Synthesis and characterization of lanthanide metal-organic framework with perylene 3,4,9,10-tetracarboxylate ligand

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Abstract. Metal-organic framework (MOF) as a semiconductor material has unique properties and potency to be utilized as a photocatalyst. The superiority of MOF compared to other semiconductor materials is due to the more possibility of adjusting its structure and properties by varying the metal type and organic ligand as the linker to create various framework building blocks, for a number of different applications. In this study, MOFs composed of lanthanide metals (samarium and dysprosium) and PTC ligand (perylene-3,4,9,10-tetracarboxylate), were synthesized and their structural and photochemical properties were characterized. MOFs synthesis were carried out using solvothermal method at 170 ºC, with the variation of metal to ligand mole ratio of 1:1, 2:1 and 1:2 for each metal. FT-IR characterization indicates that in all samples of MOF, PTC ligands coordinate with metals in bidentate ligand mode, which is supported by the existence of peak at around 1770 cm⁻¹ that resembles stretching vibration peak of conjugated C=O anhydride. XRD characterization reveals a quite good crystalline phase in at least two samples, which are Sm-PTC MOF (1:1) and Dy-PTC MOF (1:1), although their crystal types are not known yet. Characterization with UV-Vis DRS shows band gap energy for all samples of MOF ranges from 2.175 eV to 2.328 eV. The obtained band gap energy values indicate that these MOFs will have an excellent respond toward the visible or solar light and, therefore, can be considered as materials suitable for photocatalysis.

Keywords: Metal-Organic framework, lanthanide metals, perylene 3,4,9,10-tetracarboxylate, semiconductor

1. Introduction
Metal-organic framework (MOF) is a type of porous material with a crystal structure composed of metals and organic ligands as linkers between the metals so as to form its framework structure [1, 2]. MOF has more advantages compared to other porous materials due to the combination of various types of metals and organic ligands which will produce various unique MOF structures, resulting in certain physical and chemical properties. These structures can be used for several applications such as gas storage and separation, adsorption, magnetism, sensors, proton conduction, drug delivery, catalysis, and photocatalysis [3].

MOF is generally a semiconductor which has certain band gap energy, depending on the electronic properties of its constituent metals and ligands. The electronic structure of MOF produces a gap in the energy level of the valence band and the conduction band corresponding to the light energy in the range of ultraviolet and visible rays. When MOF absorbs light in accordance with its band gap energy, pairs...
of electrons (e⁻) and positive holes (h⁺) will be formed, with sufficient life time so as to initiate a redox reaction of chemicals on the surface of MOF itself. [4]. An illustration scheme of semiconductors or photocatalysts electronic system can be seen in figure 1.

In the field of photocatalysis, the value of band gap energy from photocatalyst material is of a primary concern. The smaller the value of band gap energy, the wavelength of light used to excite the electron will shift toward the visible light, which means it takes less energy to carry out the photocatalysis reaction. MOF is a potential alternative of semiconductor material for the application of photocatalysis because its tunable structure and characteristics allow the band gap energy of MOF to be controlled by modifying its constituent organic linker or metal ion [5].

Organic linker has an important role in determining the photochemical nature of MOF. By integrating organic ligand that can absorb energy in the visible light region, the band gap energy of MOF can be decreased and this MOF has the potency to be a good photocatalyst material. Organic linkers which can absorb energy in areas of visible light are those colored organic compounds whose structure have many π conjugated bonds. Several studies have shown that MOF which is incorporated with this type of organic compounds has a relatively small band gap energy compared to other semiconductor material such as TiO₂. MOF composed of dye-like ligand which has many π conjugated bonds, 3,3’,5,5’-azobenzene tetracarboxylate with lanthanide metal gadolinium (Gd) has a band gap energy of 2.35 eV [6], whereas with Dy metal the band gap energy of MOF can reach up to 2.17 eV [7].

In addition to the ligand, the constituent metal of MOF also influences its photocatalytic properties. A few researches have been focused on the developing lanthanide-based MOF because it has a unique coordination geometry, magnetic properties, and good photo-response properties [8]. Lanthanide-based MOF combined with anthracene as the organic linker which has a sufficient number of π conjugated bonds shows a good band gap energy for photocatalysis, which are 2.11 eV for Ce-MOF, 2.20 eV for Tb-MOF and 2.15 eV for Dy-MOF [9]. Therefore, the combination of lanthanide metal and dye-like ligand as the organic linker can produce MOF with excellent band gap energy for the photocatalysis reaction.

Perylene 3,4,9,10-tetracarboxylate (PTC) is a class of dyes consisting of aromatic fluorophore structures with many π conjugated bonds which has applications in various fields such as organic optoelectronics, photonics, and fluorescence sensors [10]. Research on MOF with PTC ligand has not been much developed. However, a paper reports that MOF composed of PTC ligand and potassium metal, K₂(PTC)₂(H₂O)₁.₅.₄H₂O, have been successfully synthesized and proven to have semiconductor properties with band gap energy of 2.53 eV [11].

Figure 1. Illustration scheme of a photocatalytic system.
In this study, new MOFs which are constructed of dye-like ligand perylene 3,4,9,10-tetracarboxylate (PTC) combined with lanthanide metals, samarium (Sm) and dysprosium (Dy), were synthesized and their performances as photocatalyst materials were analyzed with UV-Vis Diffuse Reflectance Spectroscopy. The combination of these types of ligand and metal was chosen based on the results of previous studies which showed that each MOF composed of lanthanide metals and PTC ligand has a relatively small band gap energy and has the potential to be used as a photocatalyst material.

2. Materials and method

2.1. Materials

The materials used in this study were Sm(NO₃)₃·6H₂O, Dy(NO₃)₃·6H₂O, perylene 3,4,9,10-tetracarboxylic dianhydride obtained from Sigma-Aldrich, and NaOH, N, N-dimethylformamide, ethanol obtained from Merck, and distilled water. All materials were used directly without any further purification.

2.2. Experimental procedures

2.2.1. PTC ligand synthesis. PTC ligand preparation was carried out using a modified method of Hariharan, et al. 2017 [10]. 0.5 gr of perylene 3,4,9,10-tetracarboxylic dianhydride (1.27 mmol) was suspended in 50 mL H₂O and 0.356 gr NaOH (8.9 mmol) was added. This mixture was then stirred constantly using a magnetic stirrer for 1 h. The resulting fluorescent greenish-brown solution was then filtered and the filtrate obtained was added with excess ethanol until a yellow precipitate was formed. The yellow precipitate, namely sodium perylene 3,4,9,10-tetracarboxylate (Na₄PTC) was then filtered, washed with ethanol, and dried at room temperature in a desiccator.

2.2.2. MOF synthesis. The synthesis of Sm-MOF-PTC and Dy-MOF-PTC was carried out using the solvothermal method which refers to the research of Sun, et al. 2016 [6]. For each Sm-MOF-PTC and Dy-MOF-PTC, the metal to ligand mole ratio, volume of the solvent, and the method used were the same.

All six MOF samples were each synthesized by dissolving a particular mass of metal and ligand according to table 1 into a mixture of 11 mL H₂O and 4 mL DMF solvents. Then, the result of this dissolution was transferred into a Teflon autoclave and stirred with constant stirring using a magnetic stirrer for 45 min. After stirring was complete, the autoclave was put into an oven at 170 °C for 6 h. The results of this reaction were cooled slowly at room temperature, then filtered and washed using a mixture of H₂O and DMF solvents with the ratio of 11:4, then dried in the oven at 70 °C for 24 h.

| Sample          | Metal mass | Ligand mass | Solvent volume |
|-----------------|------------|-------------|----------------|
| Sm-PTC (1:1)    | 0.4445 g   | 0.5163 g    | 15 mL          |
| Sm-PTC (2:1)    | 0.8890 g   | 0.5163 g    | 15 mL          |
| Sm-PTC (1:2)    | 0.4445 g   | 1.0326 g    | 15 mL          |
| Dy-PTC (1:1)    | 0.4566 g   | 0.5163 g    | 15 mL          |
| Dy-PTC (2:1)    | 0.9132 g   | 0.5163 g    | 15 mL          |
| Dy-PTC (1:2)    | 0.4566 g   | 1.0326 g    | 15 mL          |
2.2.3. **MOF characterization.** The characterization used to analyze the two MOF samples were FTIR, UV-Vis DRS, and XRD. Measurement of band gap energy of MOFs was carried out using UV-Vis DRS (Diffuse Reflectance Spectrometry) instrument, Shimadzu UV-2450 ($\lambda$ range 200 nm to 800 nm). Characterization of powder X-ray diffraction (XRD) was carried out to determine the crystallinity of MOFs structure, which used CuKα ray radiation, $\lambda = 1.5406$ Å and continuous scan type (0.0167113º per step, scan range from 4.99º to 89.99º).

3. **Results and discussion**

3.1. **PTC ligand characterization**

Perylene 3,4,9,10-tetracarboxylate (PTC) as the organic linker used in the synthesis of MOF in this study was the result of hydrolysis of the commercial compound perylene 3,4,9,10-tetracarboxylate dianhydride (PTCDA), which changed the anhydride groups in PTCDA into carboxylic anion groups in PTC ligand.

From the experimental results, a physical change where the red PTCDA turned yellow after the hydrolysis reaction was observed. Changes in the FTIR spectra of the compound before and after hydrolysis shows that PTC ligand synthesis had been successfully carried out. The FT-IR spectrum of the two compounds can be seen in figure 2. Some typical absorption peaks of anhydride groups which appear in the spectrum of PTCDA do not appear in the NaPTC spectrum. In accordance with the IR database by Sigma Aldrich, the absorption peak at around 1775 cm$^{-1}$ shows the stretching vibration of conjugated $\text{C}=\text{O}$ anhydride, while at around 1025 cm$^{-1}$ the peak shows the CO-O-CO stretching vibration of anhydride group. Both of these peaks are not found in the NaPTC IR spectrum, which indicate that the product of hydrolysis reaction has no anhydride group. The absorption peaks around 1564 cm$^{-1}$ and 1371 cm$^{-1}$ show asymmetrical and symmetrical vibrations of the COO$^-$ group [12], which proves that the anhydride group has been hydrolyzed into a carboxylic anion.

3.2. **FT-IR characterization of MOFs**

The results of FT-IR characterization for all MOF samples can be seen in figure 3. All spectra of the MOF samples show the absorption peaks at around 1770 cm$^{-1}$ for Sm-MOF, and around 1765 cm$^{-1}$ for Dy-MOF. There is no peak around these wavenumbers found in the IR spectrum of the PTC ligand.

![Figure 2. FT-IR spectra of PTCDA and NaPTC.](image-url)
Peaks around these wavenumbers in all MOF samples are similar to the stretching vibration peak of conjugated C=O anhydride in PTCDA, with lower intensity. This might be an indication that the carboxylic groups in PTC ligand forms coordination with metal that resembles the anhydride groups. All MOF spectra also exhibit absorption peaks at around 1560 cm$^{-1}$ and 1355 cm$^{-1}$, as in the PTC ligand spectrum, which show asymmetrical and symmetrical vibrations of the COO$^-$ group [12]. However, these two absorption peaks in MOF samples have lower intensity than in PTC ligand. This might indicate that in MOF, PTC ligands coordinate with metals in bidentate ligand mode, which is also supported by the existence of peak at around 1770 cm$^{-1}$ that resembles the stretching vibration peak of conjugated C=O anhydride.

3.3. UV-Vis DRS characterization of MOFs

Characterization with UV-Vis DRS for all synthesized MOF samples is presented in figure 4. The plot of energy $hv$ versus $(a/hv)^2$ (using the Tauc equation) obtained from reflectance data are presented in figure 5, while the values of band gap energy results from this plot are shown in table 2. These band gap energy values can be categorized as relatively small when compared to other types of semiconductor materials.

![Figure 3](image1.png)

Figure 3. (a) FT-IR spectrum of Sm-MOF and PTC ligand, and (b) FT-IR spectrum of Dy-MOF and PTC ligand.
Table 2. Value of band gap energy for All MOF samples

| Sample          | Band gap energy (eV) |
|-----------------|----------------------|
| Sm-PTC (1:1)    | 2.217                |
| Sm-PTC (2:1)    | 2.175                |
| Sm-PTC (1:2)    | 2.328                |
| Dy-PTC (1:1)    | 2.235                |
| Dy-PTC (2:1)    | 2.210                |
| Dy-PTC (1:2)    | 2.283                |
| PTC Ligand      | 2.362                |

Figure 4. (a) UV-Vis DRS spectra of Sm-MOF and PTC ligand, and (b) UV-Vis DRS spectra of Dy-MOF and PTC ligand.
Compared to each other, the value of band gap energy between the samples of MOF 1:1 and 2:1 does not have a significant difference. Sample of MOF 1:2 has a band gap energy value that is slightly higher than the average of MOF 1:1 and 2:1, with a magnitude close to the band gap energy value of PTC ligand. UV-Vis DRS graphs of the MOF samples and PTC ligand are compared in figure 4. From this comparison, it can be seen that there is a shift in the curve line which was originally at a wavelength of around 500 nm for the PTC ligand, to around 590–600 nm for each MOF samples. This might be an indication that there is indeed a formation of coordination between the ligand and the metal resulting in changes in the UV-Vis DRS curve. The curve shapes for all Sm-MOF and Dy-MOF samples have similarities with a slight difference in the reflectance percentage. This difference can be seen in the area of around 700 nm, where for both Sm-MOF and Dy-MOF, the MOF ratio of 1:2 has the lowest reflectance. This might be related to the band gap energy of MOF 1:2 which has the highest value. The reason of this quite significant difference in UV-Vis DRS curve and band gap energy value might be because the formation of MOF crystals for metal to ligand mole ratio of 1:2 was not as good as MOF crystals of 1:1 or 2:1. In this sample of MOF 1:2, the possibility of many ligands remaining in the product which have not been coordinated with metals in the MOF structure, might result in a higher band gap energy value observed in the experiment.

Figure 5. Tauc plot of (a) Sm-MOF and PTC ligand, (b) Dy-MOF and PTC ligand.
3.4. XRD characterization of MOFs

According to the spectra of FT-IR and UV-Vis DRS for each Sm-MOF and Dy-MOF, the comparison of metal to ligand mole ratio does not provide a significant difference in the shape of the curves, but only slightly different in the intensity of the peaks. This indicates that in general, the shapes of the MOF structure for the metal to ligand mole ratio of 1:1, 2:1 and 1:2 have similarities, with the possibility of slight differences in the structure of MOF 1:2. Taking into account these similarities and also the efficiency of materials used for synthesis, therefore, MOF 1:1 can be assumed as the sample of MOF with the most optimal ratio for the structure crystallinity characterization using X-Ray Diffraction. The results of XRD characterization for Sm-MOF 1:1 and Dy-MOF 1:1 samples can be seen in figure 6, while spectrum comparison between the two samples can be seen in figure 7.

The XRD spectrum for each MOF shows a sharp peak at 2θ around 6.34°. The presence of sharp peak indicates that the structure of the MOF is crystalline. The intensity of this peak is indeed not quite high, which means that the crystallinity of MOF is low. This is probably due to the short synthesis time (6 h) causing the incomplete crystal formation so that the resulting crystal size was still very small, with many impurities or unreacted reagents. However, all synthesized products are insoluble in various solvents such as H2O, ethanol, DMF, and DMSO, which gives an indication that the product has the framework structure of MOF, not just a metal-ligand complex. In addition, the presence of a sharp peak in the XRD spectrum also confirms the formation of the sample’s crystalline structure.

![XRD spectrum for Sm-MOF 1:1](image)

![XRD spectrum for Dy-MOF 1:1](image)

Figure 6. XRD pattern of (a) Sm-MOF 1:1 and (b) Dy-MOF 1:1.
Some small peaks which appear in both XRD spectrum can be seen at 2θ around 12.64° and 17.30°. Peaks which only appear at Sm-MOF are at 2θ around 11.82° and 18.60°, while for Dy-MOF are at 9.92° and 21.90°. The sharpest peak in both MOF spectra is in the region of about 5° to 15°, precisely at 6.34°. The 2θ value where the sharpest peak emerged, which is below 15°, is in good agreement with XRD pattern of most MOF composed of lanthanide metals and dye-like ligands in the previous researches. [6, 7, 13]. Other small peaks may indicate specific peaks for each Sm-MOF and Dy-MOF structure. In addition, the XRD spectrum of both MOFs does not show peaks at 2θ around 25°–40°, which is the area where the typical sharp peaks of each Sm and Dy crystal will appear (according to XRD spectrum simulations for Sm and Dy metals). This indicates that under conditions of MOF synthesis, the metal did not reform the same crystal structure as its metal crystal structure, but formed another structure which was a polymer-like coordination between the metal and the ligand.

4. Conclusion
From FT-IR and UV-Vis DRS characterization results, all Sm-MOF and Dy-MOF samples with different metal to ligand ratios do not show significant differences. FT-IR characterization for MOF samples shows an absorption peak around 1770 cm⁻¹, similar to the peak of conjugated C=O anhydride, which might be an indication that PTC ligands bind to metals in bidentate mode, resembling the structure of anhydride. From the results of UV-Vis DRS characterization, band gap energy values were obtained for each MOF, which values range from 2.175 eV to 2.328 eV. MOF synthesis results in this study are known to have a crystal structure even though the crystal type is still unknown. This is proven by the presence of sharp peaks in the XRD spectrum for at least two samples, namely Sm-PTC MOF (1:1) and Dy-PTC MOF (1:1).

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