Journal of Scientific Research
Banaras Hindu University, Varanasi

Vol. 63, 2019 :219-227
ISSN : 0447-9483

COVALENT ORGANIC FRAMEWORK BASED MATERIALS FOR SENSING AND SELF-ASSEMBLY APPLICATIONS

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Abstract

2D covalent organic frameworks and their few layer analouge with sub-ten nanometer thicknesses and high aspect ratios have received a great deal of attention for their graphene-like topological features, tunable optical properties. Rational synthetic strategies of these 2D covalent organic frameworks may lead to the realization of unprecedented structural precision and expected properties. Herein, a brief review of the recent literature has been presented targetting the sensing and self-assembly properties of 2D covalent organic framework based materials with suitable examples. Such 2D organic nanostructures have a brilliant future as multifunctinal materials, exhibiting great response as platforms for engineering novel optoelectronic, bioactive properties and as hybrid materials.

Keywords: covalent organic frameworks, covalent organic nanosheets, 2D-Platform, Sensing, Self-assembly.

Introduction

The 2D feature is unique and indispensable to access unprecedented physical, electronic, and chemical properties due to electron confinement in two dimensions. Since the introduction of covalent organic frameworks (COFs) by Yaghi and coworkers in 2005 [1], large numbers of different COFs have been synthesized from rationally chosen building blocks for a plethora of applications in areas such as gas separation, energy storage, catalysis, and electronics. Recently, 2D covalent organic nanosheets have emerged as a new member in the family of 2D covalent organic frameworks and in very short span of time it has received increasing attention with potential applications in chemical sensing, and antimicrobial coatings materials [2, 3].

Moreover, in quest of new 2D material, inspired by the development of 2D inorganic nanomaterials, and graphene, 2D-COFs, as well as single or few layered covalent organic nanosheets (CONs) featuring few atom-thick sheets with extended covalently bonded building blocks, have attracted great attention in recent years [4, 5]. With their unique graphene-like topological structure and the merit of structural diversity, CONs promise to possess designable properties such as; 2D-CONs with an extended π-conjugation may exhibit interesting in-plane carrier-transportation behavior, which can be a promising characteristic for optoelectronic applications. In addition, 2D-CONs can be turn into a scaffold for the construction of structurally well-defined 3D hybrid materials by wrapping, rolling, folding, or face to face induced stacking. To obtain CONs, the top-down approach facilitates is a better way compared to bottom-up approach which requires sophisticated reaction conditions and skilled techniques. The top-down approach mainly involves sonication, mechanical delamination, chemical exfoliation, self-exfoliation and solvent-assisted exfoliation leading to covalent organic nanosheets.

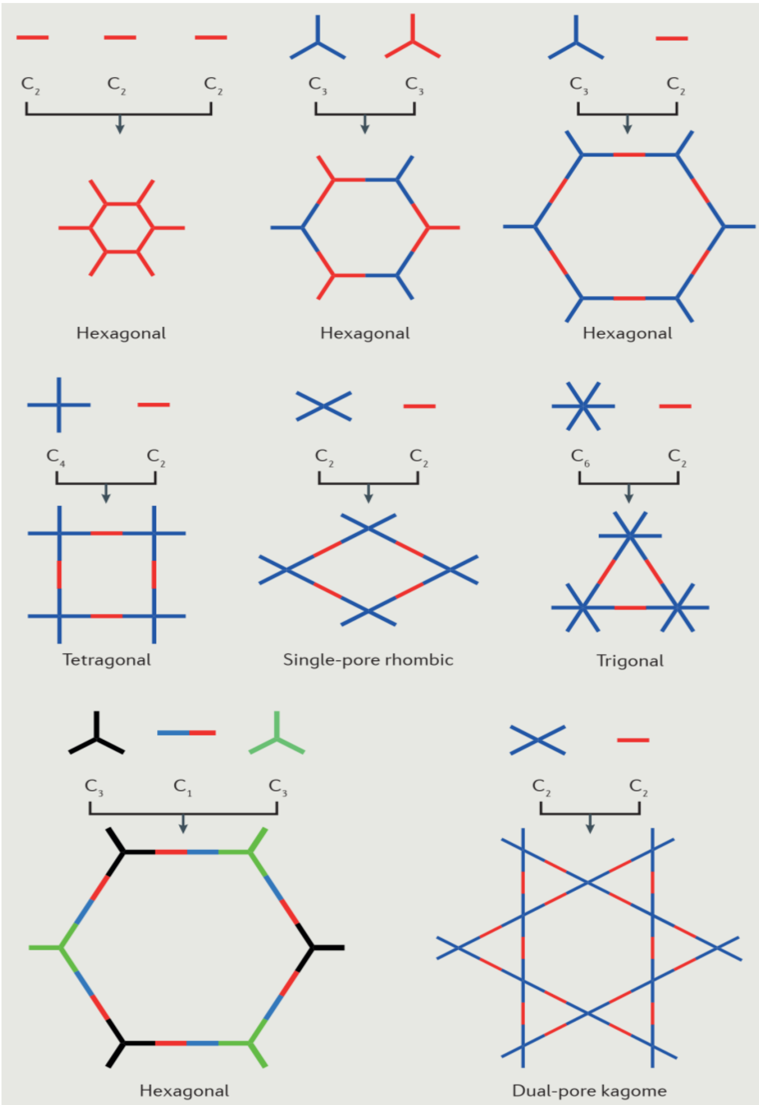

Fig. 1 Topology diagrams for designing 2D-COFs

Covalent Organic Frameworks/Nanosheets as Sensory Platform

Organic analogues of ultrathin 2D materials have recently been receiving increased attention because of their unique characteristics, such as light weight, good flexibility, high tenability, and adaptively[6]. Research into the design, synthesis, structural characterization, and material properties of synthetic 2D organic materials now represents an important branch of modern materials chemistry (Figure 1).The 2D-COFs itself or exfoliated few or single layered nanosheets (CONs) with inherent photophysical properties can serve as an effective sensory platform towards specific analytes. Han and Zhang coworkers have reported imine-linked COF (TPA-COF) which exfoliates into ultrathin 2D NSs and have demonstrated to be used as a novel fluorescence sensing platform for the highly sensitive and selective detection of DNA (Figure 2a and 2b) [7].Yan et. al. have reorted COF-based sensing platform for fluorescence turn-on detection of biomolecules such as ATP (Figure 2c) [8] while Yin and Zhang have developed the first example of a two-photon fuorescent COF nanoprobe, TpASH-NPHS, exhibiting a sensitive and selective fuorescent sensing and imaging of H_2S in live cells and deep tissues under NIR excitation (Figure 2d) [9].

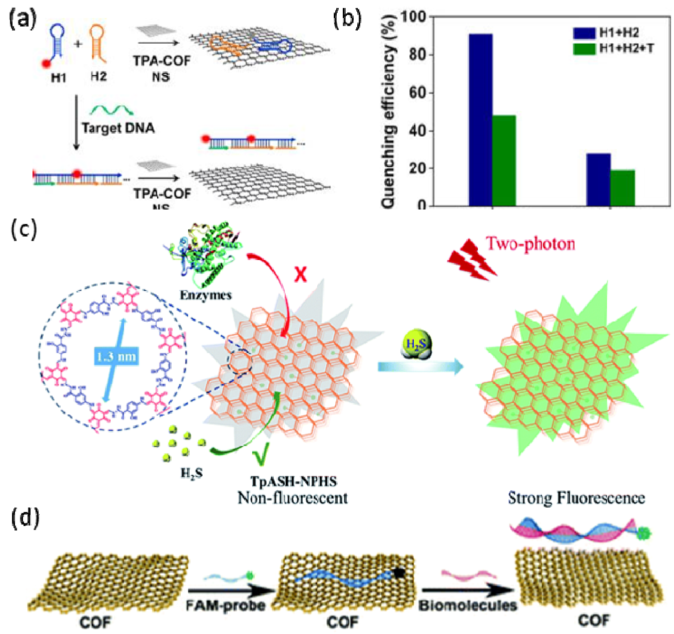

Fig. 2(a)Schematic illustration of a TPA-COF NS-based fluorescence sensor for detection of DNA.(b)Fluorescence quenching efficiency of TPA-COF NSs and bulk TPA-COF. (c) Constitution and mode of action of the COF-based nanoprobe Tp ASH-NPHS. (d) COF based probe for fluorescence turn-on detection of DNA and ATP.

Very recently Ajayaghosh et. al. have reported an ethidium bromide based self-exfoliated ionic covalent organic nanosheets (EB-TFP-iCONs) for label-free detection of dsDNA via supramolecular reassembly [10]. This DNA assisted reassembly of EB-TFP-iCONs create a hydrophobic environment over EB fragment of the iCONs, thereby preventing the excited state proton transfer process to water, thereby enhancing the emission (Figure 3). The ionic self-assembly phenomenon was also reflected in the overall surface charge of the cationic nanosheets as examined by zeta potential measurements.After adding a small amount of ctDNA concomitantly to the iCONs suspension, the positive value slowly reduced and finally a negative zeta potential value of ζ = -30.0±1.0 mV was obtained.Such reassembly process can also be used for the construction of hybrid/bio-hybrid material for advanced applications.

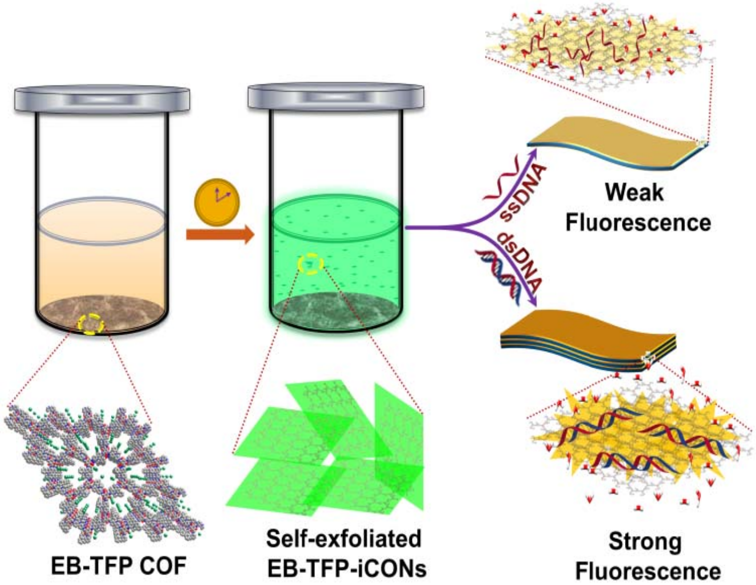

Fig. 3 Schematic representation for exfoliation of EB-TFP-iCONs and its application as a fluorescent platform for label-free detection of dsDNA.

COF based materials have also been utilized for addressing environmental issues such as removal of toxic heavy metal ions from water such as mercury and Cu^{2+}[11-13]. Recently Florian Auras's group has reported a solvatochromic covalent organic framework which exhibited a fast humidity sensor with full reversibility and stability over at least 4000 cycles [14]. A β-ketoenamine based covalent organic framework, reported by Mu and Liu co-workers demonstrated to serve as the first COF-based fluorescent pH sensor in aqueous solutions [15].Furthermore, these thin films COF materials can be utilized for the construction of smart responsive material which can respond to different external stimuli such as solvent, pH, heat, light etc.

Covalent Organic Frameworks/Nanosheets for Self-assembly Applications

Despite of substantial progress in the area of chemistry and application of covalent organic frameworks (COFs), reports on the precise construction of self-assembled nano- and microstructures as well as hybrid materials have been rare [16].These thin films COF materials can be utilized for the construction of smart responsive material which can respond to different external stimuli such as solvent, pH, heat, light etc. or can be used for supramolecular host-guest chemiistry [10].

MacLeod and Roseico-workers have demonstrated the host guest supramolecular chemistry of single layer covalent organic framework where COF synthesized from 1,4-benzenediboronic acid can act as host architecture where fullerenes guest molecules occupy the COF lattice at the solution/solid interface [17]. Rahul Banerjee et.al. have reported the single-step template-free method for hollow spherical covalent organic framework because of inside-out Ostwald ripening process (Figure 4) [18].

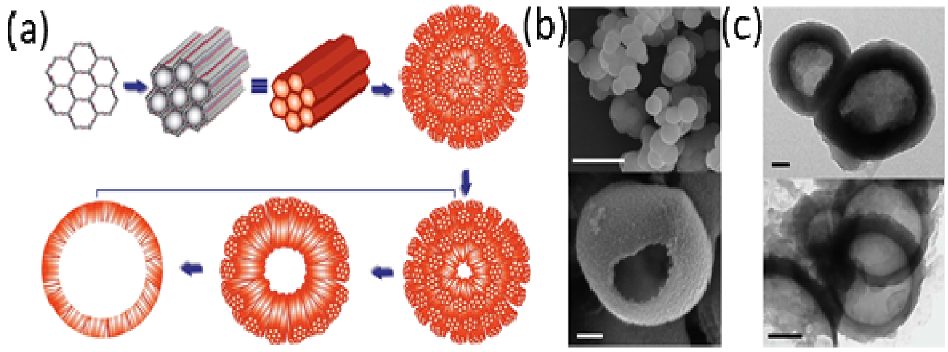

Fig. 4(a)Proposed mechanism of the formation of COF hollow spheres. (b) SEM images of COF-Dha Tab hollow spheres. (c) Transmission electron microscopy (TEM) images of COF-Dha Tab hollow spheres.

Florian Beuerleet. al. have reported the formation of Microtubular Self-Assembly. The DPP-TAPP-COF containing diketopyrrolopyrrole (DPP) and tetraphenylporphyrin (TPP) moieties exhibited a uniquehollowmicrotubular morphology with uniform diameters (Figure 5) [19]. Similar studies may open a new area in the field of covalent organic frameworks/nanosheets.

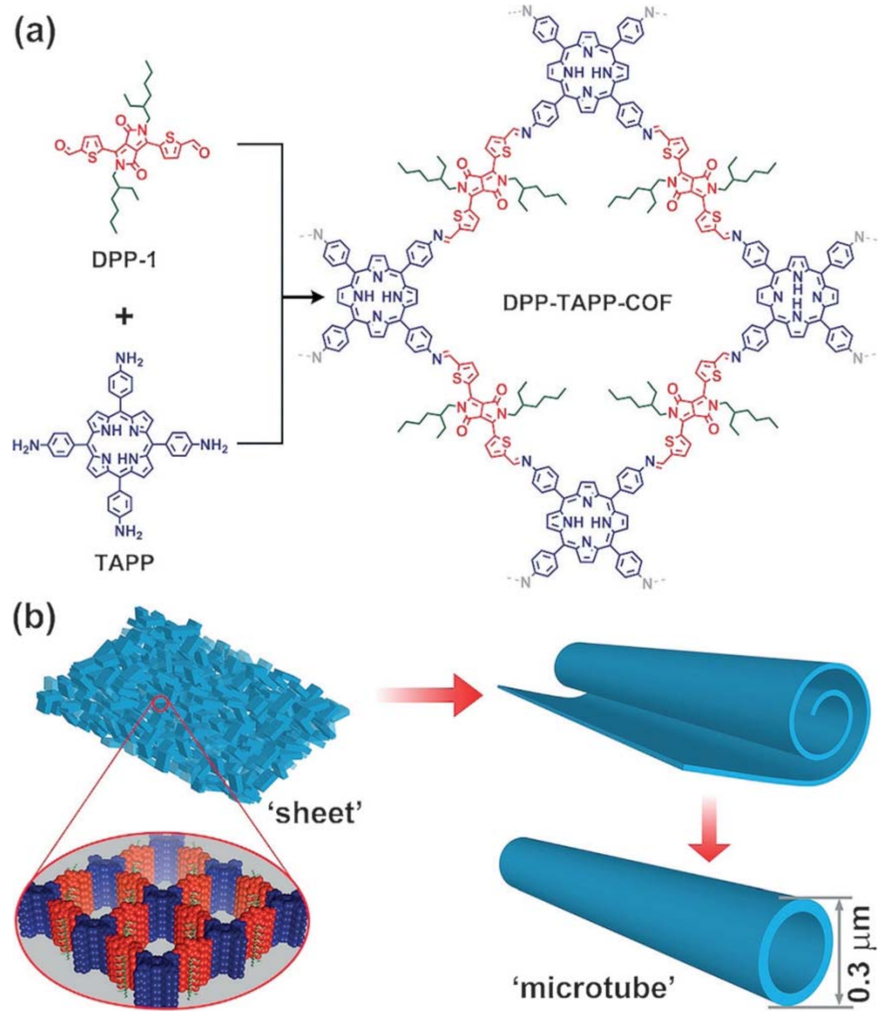

Fig. 5 (a) Synthesis and (b) proposed self-assembly of DPP-TAPP-COF into microtubes.

Challenges to be Addressed

- Development of new methodologies are still required to investigate bulk properties of the novel CON materials.
- Synthesis of new COFs/CONs of with multimodal detection properties.
- Post synthetic functionalization of 2D-CONs for different diagnostic purpose is still a challenge due to poor processability.

Conclusions

These 2D covalent organic frameworks and nanosheets are considered to be futuristic materials having potential application that could be utilized for various purposes and can provide a new paradigm in 2D materials and their applications such as;

- The water compatible covalent organic nanosheets have potential to be utilized for making aqueous self-assembly towards development of new bio-hybrid materials of wide range applications.
- Covalent organic nanosheets with Raman active properties can open a new door of fundamental research in 2D materials which can be used for various multimodal diagnostic purposes.
- The synthesized covalent organic nanosheets may serve as efficient platform for delivery of hydrophobic drugs.
- Suitable fluorescent covalent organic nanosheets/framework can be used for white light emission.
- New chiral covalent organic frameworks can be developed for heterogeneous asymmetric catalysis.

Acknowledgements

R.K.M. is thankful to DST, Govt. of India, for an INSPIRE Faculty Award (IFA-12 CH-50).

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