

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201802220 Angew. Chem. 10.1002/ange.201802220

Link to VoR: http://dx.doi.org/10.1002/anie.201802220 http://dx.doi.org/10.1002/ange.201802220

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Ultra-stable Imine-based Covalent Organic Frameworks for Sulfuric acid Recovery: An Effect of Interlayer Hydrogen Bonding**

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Abstract: Herein, we have demonstrated a rapid and scalable synthesis of six new imine-linked highly porous and crystalline COFs which showcased exceptionally high chemical stability in harsh environments including conc. H_2SO_4 (36 N), conc. HCl (12 N) and NaOH (9 N). This is because of the presence of strong interlayer C-H•••N hydrogen bonding among the individual layers which provides significant steric hindrance and a hydrophobic environment around the imine (-C=N-) bonds thus preventing their hydrolysis in such abrasive environment. These COFs were further converted into porous, crystalline, self-standing and crack-free COF membranes (COFMs) with extremely high chemical stability for their potential applications for sulfuric acid recovery. Also, the as-synthesized COFMs exhibit unprecedented permeance for acetonitrile (280 Lm²h⁻¹bar⁻¹).

Covalent organic frameworks (COFs) are pristine sets of linked periodically ordered porous networks covalently synthesized through simultaneous polymerization and crystallization of monomeric building blocks.^[1] The crystallization process of such structurally predesigned organic porous structures requires dynamic reversible bond formation, like boronic acid trimerization, boronate ester formation, Schiff base formation, etc.^[2] However, the reversible nature of these chemical bonds imparts a limit towards their chemical stability and creates a restriction towards the usage of these novel materials for expansive utilizations.^[3] Hence, the design and synthesis of porous crystalline COFs, that can sustain their crystallinity and porosity in abrasive environments including drastic humidity,

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strong acidity or basicity, is still a key challenge for modern researchers. $^{\left[4\right] }$

We have already attempted to overcome the stability issues in COFs, by introducing the enol to keto tautomerization phenomenon during the framework crystallization. By using this approach, we could achieve a set of COFs with significantly enhanced chemical (aqueous, acid and base) stability.[4a,5] However, this idea is entirely restricted to β -keto-enamine COFs, which provides minimal substrate scope and thus are limited in their widespread exploration. Hence, it is necessary to diversify this approach and extend this idea for the production of more versatile "-C=N-" (imine) linked COFs. The exploration of iminebased COFs has increased dramatically in recent years owing to their superior hydrolytic stability compared to boronic acid COFs along with their extensive substrate-library availability.^[6] However, for the widespread implementation of such chemically stable imine based COFs, the synthetic process should: 1) be devoid of toxic solvents or synthetic difficulty,^[5] 2) be rapid and easily scalable (unlike the traditional solvothermal process),^[5,7] and 3) provide the opportunity to process the as-synthesized COFs into pellets, beads as well as membranes keeping their properties intact.[5]

Keeping all these in perspective, herein, we report 2,4,6trimethoxy-1,3,5-benzenetricarbaldehyde (TpOMe) as a prime aldehyde building unit for scalable and rapid construction of six new stable imine-linked COFs via the PTSA (p-toluenesulfonic acid) mediated solid-state mixing approach (Figure 1a, Figure S4, Section S-2).^[5] The introduction of three bulky methoxy (-OCH₃) groups adjacent to the aldehyde (-CHO) functionalities provide significant steric hindrance and the hydrophobic environment around the imine bonds, promotes impregnable COF crystallization. These as-synthesized materials showcase exceptionally high chemical stability in H₂SO₄ (36 N), HCl (12 N), NaOH (9 N), boiling water and common organic solvents, for several days. To the best of our knowledge, this is the first report illustrating a series of imine based COFs with exceptionally high chemical stability in such drastic medium. Calculations with density functional theory reveal the presence of significant numbers of interlayer C-H ••• N hydrogen bonding (H-bonding)[8] between the methoxy (-OCH₃) C-H of a particular layer with the imine (-C=N-) nitrogen atoms present in the adjacent layers. The interlayer C-H ••• N H-bonding provides significant steric and hydrophobic environment around the imine bonds and protects them from being hydrolyzed in such abrasive conditions. Moreover, these COFs were further converted to self-standing, crack-free COF membranes (COFMs),^[5a] which maintain their physical appearance even after treatment with 36 N sulfuric acid solution for several days. Keeping their exceptional stability in mind these COFMs were used for sulfuric acid (12 N) recovery.

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The PTSA mediated solid-state mixing approach has opened

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Figure1. (a) General synthesis of COFs from aldehyde (TpOMe) and corresponding amines (Tab, PaNO₂, Pa1, BD(NO₂)₂, BPy and Azo) by PTSA (*p*-toluenesulfonic acid) mediated Schiff base reaction. (b) Comparison between experimental PXRD patterns (red) with simulated eclipsed (slip-AA) stacking model (blue) and Pawley refinement difference (green) for TpOMe-Pa1, TpOMe-BD(NO₂)₂, TpOMe-Azo and TpOMe-BPy COFs. The eclipsed space-filling models have shown in inset.

up a new route for rapid, processable and bulk scale production of highly crystalline porous COFs.^[5] However, the exploration of the PTSA mediated solid-state mixing approach is not straight forward for the construction of imine linked COFs. The primary concern is the chemical stability of the as-synthesized frameworks under the given reaction conditions. Owing to the intense acidic nature of PTSA (pK_a = -2.8; water), the imine-linked COF crystallites, during the framework formation, readily decompose under the experimental conditions leading to high extent of amorphization (**Figure S5, S6** and **S7**). This makes it profoundly challenging to design suitable linker units to yield the crystalline porous COFs under the aforementioned synthetic conditions. We made a prediction that the synthesis of iminelinked COFs using this approach can only be achieved by providing enough steric hindrance around the imine bonds or by incorporating significant hydrophobic environment to protect it from H^+ and H_2O attack during the COF crystallization.

The formation of TpOMe-Tab, TpOMe-PaNO₂, TpOMe-Pa1, TpOMe-BD(NO₂)₂, TpOMe-BPy and TpOMe-Azo was confirmed from their PXRD patterns (Figure 1b and Figure S11). The high intensity peak at ~4.8° (±0.1, 20), for TpOMe-Pa1 and TpOMe-PaNO₂ COFs could be assigned to the reflections from their 100 planes. In case of TpOMe-BD(NO2)2 and TpOMe-Bpy high intense peaks attributed to the 100 planes arise at \sim 3.6° (±0.1, 2θ). The **TpOMe-Azo** (with highest pore diameter in the series) and TpOMe-Tab (having lowest pore diameter) showed their 100 plane reflections at ~3.3° (2 θ) and ~ 6.1° (2 θ), respectively. All the COFs revealed their 001 plane reflections at ~27.1° (±0.2, 2 θ) in the PXRD patterns. To find the interlayer stacking constitutions, different model (eclipsed, slipped eclipsed and staggered) structures were simulated by using Materials Studio (Section S-3).^[10] The experimental PXRD pattern fits well with the simulated slipped eclipsed (AA) stacking models (Figure S12 and Table S1-S7).

The recorded FTIR spectra showed the complete disappearance of the primary -N-H (3188-3462 cm⁻¹; parent amines) and -C=O (1682 cm⁻¹; TpOMe aldehyde) stretching frequency and exhibited (**Figure S13**) the newly formed -C=N bonds stretching frequency at 1574-1623 cm⁻¹. The reference compound **TpOMe-Ani** (**Figure S8, S9**) (prepared from TpOMe aldehyde with aniline) reflected similar -C=N stretching at ~1621 cm⁻¹ (**Figure S10**). The solid-state ¹³C cross-polarization/magic-angle spinning (CP-MAS) spectra, revealed the main characteristics peak of imine (-C=N-) bonded carbon atom at ~148 ppm whereas for the aromatic and methoxy carbons it appears within the range ~141-106 ppm and 53-70 ppm respectively (**Figure S14**).

The permanent porosity of all the as-synthesized COF materials were assessed by N₂ adsorption isotherms recorded at 77 K (liq. N₂ temperature). All the COFs showed rapid N₂ uptake at the comparatively lower pressure range P/P₀<0.1. Beyond this pressure, in case of TpOMe- Tab, TpOMe-PaNO₂, TpOMe-Pa1 and **TpOMe-BD(NO₂)**₂ COFs, the isotherms got almost saturated, reflecting their dominating micro-porous nature (Figure 2c, f & Figure S18, S21). TpOMe-BPy and TpOMe-Azo, on the other hand, showed a sharp steep between the pressure P/P₀= 0.10-0.20, exhibiting the 'type-IV' adsorption isotherm, which is the characteristic of mesoporous materials (Figure S18). Moreover, based on Brunauer-Emmett-Teller (BET) model TpOMe-BPy revealed the highest surface area of 2023 m²g⁻¹, followed by 1885 m^2g^{-1} for **TpOMe-Azo**, 1164 m^2g^{-1} for **TpOMe-Pa1**, 913 m^2g^{-1} for **TpOMe-BD(NO₂)**₂, 615 m^2g^{-1} for **TpOMe-PaNO**₂ and 593 m^2g^{-1} for TpOMe-Tab. The experimental pore size distribution of TpOMe-Tab, TpOMe-PaNO₂, TpOMe-Pa1, TpOMe-BD(NO₂)₂, TpOMe-BPy and TpOMe-Azo COFs (calculated using the QSDFT model: cylindrical pore, adsorption branch), showed the pore width as 1.4, 1.4, 1.5, 1.8, 2.2 and 2.8 nm respectively **S26**). Thermogravimetric analyses (Figure (TGA) $(N_2$ atmosphere) of all the COFs showed their thermal stability in the range 320-400 °C (Figure S15).

The extent of chemical stability of any material dictates its potentiality for extensive usage. Hence, to analyze the chemical stability here, the as-synthesized COF samples (20 mg) were submerged in highly drastic media such as conc. H_2SO_4 (36 N), conc. HCI (12 N), NaOH (9 N, 24 h) and various common protic/aprotic solvents (**Section S-5**). The common solvent stability, exclusively tested for COF **TpOMe-Pa1**, reported here, exhibit almost retention of its crystallinity and porosity (**Figure**

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Figure 2. (a, d) The layered structures of **TpOMe-Pa1** and **TpOMe-BD(NO₂)**₂ (C-grey, N-blue, O-red and H-white). The interlayer C–H•••N and intralayer C–H•••O Hbonding based on distances (H to N atom or H to O atom; Å) shown with dotted line and angles (C–H•••N or C–H•••O) in degree (value assigned in green-within the range, red-outside the range and light blue exclusively for intralayer H-bonding). (b, e) Comparison of PXRD patterns (y axis intensity) and (c, f) N₂ adsorption isotherms for **TpOMe-Pa1** and **TpOMe-BD(NO₂)**₂ of as-synthesized and after treatment in H₂SO₄ (36 N) after stipulated time duration.

S29). Moreover, among all other COFs TpOMe-BD(NO₂)₂ was found to be highly sensitive towards conc. H₂SO₄ (36 N) and NaOH (9 N; here it degrades completely) (<24 hours) but found to be stable in HCI (12 N) for 7 days (Figure 2e, f and Figure S22). For other five COFs, the proper matching in the PXRD patterns (Figure S16 and S20), along with their comparatively identical FTIR spectra (Figure S17 and S20), concerning the assynthesized material, revealed their structural rigidity in such drastic media. Notably, N2 adsorption isotherms revealed the acid treated COFs maintained significantly high porosity. BET surface areas were recorded as for TpOMe-BPy (1512, 1844 and 689 m²g⁻¹), **TpOMe-Azo** (1527, 1805 and 1469 m²g⁻¹), **TpOMe-Pa1** (1014, 1112, 780 m²g⁻¹), **TpOMe-BD(NO₂)**₂ (170, 770 and 0 m²g⁻¹ ¹), **TpOMe-PaNO**₂ (603, 612 and 206 m^2g^{-1}) and **TpOMe-Tab** (584, 590 and 104 m²g⁻¹) after treating the respective COF samples in conc. H₂SO₄ (36 N, seven days), conc. HCI (12 N, seven days) and NaOH (9 N, 24h) respectively (Figure S18, S21 and S22).

Density functional tight binding (DFTB) and density functional theory (DFT) calculations were undertaken to gain more insights about the exceptionally high chemical stability of the COFs (Section S-3 and S-6). Interestingly, it was observed that the methoxy (-OCH₃) groups present in the aldehyde subunits played a very crucial role in stabilizing these materials. However, their mere presence does not impart the stability. The methoxy (-OCH₃) groups present in the COFs, except **TpOMe-BD(NO₂)**₂, were almost perpendicularly directed into the interlayer spacing in all the structures (Figure 2a and Figure S30). As a result, a significant number (6-12 H-bonding per two stacked hexagons) of interlayer C-H ••• N H-bonding were discerned between the methoxy (-OCH₃) C-H of a particular layer and the imine (-C=N-) nitrogen atom present in the adjacent layer. The calculated H-bonding distances in the slipped-AA structures for **TpOMe-Pa1** [D=3.17Å, d=2.07 Å, θ =175.2], **TpOMe-PaNO**₂ [D=3.31 Å, d=2.26 Å, θ=157.9°], TpOMe-Tab [D=3.24 Å, d=2.17 Å, θ =160.4°], **TpOMe-BPy** [D=3.24 Å, d=2.16 Å, θ =163.5°], **TpOMe-Azo** [D=3.24 Å, d=2.15 Å, θ =166.3°] suggested the existence of C-H ···· N H-bonding in these COFs (Table S9). However, in case of **TpOMe-BD(NO**₂)₂ (slip-AA), the methoxy(-OCH₃) groups lie mainly in the plane of the aldehyde phenyl ring, due to the presence of intralayer C-H•••O [D=3.27 Å,

d=2.18 Å, $\theta=167.5^{\circ}$] H-bonding between the methoxy (-OCH₃) C-H of the aldehyde and the nitro (-NO₂) oxygen atom of the $BD(NO_2)_2$ amine (Figure 2d and Table S10). The calculated distances in either cases are within the range of appreciable C-H•••N or C–H•••O ($d \le 2.7$ Å, $\theta \ge 150^\circ$) H-bondings, as evidenced from similar kind of H-bonding interactions reported in small molecule crystal structures (Figure S31).[8d-f] The presence of such C-H ... N H-bondings thereby provide significant steric hindrance and hydrophobic environment around the imine bonds making it safe from hydrolysis (Figure S23 and S24). In contrast, TpOMe-BD(NO₂)₂ lacks such interlayer C-H ···· N H-bonding, instead it maintains only intralayer C-H···O H-bonding. Hence, the imine (-C=N-) bonds, which are devoid of such stabilizing Hbonding get disrupted via the rapid attack from H⁺ or OH⁻ ions, signifying the lower chemical stability of TpOMe-BD(NO2)2 (Figure S22 and S25). Hence, the overall findings evidently indicate that the remarkable chemical stability of these materials does not depend upon the mere presence of the methoxy (-OMe) functionality in the frameworks but due to the existence of such stabilizing interlayer H-bonding.

Owing to their comparatively easy route of process-ability and high crystalline nature, self-standing TpOMe-Azo COF membranes (COFMs) and other shapes like spheres, cylinders, beads were synthesized (Figure S37 and S38). The assynthesized defect-free membranes exhibit high crystallinity and porosity similar to the parent COF. SEM images showed that the membranes (thickness ca. ~350 μ M) are composed of ~1-3 μ M crystallites, which are perfectly packed with each other (Figure 3a and Figure S40). Moreover, to address the chemical stability of the as-synthesized membrane, a coupon of 1 cm diameter and ~350 µm thickness was submerged in 3 ml of HCl (12 N, seven days), H₂SO₄ (18 N, seven days), H₂SO₄ (36 N, three days) and NaOH (9 N, 24 h). The same physical appearance (Figure S37) and other structural investigations like PXRD, FT-IR, N₂ adsorption and SEM imaging of the chemically treated membranes reflect only small alteration in the underlying framework structure (Figure 3b, c and Figure S39, S41).

We utilized this COFM as the high-performance separation membranes in a drastic environment, where toxic solvents or highly acidic solutions are involved. The COFM showed considerably high solvent flux for acetonitrile (280 Lm⁻²h⁻¹bar⁻¹),

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Figure 3: Application of **TpOMe-Azo** COFMs in waste solvent treatment. (a) Digital image of **TpOMe-Azo** COFM and its SEM images (top view). (b) Physical appearance of **TpOMe-Azo** COFM after treatment in 18 (N) H₂SO₄ for seven days and corresponding SEM images (top view). (c) PXRD patterns of different acid and base treated **TpOMe-Azo** COFM after stipulated time duration as mentioned. (d) Plot for different solvent permeance through **TpOMe-Azo** COFM (e) Physical appearance of the stated membrane before and after permeance of 12 (N) sulfuric acid. (f) Tabular representation for a quantitative test for protons in permeate through the titration test with standard aq. NaOH base.

followed by acetone (260 Lm⁻²h⁻¹bar⁻¹), methanol (200Lm⁻²h⁻¹bar⁻¹) ¹), water (170 $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$) and ethanol (150 $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$), reflecting its potentiality towards waste solvent treatment (Figure 3d and Table S11). Furthermore, sulphuric acid is a highly important manufactured chemical by many industries, not only due to its usability in various reactions but also due to its high reactivity. Although many methods have been demonstrated for its decomposition after reaction, very few attempts have been done for its recovery from the reaction mixture.^[9] In these circumstances, we believe that sulfuric acid purification via membrane permeance could be another route for its recovery process. Considering the high chemical stability of as-synthesized TpOMe-Azo COFM, we passed a different aqueous solution of H₂SO₄ with a concentration of 1 N, 3 N, 6 N and 12 N through the membrane where it shows the permeance as high as >99% (Figure 3f and Table S12). The physical appearance of the membrane was significantly intact reflecting its robustness during the process (Figure 3e). On every occasion, the strength of the eluted sulphuric acid solution was estimated via titration with the standard aqueous sodium hydroxide (0.5 N) using phenolphthalein as an acid-base titration indicator (Figure 3f, Table S13),. Furthermore, the COFMs were utilized for challenging separations (>99%) of expensive ingredients like methylene blue (MB), toxic dyes such as rhodamine b (RH), rose bengal (RB) and congo red (CR), from drinking water with high recyclability as reveled from comparative UV-Vis spectra studies between feed and the permeate of the respective dyes (Figure S42, S43 and Table S14).

In summary, we have designed and synthesized a series of imine (-C=N-) linked porous and crystalline COFs via the saltmediated crystallization process. The as-synthesized materials showcased ultra-high chemical stability in extremely drastic media such as strong acids (conc. H₂SO₄, 36 N and conc. HCl, 12 N; seven days) and base (NaOH, 9N; 24h). DFT calculations revealed that the presence of interlayer H-bonding is mainly responsible for the ultrahigh stability of these materials, as it protected the imine bond from hydrolysis by providing enough steric hindrance and hydrophobic environment. The COFs were further transformed into self-standing, continuous and defectfree covalent organic framework membranes (COFMs). These as-synthesized COFMs are highly useful for the sulphuric acid recovery, and the removal of toxic substances from drinking water. In these circumstances, we believe that the easy and large-scale production of COFs and COFMs using this approach may pave its future applications in industries.

Acknowledgements

AH & SB acknowledge CSIR, SK acknowledges UGC, India for research fellowships. AC thanks SERB NPDF (PDF/2015/000622) for a fellowship. We acknowledge Himadri S. Sasmal for single crystal data collection. RB acknowledges DST Indo-Singapore Project (INT/SIN/P-05) and DST Nanomission Project (SR/NM/NS-1179/2012 G) for funding. We acknowledge Dr. T. G. Ajithkumar & Anjali Krishna M. for the NMR; Dr. C. Ramesh & Dr. K. Guruswamy for PXRD facility.

Keywords: Covalent organic framework • Hydrogen bonding • Ultra-stable • Density functional calculations • Membranes

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In the present work, we showcase rapid and scalable construction of highly porous and crystalline iminelinked COFs with ultra-high (H₂SO₄, 36 N; HCI, 12 N; NaOH, 9N) stability. The exceptionally high chemical stability was examined due to the presence of significant no. of interlayer C-H ···· N H-bonding among the adjacent COF layers which through steric and hydrophobic environment protects and prevents imine (-C=N-) bond hydrolysis as revealed from density fuctional theory calculations (DFT) study.

4.95 Without Interlayer inter H-bonding H-2 4.95 August Au	Vith onding 2.15 2.43 (173.9 170.4 0) 2.39
As synthesized - As synthesized - In H_SO ₄ (c) for td	strong interlayer C—H···N H-Bonding - As synthesized - In H ₂ SO ₄ (c) for 7d
10 20 30 20 (Degree)	10 20 30 20 (Degree)

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Ultra-stable Imine-based Covalent Organic Frameworks for Sulfuric acid Recovery: An Effect of Interlayer Hydrogen Bonding