



# Synthesis and Characterization of Lanthanum Metal Organic Frameworks and Their Potential as Metal Cations and Oxo-Anions Sensor

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**Abstract.** This research investigates the synthesis and characterization of La-NDC/La-BDC MOF using FTIR, XRD, SEM, and the electronic response of those MOFs to metal ions and oxoanions at the UV-Vis range. This research was conducted in February-June 2022 at the Laboratory of Basic Science, Faculty of Education and Faculty of Science, University of Bengkulu, and Laboratory of Bandung Institute of Technology. MOF was synthesized using the solvothermal method from lanthanum nitrate salt ( $\text{La}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$ ) with 2,6-naphthalenedicarboxylic acid (NDC) and Benzene-1,4-dicarboxylic acid (BDC) as ligands and dimethylacetamine (DMA) as a solvent. The reaction was carried out at temperatures 120, 130, and 150 °C for 24 h. The result showed that La-NDC MOF had been obtained in the form of yellowish crystals from a reaction at temperatures 120 and 130 °C; brownish-colored crystals from a reaction at a temperature of 150 °C; and yellowish crystals from the reaction at all temperatures. The FTIR test on crystals demonstrated no wavenumber at  $2500 \text{ cm}^{-1}$  (characteristics of -OH functional groups). In addition, the absorption peak of  $\text{C}=\text{O}$  was shifted from the standard peak. This indicates that the synthesized La-NDC and La-BDC have coordination bonds between  $\text{La}^{3+}$  ions and NDC or BDC ligands. The results of the XRD test on crystals indicated a high level of crystallinity. Meanwhile, the SEM test showed that the synthesized crystals had a morphological size that was not uniform for La-NDC and a rod-like form for La-BDC. The La-NDC response test to oxoanions exhibited a new peak at a wavelength of 328 nm–368 nm indicating La-NDC MOF has the potential to be used as a sensor. Besides, La-BDC was shown to be selective toward  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  ions.

**Keywords:** Oxoanions · Metal Cations · La-NDC · Metal Organic Frameworks

## 1 Introduction

The reactive nature of free radicals can cause various potential harm to biomolecules by damaging lipids, proteins, and DNA, as well as causing oxidative stress (Pheninendra, 2014). Oxidative stress can cause cell damage and disruption to the body (Ma, 2010). The body has a mechanism to protect itself by neutralizing free radicals that are formed

using the enzymes superoxide dismutase, catalase, and glutathione peroxidase. However, in certain circumstances, free radicals can exceed the body's defense system.

*Metal organic frameworks* (MOFs) are a relatively new group of compounds built from coordination between metals and organic linkers to form unlimited one to three-dimensional (3D) structures [1]. For the last two decades, MOFs have gained more and more attention, and so far, more than ten thousand new structures of MOFs have been published. The structure variation is due to various pore sizes, surface area, and types of metal and ligand (organic linkers). MOFs have been applied as catalysts, adsorption, drug delivery, and gas storage. Several have been reported to detect environmental contaminants, such as metal ions [2–5].

MOFs developed for the sensor are MOFs with luminescence properties [5, 6]. This property emerges on a MOF when it is impregnated by a guest and triggers different electronic responses, which are then detected by a detector [5]. *Luminescence* happens when an electron in a singlet excited state returns to its ground state by photon emission [7, 8]. A MOF sensor has potential due to its sensitivity, selectivity, fast response, and ease of recycling. A sensor based on luminescence property enables integration in optical detection system and can be used for small-scale detection. A sensor material was developed where an incident of recognition of a guest is converted into a readable signal (i.e., optical signal).

LnMOFs have several advantages compared to transition metal MOFs in terms of enhancing their thermal and solvent stabilities, structural variations, and ligand conformations. The presence of more accessible *d*-orbitals and *f*-orbitals in these MOFs allows more possibilities for coordination and binding with various ligands. The accessible multi-electron *f*-orbitals energy levels make them fluorescent or photoluminescent centers for chemical sensor applications.

Linker selection for MOF synthesis is mainly based on functional groups on the organic ligands. Carboxylates are often chosen due to their possibility of forming a strong structure. Carboxylates are strong electron donors in bonding with metals and have oxophilic properties when bonding with metals, which make linkers with carboxylate functional groups good candidates for forming MOFs. Ligand with carboxylate functional groups such as 2,6-naphthalenedicarboxylate acid (NDC), and Benzene 1,4-dicarboxylic acid (BDC) offer richness in connectivity and robustness in structure and stability [9, 10].

## 2 Method

### 2.1 Synthesis of La-NDC and La-BDC MOFs

La-NDC and La-BDC MOFs were synthesized using a solvothermal method [11] with Dimethylacetamide (DMA) as solvent. As much as 2 mmol of  $\text{La}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$  dan 2 mmol NDC (for La-NDC MOF) or BDC (for La-BDC MOF) mixed with 10 ml of DMA 10 ml inside a teflon-line autoclave and then baked at 150 °C for 24 h in an oven. After 24 heating, the reactor was cooled to ambient temperature. Then, the result was washed (with water and acetone) and dried for further analysis.

## 2.2 Characterization of La-NDC and La-BDC MOF

Characterizations were conducted using Bruker Alpha-P ATR FTIR, PANalytical X'Pert PRO seri PW3040/XO, and Scanning Electron Microscope instrumentation.

## 2.3 Electronic/Optical Response of La-NDC MOF Towards Oxoanions

The optical response of La-NDC was made towards oxoanions ( $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{MnO}_4^-$ ,  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$ ). One mg of La-DND was diluted into 3 mL of methanol to form a soft suspension. Then, 100  $\mu\text{L}$  of oxoanion 300  $\mu\text{M}$  was added into that suspension. These mixtures were directly measured by spectrophotometer UV-Vis at 200–800 wavelength.

## 2.4 Electronic/Optical Response of La-BDC MOF Towards Metal Cations

The Electronic response of La-BDC MOFs was tested towards metal cations of  $\text{M}(\text{NO}_3)_m$  compounds. As much as 1 mg of La-BDC was added into 3 mL of methanol and turned into suspension. Then, 200  $\mu\text{L}$  of 100 ppm metal cations ( $\text{M}^{m+} = \text{K}^+$ ,  $\text{CO}_3^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Fe}^{3+}$ ) was added to this suspension. The mixture was placed into a cuvet and measured by Spectrophotometer UV -Vis at 200–800 nm [12].

# 3 Results and Discussion

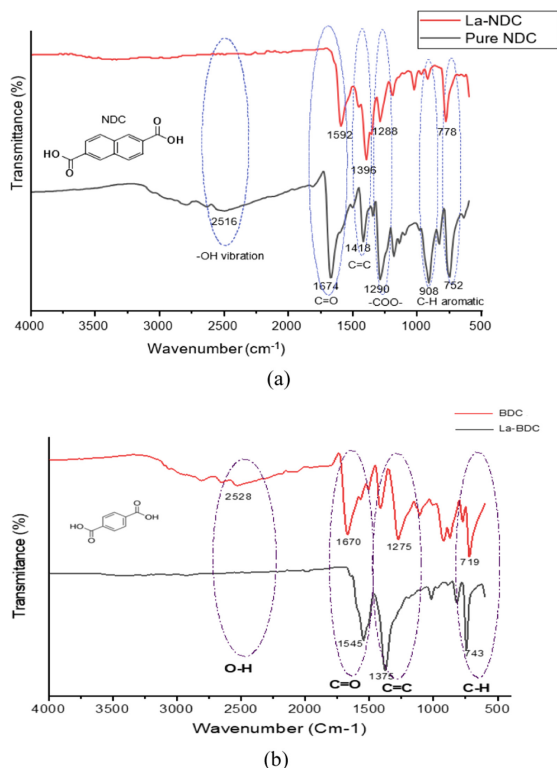
## 3.1 Lanthanum-Based MOFs Characterization

La-MOFs were synthesized using a solvothermal method since this method is known for good crystallinity results [13]. Teflon line autoclave was used to increase pressure isolation and reactant diffusion so that the reactor's energy provides the reaction's activation energy. The cooling process was done following the ambient temperature in a relatively slow process for crystal growth. Then, the products were washed using DMA, water, and acetone to eliminate excess reactants and other impurities.

La-NDC is a white crystalline powder, while La-BDC is a yellowish crystalline powder with 51.5% and 47.0% rendement at 150 °C baking temperature, respectively. The cooling process for both syntheses followed ambient temperature. This condition might affect the crystal formation compared to temperature-programmed conditions [14].

FTIR results showed the presence (or lack of) of essential functional groups of La-NDC (Fig. 1(a)) and La-BDC (Fig. 1(b)) MOFs. The presence of particular functional groups that initially comes from the linkers (ligands) shows that the structure of the ligands is maintained within the MOFs. In contrast, the lack of other functional groups might indicate the formation of bonds/connections within the MOFs. The comparison between the spectra of pure ligand and MOFs shows that  $-\text{OH}$  absorption at  $\sim 2500 \text{ cm}^{-1}$ , a distinct functional group in carboxylic acid, was eliminated in the La-NDC and La-BDC MOFs, indicating bonding formation between Lanthanum metal ion and the ligands.

The  $\text{C} = \text{O}$ ,  $\text{C} = \text{C}$  and  $\text{C-H}$  aromatics absorptions were observed on the FTIR spectra of pure NDC or BDC at  $\sim 1500\text{--}1600 \text{ cm}^{-1}$ ,  $\sim 1275\text{--}1375 \text{ cm}^{-1}$ , and  $\sim 720 \text{ cm}^{-1}$ ,

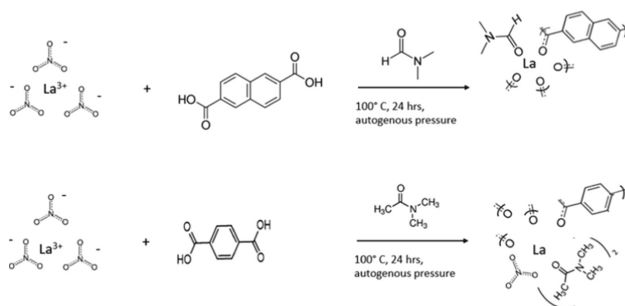


**Fig. 1.** FTIR Spectra of (a) La-NDC and (b) La-BDC MOFs

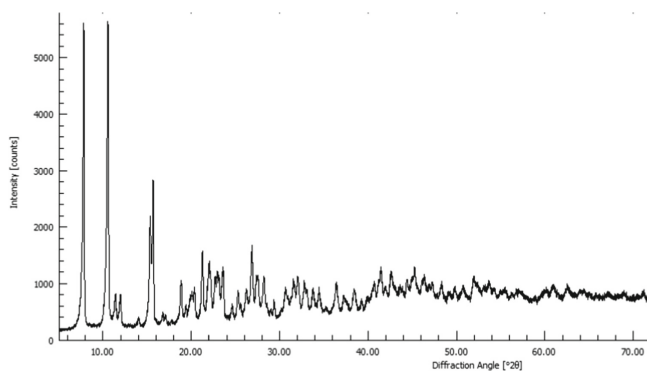
respectively. These peaks were observed to be shifted toward the lower wavenumber at La-NDC and La-BDC. The electron donation of lanthanum metal to the ligands fills in the antibonding orbitals of the La-MOFs that lower the bond order of bonds in the MOFs, thus, lowering the bond strength [15]. The elimination of -OH peak and the shifting of C = O, C = C, and C-H peaks on FTIR spectra indicate the bonding formation of lanthanum and NDC and BDC ligands. The electropositive  $\text{La}^{3+}$  from lanthanum nitrate can form bonds with all presents electronegative species, namely ligands (NDC/BDC), DMA and nitrate ions [16]. The reaction inside the Teflon line autoclave can be figuratively described in Fig. 2.

MOFs crystallinities were tested using powder x-ray diffraction. The sharp peaks in the diffractogram indicate the regularity of structure repetition (i.e., crystal definition) [17, 18] and can also be used to determine crystal purity compared to known compounds.

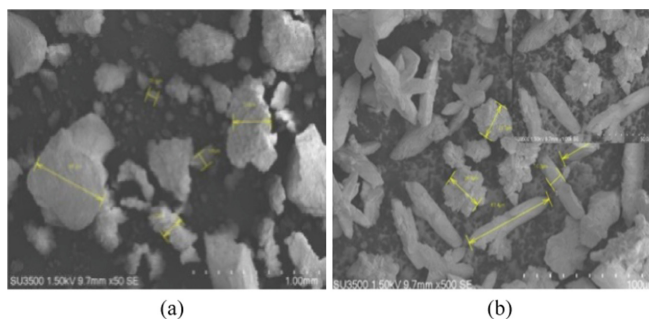
The sharp peaks shown in the PXRD results (Fig. 3) for both La-NDC and La-BDC MOFs indicate that fine crystals are present in the products. Prominent peaks are shown in  $2\theta$  around  $7^\circ$ ,  $10^\circ$ , and  $15^\circ$ . Those are similar for both La-NDC and La-BDC with slightly shifted peak positions. These results are similar to that of other reported La-NDC [18] and La-BDC [19] (using different solvents at solvothermal method), indicating that the MOFs formation was a success. Although from morphology analysis using SEM (Fig. 4), it is shown that impurities are still prominent.



**Fig. 2.** Reaction illustration inside Teflon-line autoclave



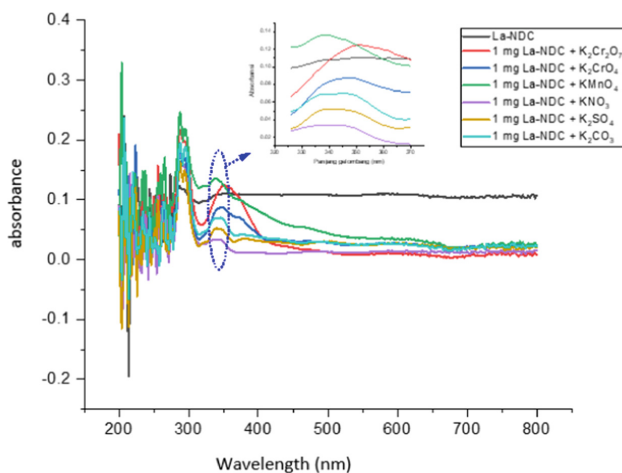
**Fig. 3.** MOFs PXRD Result of La-NDC



**Fig. 4.** SEM result of (a) La-NDC and (b) La-BDC

### 3.2 MOFs Electronic Responses

Electronic responses for La-NDC and La-BDC towards guest species were analyzed using UV-Vis Spectrophotometer. The electronic response of La-MOFs is based on the fact that Lanthanum metal series are metals with a higher principal quantum number



**Fig. 5.** Electronic response of La-NDC towards oxoanions

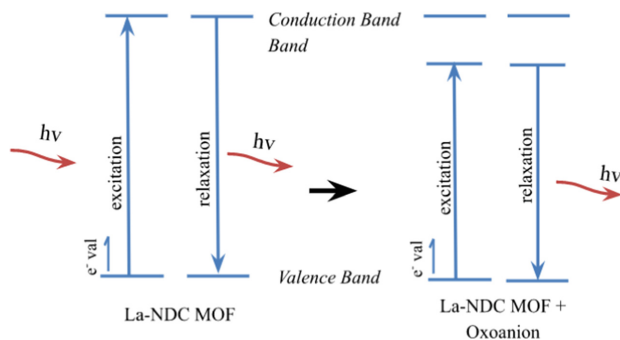
(higher period number in the periodic table), meaning that accessible multi-electron  $f$ -orbitals energy levels make them fluorescent or photoluminescent centers for chemical sensor applications. Sensing/detecting a guest molecule/species depends on the electronic responses when a guest enters MOFs pores. Ligand (NDC or BDC) will act as an “antenna” and transfer its energy to the metal center (lanthanum) and triggering excitation when radiates by UV-Vis light [19, 20]. The guest’s presents will change the electronic mapping and trigger different responses when irradiated.

Electronic responses of La-NDC towards oxoanions ( $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{MnO}_4^-$ ,  $\text{CrO}_4^{2-}$ , and  $\text{Cr}_2\text{O}_7^{2-}$ ) are given in Fig. 5. Optimum wavelength of La-NDC was obtained at 292 nm. The electronic responses of La-NDC with guests was tested at 200–800 nm.

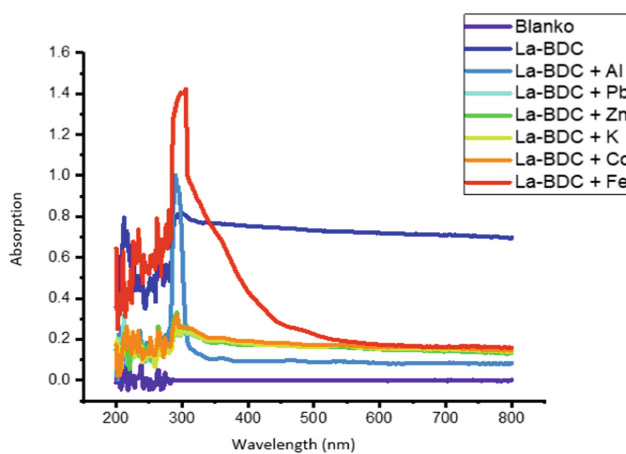
The measurement shows new peaks observed 328 nm–368 nm on every guest added. This indicates that La-NDC is not selective towards oxoanions as there is no distinct characteristic of electronic response towards specific anion. These new peaks appear due to the guests have a lower  $\pi^*$  orbital compared to La-NDC’s *lowest unoccupied molecular orbital* (LUMO), thus given a lower conduction band and a narrower band gap (Fig. 6). Therefore, the peaks appear at higher wavelengths [21].

Electronic responses of La-BDC towards metal cations can be seen on Fig. 7.

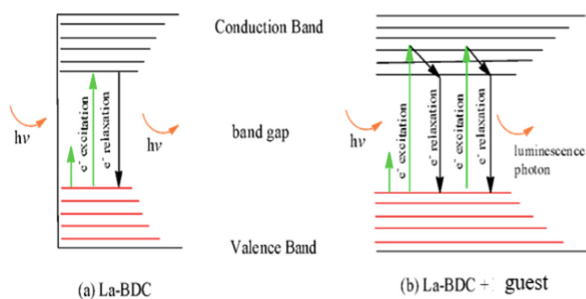
Various absorption patterns were observed when La-BDC was added with various metal cations. However,  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  have a higher intensity than other cations indicating that La-BDC is responsive toward these two ions. The interaction between metal ions and La-BDC depends on energy absorption of electrons excitation from the valence band to conducting band. The relaxation of these electrons resulted in photon emission absorbed by the spectrophotometer instrument. Higher absorbance is related to higher concentration, as stated by Lambert-Beer Law, and in this case, higher incidents of excitation-relaxation of electrons in La-BDC-Guest system (Fig. 8) [22].



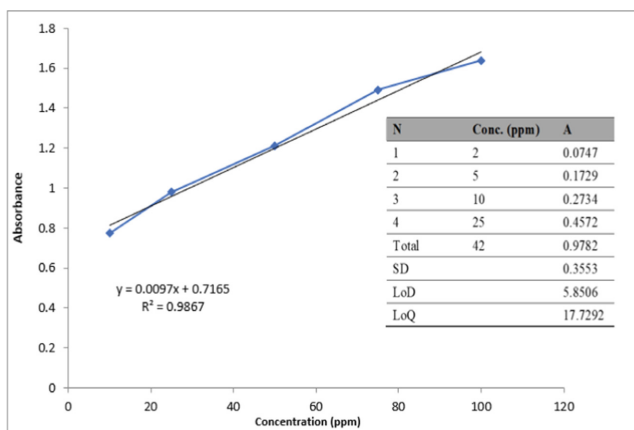
**Fig. 6.** Electron transition illustration when La-NDC added by oxoanions



**Fig. 7.** Electronic responses of La-BDC with metal cations



**Fig. 8.** Electron transition illustration when La-BDC added by metal cations



**Fig. 9.** Correlation between Absorbance and  $\text{Fe}^{3+}$  concentration

Although responses toward metal cations also show no specific characterization of specific ion, there is a strong correlation between concentration of  $\text{Fe}^{3+}$  and absorbance (Fig. 9). This correlation indicates that La-BDC is responsive towards the presents of  $\text{Fe}^{3+}$  and can be further investage for its selectivity.

## 4 Conclusions

La-NDC and La-BDC are two lanthanum-based MOFs that were synthesized based on the distinct feature of rare earth metals of their possession of  $f$  orbitals. The characterization of these two MOFs indicates MOFs crystal formation. However, an electronic response study to determine whether these MOFs can be further investigated as sensor materials shows that they are unlikely to have the necessary characteristics to detect the tested guest species. Further investigations are needed to determine their selectivity towards different guests.

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**Conflict of Interest.** The authors declare that there are no conflicts of interest.

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