COVALENT ORGANIC FRAMEWORKS AND ITS APPLICATION TOWARDS IONIC CONDUCTIVITY: A MINIREVIEW

Abstract

Covalent organic framework (COF) materials gained immense research interest since its emergence. However, two dimensional COF experiences comparatively better applications than its three dimensional counterpart and thus are reported in higher numbers. The emergence of COFs is due to its better thermal and chemical stability thereby providing opportunity towards wider applications in energy storage, catalysis, gas adsorption and separation, sensing, optics, etc. In recent days application of these materials for conduction is the growing interest of the researchers. In this minireview we aimed to describe about the applications of COFs particularly towards ionic conductivity.

Keywords: Covalent organic framework (COF), crystallinity, porous polymer, conductivity

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I. INTRODUCTION

Covalent organic frameworks (COFs) is composed of connecting various organic monomeric units (also known as building blocks/units)linked periodically across the crystal lattice via covalent bonding following the principles of reticular chemistry affording predetermined network structures [1-5].Thus the selection of suitable building blocks holding reactive functionalities that could trigger the formation of dynamic covalent bond is the vital and challenging aspect in COFs synthesis. Precisely, directing building blocks to construct discrete bonds is extremely difficult and that is why construction of such materials is imperative. Moreover, attaining the precise control over the reaction is crucial as it could lead for irregular linking of building units affording network solids with poor crystallinity. Since the entire structural architecture of COFs are constructed from lighter elements through covalent bond and are havingsufficient porous space these materials are having low density along with high chemical and thermal stability. As structure and chemical environment of COFs can be tailored made by tuning the functionality and porosity, it provides extra handle to the researchers indulging in COF chemistry. The versatile applications of COFs in various fields that includes catalysis, optoelectronic devices, environmental applications, sensing, nanoreactor,biomedicine, etc. evidence its importance in various industries [6-18].Despite being providing foundation for the reformation of many branches of industry,COFs also shape us to advance our philosophy of the functional materials.Design and synthesis of such porous system with desired properties is expected to serve as implants of new generation.

Even though this field of research under materials chemistry division emerged after the seminal work of Omar Yaghi in 2005, the huge space regarding the synthesis of COF structures is still available as reflected by the growing number of articles appearing in the reputablejournals. However, construction of large number of two dimensional 2D COFs with varied applications emerges as a remarkable development and progress in this field of research. To mention, two orthogonal processes controls the growth of 2D-COFs. First, thermodynamic control of covalent bond formation during polymerization and second,crystallization of 2D layers formed through supramolecular interactions.Although the majority of 2D COFs reported so far are in powder form the membrane/film of such materials is evolving and is of growing attractionin recent days[19].In this perspective,we particularly emphasis on the syntheticdesignand potent applications of 2D COFs in exhibiting conduction behavior. We hope this perspective could able to provide various imperative facts providing ease to better understand about 2D frameworks as conducting materials.

II. DESIGN AND SYNTHESIS OF 2D COF

The reversible linkage, shape, symmetry and size of considered monomeric/building units in a periodic manner affords the crystalline COFs with predetermined skeleton. The π–π stacking in the covalent 2D layer governs the periodicity of the 2D COFs with layered structure.Mostly, these are constructedthrough Schiff base condensation reactions. However, very recently acid and base catalyzed aldol condensation is gaining attentioninpreparation of 2D COFs.Acharjya*et al.*articulated vinylene linked 2D COFs (V-COF) viabase catalyzed aldol condensation of aryl aldehydesto be reticulated into crystalline frameworks[20].To mention the various synthetic methodsadopted in general for the synthesis of predesigned COFs are described subsequently.A triazine based cyclotrimerized covalent triazine framework has been obtained by Thomas and his groupfrom 1,4-benzenedinitrilefollowing the ionothermal process[21]. The reaction is catalyzed at high temperature (400 °C) using molten $ZnCl_2$ as catalyst to yield COF that exhibits excellent thermal stability. Conversely this process is extremely limited due to its inability to form regular ordered structure and thus till date only two COFs have been reported following this synthetic method.In another synthetic process known as solvothermal processreactants are allowed to react in a closed container at around 120 °C in common for few days under high pressure.This process allows precise control over shape, size and crystallinity behavior of the material. Research group led by Dichteldeveloped a new approach to this processby introducing single-layered graphenesheetas a supporting layer template attributing 2D COFwith good crystallinity [22] Banerjee and his research group for the first time familiarize the use of mechanochemistry towards design and synthesis of 2D COFsthrough a greener approach and an ancient idea promoting solid state reaction in supramolecular chemistry[23]. His group reported three isoreticular COFs at room temperature with higher stability in boiling water, acids and bases. These COFs are of layered morphology unlike the parent solvothermally synthesized COFs. Air water interfacial synthesis of COF film with enhanced crystallinity exhibiting better conductivity behavior is an evolving technique and is garnering wide interest [24, 25].

Post synthetic modification of the synthesized COFs provides a platform to incorporate metal ions onto it via coordination chemistry forming σ dative bonds. Such metalation is opening a new avenue of COFs towards heterogeneous catalysis.To facilitate such modification of COFs it is obligatory to haveavailable certain ligands in the COF skeleton for metalation. Some of the accessible ligands that are present so far in the post synthetic modification COFs are describedin a review article by Ramos group[26].At the onset,Ding *et al.*elucidated the modification of imine COF with Pd (II) ion that acts as an activecatalytic sites in Suzuki-Miyaura couplingreaction[27].Literature evidences various other meal ions immobilized through post treatment of COFs. However, for such modification 2D COFs revealing layered/sheet like arrangement with an efficient π–π stacking remains advantageous.Intriguingly the functionality in COF composition is also modified in recent days although such change in the backbone is limited. Haase*et al.*explored such rare conversion by substituting imine functionality by thiazole with intact chemical structure using elemental sulfur in the process through the formation of thioamide as intermediate[28].It is worthless to mention that microwave heating is another well adopted synthetic technique in organic chemistry since decades for the substantial reducion of reaction time.Wei *et al.*synthesized β-ketoenamine linkage 2D COF, TpPa-COF-1 by microwave irradiation of the monomers mixture at 100 °C for just 1 h which otherwise takes a prolong reaction time of 2-3 days and high temperature [29-31].

III. APPLICATION OF COFS AS CONDUCTING POLYMERS

Intensive studies over the last few decades on conducting polymers prove its emergence as in electronic and optoelectronic devices. However, the lack of well-defined polymeric structure precludes the efficient conductivity of the polymers. COFs having well-defined crystalline structure with extended π-conjugation and tailor-made chemical propertiesrepresents as a suitable candidate of polymeric materials that exhibits conductivity. Moreover these materials are known to maintain the bandenergy alignment, structural geometry, and π-columnar densitythat regulate the generation and separation of photogeneratedexcitonsas well as the charge carrier lifetime [32].

Banerjee and his group for the first time demonstrates the application of COFs towards proton conductivity through impregnation of phosphoric acid (H_3PO_4) into nonconductive and highly stable azo (–N=N–) based COF [33]. The high scope of extended hydrogen bonding owing to ionizable O−H bonds attributes to high proton conductivity of H_3PO_4. The mineral acid (H_3PO_4) loaded azo (–N=N–) based COF exhibits proton conductivity of 9.9×10^{-4} S cm^{-1} and 6.7×10^{-5} S cm^{-1}(Figure 1) in hydrous and anhydrous conditions respectively.His group also established mechanochemically synthesized COFsas an efficient electrolyte in polymer electrolyte membrane (PEM) fuel cells[34].

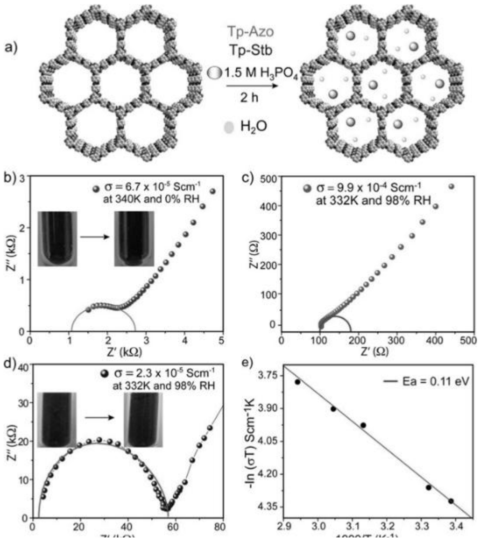

Figure 1. (a) Schematic ofH_3PO_4 doping in COFs. Proton conductivity of PA@Tp-Azo in (b) anhydrous and (c) hydrous conditions. (d) Proton conductivity of PA@Tp-Stb in hydrous conditions. (e) Arrhenius plot for PA@Tp-Azo in hydrous conditions.Reproduced with permission from ref. 30.Copyright2014 American Chemical Society.

Donglin Jiang and co-workers demonstrates a mesoporous COF (TPB-DMTP-COF) attributing proton conductivities 2-4 times higher in magnitude than microporous and non-porous polymers upon loading of *N*-heterocyclic proton carriers [35].The triazole and imidazole loaded TPB-DMTP-COF (trz@TPB-DMTP-COF and im@TPB-DMTP-COF) was observed to have good thermal stability. Unlike the proton conduction by pure triazole and imidazole molecule, the im@TPB-DMTP-COF exhibited higher conductivity than trz@TPB-DMTP-COF as triazole experiences lower concentration of proton due to two lone-paired N atoms in it as compared to one in imidazole. Furthermore, the conductivity value depends on the weight percentage of heterocycles loaded in TPB-DMTP-COF.As such im@TPB-DMTP-COF with 82 wt% imidazole exhibits conductivity of 2.03×10^{-4} S cm^{-1}, whereas with 164 wt% exhibits of 4.37×10^{-3} S cm^{-1} at 130 °Crespectively.Proton conduction via N-heterocycles loaded materials is proportional to the hydrogen bond donor ability in it. Introduction of thiophene rings into the structural architecture of imine linked COF enhances the hydrogen bonding ability of imine bond with the encapsulated imidazole thereby increasing the conduction ability of imidazole loaded COF.Shuai Li et al provides further addition to the candidature of imidazole as a good carrier of proton in COF materialsrendering as intrinsic proton conductor[36]. Vapour diffusion method was adopted to incorporate 30 % and 50 % of imidazole into pristine Py-BT-COF, Py-TT-COF, and Py-

BD-COF. The imidazole encapsulated COFs exhibit 6- to 14- fold increase in its proton conductivity as the temperature raises from 80 °C to 130 °Crespectively.

An aza-fused π-conjugated COFs with 1,10-phenanthroline-like units into the pores of the COFs skeleton wassynthesized through condensation of hexaketocyclohexane with hexa and tetra-topic amines that accomplish proton conductivity[37].“The unique features of this molecular design for proton conduction are threefold: (1) access to rigid porous scaffolds through thermally and chemically stable pyrazine linkages; (2) bottom-up synthetic assembly of structurally rigid and chemically homogeneous channels with polyaza environment that can facilitate the uptake of water molecules and provide ordered pathways for proton transport; and (3) modular approach for enhancing the proton conductivity through acidification of the aza-fused structures.” One of the unique property of 1,10-phenanthroline is that it can absorb water molecules via O−H···N hydrogen bonding. This hydrated moiety can be easily protonated by acid to accomplish proton conductivity. Proton conduction is directly proportional to the concentration and mobility of protons in the materials. In this context, the synthesized aza-fused COFs with 1,10-phenanthroline-like unitsare modified by doping with H_3PO_4, a suitable acid used in many protonconductive materials and enhanced its proton transport under 97% relative humidity (Figure 2) as analysed by impedance spectroscopy. The superior proton carrier activity of H_3PO_4 loaded COF has also been further described by Tao *et al*. exploring the 1D nanochannels with available hydrogen bonding sites in its pore wall in form of nitrogen[38].

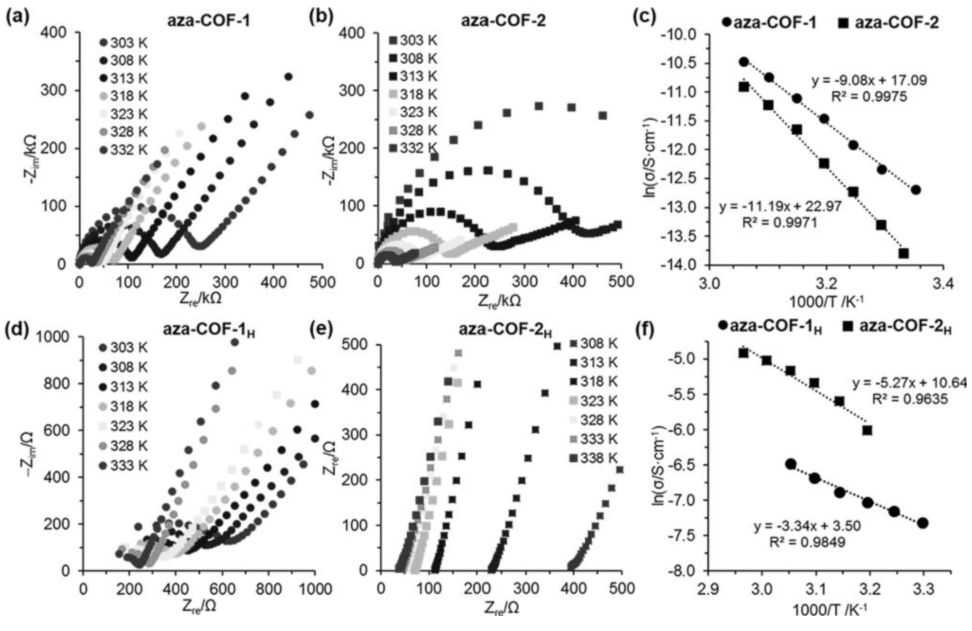

Figure 2. (a and b) Nyquist plots of aza-COF-1 and aza-COF-2 measured under 97% RH at different temperatures showing the temperature dependence of proton conductivities. (c)Arrhenius plots for aza-COF-1 and aza-COF-2 at different temperatures. (d and e) Nyquist plots of H3PO4 acidified COFs aza-COF-1H and aza-COF-2H. (f) Arrhenius plots for aza-COF-1H and aza-COF-2H. Circles and squares are experimental data; dashed lines are curve-fitting results.Reproduced with permission from ref. 34.Copyright2019 American Chemical Society.

Peng*et al.*introduced the sulfonic acid group into the 1D nanoporous channels of the 2D COF synthesized from liquid assisted mechanochemical grinding of the monomers 1,3,5-triformylphloroglucinol and 2,5-diaminobenzene-1,4-disulfonic acid[39].The well aligned sulfonic acid group into the pore walls facilitates proton conduction due to its ionization in hydrous condition. At ambient temperature this sulfonated COF exhibits intrinsic proton conductivity of 3.96 × 10^{-2} S cm^{-1}at 97% relative humidity (Figure 3) with remarkable stability.This work advocates the immense capability of sulfonated COFs to be explored as protonconductivematerials. Implementing crystallization approach Banerjee and co-workers could successfully synthesize a series of flexible and self-standing COF membraneswith the in situ loading of *p*-toluene sulfonic acid ($PTSA·H_2O$) [40].The membranes are tested as proton reservoirs for proton exchange membrane (PEM) fuel cells and measures proton conductivity of 5.3 × 10^{-2}–7.8 ×10^{-2} Scm^{-1}under 95% RH at 80 °C. This study describes an important findings that the in situ $PTSA·H_2O$ loaded COF membranes exhibits high conductivity than the ex situ loaded membranes despite of being high loading percentage of $PTSA·H_2O$. Such poor activity attributes to irregular entrapment of $PTSA.H_2O$, the proton carriers into the cavities of COF compared to regular entrapment into the COF matrix if loaded in situ.

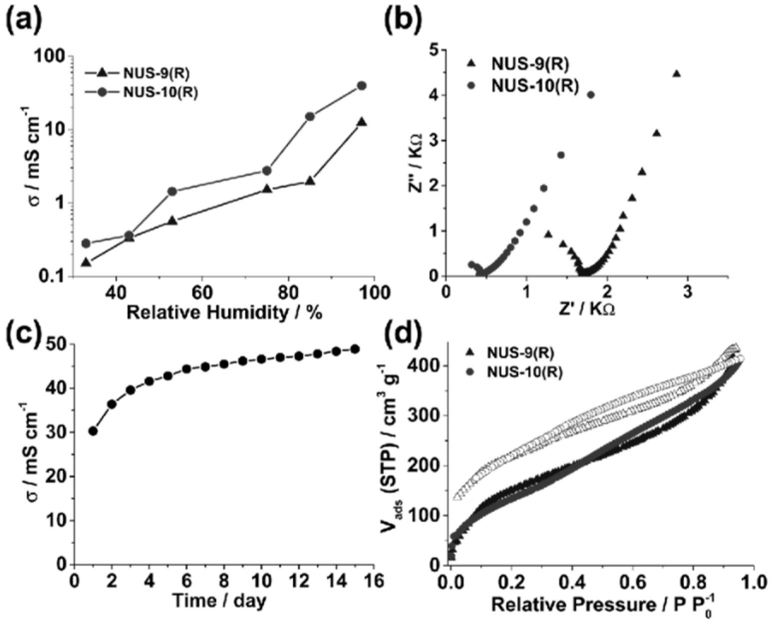

Figure 3. (a) Proton conductivity of NUS-9(R) and NUS-10(R) measured at 298 K under different relative humidity. (b) Nyquist plots of NUS-9(R) and NUS-10(R) at 298 K and 97% RH. (c) Time-dependent proton conductivity of NUS-10(R) recorded at 298 K and 97% RH. (d) Watervapor sorption isotherms of NUS-9(R) and NUS-10(R) at 273 K. Each proton conductivity test was repeated at least 3 times and an average valuewas reported.Reproduced with permission from ref. 39.Copyright2016 American Chemical Society.

The synthesis of proton conductive COFs is associated with two simple strategies. "These are: 1) Fabricating intrinsic proton conductive COFs through the covalent incorporation of proton donor groups such as sulfonate, imidazole, and phenolic hydroxyl groups into COF skeletons; 2) endowing COFs with extrinsic proton conductivity through doping of proton carriers such as H_3PO_4 into COF pores[25, 41-45].”Thus, it is anticipated for the COFs to render high proton conductivity upon assembling the above two strategies in a single system. In addition the introduction of the functional groups with high hydrophilicity into the COF skeleton could also facilitate the process of conductivity.Yang *et al*. strategically synthesized a series of 2D COFs (NKCOF-1, -2, -3, -4, NKCOF=Nankai Covalent Organic Framework) with plenty of azo and hydroxyl groups into the COFs skeleton thereby successfully fabricating both intrinsic and extrinsic proton conductivity in a system [46].Owing to the presence of azo and hydroxyl groups the NKCOFs are endowed with high hydrophilicity and enhanced absorption of water molecules into the pores with the subsequent rise in proton conductive behavior following Grotthuss mechanisms.Thus, it is worthless to mention that increase in hydrophilicity of the conductive materials evidences influence in the proton conductivity.

COFs with added advantages of tuned functionality into its skeleton represents as a potent candidate to be used in PEM fuel cells too. A sulfonic acid functionalizedCOFs (SCOFs) using the solvent thermal method was synthesized andis exfoliated into covalent organic nanosheets (CONs) using the micromechanical cleavage technique. Nafion-based composite proton exchange membranes (PEMs) were produced by incorporating well-dispersed SCONs with Nafion using a solution casting method [47].The higher sulfonic acid contentinside the SCOFs and the penetrating pore structure allow forfaster proton transport. Meanwhile, the electrostatic interaction between SCOFs and Nafion polymer molecules can inhibitthe swelling of composite membranes, reducing methanolpermeability at the same time. In order to confirm thisconjecture, multiple performances factors of compositemembranes were investigated, including proton conductivity,micro-morphology, methanol permeability and so on. Thesimple development method makes the Nafion-SCONs membrane a possible candidate for application in proton exchange membrane fuel cells (PEMFCs). The introduction of SCONs not only increased protontransport, but also inhibited methanol permeation as a resultof the evenly distributed microstructure. Once the SCONscontent reached the appropriate standard, such as in theNafion-SCONs-0.6 membrane, the composite membranecould realize improved experimental results, such as higherwater uptake, lower swelling ratio, improvement in protonconductivity, lower methanol permeability, and enhancedfuel cell performance compared with the pure Nafion membrane. Zheng group recently employed air water interfacial polymerization technique synthesizing thermally conductive COF film [25].

It is worthless to mention that the open and ordered columnar channels in 2D COFs bids huge platform for the incorporation of guest molecules rendering specific functions.Moreover, the adjustable size, shape and chemical environment of the channels is the added advantages. In addition the introduction of desired functionality into the COF skeletons could expand their scope of specific properties. However, the chemical stability of the parent COFfor such modification is an imperative factor. The reinforcement of interlayer interactions by choosing the monomers with large conjugated structure in COF synthesisis an established technique to improve its stability. Xie *et al.* demonstrates the dibenzo [*g,p*]chrysene-based heteroporous COF acting as host for the ionic conduction [48].Dibenzo [*g,p*]chrysene (DBC) being associated with large conjugation are susceptible to form columnar channels accomplished with strong interlayer interactions. Considering DBC precursor an imine based building unit with D2h symmetry was synthesized and applied to prepare the heteroporous 2D COF, DBC-2P having remarkable chemical and thermal stability. Associated with ordered heteroporous nanochannels, the DBC-2P is considered to explore as host for the confinement of a guest molecule into the nanochannels. Accordingly, polyethylene glycol (PEG) was encapsulated as a guest into the 1D columnar channels of DBC-2P. The PEG mobilized DCB-2P renders hygroscopicity for the accommodation of H_2O into it channels to exhibit ionic conductivity. Performing the electrochemical impedance spectroscopy (EIS) the ionic conductivity estimated for DBC-2P with 28 wt% PEG at 70 ºC and 98% RH is 4.50×10^{-5} Scm^{-1}. Whereas, that exhibited by DBC-2P under identical conditions is 8.49×10^{-8} Scm^{-1}. Moreover, the significant enhancement in conductivity is witnessed upon incorporation of PEG-$LiBF_4$ salt into DBC-2P. The PEG-$LiBF_4$encapsulated DBC-2P accomplished a 52-fold rise in ionic conductivity (2.31×10^{-3} Scm^{-1}) than that evaluated for DBC-2P with PEG polymer at 70 ºC and 98 % RH. Such a remarkable outcome is owed to synergistic effect of H_2O and Li^+ in the columnar nano channels [49, 50].

Guo et al engineered the pore walls of β-ketoenamine-linked COF, TpBD-Me, with quaternary ammonium (QA) ions by means of post synthetic modification with intake morphology and crystallinity of parent TpBD-Me [51]. The resultant QA functionalized TpBD-Me illustrates anion (bicarbonate) conductivity of 5.3 mS cm^{-1} and 27 mS cm^{-1} at 20 ºC and 80 °C respectively. Introduction of QA into the pore walls transform the channels in TpBD-Me into anion conducting channels by increasing the hydrophilicity of the COF material attributes enhancement in anionic conductivity. Jiang and co-workers generated ionic interfaceto facilitate ultrafast ion transport across 1D channels of COFs via engineering its pore surface with electrolytic chain [52].The engendered ionic interface constitutes for the increase in ionic mobility and transport.Employing microwave heating method, a germanate COF has been synthesized by Ashraf et al with 9,10-dimethyl-2,3,6,7-tetrahydroxy-anthracene linker. The large pore size and lower charge density of Ge perhaps provide luxury for the Li^+ hopping to exhibit better ionic conductivity [53].

IV. CONCLUSION/OUTLOOK

In this minireview we have highlighted the recent development in COF chemistry towards its application in ionic conductivity. In our thorough discussion about the subject focused we could observe that COFs advocates as a good candidature carrying species responsible for conduction with excellent stability. Although the utility of these organic framework materials rendering conduction is increasing, the majority of those are prone to proton conduction. The structure-property relationship requires more attention and research to spread the application of COFs towards other ionic conduction. With tremendous growth of COF materials for proton conduction, further development in this area of research is motivational and expected for its applications in the domain of conduction.

V. CONFLICT OF INTEREST

The authors declare no conflict of interest.

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