Construction of Crystalline 2D Covalent Organic Frameworks with Remarkable Chemical (acid/base) Stability via Combined Reversible and Irreversible Route

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Supporting Information Placeholder

**ABSTRACT:** Two new chemically stable [acid and base] 2-D crystalline COFs (T\textsubscript{P}Pa-1 and -2) were synthesized using combined reversible and irreversible organic reaction. Syntheses of COFs were done by the Schiff base reaction between Triformylphloroglucinol (\textit{TFP}) and paraphenylenediamine (\textit{Pa-1}) or 2, 5-dimethylparaphenylenediamine (\textit{Pa-2}) in mesitylene dioxane 1: 1 combination. The expected enol-imine (OH) form undergoes irreversible proton tautomerism and only keto-enamine form was observed. Due to the irreversible nature of the total reaction and the absence of imine bond in the system T\textit{P}Pa-1 and -2 show strong resistance towards acid (9N HCl) and boiling water. Moreover T\textit{P}Pa-2 shows exceptional stability in basic medium (9N NaOH) as well.

Covalent Organic Frameworks (COFs) are new class of porous crystalline material, constructed via strong covalent bonds between lighter elements like C, B, O, N, Si.\textsuperscript{1} Due to their low density and \pi-\pi stacked architecture COFs have been used as effective gas storage media,\textsuperscript{2} catalytic support\textsuperscript{3} and semiconductive and photo conductive device.\textsuperscript{4} It is believed that reversibility in covalent bond formation during synthesis is required for the successful crystallization COFs,\textsuperscript{5} which is necessary to identify their specific structural details precisely. Irreversible organic reactions always lead to the formation of amorphous polymeric materials, separately categorized as Porous Organic Polymers (POPs)\textsuperscript{6} or Porous Aromatic Frameworks (PAFs).\textsuperscript{7} Even though most of the POPs/PAFs have high thermal and chemical stability they are amorphous in nature and do not have any internal ordering. So far three reversible organic reactions eg: Boronic acid trimerisation\textsuperscript{1a}, boronate ester formation\textsuperscript{1a} and Schiff base reaction\textsuperscript{8} have been used for the synthesis of crystalline COFs. Since reversible back reactions can occur after the synthesis, COFs in general get completely decomposed even in presence of ambient humidity.\textsuperscript{9} Little improvement in water stability was achieved by pyridine doping\textsuperscript{11} and alkylation\textsuperscript{9a} of COF pore walls. However these modifications always lead to decrease in the gas adsorption properties even though it enhances the hydrolytic stability to a small extent. Hence, stability problem in COFs still remain a challenge which prevents the usage of COFs for diverse practical applications.
Schiff-base reaction between mentioned conditions. Gas adsorption property at these above as well. Both COFs retain their crystallinity and exceptional stability in basic medium (9 N NaOH) acid treatment, whereas exceptional resistance towards boiling water and same in both the cases. Shifting of bonds keeping atomic positions almost tautomerism does not affect the crystallinity of chemical stability second step (Figure 1) which enhances the irreversible enol to keto tautomerisation in the crystalline framework in the first step, followed by irreversible reaction can be divided in to two steps. Reversible Schiff-base reaction, (2) Irreversible enol to keto tautomerism.

Here we report the first time synthesis of two new COFs (TpPa-1 and -2) by a combination of reversible and irreversible organic reaction. These COFs (TpPa-1 and -2) are stable and remain crystalline in acid (9N HCl), base (9N NaOH) and water. These COFs can be synthesized by a reaction between 1, 3, 5-triformyl phloroglucinol (Tp) and Paraphenylenediamine (Pa-1) or 2, 5-dimethyl paraphenylenediamine (Pa-2). The total reaction can be divided in to two steps. Reversible Schiff base reaction leads to the formation of crystalline framework in the first step, followed by irreversible enol to keto tautomerisation in the second step (Figure 1) which enhances the chemical stability. The irreversible nature of the tautomerism does not affect the crystallinity of the COF since the transformation involve only shifting of bonds keeping atomic positions almost same in both the cases. TpPa-1 and -2 show exceptional resistance towards boiling water and acid treatment, whereas TpPa-2 shows exceptional stability in basic medium (9 N NaOH) as well. Both COFs retain their crystallinity and gas adsorption property at these above mentioned conditions.

Synthesis of TpPa-1 and -2 were done by the Schiff-base reaction between Triformylphloroglucinol (TFP) (63mg, 0.3 mmol), and Paraphenylenediamine (Pa-1) (48mg, 0.45 mmol) or 2, 5-dimethyl paraphenylenediamine (Pa-2), (61 mg, 0.45 mmol) in presence of 3 M acetic acid (0.5 mL) using (1:1) mesitylene and dioxane as solvent (3ml). Reactants were first dispersed in 3 mL of solvent combination then degassed through three freeze–pump–thaw cycles. Tubes were vacuum sealed, placed in an oven and heated at 120 °C for 3 days. After the reaction the COF powders were filtered out, washed with dry acetone and dried under vacuum at 150 °C for 12 hours. (See section S1 in SI for the detailed synthetic procedure). PXRD patterns of TpPa-1 and -2 indicate an intense peak at 4.7 ° which corresponds to 100 plane reflections (Figure 2a). PXRD patterns also show minor peaks at 8.3, 11.1 and 27 ° 2θ for TpPa-1 and 7.9, 10.9, 26.5 ° 2θ for TpPa-2 (Figure S2 in ESI). The last peak in the PXRD pattern of TpPa-1 and TpPa-2 is due to the reflection from the 001 plane. n-π stacking distance between COF layers was calculated as 3.4 Å in TpPa-1 and 3.5 Å in TpPa-2 from the d spacing between 001 plane. In order to elucidate the structure of these COFs and to calculate the unit cell parameter a possible 2-D model was built with eclipsed and staggered stacking models using the software Crystal 09. The experimental PXRD pattern matches well with the simulated pattern of the eclipsed stacking model (Figure S1 and S2 in ESI). Hence we propose a structure close to hexagonal space group (P6/m) for TpPa-1 and -2 by comparing the experimental PXRD pattern with the simulated one (Figure 2a). The slight deviation of the space group of TpPa-1 from the hexagonal system is due to the inclined stacking arrangement. The unit cell values of TpPa-1 were found to be (a=b= 22.556 Å, c= 3.5 Å), and for TpPa-2 those values are (a= b=22.506 Å, c= 3.4 Å).

FT-IR spectra of TpPa-1 and -2 indicate total consumption of starting materials due to the disappearance of N-H stretching bands (3100-3300 cm⁻¹) of PDA and carbonyl stretching bands (1639 cm⁻¹) of TFP (Figure 2b). Interestingly the FT-IR spectrum does not show the characteristic stretching bands of hydroxyl (-OH) or imine (C=N) functional groups, which should have been present if the compound, existed in the enol form. Instead it shows a strong peak at 1582 cm⁻¹ for TpPa-1 and 1587 cm⁻¹ for TpPa-2, which arises due to the C=C stretching present in keto-form similar to the FT-IR spectrum of the reference compound 2,4,6-tris((phenylamino)methylene)cyclohexane-1,3,5-trione. Most of the FT-IR peaks of TpPa-1 and 2 match well with that of the reference compound which exists in keto form (Figure 2b). But due to the peak broadening in the extended structure, C=O peaks (1616 cm⁻¹) of TpPa-1 and -2 get merged with C=C stretching band (1582 cm⁻¹) and appears as a shoulder (Figure S5 in ESI). The decreased value of frequency for C=O stretching bands (1616 cm⁻¹) in the reference compound is due to the strong intramolecular hydrogen bonding and extended conjugation in the structure. The superior intensity of C=C stretching

![Figure 1](image-url)
is due to the s-cis structure. The FT-IR spectrum of TpPa-2 shows an extra peak at 2885 cm$^{-1}$, which is due to the C-H stretching from the methyl (-CH$_3$) functionality.

The isolation of TpPa-1 and -2 as keto form was undoubtedly confirmed by $^{13}$C CP-MAS solid state NMR. Both COFs show clear signals around $\delta=180$ ppm ($\delta=182$ ppm for TpPa-1 and $\delta=181.8$ ppm for TpPa-2) which corresponds to the signal from the carbonyl (C=O) carbon. In the starting material, tri-aldehyde carbonyl (C=O) carbon resonate at a downfield position around $\delta=192$ ppm. The absence of peak at $\delta=192$ ppm in $^{13}$C CP-NMR spectrum indicates the total consumption of the starting materials. The methylated COF (TpPa-2) shows an extra peak at $\delta=14$ ppm, which corresponds to the carbon atom of methyl (-CH$_3$) group (Figure 3a). SEM image showed that TpPa-1 and -2 crystallize with a flower like morphology which is new type of morphology seen in COFs (Figure 3b). Each individual flower can be considered as a result of aggregation of large number of petals which have length in the micrometer range (1-3 µm). In the case of TpPa-1, petals (width 70-150 nm and thickness 30-40 nm) have spike shaped tips and grown epitaxially out of the core. In the case of TpPa-2, petals (width 500-800 nm and thickness 40-60 nm) are grown much broader.

**Figure 2.** (a) The observed PXRD pattern of TpPa-1 (red) was compared with simulated pattern (black). (b) FT-IR spectra of TpPa-1 (1) compared with the reference compound 2,4,6-tris((phenylamino)methylene)cyclohexane-1,3,5-trione (2), and starting material Triformyl-phloroglucinol (3), Paraphenylenediamine (4).

and longer to form plate like structure. The same flower type morphology can also be observed in the TEM images, which indicate that individual petals have sheet like structure (Figure 3c and e), which can be formed as a result of π-π stacking of COF layers.

Thermogravimetric analysis (TGA) was done for the activated TpPa-1 and -2 to determine the thermal stability and to confirm the absence of guest molecules inside the pores (Figure S19 and S20 in ESI). Both COFs show thermal stability up to 350 °C. A gradual weight loss of 40% for TpPa-1 and 50% for TpPa-2 was observed after 360 °C due to the decomposition of framework. Permanent porosity of TpPa-1 and -2 were evaluated by N$_2$ adsorption isotherm at 77 K. Activated TpPa-1 and -2 show reversible type IV adsorption isotherm. Surface area of the activated COFs calculated using Brunauer-Emmett-Teller (BET) model were found to be 535 m$^2$/g for TpPa-1 and a 339 m$^2$/g for methylated TpPa-2 (figure S10 and S11 in ESI). TpPa-1 has a higher Langmuire surface area of 815 m$^2$/g whereas for TpPa-2 it is 507 m$^2$/g (Figure S12 and S13 in ESI). Pore size distribution of TpPa-1 and TpPa-2 has been calculated on the basis of non-local density.
To our surprise both TpPa-1 and -2 remain stable while directly submerged in water for several days (7 days). To investigate stability of COFs in water, 50 mg of each COF was directly submerged in 10 mL water for 7 days. Retention of crystallinity was tested by PXRD (Figure 4a). It was found that relative peak intensity and peak position of both COFs remain same after prolonged water treatment (1, 3 and 7 days), which indicates the remarkable water stability of these COFs. All characteristic FT-IR peaks remain same after water treatment and no extra peak of the starting material was observed. N₂ adsorption isotherm shows only a small change in surface area (535 vs 520 m²/g for TpPa-1 and 339 vs 321 m²/g for TpPa-2). Since TpPa-1 and TpPa-2 show remarkable stability in water, we decided to check the effect of acid (HCl) on these materials. Acid stability of TpPa-1 and -2 was checked using HCl of different normality (1N, 3N, 6N and 9N) for one day. PXRD patterns indicate relative peak intensities and peak positions of TpPa-1 and -2 remain same even after 9N HCl treatment for 1, 3 and 7 days (Figure 4c). Similarly FT-IR peaks remain in their identical positions after the acid treatment which indicates the chemical stability of these materials towards acid treatment. Porosity and surface area measurement of the acid treated COFs show only a small change (512 m²/g for TpPa-1 and 318 m²/g for TpPa-2). Finally we had evaluated the stability of the two COFs in sodium hydroxide (NaOH) of different normality (1N, 3N, 6N and 9N) for one day. TpPa-2 shows retention of PXRD peak position after treatment of 9N NaOH for 7 days (Figure S35 in ESI). Surface area (324 m²/g) and retention of peaks shown in the FT-IR spectra confirms that TpPa-2 shows considerable resistance towards base treatment. However TpPa-1 shows loss of PXRD peaks on day 1 due to 9N NaOH treatment (Figure S33). Only 60% in weight of the material is recovered. Even though FT-IR spectroscopy shows the retention of peaks, gas adsorption analysis shows decrease in surface area by 50%.

Stability of TpPa-1 and -2 in water arises due to the irreversible nature of the enol to keto tautomerism. This type of tautomerism also exists in simple N-Salicylideneanilines, were enol form is found to be more stable (Section S12 in ESI). Two competing effects that decides which form to be more stable are, 1) aromaticity and 2) large basicity of imine nitrogen (C=N) over phenolic oxygen (O-H). In case of mono substituted N-Salicylideneanilines aromaticity is the dominating factor so the compound exists only in enol form. But in case of tris (N-salicylideneaniline) derivatives the basicity of three imine nitrogen dominates over the aromaticity factor and as a result equilibrium shifts completely towards the side of keto- form (Section S12 in ESI). The equilibrium does not revert back to the direction of enol form even after heating the sample to very high temperature, and thus this transformation can be considered as an irreversible process. TpPa-1 -2 were found to be stable even in boiling water due to this irreversible enol to keto tautomerism. The stability towards the acid arises due to the disappearance of acid labile imine

**Figure 3:** (a) Solid state ¹³C NMR of TpPa-1 (Red) and TpPa-2 (Blue) compared against the reference compound 2,4,6-tris [([phenylamino)methylene] cyclohexane-1,3,5-trione (Green). (b) SEM image of TpPa-1, (c) TEM image of TpPa-2, (d) SEM image of TpPa-1 and (e) TEM image of TpPa-2 shows nano-flower morphology.

Functional theory (NLDFT). Both COFs have a narrow pore size distribution between the range 0.8 - 1.5 nm in which the peak maxima is appearing at 1.25 nm for TpPa-1 and 1.35 nm for TpPa-2 (Figure S14 and S15 in ESI). Hydrogen uptake of TpPa-1 and -2 were found to be 1.1 wt % and 0.89 wt% (Figure S16 in ESI). These values are comparable with the performance of other reported COFs (COF-5²→0.84 wt%, COF-10²→0.82 wt%, COF-102²→1.21 wt%, and COF-103²→1.29 wt %). CO₂ uptake of TpPa-1 was measured as 78 cc/g at 273 K, this value is comparable with performance of COF-6 (85 cc/g). TpPa-2 shows a moderate CO₂ uptake of 64 cc/g at the same temperature.
(C=N) bond as a result of irreversible tautomerism. The framework instability of TpPa-1 under the influence of base (high pH) was not completely understood. We speculate that at very high basicity there is a chance of deprotonation of secondary nitrogen which leads to the back conversion of keto to enol form. The reason behind this speculation was supported by the literature report that the reference compound 2,4,6-tris((phenylamino)methylene)cyclohex-ane-1,3,5-trione upon treatment with strong base like LDA (Lithium diisopropylamide) undergo deprotonation followed by keto to enol tautomerism which then used for the chelation of BF$_2^{12}$. To overcome this base stability problem, two bulky methyl groups were positioned near the base labile secondary nitrogen centre (C-N) in TpPa-2. This strategy is almost similar to the attempt done in MOF-5 by doing 2,5-dimethylation of terephthalic acid hydrolytic stability of MOF-5 in water was enhanced. As a result of this methylation PXRD peak positions of base treated TpPa-2 were retained after 7 days treatment with 9 N NaOH eventhough small decrease in peak intensities were observed.

In summary, we for the first time could introduce a new protocol for the synthesis of highly acidic and base stable crystalline covalent-organic frameworks. Exceptional stability of these materials will make them advantageous over MOF counterparts besides its conventional properties like very low density and high thermal stability. We also showed that the problem of base stability can be solved to an extent by introducing a bulky alkyl group near to the secondary nitrogen centre with a compensation of small decrease in surface area. Even though the gas adsorption properties of these newly prepared COFs are moderate we believe that by increasing the diamine ligand length these COFs will achieve high surface area and gas adsorption properties. The sheet like petals present in these nano materials can be utilized as a support for doping of nano-particles which will be useful for catalytic application.

Figure 4: (a) PXRD pattern showing the stability of TpPa-1 in boiling water. Retention of morphology after water treatment was found out by SEM. (b) N$_2$ adsorption isotherms at 77 K of TpPa-1 before (Blue) and after treatment with water for 1 week (red). (c) PXRD pattern showing the stability of TpPa-1 towards 9N HCl (d) N$_2$ adsorption isotherms at 77 K of TpPa-1 before (Blue) and after treatment. (e) PXRD pattern showing the retention of crystallinity and (f) Retention of surface area of TpPa-2 after treatment with 9 N NaOH for 1week.

ASSOCIATED CONTENT
Supporting Information
Synthetic procedures, PXRD, $^{13}$C solid state NMR, TGA, crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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