



**INFLUENCE OF DEPROTONATING BASE ON MOLECULAR CONSTRUCTION:
CASE STUDY OF Cu^{II} /1,3,5- BENZENE TRICARBOXYLIC ACID SYSTEM**

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Abstract

The influence of deprotonating base on the properties of synthesized MOF obtained from room temperature reactions of $\text{Cu}(\text{NO}_3)_2$ and 1,3,5-benzene tricarboxylic acid was studied. Two frameworks, TF1 and TF2, were obtained by slow vapour diffusion of triethylamine or pyridine into a solution of $\text{Cu}(\text{NO}_3)_2$ and 1,3,5-benzene tricarboxylic acid in DMF at room temperature. The compounds obtained crystallized in the cubic space group with identical XRD, SEM and FT-IR spectra. The compounds however differed in optical properties when irradiated with ultraviolet radiation. TF1 exhibited blue fluorescence when irradiated under UV radiation at 365 nm.

1.0 Introduction

Metal-organic frameworks (MOFs) are a class of porous crystalline compounds obtained from the coordination of metal ions or clusters to polydentate organic ligands. These compounds have continued to attract much attention due to their intriguing molecular topologies and potential applications as functional materials (Chen *et al.*, 2024, Du *et al.*, 2005; Furukawa *et al.*, 2013; Rao *et al.*, 2004). Based on the properties of the framework, these compounds have found applications in molecular recognition, catalysis, drug delivery, gas storage and separation (Li, H, Eddaoudi, M., O’Keffe, M, Yaghi, 1999; Mori *et al.*, 2005; Noro & Nakamura, 2017; Sawaki & Aoyama, 1999; Seo *et al.*, 2000).

The framework architecture depends on a combination of several factors including the coordination geometries of the metal ions, nature of organic ligand and reaction conditions (Ding & Cai, 2019).

Metal-organic frameworks usually have high surface areas with high pore volumes and large pore sizes which can be varied by careful choice of the bridging ligands. Two classes of ligands commonly used in the construction of MOFs are carboxylic acids or carboxylates and nitrogen containing ligands such as pyridines and imidazoles, mixed ligand frameworks bearing both oxygen and nitrogen donor atoms have also been reported (Chen *et al.*, 2014). Careful adjustments of the linker length, ring substituent and geometry can be used to tune

the resulting MOF for specific applications. Aromatic polycarboxylates have been extensively applied as ligands for supramolecular materials because they are sterically rigid and chemically robust, thereby leading to coordination polymers with high thermal stability.

The use of dicarboxylic acids namely 1,4-benzenedicarboxylate and extended conjugated analogues afforded the generation of functional porous materials suitable for gas storage. By employing polycarboxylic acids such as 1,2,4,5-benzenetetracarboxylic acid, 1,3,5-benzenetricarboxylic acid (BTC) and benzene hexacarboxylic acid as ligands in the construction of metal-organic frameworks more thermally stable frameworks with interesting architecture have been obtained (Ebrahimi, 2017; Majumder et al., 2006; Nguyen et al., 2012) (Harvey et al., 2011; S.S.Y. Chui et al., 1999; Zhu et al., 2012); Kobayashi et al., 2000; Williams et al., 2000). These robust ligands generate structures with variety of topologies either through metal coordination or with organic motifs having complimenting hydrogen bonding effect. Multiple coordination modes of the carboxylate ligand are often observed within the same structure (Lu et al., 2014; Vagin et al., 2007).

Furthermore, these polycarboxylates exhibit wide variation in degree of protonation and deprotonation, which in turn affects the ligand coordination ability and the resulting topology of the framework obtained. The diverse structural chemistry of polycarboxylate aromatic ligands is sensitive to synthesis conditions requiring a thorough

systematic study of the influence of each individual factor such as pH, temperature and solvent on the ensuring framework. This knowledge would assist in generation of isoreticular materials with practical applications. While extensive research is ongoing in use of polycarboxylic acids as supramolecular ligands, systematic investigations focussing on the influence of a particular synthetic parameter are rare.

One of the most studied compound used in the investigation of MOF properties is HKUST-1, first isolated from the solvothermal reaction of copper nitrate with 1,3,5 benzenetricarboxylic acid (Chui et al., 1999). The compound is also known as MOF 199 and is commercially available as Basolite C300 (Mahmoodi & Abdi, 2019; Nguyen et al., 2012). The synthesis this MOF has been replicated under room temperature, ultrasonic and mechanochemical conditions with products having the same topology and architecture.

We are interested in the systematic study of 1,3,5-benzenetricarboxylic acid, a robust ligand with many potential applications. In this paper, we report the effect of deprotonating base on the $\text{Cu}^{2+}/1,3,5$ benzenetricarboxylic acid system.

2.0 Material and Methods

All chemicals purchased are of reagent grade and used without further purification. The IR spectra were measured using solid samples on a Bruker FT-IR tensor 27 spectrophotometer equipped with an attenuated total reflectance accessory. Elemental analyses were performed on a Perkin-Elmer automated model 2400 Series II CHNS/O analyser and Powder X-ray

diffraction on Bruker AXS D8 Diffractometer. Scanning electron microscopy images were obtained using a Scanning electron microscope JOEL-JSM-7600F.

2.1 Synthesis

[Cu₂(BTC)(H₂O)₈].0.25DMF (TF1) 1,3,5-benzenetricarboxylic acid (0.12 g, 1.0 mmol) and Cu(NO₃)₂.5H₂O (0.23 g, 1 mmol) were dissolved in dimethylformamide (DMF) (3mL) in a small vial. The small vial was placed in a bigger vial containing triethylamine (0.5 mL) in DMF (2 mL). The set up was covered and left undisturbed. After 2 weeks, turquoise blue crystalline solid was obtained. The reaction mixture was filtered, solid product washed with water and dried in a desiccator. Yield:0.324 g; Anal. Cald (%): C 23.58; H 4.21; N 0.71. Found (%): C 23.69; H 4.65; N 0.86.

[Cu₂(BTC)(H₂O)₈].0.25py (TF2) 1,3,5-benzenetricarboxylic acid (0.12 g, 1.0 mmol) and Cu(NO₃)₂.5H₂O (0.23 g, 1 mmol) were dissolved in dimethylformamide DMF (3 mL) in a small vial. The small vial was placed in a bigger vial containing pyridine (0.5 mL) in DMF (2 mL). The set up was covered and left undisturbed. After 2 weeks, green crystalline solid was obtained. The reaction mixture was filtered, solid product washed with water and dried in a desiccator. Yield 0.232 g; Anal. Cald (%): C 24.73; H 4.05; N 0.70. Found (%): C 24.99; H 4.81; N 0.89.

3.0 Result and Discussions

3.1 Synthesis

The compounds TF1 and TF2 were obtained by slow vapour diffusion of triethylamine (TEA) or pyridine into a solution of

Cu(NO₃)₂ and BTC in DMF at room temperature. TEA and pyridine were employed to facilitate the coordination reaction between the ligand and metal ion by enhancing deprotonation of the acid. As bases, they coordinate to the accumulated protons produced during the deprotonation process thus facilitating the formation of the MOF and reduction in acidity of the reacting medium. The slow diffusion process utilized promote crystal growth of the nuclides over crystal formation. The difference in ability of the deprotonating base is reflected by the different colours of the products obtained blue and green crystals for TEA and pyridine respectively (Chui et al., 1999). This is in line with observation of Shan et al., (2018) on use of TEA as deprotonating solvent in synthesis of UiO-66. The products obtained were insoluble in water and common organic solvents such as ethanol, acetonitrile, acetone or DMF. The compounds exhibited different optical properties when placed in water or polar organic solvents such as ethanol and acetone. In these media, TF1 showed blue luminescence under UV light at wavelength 365 nm (Fig. 1). This observation suggests its potential use as a sensor for detection of moisture or alcohol in matrices.

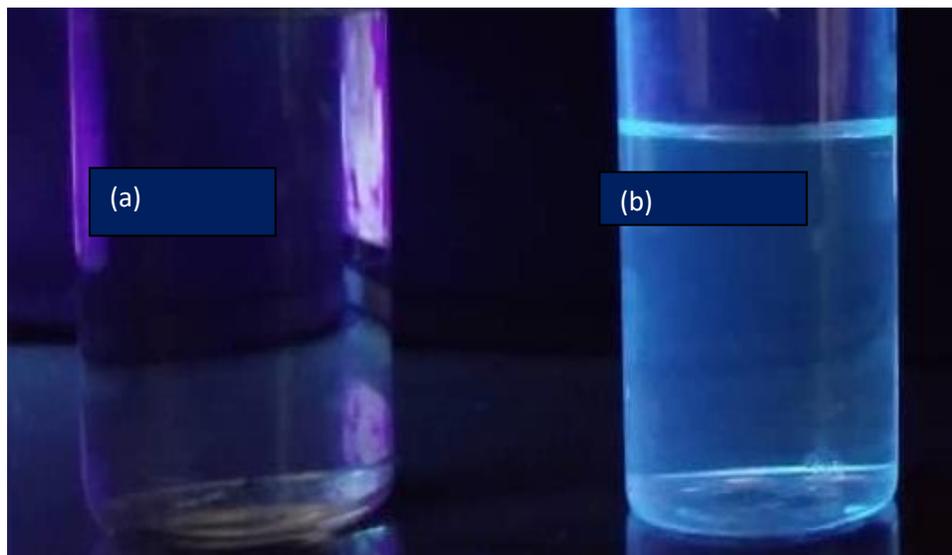


Fig. 1: View of compounds under UV light (a) TF2 (b) TF1

FT-IR

The use of Fourier transform infrared and Raman spectroscopy in characterization of MOFs provides insight into the molecular interactions present within the framework. Based on association of the organic ligand with the metal ion, the framework exhibits specific patterns of signals which can serve as fingerprints for the resulting MOF. Furthermore, many modes in the IR spectrum are sensitive to the intermolecular interactions present within the frameworks, hence can be exploited in identification of the various aggregates present within the framework.

The IR spectra of both compounds are identical (Fig. 2). The absence of bands at 1710 cm^{-1} and 1284 cm^{-1} indicate complete deprotonation of the acid linker. Comparison of the spectra with previously reported

$\text{Cu}(\text{BTC})$ complexes, reveals two sets of bands attributed to symmetric and asymmetric stretch of the carboxylate group. Bands at 1652 and 1450 cm^{-1} are assigned to carboxylate groups present in big pores while the bands at 1450 and 1374 cm^{-1} are for smaller pores (Gentile et al., 2020; Chui et al., 1999). In this case, only bands at 1450 and 1374 cm^{-1} are observed. This indicates the presence of only one type of pore in both compounds. The presence of molecular water is confirmed by the broad band at 3340 cm^{-1} and the band at 1620 cm^{-1} . In addition to the bands for molecular water, there are water molecules coordinated to copper ions as indicated by the band at 1573 cm^{-1} (Decoste et al., 2013; Gentile et al., 2020; Yaghi et al., 1996). The band at $486/489\text{ cm}^{-1}$ in both compounds, suggest that the copper ion is bonded to the ligand by a O-Cu-O paddlewheel bond.

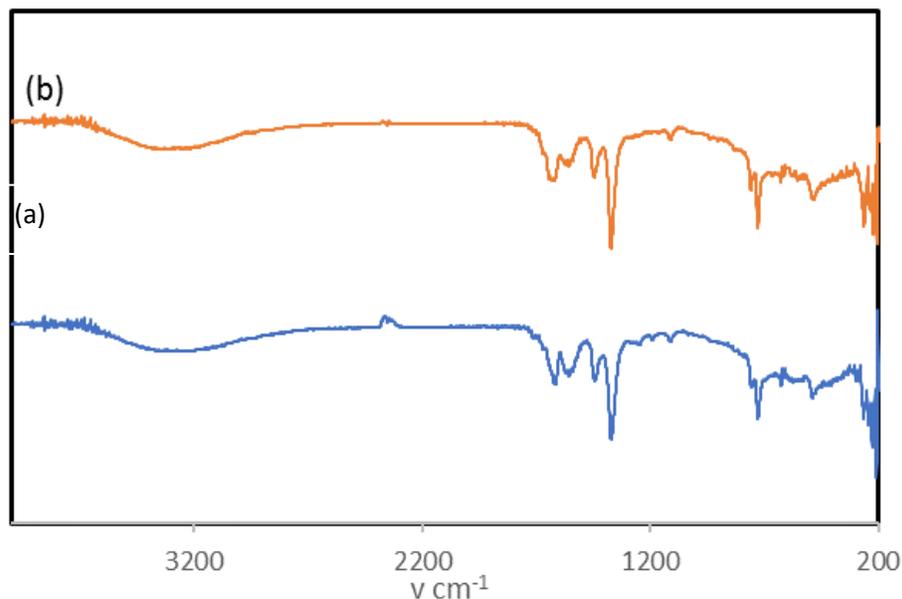


Fig. 2: IR spectra of compounds (a) TF 1 (b)TF 2

PXRD

The PXRD patterns for the compounds are shown in Fig. 3. The formation of highly crystalline samples from the slow diffusion process is reflected by the presence of high intensity peaks in low 2θ region. The spiked diffraction peaks suggest formation of large crystals in both samples. The XRD peaks were matched with the existing ICDD database. The compounds matched well with the PDF-card number 00-062-1183. This information suggests that our synthesized Cu BTC crystal structure is cubic with unit cell $a = b = c = 26.279 \text{ \AA}$ and the space angle $\alpha = \beta = \gamma = 90^\circ$. Both samples gave sharp peaks at 2θ 6.8, 9.6, 11.8, 13.5. These peaks can be indexed to corresponding signals in HKUST-1 at crystal planes (200), (220), (222), (400). Thus, indicating that the

compounds as-synthesized are isostructural with HKUST-1.

Also, the crystallite size of our prepared material (TF1 and TF2) was calculated from the XRD data using the Scherrer equation, shown below:

$$D = \frac{K\lambda}{\beta \cos\theta}$$

D= Crystallite size

K=0.9 (Scherrer constant)

$\lambda = 0.154 \text{ nm}$ (wavelength of the X-ray source)

B= FWHM (Radian)

θ = Peak position (Radian)

The full width at half maximum (FWHM) was calculated using Originpro software. Using the Scherrer equation, the average

crystallite size of the sample was calculated to be = 35.78nm.

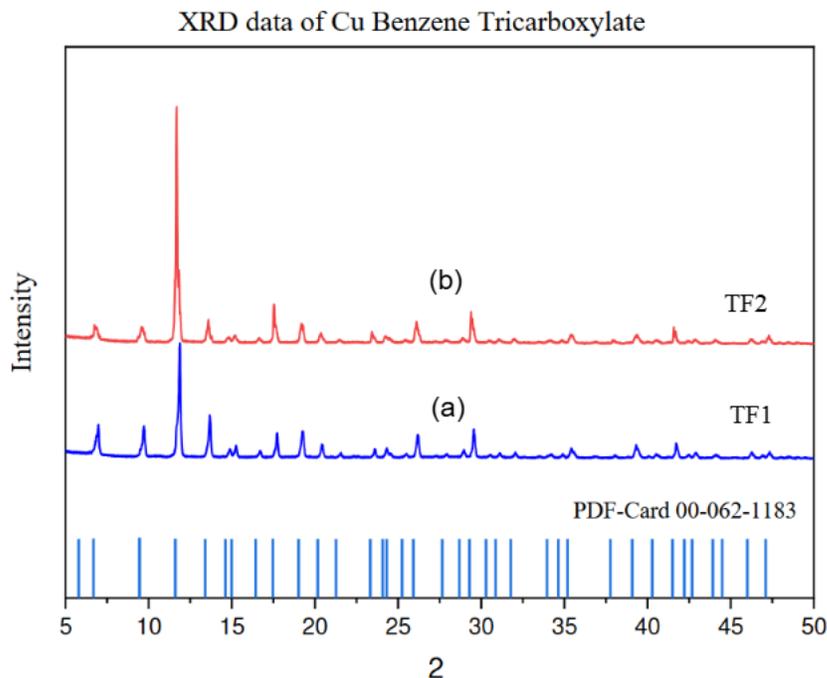


Fig. 3: XRD patterns of (a) TF1 and (b)

From the XRD data, it shows the synthesized copper benzene tricarboxylate was a single-phase crystalline material. The XRD peaks were matched with the existing ICDD database. The Cu BTC compound matched well with the PDF-card number 00-062-1183. This information suggests that our synthesized Cu BTC crystal structure is cubic with unit cell $a = b = c = 26.279 \text{ \AA}$ and the space angle $\alpha = \beta = \gamma: 90^\circ$. Also, the crystallite size of our prepared material (Copper Benzene Tricarboxylate) was calculated from the XRD data using the Scherrer equation, shown below:

$$D = \frac{K\lambda}{\beta \cos\theta}$$

D= Crystallite size

K=0.9 (Scherrer constant)

$\lambda = 0.154 \text{ nm}$ (wavelength of the X-ray source)

B= FWHM (Radian)

θ = Peak position (Radian)

The full width at half maximum (FWHM) was calculated using Originpro software. Using the Scherrer equation, the average crystallite size of the sample was calculated to be = 35.78nm.

SEM

The SEM images for the compounds are shown in Fig. 4. SEM analysis was used to

examine the morphology and particle shape of the synthesized compounds. The particles appear octahedral with etched edges.

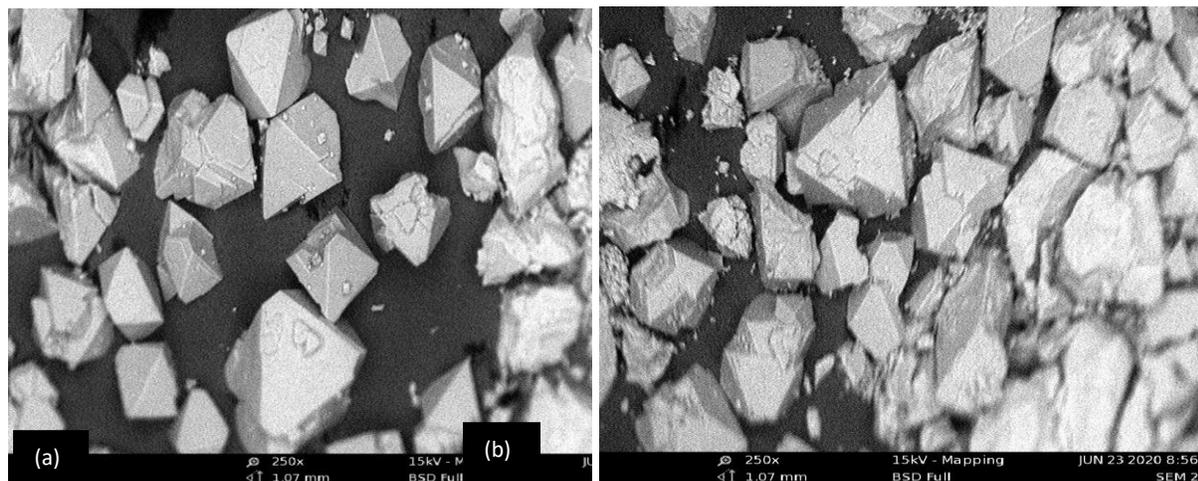


Figure 4: SEM images of (a) TF1 and (b) TF 2

4.0 Conclusions

The influence of deprotonating base on the structural properties of MOF obtained by reaction of Copper(II) nitrate with 1,3,5 BTC was studied using triethylamine and pyridine. The compounds obtained had different colours but were isostructural as shown by the IR spectra, PXRD and SEM analysis. They however exhibited different luminescence behaviour under UV light.

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