

## TCNQ-BASED POROUS COORDINATION POLYMERS SYNTHESIS AND SORPTION PROPERTIES STUDY IN MAGNETIC FIELD

Moondra Zubir<sup>1,2</sup>, Atom Hamasaki<sup>2</sup>, Sumio Ozeki<sup>2</sup>

<sup>1</sup>Department of Chemistry, Faculty of Mathematics and Natural Sciences, State University of Medan, Jl. Willem Iskandar, Pasar V Medan Estate, Medan, North Sumatera 20221, Indonesia. E-mail: Moonzuren@gmail.com. <sup>2</sup>Department of Chemistry, Faculty of Science, Shinshu University, 3-1-1, Asahi, Matsumoto, Nagano 390-8621, Japan

### ABSTRACT

Porous coordination polymers (PCPs) were synthesized with used TCNQ anion that acts as cross linker connecting and bipyridine to form a 3D framework. In these study, we use zinc and manganese metal ion as centre of complex coordination. Green crystal of Zn(TCNQ-TCNQ)bpy.1.5 benzene and Mn(TCNQ-TCNQ)bpy.1.5 benzene was successfully synthesized in no under magnetic field (0T) and under magnetic field 6T. XRD patterns of Zn(TCNQ-TCNQ)bpy.1.5 benzene 0T and 6T shown not significant different pattern that indicate no different crystal formed. XRD patterns of Mn(TCNQ-TCNQ)bpy.1.5 benzene also shown not significant different but we found five different intensity ratio peaks that possibility it was a little bit changing of crystal structure. To investigate the pores properties, adsorption isotherm was performed for oxygen gas in 77 K and the guest of benzene were removed at 413 K for 3 hours under low pressure. Zn(TCNQ-TCNQ)bpy}1.5benzene 0T and 6T oxygen adsorption isotherms shows the unique sorption isotherms by gate pressure profile. On other hand, Mn(TCNQ-TCNQ)bpy}1.5 benzene 0T and 6T shows type 1 adsorption isotherms for micropores materials. Adsorption isotherm was also determined in magnetic field 6T for all crystal, and shows shift of gate pressure for Zn compounds and enhance the amount of oxygen adsorbed for all kind of compounds.

*Key words: porous coordination polymers, polymers synthesis, magnetic field*

### INTRODUCTION

Recently, porous coordination polymers<sup>1-12</sup> have been developed which are beyond the scope of the former two classes of porous material are inorganic and carbon based material. The crystalline porous coordination polymers (PCPs) are a new family of the nanoporous crystal. They are currently receiving attention because their highly adsorption surface area and large free cage volume beside their interesting application as well including gas purification<sup>1-4</sup> and gas separation.<sup>5-7</sup> Porous coordination polymers which is composed of the self assembly of metallic ion and organic ligand is crystalline materials and has flexibility that derived from framework build with coordination bond. Designing of structure and porous property is easy because component is selectable and using this property, it is also possible to modify on

the porous surface with organic ligand which interact with specific molecules.

In this study, we prepared porous coordination polymer  $\{[M(\text{TCNQ-TCNQ})\text{bpy}]_x \text{benzene}\}_n$  with used Zn and Mn as metallic ion by reported procedures. TCNQ is a well-known multi redox active ligand that can act as a good acceptor and a weak or strong donor when its valence is 0, -1, or -2 respectively.<sup>8</sup> And we used benzene as a solvent and many solvents have been used not only as the reaction medium, but also to regulate the framework topology. In particular, in the case of microporous coordination polymers, solvent molecules are extensively contained in their micropores because nature abhors a vacuum are called "guest molecules". The large diameter space is adequate to accommodate a benzene molecule because of

the suitability of the cavity's size and thickness.<sup>9</sup>

Magnetic field may bring about serious influences on structures and properties. The crystalline was synthesized and characterized attributed to structural flexibility in magnetic field apply as 6 Tesla and without magnetic field apply as comparison. The micropores properties was observed by gas adsorption and the guest of benzene were removed at 413 K for 10 hours under low pressure and this condition will act as pretreatment condition before adsorption.

## METHOD

### Complex of (M(TCNQ-TCNQ)bpy).x benzene) Synthesis

#### Materials

7,7,8,8-tetracyano-p-quinodimethane (TCNQ) were obtained from Tokyo Kasei Industrial and 4,4'-Bypiridine (bpy) were obtained from Sigma Aldrich Corporation. Lithium Iodide (LiI), Acetonitrile, Diethyl Ether, Manganese (II) Nitrate Hexahydrate, Zinc Nitrate Hexahydrate, Benzene and Methanol were obtained from Wako Chemicals. LiTCNQ was prepared by the following procedure.

#### LiTCNQ Synthesis

To a boiling solution of 5.1 g (0,1 mole) of TCNQ in 500 ml of acetonitrile was added a boiling solution of 10 g (0.3 mol) of Lithium Iodide in 25 ml acetonitrile. The mixture stood for 1 hours at room temperature. Purple crystal separated from the dark brown solution and while still warm the purple crystal was collected and washed on the filter with acetonitrile until the washing were bright green. Then the crystal was washed with a large volume of ether.

#### Porous Coordination Polymer [M(TCNQ-TCNQ)bpy]1.5benzene 0T Synthesis.

Slow addition of a solution of LiTCNQ (2 mmol, 422 mg) and 4,4'- Bypiridine (1 mmol, 156 mg) in methanol/benzene mixture (100 mL) to a solution of  $M(NO_3)_2 \cdot 6H_2O$  (1 mmol, Zn = 297 mg and Mn = 287 mg) in methanol/benzene mixture (100 mL) at 298 K under N<sub>2</sub> atmosphere. The green powder obtained was collected by filtration.

#### Porous Coordination Polymer [M(TCNQ-TCNQ)bpy]

*1.5benzene 6T Synthesis.* Slow addition of a solution of LiTCNQ (2 mmol, 422 mg) and

4,4'- Bypiridine (1 mmol, 156 mg) in methanol/benzene mixture (100 mL) to a solution of  $M(NO_3)_2 \cdot 6H_2O$  (1 mmol, Zn = 297 mg and Mn = 287 mg) in methanol/benzene mixture (100 mL) at 298 K under N<sub>2</sub> atmosphere and conducting magnet 6 Tesla. The green powder obtained was collected by filtration.

#### Crystal Characterization.

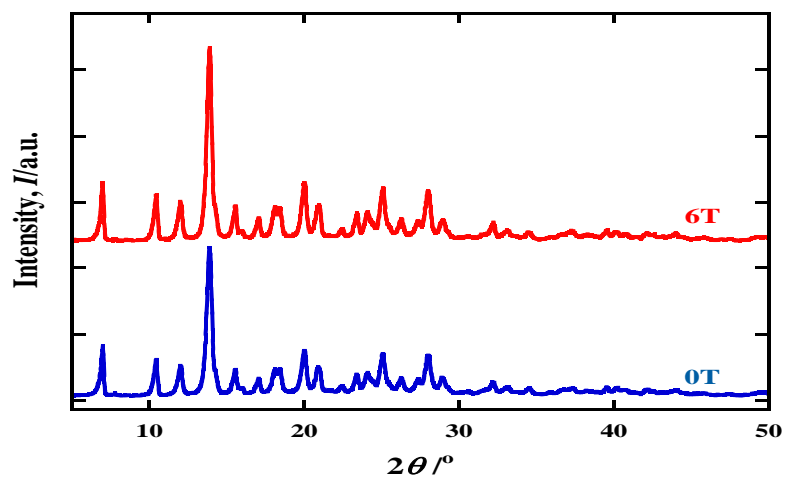
Crystal formed were characterized by X-Ray Diffraction (XRD) Rigaku Multi Flex with monochromator Cu-K $\alpha$  and morphology of complexes were observed by used Scanning Electron Microscopy (SEM) JEOL JSM-6000 F.

#### Adsorption Measurement.

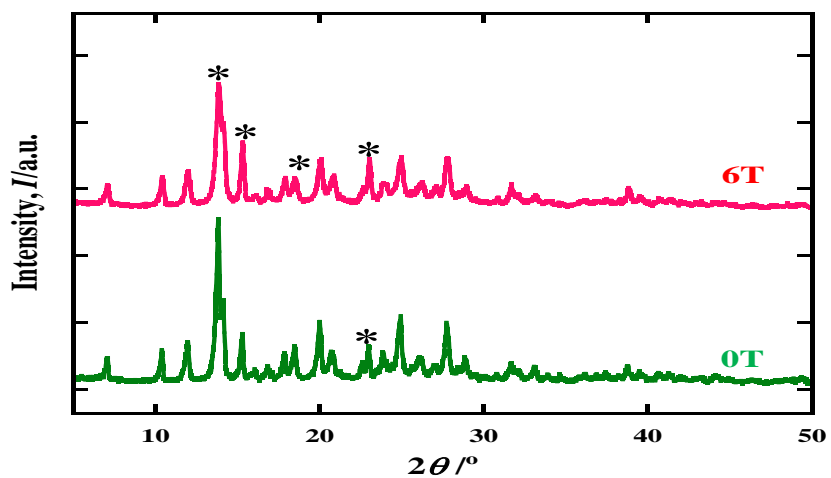
Before adsorption isotherm measurement, the guest molecules of benzene were removed at 413 K for 10 hours under low pressure and prior to the adsorption isotherm measurement, the samples (around 100 mg) were outgassed at 383 K, 1 mPa for 2 hours. The adsorption isotherms of Oxygen (O<sub>2</sub>) were measured at 77 K and 1 mPa.

## RESULTS AND DISCUSSION

LiTCNQ purple crystal was successfully synthesis with the yield as 90.7 % and this crystal will use as TCNQ anion source for MOFs crystal synthesis. Green crystal complex compounds from zinc and manganese metal ion were synthesized with MeOH/Benzene mixture solution (1 : 1). The coordination complex shows as reported paper by Kiatagawa et. al,<sup>9</sup> which is for Zn (II) as representative for both of metal ion because zinc and manganese have the same coordination number for build a complex. The large diameter space is adequate to accommodate a benzene molecule because of the suitability of the cavity's and thickness. The guest benzene molecule is accommodate strongly in the cavity with the size effect with the framework.<sup>9</sup>



**Fig. 1.** XRD patterns of porous coordination polymers of Zn[(TCNQ-TCNQ)bpy] 1.5.Benzene 0T and 6T



**Fig. 2.** XRD patterns of porous coordination polymers of Mn[(TCNQ-TCNQ)bpy] 1.5.Benzene 0T and 6T

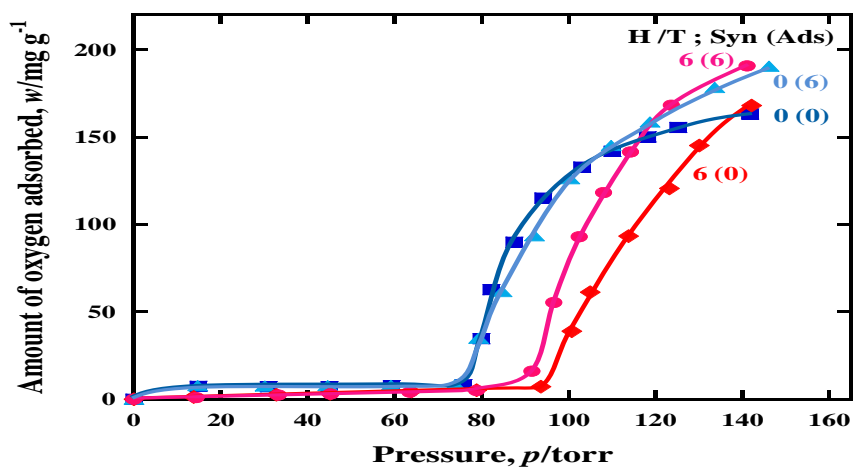


Fig. 3. Oxygen adsorption isotherms in 0T and 6T at 77 K of Zn[(TCNQ-TCNQ)bpy] 1.5.Benzene 0T and 6T

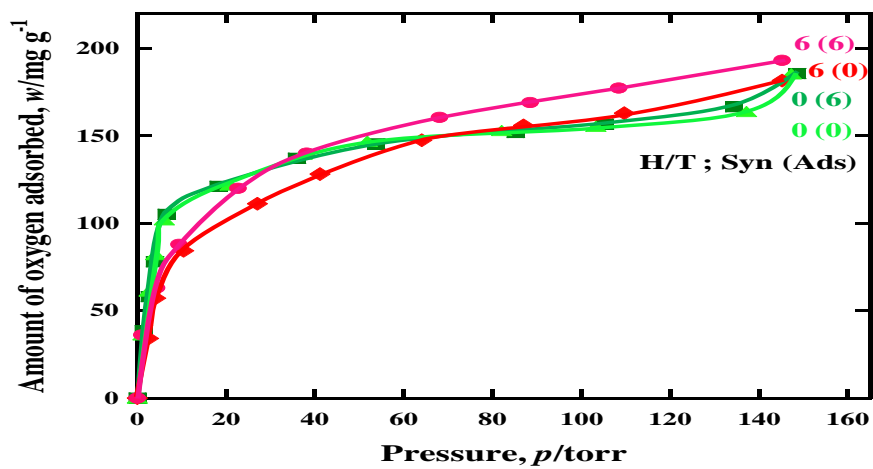


Fig. 4. Oxygen adsorption isotherms in 0T and 6T at 77 K of Zn[(TCNQ-TCNQ)bpy] 1.5.Benzene 0T and 6T.

Coordination polymer of Mn[(TCNQ-TCNQ)bpy]1.5.Benzene and Zn[(TCNQ-TCNQ)bpy]1.5.Benzene was synthesized under no magnetic field apply (0T) and under magnetic field 6 Tesla (6T). Mn[(TCNQ-TCNQ)bpy]1.5.Benzene crystal shown the dark green color than Zn[(TCNQ-TCNQ)bpy]1.5.Benzene. No significant different for visual performance between crystal that have synthesized under magnetic field 6T and no magnetic field apply. Crystal complexes formed were determined by XRD analysis. XRD pattern shows that both of metal complexes have isotypic structure each others. Only one different peak shows at 13.9 for Mn(TCNQ-TCNQ)bpy.1.5 Benzene and not appear for Zn(TCNQ-TCNQ)bpy.1.5 Benzene pattern.

XRD pattern for 0T and 6T was compared and shown that for Zn[(TCNQ-TCNQ)bpy]1.5.Benzene 0T and 6T not significant different pattern as figure 1. It is indicated no different crystal form for Zn metal ion complex between under magnetic field and no magnetic field. Diamagnetic properties of Zinc is produced a negative magnetization when exposed to an applied magnetic field. Mn[(TCNQ-TCNQ)bpy]1.5.Benzene also shown not significant different pattern for 0T and 6T but we found 5 of peaks at 13.84, 15.28, 18.48, 22.98 and 22.94 degrees shown a different intensity due to possibility impact by magnetic field synthesis as figure 2.

Before adsorption isotherm measurement, the guest molecules of benzene were removed at 413 K for 10 hours under low pressure. Zn[(TCNQ-TCNQ)bpy]1.5.Benzene 0T and 6T after pretreatment shown significant change of colour become dark green but Mn[(TCNQ-TCNQ)bpy]1.5.Benzene 0T and 6T shown not significant change the colour of crystal. Degassed process for pretreatment to removed guest molecule of benzene was shows to XRD pattern that transformed for both of complex including to 0T and 6T crystal. This sample was decomposed and intensity was decreased if compare with the crystal before pretreatment process. This X-ray diffraction (XRD) pattern show the structural flexibility of this compound, which is classified as a third-generation compound. The guest free state crystal was continue to oxygen gas adsorption isotherm as guest molecules replacement. Adsorption isotherm of oxygen shows the

unique sorption properties for Zn compounds that perform as gate pressure for both of compound in 0T and 6T synthesized compounds in 0T adsorption measurement. Zn 0T compound gate pressure found at 80.23 torr Zn 6T compound gate pressure found at 119.96 torr as figure 3. Zn 6T compound adsorption profile shown shifting the gate pressure to higher pressure if compare with Zn 0T compound. It shows that crystal preparation under magnetic field 6T influence to adsorption isotherm properties that possibility influence of the particle size different for both of compounds.

On the other hand, Mn compound shows the normal adsorption isotherm of microporous material for both of 0T and 6T compound synthesized as shows as figure 4. Although the XRD pattern a significant change by 6T synthesized but not influence to adsorption properties of them. Oxygen adsorption isotherm in magnetic filed 6T measured by continuously after finish of adsorption isotherm in 0T measurement. The same sample after degassing aims to absolutely comparison between 0T and 6T adsorption measurement. Zinc 0T and 6T compound shows the unique adsorption isotherm profile with gate pressure profile. Zn-0T compound not significant different of gate pressure at 79.89 torr for 0T Measurement and 79.82 for 6T measurement. On other hand Zn 6T compound shows a little bit shift of gate pressure as 98.77 torr for 0T measurement to 91.57 torr for 6T measurement. Manganese compounds shows the normal adsorption isotherm of microporous material for both of 0T and 6T compound synthesized prior to 0T and 6T adsorption measurement. Mn 0T and 6T sample that perform in 6T adsorption isotherm measurement shows the higher of adsorption amount.

## CONCLUSION

Zn(TCNQ-TCNQ)bpy1.5benzene and Mn(TCNQ-TCNQ)bpy1.5benzene were synthesis under 0T and 6T showed a isotypic structure with different pore properties. Zn(TCNQ-TCNQ)bpy.1.5benzene and their adsorption isotherms of oxygen measured under 6T magnetic field. Adsorption isotherms of oxygen shows specific pore properties with gate pressure profile. On the other hand, Mn(TCNQ-TCNQ)bpy1.5benzene

adsorption isotherms of oxygen shows type 1 adsorption isotherms. Magnetic fields brings changed of pore properties with sifting gate pressure for Zn-PCPs and enhance oxygen capacity of Mn-PCPs.

### REFERENCES

- Abraham F. Jalbout, Xin-Hua Li, Mohammad R. Hassan, G.M. Golzan Hossain.. *Transition Metal Chemicals* (2008) 33, 597 – 603.
- Bao-Hui Ye, Ming-Liang Tong, Xiao-Ming Chen.. *Coordination Polymer Review*, 249 (2005), 545 – 565.
- Daisuke Tanaka and Susumu Kitagawa. *Chem. Mater* (2008), 20, 922 – 931.
- Hirotohi Sakamoto, Ryotaro Matsuda, Sareeya Bureekaew, Daisuke Tanaka and Susumu Kitagawa. *Chemicals European Journal* (2009), 15, 4985 – 4989.
- Joobeom Seo, Ryotaro Matsuda, Hirotohi Sakamoto, Charlotte Bonneau and Susumu Kitagawa. *Journal of American Chemical Society* (2009), 131, 12792 – 12800.
- Ryotaro Matsuda, Ryo Kitaura, Susumu Kitagawa, Yoshiki Kubota, Tatsuo C. Kobayashi, Satoshi Horike and Masaki Takata. *Journal of American Chemical Society* 14070.
- Satoru Shimomura, Ryotaro Matsuda, Takashi Tsujino, Takashi Kawamura and Susumu Kitagawa. *Journal of American Chemical Society* (2006) 125, 1152 – 1153
- Satoru Shimomura, Satoshi Horike, Ryotaro Matsuda and Susumu Kitagawa. *Journal of American Chemical Society* (2007) 129, 1990 – 1991.
- Shin-ichiro Noro, Susumu Kitagawa, Tomoyuki Akutagawa, Takayoshi Nakamura. *Journal of Polymer Science*, 34 (2009), 240 – 279.
- Sujit K. Ghosh, Sareeya Bureekaew and Susumu Kitagawa. *Angew. Chem. Int. Ed.* (2008), 47, 3403 – 3406.
- Susumu Kitagawa, Ryo Kitaura and Shin-ichiro Noro. *Angew Chem. Int. Ed.* (2004) 43, 2334 – 2375.
- Susumu Kitagawa, Ryotaro Matsuda. *Coordination Chemistry Reviews*, 251 (2007), 2490 – 2509.