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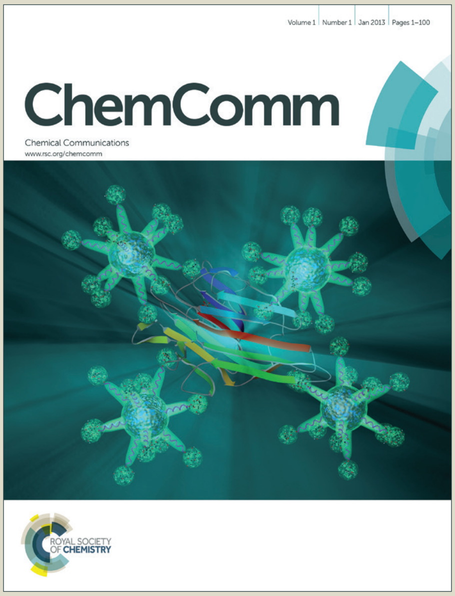

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Mechanosynthesis of Imine, β-Ketoenamine, and Hydrogen-Bonded Imine-Linked Covalent Organic Frameworks using Liquid-Assisted Grinding

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A variety of aromatic amine/hydrazide and aldehydes has been utilized for the construction of crystalline COFs at a faster rate and high yield, irrespective of their reactivity and solubility using Liquid-Assisted Grinding (LAG) method.

Mechanochemical synthesis of porous solids[1] has gained prime importance as an alternate synthetic route compared to conventional solution-based synthesis, as the process is quick, and environment friendly. Interestingly, a number of different porous materials such as metal-organic frameworks,[2] molecular cages,[3a] supramolecular assemblies, inclusion compounds etc.[4] have been synthesized using mechanochemical synthesis. However, the mechano-chemical[5] synthetic technique is still in its infancy for the synthesis of covalently bonded porous materials, especially covalent organic frameworks (COFs).[3b] COFs have already emerged as promising materials for the storage and separation of gases, as well as catalysis and charge carrier transport.[6] However, the methodologies involved for the COF synthesis need harsh experimental conditions. Moreover, traditional COF synthesis need long reaction time for crystallization.[7] Although researchers have attempted to rectify these limitations using microwave assisted and sonochemical synthesis of COFs,[8] but the challenges in COF synthesis remain active and the development of a viable synthetic process is still highly desirable. Though, mechanochemistry might become a possible alternative, until recently there has not been any attempt to synthesize COFs mechanochemically. Only recently, we successfully demonstrated the formation of few COFs *via* simple neat mechanical grinding with moderate crystallinity and porosity compared to the COFs synthesized *via* the conventional solvothermal method.[3b]

Hence, to explore the full potential of this method with proper optimized mechanochemical conditions, herein, we for the first time, demonstrate the synthesis of 2D-COFs with predetermined topological design using proper symmetry combinations (C_2+C_3 and C_2+C_4) of the building blocks and employing Liquid-Assisted Grinding **(LAG)** (Figure 1).[3b,9,10] Interestingly, **LAG** or ion- and liquid-assisted grinding **(ILAG)** methods have been considered as the most promising methodology to construct crystalline porous materials in a rapid and quantitative fashion over neat mechanochemical synthesis.[2b,5] In **LAG**, the addition of catalytic amounts of liquid enhances the rate of the reaction by bringing more reactant molecules in close proximity, which could further lead to the improved crystallinity in porous materials.[1b] Solvothermal synthesis of a COF with an unsubstituted hydrazone linkage with decent crystallinity was extremely challenging, even when solvothermal methods were employed.[11a] We have successfully synthesized a new crystalline hydrazone-linked COF [**TpTh (LAG)**] by applying the **LAG** approach (Figure 1A). We have also decided to extend this **LAG** strategy to synthesize COFs containing the porphyrin building unit [**DhaTph (LAG)**] as these COFs are known to show high charge carrier mobility and photoconductivity.[11b,c] Furthermore, we demonstrated that the COF with chemically labile Schiff base [–C=N] centers such as [**LZU-1**][12] can also be readily synthesized with decent crystallinity using the same **LAG** approach. It is pertinent to mention here that, till now, there appears to be no report of COF materials synthesized using **LAG** approach.

Powder X-ray diffraction (PXRD) patterns of **TpTh (LAG)** and **DhaTph (LAG)** showed the most intense peaks at ~3.8° and ~3.4°, which correspond to 100 plane reflections, along with minor peaks at ~6.2° and ~24-28° 2θ and ~6.9° and ~18-23° 2θ, which correspond to 200 and 001 facets respectively. The peak broadening was observed at higher 2θ (001 planes) for these COFs, which arises due to the defects in the π-π stacking between the successive COF layers. The π-π stacking distances between the COF layers were calculated to be ~3.4 Å and ~4.0 Å for **TpTh (LAG)** and **DhaTph (LAG)** respectively (Figure 2b and 2c). PXRD patterns of **LZU-1 (LAG)** showed a peak at ~4.6° (2θ), which corresponds to 100 plane reflections along with minor peaks at ~8° and ~26-28° (2θ) which corresponds to 200 and 001 facets. The π-π stacking distance was calculated as ~3.7 Å for **LZU-1 (LAG)** (Figure 2a).[13] The experimental PXRD pattern matches well with the simulated pattern of the eclipsed stacking model of **TpTh (LAG)** (Figure 2b, Section S-3 and S-4, ESI). Hence, we propose a structure close to the *P*6/*m* space group for **TpTh (LAG)**.[11a] In order to find out the unit cell parameters, Pawley refinements were done

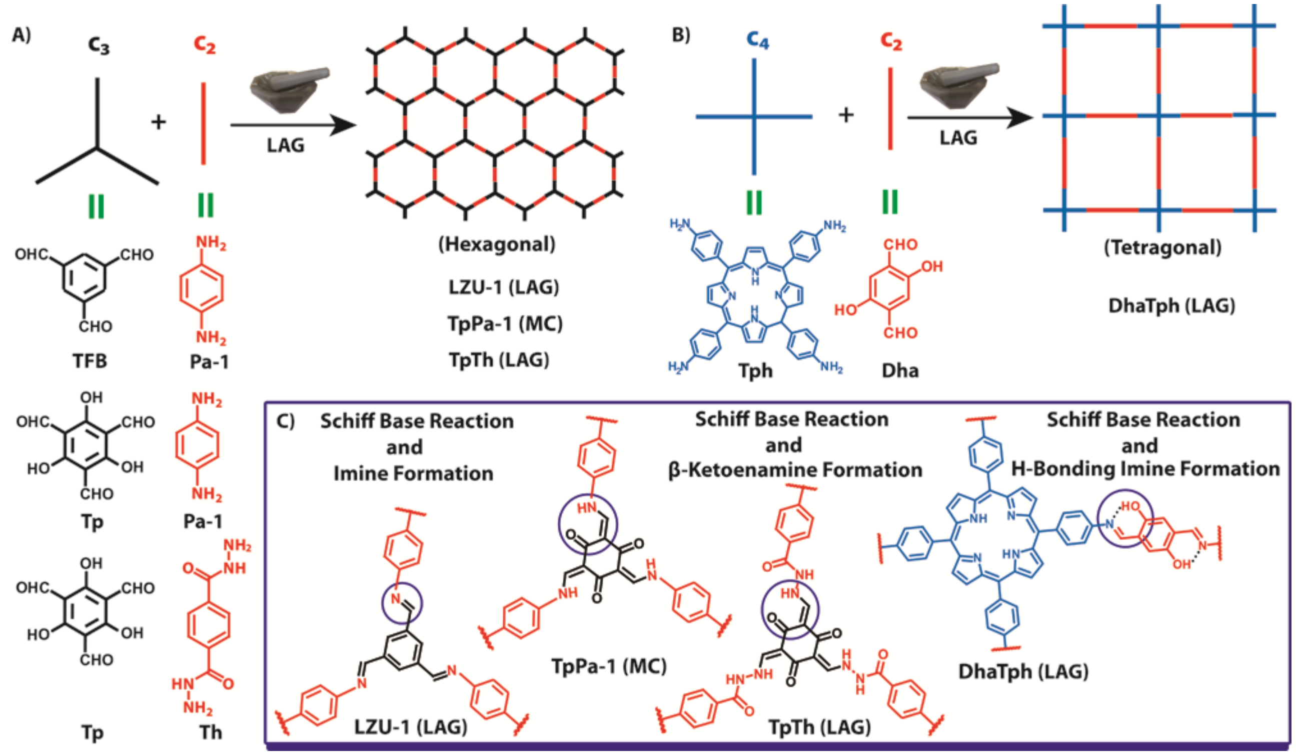

Figure 1. Schematic representation of the synthesis of A) **LZU-1 (LAG)**, **TpPa-1 (MC)**[3b] and **TpTh (LAG)**; B) **DhaTph (LAG)** through simple Schiff base reaction performed *via* liquid-assisted grinding **(LAG)** using a Ball Mill; C) Highlights the bonding moiety in these COFs **(LAG).**

for the COF **TpTh (LAG)** (Section S-3, ESI). The unit cell values of **TpTh (LAG)** were calculated to be $a = b = 29.6$ Å and $c = 3.4$ Å. The proposed structure for **DhaTph (LAG)** was close to the $P4/m$ space group, with unit cell values calculated to be $a = b = 25.6$ Å and $c = 4.0$ Å. **LZU-1 (LAG)** also crystallizes in the same eclipsed layered structures like the reported **LZU-1**[12].

The FT-IR spectra obtained for **TpTh (LAG)** clearly indicate a broad band for the characteristic N—H stretching band at (3100-3300 cm^{-1}). Simultaneously, the carbonyl (C═O) peak position at 1610 cm^{-1}, with reference to 1639 cm^{-1} for (**Tp**), becomes broad and merges with the C═C stretching frequency (1580 cm^{-1}), which happens as a result of strong hydrogen bonding in the keto form of the 2D framework (Figure 3a). The carbonyl stretching mode of the amide unit is observed as a merged band at 1660 cm^{-1}, confirming its presence in the framework. The unobserved —C═N stretching peaks and hydroxyl (O—H), as well as the new peak at 1580 cm^{-1} (C═C) observed, while forming the 2D extended framework, confirms the existence of the keto form. This aspect is further supported by the FT-IR spectra of the reference compound made for comparison (Section S-5; Figure S2, ESI). The appearance of two peaks at 1465 cm^{-1} [C═C(Ar)] and 1260 cm^{-1} (—C—N), were due to the aromatic —C═C and newly formed —C—N bond in the keto form of the **TpTh (LAG)** framework. The FT-IR spectrum of **DhaTph (LAG)** shows characteristic —C═N stretching bands at 1613 cm^{-1}, which appear almost at the same position as in COF-366[11a] (1620 cm^{-1}) (Figure S3, ESI). Hence, we can conclude that **DhaTph (LAG)** exists in the enol-imine form (Figure 1C). Similarly, the FT-IR spectrum of **LZU-1 (LAG)** shows a strong —C═N stretch at 1618 cm^{-1} indicating the formation of imine bonds. A broad band at (3020-3400 cm^{-1}) is due to the terminal aldehyde and amines present at the edges of **LZU-1 (LAG)** COF crystallites. All three COFs synthesized mechanochemically showed similar FT-IR spectra like their solvothermally synthesized counterparts (Figure 3a and Section S5, ESI). ^{13}C CP-MAS solid state NMR of **TpTh (LAG)** showed a resonance signal at δ ~182 which correspond to the carbonyl carbon of the keto form (Figure 3b). This is further supported by the ^{13}C NMR spectrum of the reference compound {2,4,6-tris [(phenylhydrazino)methylene]cyclohexane-1,3,5-trione} synthesized *via* same mechanochemical grinding approach for comparison (Section S-6; Figure S7, ESI). The peak at δ ~163 is due to the amide carbonyl (—$\underline{\text{C}}$O—NH—), in the framework. The match of ^{13}C solid state NMR pattern showcased the same local structure of COFs synthesized *via* both mechanochemical and solvothermal methods (Figure 3b). ^{13}C CP-MAS NMR of **DhaTph (LAG)** confirms the formation of the imine bond by showing the characteristic signal at δ 160, which corresponds to the chemical shift of the —$\underline{\text{C}}$═N carbon (Figure S8, ESI). Similarly, ^{13}C NMR of **LZU-1 (LAG)** showed a peak at δ ~157 which corresponds to the carbon atom of the —$\underline{\text{C}}$═N bond. The signals at δ ~122, 130, 137, and 148 can be assigned to the carbon atoms of the phenyl ring. Both **TpTh** and **TpTh (LAG)** exhibit identical thermal stability (Figure S13, ESI) up to ~300 °C with a gradual weight loss of ~70% (for **TpTh**) and ~90% [for **TpTh (LAG)**] respectively at 800 °C. **DhaTph** and **DhaTph (LAG)** were also observed to be stable up to ~300 °C. Similarly **LZU-1 (LAG)** showed a thermal stability up to 450 °C like **LZU-1**[12] with weight loss of ~62% and ~73% respectively at the end of 800 °C. These COFs **(LAG)** showed reversible type II **(TpTh** and **LZU-1)** and type IV **(DhaTph)** N_2 adsorption isotherms with low BET surface areas compared to the solvothermally synthesized COFs (Section S-7, ESI). We speculate that these mechanochemically synthesized COFs adopt a thin layer morphology compare to the flower like

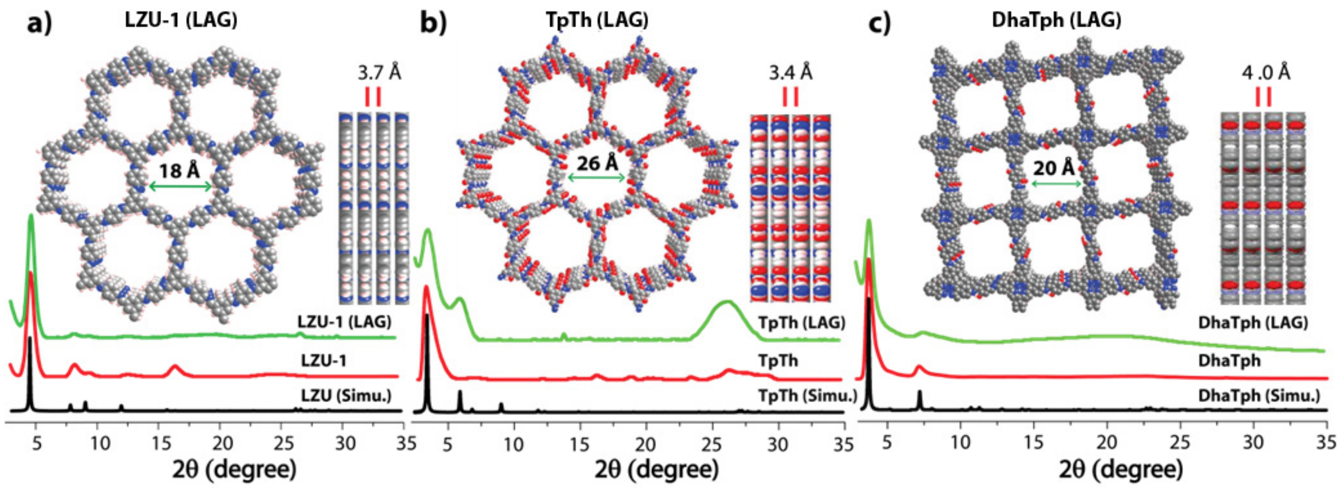

Figure 2. (a), (b) and (c) Comparison of the PXRD patterns; for **LZU-1(LAG)**, **TpTh (LAG)** and **DhaTph (LAG)** respectively (Inset images showing the pore opening and π-π staking distance between consecutive 2D layers for all three COFs).

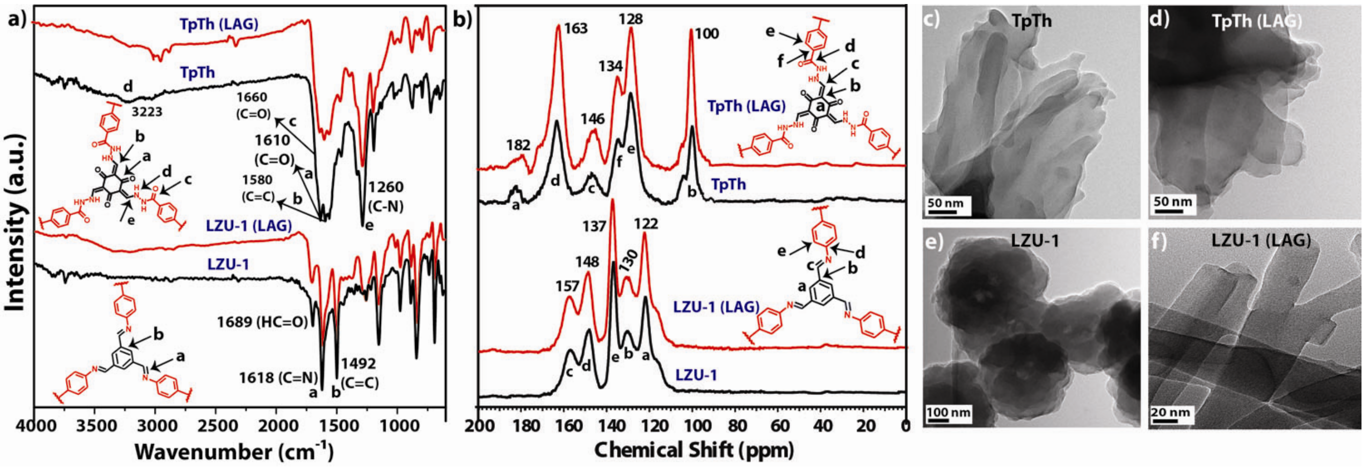

Figure 3. (a) Comparison of the FT-IR spectra for **TpTh** and **TpTh (LAG)**; **LZU-1**[12] and **LZU-1 (LAG)**; (b) ^{13}C CP-MAS solid-state NMR spectra of **TpTh** and **TpTh (LAG)**; **LZU-1** and **LZU-1 (LAG)**; [black, synthesized by solvothermal method and red, synthesized *via* mechanochemical method] (c) HR-TEM image of COF **TpTh**; (d) **TpTh (LAG)**; (e) **LZU-1** and (f) **LZU-1 (LAG)** at different magnifications.

morphology of the solvothermally synthesized one. Due to the thin-layered structures, long-range pore formation in **LAG**-synthesized COFs is hindered, rendering N_2 adsorption possible only in the shallowest, most accessible pores.[3b] Another possible reason could be the entrapment of insoluble oligomeric impurities inside the pores during the COF formation *via* mechanochemical grinding. However, no such evidence has been obtained in TGA and elemental analysis. The steep increase of N_2 uptake of **TpTh** and **TpTh (LAG)** shown at high relative pressure ($P/P_0 > 0.8$) was mainly due to the condensation in the inter-particle voids and other potentially disordered pores.

The HR-TEM images (Figure 3c and 3d) showed the layer like morphology and the boundaries of the stacked layers of both **TpTh** and **TpTh (LAG)**. HR-TEM images revealed that **DhaTph (LAG)** is composed of well-defined, square shaped particles that have almost uniform size of ~40 nm (Section S-10). As observed from the HR-TEM images, **LZU-1 (LAG)** particles were much more elongated in shape, forming thin ribbon shaped structures (width up to ~40 nm and length more than >500 nm) unlike solvothermally synthesized **LZU-1**, (Figure 3e and 3f). This observations clearly indicate that, due to the strong mechanical force the 2D layers gets delaminated, resulting into ribbon like structures. Such delamination phenomenon has already been observed in COFs during the mechanochemical grinding.[3c] The detailed investigation of the stability of these mechanochemically synthesized COFs in water, acid and base has been performed. It was observed that the relative PXRD peak intensity and peak positions of **TpTh (LAG)** and **DhaTph (LAG)** remained identical after this prolonged water treatment for 7 days (Section S-11, ESI).[11b] It was found that **DhaTph (LAG)** decomposed in acid (3N HCl), whereas **TpTh (LAG)** showed acid stability up to 7 days without affecting the crystallinity. The enol to keto tautomerism (*β*-ketoenamine formation) and O─H···N═C intramolecular hydrogen bonding is the key factor for this enhanced hydrolytic stability of **TpTh (LAG)** and **DhaTph (LAG)** respectively. However, these COFs are not stable in NaOH (3N) for more than 12 hours. It is noteworthy that, both **LZU-1** and **LZU-1 (LAG)** are not stable in water or even at humidified condition for few hours. This could be due to the presence of chemically labile Schiff base [–C=N] centers in the framework.

Overall, in this paper, we showcase that by adopting the **LAG** approach, COFs [**TpTh (LAG), DhaTph (LAG)** and **LZU-1 (LAG)**] can be synthesized in high purity and yield compared to the neat mechanical grinding method and at a faster rate compared to the conventional solvothermal methodology. We have newly synthesized a stable hydrazone-linked COF [**TpTh** (**LAG**)] using liquid-assisted mechanochemical synthesis route and crystallized the same *via* solvothermal method. Although the crystallinity and the porosity of these mechanochemically synthesized COFs are moderate, we believe that our fundamental findings will provide better insight towards the general synthetic applicability of **LAG** and will become a conventional synthetic tool for large scale COF production in the near future.

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