

Annexe I: Calibration curve used to quantify the cyclooctene and the cyclooctane oxide concentrations during the GC tests.

These calibration curves are necessary to calculate the concentrations of cyclooctene and cyclooctane epoxide. The calculations are based on the areas of these compounds in the GC chromatograms. An internal standard, being dibutyl ether was used to correct the errors in-between the manipulations. The slopes values are the response factor m as shown on the equation.

$$A_{sample}/A_{IS} = m \times C_{sample}/C_{IS}$$

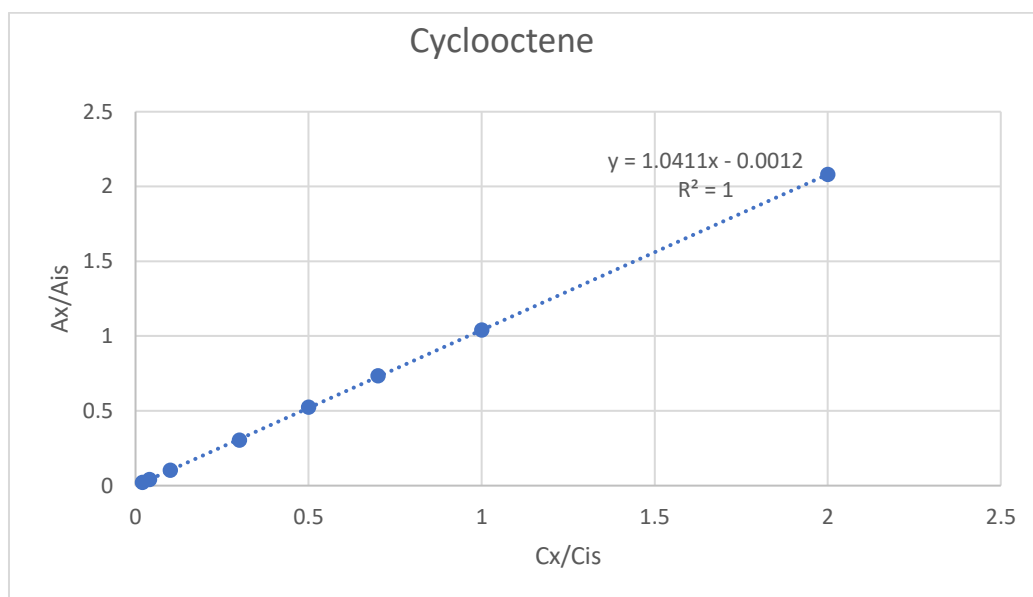


Figure 41: Calibration curve for cyclooctene. Area ratio in function of the concentration ratio

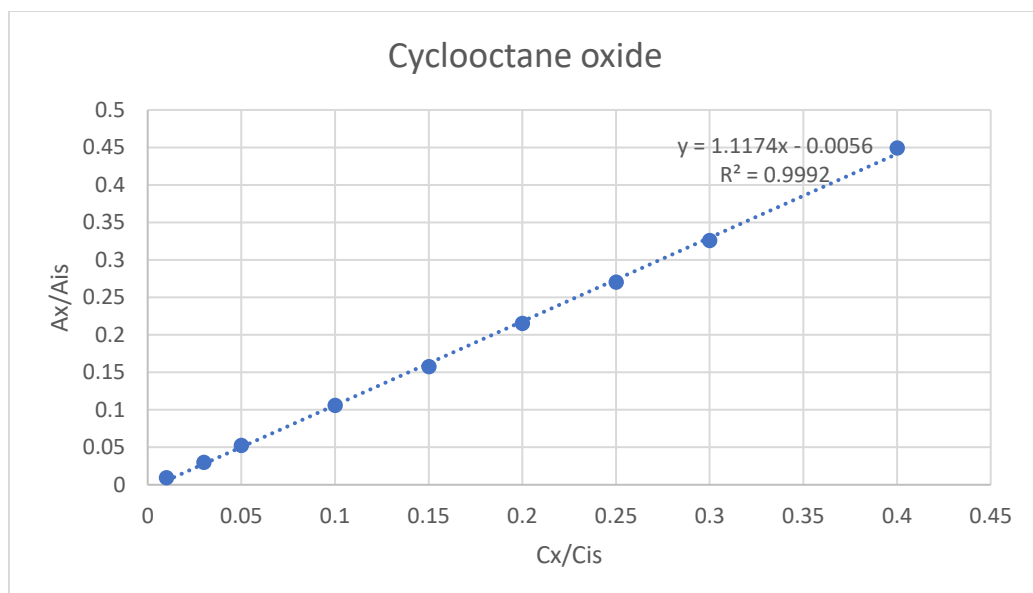


Figure 41: Calibration curve for cyclooctane oxide. Area ratio in function of

Annexe II part A: Protocol of the Ischii-Venturello synthesis to hybridize PW4 with the quaternary ammonium salt

The PW4 hybrid prepared by following exactly the same protocol is the this one: First pertungstic acid, H_2WO_4 (2.50 g, 10 mmol) is dissolved in 30 ml of water where 7 ml of 30% w/v of H_2O_2 is added and this solution is then mixed at 60°C for 15 min. Then, phosphoric acid is added, 40% w/v H_3PO_4 (0.62 ml, 2,5 mmol). After 15 more min of stirring at room temperature, a dropwise addition over 2 min at 20°C of tetrahexylammonium chloride (1.56 g, 4 mmol), dissolved in benzene is done. This will result to create a biphasic mixture where the PW4 will be formed at the interface of the two phases. Then separation of this white crystalline material is done by filtering on Büchner and washed with a small amount of water, benzene and diethyl ether and then dried over a porous plate. Recrystallization from CH_2Cl_2 - Et_2O at -25°C gives a crop of crystals, m.p. $140 - 142^\circ\text{C}$, suitable for X-ray studies. [93]

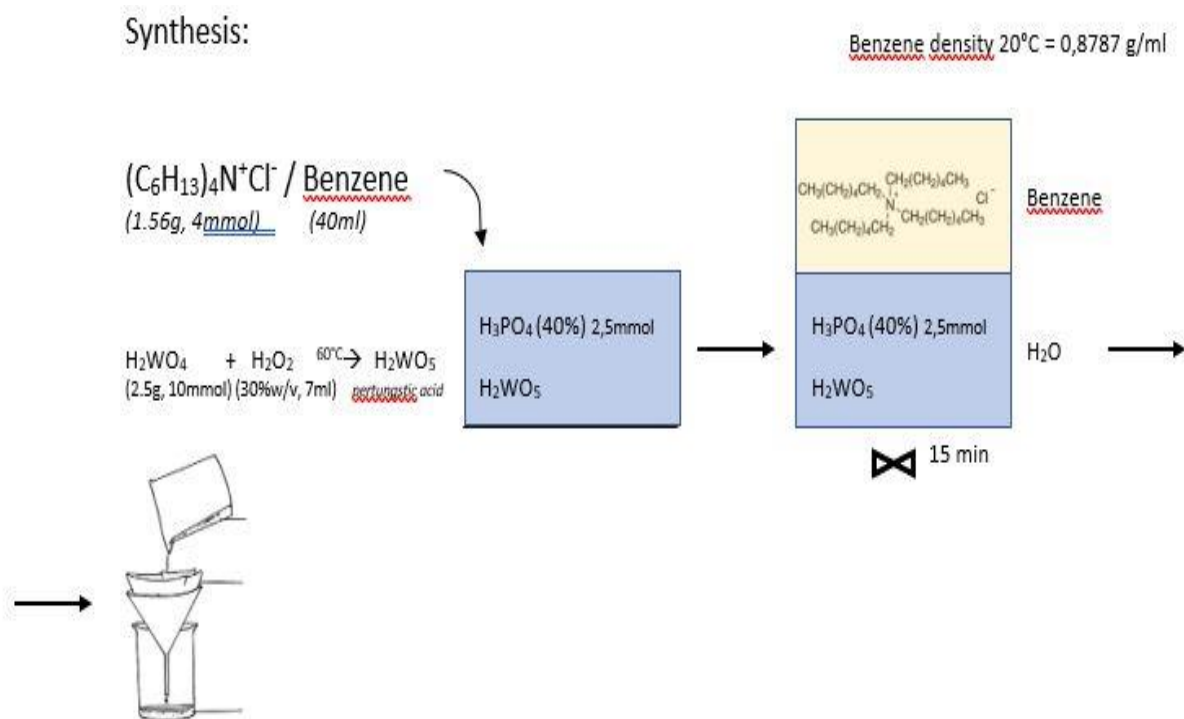


Figure 43: Schematic representation of the Ischii-Venturello synthesis

Annexe II part B: Preparation of the organic ligands according to Simon's de Crane work.

For the synthesis of phenyl terpyridine :

1 equivalent (1g) of benzaldehyde and 2 equivalents (2.2774 g) of 2-acetylpyridine were introduced in a 250 ml flask. 2 equivalents (1.0547 g) of KOH were added, as well as 35mL of NH_3 and 70 mL of ethanol. The flask was then covered, and the mixture was continuously stirred for 7 days at room conditions. The resulting suspension was filtered on a Büchner and washed 3 times with 15 ml of ethanol. The remaining solid was dried off on the same Büchner

and introduced in a new flask where it was recrystallized. This was done by dissolving it in ethanol and heating up the solution with an IR lamp, using a refrigerant on top of the flask to avoid any losses. Once the solid was completely dissolved, the heat source was removed to allow the crystallization of the solid. The resulting peaks crystals of TPY were filtered again and washed with cold ethanol to avoid redissolution.

Chlorophenylterpyridine :

Same procedure as previously, just using 1 equivalent (1g) of chlorobenzaldehyde, 2 equivalents (1.7238 g) of 2-acetylpyridine and 2 equivalents (0.7984 g) of KOH.

Fluorophenylterpyridine :

Same procedure as previously, just using 1 equivalent (1g) of fluorobenzaldehyde, 2 equivalents (1.9500 g) of 2-acetylpyridine and 2 equivalents (0.9000 g) of KOH.

Trimethoxyphenylterpyridine :

Same procedure as previously, just using 1 equivalent (1g) of 3,4,5-trimethoxybenzaldehyde, 2 equivalents (1.2350 g) of 2-acetylpyridine and 2 equivalents (0.5720 g) of KOH.

Pyridilterpyridine :

Same procedure as previously, just using 1 equivalent (2 g) of 4-pyridilcarboxaldehyde, 2 equivalents (4.5200 g) of 2-acetylpyridine and 2 equivalents (2.1000 g) of KOH.

Note: this come from Simon de Crane [64] exactly word by word from his memoire.

In the Figures below, the H-NMR spectra of the different ligands are shown.

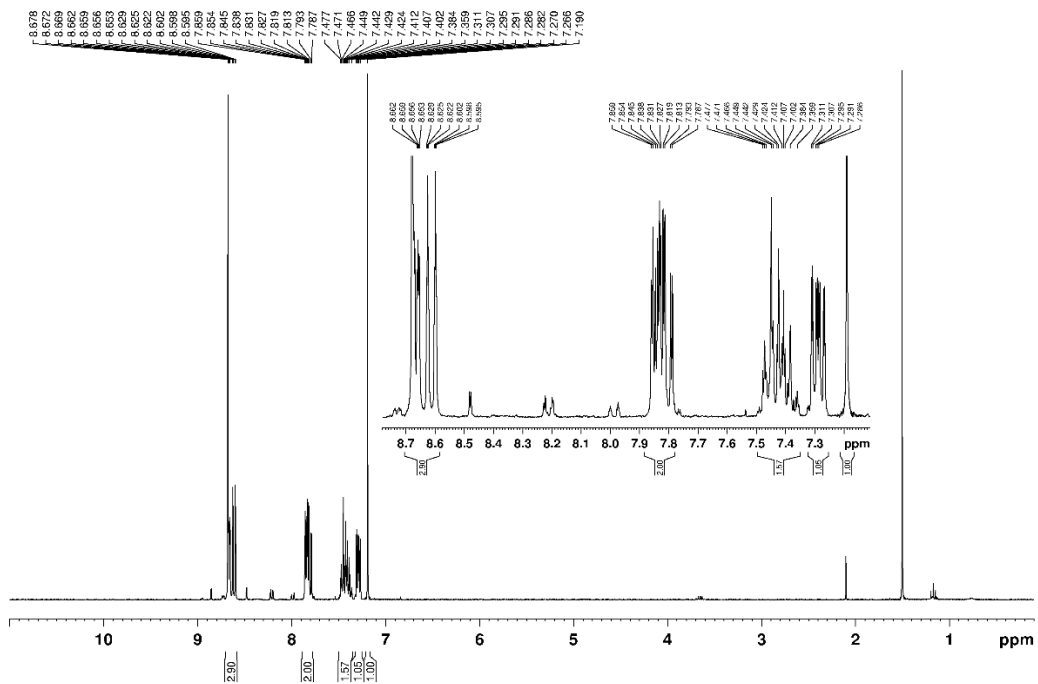


Figure 44 Ph-TPY ligand H-NMR spectrum in CDCl₃

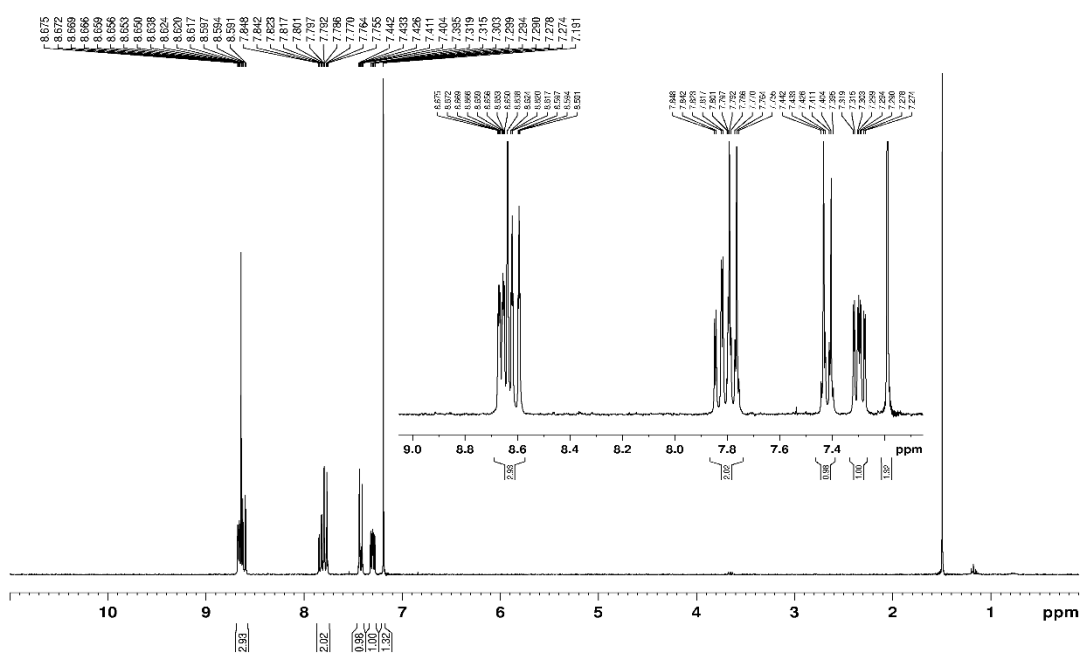


Figure 45 Cl-TPY ligand H-NMR spectrum in CDCl₃

Also, another simple test was made to confirm the following hypothesis. The IR spectrum of the short stirring time hybrid and the corresponding pure ligand are so similar that one think that in the hybrid sample, only a tiny part of the ligand has been hybridized with the PWx species and that the rest is simply the pure unreacted ligand. Since the ligand is soluble in dichloromethane and that the hybrid is not, the short stirring time hybrid (Cl-TPY) was introduced in a vial with acetonitrile and thoroughly mixed for 20 min. The suspension was then filtered and the supernatant as well as the recovered solid were analysed on ATR-IR. The spectra are illustrated in figure 48.

At first sight, the spectra look very similar with each other. However, some irregularities can be pointed out when zooming. Indeed, some peaks are shifted in some places demonstrating that maybe the 2 samples recovered after filtration might be different. Nevertheless, the shifts are so tiny that it is hard to confirm.

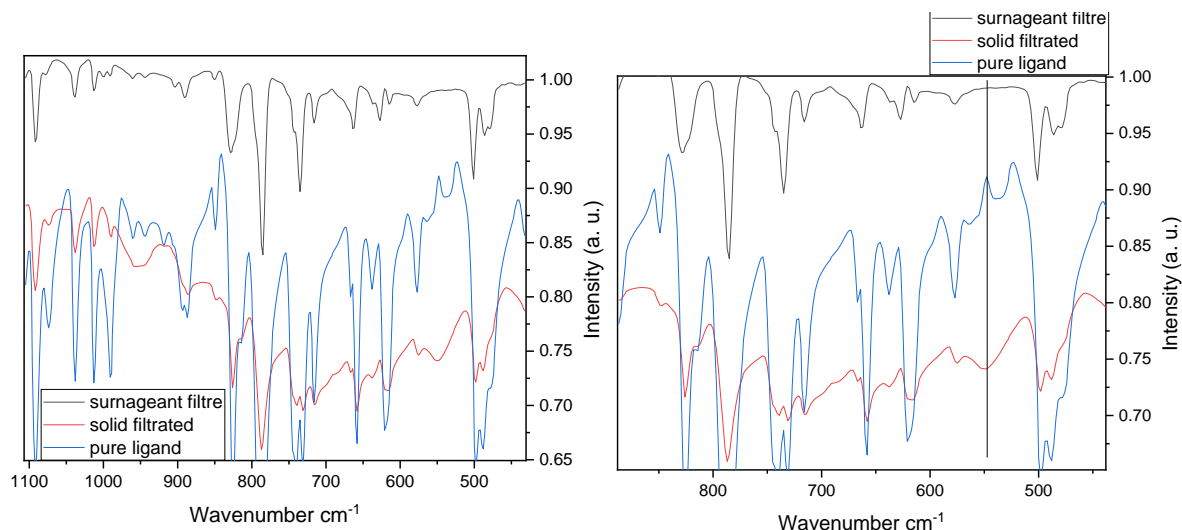


Figure 48: ATR-IR of the short stirring time hybrid (Cl-TPY) that has been washed in acetonitrile in order to try to solubilize the unreacted ligands and isolate the hybrids. The black curve corresponds to the supernatant that has been dried out in vacuum, the red curve is the recovered solid obtained after filtration and the blue curve is the pure ligand.

Annexe III: XRD diffractograms of the pure ligands and the short hybridization time hybrids

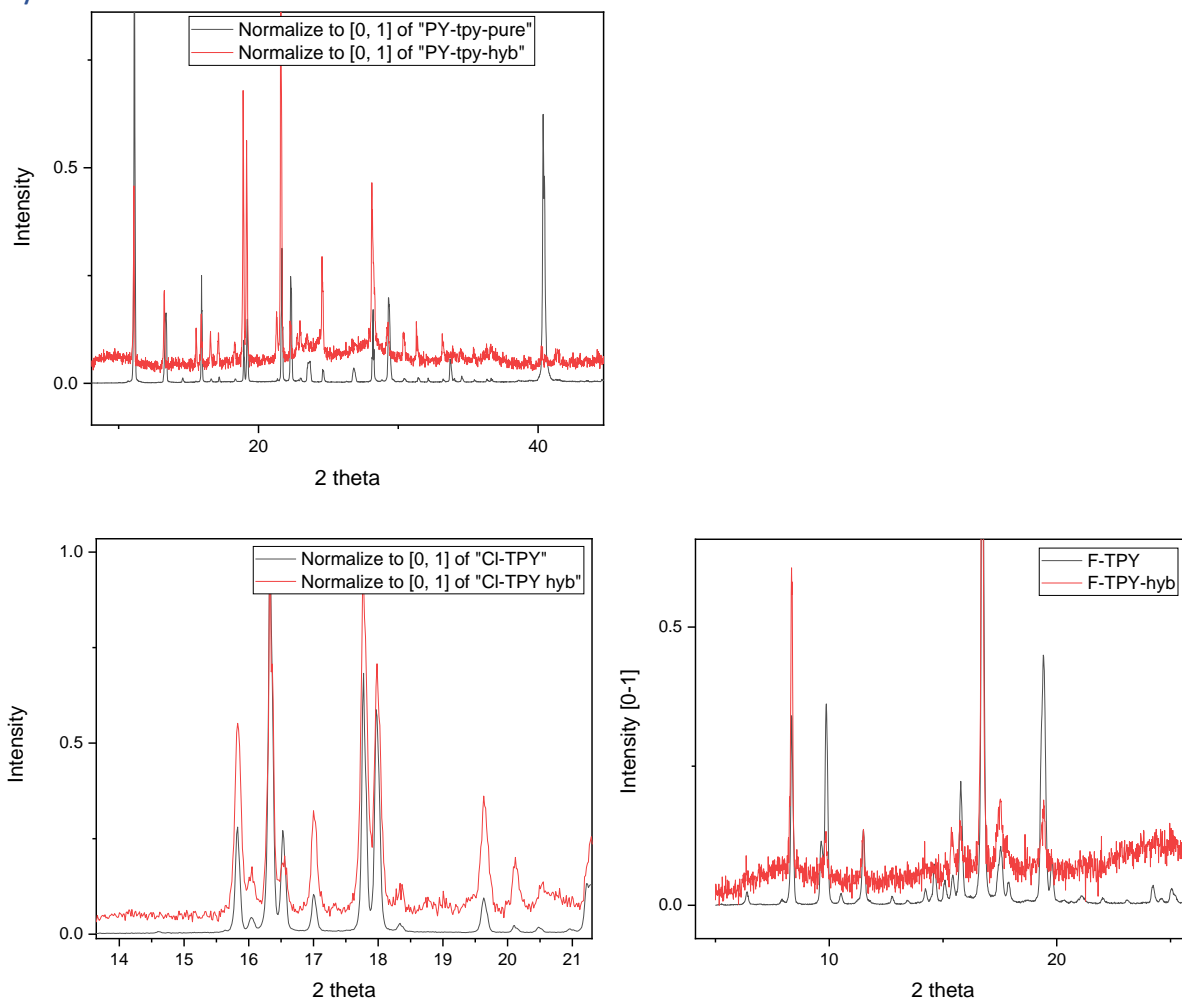


Figure 49: XRD diffractograms of the other short stirring time synthesized hybrids and their corresponding pure ligand.

Annexe IV: Infrared & TGA of the other short-stirring-time hybrids:

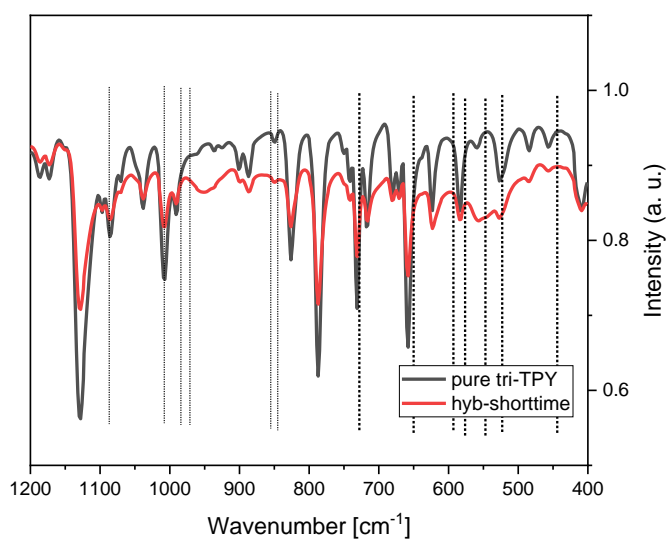


Figure 30 IR analysis

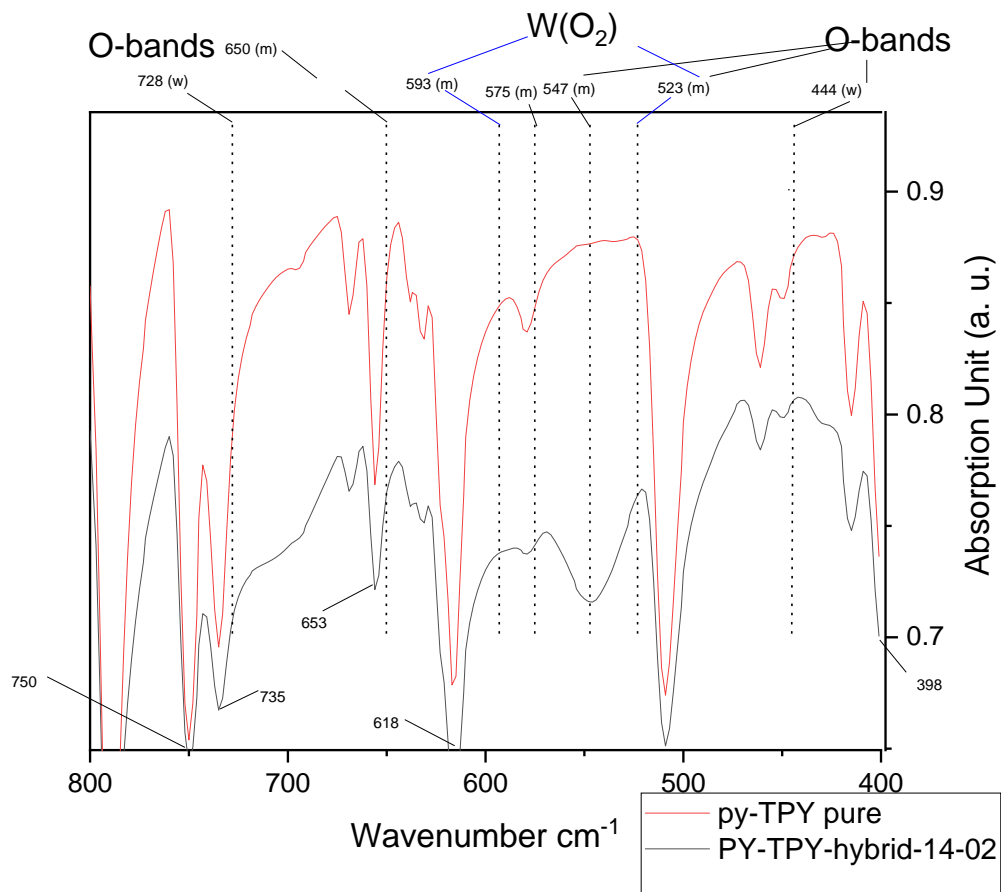


Figure 51: IR spectra of the short-stirring time Py-TPY hybrid and the pure Py-TPY ligand.

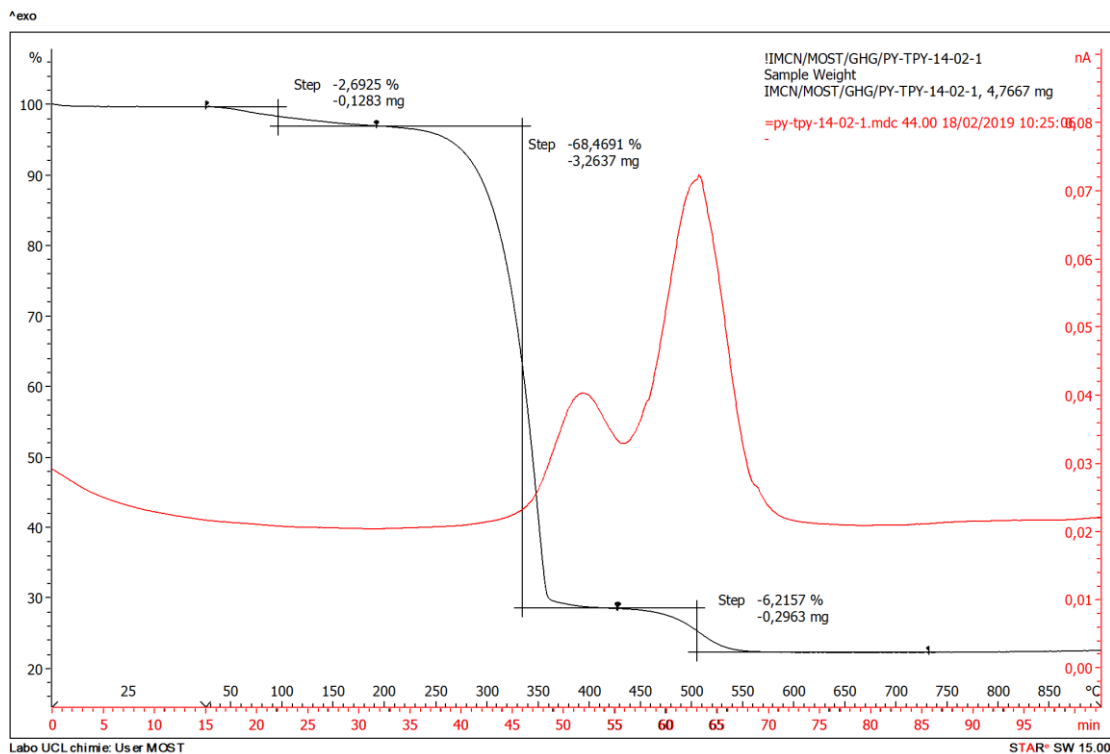


Figure 52: TGA of short the short-stirring-time hybrid Py-TPY

Annexe V: IR of the long-stirring-time hybrids

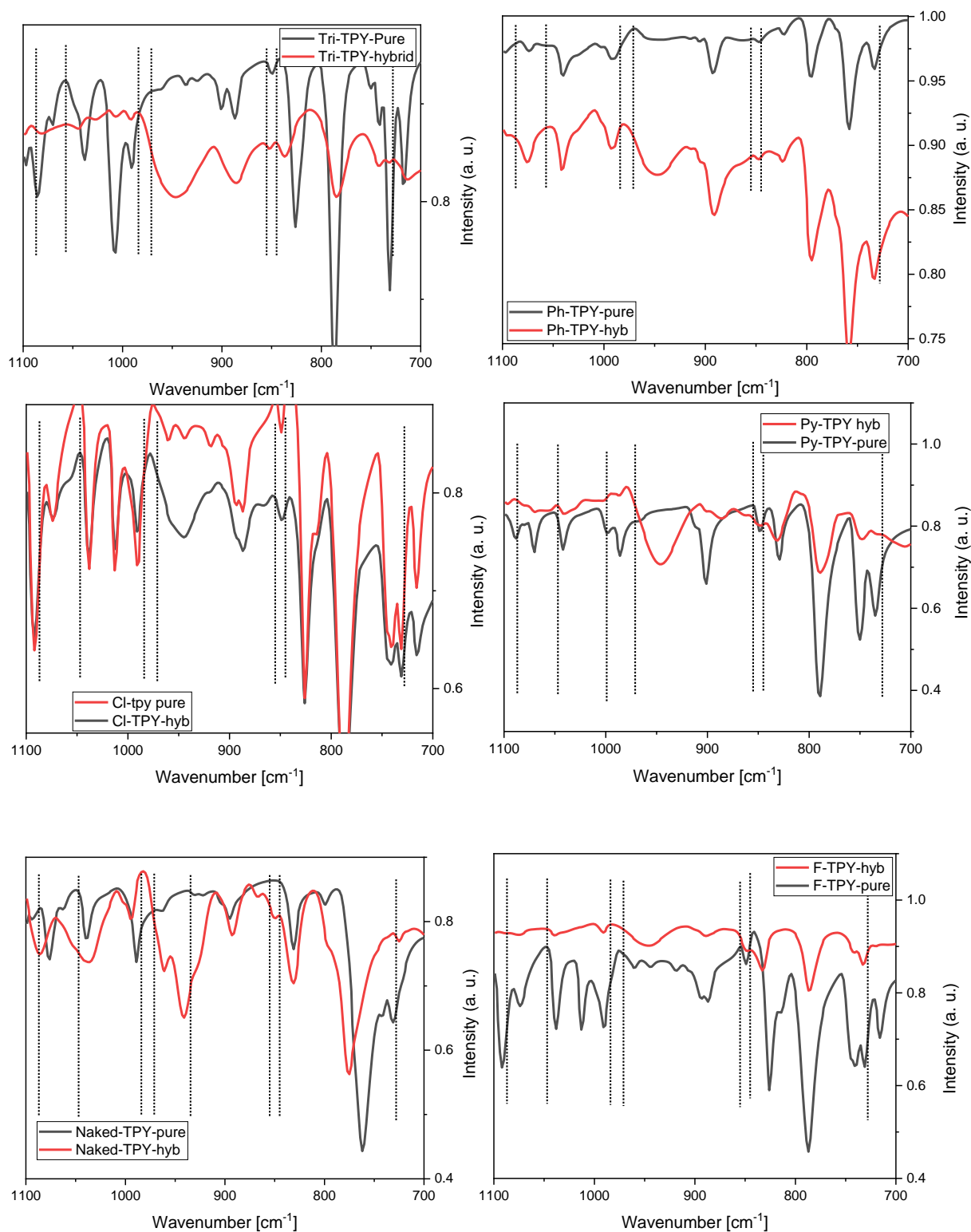


Figure 53: IR spectra of long-stirring-time hybrids and their corresponding pure ligands

Annexe VI TGA, XRD, Raman and nitrogen physisorption analysis:

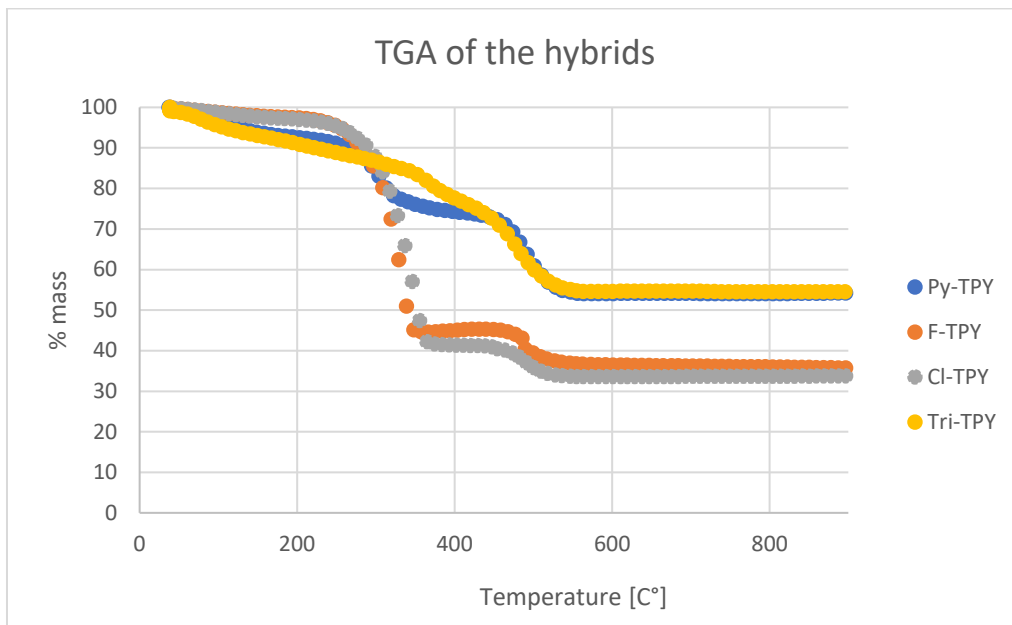


Figure 54: Thermogravitational analysis of the long hybridization time hybrids. This correspond to the first long stirring time batch. Tri-TPY hybrid (Yellow), Py-TPY hybrid (Blue), F-TPY hybrid (Brown), Cl-TPY (Grey). A mass loss of 5% of water is observed

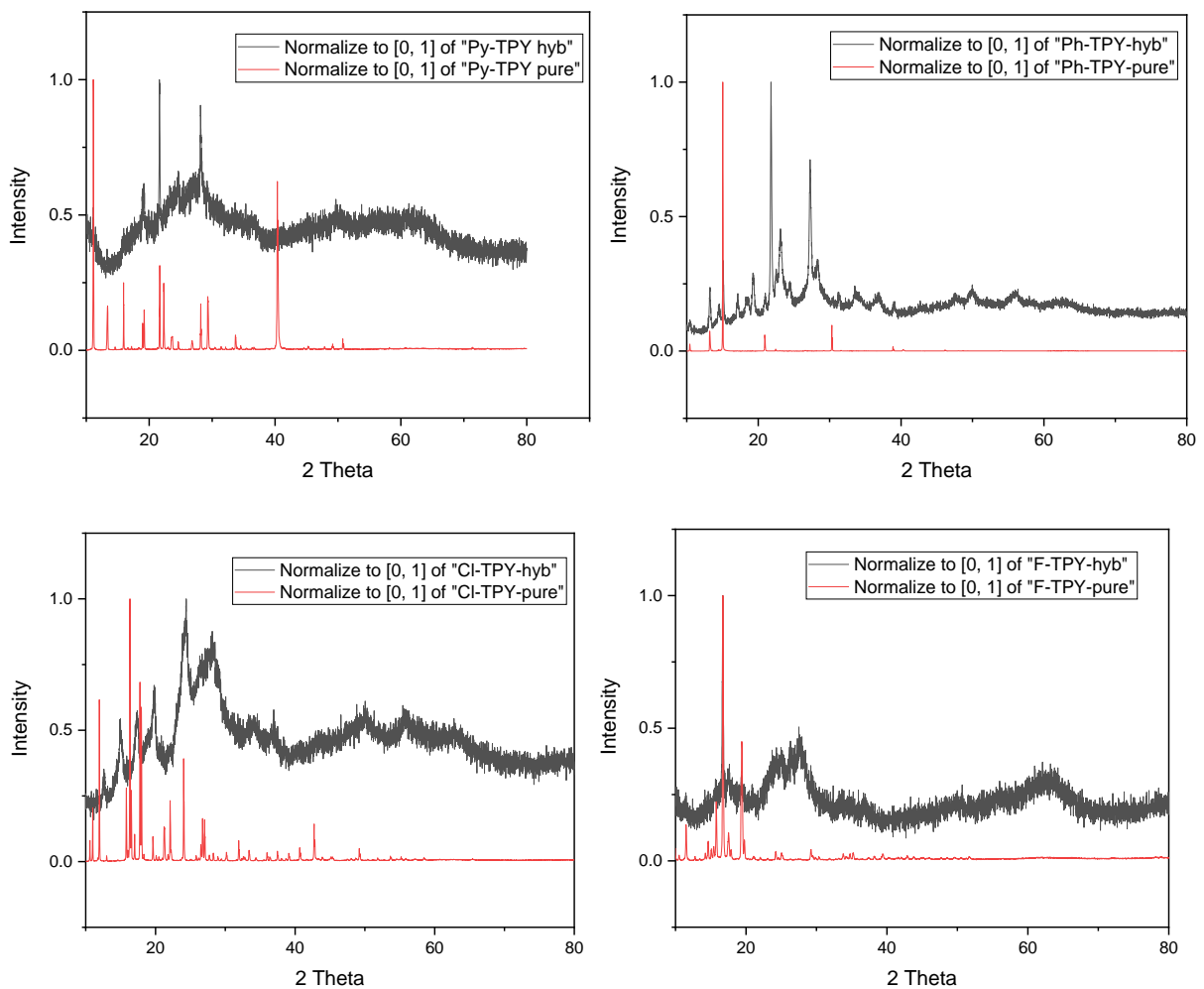


Figure 55: XRD diffractograms of the different long stirring time synthesis and their corresponding ligand.

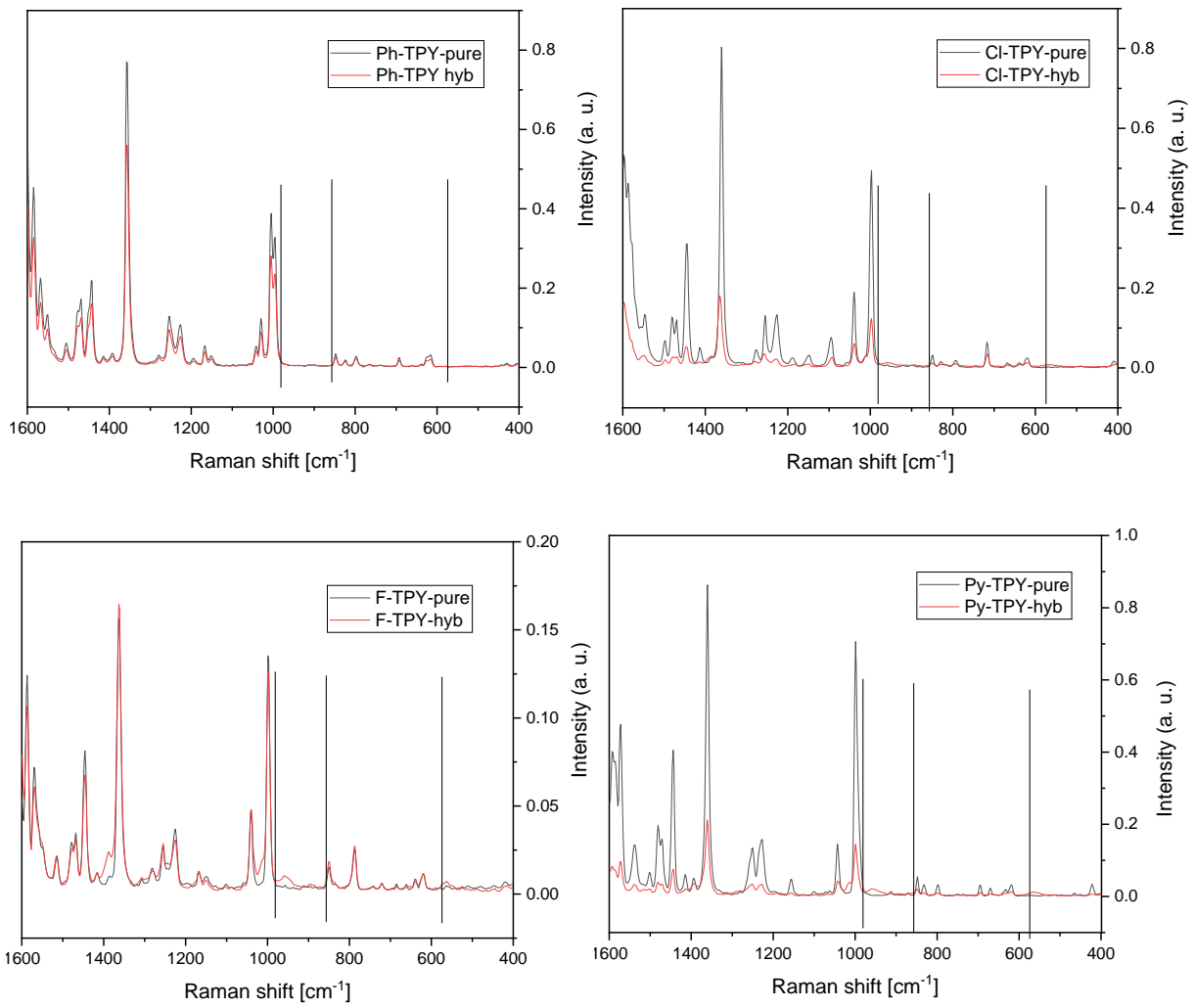
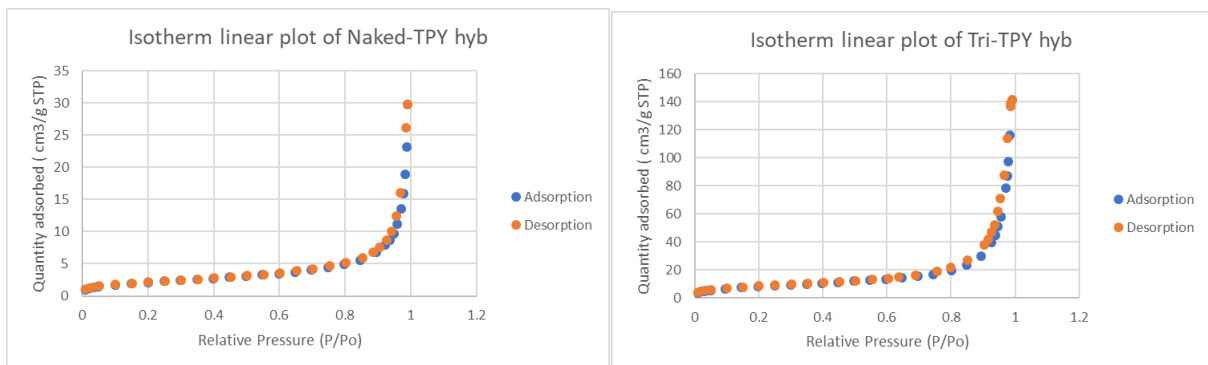


Figure 56: Solid Raman spectra of the long stirring time synthesized hybrids and their corresponding ligands. The three vertical lines represented the expected peaks of PW4 species.



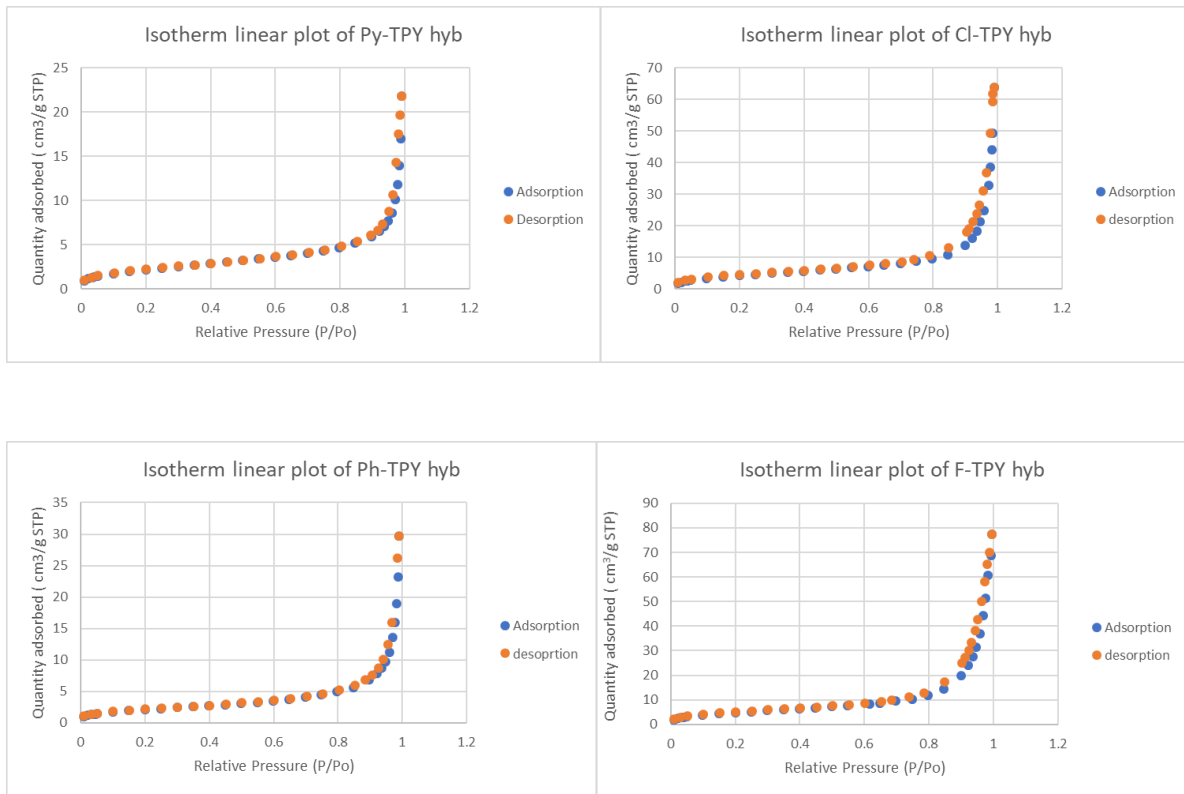


Figure 57: Isotherm of the nitrogen physisorption analyses

Annexe VII: Catalytic test

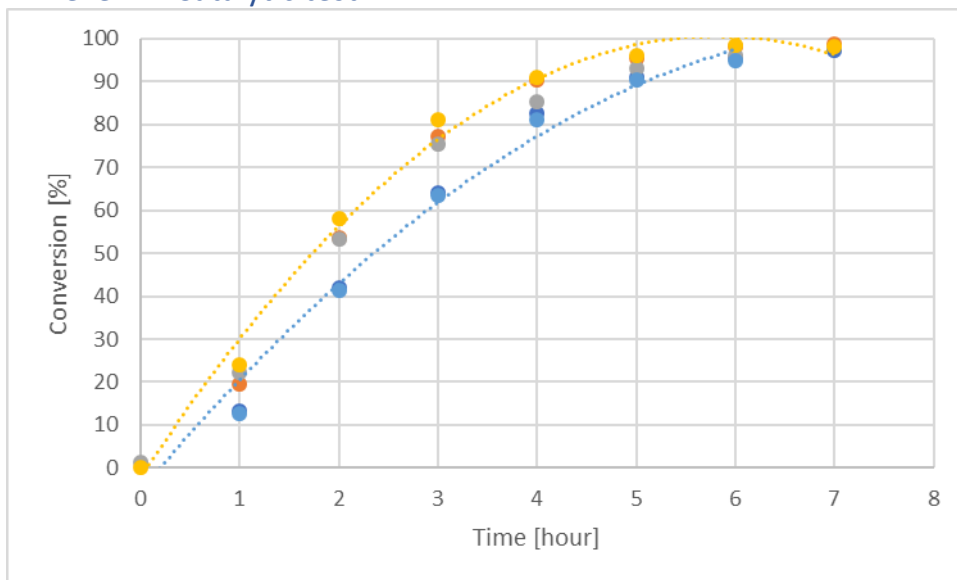


Figure 58: Statistical test to evaluate the random errors in between the measurements coming from a same batch.

In order to calculate the errors coming from the measurements and manipulation for one catalytic test. Three catalytic tests with a same catalyst were performed. To perform the calculations, the values that are represented in the next table were used. The average of the 3 measurements was calculated every time, same for the standard deviation. Consequently, an interval of confidence containing the right value with 95% of certainty. This same interval

was then transpose for every other measurement with the other catalysts. Indeed, one can consider that the error will be the same in good approximation.

Table 9 summarizing the values used to calculate the interval of confidence with alpha equal to 0.05.

Time [hour]		0	1	2	3	4	5	6	7
Conversion [%]	Test 1	- 0.0258 3	0.133 9	0.419 2	0.640 3	0.826 0	0.909 5	0.954 3	0.973 8
	Test 2	- 0.0087 8	0.194 5	0.537 3	0.771 4	0.904 0	0.953 8	0.982 1	0.987 1
	Test 3	0.143	0.221 7	0.533 8	0.753 2	0.852 8	0.931 4	0.961 6	-
Average		0.0361	0.183 3	0.496 7	0.721 6	0.860 9	0.931 5	0.966	0.980 4
Standard deviation		0.0929	0.044 9	0.067 1	0.071 0	0.039 6	0.022 1	0.014 4	0.009 4
Half of the confidence interval		0.25	5.58	8.36	8.82	4.92	2.75	1.79	0.025

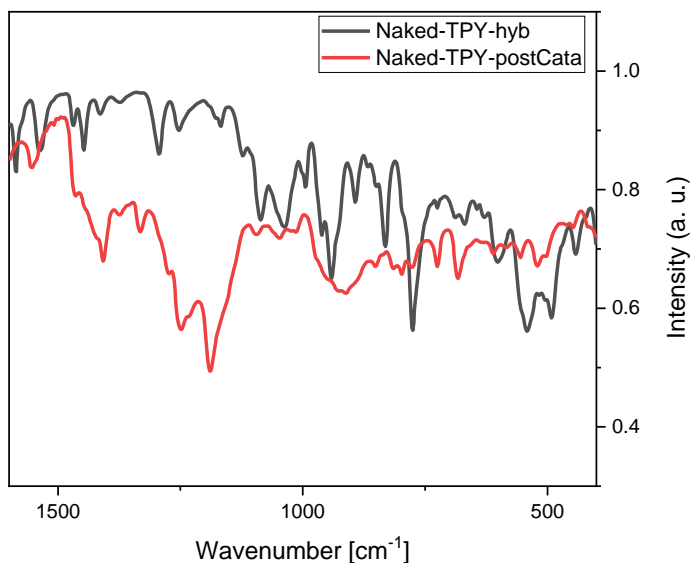


Figure 59 IR spectra of the fresh naked-TPY catalyst and the same catalyst after one catalytic test.