

Study of Charge Transfer in Photocatalytic Reduction of C1 OXYGENATED COMPOUNDS

BY

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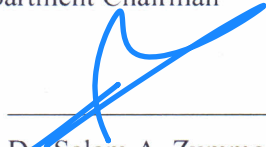
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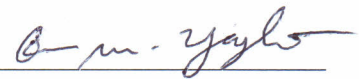
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*To my parents, dear beloved wife and kids, my brothers
& all my friends who gave me inspiration, encouragement, and valuable support for the
success of this journey.*

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LIST OF ABBREVIATIONS

BDC	:	Benzene Di-Carboxylate
CO	:	Carbon Monoxide
CO ₂	:	Carbon Dioxide
DFT	:	Density Functional Theory
DMF	:	<i>N,N</i> -Dimethylformamide
DRS	:	Diffuse Reflectance Spectroscopy
EDX	:	Energy Dispersive X-ray
EPR	:	Electron Paramagnetic Resonance
FTA	:	Femtosecond Transient Absorption
ICP	:	Inductively Coupled Plasma
PXRD	:	Powder X-ray Diffraction
Q _{st}	:	Enthalpy of Adsorption
SEM	:	Scanning Electron Microscope
TEM	:	Transmitting Electron Microscope
TEOA	:	Tri Ethanol Amine
TGA	:	Thermal Gravimetric Analysis
TiCl ₄	:	Titanium Tetra Chloride

ABSTRACT

Full Name : [Mostafa Galal ElDine Zeama].
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Despite progress in the last few years in the study of photocatalytic MOFs, there are questions in need of further investigation, such as the factors affecting the transfer of the charge carriers in the photoactive material, the role of metal doping on the bandgap energy levels, and modifications in the band edges of the photocatalyst. Indeed, a better understanding of the charge transfer mechanism and the factors affecting it will enable the research community to prepare more active photocatalysts that might make use of a greater part of the solar spectrum in producing solar fuels in the future.

This thesis targets the investigation of photocatalytic reduction of CO₂ as an example of oxygenated C1 compounds. In particular, we have prepared photocatalytically-active metal-organic frameworks (MOFs) to investigate their charge transfer mechanism, and further to tune their properties through doping with metal atoms within the secondary building units (SBUs). This allowed for the systematic study of the impact that doping has on the photocatalytic activity of these MOFs.

In this work, we investigated the prepared photocatalytic MOFs for structure and morphology using characterization techniques such as X-ray diffraction and field emission scanning electron microscopy. We studied the charge transfer in a model photoreaction using the prepared MOFs and the effect of changing the metal ions in the SBUs on the photocatalytic activity using different techniques such as femtosecond transient absorption spectroscopy and electron paramagnetic resonance spectroscopy. A computational model for the prepared samples was developed to calculate the band gap and study the effect of the metal exchange on the photocatalytic activity using density functional theory.

For the UiO-66 system, we studied different incorporation methods of titanium metal into UiO-66-NH₂ based frameworks via post-synthetic as well as *in situ* metal exchange. Each method successfully produced crystalline material with enhancement in photophysical and photocatalytic properties. The origin of the enhanced photophysical activity was investigated with electron paramagnetic resonance and ultraviolet-visible diffuse reflectance spectroscopy measurements. A detailed investigation of CO₂ reduction was then carried out with the different UiO-66 catalysts. A remarkable enhancement of the photocatalytic activity was observed by using the UiO-66-NH₂ based frameworks compared to the pristine UiO-66. A nearly doubled photocatalytic activity was obtained by the Ti-Zr mixed MOF materials regardless of the method or the ratio of incorporated titanium metal loading.

For the MIL-125 system, We studied the incorporation of zirconium metal into MIL-125-NH₂ based framework via *in situ* method. The photocatalytic activity investigation of the MIL-125-NH₂ confirms the effect of the amine linker toward better electron transfer

from the organic linker to the central metal as verified by electron paramagnetic resonance spectroscopy. The observed decrease in the electronic bandgap of the MIL-125-NH₂ and its Zr-exchange is confirmed and attributed to the effect of NH₂-functionalization that boosts the reactivity of different MOFs. On the other hand, a detailed study of CO₂ reduction was carried out with the pristine and the modified MOF catalysts to investigate the effect of NH₂ functionalization and Zr-exchange on the photocatalytic CO₂ reduction performance of MIL-125.

DFT calculations were used to study the band structure of the UiO-66 systems, the CO₂ interaction with the MOF surface, and to prepare a computational model of the charge transfer. The observed decrease in the electronic band gaps of the modified UiO-66-based MOFs is supported by density functional theory (DFT)-electronic structure calculations. The DFT-simulations also confirmed the synergistic effect between -NH₂ functionalization and titanium metal incorporation that boosts the reactivity of the respective MOFs. A computational model for the charge transfer was developed describing the light interaction with the MOF. The light is absorbed by the organic linker producing electrons. The produced electrons transfer to the metal cluster, reducing the metal centers. In the presence of the TEOA, the electron transfers from the linker to the TEOA, where the CO₂ reduction takes place. The adsorption of the CO₂ on the catalyst was studied. It was found that the produced formate blocks the active catalyst sites and prevents the reaction from converting CO₂ to higher products.

الملخص العربي

الاسم الكامل: مصطفى جلال الدين زعيمة

عنوان الرسالة: دراسة نقل الشحنات في الاختزال الكيميائي المحفز ضوئياً للمركبات ذات الأكسجين C1

التخصص: فيزياء

تاريخ الدرجة العلمية: ديسمبر 2019

تهدف هذه الرسالة إلى دراسة الاختزال الضوئي لمركبات C1 المؤكسجة. على وجه الخصوص ، سنقوم بإعداد هياكل فلزية عضوية نشطة ضوئياً (MOFs) للتحقيق في آلية نقل الشحنة وزيادة ضبط خصائصها من خلال التطعيم باستخدام ذرات معدنية داخل وحدات البناء الثانوية (SBUs) . سيسمح ذلك بإجراء دراسة منهجية للتأثير الذي يحدثه التطعيم بالمعادن على النشاط التحفيزي الضوئي لهذه MOFs .

على الرغم من التقدم المحرز في السنوات القليلة الماضية في دراسة التحفيزات الضوئية للأطر الضوئية ، هناك بعض الأسئلة التي تحتاج إلى مزيد من البحث ، مثل العوامل التي تؤثر على نقل ناقلات الشحنة في المادة المؤثرة ضوئياً ، ودور المنشطات المعدنية على مستويات الطاقة ذات فجوة الحزمة ، والتعديلات في حواف الحزمة من حفاز ضوئي. في الواقع ، يمكننا فهم أفضل لآلية نقل الشحنات والعوامل المؤثرة عليها من إعداد محفزات ضوئية أكثر نشاطاً قد تستخدم جزءاً أكبر من الطيف الشمسي في إنتاج الوقود الشمسي.

في هذا العمل ، سوف نبحت في MOFs التحفيزية المحصورة للهيكل باستخدام تقنيات التوصيف مثل حيود الأشعة السينية (XRD) ، والمجهر الإلكتروني لانبعاث الانبعاثات (FESEM) . سنقوم بدراسة نقل الشحنة في نموذج ضوئي ضوئي باستخدام MOFs المعدة وتأثير تغيير الأيونات المعدنية في وحدات SBU على نشاط التحفيز الضوئي باستخدام

تقنيات مثل مطيافية الامتصاص العابر الفمتوثاني (FET) وطيف الرنين الإلكتروني . (EPR) سيتم تطوير نموذج حاسوبي رقمي للعينات المعدة لحساب فجوة الشريط ودراسة تأثير التبادل المعدني على نشاط التحفيز الضوئي باستخدام نظرية الكثافة الوظيفية (DFT) .

نأمل أن تمكننا هذه الدراسات من تطوير فهم شامل لكيفية تحسين الحفز الضوئي كوسيلة لدراسة تخزين الطاقة الشمسية في النظم الكيميائية.

CHAPTER 1

INTRODUCTION

In the modern world, dependence on energy increases day by day. The International Energy Agency (IEA) estimates that, in 2013, total global energy consumption was 5.67×10^{20} J, equal to the average power consumption of 18.0 TW[1]. Fig. 1 shows the energy

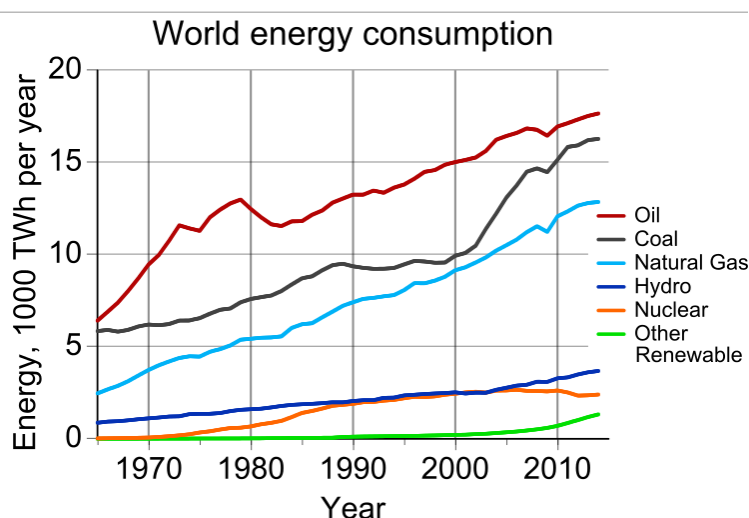


Figure 1. The growth of different types of energy sources [2].

growth for the last few decades. In the 21st century, the dependence on coal as a source of energy grew faster than that of oil and natural gas. Hydropower and renewable energy were the least to grow[2]. One of the biggest problems with fossil fuel energy sources is the emission of CO₂ as a secondary product, raising the issue of the greenhouse effect, which is theorized as a leading contributor to global warming.

To help save the environment, we need to find a clean source of energy that can replace fossil fuels. Also, we need to utilize the CO₂ and convert it into useful compounds. One of the useful techniques to do this is using solar energy (clean energy from the sun). Solar

energy can be converted and used in different ways, such as electrical energy using solar cells[3], thermal energy using solar ovens[4], or chemical energy using photocatalysis[5].

Photocatalysis is a process by which a material catalyzes an oxidation/ reduction reaction by the absorption of a photon. This material is called a photocatalyst. In photoinduced catalysis, the photocatalytic activity (PCA) depends on the ability of the catalyst to create an electron-hole pair that generates free radicals able to undergo secondary reactions.

The photocatalytic reaction takes place in three main steps (Fig. 2):

- 1- Light absorption: the light is absorbed by the photocatalyst where the photon with energy equal to, or greater than, the bandgap energy of the catalyst is used to excite an electron from the valence band to the conduction band leaving a hole in the valence band; this is called charge carrier production.
- 2- Migration of charge carrier: the produced charge carrier starts moving in the material and possibly reaches the photocatalyst surface.
- 3- Oxidation and reduction: the charge carriers at the surface of the catalyst start the reaction of the adsorbed reactants on the surface of the photocatalyst. The conduction band electrons reduce reactants while the valence band holes oxidize reactants.

Using sunlight to photocatalytically reduce such compounds produces so-called solar fuels[6, 7].

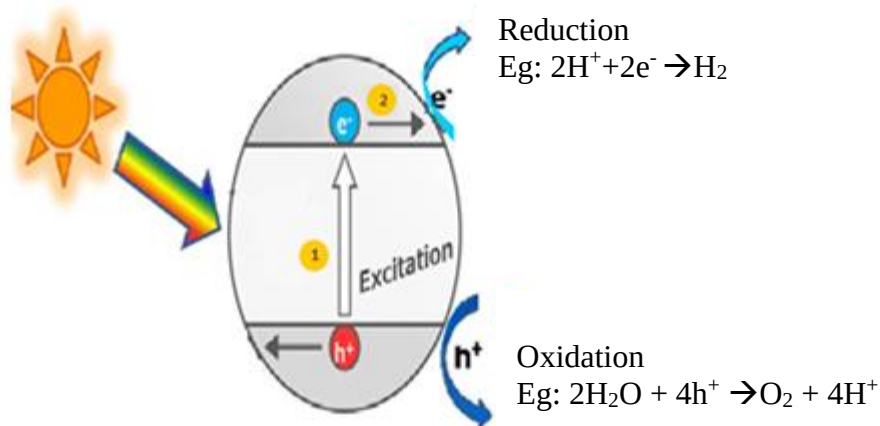


Figure 2. Steps of the photocatalytic reaction, (1) light absorption and charge carrier production, (2) migration of charge carriers, (3) oxidation and reduction reactions

For example, the photoreduction of CO₂ takes place in two main steps:

- 1- The oxidation of a proton donor: this may be water (H₂O) or alcohol (-OH). By oxidizing these materials, protons are produced and are used in the reduction step [8].
- 2- The reduction of CO₂ is a complicated process and may lead to different types of products such as CO, HCOOH, HCHO, CH₃OH, or CH₄ [9].

CO₂ was chosen in this study as an example of the C1 oxygenated compounds. The C1 oxygenated compounds contain one carbon atom with at least one atom of oxygen and hydrogen. Examples of the C1 oxygenated compounds include carbon monoxide (CO), formic acid (HCOOC), formaldehyde (HCHO), and methanol (CH₃OH).

To choose a suitable photocatalyst for carrying out a C1 reduction reaction, the photocatalyst must have an energy gap greater than the energy needed for the reduction

reaction. Moreover, the band edge of the conduction band should be higher in energy than the reduction potential of the reduced reactant, while the valence band edge should be lower in energy than the oxidation potential of the oxidized reactant.

Table 1. The steps of the reduction reaction of CO₂ and the corresponding potential with respect to the normal hydrogen electrode.

	Reaction	E ⁰ _{redox} , V vs. NHE
2H ⁺ + 2e ⁻	————→ H ₂	-0.41
H ₂ O	————→ ½ O ₂ + 2H ⁺ + 2e ⁻	0.82
CO ₂ + e ⁻	————→ CO ₂ ⁻	-1.90
CO ₂ + H ⁺ + 2e ⁻	————→ HCO ₂ ⁻	-0.49
CO ₂ + 2H ⁺ + 2e ⁻	————→ CO + H ₂ O	-0.53
CO ₂ + 4H ⁺ + 4e ⁻	————→ HCHO + H ₂ O	-0.48
CO ₂ + 6H ⁺ + 6e ⁻	————→ CH ₃ OH + H ₂ O	-0.38
CO ₂ + 8H ⁺ + 8e ⁻	————→ CH ₄ + 2H ₂ O	-0.24

The photocatalytic reduction of CO₂ often takes place using photocatalytic metal oxides such as titanium oxide (TiO₂), zinc oxide (ZnO), and copper oxide (CuO). Yet, many practical challenges face metal oxide photocatalysts, including engineering bandgap absorption, increasing charge carrier lifetime, and improving photostability.

To have a practical means for the photocatalytic reduction of C1 oxygenated compounds, it is probably best to have the reaction take place in the gaseous phase as the compounds are produced. However, most metal oxide (nano)photocatalysts usually have surface areas around 100 m²/g[10]. To photoreduce C1 oxygenated compounds in the gaseous phase, high specific area materials with high adsorption capabilities are required.

To improve the photocatalytic performance of the photocatalyst, we need to understand the charge transfer mechanism during the reaction. In a photocatalytic reaction, the charge transfer starts with the light interaction with the catalyst. After the catalyst absorbs the light, the charge carriers are generated and transfer across the catalyst to reach the active sites where the reaction takes place. The charge transfer in the catalyst is controlled by many parameters such as the charge carrier lifetime, charge carrier mobility, and charge carrier diffusion length. For better catalytic performance, we need to understand the charge transfer mechanism to optimize these parameters.

In the 1990s, Yaghi et al. produced a type of porous materials coined metal-organic frameworks (MOFs)[11]. MOFs are constructed from metal oxide units connected with organic linkers to form three-dimensional porous systems. Specific surface areas reach up to $\sim 10,000 \text{ m}^2/\text{g}$ [12]. Among the many MOFs reported, Ti- and Zr- based MOFs are advantageous for practical applications as they are stable in both water and alcohol[13]. Furthermore, these MOFs can be functionalized to improve their CO_2 adsorption capabilities. These qualities have allowed MOFs, in general, to be used in different applications such as gas storage, gas separation, catalysis, sensors, and drug delivery[14].

In photocatalytic applications, MOFs have the advantage of tuning light absorption by modification of the organic linkers by adding functional groups to the linkers such as amines (NH_2), or by coordinating with complexes like $\text{Ru}(\text{bpy})_2$ or the metal ions; this potentially allows for more efficient use of the solar spectrum[15]. Studies have shown the use of the organic linkers as antennas to absorb light and activate the metal clusters by the linker-to-metal cluster charge transfer process[16].

One interesting MOF is UiO-66-NH₂. UiO-66 was first prepared using ZrCl₄ and BDC linker. By changing the linker to BDC-NH₂, the UiO-66-NH₂ was obtained through an isorecticular functionalization technique of the parent UiO-66[17]. The structure of the UiO-66-NH₂ is shown in Fig. 3 where it is formed by cores of Zr₆O₄(OH)₄. These cores create polyhedrons that are connected with (–CO₂) from the dicarboxylic acids to form Zr₆O₄(OH)₄(–CO₂)₁₂ clusters. The clusters are linked with the organic linkers forming a three-dimensional structure[18]. The UiO-66-NH₂ is a highly porous material with associated high thermal and chemical stabilities[17, 19].

Special doping with Ti(IV) into the SBUs of the UiO-66-NH₂ has been typically used

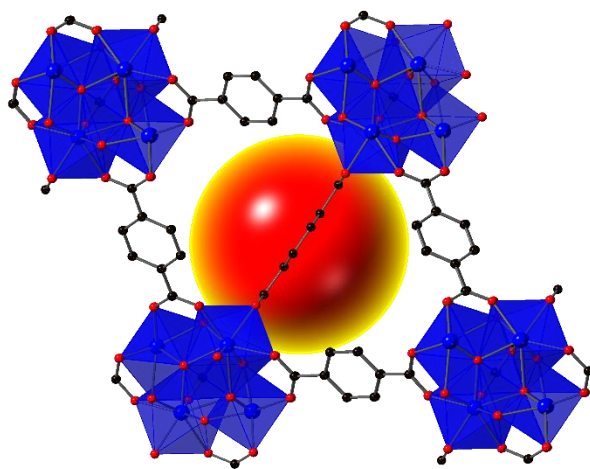


Figure 3. Crystal structure of UiO-66. The red ball represents the free space in the framework.

for studying the increase in the porosity and the CO₂ uptake[20]. However, we believe that this doping could be useful for changing the bandgap of the UiO-66-NH₂ by changing the position of the conduction band edge.

Another interesting MOF is MIL-125. It is one of the promising photocatalytic MOFs[21]. This highly porous titanium-based MOF has a basic unit of $\text{Ti}_8\text{O}_8(\text{OH})_4(-\text{CO}_2)_6$, which forms cyclic octamers by sharing between corner or edge octahedral titanium units. Each octamer is connected to 12 other octamers via the organic linkers (BDC), resulting in the formation of a quasi-cubic tetragonal structure with two cage types: octahedral (12.55 Å) and tetrahedral (6 Å), accessible through narrow triangular windows of 6 Å (Fig. 4)[21].

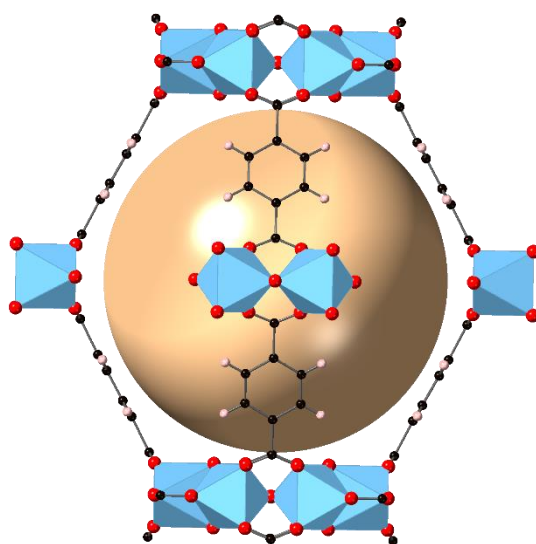


Figure 4. Crystal structure of MIL-125, The large sphere in the middle represent the pore volume.

The structure of MIL-125-NH₂ is the same as that of MIL-125 and is prepared by the same method, but with replacing the organic linker (BDC) by (BDC-NH₂). The (-NH₂) group leads to a decrease in pore size of the MOF (from 12.55 Å to 12.00 Å), which in turn leads to a decrease in its surface area. Moreover, it was found that MIL-125-NH₂ is highly stable in water; also, it has higher hydrophilicity than MIL-125; for the CO₂ adsorption, MIL-125-NH₂ has a moderate capacity (96 mg/g at 298 K) – for MIL-125 the capacity is (132 mg/g at 298 K)- due to the decrease in the surface area, with a low heat of adsorption,

which means that the CO₂ desorption is relatively easy. It was studied for 550 min at 298 K over four consecutive cycles to prove the ability of adsorption-desorption of CO₂[22]. Also, the amine has a positive impact on the photoabsorption properties of the MIL-125 as it shifts the photoabsorption to the visible region (red-shift)[23].

Although previous studies on MIL-125-NH₂ indicates that Ti³⁺ is involved in CO₂ photocatalytic reduction, the full photocatalytic process remains unclear[24-28]. To synthetically enhance the photocatalytic activity of the MOFs, we need a better understanding of the photocatalytic reduction of CO₂ with redox-active metal centers and elucidate factors influencing photocatalytic performance.

In this thesis, we will study the effect of functionalizing MOFs, and doping the metal atoms in the base units with different concentration and study the effect on the charge transfer for photocatalytic reduction of CO₂. In the next chapter, we will briefly discuss the experimental techniques used in this research and how each technique can be used in our study. In chapter 3, we will study the UiO-66 system. We will study different incorporation methods of titanium metal into the UiO-66-NH₂ framework via post-synthetic as well as *in situ* metal exchange. Also, we will study the wrapping of UiO-66-NH₂ around TiO₂ nanoparticles to use the TiO₂ photocatalytic activity and the UiO-66-NH₂ ability to adsorb CO₂ and allow easy access to the TiO₂ nanoparticles. The origin of the enhanced photophysical will be investigated with electron paramagnetic resonance and diffuse reflectance spectroscopy measurements. A detailed investigation of CO₂ reduction is then carried out with the different MOF catalysts. In chapter 4, we extend this study to the MIL-125 system. We study the incorporation of zirconium metal into MIL-125-NH₂ based

framework via *in situ* method. The photocatalytic activity investigation by electron paramagnetic resonance (EPR) spectroscopy. A detailed study of CO₂ reduction is carried out with the pristine and the modified MIL-125 catalysts to investigate the effect of NH₂ functionalization and Zr-exchange on the catalytic CO₂ reduction. Chapter 5 deals with the computational model of the CO₂ interaction with the MOF and the possible mechanism of the photocatalytic reduction of CO₂ to value-added products. In this chapter, we are going to start with the electronic structure of the UiO-66 series and study the effect of the different modifications on the bandgap. Then we will study the ground state and the first excited state charge densities, by calculating the difference in the charge densities we can get an insight on the light interaction with the catalyst and the charge transfer in the catalyst. At the end, we will study the adsorption site and energies for the reactant and products for the CO₂ reduction reaction, which will explain the CO₂ photoreduction reaction. Finally, in chapter 6, we conclude our findings and suggest future work.

CHAPTER 2

EXPERIMENTAL TECHNIQUES

In this chapter, we are going to discuss the experimental techniques used in this work, starting with the different synthesis procedures for each compound, then the experimental techniques used for the structural characterization, photoactivity measurements, and photocatalytic evaluation.

2.1 Synthesis

MOF synthesis is a chemical reaction that needs energy to take place. Usually, MOF is synthesized using solvothermal reaction, where the synthesis takes place in a solvent, and the energy required for the reaction is in the form of heat energy. The reaction takes place at temperatures ranging from room temperature to approximately 250 C. The energy form can vary between electric energy, electromagnetic energy, mechanical waves, or mechanically [29]. The energy source is closely related to the duration, pressure, and energy per molecule that is introduced into a system [30], and each of these parameters can have a strong influence on the product formed and its morphology [31].

In the microwave-assisted synthesis, the energy is introduced by microwave irradiation. This synthesis is a well-established method in synthetic chemistry [32] but has been mainly used in organic chemistry. The microwave-assisted synthesis relies on the interaction of electromagnetic waves with mobile electric charges. These can be polar solvent molecules/ions in a solution or electrons/ions in a solid.

The electrochemical synthesis of MOFs was first reported in 2005 by researchers at BASF[33]. Their main objective was the exclusion of anions, such as nitrate, perchlorate,

or chloride, during the syntheses, which are of concern to large-scale production processes. Rather than using metal salts, the metal ions are continuously introduced through an anodic dissolution to the reaction medium, which contains the dissolved linker molecules and a conducting salt.

In mechanochemical synthesis, the mechanical breakage of intramolecular bonds followed by a chemical transformation takes place. Mechanochemistry has a long history in synthetic chemistry[34], and it has recently been employed in multicomponent (ternary and higher) reactions to form pharmaceutically active cocrystals and in inorganic solid-state chemistry, organic synthesis, and polymer science [35, 36]. Its use for the synthesis of porous MOFs was first reported in 2006 [37].

Sonochemistry deals with the chemistry that takes place upon application of high-energy ultrasound to a reaction mixture[30].

After the MOF is synthesized, the washing process takes place. The washing process aims to get rid of the remaining solvent from the reaction and the unreacted organic linkers or metals that may have been blocking the MOF pores or precipitated inside the pores. The washing process usually takes place using the solvent used during the MOF preparation to get rid of the unreacted materials, then another solvent (with a low boiling point) is used to get rid of the solvent traces from the preparation and the first washing step.

After washing the prepared MOF, it is heated to evaporate the solvent and the water molecules that may be adsorbed in the MOF pores during the synthesis and the washing processes. This step is known as the MOF activation process. The MOF is usually heated up to 100 °C or higher (depending on the thermal stability of the MOF and the boiling point of the solvent used in the washing step) for one or more days under vacuum.

2.1.1 Materials.

All chemicals were used as received without further purification. Zirconium(IV) chloride, (ZrCl_4 , 99.99% purity), 2-aminoterephthalic acid (99% purity), terephthalic acid (99% purity), methanol (99.9% purity), *N,N'*-dimethylformamide (99% purity), Ti(IV) isopropoxide (97%), and glacial acetic acid (99%) were purchased from Sigma Aldrich Co. Triethanolamine (98%) was purchased from Lobal Chemie. Acetonitrile (99.93%) was purchased from Scharlau. Ethyl acetate (99%) was purchased from Eurostar. For gas sorption measurements, ultrahigh purity grade nitrogen (99.999%), helium (99.999%), and high purity CO_2 (99.9%) were obtained from Abdullah Hashem Industrial Co., Dammam, Saudi Arabia.

2.1.2 Synthesis of the UiO-66 and UiO-66-NH₂.

UiO-66 and UiO-66-NH₂ were synthesized according to the reported procedure [38]. For UiO-66, we placed 40 mL of DMF in a 150 mL high-pressure glass jar. The mixture was sonicated for 30 min, terephthalic acid (109.6 mg, 0.602 mmol) and ZrCl_4 (133.6 mg, 0.573 mmol)]. Then, 2.8 mL of acetic acid was added, and the mixture was sonicated for an additional 30 min. The mixture was subsequently heated at 120 °C in an oven for 25 h. The resulting white microcrystalline powder was then separated by centrifugation and washed with DMF (3×10 mL per d for three days) and methanol (3×10 mL per d for three days). After washing was completed, the sample was activated by heating under vacuum (10^{-2} Torr) for 1 d at 100 °C. The same procedure was used for the UiO-66-NH₂ by replacing terephthalic acid with 2-aminoterephthalic acid.

2.1.3 Synthesis of $\text{TiO}_2 \subset \text{UiO-66-NH}_2$.

The ($\subset$) sign means the incorporation of the first material inside the second one. Here we aim to incorporate the TiO_2 nanoparticle inside the UiO-66-NH_2 . Nanoparticles of TiO_2 were first prepared following a modified solvothermal method previously reported[39]. For this, $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ (0.5 mL, 1.69 mmol) was added to a mixture of distilled water (10 mL) and acetic acid (100 μL). The mixture was sonicated for one h, then heated at 180 °C in an isothermal oven for one day. The white precipitate was then collected (73% yield). To synthesize $\text{TiO}_2 \subset \text{UiO-66-NH}_2$, TiO_2 nanoparticles (40 mg, 0.501 mmol) were dispersed in 40 mL of DMF in a 150 mL high-pressure glass jar. The mixture was sonicated for 30 min, at which time the precursors to UiO-66-NH_2 [2-aminoterephthalic acid (109.6 mg, 0.602 mmol) and ZrCl_4 (133.6 mg, 0.573 mmol)] were added to the TiO_2 suspension. Then, 2.8 mL of acetic acid was added, and the mixture was sonicated for an additional 30 min. The mixture was subsequently heated at 120 °C in an oil bath for 25 h with continuous stirring at 500 rpm. The resulting yellow microcrystalline powder was then separated by centrifugation and washed with DMF (3×10 mL per day for three days) and methanol (3×10 mL per day for three days). After washing was completed, the sample was activated by heating under vacuum (10^{-2} Torr) for one day at 100 °C.

2.1.4 Post synthetic metal exchange [$(\text{Zr}_{1-x}/\text{Ti}_x)\text{UiO-66-NH}_2$], where $x = 0.07, 0.08, 0.1, 0.12, 0.13$]:

In the post-synthetic metal exchange, the exchange ratio depends on the exchange time. In our work, the exchange was done for different times (1day to 8days). After five

days of exchange, the crystal structure of the MOF was destroyed, so we just characterized the post-synthetic exchange samples from 1 day to 5 days. The general procedure for the post-synthetic exchange is as follows: UiO-66-NH₂ (274 mg) was added with TiCl₄·2THF (340 mg, 1.02 mmol) in DMF (7 mL) in a 20 mL scintillation vial. This mixture was then heated at 120 °C in an isothermal oven for 1 day (exchange time). The resulting yellow microcrystalline powder was then separated by centrifugation and washed with DMF (3 × 10 mL per day for three days) and methanol (3 × 10 mL per day for three days). After washing was completed, the samples were activated by heating under vacuum (10⁻² Torr) for 1 d at 100 °C. Modification of the post-synthetic exchange process was carried out by following the same procedure, but with different exchange times (1 day to 8 days).

2.1.5 *In situ* metal exchange [(Zr_{1-x}/Ti_x)UiO-66-NH₂], where x = 0.27, 0.59]:

In the *in situ* metal exchange process, the exchange ratio depends on the ratio between the metal salts added in the precursor. In this work, we have done two different weight ratios between the Ti salt and Zr salt (1:1) and (1:2). The *in situ* exchange process was carried out with slight modifications to a reported procedure[38]. ZrCl₄ (334 mg, 1.43 mmol) and 2-aminoterephthalic acid (274 mg, 1.51 mmol) were dissolved in a 200 mL scintillation vial containing a solvent mixture of 100 mL DMF and 7 mL acetic acid. Once added, the solids were completely dissolved after sonication for 10 min. TiCl₄·2THF (334 mg, 1.00 mmol) was then added to the solution and sonicated for 30 min. The solution was heated for five days at 120 °C in an isothermal oven. The resulting yellow microcrystalline powder was then separated by centrifugation and washed with DMF (3 × 10 mL per day for three days) and methanol (3 × 10 mL per day for three days). After washing was

completed, the sample was activated by heating under vacuum (10^{-2} Torr) for one day at 100 °C. The *in-situ* exchange process was modified by changing the amount of $\text{TiCl}_4 \cdot 2\text{THF}$ added, from 334 mg (1.00 mmol) to 167 mg (0.501 mmol).

2.1.6 Synthesis of the MIL-125

MIL-125 was synthesized according to the reported procedure with some modifications[40]. 1.5 g of BDC was added to 27 mL of DMF and sonicated for 10 min. 0.78 mL of Ti isopropoxide was added to the mixture and sonicated for 20 min. The mixture was then transferred to a 50 mL Teflon tube. Finally, 3 mL of methanol was added to the mixture, and the Teflon tube was placed in an autoclave inside the oven at 150 °C for 25 hours. The resulted powder was separated with centrifuge and washed with DMF (3 times/day for three days) to remove the unreacted materials and then washed with methanol (3 times/day for three days) to remove the excess of DMF. The sample was then activated by heating at 120 °C under vacuum for one day. The resulted microcrystalline powder was then collected and characterized.

2.1.7 Synthesis of the MIL-125-NH₂

The same procedure was used to synthesize MIL-125-NH₂ by changing the BDC with NH₂-BDC (2.16 g), and the same procedure was used.

2.1.8 Synthesis of ZrO₂@MIL-125-NH₂

Nanoparticles of ZrO₂ were first prepared following a modified solvothermal method. For this, ZrCl₄ (0.7 g) was added to distilled water (10 mL). The mixture was sonicated for 5 min, then heated at 180 °C in an isothermal oven for 1 d. The white precipitate was then collected (82% yield). To synthesize ZrO₂@MIL-125-NH₂, ZrO₂ nanoparticles (5.5 mg)

were dispersed in 13.5 mL of DMF in a 20 mL microwave vial. The mixture was sonicated for 30 min, at which time, the 2-aminoterephthalic acid (1.08g) was added to the TiO₂ suspension. The system was then closed, vacuumed, and kept under N₂ atmosphere. After that, Ti-isopropoxide (0.39 mL) was added, and the system was sonicated for 10 min. Finally, methanol (10 mL) was introduced to the system, and the mixture was sonicated for an additional 30 min. The mixture was subsequently heated at 150 °C in an oil bath for 48 h with continuous stirring at a rate of 500 rpm. After this time elapsed, the resulting yellow microcrystalline powder was then separated by centrifugation and washed with DMF (3 × 10 mL per day for three days) and methanol (3 × 10 mL per day for three days). After washing was completed, the sample was activated by heating under vacuum (10⁻³ mTorr) for one day at 120 °C.

2.1.9 *In situ* metal exchange [(Ti_{1-x}/Zr_x)Mil-125-NH₂], where x = 0.08, 0.25].

The *in situ* exchange process was carried out following the same procedure as in section 2.1.6 with slight modifications. Here a 2.16 g of NH₂- BDC was added to 27 mL of DMF and sonicated for 10 min. 0.78 mL of Ti isopropoxide was added to the mixture and sonicated for 20 min. During the sonication, 123 mg of ZrCl₄ was added to the mixture. The mixture was then transferred to a 50 mL Teflon tube. Finally, 3 mL of methanol was added to the mixture, and the Teflon tube was placed in an autoclave inside the oven at 150 °C for 25 hours. The resulted powder was separated with centrifuge and washed with DMF (3 times/day for three days) to remove the unreacted materials and then washed with methanol (3 times/day for three days) to remove the excess of DMF. The sample was then activated by heating at 120 °C under vacuum for one day. The resulted microcrystalline

powder was then collected and characterized. The *in-situ* exchange process was modified by changing the amount of ZrCl_4 added; this amount three from 123 mg to 61 mg.

2.2 Characterization Techniques

The proper characterization of materials helps in understanding the material properties and behaviors. There are a wide variety of characterization techniques in the areas of Microscopy, Spectroscopy, and thermal techniques. Each technique studies different aspects of the material. In our work, we used the characterization techniques to ensure the successful preparation, the morphology, the stability, and the composition of our prepared catalysts.

2.2.1 Powder X-ray Diffraction (PXRD)

Powder X-ray diffraction is an analytical technique used for phase identification of a crystalline material and can provide information on unit cell dimensions[41, 42]. The analyzed material is grounded, homogenized, and the average bulk composition is determined. When an X-ray is shined on a crystal, it diffracts in a spectrum characteristic of the structure. A diffraction pattern plots intensity against the angle between the source and the detector (Fig. 5a).

Basic concepts for PXRD

Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. Since most materials have unique diffraction patterns, crystals can be identified by using a database of diffraction patterns. The purity of a sample can also be determined from

its diffraction pattern, as well as the composition of any impurities present[43]. A diffraction pattern can also be used to determine the lattice parameters of a crystal structure[44].

X-ray diffraction is based on the constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. X-rays are partially scattered by atoms when they strike the surface of the powder sample. The part of the X-ray that is not scattered passes through to the next layer of atoms, where again part of the X-ray is scattered, and part passes through to the next layer. The multiple scattering causes an overall diffraction pattern, similar to how a grating diffracts a beam of light. For X-ray to diffract, the sample must be crystalline, and the spacing between atom layers must be close to the X-ray wavelength. If beams diffracted by two different layers are in phase, constructive interference occurs, and the diffraction pattern shows a peak. However, if they are out of phase,

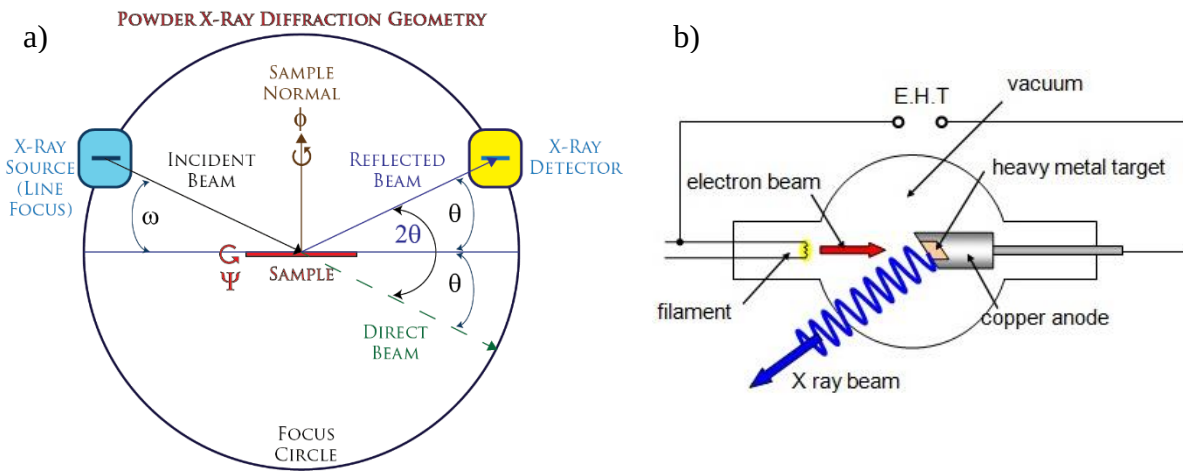


Figure 5. a) Shows a schematic diagram of the PXRD showing the components of the PXRD, the X-ray optical path, and the angle measurement between the X-ray source and detector. b) A schematic diagram of the X-ray source showing the X-ray gun and its components.

destructive interference occurs. Diffraction peaks only happen when conditions satisfy Braggs Law [45]

$$\sin \theta = \frac{n \lambda}{2 d}$$

Where (n) is a positive integer, (d) is the lattice spacing, and (λ) is the wavelength of the X-ray source. This law relates the wavelength of X-ray to the diffraction angle and the lattice spacing in a crystalline sample. The diffracted X-rays are detected by a detector, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns.

The particle size of the powder can also be determined by using the Scherrer formula [46, 47],

$$t = \frac{k \lambda}{\sqrt{B_m^2 - B_s^2} \cos \theta}$$

Where (k) is a constant depending on the material, (B_m) is the observed peak width, (B_s) is the bulk material peak width, and (t) gives a measure of the particle size.

X-ray diffractometers consist of three essential elements (Fig. 5a): an X-ray source, a sample holder, and an X-ray detector. X-rays source is a cathode ray tube (Fig. 5b). Cathode ray tube generates X-rays by heating a filament to produce electrons, accelerating

the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to free inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being K_α and K_β . The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochromators, is required to produce monochromatic X-rays needed for diffraction. Copper is the most common target material for X-ray diffraction, with CuK_α radiation = 1.5418 Å[48].

These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs, and a peak in intensity is observed. A detector records and processes the X-ray signal. The signal is then converted to a count rate, which is then sent for data storage and display.

In this work, Rigaku MiniFlex II X-ray diffractometer (XRD) with Cu K_α radiation (λ = 1.5418 Å) was used for PXRD spectroscopy.

2.2.2 Scanning Electron Microscope (SEM)

The scanning electron microscope uses electrons for image formation instead of the light that is used in ordinary optical microscopes (Fig. 6). The electron beam is generated from an electron gun containing a tungsten filament. The beam is controlled using a combination of electric and magnetic fields. These electric and magnetic fields can focus the beam and control the path of the focused beam to scan the sample. These parts should

be under a high vacuum to increase the resolution of the image. If air molecules were found in the path of the beam, the beam electrons would be scattered[49].

How does the SEM work?

1- **Electron beam generation:** When the electric current passes through the tungsten filament, thermal energy is generated. When the thermal energy is more than the work function ($E_{th} > \Phi$) of the tungsten, electrons are produced. The produced electrons are then accelerated under a potential difference towards the anode forming an electron beam.

2- **Electron beam control:** like the optical microscope, SEM needs lenses to focus the electron beam. As the electrons cannot pass through the glass, electromagnetic lenses are used. The charged electrons can be affected by the electromagnetic field, so coils inside a metal pole are used as the electromagnetic lens[50]. There are two types of

electromagnetic lenses in the SEM, the condenser lens and the objective lens. The condenser lens defines the beam size. It is placed near the electron gun; this lens converges the electron beam before the electron beam cone opens again. The objective lens converges the beam coming from the condenser lens and focus it on the sample. Scanning coils are used to raster the beam onto the sample[48].

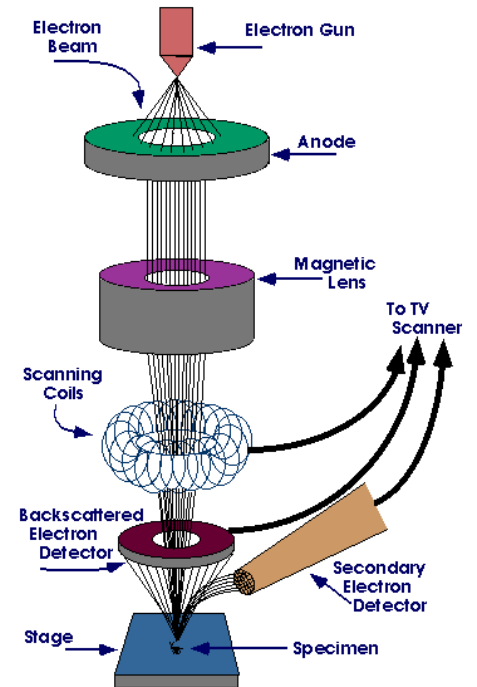


Figure 6. Schematic diagram of the SEM showing its components, the electron beam path from the electron gun to the detector, and different types of detectors.

3- Sample electron interaction: The

high energy electron beam that interacts with the sample produces three types of beams[48]; backscattered electron beam (BSE), secondary electron beam (SE), and characteristic X-ray (Fig. 7). Backscattered electrons belong to the primary electron beam and are reflected back after elastic interactions between the beam and the sample. The scattering occurs by atoms below the surface of the sample and shows

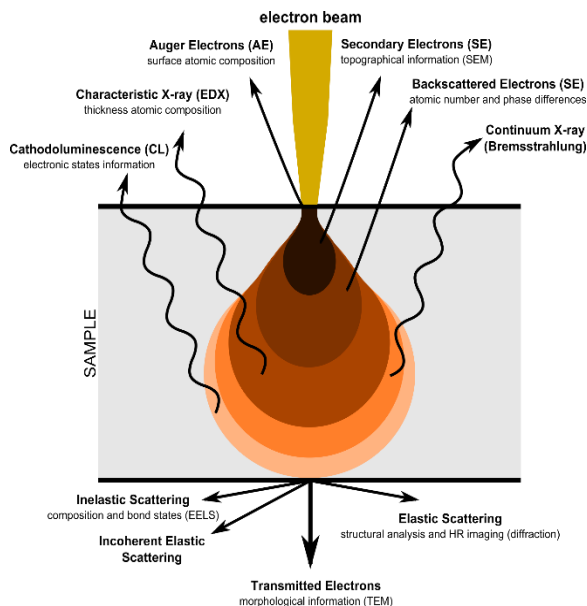


Figure 7. Types of electrons produced from the interaction of the electron beam with the sample.

high sensitivity to differences in the atomic number. On the other hand, secondary electrons originate from the atoms of the sample. They are a result of inelastic interactions between the electron beam and the surface of the sample. It gives detailed information about the surface morphology of the sample. The produced X-ray from the electron-sample interaction is used for the elemental analysis of the sample. Since each material produces characteristic X-ray differs from the other samples, the detection of the energy of the produced X-ray gives information about the composition of the sample.

In this work, a Tescan LYRA3 dual-beam field emission scanning electron microscope (FE-SEM) at an accelerating voltage of 10 kV was used to determine the particle size and morphology.

2.2.3 Gas adsorption isotherm

In 1985 IUPAC issued a manual on “Reporting Physisorption Data for Gas/Solid Systems”. This manual discussed the use of gas sorption as a tool in determining sample porosity and surface area[51]. Since then, gas adsorption is a well-established method for surface area measurement and pore size determination of porous solids.

Over the past years, nonporous materials have been widely developed with different types of pore sizes and structures such as mesoporous molecular sieves[52], carbon nanotubes[53], and nanohorns[54] and materials with categorized pore structures[55]. The characterization of these newly developed materials has led to the development of experimental protocols for the adsorption of various subcritical fluids such as nitrogen (at 77 K) and argon at (87 K). The analysis of the data obtained from these measurements has developed new techniques based on DFT calculations and the molecular simulations to analyze the pore structure[56].

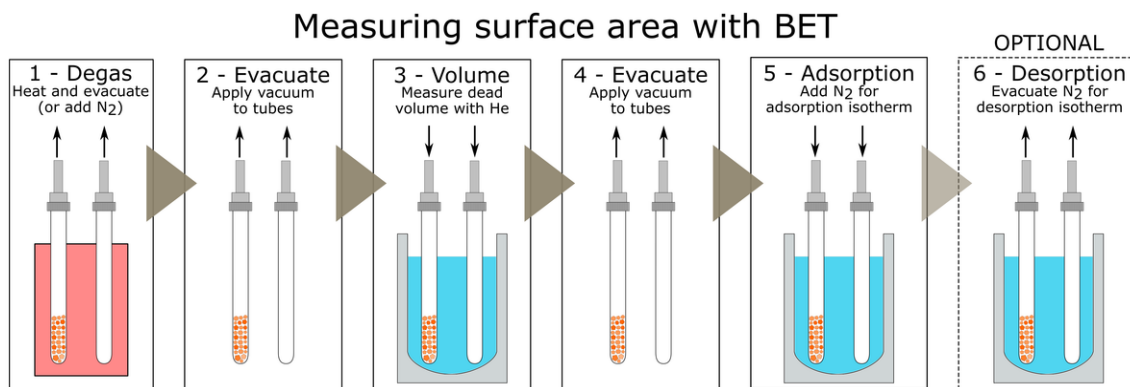


Figure 8. Gas adsorption system diagram showing the BET calculation steps for both tubes, the gas tube (empty tube) and the reference tube (colored tube).

Definitions and terminologies

- **Adsorption:** the attachment of molecules or atoms (adsorbate) to a surface of other material (adsorbent).

- **Absorption:** the penetration of the adsorbate material through the surface layer of the adsorbent.
- **Physisorption:** occurs when the attachment of the adsorbate material to the adsorbent surface takes place by physical forces (attractive force, Van der Waals forces, polarization, field-dipole, field gradient-quadrupole). It does not include the formation of chemical bonds.
- **Chemisorption:** It takes place when there is a chemical bond formation between the molecules of the adsorbent and the adsorbate.
- **The energy of liquefaction (E_L):** is the energy released from the conversion of the gas to the liquid. In our work, it is defined as the energy released from the gas molecule condensation in the multilayer adsorption.
- **Single-layer formation energy (E_s):** is the energy released from the formation of a single layer of the adsorbate on the adsorbent surface.
- **Gibbs free energy (ΔG):** the maximum amount of non-expansion work that can be extracted from a thermodynamically closed system
- **Helmholtz free energy (ΔH):** a thermodynamic potential that measures the useful work obtainable from a closed thermodynamic system at a constant temperature and volume.
- **Internal energy (U):** It is the energy necessary to create or prepare the system in any given state, but does not include the kinetic energy of motion of the system as a whole,

nor the potential energy of the system as a whole due to external force fields which include the energy of displacement of the system's surroundings.

- **Avogadro number (N_A):** is the number of molecules that are contained in one mole of the material. In SI units, it is equal to $6.02 \times 10^{23} \text{ mol}^{-1}$.
- **Pressure (P):** the force applied perpendicular to the surface of an object per unit area over which that force is distributed.
- **Capillary condensation:** is the adsorption of multilayer from the adsorbate into the pores of the adsorbent until the adsorbent pore is filled by the condensed adsorbate particles.
- **Micropores:** pores with a width of less than 2 nm.
- **Mesopores:** pores with a width between 2 nm to 50 nm.
- **Macropores:** pores with a width greater than 50 nm.

The isotherm is represented as the uptake amount of gas adsorbed (in mol/g) – mole of gas and gram of catalyst – as a function of relative pressure of vapor pressure of liquid nitrogen (P/P_0) where (P_0) is the pressure in the standard cell. According to the IUPAC classification 1985, there are 6 types of isotherms (Fig. 9) depending on the sample isotherm behavior in the gas adsorption and desorption processes[56]

Types of isotherm

Type-I isotherm: Here, the adsorbent exhibits a significant increase in the uptake at relatively low pressure and immediately saturates in the absorption as the pressure

approaches the saturation pressure (P_0). This behavior is shown when the energy of liquefaction of the adsorbate is negligible compared to the single-layer formation energy ($E_L \approx 0$), which allows the adsorbate to form a single layer on the adsorbent surface. Once the layer is formed, no more adsorbate material will attach to the adsorbent, which causes saturation in the isotherm.

Type-II isotherm: Here, the adsorbent shows a small increase in the uptake at low pressure, then saturation is achieved, and as we approach the saturation pressure, the absorption increases sharply. This behavior is shown when the energy of liquefaction of

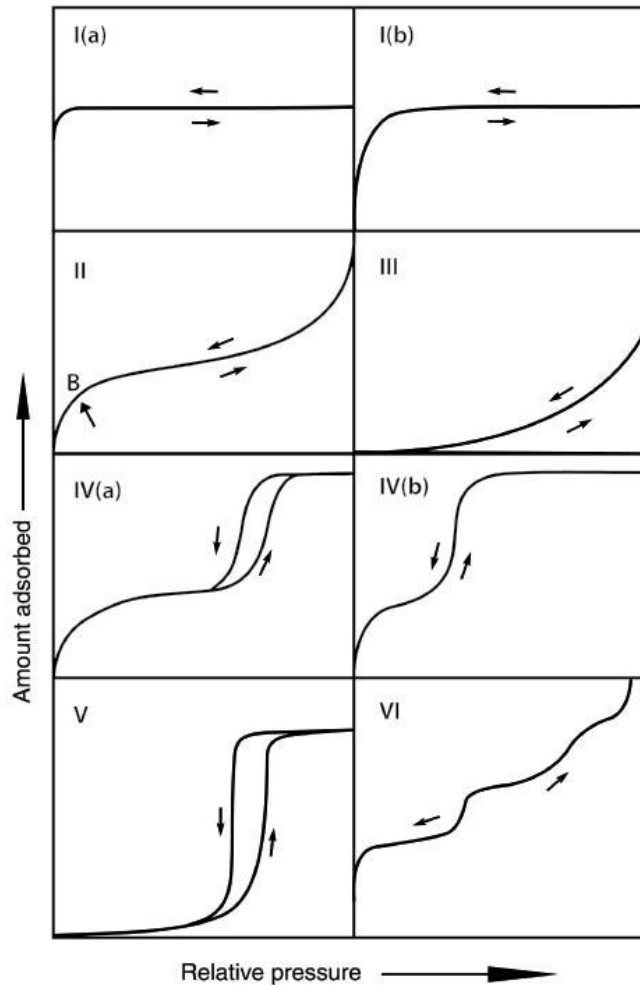


Figure 9. Graphical representation of amount adsorbed and the relative pressure for all types of isotherms.

the adsorbate is smaller than the single-layer formation energy ($E_s > E_L$). At low pressure, as the pressure increases, the uptake increases until the first layer of the adsorbate is formed on the adsorbent surface. Then a small saturation takes place before the adsorbate molecules start forming the multiple layers. This explains the sharp increase in the uptake as the pressure approaches the saturation pressure.

Type-III isotherm: In this case, the uptake increases as the pressure increases, and there is no saturation. This isotherm is obtained when the energy of liquefaction of the adsorbate is greater than the single-layer formation energy ($E_s < E_L$). So, as the pressure increases, the adsorbate molecules start condensation, and no single layer is formed.

Type-IV isotherm: This isotherm is obtained when there are some pores in the adsorbent surface. In the low-pressure region, the isotherm shows a behavior like *type-II* behavior, but as the pressure increases, the uptake reaches another saturation region as the pressure reaches the saturation pressure. This change in the isotherm is due to the capillary condensation process. At the beginning of this isotherm, the first layer is formed, then the adsorbate condensation takes place ($E_s > E_L$). After the formation of the single-layer the adsorbate molecule starts filling the pores in the surface of the adsorbent, the small pores are filled before the large pores. After the pores are filled, the saturation of the uptake is achieved.

Type-V isotherm: Similar to type-IV, this isotherm is obtained when there are some pores in the adsorbent surface. In the low-pressure region, the isotherm shows a type-III behavior, but as the pressure approaches the saturation pressure, the uptake saturation is achieved. This change in the isotherm is due to the capillary condensation process. Here

no single layer is formed, and the adsorbate condensation takes place from the beginning ($E_s < E_L$).

Type-VI isotherm: This isotherm represents the layer by layer adsorption on a nonporous adsorbent. The step height represents the capacity of each layer, while the step sharpness depends on the temperature of the system.

Origin of the hysteresis

Hysteresis takes place between the adsorption and the desorption curves in some isotherm cases. The hysteresis in the multilayer physisorption isotherm is combined with capillary condensation. The metastability of the multilayer adsorbed on the surface of the adsorbent cause the delay of the condensation in the open geometry pore (cylindrical pore). This delay results in the formation of an adsorption branch that is not in thermodynamic equilibrium. Since the desorption doesn't contain layer formation and it only depends on the liquid-vapor transition, the desorption branch is in a thermodynamic quasi-equilibrium state[56]

Surface area calculation

Many catalysts have been developed to calculate the surface area and porosity of the samples from the gas isotherm. From these catalysts, the BET model is considered one of the most reliable catalysts for the surface area calculation. BET is the initials of the three scientists' names who developed the mathematical model required for the measurement: Brunauer, Emmett, and Teller[57].

This theory is based on Langmuir's theory [58] for the monolayer adsorption but with some extensions. The model is based on the following assumption:

1. The multilayer formation for the adsorbate on the adsorbent can go infinitely.
2. The adsorbate molecule interaction is in short-range, which means that the molecules interact with adjacent layers only.
3. The Langmuir theory can be applied to each layer.

The BET equation is

$$\frac{P}{n_a(P_0 - P)} = \frac{1}{n_m C} + \frac{(C - 1)P}{n_m C P_0}$$

Where (P) is the pressure, (P₀) is the saturation pressure, (n_a) is the total uptake of the gas, (n_m) is the monolayer capacity, and (C) is the BET constant.

The data is presented as a relation between $\left(\frac{P/P_0}{n_a(1-P/P_0)}\right)$ with (P/P_0) . The BET range of values should be linear. From the slope and the y-intercept, the values of (n_m) and (C) can be calculated. The selection of the linear range is based on the following

1. The BET constant (C) must be positive, as any negative y-intercept indicates that the points are outside the BET range.
2. The relative pressure (P/P₀) must be increasing.

The total surface area (S_t) can be calculated as follows:[59]

$$S_t = \frac{n_m N_a s}{V}$$

Where (N_a) is Avogadro's number, (s) is the cross-sectional area of the adsorbate, and (V) is the molar volume of the adsorbate gas.

The BET specific surface area is calculated as follow

$$S_{BET} = \frac{S_t}{m}$$

Where (m) is the total mass of the adsorbent sample. Nitrogen is the most used adsorbate, because it is inert, well-known size (0.162 nm^2), and abundant gas. So, the N_2 -isotherm is usually done with nitrogen gas at 77 K[56].

In our research, the samples' porosity and absorptivity were investigated by low-pressure N_2 adsorption isotherms on a Quantachrome Quadrasorb Evo and CO_2 sorption isotherms on a Quantachrome Autosorb iQ2 volumetric gas adsorption analyzer, respectively. The measurement temperatures of CO_2 sorption isotherms were carried out at 273 and 298 K that was controlled with a water circulator.

2.2.4 Thermal Gravimetric Analysis (TGA)

Thermogravimetric Analysis is a technique by which the mass of a substance is monitored as a function of temperature as the specimen is subjected to a controlled temperature program in a controlled atmosphere[60].

A TGA instrument diagram is shown in Fig. 10. It consists of a sample pan that is supported by a precision balance. That pan resides in a furnace and is heated or cooled during the experiment. The mass of the sample is monitored during the experiment. A

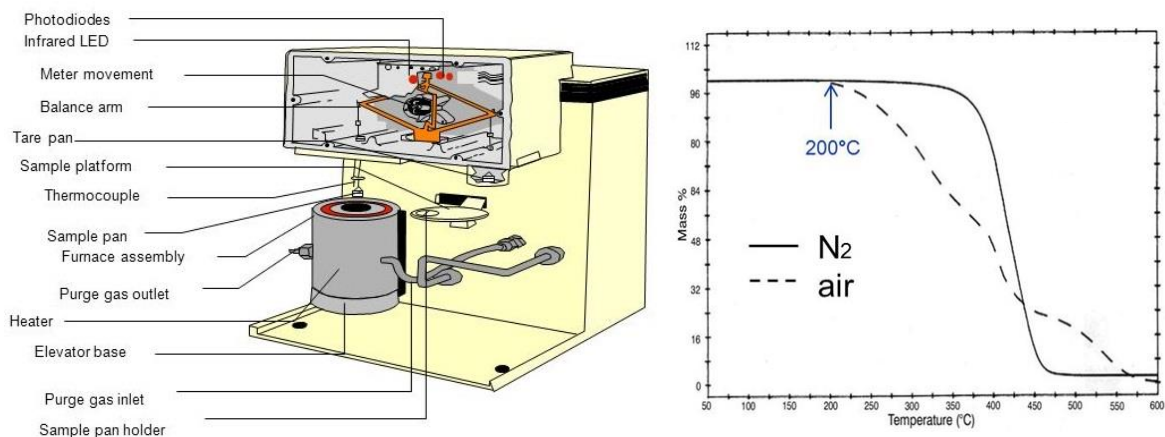


Figure 10. a) Schematic representation of TGA setup showing different components of the system. b) the TGA for carbon black.

purge gas controls the sample environment. This gas may be inert or a reactive gas that flows over the sample and exits through an exhaust[60].

This technique is used to study the thermal stability of the samples in different atmospheres (air or inert gases). In some cases, it can be used to give a rough indication of the metal content in samples[61]. The obtained data is plotted in a graph of mass with temperature, as in Fig. 10. The decrease of the mass at each temperature is attributed to the decomposition of some parts of the sample. When the sample is burned in air, the oxygen reacts with all the organic compounds forming different types of gasses (CO₂, H₂O, NO₂), leaving the metal oxides as a residue. By analyzing this residue, the metal content in the sample can be estimated.

In this work, thermal gravimetric analyses (TGA) were performed on a TA Instruments TGA Q-500 instrument with the MOFs samples placed in a platinum pan under airflow with a 10 °C per min heating rate in the range from 30 °C to 800 °C.

2.2.5 Inductively Coupled Plasma (ICP)

Inductively coupled plasma is a technique used to determine the metal traces in samples. It was first used in the late 1950s [62] and has been continuously developed since then[63]. The basic idea of this technique is to excite the metal atoms in the sample, collect the emission light, and analyze it. The excitation is achieved using a high-temperature plasma (6000 K- 10000 K). This temperature is sufficient to vaporize, excite, and ionize the sample's molecules[64].

Working principle

A schematic diagram for the ICP device is shown in Fig. 11. In ICP, argon gas is mostly used as the plasma source. A time-varying magnetic field is used to ionize the argon gas to form the plasma. This magnetic field is produced when a time-varying electric current is allowed to pass through a coil. The generated magnetic flux can be calculated as follow

$$\phi = \pi r^2 H = \pi r^2 H_0 \cos(\omega t)$$

where (r) is the radius of solenoid, (H) is the magnetic field. This time-varying magnetic field produces a time-varying electric field with strength

$$E = \frac{1}{2} \omega r H_0 \sin(\omega t)$$

This electric field is responsible for the plasma generation.

To initiate the ionization of the argon gas, a tesla coil is used. The produced electrons and ions then interact with the fluctuating magnetic field producing enough energy to ionize more argon by collision with the neutral atoms. The produced electrons accelerate in the produced electric field toward the torch. The accelerated ions collide with the argon gas atoms causing more ionization. The collision results in a significant increase in the temperature. When a high electron density steady state is achieved, the plasma will be

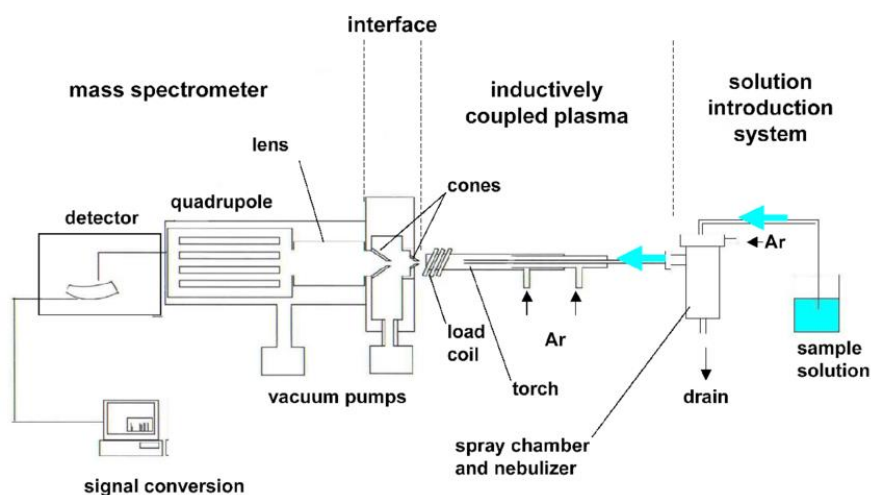


Figure 11. Schematic diagram for the ICP system shows different components of the system and the sample path from the injection point to the detector

formed at the top of the torch. The sample is digested in a strong acid (nitric acid, hydrofluoric acid, etc.,) then allowed to enter the torch from below. The torch temperature is sufficient to vaporize the sample and excite it. When the sample leaves the torch to the detector, it relaxes to the ground state emitting photons with wavelength characteristics for each metal. The produced photons are separated and analyzed using spectroscopic techniques to identify the metals[48].

In our work, ICP-OES was used to identify the actual metal content of the synthesized MOFs samples by using Analytik Jena PlasmaQuant PQ9000 ICP-OES having a radiofrequency (RF) generator power of 1200 W, auxiliary gas flow rate of 0.5 L min⁻¹, nebulizer gas flow rate of 0.5 L min⁻¹, cone gas (Ar) rate of 9 L min⁻¹, and a cold gas flow of 12 L min⁻¹.

2.2.6 Electron Paramagnetic Resonance (EPR)

Electron paramagnetic resonance spectroscopy (EPR), also called electron spin resonance (ESR), is a technique used to study chemical species with unpaired electrons based on the angular momentum of the electron.

The first evidence for electron angular momentum was observed in 1896 when Dutch physicist Zeeman observed the line splitting in optical spectra in a static magnetic field (Zeeman effect)[65]. After the availability of microwave instruments, the development of the EPR technique enhanced[66]. Between 1960 and 1980, continuous wave (CW) EPR developed while pulsed EPR was mainly studied at Bell laboratories. In the 1980s, the first commercial pulsed EPR spectrometer appeared in the market and was extensively used in the biological and medical fields. Nowadays, EPR has become a versatile and standard research tool.

EPR Working principle

The electron in an atom is a negatively charged particle that orbit around the nucleus, and also has a quantum spins. The rotation of the electron around the nucleus generates the

orbital angular momentum (L). The spin of the electron generates the spin angular momentum (S)[67].

The spin angular momentum projected on the z-axis is

$$S_z = \frac{h}{2\pi} m_s$$

Where (h) is Planck's constant, and (m_s) is the spin angular quantum number which has the values ($S, S-1, S-2, \dots, -S$); so, it has $(2S+1)$ values. For the unpaired electron, $S=1/2$. So, $m_s = +1/2$ and $-1/2$.

The magnetic moment, μ_e is directly proportional to the spin angular momentum, and one may therefore write

$$\mu_e = -g_e \mu_B S$$

Where g_e is the free electron g-factor (2.0023)[68], μ_B is the Bohr magneton which can be written as

$$\mu_B = \frac{e h}{4\pi m_e}$$

Where (e) and (m_e) are the electron charge and mass, respectively. When the atom is placed in a magnetic field, the field interacts with the electron's magnetic moment. This interaction energy can be written as

$$E = -\mu \cdot B$$

When there is no external magnetic field ($B=0$), there will be only one energy state ($E_{-1/2} = E_{+1/2} = 0$). When an external field is applied, the energy state will split into 2 states with the energy difference

$$E_{+\frac{1}{2}} = -\frac{1}{2} g \mu_B B$$

$$E_{-\frac{1}{2}} = \frac{1}{2} g \mu_B B$$

For a single unpaired electron, there will be two possible energy states with energy difference

$$\Delta E = g \mu_B B$$

This is known as the Zeeman splitting[65].

To excite an electron from the lower energy state to the higher energy state a photon of energy ($h\nu = \Delta E$) is needed, so

$$h \nu = g \mu_B B$$

The microwave frequency and the magnetic field can be controlled to achieve this condition. The other factors are known constants, and g is a constant of proportionality whose value is the property of the electron in a certain environment. So, the last equation can be written as[69]

$$g_e = \left(\frac{h}{\mu_B}\right) \left(\frac{\nu}{B}\right)$$

EPR spectrometers typically vary the magnetic field and hold the microwave frequency constant (Fig. 12)[48]. For a free electron, the value of g is constant ($g=g_e$), but when the electron is in a particular environment, for example in a transition metal ion complex, the second magnetic field produced by the nuclei, ΔB , will also influence the electron. So, the equation can be written as[70]

$$\frac{1}{g} = \left(\frac{\mu_B}{h}\right) \left(\frac{B + \Delta B}{\nu}\right)$$

From the relationship shown above, we know that there are infinite pairs of ν and B that fit this relationship. The magnetic field for resonance is not a unique “fingerprint” for the identification of a compound because spectra can be acquired at different microwave frequencies. On the other hand, the (Δg) value contains the chemical information that lies in the interaction between the electron and the electronic structure of the molecule; one can

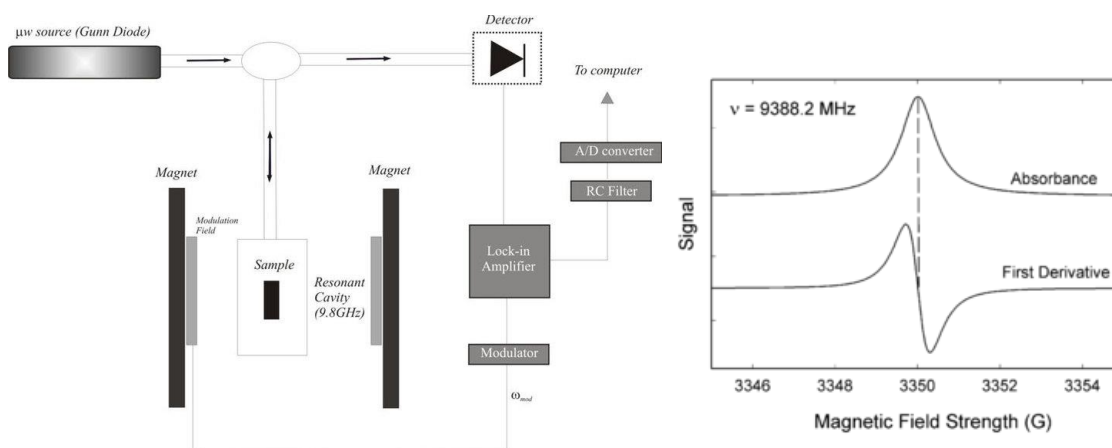


Figure 12. a) Schematic diagram of the EPR system shows the different components and the optical path of the microwave. b) graphical representation of the absorption and its derivatives.

simply take the value of ($g = g_e + \Delta g$) as a fingerprint of the molecule. For organic radicals, the g -value is very close to g_e with values ranging from (1.99-2.01)[71]. For example, the g -value for $\cdot\text{CH}_3$ (CH_3 radical) is 2.0026[71]. For transition metal complexes, the g -value

varies a lot because of the spin-orbit coupling and zero-field splitting. Usually, it ranges from 1.4-3.0 [72] depending on the geometry of the complex. For instance, the g-value of low-spin ferric heme is 2.8 {Bohan, 1977 #275}.

When the intensity of the applied magnetic field increases, the difference between the energy levels widens until it matches the microwave radiation, and results in the absorption of photons. The EPR spectrometer measures the absorption of the photons. The absorption signal then passes through a phase-sensitive detector, which converts the normal absorption signal to its first derivative. To determine the g-value, we use the center of the absorption signal. In the EPR spectrum, the point where the first derivative of the spectrum passes through zero corresponds to the center of the signal of the absorption spectrum (Fig. 12) [48].

To probe each material's interaction with light, and to gain insight into the excited state of the photocatalytic system, electron paramagnetic resonance (EPR) spectroscopy was performed. The EPR spectroscopic data were collected on a SPINSCAN X-benchtop EPR spectrometer from ADANI, Belarus, operated at the CW X-band, with an internal frequency counter, and fully auto-tuned. The spectrometer runs at a modulation frequency and amplitude of 100 kHz and 0.1 G, respectively. Its microwave frequencies were cross-checked with a Hewlett-Packard 5342 A microwave frequency counter. In a typical measurement, a sample was suspended in a solvent mixture that functions as a proton donor, as follows: 25 mg of the sample was added to a 0.2 mL mixture of ethyl acetate, acetonitrile, and water (5:1:0.1 v/v, respectively). The solution was then added to a capillary glass tube, which was then sealed and placed in the EPR device at 173 K and at room

temperature (300 K) in the dark and after irradiation with a white light source covering the visible and near-UV spectrum. When needed, the UV light was filtered out by glass.

2.2.7 Diffuse Reflectance Spectroscopy (DRS)

When light interacts with a powder sample, it is reflected in all directions. Due to the variety of powder shapes, it is reflected in many directions. The remainder of the light is refracted as it enters the powder, where it is scattered due to internal reflection, reflection from the surfaces of other powder grains, or repeated refraction entry into the powder. Some of this scattered light is emitted back into the air. As the diffuse reflected light is reflected or passes through the powder, it becomes weaker if absorption by the powder occurs[74]. This results in a diffuse reflection spectrum (Fig. 13a). However, in regions where the powder exhibits strong absorption, most of the diffuse reflected light in long light paths is absorbed, such that only the diffuse reflected light from short light paths is emitted back into the air[74]. On the other hand, in bands of weak absorption, some light is not absorbed even in long light paths, and this diffuse reflected light is emitted to the air, resulting in strong peaks.

In such a diffuse reflectance spectrum (Fig. 13b), the absorbed wavenumber positions are the same as the transmission spectrum. However, the relative intensity between peaks differs from the transmission spectrum because the weak peaks in the transmission spectrum become comparatively stronger in the diffuse reflectance spectrum. The so-called K-M function ($F(R_\infty)$) derived by Kubelka-Munk is used for quantitative analysis[75].

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{K}{S}$$

Where R_{∞} is the reflectance, K is the absorption coefficient, and S is the scattering coefficient. $F(R)$ is proportional to absorption under reasonable assumption[75]. The $F(R)$

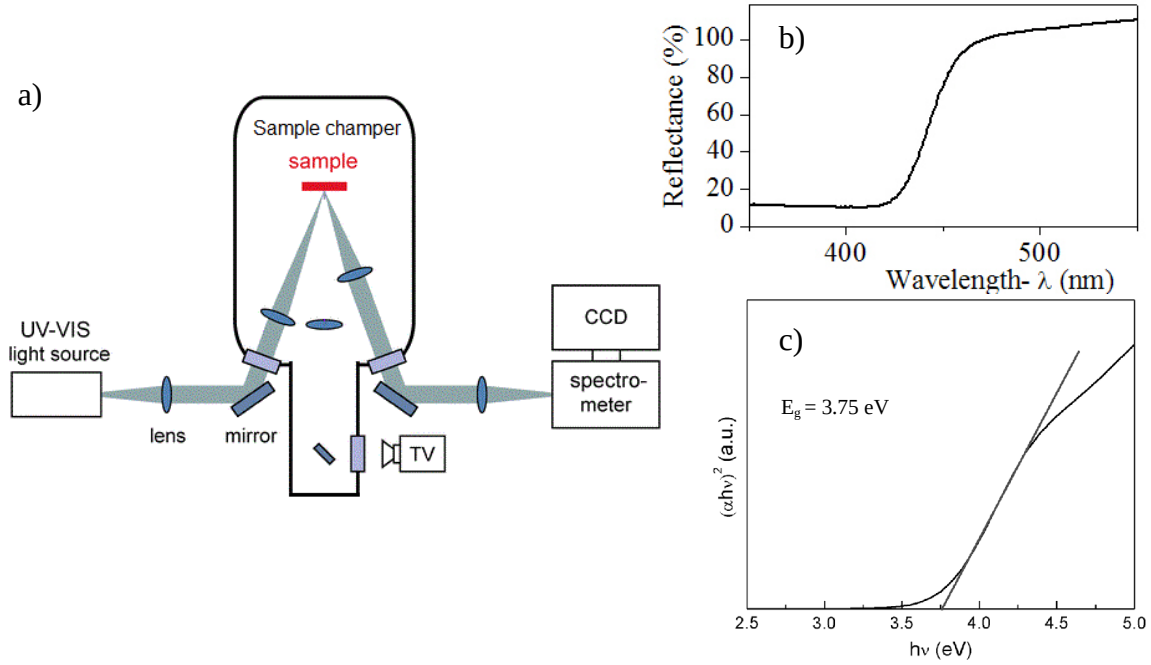


Figure 13. a) Schematic diagram for the DRS system showing different components of the system and the optical path of the incident UV-Vis beam from the source to the detector. B) Reflectance spectrum obtained from the DRS system. c) Processed Tauc plot for optical band gap calculation.

is then used to plot the Tauc plot. A Tauc plot is used to determine the optical bandgap[76, 77]. Jan Tauc showed that the optical absorption spectrum of amorphous germanium resembles the spectrum of the indirect transitions in crystalline germanium (plus a tail due to localized states at lower energies), and proposed an extrapolation to find the optical gap of these crystalline-like states. Typically, a Tauc plot (Fig. 13c) shows the absorption $(\alpha h\nu)^{1/r}$ versus the quantity $h\nu$ (the energy of the light), where α is the absorption coefficient of the material. The value of the exponent r denotes the nature of the transition[78]:

$r = 1/2$ for direct allowed transitions

$r = 3/2$ for direct forbidden transitions.

$r = 2$ for indirect allowed transitions

$r = 3$ for indirect forbidden transitions

The resulting plot has a distinct linear regime which denotes the onset of absorption. Thus, extrapolating this linear region to the energy axis yields the energy of the optical bandgap of the material.

The (DRS) measurements were performed by using a Shimadzu UV-1650PC spectrophotometer. In a typical experiment, a sample of the appropriate material was grinded and placed in the UV-DRS device equipped with a 50 W halogen lamp and a deuterium lamp. The obtained spectrum represents the absorbance of the sample as a function of the incident wavelength.

$F(R)$ was then plotted against the photon energy ($h\nu$) to create the Tauc plot. The bandgap was then obtained by fitting a straight line to the straight segment of the plot and extrapolating this line to get bandgap from the x-intercept

2.2.8 Femtosecond Transient-Absorption Spectroscopy (FTA)

Transient-absorption spectroscopy is a type of non-linear spectroscopy. It is used for the time-resolved study of excited-state molecular dynamics or molecular processes like charge and energy transfer, conformational rearrangements as well as the detection of short-living reactive intermediates in chemical reactions[79-81]. In this technique (Fig. 14), a molecular ensemble is excited to a state above the ground state at a defining moment in time (pumping). The pump event triggers the population of the excited state in the sample

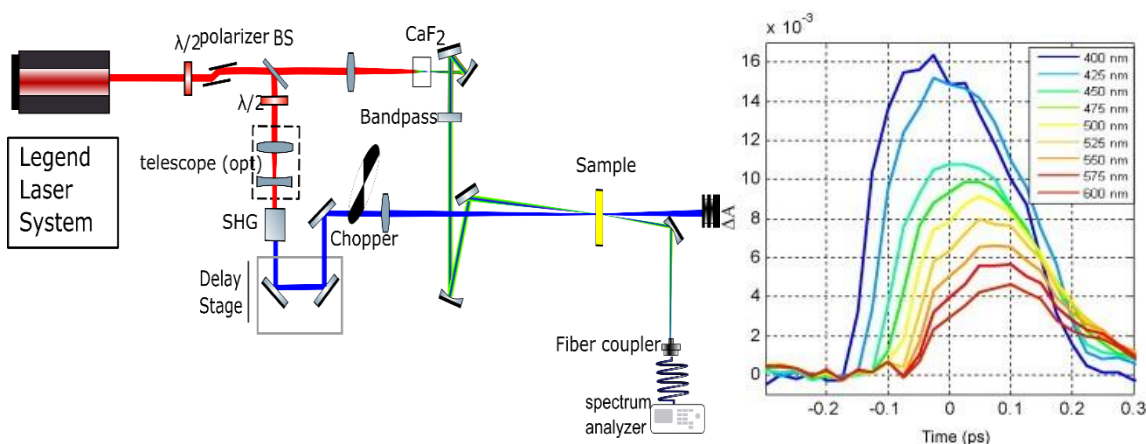


Figure 14. Schematic diagram for the FTA system showing different parts of the system and the optical path of the pump peak (red) and the probe beam (blue).

system. The excited-state dynamics are then monitored at different time intervals (probing). The results are represented as the absorbance of the sample at a specific wavelength as a function of time.

Working principle

After the development of femtosecond laser sources, pulsed laser techniques have been used for the time-resolved experiments to study the ultrafast molecular processes. In the liquid phase experiments, the absorbance of the excited sample is measured. The central wavelength of the excitation pulse is chosen to fit the linear absorption of the molecular sample under investigation.

The determination of the probe pulse spectrum is determined according to the studied molecular event. To study the electronic transitions and absorptions of photoproducts, probe spectra in the ultraviolet (UV) and visible (Vis) regime are used. In the case of examining the molecular vibrations - which is especially useful when structurally different reactive intermediates need to be distinguished- mid-infrared (MIR) probe pulses can be used[82].

After the sample excitation, a second laser pulse is used to probe the sample absorption as a function of probe wavelength λ and delay time τ . The delay time represents the time between the pumping signal and the probe signal. This time can be adjusted by adjusting the optical length of the pulse, which can be done using an adjustable mechanical stage that can delay time up to a few nanoseconds. In order to maintain the maximum spectral distribution, the two pulses (pump and probe) are derived from the same source[83].

The absorbance of the probe pulse (A) is related to the intensity of the incident (I) and the transmitted (I_0) light by Beer-Lambert law [84]

$$A = \log\left(\frac{I_0}{I}\right)$$

In this experiment, we are looking for the change in absorbance (ΔA) which can be calculated as follow

$$\Delta A = A_1 - A_2$$

Where (A_1) is the absorbance of the pumped sample, and (A_2) is the absorbance of the unpumped sample. So, (ΔA) can be written as

$$\Delta A = \log\left(\frac{I_0}{I_1}\right) - \log\left(\frac{I'_0}{I_2}\right) = \log\left(\frac{I_0 I_2}{I_1 I'_0}\right)$$

Where (I_0) and (I'_0) are the intensities of the incident pump and probe pulse respectively, while (I_1) and (I_2) is the intensity of the transmitted pulse for the pump and the probe respectively. In the real experiment both the pulses are driven from the same source, so ($I_0 = I'_0$) and

$$\Delta A = \log\left(\frac{I_2}{I_1}\right)$$

The resulting (ΔA) can be plotted as a function of wavelength or time. Plotting of (ΔA) as a function of wavelength, at different specific times, gives information about the evolution or decay of various intermediate species involved in a chemical reaction at different wavelengths[85]. Plotting of (ΔA) as a function of time, for different wavelengths, provides information regarding the number of decay processes involved at a given wavelength, and how fast or slow the decay processes are. It can provide evidence with respect to intersystem crossing, intermediate unstable electronic states, trap states, surface states, etc. [85].

2.3 Catalyst evaluation

The photocatalytic CO₂ reduction reactions were performed in a 10 mL gas-tight vial equipped with a penetrable septum. For each reaction, 50 mg of the appropriate catalyst was placed inside the vial then degassed for 5 min. Then, 5 mL of CH₃CN, functioning as the solvent, was added to the vial together with triethanolamine (0.1 mL), working as a proton donor. The mixture was then sonicated for 30 min, degassed, and flushed by bubbling CO₂ for 30 min inside the mixture at ambient pressure to ensure that no air was present. The degassing was done by the following steps: first, the vial was vacuumed and flushed by CO₂ gas for 3 times. Then the vial was connected to the CO₂ cylinder, and a syringe needle was placed in the septum to remove the access pressure to maintain the ambient pressure in the vial. Finally, the system was placed on a flat surface 30 cm below a solar simulator, with power equivalent to 460 W, for 17 h (Fig 15a).

Evolved gaseous products were monitored using a GC equipped with a methanizer and FID detector. Liquid products were analyzed by GC-MS (Fig. 15b).

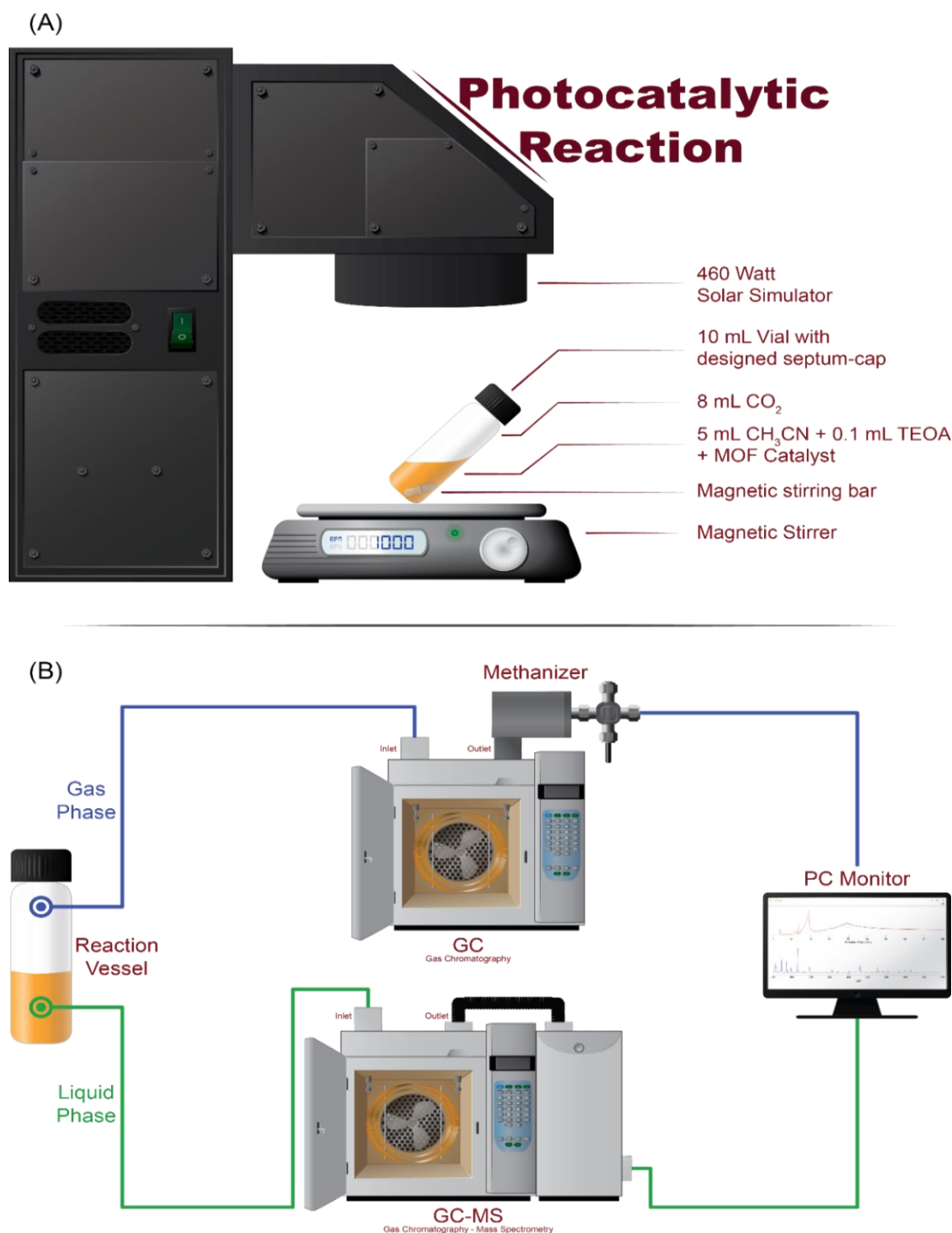


Figure 15. A) Experimental setup used in the photocatalytic reaction, and B) following analysis for both gas and liquid phases to determine the products.

The photocatalytic activity for the catalyst is evaluated according to different terms:

- The turnover number (TON), which is the number of moles of the CO₂ that a mole of catalyst can convert before becoming inactive. An ideal catalyst would have an infinite turnover number in this sense because it wouldn't ever be consumed, but in practice, one often sees turnover numbers, which go from 40 million down to 100 for the catalyst. The TON was calculated as follows:

$$TON = \frac{\text{the amount of formate produced } (\mu\text{mol})}{\text{the amount of metal active sites in the catalyst } (\mu\text{mol})}$$

The amount of active metal sites is calculated as follow

metal active site

$$= \text{no. of metal atoms per mole} * \text{the no. of catalyst moles} (\mu\text{mol})$$

- The term turnover frequency (TOF) is used to refer to the turnover per unit time. The (TOF) was calculated as follows:

$$TOF = \frac{TON}{\text{total time for the reaction (hr.)}}$$

- The product yield is the ratio between the reaction product amount and the amount of the reactants. It was calculated as follows (considering that the formate is the only product from the reaction and the amount of the other products is negligible)

$$Yield = \frac{\text{the amount of format produced } (\mu\text{mol})}{\text{the amount of CO}_2 \text{ injected in the reaction } (\mu\text{mol})} * 100$$

The amount of CO₂ injected in the reaction

$$\text{amount of CO}_2 = \frac{\text{the volume of injected CO}_2 \text{ (L)}}{22.4 \text{ (L/mole)}}$$

To measure the volume of the CO₂ in the reaction, first, 5ml of the liquid mixture and 50 mg of the catalyst were placed in the reaction vial. The vial was then vacuumed using a rotary pump. Finally, the CO₂ was added to the system using a 10ml syringe without adding any excess pressure. It was found that 8ml of the CO₂ was sucked into the system.

CHAPTER 3

UIO-66 AS A PHOTOCATALYST

3.1 INTRODUCTION

In order to synthesis a photocatalyst suitable for CO₂ reduction into value-added products, one must consider how to optimize the activity, selectivity, and efficiency of the catalyst being studied[86, 87]. Metal-organic frameworks (MOFs) are ideal in this regard as they are extended heterogeneous crystalline solids with geometrically defined organic backbones that site isolate discrete metal oxide clusters in a periodic and ordered fashion[88]. The inherent structural properties of MOFs directly address the activity concerns that molecular catalysts face as MOFs' high internal surface area, as well as their high density of spatially isolated active sites, are ideal in this regard[89]. Similarly, because of the crystalline nature of MOFs, each atom within any given framework can be modified with atomic precision, which provides a chemical handle over-optimization of its selectivity[87].

In the development of new photocatalytic MOF materials, attention has mainly focused on understanding the light absorption properties of unmodified MOF structures[90, 91]. This, in turn, has led to the targeting of MOFs that are composed of specific metals (photoactive metals) in order to shift the light absorption from the ultraviolet to the visible light region[92]. This systematic approach is akin to harnessing the photo-absorption properties of site isolated metal oxide clusters[93]. Although modifying the metal character of SBUs was successful in tuning the MOFs' light

absorption properties, photonic efficiency has remained poor[92]. To address this challenge, the electronic character of organic linkers was targeted for modification[94]. Indeed, it has been demonstrated that the light absorption properties of MOF materials can be further tuned by utilizing chromophoric linkers that extend the conjugation system, and modify the coordinating groups that connect the SBUs together[95, 96]. By the very nature of a MOF materials' structural building blocks, one has considerable handle over the resulting light absorption properties. Be that as it may, for a visible light harvesting MOF to serve as a CO₂ reduction catalyst, the absorbed photons must generate excited electrons, which, in turn, are effectively transported to MOF active sites on to which CO₂ is adsorbed and can be reduced. Generated electrons are transferred by one of four possible mechanisms: (i) linker-to-metal-cluster charge transfer (LCCT) (*e.g.* MOF-5, UiO-66, and MIL-125)[96]; (ii) intra-cluster charge transfer (ICCT) (*e.g.* MIL-101, MIL-53, and MIL-88B)[97]; (iii) simultaneous LCCT and ICCT (*e.g.* NH₂-MIL-101, NH₂-MIL-53, and NH₂-MIL-88B). This takes place in Fe-based MOFs whose linkers are functionalized with amine moieties[98]; and (iv) linker-to-linker charge transfer (LLCT) (*e.g.* Bi-mna)[99].

To better understand how a MOF photocatalyst can be optimized for CO₂ reduction, we chose to study the UiO-66 platform[100]. This MOF is well-known to be thermally and chemically stable with a high surface area and moderate CO₂ uptake capacity[20]. As a matter of fact, UiO-66 has been shown to be a photoactive catalyst[101]. In addition, with a simple functionalization of its organic linker, the photocatalytic properties can be tuned[19]. Using the tools of reticular chemistry, we sought to design, synthesize, and characterize a series of UiO-66-based MOFs in order to provide critical insights into what structural features are the most important to consider for enhancing a given MOFs

photocatalytic properties when applied to CO₂ reduction reactions. The tools we used here were comprehensive in that we carried out most of the possible structural modifications. Specifically, we synthesized UiO-66 in the following ways (Fig. 16): (i) linker functionalization (UiO-66-NH₂). It is known that by functionalizing the linker with a -NH₂ group, more visible light is absorbed as a result of a decreased bandgap;[19] (ii) core-shell construction (TiO₂@UiO-66-NH₂). By functionalizing the linker and then wrapping the MOF crystals around the photoactive TiO₂ nanoparticles, a photoactive composite is created that allows both adsorption and concentration of CO₂ near a well-known photocatalytic material (*i.e.*, TiO₂). Indeed, it is hypothesized that the composite increases the accessibility to the active surface of TiO₂[38]; (iii) post-synthetic SBU metal exchange [(Zr_{1-x}/Ti_x)UiO-66-NH₂], where $x = 0.07, 0.08, 0.10, 0.12, 0.13$]. Through a metal exchange process between Zr⁴⁺ and Ti⁴⁺, the structure and pore size will change due to a difference in the charge density (charge per unit volume) of Zr⁴⁺ and Ti⁴⁺. This difference

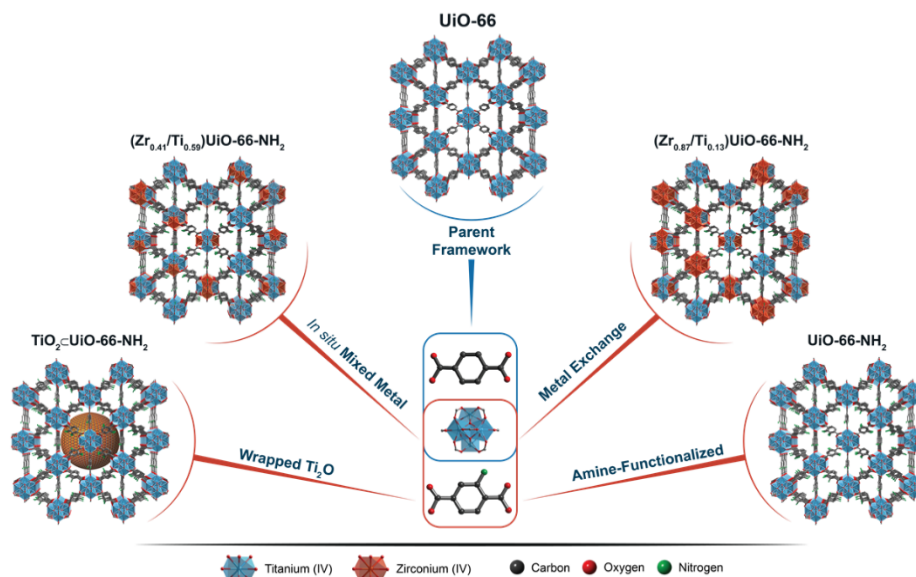


Figure 16. The series of the catalysts prepared to study the different modification on the UiO-66.

is expected to improve the polarization of CO₂ as it adsorbs, resulting in a more efficient reduction process; and (iv) *in situ* mixed-metal synthesis [(Zr_{1-x}/Ti_x)UiO-66-NH₂], where $x = 0.27, 0.59$]. With these modified UiO-66 materials in hand, the photophysical and photocatalytic properties were systematically examined in order to gain a deeper fundamental understanding of the structure-property relationships in MOF-based CO₂ reduction photocatalysts. The material synthesis was described in chapter 2, the experimental study results are explained below, while the DFT computational results are left for chapter 5.

3.2 RESULTS AND DISCUSSION

3.2.1 UiO-66 Material characterization

The structure and bulk phase purity of each member of the series was characterized by powder X-ray diffraction analysis (PXRD). The diffraction patterns for each member were in good agreement with the pattern simulated from the single crystal structure of UiO-66 (Figure 18a). It is noted that in the case of TiO₂⊂UiO-66-NH₂, the PXRD pattern included reflections at 25.3°, 37.8°, and 38.6° 2θ (Cu K_α) that were conclusively attributable to the (101), (004), and (112) anatase TiO₂ Miller indices respectively[102].

As expected, for both the post-synthetic exchanged and *in situ* generated (Zr_{1-x}/Ti_x)UiO-66-NH₂ materials, there was a noticeable consistent shift in peak positions toward higher 2θ values (Figure 18b). This uniform peak shifting is attributed to the shrinking of the MOF's lattice due to the replacement of larger Zr⁴⁺ with smaller Ti⁴⁺

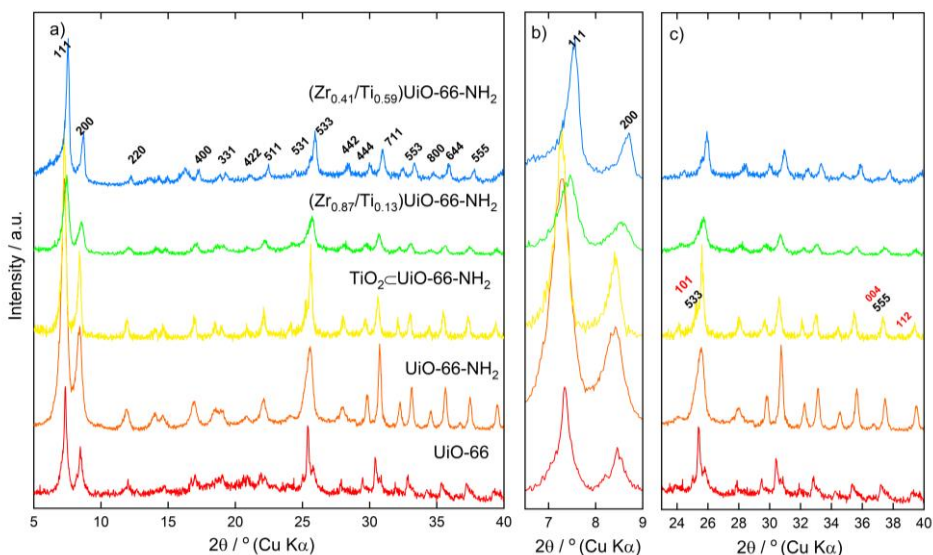


Figure 17. PXRD for the prepared samples. a) the diffraction pattern for all the samples and the peak indexing for each peak. b) the small peak shifting for the metal exchange sample ((Ti_{0.13}/Zr_{0.87})UiO-66-NH₂) and the mixed metal sample at ($2\theta = 7.2^\circ$). c) the anatase phase peaks (indexing in red) in the wrapped UiO-66-NH₂

ions[103]. The lattice shrinking upon metal exchange is a frequently observed behavior for inorganic semiconductor solid solutions[104].

To determine the amount of Ti⁴⁺ loading for these samples, inductively coupled plasma-optical emission spectroscopy measurements (ICP-OES) were performed (Table 2). It was found that for the post-synthetic exchanged analog, the percentage of Zr⁴⁺

Table 2. The ICP data for the Ti modified UiO-66-NH₂ showing the atomic percent of the Ti and the Zr in each

Metals	Wrapped	Metal Exchange				Mixed Metal	
	TiO ₂	1 day	2 days	4 days	5 days	1:2	1:1
Ti	10.6%	7.0%	7.9%	12.3%	13.3%	26.9%	58.6%
Zr	89.4%	93.0%	92.1%	87.7%	86.7%	73.1%	41.5%

replaced by Ti^{4+} increased upon increasing the incubation time with the exchange, ultimately reaching a maximum of 13% Ti^{4+} incorporation. This led to the chemical formula being determined as $(\text{Zr}_{0.87}/\text{Ti}_{0.13})\text{UiO-66-NH}_2$. For our *in-situ* analog, a range of Ti^{4+} incorporation was found, via ICP-OES, to be as low as 27% and as high as 59% depending on the molar equivalents of $\text{TiCl}_4 \cdot 2\text{THF}$ added during the synthesis. From this, the chemical formula could be calculated as $(\text{Zr}_{0.73}/\text{Ti}_{0.27})\text{UiO-66-NH}_2$ and $(\text{Zr}_{0.41}/\text{Ti}_{0.59})\text{UiO-66-NH}_2$.

From the field-emission scanning electron microscopy (FE-SEM) images (Fig. 18), the crystal morphology and size of each of the members of this series were determined. For the parent UiO-66, octahedral crystals, 100 nm in size, were observed as expected. UiO-66-NH₂ and $\text{TiO}_2 \subset \text{UiO-66-NH}_2$ were also found to have an octahedral shape, but with different crystallite sizes of ~200 and ~40 nm, respectively. For both the post-synthetic and *in situ* exchanged samples, the crystallites were found to have aggregates, and the morphology was not abundantly clear. This observation may be due to deformation upon heat treatment of the samples. Elemental mapping for $\text{TiO}_2 \subset \text{UiO-66-NH}_2$, post-synthetic $(\text{Zr}_{0.87}/\text{Ti}_{0.13})\text{UiO-66-NH}_2$, and *in situ* exchanged $(\text{Zr}_{0.41}/\text{Ti}_{0.59})\text{UiO-66-NH}_2$ was then carried out using energy-dispersive X-ray spectroscopy (SEM-EDX). The SEM-EDX results were found to be in good agreement with the ICP data regarding the atomic compositions of the samples (Table 3). Additionally, SEM-EDX mapping demonstrated that Ti was highly distributed in all the samples (Fig. 18c, 18d, and 18e). The successful encapsulation of TiO_2 nanoparticles within the UiO-66-NH₂ structure was confirmed by

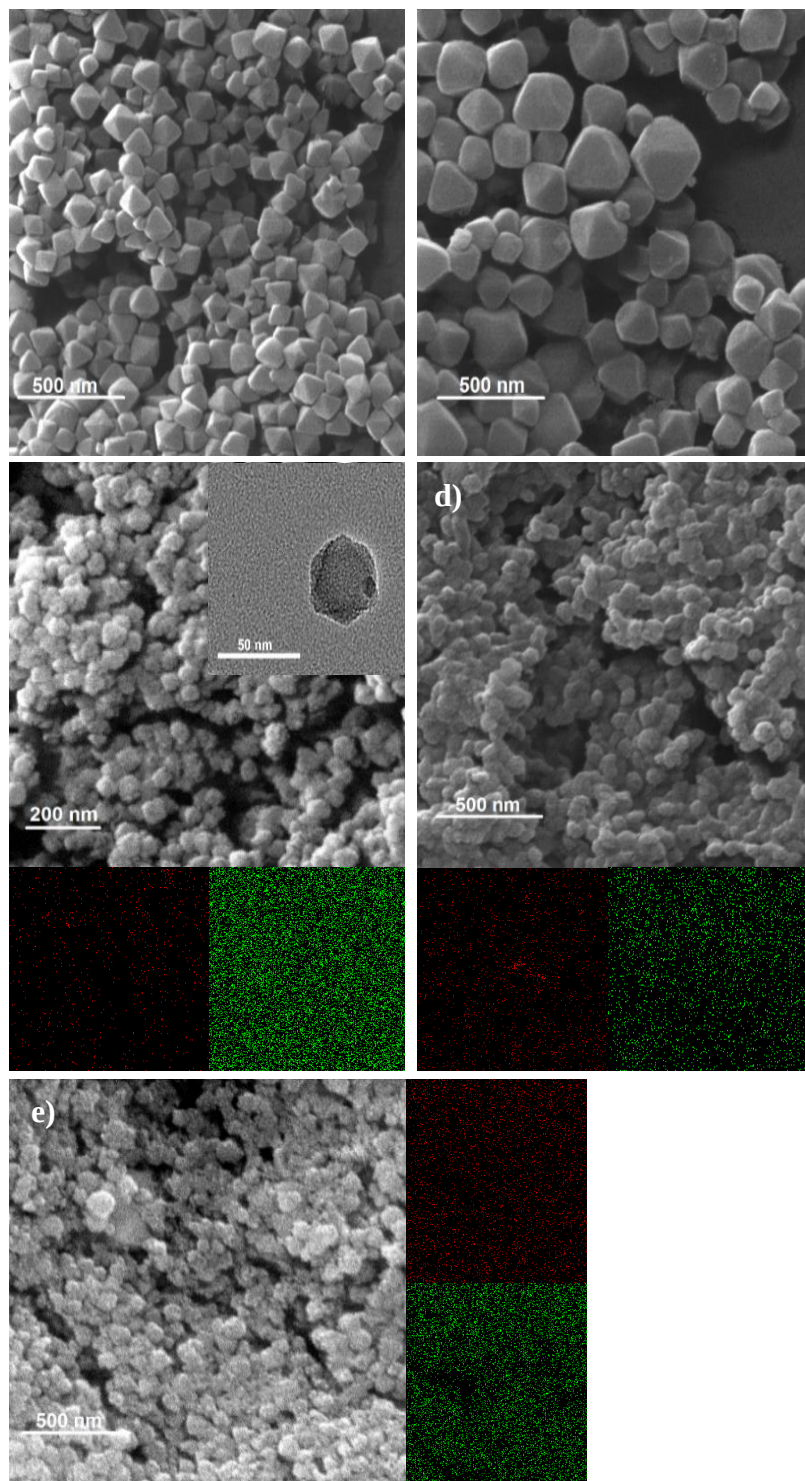


Figure 18. SEM images showing the particle size and morphology, the elemental mapping, and the EDX data for a) UiO-66, b) UiO-66-NH₂, c) TiO₂@UiO-66-NH₂, d) (Zr_{0.87}/Ti_{0.13})UiO-66-NH₂, e) (Zr_{0.41}/Ti_{0.59})UiO-66-NH₂. The inset in c) is the TEM image of TiO₂@UiO-66-NH₂ showing the TiO₂ nanoparticles inside the UiO-66-NH₂.

transmission electron microscopy (TEM) (Fig. 18). In the TEM images, the size of the TiO₂

nanoparticle was found to be ~5 nm, and the structure of anatase-phase TiO₂ was further confirmed by electron diffraction measurements (SAED).

Table 3. The metal content percentage obtained from ICP and EDX results

Catalyst	ICP result (%)		EDX result (%)	
	Zr	Ti	Zr	Ti
TiO ₂ ⊂UiO-66-NH ₂	89	11	85	15
(Zr _{0.87} /Ti _{0.13})UiO-66-NH ₂	87	13	84	16
(Zr _{0.41} /Ti _{0.59})UiO-66-NH ₂	41	59	45	55

The thermal stability and architectural robustness of each member of the series were proven by thermal gravimetric analysis and N₂ adsorption isotherms (Fig. 19 and Figure 20). In the TGA curves, all members exhibit a small decrease in weight percent up to the framework decomposition temperatures.

After the framework decomposition, the calculated weight percent of the residues for each system are shown in Table 4. The residue weight percent for UiO-66 and UiO-66-NH₂ are in line with the theoretical values calculated for the metal residue from the crystal structure. For TiO₂⊂UiO-66-NH₂, post-synthetic (Zr_{0.87}/Ti_{0.13})UiO-66-NH₂ and *in situ* exchanged (Zr_{0.41}/Ti_{0.59})UiO-66-NH₂, the residue weight percentages were higher than those found for UiO-66 and UiO-66-NH₂, due to the incorporation of Ti⁴⁺ within their structures for TiO₂⊂UiO-66-NH₂. In the case of post-synthetic (Zr_{0.87}/Ti_{0.13})UiO-66-NH₂ and *in situ* exchanged (Zr_{0.41}/Ti_{0.59})UiO-66-NH₂, this increase in residual mass was

unexpected, as the atomic mass of Ti is lower than that of Zr. The increase may be attributed to some structural defects formed because of missing linker walls during the post-synthetic and *in situ* exchange processes.

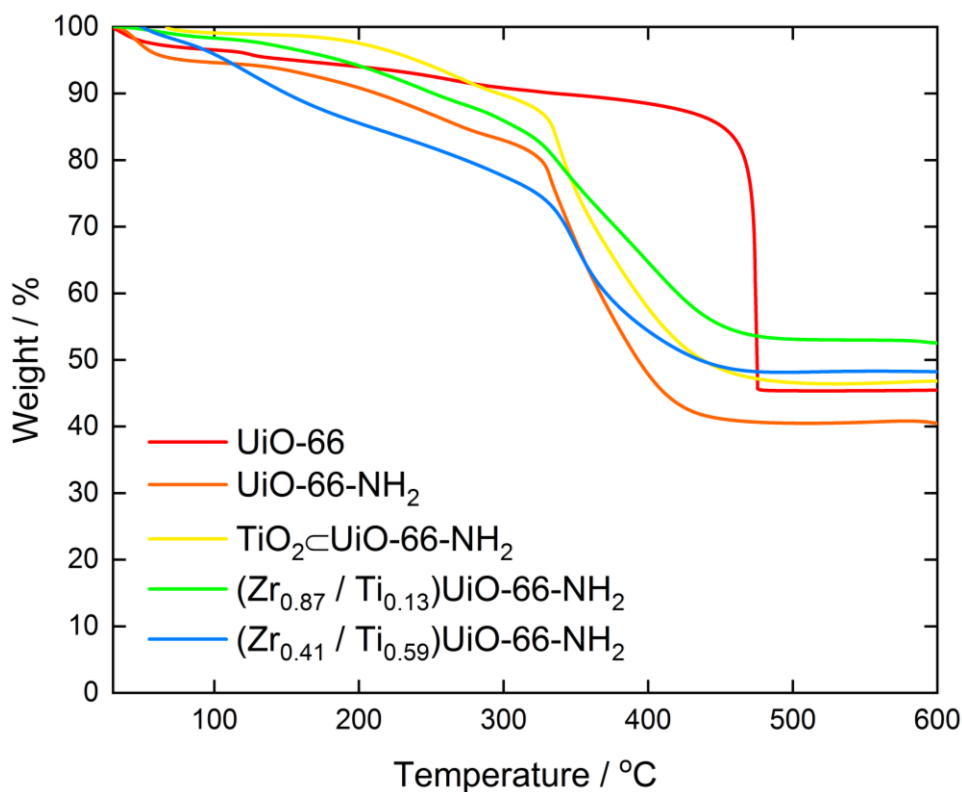


Figure 19. TGA analysis of the prepared samples in air showing the thermal stability of each MOF and the residue weight percent.

The porosity of all members of the series was proven by N₂ adsorption isotherm at 77 K (Fig. 20), which indicates Type I profiles indicative of micropores within their structures[56]. The surface areas, calculated by applying the Brunauer–Emmett–Teller (BET) model over the $P/P_0 = 0.01–0.3$ range, are shown in Table 5.

Table 4. The TGA residue calculated and experimental for the prepared UiO-66 catalysts

Catalyst	Catalyst molecular weight	No. of metals in the catalyst	Metal oxide molecular weight	Calculated TGA residue %	Experimental TGA residue %
UiO-66	1628.04	6	739.34	45.4	45
UiO-66-NH ₂	1718.16	6	739.34	43.0	41
TiO ₂ ⊂UiO-66-NH ₂	1810.01	7.15	831.19	45.9	47
(Zr _{0.87} /Ti _{0.13}) UiO-66-NH ₂	1679.15	6	700.32	41.7	52
(Zr _{0.41} /Ti _{0.59}) UiO-66-NH ₂	1575.11	6	596.27	37.9	47

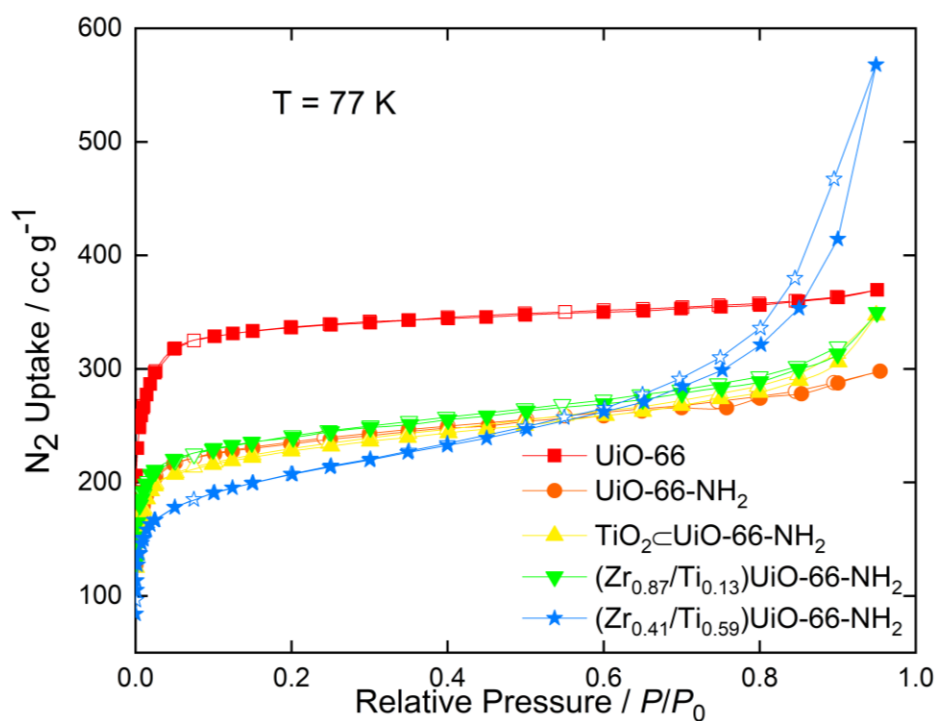


Figure 20. N₂-isotherm for the prepared samples measured at 77 K shows type 1 isotherm. The filled marks represent the adsorption and the empty marks represent the gas desorption.

Table 5. The BET surface area for the prepared samples

Catalyst	BET surface area (m ² /g)	Reported BET surface area (m ² /g)[103]
UiO-66	1300	1400
UiO-66-NH ₂	860	1000
TiO ₂ ⊂UiO-66-NH ₂	800	N/A
(Zr _{0.87} /Ti _{0.13})UiO-66-NH ₂	750	1100
(Zr _{0.41} /Ti _{0.59})UiO-66-NH ₂	650	N/A

The decrease in the BET surface area in the post-synthetic exchange is attributed to the structural defects which agree with the TGA. These defects might have resulted in removing some cluster walls (missing linkers due to post-synthetic heat treatment), which increase the pore size, as shown in Fig. 21. The increase in the pore size increases the pore volume and decreases the surface area. In addition, this decrease may be a result of the precipitation of small amounts of extremely small TiO₂ clusters in the pores of the MOF (this probably cannot be detected by PXRD). The increase in the uptake at ($P/P_0 > 0.8$) is attributed to the interparticle condensation, which means that the N₂ gas is adsorbed between the MOF nanoparticles and not only on the pores.

Prior to examining the series' photocatalytic properties, we measured CO₂ adsorption isotherms at 293 K to gain insight into the materials' uptake capacities and affinity to CO₂ (Fig. 22, Table 6). UiO-66 exhibits reasonable uptake at 293 K and atmospheric pressure.

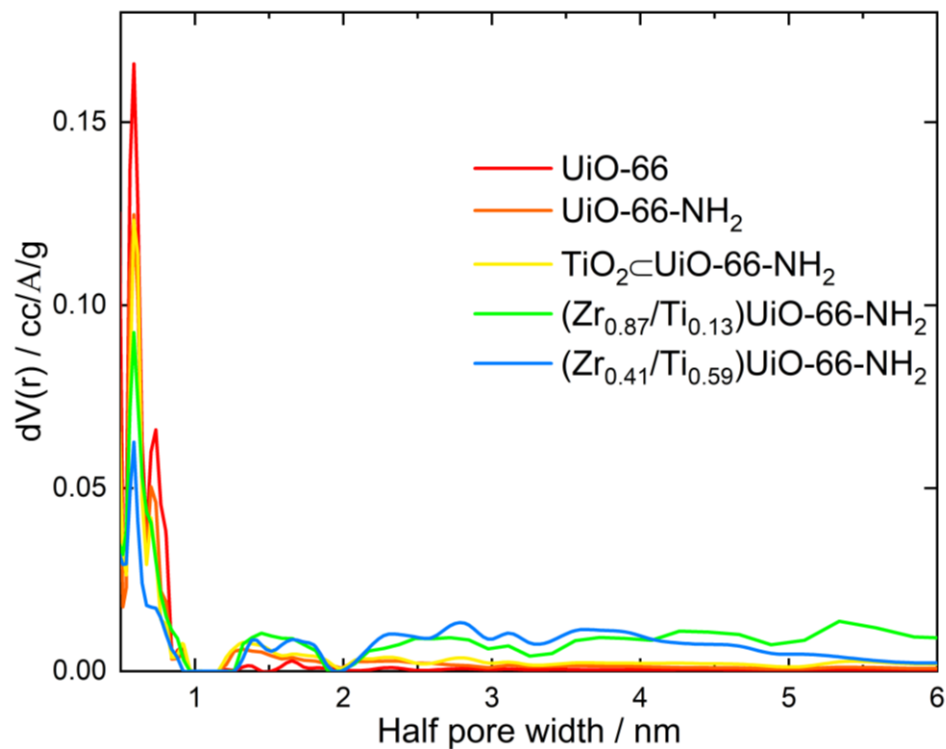


Figure 21. DFT method pore size distribution for the prepared MOFs obtained from the BET measurement

After functionalizing UiO-66 with NH_2 groups, the uptake capacity decreased by 13%. This is due to the decrease in the surface area after functionalization[105]. For $\text{TiO}_2\text{@UiO-66-NH}_2$, the uptake capacity was further decreased by 20% compared to the UiO-66-NH₂, due to the presence of the non-porous TiO_2 . In the case of post-synthetic exchange $(\text{Zr}_{0.87}/\text{Ti}_{0.13})\text{UiO-66-NH}_2$, there was no noticeable change in the uptake capacity; yet, in the case of *in situ* mixed metal $(\text{Zr}_{0.41}/\text{Ti}_{0.59})\text{UiO-66-NH}_2$ the uptake decreased by 25%. At low pressure, the amine-functionalized sample exhibits higher affinity to CO_2 , due to the presence of the $(-\text{NH}_2)$ group. So, at low pressure ($P < 20$ Torr), the CO_2 uptake for the UiO-66 is lower than the other samples (Fig. 22 inset).

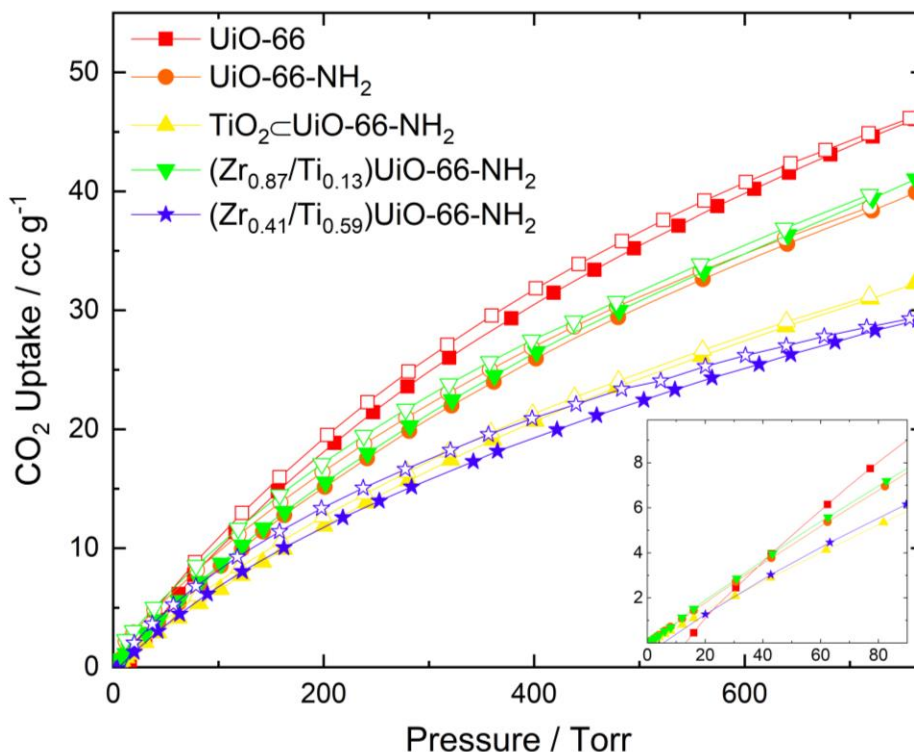


Figure 22. The CO₂ adsorption measurement for the prepared sample measured at room temperature (298 K). The filled marks represent the adsorption and the empty marks represent the gas desorption

Table 6. the CO₂ uptake measured for the prepared catalysts

Catalyst	UiO-66	UiO-66-NH ₂	TiO ₂ /UiO-66-NH ₂	(Zr _{0.87} /Ti _{0.13})UiO-66-NH ₂	(Zr _{0.41} /Ti _{0.59})UiO-66-NH ₂
CO ₂ uptake (cm ³ /g)	46	40	32	40	30

3.2.2 UiO-66 Photo-absorption characterization.

Light absorption by metal oxides is mostly associated with an excitation of electrons from the valance band to the conduction band, leaving holes behind. This transient electron-hole pair can recombine during the period of irradiation or be trapped at the surface of the solid. In some metal oxide systems, the holes are occupied by trapped oxygen anions, while the electrons are used to reduce metal cations to alter their oxidation

states[106]. If a metal-reduction induces the formation or disappearance of paramagnetic species, electron paramagnetic resonance (EPR) spectroscopy can be employed to probe such a process[107]. Accordingly, EPR spectra were obtained for all members of the series at both ambient temperatures and at 173 K under dark (no irradiation), and visible light irradiation. The EPR results are presented in Fig. 23. From these measurements, it is noticed that no EPR absorption peaks were observed for UiO-66 in the dark, nor under illumination. Thus, it is concluded that UiO-66 is not paramagnetic. In the case of UiO-66-NH₂, (Zr_{0.87}/Ti_{0.13})UiO-66-NH₂, and (Zr_{0.41}/Ti_{0.59})UiO-66-NH₂, the recorded EPR spectra did not display any EPR peaks in the dark; however, upon irradiation with visible light, the samples exhibited different responses based on the nature and type of metal oxide doping. As shown in Fig. 23, an observed EPR peak with a *g*-value of 2.0026 appears in all the modified samples. This peak is attributed to the formation of Zr³⁺ (the only paramagnetic species of zirconium ions). These findings are in agreement with the reported *g*-value for Zr³⁺ in defected polycrystalline zirconia[108]. This observation indicates that the visible light photons have enough energy to excite electrons from the valence band to the conduction band of the modified MOFs samples. Thus, Zr⁴⁺ reduces to Zr³⁺ by trapping the excited electrons. For TiO₂⊂UiO-66-NH₂, a remarkable shoulder at the sides of the Zr³⁺ EPR peak was observed upon irradiation with visible light (Fig. 23), although TiO₂ significantly absorbs light only in the UV region. This signal, at a *g*-value of 1.9910, must be attributed to the presence of Ti³⁺ ions and closely overlaps with the Zr³⁺ peak[109]. It is noted that this peak is attributed to a distorted Ti octahedral due to a tetragonal distortion of the crystal[110]. We conjecture that there is energy transfer taking place between the Zr cluster and the TiO₂, where the cluster absorbs the visible light photon producing an excited

electron that transfers its energy to the wrapped TiO_2 , hence exciting an electron there and producing Ti^{3+} .

The Ti^{3+} EPR peaks enhanced for the $(\text{Zr}_{0.87}/\text{Ti}_{0.13})\text{UiO-66-NH}_2$, as shown in Fig. 23. This enhancement is due to the replacement of the Zr^{4+} (larger size) in the SBU with a Ti^{4+}

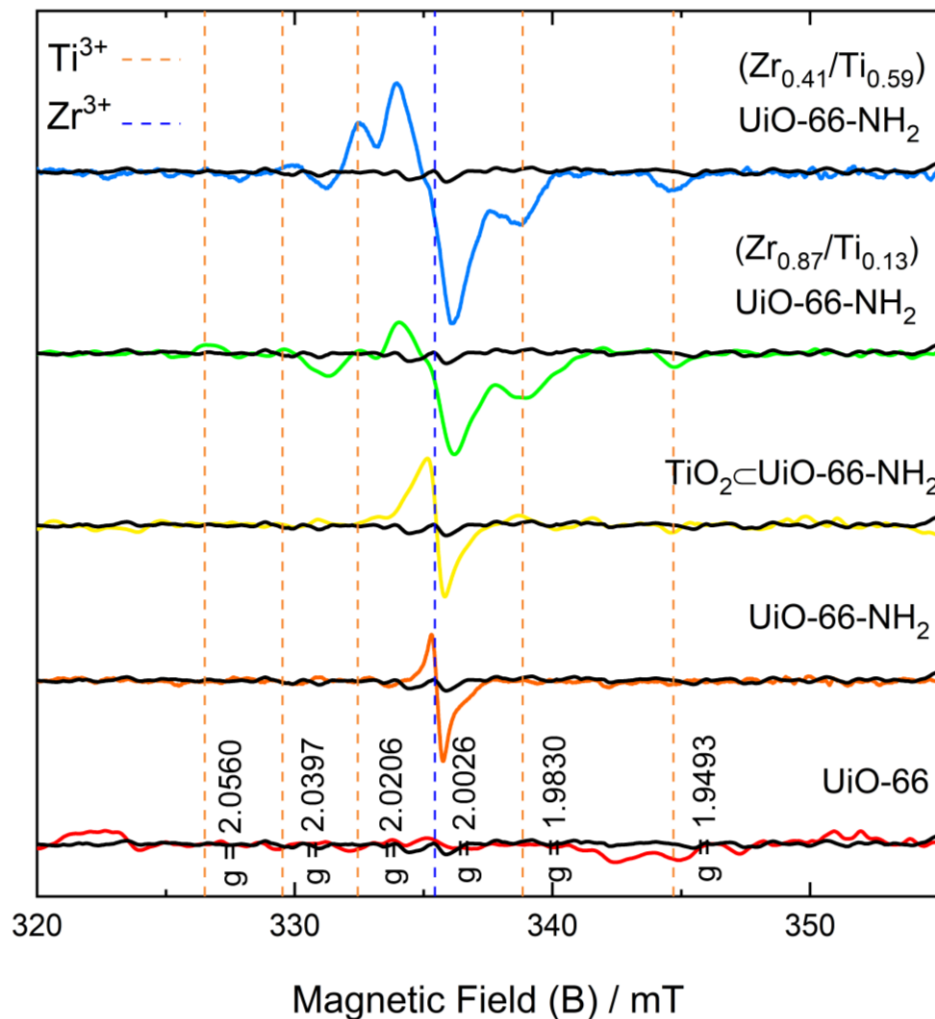


Figure 23. EPR measurement in dark (black) and under visible light irradiation for the prepared samples showing the absorption peaks for the Ti^{3+} (orange dashed line) and the Zr^{3+} (blue dashed line). The Zr^{3+} peak appears in all the samples except for the UiO-66. The Ti^{3+} peaks show different crystal fields distortions on the Ti-O bond.

(smaller size), which leads to a longer Ti-O bond, causing an overall tetragonal elongation[110].

The main characteristics of the (Zr_{0.87}/Ti_{0.13})UiO-66-NH₂ EPR response are the presence of anisotropic peaks. These peaks are formed at *g*-values of 2.0560 and 1.9493, which are ascribed to the trigonal distortion of the Ti³⁺ octahedral geometry. This distortion is attributed to the change in the Ti-O bond lengths as a result of the metal exchange. More anisotropic peaks appear, at *g*-values of 2.0397 and 1.9830, which are probably related to a tetragonal distortion of the Ti³⁺ octahedral arrangement[110]. This distortion is expected to result from the oxygen vacancy during the metal-metal exchange preparation. These distortion features increase as the incorporation of Ti⁴⁺ increases, as evidenced by the EPR spectral lines in (Zr_{0.41}/Ti_{0.59})UiO-66-NH₂ (Fig. 23). They also show a decrease in the intensity of the oxygen vacancy peaks and an increase in the intensity of the tetragonal elongation peaks. From EPR measurements, we conclude that visible light photons are responsible for the excitation of electrons that reduce the metal ions in the amine-functionalized samples. Also, the presence of Ti in different forms (TiO₂ or in the SBU) produces some distortion in the cluster. These distortions might introduce some defects in the cluster (oxygen deficiency) that cause the absence of some cage walls, hence producing macropores.

UV-Vis diffuse reflectance spectroscopy (UV-DRS) was used to compare the optical activity of each member of the series (Fig. 24). In general, ZrO₂ only absorbs UV light ($\lambda < 240$ nm)[111]. By site isolating Zr⁴⁺ oxo-clusters in UiO-66, the absorption shifts to higher wavelengths with a single absorption band being observed starting at ~350 nm. This redshift is attributed to the presence of extended π -conjugated bonds in the aromatic ring of the linker and a linker-to-linker charge transfer (LLCT) mechanism, whereby the linker

absorbs light and then transfers the excitation energy to the cluster where an excitation electron is generated[112].

After functionalization with -NH_2 , an additional absorption band appears starting at ~ 450 nm, thereby shifting the photo-absorption activity toward the visible region. This band also results mainly from the LLCT process in which light excites the non-bonding electrons of the NH_2 group into the anti-bonding p -orbitals of the linker. This electron is

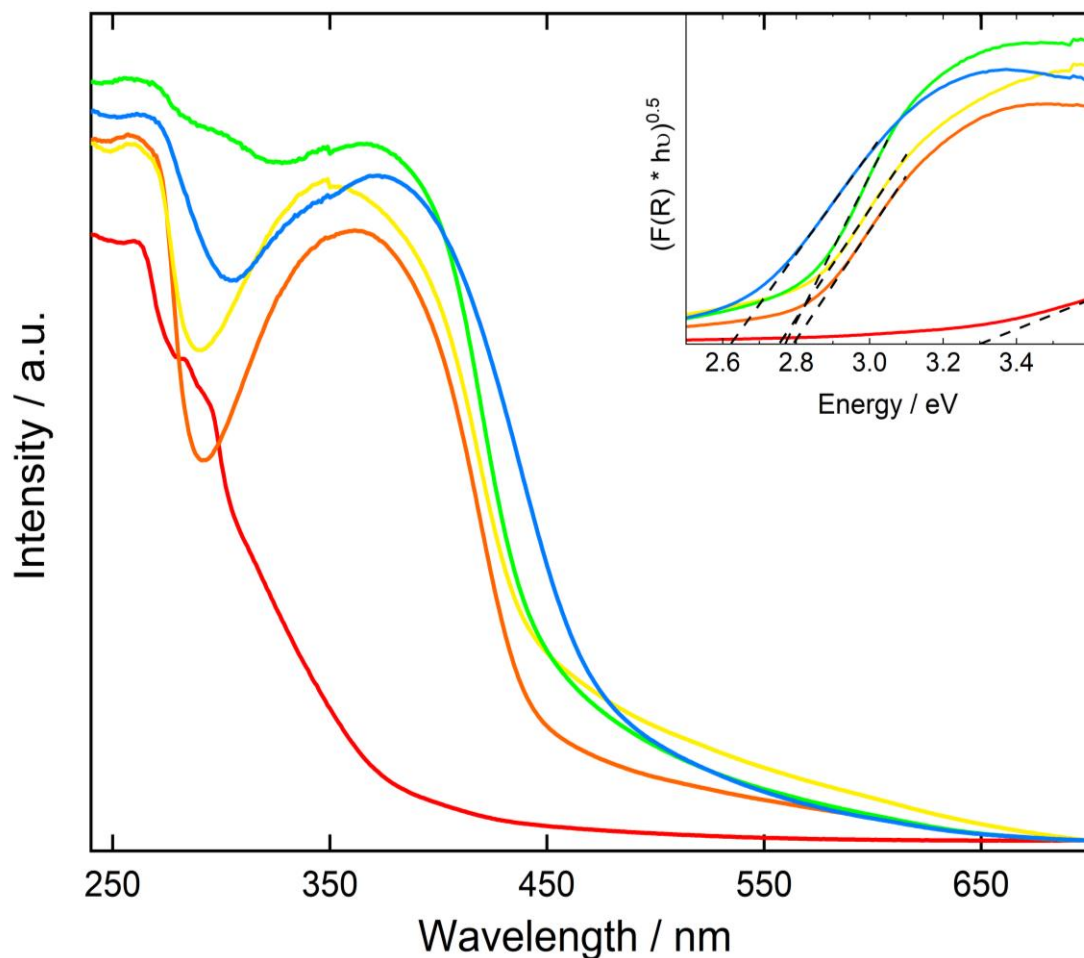


Figure 24. UV-DRS measurement for the prepared samples. for UiO-66 (red) the absorption peak starts at 350 nm. after functionalization with NH_2 (orange) another peak starts at 450 nm appears. The inset shows the Tauc's plot of the KM function for all the samples.

then transferred to the nearby metal, causing its reduction from Zr^{4+} to Zr^{3+} [113]. There was no change observed in the optical activity after wrapping UiO-66- NH_2 around TiO_2 .

This is expected, as this composite has no effect on the energy levels of the valence or conduction bands of the system (this will be discussed further in chapter 5). In the case of *in situ* metal-exchange ($\text{Zr}_{0.87}/\text{Ti}_{0.13}$)UiO-66-NH₂, the absorption band, centered at 265 nm, is broader than that of UiO-66-NH₂, which may be caused by the Ti^{4+} -containing oxo-clusters that are formed after the exchange. ($\text{Zr}_{0.41}/\text{Ti}_{0.59}$)UiO-66-NH₂ exhibited a redshift in the absorption band from around 356 nm to around 380 nm. This redshift can be attributed to the bandgap reduction, which was observed after adding Ti^{4+} . In these systems, light excites the non-bonding electrons into the vacant *d*-orbital of Ti^{4+} which populates the conduction band. In the latter systems, the bands result mainly from a linker-metal-charge-transfer (LMCT) process as will be discussed in chapter 5[114].

The fluorescence spectra were measured for the linker and for the prepared MOFs upon excitation at 350 nm (Fig. 25). It was found that the (NH₂-BDC) linker has an emission peak at 485 nm[115]. This peak results from the relaxation of the electron that was excited by the 350 nm light. In the case of the UiO-66-NH₂ series, the 485 nm emission peak decreased significantly. This decrease in the peak intensity means that the excited electron didn't relax and return back the linker. This decrease is attributed to the LMCT between the linker and the metal cluster, which means that the excited electron has transferred from the linker to the metal cluster.

The UV-DRS spectra were used in the Kubelka-Munk function to produce Tauc plots that determine the bandgap for all members of the series (Fig. 24). The bandgap of the parent UiO-66 was found to be 3.31 eV. After functionalization with -NH₂, the bandgap decreased to 2.79 eV. The bandgap was found to be 2.78 eV for $\text{TiO}_2\subset\text{UiO-66-NH}_2$. For the ($\text{Zr}_{0.87}/\text{Ti}_{0.13}$)UiO-66-NH₂, the bandgap was 2.75 eV.

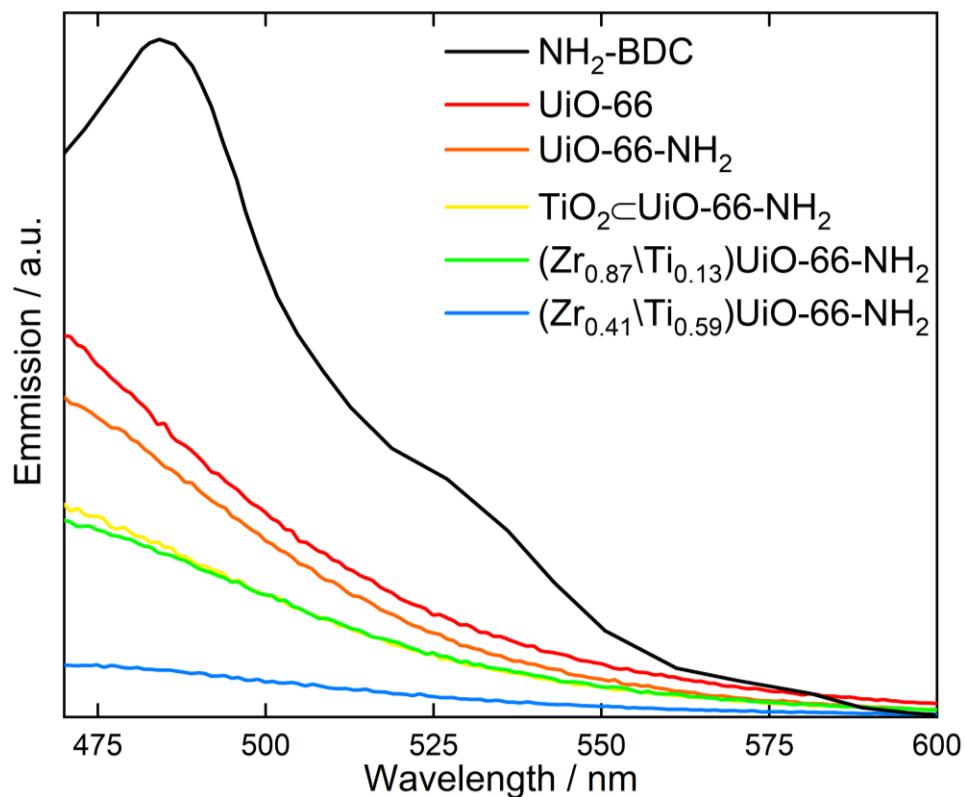


Figure 25. The fluorescence spectra for the MOF and the linkers after excitation at 350 nm.

However, the bandgap for $(\text{Zr}_{0.41}/\text{Ti}_{0.59})\text{UiO-66-NH}_2$ reduced to 2.61 eV. It is noted that the bandgap provides a good representation of the optical activity of the sample. The solar spectrum contains photons with different energies: roughly 2% in the UV region ($E > 3.2$ eV), 47% in the visible region ($3.2 > E > 1.6$ eV), and the rest is in the IR region ($E < 1.6$ eV). Photon energy is required to excite an electron from the valance band to the conduction band, overcoming the energy gap.

UiO-66 ($E_g = 3.31$ eV) can only be excited with UV photons, but for UiO-66-NH₂ ($E_g = 2.79$ eV) excitation can also occur from visible photons. This allows UiO-66-NH₂ to be active in the visible light region and have higher photoactivity than UiO-66. For

(Zr_{0.41}/Ti_{0.59})UiO-66-NH₂ ($E_g = 2.61$ eV), the bandgap is further decreased, which makes it more active for solar light absorption.

3.2.3 UiO-66 Catalyst evaluation.

To evaluate the photocatalytic activity of our samples, we studied the photocatalytic reduction of CO₂. The reaction was done in a mixture of CH₃CN and TEOA. The CH₃CN was chosen to increase the solubility of CO₂ in the mixture. The TEOA was used as a sacrificial donor, as it acts as a proton donor as well as an electron donor [116]. Also, it was used in this mixture to provide an alkaline medium for the CO₂ reduction [117].

All UiO-66 variants showed photocatalytic activity for CO₂ under visible light except UiO-66. After 17 hours of irradiation time, the produced amount of the gas product was very small (0.03 - 0.06 μ mol of CO, and negligible amounts of CH₄). The photocatalytic reduction major product was formate (HCOO⁻), which agrees with the reported CO₂ photoreduction in TEOA and acetonitrile mixture (Table 7)[118].

Table 7. The product of the CO₂ photoreduction

Product	No CO ₂	No light	No catalyst	UiO-66	UiO-66-NH ₂	TiO ₂ C UiO-66-NH ₂	(Zr _{0.87} /Ti _{0.13}) UiO-66-NH ₂	(Zr _{0.41} /Ti _{0.59}) UiO-66-NH ₂
CO	0	0	0	0	0.033	0.038	0.029	0.063
CH ₄	0	0	0	0	0.003	0.008	0.007	0
HCOO ⁻	0	0	0	0	98.655	216.047	145.251	151.236

No HCOO⁻ was produced in either the absence of light, catalyst, or CO₂. Under simulated solar radiation, the amount of the produced HCOO⁻ differed from one sample to another. For UiO-66-NH₂, the produced formate was 98 μ mol (27.7% yield). For TiO₂C/UiO-66-NH₂, the produced formate recorded the highest amount amongst the tested samples with 216 μ mol (60.5% yield), 2.2 times over that produced from UiO-66-NH₂.

Although the addition of TiO_2 to UiO-66-NH_2 didn't affect the light absorption significantly, and although the TiO_2 absorbs light only in the UV-region[119], the photocatalytic activity of the wrapped sample increased significantly. This increase is attributed to the energy transfer mechanism described in section 3.2.2. This phenomenon is known in core-shell metal oxides systems, where the shell works as an antenna to absorb light and transfers the excitation energy to the core[120]. For $(\text{Zr}_{0.87}/\text{Ti}_{0.13})\text{UiO-66-NH}_2$, the produced amount was 141 μmol (40.6% yield), 1.5 times the produced amount from UiO-66-NH_2 , which agrees with the activity reported elsewhere, for the metal exchanged samples[103]. Similarly, for $(\text{Zr}_{0.41}/\text{Ti}_{0.59})\text{UiO-66-NH}_2$, the produced amount was 151 μmol (42.3% yield), 1.5 times the amount produced from UiO-66-NH_2 . This increase in the product can be attributed to the effect of the Ti on the photoactivity.

In order to check the stability of the catalyst, PXRD analysis was performed on all catalysts after the photocatalytic reduction. Catalysts were found to remain stable and intact in all cases, as seen in Fig. 26.

After the photoreduction, it was observed that the color of $(\text{Zr}_{0.87}/\text{Ti}_{0.13})\text{UiO-66-NH}_2$ and $(\text{Zr}_{0.41}/\text{Ti}_{0.59})\text{UiO-66-NH}_2$ had turned green. This color change is believed to be due to the partial reduction of Ti^{4+} to Ti^{3+} in the oxidation process of TEOA[121]. This green color returned to yellow gradually after opening the vial because of exposure to oxygen, which oxidizes it back to its initial state, indicating the total reversibility of the process. From the variation in the amount of HCOO^- produced, it was calculated that the activity of

the catalyst enhanced by adding Ti despite the decrease in the surface area and the CO₂ uptake (Table 8).

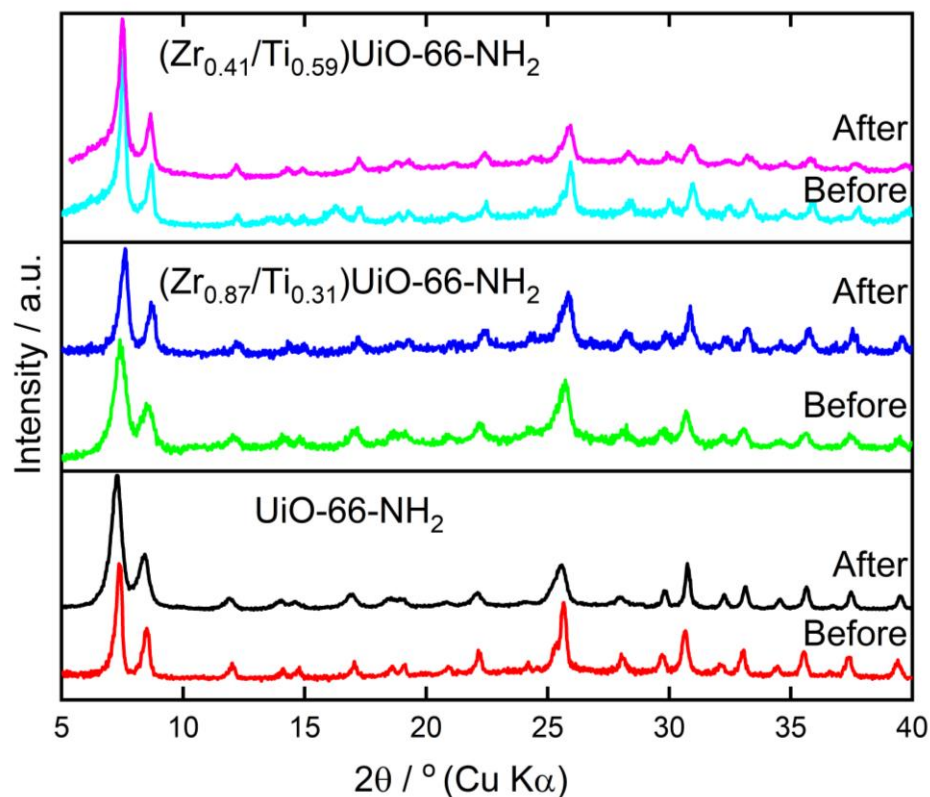


Figure 26. The PXRD of the samples after the photocatalytic reduction showing the crystallinity of the samples after the photocatalytic reduction.

Table 8. Estimated catalytic activities of the UiO-66 systems by using the possible active sites per MOF and the measured amount of formate ions

Catalyst	Molecular formula	Active site / mole ¹	Mw ² (g/mol)	The active site in 50 mg (μmol)	TON	TOF	Yield (%)
UiO-66	C ₄₈ H ₂₄ O ₃₀ Zr ₆	6	1628.04	184.3	0	0	0

¹ Number of metal atoms per mole

² Molecular weight of the unit cell

UiO-66-NH₂	C ₄₈ H ₃₀ N ₆ O ₃₀ Zr ₆	6	1718.16	174.6	0.57	0.03	27.7
TiO₂⊂ UiO-66-NH₂	C ₄₈ H ₃₀ N ₆ O ₃₀ Zr ₆ (TiO ₂) _{1.15}	7.15	1810.01	197.5	1.09	0.06	60.5
(Zr_{0.87}/Ti_{0.13}) UiO-66-NH₂	C ₄₈ H ₃₀ N ₆ O ₃₀ Zr _{5.1} Ti _{0.9}	6	1679.15	178.7	0.81	0.05	40.6
(Zr_{0.41}/Ti_{0.59}) UiO-66-NH₂	C ₄₈ H ₃₀ N ₆ O ₃₀ Zr _{2.7} Ti _{3.3}	6	1575.11	190.4	0.79	0.05	42.3

3.3 CONCLUSIONS

It is worth to emphasize the role of the different modifications of UiO-66; upon amine functionalization, the photocatalytic activity increased due to the wider absorption band. A comprehensive study was performed to tune the photophysical and photocatalytic activity of the UiO-66 platform. Amine functionalization, wrapping around TiO₂ nanoparticles, and incorporation of different ratios of Ti in the UiO-66 SBU was performed and studied using EPR and UV-Vis. The amine functionalization decreased the bandgap from 3.31 eV to 2.79 eV, shifting the light absorption to the visible region. The replacement of 59% of Zr with Ti further decreased the bandgap to 2.61 eV. The wrapping of UiO-66-NH₂ around TiO₂ nanoparticles enhanced the photocatalytic activity of UiO-66-NH₂ for CO₂ reduction, as the produced amount of formate increased by 2.2 times, although the band gap did not change much. The photocatalytic activity enhanced due to energy transfer from UiO-66-NH₂ to TiO₂.

CHAPTER 4

MIL-125 AS A PHOTOCATALYST

4.1 Introduction

One of the most interesting MOF systems for photocatalytic applications is MIL-125[40]. It is built up of cyclic octamers of corner-sharing titanium octahedral connected to 12 other octamers through the benzene-1,4-dicarboxylate (BDC) linkers. The structure has two types of cages, an octahedral cage (12.5 Å) and a tetrahedral cage (6 Å), accessible through narrow triangular windows of 6 Å width. MIL-125 was first prepared in 2009 and used for the oxidation of alcohol using UV-light [40]. Functionalization with amine (MIL-125-NH₂) makes it a good candidate for visible light photocatalytic reactions[96]. MIL-125 exhibits good photoactivity, inherent to the titanium-oxo component. In the presence of oxygen, the titanium oxo clusters are oxidized back, emphasizing a possible photocatalytic property of titanium-oxo based MOFs[94]. This material, which contains cyclic octamers of TiO₂ octahedra, is photochromic, which is related to the reduction of Ti(IV) to Ti(III) under UV irradiation[93, 122, 123].

In this study, the prepared MIL-125, its amine-functionalized, and two metal exchange derivatives were prepared and characterized by several physicochemical techniques. The crystalline forms of the produced samples confirm little changes in the morphology of the produced samples. The BET surface area, the UV-DRS data, and the CO₂ photoreduction reaction indicated the high stability of the parent MIL-125. The Zr-exchange MIL-125-NH₂ was successfully performed without any change in the framework structure. The systematic increase of the Zr-atom lowers the photocatalytic activity of the modified

materials than the pristine (amine-functionalized MOFs) that proves the role of Ti-cluster in MOF in the CO₂ reduction properties.

To unravel this role of MIL-125 as a catalyst in the CO₂ photoreduction experiment, we have synthesized four different modifications for the MIL-125 (Fig. 27); (i) linker functionalization with amine (-NH₂), as it is known that the amine group shifts the light absorption of the MOF to a longer wavelength (redshift) increasing the solar activity of the

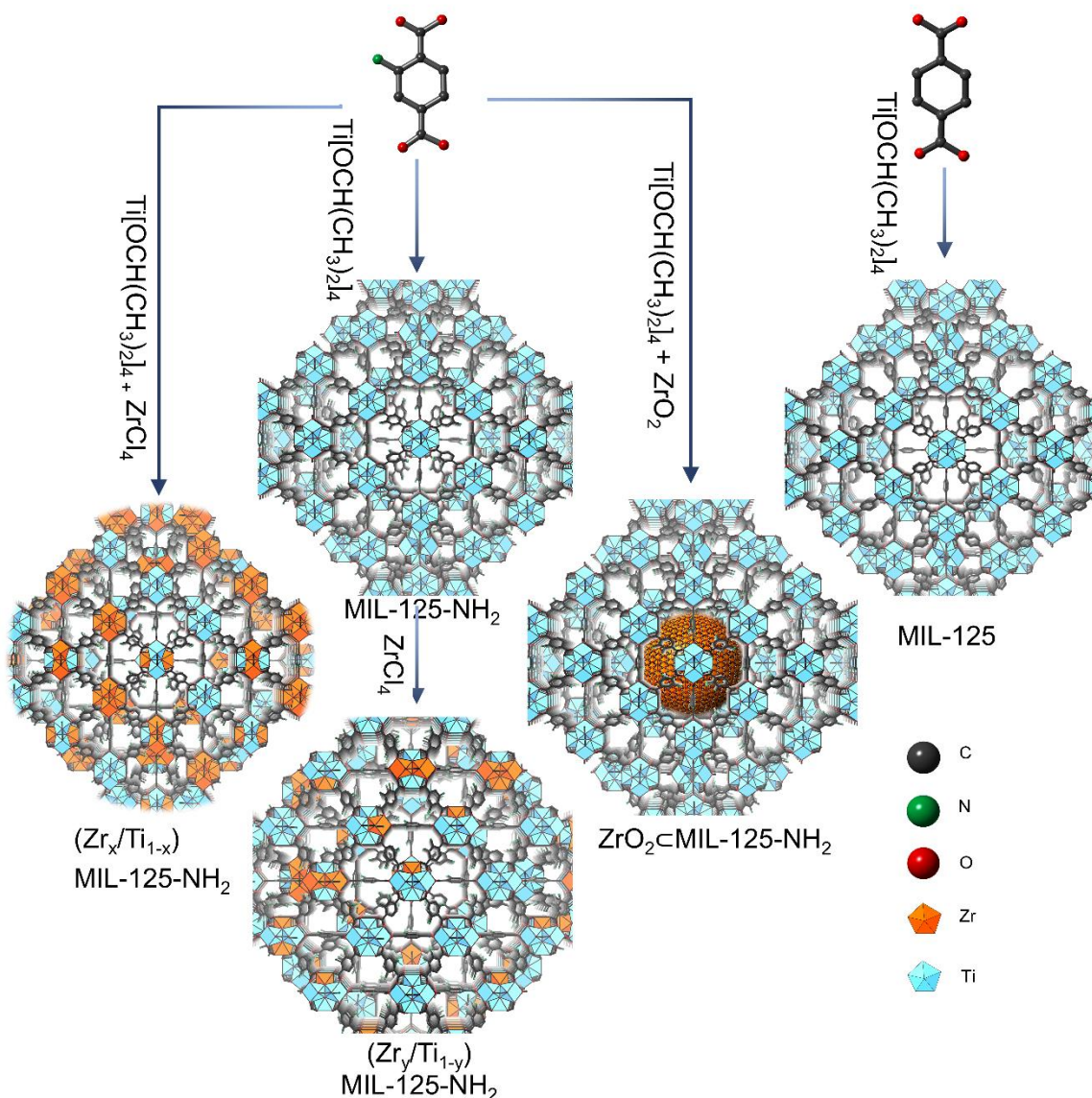


Figure 27. The series of the compounds prepared to study the different modification on the MIL-125.

MOF[96]. (ii) wrapping MOF around ZrO_2 nanoparticles, which are known to have catalytic activity in converting CO_2 to CO [124]. This wrapping will make use of the CO_2 adsorption ability of MOF to concentrate CO_2 around ZrO_2 and the catalytic ability of ZrO_2 for CO_2 conversion to CO . (iii) replacing the Ti with Zr in the SBU with a different percentage which takes place by two different procedures, post-synthetic metal exchange and *in situ* mixed metal. Exchanging the metal in the MOF SBUs is expected to affect the electronic structure and the physical properties [125-127].

4.2 Results And Discussion

4.2.1 MIL-125 Material characterization

The structure and bulk phase purity of each member of the series was then characterized by powder X-ray diffraction analysis (PXRD). The diffraction patterns for each member were in good agreement with the pattern simulated from the single crystal structure of MIL-125 (Fig. 28a). It is noted that in the case of $\text{ZrO}_2\text{-MIL-125-NH}_2$, the PXRD pattern included reflections at 24.0° , 27.9° , and 31.3° 2θ (Cu K_α) that were conclusively attributable to the (011), (11-1), and (020) Miller indices of ZrO_2 [128].

The successful encapsulation and presence of ZrO_2 nanoparticles within the MIL-125- NH_2 structure were also confirmed by transmission electron microscopy (TEM) (Fig. 29c.inset). In the TEM images, the ZrO_2 nanoparticle size was found to be ~ 5 nm, and the structure of ZrO_2 was further confirmed by electron diffraction measurements.

For the post-synthetic metal exchange, the crystallinity of MIL-125- NH_2 was destroyed, and no further characterization was performed on this sample. For the mixed

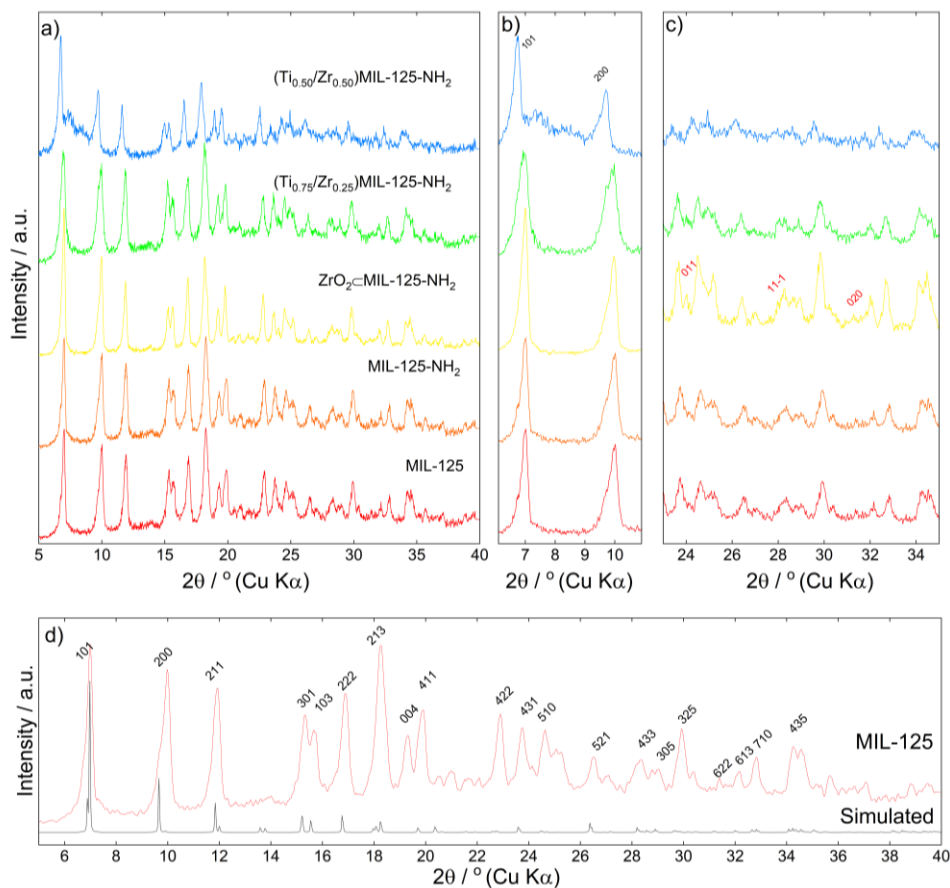


Figure 28. PXRD for the prepared samples. a) shows the diffraction pattern for all the samples. b) shows the small peak shifting for the mixed metal sample at ($2\theta = 7^\circ$ and 10°). c) Shows the wrapped ZrO_2 peaks. d) shows the crystallinity of the sample compared with the simulated structure from the CIF file and the plan indexing for each peak.

metal samples $(\text{Ti}_{1-x}/\text{Zr}_x)\text{MIL-125-NH}_2$ materials, there was a noticeable consistent shift in peak positions toward lower 2θ values (Fig. 28b). This uniform peak shifting is attributed to the expansion of the MOF's lattice due to the replacement of smaller Ti^{4+} atoms with larger Zr^{4+} atoms [103]. Lattice expansion upon metal exchange (sometimes referred to as ‘doping’) is a frequently observed behavior for inorganic semiconductor solid solutions [104].

To determine the amount of Zr^{4+} loading for these samples, inductively coupled plasma-optical emission spectroscopy measurements (ICP-OES) were performed (Table

9). For the *in-situ* analog, a range of Zr^{4+} incorporation was found to be 8% and 25%, depending on the molar equivalents of ZrCl_4 added during the synthesis. From this, the chemical formula could be calculated as $(\text{Zr}_{0.08}/\text{Ti}_{0.92})\text{MIL-125-NH}_2$ and $(\text{Zr}_{0.25}/\text{Ti}_{0.75})\text{MIL-125-NH}_2$.

From field-emission scanning electron microscopy (FE-SEM) images, the crystal morphology and size of each of the members of this series were determined (Fig. 29). For the parent MIL-125 and MIL-125-NH₂, rounded discs, 2.9 μm in size, were observed. $\text{ZrO}_2\text{C MIL-125-NH}_2$ was observed to have an octahedral shape, with different crystallite sizes of 1 μm . For mixed metal samples, the crystallites were found to be less circular and tend to be square-shaped with crystal size around 1 μm . Elemental mapping for $\text{ZrO}_2\text{C MIL-125-NH}_2$, and mixed metal samples $(\text{Zr}_{0.08}/\text{Ti}_{0.92})\text{MIL-125-NH}_2$ and $(\text{Zr}_{0.25}/\text{Ti}_{0.75})\text{MIL-125-NH}_2$ was then carried out using energy-dispersive X-ray spectroscopy (SEM-EDX). The SEM-EDX results were found to be in good agreement with the ICP data regarding the atomic compositions of the samples (Table 9). Additionally, SEM-EDX mapping demonstrated that Zr was distributed in all the samples.

Table 9. Metal content percentage obtained from ICP and EDX results for the MIL-125 samples

catalyst	ICP result (%)			EDX result (%)	
	Zr	Ti		Zr	Ti
$\text{ZrO}_2\text{C MIL-125-NH}_2$	4	96		5	95
$(\text{Zr}_{0.08}/\text{Ti}_{0.92}) \text{ MIL-125-NH}_2$	8	92		9	91

$(\text{Zr}_{0.25}/\text{Ti}_{0.75}) \text{ MIL-125-NH}_2$	25	75		26	74
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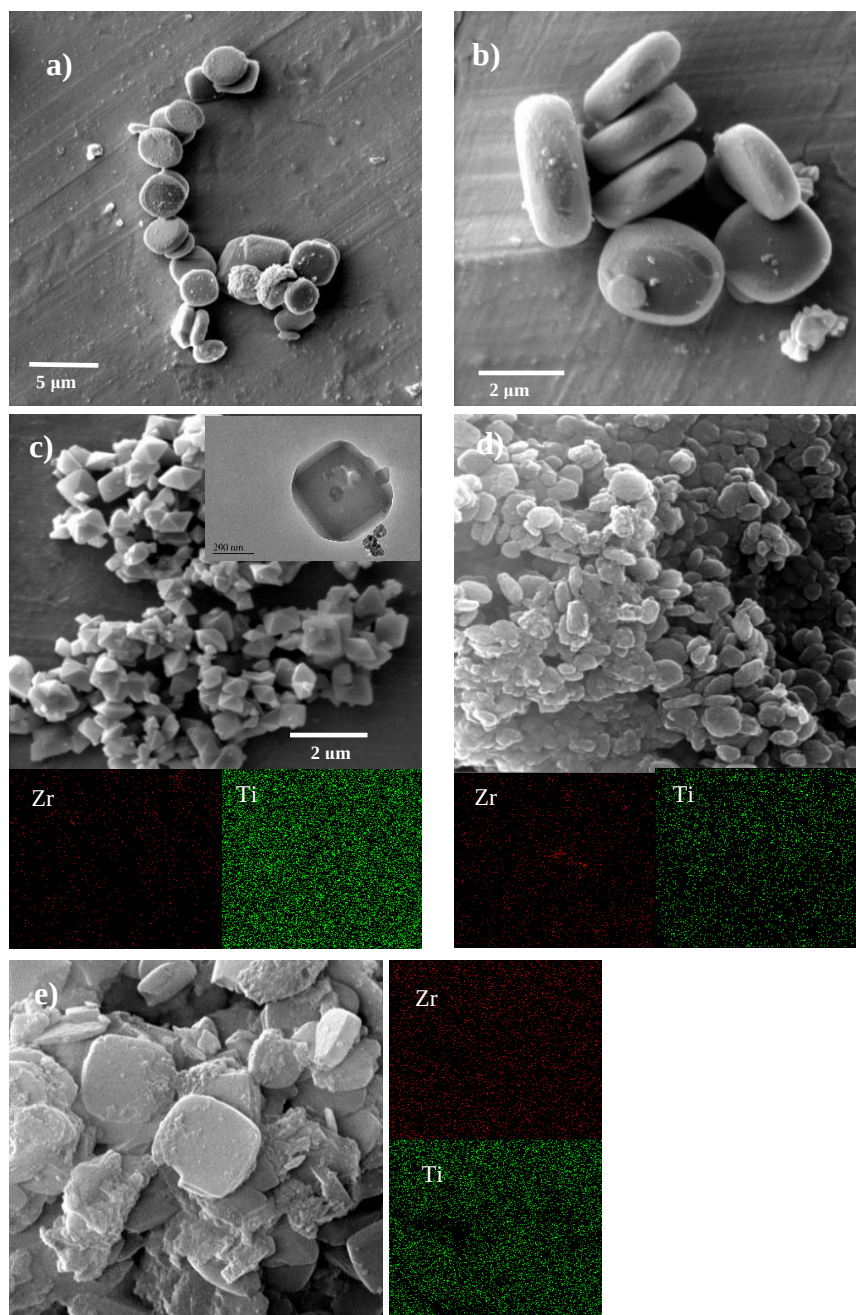


Figure 29. SEM images showing the particle size and morphology, the elemental mapping, and the EDX data for a) MIL-125, b) MIL-125-NH₂, c) ZrO₂@MIL-125-NH₂, d) (Zr_{0.08}/Ti_{0.92})MIL-125-NH₂, e) (Zr_{0.25}/Ti_{0.75})MIL-125-NH₂. The inset in c) is the TEM image of ZrO₂@MIL-125-NH₂ showing the ZrO₂ nanoparticles inside the MIL-125-NH₂.

The thermal stability and architectural robustness of each member of the series were proven by thermal gravimetric analysis (Fig. 30). In the TGA curves, all members exhibit a small decrease in weight percent up to the framework decomposition temperatures.

After framework decomposition, the calculated weight percent of the residues for the MIL-125 series are presented in Table 10. The residue weight percent for the MIL-125 series is in line with the theoretical values calculated from the crystal structure. The theoretical residue values were calculated, assuming all the residue are metal oxides (TiO_2 and ZrO_2). So, by comparing the metal oxide weight to the MOF total weight, we obtained the theoretical residue. For $\text{ZrO}_2\subset\text{MIL-125-NH}_2$, $(\text{Zr}_{0.08}/\text{Ti}_{0.92})\text{MIL-125-NH}_2$ and

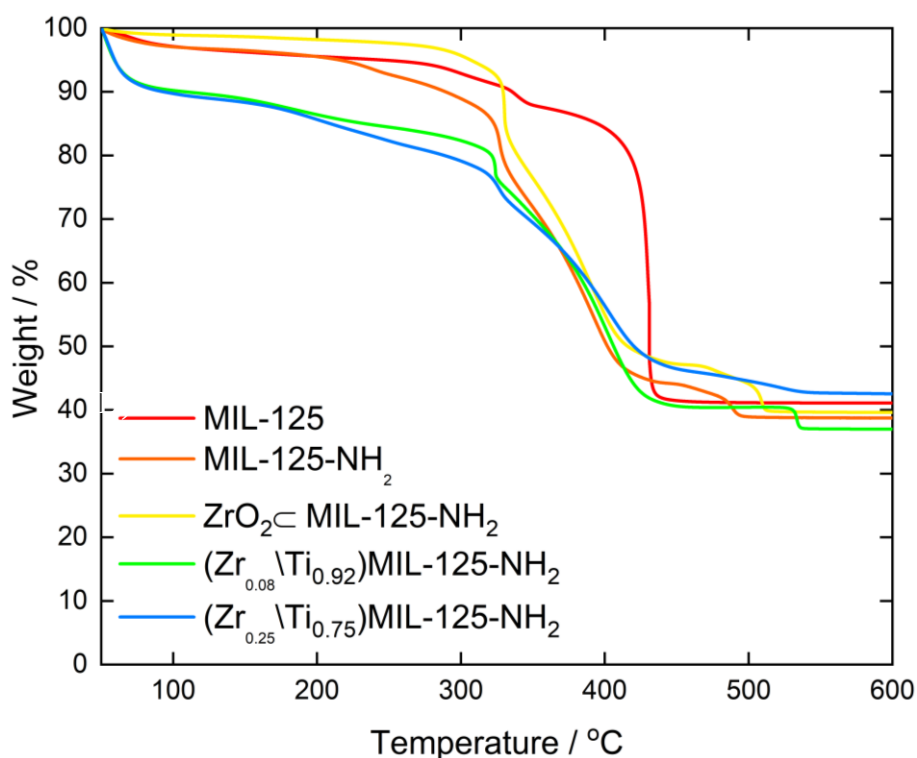


Figure 30. TGA analysis of the prepared samples in air showing the thermal stability of each MOF and the residue weight percent.

$(\text{Zr}_{0.25}/\text{Ti}_{0.75})\text{MIL-125-NH}_2$, the residue weight percent were higher than that found for

MIL-125-NH₂ due to the incorporation of Zr⁴⁺ within their structures. The Zr (91.2 u) atomic weight is higher than the atomic weight of the Ti (47.9 u). So, the residue changes from TiO₂ only to TiO₂ and ZrO₂, which explains the increase in the residue weight percent.

Table 10. TGA metal oxide residue as calculated and measured for the MIL-125.

Catalyst	Catalyst Mw	No. of metals in the catalyst	Metal oxide Mw	Calculated TGA residue %	Experimental TGA residue %
MIL-125	1563.7	8	638.94	40.9	41.3
MIL-125-NH ₂	1653.8	8	638.94	38.6	38.8
ZrO ₂ C MIL-125-NH ₂	1683.9	8.33	679.60	40.4	39.7
(Zr _{0.08} /Ti _{0.92}) MIL-125-NH ₂	1681.6	8	666.68	39.6	40.4
(Zr _{0.25} /Ti _{0.75}) MIL-125-NH ₂	1740.5	8	725.65	41.7	43.5

The porosity of all members of the series was measured by N₂ adsorption isotherm at 77 K (Fig. 31), which exhibit Type-I behavior, indicative of micropores within their structures. The surface areas calculated by applying the Brunauer–Emmett–Teller (BET) model over the $P/P_0 = 0.01–0.3$ range are presented in Table 11. These BET surface areas are in a good agreement with the surface areas previously reported[40, 129].

Table 11. The BET surface area for the MIL-125 series

Catalyst	BET surface area (m ² /g)	Reported BET surface area (m ² /g)
MIL-125	1450	1500[40]
MIL-125-NH ₂	1200	1000[129]
ZrO ₂ @ MIL-125-NH ₂	950	N/A
(Zr _{0.08} /Ti _{0.92}) MIL-125-NH ₂	1150	N/A
(Zr _{0.25} /Ti _{0.75}) MIL-125-NH ₂	650	N/A

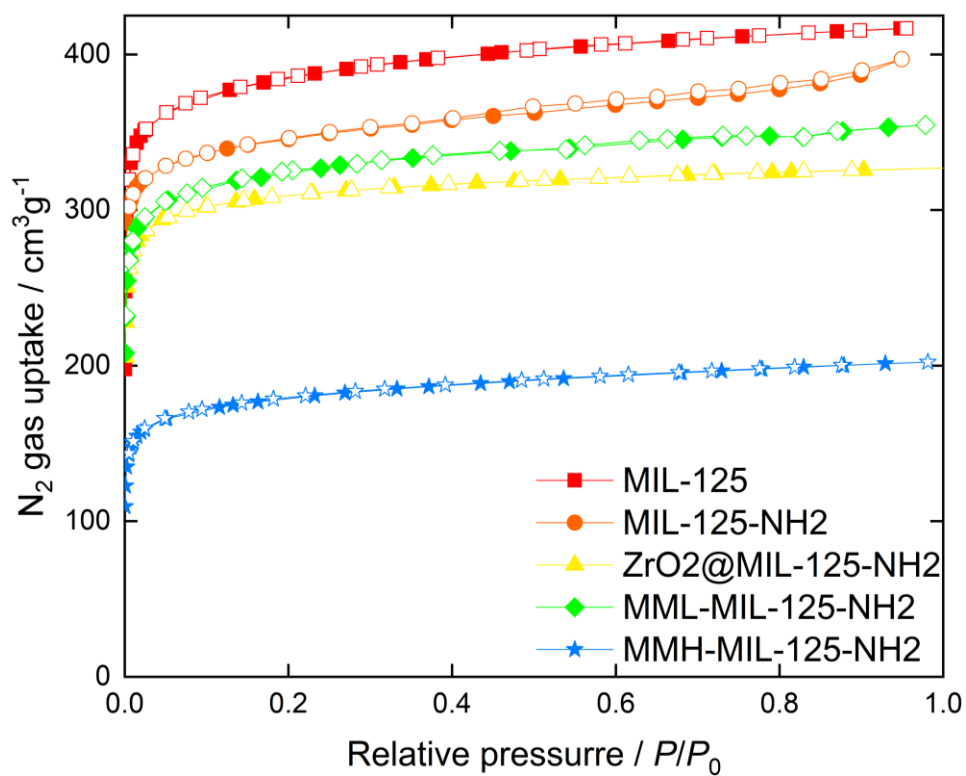


Figure 31. N₂-isotherm for the prepared samples measured at 77 K shows type 1 isotherm.

The decrease in the BET surface area in the post-synthetic exchange might be due to the existence of some ZrO_2 clusters in the pores of the MOF. The DFT method for pore size distribution shows that the MOF has micropores, and no mesopores were observed, which indicates that the pore structure didn't deform during the modifications (Fig. 32). This data agrees with that of the TGA, which shows a reasonable increase in the metal residue.

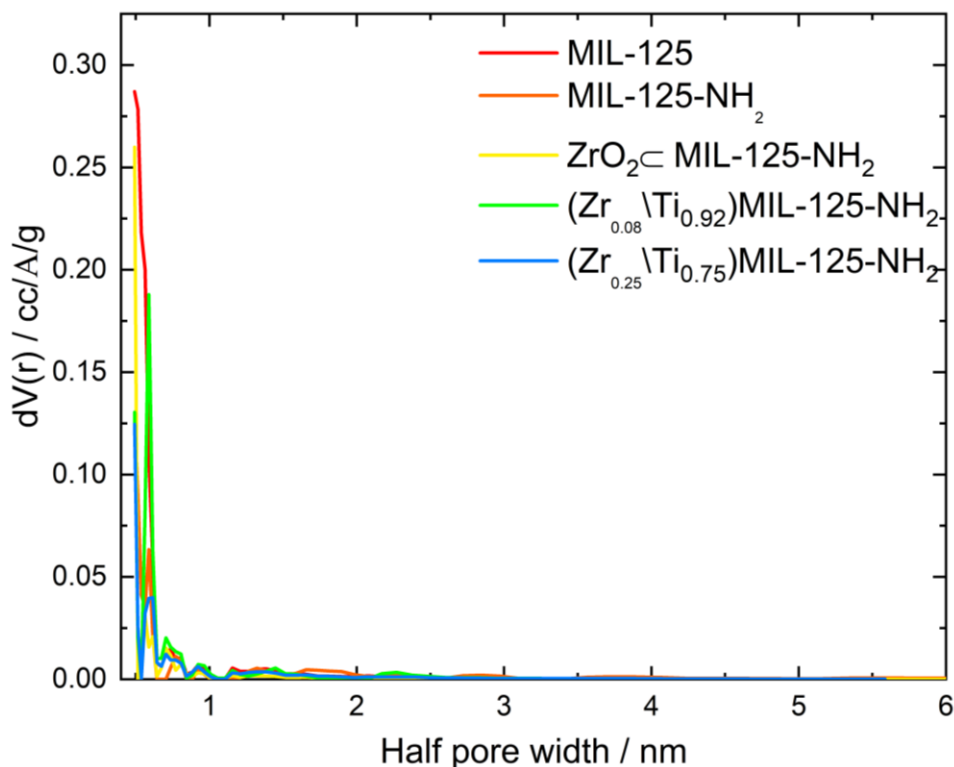


Figure 32. DFT method pore size distribution for the prepared MOFs showing the presence of micropores after modification

Prior to examining the series' photophysical properties, we measured CO_2 adsorption isotherms to gain insight into the materials' uptake capacities and affinity to CO_2 , as in Fig. 33. Table 12 states that the MIL-125 shows a good uptake at 300 K at atmospheric pressure. After functionalization with the $-\text{NH}_2$ group, the uptake remains almost the same despite

the decrease in the surface area. This is attributed to the enhanced interaction of the amine (polar) group with CO₂[130]. For ZrO₂/MIL-125-NH₂, the uptake slightly increased compared with MIL-125-NH₂. For (Zr_{0.08}/Ti_{0.92})MIL-125-NH₂, the uptake wasn't changed much, but in the case of (Zr_{0.25}/Ti_{0.75})MIL-125-NH₂, MIL-125-NH₂ the uptake decreased considerably. At low pressure, the amine-functionalized sample exhibits higher affinity to CO₂, due to the presence of the (-NH₂) group. So, at low pressure (P < 20 Torr), the CO₂ uptake for the MIL-125 is lower than the other samples (Fig. 33 inset).

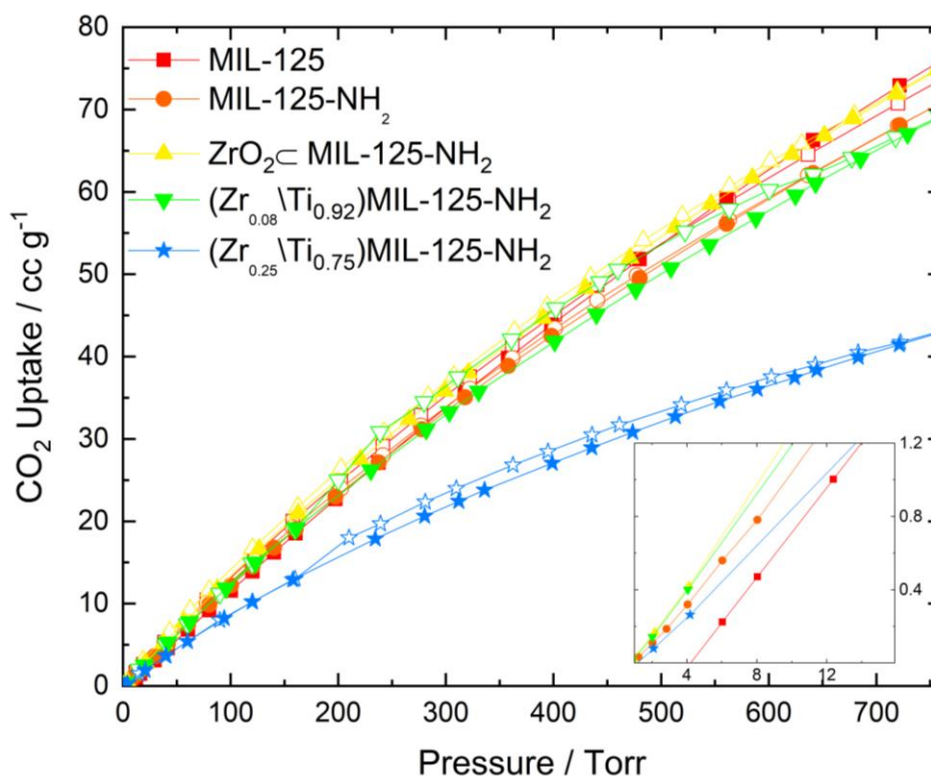


Figure 33. The CO₂ adsorption measurement for the prepared sample measured at room temperature (293 K).

Table 12. CO₂ uptake for the MIL-125 series

Catalyst	MIL-125	MIL-125-NH ₂	ZrO ₂ /MIL-125-NH ₂	(Zr _{0.08} /Ti _{0.92})MIL-125-NH ₂	(Zr _{0.25} /Ti _{0.75})MIL-125-NH ₂
CO ₂ uptake (cm ³ /g)	75	73	78	72	45

4.2.2 MIL-125 Photo-absorption characterization.

Light absorption by metal oxides is mostly associated with an excitation of electrons from the valance band to the conduction band, leaving holes behind. This transient electron-hole pair can recombine during the period of irradiation or be trapped at the surface of the solid. In some metal oxide systems, the holes are occupied by trapped oxygen anions, while the electrons are used to reduce metal cations to alter their oxidation states[131]. If a metal-reduction induces the formation or disappearance of paramagnetic species, electron paramagnetic resonance (EPR) spectroscopy can be employed to probe such a process[132].

In Fig. 34, the observed EPR spectra of MIL-125 and its amine series were obtained for all samples at 173 K in dark and under visible light irradiation. The EPR results indicate that Ti-O defects are the only reason for the formation or disappearance of paramagnetic species, as probed in similar studies of metals-MOFs[132-140].

From these measurements, three EPR peaks with g-value 2.003, are assigned to the oxygen defect in Ti-O clusters. Two other weak signals at g values of 2.150 and 2.023, which are ascribed to absorbed $\text{Ti}^{4+}\text{-O}^{2-}$ species [132, 134-138]. All the peaks exhibited very weak absorptions in the dark that drastically increased by illumination with visible light except for the parent MIL-125-MOF. The drastic increases at the characteristic EPR peak with g-value 2.003 with visible illumination in the amine derivatives may be due to electron transfer from the excited organic ligand to the metal center in the MOF

materials[139, 140]. Moreover, the absence of EPR signals at a g value of 1.988 suggests that metal reduction of Ti^{4+} to Ti^{3+} cannot form in these systems[141, 142].

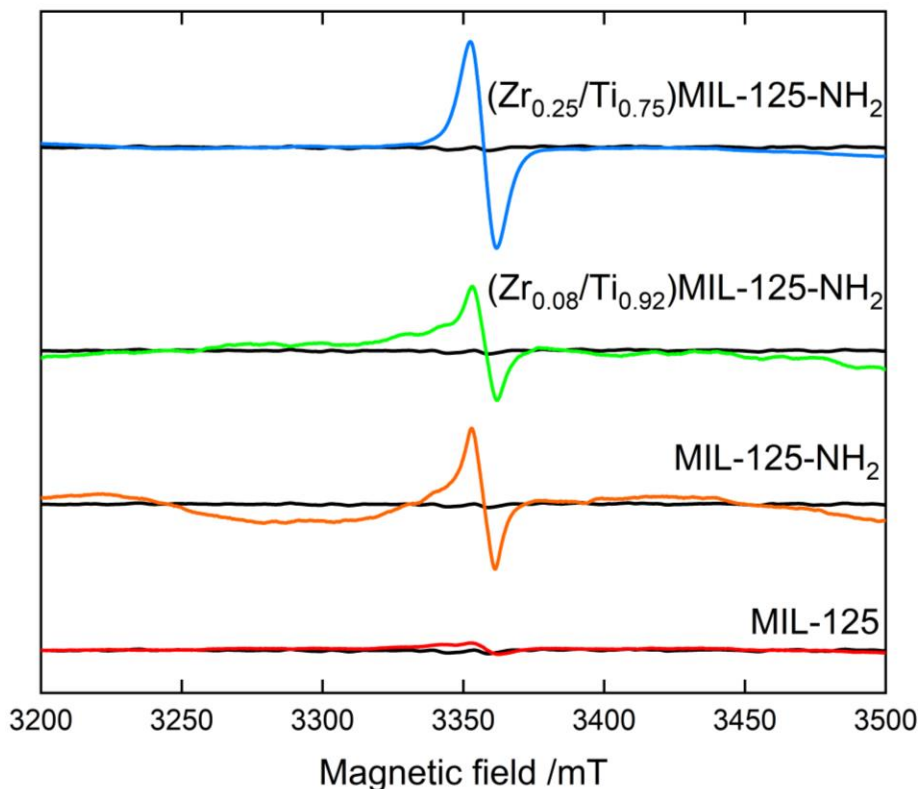


Figure 34. EPR measurement in the dark (black) and under visible light irradiation for the prepared samples (colored lines) at 173 K of the parent MIL-125-MOF and its amine and metal-metal exchanged derivatives

UV-Vis diffuse reflectance spectroscopy (UV-DRS) was used to compare the optical activity of each member of the series (Fig. 35). In general, TiO_2 only absorbs UV light [143]. By site isolating Ti^{4+} oxo-clusters in MIL-125, the absorption band is observed starting at ~ 350 nm. This absorption is attributed to the presence of extended π -conjugated bonds in the aromatic ring of the linker and a Linker-to-Metal charge transfer (LMCT) mechanism, whereby the linker absorbs light and then transfers the excitation energy to the metal cluster where an excitation electron is generated[144]. After functionalization with $-\text{NH}_2$, an additional absorption peak appears starting at ~ 550 nm and centered at ~ 370 nm,

thereby shifting the photo-absorption activity toward the visible region. This band results mainly from the LLCT process in which light excites the non-bonding electrons of the NH_2 group into the anti-bonding p -orbital of the linker. This electron is then transferred into the nearby metal, causing its reduction from Ti^{4+} to Ti^{3+} . There was a slight change observed in the optical activity after wrapping MIL-125- NH_2 around ZrO_2 . As the peak centered at 550 nm started at a lower wavelength (~ 500 nm). This results from the effect of the interface between the ZrO_2 and MIL-125- NH_2 , which may have an effect on the band structure of the system. In the case of mixed metal $[(\text{Zr}_{0.08}/\text{Ti}_{0.92})\text{MIL-125-NH}_2$ and $(\text{Zr}_{0.25}/\text{Ti}_{0.75})\text{MIL-125-NH}_2]$, the absorption band, centered at 370 nm, is broader than that of MIL-125- NH_2 , which may be caused by the Zr^{4+} containing oxo-clusters that are formed

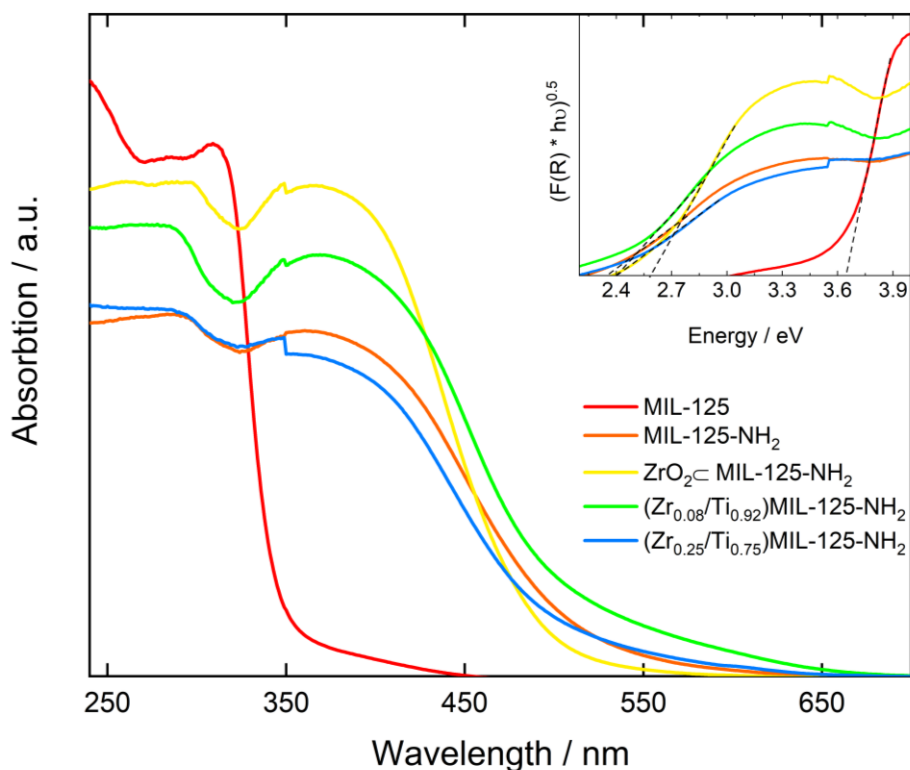


Figure 35. UV-DRS measurement for the prepared samples. The inset shows the Tauc's plot of the KM function for all the samples.

during the exchange. In these systems, light excites the non-bonding electrons into the vacant d -orbital of Ti^{4+} which populates the conduction band. In the latter systems, the bands result mainly from a linker-to-metal charge transfer (LMCT) process [145].

The UV-DRS spectra were also used in the Kubelka-Munk function to produce Tauc plots that determine the bandgap for all members of the series (inset of Fig. 35). The bandgap of the parent MIL-125 was found to be 3.61 eV. After functionalization with $-\text{NH}_2$, the bandgap decreased to 2.39 eV. In the case of $\text{ZrO}_2\text{-MIL-125-NH}_2$, the bandgap was increased to 2.61 eV, which is influenced by the effect of ZrO_2 on the MIL-125-NH₂. This effect is known for the core-shell structures[146]. The bandgap of $(\text{Zr}_{0.08}/\text{Ti}_{0.92})\text{MIL-125-NH}_2$ and $(\text{Zr}_{0.25}/\text{Ti}_{0.75})\text{MIL-125-NH}_2$ is approximately the same as the MIL-125-NH₂ (2.39 eV). The bandgap provides a good representation of the optical activity of the sample, as the solar spectrum contains: 2% in the UV region ($E > 3.20$ eV), 47% in the visible region ($3.20 > E > 1.60$ eV), and the rest is in the IR region ($E < 1.60$ eV). From the obtained band gap values, MIL-125 ($E_g = 3.61$ eV) is active in the UV region, while MIL-125-NH₂ ($E_g = 2.39$ eV) and its metal exchange MOFs are active also in the visible light region. These results are in good agreement with the EPR observations. As when the MIL-125 was shined by visible light, there was no excitation, and no peak was observed. While in the case of MIL-125-NH₂, the same light source was used, but excitation took place confirming the MIL-125-NH₂ activity in the visible region that turns Ti into a species capable of inducing photoreduction.

4.2.3 MIL-125 Catalyst evaluation

To evaluate the photocatalytic activity of our samples, we studied the photocatalytic reduction of CO₂. The reaction was done in a mixture of CH₃CN and TEOA. The CH₃CN was chosen to increase the solubility of CO₂ in the mixture. The TEOA was used as a sacrificial donor, as it acts as a proton donor as well as an electron donor[116]. Also, it was used in this mixture to provide an alkaline medium for the CO₂ reduction.

All samples showed photocatalytic activity for CO₂ under visible light except MIL-125. After 17 hours of irradiation time, the produced amount of the gas product was negligible, and the photocatalytic reduction major product was formate (HCOO⁻), which agrees with the reported CO₂ photoreduction in TEOA and acetonitrile mixture[118]. No HCOO⁻ was produced in either the absence of light, catalyst, or CO₂. Under simulated solar radiation, the amount of the produced HCOO⁻ differed from one sample to another. For MIL-125-NH₂, the produced formate was 234 μmol. For ZrO₂⊂MIL-125-NH₂, the produced formate amount was almost the same as produced from the MIL-125-NH₂ with 219 μmol. For (Zr_{0.08}/Ti_{0.92})MIL-125-NH₂, the produced amount was decreased significantly (55 μmol) 0.24 times the produced amount from MIL-125-NH₂. Similarly, for (Zr_{0.25}/Ti_{0.75})MIL-125-NH₂, the produced amount was 53 μmol, 0.24 times the amount produced from MIL-125-NH₂. This decrease in the photoreduction product is attributed to the decrease in the CO₂ uptake after adding Zr to the MIL-125-NH₂. In order to check the

stability of the catalyst, PXRD analysis was performed on all catalysts after the photocatalytic reduction. Catalysts were found to remain stable and intact in all cases.

Table 13. The product of the CO₂ photoreduction

Product	NO CO ₂	No light	No catalyst	MIL- 125	MIL-125- NH ₂	ZrO ₂ C MIL-125-NH ₂	(Zr _{0.08} /Ti _{0.92}) MIL-125-NH ₂	(Zr _{0.25} /Ti _{0.75}) MIL-125-NH ₂
CO	0	0	0	0	0.020	0.014	0.004	0.005
CH ₄	0	0	0	0	0.005	0.003	0.0	0.0
HCOO ⁻	0	0	0	0	234.0	219.7	53.8	59.7

During the photocatalytic reduction, it was observed that the color of all MIL-125-NH₂ derivatives turned green. This color change is believed to be due to the partial reduction of Ti⁴⁺ to Ti³⁺ in the oxidation process of TEOA [121]. This interesting photochromic phenomenon was observed before in the MIL-125 photocatalytic application [96]. The green color returned to yellow gradually after opening the vial because of exposure to oxygen, which oxidizes it back to its initial state, indicating the total reversibility of the process. From the variation in the amount of HCOO⁻ produced, it is concluded that the activity of the catalyst diminishes by adding Zr, with the decrease in both the surface area and the CO₂ uptake (Table 14).

Table 14. Estimated catalytic activities of the MOF systems by using the possible active sites per MOF and the measured amount of formate ions

Catalyst	Molecular formula	Active site / mole 3	Mw ⁴ (g/mol)	The active site in 50 mg (μmol)	TON	TOF	Yield (%)
MIL-125	C ₄₈ H ₂₈ O ₃₆ Ti ₈	8	1563.6	256.0	0	0	0

³ Number of metal atoms per mole

⁴ Molecular weight of the unit cell

MIL-125-NH₂	C ₄₈ H ₃₄ N ₆ O ₃₆ Ti ₈	8	1653.7	241.6	0.97	0.057	65.5
ZrO₂⊂ MIL-125-NH₂	C ₄₈ H ₃₄ N ₆ O ₃₆ Zr ₈ (TiO ₂) _{0.7}	8.7	1739.9	249.7	0.88	0.052	61.50
(Zr_{0.08}/Ti_{0.92}) MIL-125-NH₂	C ₄₈ H ₃₄ N ₆ O ₃₆ Ti _{7.4} Zr _{0.6}	8	1679.7	238.4	0.23	0.014	15.1
(Zr_{0.25}/Ti_{0.75}) MIL-125-NH₂	C ₄₈ H ₃₄ N ₆ O ₃₆ Ti ₆ Zr ₂	8	1740.4	229.6	0.26	0.015	16.7

4.3 Conclusion

A comprehensive study was performed to investigate the photophysical and photocatalytic activity of MIL-125 platform and its Zr-mixed-metal derivatives. The amine functionalization decreased the bandgap from 3.61 eV to 2.39 eV, shifting the light absorption to the visible region. The stability of the catalyst was confirmed by PXRD analysis before and after the photocatalytic reduction. The EPR measurements and the UV-DSR indicated that the visible light photons are responsible for the excitation of electrons toward the Ti-O defects, and no reduction of metal ions is possible in this system. Also, the presence of Zr did not enhance its catalytic activity.

CHAPTER 5

DFT SIMULATIONS OF DIFFERENT MOLECULES ADSORPTION AND THE CHARGE TRANSFER ON MOF CRYSTALS

5.1 Introduction

In 1926, Erwin Schrödinger published the first accounts of his now-famous wave equation[147]. He later shared the Nobel prize with Paul A. M. Dirac in 1933 for this discovery. Schrödinger's wave function seemed extremely promising, as it contains all of the information available about a system. Unfortunately, most practical systems of interest consist of many interacting electrons, and the effort required to find solutions to Schrödinger's equation increases exponentially with the number of electrons, limiting this approach to systems with a small number of relevant electrons [148]. Thus, the wave function method, which has been extremely successful in studying the properties of small molecules, is unsuitable for studies of large, extended solids. Interestingly, this difficulty was recognized by Dirac as early as 1929, when he wrote: "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the application of these laws leads to equations much too complicated to be soluble."[149].

In 1964, Hohenberg and Kohn showed that the ground state total energy of a system of interacting electrons is a unique function of the electron density[150]. Hohenberg and Kohn further identified a variational principle that appeared to reduce the problem of finding the ground state energy of an electron gas in an external potential (i.e., in the

presence of ion cores) to that of the minimization of a functional of the three-dimensional density function. Unfortunately, the definition of the function involves a set of 3N-dimensional trial wave functions.

In 1965, Kohn and Sham made a significant breakthrough when they showed that the problem of many interacting electrons in an external potential could be mapped exactly to a set of noninteracting electrons in an effective external potential[151]. This led to a set of self-consistent, single-particle equations known as the Kohn-Sham (KS) equations:

$$\left(-\frac{1}{2}\nabla^2 + v_{eff}(r) - \epsilon_j\right) \phi_j(r) = 0 \quad (1)$$

With $\phi_j(\mathbf{r})$ corresponds to the j th KS orbital of energy ϵ_j , and

$$v_{eff}(r) = v(r) + \int \frac{n(r')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + v_{xc}(r) \quad (2)$$

where $v(r)$ is the external potential, and $v_{xc}(r)$ is the exchange-correlation potential, which depends on the entire density function. Thus, the density needs to be known in order to define the effective potential so that Eq. (1) can be solved.

The ground state density is given by:

$$n(r) = \sum_{j=1}^N |\phi_j(r)|^2 \quad (3)$$

To solve Eq. (1), an initial guess is used for $\phi_j(r)$, which is used to generate Eq. (3), which is subsequently used in Eq. (2). This equation is then solved for $\phi_j(\mathbf{r})$ iteratively until the $\phi_j(\mathbf{r})$ that results from the solution of equation 1 is the same as the $\phi_j(\mathbf{r})$ that are used to define equation 2. That is, the solutions are self-consistent. Finally, the ground state energy is given by:

$$E = \sum_j \epsilon_j + E_{xc}[n(\mathbf{r})] - \int v_{xc}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} - \frac{1}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' d\mathbf{r} \quad (4)$$

where $Exc[n(\mathbf{r})]$ is the exchange-correlation energy functional. Walter Kohn shared the Nobel prize in Chemistry in 1998 for this work [148]. Provided the exchange-correlation energy functional E_{xc} is known, Eq. (4) is exact. However, the exact form of the exchange-correlation energy functional is not known; thus, approximations for this functional must be used.

5.1.1 Exchange correlation functionals

The two main types of exchange-correlation functionals used in DFT are the local density approximation (LDA) and the generalized gradient approximation (GGA). In LDA, the exchange-correlation functional is defined for an electron in a uniform electron gas of density n [151]. It is exact for a uniform electron gas and is anticipated to be a reasonable approximation for slowly varying densities. In molecules and solids, however, the density tends to vary substantially in space. Despite this, the LDA has been very successfully used in many systems [152-154]. It tends to predict overbonding in both molecular and solid systems[155], and it tends to make semiconductor systems too metallic (the bandgap problem)[156]. The generalized gradient approximation includes corrections for gradients in the electron density and is often implemented as a corrective function of the LDA. The form of this corrective function, or "exchange enhancement" function determines which functional it is (e.g., PBE, RPBE, revPBE, etc)[157].

There are increasingly new types of functionals in the literature. The so-called hybrid functionals, such as B3LYP, are more popular with Gaussian basis sets.

5.1.2 Basis sets

Briefly, the basis set is used to expand the Kohn-Sham orbitals. In a periodic lattice, one can use Bloch's theorem to show that the wave function for an electron can be

expressed as the product of a plane-wave and a function with the periodicity of the lattice[158]:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{(i\mathbf{k}\cdot\mathbf{r})}u_{n\mathbf{k}}(\mathbf{r}) \quad (5)$$

where $\mathbf{r}$ is a position vector, and $\mathbf{k}$ is a so-called wave vector that will only have certain allowed values defined by the size of the unit cell. Bloch's theorem sets the stage for using plane-waves as a basis set because it suggests a plane-wave character of the wave function. If the periodic function $u_{n\mathbf{k}}(\mathbf{r})$ is also expanded in terms of plane-waves determined by wave vectors of the reciprocal lattice vectors, $\mathbf{G}$, then the wave function can be expressed completely in terms of a sum of planewaves[159]:

$$\psi_i(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \quad (6)$$

where $c_{i,\mathbf{k}+\mathbf{G}}$ are now coefficients that can be varied to determine the lowest energy solution. This also converts Eq. (1) from an integral equation to a set of algebraic equations that can readily be solved using matrix algebra.

In a periodic system, such as systems with even one defect, or randomly ordered alloys, there is no periodic unit cell. Instead, one must represent the portion of the system of interest in a supercell, which is then subjected to the periodic boundary conditions so that a plane-wave basis set can be used. It then becomes necessary to ensure the supercell is large enough to avoid interactions between the periodic impurities. The case of the randomly ordered alloy is virtually hopeless as the energy of different configurations fluctuates statistically about an average value. These systems are discussed elsewhere [160]. Once a supercell is chosen, however, Bloch's theorem can be applied to the new artificially periodic system. To get a perfect expansion, one needs an infinite number of plane-waves. Luckily, the coefficients of the plane-waves must go to zero for high energy

plane-waves; otherwise, the energy of the wave function would go to infinity. This provides justification for truncating the plane-wave basis set above cutoff energy. Careful testing of the effect of the cutoff energy on the total energy can be done to determine suitable cutoff energy. The cutoff energy required to obtain a particular convergence precision is also element dependent. It can also vary with the "softness" of the pseudopotential. Thus, careful testing should be done to ensure the desired level of convergence of properties in different systems. These energies are rarely considered directly; it is usually differences in energy that are important. These tend to converge with the plane-wave cutoff energy much more quickly than total energies, due to cancellations of convergence errors. In this work, 520 eV was found to be suitable for the band structure calculations, but cutoff energy of 450 eV was required for CO₂ adsorption calculations.

Bloch's theorem eliminates the need to calculate an infinite number of wave functions because there are only a finite number of electrons in the supercell. However, there is still an infinite number of discrete k points that must be considered, and the energy of the unit cell is calculated as an integral over these points. It turns out that wave functions at k -points that are close together are similar; thus, an interpolation scheme can be used with a finite number of k points. This also converts the integral used to determine the energy into a sum over the k points, which are suitably weighted to account for the finite number of them. There will be errors in the total energy associated with the finite number of k , but these can be reduced and tested for convergence by using higher k -point densities[160]. The most common schemes for generating k -points are the Chadi-Cohen scheme[161], and the MonkhorstPack scheme[162]. The use of these k -point setups amounts to an expansion of the periodic function in reciprocal space, which allows a straight-forward interpolation of

the function between the points that is more accurate than with other k point generation schemes[162].

5.1.3 Pseudopotentials

The core electrons of an atom are computationally expensive with plane-wave basis sets because they are highly localized. This means that a very large number of plane-waves are required to expand their wave functions. Furthermore, the contributions of the core electrons to bonding compared to those of the valence electrons are usually negligible. In fact, the primary role of the core electron wave functions is to ensure proper orthogonality between the valence and core electrons. Consequently, it is desirable to replace the atomic potential due to the core electrons with a pseudopotential that has the same effect on the valence electrons[163]. There are essentially two kinds of pseudopotentials, norm-conserving pseudopotentials[163] and Vanderbilt ultrasoft pseudopotentials[164]. In either case, the pseudopotential function is generated from an all-electron calculation of an atom in some reference state. In norm-conserving pseudopotentials, the charge enclosed in the pseudopotential region is the same as that enclosed by the same space in an all-electron calculation. In ultrasoft pseudopotentials, this requirement is relaxed, and charge augmentation functions are used to make up the difference. As its name implies, this allows a "softer" pseudopotential to be generated, which means fewer plane-waves are required to expand it.

The pseudopotentials are not unique, and calculated properties depend on them. However, there are standard methods for ensuring the quality and transferability (to different chemical environments) of the pseudopotentials[165].

5.1.4 Fermi Temperature and band occupation numbers

At absolute zero, the occupancies of the bands of a system are well-defined step functions; all bands up to the Fermi level are occupied, and all bands above the Fermi level are unoccupied. There is a particular difficulty in the calculation of the electronic structures of metals compared to semiconductors and molecules. In molecules and semiconductors, there is a clear energy gap between the occupied states and unoccupied states. Thus, the occupancies are insensitive to changes in the energy that occurs during the self-consistency cycles. In metals, however, the density of states is continuous at the Fermi level, and there are typically a substantial number of states that are close in energy to the Fermi level.

Consequently, small changes in the energy can dramatically change the occupation numbers, resulting in instabilities that make it difficult to converge to the occupation step function. The related problem is that the Brillouin zone integral (which in practice is performed as a sum over a finite number of k points) that defines the band energy converges very slowly with the number of k points due to the discontinuity in occupancies in a continuous distribution of states for metals[166, 167]. The difficulty arises because the temperature in most DFT calculations is at absolute zero. At higher temperatures, the DOS is smeared across the Fermi level, resulting in a continuous occupation function over the distribution of states. A finite-temperature version of DFT was developed[168], which is the foundation on which one solution to this problem is based. In this solution, the step function is replaced by a smoothly varying function, such as the Fermi-Dirac function at a small but non-zero temperature[166]. The total energy is then extrapolated back to absolute zero.

5.1.5 Spin polarization and magnetism

There are two final points that need to be discussed about these calculations, spin polarization and dipole corrections. Spin polarization is important for systems that contain net spin. For example, iron, cobalt, and nickel are magnetic because they have more electrons with spin "up" than spin "down" (or vice versa). Spin polarization must also be considered in atoms and molecules with unpaired electrons, such as hydrogen and oxygen atoms, oxygen molecules, and radicals. A classically known problem involving spin polarization is the dissociation of a hydrogen molecule. In this case, the molecule starts with no net spin, but it dissociates into two atoms, each of which has an unpaired electron.

The spin-polarized solution is sensitive to the initial guess and typically converges to the closest solution. Thus, an initial magnetic guess usually must be provided to get a magnetic solution. Finally, unless an adsorbate is on a magnetic metal surface, spin polarization typically does not need to be considered, although the gas-phase reference state calculation may need to be done with spin-polarization. The downside of including spin polarization is that it essentially doubles the calculation time.

5.2 Computational Details

5.2.1 QuantumEspresso

The structure of UiO-66 and its modifications (functionalization with NH_2 and metal exchange) were optimized using the Density Functional Theory method as implemented in Quantum Espresso (QS) code[169]. We employed DFT with the generalized gradient approximation (GGA) functional in the parametrization of Perdew, Burke, and Ernzerhof (PBE) to account for exchange and correlation[170]. The projector-augmented wave

method (PAW) was used for a basis set with a cutoff energy of 520 eV[171, 172]. The valence electronic configurations as given in the atomic potential files were $5s^24d^2$ for Zr, $3p^64s^23d^2$ for Ti, $2s^22p^4$ for O, $2s^22p^3$ for N, $2s^22p^2$ for C, and $1s^1$ for H. Brillouin zone integration was performed using Blöchl's tetrahedron method, with a k-mesh generated by the Monkhorst–Pack scheme. As we are using a very large supercell, optimizations were carried out at gamma point. UiO-66 and its derivative structures were considered using a cubic supercell of 456 and 504 atoms for the pristine and functionalized amine materials, respectively. Ti^{4+}/Zr^{4+} exchange simulation was performed for 50 % atomic ratios. Geometries optimized at the experimental cell volume of the pristine UiO-66, followed by a relaxation of the cell volume and shape for all systems, was considered here. Optimizations stopped when the maximum residual force of 0.01 eV per atom was reached. The electronic wave function criterion of convergence was 10^{-7} eV. While modelling the CO_2 molecule, we have also used the implementation of the DFT-D2 approach described by Grimme to account for long-range dispersion forces. The isolated molecule was modelled in the center of the pores and near the metal sites.

The adsorption energy per molecule was calculated from the relation

$$E_{ads} = E_{complex} - (E_{MOF} + E_{mol}) \quad (7)$$

where ($E_{complex}$) is the total energy of the adsorbate-substrate system, E_{MOF} is the energy of the naked MOF cluster, and E_{mol} is the energy of the isolated adsorbate molecules. Within this definition, negative adsorption energy indicates an exothermic process.

5.2.2 VASP

The excited state and the charge transfer in the photocatalytic reduction of CO₂ for each system were studied using the Density Functional Theory method, as implemented in the VASP code[166, 173]. The PAW pseudopotential was used as implemented in the VASP code with a cutoff energy of 450 eV. We employed DFT with the generalized gradient approximation (GGA) functional in the parametrization of Perdew, Burke, and Ernzerhof (PBE) to account for exchange and correlation[170]. The relaxed structure was obtained from the QuantumEspresso code. Brillouin zone integration was performed using Blöchl's tetrahedron method, with a k-mesh generated by the Monkhorst–Pack scheme.

5.3 Results And Discussion

5.3.1 Band structure

Density functional theory simulations. DFT plane-wave calculations were carried out in order to investigate the impact of different functionalization of UiO-66 material on its electronic structures. Further, we wanted to link the electronic structures of the functionalized materials with their photocatalytic activity. Geometries were optimized in two steps, as mentioned in the Methodology section.

Upon volume and shape optimization of the pristine UiO-66 and UiO-66-NH₂, cell parameters decreased by less than 0.5% of the experimental cell parameters. In the case of the metal exchange, the cell parameters did not exceed 1.5% change of the experimental cell parameters (0.7% of UiO-NH₂-Ti-25% and 1.4% of UiO-NH₂-Ti-50%). Such shrinkage of the cell volume is manifested in PXRD (Fig. 17) and is due to the ionic size difference between Ti⁴⁺ and Zr⁴⁺.

Table 15. The change in the atomic distance after the local distortion resulted from different modifications.

	UiO-66	UiO-66-NH₂	(Ti_{0.25}/Zr_{0.75}) UiO-66-NH₂	(Ti_{0.5}/Zr_{0.5}) UiO-66-NH₂
Zr-Zr (axial)	5.03	5.02	5.00	4.98
Zr-Zr (adjacent)	3.56	3.56	3.55	3.54
Zr-O	2.24	2.22	2.21	2.23
Zr-OH	2.28	2.27	2.27	2.26
Zr-Ti	N/A	N/A	3.44	3.43
Ti-O	N/A	N/A	1.92	2.21
Ti-OH	N/A	N/A	2.19	2.19
Ti-Ti (axial)	N/A	N/A	4.74	4.72
Ti-Ti (adjacent)	N/A	N/A	N/A	3.35

In order to get an idea about the effect of the functionalization on the pore volume, we have calculated the free volume and the solvent accessible surface area of the optimized supercells. Results in Table-3 show the effect of functionalization on the pore volume. As we go from the pristine to UiO-NH₂-Ti-50%, we have a monotonic decrease in the volume and surface area. These results correlate well with the BET surface area and the CO₂-uptake data discussed in chapter 2. Such volume shrinkage can be explained by the NH₂ groups, which occupy some of the pore space, as well as the smaller ionic size of Ti⁴⁺ compared to that of Zr⁴⁺.

Table 16. The calculated and experimental band gaps of UiO-66 and its derivatives

MOF	Bandgap (eV)	Free volume (Å ³)	Surface area (Å ²)
UiO-66	2.88 (3.3)	1368	1800
UiO-66-NH ₂	1.90 (2.8)	1100	1600
(Ti _{0.25} /Zr _{0.75}) UiO-66-NH ₂	1.72 (N/A)	1019	1500
(Ti _{0.5} /Zr _{0.5}) UiO-66-NH ₂	1.61 (2.6)	960	1500

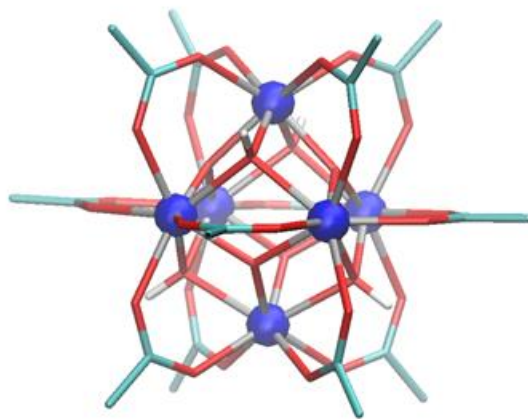


Figure 36. UiO-66 core structures Zr₆O₄OH₄ (CCOO⁻)₁₂ shown in sticks with the six Zr in blue spheres.

The optimized structures were used as inputs for the band structures and DOS calculations. It is well known that PBE functional underestimates band gaps, but here we are interested in the general trend of the bandgap upon functionalization rather than the absolute values. We did not notice any significant local structural changes at the cluster geometries level. However, there were some local distortions around the metal cores (Table 17). All modified UiO-66s have a similar structure to that of the pristine UiO-66 (see Fig. 36).

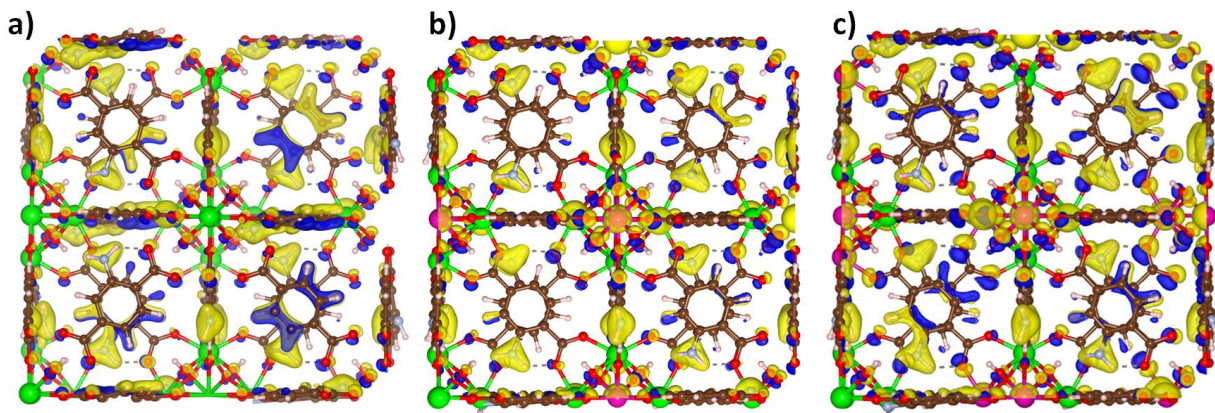


Figure 37. Charge density difference between UiO-66 and UiO-66-NH₂ (a), (Zr_{0.75}/Ti_{0.25})UiO-66-NH₂(b), (Zr_{0.5}/Ti_{0.5})UiO-66-NH₂ (c). Yellow and blue represents the electron density rich and depletion, respectively. Isosurfaces drawn at resolution of 0.08 electron/bhor³. Color code is as following; brown (C) light blue (N), white (H), green (Zr), red (O), and purple (Ti).

The band structures of UiO-66 and its derivatives are shown in Fig. 38. The band structures show a monotonic decrease in the direct bandgap from the pristine to (Zr_{0.5}/Ti_{0.5})UiO-66-NH₂ material.

This indicates that there is a synergetic effect of the amine functionalization of UiO-66 linker, which affects the top of the valence band, and the metal exchange, which affects the bottom of the conduction band (see Fig. 38). The Projected Density of States (PDOS) shown in (Fig. 39) highlights the origin of the redshift observed in the bandgap. Upon amine functionalization, electronic states generate at the top of the valence band, which are the non-bonding *p*-states of N and C atoms (see Fig. 39).

Ti⁴⁺/Zr⁴⁺ exchange generates new states at the bottom of the conduction band localized on the *d*-orbitals of Ti⁴⁺ (see Fig. 38). Further increase of Ti⁴⁺ loading leads to a smaller bandgap. On the contrary, in the pristine material, both the valence and conduction bands are localized on the linker.

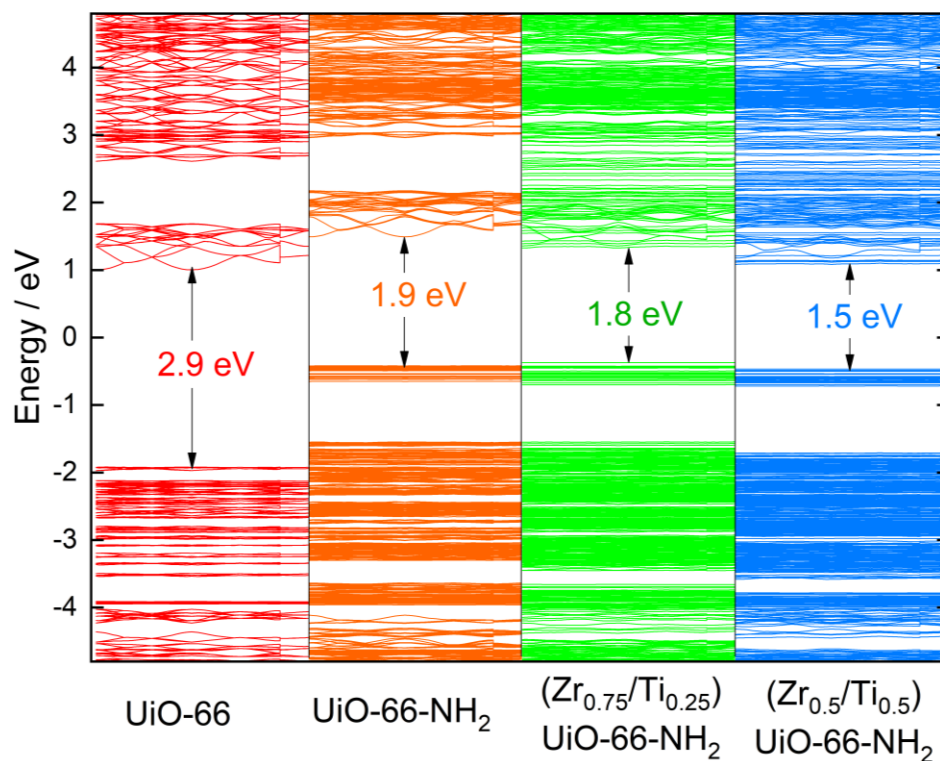


Figure 38. The computed band structure of different modification for UiO-66.

These states are located on the aromatic linker carbon atoms and the oxygen of the carboxylate groups. It is evident that the N atoms' lone pair, which is located at the top of the valence bands, has an impact on the electronic structures of the UiO-66-NH₂ series. In our study, we have modified the electronic structures of UiO-66 material using the NH₂ group and the metal exchange strategy. In the pristine UiO-66, and UiO-NH₂ the photoexcitation leads to linker-to-linker (LL) transitions while in the functionalized UiO-66-Ti⁴⁺/Zr⁴⁺, it leads to linker-to-metal (LM) transition.

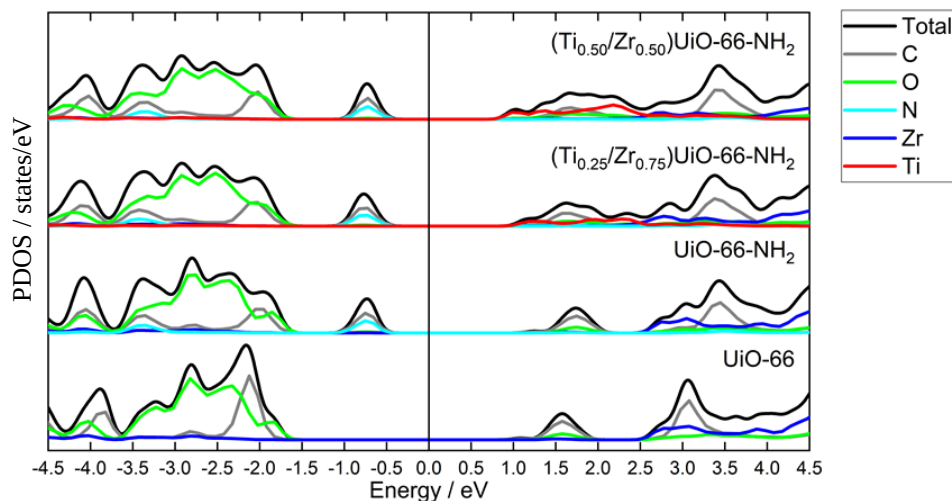


Figure 39. PDOS of the four systems investigated in our study and the total DOS are shown. The fermi level of all the systems was reset to zero.

5.3.2 CO₂ adsorption

5.3.2.1 UiO-66

We considered the supercell of the UiO-66 for CO₂ adsorption and investigated a number of initial configurations with different orientations of the CO₂ molecule. We found that the CO₂ molecule moved away from the UiO-66 surface for all configurations, except where we placed it near the Zr metal site and the OH group attached to the Zr.

metal site. In this configuration, one of the oxygen atoms, O1, of the CO₂ molecule, binds with this Zr atom, as shown in Fig. 40. The CO₂ molecule remains linear with an angle of 180°. The distance between the oxygen atom O1 of the CO₂ molecule and Zr is found to be 2.76 Å, and the C–O bond between C and this O1 atom is 1.26 Å, which is the same as the C–O₂ bond length. Zr–O bond lengths in the UiO-66 don't change with the adsorption of CO₂ where the bond length between Zr and O bonding to Zr atom is 2.08 Å, and the bond length between Zr and O bonding to C atom is 2.24 Å, while the bond

length between Zr and O bonding to H atom is 2.28 Å. The adsorption energy in this configuration is -16 kJ/mol (Table 17).

A Bader charge analysis of the supercell shows that the oxygen atom O1 of the CO₂ molecule (bonded to the coordinatively unsaturated Zr metal cluster) has 0.03e⁻, resulting from a small charge transfer from the Zr metal cluster, which becomes more oxidized after CO₂ adsorption. This very small charge transfer between the metal cluster and the CO₂ molecule, indicates weak activation of the CO₂ molecule.

By the study of the charge transfer upon light excitation of the UiO-66, it was found that the electron was transferred from the organic linkers (0.08 e) to the metal clusters (-0.08 e) leaving a partial positive charge on the linker. This finding agrees with the EPR data in our previous work; here, it shows a change in the oxidation number of the metal from Zr⁴⁺ to Zr³⁺.

OH site. In the CO₂ adsorbed near the OH group configuration, one of the oxygen atoms, O1, of the CO₂ molecule, makes a hydrogen bond with the OH group, as shown in Fig. 40. The CO₂ molecule remains linear with an angle of 180°. The distance between the oxygen atom O1 of the CO₂ molecule and H is found to be 1.81 Å, and the C–O bond between C and this O1 atom was 1.26 Å, similar to the other CO₂ bond C–O₂. Zr–O bond lengths in the UiO-66 don't change with the adsorption of CO₂, where the bond length between Zr and O bonding to Zr atom is 2.08 Å, and the bond length between Zr and O bonding to H atom is 2.27 Å. While the bond length between Zr and O bonding to C atom is 2.23 Å, which was slightly decreased to 2.21 Å after adding CO₂. The adsorption energy in this configuration is -29 kJ/mol (table 17).

A Bader charge analysis of the supercell shows that the oxygen atom O1 of the CO₂ molecule (forming a hydrogen bond with the OH group in the metal cluster) has 0.02e⁻, resulting from a small charge transfer from the OH group, which becomes more oxidized after CO₂ adsorption. This very small charge transfer between the metal cluster and the CO₂ molecule, indicates weak activation of the CO₂ molecule.

In order to assess the effect of multiple CO₂ adsorptions, we repeated our calculation by adding one more CO₂ molecule to the same UiO-66 with the CO₂ adsorbed to it. We found that the adsorption energy doesn't change for the second CO₂ molecule.

A Bader charge analysis of the supercell in the ground state (Table 18) shows that the negative charges are localized on the linkers (-2.6 e), and the positive charge is localized at the metal clusters (1.9 e), while CO₂ molecule has a very small positive charge (0.6 e). After the excitation, the negative charge was transferred to the linker (-0.08 e), leaving a positive charge on the metal cluster (0.08 e).

Our calculated geometrical parameters of the adsorbed CO₂ molecule and the binding energies are in reasonable agreement with the recent work of Tyler G. Grissom *et al.*, where they used M06-L functional utilizing an ultrafine integration grid as implemented in Gaussian09. They reported that the CO₂ has two main binding processes. CO₂ hydrogen bonds with the OH group from the metal cluster, and through dispersive interactions with the metal cluster[174]. The adsorption energy of the CO₂ was -32.5 kJ/mol.

5.3.2.2 UiO-66-NH₂

We considered the supercell of the UiO-66-NH₂ for CO₂ adsorption and investigated a number of initial configurations with different orientations of the CO₂ molecule. We found

that the CO₂ molecule moved away from the UiO-66-NH₂ surface for all configurations, except where we placed it near the Zr metal site and the NH₂ site.

metal site. In the CO₂ adsorbed near the metal configuration, one of the oxygen atoms, O1, of the CO₂ molecule binds with this Zr atom, as shown in Fig. 40. The CO₂ molecule remains linear, with an angle of 179.96°. The presence of the NH₂ group enhances the CO₂ adsorption with the metal. The distance between the oxygen atom O1 of the CO₂ molecule and Zr is found to be 2.34 Å, and the C–O bond between C and this O1 atom was 1.19 Å, similar to the other CO₂ bond C–O₂. Zr–O bond lengths in the UiO-66-NH₂ don't change with the adsorption of CO₂, where the bond length between Zr and O bonding to C atom is 2.21 Å, and the bond length between Zr and O bonding to H atom is 2.27 Å. While the bond length between Zr and O bonding to Zr atoms is 2.08 Å, which was slightly decreased after adding CO₂ to 2.07 Å. The adsorption energy in this configuration is -15 kJ/mol (table17).

A Bader charge analysis of the supercell shows that the oxygen atom O1 of the CO₂ molecule (bonded to the coordinatively unsaturated Zr metal cluster) has 0.2 e positive charge, resulting from a small charge transfer from the NH₂ function in the linker, which becomes more oxidized after CO₂ adsorption.

By the study of the charge transfer upon light excitation of the UiO-66-NH₂ it was found that the electron was localized on the organic linkers (-0.01 e), while the positive charge was located on the metal clusters (0.01 e), and a very small charge transferred to the CO₂ molecule (0.001 e).

OH site. In the CO₂ adsorbed near the OH group configuration, one of the oxygen atoms, O1, of the CO₂ molecule forms a weak hydrogen bond with the hydrogen from the

OH group, as shown in Fig. 40. The CO₂ molecule remains linear, with an angle of 179.6°. The distance between the oxygen atom O1 of the CO₂ molecule and H is found to be 2.20 Å, and the C–O bond between C and this O1 atom was slightly decreased to 1.19 Å, similar to the other CO₂ bond C–O₂. Zr–O bond lengths in the UiO-66-NH₂ don't change with the adsorption of CO₂, where the bond length between Zr and O bonding to Zr atom is 2.08 Å, and the bond length between Zr and O bonding to H atom is 2.27 Å. While the bond length between Zr and O bonding to C atom is 2.23 Å, the adsorption energy in this configuration is -30 kJ/mol (table17).

From the experimental, we have measured the CO₂ uptake for UiO-66-NH₂ at different temperatures (273 K and 293 K), and we calculated the Q_{st} value for the adsorption. The experimental Q_{st} was 28.2 kJ/mol, which is a good agreement with the calculated binding energy for the CO₂ at the OH site.

A Bader charge analysis of the supercell shows that the oxygen atom O1 of the CO₂ molecule (forming a hydrogen bond with the OH group in the metal cluster) has 0.07e⁻, resulting from a small charge transfer from the OH group, which becomes more oxidized after CO₂ adsorption. This very small charge transfer between the metal cluster and the CO₂ molecule, Indicates weak activation of the CO₂ molecule.

In order to assess the effect of multiple CO₂ adsorptions, we repeated our calculation by adding one CO₂ molecule to the same UiO-66-NH₂ with the CO₂ adsorbed to it. We found that the adsorption energy doesn't change for the second CO₂ molecule.

A Bader charge analysis of the supercell in the ground state (Table 18) shows that the negative charges are localized on the linkers (-51.6 e), and the positive charge is localized at the metal clusters (49.8 e), while CO₂ molecule has a very small positive charge (1.8 e).

After the excitation, the negative charge was transferred to the linker (-0.1 e), leaving a positive charge on the metal cluster (0.01 e).

5.3.2.3 (Ti/Zr)UiO-66-NH₂

We considered the supercell of the (Ti/Zr)UiO-66-NH₂ for CO₂ adsorption and investigated a number of initial configurations with different orientations of the CO₂ molecule. We found that the CO₂ molecule moved away from the (Ti/Zr)UiO-66-NH₂ surface for all configurations, except where we placed it near the Zr metal site and the NH₂ site.

Metal site. In the CO₂ adsorbed near the metal configuration, one of the oxygen atoms, O1, of the CO₂ molecule binds weakly with this Zr atom, as shown in Fig. 40. The CO₂ molecule remains linear, with an angle of 179.9°. The distance between the oxygen atom O1 of the CO₂ molecule and Zr is found to be 2.12 Å, and the C–O bond between C and this O1 atom was slightly decreased to 1.19 Å, and the other CO₂ bond C–O₂ was 1.19 Å. Zr–O bond lengths in the (Ti/Zr)UiO-66-NH₂ don't change with the adsorption of CO₂ where the bond length between Zr and O bonding to Zr atom is 2.09 Å, while the bond length between Zr and O bonding to H atom is 2.24 Å. While the bond length between Zr and O bonding to C atom is 2.21 Å, which was slightly decreased after adding CO₂ to 2.17 Å. The adsorption energy in this configuration is -22 kJ/mol (table 18).

A Bader charge analysis of the supercell shows that the oxygen atom O1 of the CO₂ molecule (bonded to the coordinatively unsaturated Zr metal cluster) has 0.2 e positive charge, resulting from a small charge transfer from the NH₂ function in the linker, which becomes more oxidized after CO₂ adsorption.

Similar to the UiO-66-NH₂, the charge transfer upon light excitation of the UiO-66-NH₂ was studied. It was found that the electron was localized on the organic linkers (-0.01 e), while the positive charge was located on the metal clusters (0.01 e), and a very small charge transferred to the CO₂ molecule (0.002 e).

OH site. In the CO₂ adsorbed near the OH group configuration, one of the oxygen atoms, O1, of the CO₂ molecule forms a weak hydrogen bond with the hydrogen from the OH group, as shown in Fig. 40. The CO₂ molecule remains linear, with an angle of 179.9°. The distance between the oxygen atom O1 of the CO₂ molecule and H is found to be 2.13 Å, and the C–O bond between C and this O1 atom was slightly decreased to 1.19 Å, and the other CO₂ bond C–O₂ was 1.19 Å. Zr–O bond lengths in the (Ti/Zr)UiO-66-NH₂ don't change with the adsorption of CO₂ where the bond length between Zr and O bonding to Zr atom is 2.11 Å, and the bond length between Zr and O bonding to H atom is 2.23 Å. The bond length between Zr and O bonding to C atom is 2.22 Å. The adsorption energy in this configuration is -32 kJ/mol (table18).

From the experimental, we have measured the CO₂ uptake for (Zr_{0.41}/Ti_{0.59})UiO-66-NH₂ at different temperatures (273 K and 293 K), and we calculated the Q_{st} value for the adsorption. The experimental Q_{st} was 30.7 kJ/mol, which is a good agreement with the calculated binding energy for the CO₂ at the OH site.

A Bader charge analysis of the supercell shows that the oxygen atom O1 of the CO₂ molecule (forming a hydrogen bond with the OH group in the metal cluster) has 0.1e⁻, resulting from a small charge transfer from the OH group, which becomes more oxidized after CO₂ adsorption. This very small charge transfer between the metal cluster and the CO₂ molecule, Indicates weak activation of the CO₂ molecule.

In order to assess the effect of multiple CO₂ adsorptions, we repeated our calculation by adding one CO₂ molecule to the same (Ti/Zr)UiO-66-NH₂ with the CO₂ adsorbed to it. We found that the adsorption energy doesn't change for the second CO₂ molecule.

A Bader charge analysis of the supercell in the ground state (Table 18) shows that the negative charges are localized on the linkers (-44 e), and the positive charge is localized at the metal clusters (42.50 e), while CO₂ molecule has a very small positive charge (1.5 e). After the excitation, the negative charge was transferred to the linker (-0.11 e), leaving a positive charge on the metal cluster (0.105 e).

From the above-mentioned data, we can say that the functionalization of the UiO-66 with an amine group enhances the adsorption of CO₂ on the MOF (decrease the distance between the Zr and the O) while replacing Zr with Ti further enhance the adsorption of CO₂ (increase the binding energy).

Table 17. The adsorption energy and the distances for the CO₂ on the MOF

Site	UiO-66	UiO-66-NH ₂	(Ti/Zr)UiO-66-NH ₂
Metal site (a)	2.76 Å	2.34 Å	2.12 Å
	-16 kJ/mol	-15 kJ/mol	-22 kJ/mol
OH site (b)	1.81 Å	2.20 Å	2.13 Å
	-30 kJ/mol	-30 kJ/mol	-32 kJ/mol
Q_{st} measurement		28.2 kJ/mol	30.7 kJ/mol

Table 18. The charge analysis (in e) of the MOF+CO₂ system

	UiO-66			UiO-66-NH ₂			(Ti/Zr)UiO-66-NH ₂		
	Ground	G-S	G-T	Ground	G-S	G-T	Ground	G-S	G-T
CO₂	0.631	-0.001	-0.002	1.776	0.002	0.001	1.455	0.002	0.002
Linker	-2.593	0.076	0.075	-51.6	-0.01	-0.01	-44	-0.11	-0.14
Metal	1.962	-0.075	-0.073	49.79	0.013	0.013	42.5	0.105	0.141

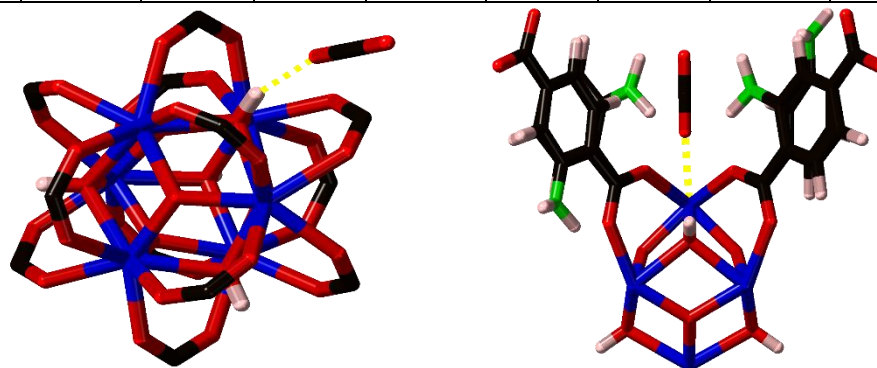


Figure 40. The adsorption site of CO₂ at different sites in the MOF crystal, showing two possible adsorption sites at the metal site (a) and at the OH group (b).

5.3.3 TEOA adsorption

5.3.3.1 UiO-66

We considered the supercell of the UiO-66 for TEOA adsorption and investigated a number of initial configurations with different orientations of the TEOA molecules (Fig. 41). We found that the TEOA molecule adsorbed in the pore of UiO-66 by bonding with two linkers in the pore. The distance between the oxygen in the TEOA and the hydrogen

from the UiO-66 is 2.03 Å and 1.33 Å. The adsorption energy of the TEOA in the UiO-66 pore is -107 kJ/mol (Table 19).

A Bader charge analysis of the supercell in the ground state (Table 20) shows that the TEOA molecule has a negative charge (-0.07 e). While the linkers have a negative charge of (-3.2 e), and the metal cluster has a positive charge of (3.2 e). After the excitation, the negative charge was transferred to the TEOA (-0.54 e) leaving a positive charge on both the linker and the metal cluster (0.52 e and 0.02 e respectively). This shows that the light excites electrons from the linkers. The excited electrons were then transferred to the TEOA.

5.3.3.2 UiO-66-NH₂

We considered the supercell of the UiO-66-NH₂ for TEOA adsorption and investigated a number of initial configurations with different orientations of the TEOA molecules (Fig. 41). We found that the TEOA molecule adsorbed in the pore of UiO-66-NH₂ by forming hydrogen bonds with linker and amine group in the pore. The distances between the oxygen in the TEOA and the hydrogen from the linker and the hydrogen from the amine are 1.38 Å and 1.81 Å, respectively. The adsorption energy of the TEOA in the UiO-66-NH₂ pore is -160 kJ/mol (Table 19).

A Bader charge analysis of the supercell in the ground state (Table 20) shows that the negative charges are localized on the linkers (-42.35 e), and the positive charge is localized at the metal clusters (42.87 e), while TEOA molecule has a very small negative charge (-0.52 e). After the excitation, the negative charge was transferred from the TEOA to the linker (-0.015 e) leaving a positive charge on both the TEOA and the metal cluster (0.002 e and 0.013 e respectively). This shows that the light excites electrons from the linkers and TEOA. The excited electrons were then transferred to the linker.

5.3.3.3 (Ti/Zr)UiO-66-NH₂

We considered the supercell of the (Ti/Zr)UiO-66-NH₂ for TEOA adsorption and investigated a number of initial configurations with different orientations of the TEOA molecules Fig. 41. We found that the TEOA molecule adsorbed in the pore of (Ti/Zr)UiO-66-NH₂ by forming hydrogen bonds with linker and amine group in the pore. The distances between the oxygen in the TEOA and the hydrogen from the linker and the hydrogen from the amine are 1.26 Å and 1.73 Å, respectively. The adsorption energy of the TEOA in the (Ti/Zr)UiO-66-NH₂ pore is -190 kJ/ mol (Table 19).

A Bader charge analysis of the supercell in the ground state (Table 20) shows that the negative charges are localized on the linkers (-41.94 e), and the positive charge is localized at the metal clusters (42.50 e), while TEOA molecule has a very small negative charge (-0.56 e). After the excitation, the negative charge was transferred to the TEOA and the linker (-0.08 e and -0.02 e respectively), leaving a positive charge on the metal cluster (0.10 e).

From the above-mentioned data, we can say that the functionalization of the UiO-66 with an amine group enhances the adsorption of TEOA on the MOF while replacing Zr with Ti further enhances the adsorption of TEOA (increase the binding energy).

Table 19. The adsorption energy and the distances for the TEOA in the MOF pores

Site	UiO-66	UiO-66-NH ₂	(Ti/Zr)UiO-66-NH ₂
Linker site (a)	1.33 Å	1.38 Å	1.26 Å
Linker site (b)	2.03 Å	1.81 Å	1.73 Å
	-107 kJ/mol	-160 kJ/mol	-190 kJ/mol

Table 20. The charge analysis (in e) of the MOF+TEOA system

	UiO-66			UiO-66-NH ₂			(Ti/Zr)UiO-66-NH ₂		
	Ground	G-S	G-T	Ground	G-S	G-T	Ground	G-S	G-T
Linker	-3.13	0.516	0.501	-42.35	-0.016	-0.016	-41.9	-0.02	-0.07
Metal	3.2	0.02	0.019	42.87	0.013	0.013	42.5	0.101	0.144
TEOA	-0.07	-0.54	-0.52	-0.52	0.002	0.003	-0.56	-0.08	-0.08

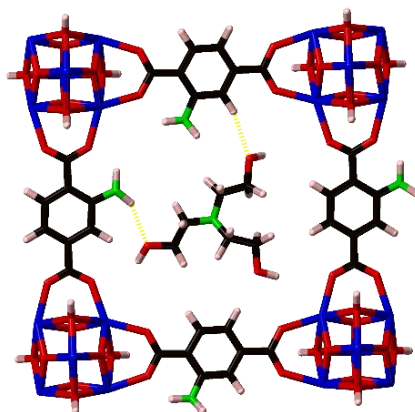


Figure 41. The adsorption site of TEOA in the MOF pores

5.3.4 TEOA+CO₂ adsorption

We evaluate the effect of TEOA on the adsorption of the CO₂ in the UiO-66 series. so, we studied the adsorption of CO₂ on a complex of MOF and TEOA.

5.3.4.1 UiO-66

We considered a complex of the supercell of the UiO-66 and TEOA for CO₂ adsorption and investigated a number of initial configurations with different orientations of the CO₂ molecule. We found that the CO₂ molecule moved away from the complex surface for all configurations, except where we placed it near the Zr metal site and the TEOA.

TEOA site. In the CO₂ adsorbed near the TEOA, one of the oxygen atoms, O1, of the CO₂ molecule forms weak hydrogen bonding with the hydrogen from the TEOA, as shown in Fig. 42. The CO₂ molecule remains almost linear, with an angle of 177.2°. The distance between the oxygen atom O1 of the CO₂ molecule and H in TEOA is found to be 2.57 Å, and the C–O bond between C and this O1 atom was 1.19 Å, similar to the other CO₂ bond C–O₂. The adsorption energy in this configuration is -35 kJ/ mol (Table 21).

OH site. In the CO₂ adsorbed near the OH group configuration, one of the oxygen atoms, O1, of the CO₂ molecule forms a weak hydrogen bond with the hydrogen from the OH group, as shown in Fig. 42. The CO₂ molecule remains linear, with an angle of 179.4°. The distance between the oxygen atom O1 of the CO₂ molecule and H is found to be 2.44 Å, and the C–O bond between C and this O1 atom was slightly decreased to 1.19 Å, similar to the other CO₂ bond C–O₂. Zr–O bond lengths in the UiO-66 don't change with the adsorption of CO₂, where the bond length between Zr and O bonding to Zr atom is 2.07 Å, and the bond length between Zr and O bonding to H atom is 2.28 Å. While the bond length between Zr and O bonding to C atom is 2.23 Å, the adsorption energy in this configuration is -30 kJ/ mol (Table 21).

A Bader charge analysis of the supercell in the ground state (Table 22) shows that the negative charges are localized on the linkers (-30.18 e), and the positive charge is localized

at the metal clusters (29.29 e), while TEOA and CO₂ molecules have a very small positive charge (0.04 e and 0.86 e respectively). After the excitation, the negative charge was transferred to the TEOA, CO₂, and the metal cluster (-0.30 e, -0.02 e, and -0.05 e respectively), leaving a positive charge on the linker (0.37 e). This shows that the light excites electrons from the linkers and TEOA. The excited electrons were then transferred to the TEOA and the metal.

In order to assess the effect of multiple CO₂ adsorptions, we repeated our calculation by adding one CO₂ molecule to the same complex with the CO₂ adsorbed to it. We found that the adsorption energy doesn't change for the second CO₂ molecule.

5.3.4.2 UiO-66-NH₂

We considered a complex of the supercell of the UiO-66-NH₂ and TEOA for CO₂ adsorption and investigated a number of initial configurations with different orientations of the CO₂ molecule. We found that the CO₂ molecule moved away from the complex surface for all configurations, except where we placed it near the Zr metal site and the TEOA.

TEOA site. In the CO₂ adsorbed near the TEOA, one of the oxygen atoms, O1, of the CO₂ molecule forms weak hydrogen bonding with the hydrogen from the TEOA, as shown in Fig. 42. The CO₂ molecule remains linear, with an angle of 179.1°. The distance between the oxygen atom O1 of the CO₂ molecule and H in TEOA is found to be 2.77 Å, and the C–O bond between C and this O1 atom was 1.19 Å, similar to the other CO₂ bond C–O₂. The adsorption energy in this configuration is -39 kJ/ mol (Table 21).

OH site. In the CO₂ adsorbed near the OH group configuration, one of the oxygen atoms, O1, of the CO₂ molecule forms a weak hydrogen bond with the hydrogen from the

OH group, as shown in Fig. 42. The CO₂ molecule remains linear, with an angle of 179.6°. The distance between the oxygen atom O1 of the CO₂ molecule and H is found to be 2.41 Å, and the C–O bond between C and this O1 atom was slightly decreased to 1.19 Å, similar to the other CO₂ bond C–O₂. Zr–O bond lengths in the UiO-66-NH₂ don't change with the adsorption of CO₂, where the bond length between Zr and O bonding to Zr atom is 2.07 Å, and the bond length between Zr and O bonding to H atom is 2.28 Å. While the bond length between Zr and O bonding to C atom is 2.22 Å, the adsorption energy in this configuration is -34 kJ/ mol (Table 21).

A Bader charge analysis of the supercell in the ground state (Table 22) shows that the negative charges are localized on the linkers (-43.30 e), and the positive charge is localized at the metal clusters (43.47 e), while TEOA and CO₂ molecules have a very small charges (-0.64 e and 0.47 e respectively). After the excitation, the negative charge was transferred to the linker (-0.02 e) leaving a positive charge on the TEOA, CO₂, and metal cluster (0.003 e, 0.0003 e, and 0.018 e respectively).

In order to assess the effect of multiple CO₂ adsorptions, we repeated our calculation by adding one CO₂ molecule to the same complex with the CO₂ adsorbed to it. We found that the adsorption energy doesn't change for the second CO₂ molecule.

5.3.4.3 (Ti/Zr)UiO-66-NH₂

We considered a complex of the supercell of the (Ti/Zr)UiO-66-NH₂ and TEOA for CO₂ adsorption and investigated a number of initial configurations with different orientations of the CO₂ molecule. We found that the CO₂ molecule moved away from the complex surface for all configurations, except where we placed it near the Zr metal site and the TEOA.

TEOA site. In the CO₂ adsorbed near the TEOA, one of the oxygen atoms, O1, of the CO₂ molecule forms weak hydrogen bonding with the hydrogen from the TEOA, as shown in Fig. 42. The CO₂ molecule remains almost linear, with an angle of 177.5°. The distance between the oxygen atom O1 of the CO₂ molecule and H in TEOA is found to be 2.58 Å, and the C–O bond between C and this O1 atom was 1.19 Å, similar to the other CO₂ bond C–O₂. The adsorption energy in this configuration is -33 kJ/ mol (Table 21).

OH site. In the CO₂ adsorbed near the OH group configuration, one of the oxygen atoms, O1, of the CO₂ molecule forms a weak hydrogen bond with the hydrogen from the OH group, as shown in Fig. 42. The CO₂ molecule remains linear, with an angle of 179.6°. The distance between the oxygen atom O1 of the CO₂ molecule and H is found to be 2.24 Å, and the C–O bond between C and this O1 atom was slightly decreased to 1.19 Å, similar to the other CO₂ bond C–O₂. Zr–O bond lengths in the (Ti/Zr)UiO-66-NH₂ don't change with the adsorption of CO₂ where the bond length between Zr and O bonding to Zr atom is 2.08 Å, and the bond length between Zr and O bonding to H atom is 2.24 Å. While the bond length between Zr and O bonding to C atom is 2.17 Å, the adsorption energy in this configuration is -35 kJ/ mol (Table 21).

A Bader charge analysis of the supercell in the ground state (Table 22) shows that the negative charges are localized on the linkers (-40.41 e), and the positive charge is localized at the metal clusters (41.06 e), while TEOA and CO₂ molecules have a very small charges (-1.34 e and 0.69 e respectively). After the excitation, the negative charge was transferred to the linker (-0.07 e) leaving a positive charge on the TEOA, CO₂, and metal cluster (0.002 e, 0.0003 e, and 0.070 e respectively).

In order to assess the effect of multiple CO₂ adsorptions, we repeated our calculation by adding one CO₂ molecule to the same complex with the CO₂ adsorbed to it. We found that the adsorption energy doesn't change for the second CO₂ molecule.

From the above-mentioned data, we can say that the presence of TEOA in the MOF pores enhance the CO₂ adsorption at the OH site of the framework. But it decreases the adsorption at the metal site and introduces another adsorption site at the TEOA molecule.

Table 21. The adsorption energy and the distances for the CO₂ on MOF in the presence of TEOA.

Site	UiO-66	UiO-66-NH ₂	(Ti/Zr)UiO-66-NH ₂
TEOA site (a)	2.75 Å	2.77 Å	2.58 Å
	-35 kJ/mol	-39 kJ/mol	-33 kJ/mol
OH site (b)	2.44 Å	2.41 Å	2.24 Å
	-30 kJ/mol	-34 kJ/mol	-35 kJ/mol

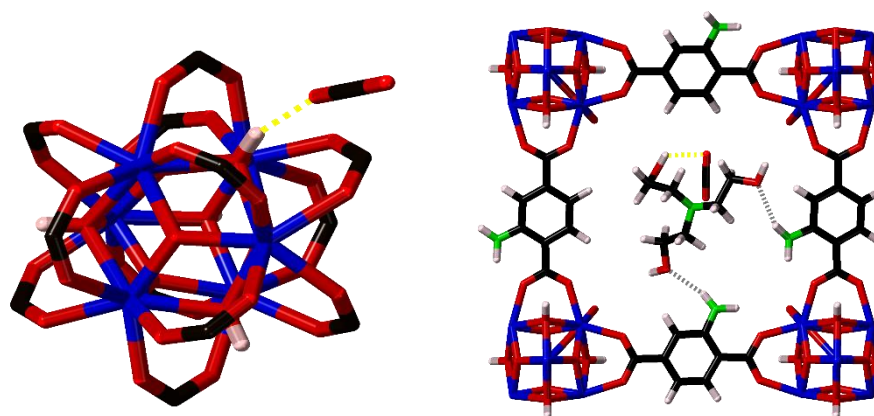


Figure 42. The adsorption sites of CO₂ on MOF in the presence of TEOA

Table 22. The charge analysis (in e) of the MOF+TEOA+CO₂ system

	UiO-66			UiO-66-NH ₂			(Ti/Zr)UiO-66-NH ₂		
	Ground	G-S	G-T	Ground	G-S	G-T	Ground	G-S	G-T
CO₂	0.86	-0.02	-0.02	0.474	3E-04	0.001	0.694	3E-04	2E-04
Linker	-30.2	0.37	0.36	-43.3	- 0.021	- 0.021	-40.4	-0.07	-0.11
Metal	29.3	-0.05	-0.06	43.47	0.018	0.018	41.06	0.07	0.109
TEOA	0.04	-0.3	-0.29	-0.64	0.003	0.002	-1.34	0.002	0.002

5.3.5 Formate adsorption

From the experimental data from the photocatalytic reduction of the CO₂, we observed that the produced formate reacts with the sacrificial agent (TEOA), forming an ester of the form ((HOCH₂CH₂)₂N(CH₂CH₂OOCH)). So, we studied the adsorption of the produced formate in the MOF pore.

5.3.5.1 UiO-66

We considered the supercell of the UiO-66 for formate adsorption and investigated a number of initial configurations with different orientations of the formate molecules (Fig. 43). We found that the formate molecule adsorbed in the pore of UiO-66 by forming hydrogen bonds with two linkers in the pore. The distance between the oxygen in the formate and the hydrogen from the UiO-66 is 1.6 Å. The adsorption energy of the formate in the UiO-66 pore is -103 kJ/ mol (Table 23).

5.3.5.2 UiO-66-NH₂

We considered the supercell of the UiO-66-NH₂ for formate adsorption and investigated a number of initial configurations with different orientations of the formate molecules (Fig. 43). We found that the formate molecule adsorbed in the pore of UiO-66-NH₂ by forming hydrogen bonds with linker and amine group in the pore. The distances between the oxygen in the TEOA and the hydrogen from the linker and the hydrogen from the amine are 1.61 Å and 1.93 Å, respectively. The adsorption energy of the TEOA in the UiO-66-NH₂ pore is -160 kJ/ mol (Table 23).

5.3.5.3 (Ti/Zr)UiO-66-NH₂

We considered the supercell of the (Ti/Zr)UiO-66-NH₂ for TEOA adsorption and investigated a number of initial configurations with different orientations of the TEOA molecules Fig. 43. We found that the TEOA molecule adsorbed in the pore of (Ti/Zr)UiO-66-NH₂ by forming hydrogen bonds with linker and amine group in the pore. The distances between the oxygen in the TEOA and the hydrogen from the linker and the hydrogen from the amine are 1.68 Å and 1.78 Å, respectively. The adsorption energy of the TEOA in the (Ti/Zr)UiO-66-NH₂ pore is -141 kJ/ mol (Table 23).

From the above-mentioned data, we can say that the adsorption of the produced formate increase after the functionalization with the amine group. While after replacing Zr with Ti in the SBU of the UiO-66-NH₂, the binding energy of the formate with the MOF decreased. This can explain the higher product yield from the CO₂ photocatalytic reduction when using (Ti/Zr)UiO-66-NH₂.

Table 23. The adsorption energy and the distances for the produced formate in the MOF pores

Site	UiO-66	UiO-66-NH ₂	(Ti/Zr) UiO-66-NH ₂
OH site (a)	1.06 Å	1.61 Å	1.68 Å
OH site (b)	2.03 Å	1.93 Å	1.78 Å
Binding energy	-103 kJ/mol	-160 kJ/mol	-141 kJ/mol

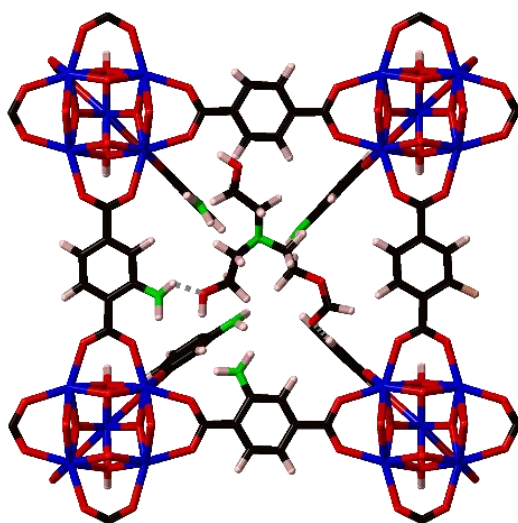


Figure 43. The adsorption of the produced formate in the MOF pores

5.4 Conclusion

DFT simulations for the band structure shed light on the origin of the experimentally observed decrease in the bandgap. The bandgap was decreased after modification. For the UiO-66-NH₂, the decrease from 2.9 eV to 1.9 eV is due to the increase in the valence band edge resulted from the amine energy levels introduced at the top of the valence band. In the case of a metal exchange, the decrease from 1.9 eV to 1.5 eV is attributed to the lower energy of the conduction band edge resulted from the Ti energy levels introduced at the

bottom of the conduction band. The change in the lattice parameters was measured, and we found that the crystal structure remains the same after modification and the change in the lattice parameter was small and consistent with the XRD data reported in Chapter 3.

DFT simulation for the CO₂ reduction reaction studied the adsorption of the chemicals on the UiO-66 systems and the charge transfer during the catalytic reaction. We found that during the reaction, when TEOA is used as a sacrificial donor, the CO₂ is adsorbed on the TEOA surface, and the reaction takes place at the TEOA site. The excited electrons transfer from the MOF linker to the TEOA, where the reaction takes place. The CO₂ photoreduction reaction is formate, which binds with the TEOA forming an ester that blocks the pores and stops the reaction.

CHAPTER 6

CONCLUSION AND PERSPECTIVES

6.1 Conclusion

A comprehensive study was performed to investigate the photophysical and photocatalytic activity of the UiO-66 platform, MIL-125 platform, and their mixed-metal derivatives. For the UiO-66 systems, the EPR measurements and the UV-DRS indicated that the visible light photons are responsible for the excitation of electrons that reduce the metal ions. Also, the presence of Ti in different forms produces some distortion in the cluster. We conjecture that this distortion introduces some defects in the cluster (oxygen deficiency) that tear down some cage's walls, hence producing macro-pores, as evidenced by a decrease in the BET surface area. Moreover, the amine functionalization decreased the bandgap from 3.31 eV to 2.79 eV, shifting the light absorption to the visible region, and the replacement of 59% of Zr with Ti further decreased the bandgap to 2.61 eV. The study also emphasizes the role of different functionalization of UiO-66, upon the photocatalytic activity. The photocatalytic activity increased remarkably due to the wider absorption band, almost doubling the photocatalytic activities using mixed-metals MOFs. However, upon Zr/Ti metal-exchange, the electronic transitions switched from ligand-ligand-charge transfer into a ligand-metal-charge transfer mechanism. Functionalization by UiO-66 wrapping around TiO₂ nanoparticles leads to further enhancement of the photocatalytic activity, due to core-shell like energy transfer mechanisms.

For the MIL-125 systems, the amine functionalization decreased the bandgap from 3.61 eV to 2.39 eV, shifting the light absorption to the visible region. The stability of the

catalyst was confirmed by PXRD analysis before and after the photocatalytic reduction. The EPR measurements and the UV-DRS indicated that the visible light photons are responsible for the excitation of electrons toward the Ti-O defects, and no reduction of metal ions is possible in this system. Also, the presence of Zr did not produce any distortion in the MIL-cluster, which in turn did not enhance its catalytic activities.

The use of DFT simulations shed light on the origin of the experimentally observed decrease in the bandgap, and the obtained DOS results proved that in UiO-66 and UiO-66-NH₂, the photoexcitation is due to linker-to-linker (LL) transitions, while in the mixed-metal catalysts the photoexcitation is due to linker-to-metal (LM) transition. Thus, upon Zr/Ti metal-exchange, the electronic transitions switch from ligand-ligand charge transfer (LLCT) into the ligand-metal charge transfer (LMCT) mechanism.

The computational calculation for the adsorption sites of the reactants and products in the MOF pores shows that the CO₂ is most probable adsorbed at the OH group in the metal cluster (which was demonstrated experimentally and computationally), while the TEOA is adsorbed at the linkers inside the MOF pore. In the CO₂ photoreduction, the CO₂ is added after adding the TEOA. The TEOA blocks the pores and adsorb CO₂ on the TEOA surface. The product of the reaction under the previously reported condition (see chapter 2) is formate. The produced formate reacts with the TEOA forming an ester. The produced ester is adsorbed at the linkers forming the pore of the MOF and blocks these pores preventing the more CO₂ from reaching the active sites and stopping the conversion of more CO₂ (no more yield). The reaction stops at the format stage and doesn't proceed to higher-value products as we need enough energy to break the bond between the TEOA, and the produced formate. In order to reach higher-value products for the CO₂ reduction, another source of

energy is needed (heat energy or electrical energy) to supply the reaction with the energy needed to liberate the formate and proceed with the reaction.

The charge transfer mechanism was studied by calculating the difference in the charge distribution between the ground state and the excited state of the UiO-66 system. Fig. 44 shows a charge analysis for the UiO-66 systems describing the charge transfer. The charge transfer analysis shows that when a photon with energy greater than the MOF energy gap reaches the MOF surface, it is absorbed by the amine group in the linker. The absorbed photon excites an electron from the amine group. The excited electron transfers to the linker through an LLCT process. Then the electron reaches the metal cluster (in the absence of TEOA) through the LMCT process. Finally, the electron transfers to the CO_2 adsorbed on the metal cluster, inducing a reduction reaction. In the presence of TEOA as a sacrificial

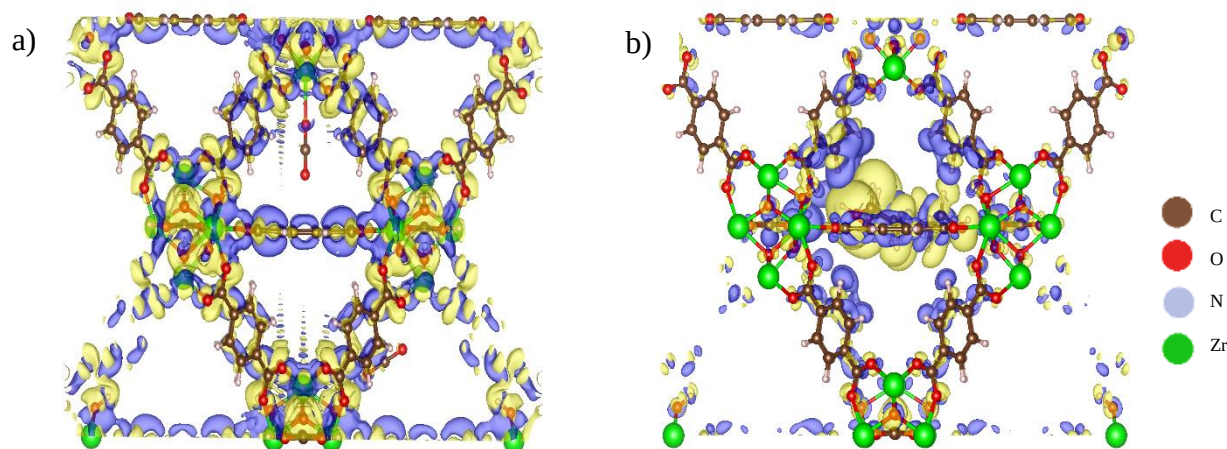


Figure 44. The charge transfer in the photoreduction process using UiO-66 a) in absence of TEOA and b) in presence of TEOA. The yellow clouds are electron rich and the blue clouds are electron deficient.

donor, the excited electron transfers from the linker to the TEOA surface. The electron then transferred to the CO_2 is adsorbed on the TEOA surface, and the reduction process takes place.

Finally, the CO₂ photocatalytic reduction using UiO-66 produce formate and don't convert the formate to a more valuable product as the produced formate block the active sites of the MOF and prevent more CO₂ from reaching the pores where the reactions take place. For this reaction to move forward, energy is needed to break the bond formed between the formate and the TEOA used as a sacrificial donor in the reaction. Regarding the light interaction with the MOF, it was found that the light was absorbed by organic linkers and produce conduction electrons there. The electrons then transferred to the metal cluster, causing the metal to be reduced. In the presence of TEOA, the electron transfer in the MOF is different. In the presence of the TEOA as a sacrificial donor, the CO₂ is adsorbed at its surface, leaving the metal site. When the light excites the electron from the organic linker in the MOF, the electron is transferred to the TEOA instead of the metal cluster. So, the photocatalytic reduction of the CO₂ takes place at the surface of the TEOA producing the formate.

6.2 Prospective:

We have studied the charge transfer in the photocatalytic reduction of CO₂ starting from the light absorption until the electron reaches the CO₂ molecule. To complete the study, the charge transfer during the reduction of CO₂ needs to be studied, so the selectivity of the reaction to a certain product can be improved. Also, our study needs to be extended to the electrocatalytic reduction of CO₂ for a better understanding of the role of each part of the MOF in the catalytic reaction. To achieve this, our prospective work can be listed as follow:

- 1- In-situ EPR needs to be done during the photocatalytic reaction to have a better understanding of the CO₂ photoreduction reaction. We need to figure out how the reaction happens, what intermediates are formed, and the stability of each intermediate. From these data, we might be able to control the selectivity of the reaction by forcing the intermediate products to direct the reaction toward a certain product.
- 2- In-situ FTA measurement for the photocatalytic reaction needs to be done. This measurement will allow us to have a better understanding of the photocatalytic reduction process. By monitoring the catalyst, the excited states, and the lifetime of each state, we can try to improve the lifetime of the produced charge carriers (electrons and holes). Increasing the lifetime of the charge carrier will increase the yield of the CO₂ photoreduction product and enhance the selectivity of the catalyst to a certain product.
- 3- Electrocatalytic reduction of CO₂ using the prepared catalysts. This will allow study of the effect of different modification on the electroactivity of MOF. By preparing thin films and measure the conductivity, resistivity, and the selectivity we can improve the charge density in the conduction band of the MOF. This will increase the electrocatalytic activity of the MOF.
- 4- Photo-electrocatalytic reduction of CO₂ needs to be performed. The light assisted electrocatalytic reduction of CO₂ will make use of the band gap decreasing and the increase in the charge density of the prepared MOFs. Performing this experiment will allow the optimization of the CO₂ reduction by engineering the band gap and enhancing the conductivity of the MOF.

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Languages

-Very Good command of reading, writing, and spoken English.

-Good reading and writing French

Computer skills & language courses

1- Computer Courses:

- Programming language (C++)
- Programming language (Python)
- Mathematica

2- TOEFL COURSE

- IBT score (96) reading (23) listening (26) speaking (22) writing (25)

3- GRE COURSE

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Teaching experience

- Lecturer B in King Fahd University for Petroleum and Minerals in Dhahran, Kingdom of Saudi Arabia. (2014- till now)
- Teaching assistant at Misr international university in Cairo, Egypt (2013-2014)
- Teaching assistant in the Canadian international college in Cairo, Egypt (2013-2014)
- Teaching assistant at the American University in Cairo, Egypt (2008-2013)

Research experience

1. Research Assistant at King Fahd University for Petroleum and Minerals in Dhahran, Kingdom of Saudi Arabia. (2014- till now)

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Experimental techniques

- 1- X-ray diffraction
- 2- Positron annihilation
- 3- Doppler broadening
- 4- Diamond anvil cell high-pressure technique
- 5- X-ray fluorescence
- 6- Liquid phase epitaxial growth
- 7- Doping by diffusion
- 8- Electron paramagnetic resonance
- 9- UV-vis spectroscopy
- 10- Density function theory

Workshop and school organization

- **March 2010:** Training program in the high-pressure technique at the University of Cologne

Publications

- 1- *Mostafa Zeama, Safwat Abdel-Azeim, and Zain H. Yamani, "Computational Study on the adsorption of CO₂ in UiO-66 modified structures", ACS Catalysis, submitted manuscript.*
- 2- *Mostafa Zeama; Ibraheem Nasser; Afaf Abdel-Hady, "Rényi, Fisher, Shannon, and their electron correlation tools for 2-electron series", J. Physica A, Just accepted manuscript.*
- 3- *Mostafa Zeama, Mohamed A. Morsy, and Zain H. Yamani, "Study of the photoactivity and photocatalytic properties of modified MIL-125", Molecular Catalysis, submitted manuscript.*
- 4- *Mostafa Zeama, Mohamed A. Morsy, Safwat Abdel-Azeim, Mahmoud M. Abdelnaby, Ahmed M. Alloush, and Zain H. Yamani, "Photophysical and Photocatalytic Properties of Structurally Modified UiO-66", Inorganica Chimica Acta, 2019, 119287.*

- 5- *Mostafa Zeama, and Zain Yamani*, “Band gap engineering of UiO-66 MOF platform as efficient method for the enhancement of CO₂ conversion”, The 11th International Conference and Exhibition on Chemistry in Industry, The Gulf Convention Center Manama, Kingdom of Bahrain (29-31 Oct 2019).
- 6- *Mostafa Zeama and Ibraheem Nasser*, “Tsallis entropy calculation for non-Coulombic helium”, *J. Physica A* 528 (2019) 121468.
- 7- *Mostafa Zeama, I. Nasser, and Afaf Abdel-Hady*, “The nonadditive entropy for ground state of helium-like ions using Hellmann potential”, *J. Molecular physics*, 2019, 1-8.
- 8- *I Nasser, M Zeama, A Abdel-Hady*, “ The Rényi entropy, a comparative study for He-like atoms using the exponential-cosine screened Coulomb potential”, *J. Results in Physics* Volume 7, 2017, Pages 3892-3900.
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