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## Bromine sequestration by advanced functional porous materials

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The capture and storage of bromine have garnered significant attention in recent years due to its widespread industrial applications as well as its environmental impact as a pollutant. Advanced functional porous materials (AFPMs)—including metal–organic frameworks (MOFs), porous organic polymers (POPs), covalent organic frameworks (COFs), and porous organic cages (POCs)—have emerged as exceptional adsorbent materials in this field. Their high surface areas, tunable porosities, controllable structures, thermal/chemical stability, versatile molecular design, and capacity for functionalization (via pre- or post-synthetic modification) make them highly promising for bromine capture. This review highlights recent advancements in AFPMs for bromine capture from both gaseous and solution phases. We analyze key strategies to enhance bromine uptake, such as redox reactions, coordination interactions, bromination, functional group oxidation, heteroatom interactions, surface area/pore volume optimization, chemical functionalization, and post-synthetic modifications. Additionally, we discuss design strategies for developing next-generation AFPMs with superior bromine adsorption performance. As research progresses, we anticipate broader adoption of these materials in bromine capture applications.

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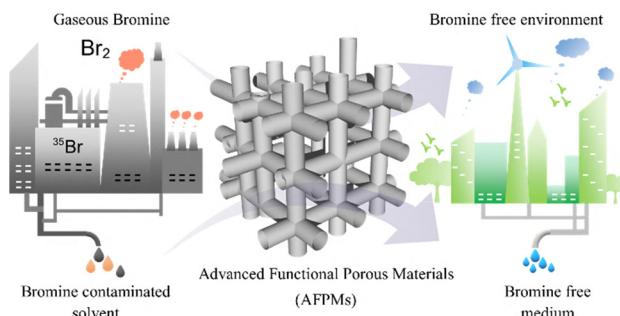
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pharmaceuticals, agriculture, water treatment, and energy storage systems such as zinc–bromine (Zn–Br) batteries.<sup>3–9</sup> However, bromine's extreme toxicity, corrosiveness, and volatility pose significant environmental and health risks. When released into the atmosphere, it contributes to ozone depletion<sup>10</sup> and respiratory hazards.<sup>11</sup> Inhalation of bromine vapor can cause severe respiratory damage, while ingestion may lead to neurological effects.<sup>11</sup> Additionally, industrial processes like coal combustion and waste incineration can emit toxic brominated compounds, including hydrogen bromide (HBr) and brominated dioxins.<sup>12</sup> Bromine emissions into the air or water pose significant risks to human health and ecosystems upon inhalation or ingestion.<sup>13</sup> Industrial activities—including chemical manufacturing, electronics production, and wastewater treatment—often release bromine-contaminated effluents, contributing to environmental pollution.<sup>14</sup> Elemental bromine and its secondary pollutants, such as brominated disinfection byproducts (DBPs), are known carcinogens and mutagens, exacerbating water contamination concerns.<sup>14–16</sup> According to the Hazardous Substance Fact Sheet, bromine gas exposure exceeding 3 ppm is considered to be dangerous to life.<sup>17,18</sup> The National Sanitation Foundation (NSF) further restricts total bromine/bromide levels in drinking water to 10 ppm due to its high toxicity.<sup>15</sup> Given these hazards, advanced bromine capture technologies—targeting both vapor and aqueous phases—are critical for mitigating environmental pollution, promoting sustainable industrial practices, and safeguarding public health. Consequently, the development of efficient bromine adsorbents has emerged as a key research focus in recent years.

There are a few traditional techniques for bromine capture that rely on chemical oxidation and subsequent recovery,<sup>19</sup> electrolysis of bromide-rich solutions to generate bromine at the anode,<sup>20</sup> precipitation as AgBr for gravimetric analysis,<sup>21</sup> etc. Among them, the most common industrial method involves oxidizing bromide (Br<sup>–</sup>) to bromine (Br<sub>2</sub>) using chlorine gas (Cl<sub>2</sub>), followed by air stripping to recover gaseous bromine.<sup>19</sup> Although the blowing-out process remains the dominant industrial method due to its efficiency, the precipitation and electrochemical methods are not economical for large-scale production. Therefore, the exploration and development of alternative techniques with high bromine adsorption performance have important academic value and application prospects. In this regard, among emerging approaches, adsorption-based sequestration has been proved to be more effective than conventional methods due to its simplicity, low maintenance cost, and avoidance of corrosive reagents. Considering this, recently, studies have been devoted to developing excellent adsorbents based on various advanced functional porous materials (AFPMs) for sequestration of bromine (Scheme 1).<sup>22–30</sup> Among them, metal–organic frameworks (MOFs),<sup>22–24</sup> porous organic polymers (POPs),<sup>25,26</sup> covalent organic frameworks (COFs)<sup>27–29</sup> and porous organic cages (POCs)<sup>30</sup> have been investigated for adsorption of bromine from the vapor phase, organic solvents and aqueous medium. These materials exhibit advantages such as high efficiency, selectivity, rapid kinetics, low energy consumption, and recyclability, making them promising candidates for sustainable bromine capture.



Scheme 1 Schematic representation of sequestration of bromine by advanced functional porous materials.

Among the aforementioned AFPMs, MOFs are solid crystalline porous materials constructed with inorganic building units (metal ions or clusters) and organic linkers connected by directional coordination bonds.<sup>31–34</sup> In contrast, POPs and COFs are amorphous and crystalline classes of advanced organic porous polymeric materials, respectively, comprising pure organic building blocks connected *via* strong covalent bonds.<sup>35–40</sup> However, POCs are a discrete class of advanced porous organic materials constructed with covalently linked small organic building units.<sup>41–44</sup> A key advantage of these AFPMs lies in their synthetic versatility—they can be engineered from diverse building blocks using various chemical approaches, allowing precise incorporation of tailored functional groups. Furthermore, they exhibit exceptional molecular design flexibility, high surface areas, tunable pore architectures, structural robustness, and opportunities for post-synthetic modification (PSM). These combined characteristics make AFPMs particularly attractive as high-performance platforms for bromine capture, offering unmatched advantages over conventional adsorbents. There are a few bromine adsorbents based on other materials that have been reported in the literature, such as vacancy-ordered perovskite<sup>45</sup> and resorcinol-formaldehyde resin nanoparticles.<sup>46</sup>

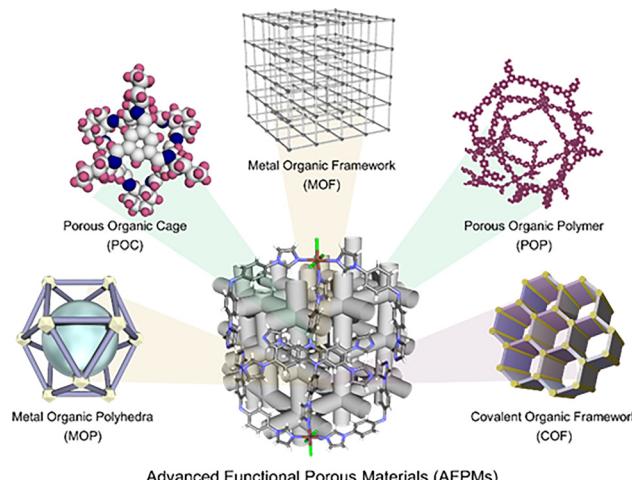
The application of advanced functional porous materials (AFPMs) for bromine adsorption has not been comprehensively reviewed before. This review highlights recent advances in bromine capture using various AFPMs as high-performance adsorbents. We provide a detailed summary of the progress in bromine adsorption using metal–organic frameworks (MOFs), porous organic polymers (POPs), covalent organic frameworks (COFs), and porous organic cages (POCs). Additionally, we discuss the principles of adsorbent design, the mechanisms of bromine–adsorbent interactions, and effective strategies to enhance capture capacity, selectivity, and recyclability. We also analyze the key challenges and issues hindering the practical application of AFPMs in bromine capture. Furthermore, we explore the potential utilization of bromine-loaded AFPMs in other critical research areas, such as catalysis, medicine, and energy-related applications. Ultimately, this review aims to guide researchers in designing and developing highly efficient porous adsorbents for the capture of environmentally and industrially important bromine related species.

## 2. Advanced functional porous materials (AFPMs) for bromine capture

Advanced functional porous materials (AFPMs) have recently garnered substantial global research interest due to their unique properties and precise molecular-level control. These materials exhibit high specific surface areas and tunable porosity, allowing for meticulous design and synthesis. Additionally, desired functional groups can be precisely incorporated into the structure of AFPMs *via* both pre and post synthetic modification methods. A key advantage is their stimuli-responsive behaviour, enabling reversible transitions between open and closed porous states under external stimuli. Unlike conventional porous solids, AFPMs benefit from diverse and straightforward synthetic strategies, functionalization and unique properties.<sup>47–49</sup> A key advantage of the synthetic strategies of AFPMs is the ability to precisely select functional moieties, enabling the design of task-specific AFPMs. By incorporating application-oriented functionalities into their framework backbone, these materials can be tailored to create interactive and functional porous scaffolds.

Generally, AFPMs are constructed *via* two primary approaches: (1) assembling organic–inorganic hybrid porous structures using functional organic linkers and inorganic metal nodes or (2) building purely organic porous materials through covalent and noncovalent interactions. Based on these methods, AFPMs can be broadly classified into two categories: inorganic–organic hybrid porous materials (*e.g.*, metal–organic frameworks (MOFs) or porous coordination polymers (PCPs), metal–organic gels (MOGs), and metal–organic polyhedra (MOP))<sup>50–52</sup> and pure organic porous materials (*e.g.*, porous organic polymers (POPs), covalent organic frameworks (COFs), supramolecular organic frameworks (SOFs), hydrogen-bonded organic frameworks (HOFs), and porous organic cages (POCs)).<sup>53–56</sup>

Among inorganic–organic hybrid AFPMs, metal–organic frameworks (MOFs) are crystalline coordination polymers featuring metal ions/clusters linked by organic ligands, creating architectures with well-defined voids.<sup>31–34</sup> Metal–organic gels (MOGs) form *via* similar coordination-driven self-assembly but develop into 3D gel networks, retaining MOF-like porosity within a flexible, gel-phase matrix.<sup>57,58</sup> Metal–organic polyhedra (MOP), a distinct subclass, are discrete polyhedral structures assembled from metal nodes and organic linkers, offering precise cavity control.<sup>59,60</sup> In contrast, purely organic AFPMs include porous organic polymers (POPs), which are three-dimensional amorphous networks synthesized through covalent polymerization of aromatic/conjugated monomers.<sup>37,61</sup> These extended networks of interconnected pores within their polymeric networks create a large surface area and diverse chemical functionalities. Unlike POPs, covalent organic frameworks (COFs) are another class of unique organic porous polymers, characterized by their crystalline structures that are designed and synthesized through the formation of robust, ordered networks, where the organic components are connected by strong covalent bonds, leading to a stable and porous framework.<sup>62,63</sup> Another class, porous organic cages (POCs),



**Scheme 2** Schematic illustration of various advanced functional porous materials (AFPMs), including a MOF, POP, COF, MOP and POC.

comprises discrete cage molecules composed of covalently connected organic building blocks with intrinsic cavities, combining tunable porosity with solution processability due to their molecular nature.<sup>41</sup> The most common AFPMs are schematically summarized in Scheme 2.

Due to their adaptable properties, AFPMs are widely employed across diverse fields, including chemistry, materials science, environmental science, and engineering. The versatility of AFPMs allows for applications in gas storage and separation, sensing, catalysis, environmental remediation, electrochemistry, and biomedicine.<sup>64–70</sup> Recently, they have also demonstrated exceptional potential for bromine capture, leveraging functionalized pores with bromine-affinity sites such as redox-active groups, electron/nitrogen-rich frameworks, and  $\pi$ -conjugated systems. These features enhance bromine adsorption capacity and selectivity, while their reversible capture–release properties facilitate bromine recovery and material regeneration. As a result, AFPMs offer sustainable solutions for bromine management in chemical processing, energy storage, and pollution control. The subsequent sections analyse the bromine adsorption performance of various AFPMs, including MOFs, POPs, COFs, and POCs (Table 1).

## 3. Methodologies for bromine adsorption in AFPMs

Bromine adsorption in advanced functional porous materials (AFPMs), such as MOFs, POPs, COFs, and POCs, is typically achieved through vapor-phase diffusion or solution-phase adsorption, both of which are widely used techniques. In vapor-phase diffusion, desolvated AFPMs and liquid bromine are placed in a sealed glass chamber at room temperature and ambient pressure. Bromine adsorption occurs over several hours to days, after which the bromine-loaded material is removed to measure uptake. The bromine adsorption capacity is calculated by comparing the weight difference before and after exposure



Table 1 Comparison table of bromine adsorption performance of various advanced functional porous materials

Materials/adsorbents	Type of material	Adsorption capacity (g g <sup>-1</sup> )	Medium of adsorption	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Ref.
Co <sub>2</sub> Cl <sub>2</sub> BTDD	MOF	0.25	Vapor	—	22
UiO-67	MOF	1.9	Cyclohexane	—	23
PCN-700	MOF	2.6	Cyclohexane	—	23
PCN-605-H	MOF	4.2	Cyclohexane	2434	23
PCN-606-OMe	MOF	3.7	Cyclohexane	1154	23
TCuCN	MOF	0.16	Vapor	—	24
Cd-MOF	MOF	0.37	Vapor	—	80
C4P-POP	POP	3.4	Cyclohexane	188 ± 20	25
C4P-POP	POP	3.6	Vapor	188 ± 20	25
POF-2	POP	2.86	Water	78.52	26
TAEDP-TA-OMe	COF	4.6	Vapor	498	27
TAP-TA-OMe	COF	3.4	Vapor	1015	27
COF-2H1	COF	3.79	Vapor	749	28
COF-2H1	COF	15.34	Cyclohexane	749	28
COF-2H1	COF	11.29	Water	749	28
COF-1	COF	4.7	Vapor	1160	29
COF-2	COF	5.1	Vapor	1331	29
COF-3	COF	4.1	Vapor	1017	29
COF-2	COF	3.92	Cyclohexane	1331	29
COF-2	COF	8.79	Water	1331	29
CC3-R	POC	0.758	Vapor	498	30
FT-RCC3	POC	0.776	Vapor	387	30

and normalizing it by the initial adsorbent mass.<sup>25–30</sup> This technique is also called the gravimetric method. Notably, gravimetric vapour phase bromine capture can be done in both static and dynamic modes. In particular, under dynamic conditions, bromine vapour is subjected to interact with the adsorbent with the help of a carrier gas such as nitrogen.<sup>29</sup> This methodology is frequently found to apply in the case of iodine adsorption by AFPMs.<sup>68,78,79</sup> Additionally, the Br<sub>2</sub> uptake capacity by AFPMs can also be measured using the iodometric titration method.<sup>30</sup> On the other hand, for solution-phase adsorption, bromine is dissolved in a nonpolar organic solvent (e.g., hexane or cyclohexane), and AFPMs are immersed to allow competitive adsorption between bromine and solvent molecules. The process is monitored using UV-vis spectroscopy to track bromine uptake.<sup>23–29</sup> Additionally, some POPs/COFs have demonstrated bromine adsorption from aqueous solutions, expanding their applicability in water treatment.<sup>25,26,28,29</sup> With these methodologies, the saturation capacity, selectivity, retention efficiency, recyclability, etc. of the bromine adsorbents (AFPMs) are determined.

#### 4. Bromine adsorption in metal–organic frameworks (MOFs)

With their unique properties such as a large surface area, chemical versatility, and ability to selectively adsorb specific molecules, MOFs have shown great promise for capturing bromine from various environments, including gaseous emissions and contaminated solutions. Several factors, such as the interaction with a metal center, the functional groups on the ligands, and the framework's porosity, make them a potential candidate for efficient and sustainable bromine removal and storage (Table 1). In this line, the first report on reversible

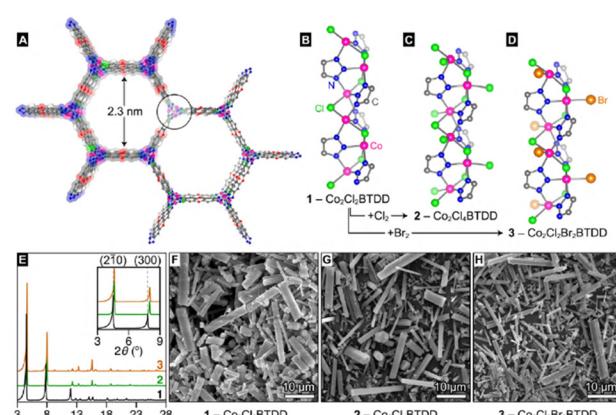


Fig. 1 (A) Schematic presentation of the structure of the Co(II) MOF Co<sub>2</sub>Cl<sub>2</sub>BTDD, (B)–(D) NPD structures of the SBU and local coordination environments of the Co metal centers Co<sub>2</sub>Cl<sub>2</sub>BTDD, Co<sub>2</sub>Cl<sub>4</sub>BTDD, and Co<sub>2</sub>Cl<sub>2</sub>Br<sub>2</sub>BTDD, respectively, and (E) PXRD data and (F)–(H) SEM images of Co(II) MOF before and after Br<sub>2</sub> and Cl<sub>2</sub> adsorption. Reproduced with permission from ref. 22. Copyright 2017, American Chemical Society.

storage of halogens such as Br<sub>2</sub> and Cl<sub>2</sub> with MOFs was demonstrated by the Dinca group.<sup>22</sup> In this study, a Co–metal based azolate MOF, namely Co<sub>2</sub>Cl<sub>2</sub>BTDD (1) (BTDD = bis(1H-1,2,3-triazolo[4,5-*b*],[4,5-*i*])dibenz[1,4]dioxin), was synthesized following a similar previously reported Mn-based analogue MOF (Mn<sub>2</sub>Cl<sub>2</sub>BTDD) protocol and used for capture and release of Br<sub>2</sub> and Cl<sub>2</sub>. The structural feature of the MOF exhibited a three-dimensional architecture with one-dimensional channels (2.3 nm pore aperture) arranged in a honeycomb fashion, where the secondary building units (SBUs) of the MOF configured with infinite -(Co–Cl)n– chains coiled into threefold spirals and interconnected by the bis(triazolate) ligands (Fig. 1a). When this MOF was treated with bromine gas



(and  $\text{Cl}_2$ ), it oxidized coordinatively unsaturated  $\text{Co}(\text{II})$  metal ions of the MOF to produce stable and safe-to handle  $\text{Co}(\text{III})$  materials featuring terminal  $\text{Co}(\text{III})\text{-Br/Cl}$  bonds (Fig. 1b-d). The successful conversion of  $\text{Co}_2\text{Cl}_2\text{BTDD}$  into  $\text{Co}_2\text{Cl}_2\text{Br}_2\text{BTDD}$  after  $\text{Br}_2$  and  $\text{Cl}_2$  sorption was quantified *via* microelemental analysis and ICP-MS analysis. Additionally, neutron powder diffraction (NPD), X-ray absorption spectroscopy (XAS), and magnetometry clearly validated the oxidation of  $\text{Co}(\text{II})$  into  $\text{Co}(\text{III})$  after  $\text{Br}_2$  and  $\text{Cl}_2$  adsorption. Also, the structural robustness of the MOF after the halogen adsorption test was monitored by performing PXRD, SEM and  $\text{N}_2$  gas sorption analysis (Fig. 1e-h). After the capture test, the release of  $\text{Br}_2$  and  $\text{Cl}_2$  from the adsorbed oxidized MOF was performed *via* thermal treatment. The thermogravimetric analysis (TGA) of the loaded MOFs indicated that sharp weight loss corresponds to the successful release of  $\text{Br}_2$  and  $\text{Cl}_2$ . The mechanistic insight into the release of  $\text{Br}_2$  and  $\text{Cl}_2$  revealed the homolytic cleavage of the  $\text{Co}(\text{III})\text{-halogen}$  bonds in the halogen loaded MOF *via* a radical mechanism, upon thermal treatment, and subsequent reduction of  $\text{Co}(\text{III})$  into  $\text{Co}(\text{II})$ . This intriguing work offers direction for investigating possible adsorbents that function through a redox mechanism, which may be useful in the storage and capture of various other harmful and corrosive gases.

Among various types, one of the important subclasses of MOFs is flexible MOFs (FMOFs) that exhibit structural adaptability in response to external stimuli, such as changes in temperature, pressure, or gas adsorption.<sup>71</sup> Unlike traditional rigid MOFs, flexible MOFs can undergo reversible changes in their structure, such as breathing or gating behaviours, which can enhance their performance in applications like gas storage, separation, and sensing. This flexibility allows for greater efficiency in capturing or releasing specific molecules, making flexible MOFs particularly valuable for dynamic environments where responsiveness is crucial.<sup>71</sup> In order to explore the advantage of the framework's flexibility towards tunable and enhanced adsorption of bromine, in a report, a series of flexible MOFs such as PCN-605, PCN-606 and PCN-700 have been utilized for reversible storage and release of bromine.<sup>23</sup> In this work, using the  $\text{Zr}_6$  oxocluster along with the aforementioned topology guided designed flexible MOFs, a rigid 12-connected MOF with similar porosity, named UiO-67, has also been synthesized, and its bromine adsorption properties were compared with those of the others. In the cyclohexane phase bromine adsorption study, all the four crystalline MOF samples were treated with 1 mol  $\text{L}^{-1}$  solution, and their corresponding UV-vis results were recorded. The UV-vis spectra indicated, for all MOFs, that the concentration of bromine in the cyclohexane solution decreased upon an increase in time. The capacity measurement analysis revealed total bromine uptake of 4.2, 3.7, 2.6 and 1.9 g  $\text{g}^{-1}$  for PCN-605-H, PCN-606-OMe, PCN-700, and UiO-67, respectively.

The values clearly indicated the relatively lower  $\text{Br}_2$  adsorption uptake by the rigid MOF (UiO-67) compared to the flexible MOFs, which was because of the larger pore configuration of the FMOFs when treated with  $\text{Br}_2$  cyclohexane solution. Additionally, the authors compare the  $\text{Br}_2$  adsorption capacity of

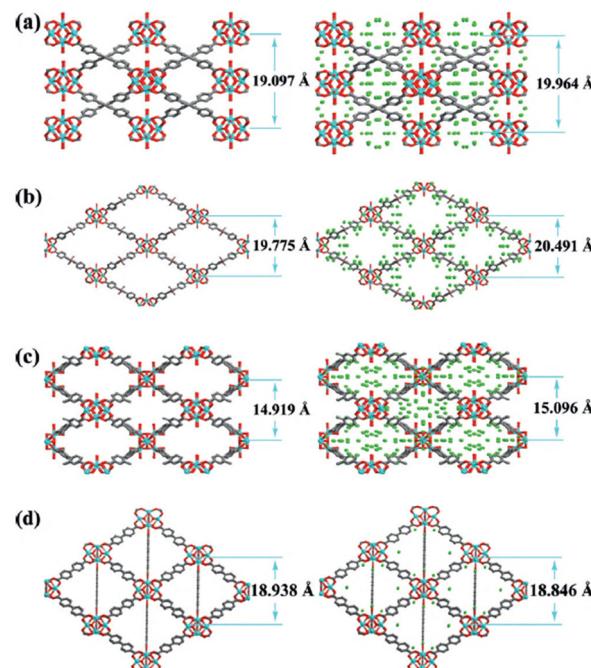


Fig. 2 The structures with their pore size of the MOFs: (a) PCN-605-H, (b) PCN-606-OMe, (c) PCN-700, and (d) UiO-67 before and after bromine adsorption. Reproduced with permission from ref. 23. Copyright 2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

activated carbon (14.1 g  $\text{g}^{-1}$ ), which is much higher than these MOFs. Most interestingly, the single crystal (SC) data of the post  $\text{Br}_2$  adsorption MOFs were recorded, which directly evidenced the encapsulation of bromine molecules into the pores of the MOFs (Fig. 2a-d). The SC data showed that all of the FMOFs' pores expanded during bromine adsorption, but the rigid framework UiO-67's unit cell characteristics stayed essentially the same (Fig. 2a-d). Thereafter, these  $\text{Br}_2$  adsorbed MOFs were used as bromine-nanocontainers for the bromination reaction under ambient conditions. To test this, the bromine adsorbed MOFs were treated as halogenation agents for binaphthol. Remarkably, the results demonstrate that the efficiency of binaphthol bromination using flexible MOFs that have been pre-absorbed with bromine is significantly higher than that of rigid MOFs and even higher than that of utilizing liquid bromine directly. Furthermore, it was found that the bromination reaction for PCN-606-OMe-Br and PCN-700-Br MOFs was repeatable in nature with excellent capture and release efficiency. It was discovered that these two MOFs worked well for brominating additional substrates, including anilines and biphenols, under ambient conditions. According to this study, these flexible MOFs have the potential to collect bromine and then be used for practical uses like the controlled release in a bromination reaction that is significant to industry.

In another report, adsorption of bromine vapor has been demonstrated by developing a series of four MOFs, named  $\text{TCuCN}$ ,  $\text{TCuCl}$ ,  $\text{TCuBr}$  and  $\text{TCuI}$ .<sup>24</sup> In this study, a new MOF,  $[\text{CuCN}(\text{TMBP})\text{-H}_2\text{O}]_n$  or  $(\text{TCuCN})$ , has been synthesized by reacting a functional bipyrazole organic ligand with  $\text{CuCN}$



metal salt. The developed MOF was characterized and found to be isostructural with previously reported MOFs such as  $\text{TCuCl}$ ,  $\text{TCuBr}$  and  $\text{TCuI}$ . All these MOFs demonstrated reversible adsorption of  $\text{Br}_2$  vapor, with  $\text{TCuI}$  showing the highest  $\text{Br}_2$  sorption capacity of 15.7 wt%. Interestingly, the MOFs exhibited retention of structural integrity even following the  $\text{Br}_2$  adsorption test. The reversible  $\text{Br}_2$  absorption of every MOF was confirmed through TGA, elemental analysis (EA), and PXRD analysis. Finally, the authors explained the reason for the varying uptake of  $\text{Br}_2$  by the four MOFs, primarily due to the distinct intermolecular interactions between the halogen in the MOFs and the  $\text{Br}_2$  molecule.

## 5. Bromine adsorption in porous organic polymers (POPs)

POPs are an excellent class of three-dimensional pure organic polymeric materials featuring unique characteristic features, including their large surface area, tunable functionality and robust chemical structure.<sup>37</sup> A large number of POPs have been synthesized using various organic chemical reactions and utilized for numerous potential applications.<sup>72</sup> Recently, POPs have been exclusively used for iodine capture from both the vapor and solution phases.<sup>73</sup> Among various classes of POPs, calixarene-based POPs have been explored as one of the potential candidates for adsorption, separation and identification of different chemicals.<sup>74–76</sup> Of them, out of their various promising applications, calix[4]pyrrole based POPs have been found to be efficient towards iodine capture from gaseous and solution media.<sup>77</sup> Inspired by the unique structural design of the strategic molecular configuration of these types of POPs, Chi, Sessler and co-workers postulated that resorcinol functionalized calix[4]pyrrole based POPs might work as an efficient adsorbent for bromine capture also.<sup>25</sup> In order to investigate this, an azo-bridged calix[4]pyrrole-based POP (C4P-POP) has been synthesized *via* a one-pot diazo-coupling reaction between resorcinol-functionalized calix[4]pyrrole (C4P) and biphenyldiamine monomers (Fig. 3a). Following successful structural and morphological characterization, the developed POP was employed for bromine capture. In this first study of POP-based bromine adsorption, C4P-POP was found to be an effective adsorbent in the vapor phase at room temperature under ambient pressure. The polymer exhibits a gravimetric saturation  $\text{Br}_2$  uptake capacity of  $3.6 \text{ g g}^{-1}$ , which was found to be significantly higher compared to MOF-based  $\text{Br}_2$  adsorbents. Moreover, apart from the high capture capacity, the retention efficiency or  $\text{Br}_2$  storage performance of C4P-POP was found to be good as  $\geq 97.5\%$  of the adsorbed  $\text{Br}_2$  was retained even after 96 h of exposure. After that, the potential of the POP for adsorbing  $\text{Br}_2$  from the solution phase was explored. As a result of the bromine capture test in cyclohexane, C4P-POP demonstrates fast adsorption kinetics as almost 95% removal efficiency was observed within 7 h of contact time (Fig. 4b).

Inspired by such rapid  $\text{Br}_2$  sorption kinetics, the authors further performed bromine capture from cyclohexane under

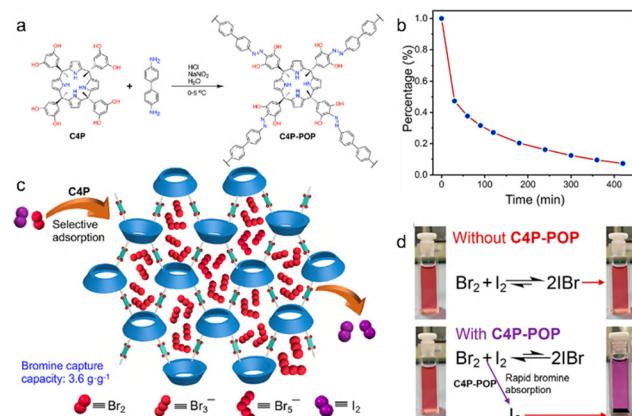


Fig. 3 (a) Schematic representation of the synthesis of C4P-POP. (b) Percentage of bromine remaining in the cyclohexane solution after capture with respect to time. (c) Schematic illustration of selective bromine uptake by C4P-POP. (d) Digital images and a scheme showing the separation of bromine and hence scrubbing of  $\text{IBr}$  from a mixture of  $\text{Br}_2$  and  $\text{I}_2$  cyclohexane solution. Reproduced with permission from ref. 25. Copyright 2022, American Chemical Society.

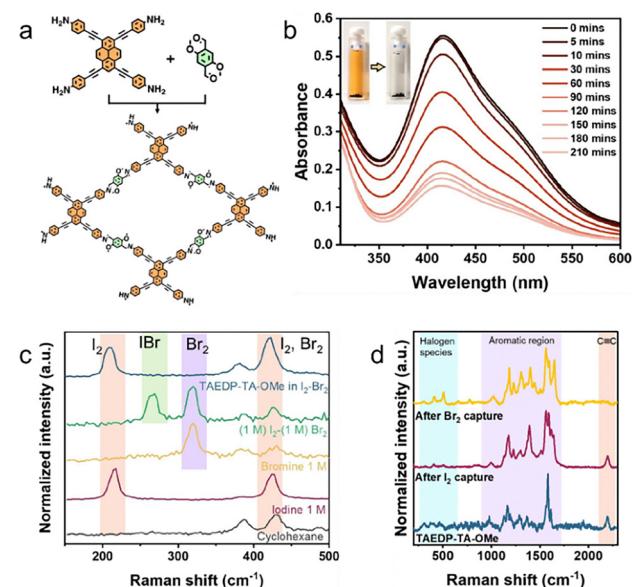


Fig. 4 (a) The chemical structure of the TAEDP-TA-OMe COF. (b) Time-dependent UV-vis spectra of bromine capture in the cyclohexane solution. (c) Raman spectra of bromine, iodine and a mixture of  $\text{Br}_2$  and  $\text{I}_2$  in cyclohexane before and after COF treatment. (d) Solid state Raman spectra of TAEDP-TA-OMe before and after the  $\text{Br}_2$  and  $\text{I}_2$  capture test. Reproduced with permission from ref. 27. Copyright 2024, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

dynamic conditions. As a result of this test, the UV-vis spectroscopy data indicated that C4P-POP was able to eliminate almost 80% of bromine from the cyclohexane solution under flow-through conditions. Recyclability is an important parameter for an effective adsorbent. Therefore, in order to test the reusability of C4P-POP towards multiple cycles of bromine capture, the  $\text{Br}_2$  adsorb polymer was desorbed upon treatment with a polar solvent (DMF) and further used for four consecutive cycles.



As mentioned above, apart from storage, separation of bromine from other halogens like iodine is highly important from an industrial point of view. Keeping this in mind, and motivated by the faster  $\text{Br}_2$  adsorption kinetics compared to that of iodine in cyclohexane, in this study, C4P-POP was applied for capture of  $\text{Br}_2$  (and IBr) from a mixture of  $\text{Br}_2$  and  $\text{I}_2$  (Fig. 3c). The UV-vis spectroscopic result indicated that the absorption maximum associated with the mixture of  $\text{Br}_2$ ,  $\text{I}_2$  and IBr in cyclohexane was found to shift towards a higher wavelength with increasing time. After final treatment, the observed spectra were found to be similar to those of  $\text{I}_2$  in cyclohexane. These changes were also observed by the naked eye as the colour of the mixture (orange) was found to change to purple (the colour of iodine in cyclohexane) (Fig. 3d). In light of these findings, the authors hypothesized that their polymer would be useful for isolating  $\text{Br}_2$  from possible contaminants like  $\text{I}_2$  and IBr. Finally, the mechanism of bromine capture by C4P-POP was investigated. Both the FT-IR and XPS analyses of  $\text{Br}_2$  loaded POP ( $\text{Br}_2@$ C4P-POP) indicated that the oxidation of phenolic hydroxyl units into the  $\text{C}=\text{O}$  group upon bromine adsorption was responsible for effective interaction with bromine. Additionally, the electron rich macrocycle moiety helps enhance  $\text{Br}_2$  sorption. This study explores the potential of POP-based materials for addressing the challenge of capture, storage and purification of bromine.

As an electrophilic species, bromine readily interacts with electron-rich adsorbents. Leveraging this property, a recent study reported the development of an electron-rich, thiophene-group-containing, imine-functionalized porous organic polymer (POF-2) for bromine capture from aqueous solutions.<sup>26</sup> Due to its multiple interactive sites—including electron-rich benzene rings, heteroatoms (S, N), and imine groups—POF-2 exhibits a high  $\text{Br}_2$  adsorption capacity ( $2.86 \text{ g g}^{-1}$ ) with rapid uptake kinetics in water, driven by noncovalent charge-transfer interactions. Furthermore, in cyclohexane, POF-2 demonstrates preferential bromine separation from  $\text{Br}_2/\text{I}_2$  mixtures.

## 6. Bromine adsorption in covalent organic frameworks (COFs)

In addition to MOFs and POPs, bromine capture by covalent organic frameworks (COFs) has emerged as a promising approach for environmental remediation and resource recovery.<sup>27–29</sup> COFs, characterized by their high surface area, tunable pore sizes, and robust chemical stability, offer an ideal platform for selectively trapping bromine and its related species from various media. In order to investigate the role of functional COFs towards bromine capture, in a recent study, De *et al.* reported the synthesis of an alkyne group functionalized 2D imine COF, named TAEDP-TA-OMe.<sup>27</sup> The developed COF featured multiple electron rich sites, including a  $\pi$ -conjugated structure, heteroatom N-based imine linkages and C–C triple bonds, all of which are favourable for efficient capture of bromine (Fig. 4a). Initially, the crystalline, stable mesoporous structure of the COF was established by PXRD, FT-IR, HRTEM and low temperature (77 K) nitrogen gas sorption analysis. The structural

characteristics of the COF mentioned earlier led the authors to conduct  $\text{Br}_2$  adsorption tests in both the vapor and solution phases. Under static conditions, the COF was observed to adsorb  $4.6 \text{ g g}^{-1}$  of gaseous bromine from the vapor phase, which is nearly 1.5 times greater than the theoretical capacity due to the COF's porosity, as well as higher than the iodine adsorption capacity ( $2.7 \text{ g g}^{-1}$ ). The vapor phase bromine adsorption of TAEDP-TA-OMe was recyclable in nature. Next, to test the solution phase  $\text{Br}_2$  adsorption ability of the COF, it was treated with bromine in a cyclohexane solution. The UV-vis results indicated that almost 60% bromine was captured from the 2 mM stock within 90 minutes of capture time (Fig. 4b). On the other side, the COF was found to capture significantly lower amounts of iodine from the cyclohexane solution under similar capture conditions. The comparison data indicated almost 75% bromine and only 15% iodine capture efficiency in cyclohexane by TAEDP-TA-OMe. This difference in the removal percentage between  $\text{Br}_2$  and  $\text{I}_2$  inspired the authors further to perform the selectivity test of the COF. The selectivity test resulted in preferential capture of bromine over iodine, which has been experimentally characterized by solution phase Raman spectroscopy analysis (Fig. 4c). Furthermore, the role of different functionalities of the COF toward the selective bromine capture mechanism was investigated. The Raman spectra of the COF sample treated with  $\text{Br}_2$  and  $\text{I}_2$  showed that the vibration of the C–C triple bond at  $2191 \text{ cm}^{-1}$  vanished only after bromine was captured, indicating a significant role of the alkyne bridge in the bromine capture process. Interestingly, the signal for iodine remained unaffected (Fig. 4d). This observation was further confirmed by conducting FT-IR, XPS, and density functional theory studies. This collectively demonstrated the participation of various functionalities (including electron-rich alkyne, imine, and phenyl groups) alongside the COF's porosity for selective binding interactions with bromine through both chemisorption and physisorption mechanisms. This research offers a framework for the strategic design of adsorbents aimed at capturing environmentally detrimental halogens like bromine in this context.

In another research, Das *et al.* reported efficient removal of bromine from gaseous and solution media using an imine and hydrazone-dual linkage covalent organic framework (COF-2H1).<sup>28</sup> In this study, a COF with multiple functionalities, including heteroatomic hydrazone, imine, ether and triazine groups, was developed *via* a facile and scalable synthesis procedure (Fig. 5a). After successful characterization, COF-2H1 was applied for the removal of bromine from water. The UV-vis data revealed a rapid decrease in the concentration of  $\text{Br}_2$  with an increase in time upon treatment with the COF. Notably, such elimination of trace  $\text{Br}_2$  from water was noticed by the naked eye using the KI starch paper test (Fig. 5b). Moreover, COF-2H1 was found to remove bromine from contaminated water from different sources. After that, COF-2H1 was used for bromine capture from the cyclohexane solution, which revealed fast sorption kinetics with high adsorption capacity. The  $\text{Br}_2$  uptake capacities of  $11.29$  and  $15.34 \text{ g g}^{-1}$  were recorded for COF-2H1 in water and cyclohexane,



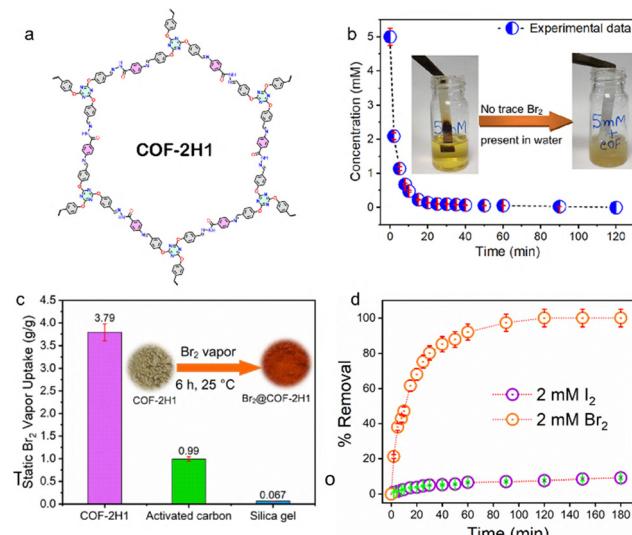


Fig. 5 (a) Chemical structure of COF-2H1, (b) decreases in the concentration of bromine in water with time (inset: the KI starch paper test before and after bromine capture), (c) result of vapor phase static  $\text{Br}_2$  uptake capacities, and (d)  $\text{Br}_2$  and  $\text{I}_2$  removal kinetics of COF-2H1 in cyclohexane. Reproduced with permission from ref. 28. Copyright 2024, American Chemical Society.

respectively. Apart from the solution phase, the adsorbent was also found to sequester gaseous bromine from the vapor phase. The result of the static  $\text{Br}_2$  vapor capture test exhibited  $3.79 \text{ g g}^{-1}$  capacity, which was found to be higher than those of commercial activated carbon ( $0.99 \text{ g g}^{-1}$ ) and silica gel ( $0.067 \text{ g g}^{-1}$ ) adsorbents (Fig. 5c). Furthermore, the separation of molecular bromine from a mixture of 1:1 molar ratio of  $\text{Br}_2$  and  $\text{I}_2$  in the cyclohexane solution was performed. The individual kinetic sorption test exhibited rapid removal efficiency of bromine over iodine in cyclohexane (Fig. 5d). Finally, the  $\text{Br}_2$  adsorption mechanism of COF-2H1 was investigated by FT-IR, Raman and XPS analyses.

The above studies explored the potential role of COFs as effective adsorbents for bromine capture from both the vapor and solution phases. However, studies that show the fundamental understanding of framework integrated functionalities along with their textural properties upon the bromine adsorption process are scarce in the literature. In this direction, in order to investigate the structure–property correlation of the adsorbents (COFs) with insightful mechanism toward bromine adsorption, in a recent study, our group demonstrated a strategy-driven systematic study aimed at significantly enhancing multiple host–guest interactions to obtain a series of framework-engineered COFs for the efficient sequestration of bromine.<sup>29</sup> In this study, three  $\beta$ -ketoenamine COFs (COF-1, COF-2 and COF-3) with different numbers of phenolic hydroxyl (-OH) groups were synthesized (Fig. 6a–c). The three COFs exhibited alteration of intramolecular interactions along with conjugation, aromaticity, hydrogen bonding, and steric effect, which altogether were found to affect the total bromine adsorption capacity. These chemically stable, electronically abundant, heteroatom (triazine, imine groups) functionalized porous

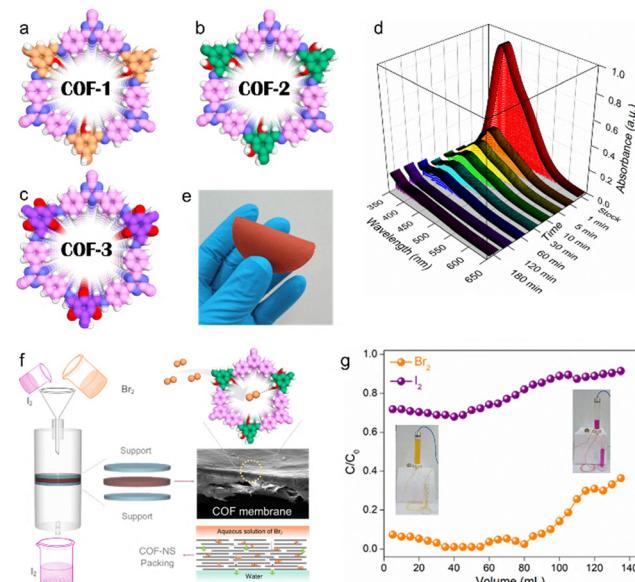


Fig. 6 (a)–(c) Schematic illustration of structures of COF-1, 2 and 3. (d) UV-vis result of  $\text{Br}_2$  capture in the cyclohexane solution. (e) Digital image of a self-standing membrane of COF-2. (f) Schematic representation of COF-2 membrane based flow-through capture of  $\text{Br}_2$  and  $\text{I}_2$ . (g) Result of flow-through  $\text{Br}_2$  and  $\text{I}_2$  capture in cyclohexane under dynamic conditions. Reproduced with permission from ref. 29. Copyright 2025, the Royal Society of Chemistry.

COFs with adjustable electron-accepting carbonyl functionalities have been shown to demonstrate variable gaseous  $\text{Br}_2$  adsorption capacities in the vapor phase. Among all, COF-2 functionalized with two -OH groups was found to exhibit the highest  $\text{Br}_2$  sorption capacity of  $5.16 \text{ g g}^{-1}$  with high retention efficiency and recyclability. In addition to dry conditions, the static adsorption capacity under the humid condition was found to be the highest for COF-2. COF-2 exhibited  $2.79 \text{ g g}^{-1}$   $\text{Br}_2$  capture capacity under the vapor phase dynamic condition. Apart from the gaseous phase, COF-2 was found to separate bromine from both organic (cyclohexane) and aqueous solutions. The UV-vis result of bromine capture in the cyclohexane medium indicated rapid elimination with high adsorption capacity (Fig. 6d). On the flip side, the iodine adsorption efficiency in cyclohexane by COF-2 was found to be significantly less than that of bromine, which motivated us to further perform the preferential removal of bromine over iodine. The result of this test showed adsorption of  $\text{Br}_2$  (and  $2\text{IBr}$ ) from an equal concentration mixture of  $\text{Br}_2$  and  $\text{I}_2$  in cyclohexane. Moreover, COF-2 exhibited selective and fast adsorption kinetics with high capacity toward bromine in a water medium. Additionally, COF-2 was found to remove trace bromine in aqueous medium. Inspired by these results, we further demonstrated the continuous flow through based capture of bromine from both cyclohexane and aqueous medium under dynamic conditions by developing the self-standing membrane of COF-2 (Fig. 6e and f). The COF-2 membrane was found to extract molecular bromine from water with high removal efficiency and good permeability even after passing 250 mL of  $\text{Br}_2$

contaminated aqueous solution. Interestingly, the membrane showed significantly higher removal efficiency towards bromine over iodine up to a large amount of cyclohexane solution under the dynamic conditions (Fig. 6g). Finally, the mechanistic understanding revealed that upon interaction with bromine, the oxidation of the phenolic hydroxyl group into carbonyl promotes adsorption within the heteroatom functionalized large porous structures of the COFs. This study emphasizes how important it is to balance robust host–guest interactions with textural properties when developing adsorbents such as COFs that are rationally engineered to efficiently sequester halogens like bromine.

## 7. Bromine adsorption in porous organic cages (POCs)

Owing to their unique characteristic properties such as good processability and synthetic scalability, discrete ultra/micro-porous organic cages (POCs) were found to apply in various applications, including gas storage and separation, catalysis, toxic gases and pollutant sequestration, sensing, *etc.* Among various POCs, heteroatomic functionalized (N-containing) organic cages are promising towards host–guest interaction mediated sequestration or separation applications.<sup>41</sup> Heteroatomic functionalized POCs have also been used as potential adsorbents for highly efficient capture and storage of gaseous bromine (Table 1).<sup>30</sup> In their study, Koh and Chung *et al.* synthesized for the first time an N-containing imine functionalized organic cage (CC3-R) *via* a [4+6] cyclo-condensation reaction of 1,3,5-triformylbenzene (TFB) and (1R,2R)-cyclohexane-1,2-diamine (CHDA). Furthermore, another POC (FT-RCC3) has been synthesized utilizing post-synthetic modification of CC3-R *via* reducing the imine group of CC3-R, followed by the “tying” method with formaldehyde, as schematically represented in Fig. 7a. Both these isostructural cages were isolated as pure crystalline forms with sharp octahedral morphologies. The crystal structure information indicated tetrahedral space groups of the cages with three-dimensional packing, resulting in a diamondoid pore network. Moreover, the structural configuration and the successful post-synthetic modification of the cages were carried out using various characterization studies. The low temperature nitrogen gas sorption data indicated ultra-microporous structures of the cages. Thereafter, these developed POCs were applied for bromine vapor adsorption under static conditions. The gravimetric measurements revealed total Br<sub>2</sub> adsorption capacities of 11.02 and 11.64 mmol g<sup>-1</sup> for CC3-R and FT-RCC3, respectively, within 48 hours of adsorption time (Fig. 7b). Interestingly, these Br<sub>2</sub> adsorption capacity values were found to be higher compared to the values determined through GCMC simulation studies. The authors stated that two main mechanisms, including the development of polybromide species and the increase in cage-to-cage channel distance, control the difference in these capacities and may be responsible for the increased adsorption of Br<sub>2</sub> molecules. More importantly, the adsorption data indicated faster kinetics for FT-RCC3 (the cage with a tertiary amine group) than the CC3-R

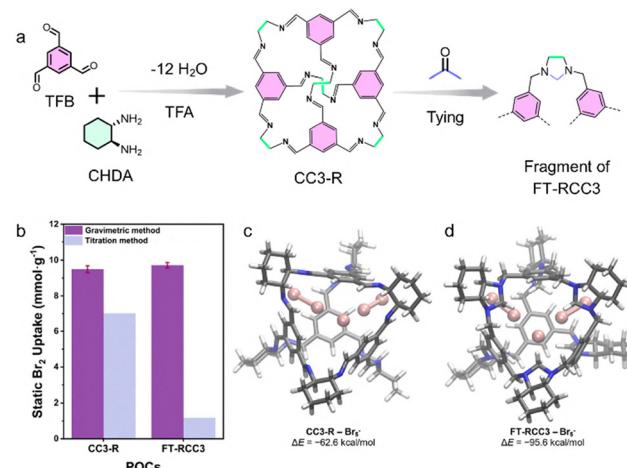


Fig. 7 (a) Schematic representation of the synthesis of CC3-R and FT-RCC3 porous organic cages. (b) Result of static Br<sub>2</sub> capture capacities of both the POCs determined through the gravimetric and titration methods. (c) and (d) DFT optimized structures and their corresponding binding energies of CC3-R and FT-RCC3, respectively with adsorbed polybromide Br<sub>5</sub><sup>-</sup>. Reproduced with permission from ref. 30. Copyright 2022, the Royal Society of Chemistry.

cage with an imine group. The Br<sub>2</sub> adsorption kinetics of both the POCs were found to follow the pseudo-second-order model with high correlation coefficient values, indicating chemisorption of bromine molecules. Furthermore, in addition to the gravimetric method, the adsorption capacities of the POCs were calculated using the titration method (Fig. 7b).

Notably, the difference between the uptake capacities obtained through these two methods was higher in the case of FT-RCC3 than CC3-R, which is owing to the stronger irreversible chemisorption for FT-RCC3. Finally, the Br<sub>2</sub> adsorption mechanism of both the cages was investigated by performing various experimental (such as FT-IR, XPS and Raman analyses) and theoretical studies. The time-resolved FT-IR spectra indicated a strong interaction between different functional groups (such as imine, cyclohexane, and phenyl ring) of both the host POCs with guest bromine molecules, which further resulted in the formation of charge-transfer complexes.

Such host–guest interaction driven charge-transfer complex formation between POCs and Br<sub>2</sub> molecules was also verified by XPS analysis. The XPS result exhibited involvement of different functional sites, especially N-sites of the POCs, towards interaction with Br<sub>2</sub> as well as the generation of polybromide species, including Br<sup>-</sup> and Br<sub>3</sub><sup>-</sup>. The presence of these polybromide species within the structure of the POCs upon interaction with bromine molecules was further thoroughly investigated by Raman analysis. Moreover, DFT calculations were carried out to compute the binding and formation energies of the developed complexes. The detailed analysis of the calculation showed different favourable binding energies between the two cages (CC3-R and FT-RCC3) and polybromide species (Br<sub>3</sub><sup>-</sup> and Br<sub>5</sub><sup>-</sup>), as well as HBr, are the most energetically stable species compared with other bromine species within the POCs after bromine capture (Fig. 7c and d). This study



investigated the possible application of N-heteroatomic functionalized POCs as potential adsorbents for the capture and storage of volatile and hazardous halogen gases through appropriate host–guest interaction. Finally, all the reported studies (to date) of bromine capture by various advanced functional porous materials have been summarized in Table 1.

## 8. Summary and future outlooks

The capture and storage of bromine are essential because of its extensive industrial uses and environmental effects. Bromine finds application in flame retardants, pharmaceuticals, and agriculture, so its effective recovery is crucial for sustainable manufacturing. Furthermore, uncontrolled bromine releases can lead to air contamination. Effective capture and storage mitigate these environmental hazards while securing a consistent supply for essential industries. In this context, advanced porous materials like MOFs, COFs, POPs, and POCs exhibit remarkable potential for applications in the adsorption of bromine. In comparison with conventional porous materials, advanced functional porous materials possess several clear benefits. The reticular chemistry driven varying building blocks allow the creation of different numerous tailored structures. Their surface areas, pore sizes, and pore volumes can be altered, making it simple to adjust their internal pores and surfaces.<sup>81</sup> In the past few years, numerous advanced functional porous materials have been reported, showcasing their potential for capturing and storing bromine from both vapor and solution phases. In this review article, we focused on the applicability of these functional porous materials (MOFs, COFs, POPs, and POCs) for bromine capture with various robust mechanisms such as redox reactions, coordination interactions, bromination reaction, oxidation of functional groups, interaction with heteroatoms, *etc.* We also illustrate effective methods for improving the capture of bromine from both gas and liquid phases. Although these adsorbents are highly praised for their excellent bromine capture performance, their industrial-scale application for bromine trapping and treatment remains challenging. This is particularly true due to bromine's reactive properties, as well as the need for stability and challenges in characterizing the AFPM-based host–guest systems. To date, most of these materials have only been developed at the laboratory scale and are produced in limited quantities at high costs. Despite significant advancements, further research is needed to improve key aspects such as efficiency, adsorption capacity, selectivity, high-temperature and humidity stability, performance in the presence of interfering molecules, reusability, and cost-effectiveness. In the following section, we outline a few potential strategies to consider when designing an effective bromine adsorbent.

(1) Emerging design strategies are aimed to tailor advanced porous materials at the molecular level to optimize the interactions with bromine. This is one of the most effective consideration for the development of superior adsorbents.<sup>29</sup> The introduction of halogenophilic sites such as nitrogen-containing heterocycles,<sup>30</sup> sulfur containing sites, interactive

metal clusters and polarizable electron-rich aromatic rings is expected to increase bromine uptake capacity and selectivity. Future materials may incorporate dynamic binding sites or stimuli-responsive elements that enhance performance under varying operational conditions.

(2) Development of hybrid composite porous materials could be an effective strategy for highly efficient halogen-bromine capture. Combining MOFs, COFs, or POPs with other functional materials such as cages, ionic liquids, metal nanoparticles, or carbon-based materials could lead to hybrid systems with synergistic properties.<sup>82,83</sup> These hybrid composite materials may offer improved structural stability, higher sorption kinetics, selectivity and potential for bromine capture with a high enrichment index.

(3) Dynamic capture measurements are recommended for evaluating adsorbents, as they enable precise control of concentration and temperature while incorporating multiple components to simulate real-world conditions.<sup>84</sup> This approach allows for the study of competitive adsorption between bromine and other halogens or coexisting species. However, systematic research on such competitive adsorption remains limited. Additionally, further studies should assess bromine capture adsorbents under conditions that closely mimic real applications.

(4) Given the environmental impact of aqueous bromine, its capture from water sources presents significant potential.<sup>85</sup> While a few studies have explored bromine removal from water, more in-depth investigations are needed to understand the sequestration of molecular bromine from contaminated aqueous systems. Additionally, when conducting bromine capture tests in organic solvents such as hexane or cyclohexane (*e.g.*, *via* UV-vis measurements), precautions must be taken to prevent photodegradation. These experiments should be performed under dark conditions to avoid light-induced decomposition of molecular bromine in these solutions.

(5) Since bromine is reactive and corrosive, considering the practical utility of the developed materials for real-world bromine capture, researchers should pay more attention to the creation of highly stable adsorbents. The physicochemical durability of various advanced functional porous materials (*i.e.*, MOFs)<sup>94–98</sup> for the sequestration of bromine from complex systems such as industrial effluents or strong chemical media should be investigated thoroughly.

(6) Another important aspect is the long-term feasibility of the adsorbents, which depends on the ability to regenerate and reuse with minimal loss in performance. Advances in mild regeneration techniques, such as vacuum cycling or low-temperature desorption, are necessary to ensure cost-effectiveness.

(7) A major challenge for practical deployment of adsorbents for bromine capture is the development of scalable, cost-effective, and environmentally benign synthesis routes. Future research should likely focus on green chemistry approaches, such as solvent-free synthesis, bio-derived linkers, and low-energy processing. These developments will be crucial for translating laboratory-scale materials to industrial applications.<sup>86,87</sup>

(8) Greater integration of computational chemistry, including machine learning and molecular dynamics simulations, is



expected to accelerate the discovery of new advanced porous materials as more effective adsorbents for bromine capture. By providing detailed mechanistic insights into bromine–host interactions, these tools can guide the rational design of frameworks with enhanced capture performance.

(9) The performance needs for halogen–bromine capture differ between applications, ranging from industrial leak prevention to environmental clean-up. Consequently, future materials need to be tailored for particular operational situations, such as high humidity conditions, elevated temperatures, and the existence of co-contaminants. Creating adsorbents specifically designed for various capture scenarios will be a significant focus for applied research.

Looking towards the future, the newly developed characteristics of bromine-infused advanced porous materials also signify significant potential for further practical industrial applications, such as bromination reactions.<sup>23</sup> Conversely, regarding the medical and microbial use of bromine, Br<sub>2</sub> adsorbed porous materials may act as a promising platform for such applications as well. Moreover, bromine-loaded porous sorbents can serve as a potential material for bromine–sulphur-based battery development/application.<sup>88–93</sup> Ultimately, we intend for this review to provide useful insights for researchers and to broaden the research field related to the development of various advanced functional porous material (AFPM)-based adsorbents for trapping different toxic species.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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