

Supporting Information for Dalton Trans.,

Micro and Mesoporous Metal-Organic Frameworks for Catalysis Applications

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Experimental 1. Preparation of complex **2** and **3**.

Experimental 2: Experimental details of alkylation and benzylation of Toluene and biphenyl using MOF's **2-4**.

Experimental 3: Leaching experiments using MOFs **2-4**

Figure 1. Two interpenetrated Adamantanoid network of complex **2** generated with trapped solvent molecules.

Figure 2. Two-fold interpenetrated Lonsdaleite network of complex **3** generated from tetrahedral building block, **1** and Zn₂ clusters.

Figure 3. PtS network structure of complex **4**.

Figure 4. Thermal analysis of complex **2** with a heating rate of 5 deg/min.

Figure 5. Thermal analysis of complex **3**.

Figure 6. BET surface area analysis of **2** using liquid nitrogen at 77K.

Figure 7. BET surface area measurements of complex **3**.

Figure 8. Powder diffraction patterns (PXRD) patterns of complex **3** before and after catalysis.

Figure 9. Powder diffraction patterns of complex **2** before and after catalysis.

Figure 10. Powder diffraction patterns of complex **4** before and after catalysis. Notice no change in PXRD was observed.

Figure 11. IR spectra of complex **2** before and after catalysis reaction.

Figure 12. IR spectra of complex **3** before and after catalysis reaction.

Experimental 1: Tetrahedral organic linker, **1** was successfully synthesized using the reported procedure.¹

Complex 2 (with Pyrazine): Equi-molar ratio of **1** (61.6 mg, 0.1mmol), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (29.7 mg, 0.1 mmol, Aldrich) and Pyrazine (8.0 mg, 0.1 mmol) were dissolved in 10ml DMF in a 20 ml vial. The reaction mixture was ultrasonicated until homogeneous (approx. for 1 min). The reaction vial was capped tightly and placed in an oven at 103 °C. After 24 hours, the sample was removed from the oven and allowed to cool to RT. The mother liquor was decanted to get the transparent crystals, which were washed with DMF (3 mL $\times$ 3) and dried in air for 10 min.

Complex 3 (with DABCO): Equi-molar ratio of **1** (61.6 mg, 0.1mmol), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (29.7 mg, 0.1 mmol, Aldrich) and Diazabicyclo[2,2,2]octane (11.2 mg, 0.1 mmol) were dissolved in 10ml DMF in a 23 ml Teflon lined autoclave. The reaction mixture was ultrasonicated for a minute to get homogeneous. Then the autoclave heated at 110 °C for 24h and then gradually cooled to RT at the rate of 10 °C/hr. The crystals were washed with DMF and air dried.

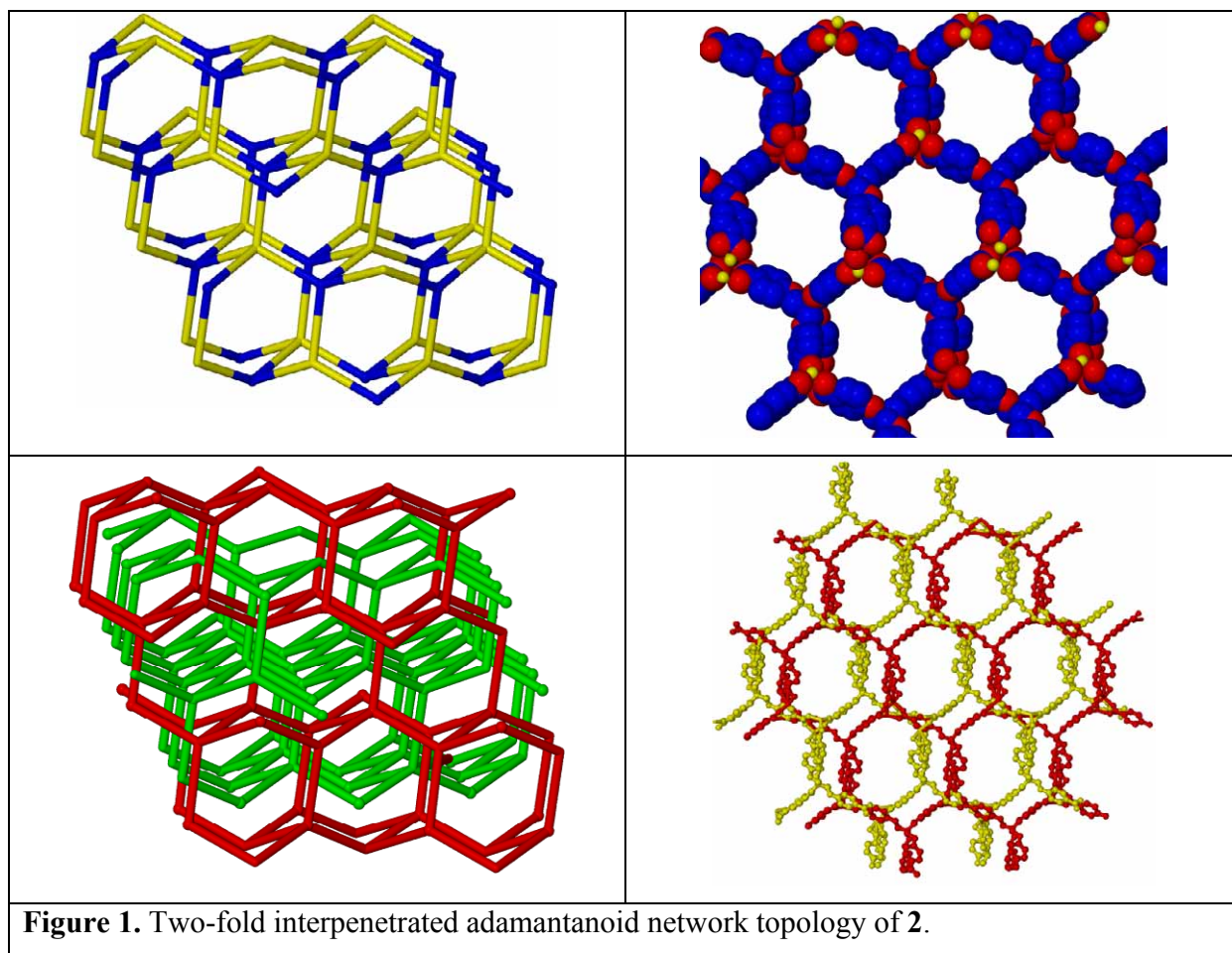
Experimental 2:

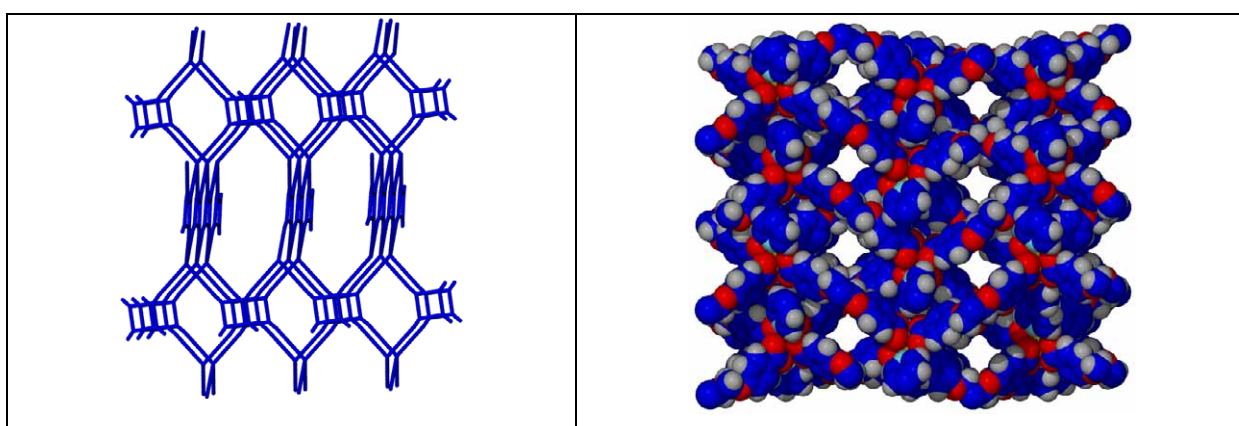
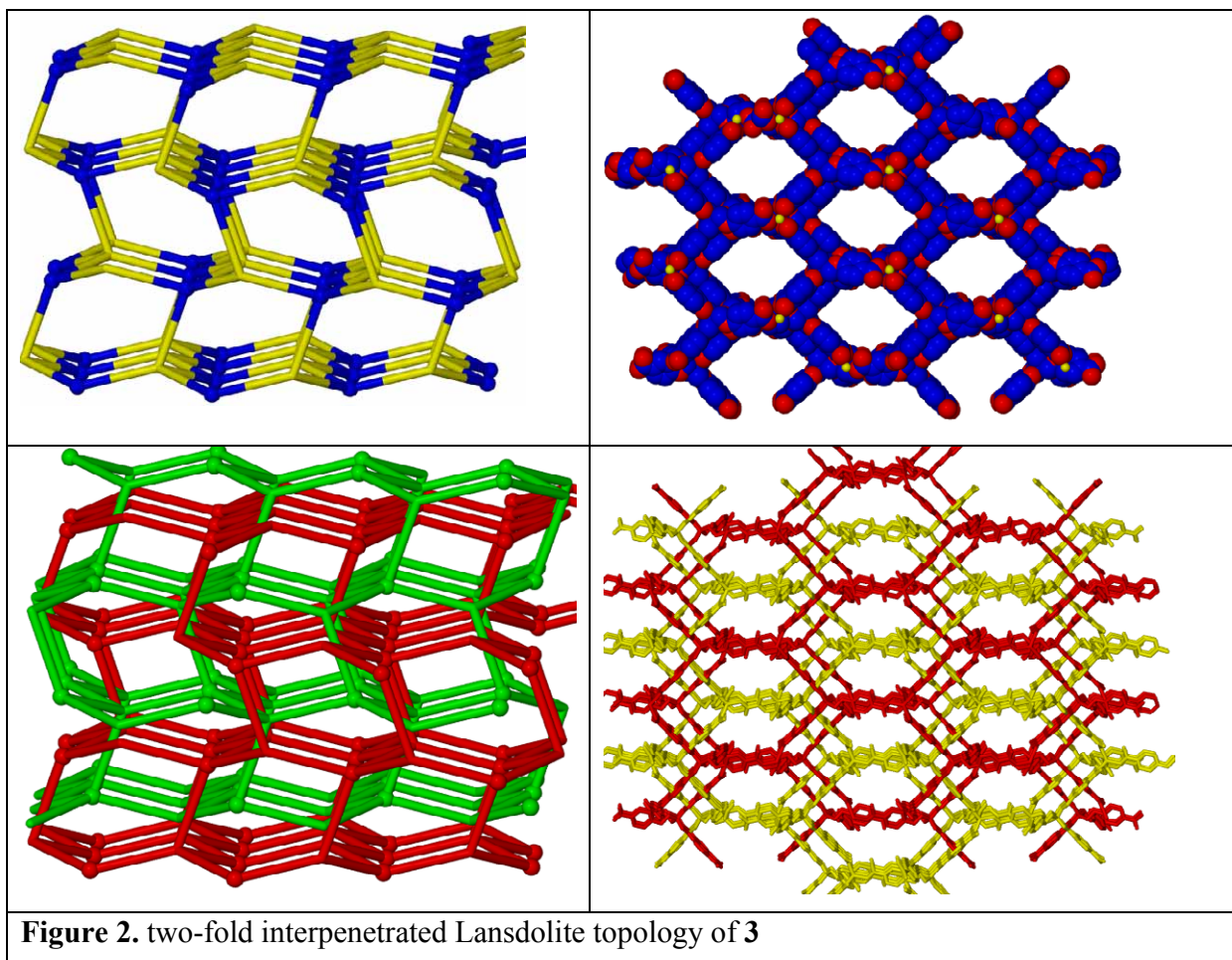
Alkylation and Benzylation using MOF's 2-4:

The reactions were performed as follow. In a 25 ml autoclave 1.04 ml (9.6 mmol) of toluene were mixed with 0.52 ml of *tert*-butyl chloride (4.7 mmol) in 3.7 ml of decane solution (molar ratio toluene : *tert*butyl chloride = 2:1). Then, 20 mg of catalyst was added, the autoclave was sealed and the reaction mixture stirred for 2 hrs at 170 °C. Similarly, the reaction between biphenyl (1.48 g, 9.6 mmol) and *tert*-butyl chloride (0.52 ml, 4.7 mmol) in 3.65 ml of decane was performed in an autoclave using 20 mg of catalyst and stirring for 2 h at 170 °C. Similar method has been adopted for benzylation of toluene and biphenyl {0.54 mL (4.7 mmol) of benzyl chloride added to 1.04 mL (9.6 mmol) of toluene in 3.7 mL of decane (toluene : benzyl chloride ratio 2:1)}.

Leaching Experiments:

The leaching experiments were done to test the heterogeneity of the reaction. A blank reaction was carried out in the absence of solid catalyst, resulted little or no conversion of the reactants as shown in Table I and II. In another experiment, the reaction mixtures were filtered off after the completion of the alkylation reactions and the solid catalyst, reaction solution recovered separately. Then the new reaction started with fresh reactants of Toluene (9.6 mmol) and tert-butyl chloride (4.7 mmol) to the recovered solution and heated the reaction mixture in autoclave at 170 C for 2h. There is no further enhancement in the conversion of the reactants observed.





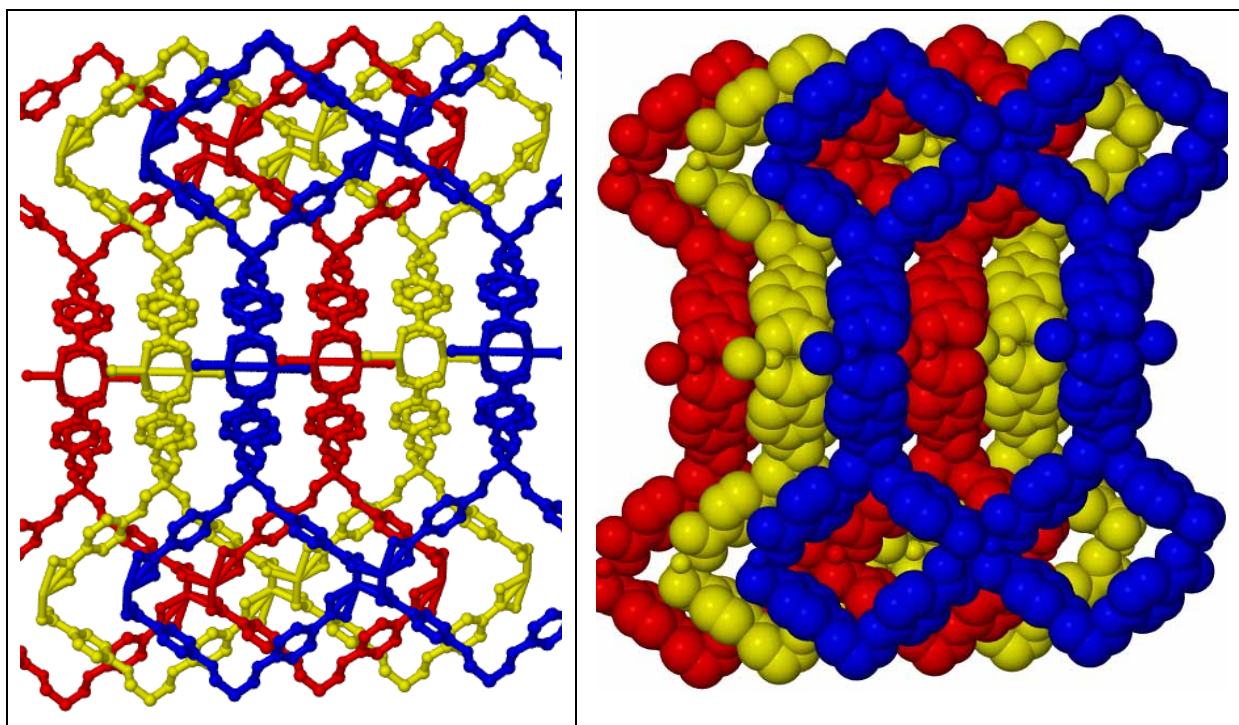


Figure 3. Three-fold interpenetrated PtS network structure of **4**.

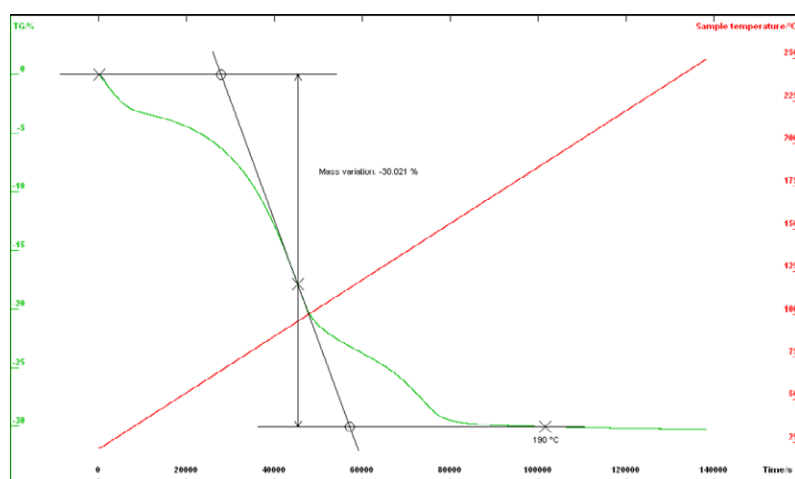


Figure 4. Thermal analysis of complex **2** with a heating rate of 5 deg/min reported earlier ((Ref. 19 in the manuscript).

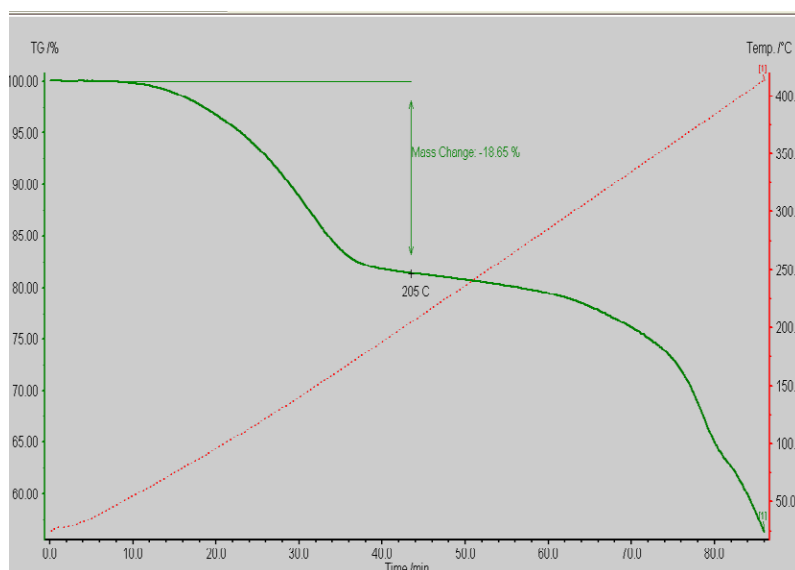


Figure 5. Thermogravimetric analysis of complex 3 reported earlier (Ref. 19 in the manuscript).

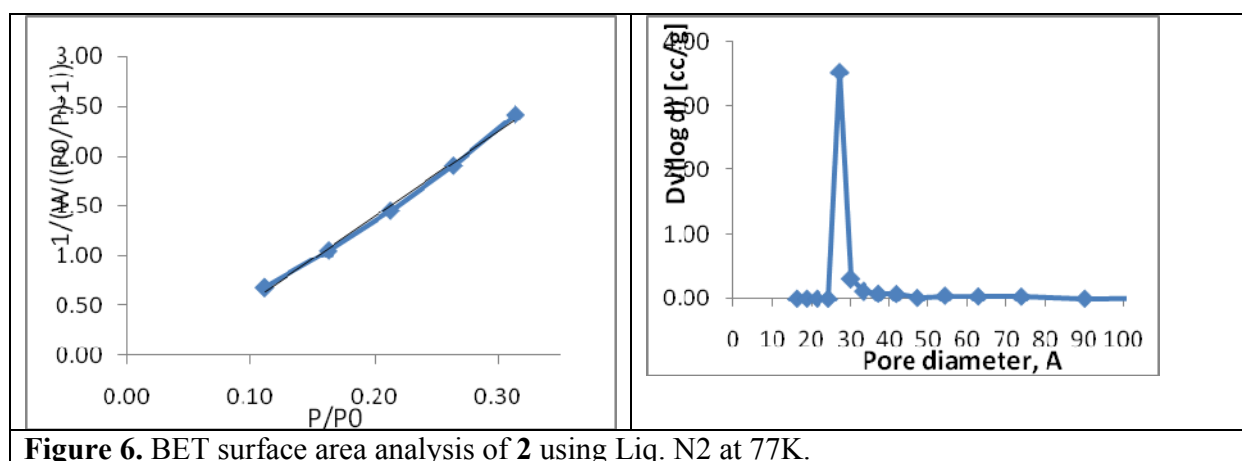


Figure 6. BET surface area analysis of **2** using Liq. N₂ at 77K.

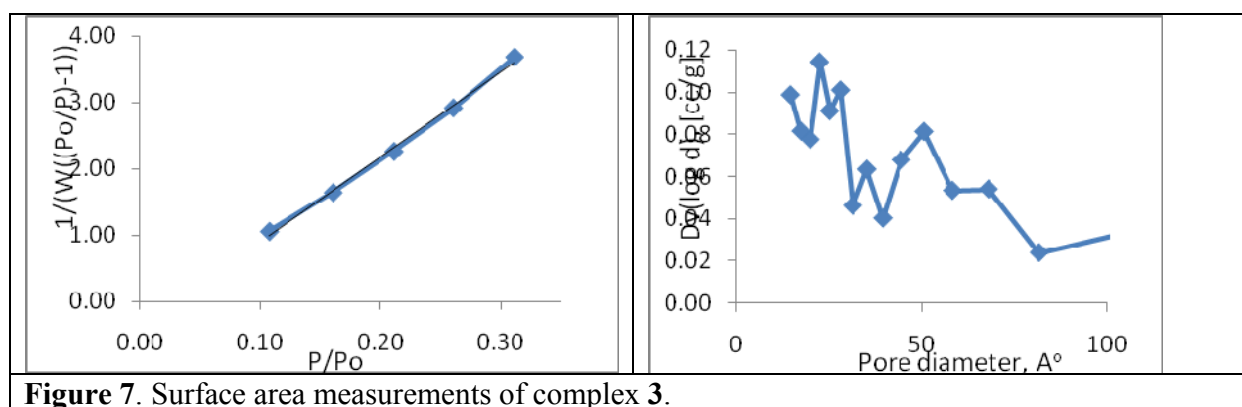


Figure 7. Surface area measurements of complex **3**.

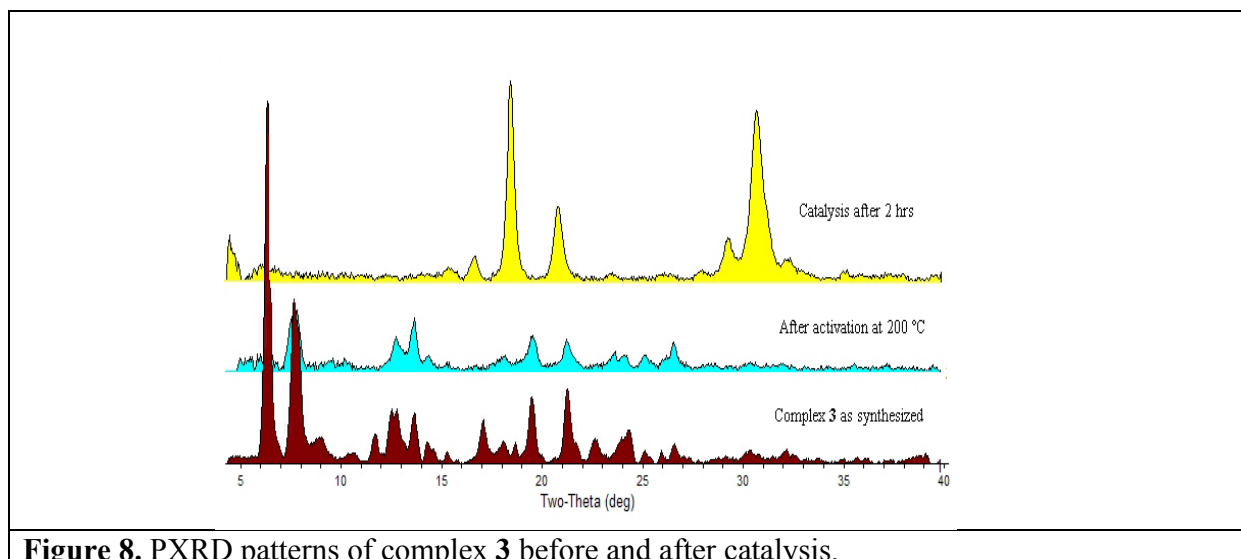


Figure 8. PXRD patterns of complex 3 before and after catalysis.

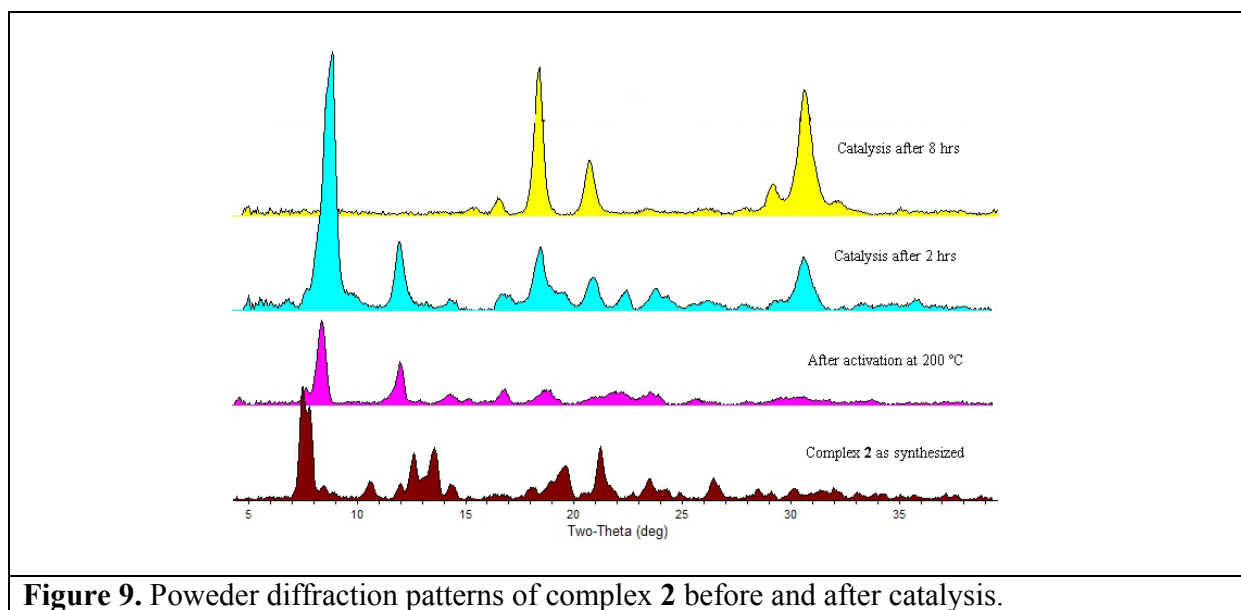
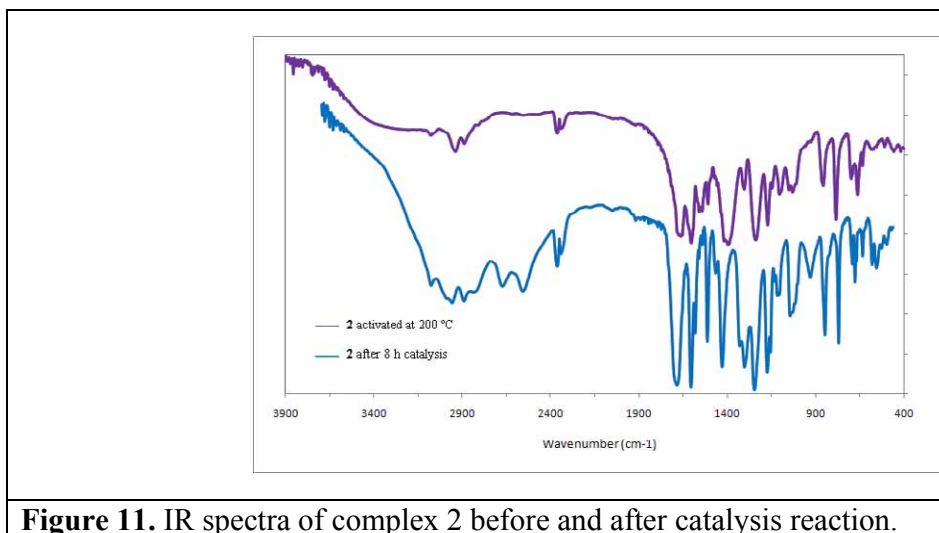
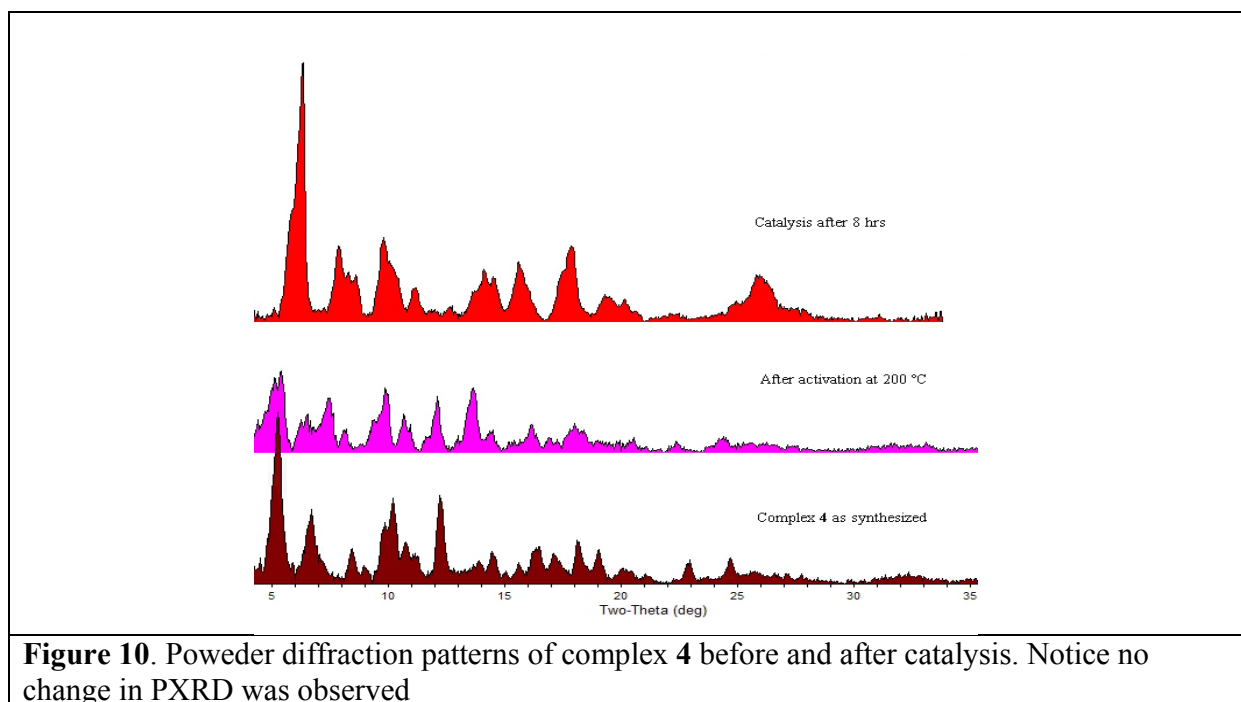
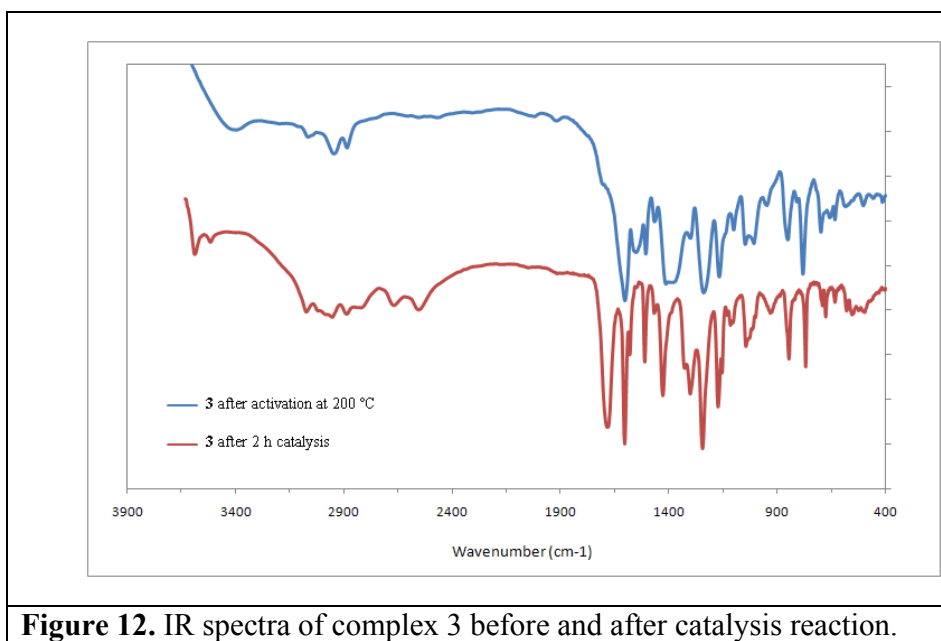


Figure 9. Powder diffraction patterns of complex 2 before and after catalysis.





1. D. Laliberte, T. Maris and J. D. Wuest, *Journal of Organic Chemistry*, 2004, **69**, 1776-1787.