Electronic Supplementary Material (ESI) for ChemComm.

# Electronic Supporting Information (ESI)

## Mechanosynthesis of Imine, *β*-Ketoenamine, and Hydrogen-Bonded Imine-Linked Covalent Organic Frameworks using Liquid-Assisted Grinding

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## Section S-1: General Information

***General Remarks*:** 1,3,5-Triformylphloroglucinol (**Tp**) was prepared from Phloroglucinol using literature procedure (Chong *et al.*, *Org. Lett.* **2003**, *5*, 3823), Terephthalic dihydrazide was synthesized by diethyl terephthalate and hydrazine monohydrate by reported procedure (*Journal of Molecular Structure*, **2007,** 846, 55) and 2, 5-dihydroxyterephthalaldehyde (**Dha**) was synthesized by 1, 4-dimethoxybenzene (*Naturforsch.* **2007**, *62b*, 66), All other reagents and solvents were commercially available and used as received. Powder X-ray diffraction (PXRD) patterns were recorded on a Phillips PANalytical diffractometer for Cu $K_\alpha$ radiation ($\lambda$ = 1.5406 Å), with a scan speed of 1° $min^{-1}$ and a step size of 0.02° in 2$\theta$. Fourier transform infrared (FT-IR) spectra were taken on a Bruker Optics ALPHA-E spectrometer with a universal Zn-Se ATR (attenuated total reflection) accessory in the 600-4000 $cm^{-1}$ region or using a Diamond ATR (Golden Gate). Thermogravimetric analyses (TGA) were carried out on a TG50 analyzer (Mettler-Toledo) or a SDT Q600 TG-DTA analyzer under $N_2$ atmosphere at a heating rate of 10 ºC $min^{-1}$ within a temperature range of 30-900 °C. SEM images were obtained with a Zeiss DSM 950 scanning electron microscope and FEI, QUANTA 200 3D Scanning Electron Microscope with tungsten filament as electron source operated at 10 kV. The samples were sputtered with Au (nano-sized film) prior to imaging by a SCD 040 Balzers Union. HRTEM images were recorded using FEI Tecnai G2 F30 X-TWIN TEM at an accelerating voltage of 300 kV.The TEM Samples were prepared by dropcasting the sample from isopropanol on copper grids TEM Window (TED PELLA, INC. 200 mesh). $N_2$ adsorption experiments (up to 1 bar) were performed on a *Quantachrome Quadrasorb* automatic volumetric instrument. $^{13}C$ solid state NMR (CP/MAS-SSNMR) was taken in a Bruker 300 MHz NMR spectrometer and Ligand NMR data were taken in Bruker 200 MHz NMR spectrometer.

## Section S-2: Synthetic procedures

**2,4,6-tris-[(phenylhydrazino)methylene] cyclohexane-1,3,5-trione (Reference compound for TpTh):** 1,3,5-Triformylphloroglucinol (**Tp**) (63.0 mg, 0.3 mmol) and phenyl hydrazide (**Ph**) (97.2 mg, 0.9 mmol) was placed in a 5 mL stainless steel jar, with one 7 mm diameter stainless steel ball, 1-2 drop (~100 µL) of ethanol and 1 drop (~50 µL) of 3 M acetic acid. The mixture was milled at room temperature for 30 minutes in a Retsch MM400 mill operated at 25 Hz. The powder formed was collected and washed with ethanol, and dried under vacuum to give a dark red solid (yield 84%); **IR (powder, cm$^{-1}$):** 1594, 1565, 1436, 1273, 1170, 1109, 986, 812, 710.

**TpTh (LAG):** 1,3,5-triformylphloroglucinol (**Tp**) (63.0 mg, 0.3 mmol), Terephthalic dihydrazide (**Th**) (87.4 mg, 0.45 mmol) was placed in a 5 mL stainless steel jar, with one 7 mm diameter stainless steel ball, 1-2 drop (~100 μL) of mesitylene : dioxane (2:1) and 1 drop (~50 μL) of 3 M acetic acid. The mixture was milled at room temperature for 90 minutes in a Retsch MM400 mill operated at 25 Hz. A yellow colour powder formed was collected and washed with DMA, DMF and finally with acetone repeatedly for 3 days. Further purification was carried out by Soxhlet extraction in DMA for 48 h and then dried at 180 °C under vacuum for 24 hours to give a yellow colour powder in ~78 % (105 mg) isolated yield. **IR (powder, cm$^{-1}$):** 3223, 1660, 1610, 1580, 1542, 1444, 1337, 1260, 1180, 995, 855. **Anal. Calcld (%)**. For $(C_7O_2N_2H_4)_n$ : C, 57.75; H, 3.7; N, 18.9; found : C, 50.33; H, 3.87; N, 18.87.

**TpTh:** A pyrex tube ( o.d. × i.d. = 10 × 8 mm$^2$ and length 18 cm) is charged with 1,3,5-triformylphloroglucinol (**Tp**) (63.0 mg, 0.3 mmol), Terephthalic dihydrazide (87.4 mg, 0.45 mmol), 3.0 mL of mesitylene, 1.5 mL of dioxane, 0.5 mL of 3 M aqueous acetic acid. This mixture was sonicated for 10 minutes in order to get a homogenous dispersion. The tube was then flash frozen at 77 K (liquid $N_2$ bath) and degassed by three freeze-pump-thaw cycles. The tube was sealed off and then heated at 120 °C for 3 days. A yellow colour precipitate formed was collected by filtration and washed with DMA, DMF and finally with acetone repeatedly for 3 days. Further purification was carried out by Soxhlet extraction in DMA for 48 h and then dried at 180 °C under vacuum for 24 hours to give a yellow powder in ~70 % (94 mg) isolated yield. **IR (powder, cm$^{-1}$):** 3223, 1660, 1610, 1580, 1542, 1444, 1337, 1260, 1180, 995, 855. **Anal. Calcld (%)**. For $(C_7O_2N_2H_4)_n$ : C, 57.75; H, 3.7; N, 18.9; found : C, 49.69; H, 3.89; N, 19.66.

**DhaTph (LAG):** 2,5-Dihydroxyterephthalaldehyde (**Dha**) (13.3 mg, 0.08 mmol) and tetra(*p*-amino-phenyl)porphyrin (**Tph**) (27.0 mg, 0.04 mmol) was placed in a 5 mL stainless steel jar, with one 7 mm diameter stainless steel ball, in that 6 M acetic acid (1 drop) and dichlorobenzene, ethanol (1:1) as solvent combination (2 drop) was added. The mixture was milled at room temperature for 90 minutes in a Retsch MM400 mill operated at 25 Hz. After the reaction the COF powders washed with ethanol 5-7 times and dried under vacuum at 150 °C for 12 hours to give purple colored powder in ~75 % (28 mg) isolated yield based on

**Tph**. **IR (powder, cm$^{-1}$)**: 1613, 1590, 1491, 1399, 1338, 1313, 1213, 1149, 968, 888, 849, 797, 718.

**DhaTph:** The detailed synthetic procedure was described by S. Kandambeth *et al.* in *Angew. Chem., Int. Ed.* **2013,** 52**,** 13052**.**

**LZU-1 (LAG):** 1,3,5-triformylbenzene (**TFB**) (48.0 mg, 0.3 mmol), p-phenylenediamine (**Pa-1**) (48.0 mg, 0.45 mmol) was placed in a 5 mL stainless steel jar, with one 7 mm diameter stainless steel ball, 1-2 drop of mesitylene : dioxane (1:1) and 1 drop of 3M acetic acid. The mixture was milled at room temperature for 90 minutes in a Retsch MM400 mill operated at 25 Hz. The dark yellow powders collected was then washed with anhydrous DMF and THF, 5-6 times to remove some unreacted starting material and oligomeric impurities. Further purification was carried out by Soxhlet extraction in THF for 48 h and dried at 160 ºC under vacuum for 24 h to yield COF-LZU-1 (LAG) as a dark yellow powder (68.5 mg, ~86% yield). Reaction was repeated to ensure reproducibility. **IR (powder, cm$^{-1}$);** 3382, 2863, 1689, 1618, 1492, 1444, 1250, 1146, 968, 880, 832, 730, 685. **Anal. Calcld (%)**. For $(C_6H_4N)_n$ : C, 80.0; H, 4.44; N, 15.55; found : C, 72.31; H, 4.59; N, 13.79.

**COF-LZU-1:** The detailed synthetic procedure was described by Ding *et al.* in *J. Am. Chem. Soc.* **2011**, *133*, 19816.

## Section S-3: Structure Modeling and Atomic Coordinates of COFs.

Atomic positions and cell sizes of modeled COF layers were optimized using Self-Consistent Charge Density Functional Tight-Binding (SCC-DFTB) Method. Stacking of layers are affected by the Coulomb repulsion between the partial atomic charges in adjacent layers. Hence, we performed Mulliken population analysis for the charges. The adjacent layers were shifted with respect to each other in different directions in order to avoid Coulomb repulsion from charges alike. Several possibilities were considered, however, the best was taken from comparison of simulated PXRD pattern with the experimental. Interlayer separation was also determined from the comparison of PXRD patterns. The fractional coordinates of **TpTh (LAG)** is given in **Table S1**.

## Table S1. Fractional atomic coordinates for the unit cell of TpTh (LAG)

| **TpTh (LAG)** | | | |
|---|---|---|---|
| **Hexagonal-*P*6/*m***<br>**a = b = 29.97 Å, c = 3.4 Å**<br>**α = 90º, β = 90º and γ = 120º** | | | |
| C1 | 0.38352 | 0.67953 | 0 |
| C2 | 0.37095 | 0.71716 | 0 |
| C3 | 0.46151 | 0.44892 | 0 |
| C4 | 0.45120 | 0.48802 | 0 |
| C5 | 0.46878 | 0.57675 | 0 |
| C6 | 0.48730 | 0.53952 | 0 |
| C7 | 0.35904 | 0.58914 | 0 |
| N1 | 0.41908 | 0.56296 | 0 |
| N2 | 0.40520 | 0.59983 | 0 |
| O1 | 0.57173 | 00.30789 | 1.00668 |
| O2 | 0.49804 | 0.62101 | 0 |

## Section S-4: Powder X-Ray Diffraction Analysis (PXRD)

In order to elucidate the structure of these COFs and to calculate the unit cell parameters, possible 2D models were optimized using Density Functional Tight-Binding method. Several stacking possibilities were considered for reasons reported in the literature.[1] The experimental PXRD patterns are agreeable with the simulated patterns of some near-eclipsed stacking models (Figure S1). Hence we propose structures close to hexagonal space group (*P*6/*m*) for **TpTh (LAG)** by comparing the experimental and simulated PXRD patterns.

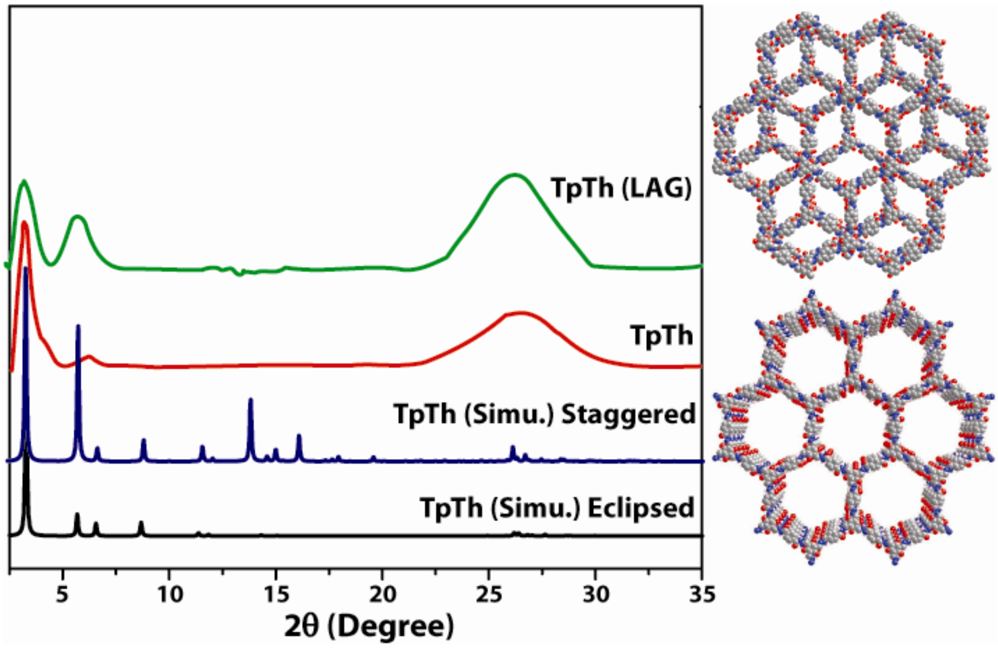

**Figure S1:** PXRD pattern of as-synthesized **TpTh (LAG)** (green), **TpTh** (red), compared with the staggered (blue) and eclipsed (black) stacking models.

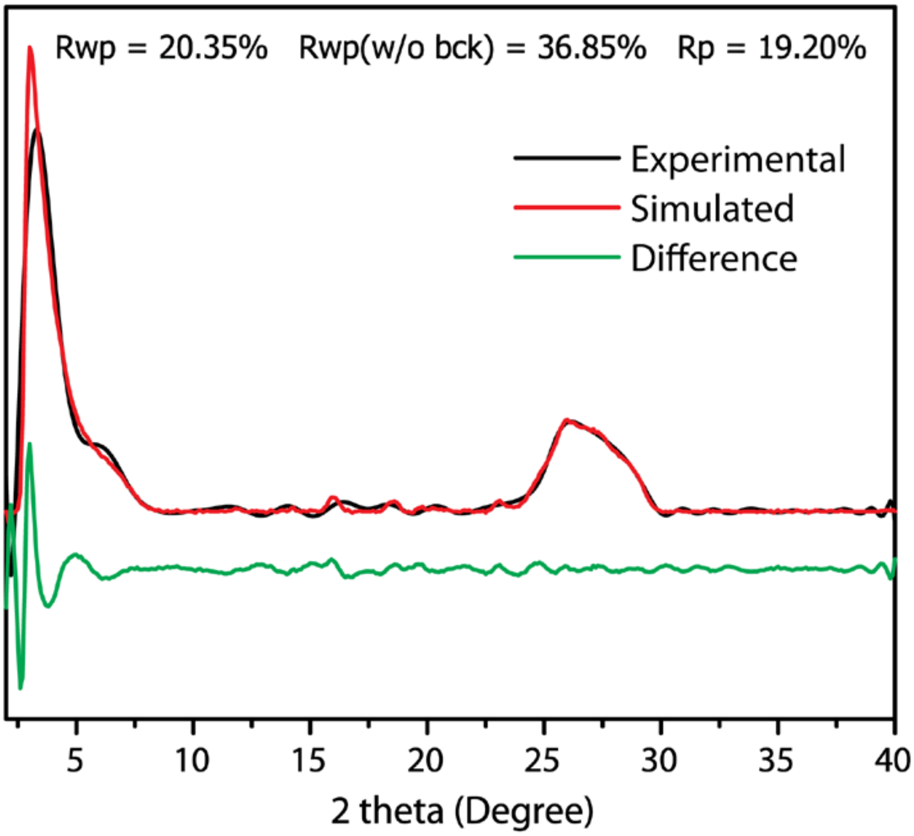

**Figure S1a:** Experimental (Red) compared with refined (Black) PXRD profiles of COF-**TpTh** with an eclipsed arrangement; difference plot is given in (Green).

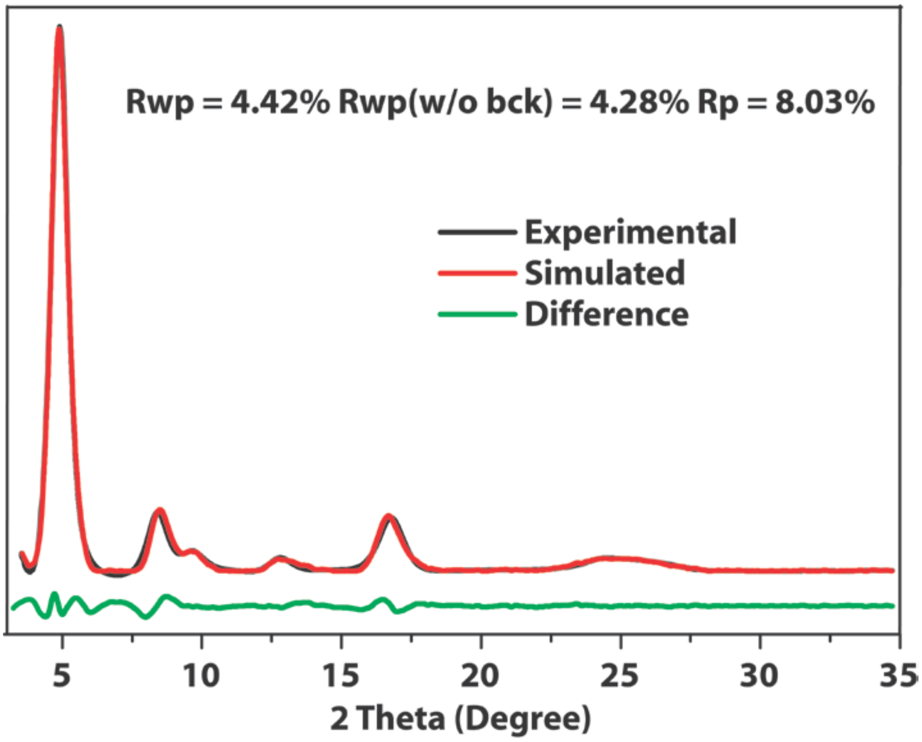

**Figure S1b:** Experimental (Black) compared with refined (Red) PXRD profiles of COF-**LZU-1** with an eclipsed arrangement; difference plot is given in (Green).

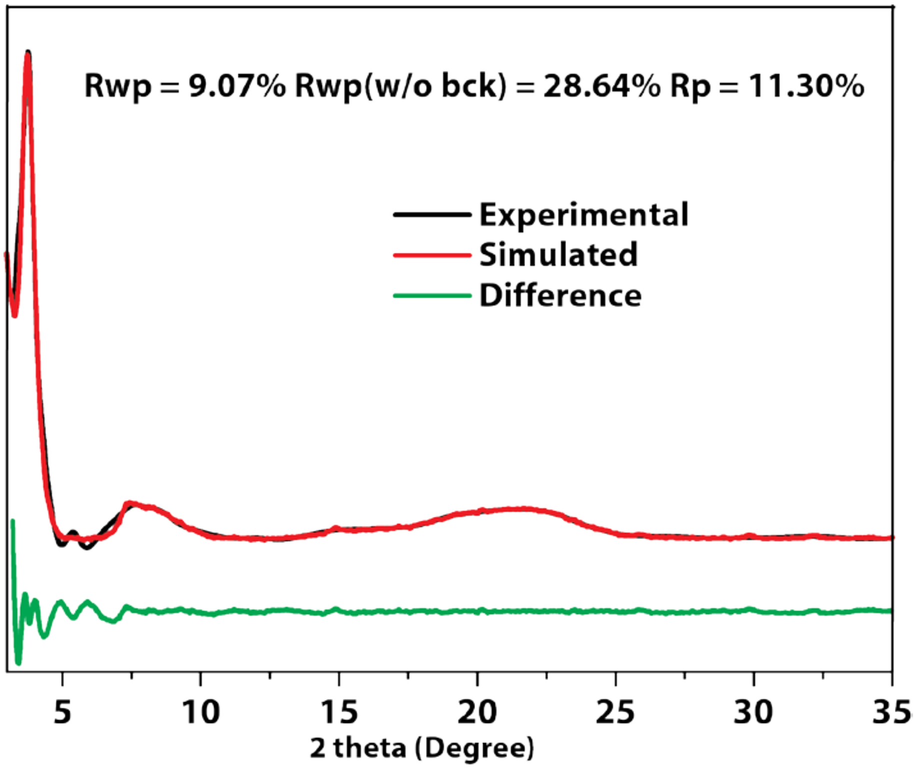

**Figure S1c:** Experimental (Black) compared with refined (Red) PXRD profiles of COF-**DhaTph (LAG)** with an eclipsed arrangement; difference plot is given in (Green).

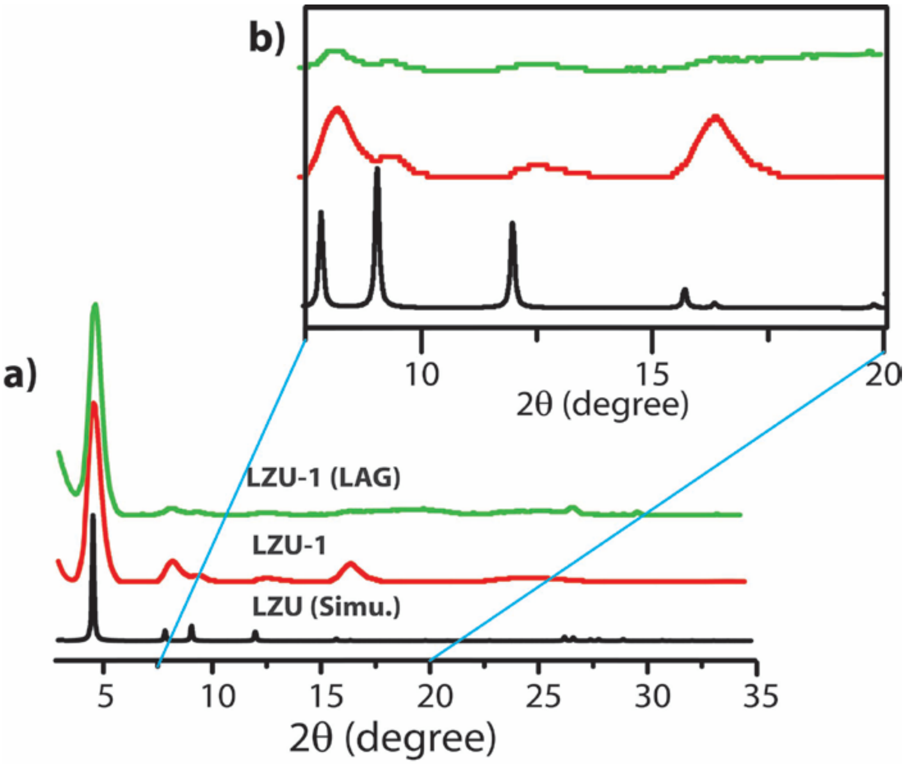

**Figure S1d: a)** PXRD pattern of as-synthesized **LZU-1 (LAG)** (green), **LZU-1** (red), compared with the staggered simulated one (black); **b)** Zoomed patterns from 7.5 to 20 2θ.

## Section S-5: FT-IR Spectra

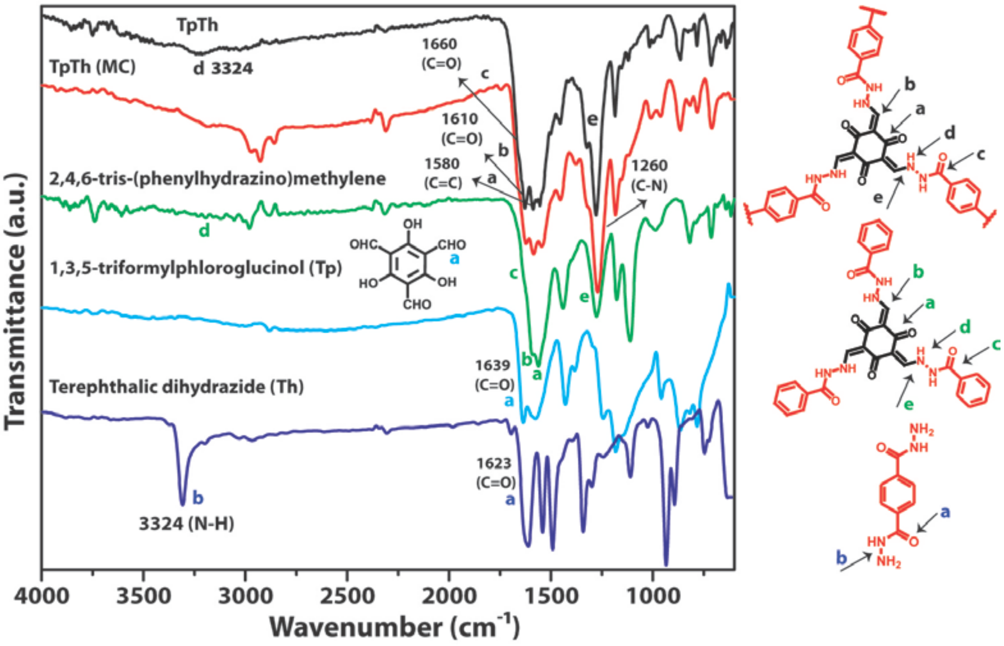

**Figure S2**: FT-IR spectra of **TpTh** (Black), **TpTh (LAG)** (red), 2,4,6-tris-[(phenylhydrazino)methylene]cyclohexane-1,3,5-trione (**TpPh, reference compound**) (green), 1,3,5-triformylphloroglucinol (**Tp**) (cyano) and Terephthalic dihydrazide (**Th**) (blue).

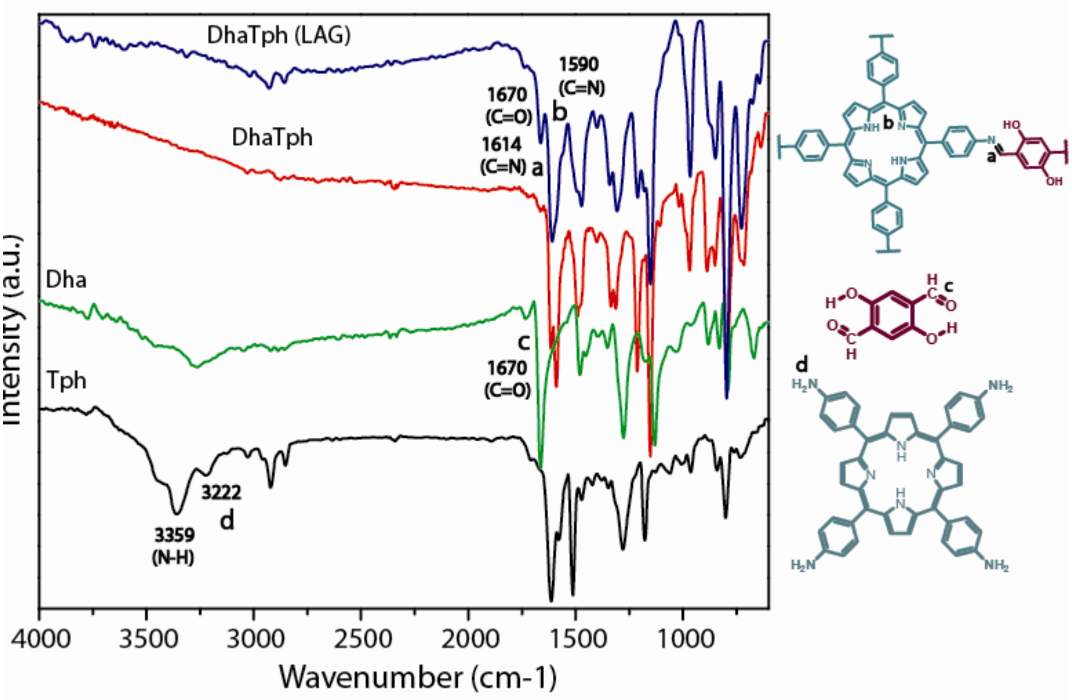

**Figure S3**: FT-IR spectra of **DhaTph (LAG)** (blue), **DhaTph** (red), 2, 5-dihydroxyterephthalaldehyde (**Dha**) (green), and 5, 10, 15, 20-Tetrakis-(4-aminophenyl)-21H, 23H-porphine (**Tph**) (black).

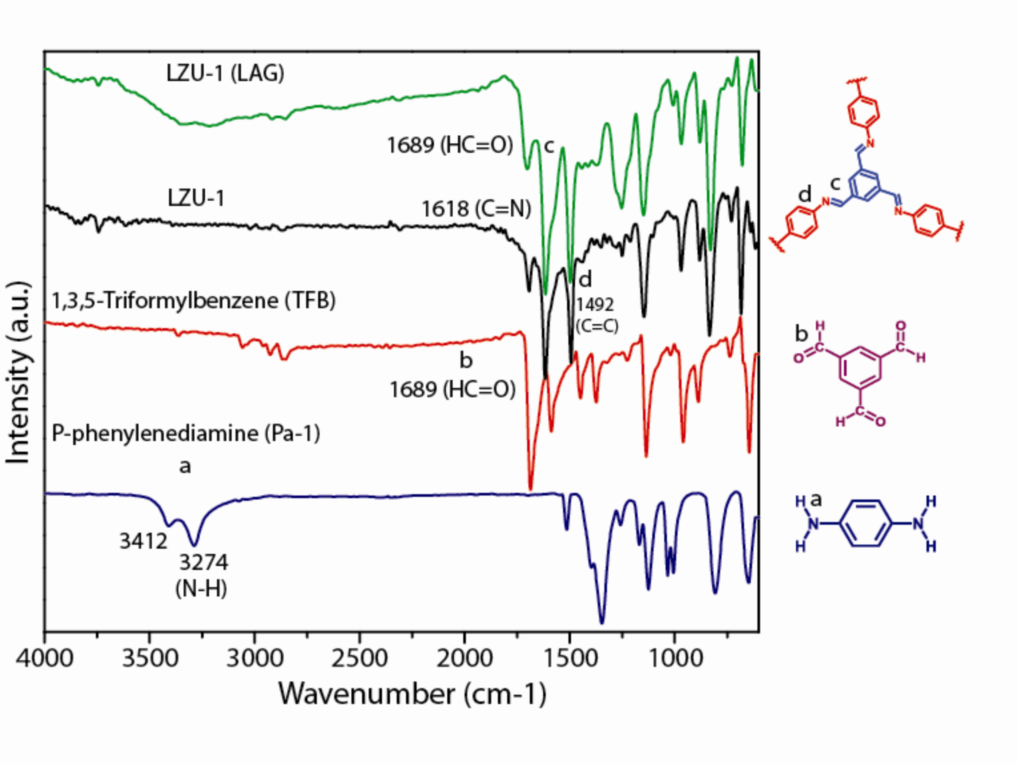

**Figure S4**: FT-IR spectra of **LZU-1 (LAG)** (green), **LZU-1** (black), 1,3,5-triformylbenzene (**TFB**) (red) and P-phenylenediamine (**Pa-1**) (blue).

## Section S-6: $^{13}$C CP/MAS NMR Spectra

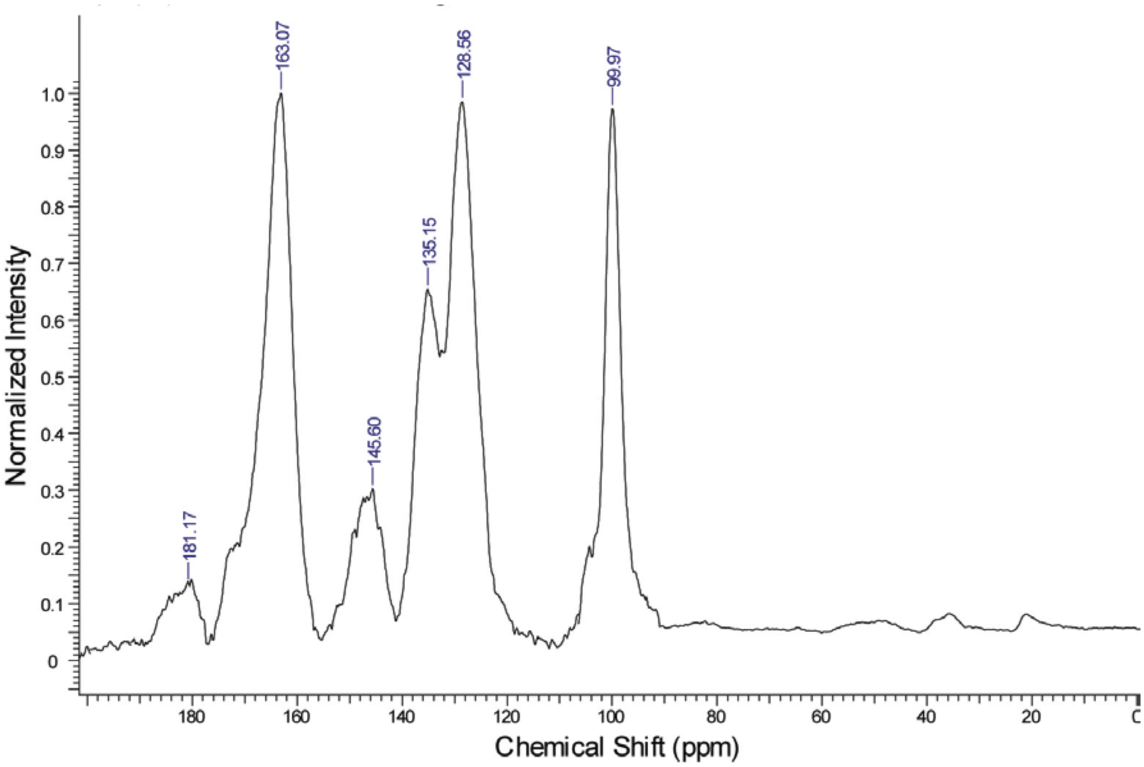

**Figure S5:** $^{13}$C CP-MAS spectrum of **TpTh (LAG)**.

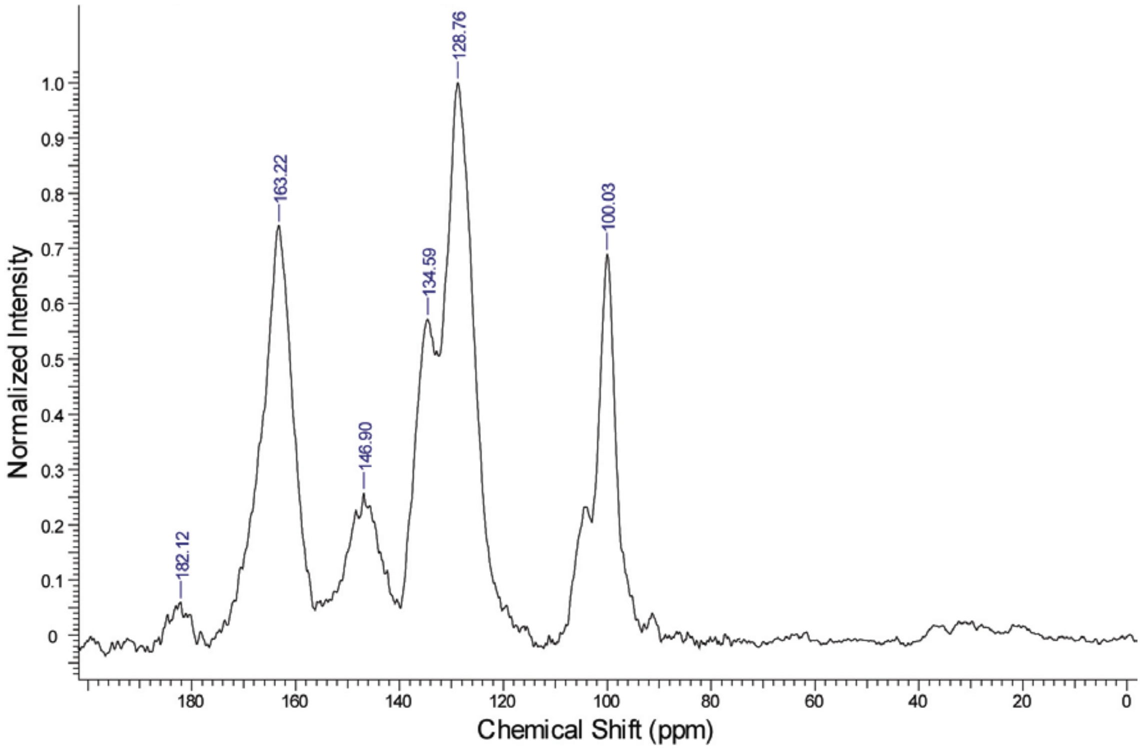

**Figure S6:** $^{13}$C CP-MAS spectrum of **TpTh**.

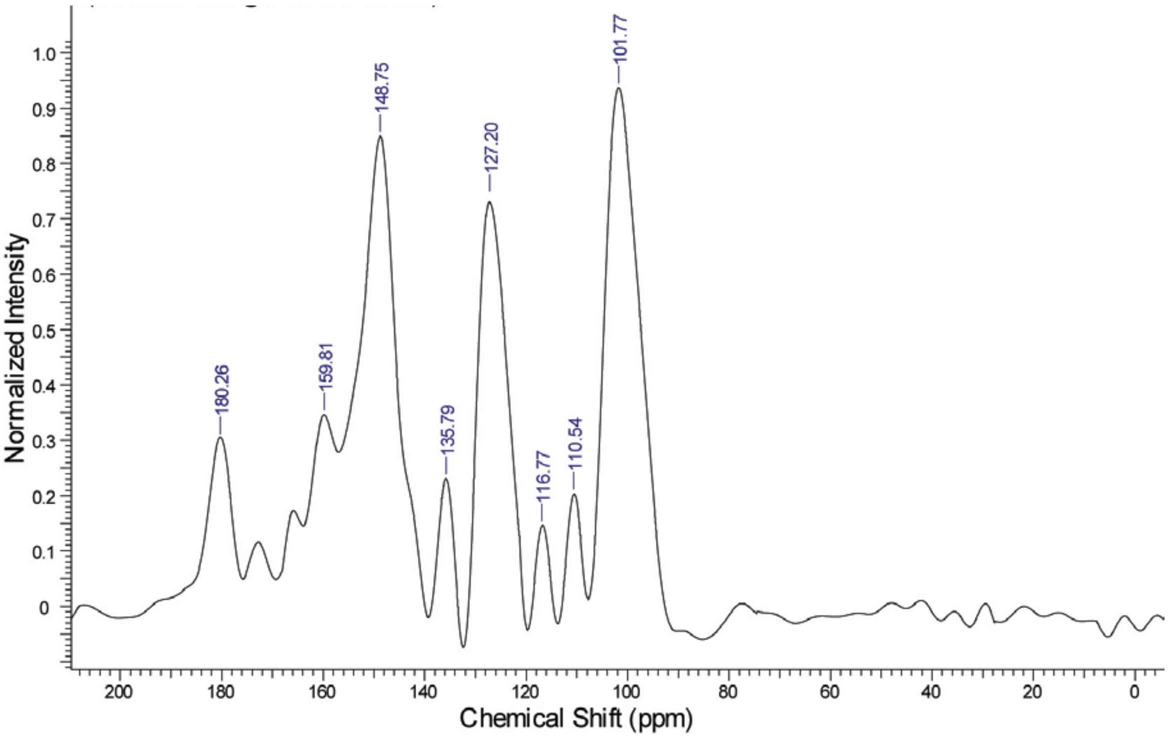

**Figure S7:** $^{13}$C CP-MAS spectrum of 2,4,6-tris-[(phenylhydrazino)methylene]cyclohexane-1,3,5-trione (Reference compound for **TpTh**).

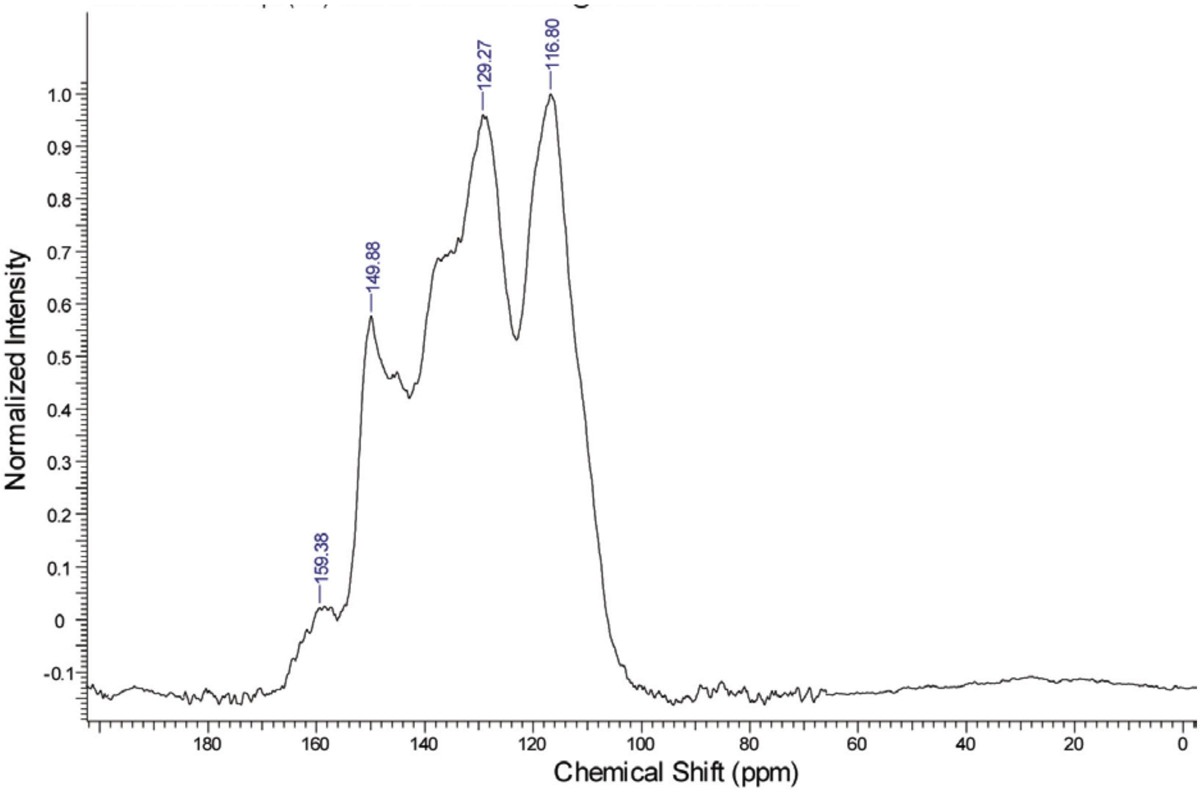

**Figure S8:** $^{13}$C CP-MAS spectrum of **DhaTph (LAG)**.

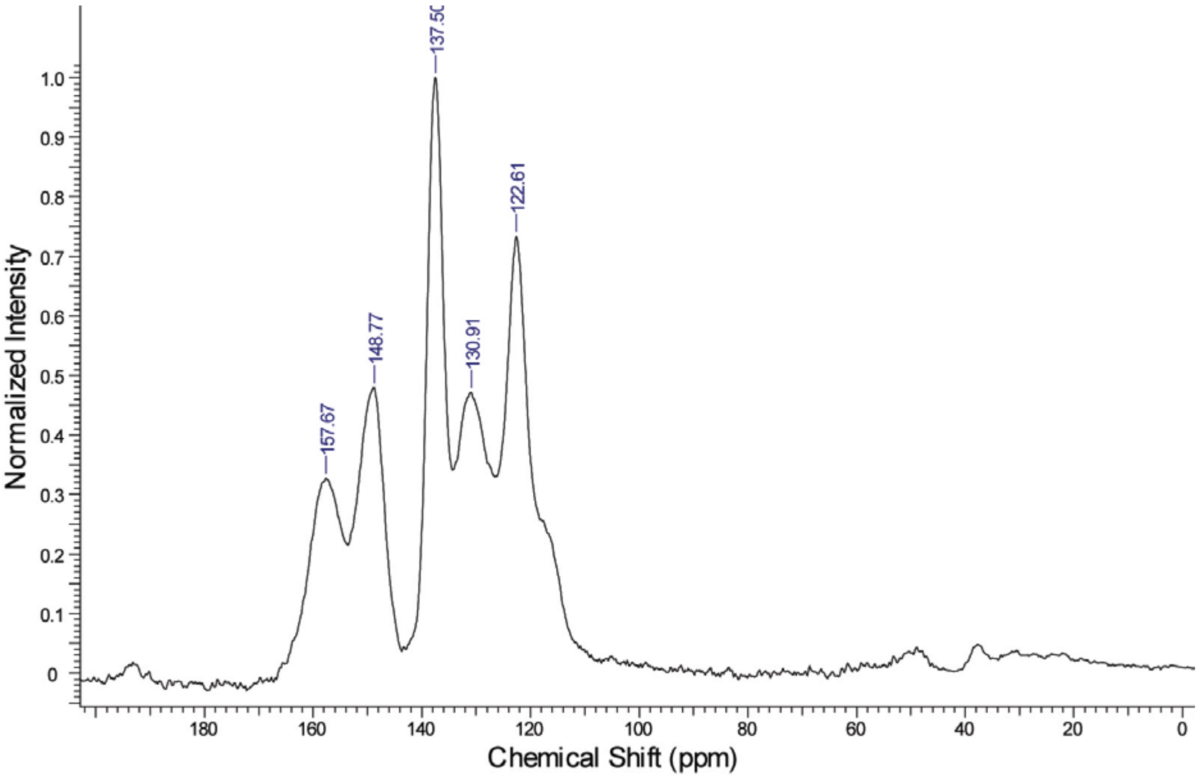

**Figure S9:** $^{13}$C CP-MAS spectrum of **LZU-1 (LAG)**.

## Section S-7: $N_2$ Adsorption Studies of TpTh, LZU-1 and DhaTph

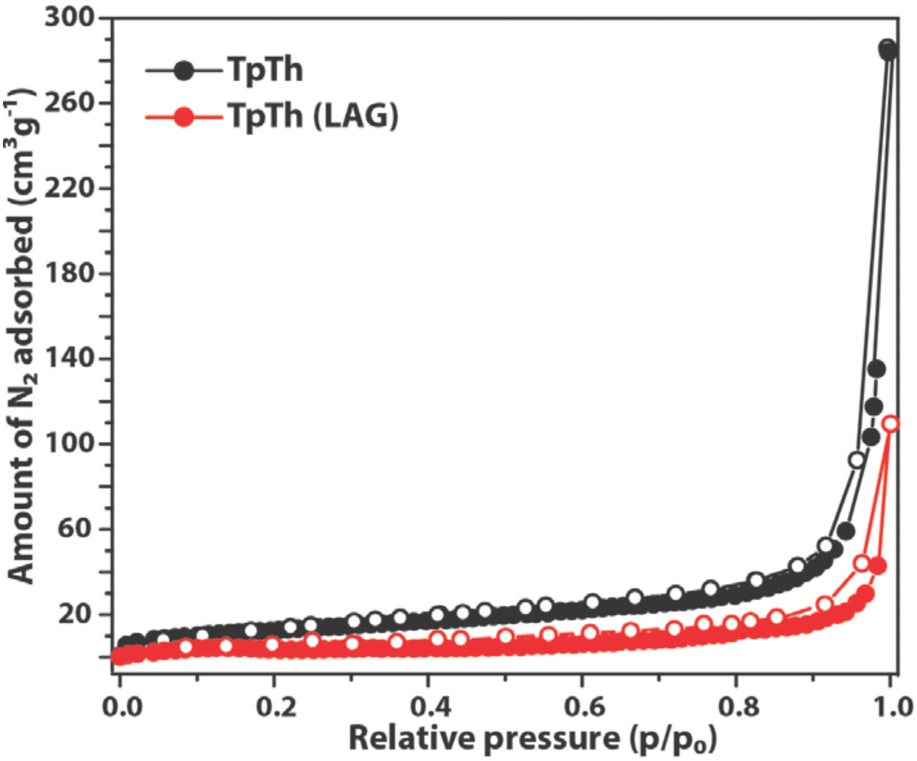

**Figure S10**: $N_2$ adsorption isotherm of **TpTh** and **TpTh (LAG).**

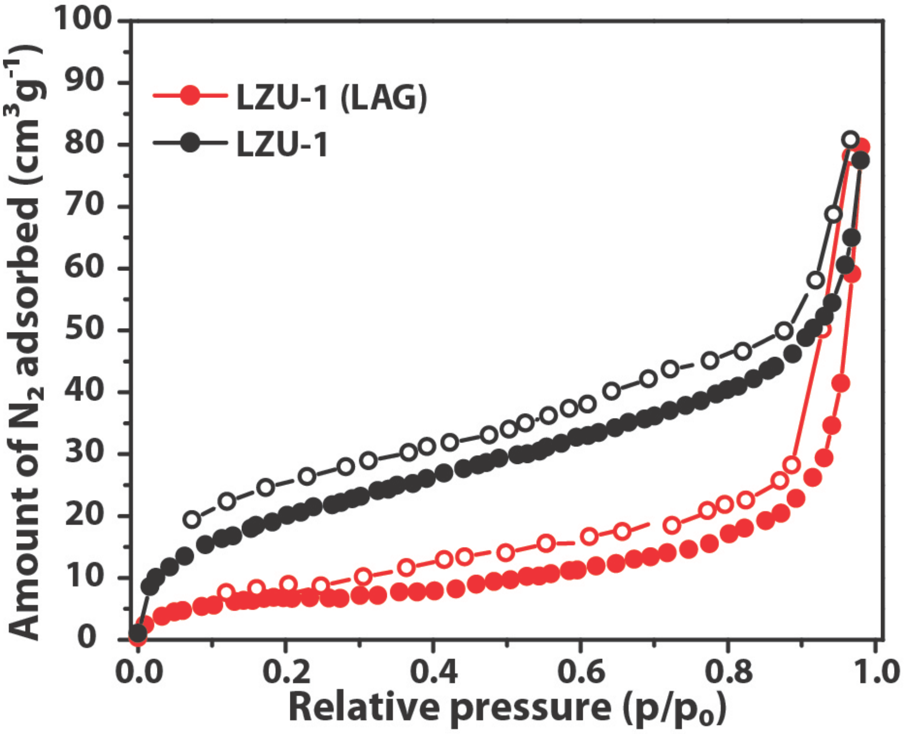

**Figure S11**: $N_2$ adsorption isotherm of **LZU-1** and **LZU-1 (LAG)**.

**Note:** We have synthesized COF LZU-1 solvothermally by using the literature procedure reported by Ding *et al*., in *J. Am. Chem. Soc.* 2011, **133**, 19816. However the $N_2$ adsorption as well as the surface area value for LZU-1 reported by Ding *et al*. (*J. Am. Chem. Soc.* 2011, **133**, 19816) is much higher than what we could obtain during our experiment.

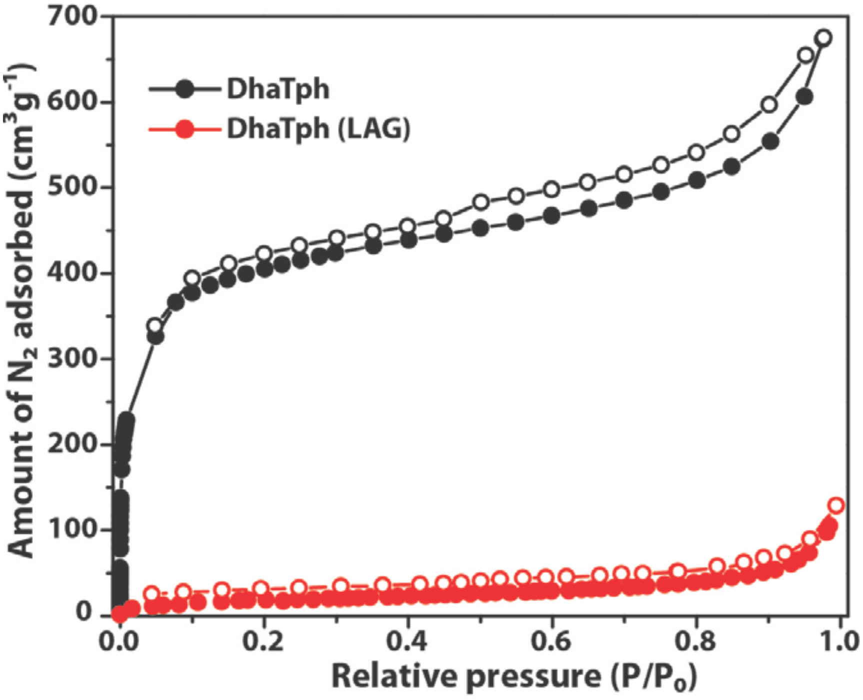

**Figure S12**: $N_2$ adsorption isotherm of **DhaTph** and **DhaTph (LAG).**

## Section S-8: Thermogravimetric Analysis (TGA)

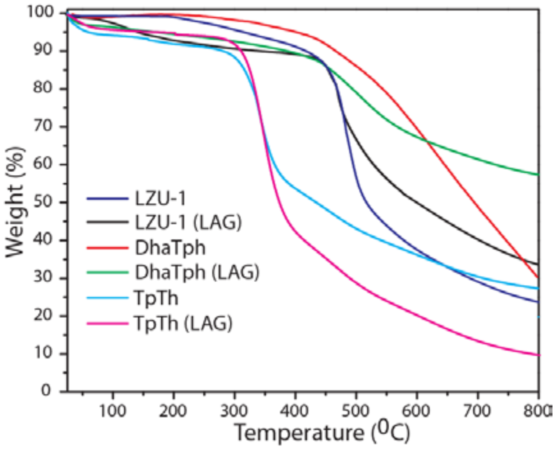

**Figure S13:** TGA data of all **COFs (ST and LAG)** under $N_2$ atmosphere.

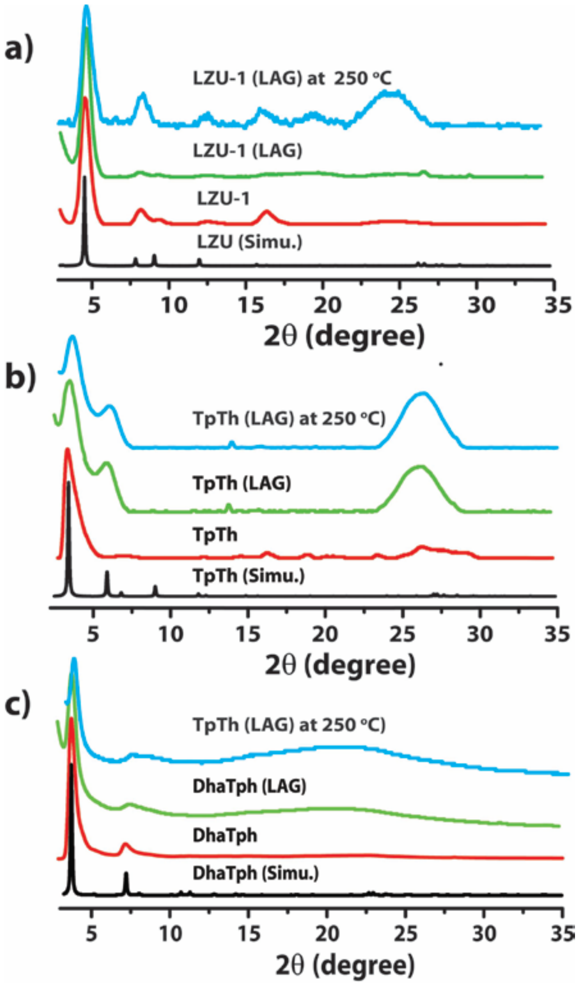

**Figure S13a: a)**, **b)** and **c)** PXRD of **LZU-1 (LAG)**, **TpTh (LAG)** and **DhaTph (LAG)** (cyan) taken after heating at 250 ºC for 3 h in a furnace under $N_2$ atmosphere.
This indicates that these COFs (LAG) are thermally stable at high temerature (>250 ºC) as indicated by TGA analysis.

## Section S-9: <u>Scanning Electron Micrographs (SEM)</u>

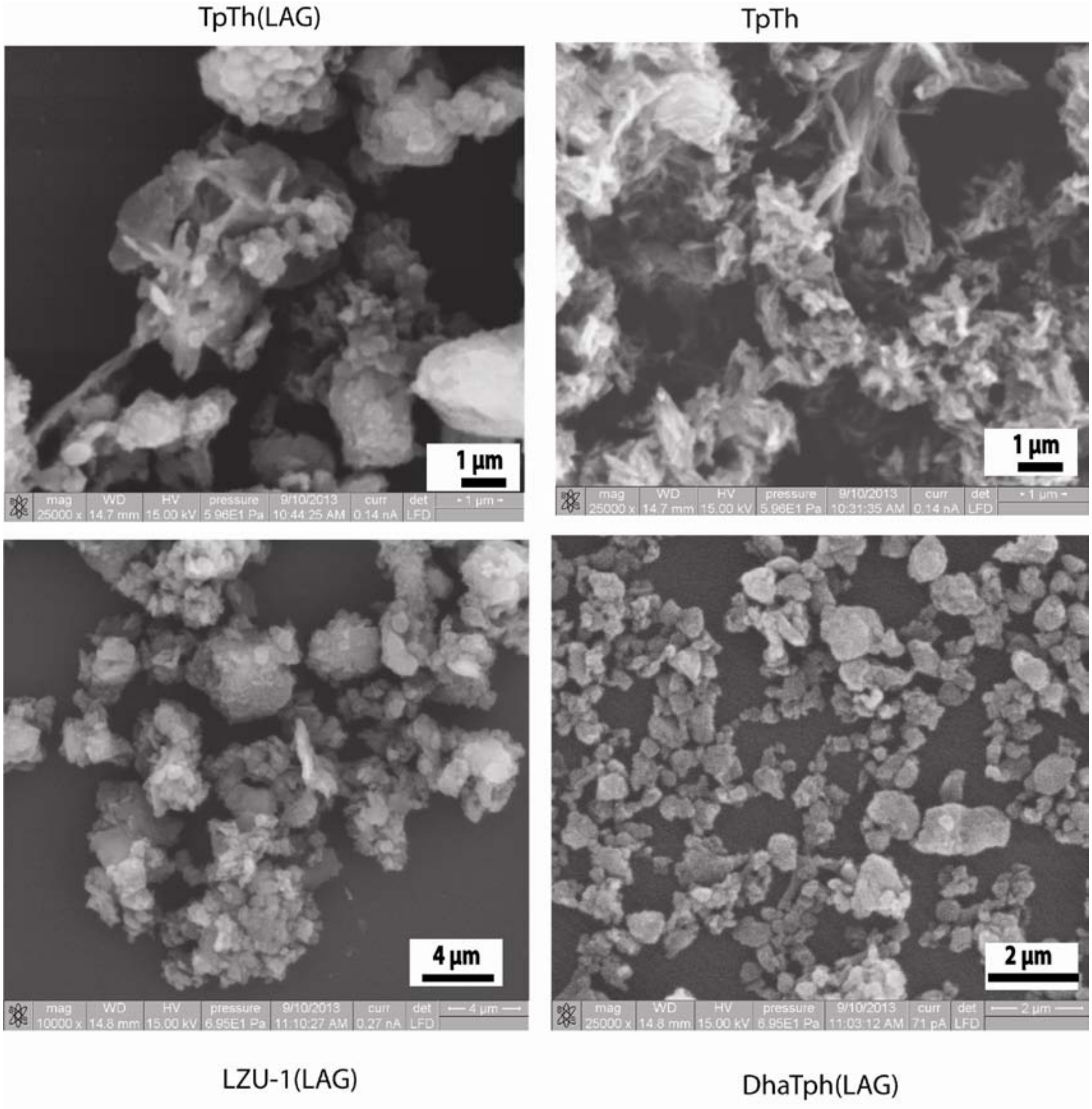

**Figure S14:** SEM images of **TpTh (LAG), TpTh  b) LZU-1 (LAG), c) DhaTph (LAG).**

## Section S-10: High Resolution Transmission Electron Micrographs (HRTEM)

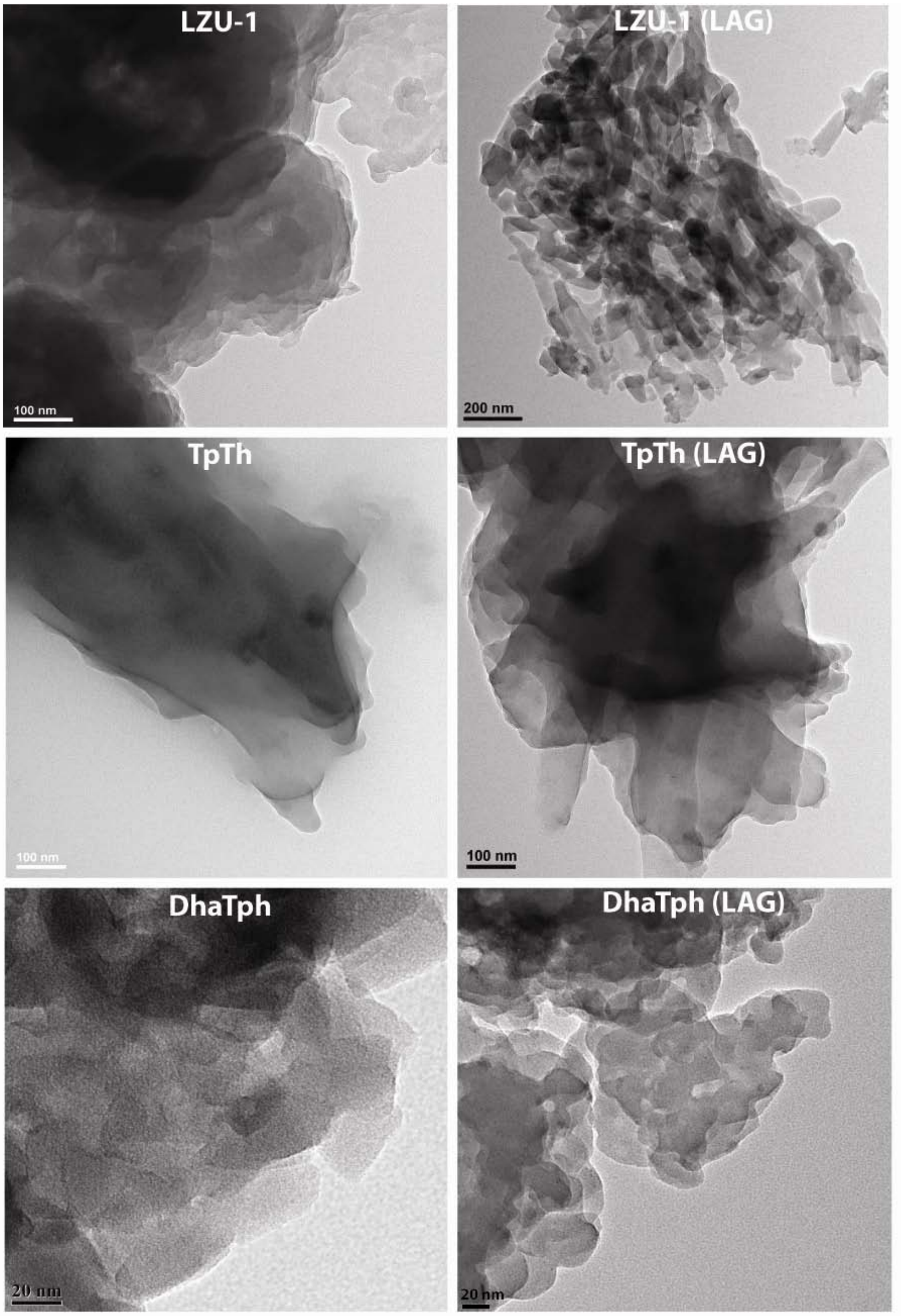

**Figure S15:** HR-TEM images of **LZU-1, LZU-1 (LAG), TpTh, TpTh (LAG), DhaTph,** and **DhaTph (LAG)** respectively**.**

## Section S-11: Stability test for TpTh (LAG)

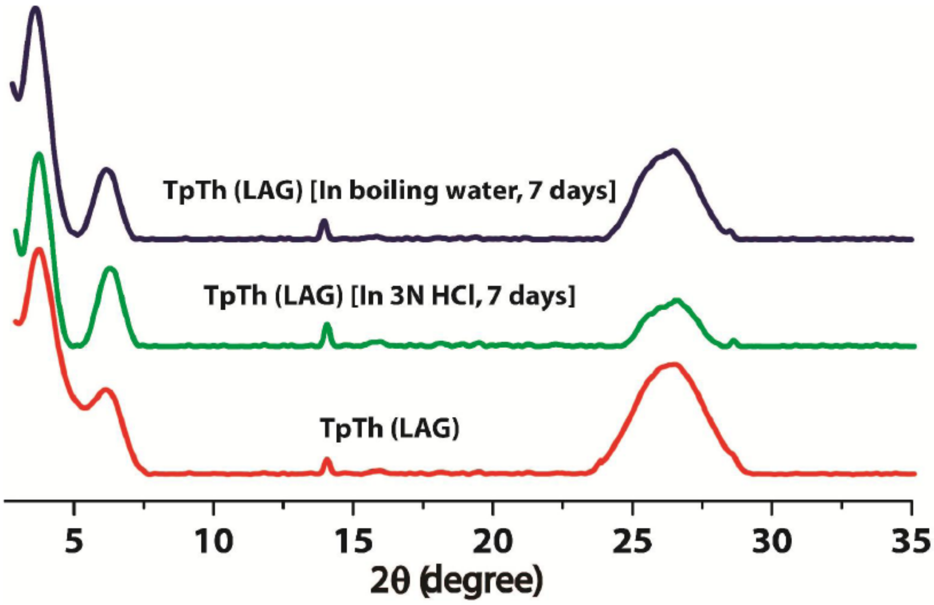

**Figure S16:** PXRD of **TpTh (LAG)** after treatment with water and acid for 7 days.

## Section S-12: References

**1)** Lukose, B.; Kuc, A.; Heine, T. *Chem. Eur. J.* 2011, ***17***, 2388.