Porphyrin-Based Porous Sheet: Electronic Property and Hydrogen Storage

Guizhi Zhu¹, Qiang Sun^{1,2,4,*}, Yoshiyuki Kawazoe³, Puru Jena⁴

¹Department of Materials Science and Engineering, Peking University, Beijing 100871, PR China

²Center for Applied Physics and Technology, Peking University, Beijing 100871, PR China

³Institute for Material Research, Tohoku University, Sendai, 980-8577, Japan

⁴Department of Physics, Virginia Commonwealth University, Richmond, VA 23284

ABSTRACT

The exploration of two-dimensional (2D) sheets beyond graphene has been gaining increasing interest. In this work, using first-principles calculations combined with grand canonical Monte Carlo (GCMC) simulations we systematically study the stability, electronic structure, optical absorbance and hydrogen adsorption of porphyrin (Por)-based nanosheets. We find these sheets to be thermally and mechanically stable. In addition, their electronic structure can be tuned from semiconductor to metal by doping different metal atoms, and the sheets can absorb near infrared (NIR) light. We also calculate the hydrogen storage capacities of the MPor (M=Mg, Ca, Sc) at 298 K and 100 bar pressure and find that the hydrogen gravimetric density of ScPor nanosheet can reach 6.71 wt% which represents an enhancement of 45% as compared to the Sc-phthalocyanine sheet.

* *Corresponding author.* Tel: +86 (010) 6275 2043.

E-mail address: sunqiang@pku.edu.cn.

Introduction

Due to the special geometry and unique properties of two-dimensional (2D) materials and certain inherent limitations of graphene, there is an increasing interest in looking for materials beyond graphene to meet specific needs. Among these, 2D metal-organic sheets, based on the extended π -conjugation units such as porphyrin and phthalocyanine, have attracted considerable attention. Here the tetrapyrrole skeletons with π -electron conjugated macrocycles exhibit good coordinating ability to bind most metal ions, showing potential applications in novel photoelectric functional materials,[1] molecular magnets,[2, 3] organo-synthetic catalysts,[4, 5] and molecular machines.[6] Nakamura *et al.* recently reported a meso-meso-, β - β -, and β - β -linked porphyrin sheet[7] by oxidizing meso-meso linked cyclic porphyrin tetramers. The corresponding transport properties[8] and magnetism[9] have also been studied theoretically. Abel *et al.*[10] fabricated a 2D Fe-phthalocyanine sheet on NaCl(100) thin film where the central Fe atom can be flexibly substituted by other 3d transition metal (TM) atoms. This extension of the substrate from the metal surface to the insulating surface provides a new platform to study 2D metal-organic sheets because the insulating NaCl substrate only affects slightly their electronic and magnetic properties. The biggest advantage of 2D organometallic sheets is the exposed metal sites which are uniformly distributed in the sheets, thus providing active sites for gas storage[11] and catalysis[12]. Using first-principles theory and grand canonical Monte Carlo simulation, Lv *et al.*[13] carried out a systematic study of 3d transition metals (Sc~Zn) phthalocyanine porous sheets and found that Sc-phthalocyanine can store 4.6 wt% hydrogen at 298K and 100 bar, which is much lower than the revised target set for 2015, namely 5.5 wt%.[14]

In this work we explore the design of a new sheet with improved hydrogen storage capacity by carrying out a comprehensive study of the doubly β - β -linked 2D porphyrin nanosheets impregnated with divalent alkaline-earth and rare-earth metals. Since porphyrin is lighter in mass than phthalocyanine we can expect the former to store hydrogen with higher gravimetric density. This is indeed confirmed by our detailed studies. Furthermore, we also show that the studied 2D porphyrin nanosheet

can display intriguing optical properties.

Computational method

Geometry optimizations of the structures were carried out using the Vienna Ab initio Simulation Package (VASP) code[15, 16] and the projector-augmented wave (PAW) method.[17, 18] The atoms were relaxed using the conjugate gradient method with a stringent force convergence criterion (0.01 eV/Å). Energies were minimized with a tolerance of 10^{-4} eV and convergence was accelerated with a Gaussian smearing of the Fermi surface by 0.01 eV. The Monkhorst-Pack $5 \times 5 \times 1$ and $7 \times 7 \times 1$ special k-point meshes[19] were used for modeling unit cell of H₂Por and MPor, respectively. The cutoff energy was set to be 400 eV. The vacuum space between two layers is 20 Å. For the geometry optimization, the exchange and correlation potential was treated within the generalized gradient approximation (GGA) using Perdew–Burke–Ernzerhof (PBE) functional,[20] while for electronic band structures and optical properties we use the hybrid Heyd–Scuseria–Ernzerhof (HSE06) functional[21, 22] since the GGA-PBE method is known to underestimate the band gap. Optical absorption spectrum was obtained by calculating the frequency dependent dielectric matrix after the electronic ground state had been determined.[23] The imaginary part $\epsilon^{(2)}$ was determined by a summation over empty states using the equation:

$$\epsilon_{\alpha\beta}^{(2)}(\omega) = \frac{4\pi^2 e^2}{\Omega} \lim_{q \rightarrow 0} \frac{1}{q^2} \sum_{c,v,k} 2\omega_k \delta(\epsilon_{ck} - \epsilon_{vk} - \omega) \times \langle u_{ck} + e_{\alpha q} | u_{vk} \rangle \langle u_{ck} + e_{\beta q} | u_{vk} \rangle^*,$$

The real part of the dielectric tensor $\epsilon^{(1)}$ was obtained using Kramers-Kronig transformation:

$$\epsilon_{\alpha\beta}^{(1)}(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\epsilon_{\alpha\beta}^{(2)}(\omega') \omega'}{\omega'^2 - \omega^2 + i\eta} d\omega',$$

where the indices c and v refer to conduction and valence band states respectively, and u_{ck} defines the periodic cell part of the wavefunction at the k-point, $\mathbf{k}$. P denotes the principle value. The complex shift η is set to be 0.1. This method has been widely used and confirmed to well reproduce the experimental observations for similar 2D

organometallic materials.[24, 25]

To explore the H₂ storage capability of the metalloporphyrin (MPor, M=Mg, Ca, Sc) nanosheets, we fitted the force field (FF) parameters for the interactions of H₂. In order to include long-range correlation effects, we employed hybrid Lee-Yang-Parr correlation functional (B3LYP)[26] and the 6-31G* basis set to optimize the adsorption configuration. We further used the 6-311+G* basis set at the second-order Møller-Plesset perturbation theory (MP2) level to scan the potential energy surface (PES) for higher accuracy. Based on the first-principles-derived FF parameters, we used grand canonical Monte Carlo (GCMC) simulations to calculate the hydrogen adsorption isotherms with the Multipurpose Simulation Code (MuSiC),[27] which has been widely used to evaluate the hydrogen storage capacities[28-30]

Results and discussion

Geometric structures and stabilities

We begin with a discussion of the geometry and stability of porphyrin nanosheets. The ground state geometry of metal-free porphyrin (H₂Por) nanosheet is shown in Fig. 1(a) where the orientation of H...H is vertical to that of its neighboring units. Similar to pristine graphene, the H₂Por nanosheet is planar with a crystallographic space group of p4/mbm (D_{4h}^{5}). When metal atoms are embedded, the symmetry becomes p4mm (C_{4v}^1) and the metal atoms protrude slightly out of the basal plane. The lattice constants are found to be 17.15, 8.57, 8.64 and 8.60 Å in side length for H₂Por, MgPor, CaPor and ScPor nanosheets, respectively. Both lattice parameters and the bond lengths between the central metal atoms and the neighboring N atoms (D_{TM-N}) exhibit a similar trend, increasing successively from MgPor to ScPor to CaPor. This is consistent with the atomic radii of the metal atoms. Table 1 summarizes the geometrical parameters.

We first examine the mechanical stability of the materials. In the linear elastic range, the elastic constant tensor C forms a symmetric 6×6 matrix with 21 independent components. According to Born criteria,[31] the elastic constants of a tetragonal crystal need to satisfy:

$$C_{11}-C_{12}>0;$$

$$C_{11}, C_{33}, C_{44}, C_{66}>0;$$

$$C_{11}+C_{33}-2C_{13}>0;$$

$$2C_{11}+C_{33}+2C_{12}+4C_{13}>0.$$

Due to the symmetry of porphyrin-based nanosheets only three elastic constants need to be considered, namely, C_{11} , C_{12} , and C_{66} . These are listed in Table 1 and indeed satisfy the Born criteria, namely $C_{11}-C_{12}>0$, $C_{11}>0$, $C_{66}>0$, $2C_{11}+2C_{12}>0$. Thus, the studied sheets are mechanically stable. We also see that when metal atoms are introduced C_{11} and C_{66} are increased while C_{12} is decreased. C_{11} and C_{12} monotonically change with the atomic number of metal atoms whereas C_{66} displays slight oscillations, depending on metal species.

Table 1 - Lattice parameters, bond lengths between the central metal atoms and the neighboring N atoms (D_{TM-N} , in Å), Elastic constants, and Energy Band Gaps (E_g , in eV) of 2D porphyrin nanosheets

Structure	Lattice/Å	$D_{TM-N}/\text{Å}$	Elastic constants/GPa·nm			E_g/eV
			C_{11}	C_{12}	C_{66}	
H ₂ Por	17.15	-	119.52	57.07	51.06	0.58
MgPor	8.57	2.09	156.07	59.49	75.92	0.52
CaPor	8.64	2.29	130.82	47.62	70.79	0.61
ScPor	8.60	2.13	166.87	35.38	75.40	Metal

To check the thermal stability, we perform *ab initio* molecular dynamics (MD) simulations at 500 K for 5000 steps with a time step of 1 fs by using the Nse–Hoover heat bath scheme.[32] The value of total energy remains nearly constant even after 5000 steps during the simulation (see Fig. 1 (c)). These results demonstrate that the porphyrin-based nanosheets, once synthesized, are both mechanically and thermodynamically stable above room temperature.

Fig. 1 - Geometric structures and MD simulations of 2D porphyrin nanosheets. The top view of H_2Por (a) and $MPor$ (b) nanosheets; the energy fluctuation (c) with respect to time in MD simulations at 500 K and the well sustained geometric structure after 5000 fs.

Electronic structure

To understand the electronic structure of the porphyrin-based sheets, we calculated the band structures and the corresponding partial densities of states (PDOS). The results are shown in Fig. 2. In the first Brillouin Zone of the reciprocal space the

bands are plotted along the high symmetry path: $\Gamma(0,0,0) \rightarrow X(0,1/2,0) \rightarrow M(1/2,1/2,0) \rightarrow \Gamma(0,0,0)$. A common feature in H₂Por, MgPor and CaPor nanosheets is that they all are direct-gap semiconductors with band gaps at the Γ point, the corresponding gaps being 0.58, 0.52 and 0.61 eV, respectively (listed in Table 1). The narrow band gap feature suggests potential applications of these materials in NIR optoelectronic devices which will be discussed in next section.

Fig. 2 - Electronic band structures (a)-(d) and the corresponding partial densities of states (PDOS) of MgPor, CaPor and ScPor nanosheets (e)-(g) calculated with HSE06 hybrid functional. The *s*, *p*, *d* orbitals are denoted as blue, red and green, respectively. Fermi level is shifted to 0 eV and marked with a dotted line.

It is interesting to note that the ScPor nanosheet shows strong metallicity where two electronic bands cross the Fermi level. To understand the origin of this metallicity

we calculate the PDOS of the primitive cell (see Fig. 2 (g)). The electronic states near the Fermi level are mainly contributed by the hybridization of p and d orbitals. Spin polarized DFT calculations indicate no magnetism in the sheet, suggesting that the moment of $3d^1$ electron is quenched when embedded in the sheet.

The band structures in Fig. 2 indicate that metal-doping can tune the band from flat to highly disperse. The calculated PDOS suggests that near the Fermi level the p -electrons dominate the bands in MgPor and CaPor sheets. Detailed analysis suggests that both the valence band maximum (VBM) and the conduction band minimum (CBM) of MgPor and CaPor sheets arise mainly from the C and N $2p$ electrons in the host porphyrin frameworks while the d electrons participate in the hybridization in ScPor sheet.

Fig. 3 - Charge density slices from left to right in MgPor, CaPor and ScPor, respectively. Panels (a)-(c) are viewed from [001] direction and panels (d)-(f) from the [010] direction in the unit cells.

Electron densities are calculated to visualize the charge distribution in the occupied band near the Fermi level. The electron density plots provide a good description of electron delocalization in molecules and solids and are a useful tool for chemical bond classification. As shown in Fig. 3 (a)-(f), we find that the main contribution to the charge density comes from the metal atoms and the π -conjugated macrocycles formed by the electrons in the $2p$ orbitals of C and N atoms. The electron cloud around N atoms is much denser because the electronegativity of N is larger than that of C. We note that the charge density slices in (a)-(c) are projected onto the porphyrin organic plane. Due to the spatial protrusion of 0.86 Å and 0.22 Å of Ca and Sc atoms, respectively, the side views as shown in (d)- (f) from the [010] direction are

necessary to give a full picture of the charge density distribution. We further find that the metal sites are positively charged due the charge transfer to the substrate. Consequently, the metal cations can trap gas molecules.

Optical properties

Porphyrin has good light-harvesting property. To investigate the optical properties of functionalized 2D porphyrin sheets, we have calculated the imaginary part of the dielectric function. The results are displayed in Fig. 4 (a). As expected, the absorption spectra of MPor sheets are different from that of the normal aromatic porphyrins which usually exhibit an intense B band and a weak Q band.[33] A red-shift of the optical absorption peak is observed from the Vis-NIR transmission spectra (400-3000 nm). We also find that three absorption peaks are observed for MgPor and CaPor sheets as opposed to only two peaks for ScPor sheet. A common feature is that the metal doped porphyrin sheets show palpable absorption in both NIR and visible light region. The first peak for MgPor, CaPor and ScPor nanosheets located at 2389 nm (0.52 eV), 2037 nm (0.61 eV) and 2680 nm (0.46 eV), respectively falls in NIR domain. For metal free H₂Por sheet, weak absorbance uniformly pervades from 600 nm to 2200 nm. By comparing the optical spectroscopy of ScPor with CaPor sheet, we find that after the doping of 3d¹ electron, the optical absorption of ScPor decreases although the electroconductibility becomes relatively strong. This is similar to the optical properties of conducting polymers.[34]

On the basis of the band structures and charge densities in Fig. 2 and 3, the dominant optical transitions in different energy regions of the optical spectrum can be determined. The adsorption from 0.46 to 2.0 eV comes from the 2p $\pi \rightarrow \pi^*$ transition, since the VBM and CBM mainly consist of the π -conjugated 2p electrons as discussed in the above. The introduction of metal atoms widens the original flat bands in metal free porphyrin nanosheet and increases the transition energy between neighboring bands. We find that the doping of metal atoms, especially alkali-earth metal, can clearly enlarge the strength of optical absorbance of 2D porphyrin sheets, providing a possible means to tune optical performance.

On the basis of the calculated dielectric functions using the HSE06 functional,

we can further obtain the static refractive index $n(\omega)$ using the following equation,

$$n(\omega) = \sqrt{\frac{|\varepsilon(\omega)| + \text{Re} \varepsilon(\omega)}{2}},$$

where $\varepsilon(\omega)$ and $\text{Re} \varepsilon(\omega)$ denote dielectric function and its real part, respectively. The derived maximum refractive indices (see Fig. 4 (b)) of H₂Por, MgPor, CaPor and ScPor are 3.45, 3.10, 2.50 and 2.32, respectively. This tunable refractive index may meet the diverse needs of different optical devices.

Fig. 4 - Wavelength-dependent optical absorption spectra (a) and refractive index (b) of 2D porphyrin nanosheets calculated using HSE06 functional. Black, red, green and blue line denote to H₂Por, MgPor, CaPor and ScPor, respectively.

Hydrogen storage

Hydrogen is one of the leading candidates as an alternate energy source to meet the needs of the transportation industry. However, hydrogen storage presents a formidable scientific and engineering challenge. Currently no materials can satisfy the target set by DOE.[14] In the following we discuss the hydrogen adsorption in the studied systems.

The adsorption energies of H₂ on MgPor, CaPor, ScPor substrates at the MP2/6-311+G* level are calculated to be -1.55, -2.06 and -5.43 kcal/mol, respectively. The corresponding distances between the hydrogen molecules to the substrate are 2.68, 2.75 and 2.32 Å. To reduce the computational cost in scanning the potential energy surface (PES) of H₂ interacting with functionalized porphyrin nanosheets, we adopt a

commonly used cluster model, as shown in Fig. 5. To describe the vdW interactions of H₂ with the substrate the following Lennard–Jones potential is used to fit the force field (FF) parameters,

$$U_{ij}(r_{ij}) = 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right],$$

where ε represents the depth of the potential well, σ denotes the equilibrium distance at which the inter-particle potential is zero, and r_{ij} is the actual distance. Examination of the unit cell revealed 6 chemically distinct atoms (N, C_m, C_a, C_b, H_a and M, M=Mg, Ca or Sc) which reproduce the entire 25-atoms unit cell upon crystallographic symmetry operations. The potential curves are shown in Fig. 5 (a)-(c), and the fitted FF parameters are listed in Table 2.

It is worth noting that for light alkali metal and alkali-earth metal, MP2/6-311+G* level has been used earlier for calculating the adsorption energy of H₂ molecules with high accuracy.[30, 35] To check its accuracy for the transition metal, we performed additional calculations. In the previous study on Sc-Pc porous sheet,[13] long range correlated hybrid functional WB97XD[36] has been adopted. In addition, Los Alamos effective core potential (ECP) has been used to represent the inner core electrons, while the outermost core orbitals have been treated utilizing a double-zeta contraction (LANL2DZ)[37, 38] which has been widely used for metal atoms.[39, 40] So we recalculated the PES for ScPor sheet using the WB97XD/LANL2DZ level of theory. The adsorption energy is calculated to be 0.25 eV compared with the value of 0.24 eV obtained at the MP2/6-311+G* level. The equilibrium distance between the hydrogen molecule and the substrate is 2.32 Å at the WB97XD/LANL2DZ level of theory, which is in a good agreement with the result obtained at the MP2/6-311+G* level. Therefore, the method we use for fitting the FF parameters is good for light alkali and alkali-earth metals as well as for transition metal Sc.

Using the first-principles-derived FF parameters we further performed the GCMC simulation. The simulation was conducted in a constant volume system which allowed the number of the total molecules, N and configurational energy, E to

fluctuate at a given temperature and chemical potential. For each given pressure (P) and temperature (T), 6×10^6 steps are used to sample and calculate the thermodynamic properties. Then average loading of H₂ molecules in each unit cell is converted to the excess uptake which is defined as follows,

$$m_{ex} = m_{abs} - \rho(T, P) \cdot V_{free},$$

where m_{ex} and m_{abs} denote the mass of excess H₂ uptake and absolute uptake, respectively, $\rho(T, P)$ is the density of H₂ calculated by using the Peng–Robinson state formulation,[41] and V_{free} is the free volume of the substrate.

Table 2 - The first-principles-derived FF parameters [* C_m and H_a are located at the bridge site connecting neighboring pyrrole rings; C_a represents the carbon atoms linked to N atoms in the pyrrole rings, whereas C_b is the β -linked site between different porphyrin ring; H_a denotes H binding to pyrrole N atoms in the center of the H₂Por macrocycle].

Term(H_)	$\epsilon(\text{kcal/mol})$			$\sigma(\text{\AA})$		
Atom type*	MgPor	CaPor	ScPor	MgPor	CaPor	ScPor
H_	0.0152	0.0152	0.0152	2.8460	2.8460	2.8460
N	0.3439	0.2478	0.5399	2.1827	2.6376	2.0135
C_m	0.1030	0.1610	0.2018	3.9800	3.2427	2.9919
C_a	0.1079	0.1791	0.2079	2.1958	2.3611	2.1212
C_b	0.1618	0.1753	0.5410	2.7635	3.6541	3.2770
H_a	0.0233	0.0556	0.0402	2.5329	2.6501	2.7944
Mg	0.5505	-	-	2.0338	-	-
Ca	-	0.5145	-	-	3.7186	-
Sc	-	-	1.2569	-	-	3.1304

Since safety concerns for a storage device in the industry may limit the maximum allowed pressure to 100 bar[42] we simulated the H₂ adsorption isotherms

of MgPor, CaPor and ScPor nanosheets at 298 K from 0 to 100 bar. The results are shown in Fig. 5 (d). We find that the excess H_2 uptake of the ScPor nanosheet (6.71 wt%) is much higher than that of MgPor (1.25 wt%) and CaPor (3.99 wt%) at 298 K and 100 bar, surpassing the target (5.5 wt%) set by the US Department of Energy (DOE) for 2015.[14] The interactions between H_2 and ScPor follows the Kubas mechanism where the charge donations occur from the bonding state of H_2 to the unoccupied states of Sc, while the back donation takes place from the occupied d orbital to the anti-bonding state of H_2 . We note that the hydrogen atoms are bound in quasi-molecular form resulting in good adsorption thermodynamics. It should be pointed out that the quasi-molecular adsorption of hydrogen on a positively-charged metal atom was also demonstrated independently by Niu *et. al*[43, 44] where the electric field associated with the metal cation polarizes the H_2 molecule. However, the ultimate target of 7.5 wt% for the total storage system is yet to be reached.[14]

Fig. 5 - (a)-(c) The PES of H_2 derived from first-principles calculations and fitting FF parameters using a cluster model for the substrate. (d) The H_2 adsorption isotherms of the MgPor, CaPor and ScPor nanosheets at 298 K from 0 to 100 bar.

Conclusion

In summary, we have used DFT combined with the grand canonical Monte Carlo

(GCMC) method to investigate the band structure, optical property and H₂ adsorption in metallo-porphyrin sheets. The following conclusions are drawn: (1) All the studied sheets are thermally stable and mechanically robust. (2) The electronic structures of the sheet can be flexibly tuned from semiconductor to metal by doping different metal atoms. (3) The first peaks of optical spectra in various 2D porphyrin sheets are located in near infrared (NIR) region, suggesting their potential applications in NIR-related devices. (4) The ScPor sheet is identified as a promising material for hydrogen storage exhibiting 6.71 wt% hydrogen gravimetric density at 298 K and 100 bar, which is much higher than that of ScPc sheet (4.6wt%). From ScPc sheet to ScPor sheet, the hydrogen storage performance is enhanced by 45%, which is consistent with the mole mass reduction of 40%.

Acknowledgment

This work is partially supported by grants from the National Natural Science Foundation of China (NSFC-21173007 and 11274023), and from the National Grand Fundamental Research 973 Program of China (2012CB921404). PJ acknowledges the support of the Department of Energy, Office of Basis Energy Sciences, Division of Materials Sciences and Engineering under Award # DE-FG02-96ER45579.

REFERENCES

- [1] Chen Y, Su W, Bai M, Jiang J, Li X, Liu Y, et al. High Performance Organic Field-Effect Transistors Based on Amphiphilic Tris(phthalocyaninato) Rare Earth Triple-Decker Complexes. *Journal of the American Chemical Society* 2005;127:15700-1.
- [2] Bogani L, Sangregorio C, Sessoli R, Gatteschi D. Molecular Engineering for Single-Chain-Magnet Behavior in a One-Dimensional Dysprosium–Nitronyl Nitroxide Compound. *Angewandte Chemie International Edition* 2005;44:5817-21.
- [3] Liu Z, Yasseri AA, Lindsey JS, Bocian DF. Molecular Memories That Survive Silicon Device Processing and Real-World Operation. *Science* 2003;302:1543-5.
- [4] Cui W, Zhang XP, Wayland BB. Bimetallo-Radical Carbon–Hydrogen Bond Activation of Methanol and Methane. *Journal of the American Chemical Society* 2003;125:4994-5.
- [5] Zhu S, Xu X, Perman JA, Zhang XP. A General and Efficient Cobalt(II)-Based Catalytic System for Highly Stereoselective Cyclopropanation of Alkenes with α -Cyanodiazooacetates. *Journal of the American Chemical Society* 2010;132:12796-9.
- [6] Takami T, Ye T, Pathem BK, Arnold DP, Sugiura K-i, Bian Y, et al. Manipulating Double-Decker Molecules at the Liquid–Solid Interface. *Journal of the American Chemical Society*

2010;132:16460-6.

[7] Nakamura Y, Aratani N, Shinokubo H, Takagi A, Kawai T, Matsumoto T, et al. A Directly Fused Tetrameric Porphyrin Sheet and Its Anomalous Electronic Properties That Arise from the Planar Cyclooctatetraene Core. *Journal of the American Chemical Society* 2006;128:4119-27.

[8] Yamaguchi Y. Transport properties of two-dimensionally fused zinc porphyrins from linear-response approach. *International Journal of Quantum Chemistry* 2011;111:3230-8.

[9] Tan J, Li W, He X, Zhao M. Stable ferromagnetism and half-metallicity in two-dimensional polyporphyrin frameworks. *RSC Advances* 2013;3:7016-22.

[10] Abel M, Clair S, Ourdjini O, Mossoyan M, Porte L. Single Layer of Polymeric Fe-Phthalocyanine: An Organometallic Sheet on Metal and Thin Insulating Film. *Journal of the American Chemical Society* 2010;133:1203-5.

[11] Budd PM, Butler A, Selbie J, Mahmood K, McKeown NB, Ghanem B, et al. The potential of organic polymer-based hydrogen storage materials. *Physical Chemistry Chemical Physics* 2007;9:1802-8.

[12] Li Y, Sun Q. The superior catalytic CO oxidation capacity of a Cr-phthalocyanine porous sheet. *Sci Rep* 2014;4.

[13] Lu K, Zhou J, Zhou L, Wang Q, Sun Q, Jena P. Sc-phthalocyanine sheet: Promising material for hydrogen storage. *Applied Physics Letters* 2011;99:163104-3.

[14] DOE Targets for onboard hydrogen storage systems for light-duty vehicles 2009; http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_onboard_hydro_storage.pdf.

[15] Kresse G, Furthmüller J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational Materials Science* 1996;6:15-50.

[16] Kresse G, Furthmüller J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical Review B* 1996;54:11169-86.

[17] Blöchl PE. Projector augmented-wave method. *Physical Review B* 1994;50:17953-79.

[18] Kresse G, Joubert D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Physical Review B* 1999;59:1758-75.

[19] Monkhorst HJ, Pack JD. Special points for Brillouin-zone integrations. *Physical Review B* 1976;13:5188-92.

[20] Perdew JP, Burke K, Ernzerhof M. Generalized Gradient Approximation Made Simple. *Physical Review Letters* 1996;77:3865-8.

[21] Heyd J, Scuseria GE, Ernzerhof M. Hybrid functionals based on a screened Coulomb potential. *The Journal of Chemical Physics* 2003;118:8207-15.

[22] Heyd J, Scuseria GE, Ernzerhof M. Erratum: "Hybrid functionals based on a screened Coulomb potential" [*J. Chem. Phys.* [bold 118], 8207 (2003)]. *The Journal of Chemical Physics* 2006;124:219906-1.

[23] Gajdoš M, Hummer K, Kresse G, Furthmüller J, Bechstedt F. Linear optical properties in the projector-augmented wave methodology. *Physical Review B* 2006;73:045112.

[24] Du A, Sanvito S, Li Z, Wang D, Jiao Y, Liao T, et al. Hybrid Graphene and Graphitic Carbon Nitride Nanocomposite: Gap Opening, Electron-Hole Puddle, Interfacial Charge Transfer, and Enhanced Visible Light Response. *Journal of the American Chemical Society* 2012;134:4393-7.

[25] Zhu G, Kan M, Sun Q, Jena P. Anisotropic Mo₂-Phthalocyanine Sheet: A New Member of the Organometallic Family. *The Journal of Physical Chemistry A* 2013;118:304-7.

- [26] Xu X, Goddard WA. The X3LYP extended density functional for accurate descriptions of nonbond interactions, spin states, and thermochemical properties. *Proceedings of the National Academy of Sciences of the United States of America* 2004;101:2673-7.
- [27] Gupta A, Chempath S, Sanborn MJ, Clark LA, Snurr RQ. Object-oriented Programming Paradigms for Molecular Modeling. *Molecular Simulation* 2003;29:29-46.
- [28] Garberoglio G, Skoulidas AI, Johnson JK. Adsorption of Gases in Metal Organic Materials: Comparison of Simulations and Experiments. *The Journal of Physical Chemistry B* 2005;109:13094-103.
- [29] Han SS, Goddard WA. Lithium-Doped Metal-Organic Frameworks for Reversible H₂ Storage at Ambient Temperature. *Journal of the American Chemical Society* 2007;129:8422-3.
- [30] Zhu G, Li Y, Lü K, Sun Q. Phthalocyanine-Based Organometallic Nanocages: Properties and Gas Storage. *ChemPhysChem* 2014;15:126-31.
- [31] Zhang S, Wang Q, Chen X, Jena P. Stable three-dimensional metallic carbon with interlocking hexagons. *Proceedings of the National Academy of Sciences* 2013;110:18809-13.
- [32] Nosé S. A unified formulation of the constant temperature molecular dynamics methods. *The Journal of Chemical Physics* 1984;81:511-9.
- [33] Shimizu S, Ito Y, Oniwa K, Hirokawa S, Miura Y, Matsushita O, et al. Synthesis of 5,10,15-triazaporphyrins-effect of benzo-annulation on the electronic structures. *Chemical Communications* 2012;48:3851-3.
- [34] Patil AO, Heeger AJ, Wudl F. Optical properties of conducting polymers. *Chemical Reviews* 1988;88:183-200.
- [35] Zhu G, Lü K, Sun Q, Kawazoe Y, Jena P. Lithium-doped triazine-based graphitic C₃N₄ sheet for hydrogen storage at ambient temperature. *Computational Materials Science* 2014;81:275-9.
- [36] Chai J-D, Head-Gordon M. Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections. *Physical Chemistry Chemical Physics* 2008;10:6615-20.
- [37] Hay PJ, Wadt WR. Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. *The Journal of Chemical Physics* 1985;82:270-83.
- [38] Hay PJ, Wadt WR. Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. *The Journal of Chemical Physics* 1985;82:299-310.
- [39] Bordiga S, Vitillo JG, Ricchiardi G, Regli L, Cocina D, Zecchina A, et al. Interaction of Hydrogen with MOF-5. *The Journal of Physical Chemistry B* 2005;109:18237-42.
- [40] Adams BD, Ostrom CK, Chen S, Chen A. High-Performance Pd-Based Hydrogen Spillover Catalysts for Hydrogen Storage. *The Journal of Physical Chemistry C* 2010;114:19875-82.
- [41] Peng D-Y, Robinson DB. A New Two-Constant Equation of State. *Industrial & Engineering Chemistry Fundamentals* 1976;15:59-64.
- [42] Dincă M, Long JR. Hydrogen Storage in Microporous Metal–Organic Frameworks with Exposed Metal Sites. *Angewandte Chemie International Edition* 2008;47:6766-79.
- [43] Niu J, Rao BK, Jena P. Binding of hydrogen molecules by a transition-metal ion. *Physical Review Letters* 1992;68:2277-80.
- [44] Niu J, Rao BK, Jena P, Manninen M. Interaction of H₂ and He with metal atoms, clusters, and ions. *Physical Review B* 1995;51:4475-84.