Heterogenization of Pt complexes inside Metal Organic Frameworks using facile Postsynthetic Modification for visible-light driven hydrogen evolution

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Abstract: Integration of polypyridyl complexes inside Metal Organic Frameworks (MOFs) backbone has been so far mostly done by utilization of bipyridine dicarboxylic acid as a linker. This limit the possibility of hosts that can be used only to 2 choices amongst the countless MOFs existing. Hence another pathway was used for heterogenization in this study; postsynthetic modification (PSM) of amino groups in linkers using 2-pyridinecarboxaldehyde was applied to create a pyridylimine anchor for simultaneous coordination of Pt^{2+} ions in a one-pot approach. The resulting materials showed activity towards photocatalytic hydrogen production evolution reaction (HER) under visible light irradiation

Keywords: Metal Organic Frameworks, H_2 evolution, photocatalysis

1. Introduction

Homogeneous metal complexes are alluring catalysts whose selectivity and properties can readily change by varying the chemical environment surrounding them. Unfortunately, they suffer from poor stability and their recyclability can be arduous. Thus, immobilizing molecular complexes inside stable hosts could greatly improve their practical uses and develop novel properties. Metal-Organic Frameworks (MOFs), are captivating candidate for heterogenization applications; the chemical and physical properties of the materials can be altered by designing the organic linkers or inorganic secondary building unit (SBU), creating pores with diversified environment which can be used as nanoreactors. To integrate polypyridyl complexes inside MOFs, one of the most used method is to use bipyridine dicarboxylic acid which possesses the dual role of linker and anchor thanks to respectively the carboxylic acid and pyridine functions. However only a few MOFs using this linker have been reported so far. The limitation in available platform greatly inhibits the development of heterogenized photocatalysts within MOFs. We propose here a versatile methodology for heterogenization of polypyridyl analog complexes into various MOFs. Nucleophilic attack of the amino function of 2-aminoterephtalic acid into a pyridinecarboxaldehyde creates an imine linked to a pyridine function. The designed molecular structure possesses 2 free nitrogen atoms which can coordinate a metal similarly to the bipyridine ligand.

2. Experimental

A zirconium MOF called UiO-66-NH_2 was synthesized using solvothermal method by mixing zirconium salt, 2-aminoterephtalic acid and concentrated HCl in dimethylformamide at 393 K for 24 h. The dim yellow powder was recovered by filtration and suspended in MeOH for 16 h under vigorous stirring to remove any unreacted linker or Zr salt. After another filtration step the powder was dried at 353 K in air. Next, the Pt complex called $[Pt(PTA)Cl_2]$ (PTA = 2-pyridylimine terephtalic acid) (**Figure 1**) was constructed into the framework through postsynthetic modification and metalation at room temperature. Reaction of K_2PtCl_4 with the formyl function 2-pyridinecarboxaldehyde creates of a reactive intermediate whose carbonyl function can be attacked by the NH_2 of the MOF linker. The synthesized imine and the nitrogen atom of the pyridine coordinate together the Pt^{2+} ion creating the desired complex. The obtained powder was heavily washed with water and methanol to remove

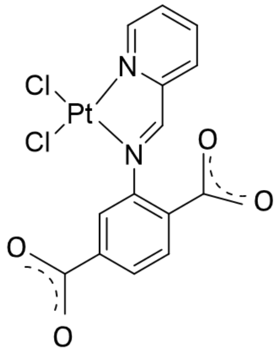

Figure 1. Molecular structure of $Pt(PTA)Cl_2$

unreacted chemicals. Photocatalytic H_2 evolution reaction was carried out in a pyrex vessel at room temperature using white LED as a photon source and an aqueous solution of ethylenediaminetetraacetate (EDTA) 0.01 M at pH = 5.3. Other pH (2, 3, 4, 7.3) were also studied but less or no H_2 was measured.

3. Results and discussion

After the reaction, a clear variation in colour could be observed in the powder, from dim yellow to orange. Such phenomenon is attributed to a ^{3}MLCT between Pt^{2+} and the pyridylimine ligand. This was further confirmed by UV-Vis spectroscopy which showed the apparition of a new band in the visible region extending to 600 nm (Figure 2). Furthermore, the absorption spectrum matches well with the homogeneous counterpart [Pt(PTA)Cl2], stressing the close structure between homo and heterogenous catalysts. PXRD patterns and N_2 adsorption-desorption isotherms of $Pt(PTA)Cl_2@UiO\text{-}66\text{-}NH_2$ were measured before and after the PSM, proving the successful formation of the porous crystalline structure and its conservation even after the heterogenization of Pt^{2+} complex. Nonetheless the specific surface are of the MOF which was calculated by BET method was reduced from 1123 $m^2.g^{-1}$ to 947. $m^2.g^{-1}$ due to the complexes blocking the windows of the pores. To understand how much NH_2 moieties were converted by the PSM, ^{1}H NMR was carried out with HF-digested MOF. According to integration peaks, around 10% of the amino function was found to become an imine. Under visible light irradiation, the material showed good activity, up to 60 μmol of hydrogen in 9 hours, without any loss of activity or leaching even after 3 cycles (**Figure 3**). Thanks to this method, the same complexes can be integrated into various MOFs possessing a free NH_2 function. Therefore, by employing the same methodology $Pt(PTA)Cl_2$ was integrated inside MIL-101(Al)-NH_2, MIL-53(Al)-NH_2 and MIL-101(Cr)-NH_2. All Al-MOFs showed the lowest activity with less than 1 μmol produced while Cr-MOF displayed exceptional efficiency, with 142 μmol of H_2 produced in the same experimental time. Although the details concerning the divergence in activity are not yet fully understood, the most probable hypothesis is that the reactivity of the NH_2 function, meaning its nucleophilicity, greatly varies based on the inorganic SBU. Another possibility would be the effect of the structure, in the case of Pt molecular photocatalyst, since creating a Pt-Pt bond is necessary to possess activity, a packed structure such as UiO-66 may promote such interactions.

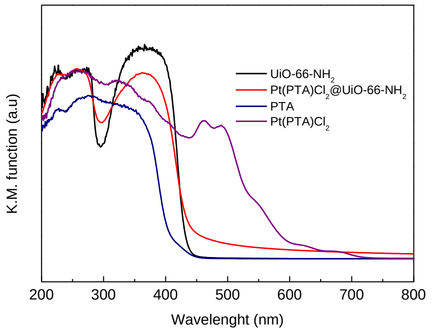

Figure 2. UV-Vis of $Pt(PTA)Cl_2$ at homogeneous state (purple) and heterogeneous state (red)

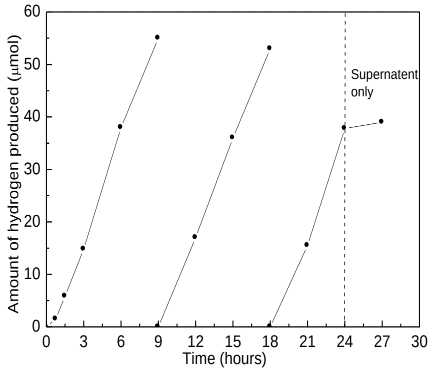

Figure 3. Time course plot, recyclability and leaching test of H_2 production of $Pt(PTA)Cl_2@UiO\text{-}66\text{-}NH_2$ under visible light irradiation

4. Conclusions

By using a simple and versatile PSM on the NH_2 moieties of the linker; we managed to introduce $Pt(PTA)Cl_2$ inside UiO-66-NH_2. Conservation of the crystalline porous structure and its high mean specific surface was confirmed by PXRD and N_2 isotherms. Thanks to the ^{3}MLCT of the complex, the material could absorb visible light until 600 nm. Furthermore, the molecular photocatalyst showed good photocatalytic activity for HER under visible light without any loss of activity or leaching even after 3 cycles. Prompted by this discovery, the same complex was integrated to different MOF, each one developing its own activity towards HER. While those disparities are not fully understood, the introduction of polypyridyl analog complexes using PSM is clearly an attractive method owing its flexible application. Heterogenization of other metals using the same protocol may help to develop the photocatalytic application of MOF in the long term.