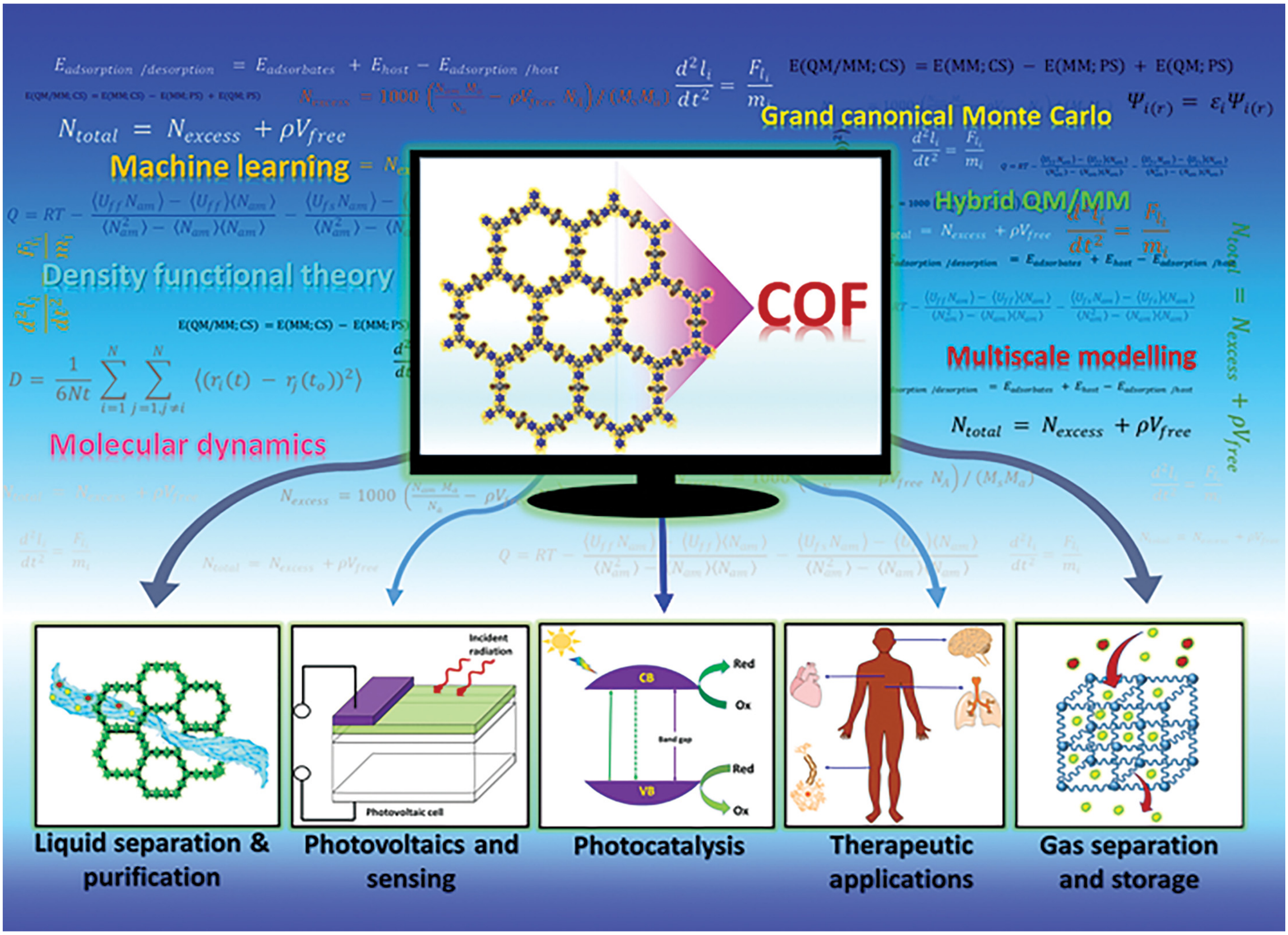

Showcasing research from Professor Swapnali Hazarika's laboratory, Chemical Engineering Group and Centre for Petroleum Research, CSIR-North East Institute of Science and Technology, Jorhat – 785006, Assam, India.

Exploring covalent organic frameworks through the lens of computational chemistry

The review explores the critical role of computational chemistry during the design, modelling, and applications of COFs, unveiling their exciting potential and providing a profound understanding of the existing experimental and hypothetical COFs at the atomic scale. Emphasizing the key challenges and future perspectives, this review may serve as a stepping stone for future advancements that ultimately guide the design and development of COF-based tailored materials for their ubiquitous applications in research and industrial domains, thereby mitigating current challenges.

Image reproduced by permission of Swapnali Hazarika from *Mater. Adv.*, 2026, **7**, 682.
Cover artwork designed by: Parashmoni Rajguru, Prarthana Bora, Chinmoy Bhuyan and Swapnali Hazarika.

As featured in:

See Swapnali Hazarika *et al.*, *Mater. Adv.*, 2026, **7**, 682.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/materials-advances

Registered charity number: 207890

Materials Advances

ROYAL SOCIETY OF CHEMISTRY

REVIEW

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Mater. Adv.*, 2026, 7, 682

Received 3rd August 2025,
Accepted 25th November 2025

DOI: 10.1039/d5ma00843c

rsc.li/materials-advances

Exploring covalent organic frameworks through the lens of computational chemistry

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

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 and higher-order architectures, and their unique properties make them a groundbreaking class of materials in the current scientific research. The advantageous properties of COFs include easily tunable porous structures, high surface area, low density, and exceptional chemical and thermal stability. With their 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 dynamics (MD) simulations, density functional theory (DFT), hybrid quantum mechanical/molecular mechanics (QM/MM), multiscale modelling and machine learning (ML) approaches, researchers provided a profound understanding of the interaction/adsorption mechanisms, performance–structure relationships and electronic behaviour of COFs even at the atomic level, which is often unattainable through conventional experimental methods. Currently, emerging computational methodologies play more imperative roles in unveiling the exciting potential of COFs in mitigating global challenges pertaining to environment, energy and sustainability. This review explores the critical role of computational chemistry in the 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 class of porous materials with exceptional physicochemical properties

Parashmoni Rajguru

Parashmoni Rajguru is a CSIR-Senior Research Fellow and PhD student in the Centre for Petroleum Research at CSIR-North East Institute of Science and Technology, Jorhat, Assam, India. He completed his MSc in Chemistry from Mizoram University in 2020. His research area focuses on experimental and computational approaches including synthesis and functionalization of nanomaterials like covalent organic frameworks, metal organic frameworks, carbon nanotubes, graphene oxide, carbon dots, layered double hydroxides, and cellulose nanocrystal, fabrication of functionalized membranes, computational modelling and study of interaction energy for environmental remediation such as wastewater treatment and gas separation.

Prarthana Bora

Prarthana Bora is a DST-INSPIRE fellow and PhD student in the Centre for Petroleum Research at CSIR-North East Institute of Science and Technology, Jorhat, Assam, India. She obtained her MSc in Chemistry from Dibrugarh University in 2020. Her research interest includes the design and development of nanomaterial-based gas separation membranes for carbon capture and olefin/paraffin separation. She also has expertise in the synthesis of various nanomaterials such as carbon dots, boron nitride, nanocellulose, zeolitic imidazolium frameworks, and layered double hydroxides.

---

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

and fully predesignable nature.[1] The advantages of COFs include extensive surface area, easy modifiability, tunable pores, and 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-saving and environmentally benign synthetic procedures such as microwave irradiation, electron beam irradiation, and ultrasound irradiation.[4] COFs came into focus at the beginning of 2000s and were synthesized based on the combined concept of organic chemistry synthesis and coordination chemistry. This synergistic approach was carried out to design novel materials 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 COFs (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 and self-condensation reactions of tetrahedral tetra(4-dihydroxyborylphenyl)methane (TBPM), silane analog of TBPM, *i.e.* TBPS, and triangular hexahydroxytriphenylene (HHTP). Among the designed COFs, COF-108 had the lowest density as compared to the 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 Fig. 1.[8] A survey on the number of publications on "covalent organic frameworks" between 2015 and 2025 was conducted, which is represented in Fig. 2. It is clearly observed that the demand for covalent organic frameworks has been increasing day by day. In the literature, there are approximately 500 000 different types of reported COFs, where the majority of them exhibit pore sizes ranging from 1 to 3 nm.[9] With their 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 potential candidates 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 COFs (CURATED COFs), and (iii) hypothetical COFs (hypoCOFs) database.[13] While discussing COFs, their design, synthesis routes, structures and

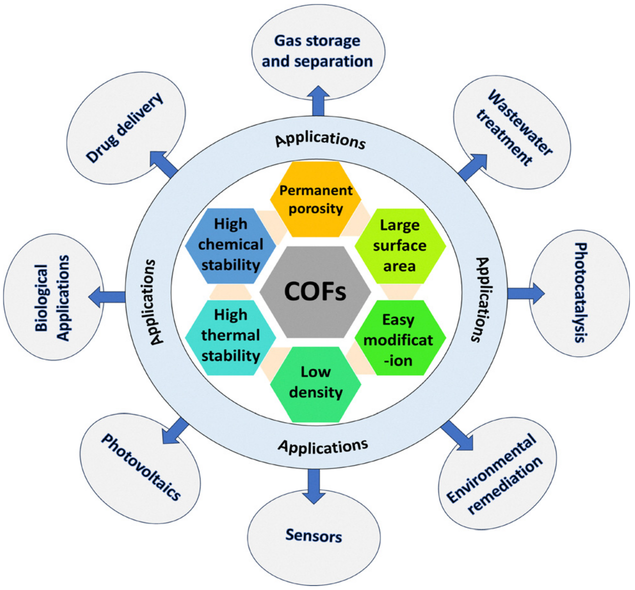

Fig. 1 Diverse properties and applications of COFs.

Chinmoy Bhuyan

Chinmoy Bhuyan is a CSIR-Senior Research Fellow and PhD student in the Centre for Petroleum Research at CSIR-North East Institute of Science and Technology, Jorhat, Assam, India. He completed his MSc in Chemistry from Gauhati University in 2020. His research area focuses on the design of polymeric nanocomposite membranes and hybrid membrane systems for the treatment of industrial wastewater. His work interest also covers the synthesis of MXenes, layered double hydroxides, metal organic frameworks, graphene oxide, graphitic carbon nitride and carbon dots.

Swapnali Hazarika

Swapnali Hazarika is Head of the Centre for Petroleum Research and Senior Principal Scientist at CSIR-North East Institute of Science and Technology, Jorhat, Assam, India. She received her MSc in Chemistry from Dibrugarh University in 1996. She received her PhD in Chemistry & Chemical Engineering from CSIR-NEIST, Dibrugarh University in 2002. Her research area covers separation science and technology, design of customized membranes, membrane separation studies, including chiral separation, biomolecule separation, and gas separation, wastewater treatment, membrane-based isolation and purification of natural products, biochemical reaction engineering and mechanism, kinetic analysis of reaction diffusion, modelling and simulation, and QSAR-QSPR studies.

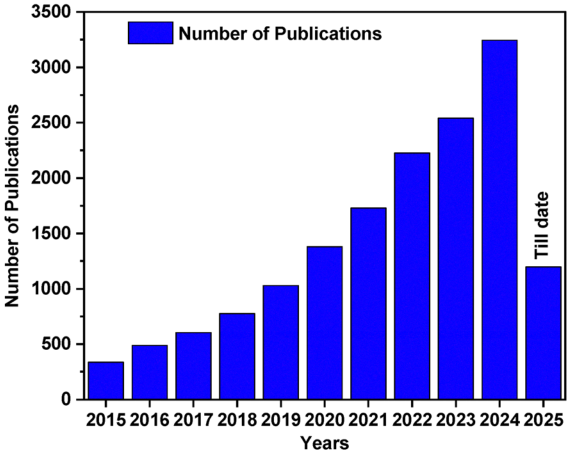

Fig. 2 Publications on covalent organic frameworks in the last ten years (data were collected from the Web of Science employing the term "covalent organic framework", accessed on 9th April, 2025).

functions are very important aspects to consider. A hierarchical diagram showcasing these important features of COFs and the corresponding research scopes is given in Fig. 3.

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 Fig. 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, optimization 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 wide range of applications.[16]

Before synthesis, computational studies can provide predictions of topologies and structural stability of a COF framework. Density Functional Theory (DFT) and Molecular Dynamics (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] Grand Canonical Monte Carlo (GCMC) and MD simulations provide insights into the 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.[17,18] Non-equilibrium molecular dynamics (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 the integration of COFs into 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 COFs 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 offers the researchers a nuanced understanding of the existing experimental and 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 the optimization of molecular structures, it offers 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

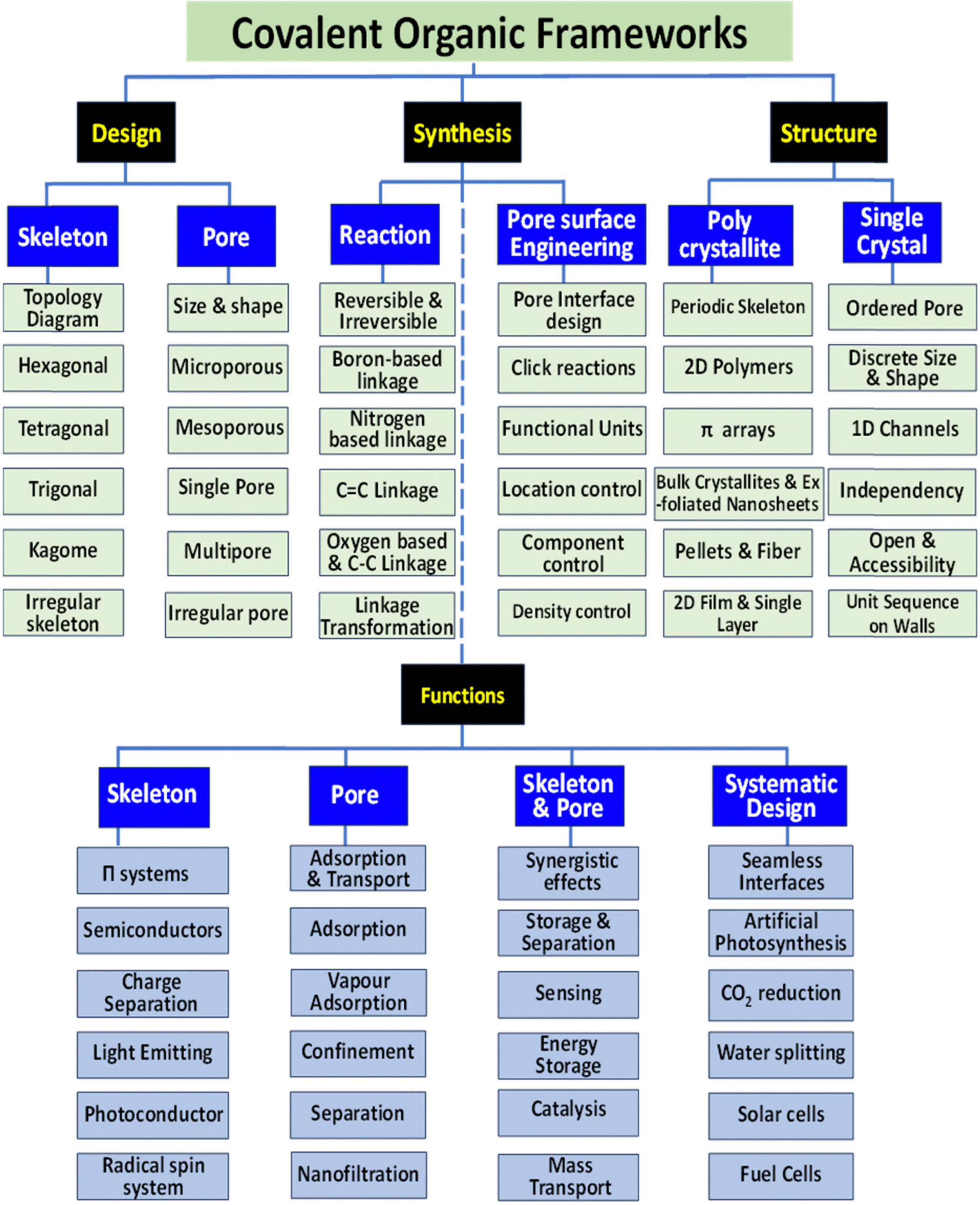

Fig. 3 Research scope of COFs in various domains. Reproduced from ref. 5 with permission from the Royal Society of Chemistry, Copyright 2021.

(eqn (1)) is given as follows:[22,23]

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

where 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 $V_{(r)}$, $V_{\mathrm{H}(r)}$ and $V_{\{\mathrm{XC}\}(r)}$, respectively.

The external potential considers the repulsive potential of the nucleus with external field potentials and the 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 using eqn (2):[22,24]

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

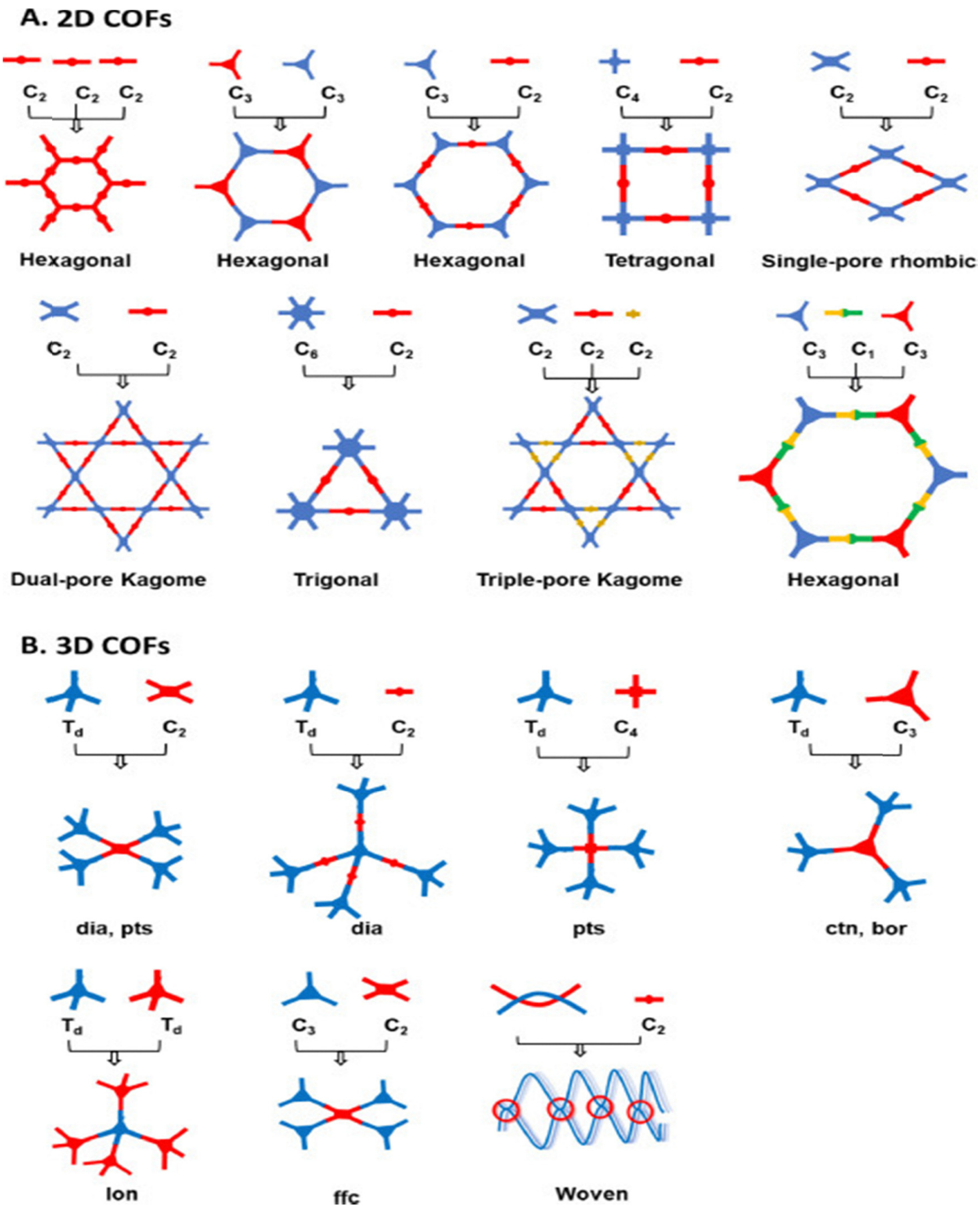

Fig. 4 Various reported 2D (A) and 3D (B) COFs based on their shapes/structures. Reproduced from ref. 15 with permission from Elsevier, Copyright 2021.

where $E_{\text{adsorbates}}$, E_{host} and $E_{\text{adsorption/host}}$ 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 such as 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 dynamics (MD) simulations 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, an experimental study and DFT-based calculations were carried out to evaluate the removal of naproxen (a pain-relieving medication), owing to its environmental concern, using an ionic guanidinium-based COF. The COF was found to exhibit excellent adsorption towards naproxen (308 mg g^{-1}), where physical adsorption was dominant over the chemical adsorption. The pi–pi and electrostatic interactions played an important role during the adsorption process, which was found to be exothermic and spontaneous. The guanidium-based COF architecture was reported as an effective and expeditious approach to mitigate the urgent issue of contamination of an 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 the 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]

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, up to 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 calculations 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 of 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 the MM approach. The QM/MM energy of the complete system can be obtained by employing the following expression:[47,48]

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

where E(MM;CS) and E(MM;PS) denote the MM analysis of the complete system and the primary subsystem and E(QM;PS) represents the 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 charges close to the borders, and modifying the borderline throughout the simulation. The versatility of the QM/MM approach was reported for studying the substituent effect on the enantioselectivity and reactivity of (salen)Mn catalysts within MOFs.[45] The crucial factors such as steric hindrance and electronic effects reducing enantioselectivity were 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. Moreover, 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 the simulation of modelling purposes of various systems, classical force field methods primarily harness (predefined) potential energy functions to examine molecular behaviours under different 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 and 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 in different parameters such as pressure and temperature (*i.e.* simulating a real-world environment).[54–58] Moreover, the 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 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]

$$N_{\text{total}} = N_{\text{excess}} + \rho V_{\text{free}} \tag{4}$$

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

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

$$N_{\text{excess}} = 1000\left(\frac{N_{\text{am}}M_{\text{a}}}{N_{\text{a}}} - \rho V_{\text{free}}N_{\text{A}}\right)/(M_{\text{s}}M_{\text{a}}) \tag{5}$$

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

$$\begin{aligned} Q = RT &- \frac{\langle U_{\text{ff}}N_{\text{am}}\rangle - \langle U_{\text{ff}}\rangle\langle N_{\text{am}}\rangle}{\langle N_{\text{am}}{}^2\rangle - \langle N_{\text{am}}\rangle\langle N_{\text{am}}\rangle} \\ &- \frac{\langle U_{\text{fs}}N_{\text{am}}\rangle - \langle U_{\text{fs}}\rangle\langle N_{\text{am}}\rangle}{\langle N_{\text{am}}{}^2\rangle - \langle N_{\text{am}}\rangle\langle N_{\text{am}}\rangle} \end{aligned} \tag{6}$$

where 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 the adsorbent, thereby indicating a stable adsorption process between the two.

Upon integration with advanced and emerging technologies, including data mining and ML, the GCMC simulation becomes a robust and more powerful platform, paving the way for 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 a 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) simulations. To gain crucial insights into the different systems, the MD simulation promotes computational investigations of atomic dynamics and interactions within the COF framework under different operating conditions.[76] The 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 follows:[22,80]

$$\frac{\mathrm{d}^2 l_i}{\mathrm{d}t^2} = \frac{F_{l_i}}{m_i} \tag{7}$$

where the 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]

$$D = \frac{1}{6Nt}\sum_{i=1}^{N}\sum_{j=1, j\neq i}^{N}\left\langle \left(r_i(t) - r_j(t_0)\right)\right\rangle^2 \tag{8}$$

In the above equation, $\langle\ \rangle$ denotes the overall average, and N, t, $r_i(t)$ and $r_j(t_0)$ denote the number of adsorbates, time of simulation, position of ith and jth molecule at time t and t_0, respectively.

To tackle nanoplastic pollution, the role of COF was evaluated by Shang *et al.* using MD simulations.[82] MD simulations were employed to study the adsorption behaviour of nanoplastics such as polyethylene (PE), polyethylene terephthalate (PET) and nylon-6 (PA 6) on functionalized COFs. It was observed that van der Waals interaction and electrostatic interaction play a key role in the adsorption process. Two-dimensional 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 the incorporation of C60 into 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 simulations, which revealed their low thermal conductivity. The limited phonon mean free path was identified as the primary responsible factor for 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 compared to equilibrium MD (EMD) simulations, as NEMD considers real transport effects such as the pore entrance and 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 highly based on their 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, have demonstrated the influence of functional groups and pore sizes on 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 thermoelectric candidates, 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, and graph neural networks) are employed by the researchers to gather various COF's structural parameters, including the presence of functional groups, surface area, and pore sizes, from a huge database, which is also termed 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 403 959 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 using the AutoML method 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, the 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 the 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 tunable band gap and semiconducting behaviour of the 2D COFs were substantiated, rendering them highly suitable for electronic applications. 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 gaining an in-depth understanding of boron-based COFs, including their structural, thermal, mechanical and adsorption behaviours.[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 (GCMC) simulations are mostly employed. Owing to the flexibility of permitting variation in 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 the separation of industrial gas mixtures 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

Table 1 Computational approaches for COFs or COF-based materials, investigating their gas separation and storage potential with structural and dynamic analyses

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 membranes) for CH_4 and CO_2; CO_2 /H_2 separation performance	–NH_2 group incorporated COFs	GCMC simulations, modelling	Adsorption behaviour, separation efficiency, experimental validation, membrane stability	Structural analysis	124
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

computational approaches for COFs or COF-based materials, investigating gas separation and storage with structural and dynamic analyses.

The adsorption study of gas molecules on COF can proceed in two phases. First, the COF or COF-based material structure can be validated through modelling, ensuring its structural correspondence to reality. Second, the adsorption simulation study can be used 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 designs 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 were 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 peaks at 5.8°, 10.0°, 11.6°, 15.3°, and 25.9°, confirming better crystallinity with strong π–π stacking. Again, the Brunauer–Emmett–Teller (BET) analysis revealed the microporous structures of all three COFs, with pore volumes of 0.395, 0.442, and 0.549 cm^3 g^{-1}, 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 298 K) 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 pressures, while at high pressures, 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 and 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 simulations and GC simulations.[115] The potential of 572 COFs in the separation of binary gas mixtures such as methane/hydrogen, methane/nitrogen and ethane/methane was investigated. These COFs outperformed traditional adsorbents in separation performance. The COF-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 under the condition of pressure up to 50 bars. The study underscores the significance of classical DFT for the prediction of adsorption of long hydrocarbons in the 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 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 investigative study 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, 3D-Sp-COF-1 exhibited excellent helium adsorption ability

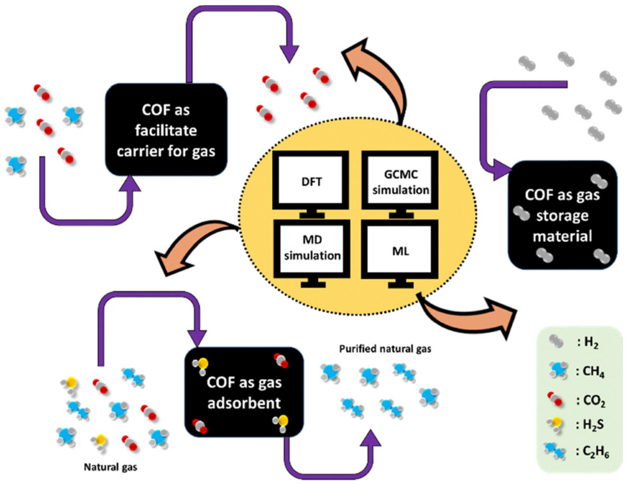

Fig. 5 Representation of the most commonly used methods for various gas storage and separation applications.

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 represents the most commonly employed computational approaches to investigate the gas storage and separation performance of COFs.

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 COF architectures (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 remained unchanged. The 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 and diffusion phenomena 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 such as methane, hydrogen and argon was 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 different 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.

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 simulations 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, under different pressure and temperature conditions.[130,131] An ML-assisted screening approach was carried out computationally to assess the potential of 597 synthesized and 7737 hypoCOFs (*i.e.* screened out from 69 840 hypothetical COFs), in CH_4/H_2 separation applications.[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 than that of 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 COFs were 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 (up to 73.4% and 32.9%) as compared to the pure polymeric membrane, which was further validated by DFT calculations and GCMC simulations.

A 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 up to 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 COFs in CO_2 separation as well as capture was analyzed using DFT and MD approaches. Their tunable structural properties, strong CO_2 interaction and effective sieving effect position them as potential candidates 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 simulations can complement the GCMC simulations.[139] The 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, the 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]

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

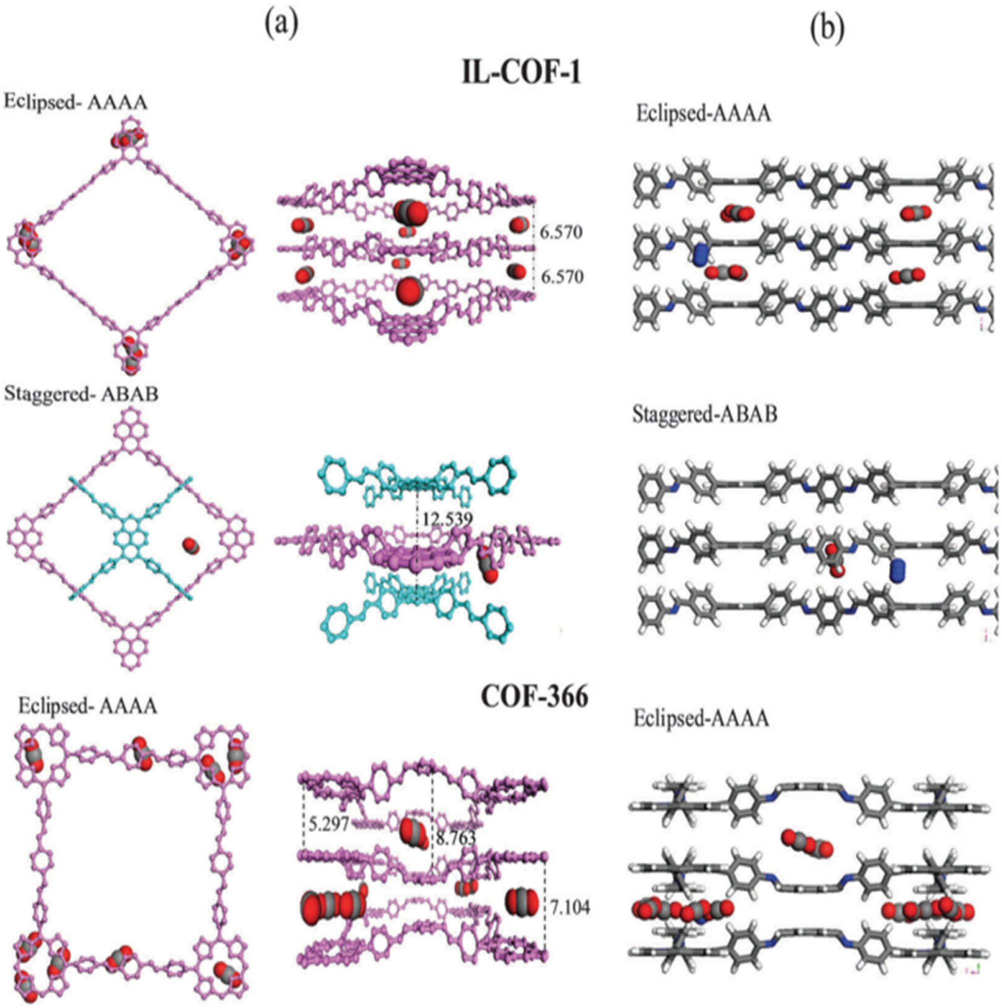

Fig. 6 Adsorption of CO_2 and N_2 on IL-COF-1 and COF-366, showing (a) only CO_2 and (b) gas mixture. Reproduced from ref. 143 with permission from the Royal Society of Chemistry, Copyright 2014.

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 37 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 Fig. 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]

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 the 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 and 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 (Fig. 7).[18,147]

These studies collectively confirmed/highlighted the immense potential of various COFs in gas separation/storage and carbon capture applications, 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 (up to 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 simulations, 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 (up to 99%) from acidic water was obtained when a COF-supported silver nanoparticle was employed as an adsorbent material (further validated by DFT calculations), which was highly stable and regenerable in nature.[151]

By conducting DFT calculations, the boroxine-based COFs were tested for their use in the removal of toxic heavy metals

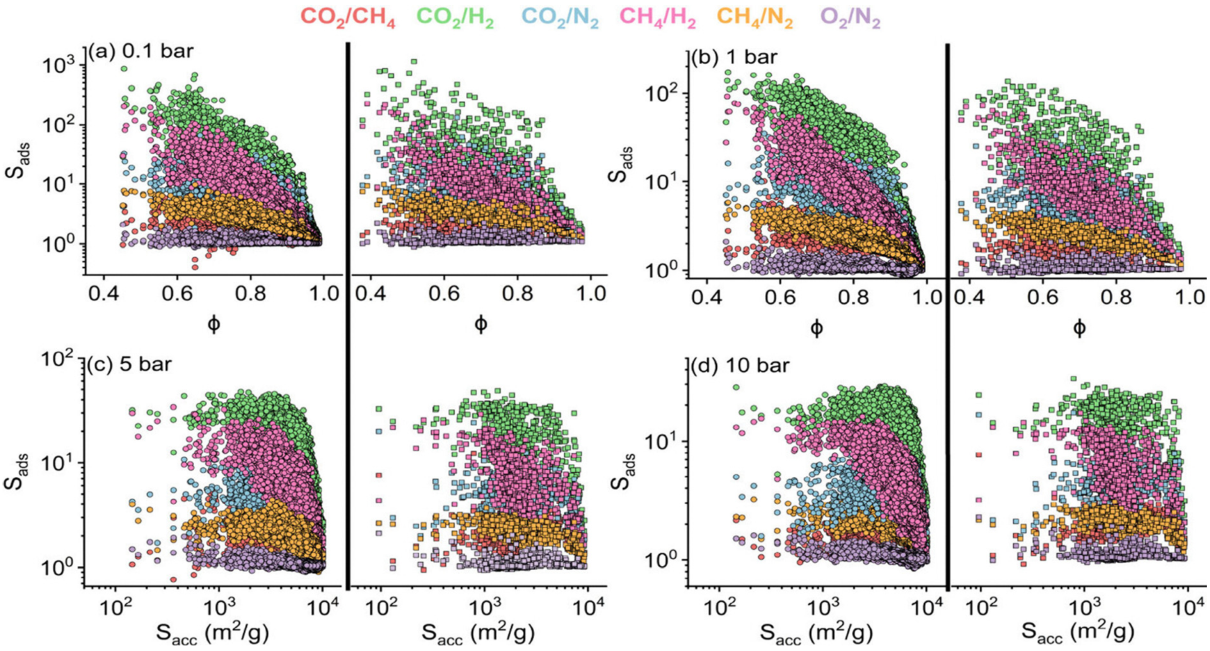

Fig. 7 Selectivities of the COF materials for CO_2/CH_4, CO_2/H_2, CO_2/N_2, CH_4/H_2, CH_4/N_2, and O_2/N_2 separations. Selectivities of 68 724 hypoCOFs (left panel) and 1060 CoRE COFs (right panel) were computed at (a) 0.1, (b) 1, (c) 5, and (d) 10 bars. Reproduced from the ref. 18. Copyright © 2025, American Chemical Society.

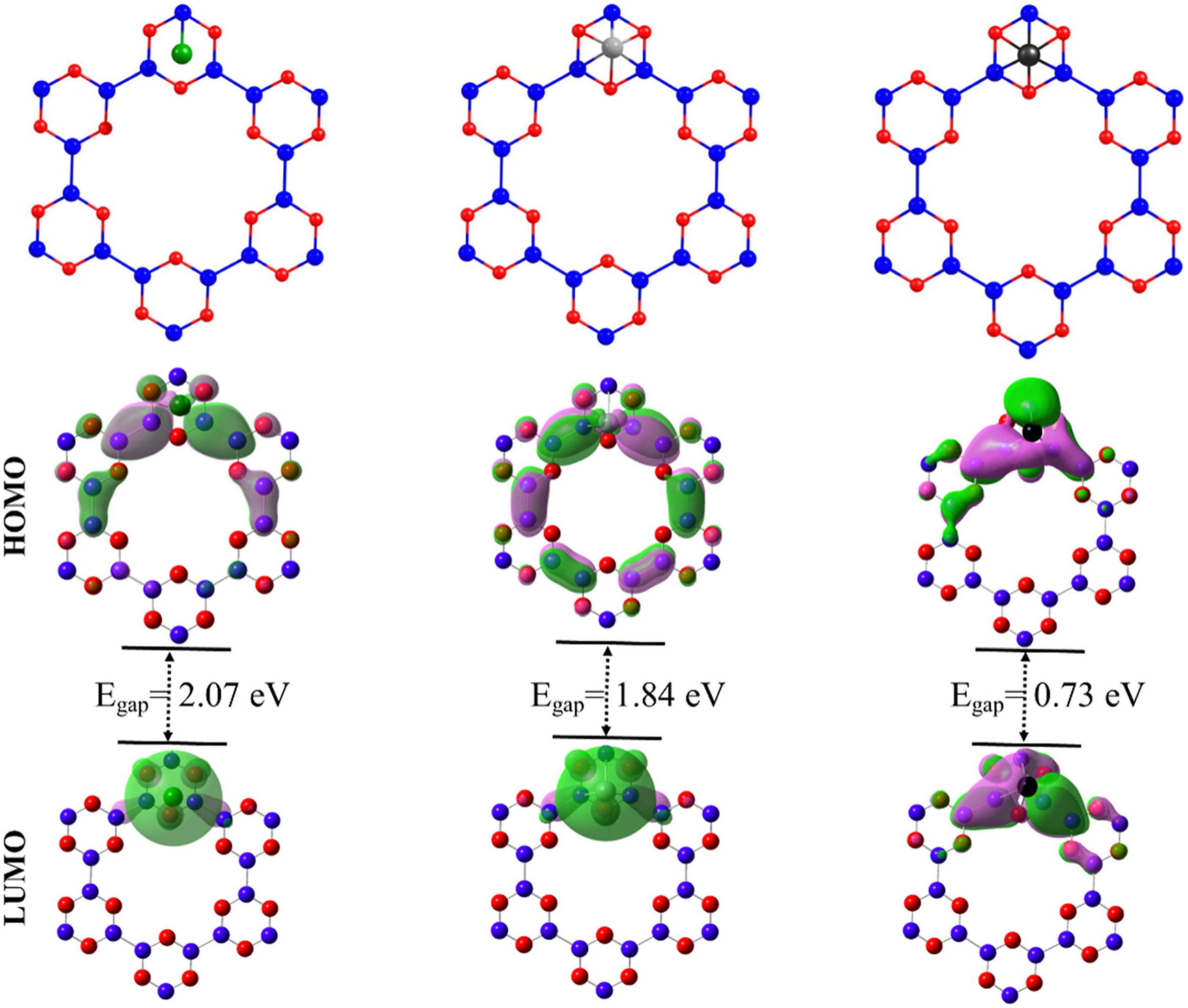

Fig. 8 Optimized structures, HOMOs and LUMOs, and E_{gap} values of the heavy metal@boroxine complexes. B, O, Cd, Hg, and Pb atoms are shown in blue, red, green, gray, and black colors, respectively. Reproduced from ref. 152 with permission from Elsevier, Copyright 2021.

(Hg(II), Pb(II) and Cd(II)) from wastewater, and the charge transfer from boroxine to metal ions was discussed (as shown in Fig. 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, the utilization of various COFs and COF-based materials for the removal of palladium,[153] lead[29] and Cr(VI)[154] from water streams and the recovery of Au(I) from the solution of thiosulfate[155] were 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.

The dye (methylene blue) adsorption properties of Schiff base network1 (SNW1) (a series of COFs synthesized by Mullen *et al.*[156] *via* the reaction of terephthaldehyde and melamine) 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 shows colour change with pH, for effective removal of dyes and salts from the wastewater stream. The membrane showed good removal efficacy with excellent water flux, especially at high pH values. The MD simulation was carried out to demonstrate the separation of dye molecules using 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 the aqueous phase was studied using molecular simulations. COF-1 exhibits better interaction with the dye molecules, resulting in 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 dyes 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 the membrane thickness was also emphasized in the study.[9] The impact of functional groups and pore sizes on the dye (bisphenol A) adsorption efficiency of COFs (in both 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. The 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(4-formylphenyl)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 the 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 (RhB), brilliant green (BG), gentian violet (GV), tolonium chloride (TC), methylene blue (MB) and methyl orange (MO) from the aqueous phase (as shown in Fig. 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

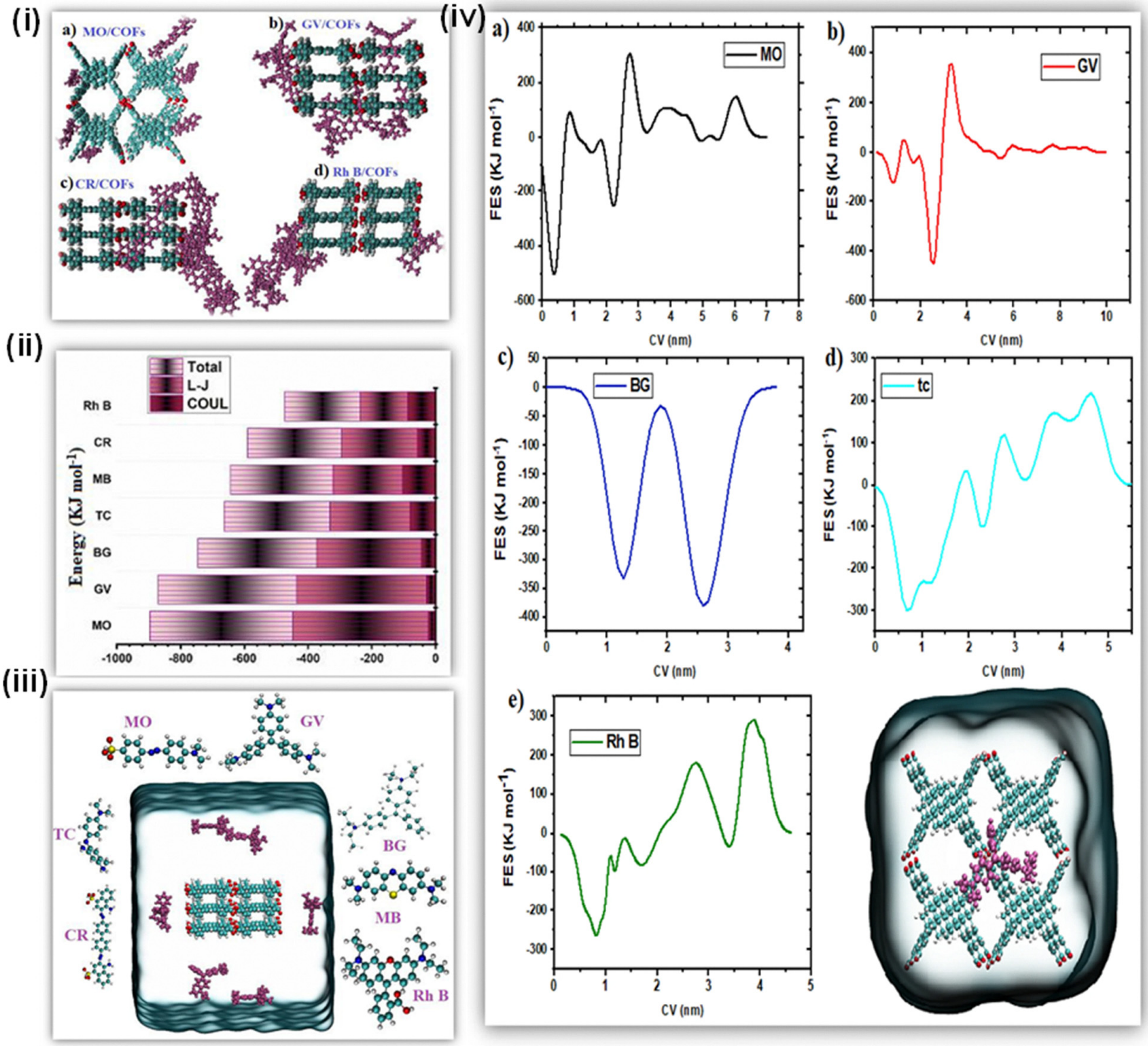

Fig. 9 (i) Final snapshots of the dyes/COFs (water molecules are not shown for clarity). (ii) Interaction energy between dye molecules and COFs (total, Lennard-Jones (L-J), and Coulombic energies for the adsorption). (iii) Initial snapshot of the studied systems for COFs/dyes. Color code-carbon: cyan, hydrogen: gray, sulfur: yellow, and nitrogen: blue. (iv) FES patterns for transferring dye molecules (a–e: MO, GV, BG, TC and RhB) towards the COFS materials. Reproduced from ref. 164 with permission from Springer Nature, Copyright 2024.

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 on the separation/adsorption, energy storage/conversion and catalytic applications of COFs 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 COFs showed excellent uranium extraction capability. Other various COFs or COF-based frameworks were reported for the extraction/removal of radioactive uranium from the aqueous stream using an 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 an experimental study and MD simulations. SCU-COF-1 possesses excellent radiation resistance with very high acid stability and effective 99TcO4$^-$ removal capability.[173] Cationic COFs were also investigated for effective elimination of radioactive $^{99}TcO_4^-$ (from the water stream), and its adsorption/interaction (at the 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 them an emerging pollutant demanding effective removal strategies.[151,177] The role and importance of various *in silico* approaches such as GCMC simulations, 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] The van der Waals interaction and hydrogen bond formation were identified as the key factors for the effective adsorption. MD simulations incorporated with coarse-grained (CG) simulations alongside DFT calculations were employed to study the removal of the drug phenazopyridine from the aqueous phase, using MOF/COF hybrid architectures.[180] Additionally, a carbon nanotube-incorporated COF-based composite was reported for the removal of pefloxacin, ofloxacin and norfloxacin from an aqueous stream. Employing MD and metadynamics simulations,[151] it was observed that the van der Waals interaction played a dominant role, whereas hydrophobic and electrostatic interactions also significantly influenced 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 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 a triazine-based COF (C_6N_6) as an anti-cancer drug (fluorouracil and nitrosourea) carrier was reported, and the adsorption energies of the drug towards the COF and the drug release profiles were illustrated using DFT calculations.[184] The study showcased that the adsorption of drugs onto 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 than 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 the B6N6 COF were evaluated by 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 were evaluated with and without 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, the drug release also 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 multi-scale 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 the 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,

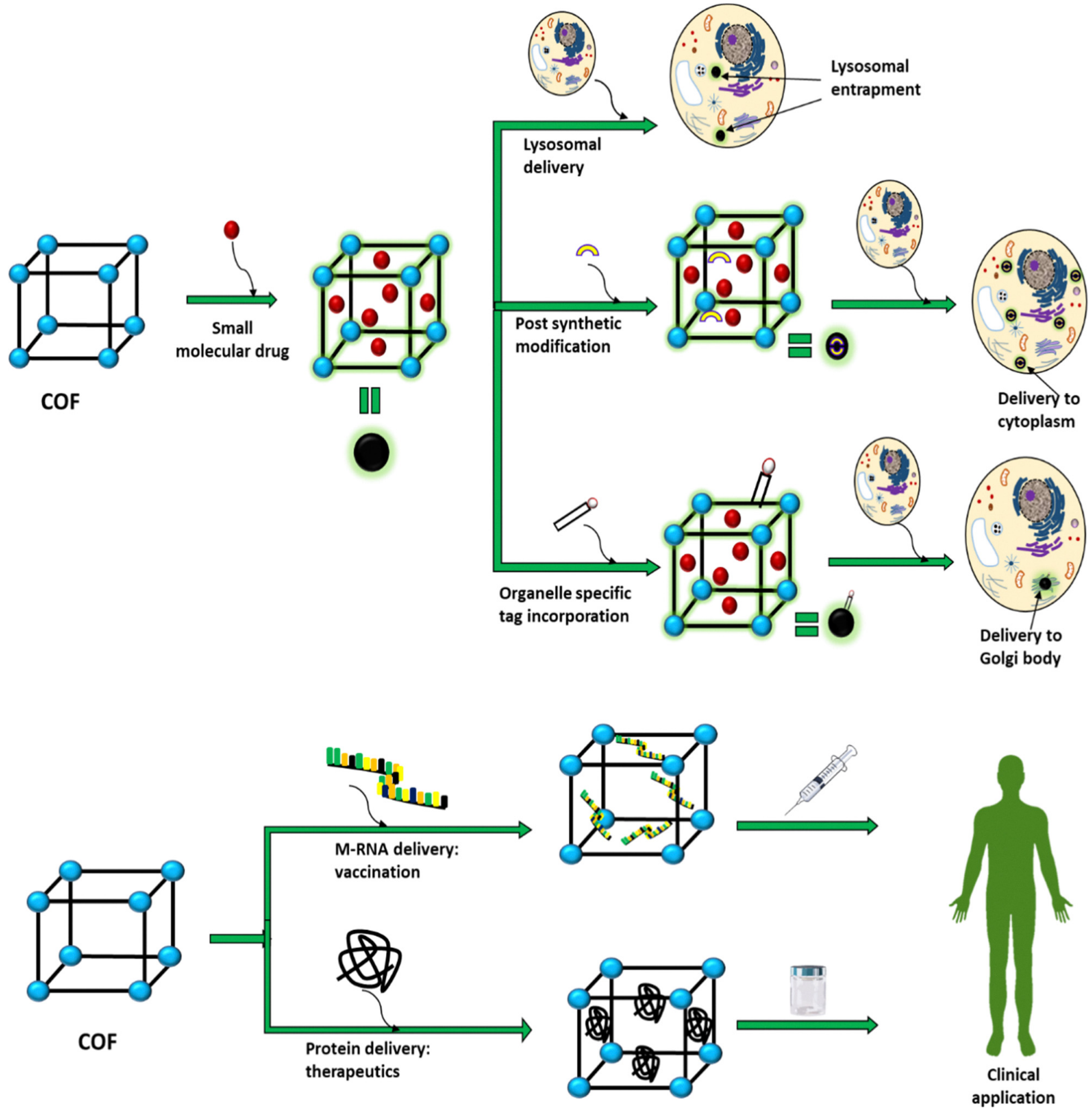

Fig. 10 Schematic showing the potential of COFs in various drug delivery applications.

through C–H–π and hydrogen bonding interactions, was further discussed employing DFT calculations, suggesting the potential of the COF in drug delivery and drug design applications.[189] Employing DFT calculations (at the 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] Fig. 10 depicts the potential of COFs in various drug delivery applications.

3.4. Photocatalysis

Fei Xie and team members have 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) COFs in photocatalytic reduction of CO_2.[192] The photocatalytic performance enhancement of COFs 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 bonds, 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.

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 the 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] Diverse 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 COFs 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 has been 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 the 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] Two-dimensional 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 up to 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 were 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 cluster-incorporated COFs[216] and isoelectronic organic dye-based COFs[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 on photocatalytic hydrogen peroxide evolution was also discussed using experimental and DFT-based approaches (Fig. 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 enhanced 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 into imines within 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

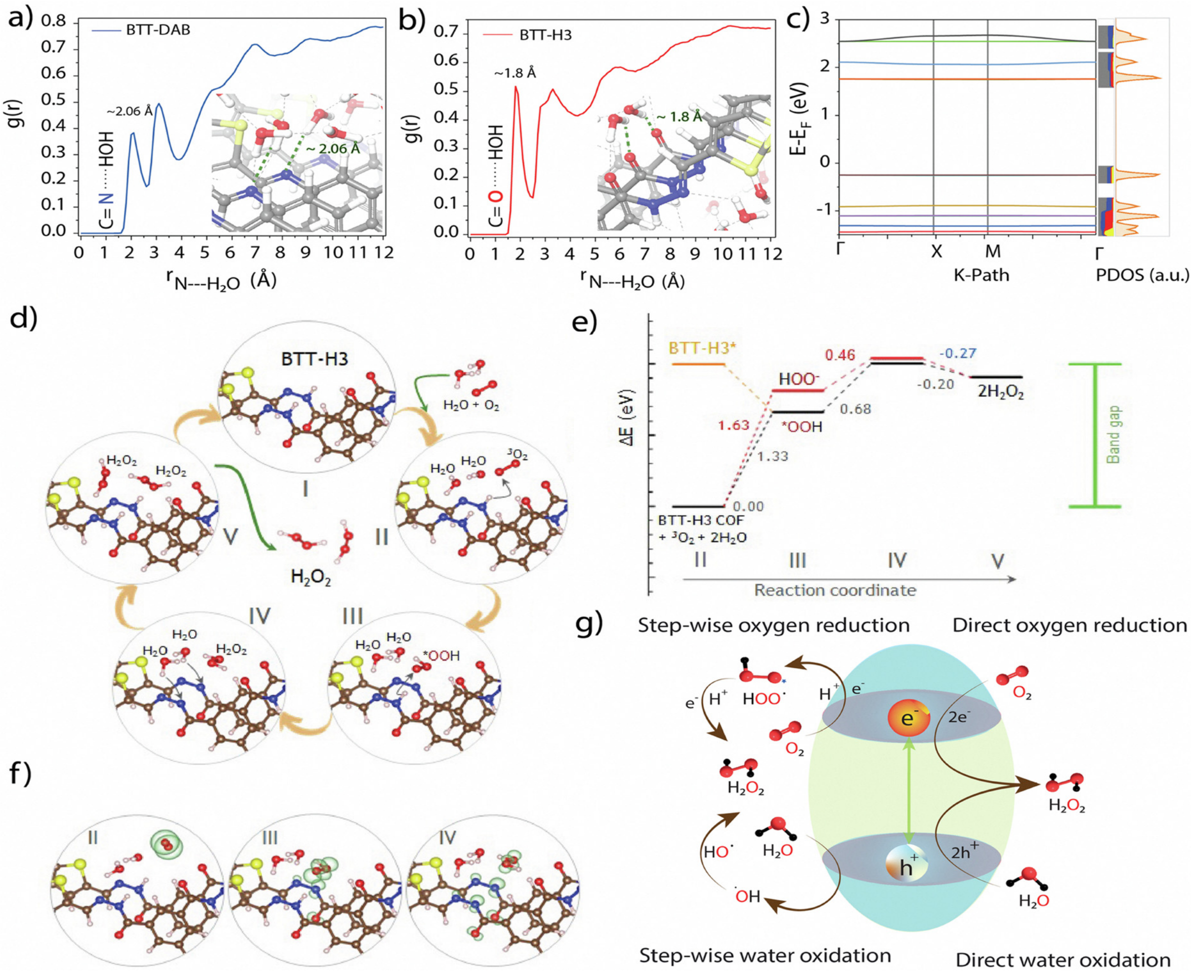

Fig. 11 Photocatalytic H_2O_2 evolution study employing computational analysis: (a) N center of BTT-DAB (Benzo[1,2-*b*:3,4-*b*′:5,6-*b*″] trithiophene-2,5,8-tricarbaldehyde and 4-diaminobenzene) COFs, (b) O center of BTT-H3 (hydrazone-linked COF), (c) band structure and projected density of states (PDOS) 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 (semi-transparent light green blobs) of the radical species, and (g) representation of the overall photocatalytic mechanism of H_2O_2 generation through the water oxidation reaction and oxygen reduction reaction. Reproduced from ref. 220 with permission from Springer Nature, Copyright 2025.

activity of COFs utilizing an integrated approach of experimental studies and DFT calculations.[224]

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, which have been 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

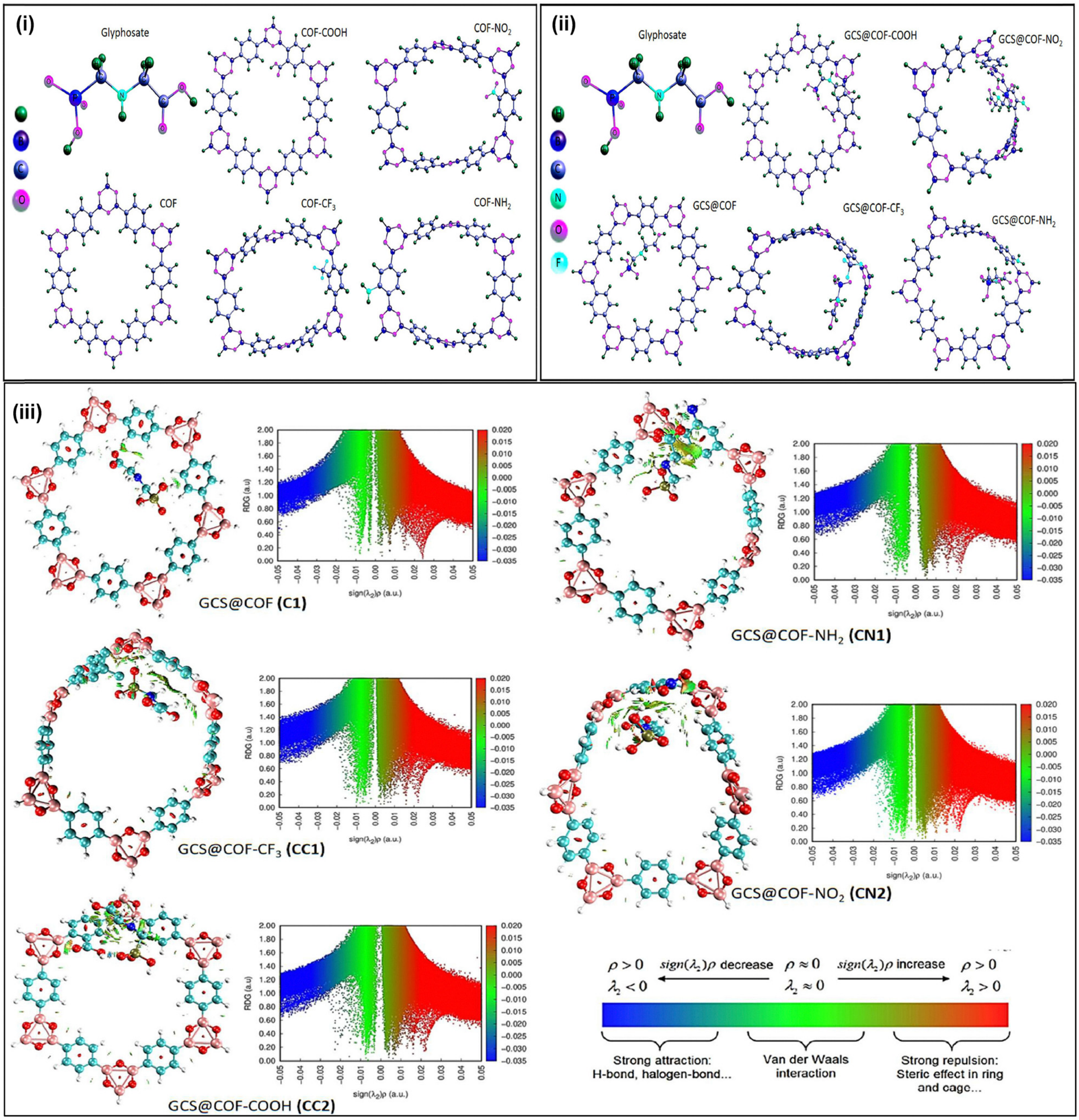

Fig. 12 (i) Optimized structures of the GCS with the pure and functionalized COFs, (ii) optimized structures of the stable configurations of the stable complexes (complexes of the COFs with GCS) studied at the M06-2X/ LanL2DZ level of theory, and (iii) 3D NCI isosurfaces and 2D RDG scatter maps for all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

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 fullerene, displayed enhanced photovoltaic performance, achieving a balance between long-range order and surface area.[232] The evaluation of electronic properties, 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, a 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 and 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 and hydrogen sulfide,[242] and volatile organic compounds.[243] Employing DFT calculations (utilizing the M06-2X/Gen/6-311G(d)/LanL2DZ method), the adsorptive behaviour of glyphosate (GCS), one of the most commonly used herbicide, on the TpBD-based COF architecture and its potential sensing application were studied, as shown in Fig. 12.[244] The study explores the impact of various functional derivatives such as $-NO_2$, $-NH_2$, $-CF_3$ and $-COOH$, when incorporated into the COF, in the adsorption process. Out of all the studied systems, GCS@COF–NH_2 possessed the highest negative value of adsorption energy. Two-dimensional reduced density gradient (RDG) scatter plots and 3D non-covalent interaction (NCI) isosurface plots were visualized, revealing the variations of interaction in all the studied complex systems. In 3D visualization as represented in Fig. 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 materials in the current scientific research, showcasing their significant potential in various applications such as gas separation/storage, wastewater treatment, drug delivery, photocatalysis, sensing, 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 and separation processes and catalytic activities, from the perspective of computational chemistry, was discussed in this review article.

Future studies should focus on linkage engineering to enhance the stability 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. The 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 printing techniques could be employed to build COFs with complex designs and 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 achieve their large-scale application 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 the COF design, ultimately guiding the design and development of tailored COF-based materials for numerous applications. 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. The authors also declare that they have no conflicts of interest.

Data availability

All the relevant data have been presented in the manuscript.

Acknowledgements

Parashmoni Rajguru and Chinmoy Bhuyan acknowledge CSIR, India for SRF-Direct fellowship (ID numbers: 35110903 & 35110313, respectively). Prarthana Bora acknowledges DST, India for INSPIRE fellowship (grant no. IF200403 (GAP0811)). All authors acknowledge the Department of Chemicals and Petrochemicals, Ministry of Chemicals and Fertilizers, Govt. of India, for the research grant GPP-373, vide F. No. 25012/01/2020-PC-II (FTS:16020). The authors acknowledge Prof. G. Narahari Sastry for his unwavering guidance and invaluable suggestions throughout the work. The authors further acknowledge the Director, CSIR-NEIST, Jorhat, for the encouragement and timely discussion. The work has been approved by the Publication & Intellectual Property Rights Committee, CSIR-NEIST and assigned the manuscript number: CSIR-NEIST/PUB/2025/207.

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, *J. Am. Chem. Soc.*, 2024, **147**, 1709–1720, DOI: 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, *Chem. Soc. Rev.*, 2025, **54**, 484–514, DOI: 10.1039/D4CS00703D.

3 T. Wu, Y. Qian, Z. Zhu, W. Yu, L. Zhang, J. Liu, X. Shen, X. 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, *Adv. Mater.*, 2025, **37**, 2415509, DOI: 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, *Sep. Purif. Technol.*, 2024, **339**, 126636, DOI: 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, *Chem. Soc. Rev.*, 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, DOI: 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 Mesoporous Mater.*, 2023, **349**, 112417, DOI: 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, *Rev. Inorg. Chem.*, 2024, **44**, 117–133, DOI: 10.1515/revic-2023-0018.

11 X. Zhao, P. Pachfule and A. Thomas, Covalent organic frameworks (COFs) for electrochemical applications, *Chem. Soc. Rev.*, 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, *Chem. Soc. Rev.*, 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, *J. CO2 Util.*, 2022, **62**, 102077, DOI: 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 Appl. Mater. Interfaces*, 2025, **17**, 10108–10117, DOI: 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, DOI: 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, *Appl. Mater. Today*, 2025, **44**, 102694, DOI: 10.1016/j.apmt.2025.102694.

17 N. Keller and T. Bein, Optoelectronic processes in covalent organic frameworks, *Chem. Soc. Rev.*, 2021, **50**(3), 1813–1845, DOI: 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 Mater. Lett.*, 2025, **7**, 954–960, DOI: 10.1021/acsmaterialslett.4c02594.

19 S. Velioglu and S. Keskin, Simulation of H2/CH4 mixture permeation through MOF membranes using non-equilibrium molecular dynamics, *J. Mater. Chem. A*, 2019, **7**(5), 2301–2314, DOI: 10.1039/C8TA10167A.

20 D. Sen, The uncertainty relations in quantum mechanics, *Curr. Sci.*, 2014, 203–218.

21 C. de Ronde, R. Fernández Mouján and C. Massri, Everything is entangled in quantum mechanics: on the measures of quantum entanglement, *Eur. Phys. J. Plus*, 2024, **139**, 1039, DOI: 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, DOI: 10.1021/acs.energyfuels.4c02206.

23 H. J. F. Jansen, Many-body properties calculated from the Kohn-Sham equations in density-functional theory, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1991, **43**, 12025, DOI: 10.1103/PhysRevB.43.12025.

24 S. Wang, G. Zhou, Y. Ma, L. Gao, R. Song, G. Jiang and G. Lu, Molecular dynamics investigation on the adsorption behaviors of H2O, CO2, CH4 and N2 gases on calcite (1 1 0) surface, *Appl. Surf. Sci.*, 2016, **385**, 616–621, DOI: 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, DOI: 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**, e32861, DOI: 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, *Adv. Funct. Mater.*, 2023, **33**, 2301594, DOI: 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, *Inorg. Chem.*, 2019, **58**, 9303–9315, DOI: 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, *Sep. Purif. Technol.*, 2023, **307**, 122783, DOI: 10.1016/j.seppur.2022.122783.

30 P. Zhu and V. Meunier, Electronic properties of two-dimensional covalent organic frameworks, *J. Chem. Phys.*, 2012, 137, DOI: 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, DOI: 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, *Sep. Purif. Technol.*, 2025, **357**, 130182, DOI: 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, *Chem. Eng. J.*, 2025, 159249, DOI: 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, *Phys. Chem. Chem. Phys.*, 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 Appl. Mater. Interfaces*, 2017, **9**, 31129–31141, DOI: 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, *Nat. Commun.*, 2022, **13**, 6317, DOI: 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, *Sci. China Chem.*, 2025, 1–9, DOI: 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, *Chem. Eng. Sci.*, 2024, **298**, 120380, DOI: 10.1016/j.ces.2024.120380.

39 A. S. Christensen, T. Kubar, Q. Cui and M. Elstner, Semi-empirical quantum mechanical methods for noncovalent interactions for chemical and biochemical applications, *Chem. Rev.*, 2016, **116**, 5301–5337, DOI: 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), *J. Chem. Theory Comput.*, 2017, **13**, 1989–2009, DOI: 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, *Mater. Today Commun.*, 2025, **44**, 111951, DOI: 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, *J. Chem. Theory Comput.*, 2011, **7**, 931–948, DOI: 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, *J. Comput. Chem.*, 2024, **45**, 2786–2792, DOI: 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, *J. Chem. Theory Comput.*, 2007, **3**, 1349–1367, DOI: 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, *Ind. Eng. Chem. Res.*, 2010, **49**, 10965–10973, DOI: 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-Rev. Med. Chem.*, 2022, **22**, 1096–1107, DOI: 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, *Angew. Chem., Int. Ed.*, 2009, **48**, 1198–1229, DOI: 10.1002/anie.200802019.

49 G. Groenhof, Introduction to QM/MM simulations, *Biomolecular simulations: methods and protocols*, 2012, pp. 43–66, DOI: 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, *J. Phys. Chem. C*, 2021, **125**, 26832–26846, DOI: 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, *J. Mol. Liq.*, 2025, **422**, 126904, DOI: 10.1016/j.molliq.2025.126904.

52 *Biomolecular simulations: methods and protocols*, ed L. Monticelli and D. P. Tieleman, Humana Press, Totowa, NJ, Vol. 924, 2013, DOI: 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?, *J. Chem. Theory Comput.*, 2017, **13**, 4636–4648, DOI: 10.1021/acs.jctc.7b00777.

54 E. Tylianakis and G. E. Froudakis, Grand canonical Monte Carlo method for gas adsorption and separation, *J. Comput. Theor. Nanosci.*, 2009, **6**, 335–348, DOI: 10.1166/jctn.2009.1040.

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, *Angew. Chem.*, 2025, **137**, e202420801, DOI: 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, *Appl. Organomet. Chem.*, 2023, **37**, e7199, DOI: 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, *J. Phys. Chem. C*, 2013, **117**, 5861–5872, DOI: 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, *J. Phys. Chem. C*, 2012, **116**, 3492–3502, DOI: 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, *J. Am. Chem. Soc.*, 2018, **140**, 10094–10098, DOI: 10.1021/jacs.8b05136.

60 Z. Xia, Y. Zhao and S. B. Darling, Covalent organic frameworks for water treatment, *Adv. Mater. Interfaces*, 2021, **8**, 2001507, DOI: 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, *Adv. Mater.*, 2024, **36**(49), 2412653, DOI: 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, *Int. J. Biol. Macromol.*, 2025, **294**, 139541, DOI: 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, *Adv. Mater.*, 2024, 2405532, DOI: 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), *Appl. Catal., B*, 2025, **362**, 124721, DOI: 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, *Angew. Chem., Int. Ed.*, 2025, **64**(2), e202414118, DOI: 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, DOI: 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, *Chem. Phys.*, 2019, **516**, 71–83, DOI: 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, *Chem. Eng. J.*, 2021, **415**, 128824, DOI: 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 Mesoporous Mater.*, 2022, **341**, 112081, DOI: 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, *Ind. Eng. Chem. Res.*, 2022, **61**(25), 8809–8820, DOI: 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, *Geophys. J. Int.*, 2020, **220**(1), 37–58, DOI: 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 Appl. Mater. Interfaces*, 2017, **9**(39), 33419–33428, DOI: 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, *Int. J. Heat 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, *Chem. Eng. Sci.*, 2011, **66**, 6297–6305, DOI: 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 Appl. Nano Mater.*, 2023, **6**, 13363–13373, DOI: 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 Interface Sci. Commun.*, 2024, **62**, 100798, DOI: 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, *Chem. Sci.*, 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, DOI: 10.1021/acsnano.3c11787.

79 H. C. Andersen, Molecular dynamics simulations at constant pressure and/or temperature, *J. Chem. Phys.*, 1980, **72**, 2384–2393, DOI: 10.1063/1.439486.

80 S. Alavi, Statistical Mechanics: Theory and Molecular Simulation. By Mark E. Tuckerman, *Angew. Chem., Int. Ed.*, 2011, 12138–12139, DOI: 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, *J. Phys. Chem. B*, 2023, **127**, 7983–7987, DOI: 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, *J. Hazard. Mater.*, 2022, **421**, 126796, DOI: 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, *J. Phys. Chem. C*, 2020, **124**, 8386–8393, DOI: 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, *Int. J. Heat Mass Transfer*, 2024, **225**, 125404, DOI: 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, *J. Phys. Chem. C*, 2016, **120**, 17060–17068, DOI: 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 Appl. Mater. Interfaces*, 2025, **17**(10), 15372–15384, DOI: 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+, *J. Membr. Sci.*, 2024, **712**, 123247, DOI: 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, *Adv. Theory Simul.*, 2025, e01576, DOI: 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 Appl. Mater. Interfaces*, 2024, **16**, 19806–19818, DOI: 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, *J. Phys. Chem. C*, 2020, **124**, 19538–19547, DOI: 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, *Chem. Mater.*, 2024, **36**, 4315–4330, DOI: 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, *J. Phys. Chem. C*, 2024, **128**, 11355–11366, DOI: 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 Chem.*, 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, DOI: 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, *J. Phys. Chem. Lett.*, 2023, **14**, 6757–6764, DOI: 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 Appl. Mater. Interfaces*, 2024, **16**, 71048–71059, DOI: 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, *Chem. Mater.*, 2024, **36**, 9535–9546, DOI: 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, *Appl. Surf. Sci.*, 2023, **638**, 157947, DOI: 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, *J. Mol. Model.*, 2025, **31**, 1–12, DOI: 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, **4**, 3351–3362, DOI: 10.1039/D5DD00126A.

102 J. A. Elliott, Novel approaches to multiscale modelling in materials science, *Int. Mater. Rev.*, 2011, **56**, 207–225, DOI: 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 Digit. Med.*, 2019, **2**, 115, DOI: 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 Appl. Mater. Interfaces*, 2021, **13**, 26411–26420, DOI: 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, DOI: 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, *J. Phys. Chem. C*, 2012, **116**, 4921–4929, DOI: 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 Mesoporous Mater.*, 2015, **210**, 142–148, DOI: 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, *Chem. Eng. Sci.*, 2025, **305**, 121175, DOI: 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, *Front. Energy Res.*, 2019, **7**, 77, DOI: 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, DOI: 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, *Ind. Eng. Chem. Res.*, 2025, **64**(35), 17014–17025, DOI: 10.1021/acs.iecr.4c04786.

114 B. Dash, Carbon dioxide capture using covalent organic frameworks (COFs) type material—a theoretical investigation, *J. Mol. Model.*, 2018, **24**, 120, DOI: 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, *Ind. Eng. Chem. Res.*, 2021, **60**, 12999–13012, DOI: 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 Mesoporous Mater.*, 2021, **324**, 111263, DOI: 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, *Ind. Eng. Chem. Res.*, 2024, **63**, 8369–8382, DOI: 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 J. Chem.*, 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, *J. Mater. Sci.*, 2022, **57**, 6282–6292, DOI: 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 Mesoporous Mater.*, 2021, **326**, 111386, DOI: 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, *Chem. Phys. Rev.*, 2023, 4, DOI: 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, *Ind. Eng. Chem. Res.*, 2023, **62**, 12291–12304, DOI: 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, *Mol. Simul.*, 2018, **44**, 1244–1251, DOI: 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, *Adv. Funct. Mater.*, 2023, **33**, 2300219, DOI: 10.1002/adfm.202300219.

125 S. Keskin, Adsorption, diffusion, and separation of CH4/H2 mixtures in covalent organic frameworks: molecular simulations and theoretical predictions, *J. Phys. Chem. C*, 2012, **116**, 1772–1779, DOI: 10.1021/jp209804x.

126 G. Garberoglio, Computer simulation of the adsorption of light gases in covalent organic frameworks, *Langmuir*, 2007, **23**, 12154–12158, DOI: 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, *J. Phys. Chem. A*, 2010, **114**, 10824–10833, DOI: 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, *Chem. Soc. Rev.*, 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 Mesoporous Mater.*, 2010, **133**, 59–65, DOI: 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, *Int. J. Hydrogen Energy*, 2022, **47**, 29390–29398, DOI: 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, *Mater. Today Commun.*, 2022, **33**, 104374, DOI: 10.1016/j.mtcomm.2022.104374.

132 G. O. Aksu and S. Keskin, Advancing CH4/H2 separation with covalent organic frameworks by combining molecular simulations and machine learning, *J. Mater. Chem. 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, *J. Membr. Sci. Res.*, 2022, 8, DOI: 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, *Chem. Eng. Sci.*, 2025, **301**, 120801, DOI: 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, *Mater. Today Energy*, 2025, **48**, 101771, DOI: 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 Models, *ACS Appl. Mater. Interfaces*, 2024, **16**, 61995–62009, DOI: 10.1021/acsami.4c11953.

137 Y. Zeng, R. Zou and Y. Zhao, Covalent organic frameworks for CO_2 capture, *Adv. Mater.*, 2016, **28**(15), 2855–2873, DOI: 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, *Appl. Surf. Sci.*, 2022, **571**, 151355, DOI: 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, *Phys. Chem. Chem. Phys.*, 2024, **26**, 8577–8603, 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, *Phys. Chem. Chem. Phys.*, 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, *Chem. Mater.*, 2019, **31**, 1584–1596, DOI: 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, *J. Mol. Model.*, 2014, **20**, 1–6, DOI: 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, *Phys. Chem. Chem. Phys.*, 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, *J. Mol. Graphics Modell.*, 2019, **86**, 84–94, DOI: 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, *Ind. Eng. Chem. Res.*, 2022, **61**, 11116–11123, DOI: 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 Appl. Mater. Interfaces*, 2024, **16**, 27360–27367, DOI: 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, *Environ. Sci. Technol.*, 2025, **59**(13), 6361–6378, DOI: 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, *Phys. Chem. Chem. Phys.*, 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, *J. Chem. Phys.*, 2024, 161, DOI: 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, DOI: 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, *J. Hazard. Mater.*, 2020, **389**, 121824, DOI: 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, *J. Mol. Liq.*, 2021, **336**, 116326, DOI: 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, DOI: 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), *Sep. Purif. Technol.*, 2025, **359**, 130544, DOI: 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, *Sep. Purif. Technol.*, 2025, **353**, 128329, DOI: 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, *J. Am. Chem. Soc.*, 2009, **131**, 7216–7217, DOI: 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, *Int. J. New Chem.*, 2023, **9**, 383–392, DOI: 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, DOI: 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, *Appl. Water Sci.*, 2024, **14**, 184, DOI: 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, *J. Membr. Sci.*, 2025, **715**, 123487, DOI: 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, *J. Mol. Liq.*, 2023, **392**, 123475, DOI: 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, *J. Mol. Liq.*, 2020, **301**, 112431, DOI: 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 Appl. Mater. Interfaces*, 2022, **14**, 57180–57188, DOI: 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, DOI: 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, DOI: 10.1038/s41545-022-00173-2.

166 Z. Li, T. He, Y. Gong and D. Jiang, Covalent organic frameworks: pore design and interface engineering, *Acc. Chem. Res.*, 2020, **53**, 1672–1685, DOI: 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 Appl. Mater. Interfaces*, 2021, **13**, 48700–48708, DOI: 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, *J. Am. Chem. Soc.*, 2024, **146**, 23566–23573, DOI: 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, *Chem. Eng. J.*, 2025, **503**, 158513, DOI: 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, *Adv. Funct. Mater.*, 2024, **34**, 2313314, DOI: 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 Res.*, 2024, **265**, 122320, DOI: 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, *Sep. Purif. Technol.*, 2024, **338**, 126501, DOI: 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, *Chem. Sci.*, 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, *Environ. Sci.: Nano*, 2023, **10**, 611–624, DOI: 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, *Sep. Purif. Technol.*, 2025, **354**, 128786, DOI: 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), *Sep. Purif. Technol.*, 2025, **356**, 129947, DOI: 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 Rev.*, 2024, **43**, 277–299, DOI: 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, *J. Mol. Liq.*, 2024, 125513, DOI: 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, DOI: 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, *Appl. Mater. Today*, 2021, **25**, 101196, DOI: 10.1016/j.apmt.2021.101196.

181 P. Ghosh and P. Banerjee, Drug delivery using biocompatible covalent organic frameworks (COFs) towards a therapeutic approach, *Chem. Commun.*, 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, *Comput. Mater. Sci.*, 2024, **237**, 112882, DOI: 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, *J. Phys. D: Appl. Phys.*, 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, DOI: 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, *J. Inorg. Organomet. Polym. Mater.*, 2022, **32**, 4216–4222, DOI: 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, *Comput. Theor. Chem.*, 2023, **1220**, 113990, DOI: 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, *J. Taiwan Inst. Chem. Eng.*, 2021, **125**, 15–22, DOI: 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, *Adv. Healthcare Mater.*, 2021, **10**, 2100775, DOI: 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 Mesoporous Mater.*, 2020, **294**, 109850, DOI: 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 Appl. Bio Mater.*, 2022, **5**, 5887–5900, DOI: 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 Appl. Mater. Interfaces*, 2024, **16**, 28245–28262, DOI: 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, *J. Mater. Sci. Technol.*, 2024, **170**, 87–94, DOI: 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, DOI: 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 non-adiabatic excited-state dynamics, *J. Mater. Chem. 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, *Adv. Funct. Mater.*, 2024, **34**, 2411077, DOI: 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, *J. Am. Chem. Soc.*, 2020, **142**, 16723–16731, DOI: 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, *Phys. Chem. Chem. Phys.*, 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, *J. Am. Chem. Soc.*, 2025, **147**, 3776–3785, DOI: 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, *J. Mater. Chem. 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, *Adv. Funct. Mater.*, 2024, **34**(43), 2309060, DOI: 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, *Chin. J. Struct. Chem.*, 2024, **43**, 100375, DOI: 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, *Nat. Commun.*, 2023, **14**, 3083, DOI: 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, *Angew. Chem.*, 2025, **137**, e202416240, DOI: 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, *J. Phys. Chem. Lett.*, 2024, **15**, 5467–5475, DOI: 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, *J. Mater. Chem. 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, *Nat. Rev. Methods Primers*, 2023, **3**(1), 42, DOI: 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 Appl. Mater. Interfaces*, 2025, **17**, 5038–5046, DOI: 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, *J. Phys. Chem. Lett.*, 2023, **14**, 7411–7420, DOI: 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, *J. Am. Chem. Soc.*, 2024, **146**, 20107–20115, DOI: 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, *J. Am. Chem. Soc.*, 2020, **142**, 12146–12156, DOI: 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, *Angew. Chem.*, 2025, **137**, e202414229, DOI: 10.1002/ange.202414229.

212 F. Duan, J. Sheng, S. Shi, 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, *J. Colloid Interface Sci.*, 2024, **675**, 620–629, DOI: 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, *J. Colloid Interface Sci.*, 2024, **653**, 1650–1661, DOI: 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, *J. Mater. Chem. 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 Catal.*, 2021, **11**, 13266–13279, DOI: 10.1021/acscatal.1c03441.

216 Y. Li, L. Yang, H. He, L. Sun, H. Wang, X. Fang, Y. Zhao, D. Zheng, Y. Qi, Z. Li and W. Deng, In situ photodeposition of platinum clusters on a covalent organic framework for photocatalytic hydrogen production, *Nat. Commun.*, 2022, **13**, 1355, DOI: 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 Appl. Polym. Mater.*, 2025, **7**, 1338–1346, DOI: 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, *Mater. Res. Bull.*, 2024, **173**, 112697, DOI: 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, *Angew. Chem.*, 2024, **136**, e202408802, DOI: 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, *Nat. Commun.*, 2025, **16**, 503, DOI: 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, *Angew. Chem., Int. Ed.*, 2025, e202421821, DOI: 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, *J. Am. Chem. Soc.*, 2024, **146**, 3396–3404, DOI: 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, *Chem. Eng. J.*, 2022, **430**, 132833, DOI: 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, *Appl. Catal., B*, 2025, **365**, 124933, DOI: 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, *Appl. Catal., B*, 2022, **301**, 120814, DOI: 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, *Angew. Chem., Int. Ed.*, 2024, **63**, e202409925, DOI: 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, *Appl. Catal., B*, 2025, **361**, 124583, DOI: 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, *Sep. Purif. Technol.*, 2025, **361**, 131461, DOI: 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, *J. Phys. Chem. C*, 2020, **124**, 9126–9133, DOI: 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, DOI: 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, *Surf. Interfaces*, 2021, **27**, 101587, DOI: 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, *J. Mol. Liq.*, 2022, **358**, 119191, DOI: 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, *Inorg. Chem. Commun.*, 2022, **146**, 110205, DOI: 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, *Nat. Commun.*, 2023, **14**, 2133, DOI: 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, *Mater. Today Commun.*, 2024, **38**, 108363, DOI: 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, *J. Colloid Interface Sci.*, 2024, **659**, 665–675, DOI: 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, *Nat. Commun.*, 2019, **10**, 3228, DOI: 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 Appl. Mater. Interfaces*, 2024, **16**, 30408–30420, DOI: 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 Mesoporous Mater.*, 2020, **300**, 110146, DOI: 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, *Coord. Chem. Rev.*, 2024, **521**, 216163, DOI: 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, *Chem. Phys. Impact*, 2024, **8**, 100510, DOI: 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, *Acc. Mater. Res.*, 2024, **5**(10), 1263–1278, DOI: 10.1021/accountsmr.4c00195.