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A comparative study on the interaction between tin(II) porphyrin and selected group 8B metals for potential application as reduction catalysts

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Abstract. We study the interaction between tin(II) porphyrin (SnPor) with platinum and non-precious Group 8B metals (iron, cobalt and nickel) by density functional theory and discuss the electronic properties of the resulting products. We also model the interaction of the resulting compounds with water where applicable. Our studies indicate that, SnPor-Ni possesses electronic properties similar to SnPor-Pt, suggesting that it may possess similar photocatalytic properties for reduction reactions, such as converting water to hydrogen gas.

PACS. 72.80.Ga Transition-metal compounds – 73.22.-f Electronic structure of nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals

1 Introduction

Recently, it was shown that platinum (Pt) can be deposited on the surface of nanomaterials using tin porphyrins as photocatalysts [1]. The resulting complex demonstrated the capability to photocatalyze the reduction of water into hydrogen gas. In our previous paper, we used density functional theory to study the interaction between tin (II) porphyrin and platinum and the electronic characteristics of their reaction product [2]. Our calculations indicate that Pt binds strongly on SnPor and enhances the catalytic property of Pt.

Interestingly, experimental studies have shown that SnPor can deposit other metals, such as iron (Fe), magnesium (Mg) and cobalt (Co), on its surface. Unlike metals bonded directly to porphyrins, metals bonded on SnPor are neutral. The Mg and Co deposited on SnPor can further bond with metals such as mercury (Hg), manganese (Mn), cadium (Cd), cobalt (Co) or zinc (Zn). The structures of these compounds have been confirmed by X-ray diffraction [3,4].

As a continuation of our search for alternative catalysts for hydrogen production, we shall compare SnPor-Pt with SnPor-Fe, -Co, and -Ni (nickel) in this study. We will compare their electronic properties and also their interaction with water where applicable. Dispersing metals on SnPor will not only lower quantities of the metal needed to make catalytic surfaces but also — we believe — enhance their performance. The reasons for our belief are as follows: the top metal (as shown in Fig. 1) has minimal steric hindrances for incoming molecules compared to metals in surfaces or porphyrins; presence of a porphyrin chromophore can trap light energy possibly assisting catalytic reduction processes; and perturbation on the electronic structure of the top metal by the SnPor may alter its catalytic properties [2].

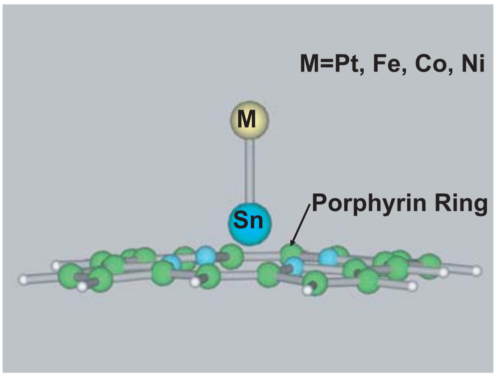

Fig. 1. (Color online) Geometry of SnPor-M.

2 Calculations

In our previous paper, we calculated the interaction between SnPor and Pt [2]. In this study, we show the results of our calculations for SnPor-Fe, SnPor-Co, and SnPor-Ni and compare them with those previously obtained for SnPor-Pt.

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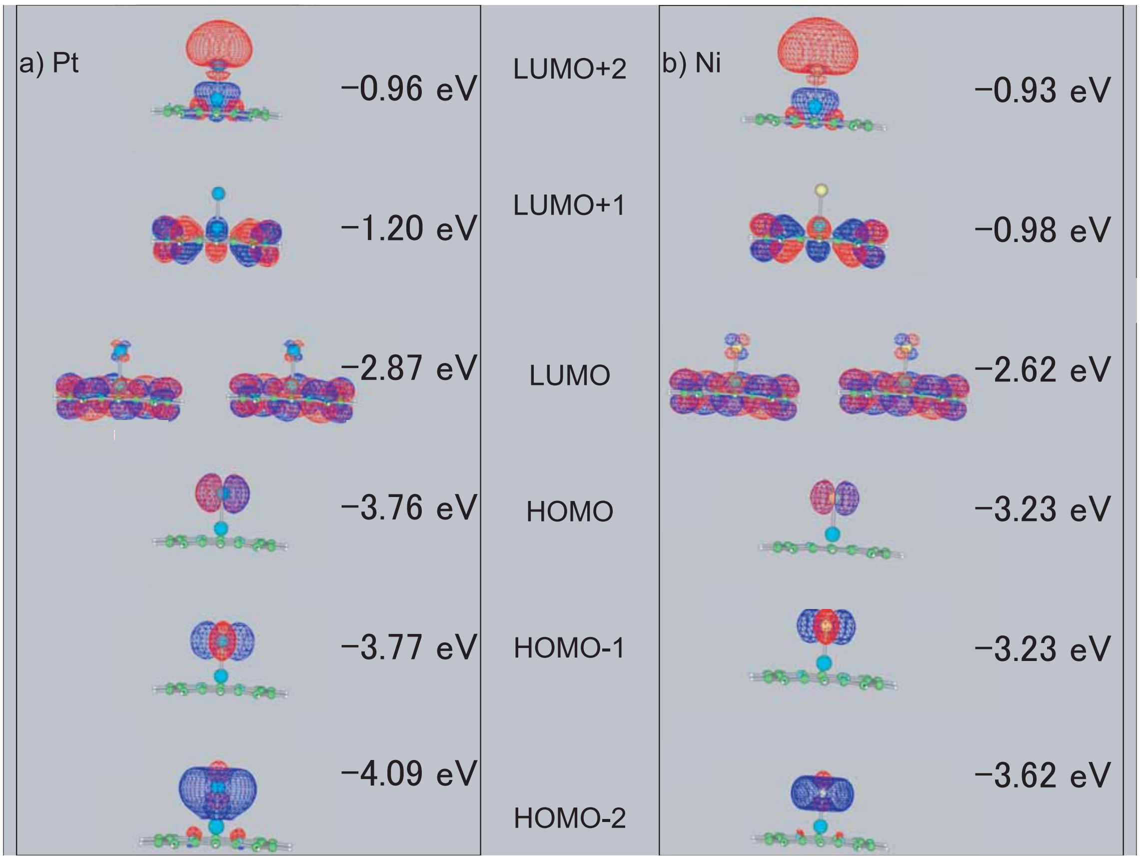

Fig. 2. (Color online) Comparison between frontier molecular orbitals of SnPor-Pt (a) and SnPor-Ni (b).

We performed density functional calculations with Gaussian03 [6] using the LANL2DZ basis set and the Becke-Lee-Yang-Parr (B3LYP) exchange-correlation functionals. We consider SnPor-Ni and SnPor-Fe in spin multiplicities of 1, 3, 5 and 7 to determine the ground state of these compounds. We considered SnPor-Co with spin multiplicities of 2, 4, 6 and 8 to determine its ground state. We fully relaxed the geometry at each spin state. We also calculated the energies and optimized geometries of SnPor-MH_2O where applicable and the energies of their corresponding anionic (−1 charge) states.

3 Results and discussion

The relative energies for each spin state of SnPor-M (M = Fe, Co, Ni, Pt) are reported in Table 1. For cobalt, spin contamination was significantly observed in the doublet state using unrestricted density functional theory. This leads us to believe that the energy of the doublet state is artificially stable. Attempts to calculate the doublet SnPor-Co with restricted open-shell algorithms, on the other hand, failed to converge. Regardless of its true ground state, binding energies of SnPor-Co for all cases of spin multiplicities were negative (unstable) — even for the artificially stable doublet. Consequently, we can conclude at this point that SnPor-Co is not a suitable catalyst material.

Table 1. Relative energies versus spin multiplicities of SnPor-M.

Spin multiplicity	Energy (eV)			
	SnPor-Pt [2]	SnPorFe	SnPorCo	SnPorNi
1	**0**	2.17		**0**
2			**0***	
3	2.53	**0**		1.29
4			0.45	
5	2.87	1.96		0.83
6			0.33	
7	5.02	1.40		2.66
8			1.61	

*Significant spin contamination.

Table 2. Calculated geometric parameters of SnPor-M.

	SnPor-Pt	SnPor-Fe	SnPor-Co	SnPor-Ni
Bondlength (Å)				
M-Sn	2.42	2.63	2.56	2.34
Sn-N Plane	0.82	0.63	0.63	0.86
N1-αC	1.40	1.41	1.41	1.40

The relaxed geometries for SnPor-M (M = Pt [2], Fe, Co, Ni,) are summarized in Table 2. The bond distances between Sn and Fe, Co and Ni are accounted for by the differences in atomic radius between the metals. The relatively small bond distance between Sn and Pt can be

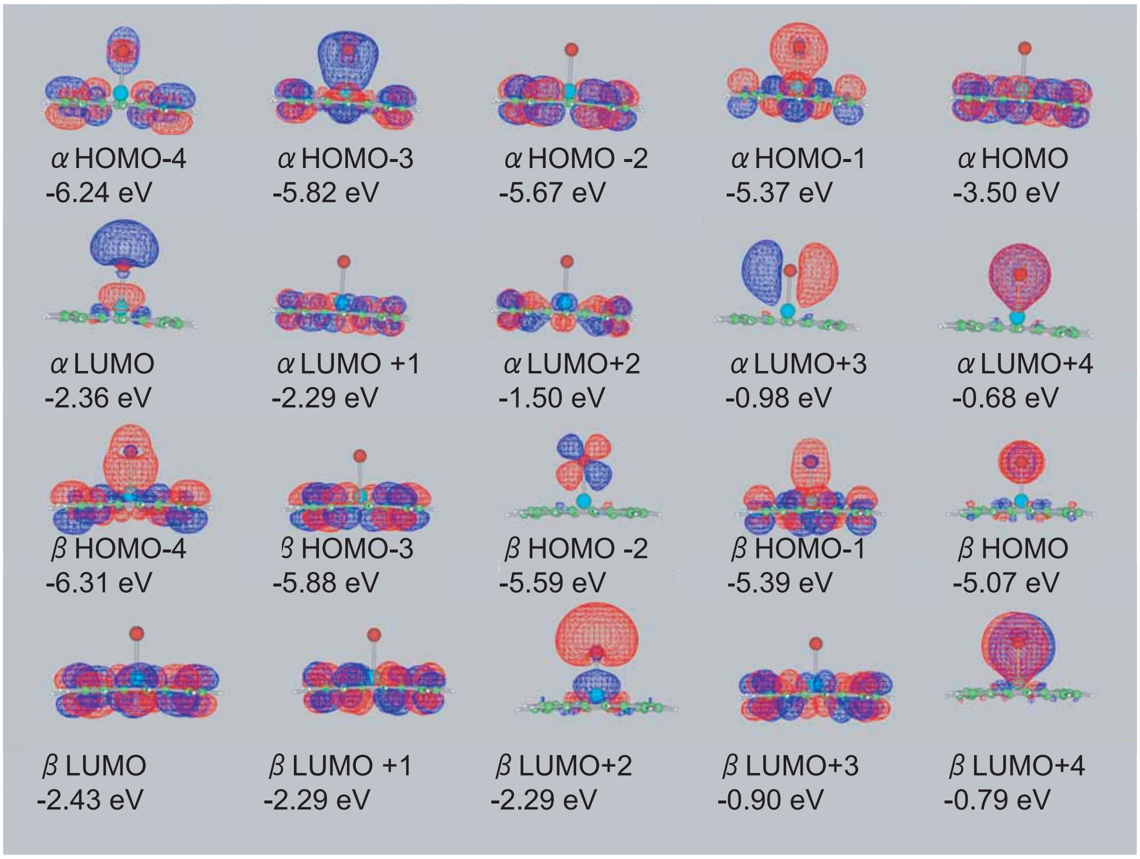

Fig. 3. (Color online) Frontier molecular orbitals of SnPor-Fe.

Table 3. Mulliken charge distribution of neutral SnPor-Pt, SnPor-Fe, and SnPor-Ni and electronegativities of the central metals.

	SnPor-Pt	SnPor-Fe	SnPor-Ni
Por	−1.41	−1.41	−0.99
Sn	0.78	1.41	1.29
M	−0.63	0.0	−0.30
EN	2.28	1.83	1.91

attributed to the strong interaction between Pt and SnPor. (Our calculations gave energies of 3.13 [2], 1.29, −0.48 and 0.38 eV respectively for the binding Pt, Fe, Co, Ni on SnPor.) For the partial charges of Fe, Ni and Pt in SnPor-M as shown in Table 3, electronegativity accounts for the observed trend — i.e., the most electronegative metal, Pt, has the highest partial negative charge.

The frontier molecular orbitals of SnPor-Pt and SnPor-Ni are compared in Figure 2. As can be seen from the figure, the frontier molecular orbital wave functions of SnPor-Pt and SnPor-Ni are quite similar except the valence *d*-electron of Ni is from the 3*d* level and those of Pt is from 5*d*. This explains the differences in energy gaps between the frontier molecular orbitals of SnPor-Pt and SnPor-Ni. The d-orbitals of the central Ni and Pt atoms are shown to predominate near HOMO and LUMO levels. The frontier molecular orbitals of SnPor-Fe (Fig. 3), on the other hand, are very different from SnPor-Ni and SnPor-Pt because of the singly-filled *d*-orbitals of Fe.

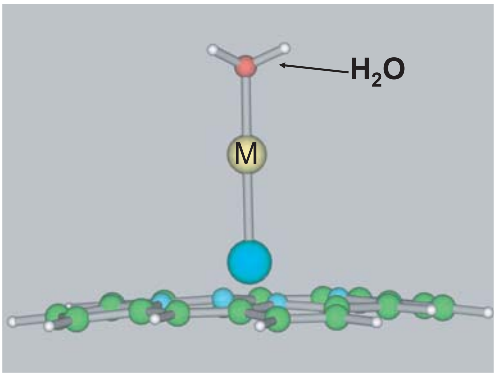

Fig. 4. (Color online) Geometry of SnPor-M with H_2O.

We proceed to the interaction of Pt, Fe and Ni on SnPor with water. As briefly mentioned in our previous paper [2], the H_2O will attach via its O on top of the Pt (opposite SnPor) axially with a binding energy of 0.73 eV. Here we show the geometry (Fig. 4). Similar stable positions were found for SnPor-Pt, SnPor-Ni and SnPor-Fe — water binds axially on top of M. The binding energies for SnPor-Ni and SnPor-Fe are 1.13 and 1.19 eV. We calculated the electron affinity (EA) of the hydrated SnPor-Pt, -Ni and -Fe to be 1.04, 2.1 and 1.2 eV respectively. This

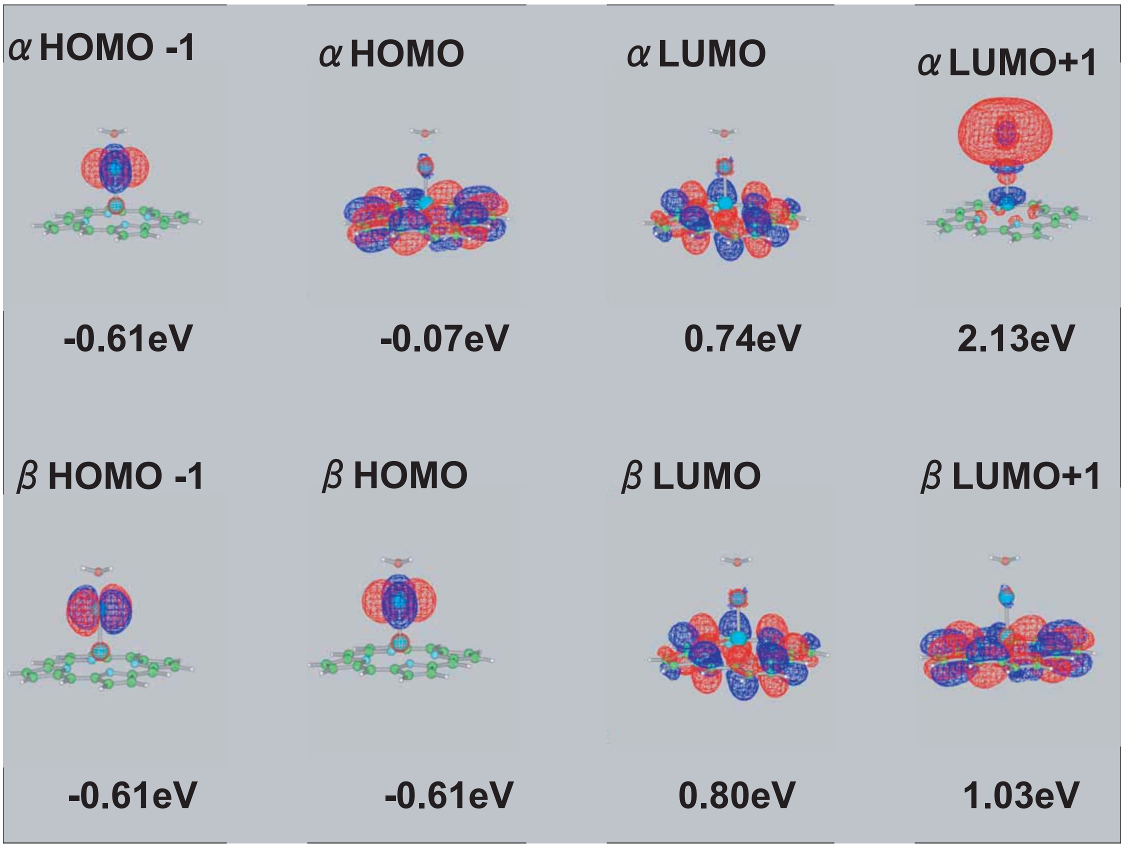

Fig. 5. (Color online) Frontier molecular orbitals of SnPor-$Pt^{-1}\cdot H_2O$.

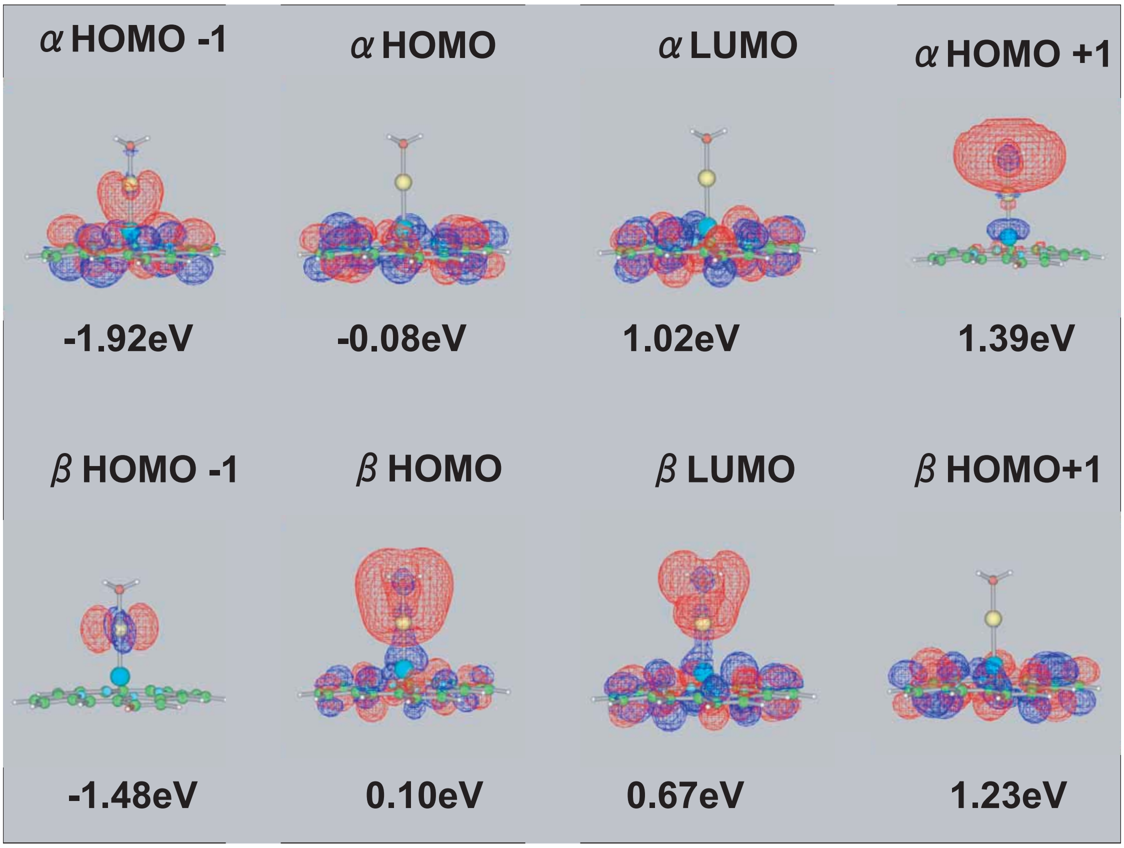

Fig. 6. (Color online) Frontier molecular orbitals of SnPor-$Ni^{-1}\cdot H_2O$.

indicates that they all will interact with H_2O and readily accept an extra electron for reduction reactions.

Lastly, Figures 5 and 6 show the frontier molecular orbitals of both SnPor-Pt·H_2O and SnPor-Ni·H_2O with a net -1 charge. In both cases, it can be seen that the extra electron (in the HOMO) can transfer from the porphyrin to the hydrogen atoms of H_2O by excitation from the HOMO to the LUMO+1. For SnPor-Pt·H_2O, the excitation energy is of 2.19 toexcitation at 565 nm. Due to similarities between the frontier molecular orbitals of SnPor-Pt·H_2O^{-1} and SnPor-Ni·H_2O^{-1}, we think that SnPor-Ni may have similar photocatalytic properties as SnPor-Pt. The main difference is that the excitation energy needed to transfer the HOMO electron from the porphyrin ring to the hydrogen atoms of water in (LUMO+1) is lower (1.47 eV). It corresponds to longer wavelengths of the electromagnetic spectrum (843 nm), but this is not a problem as sunlight, our preferred excitation source for H_2 gas generation, emits radiation significantly in this region.

In conclusion, we compared the interaction of SnPor and Pt with Co, Fe and Ni. Our calculations indicate that SnPor-Co is not stable and, hence, not a suitable catalyst material. The distance between SnPor and Pt is smaller than between SnPor with Ni or Fe. This can be attributed to the fact that SnPor binds strongly to Pt. The partial charges of the metals in SnPor-M can be attributed to its electronegativity; Pt, being the most electronegative has the highest partial negative charge. Lastly, think that SnPor-Ni may possess similar photocatalytic properties as SnPor-Pt due to similarities in relevant electronic properties. This suggests that SnPor-Ni may be used together with (or as a replacement of) SnPor-Pt as catalysts for solar hydrogen production. SnPor-Ni will utilize wavelengths different from SnPor-Pt; hence when used together a broader spectrum of solar energy can be utilized and therefore increased H_2 production efficiency can be achieved.

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