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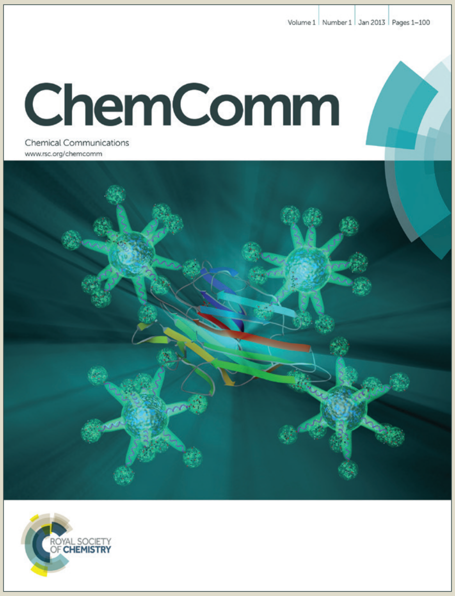

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Bifunctional Covalent Organic Frameworks with Two Dimensional Organocatalytic Micropores

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We report the successful incorporation of bifunctional (acid/base) catalytic sites in crystalline organocatalytic porous COF (2,3-DhaTph). Due to the presence of acidic (catachol) and basic (porphyrin) sites, 2,3-DhaTph shows significant selectivity, reusability, and excellent ability to perform the cascade reaction.

Covalent organic frameworks (COFs)[1] are a new class of crystalline porous material constructed from light elements like H, B, C, N, O, Si, etc.[2] Although, research on these materials received immense attention for their potential applications in gas adsorption, charge carrier transport, and optoelectronics,[3] these porous materials are less explored as catalysts owing to their limited stability in aqueous, acidic and alkaline mediums.[4] In principle, COFs can be used as catalysts in mainly two ways: 1) as a support for catalytically active nanoparticles,[5] and 2) direct oragnocatalysis using catalytically active organic building units within the COF framework.[6] Among these catalytic applications, heterogenous organocatalytic COFs are more promising, because it has high scope in pharmaceutical and food industries.[7] Here, we report, the successful synthesis of a bifunctional catachol-porphyrin COF, consisting of both acidic and basic sites, which can act as heterogeneous catalyst for one pot deprotection of acetal groups followed by Knoevenagel condensation reaction.[8] Even though there has been a report of porphyrin COF ([Pyr]$_X$-H$_2$P-COF) used as an organocatalyst,[6b] but the incorporation of the bifunctionality inside COF backbone for catalysis is still unprecedented.

Bifunctional heterogeneous catalysts are more preferred for cascade/tandem/one-pot synthesis reactions, because of the fixed location of the acidic and basic sites, within the framework. Also high surface area, chemical stability and ordered crystalline structure with separated antagonist sites are the essential requirements of a heterogeneous bifunctional catalyst to achieve highest catalytic activity. High surface area will provide greater exposure of the catalytic sites towards the incoming reactants. The chemical stability will help to avoid the contamination due to catalyst degradation; whereas high crystallinity will provide the knowledge of the structure and the exact position as well as the distance between the antagonist catalytic sites. Although, few polymer based organocatalysts are reported in the literature for the cascade reaction, due to the amorphous nature of the catalysts, the exact position of the antagonist catalytic sites and the spatial separation between them were very poorly understood.[8] Moreover, the reported post functionalization strategy does not ensure 100 % incorporation of the catalytic sites in the framework.[6b,9] Thus, the synthesis of bifunctional heterogeneous catalysts having high crystallinity, porosity and chemical stability is still a challenging task.[10] The COFs reported in this paper, **2,3-DhaTph** and **2,3-DmaTph**, were synthesized by reversible Schiff-base reaction using 2,3-dihydroxyterephthalaldehyde (**2,3-Dha**)/ 2,3-dimethoxyterephthalaldehyde (**2,3-Dma**) and 5,10,15,20-tetrakis(4-aminophenyl)- 21H,23H-porphine unit (**Tph**) in dichlorobenzene (o-DCB,) and dimethylacetamide (DMAc) with catalytic amount of 6.0 M acetic acid (Figure 1) (ESI Section 2). The PXRD patterns of the as synthesized COFs showed good crystallinity with a high intense peak at ~3.6° 2θ corresponding to the [100] plane reflections and low intense peaks at ~7.3° and ~19–25° 2θ, which were assigned to [200] and [001] facets (d spacing = 4.0 Å). The diffraction patterns of the synthesized COFs are similar to that of eclipsed stacking model of the COF structures built using SCC-DFTB method (Figure 2a, S-4, ESI).[11] From the Pawley refinement, we could conclude that the unit cell values for **2,3-DhaTph** are ((a = 24.7, b = 24.6, c = 4.0 Å; α = 92.9, β = 90.2, γ = 92.7; $P1$ space group); and for **2,3-DmaTph** are a = 25.2, b = 24.6, c = 4.1Å; α = 90.1, β = 89.7, γ = 88.4; $P1$ space group) (Section S-3, ESI). The Crystal structure analysis of the monomers of **2,3-DhaTph** and **2,3-DmaTph** indicated that, these COFs exist only in the enol-imine form (Figure 1 and S-11, ESI). The presence of trans conformation of imine bonds and the presence of intramolecular hydrogen bonding [–O–H•••N=C; D = 2.579 (2), d = 1.858 (2) Å, and θ= 146.1°(3)] in **2,3-DhaTph** has been confirmed from the monomer crystal structure, which leads to the rigid structure enhancing the crystallinity (Figure 1).[10b,12] As a result, the PXRD pattern of **2,3-DhaTph** is much more intense than that of **2,3-DmaTph**, since the intramolecular H-bonding is absent in **2,3-DmaTph** (Figure 1). The appearance of strong characteristic imine –C=N stretching frequency in the FT-IR spectrum at 1612 cm^{-1} for **2,3-DhaTph**

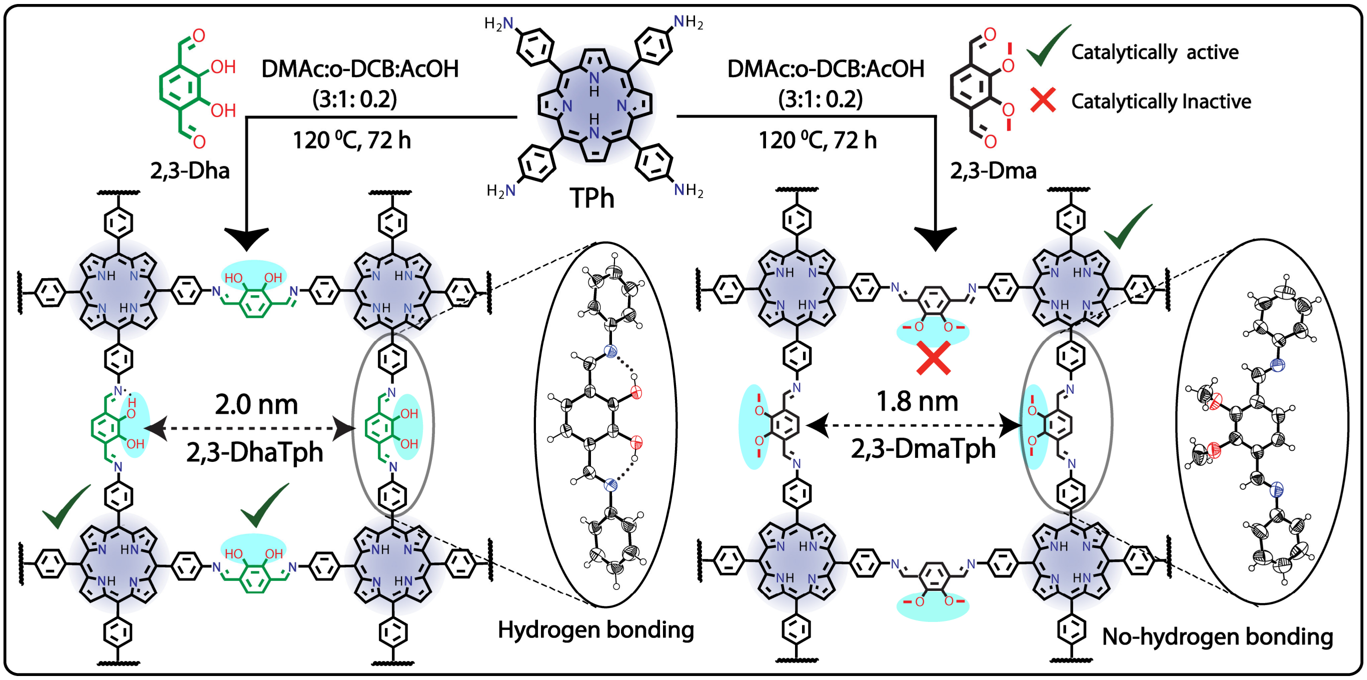

Figure 1. The synthesis of **2,3-DhaTph** and **2,3-DmaTph** by the condensation of **Tph** and **2,3-Dha/2,3-Dma**.. The catalytically active porphyrin and catacholic –OH groups is shown in coral and cyan colors, respectively. ORTEP diagram of **2,3-DhaTph** and **2,3-DmaTph** monomer unit

(Figure S5, ESI) and 1608 cm^{-1} for **2,3-DmaTph** (Figure S6, ESI) confirmed the formation of COFs. Also, the disappearance of stretching frequency of –C=O group (1661 of **2,3-Dha**, 1676 cm^{-1} of **2,3-Dma**) and –NH$_2$ group (3100-3400 cm^{-1}) of **Tph** in the FT-IR spectrum of **2,3-DhaTph** and **2,3-DmaTph** confirmed the formation of imine –C=N bonds. The solid state ^{13}C CP-MAS NMR spectrum confirmed the formation of imine –C=N bonds, as it shows the characteristics signals at δ 160.8 (Figure S7, ESI) and 154.2 (Figure S8, ESI) ppm respectively. These chemical shifts of imine –C=N appears closer to the monomer unit values of **2,3-DhaTph** (δ 161.3) (Figure S10, ESI) and **2,3-DmaTph** (δ 154.9) (Figure S12, ESI). The morphological analysis of **2,3-DhaTph** and **2,3-DmaTph** done using SEM and TEM imaging indicate that the **2,3-DhaTph** is composed of 100–200 nm thin platelet like morphology; whereas **2,3-DmaTph** consists of 30–50 nm average sized sheet like morphology (Section S-10, ESI).

The thermal stability of the activated COFs was confirmed by TGA analysis, which showed high thermal stability up to 300 °C (Section S-9, ESI). The N$_2$ adsorption isotherms collected at 77 K for the activated COFs showcase typical Type-IV isotherm (Figure 3a) with the Brunauer-Emmett-Teller (BET) surface area of 1019 and 668 m^{2}g^{-1}, respectively (Figure S14 and S17, ESI). The pore width calculated using NLDFT method found to be 2.2 and 1.4 nm which is in close agreements with the theoretically predicted pore width (Figure 1). The lower surface area and pore size of **2,3-DmaTph** than that of **2,3-DhaTph** is well justified as twisted confirmation of phenyl rings in former case shows disturbed stacking of 2D layers, which finally reduces the crystallinity as well as porosity. We have analyzed the chemical stability of these COFs in aqueous, acidic (3N HCl) and alkaline (3N NaOH) mediums. Both COFs showed good aqueous stability for more than 7 days, which was confirmed by PXRD, FT-IR and porosity studies. The presence of –OH and –OCH$_3$ groups adjacent to the imine bonds in these COFs probably helped to improve the hydrolytic stability. Similarly, the stability of these COFs in 3N HCl was further confirmed by FT-IR, PXRD and SEM studies (Section S-12, ESI).[10] **2,3-DhaTph** showed higher structural integrity than **2,3-DmaTph**, probably due to the strong intramolecular hydrogen bonding [–O–H•••N=C].[10b,12] Due to the protonation of inner porphyrin core by acid the decrease in surface area, have been observed (before 1019, after 652 m^{2}g-1 for **2,3-DhaTph** and before 668, after 307 m^{2}g^{-1} for **2,3-DmaTph**).[10b] Both **2,3-DhaTph** and **2,3-DmaTph**, are unstable in basic medium (3N NaOH).

The **2,3-DhaTph** COF possesses separated antagonist catalytic sites in which catacholic –OH act as weak acidic sites,[13] whereas porphyrin units and imine bonds act as basic sites, with high chemical stability in aqueous/acidic mediums along with high crystallinity and porosity. Hence, we have decided to explore the catalytic activity of this COF for the acid-base catalyzed one-pot cascade reactions.[8] The catalytic activity of **2,3-DhaTph** was analyzed in presence of 10 mg of COF catalyst using a model reaction (Figure 3c), wherein benzaldehydedimethylacetal (**1a**) (152 mg, 0.1 mmol) reacts with malononitrile (72.6 mg, 0.11 mmol) in toluene (1.5 mL) and water (0.5 mL) at 80 °C. In the case of **2,3-DhaTph** the formation of the desired product 2-benzylidenemalononitrile (**3a**) with excellent isolated yield (96%) was observed. The detailed kinetic study show that the completion of reaction occurs within 90 min (Figure 3d). It was understood, from the controlled experiments that this cascade reaction proceeds through two sequential steps: 1) the acid catalyzed deacetalization of benzaldehydedimethylacetal (**1a**) to yield benzaldehyde (**2a**); and 2) the base catalyzed Knoevenagel condensation reaction to yield 2-benzylidenemalononitrile (**3a**). (Figure 3c and Section S13, ESI).

In order to analyze the necessity of the catalyst for the cascade reaction, the model reaction was performed without the addition of the catalyst. The reactions without catalyst yielded only 5% product **3a** during the estimated time span of 90 min.

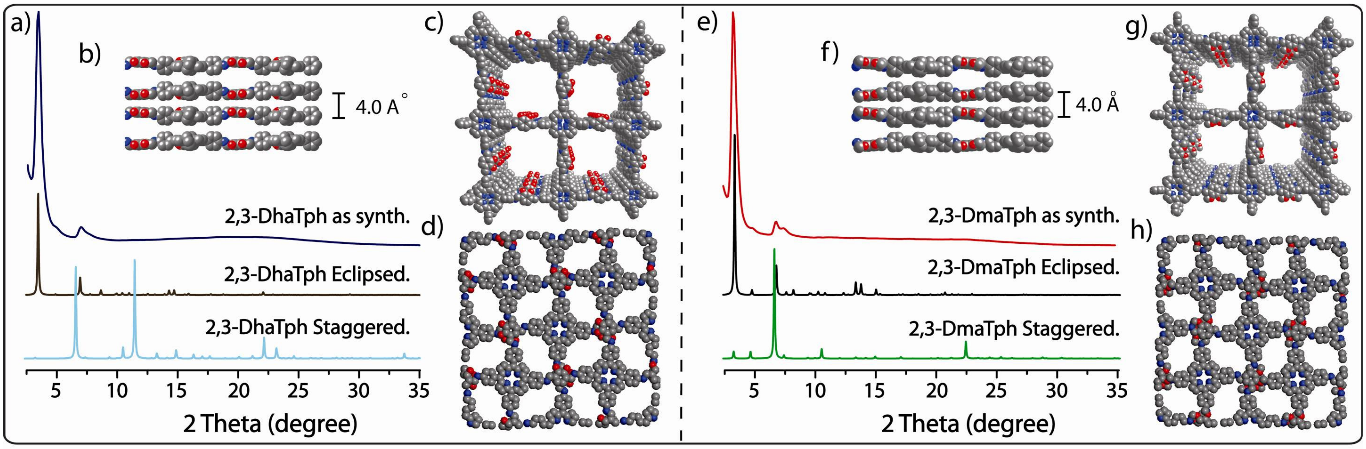

Figure 2. (a) The PXRD pattern of **2,3-DhaTph** compared with simulated eclipsed, and staggered, (b and c) Stacking diagram and eclipsed stacking model of **2,3-DhaTph**. (d) Staggered stacking model of **2,3-DhaTph**. (e) PXRD pattern of **2,3-DmaTph** compared with simulated eclipsed and staggered. (f and g) Stacking diagram and eclipsed stacking model of **2,3-DmaTph**. (h) Staggered stacking model of **2,3-DmaTph**.

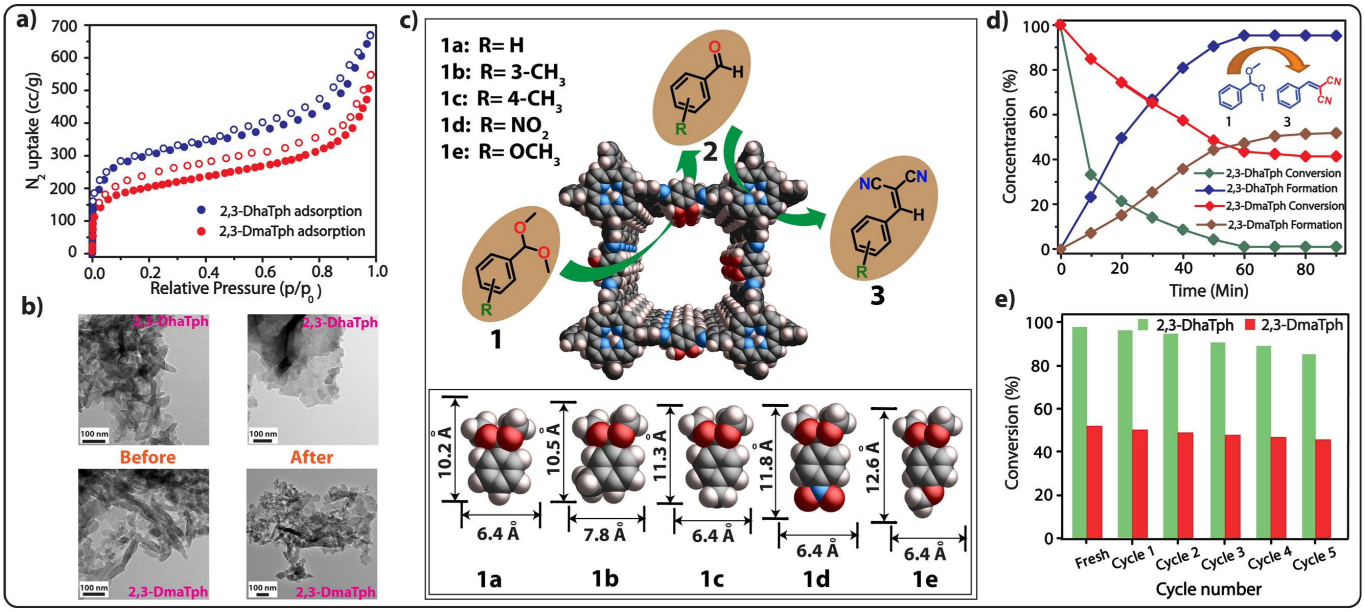

Figure 3. (a) N_2 adsorption isotherms for **2,3-DhaTph** and **2,3-DmaTph**. (b) Comparative TEM images, as synthesized and after 3rd cycle **2,3-DhaTph** and **2,3-DmaTph**. (c) The catalytic activity towards acid-base catalyzed reaction with various reactants (d) Kinetics of the cascade reaction between **1** and malononitrile. (e) Comparison of the recyclability studies performed for **2,3-DhaTph** and **2,3-DmaTph.**

The reaction performed without catalyst (blank) (Section S-13, ESI Table 3, entry 1) under the same condition yielded only 25% intermediate **2a**, probably due to the deacetalization of **1a** by water, which has been used as a solvent. We have explored the substrate scope of **2,3-DhaTph** catalyst using a number of substituted dimethyl acetal of reactants, keeping all other reaction conditions same. In general, excellent conversions (> 80%) to the desired products were observed (Section S13, ESI, Table 4, entries 2–5); despite of the presence of electron donating (–Me, –OMe) or withdrawing group (–NO_2) on the acetal based reactants. As shown in figure. 3c, the reactant size (molecular dimensions) didn't affect on the reactivity the starting materials, which emphasizes the utility of the **2,3-DhaTph** for the broad spectrum of the catalytic reactions. The kinetics of the cascade reaction after addition of the catalyst shows that as the rate of the reaction increases with time and the amount of reactant **1a** starts decreasing along with a related increase in the corresponding product **3a**. As shown in Figure. 2d, with increasing time formation of **3a** steadily increases up to 60 min yielding ~ 90 % product for the **2,3-DhaTph** catalyst. The probable reason of the significant activity shown by **2,3-DhaTph** catalyst may be the fine distribution of acidic and basic sites in crystalline COF framework and periodic arrangement of these centres distributed over the entire COF matrix. In order to prove the necessity of acidic and basic sites for catalyzing the cascade reaction,[14] we have repeated the similar catalytic reaction in presence of **2,3-DmaTph** as a catalyst, which holds only basic porphyrin centers; but lacks acidic catacholic –OH functionality, which have been replaced by –OMe functionality. In this case, reaction proceeds very slowly giving only 52 % yield of **3a** in 90 min (Section S13, ESI, Table 3); as shown in Figure 3d. Hence, it is clear that only basic sites are not sufficient to catalyze the cascade reaction (Figure 3). The solid catalysts can be recycled for more than five times without loss in product yield as shown in figure. 3e. **2,3-DhaTph** has showed excellent recyclability for more than five catalytic cycles giving yields over ~ 81% in an estimated time span of 90 min. In the case of **2,3-DmaTph**, as expected, we have also observed the recyclability upto 5 cycles, but very limited yield up to ~ 42%. (Figure 3d, 3e and Section S13, ESI).

In conclusion, we have synthesized of a catalytically active COF **2,3-DhaTph** with weak acidic and basic sites for catalyzing the cascade reaction. The **2,3-DhaTph** showed high surface area high crystallinity as well as porosity than **2,3-DmaTph**, which lacks intramolecular hydrogen bonding within the framework. The potential of **2,3-DhaTph** for catalyzing the cascade reaction is validated by the good catalytic activity shown towards the cascade reaction with very high product yield and recyclability over 5 cycles. The necessity of the basic and acidic sites in a catalyst for catalyzing the cascade reaction has been further validated by utilization of methoxy functionalized **2,3-DmaTph**.

Notes and references

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14. The concept of necessity of both acidic (quinolic−OH) and basic (porphyrin) groups for catalyzing aforementioned catalytic reaction was confirmed by using literature reported **DhaTph** catalyst, which have both acidic as well as basic centers, with similar stability.[10b] In the case of **DhaTph** also, we have observed the similar yield of ~ 94 % of product **3a** (ESI, Section S13).