Materials Advances

Accepted Manuscript

Materials Advances

rsc.li/materials-advances

Volume 01
Number 1
February 2020
Pages 001-200

ISSN 2633-5409

ROYAL SOCIETY
OF CHEMISTRY

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

ROYAL SOCIETY
OF CHEMISTRY

rsc.li/materials-advances

Materials Advances

Materials
Advances

Review

Exploring Covalent Organic Frameworks through the Lens of Computational Chemistry

Parashmoni Rajguru,[a,b] Prarthana Bora,[a,b] Chinmoy Bhuyan[a,b] and Swapnali Hazarika*[a,b]

Covalent Organic Frameworks (COFs) are a special class of porous polymeric architectures with robust covalent bonds that can have two- or three-dimensional frameworks. They can easily be utilised for designing primary as well as higher-order architectures, and their unique properties make them a groundbreaking class of current scientific research. The advantageous properties of COFs include easily tunable porous structures, high surface area, low density, with great chemical and thermal stability. Having diverse molecular structures, they are promising candidates for ubiquitous applications, including energy and the environment. Employing various advanced computational methods such as grand canonical Monte Carlo (GCMC) simulations, molecular dynamic (MD) simulation, density functional theory (DFT), hybrid quantum mechanical/molecular mechanics (QM/MM), multiscale modelling and machine learning (ML) approaches, researchers provided profound understanding of interaction/adsorption mechanisms, performance-structure relationships and electronic behaviour of COFs even at atomic level, which often unattainable through conventional experimental methods. Currently, with emerging computational methodologies, computational techniques play a more imperative role in unveiling the exciting potential of COFs for global challenges-oriented applications, including environment, energy and sustainability. The review explores the critical role of computational chemistry during design, modelling, and applications of COFs, including key challenges and future perspectives, serving as a stepping stone for future advancements.

1. Introduction

Covalent Organic Frameworks (COFs) are an attractive branch of porous materials with exceptional physicochemical properties and is fully predesignable nature.[1] The advantages of COFs include extensive surface area, easy modifiability, tuneable pores, exceptional mechanical, thermal and chemical stability.[2,3] Nowadays, for the synthesis of COFs, trends have shifted from energy-intensive hydrothermal/solvothermal approaches to more energy and environmentally benign synthetic procedures such as microwave irradiation, electron beam irradiation, and ultrasound irradiation.[4] The COFs came into focus at the beginning of the 2000s and were synthesized based on the combined concept of organic chemistry synthesis with coordination chemistry. The synergistic approach was carried out to design a novel material having zeolite or MOF-type porous architectures, which also have the advantages of easy tunability as well as flexibility like organic polymers.[5] Yaghi et al., in 2005, designed the first 2D COF (COF-1 and COF-5), where a boronate-Ester linkage was used for the synthesis. They set the benchmark for the use of porous materials in material science research.[6] Again in 2007, Yaghi and colleagues became

the first to design 3D COFs (COF-102, COF-103, COF-105, and COF-108), employing co-condensation as well as self-condensation reactions of tetrahedral tetra(4-dihydroxyborylphenyl)methane (TBPM), silane analog of TBPM i.e. TBPS, and triangular hexahydroxytriphenylene (HHTP). Out of the designed COFs, COF-108 reportedly had the lowest density as compared to other reported crystalline materials at that time.[7] A pictorial representation of the advantageous properties of COFs and their broad range of applications is shown in Figure 1.[8]

From 2015 to 2025, a survey on the number of publications on "covalent organic frameworks" was conducted, which is represented in Figure 2. It is clearly observed that the demand for covalent organic frameworks has been increasing day by day. From the literature, there are approximately 500,000 different types of reported COFs, where the majority of them exhibited pore sizes ranging from 1 to 3 nm.[9] With the adjustable porous nature, extraordinary stability and high surface area, COFs are suitable for a wide range of separation and adsorption-based applications such as sensing, catalysis, gas separation, and storage applications.[10-12] Due to their high chemical and thermal stability, COFs can withstand harsh physicochemical conditions, which also makes them a potential candidate for various industrial applications. To screen out the application-specific materials in computational COF research, the primarily used databases are i) Computation-Ready and Experimental COFs (CoRE COFs), ii) Clean, Uniform, and Refined with Automatic Tracking from Experimental Database (CURATED COFs), and iii) hypothetical COF (hypoCOF) database,

[a]Chemical Engineering Group and Centre for Petroleum Research
CSIR-North East Institute of Science and Technology, Jorhat – 785006, Assam, India
Email: shrrljt@yahoo.com (Swapnali Hazarika)
[b]Academy of Scientific and Innovative Research (AcSIR), Ghaziabad – 201002, India
*Author for correspondence

Materials Advances Accepted Manuscript

etc.[13] While discussing COFs, their design, synthesis routes, structures and functions are very important aspects to consider. A hierarchical diagram showcasing these important features of COFs and the corresponding research scopes is given in Figure 3.
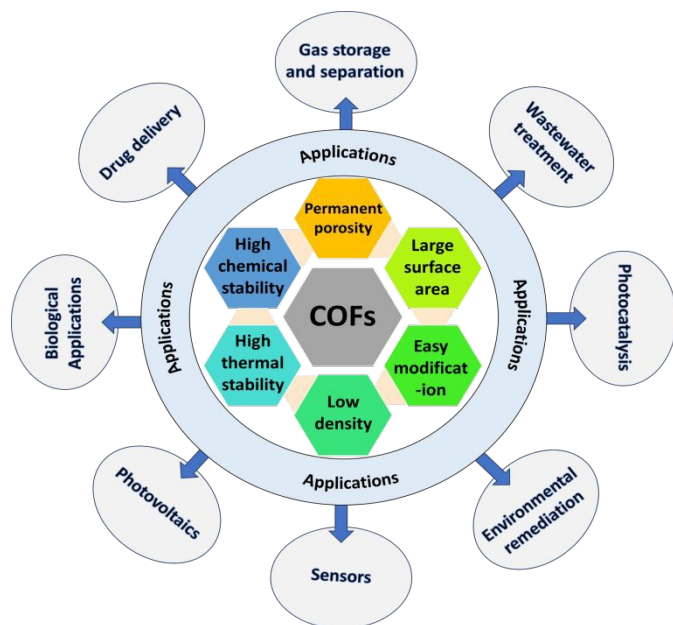

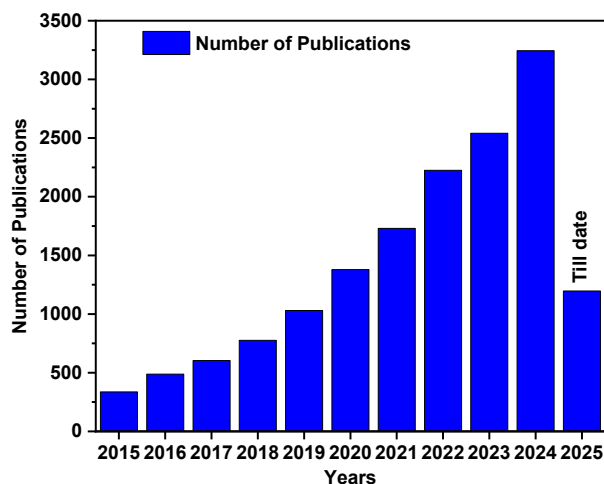**Fig. 1** Diverse properties and applications of COF.

Fig. 2 Publications on covalent organic frameworks in the last ten years (data was collected from Web of Science employing the term "covalent organic framework", accessed on 9th April, 2025).

To understand the design conditions and principles of COF synthesis at the atomic scale, the computational approaches are highly effective, offering hazard-free, cost-efficient and safer alternatives to conventional methodologies that require

expensive and hazardous chemicals.[13,14] As already mentioned, COFs can have both 2D and 3D structures. Various reported 2D and 3D COFs based on their shapes/structures are shown in Figure 4.[15] Evaluating the exciting potential of COFs from the computational point of view prior to carrying out experimental work allows us to delve into the change in material's behaviour or properties at molecular/atomic levels (under various modifications). Herein, a holistic up-to-date review, mainly focusing on using various computational tools for screening the structure, optimisation and property evaluation for numerous applications of COFs, is presented.

Owing to high surface area and tunable pore structures, COFs are extensively used in gas storage and separation applications, where computational studies can effectively boost their performance by exploring new possible designs. Ease of structural control and functionalization with meticulously arranged porous structure and enhanced selectivity make COFs attract tremendous interest from the scientific community. Computational screening of the building blocks and in-depth grasp of structural parameters as well as functional groups, may lead to the design of novel COFs for a broad range of applications.[16]

Before synthesis, computational studies can provide predictions of topologies and structural stability of a COF framework. DFT and MD simulations can reveal the stability, bonding and energetics of a COF architecture. Moreover, DFT and hybrid functionals can elucidate the electronic properties, such as frontier orbitals, band gaps, and charge distributions in COFs, which are highly essential for designing effective COF-based tailored materials for their applications in sensing, energy harvesting, and photocatalysis.[17] GCMC and MD simulations provide insights into adsorption, separation and diffusion behaviour of COFs, narrowing down the need for substantial experimental validation. From a huge database, computationally assisted screening can effectively pinpoint the most suitable COFs with superior (optimal) properties for particular applications.[18,17] Non-Equilibrium Molecular Dynamic (NEMD) simulations can provide an understanding of heat and mass transfer in COF membranes, including diffusivity, thermal conductivity and permeability.[19] In-depth computational studies can explore charge transfer and storage in COFs, and simulations of COFs integration to advanced battery systems, which may provide a new avenue for the development of next-generation batteries. Computational investigation of the electronic structure-property relationship may accelerate the design of COFs for green catalysis, environmental monitoring and biosensor applications. Computational interaction analysis of COF with drugs and biomolecules can provide a pathway for their use in effective and controlled drug delivery applications.[16] This account may inspire COF-based research and may introduce a new paradigm guiding the innovation of COF-based tailored materials with superior properties in the upcoming years. Furthermore, the study also allows the researchers a nuanced understanding of the existing experimental and

Materials Advances

<div align="right">

Review

</div>

hypothetical COFs (with their property-performance relationship), and their implementation across diverse domains, providing strategies to design novel COFs for their future prospects in research and industrial applications.

2. Computational Framework for COF research

2.1. Quantum Mechanical Approaches

Quantum mechanical (QM) approaches are powerful and widely used tools that leverage the concept of the uncertainty principles, quantum entanglement and dual nature of wave unveiling insights into the atomic and electronic behaviour within the COF frameworks.[20,21] Density Functional Theory (DFT) and hybrid quantum mechanical or molecular mechanical approaches are the most widely employed QM methods for modelling as well as accurate prediction of various properties of COFs, as discussed in the following sections of this review.

2.1.1. Density Functional Theory (DFT)

DFT is one of the most widely accepted, reliable and powerful computational tools to study many-body systems. Through precise calculations of total energy, electron density and optimization of molecular structures, it facilitates an in-depth understanding of the electronic behaviour of complex systems such as COFs. Meanwhile, it figures out the most stable COF architecture for particular applications, with optimal precision (through energy optimization). Additionally, band gap study using Frontier molecular orbital (FMO) analysis and conductivity analysis of COFs can also be carried out utilizing DFT. In order to optimize the geometrical structures and total energy calculations, the Kohn–Sham equation is employed.

The Kohn–Sham equation (Equation 1) is given below[22,23]–

$$\left[-\left(\frac{\hbar^2}{2m}\right)\nabla^2 + V_{(r)} + V_{H(r)} + V_{\{XC\}(r)} \right]\Psi_{i(r)} = \varepsilon_i \Psi_{i(r)} \quad (1)$$

The wave function is denoted by $\Psi_{i(r)}$ that characterizes the dynamics of the ith electron, where ε_i denotes the associated energy. In the above expression, external potential, Hartree potential and exchange-correlation potential are indicated by $V_{(r)}$, $V_{H(r)}$ and $V_{\{XC\}(r)}$ respectively.

The external potential considers the nucleus' repulsive potential with external field potentials, Hartree potential demonstrates the electrostatic interaction of electrons. The electron correlation and electron exchange effects are taken into account by the exchange-correlation potential.

DFT models are used to calculate the adsorption/desorption energies of various systems utilizing the Equation 2,[22, 24]

$$E_{adsorption/desorption} = E_{adsorbates} + E_{host} - E_{adsorption/host} \quad (2)$$

$E_{adsorbates}$, E_{host} and $E_{adsorption/host}$ denote the energies of the adsorbates, host and host-guest system, respectively.

BLYP and PBE are the most widely used generalized gradient approximation (GGA) used in DFT for the calculation of electron density. Even though they are commonly used, they have some limitations like higher computational cost, and may produce some errors. Hybrid DFT functionals for instance B3LYP and PBE0 can overcome these limitations up to a good extent, during the study of the electronic properties of COFs.[25-30] Experimental investigations integrated with DFT calculations and molecular dynamic (MD) simulation were reported for the exploration of electronic properties, layer interactions and charge carrier dynamics in benzodithiophene-COF thin films.[31] From the findings, it can be concluded that the films with less thickness exhibit significantly higher hole mobilities (especially under light), indicating their potential in optoelectronics applications. In another study, as an environmental concern, experimental study as well as DFT-based calculations were carried out to evaluate the removal of naproxen (a pain-relieving medication) using ionic COF (guanidinium-based). The COF was found to exhibit excellent adsorption towards naproxen (308 mg/g), where physical adsorption was dominant over the chemical one. The pi-pi and electrostatic interactions played an important role during the adsorption process, which was found to be exothermic and spontaneous.

Guanidium-based COF architecture was reported as an effective and expeditious approach to mitigate the urgent issue of contamination of aqueous stream by the naproxen drug (mainly after the COVID-19 pandemic). Meanwhile, the interaction of naproxen with the guanidium based COF architecture (especially between the -COOH group of the naproxen molecules and the guanidinium of the COF) was thoroughly inspected harnessing advanced computational techniques such as Gradient Model based on Hirshfeld partition and electrostatic potential analysis.[32] The synthesis of fluorescent COFs, their fluorescence mechanism (analyzed employing DFT) and excellent heavy metal detection capabilities were envisioned in another work.[33] The intriguing impact of the intercalation of first-row transition metals into 31 COFs, their electronic properties, and structural changes revealing stable configurations was comprehensively investigated leveraging DFT calculations.[34] The study provided crucial insights into the structure-property relationships of transition metal intercalated COFs and enhanced conductivity of COFs upon intercalation. Further, DFT studies (with the support of electron density mapping), provided insights into the structural properties, electrostatic properties and specific interlayer interaction of 2D COFs.[35]
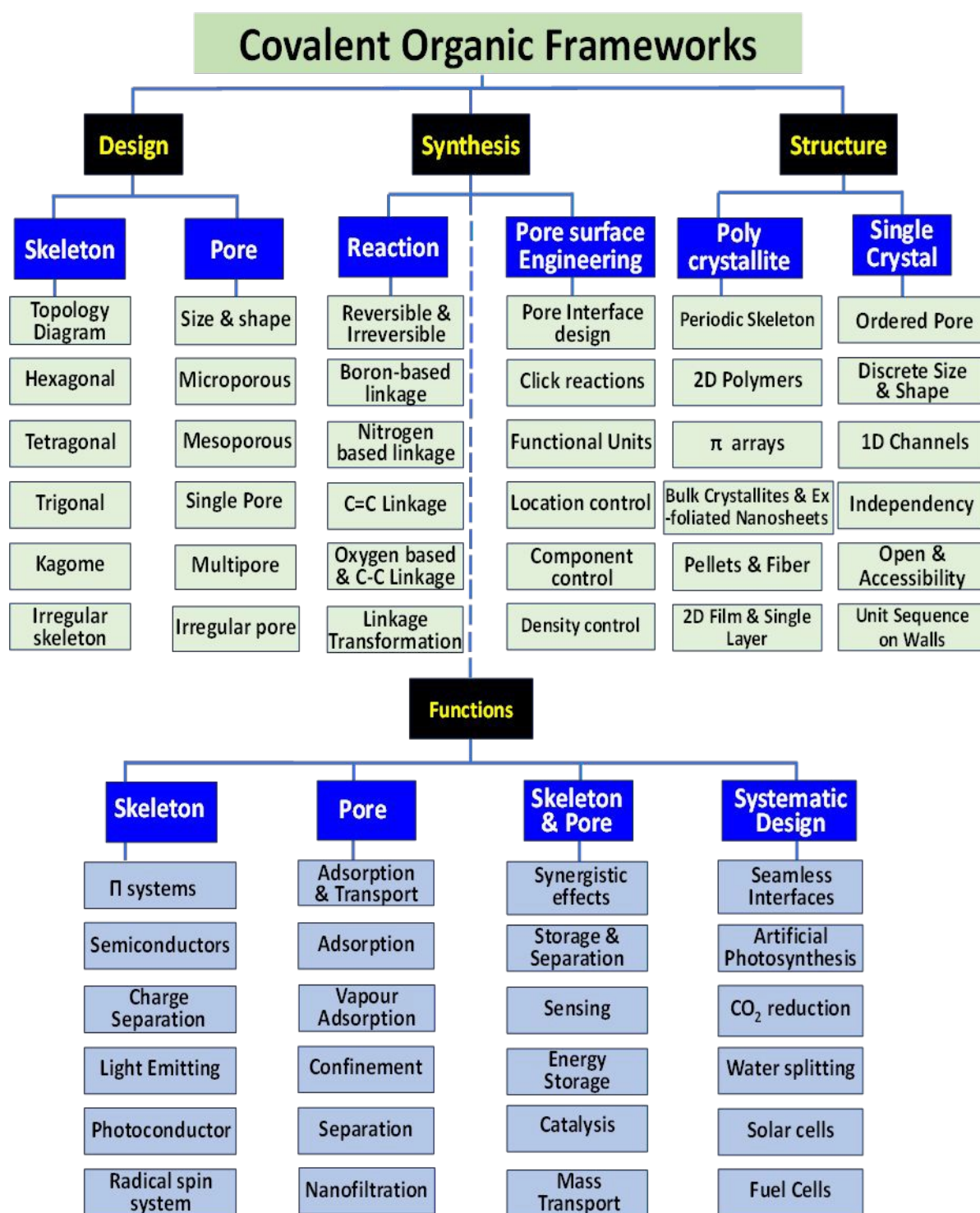
Fig. 3 The research scope of COFs in various domains. Reproduced from ref.[5] with permission from Royal Society of Chemistry, Copyright 2021.
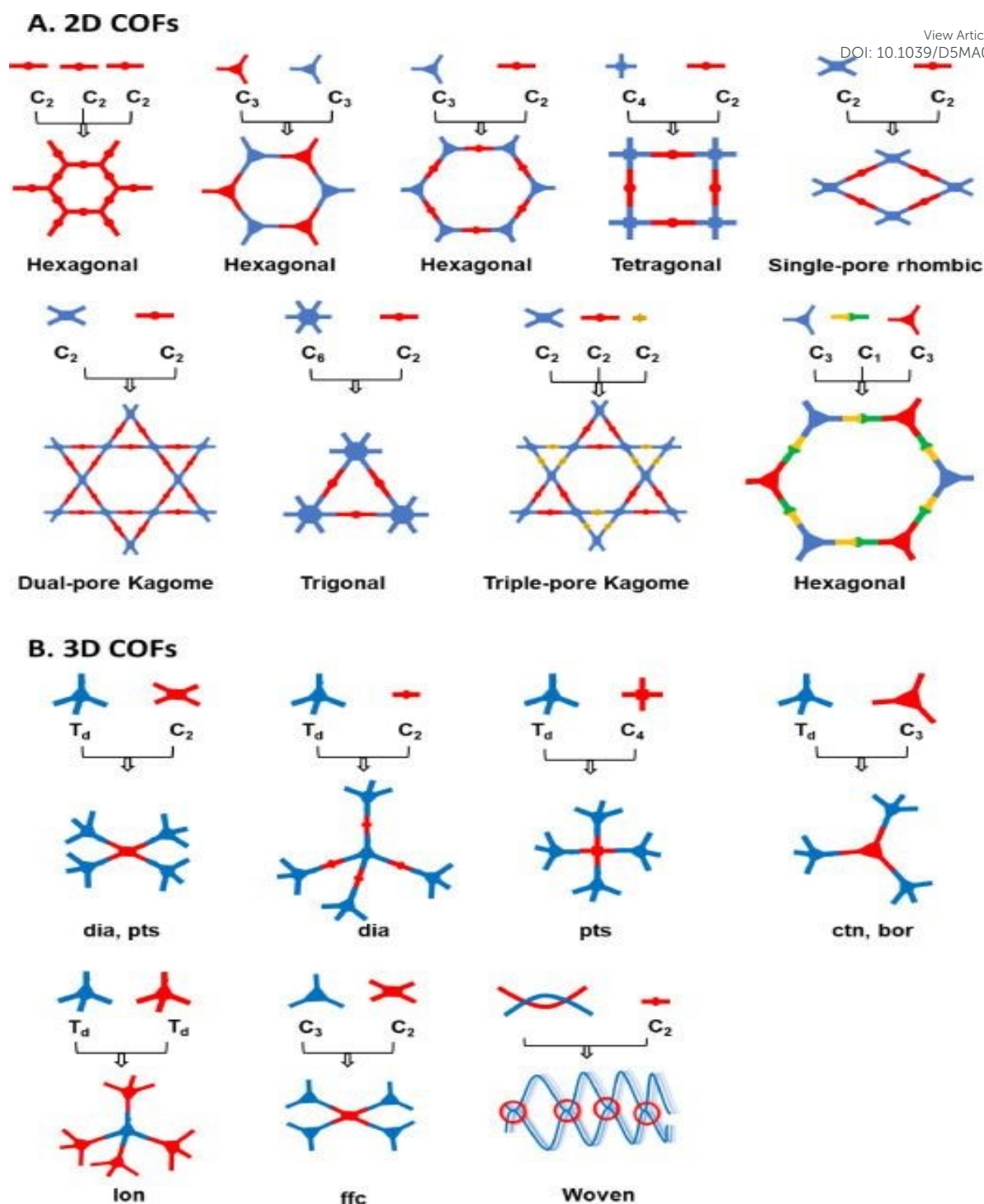
Materials Advances Accepted Manuscript

Fig. 4 Various reported 2D and 3D COFs based on their shapes/structures. Reproduced from ref.[15] with permission from Elsevier, Copyright 2021.

The impact of protonation and structural variation on donor-acceptor COFs was also reported, revealing that upon protonation, the energy gap gets lowered and alters the electron dynamics within the COF framework, which was validated by experimental findings.[36] Notably, upto 98% of enantiomeric excess of racemic drugs was achieved by performing enantioselective separations using 3D chiral COFs (which are recyclable in nature), with tailored pore surfaces and their chiral recognition mechanisms were elucidated with the aid of DFT approaches.[37]

The integration of machine learning (ML) (specifically neural networks) has further revolutionized the field by improvising and simplifying the classical DFT computations and boosting the calculation process. The use of classical DFT with the

advantages of ML was discussed to analyze the gas adsorption behaviour of COFs following the Helmholtz energy model.[38]

The semi-empirical approach uses experimental data to make the quantum mechanical calculation that reduces the computational cost.[39] By considering the core electrons as a part of the atomic nucleus, it omits the core electron integrals and only valence electrons are taken into account. AM1, PM3, PM6, OMx and NDO are the most frequently used semi-empirical methods, which are computationally way much faster than the ab initio methods, although there are certain trade-offs in accuracy in comparison to ab initio methods.[39,40] A semi-empirical method termed the tight binding approach combines the wavefunctions produced by individual/constituent atoms to represent the wave functions of the whole system, in order to strike a balance between accuracy with optimum speed (with an accuracy that is comparable to DFT).[39-42] DFTB is an extension of the tight-binding approach incorporated with advanced DFT principles. It uses precomputed interaction parameters, making the whole process significantly faster than traditional DFT. Despite the advantages, the dependence on various parameters for various elements and spin-polarization restricts their use on a broad scale.[43-44]

2.1.2. Hybrid Quantum Mechanical/Molecular Mechanics (QM/MM) Approaches

To study complex systems including COFs or modified COF-based architectures, QM/MM is considered as an emerging and powerful computational tool. This approach allows researchers to predict the molecular interaction and explore the electronic nature of massive systems while maintaining the computational cost.[45,46] It seamlessly combines the quantum mechanical approach with molecular mechanics to fill the gap of the molecular mechanical (MM) approach with the quantum mechanical (QM) approach or vice versa. Using these approaches, quantum-level calculations can be achieved with the speed of classical mechanics (bridging the limitations of each method), for in-depth (with good precision) atomic-level calculations of molecular systems.[46-48] The hybrid QM/MM approach utilizes quantum mechanical calculation for analysis of the focussed site of the system, while classical molecular mechanics evaluates the surrounding environment. An overall or detailed understanding of different massive systems like COFs can be achieved by employing this strategic synergistic approach, thereby effectively reducing the complexity of the calculation as well as the computational time. In this approach, during the computations of large/complex frameworks, additive and subtractive coupling pathways are often employed.[47,48] The first pathway generally estimates the total energy obtained through the addition of the energies obtained by QM as well as MM approaches, therefore it is termed as additive coupling. On the other way in case of the subtractive coupling, the entire system energy is calculated and then the QM component is added considering the overlapping the QM as well as MM computations.[47-49]

In this approach, a complete system (CS) is partitioned into two parts, primary subsystem (PS) and secondary subsystem (SS), where PS is illustrated utilizing QM and SS is treated using MM approach. The QM/MM energy of the complete system can be obtained by employing the following expression:[47,48]

$$E(QM/MM;CS) = E(MM;CS) - E(MM;PS) + E(QM;PS) \quad (3)$$

Here, $E(MM;CS)$ and $E(MM;PS)$ denote MM analysis of the complete system, MM analysis of the primary subsystem and $E(QM;PS)$ represents QM analysis of the primary subsystem respectively.

Even though, the hybrid QM/MM approaches are crucial in biological and material science applications, in some cases the line of separation between QM and MM approaches can be tricky based on different systems. To overcome these challenges, various strategies can be followed such as introducing linker atoms like hydrogen to cap the damaged bonds, regulating the effect of charge close to the borders, and modifying the borderline throughout the simulation. The versatility of QM/MM approach was reported for studying the substituent effect, on enantioselectivity and reactivity of (salen)Mn catalysts within MOFs.[45] The crucial factors such as Steric hindrance and electronic effects reducing enantioselectivity, was portrayed in the study. Furthermore, the study depicted the impact of electronic and configurational changes on the catalytic performances of COFs, by adopting hybrid QM/MM approaches. Also, these methods can effectively explore the chemical reactions and interactions,[46] even at atomic/molecular levels, offering a new avenue of COFs or COF-based functional materials for their future advancements in a variety of domains, including drug design.

2.2. Classical Force Field Methods

For simulation of modelling purposes of various systems, classical force field methods primarily harness (predefined) potential energy functions to examine molecular behaviours at varying conditions. These approaches can play a pivotal role in the thorough computational investigations of configurational/conformational properties, dynamic nature as well as in understanding numerous dynamic responses of COFs. This study presents various reported popular classical force field methods, analyzing the advantageous (electronic and structural) properties of numerous COFs, their potential applications with the ultimate goal of environmental remediations and sustainability.[50-53]

2.2.1. Grand Canonical Monte Carlo (GCMC) Simulations

GCMC simulations are pivotal in studying the real dynamics of systems by allowing the particles of the system to add, remove and move under energy considerations. Three distinct types of trial movements – formation, destruction and rotation/displacement of particles are attempted while conducting GCMC simulations.[54] Through this approach,

computer simulation is employed to understand the interaction/adsorption of gas molecules (or other various molecules) on the COF architecture with the variation of different parameters such as pressure and temperature (i.e. simulating a real-world environment).[54-58] Moreover, the ML approach is suitable for the prediction/evaluation of adsorption isotherm, adsorption behaviour of various gases on different COF structures and selectivity parameter of different COFs towards some specific gases over other gases. Additionally, the GCMC approach is also widely utilized by researchers to predict the impact of various functional sites, structures and pore sizes of the COFs on their efficiencies, providing valuable strategies to optimize these parameters.[12,59-66] By optimizing these parameters of COFs, significant enhancement in selectivity, separation/adsorption, sensor applications, photovoltaic applications and photocatalytic activities were reported.[67-70] This approach can be extensively used to understand the dynamic behaviour of the gas molecules within the porous COF framework/structure and for in-depth analysis of COF-gas interactions.

The algorithms mainly used by GCMC include the Metropolis and Gibbs algorithms. Metropolis algorithms are mainly employed for simulations of solid-liquid systems, whereas Gibbs algorithms are useful in the simulation of gas systems.[22,71]

Employing the following expressions, the total adsorption value, for any system, can be defined,[22,72,73]

$$N_{total} = N_{excess} + \rho V_{free} \qquad (4)$$

Where the N_{total} and N_{excess} denote total and excess adsorption values, V_{free} denotes the single crystal cell's free volume, and ρ denotes bulk density or packing density.

Again, the excess adsorption value can be calculated by employing the following equation,

$$N_{excess} = 1000 \left(\frac{N_{am} M_a}{N_a} - \rho V_{free} N_A \right) / (M_s M_a) \qquad (5)$$

N_{am}, M_s, M_a, N_a, and N_A represent the amount of adsorbate molecules (the final number), the quantity of materials of the single crystal cell, the adsorbate's relative molecular mass, the number of structure cell and Avogadro's number respectively.

Additionally, harnessing GCMC simulations, heat of adsorption (Q) can be calculated by solving the given equation,[22,74]

$$Q = RT - \frac{\langle U_{ff} N_{am} \rangle - \langle U_{ff} \rangle \langle N_{am} \rangle}{\langle N_{am}^2 \rangle - \langle N_{am} \rangle \langle N_{am} \rangle} - \frac{\langle U_{fs} N_{am} \rangle - \langle U_{fs} \rangle \langle N_{am} \rangle}{\langle N_{am}^2 \rangle - \langle N_{am} \rangle \langle N_{am} \rangle} \qquad (6)$$

R is the gas constant, $\langle\ \rangle$ denotes the overall average, U_{ff} represents the potential energy of adsorbate molecules and the adsorbate-adsorbent potential energy is denoted by U_{fs}.

A larger value of Q indicates a strong affinity between the adsorbate and adsorbent, thereby indicating a stable adsorption process between the two.

Upon integration with advanced and emerging technologies, including data mining and ML, GCMC simulation becomes a robust and more powerful platform, paving the way towards the synthesis of next-generation materials for gas storage/separations and environmental remediation. ML speeds up the evaluation process of complex systems, playing a crucial role in high-quality COF design strategies. The capabilities of COFs and MOFs, towards efficient energy storage, were compared by comparing their performances. Even though MOFs typically have higher energy storage efficiency, the study highlights the potential of COFs to surpass MOFs in superior energy storage performance, through appropriate design strategies.[75]

2.2.2. Molecular Dynamics (MD) Simulation

To understand crucial insights of the different systems, MD simulation promotes computational investigations of atomic dynamics and interactions within the COF framework at varying operating conditions.[76] MD simulation guides the synthesis of defect-free and high-quality 2D COFs, by highlighting the optimization requirement of some key parameters such as temperature, speed of bond formation and surface movement.[77] This approach explains how the 2D COFs can grow on a sheet of graphene, explaining the underlying mechanisms, emphasizing the significance of reaction temperature, van der Waals (vdW) interactions and monomer arrangements.[78] During MD simulations, the particles (atoms and molecules) follow Newton's equation of motion, which can be solved using integral iteration. The velocity and position coordinates of the particles at various moments can be obtained from the trajectory files of the simulation outputs.[79] In MD simulations, the trajectory of atoms can be obtained by employing Newton's equation of motion as given below:[22,80]

$$\frac{d^2 l_i}{dt^2} = \frac{F_{l_i}}{m_i} \qquad (7)$$

Mass, position and force of the ith particle (in one direction) are denoted by m_i, l_i and F_{l_i} respectively.

Additionally, the coefficient of self-diffusion in a system can be calculated using the following equation,[22,81]

$$D = \frac{1}{6Nt} \sum_{i=1}^{N} \sum_{j=1,j \neq i}^{N} \langle (r_i(t) - r_j(t_o))^2 \rangle \qquad (8)$$

In the above equation, $\langle\ \rangle$ denotes the overall average. Where N, t, $r_i(t)$ and $r_j(t_o)$ denote the number of adsorbates, time of simulation, position of ith and jth molecule at time t and t_o, respectively.

To tackle nanoplastic pollution, the role of COF was evaluated by Shang et al. using MD simulations.[82] MD simulation was employed to study the adsorption behaviour of nanoplastics such as polyethylene (PE), polyethylene terephthalate (PET) and nylon-6 (PA 6) on functionalized COF. It was observed that van der Waals interaction and electrostatic interaction play a key role in the adsorption process. The 2D

COF-1 and COF-5 were evaluated for their thermal conductivity using MD simulations and it was found that they have very low thermal conductivity.[83,84] A remarkable enhancement of thermal conductivity was observed upon incorporation of C60 to COF-1, whose insight mechanism was also discussed in the study.[83] The findings have great importance in the practical use of COFs. For the first time, Liu et al. investigated the thermal conductivity/behaviour of 3D-boron based COFs (COF-102, COF-103, COF-105, and COF-108) using MD simulation which reveals their low thermal conductivity. The limited phonon mean free path was identified as the primary responsible factor behind this.[85] The mechanical properties of the two-dimensional COFs (COF-1 and COF-5) and the effect of temperature on their elastic behaviour were evaluated using machine learning and MD simulation approaches.[86]

To predict the transport of gas molecules through a porous framework, non-equilibrium MD (NEMD) simulations stand superior as compared to equilibrium MD (EMD) simulations, as NEMD considers real transport effects such as the pore entrance as well as mass transfer resistances. NEMD simulations enable the investigation of gas flow behaviour through a nanoporous architecture, directly from the simulation itself, which can effectively consider pressure and concentration gradient, demonstrate high accuracy and provide deeper insights.[87] In a study by Velioglu and Keskin, the GCMC+EMD approach was compared with the NEMD approach during the permeation study of CH_4 and H_2 through MOF membranes.[19] It was observed that, as compared to the results obtained from the GCMC+EMD approach, the results from the NEMD approach showcased a close alignment with the experimental findings, highlighting the efficacy of the NEMD approach in revealing realistic gas transport mechanisms.

In a recently reported work, H_2 and CH_4 transport through COF membranes (COF-320 and COF-300) was evaluated leveraging the NEMD method. It was observed that the findings of the NEMD simulations closely match the experimental findings, as compared to the GCMC+EMD approach. The study also demonstrates the pivotal role of pore sizes for COF membrane's computational analysis and reveals the prominent COFs for the effective separation of CH_4 and H_2. As the diffusion and adsorption characteristics of the COF membranes are influenced by their pore sizes, the selectivity and permeation of the gases are greatly impacted based on the pore size range. The study showcased the importance of a simulation method for such studies, highlighting the robustness of the CGD-MD approach (gradient-driven molecular dynamics, a NEMD approach) for its reliable results with minimal error profiles.[87] In another study, the significance of the hydrophilicity of COF membranes during the permeation of Mg^{2+} and Li^+, was investigated leveraging NEMD simulations. The study demonstrated that the membrane can effectively trap/adsorb Li+, while allowing Mg^{2+} to pass through it. The study may guide the fabrication of nanofiltration membranes for effective

lithium extraction (or other ion sieving applications), which has the potential to meet the requirement for lithium in new energy sectors.[88] Wei et al., in a recently reported work, demonstrated the influence of functional group and pore sizes for the effective separation of salt, employing NEMD simulations. The COF membrane TpPa-SO_3H displayed more than 98% rejection of Na_2SO_4, rivaling commercial membranes. The study may pave the way for next-generation membrane design, employing a simulation-based approach, without any experimental setup.[89]

2.2.3 Machine Learning (ML) Approaches

As an emerging transformative paradigm and a powerful tool, ML prominently screens COFs that possess optimal efficiency across various domains. By leveraging specific algorithms, ML can efficiently figure out the potential candidates for a particular application, from a huge database, obtained from simulations like GCMC or MD.[90-92] By employing the XGB model of ML (combined with simulation), the SF_6 and N_2 separation performance by COF-638 was investigated, underscoring the significance of porosity and adsorption heat.[93] The critical role of COF's building blocks and the impact of appropriate solvent selection during the synthesis of defect-free and high-quality COFs were demonstrated using ML approaches.[94] The automated ML approach outperforming traditional methods was reported for the prediction of the methane storage capacity of 403,959 COFs.[95]

The integration of ML and first-principles calculations was reported for the prediction of the band-edge of 2D COFs (achieving high accuracy) in a fast and efficient manner.[96] In a recently reported work, ML facilitated the development of iron porphyrin COFs possessing enzymatic activity for the detection and identification of thiols, showcasing their potential in disease diagnosis applications.[97] The movement of protons in COFs was investigated using ML and MD simulations, revealing that the fastest movement was found in the pores, which may vary based on the side chain length, sulphonic acid concentration, and the water content.[98] It was seen that by reducing the side chain length, and sulphonic acid concentration, while increasing the water levels, the proton mobility was significantly enhanced, demonstrating the potential of COFs in fuel cell applications. Moreover, ML and first-principles calculations were carried out for 2D porphyrin COFs to analyze their potential as a thermoelectric candidate and it was observed that the incorporation of metal atoms enhanced the stability and reduced the thermal conductivity, thereby improving thermoelectric performance.[99] Another study employed ML and first-principles calculations to provide a strategy for the predictions of band gap positions in 2D COFs, more precisely,[96,100] facilitating advanced COF design strategies for their applications in nanoelectronics as well as in photocatalysis.

AI and ML-based advanced deep learning models (such as transformer-based models, convolutional neural networks, Graph Neural Networks etc.) are employed by the researchers to gather

various COF's structural parameters, including the presence of functional groups, surface area, pore sizes, etc., from a huge database, which is also termed as parameter loading. Reliable parameter loading from open databases (for instance CoRE-COF), employing automated tools such as molecular-level simulation and Python-based libraries, enhances the accuracy of the model. Specifically, physical, chemical and geometrical properties are the key parameters for this type of study, where the automated tools save time, reduce human effort and boost the material screening throughput. The data for a known COF obtained from a database are collected with their associated properties. From this, the model learns the pattern of chemical and structural features, enabling the system to understand the insightful structure-property relationship, a process known as model training. The model was then subjected to screening of huge databases to find the best-performing COFs with quantitative prediction of the desired properties, in a rapid manner. Yang et al. reported the efficiency of automated ML (AutoML) as compared to other conventional ML approaches, to analyse/predict the methane uptake capability of various COFs.[95] The study evaluated 4,03,959 COFs depending on their various chemical and physical properties. Furthermore, the study compared various conventional ML tools such as random forest, support vector machine, decision tree and multiple linear regression with the AutoML tool tree-based pipeline optimization tool (TPOT). The study highlights the potential of TPOT in terms of accuracy and speed that does not require any manual tuning, demonstrating superior prediction capability and precision, making the approach more convenient and effective for COF research. In another work, attention-based ML approach was employed to predict the thermal conductivity of COFs with high accuracy, emphasizing the role of dangling molecular branches. The transformer-based deep learning model (incorporated with multi-head attention mechanism) was found to be more effective than the conventional ensemble-based regression approaches.[101] The study evaluated 2471 two-dimensional COFs and it was observed that COFs containing more dangling atoms have lower heat transfer capability owing to the disrupted pathways, which was further validated by vibrational analysis. The study showcased the potential of advanced deep learning methods to reveal the structure-property correlation of COFs, guiding researchers for quick and precise design of next-generation tailored COFs or COF-based materials, with desired properties.

2.3. Multiscale Modelling Techniques

The multiscale modelling techniques promote integrating diverse computational methods from multiple domains to address one specific issue.[102-105] A study leverages a multiscale modelling approach to demonstrate the formation of 2D COFs at the interface of water and air.[105] The study involved an experimental study validated by an in-silico approach. To achieve COFs with superior quality, preferential alignment of the building blocks at the interface, which promotes the polymerization process, was discussed. Through electronic and structural evaluations, the tuneable band gap and

semiconducting behaviour of the 2D COFs were substantiated, rendering them highly suitable for electronic applications.[106] In tandem approach of various computational methods was reported to analyse the high efficacy of COFs in H_2 storage applications.[106,107] Again, advanced quantum mechanical and classical force field methods were utilized for an in-depth understanding of boron-based COFs, including their structural, thermal, mechanical and adsorption behaviour.[108]

3. Applications of Computational Studies on COFs

3.1. Gas Separation and Storage

To study the adsorption behaviour of various gases on COFs, Grand Canonical Monte Carlo Simulations (GCMC) approach is mostly employed. Owing to the flexibility of permitting variation of the total number of particles for adsorption analysis, it serves as a highly useful and frequently utilized tool for studying gas separation and storage applications.[54-58]

Many COFs possess superior efficiency in gas separation applications in comparison to conventional porous materials like MOFs or Zeolites,[109,110] which is established by computational evaluation. The exceptional performance of COFs towards industrial gas mixtures separation, such as He/N_2, He/CH_4, CO_2/CH_4, CO_2/H_2 and CH_4/H_2 was observed, making them potential candidates in industrial gas separation and carbon capture applications. Table 1 shows the reported computational approaches for COFs or COF-based materials, investigating gas separation and storage with structural and dynamic analysis.

The adsorption study of gas molecules on COF can proceed in two phases. Firstly, the COF or COF-based material structure can be validated through modelling, ensuring its structural correspondence to reality. Secondly, the adsorption simulation study to investigate the gas uptake capability or efficiency of the structure. This approach correlates the material's structure with their properties, aiding efficient COF or COF-based material discovery, with superior gas storage and adsorption/separation ability.[111] Dong et al. demonstrated the role of BET and PXRD analysis for efficient monomer design during the development of effective COF or COF-based materials.[112] Three types of two-dimensional isoreticular COFs such as 1,3,5-tris(4-aminophenyl) benzene (P-COF), tris(4-aminotriphenyl) amine (N-COF) and 2,4,6-tris(4-aminophenyl)-s-triazine (T-COF) were prepared from 1,3,5- benzenetricarbaldehyde (BTCA). The study compared the experimental PXRD (powder X-ray diffraction) pattern of COF structures with the pattern of structural simulations, confirming the material structure. The PXRD peaks for N-COF was observed at 6.8°, 11.8°, and 22.5°, while in the case of P-COF, the peaks were observed at 5.7°, 9.9°, 11.7°, and 25.1°. The experimental PXRD patterns match well with AB staggered and AA staggered stacking patterns of simulated N-COF and P-COF, respectively. Both structures possess low crystallinity owing to the presence of flexible amine linkages. Considering this fact, to improve the crystallinity of the COF structure, a rigid triazine-based linkage was introduced to produce T-COF. T-COF showed sharper PXRD

Review

peaks at 5.8°, 10.0°, 11.6°, 15.3°, and 25.9°, confirming better crystallinity with strong π–π stacking. Again, Brunauer–Emmett–Teller (BET) analysis revealed the microporous structures of all three COFs, with pore volumes of 0.395, 0.442, and 0.549 cm³/g, and BET surface areas of 692, 435 and 1149 m^2 g^{-1}. Nonlocal density functional theory-based calculation of pore width distribution showcased the framework's good match with the proposed crystalline structure. It was observed that the COF with planar amine linkages possess more crystallinity and high porosity, thereby exhibiting more hydrocarbon uptake capability. On the other hand, the N-COF possessing the smallest pore sizes demonstrates C_2H_6/ CH_4 separation with the highest efficiency (as compared to the other two COF structures). Again, in another study, the gas storage and separation capability (for the mixture CO_2/CH_4) of N-COF, P-COF and T-COF was assessed employing GCMC and MD simulations.[113] The adsorption isotherms (for C_2H_6 and CH_4, at 298K) derived from the simulations are in good agreement with the experimental results as reported by Dong et al., for all three types of COFs. Owing to the smallest pore channels, N-COF demonstrated superior CO_2/CH_4 separation. Moreover, N-COF can effectively store CO_2 at low pressure, while at high pressure, P-COF and T-COF are the better candidates for CO_2 storage. This may be attributed to the dominant role of adsorbate-adsorbent interactions at low pressure and the key role of pore sizes in the case of high pressure. This type of experimental as well as computational study may guide future studies on gas storage and separation, using various COFs or COF-based tailored materials.

A study investigates the interaction of N_2 and CO_2 gas with nitrogen-containing COFs by calculating the binding energies of the gas molecules with the COF architecture employing the DFT approach.[114] The capability of 580 synthesized and 891 hypoCOFs, for the separation of carbon dioxide and hydrogen sulfide from natural gas and their selectivity towards them was explored utilizing computational investigations such as DFT and MD simulations (considering industrial-related environments).[13] The study concluded that some of the synthesized and hypoCOFs exhibit excellent carbon dioxide and hydrogen sulfide selectivities outperforming conventional adsorbents. COFs hold emerging opportunities for their diverse applications in methane separation from industrially relevant gas mixtures, including nitrogen, hydrogen and ethane, which were assessed through DFT calculations, MD and GC simulations.[115] The potential of 572 COFs in the separation of binary gas mixtures was investigated, such as methane/hydrogen, methane/nitrogen and ethane/methane. These COFs outperformed traditional adsorbents in separation performance. The COFs incorporated membrane showed excellent hydrogen permeability with favourable selectivity, which makes them superior to polymeric and MOF-based membranes. The adsorption of gases (n-butane, ethane and methane) in COFs (2,3-DhaTph and TpPa-1) was modelled using classical DFT and GCMC simulations. The findings showed good agreement between the two methods when studied upto 50

bar of pressure condition. The study underscores the significance of classical DFT for the prediction of adsorption of long hydrocarbons in COF architecture.[116] Integrating molecular simulations with an ML approach was followed for the rapid screening of 10 top-performing COFs out of 70,000 COFs, for the application of deacidification (acid gas removal from natural gas).[117] The study showed the high separation performance of COF-incorporated membranes surpassing the efficiency of the MOF fillers. In another GCMC simulation study, a novel MOF was designed where carbon flakes were used to modify IRMOF-1, which showed enhanced gas storage efficiency.[118] The circular-shaped carbon flakes demonstrated the best CO_2 storage capacity, while rhombus flakes exhibited the best H_2 storage. These findings could greatly benefit the design of novel, highly efficient COFs/MOFs for gas storage/separation applications. DFT and GCMC simulations were employed to evaluate the adsorption behaviour of Polyarylether-based COFs (functionalized with -CN, −C(NH$_2$) NOH and -COOH groups) towards CO_2, thereby showcasing their promising potential in gas storage and carbon capture.[119] Using GCMC simulation an investigation was carried out to analyze the potential of the 2-dimensional imine COFs (1171 COFs with various configurations) for the separation of methane and ethane.[120] MD simulations and ML were employed in a recently reported work to screen out the best-performing COF or MOF-based membranes for the separation of Helium from natural gas. Among all, the 3D-Sp-COF-1 exhibited excellent helium adsorption ability and separation efficiency for the binary mixtures of He/N_2 and He/CH_4.[110] The findings emphasized that the COFs having 3D structures, high surface area and larger pore volumes play a major role in effective helium separation. The role of computational simulations and ML approaches in exploring the effectiveness of COFs/MOFs and further design strategies of such materials for gas separation, storage and delivery applications was reported.[121]
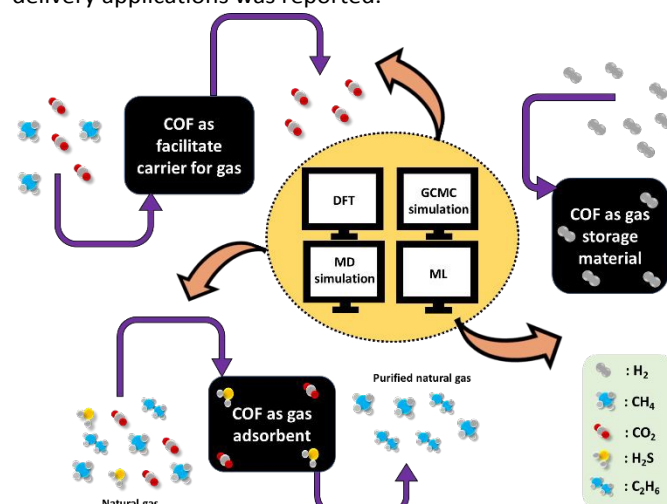

Fig. 5 A representation of the most commonly used methods for various gas storage and separation applications

Strategies for the separation of CH_4 and CO_2 using a COF-based membrane were discussed employing MD and GCMC simulations, investigating the potential impact of temperatures, pore sizes and functional groups in enhancing the separation process.[122] Gas diffusion and adsorption behaviour within $-NH_2$ group incorporated COFs architecture (for CH_4 and CO_2) and their interactions were evaluated.[123] Upon incorporation of -NH_2 group into the COF architecture, CO_2 adsorption capability improved, however, the dynamic behaviours of the gas molecules within the architecture remain unchanged. GCMC simulation further validates the excellent CO_2-H_2 separation performance of a COF-based self-standing membrane possessing enhanced H_2 permeance.[124] In another study by Keskin et. al., it was observed that COF-6 outperformed various nanoporous materials, towards the effective separation of CH_4 and H_2.[125] The adsorption as well as diffusion phenomenon of gas molecules within various COF frameworks were analyzed employing GCMC and Equilibrium molecular dynamics (EMD) simulations. In another study, by considering COF-102, COF-103, COF-105, and COF-108 architectures, the adsorption of various gases like methane, hydrogen and argon were presented.[121] Out of the COFs used, COF-102 performed with exceptional methane storage capability, whereas most of the COFs exhibited strong hydrogen adsorption behaviour. The methane adsorption behaviour of various 2D and 3D COFs, under varying pressure conditions, with their insight mechanisms was discussed employing an experimental study validated by computer simulations.[126, 127] The highest methane storage capacity by COF-1 (2D) and methane delivery efficiency by COF-102 (3D) and COF-103 (3D) were showcased in the study.

The key factors such as pore size optimization, impregnation and structure modifications responsible for hydrogen storage applications of porous materials (including MOFs and COFs, both 2D and 3D), and their improvement strategies were explored using quantum calculations, MD and GCMC simulations.[128,129] The efficient hydrogen storage/separation abilities of novel COFs (boron-phosphorus and borophosphonate-based) possessing high valency were investigated by harnessing DFT and molecular simulations, at varying pressure and temperature conditions.[130,131] ML-assisted screening approach was carried out computationally to assess the potential of 597 synthesized and 7737 hypo COFs (i.e. screened out from 69,840 hypothetical COFs), in CH_4/H_2 separation application.[132] Identifying the best-performing COFs (considering adsorption and regeneration capability), the impact of structural features and pressure variations on the adsorption capability of the COFs was emphasized in the study, employing GCMC simulations. The findings demonstrated better CH_4/H_2 separation efficiency of the hypothetical COFs as compared to the synthesized COFs and MOFs. The quick separation performance predictions based on the structural features of the COFs were carried out using ML models. These studies suggest various pathways and strategies for accelerating

further advancements of COFs in hydrogen separation and storage applications.

The role of fillers, including COFs and MOFs, in polymeric mixed matrix membranes was reported for enhanced separation of gases with the help of high-throughput computational screening (to find out the best filler materials), where the interactions of the gas molecules with the membrane were evaluated using molecular simulations.[133] Tentacle-like COF was incorporated as fillers into the Pebax polymeric matrix (used as a mixed matrix membrane) to obtain improved separation of CO_2 and CH_4.[134] The COFs introduced various nanotraps for capturing CO_2, with the best CO_2 separation performance observed at 3% COF loading into the polymeric matrix. The significance of COF loading into the polymeric matrix was demonstrated by the enhanced separation efficiency of the COF-incorporated membrane (upto 73.4% and 32.9 %) as compared to the pure polymeric membrane, which was further validated by DFT calculation and GCMC simulation. Photo-responsive COF-based architecture (NUT-105@COF-OCH_3) was designed by Yang et al. for improved and controlled CO_2 capture application (achieving upto 29.2% of CO_2 adsorption, with better light response).[135] The alternation of pore sizes upon irradiation of UV- and Vis-light (leading to regulated CO_2 adsorption) was further illustrated using GCMC simulations. The hydrogen storage applicability of COFs functionalized with Mg-alkoxide was explored in another study using thorough computational screening employing simulations and ML approaches.[136] Enhanced CO_2 uptake capacities of the COFs, concerning the temperature and pressure variations (and the impact of functionalization) were predicted, showing that COFs having small pore sizes exhibited better CO_2 capture capabilities.[132,137]

The role of hydrazone-based COF towards CO_2 separation as well as capture was analyzed using DFT and MD approaches. Their tuneable structural properties, strong CO_2 interaction and effective sieving effect position them as a potential candidate in CO_2 separation and storage applications.[138] With the advantages of illustrating the time-dependent dynamic nature of gas molecules within the COF framework, MD simulation can complement the GCMC simulations.[139] MD approach enables the analysis of gas transport mechanisms within the framework, including the diffusion of gas molecules and the influence of the structural framework on these processes.

Employing DFT and MD simulations, CO_2/N_2 separation efficiency and gas adsorption performances of diamine-linked 2D COFs (building units: 1,3,5-tris(chloromethyl)benzene; linkers: p-diaminobenzene and hydrazine) were discussed in detail. By maintaining the typical thermodynamic conditions of industrial flue gas after combustion, the remarkable CO_2 capture ability of the COFs was assessed.[140] In order to identify and optimize the crucial parameters (such as pores and surface areas), for efficient hydrogen storage applications, a combined approach of ab initio calculations, MD and GCMC simulations was harnessed.[106]

Review

Materials Advances

These investigations may pave the way for future advancements of novel COFs or COF-based materials endowed with high hydrogen storage capabilities, for cutting-edge research. The impact of tiny porous architectures of COFs in enhancing their CO_2 separation and capture ability was also demonstrated, utilizing Triazine-based benz-bis(imidazole)-bridged COFs.[141] Again, in another work, ML accelerated high-throughput screening was carried out, figuring out the top-performing COFs, and showcasing their CO_2 separation potential from flue gases. The study revealed the role of various linkages and pore sizes/distributions in COF architectures, influencing CO_2 capture capabilities. The significance of 2D COFs possessing fluoro groups and imide linkages (remarkably enhancing their selectivity towards CO_2) was reported in the study and it was also observed that 3D COFs with approximately 1 nm pore diameter exhibited excellent CO_2 capture ability.[92] Modelling adsorption of volatile organic compounds (VOCs) on COFs was carried out utilizing DFT calculations and MD simulations, revealing the potential of COFs in the mitigation of indoor air quality issues.[142]

The studied VOCs in the work include benzene, toluene and formaldehyde, whose selectivity and adsorption on screened-out COFs (obtained from experimental data) were reported (over N_2), providing insights into adsorption mechanisms. The adsorption of CO_2 and N_2 on IL-COF-1 and COF-366 was discussed,[143] emphasizing the importance of COFs in gas separation applications, as shown in Figure 6. These studies may pave the way for further advancements of COFs in broad-scale gas storage/separation, and hydrocarbon separation/purification applications.

MD simulations were further employed to analyze the removal of CCl_4 from gas mixtures/air effectively, using COFs, ZIFs and IRMOFs. The effective role of the architectural design of the materials in enhancing adsorption-based separation was also discussed.[144] Additionally, ML integrated with simulation approaches was employed to study the industrially challenging separation of ethane from ethene using optimal COFs.[145,146]
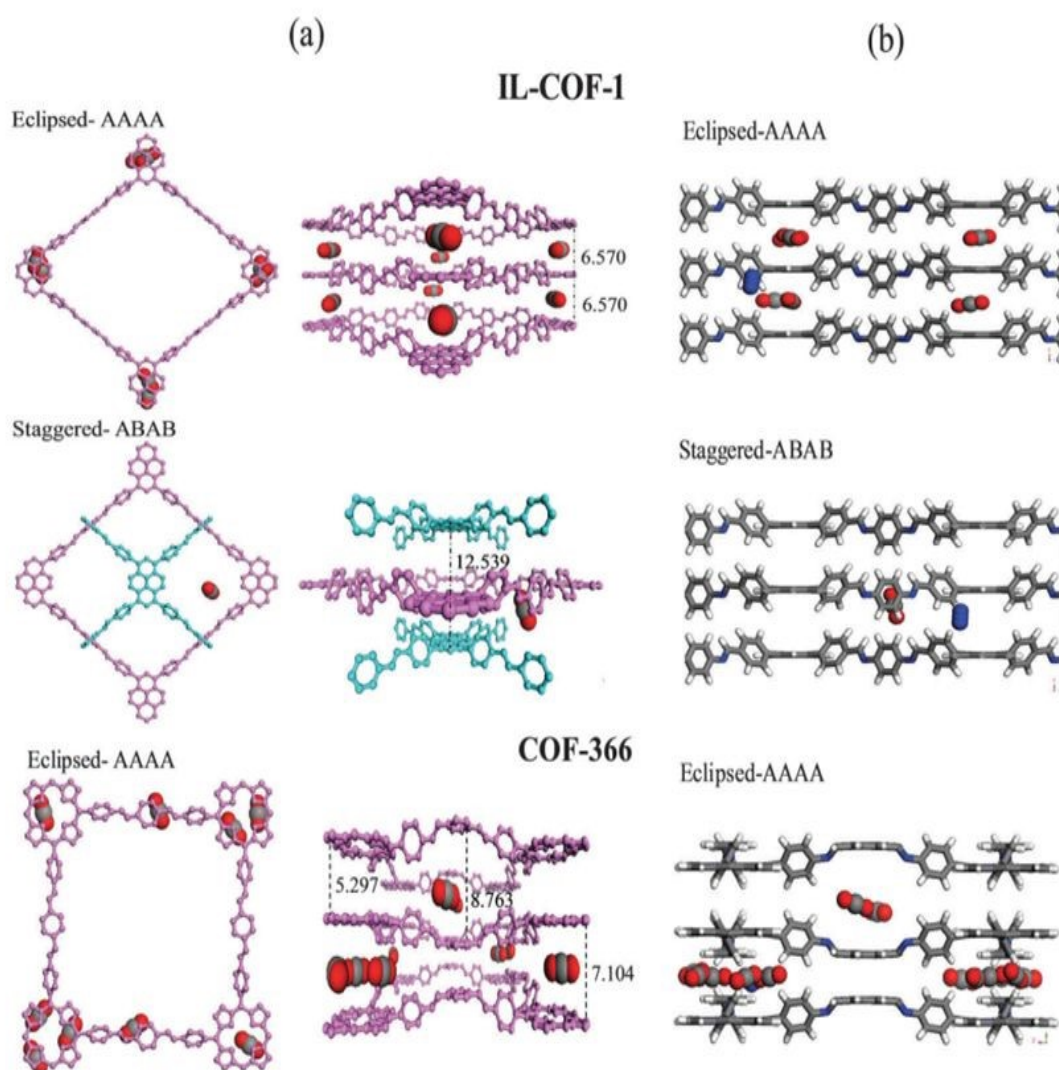
Fig. 6 Adsorption of CO_2 and N_2 on IL-COF-1 and COF-366. Reproduced from ref.[143] with permission from Royal Society of Chemistry, Copyright 2014.

Table 1: Computational approaches for COFs or COF-based materials, investigating gas separation and storage with structural and dynamic analysis.

Topic of study	COF/COF-based materials studied	Computational methods & algorithms	Studied parameters	Structural/dynamic testing	Ref.
Interaction of N_2 and CO_2 with COF	Nitrogen-containing COFs	Ab initio and DFT approach	Binding energy	Structural analysis	114
Separation of CO_2 & H_2S from natural gas	580 synthesized and 891 hypoCOFs	DFT, GCMC simulations, multi-level computational screening	Separation, selectivity, structure-property correlation	Structural and dynamic analysis	13
Separation of CH_4/H_2, CH_4/N_2 and C_2H_6/CH_4 binary mixtures with 572 COFs	572 COFs	DFT calculations, MD and GC simulations, Nucleus-Independent Chemical Shift analysis	Adsorption, Separation, Binding energy	Structural and dynamic analysis	115
Adsorption of gases (n-butane, ethane and methane)	COFs (2,3-DhaTph and TpPa-1)	Classical DFT and GCMC simulations	Adsorption, Selectivity, Isotherms	Structural analysis	116
Acid gas removal from natural gas	10 top-performing COFs out of 70,000 COFs	Integrated molecular simulations with an ML approach	Deacidification/ Separation efficiency, structure-property correlation	Structural analysis	117
Adsorption behaviour of COF towards CO_2	Polyarylether-based COFs (functionalized with -CN, –C(NH_2) NOH and -COOH groups)	DFT and GCMC simulation, interaction energy and radial distribution analysis	Adsorption behaviour, gas storage and carbon capture, Interaction energy, Gas distribution analysis	Structural analysis	119
Separation of CH_4 and C_2H_6	2-dimensional imine COFs(1171 COFs with various configurations)	GCMC simulation	Adsorption and Separation efficiency, structural parameters, nitrogen content, node type and monomer structure effect	Structural analysis	120
Separation of Helium from natural gas	3D-Sp-COF-1	GCMC simulations and ML, MD simulations	Separation efficiency of binary mixtures of He/N_2 and He/CH_4, structure-property correlation	Structural and dynamic analysis	113
Separation of CH_4 and CO_2	COF-based membrane	MD and GCMC simulations, thermodynamic analysis	Separation efficiency, Effects of pressure, temperature and structure	Structural and dynamic analysis	122
Gas diffusion and adsorption behaviour of COF membranes (2D N-COF and 3D COF-300	-NH_2 group incorporated COFs	GCMC simulations, Modelling	Adsorption behaviour, Separation efficiency, Experimental validation, Membrane stability	Structural analysis	124

| membranes) for CH_4 and CO_2 ; CO_2 /H_2 separation performance					
Adsorption of various gases like methane, hydrogen and argon	COF-102, COF-103, COF-105, and COF-108	GCMC simulations	Adsorption behaviour, Experimental validation	Structural analysis	126
Hydrogen storage/separation of COF	COFs (boron-phosphorus and borophosphonate based)	GCMC simulations and DFT	Adsorption, Storage and separation efficiency, structure-property correlation	Structural analysis	130, 131
CH_4/H_2 separation application	597 synthesized and 7737 hypo COFs	GCMC simulations, ML-assisted screening approach	Adsorption, Separation efficiency, structure-property correlation	Structural analysis	132
COF incorporated Pebax polymeric matrix For separation of CO_2 and CH_4	Tentacle-like COF	DFT calculation and GCMC simulation	Separation efficiency, Effect of pressure, temperature and COF loading on the membrane's efficiency, CO_2 capture	Structural analysis	134
Controlled CO_2 capture application	Photo-responsive COF-based architecture (NUT-105@COF-OCH$_3$)	GCMC simulations	Adsorption capacity	Structural analysis	135
Hydrogen storage applicability of COFs	2902 COFs functionalized with Mg-alkoxide	Force-Field modelling, GCMC simulations, ML approaches	Hydrogen storage/adsorption capacity, Binding energy, Structure-property correlation,	Structural analysis	136
CO_2 separation	Hydrazone-based COF	DFT and MD approaches	Adsorption/Separation efficiency, Structure-property correlation,	Structural and dynamic analysis	138
CO_2/N_2 separation efficiency and gas adsorption performances of COF	Diamine-linked 2D COFs (building units: 1,3,5-tris(chloromethyl)benzene; linkers: p-diaminobenzene and hydrazine)	DFT and MD simulations	Adsorption capacity, Separation efficiency, Adsorption isotherms, permeability and selectivity	Structural and dynamic analysis	140
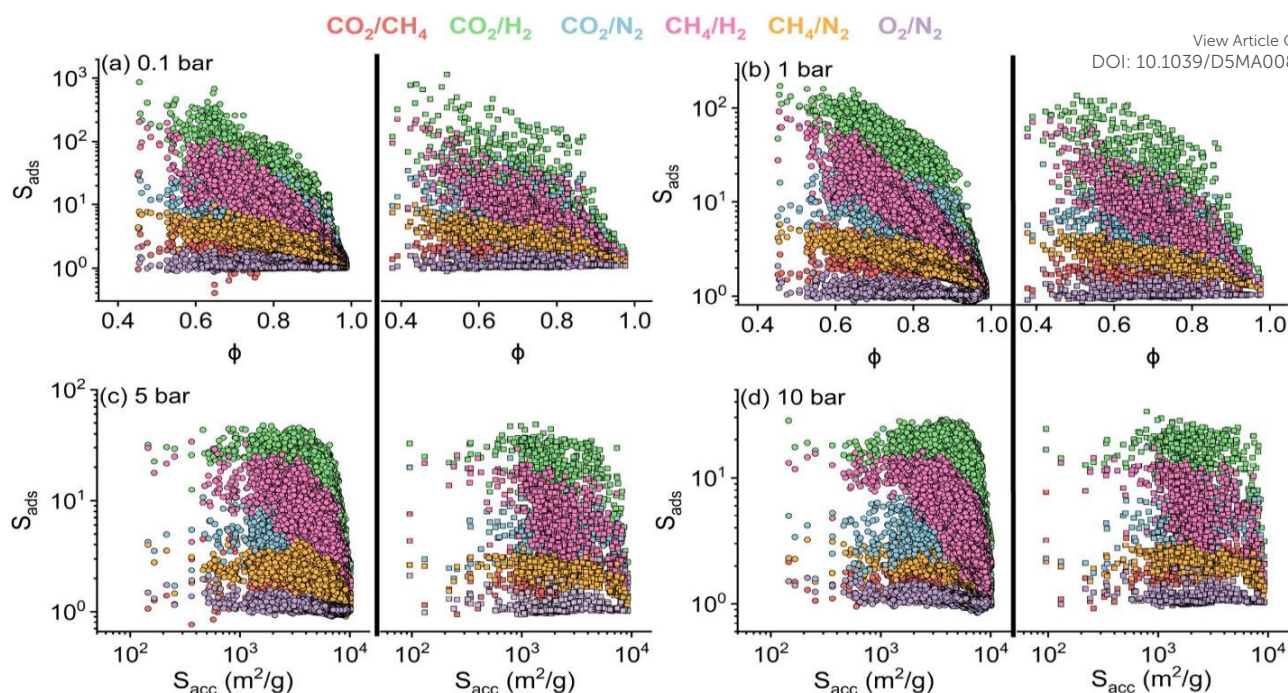
Fig. 7 Selectivities of the COF space for CO_2/CH_4, CO_2/H_2, CO_2/N_2, CH_4/H_2, CH_4/N_2, and O_2/N_2 separations. Selectivities of 68,724 hypoCOFs (left panel) and 1,060 CoRE COFs (right panel) were computed at (a) 0.1, (b) 1, (c) 5, and (d) 10 bar. Reproduced from the ref.[18]. Copyright © 2025, American Chemical Society.

Further, the study emphasized the substantial impact of COF density on the selectivity of the gases and enhanced selectivity of COF-303 upon introduction of fluorine.[145] Again, optimal fluorinated ionic liquid (FIL)-COFs were screened, using ML approaches, for effective separation of ethane and ethene.[146] In another study, employing XGB model of ML, four COFs were identified from the CURATED database for the effective separation of SF_6 and N_2. Subsequently, employing GCMC simulations as well as DFT calculations, the adsorption performance of the COFs and underlying mechanisms were explored.[93] A Combined approach of ML and molecular simulations was employed in another study to assess the gas adsorption properties of 69,784 COFs, from various gas mixtures such as O_2/N_2, CO_2/N_2, CH_4/N_2, CH_4/H_2, CO_2/H_2 and CO_2/CH_4, revealing the chemical and structural features of the top-performing COFs.[18, 147]

These studies collectively confirmed/highlighted the immense potential of various COFs in gas separation/storage and carbon capture applications and guiding future advancements in COF design.

3.2. Liquid Separation and Purification

The MD approach was utilized to evaluate the water desalination application of a three-dimensional COF framework, named 3D-OH-COF, emphasizing the underlying mechanism of the separation process.[148] In this study, the COF demonstrated excellent salt rejection ability (upto 100%) with very high-water flux, even better than commercial RO membranes. The transport of ions as well as water through the nanochannel of COF was also examined employing MD simulation, highlighting their significant potential in desalination applications.[149] In another study, Guan et al. discussed the effect of layer spacing on the ion's interaction and water flow during desalination using COF-based membranes.[150] The effective removal of mercury (upto 99%) from acidic water was obtained when COF-supported silver nanoparticle was employed as an adsorbent material (further validated by DFT calculations), which was highly stable and regenerable in nature.[151]
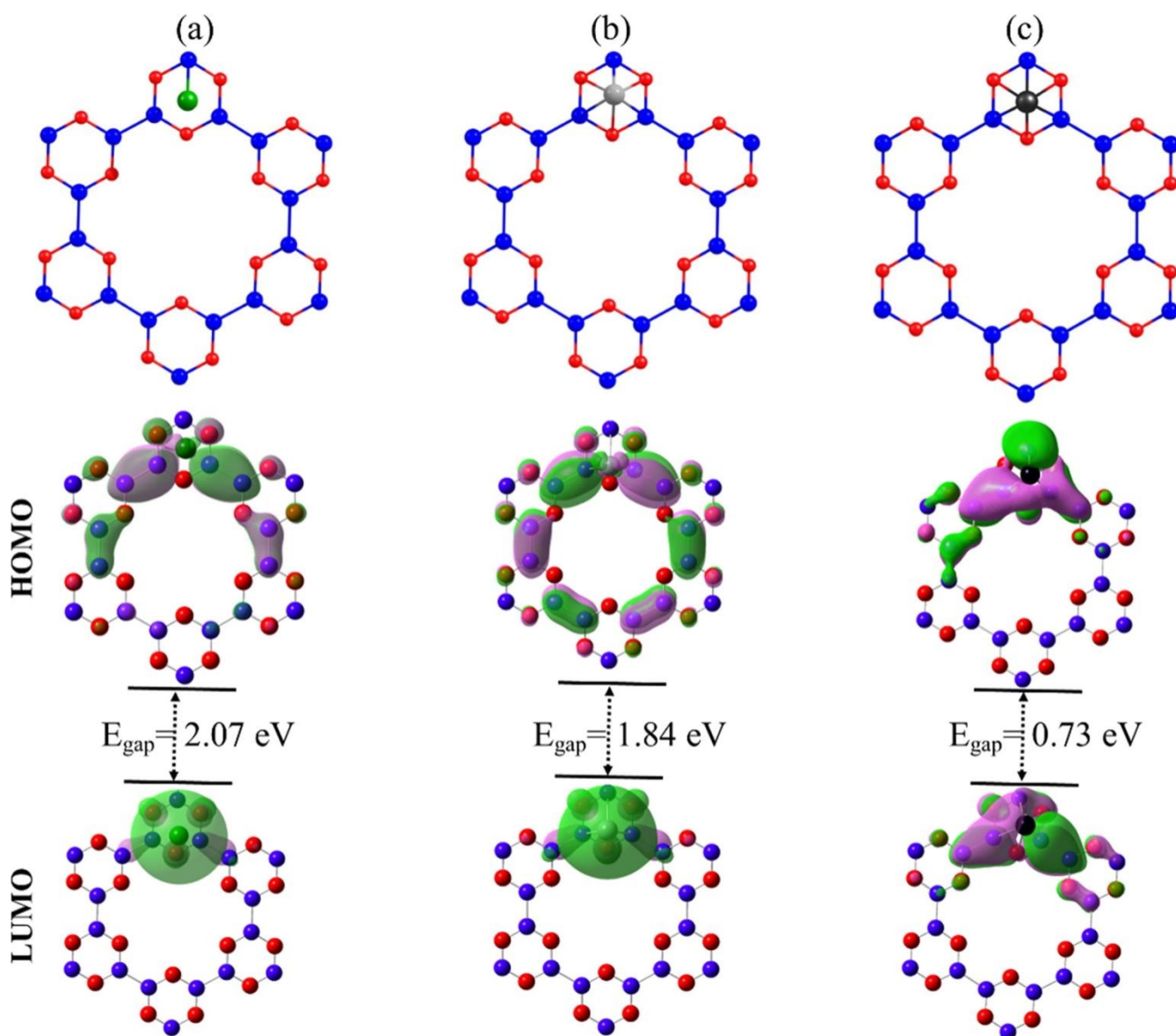
Materials
Advances

Review

Fig. 8 The optimized structures, HOMOs and LUMOs, and E_{gap} values of the heavy metal@boroxine complexes. B, O, Cd, Hg, and Pb atoms are shown in blue, red, green, gray, and black, respectively. Reproduced from ref.[152] with permission from Elsevier, Copyright 2021.

By conducting DFT calculations, the boroxine-based COFs were tested for their use in toxic heavy metals (Hg (II), Pb (II) and Cd (II)) removal from wastewater, and discussed the charge transfer from the boroxine to the metal ions (as shown in Figure 8).[152] It was observed that upon adsorption of the metal ions, the HOMO-LUMO gap reduced, enhancing the electron transport with effective binding affinity between the COF and the heavy metal ions. Again, utilization of various COFs and COF-based materials for removal of palladium,[153] lead[29] and Cr (VI)[154] from water streams, as well as recovery of Au(I) from solution of thiosulfate[155] was reported using experimental and DFT approaches. These studies underscore the remarkable versatility of COFs in environmental remediation and recovery of precious metals, providing an in-depth understanding of the separation mechanisms.

Dye (Methylene Blue) adsorption properties of Schiff base network1 (SNW1) (a series of COFs synthesized by reaction of terephthaldehyde and melamine, synthesized by Mullen et al.[156]) were evaluated using DFT, which showed a thermodynamically favourable spontaneous and exothermic interaction of the COFs with the dye molecules.[157] Zhao et al. reported a pH-responsive COF-based membrane (fabricated through an interfacial polymerization approach) that changes colour with pH, for effective removal of dye and salts from the wastewater stream. The membrane showed good removal efficacy with excellent water flux, especially at high pH. MD simulation was carried out to demonstrate the separation of dye molecules through the COF membrane architecture.[158] The effective role of COF-1 and COF-2 nanostructures in the removal of alizarin dye and its derivatives from aqueous phase was studied using molecular simulations. COF-1 exhibits better interaction with the dye molecules, resulting more effective removal, where π-π and van der Waals interactions played a significant role.[159] The fabrication of TpPa COF membranes and their performance were evaluated for the separation of dye from industrial wastewater.[9,160] From the observation, it was concluded that pi-pi interaction and surface adsorption are the key factors behind the enhanced separation performance of the membrane. The separation efficiency of the membrane with respect to the structure of dye molecules and membrane thickness is also emphasized in the study.[9] The impact of functional groups and pore sizes on COF's dye (bisphenol A) adsorption efficiency (both in liquid and gas environments) was discussed by Wang et al. using DFT, GCMC and MD simulations.[161] The COFs functionalized with -COOH groups stand best in terms of the dye uptake capacity and it was seen that high temperatures reduce the adsorption performance. Removal of dye pollutants (such as Congo red, Gentian violet cat, brilliant green, methyl orange, rhodamine b, tolonium chloride and methylene blue) from water using 1, 3, 6, 8-tetrakis (4formylphenyl) pyrene -COF (3D) was evaluated using computer simulations. DFT and MD simulations (with experimental study) were carried out to study the adsorption of bisphenol-A[162] and removal of Malachite Green from the water stream,[163] using COF-based materials. Harnessing MD and well-tempered metadynamics simulations the dye removal capability of 3D TFPPy-COFs (with underlying dye adsorption mechanisms) was analyzed for different dye contaminants including congo red (CR), rhodamine b (Rh B), brilliant green (BG), Gentian violet (GV), tolonium chloride (TC), methylene blue (MB) and methyl orange (MO) from aqueous phase (as shown in Figure 9).[164] From the metadynamics simulations negative free energy surface (FES) was observed, indicating energetically favourable interactions, as the proposed dye molecules approach the COF architecture. The COFs demonstrated rapid adsorption and promising reusability, showcasing their potential in dye separation or water purification applications.

Classical MD simulation was employed to evaluate the phenol adsorption mechanism on COFs, under the influence of electric field. It was observed that the interaction between the -OH and -NH groups present on the phenol and COFs remarkably enhances the adsorption process.[165] The strategies/influence of optimization of structural parameters, pore design and pore interface engineering in separation/adsorption, energy storage/conversion and catalytic applications of COF was discussed, to achieve their ultimate efficiency.[166] β-cyclodextrin COF demonstrated excellent adsorption capacity (with efficient regeneration ability) towards Perfluoroalkanesulfonates (a toxic organic chemical) for their rapid elimination from the aqueous phase (outperforming conventional adsorbents), which was further validated by DFT calculations.[167]

Research is also going on using COF-based materials, exploring various ways to utilize nuclear power that can help to accomplish the goal of net-zero emissions by 2050. COF nanowires are reported for their excellent uranium capture ability when exposed to sunlight.[168] The growth of the COF nanowires in different solvents was evaluated using MD simulations, where n-butanol stands out best, helping the formation of long nanowires by guiding their growth in specific directions. The uranium capture ability of three novel COFs (incorporated with N-donor heterocycles), over competing ions, from nuclear wastewater and seawater was analyzed using theoretical and experimental studies,[169] where imidazoline-based COF performed excellent uranium extraction capability. Other various COFs or COF-based frameworks were reported for extraction/removal of radioactive uranium from the aqueous stream using experimental study and DFT calculations.[170-172] The effective role of a 2D cationic COF, SCU-COF-1 for nuclear waste management was investigated using experimental as well as MD simulation. The SCU-COF-1 possesses excellent radiation resistance with very high acid stability and effective $99TcO_4^-$ removal capability.[173] Cationic COFs were also investigated for effective elimination of radioactive $^{99}TcO_4^-$ (from water stream) and its adsorption/interaction (at molecular level) with the COF was demonstrated using DFT calculations and MD simulations.[174,175] The adsorption (of imine-linked cationic COFs) was enhanced upon increasing the $^{99}TcO_4^-$ concentration; however, complete removal was difficult due to the presence of tightly held counter anions.

MD simulations were extensively employed to study the separation efficiency of TpPa and functionalized TpPa-R based membranes for the separation of some of the most commonly used solvents (acetone, methanol and ethanol).[176] The study emphasized the critical role of solvent-solvent interactions during the separation process offering valuable insights into the fabrication or design of COF-based organic solvent nanofiltration membranes.

Antibiotics are poorly biodegradable due to their intricate synthetic structure and tend to persist in water phase, making

Review

Materials Advances

them an emerging pollutant demanding effective removal strategies.[151,177] The role and importance of various in-silico
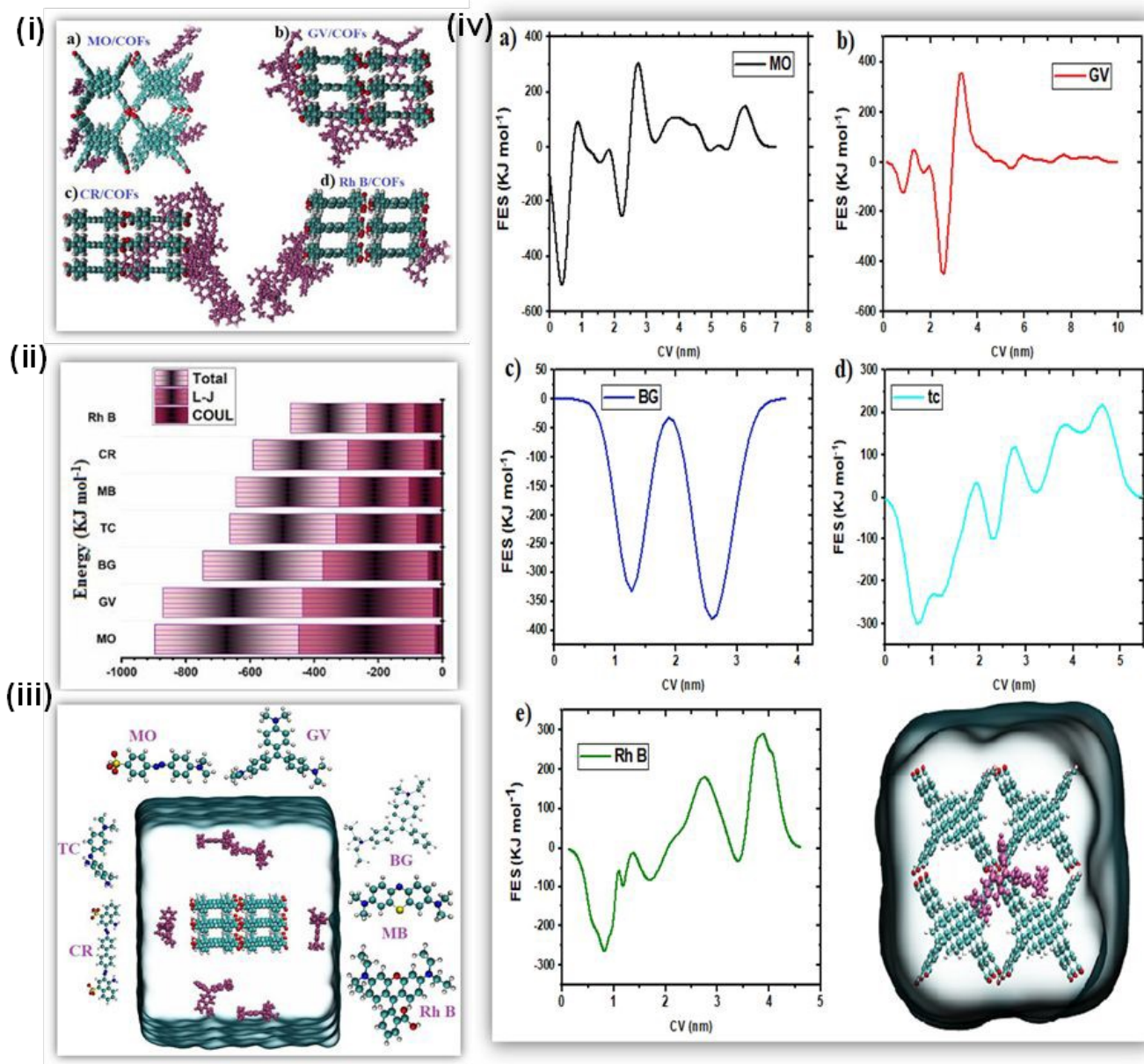
Fig. 9 (i) The final snapshots of the dyes-COFs. (water molecules are not shown for clarity), (ii) the interaction energy between dye molecules and COFs (Total, Lennard-Jones (L-J), and coulombic energies for the adsorption), (iii) the initial snapshot of the studied systems, for COFs/dyes, Color code Carbon: cyan, Hydrogen: gray, Sulfur: yellow, and Nitrogen: blue, and (iv) the FES patterns. For transferring dye molecules (MO/GV/BG/TC and Rh B) towards the COFS materials. Reproduced from ref.[164] with permission from Springer Nature, Copyright 2024.

approaches such as GCMC, MD simulations and quantum mechanical calculations and their synergistic potentials were emphasised to investigate the adsorption efficiency of pharmaceutical pollutants by various surfaces, considering the environmental conditions.[178]

In another study, MD simulations and DFT calculations were conducted to assess the pharmaceutical removal efficiency of three reusable COFs (such as COF-OEt, COF-78

and DAAQ-TFP), from wastewater streams.[70,179]. Van der Waals interaction and hydrogen bond formation were identified as the key factors behind the effective adsorption. MD simulation incorporated with coarse-grained (CG) simulations alongside DFT calculations was employed to study the removal of the drug phenazopyridine from the aqueous phase, using MOF/COF hybrid architecture.[180] Additionally, carbon nanotube incorporated COF-based

composite was reported for the removal of pefloxacin, ofloxacin and norfloxacin from aqueous stream. Employing MD and metadynamics simulations,[151] it was observed that the van der Waals interaction played the dominant role whereas hydrophobic and electrostatic interactions also significantly influence the separation process.

3.3. Drug delivery/Therapeutic application

COFs with metal free tunable porous architectures, high surface area and ease of functionalization make them suitable for drug delivery/therapeutic applications.[181] The effect of temperature and substitution on the drug (doxorubicin) release phenomena of various COFs was examined using MD simulations.[182] In another study, quantum mechanical calculations in tandem with MD simulations were employed to analyze the adsorption behaviour of a drug molecule, 5-fluorouracil (5-Fu) on the PI-3-COF.[183] Stable binding of the COF with the drug, 5-Fu was presented, revealing an exothermic adsorption process, primarily attributed to hydrogen bonding and pi-pi interactions. The slow diffusion of 5-Fu into the COF's porous framework suggested the potential controlled drug delivery applications of the COFs.

Furthermore, the role of triazine-based COF (C_6N_6) as an anti-cancer drug (fluorouracil and nitrosourea) carrier was reported, and the adsorption energies of the drugs towards the COF and the drug release profiles were illustrated using DFT calculations.[184] The study showcased that the adsorption of drugs onto the C_6N_6 occurred primarily due to the van der Waals interactions with fluorouracil, showing stronger interactions and efficient release in an acidic environment (cancerous cells are more acidic compared to normal cells), thereby indicating the potential of the COF (C_6N_6) in anticancer drug delivery applications. In another study, sensor and anticancer drug (lomustine) delivery applications of B6N6 COF were evaluated, employing DFT calculations. It was observed that upon adsorption of the drug, the band gap of the COF gets reduced and the release of the drug was triggered by an external electric field.[185] The anticancer drug (Tegafur) delivering applications of triazine-based COFs was evaluated both in the presence and absence of boron doping. The study highlighted the impact of boron doping (into the COF), in improving the drug adsorption efficacy and enhancing drug recovery.[186] Molecular dynamics and metadynamics simulations were carried out to monitor the impact of -OH functionalization on the 2D COFs during the adsorption of doxorubicin, with pi-pi interactions and hydrogen bonding interactions playing a critical role. In this case, also the drug release favoured an acidic environment, reinforcing the therapeutic applications of the COFs.[187]

Furthermore, a study investigated the therapeutic potential of 2D COFs in treating Alzheimer's disease through a multiscale simulation approach.[107] Alzheimer's disease is mainly caused by the aggregation of β-amyloid (Aβ) protein. To mitigate this, a multi-scale computational strategy was adopted to assess the interaction of the 2D COF with Aβ protein, thereby disrupting their aggregation. Apparently, surface area and functional groups play a crucial role in the inhibitory impact of the 2D COFs. The significance of COF-based architecture in photodynamic therapy applications (having exceptional antimicrobial activities) was studied through experimental investigation and MD simulations.[188] A novel amine-based COF was reported for its excellent drug loading capacity (31.32%) and carboplatin (antineoplastic drug) release efficiency at pH 5, making it effective in anticancer therapy. The adsorption mechanism of the drug on the COF architecture, through C–H–π and hydrogen bonding interactions, was further discussed employing DFT calculations, suggesting the potential of the COF in drug delivery as well as drug design applications.[189] Employing DFT calculations (at ωB97XD/6-311+G (d, p) level), the nature of the interaction of aluminium and boron-modified COFs with metformin and biguanide drugs was addressed thoroughly.[190] The study revealed the robust interaction of boron-doped COF with biguanides, whereas the aluminium-doped COF exhibited effective binding with metformin drugs. Additionally, for dual drug delivery including chemotherapy and photothermal therapy applications, silica core-shell template-based COF nanoplatforms were introduced, demonstrating significant drug loading and synergistic anticancer effects.[191] This novel approach paves the way for extensive applications of such structurally engineered COFs as multimodal therapeutic agents and hydrophobic/hydrophilic drug carriers. Moreover, owing to their lightweight nature as compared to MOFs, COFs are considered more suitable for drug delivery applications.[181] Figure 10 depicts the potential of COFs in various drug delivery applications.

3.4. Photocatalysis

Fei Xie and team members recently reported a DFT study to explore the role of 1,3,5-tris(4-formylphenyl)-triazine (TFPT) and 2,4,6-trimethyl-1,3,5-triazine (TMT) COF in photocatalytic reduction of CO_2.[192] The photocatalytic performance enhancement of COF by single platinum atom modification was analyzed, where it was observed that the modification decreased the energy barrier and band gap, thereby significantly improving the adsorption of light and carbon capture.

Employing DFT calculations, a complete assessment of the interaction behaviour of the Platinum atom with the COF architecture mediated through Pt-C and Pt-N bond, along with the changes in Gibbs free energy during the CO_2 reduction and the adsorption energy of CO_2 on the Pt-COF were thoroughly carried out. The study offers a detailed

understanding of the role of COF in photocatalysis and CO_2 reduction.
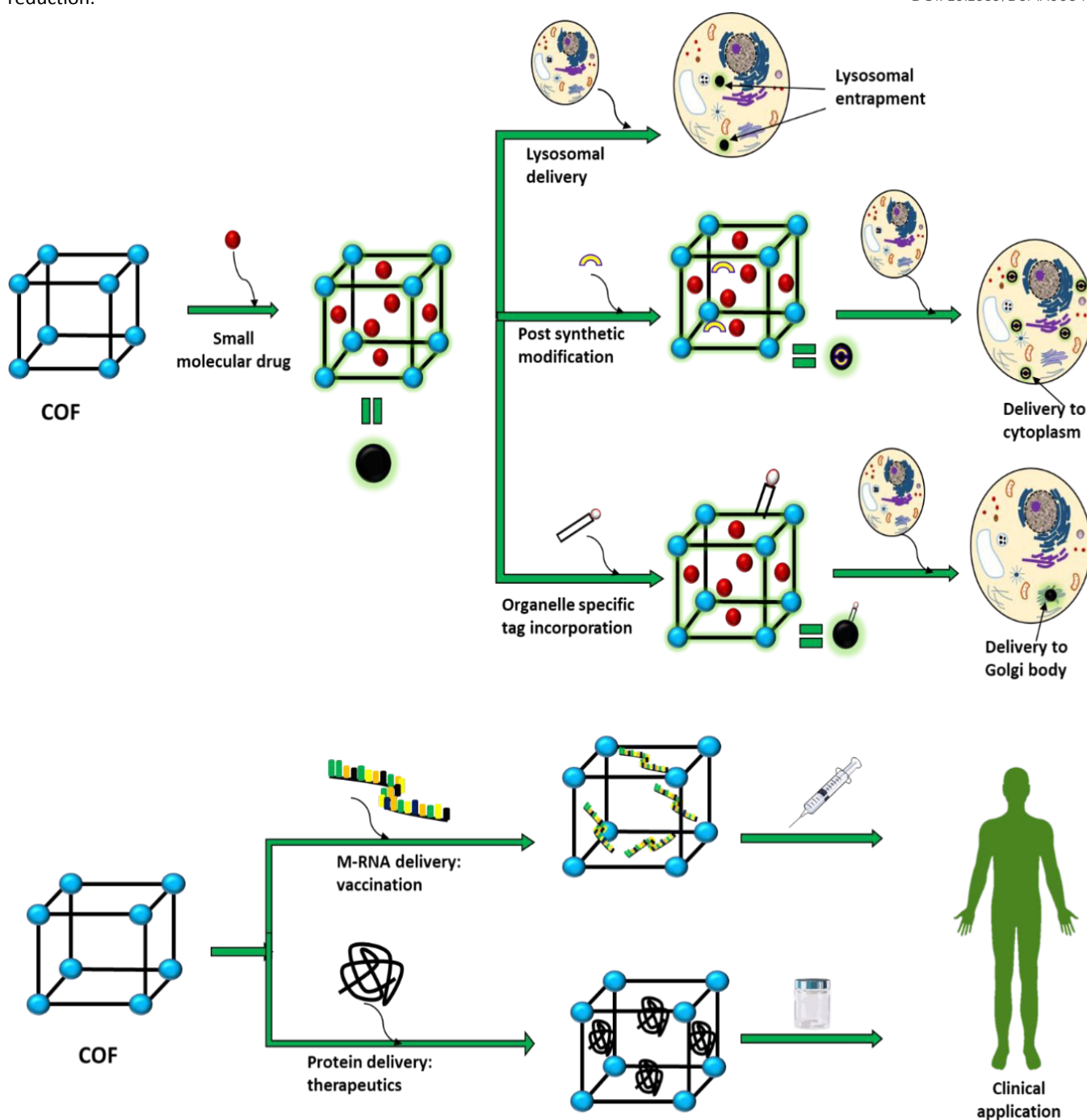
Fig. 10 Representative figure showing the potential of COFs in various drug delivery applications.

Furthermore, the significant effect of interlayer interactions in squaric-acid-linked zwitterionic COFs on their photocatalytic performance was discussed employing DFT.[193] The study suggested that improving the planarity, thereby aiding interlayer interactions, may enhance the photocatalytic performance of the COFs, owing to enhanced charge carrier transport. In another recently reported work, MD simulation underscored the potential of an S-scheme heterostructure of SnS_2/COF during the photocatalytic water-splitting activity. Using sunlight, up to 54.18% of water-splitting efficiency was attained, when pH ranges from 0 to 7.[194] The study highlights the key factors to improve the performance of COFs in photocatalysis applications. Again, in another work, a strategy for enhancing the photocatalytic efficiency of the COFs was presented (using experimental and DFT study) by optimizing the 3D donor-acceptor systems in COFs for improved energy as well as electron transfer.[195] Diverge strategies were reported (through experimental and

DFT approaches) for improving the photocatalytic activities of COFs, focusing on spin-state manipulation, metal ion tuning, local electric fields and conformational/structural modifications. The studies demonstrated that tweaking these factors boosts the photocatalysis applications of COFs such as CO_2 reduction and water splitting.[63,196-201] With respect to the structures of the COFs, their photocatalytic performances were discussed using the DFT and time-dependent DFT study. From the DFT calculations, it was concluded that COF having a narrower bandgap, delocalized HOMO over the naphthalene linker and more positive potential possessed enhanced energy and charge transfer, which fosters effective electron excitations facilitating the photocatalysis process. Additionally, DFT calculations were carried out to assess the charge transfer as well as band alignment in donor-acceptor COFs which revealed a strategy to minimize the exciton binding energy aiding the photocatalytic activities of the COFs.[202,203] In a recently reported work, MD simulation was employed to underscore the role of an S-scheme heterostructure of SnS_2/COF during the photocatalytic water-splitting activity. Using sunlight, up to 54.18% of water-splitting efficiency was attained when pH ranges from 0 to 7.[194] The role of altering the connection of imine linkers in enhancing the photocatalytic efficiency of 2D COFs was explored by Luo et al. The study displayed that optimizing the imine linker connections enhanced the solar-to-hydrogen efficiency from 2.76% to 4.24%.[204] The role of 2D COFs and COF-based architectures was evaluated for photocatalytic water-splitting applications.[205-207] Electronic and light absorption properties of SnS_2/COFs S-scheme van der Waals heterostructures and the impact of strain on these properties were discussed using DFT and time-domain nonadiabatic MD simulations.[205] 2D imine-based COFs with their light absorption and hydrogen production capabilities were presented in another study using an integrated approach of first-principles calculations and MD simulations.[204]

A study presented, β-ketoamine 2D COFs for their effective photocatalytic water-splitting activities achieving upto 13.01% of energy conversion efficiency.[207] Studies on, 3D (fully conjugated) COFs utilizing sunlight, showed enhanced water-splitting behaviour when investigated with the help of first-principles calculations. The 3D COFs showcased excellent light absorption and charge transport even higher than the 2D COFs.[208] Researchers developed hydrophilic COFs having aliphatic linkers to enhance their light absorption and interaction with water, thereby improving photocatalytic activity towards H_2O_2 and H_2 production, which was further validated by DFT calculations.[209] To fulfill the indisputable requirement of novel H_2 evolution catalysts (light-driven in nature) that can replace expensive platinum-based catalysts, a thorough in-

silico study was conducted.[210] In particular, the unique integration of cobaloxime-based H_2 evolution cocatalysts with hydrazone-based COF-42, and their effective photocatalytic H_2 evolution efficiency was presented, providing a new avenue of cobaloxime-tethered COFs in advancing next-generation solar fuel applications. Moreover, employing DFT calculation fused with experimental studies, the crucial atomic-scale analysis of photocatalytic H_2 evolution by H-bonded organic frameworks/COF S-scheme heterojunctions,[211] protonated Z-scheme CdS-COF heterojunction,[212] COF/2D g-C3N4 heterostructure,[213] Arylboron functional COFs,[214] Pt single atom[215] and Pt clusters incorporated COFs[216] and isoelectronic organic dye-based COF[217] for photocatalytic H_2 production was extensively discussed. These study offers an in-depth understanding of COFs in photocatalytic H_2 production applications, providing insights into the charge transfer pathways/mechanisms.[211-217] Mourino et al. reported a screening approach (based on low-cost DFT calculations) on the CURATED COFs database and identified the most promising COF candidates (13 numbers) having effective water-splitting capability. The study also highlighted the best-performing COF materials (N_x-COF (x = 0–3)) for potential applications in H_2 evolution.[27] The impact of multipolar structures, functional groups and hydrazone linkage density in photocatalytic hydrogen peroxide evolution was also discussed using experimental as well as DFT-based approaches (Figure 11).[218-220]

Electrocatalytic nitrate reduction and synthesis of ammonia by Copper-Bipyridine 2D COF films were investigated using experimental and theoretical approaches where it was found that the structural features of the film effectively enhance mass transfer and ammonia production.[221] Computer simulations demonstrated the photocatalytic conversion of nitrogen into ammonia using 3D COFs. After screening the experimental COF database, COF-300 is identified as the most promising candidate owing to its electronic properties and nitrogen uptake capabilities.[222] In an attempt to enhance the (aerobic) photocatalytic oxidation processes, COFs with three-motif molecular junctions were designed and studied employing experimental study and DFT calculations.[223]

It was observed that the best-performing COF effectively converted benzylamine to imines in just 2.5 hours with 99.9% conversion efficiency, owing to high light absorption capability and a synergistic electron transfer pathway. Excellent bisphenol degradation was achieved using the photocatalytic activity of COFs utilizing an integrated approach of experimental studies and DFT calculations.[224]
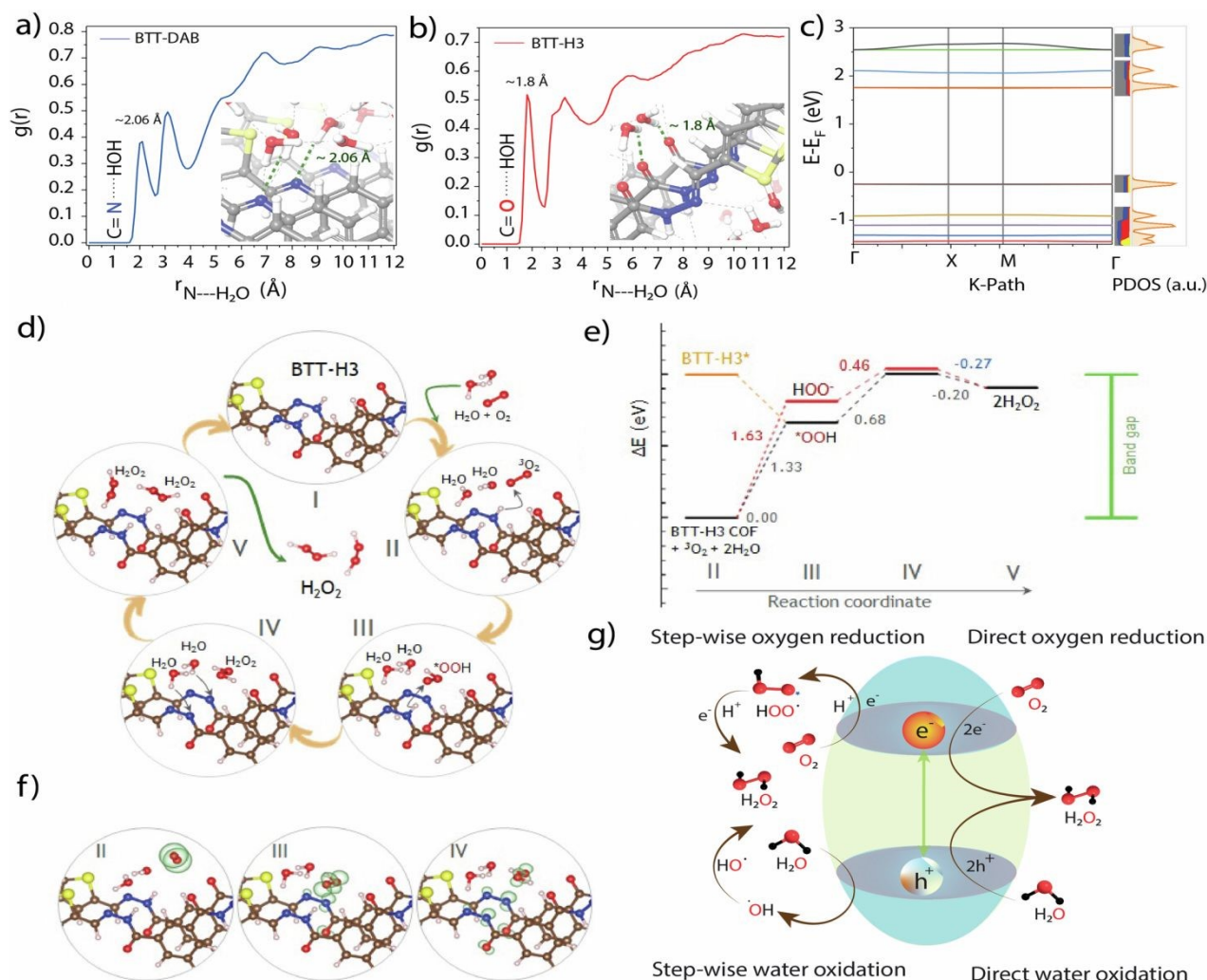
Materials
Advances

Review

Fig. 11 Photocatalytic H_2O_2 evolution study employing computational analysis **(a)** N center of BTT-DAB (Benzo[1,2-b:3,4-b':5,6-b"] trithiophene-2,5,8-tricarbaldehyde and 4-diaminobenzene) COFs, **(b)** O center of BTT-H3 (hydrazone-linked COF), **(c)** Band structure and projected density of states (PDOS) for BTT-H3, **(d)** Molecular mechanism of the generation of H_2O_2 from oxygen and water at the hydrazone center of the BTT-H3 COFs, **(e)** Electronic energy profile of the hydrogen peroxide generation reaction path, **(f)** Spin densities (semitransparent light green blobs) of the radical species, **(g)** Representation of the overall photocatalytic mechanism of H_2O_2 generation through water oxidation reaction and oxygen reduction reaction. Reproduced from ref.[220] with permission from Springer Nature, Copyright 2025.

Recent studies have focused on the development of COFs and metal-based COFs for numerous applications, including environmental remediation, reduction of CO_2 and extraction of uranium from seawater, that are extensively evaluated using experimental, DFT and ML approaches.[225-231] These studies may play a crucial role in leveraging advanced design strategies for next-generation COF-based photocatalysts and their future advancements in the domains of optoelectronic, photocatalytic, and environmental remediation applications.

3.5. Photovoltaics and Sensors

The electronic properties and charge dynamics of 2D aza-COFs were analyzed with the help of time domain DFT calculations and non-adiabatic MD simulations. The direct band gap, prolonged electron-hole recombination, and

exceptional light absorption of the COF and its potential for effective solar-energy harvesting and future applications in photovoltaic devices were also discussed in the study.[178] A novel subphthalocyanine-based 3D COF, co-crystallized with
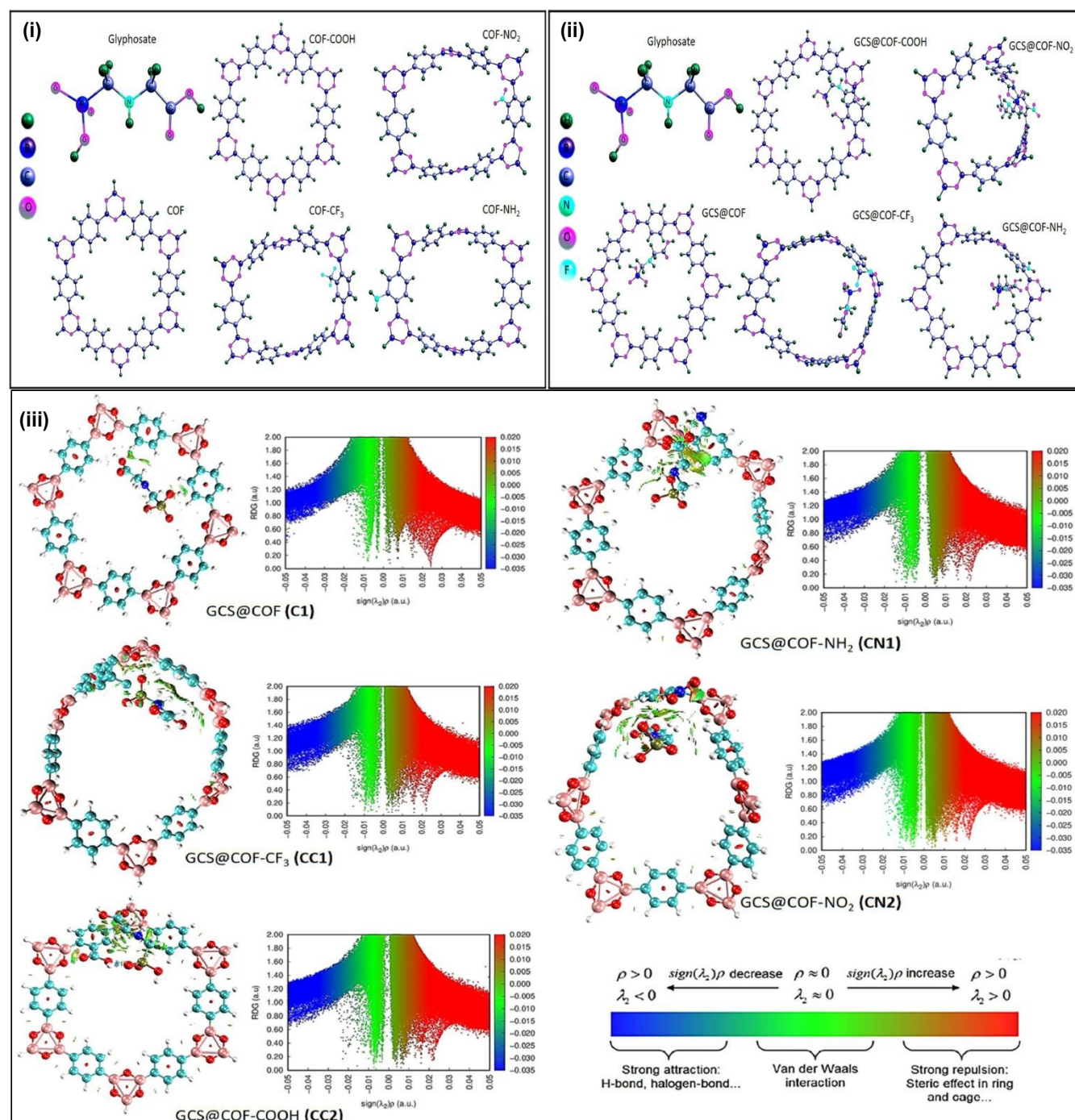

Figure 12: (i) Optimized structures of the GCS with the pure and functionalized COFs, (ii) Optimized structures of stable configurations of the stable complexes (complexes of the COFs with GCS) studied at M06-2X/ LanL2DZ level of theory, and (iii) 3D NCI isosurface and the 2D RDG scatter maps for all studied complexes. Reproduced from ref.[233] with permission from Elsevier, Copyright 2025.

fullerene, displayed enhanced photovoltaic performance, achieving a balance between long-range order and surface area.[232] The electronic properties evaluation, insights into charge transfer, structural optimization and separation

mechanisms of the COFs were explored using DFT and MD simulations. The recent advancements in photovoltaic applications utilizing COFs and MOFs were also reviewed in

another study, owing to their exceptional stability and tunable electronic properties.[233]

Furthermore, DFT study explored the detection of nitroaniline isomers (which are toxic in nature), using 2D B6N6 (boron nitride) COFs.[234] The study revealed the binding behaviour of the COFs with the nitroaniline isomers through weak van der Waals interaction, which pointed out their potential towards sensor applications. The chemical and thermal properties of imine-linked COFs were characterized through computational as well as experimental approaches.[235] B_6N_6 COFs were reported for their effective sensing capabilities in detecting cathinone drugs (showing significant conductivity changes) and adsorption energies were calculated using the DFT approach.[236] Various COF-based architectures were reported employing experimental study, DFT calculations, GCMC and MD simulations for their use in sensor applications. These include selective sensing of nitrogen dioxide,[237] ethane and carbon monoxide,[238] dopamine in serum,[239] HCl vapours,[240] formic acid,[241] nitric oxide & hydrogen sulfide,[242] and volatile organic compounds.[243] Employing DFT calculations (utilizing M06-2X/Gen/6-311G(d)/LanL2DZ method), the adsorptive behaviour of glyphosate (GCS), one of the mostly used herbicide, on the e TpBD-based COF architectures and its potential sensing application was studied (as shown in Figure 12).[244] The study explores the impact of various functional derivatives such as -NO₂, -NH₂, -CF₃ and -COOH, when incorporated to the COF, in the adsorption process. Out of all the studied systems, GCS@COF–NH₂ possessed the highest negative value of adsorption energy. 2D reduced density gradient (RDG) scatter plots and 3D non-covalent interactions (NCI) isosurface plots were visualized, revealing the variations of interaction in all the studied complex systems. In 3D visualization as represented in Figure 12, the green and blue regions indicate weak vdW and H-bonding interactions, respectively, whereas the repulsive forces in the systems are indicated by the red patches.

4. Conclusion

COFs are emerging as a groundbreaking class of current scientific research showcasing their significant potential in various applications, such as in gas separation/storage, wastewater treatment, drug delivery, photocatalysis, sensor, photovoltaics and environmental remediation. To advance the understanding of COFs, computational chemistry plays an imperative role, providing molecular-level insights and highlighting the promising features of COFs that make them suitable for a broad range of research domains. Computational chemistry is a powerful tool providing an in-depth evaluation of interaction/adsorption mechanisms, electronic properties and performance-

structure relationships. The impact of the pore sizes, topology, functional groups and configurational modifications of COFs on the gas storage, adsorption, separation processes and catalytic activities, from the perspective of computational chemistry, are discussed in this review article.

Future studies should focus on linkage engineering to enhance the stabilities and properties of COFs, making them more effective in real-world applications. Proper planning of a functionalization strategy with precise positioning within the COF architecture is indeed valuable without disturbing its original framework, which may be carried out through host-guest interactions, metalation, and click chemistry. Further research should be carried out on chemical locking (by converting the linkages to a more stable form) and protective coating of COFs, which may enhance their lifespan to a great extent, even under harsh physical and chemical conditions. Designing of hybrid materials should also be anticipated, by integrating COFs with other materials such as graphene, CNT and MOFs, resulting in advanced composites with unprecedented properties and performance. Upcoming studies should aim to develop computational high-throughput screening approaches to find out the most suitable COFs for particular applications. Moreover, advanced 3D paining techniques could be employed to build COFs with complex designs with tailored properties for specific applications. Machine learning integrated with computational modelling can facilitate the discovery of novel COF-based materials by predicting their behaviour and properties. Overall, future research should focus on computational and experimental strategies for tuning pore sizes, chemical functionalities and surface area of COFs or COF-based materials, to make their large-scale applicability in industrial as well as scientific domains.[16,245]

It is noteworthy that, in contrast to several advancements, hurdles remain in combining computational and experimental findings and attaining effective/accurate multiscale modelling, which should be properly addressed to fully unveil or unlock the exciting potential of COFs in diverse domains. The potential of various advanced computational strategies was critically reviewed while addressing the optimization approaches and key challenges during COF design, ultimately guiding the design and development of tailored COF-based materials for numerous applications. By bridging ML and simulations with experimental feedback may lead to an era of more rational COF design. Meanwhile, we believe that this study can serve as a stepping stone for future advancements, accelerating the design of novel next-generation COF-based materials (both experimentally and computationally) and paving the way for their applications in real-world scenarios, tackling global challenges.

Author contributions

Parashmoni Rajguru: Drafting the original Manuscript, Editing, Reviewing, Formal analysis, software.

Prarthana Bora: Software, Formal analysis.

Chinmoy Bhuyan: Software, Formal analysis

Swapnali Hazarika: Conceptualization, Investigation, Writing – review & editing, Supervision.

Conflicts of interest

The authors declare that this work has not been published previously, and it is not under consideration for publication elsewhere. We also declare that we have no conflicts of interest.

Data availability statement

All the relevant data have been presented in the manuscript.

Acknowledgments

Funding Statement

Notes

The authors declare no competing financial interest.

References

[1] X. Zhang, J. Hu, H. Liu, T. Sun, Z. Wang, Y. Zhao, Y. B. Zhang, P. Huai, Y. Ma and S. Jiang, Determining covalent organic framework structures using electron crystallography and computational intelligence, Journal of the American Chemical Society, 2024, 147, 1709-1720. https://doi.org/10.1021/jacs.4c12757

[2] F. Chen, H. Zheng, Y. Yusran, H. Li, S. Qiu, and Q. Fang, Exploring high-connectivity three-dimensional covalent organic frameworks: topologies, structures, and emerging applications, Chemical Society Reviews, 2025, 54, 484-514. https://doi.org/10.1039/D4CS00703D

[3] T. Wu, Y. Qian, Z. Zhu, W. Yu, L. Zhang, J. Liu, X. Shen, Xi. Zhou, T. Qian and C. Yan, Imine-Linked 3D Covalent Organic Framework Membrane Featuring Highly Charged Sub-1 nm Channels for Exceptional Lithium-Ion Sieving, Advanced Materials, 2025, 37, 2415509. https://doi.org/10.1002/adma.202415509

[4] S. Ma, Z. Zhou, Y. Zhang, R. Rao, H. Han, J. Liang, Z. Zhao, F. Bi, N. Liu and X. Zhang, Review of irradiation treatments on MOFs and COFs: Synthesis, modification, and application, Separation and Purification Technology, 2024, 339, 126636. https://doi.org/10.1016/j.seppur.2024.126636

[5] R. Liu, K. T. Tan, Y. Gong, Y. Chen, Z. Li, S. Xie, T. He, Z. Lu, H. Yang and D. Jiang, Covalent organic frameworks: an ideal platform for designing ordered materials and advanced applications, Chemical Society Reviews, 2021, 50, 120-242. DOI: 10.1039/D0CS00620C

[6] A. P. Cote, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger and O. M. Yaghi, Porous, crystalline, covalent organic frameworks, Science, 2005, 310, 1166-1170. DOI: 10.1126/science.1120411

[7] H. M. El-Kaderi, J. R. Hunt, J. L. Mendoza-Cortés, A. P. Côté, R. E. Taylor, M. O'Keeffe and O. M. Yaghi, Designed synthesis of 3D covalent organic frameworks, Science, 2007, 316, 268-272. DOI: 10.1126/science.1139915

[8] H. Vardhan, G. Rummer, A. Deng and S. Ma, Large-scale synthesis of covalent organic frameworks: challenges and opportunities. Membranes, 2023, 13, 696. https://doi.org/10.3390/membranes13080696

[9] X. Zhu, B. Ma, Y. Ai, L. Zhang, X. Wang, L. Liang and J. W. Shen, Investigation on dye separation mechanism in covalent-organic framework membranes with molecular dynamics simulation, Microporous and Mesoporous Materials, 2023, 349, 112417. https://doi.org/10.1016/j.micromeso.2022.112417

[10] A. Shahbaz, K. Ahmad, K. Qureshi, H. Majeed, I. Arshad, T. Tabinda, T. Iftikhar, K. U. Khair, M. Ashfaq, H. U. R. Shah, M. Z. Ahmad and S. L. Lee, Porous materials: covalent Organic Frameworks (COFs) as game-changers in practical applications, a review, Reviews in Inorganic Chemistry, 2024, 44, 117-133. https://doi.org/10.1515/revic-2023-0018

[11] X. Zhao, P. Pachfule and A. Thomas, Covalent organic frameworks (COFs) for electrochemical applications, Chemical Society Reviews, 2021, 50, 6871-6913. DOI: 10.1039/D0CS01569E

[12] Z. Wang, S. Zhang, Y. Chen, Z. Zhang and S. Ma, Covalent organic frameworks for separation applications, Chemical

View Article Online
DOI: 10.1039/D5MA00843C

Materials Advances Accepted Manuscript

Society Reviews, 2020, 49, 708-735. DOI: 10.1039/C9CS00827F

[13] G. O. Aksu, I. Erucar, Z. P. Haslak and S. Keskin, Exploring covalent organic frameworks for H2S+ CO2 separation from natural gas using efficient computational approaches, Journal of CO2 Utilization, 2022, 62, 102077. https://doi.org/10.1016/j.jcou.2022.102077

[14] L. Zhao, C. Yu, X. Wu, M. Zuo, Q. Zhang, Q. Dong and L. Ding, Computational Screening Guiding the Development of a Covalent-Organic Framework-Based Gas Sensor for Early Detection of Lithium-Ion Battery Electrolyte Leakage, ACS Applied Materials & Interfaces, 2025. https://doi.org/10.1021/acsami.4c19321

[15] H. R. Abuzeid, A. F. EL-Mahdy and S. W. Kuo, Covalent organic frameworks: Design principles, synthetic strategies, and diverse applications, Giant, 2021, 6, 100054. https://doi.org/10.1016/j.giant.2021.100054

[16] S. Raghav, J. Raghav, M.A.A. Muhammad, M.B. Singh, P. Jain and D. Kumar, Recent advancements in synthesis and applications of covalent organic frameworks. Applied Materials Today, 2025, 44, 102694. https://doi.org/10.1016/j.apmt.2025.102694

[17] N. Keller and T. Bein, Optoelectronic processes in covalent organic frameworks, Chemical Society Reviews, 2021, 50(3), 1813-1845. https://doi.org/10.1039/D0CS00793E

[18] G. O. Aksu and S. Keskin, The COF Space: Materials Features, Gas Adsorption, and Separation Performances Assessed by Machine Learning, ACS Materials Letters, 2025, 7, 954-960. https://doi.org/10.1021/acsmaterialslett.4c02594

[19] S. Velioglu and S. Keskin, Simulation of H2/CH4 mixture permeation through MOF membranes using non-equilibrium molecular dynamics, Journal of Materials Chemistry A, 2019, 7(5), 2301-2314. https://doi.org/10.1039/C8TA10167A

[20] D. Sen, The uncertainty relations in quantum mechanics, Current Science, 2014, 203-218. https://www.jstor.org/stable/24103129

[21] C. de Ronde, R. Fernández Mouján and C. Massri, Everything is entangled in quantum mechanics: on the measures of quantum entanglement, The European Physical Journal Plus, 2024, 139, 1039. https://doi.org/10.1140/epjp/s13360-024-05824-6

[22] Y. Sun, Y. Ma, B. Yu, W. Zhang, L. Zhang, P. Chen and L. Xu, Perspectives on Molecular Simulation of CO2/CH4 Competitive Adsorption in a Shale Matrix: A Review, Energy & Fuels, 2024, 38, 15935-15971. https://doi.org/10.1021/acs.energyfuels.4c02206

[23] H. J. F. Jansen, Many-body properties calculated from the Kohn-Sham equations in density-functional theory, Physical Review B, 1991, 43, 12025. DOI: https://doi.org/10.1103/PhysRevB.43.12025

[24] S. Wang, G. Zhou, Y. Ma, L. Gao, R. Song, G. Jiang, G. Lu, Molecular dynamics investigation on the adsorption behaviors of H2O, CO2, CH4 and N2 gases on calcite (1 1 0)

surface, Applied Surface Science, 2016, 385, 616-621. https://doi.org/10.1016/j.apsusc.2016.05.026

[25] K. P. Zois and D. Tzeli, A Critical Look at Density Functional Theory in Chemistry: Untangling Its Strengths and Weaknesses, Atoms, 2024, 12, 65. https://doi.org/10.3390/atoms12120065

[26] N. E. Fard, N. S. Ali, N. M. C. Saady, T. M. Albayati, I. K. Salih, S. Zendehboudi, H. N. Harharah and R. H. Harharah, A review on development and modification strategies of MOFs Z-scheme heterojunction for photocatalytic wastewater treatment, water splitting, and DFT calculations, Heliyon, 2024. 10.1016/j.heliyon.2024.e32861

[27] B. Mourino, K. M. Jablonka, A. Ortega-Guerrero and B. Smit, In Search of Covalent Organic Framework Photocatalysts: A DFT-Based Screening Approach, Advanced Functional Materials, 2023, 33, 2301594. https://doi.org/10.1002/adfm.202301594

[28] A. Dittmer, R. Izsak, F. Neese and D. Maganas, Accurate band gap predictions of semiconductors in the framework of the similarity transformed equation of motion coupled cluster theory, Inorganic chemistry, 2019, 58, 9303-9315. https://doi.org/10.1021/acs.inorgchem.9b00994

[29] S. Wang, H. Wang, S. Wang, L. Fu and L. Zhang, Novel magnetic covalent organic framework for the selective and effective removal of hazardous metal Pb (II) from solution: Synthesis and adsorption characteristics, Separation and Purification Technology, 2023, 307, 122783. https://doi.org/10.1016/j.seppur.2022.122783

[30] P. Zhu and V. Meunier, Electronic properties of two-dimensional covalent organic frameworks, The Journal of chemical physics, 2012, 137. https://doi.org/10.1063/1.4772535

[31] D. D. Medina, M. L. Petrus, A. N. Jumabekov, J. T. Margraf, S. Weinberger, J. M. Rotter, T. Clark and T. Bein, Directional charge-carrier transport in oriented benzodithiophene covalent organic framework thin films, ACS nano, 2017, 11, 2706-2713. https://doi.org/10.1021/acsnano.6b07692

[32] Y. Jin, S. Zheng, Z. Lin, S. Chen, Z. Xiao, Y. Mi, S. Fan, Y. Zou, D. Zeng, J. Gong, H. Zhang and G. Liu, An innovative guanidinium-based ionic covalent organic frameworks with abundant aromatic rings for high-efficiency naproxen removal: Adsorption behavior, mechanisms, and density functional theory calculations, Separation and Purification Technology, 2025, 357, 130182. https://doi.org/10.1016/j.seppur.2024.130182

[33] Y. Wang, L. He, W. Wei, X. Zhang, L. Zeng, T. Jiang, J. Li, S. Chen and Z. Gao, A review of fluorescent covalent organic frameworks for heavy metal ion sensors, Chemical Engineering Journal, 2025, 159249. https://doi.org/10.1016/j.cej.2025.159249

[34] S. Pakhira and J. L. Mendoza-Cortes, Intercalation of first row transition metals inside covalent-organic frameworks (COFs): a strategy to fine tune the electronic properties of

porous crystalline materials, Physical chemistry chemical physics, 2019, 21, 8785-8796. DOI: 10.1039/C8CP07396A

[35] K. Gontarczyk, W. Bury, J. Serwatowski, P. Wiecinski, K. Wozniak, K. Durka and S. Lulinski, Hybrid triazine-boron two-dimensional covalent organic frameworks: Synthesis, characterization, and DFT approach to layer interaction energies, ACS Applied Materials & Interfaces, 2017, 9, 31129-31141. https://doi.org/10.1021/acsami.7b09061

[36] J. Yang, S. Ghosh, J. Roeser, A. Acharjya, C. Penschke, Y. Tsutsui, J. Rabeah, T. Wang, S.Y.D. Tameu, M.Y. Ye, J. Grüneberg, S. Li, C. Li, R. Schomäcker, R.V.D. Krol, S. Seki, P. Saalfrank and A. Thomas, Constitutional isomerism of the linkages in donor–acceptor covalent organic frameworks and its impact on photocatalysis, Nature Communications, 2022, 13, 6317. https://doi.org/10.1038/s41467-022-33875-9

[37] S. Fu, X. Zhang, K. Wang, L. Chen, F. Xia, Y. Cui and Y. Liu, Synthetic control of chiral pore surfaces in covalent organic frameworks for enantioselective separation of chiral drugs, Science China Chemistry, 2025, 1-9. https://doi.org/10.1007/s11426-024-2452-x

[38] R. Stierle, G. Bauer, N. Thiele, B. Bursik, P. Rehner and J. Gross, Classical density functional theory in three dimensions with GPU-accelerated automatic differentiation: Computational performance analysis using the example of adsorption in covalent-organic frameworks, Chemical Engineering Science, 2024, 298, 120380. https://doi.org/10.1016/j.ces.2024.120380

[39] A. S. Christensen, T. Kubar, Q. Cui and M. Elstner, Semiempirical quantum mechanical methods for noncovalent interactions for chemical and biochemical applications, Chemical reviews, 2016, 116, 5301-5337. https://doi.org/10.1021/acs.chemrev.5b00584

[40] S. Grimme, C. Bannwarth and P. Shushkov, A robust and accurate tight-binding quantum chemical method for structures, vibrational frequencies, and noncovalent interactions of large molecular systems parametrized for all spd-block elements (Z= 1–86), Journal of chemical theory and computation, 2017, 13, 1989-2009. https://doi.org/10.1021/acs.jctc.7b00118

[41] P. Rajguru, K. D. Dihingia, A. Konwar, P. Bora, C. Bhuyan, S. Saha, G. N. Sastry and S. Hazarika. Carbon nanotube/Fe2O3 nanocomposites for optimizing membrane-based separation of antibiotics: Experimental and computational approach, Materials Today Communications, 2025, 44, 111951. https://doi.org/10.1016/j.mtcomm.2025.111951

[42] M. Gaus, Q. Cui and M. Elstner, DFTB3: Extension of the self-consistent-charge density-functional tight-binding method (SCC-DFTB), Journal of chemical theory and computation, 2011, 7, 931-948. https://doi.org/10.1021/ct100684s

[43] S. Moradi, R. Tomann, J. Hendrix, M. Head-Gordon and C. J. Stein, Spin parameter optimization for spin-polarized extended tight-binding methods, Journal of Computational Chemistry, 2024, 45, 2786-2792. https://doi.org/10.1002/jcc.27482

[44] G. Zheng, H. A. Witek, P. Bobadova-Parvanova, S. Irle, D. G. Musaev, R. Prabhakar, K. Morokuma, M. Lundberg, M. Elstner, C. Köhler and T. Frauenheim, Parameter calibration of transition-metal elements for the spin-polarized self-consistent-charge density-functional tight-binding (DFTB) method: Sc, Ti, Fe, Co, and Ni, Journal of chemical theory and computation, 2007, 3, 1349-1367. https://doi.org/10.1021/ct600312f

[45] G. A. Oxford, R. Q. Snurr and L. J. Broadbelt, Hybrid quantum mechanics/molecular mechanics investigation of (salen) Mn for use in metal– organic frameworks, Industrial & engineering chemistry research, 2010, 49, 10965-10973. https://doi.org/10.1021/ie100165j

[46] P. U. Kulkarni, H. Shah and V. K. Vyas, Hybrid quantum mechanics/molecular mechanics (QM/MM) simulation: a tool for structure-based drug design and discovery, Mini reviews in medicinal chemistry, 2022, 22, 1096-1107. https://doi.org/10.2174/1389557521666211007115250

[47] H. Lin, QM/MM Methods. American Chemical Society, 2024.

[48] H. M. Senn and W. Thiel, QM/MM methods for biomolecular systems, Angewandte Chemie International Edition, 2009, 48, 1198-1229. https://doi.org/10.1002/anie.200802019

[49] G. Groenhof, Introduction to QM/MM simulations, Biomolecular simulations: methods and protocols, 2012, 43-66. https://doi.org/10.1007/978-1-62703-017-5_3

[50] S. E. Boulfelfel, J. M. Findley, H. Fang, A. S. Daou, P. I. Ravikovitch and D. S. Sholl, A transferable force field for predicting adsorption and diffusion of small molecules in alkali metal exchanged zeolites with coupled cluster accuracy, The Journal of Physical Chemistry C, 2021, 125, 26832-26846. https://doi.org/10.1021/acs.jpcc.1c07790

[51] A. A. Glushak, E. V. Tararushkin and G. S. Smirnov, A classical force field for selenium oxyanions in aqueous solutions and minerals, Journal of Molecular Liquids, 2025, 422, 126904. https://doi.org/10.1016/j.molliq.2025.126904

[52] L. Monticelli and D. P. Tieleman, eds. Biomolecular simulations: methods and protocols. Vol. 924. Totowa, NJ: Humana Press, 2013. https://doi.org/10.1007/978-1-62703-017-5

[53] O. Andreussi, I. G. Prandi, M. Campetella, G. Prampolini and B. Mennucci, Classical force fields tailored for QM applications: Is it really a feasible strategy?, Journal of chemical theory and computation, 2017, 13, 4636-4648. https://doi.org/10.1021/acs.jctc.7b00777

[54] E. Tylianakis and G. E. Froudakis, Grand canonical Monte Carlo method for gas adsorption and separation, Journal of Computational and Theoretical Nanoscience, 2009, 6, 335-348. https://doi.org/10.1166/jctn.2009.1040

Materials Advances Accepted Manuscript

[55] X. Wang, H. Liu, M. Sun, F. Gao, X. Feng, M. Xu, W. Fan and D. Sun, Functionalization of covalent organic frameworks with cyclopentadienyl cobalt for C2H2/CO2 separation, Angewandte Chemie, 2025, 137, e202420801. https://doi.org/10.1002/ange.202420801

[56] L. Li, Y. Zhu, Z. Qi, X. Li, H. Pan, B. Liu and Y. Liu, GCMC simulations to study the potential of MOFs as drug delivery vehicles, Applied Organometallic Chemistry, 2023, 37, e7199. https://doi.org/10.1002/aoc.7199

[57] D. W. Siderius and V. K. Shen, Use of the grand canonical transition-matrix Monte Carlo method to model gas adsorption in porous materials, The Journal of Physical Chemistry C, 2013, 117, 5861-5872. https://doi.org/10.1021/jp400480q

[58] T. R. Zeitler, M. D. Allendorf and J. A. Greathouse, Grand canonical Monte Carlo simulation of low-pressure methane adsorption in nanoporous framework materials for sensing applications, The Journal of Physical Chemistry C, 2012, 116, 3492-3502. https://doi.org/10.1021/jp208596e

[59] H. Fan, A. Mundstock, A. Feldhoff, A. Knebel, J. Gu, H. Meng and J. Caro, Covalent organic framework–covalent organic framework bilayer membranes for highly selective gas separation, Journal of the American Chemical Society, 2018, 140, 10094-10098. https://doi.org/10.1021/jacs.8b05136

[60] Z. Xia, Y. Zhao and S. B. Darling, Covalent organic frameworks for water treatment, Advanced Materials Interfaces, 2021, 8, 2001507. https://doi.org/10.1002/admi.202001507

[61] B. B. Luan, X. Chu, Y. Wang, X. Qiao, Y. Jiang and F. M. Zhang, Construction of COF/COF Organic S-Scheme Heterostructure for Enhanced Overall Water Splitting, Advanced Materials, 2024, 36, 49 2412653. https://doi.org/10.1002/adma.202412653

[62] Y. Ju, K. Zhang, P. Gan, B. Guo, H. Xia, L. Zhang, B. Wang, L. Zhang and J. Chen, Functionalized covalent organic frameworks for catalytic conversion of biomass-derived xylan to furfural, International Journal of Biological Macromolecules, 2025, 294, 139541. https://doi.org/10.1016/j.ijbiomac.2025.139541

[63] H. Daglar, H. C. Gulbalkan, G. O. Aksu and S. Keskin, Computational simulations of metal–organic frameworks to enhance adsorption applications, Advanced Materials, 2024, 2405532. https://doi.org/10.1002/adma.202405532

[64] Q. Huang, H. Zhang, H. Yang, Z. Yu, Z. Xu, Z. Li, Z. Gao and J. P. Zou, Site engineering of covalent organic frameworks to increase charge transfer channels and provide hydrogen bond toward enhanced photocatalytic reduction of U(VI), Applied Catalysis B: Environment and Energy, 2025, 362, 124721. https://doi.org/10.1016/j.apcatb.2024.124721

[65] J. He, S. Yang, C. Luo, F. Li, X. Jiang, Z. Liu, Y. Feng, R. Wu, Z. R. Lan, M. Tao, G. Niu, K. Yang, Y. Yuan, Y. Wang, X. Deng, Y. Chen, S. Zeng, Y. Zhao, F. Wang, Y. W. Zhong, W. Zhang, Q. Zhao, F. Liu, G. Yu and J. Wang, Cyclic Multi-Site Chelation for Efficient and Stable Inverted Perovskite Solar Cells, Angewandte Chemie International Edition, 2025, 64, 2 , e202414118. https://doi.org/10.1002/anie.202414118

[66] J. L. Sheng, H. Dong, X. B. Meng, H. L. Tang, Y. H. Yao, D. Q. Liu, L. L. Bai, F. M. Zhang, J. Z. Wei and X. J. Sun, Effect of different functional groups on photocatalytic hydrogen evolution in covalent-organic frameworks, ChemCatChem, 2019 11 (9) 2313-2319. https://doi.org/10.1002/cctc.201900058

[67] A. Abedini, E. Crabtree, J. E. Bara and C. H. Turner, Molecular analysis of selective gas adsorption within composites of ionic polyimides and ionic liquids as gas separation membranes, Chemical Physics, 2019, 516, 71-83. https://doi.org/10.1016/j.chemphys.2018.08.039

[68] H. Chen, Y. Guo, Y. Du, X. Xu, C. Su, Z. Zeng and L. Li, The synergistic effects of surface functional groups and pore sizes on CO2 adsorption by GCMC and DFT simulations, Chemical Engineering Journal, 2021, 415, 128824. https://doi.org/10.1016/j.cej.2021.128824

[69] Y. Jiang, X. Xu, B. Liu, C. Zhou, H. Wang, J. Qiu, Z. Zeng, Y. Ge and L. Li, Optimal pore size design guided by GCMC molecular simulation for VOCs adsorption, Microporous and Mesoporous Materials, 2022, 341, 112081. https://doi.org/10.1016/j.micromeso.2022.112081

[70] M. Ghasemi, M. Khedri, M. Didandeh, M. Taheri, E. Ghasemy, R. Maleki, H. K. Shon and A. Razmjou, Removal of pharmaceutical pollutants from wastewater using 2D covalent organic frameworks (COFs): an in silico engineering study Industrial & Engineering Chemistry Research, 2022, 61 (25), 8809-8820. https://doi.org/10.1021/acs.iecr.2c00924

[71] M. D. Wigh, T. M. Hansen and A. Døssing, Inference of unexploded ordnance (UXO) by probabilistic inversion of magnetic data, Geophysical Journal International, 2020, 220(1), 37-58. https://doi.org/10.1093/gji/ggz421

[72] D. A. Gómez-Gualdrón, T. C. Wang, P. García-Holley, R. M. Sawelewa, E. Argueta, R. Q. Snurr, J. T. Hupp, T. Yildirim and O. K. Farha, Understanding volumetric and gravimetric hydrogen adsorption trade-off in metal–organic frameworks, ACS applied materials & interfaces, 2017, 9(39), 33419-33428. https://doi.org/10.1021/acsami.7b01190

[73] H. Wang, Z. G. Qu, W. Zhang, Q. N. Yu and Y. L. He, Experimental and numerical study of CO2 adsorption on copper benzene-1, 3, 5-tricarboxylate (Cu-BTC) metal organic framework, International Journal of Heat and Mass Transfer, 2016, 92, 859-863.

[74] H. Huang, W. Zhang, D. Liu, B. Liu, G. Chen and C. Zhong, Effect of temperature on gas adsorption and separation in ZIF-8: A combined experimental and molecular simulation study, Chemical engineering science, 2011, 66, 6297-6305. https://doi.org/10.1016/j.ces.2011.09.009

[75]   W. Li, Y. Lin, S. Li, T. Liang, Z. Cai and W. Wu, Sorption Thermal Energy Storage Performance of Nanoporous Metal–Organic Frameworks and Covalent Organic Frameworks by Grand Canonical Monte Carlo Simulations, ACS Applied Nano Materials, 2023, 6, 13363-13373. https://doi.org/10.1021/acsanm.3c02041

[76]   S. Bandehali, S. Moradi, M. Khalili, M. Bandehali and A. Alimadadi, Molecular dynamic simulation (MD) for COF-based membrane in water treatment, Colloid and Interface Science Communications, 2024, 62, 100798. https://doi.org/10.1016/j.colcom.2024.100798

[77]   Z. Wang, H. Du, A. M. Evans, X. Ni, J. L. Bredas and H. Li, Growth of two-dimensional covalent organic frameworks on substrates: insight from microsecond atomistic simulations, Chemical Science, 2024, 15, 17629-17641. DOI: 10.1039/D4SC05168H

[78]   W. Hao, C. Sui, G. Cheng, J. Li, L. Miao, G. Zhao, Y. Sang, J. Li, C. Zhao, Y. Zhou, Z. Zang, Y. Zhao, X. He and C. Wang, Dynamic Insights into the Growth Mechanisms of 2D Covalent Organic Frameworks on Graphene Surfaces, ACS nano, 2024, 18, 10485-10494. https://doi.org/10.1021/acsnano.3c11787

[79]   H. C. Andersen, Molecular dynamics simulations at constant pressure and/or temperature, The Journal of chemical physics, 1980, 72, 2384-2393. https://doi.org/10.1063/1.439486

[80]   S. Alavi, Statistical Mechanics: Theory and Molecular Simulation. By Mark E. Tuckerman, 2011, 12138-12139. https://doi.org/10.1002/anie.201105752

[81]   J. Busch and D. Paschek, OrthoBoXY: A simple way to compute true self-diffusion coefficients from MD simulations with periodic boundary conditions without prior knowledge of the viscosity, The Journal of Physical Chemistry B, 2023, 127, 7983-7987. https://doi.org/10.1021/acs.jpcb.3c04492

[82]   S. Shang, Y. Liu, M. Liu, Y. Bai, X. Wang, B. Wu, J. Chen, J. Dong and Y. Liu, Studying the adsorption mechanisms of nanoplastics on covalent organic frameworks via molecular dynamics simulations, Journal of Hazardous Materials, 2022, 421, 126796. https://doi.org/10.1016/j.jhazmat.2021.126796

[83]   D. Feng, Y. Feng, Y. Liu, W. Zhang, Y. Yan and X. Zhang, Thermal conductivity of a 2D covalent organic framework and its enhancement using fullerene 3D self-assembly: a molecular dynamics simulation, The Journal of Physical Chemistry C, 2020, 124, 8386-8393. https://doi.org/10.1021/acs.jpcc.0c00448

[84]   Z. Li, H. Dong, J. Wang, L. Liu and J. Y. Yang, Active learning molecular dynamics-assisted insights into ultralow thermal conductivity of two-dimensional covalent organic frameworks, International Journal of Heat and Mass Transfer, 2024, 225, 125404. https://doi.org/10.1016/j.ijheatmasstransfer.2024.125404

[85]   Y. Liu, Y. Feng, Z. Huang and X. Zhang, Thermal conductivity of 3D boron-based covalent organic frameworks from molecular dynamics simulations, The Journal of Physical Chemistry C, 2016, 120, 17060-17068. https://doi.org/10.1021/acs.jpcc.6b04891

[86]   B. Wang, P. Ying and J. Zhang, The thermoelastic properties of monolayer covalent organic frameworks studied by machine-learning molecular dynamics, Nanoscale, 2024, 16, 237-248. DOI: 10.1039/D3NR04509A

[87]   P. Jamshidi Ghaleh, Z. P. Haslak, M. Batyrow and I. Erucar, Harnessing Pore Size in COF Membranes: A Concentration Gradient-Driven Molecular Dynamics Study on Enhanced H2/CH4 Separation, ACS Applied Materials & Interfaces, 2025, 17(10), 15372-15384. https://doi.org/10.1021/acsami.4c20420

[88]   M. Liu, M. Wei, G. Liu, D. Li, Z. Zhang and Y. Wang, Covalent organic framework membranes achieving Mg/Li separation by permeating Mg2+ while retaining Li+, Journal of Membrane Science, 2024, 712, 123247. https://doi.org/10.1016/j.memsci.2024.123247

[89]   G. Wei, A. Narayanan Krishnamoorthy, G. Sivaraman and L.Valentino, Molecular Simulation of Functionalized Covalent Organic Framework Membranes for Inorganic Salt Separation. Advanced Theory and Simulations, 2025, e01576. https://doi.org/10.1002/adts.202501576

[90]   G. O. Aksu and S. Keskin, Rapid and Accurate Screening of the COF Space for Natural Gas Purification: COFInformatics, ACS Applied Materials & Interfaces, 2024, 16, 19806-19818. https://doi.org/10.1021/acsami.4c01641

[91]   S. Y. Kim, S. I. Kim and Y. S. Bae, Machine-learning-based prediction of methane adsorption isotherms at varied temperatures for experimental adsorbents, The Journal of Physical Chemistry C, 2020, 124, 19538-19547. https://doi.org/10.1021/acs.jpcc.0c01757

[92]   J. S. De Vos, S. Ravichandran, S. Borgmans, L. Vanduyfhuys, P. Van Der Voort, S. M. Rogge and V. Van Speybroeck, High-throughput screening of covalent organic frameworks for carbon capture using machine learning, Chemistry of Materials, 2024, 36, 4315-4330. https://doi.org/10.1021/acs.chemmater.3c03230

[93]   J. Ning, K. Shen, R. Zhao, K. Gao, J. Cai and L. Hou, Computer-aided design of covalent organic frameworks for SF6 capture: the combination of high-throughput screening and machine learning, The Journal of Physical Chemistry C, 2024, 128, 11355-11366. https://doi.org/10.1021/acs.jpcc.4c01825

[94]   S. Kumar, G. Ignacz and G. Szekely, Synthesis of covalent organic frameworks using sustainable solvents and machine learning, Green Chemistry, 2021, 23, 8932-8939. DOI: 10.1039/D1GC02796D

[95]   P. Yang, H. Zhang, X. Lai, K. Wang, Q. Yang and D. Yu, Accelerating the selection of covalent organic frameworks

with automated machine learning, ACS omega, 2021, 6, 17149-17161. https://doi.org/10.1021/acsomega.0c05990

[96] D. Wang, H. Lv, Y. Wan, X. Wu and J. Yang, Band-edge prediction of 2D covalent organic frameworks from molecular precursor via machine learning, The Journal of Physical Chemistry Letters, 2023, 14, 6757-6764. https://doi.org/10.1021/acs.jpclett.3c01419

[97] C. Hu, W. Xie, J. Liu, Y. Zhang, Y. Sun, Z. Cai and Z. Lin, Bioinspired Iron Porphyrin Covalent Organic Frameworks-Based Nanozymes Sensor Array: Machine Learning-Assisted Identification and Detection of Thiols, ACS Applied Materials & Interfaces, 2024,16, 71048-71059. https://doi.org/10.1021/acsami.4c18284

[98] S. Minami, M. Kin, K. Takahashi, T. Sato and R. Jinnouchi, Impact of Local Water Uptake on Proton Conduction in Covalent Organic Framework Revealed by Machine-Learning Potentials, Chemistry of Materials, 2024, 36, 9535-9546. https://doi.org/10.1021/acs.chemmater.4c01351

[99] C. W. Wu, F. Li, Y. J. Zeng, H. Zhao, G. Xie, W. X. Zhou, Q. Liu and G. Zhang, Machine learning accelerated design of 2D covalent organic frame materials for thermoelectrics, Applied Surface Science, 2023, 638, 157947. https://doi.org/10.1016/j.apsusc.2023.157947

[100] A. P. Srivastava and B. K. Pandey, DFT-based evaluation of covalent organic frameworks for adsorption, optoelectronic, clean energy storage, and gas sensor applications, Journal of Molecular Modeling, 2025, 31(11), 1-12. https://doi.org/10.1007/s00894-025-06535-0

[101] P. Thakolkaran, Y. Zheng, Y. Guo, A. Vashisth, and S. Kumar, Deep learning reveals key predictors of thermal conductivity in covalent organic frameworks, Digital Discovery, 2025. https://doi.org/10.1039/D5DD00126A

[102] J. A. Elliott, Novel approaches to multiscale modelling in materials science." International Materials Reviews, 2011, 56, 207-225. https://doi.org/10.1179/1743280410Y.0000000002

[103] E. Weinan, Principles of multiscale modeling. Cambridge University Press, 2011.

[104] M. Alber, A. Buganza Tepole, W. R. Cannon, S. De, S. Dura-Bernal, K. Garikipati, G. Karniadakis, W. W. Lytton, P. Perdikaris, L. Petzold and E. Kuhl, Integrating machine learning and multiscale modeling—perspectives, challenges, and opportunities in the biological, biomedical, and behavioral sciences, NPJ digital medicine, 2019, 2, 115. https://doi.org/10.1038/s41746-019-0193-y

[105] A. Ortega-Guerrero, H. Sahabudeen, A. Croy, A. Dianat, R. Dong, X. Feng and G. Cuniberti, Multiscale modeling strategy of 2d covalent organic frameworks confined at an air–water interface, ACS Applied Materials & Interfaces, 2021, 13, 26411-26420. https://doi.org/10.1021/acsami.1c05967

[106] E. Tylianakis, E. Klontzas and G. E. Froudakis, Multi-scale theoretical investigation of hydrogen storage in covalent

organic frameworks, Nanoscale, 2011, 3, 856-869. DOI: 10.1039/C0NR00505C

[107] R. Maleki, M. Khedri, S. Rezvantalab, F. Afsharchi, K. Musaie, S. Shafiee and M. A. Shahbazi, β-amyloid targeting with two-dimensional covalent organic frameworks: Multi-scale in-silico dissection of nano-biointerface, ChemBioChem, 2021, 22, 2306-2318. https://doi.org/10.1002/cbic.202100075

[108] S. Amirjalayer, R. Q. Snurr and R. Schmid, Prediction of structure and properties of boron-based covalent organic frameworks by a first-principles derived force field, The Journal of Physical Chemistry C, 2012, 116, 4921-4929. https://doi.org/10.1021/jp211280m

[109] M. Tong, Q. Yang and C. Zhong, Computational screening of covalent organic frameworks for CH4/H2, CO2/H2 and CO2/CH4 separations, Microporous and Mesoporous Materials, 2015, 210, 142-148. https://doi.org/10.1016/j.micromeso.2015.02.034

[110] Y. Lang, L. Sun, Y. Pan, M. Xu, D. Zhai, J. Liu, W. Deng and L. Yang, A universal model for predicting helium separation in covalent organic frameworks and Metal–organic frameworks, Chemical Engineering Science, 2025, 305, 121175. https://doi.org/10.1016/j.ces.2024.121175

[111] J. Ozdemir, I. Mosleh, M. Abolhassani, L. F. Greenlee, R. R. Beitle Jr and M. H. Beyzavi, Covalent organic frameworks for the capture, fixation, or reduction of CO2. Frontiers in Energy Research, 2019, 7, 77. https://doi.org/10.3389/fenrg.2019.00077

[112] J. Dong, Y. Wang, G. Liu, Y. Cheng and D. Zhao, Isoreticular covalent organic frameworks for hydrocarbon uptake and separation: the important role of monomer planarity, CrystEngComm, 2017, 19(33), 4899-4904. https://doi.org/10.1039/C7CE00344G

[113] H. Akbarzadeh, M. Abbaspour, S. Amiri, E. Mehrjouei and C. Izanloo, Increasing the Performance of Covalent Organic Frameworks in the Separation of the CO2/CH4 Mixture by Tuning the Structural Arrangement of Layers and Pore Size: An MD/GCMC Simulation Study, Industrial & Engineering Chemistry Research, 2025, 64(35), 17014-17025. https://doi.org/10.1021/acs.iecr.4c04786

[114] B. Dash, Carbon dioxide capture using covalent organic frameworks (COFs) type material—a theoretical investigation, Journal of Molecular Modeling, 2018, 24, 120. https://doi.org/10.1007/s00894-018-3646-3

[115] O. F. Altundal, Z. P. Haslak and S. Keskin, Combined GCMC, MD, and DFT approach for unlocking the performances of COFs for methane purification, Industrial & Engineering Chemistry Research, 2021, 60, 12999-13012. https://doi.org/10.1021/acs.iecr.1c01742

[116] C. Kessler, J. Eller, J. Gross and N. Hansen, Adsorption of light gases in covalent organic frameworks: comparison of classical density functional theory and grand canonical Monte Carlo simulations, Microporous and Mesoporous

Materials, 2021, 324, 111263. https://doi.org/10.1016/j.micromeso.2021.111263

[117] B. Xin, M. Feng, M. Cheng, Z. Dai, S. Ye, L. Zhou, Y. Dai and X. Ji, Combining Interpretable Machine Learning and Molecular Simulation to Advance the Discovery of COF-Based Membranes for Acid Gas Separation, Industrial & Engineering Chemistry Research, 2024, 63, 8369-8382. https://doi.org/10.1021/acs.iecr.4c00855

[118] K. Gopalsamy and V. Subramanian, Carbon flakes based metal organic frameworks for H 2, CH 4 and CO 2 gas storage: a GCMC simulation study, New Journal of Chemistry, 2018, 42, 4240-4250. DOI: 10.1039/C7NJ04538G

[119] H. Xin, S. Zhou, S. Xu, W. Zhai, S. Liu, S. Liu, Z. Wang, X. Lu and S. Wei, Functionalized linker to form high-symmetry adsorption sites in micropore COF for CO2 capture and separation: insight from GCMC simulations, Journal of Materials Science, 2022, 57, 6282-6292. https://doi.org/10.1007/s10853-022-07008-y

[120] H. Wang, Y. Liu, Y. Liu, Z. Wang, C. Li, S. Sun, Q. Lyu and S. Hu, Two-dimensional imine covalent organic frameworks for methane and ethane separation: a GCMC simulation study, Microporous and Mesoporous Materials, 2021, 326, 111386. https://doi.org/10.1016/j.micromeso.2021.111386

[121] M. Ernst, J. D. Evans and G. Gryn'ova, Host–guest interactions in framework materials: Insight from modeling, Chemical Physics Reviews, 2023, 4. https://doi.org/10.1063/5.0144827

[122] C. Yu, C. Lu, X. Wang, W. Zhou, Z. Yang, X. Yu, E. Wang and R. Lin, Simulation study of mass transfer characteristics of CH4/CO2 separation in multiple types of covalent organic framework membrane materials, Industrial & Engineering Chemistry Research, 2023, 62, 12291-12304. https://doi.org/10.1021/acs.iecr.3c01730

[123] H. Zeng, Y. Liu and H. Liu, Adsorption and diffusion of CO2 and CH4 in covalent organic frameworks: an MC/MD simulation study, Molecular Simulation, 2018, 44, 1244-1251. https://doi.org/10.1080/08927022.2018.1481959

[124] B. Li, Z. Wang, Z. Gao, J. Suo, M. Xue, Y. Yan, V. Valtchev, S. Qiu and Q. Fang, Self-standing covalent organic framework membranes for H2/CO2 separation, Advanced Functional Materials, 2023, 33, 2300219. https://doi.org/10.1002/adfm.202300219

[125] S. Keskin, Adsorption, diffusion, and separation of CH4/H2 mixtures in covalent organic frameworks: molecular simulations and theoretical predictions, The Journal of Physical Chemistry C, 2012, 116, 1772-1779. https://doi.org/10.1021/jp209804x

[126] G. Garberoglio, Computer simulation of the adsorption of light gases in covalent organic frameworks, Langmuir, 2007, 23, 12154-12158. https://doi.org/10.1021/la701736m

[127] J. L. Mendoza-Cortés, S. S. Han, H. Furukawa, O. M. Yaghi and W. A. Goddard III, Adsorption mechanism and uptake of methane in covalent organic frameworks: theory and experiment, The Journal of Physical Chemistry A, 2010, 114, 10824-10833. https://doi.org/10.1021/jp1044139

[128] S. S. Han, J. L. Mendoza-Cortés and W. A. Goddard Iii, Recent advances on simulation and theory of hydrogen storage in metal–organic frameworks and covalent organic frameworks, Chemical Society Reviews, 2009, 38, 1460-1476. DOI: 10.1039/B802430H

[129] B. Assfour and G. Seifert, Adsorption of hydrogen in covalent organic frameworks: Comparison of simulations and experiments, Microporous and mesoporous materials, 2010, 133, 59-65. https://doi.org/10.1016/j.micromeso.2010.04.015

[130] L. Y. Bian, X. D. Li, X. Y. Huang, P. H. Yang, Y. D. Wang, X. Y. Liu and Z. Chen, Molecular simulation on hydrogen storage properties of five novel covalent organic frameworks with the higher valency, International Journal of Hydrogen Energy, 2022, 47, 29390-29398. https://doi.org/10.1016/j.ijhydene.2022.06.285

[131] X. D. Li, P. H. Yang, X. Y. Huang, X. Y. Liu, J. X. Yu and Z. Chen, Computational simulation study on adsorption and separation of CH4/H2 in five higher-valency covalent organic frameworks, Materials Today Communications, 2022, 33, 104374. https://doi.org/10.1016/j.mtcomm.2022.104374

[132] G. O. Aksu and S. Keskin, Advancing CH 4/H 2 separation with covalent organic frameworks by combining molecular simulations and machine learning, Journal of Materials Chemistry A, 2023, 11, 14788-14799. DOI: 10.1039/D3TA02433D

[133] P. Ortiz-Albo, H. Takaba, I. Kumakiri, J. G. Crespo and L. A. Neves, An Overview of Molecular Simulations Studies in Mixed Matrix Membranes for Gas Separation Processes, Journal of Membrane Science and Research, 2022, 8. 10.22079/JMSR.2022.549436.1536

[134] C. Liang, K. Li, T. Chen, Y. Zhang, J. Yu, Z. Wang, H. Li and X. Li, Constructing CO2 capture nanotraps via tentacle-like covalent organic frameworks towards efficient CO2 separation in mixed matrix membrane, Chemical Engineering Science, 2025, 301, 120801. https://doi.org/10.1016/j.ces.2024.120801

[135] T. Yang, M. Zuo, C. Li, Y. Liu, Z. J. Diao, X. Q. Liu, G. Liu, L. Ding and L. B. Sun, Incorporating a photo-responsive metal-organic cage into covalent organic framework for controllable CO2 adsorption, Materials Today Energy, 2025, 48, 101771. https://doi.org/10.1016/j.mtener.2024.101771

[136] Y. Chen, G. Zhao, S. Yoon, P. Habibi, C. S. Hong, S. Li, O. A. Moultos, P. Dey, T. J. H. Vlugt and Y. G. Chung, Computational Exploration of Adsorption-Based Hydrogen Storage in Mg-Alkoxide Functionalized Covalent-Organic Frameworks (COFs): Force-Field and Machine Learning

Materials Advances Accepted Manuscript

Models, ACS applied materials & interfaces, 2024, 16, 61995-62009. https://doi.org/10.1021/acsami.4c11953

[137] Y. Zeng, R. Zou and Y. Zhao, Covalent organic frameworks for CO₂ capture, Advanced Materials, 2016, 28(15), 2855-2873. https://doi.org/10.1002/adma.201505004

[138] Y. Wang, W. Wang, Z. Zhang and P. Li, The sorption and separation mechanism of CO2 in covalent organic frameworks with different aligned structures: DFT and molecular dynamic simulations, Applied Surface Science, 2022, 571, 151355. https://doi.org/10.1016/j.apsusc.2021.151355

[139] H. Sajid, Effect of interlayer slipping on the geometric, thermal and adsorption properties of 2D covalent organic frameworks: a comprehensive review based on computational modelling studies, Physical Chemistry Chemical Physics, 2024. DOI: 10.1039/D4CP00094C

[140] Y. B. Apriliyanto, N. Darmawan, N. Faginas-Lago and A. Lombardi, Two-dimensional diamine-linked covalent organic frameworks for CO 2/N 2 capture and separation: theoretical modeling and simulations, Physical Chemistry Chemical Physics, 2020, 22, 25918-25929. DOI: 10.1039/D0CP04258G

[141] P. Das and S. K. Mandal, In-depth experimental and computational investigations for remarkable gas/vapor sorption, selectivity, and affinity by a porous nitrogen-rich covalent organic framework, Chemistry of Materials, 2019, 31, 1584-1596. https://doi.org/10.1021/acs.chemmater.8b04683

[142] W. Li, Y. Pang and J. Zhang, Modeling the selectivity of indoor pollution gases over N 2 on covalent organic frameworks, Journal of molecular modeling, 2014, 20, 1-6. https://doi.org/10.1007/s00894-014-2346-x

[143] M. Tong, Q. Yang, Y. Xiao and C. Zhong, Revealing the structure–property relationship of covalent organic frameworks for CO 2 capture from postcombustion gas: a multi-scale computational study, Physical Chemistry Chemical Physics, 2014, 16, 15189-15198. DOI: 10.1039/C4CP02047B

[144] E. Gulcay and I. Erucar, Molecular simulations of COFs, IRMOFs and ZIFs for adsorption-based separation of carbon tetrachloride from air." Journal of Molecular Graphics and Modelling, 2019, 86, 84-94. https://doi.org/10.1016/j.jmgm.2018.10.006

[145] X. Cao, Z. Zhang, Y. He, W. Xue, H. Huang and C. Zhong, Machine-learning-aided computational study of covalent organic frameworks for reversed C2H6/C2H4 separation, Industrial & Engineering Chemistry Research, 2022, 61, 11116-11123. https://doi.org/10.1021/acs.iecr.2c01385

[146] X. Cao, Q. Han, R. Han, S. Zhang, M. Wang, Z. Zhang and C. Zhong, Integrating Multiscale Simulation with Machine Learning to Screen and Design FIL@ COFs for Ethane-Selective Separation, ACS Applied Materials & Interfaces, 2024, 16, 27360-27367. https://doi.org/10.1021/acsami.4c03089

[147] H. Wang, Y. Li, X. Xuan, K. Wang, Y.F. Yao and L. Pan, Machine learning accelerated discovery of covalent organic frameworks for environmental and energy applications, Environmental Science & Technology, 2025, 59(13), 6361-6378. https://doi.org/10.1021/acs.est.5c00390

[148] Y. Zhang, T. Fang, Q. Hou, Z. Li and Y. Yan, Water desalination of a new three-dimensional covalent organic framework: a molecular dynamics simulation study, Physical Chemistry Chemical Physics, 2020, 22, 16978-16984. DOI: 10.1039/D0CP01792B

[149] Y. Xie, C. Q. Huang, K. Zhou and Y. Liu, Elucidating the transport of water and ions in the nanochannel of covalent organic frameworks by molecular dynamics, The Journal of Chemical Physics, 2024, 161. https://doi.org/10.1063/5.0195205

[150] M. Guan, D. Yang, H. Zhang, Q. Li, J. Xu, M. Cai, Q. Liu and L. Wu, Understanding the effect of layer spacing on water desalination through two-dimensional covalent organic framework membranes via molecular dynamics simulation, Desalination, 2024, 580, 117512. https://doi.org/10.1016/j.desal.2024.117512

[151] L. Wang, H. Xu, Y. Qiu, X. Liu, W. Huang, N. Yan and Z. Qu, Utilization of Ag nanoparticles anchored in covalent organic frameworks for mercury removal from acidic waste water." Journal of hazardous materials, 2020, 389, 121824. https://doi.org/10.1016/j.jhazmat.2019.121824

[152] F. Li and G. Zhang, Effective removal of toxic heavy metal ions from wastewater using boroxine covalent organic framework, Journal of Molecular Liquids, 2021, 336, 116326. https://doi.org/10.1016/j.molliq.2021.116326

[153] W. Junli, L. Chen, W. Wentao, W. Hui, S. Jiaxuan, Y. Taihong and L. Jianwei, The Functionalized N-Rich Covalent Organic Framework for Palladium Removal from Nuclear Wastewater, Langmuir, 2024, 40, 22006-22014. https://doi.org/10.1021/acs.langmuir.4c02071

[154] R. Ding, J. Liu, Q. Meng, T. Wang and X. Zhang, Dual-functional flexible cationic porphyrin-based covalent organic frameworks for selective adsorption and sensitive detection of Cr (VI), Separation and Purification Technology, 2025, 359, 130544. https://doi.org/10.1016/j.seppur.2024.130544

[155] J. Xiong, Y. Zhou, B. Ren, Z. Zhang, Y. Zhang, J. Zhang, J. Chang, X. Yang and S. Wang, Protonated covalent organic frameworks for green and effective recovery of Au (I) from thiosulfate solutions: Performance, DFT calculations, and mechanism insights, Separation and Purification Technology, 2025, 353, 128329. https://doi.org/10.1016/j.seppur.2024.128329

[156] M. G. Schwab, B. Fassbender, H. W. Spiess, A. Thomas, X. Feng and K. Mullen, Catalyst-free preparation of melamine-based microporous polymer networks through Schiff base

chemistry, Journal of the American Chemical Society, 2009, 131, 7216-7217. https://doi.org/10.1021/ja902116f

[157] R. Farahani, T. Madrakian and A. Afkhami, Investigating the performance of a recently synthesized covalent organic framework as an adsorbent for methylene blue: A DFT Study, International Journal of New Chemistry, 2023, 9, 383-392. https://doi.org/10.22034/ijnc.2023.706008

[158] B. Zhao, C. Luo, Y. Feng, B. Wang, Z. Chen and J. Hu, A pH-responsive covalent organic framework membrane based on flexible building blocks for superhigh-flux dye/salt separation, Desalination, 2025, 606, 118783. https://doi.org/10.1016/j.desal.2025.118783

[159] A. Nakhaei, H. Raissi and F. Farzad, Advanced porous covalent organic framework (COF) materials for the capture of alizarin dye and its derivatives from the aquatic environment, Applied Water Science, 2024, 14, 184. https://doi.org/10.1007/s13201-024-02242-y

[160] C. Zhang, G. Wang, Y. Qiu, C. Wang, F. Li, L. F. Ren, J. Shao and Y. He, Rapid preparation and mechanism investigation of covalent organic framework membranes by 3D printing based on electrostatic spraying, Journal of Membrane Science, 2025, 715, 123487. https://doi.org/10.1016/j.memsci.2024.123487

[161] Y. Wang, W. Wang, Z. Zhang and P. Li, Adsorption performance of the functional COFs for removal of bisphenol A: Molecular dynamic simulations, Journal of Molecular Liquids, 2023, 392, 123475. https://doi.org/10.1016/j.molliq.2023.123475

[162] D. Wei, J. Li, Z. Chen, L. Liang, J. Ma, M. Wei, Y. Ai and X. Wang, Understanding bisphenol-A adsorption in magnetic modified covalent organic frameworks: Experiments coupled with DFT calculations, Journal of Molecular Liquids, 2020, 301, 112431. https://doi.org/10.1016/j.molliq.2019.112431

[163] M. Li, J. Ma, B. Pan and J. Wang, Cage-based covalent organic framework for the effective and efficient removal of malachite green from wastewater, ACS Applied Materials & Interfaces, 2022, 14, 57180-57188. https://doi.org/10.1021/acsami.2c17878

[164] A. Ghahari, F. Farzad and R. Azadnejad, The strategy of three-dimensional Covalent Organic Frameworks to exclude dye contaminants in aqueous solutions, npj Clean Water, 2024, 7, 27. https://doi.org/10.1038/s41545-024-00311-y

[165] A. Ghahari, H. Raissi, S. Pasban and F. Farzad, Proposing two-dimensional covalent organic frameworks material for the capture of phenol molecules from wastewaters, npj Clean Water, 2022, 5, 28. https://doi.org/10.1038/s41545-022-00173-2

[166] Z. Li, T. He, Y. Gong and D. Jiang, Covalent organic frameworks: pore design and interface engineering, Accounts of Chemical Research, 2020, 53, 1672-1685. https://doi.org/10.1021/acs.accounts.0c00386

[167] W. Wang, H. Shao, S. Zhou, D. Zhu, X. Jiang, G. Yu and S. Deng, Rapid removal of perfluoroalkanesulfonates from water by β-cyclodextrin covalent organic frameworks, ACS Applied Materials & Interfaces, 2021, 13, 48700-48708. https://doi.org/10.1021/acsami.1c14043

[168] X. Ma, K. R. Meihaus, Y. Yang, Y. Zheng, F. Cui, J. Li, Y. Zhao, B. Jiang and Y. Yuan, Photocatalytic extraction of uranium from seawater using covalent organic framework nanowires, Journal of the American Chemical Society, 2024, 146, 23566-23573. https://doi.org/10.1021/jacs.4c07699

[169] R. Yao, J. Wang, Y. Li, W. Qu, B. Yang, J. Lu, Z. Wu, Y. Li, Z. Lu, Z. Geng and Z. Wang, Engineering N-donor heterocycles on dioxin-linked covalent organic frameworks to in situ improvement uranium separation and extraction selectivity in wastewater and seawater, Chemical Engineering Journal, 2025, 503,158513. https://doi.org/10.1016/j.cej.2024.158513

[170] D. Mei and B. Yan, β-Ketoenamine and Benzoxazole-Linked Covalent Organic Frameworks Tailored with Phosphorylation for Efficient Uranium Removal from Contaminated Water Systems, Advanced Functional Materials, 2024, 34, 2313314. https://doi.org/10.1002/adfm.202313314

[171] J. Sun, Z. Hou, J. Wang, P. Yang, S. Li, C. Liu, C. Shen and Z. Liu, A robust amphiphilic ionic covalent organic framework intercalated into functionalized graphene oxide hybrid membranes for ultrafast extraction uranium from wastewater, Water Research, 2024, 265, 122320. https://doi.org/10.1016/j.watres.2024.122320

[172] M. Zhou, S. Wang, F. Liu and B. Hu, Effective separation and immobilization of uranium (VI) from wastewater using amino and carboxyl groups functionalized covalent organic frameworks, Separation and Purification Technology, 2024, 338, 126501. https://doi.org/10.1016/j.seppur.2024.126501

[173] L. He, S. Liu, L. Chen, X. Dai, J. Li, M. Zhang, F. Ma, C. Zhang, Z. Yang, R. Zhou, Z. Chai, and S. Wang, Mechanism unravelling for ultrafast and selective 99 TcO 4– uptake by a radiation-resistant cationic covalent organic framework: a combined radiological experiment and molecular dynamics simulation study, Chemical science, 2019, 10, 4293-4305. DOI: 10.1039/C9SC00172G

[174] C. Zhao, X. Ma, X. Wei, W. Liu, L. Sun and Y. Ai, Effective strategies toward imine-linked cationic covalent organic frameworks for rapid and selective removal of 99 TcO 4– from water: insights from DFT and MD calculations, Environmental Science: Nano, 2023, 10, 611-624. DOI https://doi.org/10.1039/D2EN01049F

[175] Q. Tang, Q. Y. Wu, W. Q. Shi, G. Han, X. H. Pan, M. J. Jin, D. R. Zheng, G. Z. G. Zhou and J. H. Zu, Cationic covalent organic frameworks based on pyridine and triazine for selective extraction of radioactive 99TcO4-from contaminated water, Separation and Purification

Review

Materials Advances

Technology, 2025, 354, 128786. https://doi.org/10.1016/j.seppur.2024.128786

[176] S. Li, B. Liu, M. Wei, M. Liu, J. Cao, W. Xing and Y. Wang, Insights into the mixing effect in organic solvent nanofiltration from simulations on covalent organic frameworks (COFs), Separation and Purification Technology, 2025, 356, 129947. https://doi.org/10.1016/j.seppur.2024.129947

[177] S. S. A. Shah, N. A. Khan, A. U. Rehman, G. Murtaza, S. Ashiq, M. A. Nazir, T. Najam and M. Sohail, Removal of antibiotics from wastewater via metal-organic frameworks (MOFs) as adsorbents, Toxin Reviews, 2024, 43, 277-299. https://doi.org/10.1080/15569543.2024.2329921

[178] I. Salahshoori, S. Mahdavi, Z. Moradi, M. Otadi, F. Z. Kazemabadi, M. A. Nobre, H. A. Khonakdar, A. Baghban, Q. Wang and A. H. Mohammadi, Advancements in molecular simulation for understanding pharmaceutical pollutant Adsorption: A State-of-the-Art review, Journal of Molecular Liquids, 2024, 125513. https://doi.org/10.1016/j.molliq.2024.125513

[179] S. Akhzari, H. Raissi and A. Ghahari, Architectural design of 2D covalent organic frameworks (COFs) for pharmaceutical pollutant removal, npj Clean Water, 2024, 7(1), 31. https://doi.org/10.1038/s41545-024-00315-8

[180] M. Khedri, R. Maleki, S. G. Khiavi, M. Ghasemi, E. Ghasemy and A. M. Jahromi, Removal of phenazopyridine as a pharmacological contaminant using nanoporous metal/covalent-organic frameworks (MOF/COF) adsorbent, Applied Materials Today, 2021, 25, 101196. https://doi.org/10.1016/j.apmt.2021.101196

[181] P. Ghosh and P. Banerjee, Drug delivery using biocompatible covalent organic frameworks (COFs) towards a therapeutic approach, Chemical Communications, 2023, 59, 12527-12547. DOI: 10.1039/D3CC01829F

[182] M. Darparesh and R. Ghadari, Analyzing the impact of substitution on the temperature-sensitive release of doxorubicin in an imine-based covalent organic framework using molecular dynamics, Computational Materials Science, 2024, 237, 112882. https://doi.org/10.1016/j.commatsci.2024.112882

[183] H. Hashemzadeh and H. Raissi, Covalent organic framework as smart and high efficient carrier for anticancer drug delivery: a DFT calculations and molecular dynamics simulation study, Journal of Physics D: Applied Physics, 2018, 51, 345401. **DOI** 10.1088/1361-6463/aad3e8

[184] M. A. Alkhalifah, M. Yar, I. Bayach, N. S. Sheikh and K. Ayub, Covalent organic framework (C6N6) as a drug delivery platform for fluorouracil to treat cancerous cells: a DFT study, Materials, 2022, 15, 7425. https://doi.org/10.3390/ma15217425

[185] M. Heidari and M. Solimannejad, The porous B6N6 boron nitride covalent organic framework as a potential platform for sensing and delivering lomustine anticancer drug: a first-principles study, Journal of Inorganic and Organometallic Polymers and Materials, 2022, 32, 4216-4222. https://doi.org/10.1007/s10904-022-02407-9

[186] A. Allangawi, H. Sajid, K. Ayub, M. A. Gilani, M. S. Akhter and T. Mahmood, High drug carrying efficiency of boron-doped Triazine based covalent organic framework toward anti-cancer tegafur; a theoretical perspective, Computational and Theoretical Chemistry, 2023, 1220, 113990. https://doi.org/10.1016/j.comptc.2022.113990

[187] A. Ghahari, H. Raissi and F. Farzad, Design of a new drug delivery platform based on surface functionalization 2D covalent organic frameworks, Journal of the Taiwan Institute of Chemical Engineers, 2021, 125, 15-22. https://doi.org/10.1016/j.jtice.2021.05.048

[188] C. Zhang, J. Guo, X. Zou, S. Guo, Y. Guo, R. Shi and F. Yan, Acridine-based covalent organic framework photosensitizer with broad-spectrum light absorption for antibacterial photocatalytic therapy, Advanced Healthcare Materials, 2021, 10, 2100775. https://doi.org/10.1002/adhm.202100775

[189] L. Akyuz, An imine based COF as a smart carrier for targeted drug delivery: From synthesis to computational studies, Microporous and Mesoporous Materials, 2020, 294, 109850. https://doi.org/10.1016/j.micromeso.2019.109850

[190] S. A. Adalikwu, H. Louis, A. C. Iloanya, H. O. Edet, M. U. Akem, E. A. Eno and A. L. E. Manicum, B-and Al-doped porous 2D covalent organic frameworks as nanocarriers for biguanides and metformin drugs, ACS Applied Bio Materials, 2022, 5, 5887-5900. https://doi.org/10.1021/acsabm.2c00855

[191] N. Rahmani Khalili, A. Banitalebi Dehkordi, A. Amiri, G. Mohammadi Ziarani, A. Badiei and P. Cool, Tailored Covalent Organic Framework Platform: From Multistimuli, Targeted Dual Drug Delivery by Architecturally Engineering to Enhance Photothermal Tumor Therapy, ACS Applied Materials & Interfaces, 2024, 16, 28245-28262. https://doi.org/10.1021/acsami.4c05989

[192] F. Xie, C. Bie, J. Sun, Z. Zhang and B. Zhu, A DFT study on Pt single atom loaded COF for efficient photocatalytic CO2 reduction, Journal of Materials Science & Technology, 2024, 170, 87-94. https://doi.org/10.1016/j.jmst.2023.06.028

[193] G. Yan and X. Zhang, Interlayer Interactions and Macroscopic Property Calculations of Squaric-Acid-Linked Zwitterionic Covalent Organic Frameworks: Structures, Photocatalytic Carrier Transport, and a DFT Study, Molecules, 2024, 29, 2739. https://doi.org/10.3390/molecules29122739

[194] Y. Tang, H. Zhang, X. Cheng and Y. Wang, SnS 2/covalent organic framework S-scheme heterostructures for photocatalytic water splitting: insights from ground-state properties and nonadiabatic excited-state

dynamics, Journal of Materials Chemistry A, 2025, 13, 3350-3358. DOI: 10.1039/D4TA07330D

[195] Y. Xie, F. Mao, Q. Rong, X. Liu, M. Hao, Z. Chen, H. Yang, G. I. N. Waterhouse, S. Ma and X. Wang, Rational design of 3D space connected donor–acceptor system in covalent organic frameworks for enhanced photocatalytic performance, Advanced Functional Materials, 2024, 34, 2411077. https://doi.org/10.1002/adfm.202411077

[196] Y. N. Gong, W. Zhong, Y. Li, Y. Qiu, L. Zheng, J. Jiang and H. L. Jiang, Regulating photocatalysis by spin-state manipulation of cobalt in covalent organic frameworks, Journal of the American Chemical Society, 2020, 142, 16723-16731. https://doi.org/10.1021/jacs.0c07206

[197] K. Chen, L. Yang, Z. Wu, C. Chen, J. Jiang and G. Zhang, A computational study on the tunability of woven covalent organic frameworks for photocatalysis, Physical Chemistry Chemical Physics, 2019, 21, 546-553. DOI: 10.1039/C8CP04373F

[198] Y. Zhang, X. Guan, Z. Meng and H. L. Jiang, Supramolecularly Built Local Electric Field Microenvironment around Cobalt Phthalocyanine in Covalent Organic Frameworks for Enhanced Photocatalysis, Journal of the American Chemical Society, 2025. https://doi.org/10.1021/jacs.4c16538

[199] M. Ran, X. Zhang, J. Lin, R. A. Borse, L. Zhang and Y. Wang, Conformation-driven exciton transfer in pyrene-sulfone covalent organic frameworks for bifunctional photocatalysis, Journal of Materials Chemistry A, 2025, 13, 1123-1134. DOI: 10.1039/D4TA06978A

[200] B.B. Rath, S. Krause and B.V. Lotsch, Active site engineering in reticular covalent organic frameworks for photocatalytic CO$_2$ reduction, Advanced Functional Materials, 2024, 34(43),2309060. https://doi.org/10.1002/adfm.202309060

[201] Y. Wu, H. Lv and X. Wu, Design of two-dimensional porous covalent organic framework semiconductors for visible-light-driven overall water splitting: A theoretical perspective, Chinese Journal of Structural Chemistry, 2024, 43, 100375. https://doi.org/10.1016/j.cjsc.2024.100375

[202] Y. Qian, Y. Han, X. Zhang, G. Yang, G. Zhang and H. L. Jiang, Computation-based regulation of excitonic effects in donor-acceptor covalent organic frameworks for enhanced photocatalysis, Nature Communications, 2023, 14, 3083. https://doi.org/10.1038/s41467-023-38884-w

[203] J. Liu, C. Tuo, W. Y. Xiao, M. Y. Qi, Y. Yusran, Z. Wang, H. Li, C. Guo, J. Song, S. Qiu, Y.J. Xu and Q. Fang, Constructing Donor-Acceptor Covalent Organic Frameworks for Highly Efficient H2O2 Photosynthesis Coupled with Oxidative Organic Transformations, Angewandte Chemie, 2025, 137, e202416240. https://doi.org/10.1002/ange.202416240

[204] X. Luo, Y. Wang, H. Lv and X. Wu, Asymmetric Potential Model of Two-Dimensional Imine Covalent Organic Frameworks with Enhanced Quantum Efficiency for Photocatalytic Water Splitting, The Journal of Physical

Chemistry Letters, 2024, 15, 5467-5475. https://doi.org/10.1021/acs.jpclett.4c00980

[205] Y. Tang, Y. Wang, X. Cheng and H. Zhang, SnS 2/covalent organic framework S-scheme heterostructures for photocatalytic water splitting: insights from ground-state properties and nonadiabatic excited-state dynamics, Journal of Materials Chemistry A, 2025, 13, 3350-3358. DOI: 10.1039/D4TA07330D

[206] S. Nishioka, F. E. Osterloh, X. Wang, T. E. Mallouk and K. Maeda, Photocatalytic water splitting, Nature Reviews Methods Primers, 2023, 3(1), 42. https://doi.org/10.1038/s43586-023-00226-x

[207] Y. W. Yang, H. D. Ren, H. Y. Zhang, Y. N. Zhao, H. Q. Tan and Z. L. Lang, Linkage Regulation of β-Ketoamine Covalent Organic Frameworks for Boosting Photocatalytic Overall Water Splitting, ACS Applied Materials & Interfaces, 2025, 17, 5038–5046. https://doi.org/10.1021/acsami.4c20472

[208] Y. Wan, P. Sun, L. Shi, X. Yan and X. Zhang, Three-dimensional fully conjugated covalent organic frameworks for efficient photocatalytic water splitting, The Journal of Physical Chemistry Letters, 2023, 14, 7411-7420. https://doi.org/10.1021/acs.jpclett.3c01850

[209] T. Xu, Z. Wang, W. Zhang, S. An, L. Wei, S. Guo, Y. Huang, S. Jiang, M. Zhu, Y. B. Zhang and W. H. Zhu, Constructing photocatalytic covalent organic frameworks with aliphatic linkers, Journal of the American Chemical Society, 2024, 146, 20107-20115. https://doi.org/10.1021/jacs.4c04244

[210] K. Gottschling, G. Savasci, H. Vignolo-González, S. Schmidt, P. Mauker, T. Banerjee, P. Rovó, C. Ochsenfeld and B. V. Lotsch, Rational design of covalent cobaloxime–covalent organic framework hybrids for enhanced photocatalytic hydrogen evolution, Journal of the American Chemical Society, 2020, 142, 12146-12156. https://doi.org/10.1021/jacs.0c02155

[211] R. Gao, R. Shen, C. Huang, K. Huang, G. Liang, P. Zhang and X. Li, 2D/2D Hydrogen-Bonded Organic Frameworks/Covalent Organic Frameworks S-Scheme Heterojunctions for Photocatalytic Hydrogen Evolution, Angewandte Chemie, 2025, 137, e202414229. https://doi.org/10.1002/ange.202414229

[212] F. Duan, J. Sheng, J. Shi, S. Yi, Y. Li, W. Liu, S. Lu, H. Zhu, M. Du, X. Chen and J. Wang, Protonated Z-scheme CdS-covalent organic framework heterojunction with highly efficient photocatalytic hydrogen evolution, Journal of Colloid and Interface Science, 2024, 675, 620-629. https://doi.org/10.1016/j.jcis.2024.07.051

[213] A. E. Hassan, A. M. Elewa, M. S. Hussien, A. F. El-Mahdy, I. M. Mekhemer, I. S. Yahia, T. A. Mohamed, H. H. Chou and Z. Wen, Designing of covalent organic framework/2D g-C3N4 heterostructure using a simple method for enhanced photocatalytic hydrogen production, Journal of Colloid and

Interface Science, 2024, 653, 1650-1661. https://doi.org/10.1016/j.jcis.2023.10.010

[214] X. Wu, M. Zhang, Y. Xia, C. Ru, P. Chen, H. Zhao, L. Zhou, C. Gong, J. Wu and X. Pan, Arylboron functional covalent organic frameworks for synergistic photocatalytic hydrogen evolution, Journal of Materials Chemistry A, 2022, 10, 17691-17698. DOI: 10.1039/D2TA04748A

[215] P. Dong, Y. Wang, A. Zhang, T. Cheng, X. Xi and J. Zhang, Platinum single atoms anchored on a covalent organic framework: boosting active sites for photocatalytic hydrogen evolution, Acs Catalysis, 2021, 11, 13266-13279. https://doi.org/10.1021/acscatal.1c03441

[216] Y. Li, L. Yang, H. He, L. Sun, H. Wang, X. Fang, Y. Zhao, D. Zheng, Yu. Qi, Z. Li and W. Deng, In situ photodeposition of platinum clusters on a covalent organic framework for photocatalytic hydrogen production, Nature Communications, 2022, 13, 1355. https://doi.org/10.1038/s41467-022-29076-z

[217] H. Han, Q. Xue, J. Ding, J. Han, H. Li, Y. Li, and X. Zhou. Isoelectronic Organic Dye-Based Covalent Organic Framework with Varied Nitrogen Content for Tuning Optoelectronic Properties and Photocatalytic H2 Evolution, ACS Applied Polymer Materials, 2025. https://doi.org/10.1021/acsapm.4c03047

[218] C. Li, H. Xie, S. Zhou, H. Hu, G. Chen, Z. Wei, J. Jiang, J. Qin, Z. Zhang and Y. Kong, The structure-activity relationship for the electron-donating functional groups in hydrazone-linked COFs and their photocatalytic H_2O_2 production, Materials Research Bulletin, 2024, 173, 112697. https://doi.org/10.1016/j.materresbull.2024.112697

[219] H. Xu, Y. Wang, Y. Xu, Q. Wang, M. Zhuang, Q. Liao and K. Xi, Integrating Multipolar Structures and Carboxyl Groups in Sp2-Carbon Conjugated Covalent Organic Frameworks for Overall Photocatalytic Hydrogen Peroxide Production, Angewandte Chemie, 2024, 136, e202408802. https://doi.org/10.1002/ange.202408802

[220] A. Chakraborty, A. Alam, U. Pal, A. Sinha, S. Das, T. Saha-Dasgupta and P. Pachfule, Enhancing photocatalytic hydrogen peroxide generation by tuning hydrazone linkage density in covalent organic frameworks, Nature Communications, 2025, 16, 503. https://doi.org/10.1038/s41467-025-55894-y

[221] Y. Zhu, H. Duan, C. G. Gruber, W. Qu, H. Zhang, Z. Wang, J. Zhong, X. Zhang, L. Han, D. Cheng, D. D. Medina, E. Cortés and D. Zhang, Boosting Electrocatalytic Nitrate Reduction through Enhanced Mass Transfer in Cu-Bipyridine 2D Covalent Organic Framework Films, Angewandte Chemie International Edition, 2025, e202421821. https://doi.org/10.1002/anie.202421821

[222] A. M. Mohamed and Y. Bicer, 3D COFs FOR PHOTOCATALYTIC N2 FIXATION: A COMPUTATIONAL STUDY, In 23rd World Hydrogen Energy Conference:

Bridging Continents by H2, WHEC, 2022, 571-573. International Association for Hydrogen Energy, IAHE, 2022.

[223] M. Y. Yang, S. B. Zhang, M. Zhang, Z. H. Li, Y. F. Liu, X. Liao, M. Lu, S. L. Li and Y. Q. Lan, Three-motif molecular junction type covalent organic frameworks for efficient photocatalytic aerobic oxidation, Journal of the American Chemical Society, 2024, 146, 3396-3404. https://doi.org/10.1021/jacs.3c12724

[224] F. Liu, Q. Dong, C. Nie, Z. Li, B. Zhang, P. Han, W. Yang and M. Tong, Peroxymonosulfate enhanced photocatalytic degradation of serial bisphenols by metal-free covalent organic frameworks under visible light irradiation: mechanisms, degradation pathway and DFT calculation, Chemical Engineering Journal, 2022, 430, 132833. https://doi.org/10.1016/j.cej.2021.132833

[225] K. X. Chen, Y. Wang, Y. Q. Dong, Z. H. Zhao, Y. Zang, G. L. Zhang, Y. Liu and F. M. Zhang, Theoretical design of dual-site metallo-covalent organic frameworks for efficient CO2 photoreduction into C2H4, Applied Catalysis B: Environment and Energy, 2025, 365, 124933. https://doi.org/10.1016/j.apcatb.2024.124933

[226] J. Wang, Y. Yu, J. Cui, X. Li, Y. Zhang, C. Wang, X. Yu and J. Ye, Defective g-C3N4/covalent organic framework van der Waals heterojunction toward highly efficient S-scheme CO2 photoreduction, Applied Catalysis B: Environmental, 2022, 301, 120814. https://doi.org/10.1016/j.apcatb.2021.120814

[227] S. Li, C. Gao, H. Yu, Y. Wang, S. Wang, W. Ding, L. Zhang and J. Yu, Vinylene-Linked Donor-π-Acceptor Metal-Covalent Organic Framework for Enhanced Photocatalytic CO2 Reduction, Angewandte Chemie International Edition, 2024, 63, e202409925. https://doi.org/10.1002/anie.202409925

[228] C. Wang, W. Lu, W. Song, Z. Zhang, C. Xie, Y. Li and J. Wang, Highly crystalline benzothiadiazole covalent organic framework for enhanced Cr (VI) photocatalytic reduction by constructing donor-acceptor structure, Applied Catalysis B: Environment and Energy, 2025, 361, 124583. https://doi.org/10.1016/j.apcatb.2024.124583

[229] Y. Liu, Q. Deng, Y. Yu, H. Chen, C. Liu, L. Li, Q. Cai and D. Zhen, Novel amidoxime-functionalized covalent organic frameworks synergistically promote UO22+ removal via photocatalytic reduction and adsorption, Separation and Purification Technology, 361, 2025, 131461. https://doi.org/10.1016/j.seppur.2025.131461

[230] S. Zhang, L. Chen, Z. Qu, F. Zhai, X. Yin, D. Zhang, Y. Shen, H. Li, W. Liu, S. Mei, G. Ji, C. Zhang, X. Dai, Z. Chai and S. Wang, Confining Ti-oxo clusters in covalent organic framework micropores for photocatalytic reduction of the dominant uranium species in seawater, Chem, 2023, 9, 3172-3184. DOI: 10.1016/j.chempr.2023.06.008

[231] G. Wen, Q. Peng, C. Yuan, J. He and X. Hou, Nickel single atoms anchored on a bipyridine-based covalent organic framework: boosting active sites for photodegradation of

acetaminophen, Nanoscale, 2025, 17, 322-332. DOI: 10.1039/D4NR02759K

[232] J. M. Cox, B. Mileson, A. Sadagopan and S. A. Lopez, Molecular recognition and band alignment in 3D covalent organic frameworks for cocrystalline organic photovoltaics, The Journal of Physical Chemistry C, 2020, 124, 9126-9133. https://doi.org/10.1021/acs.jpcc.0c00087

[233] O. Yildirim, M. Bonomo, N. Barbero, C. Atzori, B. Civalleri, F. Bonino, G. Viscardi and C. Barolo, Application of metal-organic frameworks and covalent organic frameworks as (photo) active material in hybrid photovoltaic technologies, Energies, 2020, 13, 5602. https://doi.org/10.3390/en13215602

[234] H. Sajid, M. Asif, K. Ayub, M. A. Gilani, M. S. Akhter and T. Mahmood, Novel microporous B6N6 covalent organic framework (COF) as an electrochemical sensor for the ultra-selective detection of nitroaniline isomers; a DFT outcome, Surfaces and Interfaces, 2021, 27, 101587. https://doi.org/10.1016/j.surfin.2021.101587

[235] E. A. Gendy, A. I. Khodair, A. M. Fahim, D. T. Oyekunle and Z. Chen, Synthesis, characterization, antibacterial activities, molecular docking, and computational investigation of novel imine-linked covalent organic framework, Journal of Molecular Liquids, 2022, 358, 119191. https://doi.org/10.1016/j.molliq.2022.119191

[236] M. Heidari and M. Solimannejad, Sensing behavior of porous B6N6 boron nitride covalent organic framework toward cathinone drugs: A DFT study, Inorganic Chemistry Communications, 2022, 146, 110205. https://doi.org/10.1016/j.inoche.2022.110205

[237] W. Ye, L. Zhao, H. Z. Lin, L. Ding, Q. Cao, Z. K. Chen, J. Wang, Q. M. Sun, J. H. He and J. M. Lu, Halide Perovskite glues activate two-dimensional covalent organic framework crystallites for selective NO2 sensing, Nature Communications, 2023, 14, 2133. https://doi.org/10.1038/s41467-023-37296-0

[238] I. O. Amodu, M. Raimi, M. N. Ogbogu, I. Benjamin, A. O. Gulack, A. S. Adeyinka, H. Louis, I. O. Amodu, M. Raimi, M. N. Ogbogu, I. Benjamin, A. O. Gulack, A. S. Adeyinka and H. Louis, Mn-doped covalent organic framework (COF), graphene, and their nanocomposite (Mn@ GP/COF) as sensors for oil-dissolved gases in transformer: A computational study, Materials Today Communications, 2024, 38, 108363. https://doi.org/10.1016/j.mtcomm.2024.108363

[239] X. Ma, J. Kang, W. Cao, Y. Wu, C. Pang, S. Li, Z. Yi, Y. Xiong, C. Li, M. Wang, Z. Xu and J. Li, Anthracene-based dual channel donor-acceptor triazine-containing covalent organic frameworks for superior photoelectrochemical sensing, Journal of Colloid and Interface Science, 2024, 659, 665-675. https://doi.org/10.1016/j.jcis.2024.01.050

[240] R. Kulkarni, Y. Noda, D. Kumar Barange, Y. S. Kochergin, P. Lyu, B. Balcarova, P. Nachtigall and M. J. Bojdys, Real-time optical and electronic sensing with a β-amino enone linked, triazine-containing 2D covalent organic framework, Nature Communications, 2019, 10, 3228. https://doi.org/10.1038/s41467-019-11264-z

[241] L. R. Ahmed, J. Lüder, C. H. Chuang and A. F. El-Mahdy, Covalent-Organic-Framework-Modified Quartz Crystal Microbalance Sensor for Selective Detection of Hazardous Formic Acid, ACS Applied Materials & Interfaces, 20244, 16, 30408-30420. https://doi.org/10.1021/acsami.4c04630

[242] M. Yar and K. Ayub, Expanding the horizons of covalent organic frameworks to electrochemical sensors; A case study of CTF-FUM, Microporous and Mesoporous Materials, 2020, 300,110146. https://doi.org/10.1016/j.micromeso.2020.110146

[243] Z. Golshadi, M. Dinari, A. Knebel, J. Lützenkirchen and B. H. Monjezi, Metal organic and covalent organic framework-based QCM sensors for environmental pollutant detection and beyond, Coordination Chemistry Reviews, 2024, 521, 216163. https://doi.org/10.1016/j.ccr.2024.216163

[244] A. O. Rajee, I. O. Amodu, M. K. Abdlateef, M. N. Ogbogu, R. H. Ibrahim, K. T. Adesope, I. Benjamin and H. Louis, Chemically effect of small molecules (X= CF3, COOH, NH2, NO2) functionalized covalent organic framework (X–COF) as sensors for glyphosate: A computational study, Chemical Physics Impact, 2024, 8, 100510. https://doi.org/10.1016/j.chphi.2024.100510

[245] Y. Yusran, B. Miao, S. Qiu and Q. Fang, Functional covalent organic frameworks: design principles to potential applications. Accounts of Materials Research, 2024, 5(10), 1263-1278. https://doi.org/10.1021/accountsmr.4c00195

Data availability statement

All the relevant data have been presented in the manuscript.

Materials Advances Accepted Manuscript