

**SYNTHESIS, CHARACTERIZATION AND
HYDROGEN STORAGE STUDIES OF METAL-
ORGANIC FRAMEWORKS CONTAINING
MONOAMIDE LIGAND**

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**MASTER OF SCIENCE
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MONOAMIDE LIGAND**

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Metal organic frameworks (MOFs) are commonly designed and investigated as materials for hydrogen storage applications. The abilities of MOFs to absorb and separate of gas depends on compounds that have nitrogen (N) and oxygen (O) containing group due to interaction between localized dipoles of nitrogen and quadrupole moment of oxygen. Therefore, in this study, one reported ligand and five new monoamide ligands containing N and O atom donors were synthesized from reactions between *N*-aminopyridine and dimethyl-2,6-pyridinedicarboxylate to give *N*-6-[(4-pyridylmethylamino)carbonyl]-2-pyridinecarboxylic acid methyl ester (L1), 6-(pyrimidin-2-ylcarbamoyl)-pyridine-2-carboxylic acid methyl ester (L2), 6-(3-methyl-pyridin-2-ylcarbamoyl)-pyridine-2-carboxylic acid methyl ester (L3), 6-(4-methyl-pyridin-2-ylcarbamoyl)-pyridine-2-carboxylic acid methyl ester (L4), 6-(5-methyl-pyridin-2-ylcarbamoyl)-pyridine-2-carboxylic acid methyl ester (L5) and 6-(6-methyl-pyridin-2-ylcarbamoyl)-pyridine-2-carboxylic acid methyl ester (L6), respectively. These ligands were characterized by typical spectroscopic techniques such as Fourier Transform Infrared (FTIR), ¹H and ¹³C Nuclear Magnetic Resonance (NMR), Ultraviolet-visible (UV-vis) and formulation of each compounds were

confirmed by elemental analysis. The infrared analysis showed the presence of five significant peaks for $\nu_{\text{str}}(\text{N-H})$, $\nu_{\text{str}}(\text{C-H})$, $\nu(\text{C=O})$, $\nu_{\text{bend}}(\text{N-H})$ and $\nu_{\text{bend}}(\text{C-H})$ at range of 3254-3358 cm^{-1} , 2920-2964 cm^{-1} , 1668-1749 cm^{-1} , 1525-1607 cm^{-1} , and 1301-1324 cm^{-1} , respectively. Whilst for ^1H NMR results, the presence of methyl, methoxy, C-H aromatic protons and N-H were indicated at range of $\delta_{\text{H}} = 2.36\text{-}2.53$ ppm, $\delta_{\text{H}} = 4.0\text{-}4.06$ ppm, $\delta_{\text{H}} = 6.96\text{-}8.49$ ppm and $\delta_{\text{H}} = 10.28\text{-}10.59$, respectively. The ^{13}C NMR detects the methyl carbon, pyridine carbon and carbonyl carbon at $\delta_{\text{C}} = 17.93\text{-}53.05$ ppm, $\delta_{\text{C}} = 111.13\text{-}157.28$ ppm and $\delta_{\text{C}} = 161.27\text{-}164.99$ ppm, respectively. The overlapping of pyridine and carbonyl absorptions at range 272.5-292.5 nm were indicated in the UV spectra of the respective ligands. Ligands L1-L6 were utilized as a organic linker in the construction of MOFs *via* reaction with cadmium nitrate (II) tetrahydrate. The complexes are prepared using solvothermal method, a common technique for MOF's synthesis. By using this method, three MOFs (MOF-L1 – MOF-L3) were obtained. In the FTIR spectra of MOF-L1 – MOF-L3, several distinctive peaks of $\nu_{\text{str}}(\text{N-H})$, $\nu(\text{C=O})$, $\nu_{\text{bend}}(\text{N-H})$, $\nu(\text{N-O})$, $\nu(\text{Cd-O})$ and $\nu(\text{Cd-N})$ were indicated at range of 3303-3409 cm^{-1} , 1655-1597 cm^{-1} , 1424-1566 cm^{-1} , 1382-1384 cm^{-1} , 596-430 cm^{-1} and 501-434 cm^{-1} , respectively. X-ray crystallography shows that crystals of MOF-L1 crystallizes in monoclinic with space group, $P21/n$. MOF-1 has two dimensional close-packed frameworks which expected to have limited potential in storing hydrogen. Crystals of MOF-L3 on the other hand crystallizes in orthorhombic crystal system with space group $Pbcn$ and exhibits a one dimensional framework. X-ray crystallography reveals that ligands L1 and L3 (as well as L4, L5) underwent hydrolysis as expected and formed *in situ* carboxylic acid ligands with tridentate O, N, and O donors. TGA analysis indicated that the synthesized MOFs have two degradation steps, showing decomposition of water and

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solvent at first stage, and ligand at the second stage. Further investigation on the hydrogen uptake studies using Pressure-Composition Temperature (PCT) resulted to interesting properties of MOF-L1 and MOF-L2 with their capability to store hydrogen up to 0.5 wt. % and 0.3 wt. %, at 373 K and 60 bar, respectively. However, the hydrogen uptake for MOF-L3 is zero due the absence of pyridine rings in the linker's structure. This study reveals that MOF-L1 and MOF-L2 have promising potential to store hydrogen compared to MOF-L3. This study also suggested that the new monoamide ligands, L3-L6 is not suitable for use as linker in MOFs because it can be easily hydrolysed and led to decomposition of ligands in the reaction.

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**SINTESIS, PENCIRIAN DAN KAJIAN PENYIMPANAN HIDROGEN
JARINGAN LOGAM-ORGANIK MENGANDUNGI LIGAN MONOAMIDA**

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Jaringan logam organik (MOFs) biasanya direka dan dikaji sebagai bahan untuk aplikasi penyimpanan hidrogen. Kebolehan MOFs untuk menyerap dan memisahkan gas bergantung kepada sebatian yang mengandungi kumpulan nitrogen (N) dan oksigen (O) kerana interaksi antara dwikutub setempat nitrogen dan momen kuadrupol oksigen. Oleh itu, dalam kajian ini, satu ligan yang telah dilaporkan dan lima ligan monoamida baru yang mengandungi atom penderma N dan O telah disintesis daripada tindak balas antara *N*-aminopiridina dan dimetil-2,6-piridinakarboxilat, masing-masing untuk menghasilkan *N*-6-[(4-piridilmetilamino)karbonil]-2-piridinakarboxilik asid metil ester (L1), 6-(pirimidin-2-ilkarbamoil)-piridina-2-karboxilik asid metil ester (L2), 6-(3-metil-piridin-2-ilkarbamoil)-piridina-2-karboxilik asid metil ester (L3), 6-(4-metil-piridin-2-ilkarbamoil)-piridina-2-karboxilik asid metil ester (L4), 6-(5-metil-piridin-2-ilkarbamoil)-piridina-2-karboxilik asid metil ester (L5) dan 6-(6-metil-piridin-2-ilkarbamoil)-piridina-2-karboxilik asid metil ester (L6). Ligan yang diperolehi telah dicirikan menggunakan teknik spektroskopi seperti Inframerah Penukar Fourier (FTIR), ^1H dan ^{13}C Resonans Magnet Nukleus (RMN), Ultra-Lembayung sinar nampak (UV-vis) dan formula molekul bagi setiap sebatian disahkan menggunakan

analisis unsur. Analisis inframerah menunjukkan kehadiran lima puncak penting iaitu $\nu_{\text{str}}(\text{NH})$, $\nu_{\text{str}}(\text{CH})$, $\nu(\text{C}=\text{O})$, $\nu_{\text{bend}}(\text{NH})$ dan $\nu_{\text{bend}}(\text{CH})$ masing-masing pada julat $3254\text{-}3358\text{ cm}^{-1}$, $2920\text{-}2964\text{ cm}^{-1}$, $1668\text{-}1749\text{ cm}^{-1}$, $1525\text{-}1607\text{ cm}^{-1}$, dan $1301\text{-}1324\text{ cm}^{-1}$. Manakala untuk keputusan $^1\text{H NMR}$, kehadiran proton metil, metoksi, CH proton aromatik dan NH telah dinyatakan masing-masing pada julat $\delta_{\text{H}}= 2.36\text{-}2.53\text{ ppm}$, $\delta_{\text{H}}= 4.0\text{-}4.06\text{ ppm}$, $\delta_{\text{H}}= 6.96\text{-}8.49\text{ ppm}$ dan $\delta_{\text{H}}= 10.28\text{-}10.59$. $^{13}\text{C NMR}$ mengesan karbon metil, karbon piridina dan karbon karbonil masing-masing pada $\delta_{\text{C}}= 17.93\text{-}53.05\text{ ppm}$, $\delta_{\text{C}}= 111.13\text{-}157.28\text{ ppm}$ dan $\delta_{\text{C}}= 161.27\text{-}164.99\text{ ppm}$. Pertindihan serapan piridina dan karbonil pada julat $272.5\text{-}292.5\text{ nm}$ telah diperolehi dalam spektrum UV. Ligan, L1-L6 yang disintesis telah digunakan sebagai penghubung organik dalam pembinaan jaringan logam organik (MOFs) melalui tindak balas dengan kadmium nitrat (II) tetrahidrat. Kompleks disediakan dengan menggunakan kaedah solvotermal, teknik yang biasa digunakan untuk sintesis MOFs. Dengan menggunakan kaedah ini, tiga MOFs (MOF-L1 - MOF-L3) telah berjaya diperolehi. Dalam spektrum FTIR MOF-L1 - MOF-L3, beberapa puncak yang penting iaitu $\nu_{\text{str}}(\text{NH})$, $\nu(\text{C}=\text{O})$, $\nu_{\text{bend}}(\text{NH})$, $\nu(\text{NO})$, $\nu(\text{Cd-O})$ dan $\nu(\text{Cd-N})$ telah ditunjukkan pada julat $3303\text{-}3409\text{ cm}^{-1}$, $1655\text{-}1597\text{ cm}^{-1}$, $1424\text{-}1566\text{ cm}^{-1}$, $1382\text{-}1384\text{ cm}^{-1}$, $596\text{-}430\text{ cm}^{-1}$ dan $501\text{-}434\text{ cm}^{-1}$. Kristalografi sinar-X menunjukkan bahawa hablur MOF-L1 mengablur dalam system hablur monoklinik dengan kumpulan ruang, $P21/n$. MOF-L1 adalah MOF dua dimensi yang tertutup penuh dan dianggap mempunyai limitasi dalam menyimpan hidrogen. hablur MOF-L3 pula mengablur dalam sistem hablur ortorombik dengan kumpulan ruang $Pbcn$ dan mempunyai jaringan satu dimensi. Kristalografi sinar X menunjukkan bahawa ligan L1 dan L3 (serta L4, L5) menjalani hidrolisis seperti yang dijangka dan menghasilkan ligan ini situ asid karboksilik dengan penderma tridentat O, N, dan O.

Kedua-dua kajian menunjukkan bahawa ligan mengalami hidrolisis dan membentuk in situ ligan asid karboksilik dengan tridentat O, N, O penderma. Analisis TGA menunjukkan bahawa MOFs mempunyai dua langkah degradasi, penguraian air dan pelarut pada peringkat pertama dan ligan pada peringkat kedua. Kajian lanjut mengenai kajian pengambilan hidrogen menggunakan Suhu Tekanan Komposisi (PCT) menunjukkan keupayaan untuk menyimpan hidrogen masing-masing sebanyak 0.5 wt. % dan 0.3 wt. %, pada 373 K dan 60 bar. Walau bagaimanapun, pengambilan hidrogen untuk MOF-L3 adalah sifar kerana ketiadaan gelang piridina dalam struktur penghubung organik itu. Kajian ini membuktikan bahawa MOF-L1 dan MOF-L2 mempunyai potensi untuk menyimpan hidrogen berbanding MOF-L3. Kajian ini juga mencadangkan bahawa monoamida ligan yang baru iaitu L3-L6 tidak sesuai untuk digunakan sebagai penghubung dalam pembinaan MOF kerana ia mudah terhidrolisis dan menyebabkan penguraian ligan dalam tindak balas.