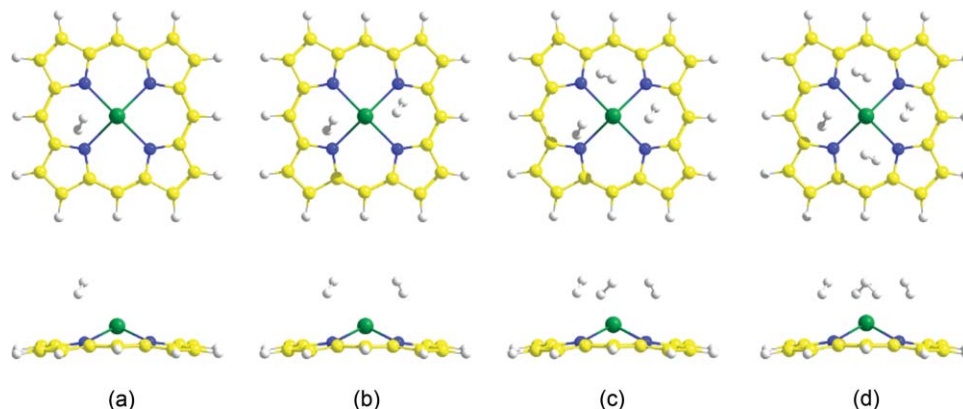


FIG. 1. Optimized configurations of H₂ molecules adsorbed on Ca-porphyrin. The upper and lower panels show top and side views of optimized structures, respectively. Yellow, blue, green, and white balls represent carbon, nitrogen, calcium, and hydrogen atoms, respectively.

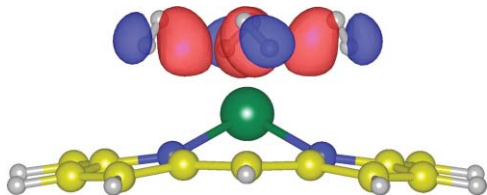


FIG. 3. Isosurface plot of charge difference between the total electron density of 4H₂/Ca-porphyrin and the sum of those of isolated 4H₂ and Ca-porphyrin. Charge accumulation and depletion are represented by red and blue, respectively. The isosurface levels are ± 0.0025 electrons/bohr³. A slight electric displacement of hydrogen molecules is shown.

For our LDA results of Ca-porphyrin, the bond lengths of H₂ molecules were slightly elongated to ~ 0.78 Å from 0.765 Å (by $\sim 2\%$), and the distances between H and Ca atoms were 2.35–2.52 Å, which are very similar to the sum of atomic radii of H (0.53 Å) and Ca (1.94 Å). It means that there is no practical covalent bonding between H and Ca.

Compared with results of Ca-porphyrin, the energetics of H₂ adsorption on Ti-porphyrin was also studied. The LDA and GGA results for the H₂ binding energy on Ti-porphyrin are summarized in Table I. Although the number of H₂ adsorbed on porphyrin are only two, the binding energy is even larger than that for Ca-porphyrin. The LDA (GGA) binding energies per H₂ are 0.63 eV (0.32 eV) up to two H₂ molecules.

Next, we considered a binding mechanism between adsorbed H₂ molecules and the Ca atom. Though there are several energy levels aligned at the same positions in the projected density of states (PDOS) of H₂/Ca-porphyrin (Fig. 3 in Ref. 35) as well as 4H₂/Ca-porphyrin, no significant overlap (i.e., orbital hybridization) was found between *d* orbitals of Ca and σ orbitals of H₂ in the wave functions. We calculated the charge difference, $\Delta\rho$, between the configurations before and after adsorption of a hydrogen molecule

$$\Delta\rho = \rho_{n\text{H}_2/\text{M-porphyrin}} - \rho_{n\text{H}_2} - \rho_{\text{M-porphyrin}}$$

From the Löwdin charge difference between total charge density of 4H₂/Ca-porphyrin and the sum of those of Ca-porphyrin and 4H₂, as shown in Fig. 3, we found that there is small electric polarization in each hydrogen molecule, which is associated with a weak interaction between H₂ molecules and the Ca ion. According to our charge analysis, Ca donates about 0.8–1.0 e to porphyrin, and becomes a positive ion (Ca⁺). Consequently, the tilting shape gives rise to the weak electric polarization in a H₂ molecule under the influence of electric field by the Ca ion. The average difference in the charge in the two H atoms of H₂ is 0.015 e . It is hard to assign the number of electrons clearly to a specific atom using the Löwdin charge analysis as well as other charge analysis methods. Thus, we have to accept the value of charge with caution. This phenomenon was also reported in H₂ binding to a Ca-hydroxyl group complex.³⁹

Then, we examined interaction between H₂ and Ti-porphyrin. Similar to Ca-porphyrin, we considered a charge difference between the total electron density of 2H₂/Ti-porphyrin and the sum of those of two isolated H₂ and Ti-porphyrin. As shown in the charge difference plot in Fig. 4, an electric displacement around both Ti and two H₂ occurs along the vertical line to the porphyrin. Such relatively large and

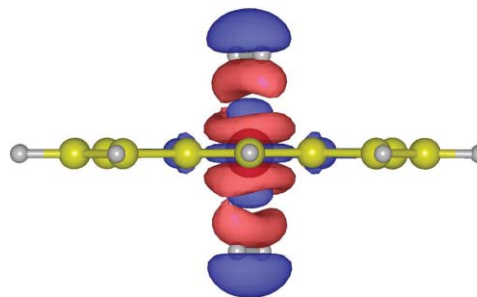


FIG. 4. Isosurface plot of charge difference between the total electron density of 2H₂/Ti-porphyrin and the sum of those of isolated 2H₂ and Ti-porphyrin. Charge accumulation and depletion are represented by red and blue, respectively. The isosurface levels are ± 0.0025 electrons/bohr³. Complicated and relatively large electric polarization is shown around Ti and H₂ molecules.

complicated electric displacement is related to the Kubas interaction, which is roughly defined by a sort of interaction between *d* orbitals of metal atom and σ (or σ^*) orbitals of H₂.⁴⁰ In addition, it shows that charge redistribution takes place in the Ti orbitals (especially for *d*_{z²) because of adsorption of H₂. For the case of Ti-porphyrin using LDA, the bond lengths of H₂ were considerably elongated to 0.796–0.810 Å from 0.765 Å (by $\sim 4\%$ – 6%), and the distances between H and Ti atoms were 1.9–2.0 Å, which are shorter than the sum of atomic radii of H (0.53 Å) and Ti (1.76 Å). It implies that H₂–Ti binding is stronger than H₂–Ca binding.}

To understand interaction between H₂ and Ti atom in more detail, we considered the electronic properties of the 2H₂/Ti-porphyrin system such as the PDOS and wave function characters. The PDOS of Ti, adsorbed H₂ molecules, and surrounding N atoms is shown in Fig. 5(a), where some (apparent) hybridization are seen between *d* orbitals of Ti and *s* orbital of H (or N). After detailed investigations of wave function characters for the coincident energy levels, following a previous study,⁴¹ we obtained a hybridization diagram in Fig. 5(b), where we found the bonding and anti-bonding states between Ti 3*d* orbitals and σ (or σ^*) orbitals of H₂. Each wave function character labeled “*a*”–“*d*” corresponds to each denoted electronic states having the same label in Fig. 5(a).⁴²

Three hybridizations labeled “*a*”–“*c*” are clearly noticeable. The first one denoted by “*a*” is a hybridized bonding state of the empty *d*_{z²} orbital of Ti with filled σ orbitals of H₂, where the filled σ orbital donates electrons to empty *d*_{z²} orbital. The second one denoted by “*b*” just below the Fermi energy is another hybridized bonding state of the filled *d* orbitals (*d*_{zx}, *d*_{zy}) of Ti with empty σ^* orbitals of H₂, where the filled *d* orbitals (*d*_{zx}, *d*_{zy}) back-donate electrons to empty σ^* orbitals. This bonding state has a “twin” anti-bonding state denoted by “*b*” which is located just above the Fermi level: Due to surrounding environments around Ti–H₂, these two states (*b* and *b*′) would be split from an original bonding state hybridized from the filled *d* orbitals (*d*_{zx}, *d*_{zy}) of Ti with empty σ^* orbitals of H₂. On the other hand, we have a distinct anti-bonding state (denoted by “*c*”) obtained from the *d*_{z²} – σ hybridization. Another anti-bonding state between *d* orbitals (*d*_{zx}, *d*_{zy}) and σ^* of H₂ is not clearly shown. As a result, we conclude that H₂ binds strongly to Ti atom through the Kubas interaction. It should be compared with a weak interaction between H₂ and

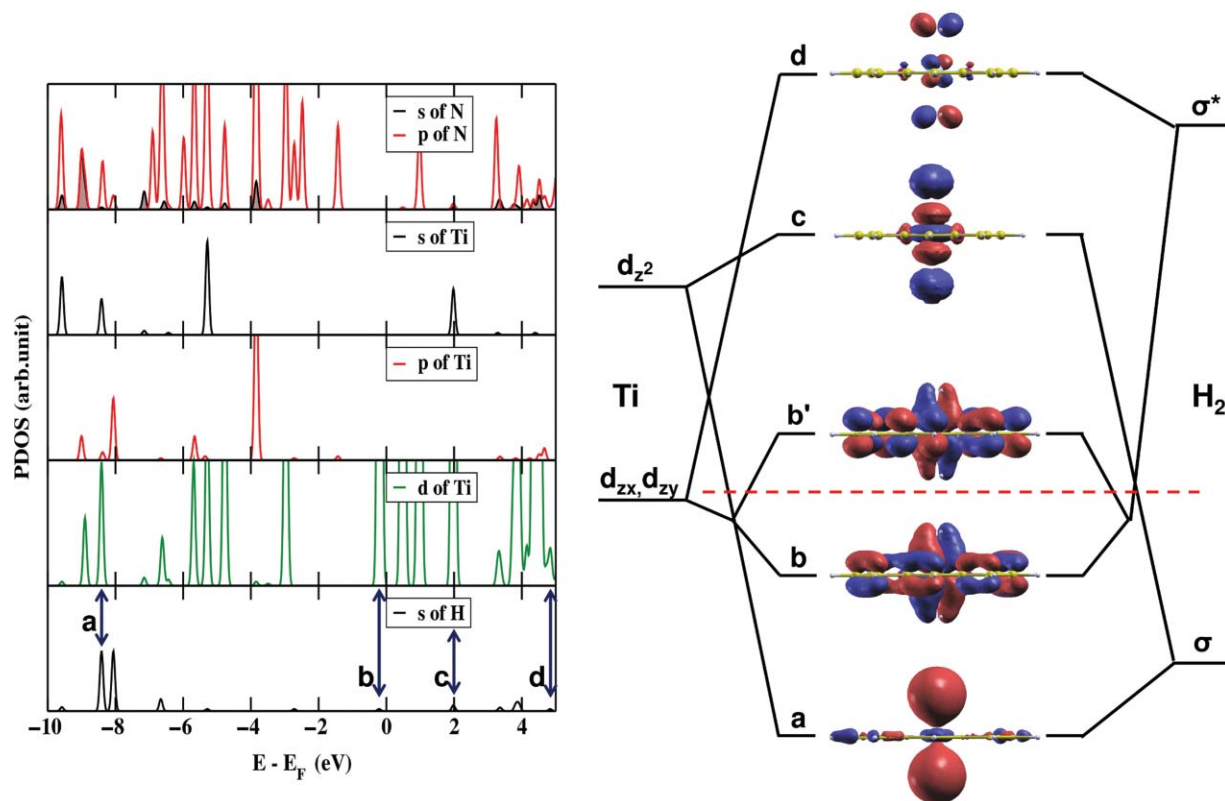


FIG. 5. (a) PDOS and (b) hybridization diagram for $2\text{H}_2/\text{Ti}$ -porphyrin. The dotted line in the right panel represents the Fermi level.

Ca through slight polarization of hydrogen molecules. A difference in the interaction types between Ti- and Ca-porphyrin molecules may be attributed to the presence of d orbital in Ti.

Finally, we turned our interest to a possibility of metalloporphyrin as a hydrogen storage material by calculating the hydrogen storage capacity. When hydrogen molecules are directly adsorbed on the Ca atom, the storage capacity is estimated to about 2.3 wt% for $4\text{H}_2/\text{Ca}$ -porphyrin. On the other hand, the hydrogen storage capacity of Ti-porphyrin is about 1.1 wt% for $2\text{H}_2/\text{Ti}$ -porphyrin. Unfortunately, these values are much smaller than the requirement for practical applications of hydrogen storage. Whereas model systems of other research groups are carbon-based structures with metal adatom, our model has strong covalent bonding between the Ca (or Ti) atom and four nitrogen atoms in porphyrin. Thus, there are not so reactive electronic orbitals to interact with H_2 in metalloporphyrin. Consequently, the storage capacity of metal-incorporated porphyrin is not as high as those of metal-decorated carbon nanostructures. If metal organic frameworks (MOFs) are constructed using metal-incorporated porphyrins,⁴³ the storage capacity could increase even in ambient conditions. Therefore, further investigations are needed for metal-incorporated porphyrin molecules to seek high-capacity H_2 storage materials. At present, gravimetric storage capacities of MOFs are much smaller than 1 wt% at ambient pressures and room temperature.^{44,45}

IV. CONCLUSION

In summary, we have investigated non-dissociative molecular hydrogen binding onto M-inserted ($M = \text{Ca}, \text{Ti}$)

porphyrin, and have compared the differences in the origins of dihydrogen binding to Ca- and Ti-porphyrin, using density functional theory calculations. By successively increasing the number of adsorbed hydrogen molecules on a Ca-porphyrin or Ti-porphyrin, we obtained the optimized structures and the H_2 binding energies. According to our LDA (GGA) calculations, the binding energy of H_2 to the Ca atom is about 0.25 (0.1) eV/ H_2 up to four H_2 molecules while that to the Ti atom is about 0.6 (0.3) eV/ H_2 up to two H_2 molecules. Our results demonstrate that a calcium atom incorporated into porphyrin with H_2 molecules forms a dihydrogen complex mainly through a weak polarization of H_2 . In contrast, Ti-porphyrin generates a Kubas-type dihydrogen complex with H_2 . The presence of d orbital in the Ti element may explain the difference in the interaction types.

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