**ORIGINAL PAPER** 



### Immobilization and DFT studies of Tin chloride on UiO-66 metal–organic frameworks as active catalyst for enamination of acetylacetone

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#### Abstract

An efficient synthetic method for the preparation of  $\beta$ -enaminones catalyzed by immobilization of SnCl<sub>2</sub> on Zr-metal–organic frameworks (UiO-66 MOF) and designated as SnUiO66 is described. Also the prepared catalyst was characterized by Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy (XPS), energy-dispersive X-ray spectroscopy and N<sub>2</sub> adsorption and desorption techniques. XPS and DFT studies on Sn UiO66 were consistent with the immobilization of Sn chloride as Sn<sup>IV</sup> on MOF. A variety of  $\beta$ -enaminones were synthesized via reaction of primary aromatic amines with acetylacetone. It was found that SnUiO66 shows moderate-to-high catalytic activity for enamination reactions. The catalyst was found to be reusable up to four catalytic cycles without any appreciable loss in activity.

Keywords Modification · Metal-organic frameworks · Enamination · SnUiO-66

#### Introduction

An increasing interest has been directed toward the enamination of 1,3-dicarbonyl compounds to  $\beta$ -enamino ketones and esters due to their importance in organic synthesis [1]. These compounds are significant intermediates in the synthesis of heterocyclic compounds and also in medicinal applications, and they are also known as anticonvulsant, anti-inflammatory, antitumor and analgesic agents [2]. There are a few reported methods for the synthesis of  $\beta$ -enaminones through reaction of dicarbonyl compounds with amines using catalysts such as metal oxides under microwave or ultrasound irradiation [3, 4]. Several homogeneous and heterogeneous catalysts have also been used for enamination reactions. Examples of homogeneous catalysts include Ca(CF<sub>3</sub>COO)<sub>2</sub>

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[5], BF<sub>3</sub>•OEt<sub>2</sub> [6], Zn(ClO<sub>4</sub>)•6H<sub>2</sub>O [7], ceric ammonium nitrate [8] and Bi(OTF)<sub>3</sub> [9]. Utilization of homogeneous catalysts is associated with certain drawbacks like use of moisture-sensitive metal triflates and tedious workup, use of harmful reagents and nonrecyclable catalysts. On the other hand, heterogeneous catalysts such as clays [10], supported tungstophosphoric acid [11], silica-supported perchloric acid [12] and silica chloride [13] have been used for enamination reactions. Due to the significantly more expensive non-recoverable catalysts, use of the more attracting, easily separable and recyclable heterogeneous systems has been developed [14–18].

A new class of microporous materials known as metal–organic frameworks (MOFs) has emerged in recent years which are comprised of metal "nodes" linked with "rod"-shaped organic linkers. These materials have attracted considerable attention due to their profound range of applications including separation, gas storage and catalysis [19]. The use of MOFs as heterogeneous catalysts is particularly interesting since the pore size and functionality of the framework can be adjusted over a wide range for a variety of catalytic reactions [20].

Modification of some MOFs to increase their acidity and use as catalyst in the synthesis of  $\beta$ -enaminones via reaction of primary aromatic amines with acetylacetone is described in this presentation. The DFT calculation on

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all studied complexes has been carried out for comparison of the experimental and theoretical results. The DFT as a suitable and popular method can be used for calculation of compounds including metals. The most important advantage of using the DFT methods is obtaining a significant increase in computational accuracy without the additional increase in computing time.

#### **Experimental section**

#### Materials and characterization

All materials were of commercial reagent grade and used without further purification. FT-IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer using KBr pellets over the range of 4000–400 cm<sup>-1</sup>. The catalysts were analyzed by powder X-ray diffractometer (XRD) PHILIPS PW 1800, using Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm) and in the  $2\theta$ range of 0°-60°. The percentages of immobilized metal ions were determined by atomic absorption double-beam instrument. Energy-dispersive X-ray spectroscopy (EDX) VEGA3 LMU analysis was performed by TESCAN Company. The X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Scientific ESCALAB 250Xi analyzer equipped with Mg X-ray source. Products were analyzed by GC and GC-Mass using Agilent 6890 series with a FID detector, HP-5,5% phenylmethylsiloxane capillary and Agilent 5973 network, mass selective detector, HP-5 MS 6989 network GC.

#### Synthesis of UiO-66

The UiO-66 was prepared via modification of the previously reported procedure [21]. To a suspension of  $ZrCl_4$  (0.63 g, 2.7 mmol) in DMF (25 mL) was added concentrated HCl (5 mL) and the mixture sonicated with ultrasound for several minutes until it becomes clear. Terephthalic acid (0.62 g; 3.75 mmol) dissolved in DMF (50 mL) was then added into the  $ZrCl_4$  and the mixture stirred at 80 °C for 24 h. After cooling to RT, the white solid was separated and resuspended in DMF. After stirring for 24 h in RT, the precipitate was separated by filtration and washed with DMF (4×10 mL). It was then resuspended in MeOH and stirred for 24 h at RT followed by filtration and washing the solid with MeOH. This procedure was repeated twice in order to remove all impurities.

#### Preparation of Sn UiO-66

To a dispersed UiO-66 (0.1 g) in MeOH (1 mL) was added  $SnCl_2 H_2O$  (0.01 g; 10 wt%) dissolved in MeOH (1 mL) and the mixture stirred for 4 h at RT. The white solid was

subsequently filtered, washed with MeOH for several times and dried at 110  $^{\circ}$ C within 4 h.

## Typical method for the synthesis of $\beta$ -enaminones and $\beta$ -enamino esters

To a 25-ml round-bottom flask containing MeOH (5 mL) were added dicarbonyl compound (1 mmol), amine (1 mmol, 1.1 mmol) and catalyst (20 mg) and the mixture heated at reflux for 2 h. After separation of the catalyst by filtration, the filtrate was subjected to GC and GC–Mass analyses. The GC–Mass of products was reported in supplementary.

#### **Computational details**

The structures and energy of all studied compounds including  $[Zr_6O_4(OH)_4]$  clusters and the complexes between Tin and  $[Zr_6O_4(OH)_4]$  from different positions with different oxidation numbers were calculated by using the density functional theory (DFT) [22] without any symmetry constraints. The hybrid of Beck's nonlocal three-parameter exchange and corrected functional with Lee-Yang-Parr correlation functional (B3LYP) [23] for the closed shell system has been used. The  $6-311 + +G^{**}$  basis set was used for H and O atoms. Moreover, the effective core potentials (ECPs) of Hay and Wadt with double- $\zeta$  valance basis set (Lan12DZ) [24-26] were chosen to describe the Zr and Tin atoms. The core behavior parameter controls the electrons treatment modes in the lowest lying atomic orbitals. In the case of heavier elements especially in MOF, it is important to take into account the relativistic effects of the central electrons. One prevalent method to incorporate these effects is replacing the complex effects of the core electrons with an effective potential or pseudo-potential [27, 28]. This method which is named effective core potential (ECP) approximates the Schrodinger equation in heavy systems [29].

The harmonic vibrational frequencies have been computed to confirm that an optimized geometry correctly corresponds to a local minimum that has only real frequencies. In addition, the results of frequency calculations have been employed to calculate thermodynamic functions such as enthalpies and Gibbs free energies at 298.15 K and 1.0 atmosphere pressure. All reported enthalpies were zero-point (ZPE) corrected with unscaled frequencies. The solvent effects on the conformational equilibrium and contribution to the total enthalpies were investigated by using polarized continuum (overlapping spheres) model (PCM) of Tomasi and coworkers [30] at the same level for the methanol solvent. All calculations were performed using the Gaussian 2003 [31] software.

#### **Results and discussion**

In this study, the UiO-66 was prepared with  $ZrCl_4$  and terephthalic acid based on the report of [21], followed by immobilization SnCl<sub>2</sub> on it.

#### **Characterization of prepared catalyst**

The FTIR spectra of ZrCl<sub>4</sub>, terephthalic acid and UiO-66 are shown in Fig. S1. The spectrum of acid shows two peaks at 3742 and 3389 cm<sup>-1</sup> related to the O–H stretching vibrations of COOH. Whereas two peaks appeared at 1424 cm<sup>-1</sup> and 1568 cm<sup>-1</sup> are due to the symmetric and asymmetric vibrations of carboxylate anions, the band observed around 1682 cm<sup>-1</sup> can be significantly assigned to acidic C=O stretching vibration (Fig. S1b). After formation of MOF (UiO-66), the C=O vibration is shifted to 1581 cm<sup>-1</sup> (Fig. S1c).. Zr–O vibrations are observed at 482, 545, 661 and 745 cm<sup>-1</sup>. The strong and weak peaks located at 1399 and 1508 cm<sup>-1</sup> are attributed to C–O and aromatic organic linker C=C stretchings, respectively [32–34].

The FTIR spectra of UiO-66, Sn UiO-66 before and after being used as a catalyst are shown in Fig. 1a–c, respectively. No significant change in catalyst is observed on the basis of these spectra.

The XRD patterns of UiO-66, SnUiO-66 before and after being used as a catalyst exhibit a typical diffraction at  $2\theta = 7.45^{\circ}$ , 8.58°, similar to those reported previously for UiO-66 [28] (Fig. 2a–c). Observation of no change in the XRD patterns after immobilization of SnCl<sub>2</sub> significantly confirms the stability of the prepared MOF crystal structure.



Fig. 1 FTIR spectra of (a) UiO-66, (b) SnUiO-66 before and (c) after being used as catalyst



Fig. 2 XRD patterns for UiO-66, SnUiO-66 before and (c) after being used as catalyst

The energy-dispersive X-ray (EDX) for SnUiO-66 is shown in Fig. 3. The presence of C, O, Cl, Zr and Sn is clearly observed in EDX map. Significantly, the immobilized amount for Sn before and after reaction was determined by ICP techniques and found to be 0.2697 and 0.2511 weight percentage, respectively.

In order to obtain support for immobilization of metal ions on UiO-66, the SnUiO-66 was used as a model for this study. The N<sub>2</sub> adsorption/desorption isotherms of UiO-66 and Sn UiO-66 are exhibited in Fig. 4a, b. It seems that the isotherms of two samples are type I according to the IUPAC classification. This type of isotherm is observed for solids with micropores such as activated carbons or zeolites [35]. As seen in Fig. 4, the amount of nitrogen adsorption



Fig. 3 EDX image of SnUiO-66



Fig. 4 N2 adsorption/desorption of UiO-66 and SnUiO-66

for the immobilized SnUiO-66 is less than that of UiO-66. The specific surface area and pore size distribution were determined using Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods. The measured BET surface area, pore volume, mean pore diameter and the volume of a monolayer were determined as 1377.1 [m<sup>2</sup> g<sup>-1</sup>], 0.851 [cm<sup>3</sup> g<sup>-1</sup>], 2.47 nm and 316.39 [m<sup>3</sup> (STP) g<sup>-1</sup>], respectively (Table 1). The textural parameters calculated by N<sub>2</sub> adsorption–desorption isotherms were found to be reduced

Table 1 Texture parameters of UiO-66 and Sn<sup>2+</sup>/UiO-66

MOF	$\frac{V_m}{[m^3(\text{STP}) \text{ g}^{-1}]}$	$a_{s, \text{BET}}$ (m <sup>2</sup> g <sup>-1</sup> )	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Mean pore diameter (nm)
UiO-66	316.39	1377.1	0.851	2.47
Sn <sup>2+</sup> /UiO- 66	276.92	1205	0.7262	2.41

to 1205  $[m^2 g^{-1}]$ , 0.7262  $[cm^3 g^{-1}]$ , 2.41 nm and 276.92  $[m^3(STP) g^{-1}]$  after immobilization of Sn within UiO-66. These results indicate that whereas the most Sn atoms of complex are located on the surface of MOF, some are located at internal surface based on the obtained results. Although such a decrease in the textural parameters is observed, the structure of UiO-66 remained unchanged after immobilization of SnCl<sub>2</sub>, consistent with XRD and FTIR characterization results.

XPS spectra were used for analyses of the SnUiO-66 chemical status and surface chemical composition. Figure 5a shows the survey scan of sample, which indicates that Sn, Cl, Zr, O and C elements exist in the SnUiO-66. Figure 5b indicates the binding energies of Zr  $3d_{5/2}$  and Zr  $3d_{3/2}$ , which are observed at approximately 182.96 eV and 185.33 eV. This binding energy confirmed the existence of Zr<sup>IV</sup> for the zirconium-oxo cluster [36, 37].

The Gaussian fit of the C1s spectrum of SnUiO-66 (Fig. 5c) exhibited two peaks as follows: non-oxygenated C–C (284.94 eV) and O–C=O (288.90 eV) components that both of them were attributed species [38, 39]. Figure 5d presents  $Sn3d_{5/2}$  and  $Sn3d_{3/2}$  binding energies of 487.28 and 495.69 eV, respectively. The peak positions agree well with the presence of  $Sn^{IV}$  species as SnUiO-66 [40, 41]. The presence of chloride and oxygen is confirmed by the energy binding peak of Cl2p and O1s at 198.86 eV and 531.89 eV in Fig. 5e, d [36, 42].

#### **Optimization of enamination reaction conditions**

Synthesis of  $\beta$ -enaminone via reaction of aniline with acetylacetone was selected as model to study the catalytic activity of SnUiO-66 at RT. The effects of various reaction parameters including time, catalyst amount and solvent were studied (Figs. 6, 7 and Table 2). High reaction yield was obtained using 20 mg of catalyst in refluxing MeOH within 2 h. As seen in Fig. 7, increasing the amount of catalyst from 5 to 20 mg enhances the conversion from 64 to 93% with 100% selectivity (Fig. 7).

Table 2 presents the influence of solvent on the condensation reaction condition for the synthesis of  $\beta$ -enaminone using SnUiO-66 as catalyst. Based on the obtained results, better yield was obtained in ethanol and methanol if an



Fig. 5 XPS spectra of SnUiO-66 a survey scan, b Zr3d, c C1s, d Sn3d, e O1s and f Cl2p

excess amount of acetylacetone with respect to aniline (1.2/1) was used (entries 4–5, Table 2).

Enamination of acetylacetone with various amines was then investigated under optimized reaction conditions. As seen in Table 3, utilization of aniline (entry 1, Table 3) and substituted aniline either with strong electron-donating (entries 2–3, Table 3) or modest electron-withdrawing substituents (entries 4–6, Table 3) affords the corresponding



Fig. 6 Conversion and selectivity of  $\beta$ -enaminones at different times in the presence of the SnUiO-66 as catalyst. Reaction conditions: acetylacetone (1.1 mmol), aniline (1 mmol), catalyst amount (20 mg), methanol (5 mL) and temperature (60 °C)



Fig.7 Conversion and selectivity of  $\beta$ -enaminones at different amounts of SnUiO-66 as catalyst. Reaction conditions: acetylacetone (1.1 mmol), aniline (1 mmol), methanol (5 mL) and temperature (60 °C), time 2 h

 $\beta$ -enaminones in excellent yields. On the other hand, aldehydes containing strong electron-withdrawing substituents are totally inefficient toward the formation of  $\beta$ -enaminone (entries 7–8, Table 3).

Particularly significant are the stability and reusability of the prepared catalyst since the obtained results indicate that not only the activity in methanol solvent is remarkable, but also it is recycled up to four consecutive cycles without any notable loss in catalytic activity (Fig. 8). Table 2 Effect of solvent on enaminone 2a obtained via reaction of acetylacetone with amine 1a catalyzed by SnUiO-66



Conversion (%)	

Acetylacetone (1.1 mmol), aniline (1 mmol), catalyst amount (20 mg), solvent (5 mL), temperature (60  $^{\circ}$ C) and time (2 h)

Based on the obtained results, SnUiO-66 has been used in further theoretical studies to find the position of immobilized tin chloride on UiO-66.

UiO-66 is known to have missing some linkers due to coordinating water and solvent molecules as reported before [43, 44]. Huong Giang indicated that vanadium (V) can be directly incorporated onto the  $[Zr_6O_4(OH)_4]$  clusters of UiO-66 by reacting with exposed OH groups, especially the OH groups arisen from missing linkers. According to this article, five complexes are formed from three proposed structures A, B and C (Fig. 9) [43]. Based on the above-mentioned article, in the present study, ten different complexes that arise from the connection between two ions (Sn<sup>II</sup> and Sn<sup>IV</sup>) onto  $[Zr_6O_4(OH)_4]$  clusters of UiO-66 from different positions have been investigated using density functional theory (Fig. 10). Our goal is to determine the geometrical details and energetic state of the most stable complex based on thermodynamic point of view.

#### Geometry optimization of $[Zr_6O_4(OH)_4]$ cluster

The  $[Zr_6O_4(OH)_4]$  cluster from UiO-66 (Zr) was assembled by using the crystallographic structure available in literature [44] and has been selected as a model system. Comparison of the average bond distances obtained from X-ray

# Table 3Enaminones 2a-h obtained via reaction ofacetylacetone with amines 1a-hcatalyzed by Sn UiO-66.a



Acetylacetone (1.1 mmol), aniline (1 mmol), catalyst amount (20 mg), methanol (5 mL), temperature (60  $^{\circ}C)$  and time (2 h)



Fig. 8 Effect of recycling of Sn UiO-66 as catalyst in enamination of acetylacetone with aniline

crystallography and optimized structure is shown in Table 4. The structure of  $[Zr_6O_4(OH)_4]$  cluster was optimized at B3LYP/6311 + G\*U Lan12DZ level with no initial symmetry restrictions. The average bond distance between Zr and O atoms at the optimized structure and X-ray crystallography data was found to be 2.28Å and 2.26Å, respectively. The result indicates a good accuracy between experimental and theoretical prediction which is about 0.0099 standard deviation of bond distances at the B3LYP/6311 +  $G^*U$  Lan12DZ, Table 4.

#### Interaction between Tin and [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>] clusters

According to the experimental data, different complexes from different positions of  $[Zr_6O_4(OH)_4]$  cluster and tin (state of Sn<sup>II</sup> and Sn<sup>IV</sup>) have been constructed and were named as Com I, Com II, Com III, Com IV, Com V (Fig. 10a and b). To analyze the interaction between  $[Zr_6O_4(OH)_4]$ cluster and tin (state of Sn<sup>II</sup> and Sn<sup>IV</sup>) in the optimized geometries, the complexation energy ( $\Delta E_{com}$ ) of ten possible complexes that is presented in Table 5 is calculated by using Eq. 1:

$$\Delta E_{\rm com} = E_{\rm opt[Zr6O4(OH4)]/Sn} - \left(E_{\rm opt[Zr6O4(OH4)]} + E_{\rm opt\ sn}\right)$$
(1)

The complexation energy has been calculated as the difference in energies of isolated  $[Zr_6O_4(OH)_4]$  cluster and Tin (state of Sn<sup>II</sup> and Sn<sup>IV</sup>) at their optimized geometry and the optimized complex,  $[Zr_6O_4(OH)_4]/Sn$  (Eq. 1).

 $\Delta E_{\rm com}^{\circ}$  and all thermodynamic data of the complexation including enthalpies ( $\Delta H_{\rm com}^{\circ}$ ), Gibbs free energies ( $\Delta G_{\rm com}^{\circ}$ ) and entropies ( $\Delta S_{\rm com}^{\circ}$ ) are calculated in the solvents for ten formed complexes with Sn<sup>II</sup> and Sn<sup>IV</sup> (Table 5). As seen



Fig. 9 Left: structure of UiO-66 and its (A) proposed idealized and (B, C) defective linker presenting nodes. Right: proposed possible products (I, II, III, IV, V)



Fig. 10 a, b Comparison of the stability order of complexes  $[Zr_6O_4(OH)_4]$ -Sn<sup>IV</sup> and  $[Zr_6O_4(OH)_4]$ -Sn<sup>II</sup> based on the thermodynamic data  $\Delta E_{con}^{\circ}$ 

in Table 5, the calculated results show the negative  $\Delta E_{\rm com}$  value for all possible complexes and also enthalpy result demonstrated the exothermic interaction between tin and  $[{\rm Zr}_6{\rm O}_4({\rm OH})_4]$  cluster. According to thermodynamic data in Table 5, the stability order of different complexes of  $[{\rm Zr}_6{\rm O}_4({\rm OH})_4]/{\rm Sn}$  is Com(II) > Com(I) > Com(II) > Com (IV) > Com(V) for both states of Sn<sup>II</sup> and Sn<sup>IV</sup> (Fig. 10a, b). So, the Com (III) complex was selected as the most stable complex for both states of Sn<sup>II</sup> and Sn<sup>IV</sup>. Comparison result between  $\Delta E_{\rm com}$  of two Com (III)-Sn<sup>II</sup> and Com (III)-Sn<sup>IV</sup> complexes indicates that Sn<sup>IV</sup> is more stable than Sn<sup>III</sup> by about 47.11 kcal/mol. On the other hand, the Com (III)-Sn<sup>IV</sup> complex was determined as the most stable complex between ten possible complexes (Table 5). Therefore, the Com (III)-Sn<sup>IV</sup> complex is formed via connection of SnCl<sub>2</sub>, to the O atom of  $[{\rm Zr}_6{\rm O}_4({\rm OH})_4]$  cluster

and formation of one coordination bond. This observation is consistent with the result of Sn ion obtaind using XPS analysis that shows the existence of Sn with oxidation numer of four. The good agreement between theoretical and experimental results confirms the accuracy of selected method for calculations of these kinds of compounds.

#### Conclusion

In conclusion, a high-performance catalyst for the synthesis of  $\beta$ -enaminones from acetylacetone and primary aromatic amines with SnUiO-66 was prepared. Interestingly, the prepared SnUiO66 as catalyst revealed a remarkable activity in methanol solvent and was recycled up to four consecutive cycles without any notable loss in catalytic

**Table 4** Comparison between some selected experimental (Exp. and<br/>calculated The.) geometrical parameters of  $[\mathrm{Zr}_6\mathrm{O}_4(\mathrm{OH})_4]$  cluster

	Exp.	The.	
Bond distance (Å)			
Zr9-013	2.261	2.267	
Zr6-013	2.261	2.266	
Zr10-012	2.261	2.264	
Zr9-O2	2.261	2.262	
Zr4–O2	2.261	2.261	
Zr4–O5	2.261	2.262	
Zr9–O11	2.261	2.263	
Zr6-011	2.261	2.260	
Zr6-O7	2.261	2.262	
Zr10-07	2.261	2.265	
Zr8–O7	2.261	2.263	
SD		0.0099	
Bond angle (°)			
O2-Zr1-O13	76.60	73.32	
O14–Zr4–O5	76.60	73.27	
O5–O14–Zr4	76.60	73.54	
Zr1-014-Zr9	102.27	100.45	
Zr10-011-Zr6	102.28	107.24	
SD		7.68	

**Table 5** Calculated thermodynamic data for the different optimized complexes at B3LYP/6-311++G<sup>\*\*</sup> U LANL2DZ level, including enthalpies ( $\Delta H_{\rm com}$ ), Gibbs free energies ( $\Delta G_{\rm com}$ ) and entropies ( $\Delta S_{\rm com}$ )

	$^{a}\Delta E_{\rm com}^{\circ}$	$^{c}\Delta H_{\rm com}^{\circ}$	$^{\rm d}\Delta G^{\circ}_{ m com}$	$\Delta S_{\rm com}^{\circ}$
Complex I (Sn <sup>II)</sup>	- 79.88	- 80.47	-74.76	-0.023
Complex II (Sn <sup>II)</sup>	-74.24	-74.83	-69.37	-0.022
Complex III (Sn <sup>II)</sup>	-88.21	- 88.79	- 82.60	-0.025
Complex IV(SnII)	-61.32	-61.91	- 58.44	-0.014
Complex V (Sn <sup>II)</sup>	-24.82	-25.41	-20.45	-0.020
Complex I (SnIV)	-122.54	-123.13	-117.67	-0.022
Complex II (Sn <sup>IV)</sup>	-107.32	- 107.91	- 103.69	-0.017
Complex III (Sn <sup>IV)</sup>	-135.32	- 135.91	- 129.95	-0.024
Complex IV(Sn <sup>IV)</sup>	-73.82	-74.41	-70.93	-0.014
Complex V (Sn <sup>IV)</sup>	-23.15	-23.74	- 18.53	-0.021

 ${}^{a}\Delta E_{com}^{\circ} = Eopt \ [Zr6O4(OH)4] - V - (Eopt \ [Zr6O4(OH)4] + Eopt \ V),$  ${}^{c}\Delta H_{com} = \Delta E + \Delta nRT, {}^{d}\Delta G_{com} = \Delta H - T\Delta S$ 

activity. The XPS and DFT studies on SnUiO66 were consistent with the immobilization of Sn chloride as Sn<sup>IV</sup> on MOF due to coordination with oxygen atoms of UiO-66.

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