Eng. Sci., 2025, **35**, 1525

Engineered Science
DOI: https://dx.doi.org/10.30919/es1525

Rational Design of Porous Organic Polymers for Cycloaddition between Carbon Dioxide and Epoxides

Lingling Wang,[1,#] Yang Liu,[1,#] Zhangting Dang,[1] Qingqing Hou,[1] Zhengjiao Zhang,[1] Zhihua Feng,[1] Yue Yu,[1] Xiufu Hua[1, 2, 3,*] and Renbo Wei[1,*]

Abstract

The catalytic cycloaddition between carbon dioxide (CO_2) and epoxides represents one of the most efficient and eco-friendly strategies to advance carbon neutrality in the industrial sector. Recently, porous organic polymers (POPs) have gained prominence as pivotal porous materials extensively utilized for efficient capture and conversion of CO_2. To address the multifaceted requirements of CO_2 capture, activation, and immobilization, the design of functionally stable and structurally ordered POPs presents a viable and promising substitute to metal-organic frameworks (MOFs). This review delivers a thorough and in-depth examination of the latest advancements in designing and synthesizing POPs catalysts tailored for converting CO_2 into cyclic carbonate. Recent developments in POPs can be categorized into two primary groups according to the catalytic mechanisms: single activation mechanism POPs and multi-activation mechanism POPs. These groups highlight four key types of catalysts: triazine ring-structured catalysts, hydrogen bond donor (HBD)-based catalysts, ionic liquid-modified catalysts, and metal-complex catalysts. Considerable attention has been dedicated to the rational design, pre-synthetic methodologies, and post-synthetic modification strategies of organic polymer monomers. This review seeks to offer an exhaustive perspective that informs the cycloaddition-based conversion for CO_2 into cyclic carbonates, driving the innovation and development of diverse POPs with expansive industrial potential.

Keywords: Cesium tungsten bronze; Silver nanowires; Near infrared blocking; Energy saving.
Received: 05 April 2025; Revised: 04 May 2025; Accepted: 15 May 2025.
Article type: Review article.

1. Introduction

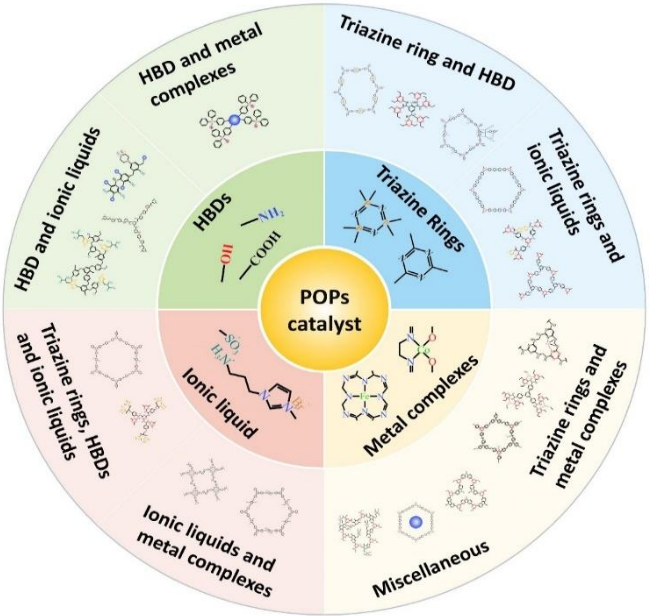
The increase in global carbon dioxide (CO_2) emissions is an unavoidable consequence of both industrialization and urbanization. Based on the International Energy Agency (IEA) report, fossil fuel combustion constitutes the primary source of CO_2 emissions, accounting for approximately 70% of global emissions.[1] Moreover, industrial production, transportation, and agricultural activities considerably contribute to the overall CO_2 emissions.[2] These activities not only severely pollute the environment but also intensify global climate change. To address this pressing global environmental challenge, scientists and policymakers have proposed a range of solutions. First and foremost, the reduction of fossil fuel consumption is essential for mitigating CO_2 emissions. This objective can be accomplished by improving energy efficiency and advancing clean energy sources, including solar, wind, and biomass.[3-6] In addition to reducing CO_2 emissions, technologies for CO_2 capture and storage (CCS) perform a vital part in mitigating climatic variation.[7-9] CCS technology effectively reduces atmospheric CO_2 concentrations by capturing CO_2 emissions from industrial sources and subsequently storing it underground. Moreover, converting CO_2 into high-value organic compounds represents another highly effective strategy for mitigating CO_2 levels, with catalytic cycloaddition reactions serving as a pivotal mechanism. These reactions enable the transformation of CO_2 into organic products like cyclic carbonates, which hold

---

[1] *School of Chemical Engineering, Northwest University, Xi'an 710069, China*
[2] *Shaanxi Hydrogen Energy Industry Development Co, Ltd, Shaanxi, Yulin, 719054, China*
[3] *Yangtze Delta Region Institute of Tsinghua University, Jiaxing, 314006, China*
[#] *These authors contribute equally to this work.*
* *E-mail:* huaxf@nwu.edu.cn (X. Hua); weirb10@nwu.edu.cn (R. Wei)

substantial economic and industrial value.[10,11] In the domain of CO_2 conversion technology, POPs have garnered considerable attention owing to their distinct structures and remarkable properties. POPs, as functional porous materials linked by covalent bonds, offer advantages including porous structural stability, high specific surface area, and ease of active site modification.[12-17] Based on their structural attributes, POPs are categorized into crystalline covalent organic frameworks (COFs),[18,19] and amorphous POPs.[20,21] Amorphous POPs present distinct advantages, including enhanced dispersibility and chemical stability, which support the development of catalysts with superior performance. By contrast, tailored COFs exhibit a well-defined architecture characterized by regularly arranged nanopores and accessible open channels, providing a homogeneous surface environment and a pronounced spatial confinement effect.[22] Substantial advancements have been made in designing and synthesizing POPs catalysts. Researchers have attained various porosities and chemical compositions by optimizing organic monomer types and employing diverse crosslinking strategies.[23-27] Moreover, the enhancement of catalytic activity and selectivity has been realized through the incorporation of active sites.[28-32] However, challenges continue to exist regarding the stability and recyclability of these catalysts. To address these challenges, researchers are investigating innovative preparation methods and modification strategies designed to enhance catalyst stability and recyclability.[33-36] With regard to applications in CO_2 conversion technology, catalytic ring addition reactions have been successfully industrialized. Nonetheless, technological innovation remains essential owing to stringent production conditions and intrinsic limitations of the catalysts.[37] In conclusion, CO_2 capture and conversion technologies constitute a vital strategy for combating global climate change. POPs catalysts, characterized by their unique structures and performance attributes, exhibit considerable potential in CO_2 conversion applications. Continued research and technological innovation are anticipated to yield more efficient, stable, and sustainable CO_2 conversion technologies, thus helping mitigate the greenhouse effect and fostering a green, low-carbon society.

This review provides a thorough examination of recent advances in designing and synthesizing POPs for capturing and converting CO_2 into cyclic carbonates. The classification and analysis of POPs are based on the catalytic mechanisms and active components, as illustrated in Scheme 1.[38-41] Additionally, this paper delves into pivotal elements involving specific surface area, average pore size, CO_2 adsorption capacity, elucidating the prevailing understanding of the structure-property relationship of catalysts. Finally, this review summarizes the challenges and future perspectives in catalyst design, offering valuable insights alongside a comprehensive overview. The objective is to furnish both theoretical and practical guidance for advancing development in CO_2 resource utilization technologies.

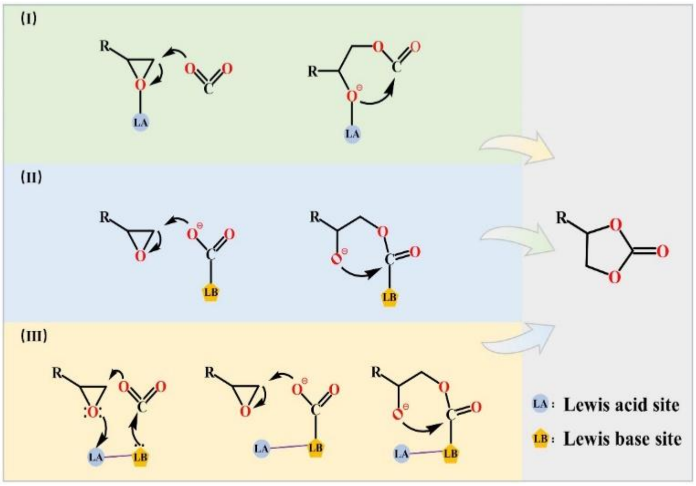


Scheme 1: Schematic illustration of tailored POPs in the cycloaddition reaction of CO_2 to epoxides.

2. Catalytic mechanisms of CO_2 and epoxide cycloaddition reactions

Within the realm of capturing and converting CO_2, the transformation into compounds with practical application value holds profound strategic importance. Notably, converting CO_2 and epoxides into cyclocarbonates through cycloaddition reactions has emerged as an efficient and promising avenue for CO_2 utilization. This reaction attains 100% atom economy, thereby maximizing efficiency while yielding cyclocarbonate products with significant economic value. Such processes align closely with the principles of sustainable chemistry. Cyclocarbonates are widely recognized as optimal polar solvents due to the impressive physicochemical properties, such as high dipole moment, high dielectric constant, high boiling point, excellent stability, and good solubility. Moreover, as a critical intermediate in chemical synthesis, cyclocarbonates serve a multitude of applications. Cyclocarbonates play pivotal roles in the synthesis of polymer materials such as polyurethane, polycarbonate, and polyglycerol. Additionally, in industrial applications, carbonates serve as raw materials for engineering plastics, additives, and fixatives for synthetic fibers, and dispersants for water-soluble dyes, thereby underscoring their versatility and importance within the chemical industry.[42-45]

Among various synthetic processes, the cycloaddition reaction of CO_2 with epoxides is distinguished via its unique capability to produce cyclocarbonates without generating any by-products, thus achieving high carbon atom utilization and substantial economic benefits.[46-49] Extensive studies have investigated the active mechanisms of various catalysts employed in CO_2 cycloaddition reactions.[50] However, to accurately elucidate the fundamental mechanism underlying the CO_2 cycloaddition reaction, comprehensive physicochemical investigations are indispensable. This encompasses detailed analyses of reaction kinetics and theoretical calculations employing density functional theory (DFT), which are critical for elucidating reaction pathways and guiding catalyst design.[51] Broadly, the mechanisms on cycloaddition reactions can be categorized into three primary aspects: (1) activation of epoxy compounds, (2) activation of carbon dioxide, (3) synchronous activation of CO_2 and epoxy compounds as illustrated in Scheme 2.



Scheme 2: Three kinds of possible activation models for the cycloaddition reaction of CO_2 with epoxides.

2.1 Activation of epoxides

The activation of epoxy compounds represents a crucial step in the synthesis of cyclocarbonates. According to extensive research, Lewis acidic catalysts have been demonstrated to be effective in this activation process. The catalytic cycle diagram elucidates this mechanism: initially, the Lewis acid catalyst coordinates with oxygen atoms in the epoxy compounds, facilitating nucleophilic attack and resulting in the ring cleavage of the epoxides.[52-56] Afterwards, the ring-opening intermediate reacts with CO_2, yielding a cyclic carbonate intermediate. Finally, the cyclization reaction produces desired cyclic carbonate products, releasing the nucleophile and catalyst. Central to this mechanism are two nucleophilic substitution reactions occurring on the identical carbon atom. The reaction is an Sn2 mechanism, typically favored at less hindered sites within the epoxide structure, followed by an intramolecular substitution reaction. The rate of this two-step process has been demonstrated through DFT calculations to depend significantly on the characteristics of the catalyst, nucleophile, and substrate used.[57]

2.2 Activation of CO_2

The activation of CO_2 also performs a vital part in cycloaddition reactions. Generally, the activation process of CO_2 can be categorized into three distinct steps: (a) The catalyst interacts with CO_2, forming carboxylate or carbonic acid intermediates. (b) These CO_2 activation intermediates function as nucleophiles, thereby facilitating the ring-opening of epoxides. (c) A subsequent intramolecular reaction occurs at the carbonyl group, yielding the final product cyclocarbonate, while simultaneously regenerating the catalyst. Catalysts that facilitate these reactions encompass nitrogen-based organics and metal complexes, such as those incorporating amino and sulfonic acid groups as HBDs, triazine structures, tertiary amines, guanidine, amidines, and various metal complexes.[58-61] These catalysts significantly enhance reaction efficiency and selectivity by promoting the effective binding of CO_2 to epoxides, thereby creating novel opportunities for synthesizing high-value cyclocarbonates.

2.3 Simultaneous activation of epoxide and CO_2

The mechanisms delineated earlier represent partial aspects of the activation of the reaction system. Although these mechanisms significantly enhance the rate of CO_2 cycloaddition, they are inadequate in isolation to facilitate the reaction under mild conditions. Contemporary catalyst design emphasizes the integrating of these activation mechanisms. Illustrative examples include synergistic approaches involving nucleophilic systems and activated epoxides,[62-66] and strategies prioritizing simultaneous activation of both CO_2 and epoxides.[67-70] These integrated approaches not only augment cyclocarbonate yield but also strive to advance the industrialization of the catalytic cycloaddition between CO_2 and epoxides.

3. POPs with a single activation mechanism

3.1 Triazine rings and the derivatives-modified POPs

Triazines belongs to six-membered aromatic heterocyclic compounds possessing three nitrogen atoms, endowing it with abundant alkaline sites due to its high nitrogen content. This characteristic allows triazine to interact with CO_2 molecules through lewis acid-base interactions, effectively activating inert CO_2 molecules and facilitating their adsorption and transformation. Additionally, triazine exhibits remarkable chemical stability, preserving its structure and properties even under rigorous reaction conditions.[71-74] Furthermore, triazine rings can be utilized to construct porous materials with regular pores, such as covalent triazine polymer frameworks (CTFs). These frameworks enhance the diffusion and adsorption of CO_2 molecules, thereby markedly improving their catalytic efficiency.

3.1.1 POPs with Triazine ring

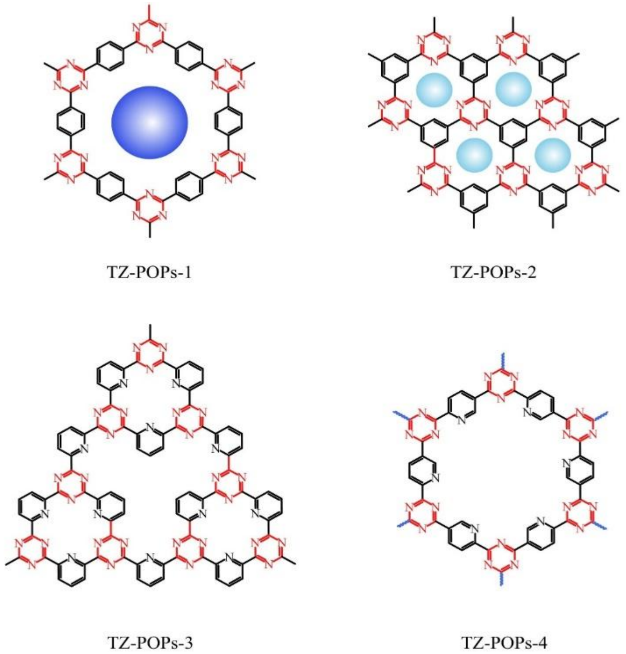
In 2012, Roeser *et al*. synthesized multi-alkali CTFs (Scheme 3 TZ-POPs-1) utilizing dicyan compound precursors via a $ZnCl_2$ melting process. They first applied these materials in the cycloaddition reactions involving CO_2 with linear and cyclic carbonate compounds. Benefiting from large specific surface areas, controllable pore structure, and sufficient alkaline sites, the heterogeneous catalysts exhibited exceptional catalytic activity and stability. It is worth noting that the catalysts can still maintain over 90% of the catalytic activity after 6 cycles, with no significant structural changes. The study further emphasized that increasing the pyridine groups in CTFs significantly boosted the catalytic activity at lower reaction temperatures, highlighting the pivotal role of basic sites in the activation of CO_2. The architecture of the polymer monomer profoundly influences the structure and porosity of the triazinyl network. Roeser's team polymerized 1,3,5-benzenetrinitrile within melted $ZnCl_2$, modifying the polymer monomeric structure to synthesize CTF-0 (Scheme 3 TZ-POPs-2). They also found that the ratio of monomer to $ZnCl_2$, reaction time, and temperature notably affect construction, porosity, and pore volume. Elevated reaction temperatures facilitated the formation of amorphous samples with surface areas reaching 2000 m^2/g, thereby demonstrating enhanced catalytic activity and achieving complete CO_2 conversion under comparable conditions.[75] Furthermore, Roeser *et al*. synthesized CTF P-HAS (Scheme 3 TZ-POPs-3) utilizing 2,6-dicyanopyridine at 600 °C, yielding a material with large nitrogen content (15.9 wt%) and a specific surface area (1745 m^2/g), along with superior microporous and mesoporous properties. The introduction of pyridine groups augmented the basic sites in CTF P-HAS, enhancing CO_2 activation and catalytic performance. Notably, CTF P-HAS accomplished 100% epichlorohydrin conversion and 94.6% selectivity at 130 °C, 0.69 MPa CO_2 pressure over 4 hours.[76] Additionally, Li *et al*. fabricated serial metal-free covalent triazine frameworks (Scheme 3 TZ-POPs-4) employing 2,5-dicyanopyridine (2,5-DCP) as a precursor. These frameworks exhibited exceptional thermal stability, multilayer pore structure, and elevated nitrogen content. The BET specific surface area of 2,5-DCP-CTFs reached up to 1768 m^2/g. When combined with metal-free conditions and a co-catalyst, these materials exhibited robust catalytic activity in converting CO_2 and epichlorohydrin into cyclocarbonates, achieving optimal conversion and selection rates of 99.1% and 95.5%, under conditions of 130 °C and 7.0 bar CO_2 pressure over 4 hours.[77]

While the mentioned method can produce triazine ring materials with a certain degree of crystallinity, the high-temperature reaction conditions may result in partial carbonization of the materials, consequently restricting their performance in specific applications. In 2017, Tan *et al*. introduced an innovative synthesis method for triazine rings, founded upon the polycondensation reaction of aromatic aldehydes and amidines. This methodology resulted in CTF-HUST-3, characterized by a considerable number of micropores and mesopores, with a CO_2 adsorption capacity of 13.91 wt% at 297 K. Notably, the heat of CO_2 adsorption associated with CTF-HUST-3 surpasses that of the majority of other nitrogen-rich porous organic frameworks, underscoring its potential in CO_2 capture applications.[78] To address the limitations of amorphous CTF structures synthesized using previous methods, Tan *et al*. further refined their synthesis approach in 2018. They achieved enhanced crystallinity via in situ oxidization of alcohols to aldehyde groups, resulting in series of CTF materials with improved thermal stability and catalytic activity.[79]

3.1.2 POPs with Phosphazene ring

The phosphazene ring structure, akin to the triazine framework, exhibits potential for applications in CO_2 capture and conversion. Notable differences of phosphazene ring and triazine framework lie in CO_2 adsorption mechanisms, catalytic active sites, and reaction conditions. The triazine framework primarily relies on nitrogen atoms to adsorb and interact with CO_2 molecules via Lewis acid-base interactions at higher temperatures and pressures, while the phosphazene ring with highly electron-enriched phosphazene core and surrounding aromatic rings as active sites, can more effectively adsorb and activate CO_2 molecules under milder conditions.[37]

In 2022, Vengatesan M. Rangaraj *et al*. pioneered the synthesis of phosphazene-core-containing covalent triazine frameworks (Pz-CTFs), marking the inaugural application in CO_2 capture. Pz-CTFs are distinguished by the exceptional porosity, specific surface area (1009 m^2/g), ultra-microporous architecture, and a highly electron-enriched phosphazene core, substantially augmenting the CO_2 adsorption performance. The breakthrough lays the groundwork for the advancement of catalyst designs.[80]


TZ-POPs-1 TZ-POPs-2

TZ-POPs-3 TZ-POPs-4

Scheme 3: POPs with Triazine rings.

3.2 HBD-modified POPs

3.2.1 Hydroxyl group

HBDs are crucial to catalyze the cycloaddition reactions of CO_2 with epoxides to synthesize cyclic carbonates.[81-83] One category of HBD facilitates the ring-opening of epoxides via composing hydrogen bonds with substrate molecules, while another category excels in activating CO_2 to promote the reaction.[84,85] In 2019, Kewei H *et al*. achieved precise control over the positioning of catalytic functional groups in porous organic materials through molecular engineering techniques. They integrated hydroxyl groups with phosphonium salts to greatly enhance the activity of cycloaddition reactions involving epoxides and CO_2. The incorporation of a hydroxyl group into the phosphate and indium salt molecule as an HBD effectively activated epoxy ring-opening process, as depicted in scheme 4 (HBD-POPs-1).[86] Jiang *et al*. synthesized a multifunctional super-crosslinked ionic polymer, PDCX-OH, exhibiting a high affinity for CO_2 through self-condensation, quaternary ammonium, and ion exchange processes. Under metal-free and solvent-free conditions, PDCX-OH (Scheme 4 HBD-POPs-2) achieved an impressive yield of 93%.[87] Additionally, Guo *et al*. designed and successfully synthesized two novel hydroxyl-rich POPs, PPDA-P5 and TB-P5, featuring azo bridging. PPDA-P5 and TB-P5 (Scheme 4 HBD-POPs-3) were synthesized employing fully hydroxylated aromatic hydrocarbon macrocycles as cores, p-phenylenediamine and Troger base (TB) diamines as linkers, respectively. These polymers exhibit strong nitrogen affinity, rendering them effective heterogeneous catalysts for CO_2. TB-P5, demonstrated superior catalytic performance compared to PPDA-P5, highlighting the advantageous role of TB as an organic base.[88]

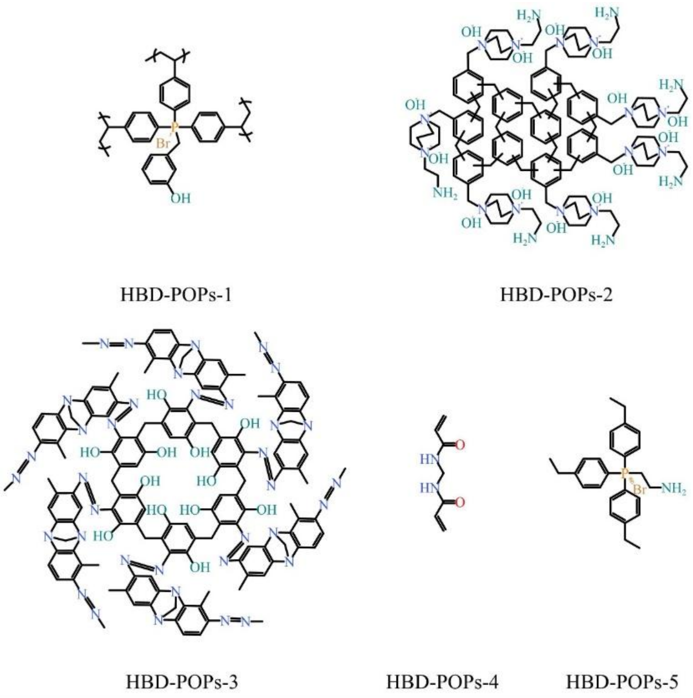
3.2.2 Amino groups and their derivative groups

In contrast to the studies, Wan *et al*. focused on CO_2 activation via HBDs and successfully synthesized a series of innovative polymer catalysts incorporating amide functional groups and bromine ions (Scheme 4 HBD-POPs-4). The catalysts were prepared using N, N'-methylenebisacrylamide (MBA) and polyvinylimidazole bromide salt (VxBr) as raw materials. The polymers exhibit large specific surface areas, controllable pore structure, abundant amide-HBDs and bromide ion nucleophilic sites, contributing to exceptional catalytic activity and stability, and could be reused at least 10 times without significant activity loss. Increasing the number of amide units significantly enhanced catalytic performance even at lower reaction temperatures, underscoring the crucial role of amide units in facilitating CO_2 activation.[89] Dai's team also contributed by synthesizing POP-PA-NH2 functionalized with -NH2 groups, as illustrated in Scheme 4 (HBD-POPs-5). This material exhibits exceptionally efficient catalytic activity in cycloaddition reactions under mild conditions, showcasing its capability to function without the necessity of co-catalysts.[90]

The formation of hydrogen bonds markedly diminishes the activation energy required for reactions, accelerates reaction kinetics, and stabilizes transition states, thereby enhancing the yield of cyclic carbonate products. HBDs serve an indispensable function in catalytic systems designed to facilitate CO_2 conversion, constituting a pivotal element in achieving efficient and environmentally sustainable CO_2 utilization. Through meticulous design of catalysts incorporating HBDs, the cycloaddition reaction of CO_2 can be optimized, offering an effective pathway for synthesizing cyclic carbonates with diverse applications.

3.3 Ionic liquids-modified POPs

Ionic liquids (IL) are defined as room temperature melting salts, consisting of organic cations and inorganic/organic anions, renowned for its unique physicochemical properties.[91-94] IL has been widely investigated as a catalyst for immobilizing CO_2 attributed to its exceptional solvent properties and adaptable chemical structure. In 2016, Wang's team synthesized a series of multi-active COF polymers incorporating ionic liquids, zinc salts (ZnX_2), and triphenylphosphine (PPh3) via post-synthetic metallization (Scheme 5 IL-POPs-1). These POPs catalysts capitalize on the synergistic effects of ionic liquids and uniformly dispersed



Scheme 4: POPs with HBD.

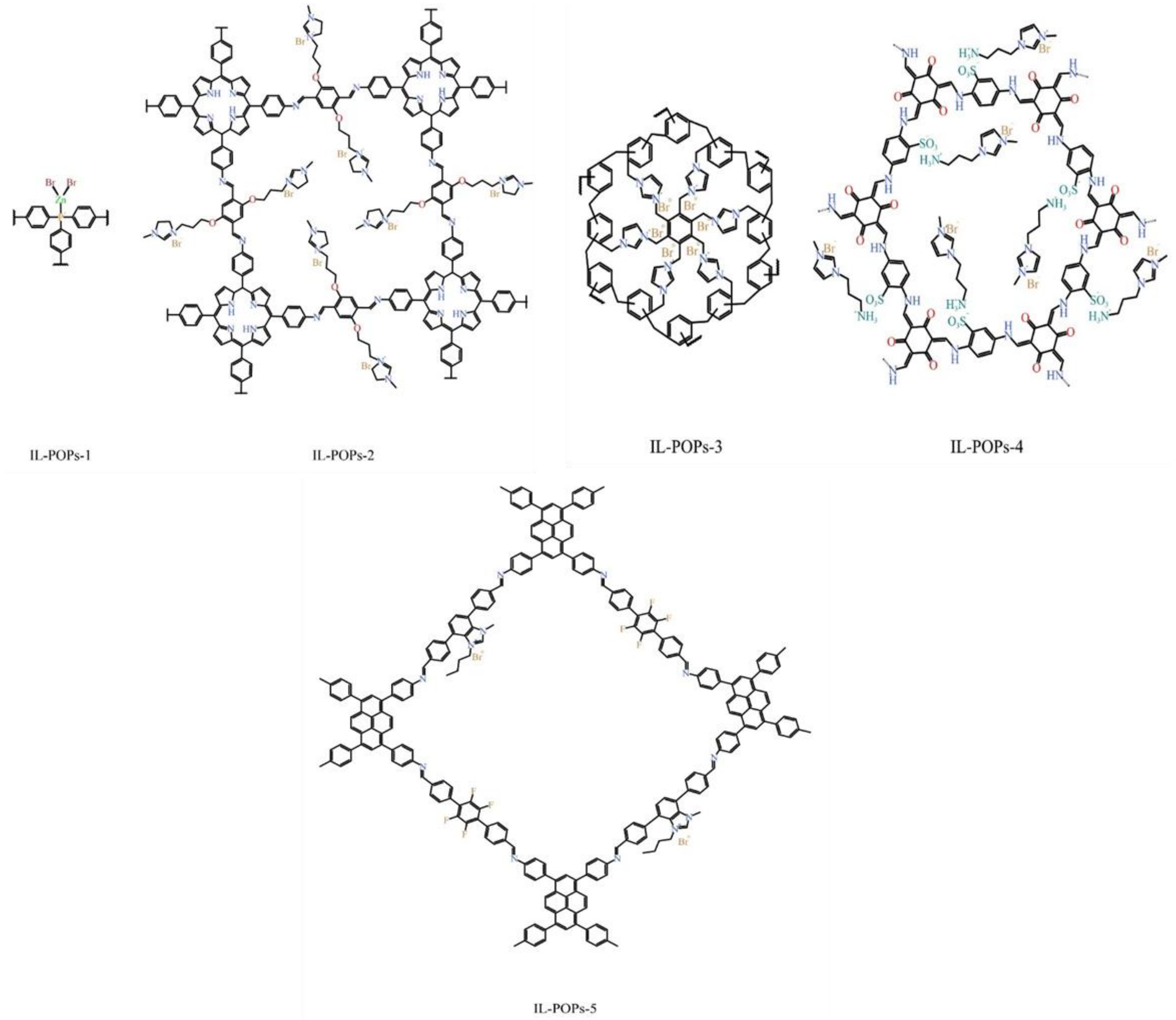
Zn-PPh3, embedded within a microporous and flexible framework. Consequently, they exhibit exceptional performance in CO_2 capture and conversion, achieving the highest activity levels reported for heterogeneous catalysts (initial conversion frequencies up to 5200 h^{-1}). Furthermore, the catalyst can be easily recovered and reused five times without a significant loss of activity.[95] Imidazolium-based ionic liquids have garnered significant attention for their exceptional activation properties in epoxide reactions. In 2020, Zhang *et al*. synthesized AMIMBr@H2P-DHPhCOF (Scheme 5 IL-POPs-2) by grafting 1-alkyl-3-methylimidazolinium-based IL (AMIMBr) on channel walls of two-dimensional covalent organic frameworks (2D-COF), H2P-DHPh COF, employing a post-synthesis strategy. The active sites on the imidazolium group were crucial for the efficient ring-opening of epoxides, significantly enhancing catalytic activity compared to the original H2P-DHPh COF.[96] Liao's team synthesized [HBIM-6]Br-DCX(3) (Scheme 5 IL-POPs-3), an imidazole hyperionic polymer (HIP) with high ionic density through the Friedel-Crafts reaction of α-dichloro-paraxylene and the monomer [BIM-6]Br.

This material demonstrated exceptional catalytic properties in cycloaddition reactions between CO_2 and epichlorohydrin without auxiliary catalysts and solvents, acquiring a productivity and selectivity of 99% in 1 hour.[97] Similarly, Zhao *et al*. introduced a new approach involving grafting imidazolium salts into COFs through acid-base neutralization strategies, which is depicted in Scheme 5 (IL-POPs-4).[98] Additionally, Yan *et al*. successfully synthesized BMIM4F-Py-COF (Scheme 5 IL-POPs-5), a novel ionic liquid-immobilized COF, by immobilizing imidazolium ionic liquid precursors onto a COF via quaternary ammonium reactions. The material exhibited outstanding catalytic properties in cycloaddition reactions between CO_2 and epoxide in the absence of solvents or co-catalysts, owing to its high specific surface area, unidimensional open channel construction, and catalytic activity of IL.[99]

3.4 Metal complexes POPs

3.4.1 Porphyrin-based POPs

Well-engineered metal-functionalized POPs have demonstrated superior catalytic activity when compared to conventional organocatalysts derived from ionic liquids.[100-102] Recently, there has been notable advancement in metal complex catalysts, especially in integrating Salen and porphyrin structures into highly stable porous organic frameworks, which has attracted considerable attention.[103,104] Metalloporphyrin complexes demonstrate outstanding performance in catalyzing oxidation, cycloaddition reactions, C-H bond activation, and various other processes.[105] Their diverse and adjustable structures enable the design of catalysts with precise functionalities, particularly in adsorbing and activating CO_2 during cycloaddition reactions with epoxides.[106,107] In 2017, Tan and colleagues successfully synthesized a porphyrin-based highly cross-linked polymer known as HUST-1 using an $AlCl_3$-catalyzed Friedel-Crafts reaction. Subsequently, cobalt ions were introduced into the central coordination site of porphyrins, resulting in HUST-1-

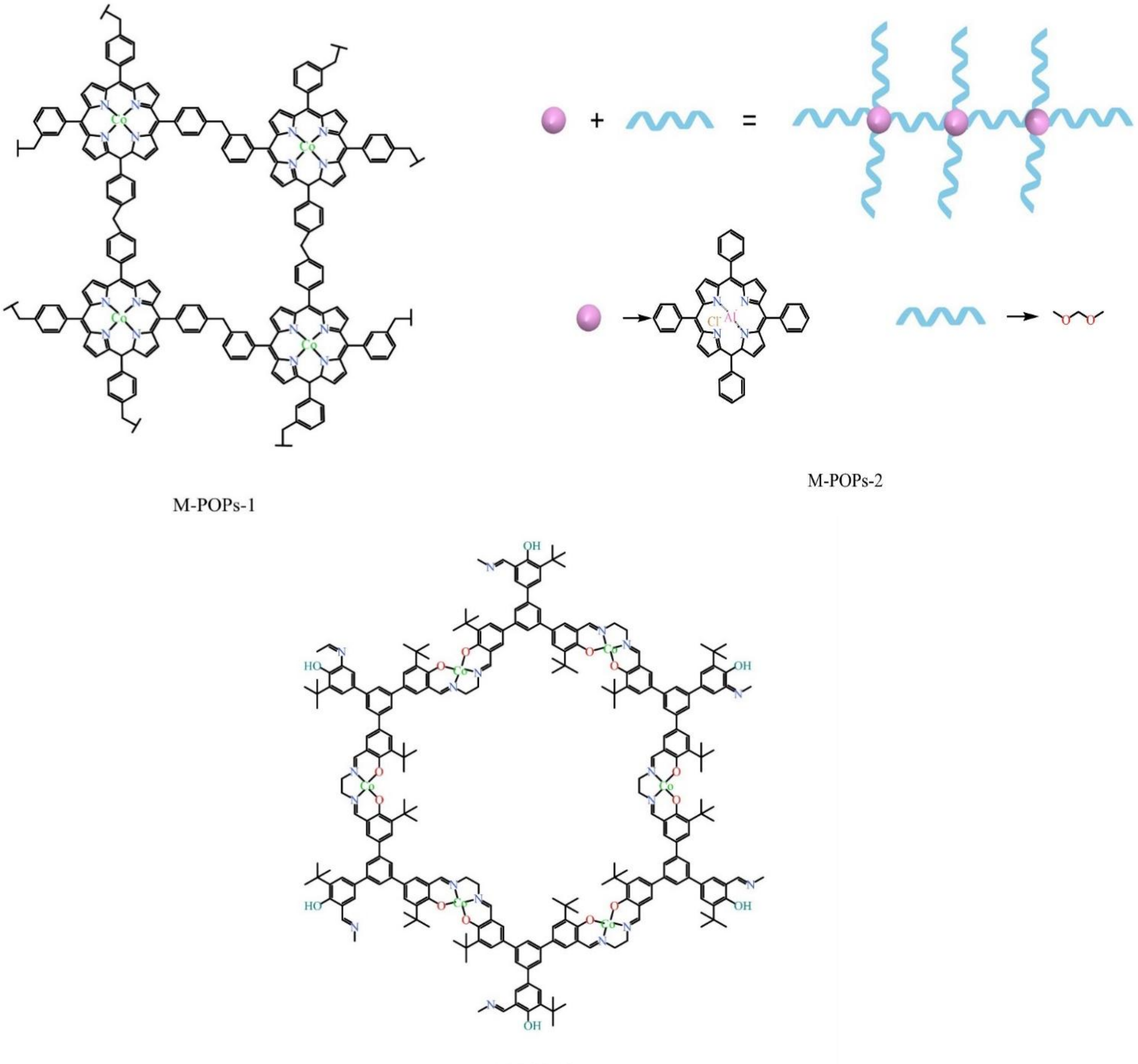


Scheme 5: POPs with Ionic liquid.

Co (Scheme 6 M-POPs-1) owning cobalt loadings of 0.39 mmol/g. HUST-1 and HUST-1-Co possess microscopic pore sizes of 0.68 nm and 1.17 nm, as well as successive medium and large pore construction that promote interactions between pore walls and CO_2, thereby facilitating catalytic processes.[108] Recently, Chen and colleagues synthesized metalloporphyrin-based high crosslinked polymers (Scheme 6 M-POPs-2) via Friedel-Crafts reaction. These M-HCPs feature numerous steady nano-sized pores, a large BET surface area, and outstanding CO_2/N_2 adsorption separability. Experimental effects showed the turnover frequency (TOF) of Al-HCP in propylene oxide (PC) is 14,880 h^{-1} under conditions of 100 °C and 3.0 MPa. Furthermore, these catalysts are capable of being recovered and reused exceeding 35 times using straightforward filtration or centrifugation methods avoiding loss of catalytic properties, suggesting promising potential for industrial applications.[109]

3.4.2 Salen-based POPs

Given the complexity and rigidity inherent in porphyrin synthesis, catalytic systems utilizing Salen structures with metal complexes have emerged as promising alternatives. Salen, known as Schiff base ligands, exhibit a quadrilateral ring structure composed of two nitrogen atoms and two oxygen atoms. The versatile and adaptable nature of Salen structures renders them ideal for designing innovative catalysts and functional materials. Li *et al*. successfully synthesized COF-Salen, a novel Salen-based COF characterized by large surface area (1646 m^2/g), consistent pore diameter (1.86 nm), and a layer crystal construction of



M-POPs-1

M-POPs-2

M-POPs-3

Scheme 6: POPs with Metal complexes.

AA stacking, demonstrating exceptional stability in acid-base environments while preserving a well-ordered crystal structure. Metallizing COF-Salen with metals such as Co enables the transformation into COF-Salen-Co (Scheme 6 M-POPs-3) catalysts possessing high BET surface areas and crystalline structures. The catalysts not only exhibited high catalytic activity but also showed good stability, with no significant loss of activity after 5 cycles. Li *et al*. proposed that the distinctive layered crystal structure of COF-Salen-M efficiently immobilizes active sites.[110] Conjugated microporous polymers (CMPs) represent a new type of porous materials distinguished by high specific surface areas, extensively utilized in heterogeneous catalysis and gas separating. Zou *et al*. recently reported Zn-Salen-CMP, a novel conjugated microporous polymer synthesized via Sonogashira coupling reaction using Zn-Salen compounds. Zn-Salen-CMP demonstrated outstanding catalytic properties, particularly in the chemical solidification between CO_2 and epoxides, especially when used in conjunction with the cocatalyst TBAB.[111]

3.4.3 Titanyl POPs

Maya *et al*. utilized Friedel-Crafts reaction to fabricate FePc-POP, a microporous-mesoporous organic polymer derived from commercially available iron phthalocyanine (FePc) and biphenyls. FePc-POP features a specific surface area of 427 m^2/g and an iron loading of 5.42%. This method enables the direct synthesis of heterogeneous catalysts from ferrous

Table 1: Results of CO_2 cycloaddition with substrate over a variety of POPs.

Entry	Catalyst	Cocatalyst	Substrate	Reaction condition	Yield (%)	Selectivity (%)	Ref.
TZ-POPs-1/2	CTF-0/1	NONE	ECH	0.7 MPa, 130 °C, 4 h	81.2	94.4	[75]
TZ-POPs-3	CTF P-HAS	NONE	ECH	0.7 MPa, 130 °C, 4 h	100	95.8	[76]
TZ-POPs-4	2,5-DCP-CTF	NONE	ECH	0.7 MPa, 120 °C, 4 h	95	95.9	[77]
HBD-POPs-1	PPS-mOH-Bn	NONE	1,2-Epoxybutane	0.1 MPa, 50 °C, 3 d	98	99	[86]
HBD-POPs-2	PDCX-OH	NONE	PO	0.5 MPa, 60 °C, 6 h	91	99	[87]
HBD-POPs-3	TB-P5	TBAB	PO	1.0 MPa, 80 °C, 48 h	96.0	99	[88]
HBD-POPs-4	P(MBA-V3Br)−2	NONE	PO	0.1 MPa, 80 °C, 12 h	95	99.7	[89]
HBD-POPs-5	POP-PA-NH2	NONE	ECH	0.1 MPa, 60 °C, 96 h	84.7	99	[90]
IL-POPs-1	PPh3-ILBr-ZnBr2@POPs	NONE	PO	3.0 MPa, 120 °C, 6 h	92	99	[95]
IL-POPs-2	AMIMBr@H2P-DHPh COF	NONE	PO	1.0 MPa, 120 °C, 24 h	95	95	[96]
IL-POPs-3	[HBIM-6]Br-DCX(3)	NONE	ECH	0.1 MPa, 140 °C, 1 h	99	99	[97]
IL-POPs-4	COF-HNU14	NONE	PO	2.0 MPa, 120 °C, 24 h	96	99	[98]
IL-POPs-5	BMIM4F-Py-COF	NONE	ECH	4.0 MPa, 120 °C, 24 h	99	99	[99]
M-POPs-1	HUST-1-Co	NONE	PO	0.1 MPa, 25 °C, 48 h	94.6	99	[108]
M-POPs-2	Al-HCP	TBAB	PO	1.0 MPa, 40 °C, 1 h	99	99	[109]
M-POPs-3	COF-salen-Co	TBAB	PO	2.0 MPa, 120 °C, 3 h	95	99	[110]
M-POPs-4	Zn-salen-CMP-2	TBAB	PO	3.0 MPa, 120 °C, 1.5 h	92	99	[111]
M-POPs-5	FePc-POP	NONE	ECH	0.3 MPa, 90 °C, 3 h	94	99	[112]

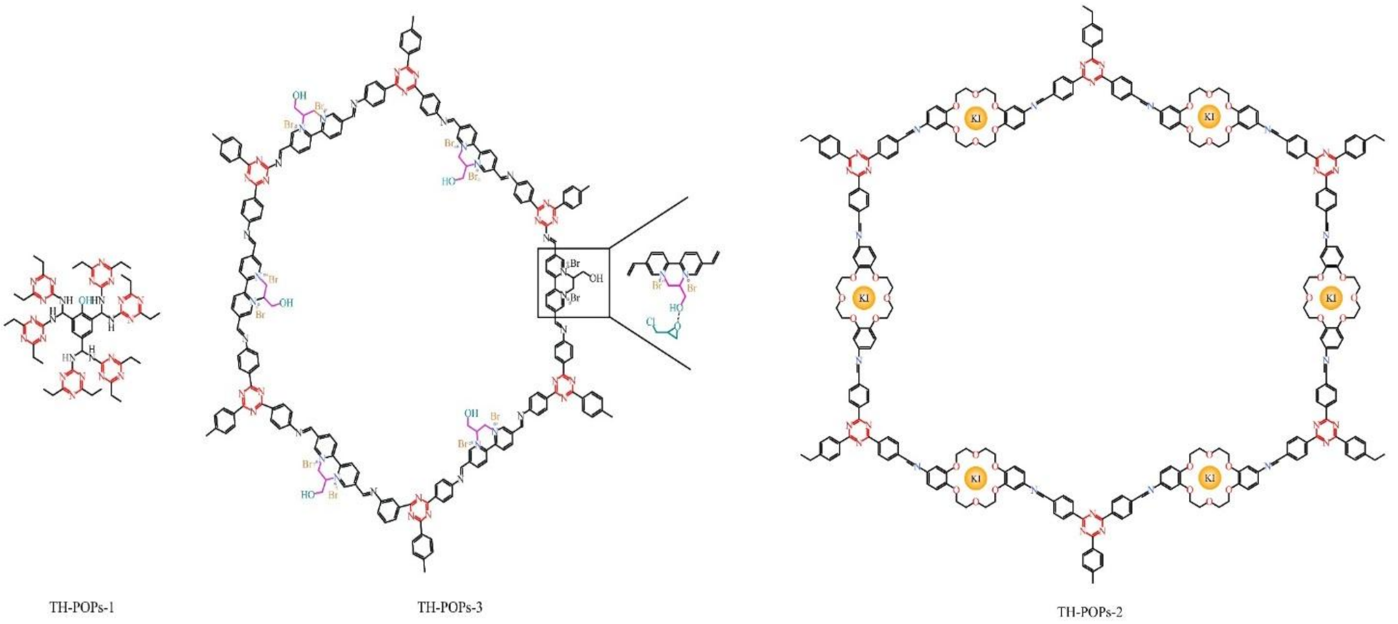
monomers. FePc-POP incorporates a "Fe-N" bond and, in combination with DMAP (4-(dimethylamino)pyridine), effectively activates CO_2 to facilitate cycloaddition reactions. Under relatively mild conditions (90 °C and 3 bar CO_2 for 3 hours, without solvent), FePc-POP achieves turnover numbers (TON) up to 2700.[112] Table 1 presents the key consequences of various POPs which catalyzing epoxide versus CO_2 cycloaddition.

4. Multi-activation mechanisms

Instead of concentrating solely on individual activator groups or structures tailored to activate either epoxides or CO_2, researchers are progressively investigating novel catalytic approaches. The strategy entails leveraging the synergistic interplay of two or more active groups to craft catalysts that exhibit superior overall performance. This trend has spurred the creation of catalysts proficient not only in intensifying the activation of epoxides or CO_2 individually but also in concurrently activating both species.

4.1 POPs with Triazine ring and HBD

Mohanty *et al*. employed melamine and 2-hydroxy-1,3,5-benzentricarboxaldehyde to synthesize multifunctional nitrogen-rich nanoporous polymers (Scheme 7 TH-POPs-1). -OH, -NH, and triazine moieties within the polymers act as potent functional groups. Specifically, the triazine ring interacts with CO_2 molecules through the nitrogen atoms, activating CO_2 via Lewis acid-base interactions. Meanwhile, the -OH serve as HBDs, forming hydrogen bonds with the epoxy groups of epoxides, thereby reducing the activation energy required for ring-opening and promoting the cycloaddition reaction.[113] Liu's group synthesized crown ether-functionalized porous organic polymers (CE-POPs) via a Schiff base condensation reaction, wherein trans-di(aminodibenzo)-18-crown-6 was linked to a trialdehyde-type monomer and the synthesis was performed in DMF solvent under reflux conditions. KI@CE-POPs (Scheme 7 TH-POPs-2) modified with potassium ions, phenolic hydroxyl and triazine units, exhibited synergistic catalytic activity,



Scheme 7: POPs with Triazine rings and HBD.

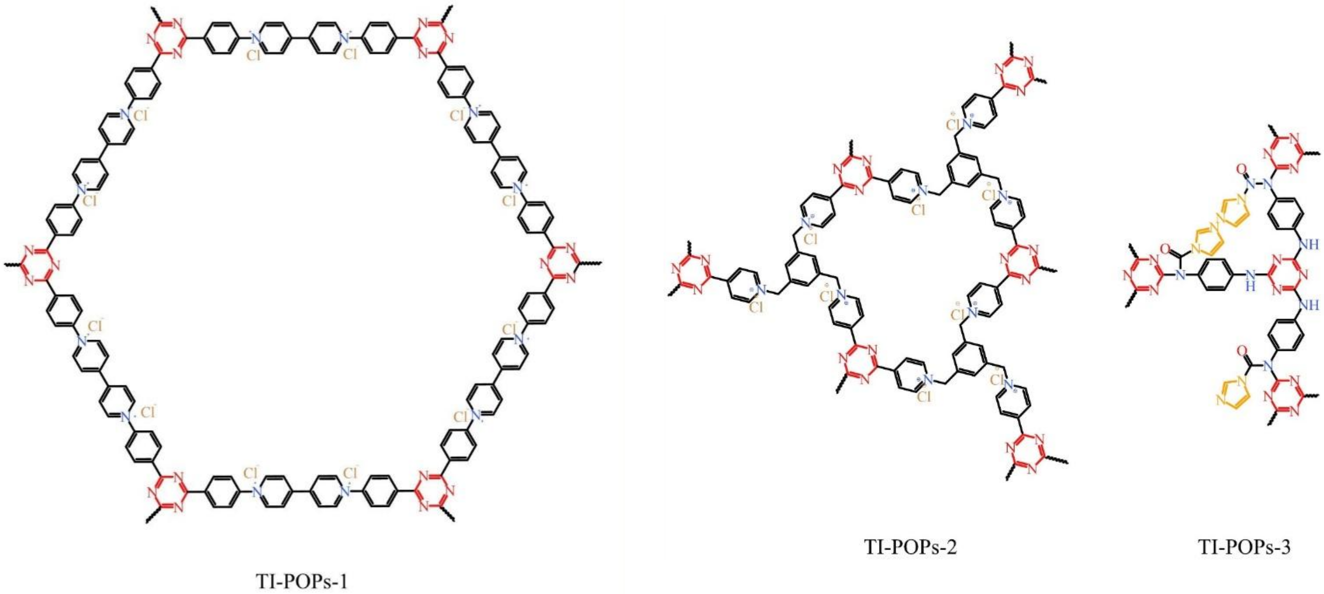
exceptional catalytic efficiency and broad substrate compatibility in a moderate environment (100 °C and 1.0 MPa), alongside excellent recyclability and stability.[114] Yin *et al*. also contributed to advancing crystalline COF materials. They rapidly synthesized bipyridine-based TAPT-BP-COF with high crystallinity as backbones within just 1 h using supercritical CO_2 ($scCO_2$) activation. Subsequently, they completed the preparation of doubly cationic TAPT-BP2+-COF (Scheme 7 TH-POPs-3) through quaternization reactions. Featuring CO_2-philic groups (imine and triazine), a charged backbone, and appropriate pore sizes, TAPT-BP2+-COF showed 55.6% increase in CO_2 capture capacity, along with improved conversion rates and yields. Moreover, it exhibited excellent stability, allowing for ten cycles of reuse without significant loss of activity.[115]

4.2 POPs with Triazine rings and ionic liquids

In 2017, Ali Coskun *et al*. pioneered the synthesis of charged covalent triazine backbone catalysts (cCTFs). The resulting cCTF-500 (Scheme 8 TI-POPs-1) exhibited an impressive specific surface area of 1247 m^2/g. The ionic functional groups incorporated into POPs significantly enhance CO_2 adsorption capacity. Specifically, the positively charged pyridine groups in cCTFs can interact with CO_2 through electrostatic interactions, facilitating CO_2 adsorption. Meanwhile, the triazine ring structure provides additional adsorption sites and promotes the activation of CO_2. The dual-action mechanism, combining electrostatic interactions and Lewis acid-base interactions, significantly improves the overall catalytic performance.[116] Hongliang Huang's team synthesized 1,3,5-tris(4-cyanopyridine-1-methyl)-tribromobenzene (TPM) cationic CTFs (CCTFs) exploiting $ZnCl_2$ as both catalyst and reacting media for prussiate terpolymerization. CCTF-TPM-400 (Scheme 8 TI-POPs-2) exhibited characteristics including high-density pyridine cation sites, a substantial specific surface area (1206 m^2/g), excellent CO_2 adsorption ability (61.4 cc/g at 1 bar, 273 K), and outstanding catalytic efficiency in cycloaddition reactions in a moderate environment (0.7 MPa CO_2, 100 °C, 24 h).[117] Additionally, Dai *et al*. synthesized hierarchical structured CTFs through a straightforward solvothermal approach employing melamine and 1,4-phenylenediamine. The CTFs were further functionalized with imidazole groups to yield CTF-IM (Scheme 8 TI-POPs-3), which displayed exceptional catalytic activity in metal-free, halogen-free, and solvent-free environments. Under optimized conditions (120 °C, 2.0 MPa, 2.5 h), CTF-IM achieved an impressive productivity 94.6%, and exhibited good stability, with no significant decline in catalytic performance after 5 cycles. Dai underscored the contributions of Lewis acidic and basic groups within CTF-IM, which facilitated the activation of epoxides and CO_2, respectively.[118]

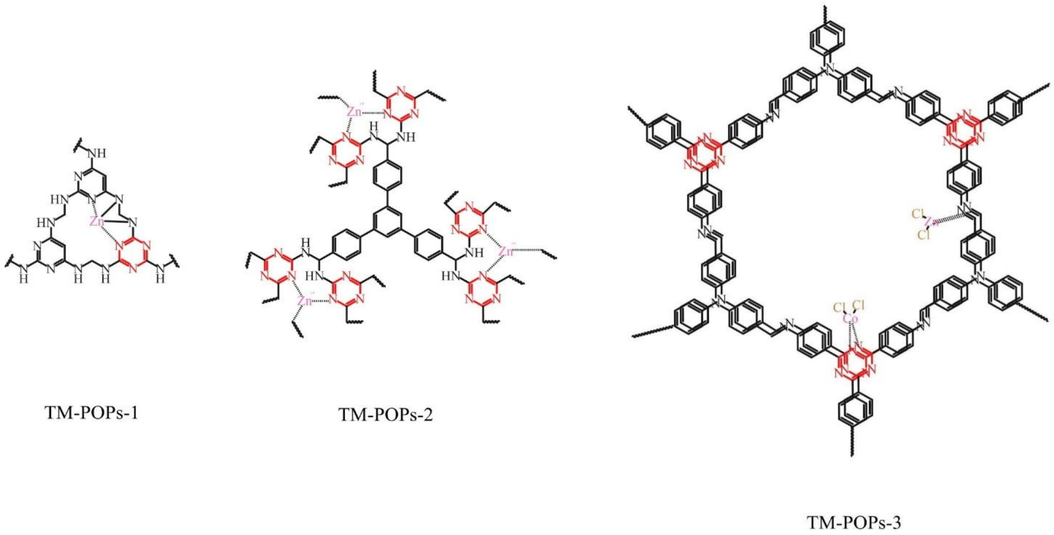
4.3 POPs with Triazine rings and metal complexes

Meng *et al*. investigated layered porous metallized melamine-formaldehyde (PMF) catalysts, engineered to enhance mass transport in catalytic reactions. PMFs were metallized to produce hierarchical porous Zn@ah-PMFs (Scheme 9 TM-POPs-1), featuring BET surface area of 497.01 m^2/g. Increased Zn^{2+} correlated with accelerated adsorption rates.

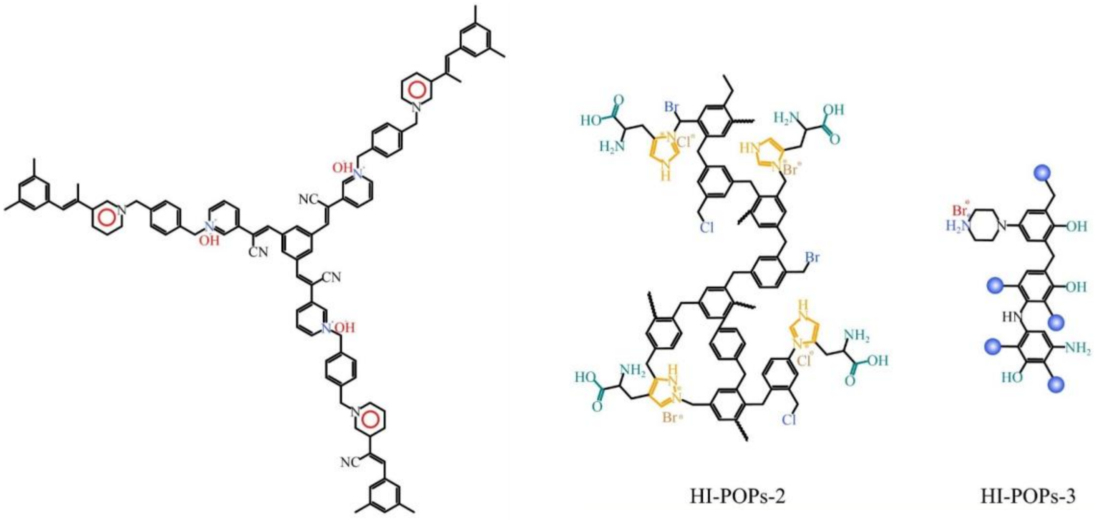


Scheme 8: POPs with Triazine rings and ionic liquids.

The catalyst was employed in CO_2 cycloaddition experiments with co-catalyst TBAB, achieving a remarkable 99% conversion rate and separability at 100 °C and 2.0 MPa CO_2 pressure within 0.5 hours. The metal ions (Zn^{2+}) in the catalysts interact with the epoxy groups of epoxides, stabilizing the reaction intermediates. Meanwhile, the triazine ring structure provides additional activation sites, promoting the adsorption and activation of CO_2. The synergistic effect between the metal ions and the triazine ring enhances the overall catalytic efficiency.[119] Similarly, Liu *et al*. synthesized two metal-containing triazine polymer catalysts (Zn-TPAMP and Zn-TPBMP) from melamine and various aldehyde precursors. N_2 adsorption choroisotherm and pore diameter compositions of TPAMP and TPBMP (Scheme 9 TM-POPs-2), revealed the microporous and mesoporous structures. Both catalysts exhibited excellent CO_2 adsorption capacities, with Zn-TPAMP displaying high catalytic activity (TOF: 1383 h^{-1}) owing to plentiful mesopores and zinc ions. With the addition of tetrabutylammonium bromide, at 100 °C, 2.0 MPa CO_2 pressure lasting 1 h, Zn-TPAMP achieved better yields of cyclic carbonate with CO_2 and propylene oxide.[120] Furthermore, Ahn *et al*. synthesized covalent imine backbone (CIF) materials, specifically TPA-TCIFs (Scheme 9 TM-POPs-3). The CIFs were subsequently functionalized with M^+ (Zn^{2+} and Co^{2+}) for cycloaddition reactions. While surface areas of specimens partially decreased after functionalization, the catalytic activity was significantly enhanced, showcasing outstanding structural properties and improved catalytic efficiency, and the activity was sustained after five rounds of recycling.[121]



Scheme 9: POPs with Triazine rings and metal complexes.



HI-POPs-1

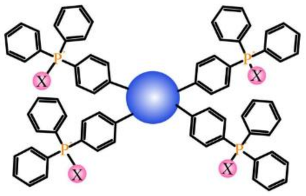
HI-POPs-2

HI-POPs-3

Scheme 10: POPs with HBD and ionic liquids.

4.4 POPs with HBD and ionic liquids

Liu and colleagues synthesized pyridyl ionic porous organic polymers (Py-iPOPs) incorporating hydroxyl and pyridyl radicals in situ, employing an acetonitrile-functionalized pyridinium ionic liquid and polyaldehyde monomer via alkali-catalyzed Knoevenagel condensation. Py-iPOP-1 (Scheme 10 HI-POPs-1) exhibited outstanding catalytic activity, achieving 99% yield and selectivity in converting CO_2 and glycerol carbonate to cyclic carbonate in moderate environments (0.1 MPa CO_2, 60 °C, 48 hours). The hydroxyl groups as HBDs facilitates epoxide ring opening, synergistically enhanced by the pyridine groups. Specifically, the pyridine groups provide the additional nucleophilic sites to interact with CO_2 and promote its activation. The dual-action mechanism, combining hydrogen bonding and nucleophilic activation, significantly improves the overall catalytic performance.[122] Guo *et al*. synthesized a novel multifunctional histidine-based supercross-linked polymer, HIPs-Br-His (Scheme 10 HI-POPs-2), integrating multiple hydrogen bond donors, nucleophilic ion sites, and Lewis bases. In moderate environments (70 °C, 1 MPa), devoid of metal catalysts or solvents, HIPs-Br-His exhibited robust catalytic properties.[123] Additionally, Cai *et al*. synthesized resorcinol/formaldehyde resin via solvent-free self-assembly, subsequently modifying by HBr to yield nitrogen-doped POP featuring protonation IL locus, PIP-HP-HBr (Scheme 10 HI-POPs-3). The material retained a large surface area following the formation of ionic sites and demonstrated synergistic effects of hydroxyl groups and Br^- ions, facilitating high catalytic activity without metals, solvents, or co-catalysts. Additionally, PIP-HP-HBr achieved a maximum yield of 99% and can be reused with performance remaining largely unchanged after five cycles.[124]



HM-POPs-1

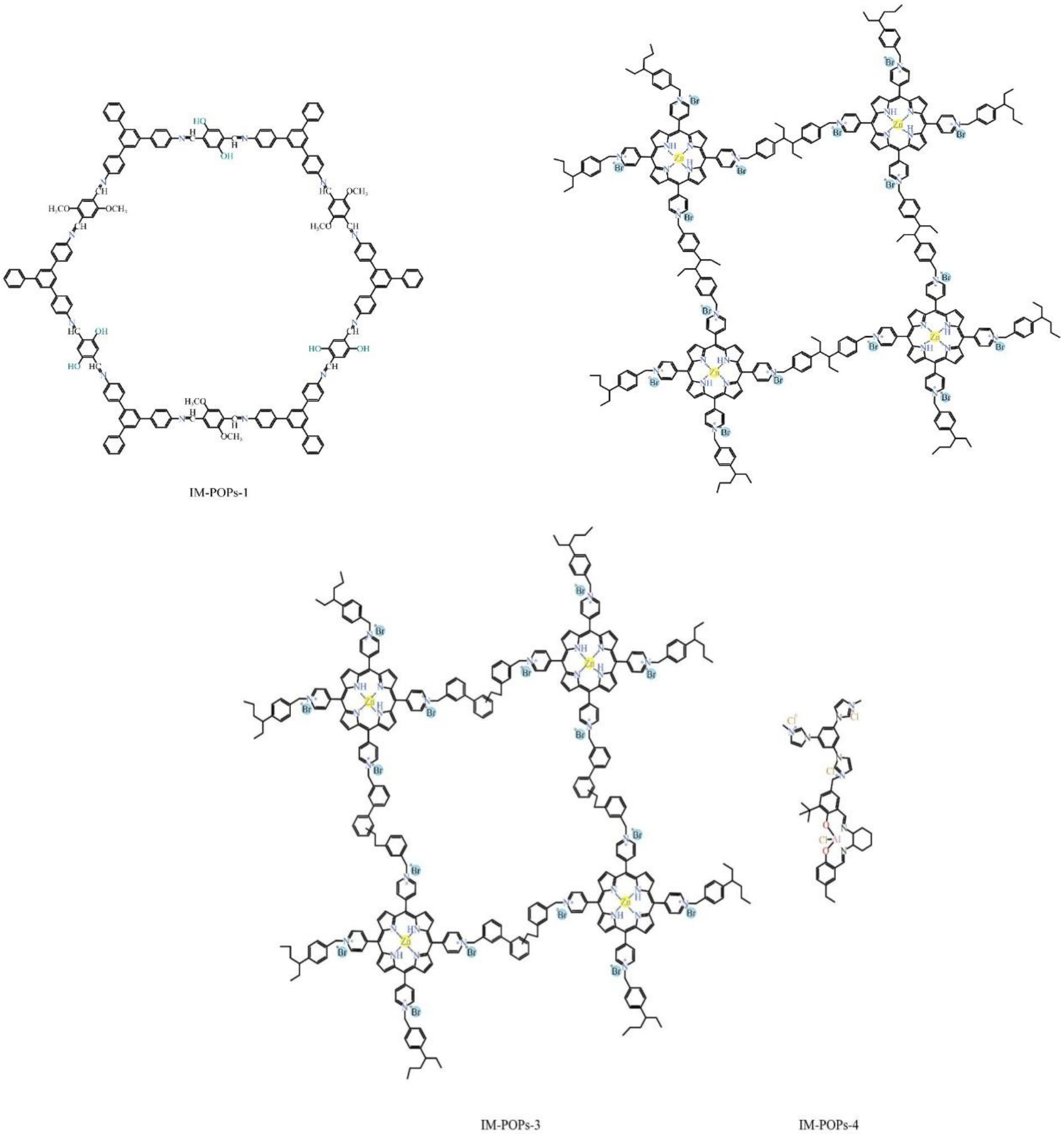
Scheme 11: POPs with HBD and metal complexes.

4.5 POPs with HBD and metal complexes

Recently, Chen *et al*. synthesized phosphorus-ion-based porous hypercrosslinking polymers (Scheme 11 HM-POPs-1) using octavinylsesquioxane (VPOSS) and the cost-effective organic ionic salt methyltriphenylphenyl bromide ([Ph3PMe]Br) through an $AlCl_3$-catalyzed Friedel-Crafts reaction. These polymers incorporate various active centers, comprising uncombined Cl^- and Br^-, POSS-rich Si-OH HBDs groups formed from POSS cage cleavage during synthesis, and metal halide complex anion $[AlCl_3Br]^-$. The HBDs (Si-OH groups) form hydrogen bonds with the epoxy groups of epoxides, reducing the activation energy required for ring-opening. Meanwhile, the metal halide complex anion $[AlCl_3Br]^-$ activates and interacts with CO_2.[125]

4.6 POPs with Ionic liquids and metal complexes

Beyond the above mentioned studies, the covalent modification strategy with metal complexes has surfaced as a promising research avenue, facilitating the seamless integration of active groups. Zhang and co-workers devised the innovative multi-component heterogeneous catalyst, POM@ImTD-COF (Scheme 12 IM-POPs-1), through immobilizing imidazole ionic liquids (ImTD) onto COFs, exploiting electrostatic interactions with polyoxymetalate (POMs). The exceptional catalytic efficacy of POM@ImTD-COF arises from synergies between the ionic liquids and



Scheme 12: POPs with Ionic liquids and metal complexes.

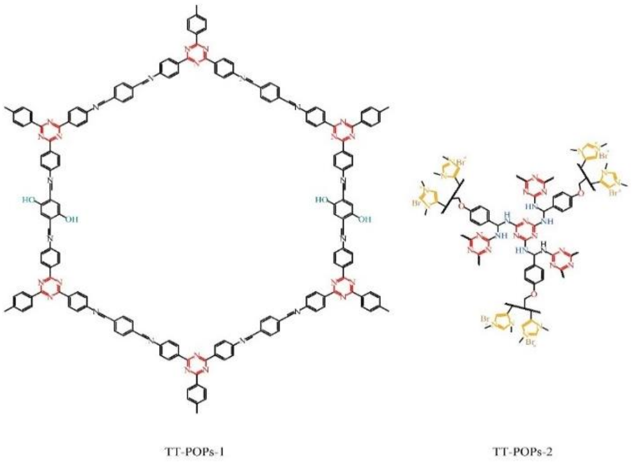
POMs. In cycloaddition reactions, the ionic liquid, alongside the co-catalyst n-Bu4NBr, facilitates the breaking of C-O within epoxy compounds, whereas Lewis acidic POMs drive the process of ring-opening. These diverse activation pathways enhance the robust catalytic efficiency of POM@ImTD-COF.[126]

Ma *et al*. prepared the zinc porphyrin-based ionic POP (Scheme 12 IM-POPs-2) catalyst employing a newly devised pyridine-functionalized cationic zinc porphyrin monomer (ZnTPyPBr4). The bimodal heterogeneous catalyst, endowed with zinc (II) active centers and nucleophilic Br-, demonstrated robust catalytic properties in the absence of solvent and cocatalyst. Particularly notable are its remarkable turnover frequency (TOF) values, reaching as high as 15,500 h^{-1} for CO_2 and epichlorohydrin at 120 °C and 1.0 MPa.[127] Wang *et al*. utilized a solvothermal approach to copolymerize pyridine-functionalized zinc porphyrin (ZnTPyPBr4) with divinylbenzene (DVB), yielding ZnTPyPBr4/DVB (1:30)-iPOP (Scheme 12 IM-POPs-3) possessing large specific surface areas, superior CO_2 adsorption efficiency, plentiful bifunctional Zn and Br- sites. This catalyst demonstrated best catalytic property reported thus far in cycloaddition reactions, achieving 99% conversion rate.[128]

Cao *et al*. engineered and synthesized a pioneering cationic POP, Al-CPOP, integrating Salen-(Al) and imidazole effectiveness. The porous polymer plays a dual role as catalysts and excels at facilitating cycloaddition reactions. Al-CPOP (Scheme 12 IM-POPs-4) efficiently synthesizes cyclic carbonates under atmospheric pressure without requiring additional co-catalysts. Within Al-CPOP, Salen-(Al) functions as a Lewis acid, complemented by imidazole chloride serving as a Lewis base. Collectively, the components catalyze the cycloaddition reaction by activating epoxides and facilitating the nucleophilic attack on C-O bonds by chloride ions derived from imidazole. This process initiates the ring-opening reaction, generating new intermediates. The nitrogen-rich backbone of Al-CPOP enhances the capacity for CO_2 adsorption, thereby enhancing CO_2 capture efficiency and accelerating overall reaction rate.[129]

4.7 POPs with Triazine rings, HBDs and ionic liquids

Besides integrating two catalytic strategies, current research explores the integration of three simultaneous catalytic active sites. For example, Sun *et al*. successfully engineered a series of multifunctional ionic COFs through the covalent grafting of functionalized imidazole onto the triazinyl COF backbone using a post-synthetic modification strategy. IM-COF-Br-Vinyl (Scheme 13 TT-POPs-1) features multiple active sites, including CO_2-affinity basic sites, hydrogen bond donors, and nucleophilic anions. Specifically, the triazine ring provides basic sites that interact with CO_2, promoting its adsorption and activation. The hydroxyl groups act as HBDs, forming hydrogen bonds with the epoxy groups of epoxides, reducing the activation energy required for ring-opening. Meanwhile, the nucleophilic anions (Br^-) interact with the epoxy groups, further promoting the ring-opening process. The framework demonstrates outstanding catalytic performance in a moderate environment without solvent, co-catalyst, and metal. Optimization of conditions enabled IM-COF-Br-Vinyl to achieve a conversion rate of 96.49% for epichlorohydrin with a selectivity exceeding 99% at 100 °C, 0.5 MPa, and 6 h.[130] Furthermore, Liu *et al*. synthesized an alkene-modified melamine-based POP (MPOP-4A) using a one-pot method, subsequently modifying with imidazole ions to produce the final catalyst (Scheme 12 TT-POPs-2). The structure of MPOP-4A-IL incorporates an array of active centers, including hydrogen bond donors, nitrogen centers, and nucleophilic groups, which collectively enhance efficiency and catalytic activity in chemical reactions. The MPOP-4A-IL catalyst was found to retain high catalytic activity even after being recycled six times.[131]

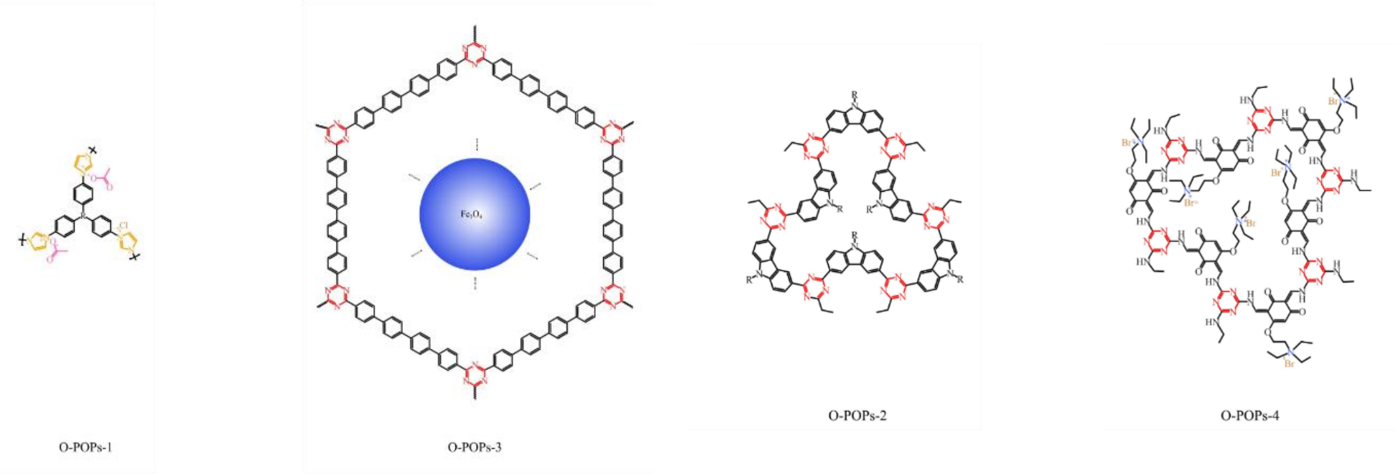


Scheme 13: POPs with Triazine rings, HBDs and ionic liquids.

4.8 Miscellaneous POPs

Lin *et al*. have made a significant contribution to the field of catalysis by developing a novel class of materials known as ionic conjugated microporous polymers (iCMPs). They synthesized these polymers through a simplified one-step Debus-Radziszewski reaction, which is a significant advancement in the synthesis of such materials. The resulting Imidazole-linked iCMP-1@Cl (referred to as Scheme 14 O-POPs-1) was obtained through a direct anion exchange process with halides. This innovative method not only simplifies the synthesis but also introduces a unique feature: the imidazole group's interaction with the halogen anion. This synergy effect markedly enhances catalytic efficiencies of the material, particularly in the process of epoxides ring-opening, a reaction of great importance in the chemical industry. The efficiency of this catalyst is highlighted by its performance.[132] In a parallel development, Yu *et al*. have synthesized covalent triazine frameworks (Scheme 14 O-POPs-2) with remarkable properties. The frameworks, prepared at 400 °C using 3,6-dicyanocarbazole as the monomeric precursor, boast a substantial specific surface area of 982 m^2/g and a high nitrogen content of 15.33 wt%. These characteristics make them highly effective catalysts for epoxides ring-opening reactions. When combined with the cocatalyst TBAB (tetrabutylammonium bromide), the performance of catalysts is further enhanced, demonstrating exceptional catalytic properties in CO_2 activation. In a moderate environment of 25 °C and 0.1 MPa CO_2 pressure, these catalysts achieve a conversion efficiency of over 96% in cycloaddition reactions, thereby effectively contribute to forming cyclic carbonates.[133] For application in CO_2 capture and catalysis, Ahn and collaborators have also made strides in the synthesis of porous matters. They have developed triazine polymers (QP-CTP) through a process involving cyanochloride and tetraphenyl substitution, and further integrated these polymers with ferric oxide nanoparticles to create porous Fe_3O_4@QP-CTP architectures. At 273 K and 1 bar, these materials, as depicted in Scheme 14 O-POPs-3, exhibit an impressive CO_2 adsorption amount of 83 mg/g.

When used in conjunction with tetrabutylammonium bromide, they catalyze the reaction at 0.1 MPa CO_2 pressure and 50 °C for 12 hours, achieving a conversion rate of 91% and a selectivity of 98% for propylene oxide, as described in reference.[134] Sarkar and colleagues have demonstrated quaternary ammonium salts can be effectively immobilized onto a microporous COFs. By harnessing the synergistic effects among multiple active centers within the COFs, such as Br^- and NH^{3+}, along with highly accessible microporous channels and excellent CO_2 enrichment capacity of the frameworks, these modified COFs (Scheme 14 O-POPs-4) have been shown to facilitate the coupling of CO_2 with various epoxides. Notably, cyclic carbonates can be acquired in yields surpassing 99% with selectivity exceeding 99%. The catalytic system can be reused at least five times, maintaining nearly



Scheme 14: Miscellaneous POPs.

the same level of catalytic performance, as reported in reference.[135] These advancements showcase the innovative approaches being taken to develop materials with enhanced catalytic properties for CO_2 capture and conversion, which are crucial in sustainable chemical processes and the development of green technologies. The work of Lin *et al*. highlights the importance of interdisciplinary collaboration and the integration of novel synthetic strategies to address contemporary challenges in catalysis and material science.

Table 2 provides a comprehensive summary of the principal outcomes the principal outcomes associated with the diverse POPs discussed earlier concerning their performance

Table 2: Results of CO_2 cycloaddition with substrate over a variety of POPs.

Entry	Catalyst	Cocatalyst	Substrate	Reaction condition	Yield (%)	Selectivity (%)	Ref.
TH-POPs-1	MNENP	NONE	ECH	120 °C, 0.4 MPa, 20 h	100	100	[113]
TH-POPs-2	KI@CE-POP-2	NONE	ECH	100 °C, 1.0 MPa, 12 h	96	unknown	[114]
TH-POPs-3	TAPT-BP^{2+}-COF	NONE	ECH	120 °C, 2.0 MPa, 12 h	99.3	99	[115]
TI-POPs-1	cCTF-500	NONE	PO	90 °C, 1.0 MPa, 12 h	99	unknown	[116]
TI-POPs-2	CTF-TPM-400	NONE	ECH	100 °C, 0.7 MPa, 24 h	99	unknown	[117]
TI-POPs-3	CTF-IM	NONE	ECH	120 °C, 2.0 MPa, 2.5 h	94.6	100	[118]
TM-POPs-1	Zn@ah-PMF	TBAB	PO	100 °C, 2.0 MPa, 0.5 h	99	99	[119]
TM-POPs-2	Zn-TPBMP	TBAB	PO	100 °C, 2.0 MPa, 1 h	99	unknown	[120]
TM-POPs-3	Zn/TPA-TCIF(BD)	NONE	PO	40 °C, 0.5 MPa, 10 h	99.3	99.7	[121]
HI-POPs-1	Py-iPOP-1	NONE	glycidol	60 °C, 0.1 MPa, 48 h	99	99	[122]
HI-POPs-2	HIPs-Br-His	NONE	PO	110 °C, 1.0 MPa, 1 h	97	unknown	[123]
HI-POPs-3	PIP-HP-HBr	NONE	EH	120 °C, 1.0 MPa, 8 h	99	unknown	[124]
HM-POPs-1	P-iPHCP-14	NONE	EH	60 °C, 0.1 MPa, 48 h	96	99	[125]
IM-POPs-1	POM@ImTD-COF	NONE	ECH	80 °C, 0.1 MPa, 24 h	99	99	[126]
IM-POPs-2	ZnTPyPBr4-iPOP	NONE	ECH	120 °C, 1.0 MPa, 6 h	99	99	[127]
IM-POPs-3	ZnTPyPBr4/DVB-iPOP	NONE	ECH	80 °C, 0.5 MPa, 18 h	99	99	[128]
IM-POPs-4	Al-CPOP	NONE	ECH	120 °C, 0.1 MPa, 24 h	99	95	[129]
TT-POPs-1	IM-COF-Br-Vinyl	NONE	ECH	100 °C, 0.5 MPa, 6 h	96.49	99	[130]
TT-POPs-1	MPOP-4A-IL	NONE	ECH	120 °C, 1.0 MPa, 8 h	95	99	[131]
O-POPs-1	iCMP-1@Cl	NONE	ECH	130 °C, 1.0 MPa, 8 h	98	99	[132]
O-POPs-2	CTF-CSU19	TBAB	ECH	90 °C, 1.0 MPa, 48 h	96	unknown	[133]
O-POPs-3	Fe3O4@QP-CTP	TBAB	PO	50 °C, 0.1 MPa, 12 h	91	98	[134]
O-POPs-4	MA-PDA IL@COF	NONE	ECH	90 °C, 0.1 MPa, 12h	99	99	[135]

in catalyzing epoxide versus CO_2 cycloaddition reactions. From the viewpoint of chemical reaction engineering, a catalyst must exhibit three fundamental attributes-high efficiency, specificity, and reliability-to meet the stringent requirements of industrial applications. These attributes serve as the foundation for the industrial implementation of POPs. Achieving high-performance catalysts necessitates finely optimizing preparation conditions and meticulously designing functional monomers to develop tailored POPs with active catalytic sites. Nevertheless, this approach escalates the expenses associated with synthesizing porous organic polymers. Hence, substantial advancements are imperative before attaining industrial-scale production of these materials.

5. Conclusion and outlook

In summary, customized POPs are emerging as highly effective and readily recyclable heterogeneous catalysts adept at capturing carbon dioxide and converting it into cyclic carbonates in a moderate environment. Incorporating functional groups like triazine structures, H-bond donors, ionic liquids, and metal complexes into the POPs framework not only augments the efficiency of CO_2 capture and conversion but also facilitates the activation of epoxy compound ring-opening reactions. The triazine basic unit in covalent triazine frameworks can capture and activate CO_2, underscoring the importance of optimizing nitrogen content, preserving crystal structure integrity, and selecting appropriate functional groups during CTF synthesis. Precise design is essential to enhance material properties while maintaining structural integrity.[136-139] Introducing HBD modifications on POPs engenders synergistic effects in the activation pathway of epoxy compounds, thereby enhancing their ring-opening reactions.[140-142] Ionic liquid-modified POPs possess the ability to incorporate both anions and cations as a viable strategy to tailor ionic functionalities through either pre- or post-synthesis modifications.[143-146] Metal complex-modified POPs can catalyze reactions under ambient conditions, attributable to interactions involving metal-oxygen coordination bonds.[147-149] The preceding analysis clearly indicates that, although catalysts designed for the activation of epoxides or the fixation and conversion of CO_2 are capable of facilitating these processes, their catalytic efficacy requires enhancement to satisfy industrial requirements. Consequently, developing catalysts proficient in activating both epoxide and CO_2 simultaneously warrants the attention of researchers. For instance, increasing the CO_2 adsorption ability of POPs facilitates the concurrent capture and conversion of CO_2.[150] The catalytic activity of POPs has been augmented by preparing high-performance bifunctional catalysts capable of simultaneously activating CO_2 and promoting the ring opening of epoxides.[151]

Nonetheless, the advancement of metal complexes and ionic liquid-modified POPs remains nascent, and further research in this direction should be encouraged. From the viewpoint of driving the innovation and development of diverse POPs with expansive industrial potential, the research on POPs needs to focus on four aspects: simplicity of preparation method, industrial applicability of structure, operability of catalytic conditions, and recyclability of catalytic performance to meet the stringent requirements of industrial applications. Specifically, it is crucial to highlight that the stability and cycle numbers of the POPs are of paramount importance for practical industrial applications. Although most of the POPs reported in this article show good performance in single reactions, the long-term stability and recyclability over multiple cycles are essential for sustainable and cost-effective industrial processes. Future research should focus on developing catalysts that can maintain high performance over numerous cycles while minimizing structural degradation and loss of activity. The long-term stability and recyclability will pave the way for the large-scale application of POPs catalysts in CO_2 capture and conversion technologies. As the synthesis of porous organic polymers continues to innovate and advance, we confidently anticipate the emergence of more highly customized POPs catalysts in the near future. Given the exceptional properties, these innovative materials will significantly contribute to mitigating the greenhouse effect and promoting environmental sustainability.

Acknowledgements

The financial support from Ministry of Science and Technology, China (MOST 2024YFB4006704), Natural Science Foundation of Shaanxi Province (2023-JC-YB-370, 2024-JC-YBQN-0140) and Key R&D Program Projects in Shaanxi Province (2023JBGS-22) are gratefully acknowledged.

Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

References

[1] B. Li, N. Haneklaus, The role of renewable energy, fossil fuel consumption, urbanization and economic growth on CO_2 emissions in China, *Energy Reports*, 2021, **7**, 783-791, doi: 10.1016/j.egyr.2021.09.194.

[2] H. Zhu, S. Jiang, Innovating for cleaner skies: a study on the impact of China's national innovation demonstration zones on urban air quality from the perspective of energy consumption, *Energy Strategy Reviews*, 2024, **54**, 101438, doi: 10.1016/j.esr.2024.101438.

[3] P. Peng, A. Yu, J. Ren, F. Li, Electrolytic carbons from CO and their applications, *ES Energy & Environment*, 2018, **2**, 9-20, doi: 10.30919/esee8c205

[4] Y. Liu, B. Tang, Z. Wang, Y. Jiao, Q. Hou, Z. Dang, X. Hua, L. Wei, L. Wang, R. Wei, Enhanced dielectric performances of strontium barium titanate nanorod composites *via* improved

interfacial compatibility, *Journal of Colloid and Interface Science*, 2025, **680**, 85-95, doi: 10.1016/j.jcis.2024.11.088.

[5] H. Hong, L. Gao, Y. Zheng, X. Xing, F. Sun, T. Liu, V. Murugadoss, Z. Guo, M. Yang, H. Zhang, A path of multi-energy hybrids of concentrating solar energy and carbon fuels for low CO_2 emission, *ES Energy & Environment*, 2021, **13**, 1-7, doi: 10.30919/esee8c520.

[6] R. Wei, K. Liu, Y. Liu, Z. Wang, Y. Jiao, Q. Huo, X. Hua, L. Wang, X. Wang, Controlled distribution of MXene on the pore walls of polyarylene ether nitrile porous films for absorption-dominated electromagnetic interference shielding materials, *Small*, 2025, **21**, e2407142, doi: 10.1002/smll.202407142.

[7] S. P. Thota, P. P. Bag, P. V. Vadlani, S. K. Belliraj, Plant biomass derived multidimensional nanostructured materials: a green alternative for energy storage, *Engineered Science*, 2022, **18**, 31-38, doi: 10.30919/es8d664.

[8] R. Béres, M. Junginger, M. van den Broek, Assessing the feasibility of CO_2 removal strategies in achieving climate-neutral power systems: Insights from biomass, CO_2 capture, and direct air capture in Europe, *Advances in Applied Energy*, 2024, **14**, 100166, doi: 10.1016/j.adapen.2024.100166.

[9] Y. Lin, T. A. Gunawan, C. Isaac, H. Luo, F. Cheng, E. D. Larson, C. Greig, L. Ma, Z. Li, A preliminary assessment of CO_2 capture, transport, and storage network for China's steel sector, *Journal of Cleaner Production*, 2024, **454**, 142280, doi: 10.1016/j.jclepro.2024.142280.

[10] Y. Fu, Y. Xu, Z. Zeng, A. R. Ibrahim, J. Yang, S. Yang, Y. Xie, Y. Hong, Y. Su, H. Wang, Y. Wang, L. Peng, J. Li, W. L. Queen, Mesoporous poly(ionic liquid)s with dual active sites for highly efficient CO_2 conversion, *Green Energy & Environment*, 2023, **8**, 478-486, doi: 10.1016/j.gee.2021.05.013.

[11] Y. Cui, X. Wang, L. Dong, Y. Liu, S. Chen, J. Zhang, X. Zhang, Tunable and functional phosphonium-based deep eutectic solvents for synthesizing of cyclic carbonates from CO_2 and epoxides under mild conditions, *Journal of CO_2 Utilization*, 2023, **70**, 102442, doi: 10.1016/j.jcou.2023.102442.

[12] M. Shit, S. Paul, T. Chatterjee, B. Dutta, C. Sinha, Towards design of energy efficient semiconducting material: an example of 1D Cd(II)-2, 5-thiophene dicarboxylato co-ordination polymer, *ES Energy & Environment*, 2022, **16**, 40-46, doi: 10.30919/esee8c740.

[13] S. Qiao, H. Jin, A. Zuo, Y. Chen, Integration of enzyme and covalent organic frameworks: from rational design to applications, *Accounts of Chemical Research*, 2024, **57**, 93-105, doi: 10.1021/acs.accounts.3c00565.

[14] A. Karn, C. Yadav, A. Kumar Sahoo, J. Narasimha Moorthy, Porous organic polymer with free carboxylic acids (carboxy-POP) for heterogeneous catalytic one-pot synthesis of xanthenes and acridines, *ChemCatChem*, 2023, **15**, e202300727, doi: 10.1002/cctc.202300727.

[15] N. Li, B. Yao, X. Xiong, P. Zhu, L. Xi, Recent advances in adsorptive removal and photocatalytic reduction of Cr(VI) by porous organic polymers (POPs), *European Polymer Journal*, 2023, **200**, 112530, doi: 10.1016/j.eurpolymj.2023.112530.

[16] K. Z. Abdiyev, M. B. Zhursumbayeva, N. Z. Seitkaliyeva, G. K. Kussainova, M. N. Mohamad Ibrahim, D. N. Shakhmetova, M. Y. Yermaganbetov, Z. Toktarbay, Synthesis and characterization of N, N-dimethylacrylamide and [(3-methacryloyl-amino)propyl] trimethylammonium chloride copolymers: kinetics, reactivity, and biocidal properties, *Engineered Science*, 2024, **30**, 1217, doi: 10.30919/es1217.

[17] H. Zhong, Y. Su, X. Chen, X. Li, R. Wang, Imidazolium- and triazine-based porous organic polymers for heterogeneous catalytic conversion of CO_2 into cyclic carbonates, *ChemSusChem*, 2017, **10**, 4855-4863, doi: 10.1002/cssc.201701821.

[18] S. Ding, W. Wang, Covalent organic frameworks (COFs): from design to applications, *Chemical Society Reviews*, 2013, **42**, 548-568, doi: 10.1039/C2CS35072F.

[19] S. Tao, D. Jiang, Covalent organic frameworks for energy conversions: current status, challenges, and perspectives, *CCS Chemistry*, 2021, **3**, 2003-2024, doi: 10.31635/ccschem.020.202000491.

[20] S. Qi, G. Yu, D. Xue, X. Liu, X. Liu, L. Sun, Rigid supramolecular structures based on flexible covalent bonds: a fabrication mechanism of porous organic polymers and their CO_2 capture properties, *Chemical Engineering Journal*, 2020, **385**, 123978, doi: 10.1016/j.cej.2019.123978.

[21] S. Qi, Y. Liu, A. Peng, D. Xue, X. Liu, X. Liu, L. Sun, Fabrication of porous carbons from mesitylene for highly efficient CO_2 capture: a rational choice improving the carbon loop, *Chemical Engineering Journal*, 2019, **361**, 945-952, doi: 10.1016/j.cej.2018.12.167.

[22] N. Huang, P. Wang, D. Jiang, Covalent organic frameworks: a materials platform for structural and functional designs, *Nature Reviews Materials*, 2016, **1**, 16068, doi: 10.1038/natrevmats.2016.68.

[23] R. D. Prasad, N. R. Prasad, N. Prasad, S. R. Prasad, R. S. Prasad, R. B. Prasad, R. R. Prasad, R. G. Prasad, C. B. Desai, A. K. Vaidya, Y. I. Shaikh, G. M. Nazeruddin, V. Shaikh, R. S. Pande, P. M. Mamidpelliwar, R. N. Deshmukh, V. N. Patil, A. Samant, C. Chiplunkar, Z. Guo, P. Sarvalkar, A. A. Ramteke, A. D. Shaikh, A review on scattering techniques for analysis of nanomaterials and biomaterials, *Engineered Science*, 2024, **33**, 1332, doi: 10.30919/es1332.

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

[25] A. Dong, Y. Zhu, M. Ren, X. Sun, V. Murugadoss, Y. Yuan, J. Wen, X. Wang, Q. Chen, Z. Guo, N. Wang, Remarkably enhanced CO_2 uptake and uranium extraction by functionalization of cyano-bearing conjugated porous polycarbazoles, *Engineered Science*, 2019, **6**, 44-52, doi: 10.30919/es8d688.

[26] R. Wei, F. Gao, H. Hou, B. X. Ben, H. Yang, X. Zhang, Z. Guo, L. Wang, Triazine and urea constructed polyurea microsphere as a promising catalyst for CO_2 conversion to cyclic carbonates, *Journal of Environmental Chemical Engineering*,

2025, **13**, 116312, doi: 10.1016/j.jece.2025.116312.

[27] M. Yin, L. Wang, S. Tang, Amino-functionalized ionic-liquid-grafted covalent organic frameworks for high-efficiency CO_2 capture and conversion, *ACS Applied Materials & Interfaces*, 2022, **14**, 55674-55685, doi: 10.1021/acsami.2c18226.

[28] B. Guo, L. Liu, A. Li, X. Li, Y. Chang, Z. Jiao, M. Han, Insights into the effect of Ni doping on In_2S_3 for enhanced activity and selectivity of photocatalytic CO_2 reduction, *Journal of Alloys and Compounds*, 2024, **995**, 174741, doi: 10.1016/j.jallcom.2024.174741.

[29] S. Chanthee, C. Asavatesanupap, D. Sertphon, T. Nakkhong, N. Subjalearndee, M. Santikunaporn, Surface transformation of carbon nanofibers *via* co-electrospinning with natural rubber and Ni doping for carbon dioxide adsorption and supercapacitor applications, *Engineered Science*, 2023, **27**, 975, doi: 10.30919/es975.

[30] J. Wang, Y. Tian, S. Zhang, Y. Zhang, Chiral porous poly(ionic liquid)s: Facile one-pot, one-step synthesis and efficient heterogeneous catalysts for asymmetric epoxidation of olefins, *Applied Catalysis A: General*, 2022, **631**, 118477, doi: 10.1016/j.apcata.2021.118477.

[31] G. K. Dam, S. Let, V. Jaiswal, S. K. Ghosh, Urea-tethered porous organic polymer (POP) as an efficient heterogeneous catalyst for hydrogen bond donating organocatalysis and continuous flow reaction, *ACS Sustainable Chemistry & Engineering*, 2024, **12**, 3000-3011, doi: 10.1021/acssuschemeng.3c06108.

[32] M. Liu, B. Liu, L. Liang, F. Wang, L. Shi, J. Sun, Design of bifunctional NH_3I-Zn/SBA-15 single-component heterogeneous catalyst for chemical fixation of carbon dioxide to cyclic carbonates, *Journal of Molecular Catalysis A: Chemical*, 2016, **418**, 78-85, doi: 10.1016/j.molcata.2016.03.037.

[33] N. Pannucharoenwong, S. Echaroj, K. Duanguppama, S. Hemathulin, C. Turakarn, K. Chaiphet, P. Rattanadecho, Addition of hydrocarbon components to products in the catalytic pyrolysis of sawdust by natural catalysts, *Engineered Science*, 2024, **31**, 1194, doi: 10.30919/es1194.

[34] L. Wang, Z. Feng, Q. Hou, Z. Dang, Y. Yu, C. Yang, B. Tang, Q. Zhou, X. Hua, R. Wei, T. X. Liu, Quaternary ammonium salt functionalized copper phthalocyanine-graphene oxide hybrids for cocatalyst-free carbon dioxide cycloaddition, *Advanced Composites and Hybrid Materials*, 2024, **8**, 40, doi: 10.1007/s42114-024-01081-4.

[35] Y. Liu, S. Hu, Y. Zhi, T. Hu, Z. Yue, X. Tang, S. Shan, Non-metal and non-halide enol PENDI catalysts for the cycloaddition of CO_2 and epoxide, *Journal of CO_2 Utilization*, 2022, **63**, 102130, doi: 10.1016/j.jcou.2022.102130.

[36] H. Büttner, J. Steinbauer, T. Werner, Synthesis of cyclic carbonates from epoxides and carbon dioxide by using bifunctional one-component phosphorus-based organocatalysts, *ChemSusChem*, 2015, **8**, 2655-2669, doi: 10.1002/cssc.201500612.

[37] R. Luo, M. Chen, X. Liu, W. Xu, J. Li, B. Liu, Y. Fang, Recent advances in CO_2 capture and simultaneous conversion into cyclic carbonates over porous organic polymers having accessible metal sites, *Journal of Materials Chemistry A*, 2020, **8**, 18408-18424, doi: 10.1039/D0TA06142E.

[38] D. Yang, Y. Tao, X. Ding, B. Han, Porous organic polymers for electrocatalysis, *Chemical Society Reviews*, 2022, **51**, 761-791, doi: 10.1039/d1cs00887k.

[39] X. Zhang, J. Wang, Y. Bian, H. Lv, B. Qiu, Y. Zhang, R. Qin, D. Zhu, S. Zhang, D. Li, S. Wang, W. Mai, Y. Li, T. Li, A novel conjugated microporous polymer microspheres comprising cobalt porphyrins for efficient catalytic CO_2 cycloaddition under ambient conditions, *Journal of CO_2 Utilization*, 2022, **58**, 101924, doi: 10.1016/j.jcou.2022.101924.

[40] G. Li, X. Zhou, Z. Wang, CO_2 capture and conversion to di-functional cyclic carbonates in metalloporphyrin-based porous polyaminals with large surface area, *Microporous and Mesoporous Materials*, 2022, **343**, 112119, doi: 10.1016/j.micromeso.2022.112119.

[41] G. M. Eder, D. A. Pyles, E. R. Wolfson, P. L. McGrier, A ruthenium porphyrin-based porous organic polymer for the hydrosilylative reduction of CO_2 to formate, *Chemical Communications*, 2019, **55**, 7195-7198, doi: 10.1039/C9CC02273B.

[42] J. Zhang, Y. Zhao, X. Guo, C. Chen, C. Dong, R. Liu, C. Han, Y. Li, Y. Gogotsi, G. Wang, Single platinum atoms immobilized on an MXene as an efficient catalyst for the hydrogen evolution reaction, *Nature Catalysis*, 2018, **1**, 985-992, doi: 10.1038/s41929-018-0195-1.

[43] J. Zhang, Y. Liu, C. Sun, P. Xi, S. Peng, D. Gao, D. Xue, Accelerated hydrogen evolution reaction in CoS_2 by transition-metal doping, *ACS Energy Letters*, 2018, **3**, 779-786, doi: 10.1021/acsenergylett.8b00066.

[44] J. Hou, Y. Wu, B. Zhang, S. Cao, Z. Li, L. Sun, Rational design of nanoarray architectures for electrocatalytic water splitting, *Advanced Functional Materials*, 2019, **29**, 1808367, doi: 10.1002/adfm.201808367.

[45] N. Bektenov, A. Baidullayeva, T. Chalov, T. Jumadilov, S. Kanat, Modified adsorbents based on glycidyl methacrylate copolymers for the removal of copper and lead ions from wastewater, *Engineered Science*, 2024, **31**, 1237 doi: 10.30919/es1237.

[46] Y. Liu, J. Zhang, Y. Li, Q. Qian, Z. Li, Y. Zhu, G. Zhang, Manipulating dehydrogenation kinetics through dual-doping Co3N electrode enables highly efficient hydrazine oxidation assisting self-powered H_2 production, *Nature Communications*, 2020, **11**, 1853, doi: 10.1038/s41467-020-15563-8.

[47] Z. Feng, B. Tang, K. Liu, Q. Hou, Z. Dang, C. Yang, X. Hua, Q. Yu, L. Wang, R. Wei, One-pot synthesis of copper phthalocyanine polymer: an efficient CO_2 fixation catalyst, *Materials Today Communications*, 2024, **41**, 110875, doi: 10.1016/j.mtcomm.2024.110875.

[48] Z. Wu, J. Wang, L. Liu, S. Guo, J. Li, X. Zhang, C2-phenyl-substituted benzimidazolium-based covalent organic framework as efficient catalyst for CO_2 conversion without solvents, metals, and cocatalysts, *Science China Chemistry*, 2024, **67**, 551-557, doi: 10.1007/s11426-023-1754-5.

[49] Y. Du, G. Ding, Y. Wang, B. Xu, S. Zhang, Construction of

a PPIL@COF core–shell composite with enhanced catalytic activity for CO_2 conversion, *Green Chemistry*, 2021, **23**, 2411-2419, doi: 10.1039/D1GC00267H.

[50] X. Zheng, P. Cui, Y. Qian, G. Zhao, X. Zheng, X. Xu, Z. Cheng, Y. Liu, S. X. Dou, W. Sun, Multifunctional active-center-transferable platinum/lithium cobalt oxide heterostructured electrocatalysts towards superior water splitting, *Angewandte Chemie*, 2020, **59**, 14533-14540, doi: 10.1002/anie.202005241.

[52] P. Zhou, X. Lv, Y. Gao, Z. Cui, Y. Liu, Z. Wang, P. Wang, Z. Zheng, Y. Dai, B. Huang, Enhanced electrocatalytic HER performance of non-noble metal nickel by introduction of divanadium trioxide, *Electrochimica Acta*, 2019, **320**, 134535, doi: 10.1016/j.electacta.2019.07.046.

[53] H. Zhong, J. Gao, R. Sa, S. Yang, Z. Wu, R. Wang, Carbon dioxide conversion upgraded by host-guest cooperation between nitrogen-rich covalent organic framework and imidazolium-based ionic polymer, *ChemSusChem*, 2020, **13**, 6050, doi: 10.1002/cssc.202002411.

[54] X. Liao, B. Pei, R. Ma, L. Kong, X. Gao, J. He, X. Luo, J. Lin, Hypercrosslinked ionic polymers with high ionic content for efficient conversion of carbon dioxide into cyclic carbonates, *Catalysts*, 2022, **12**, 62, doi: 10.3390/catal12010062.

[55] J. Li, Y. Han, T. Ji, N. Wu, H. Lin, J. Jiang, J. Zhu, Porous metallosalen hypercrosslinked ionic polymers for cooperative CO_2 cycloaddition conversion, *Industrial & Engineering Chemistry Research*, 2020, **59**, 676-684, doi: 10.1021/acs.iecr.9b05304.

[56] H. Ouyang, K. Song, I. Hussain, B. Tan, Amine-impregnated porous organic polymers with chemisorption sites for highly efficient CO_2 chemical conversion under ambient conditions, *ACS Applied Polymer Materials*, 2023, **5**, 3574-3584, doi: 10.1021/acsapm.3c00235.

[57] J. Kim, S. N. Kim, H. G. Jang, G. Seo, W. S. Ahn, CO_2 cycloaddition of styrene oxide over MOF catalysts, *Applied Catalysis A: General*, 2013, **453**, 175-180, doi: 10.1016/j.apcata.2012.12.018.

[58] D. Ji, L. Peng, J. Shen, M. Deng, Z. Mao, L. Tan, M. Wang, R. Xiang, J. Wang, S. S. Ahmad Shah, Inert V_2O_3 oxide promotes the electrocatalytic activity of Ni metal for alkaline hydrogen evolution, *Chemical Communications*, 2019, **55**, 3290-3293, doi: 10.1039/C8CC10128K.

[59] W. Wang, Y. Wang, C. Li, L. Yan, M. Jiang, Y. Ding, State-of-the-art multifunctional heterogeneous POP catalyst for cooperative transformation of CO_2 to cyclic carbonates, *ACS Sustainable Chemistry & Engineering*, 2017, **5**, 4523-4528, doi: 10.1021/acssuschemeng.7b00947.

[60] X. Bai, Z. Su, J. Wei, L. Ma, S. Duan, N. Wang, X. Zhang, J. Li, Zinc(II)porphyrin-based porous ionic polymers (PIPs) as multifunctional heterogeneous catalysts for the conversion of CO_2 to cyclic carbonates, *Industrial & Engineering Chemistry Research*, 2022, **61**, 5093-5102, doi: 10.1021/acs.iecr.2c00161.

[61] S. Rat, A. Chavez-Sanchez, M. Jerigov , D. Cruz, M. Antonietti, Acetic anhydride polymerization as a pathway to functional porous organic polymers and their application in acid-base catalysis, *ACS Applied Polymer Materials*, 2021, **3**, 2588-2597, doi: 10.1021/acsapm.1c00202.

[62] Y. Chen, F. Li, L. Liu, Y.-H. Zhou, Implanting multi-functional ionic liquids into MOF nodes for boosting CO_2 cycloaddition under solventless and cocatalyst-free conditions, *Chemical Engineering Journal*, 2024, **490**, 151657, doi: 10.1016/j.cej.2024.151657.

[63] X. Liu, N. Li, Y. Zhang, Y. Hao, Z. Zhu, T. Chang, S. Liu, X. Wang, S. Qin, Synthesis of PEI grafted poly (ionic liquid)s: optimization and kinetics modeling of effective CO_2 fixation reactions, *ChemistrySelect*, 2024, **9**, e202303765, doi: 10.1002/slct.202303765.

[64] X. Du, Z. Liu, Z. Li, X. Yuan, C. Li, M. Zhang, Z. Zhang, X. Hu, K. Guo, Aminocyclopropenium as a novel hydrogen bonding organocatalyst for cycloaddition of carbon disulfide and epoxide to prepare cyclic dithiocarbonate, *RSC Advances*, 2024, **14**, 10378-10389, doi: 10.1039/D4RA00937A.

[65] Y. Luo, F. Chen, H. Zhang, J. Liu, N. Liu, Catalysis conversion of carbon dioxide and epoxides by tetrahydroxydiboron to prepare cyclic carbonates, *The Journal of Organic Chemistry*, 2023, **88**, 15717-15725, doi: 10.1021/acs.joc.3c01702.

[66] Y. Qu, L. Lu, Z. Li, J. He, H. Yu, N. Shi, B. Liu, J. Sun, J. Huang, K. Guo, Polybenzoxazine bearing phosphonium and phenol functions catalyzed the cycloaddition of CO_2 into epoxide reactions, *Polymer*, 2023, **282**, 126128, doi: 10.1016/j.polymer.2023.126128.

[67] P. Qin, C. Zhang, Y. Guo, D. Zhang, Q. Liu, Y. Li, H. Song, Z. Lv, Hydroxyl and amino dual-functionalized core-shell molecular sieves featuring hydrogen bond donor groups for efficient CO_2 cycloaddition, *Journal of Colloid and Interface Science*, 2024, **656**, 68-79, doi: 10.1016/j.jcis.2023.11.088.

[68] J. Wang, J. Chen, D. Li, J. Liu, Z. Shi, L. Xu, Y. Zang, A novel bifunctional metalloporphyrin-based hyper-crosslinked ionic polymer as heterogeneous catalyst for efficiently converting CO_2 into cyclic carbonates, *Journal of Materials Science*, 2024, **59**, 1235-1252, doi: 10.1007/s10853-023-09280-y.

[69] M. Li, L. Shi, Y. Liu, S. Li, W. Cui, W. Li, Y. Zhi, S. Shan, Y. Miao, A dual-ionic hyper-crosslinked polymer for efficient CO_2 fixation and conversion, *Chemical Engineering Journal*, 2024, **481**, 148550, doi: 10.1016/j.cej.2024.148550.

[70] M. Fu, W. Ding, Q. Zhao, Z. Xu, W. Hua, Y. Li, Z. Yang, L. Dong, Q. Su, W. Cheng, Dual hydrogen bond donor functionalized hierarchical porous poly(ionic liquid)s for efficient CO_2 fixation into cyclic carbonates, *Separation and Purification Technology*, 2024, **344**, 127174, doi: 10.1016/j.seppur.2024.127174.

[71] J. Huang, S. Peng, Y. Du, J. Feng, J. Li, J. Su, G. Zhang, Quaternary ammonium-functionalized mesoporous covalent organic frameworks for effective catalytic CO_2 cycloaddition, *ACS Applied Polymer Materials*, 2024, **6**, 4607-4614, doi: 10.1021/acsapm.4c00164.

[72] L. Ding, B. Yao, F. Li, S. Shi, N. Huang, H. Yin, Q. Guan, Y. Dong, Ionic liquid-decorated COF and its covalent composite aerogel for selective CO_2 adsorption and catalytic conversion, *Journal of Materials Chemistry A*, 2019, **7**, 4689-4698, doi:

10.1039/C8TA12046C.

[73] Y. Zhao, Y. Zhao, J. Qiu, Z. Li, H. Wang, J. Wang, Facile grafting of imidazolium salt in covalent organic frameworks with enhanced catalytic activity for CO_2 fixation and the Knoevenagel reaction, *ACS Sustainable Chemistry & Engineering*, 2020, **8**, 18413-18419, doi: 10.1021/acssuschemeng.0c05294.

[74] J. Cao, W. Shan, Q. Wang, X. Ling, G. Li, Y. Lyu, Y. Zhou, J. Wang, Ordered porous poly(ionic liquid) crystallines: spacing confined ionic surface enhancing selective CO_2 capture and fixation, *ACS Applied Materials & Interfaces*, 2019, **11**, 6031-6041, doi: 10.1021/acsami.8b19420.

[75] J. Roeser, K. Kailasam, A. Thomas, Covalent triazine frameworks as heterogeneous catalysts for the synthesis of cyclic and linear carbonates from carbon dioxide and epoxides, *ChemSusChem*, 2012, **5**, 1793-1799, doi: 10.1002/cssc.201200091.

[76] P. Katekomol, J. Roeser, M. Bojdys, J. Weber, A. Thomas, Covalent triazine frameworks prepared from 1, 3, 5-tricyanobenzene, *Chemistry of Materials*, 2013, **25**, 1542-1548, doi: 10.1021/cm303751n.

[77] Y. Li, L. Yang, L. Sun, L. Ma, W. Deng, Z. Li, Chemical fixation of carbon dioxide catalyzed *via* covalent triazine frameworks as metal free heterogeneous catalysts without a cocatalyst, *Journal of Materials Chemistry A*, 2019, **7**, 26071-26076, doi: 10.1039/C9TA07266G.

[78] K. Wang, L. Yang, X. Wang, L. Guo, G. Cheng, C. Zhang, S. Jin, B. Tan, A. Cooper, Covalent triazine frameworks *via* a low-temperature polycondensation approach, *Angewandte Chemie*, 2017, **56**, 14149-14153, doi: 10.1002/anie.201708548.

[79] M. Liu, Q. Huang, S. Wang, Z. Li, B. Li, S. Jin, B. Tan, Crystalline covalent triazine frameworks by *in situ* oxidation of alcohols to aldehyde monomers, *Angewandte Chemie*, 2018, **57**, 11968-11972, doi: 10.1002/anie.201806664.

[80] V. M. Rangaraj, K. S. K. Reddy, G. N. Karanikolos, Ionothermal synthesis of phosphonitrilic-core covalent triazine frameworks for carbon dioxide capture, *Chemical Engineering Journal*, 2022, **429**, 132160, doi: 10.1016/j.cej.2021.132160.

[81] W. Dai, L. Chen, S. Yin, W. Li, Y. Zhang, S. Luo, C. Au, High-efficiency synthesis of cyclic carbonates from epoxides and CO_2 over hydroxyl ionic liquid catalyst grafted onto cross-linked polymer, *Catalysis Letters*, 2010, **137**, 74-80, doi: 10.1007/s10562-010-0346-8.

[82] C. Liu, L. Shi, J. Zhang, J. Sun, One-pot synthesis of pyridine-based ionic hyper-cross-linked polymers with hierarchical pores for efficient CO_2 capture and catalytic conversion, *Chemical Engineering Journal*, 2022, **427**, 131633, doi: 10.1016/j.cej.2021.131633.

[83] Y. Du, X. Yang, Y. Wang, P. Guan, R. Wang, B. Xu, Immobilization poly(ionic liquid)s into hierarchical porous covalent organic frameworks as heterogeneous catalyst for cycloaddition of CO_2 with epoxides, *Molecular Catalysis*, 2022, **520**, 112164, doi: 10.1016/j.mcat.2022.112164.

[84] D. Jia, L. Ma, Y. Wang, W. Zhang, J. Li, Y. Zhou, J. Wang, Efficient CO_2 enrichment and fixation by engineering micropores of multifunctional hypercrosslinked ionic polymers, *Chemical Engineering Journal*, 2020, **390**, 124652, doi: 10.1016/j.cej.2020.124652.

[85] W. Zhang, F. Ma, L. Ma, Y. Zhou, J. Wang, Imidazolium-functionalized ionic hypercrosslinked porous polymers for efficient synthesis of cyclic carbonates from simulated flue gas, *ChemSusChem*, 2020, **13**, 341-350, doi: 10.1002/cssc.201902952.

[86] K. Hu, Y. Tang, J. Cui, Q. Gong, C. Hu, S. Wang, K. Dong, X. Meng, Q. Sun, F. Xiao, Location matters: cooperativity of catalytic partners in porous organic polymers for enhanced CO_2 transformation, *Chemical Communications*, 2019, **55**, 9180-9183, doi: 10.1039/c9cc05051e.

[87] B. Jiang, J. Liu, W. Xiong, M. Weng, J. An, Y. Fan, L. Zheng, G. Yang, Z. Zhang, A halogen-free hyper-crosslinked ionic polymer for efficient multi-conversion of CO_2 into carbonates under mild conditions, with a combination of theoretical study, *Chemical Engineering Journal*, 2023, **476**, 146873, doi: 10.1016/j.cej.2023.146873.

[88] Q. Guo, S. Zhang, W. Gong, Azo-bridged hydroxyl-rich porous pillar [5] arene polymers for efficient carbon dioxide conversion, *Journal of Polymer Science*, 2024, **62**, 1664-1672, doi: 10.1002/pol.20230263.

[89] Y. Wan, L. Wang, L. Wen, Amide-functionalized organic cationic polymers toward enhanced catalytic performance for conversion of CO_2 into cyclic carbonates, *Journal of CO_2 Utilization*, 2022, **64**, 102174, doi: 10.1016/j.jcou.2022.102174.

[90] Z. Dai, Y. Bao, J. Yuan, J. Yao, Y. Xiong, Different functional groups modified porous organic polymers used for low concentration CO_2 fixation, *Chemical Communications*, 2021, **57**, 9732-9735, doi: 10.1039/d1cc03178c.

[91] T. Liu, R. Xu, J. Yi, J. Liang, X. Wang, P. Shi, Y. Huang, R. Cao, Imidazolium-based cationic covalent triazine frameworks for highly efficient cycloaddition of carbon dioxide, *ChemCatChem*, 2018, **10**, 2036-2040, doi: 10.1002/cctc.201800023.

[92] J. Chen, L. Jiang, W. Wang, Z. Shen, S. Liu, X. Li, Y. Wang, Constructing highly porous carbon materials from porous organic polymers for superior CO_2 adsorption and separation, *Journal of Colloid and Interface Science*, 2022, **609**, 775-784, doi: 10.1016/j.jcis.2021.11.091.

[93] Q. Xue, P. Wang, L. Cheng, Y. Wei, Y. Wang, J. Lin, Z. Zhang, C. Fang, H. Li, J. Ding, H. Wan, G. Guan, Triazole-based COF tightly hugging ionic liquids through interactions of hydrogen bonds for enhanced atmospheric CO_2 conversion, *Separation and Purification Technology*, 2025, **352**, 128175, doi: 10.1016/j.seppur.2024.128175.

[94] L. Wang, M. Yin, R. Li, S. Tang, Hydroxyl-functionalized ionic liquid-modified covalent organic frameworks for efficient CO_2 cycloaddition conversion, *Molecular Catalysis*, 2024, **564**, 114331, doi: 10.1016/j.mcat.2024.114331.

[95] W. Wang, C. Li, L. Yan, Y. Wang, M. Jiang, Y. Ding, Ionic liquid/Zn-PPh_3 integrated porous organic polymers featuring multifunctional sites: highly active heterogeneous catalyst for cooperative conversion of CO_2 to cyclic carbonates, *ACS Catalysis*, 2016, **6**, 6091-6100, doi: 10.1021/acscatal.6b01142.

[96] Y. Zhang, H. Hu, J. Ju, Q. Yan, V. Arumugam, X. Jing, H.

Cai, Y. Gao, Ionization of a covalent organic framework for catalyzing the cycloaddition reaction between epoxides and carbon dioxide, *Chinese Journal of Catalysis*, 2020, **41**, 485-493, doi: 10.1016/S1872-2067(19)63487-X.

[97] X. Liao, Z. Wang, Z. Li, L. Kong, W. Tang, Z. Qin, J. Lin, Tailoring hypercrosslinked ionic polymers with high ionic density for rapid conversion of CO_2 into cyclic carbonates at low pressure, *Chemical Engineering Journal*, 2023, **471**, 144455, doi: 10.1016/j.cej.2023.144455.

[98] R. Sani, T. K. Dey, M. Sarkar, P. Basu, S. M. Islam, A study of contemporary progress relating to COF materials for CO_2 capture and fixation reactions, *Materials Advances*, 2022, **3**, 5575-5597, doi: 10.1039/D2MA00143H.

[99] Q. Yan, H. Liang, S. Wang, H. Hu, X. Su, S. Xiao, H. Xu, X. Jing, F. Lu, Y. Gao, Immobilization of ionic liquid on a covalent organic framework for effectively catalyzing cycloaddition of CO_2 to epoxides, *Molecules*, 2022, **27**, 6204, doi: 10.3390/molecules27196204.

[100] B. Jiang, J. Liu, G. Yang, Z. Zhang, Efficient conversion of CO_2 into cyclic carbonates under atmospheric by halogen and metal-free poly(ionic liquid)s, *Chinese Journal of Chemical Engineering*, 2023, **55**, 202-211, doi: 10.1016/j.cjche.2022.05.018.

[101] T. Ying, X. Tan, Q. Su, W. Cheng, L. Dong, S. Zhang, Polymeric ionic liquids tailored by different chain groups for the efficient conversion of CO_2 into cyclic carbonates, *Green Chemistry*, 2019, **21**, 2352-2361, doi: 10.1039/c9gc00010k.

[102] J. Liu, G. Zhao, O. Cheung, L. Jia, Z. Sun, S. Zhang, Highly porous metalloporphyrin covalent ionic frameworks with well-defined cooperative functional groups as excellent catalysts for CO_2 cycloaddition, *Chemistry*, 2019, **25**, 9052-9059, doi: 10.1002/chem.201900992.

[103] W. Zhou, W. Deng, X. Lu, Metallosalen covalent organic frameworks for heterogeneous catalysis, *Interdisciplinary Materials*, 2024, **3**, 87-112, doi: 10.1002/idm2.12140.

[104] T. Wang, Z. Mu, X. Ding, B. Han, Functionalized COFs with quaternary phosphonium salt for versatilely catalyzing chemical transformations of CO_2, *Chemical Research in Chinese Universities*, 2022, **38**, 446-455, doi: 10.1007/s40242-022-1495-1.

[105] X. Gu, B. Wang, Y. Pang, H. Zhu, R. Wang, T. Chen, Y. Li, X. Yan, Crown ether-based covalent organic frameworks for CO_2 fixation, *New Journal of Chemistry*, 2023, **47**, 2040-2044, doi: 10.1039/D2NJ05372A.

[106] Y. Li, J. Zhang, K. Zuo, Z. Li, Y. Wang, H. Hu, C. Zeng, H. Xu, B. Wang, Y. Gao, Covalent organic frameworks for simultaneous CO_2 capture and selective catalytic transformation, *Catalysts*, 2021, **11**, 1133, doi: 10.3390/catal11091133.

[107] Y. Pang, B. Wang, X. Gu, H. Shen, X. Yan, Y. Li, L. Chen, Hydroxy-rich covalent organic framework for the efficient catalysis of the cycloaddition of CO_2, *Langmuir*, 2023, **39**, 16721-16730, doi: 10.1021/acs.langmuir.3c01719.

[108] S. Wang, K. Song, C. Zhang, Y. Shu, T. Li, B. Tan, A novel metalporphyrin-based microporous organic polymer with high CO_2 uptake and efficient chemical conversion of CO_2 under ambient conditions, *Journal of Materials Chemistry A*, 2017, **5**, 1509-1515, doi: 10.1039/C6TA08556C.

[109] Y. Chen, R. Luo, Q. Xu, J. Jiang, X. Zhou, H. Ji, Charged metalloporphyrin polymers for cooperative synthesis of cyclic carbonates from CO_2 under ambient conditions, *ChemSusChem*, 2017, **10**, 2534-2541, doi: 10.1002/cssc.201700536.

[110] H. Li, X. Feng, P. Shao, J. Chen, C. Li, S. Jayakumar, Q. Yang, Synthesis of covalent organic frameworks *via in situ* salen skeleton formation for catalytic applications, *Journal of Materials Chemistry A*, 2019, **7**, 5482-5492, doi: 10.1039/C8TA11058A.

[111] F. Zhou, Q. Deng, N. Huang, W. Zhou, W. Deng, CO_2 fixation into cyclic carbonates by a Zn-salen based conjugated microporous polymer, *ChemistrySelect*, 2020, **5**, 10516-10520, doi: 10.1002/slct.202001538.

[112] E. M. Maya, A. Valverde-Gonz lez, M. Iglesias, Conversion of CO_2 into chloropropene carbonate catalyzed by iron (II) phthalocyanine hypercrosslinked porous organic polymer, *Molecules*, 2020, **25**, 4598, doi: 10.3390/molecules25204598.

[113] R. Sharma, A. Bansal, C. N. Ramachandran, P. Mohanty, A multifunctional triazine-based nanoporous polymer as a versatile organocatalyst for CO_2 utilization and C-C bond formation, *Chemical Communications*, 2019, **55**, 11607-11610, doi: 10.1039/C9CC04975D.

[114] X. Liu, M. Chen, W. Xu, R. Luo, Potassium-ion-bound porous organic polymers having crown ether struts enable cooperative conversion of CO_2 to cyclic carbonates under mild conditions, *Journal of Polymer Science*, 2024, **62**, 1578-1587, doi: 10.1002/pol.20220638.

[115] M. Yin, L. Wang, S. Tang, Stable dicationic covalent organic frameworks manifesting notable structure-enhanced CO_2 capture and conversion, *ACS Catalysis*, 2023, **13**, 13021-13033, doi: 10.1021/acscatal.3c02796.

[116] O. Buyukcakir, S. H. Je, S. N. Talapaneni, D. Kim, A. Coskun, Charged covalent triazine frameworks for CO_2 capture and conversion, *ACS Applied Materials & Interfaces*, 2017, **9**, 7209-7216, doi: 10.1021/acsami.6b16769.

[117] Y. Zhao, H. Huang, H. Zhu, C. Zhong, Design and synthesis of novel pyridine-rich cationic covalent triazine framework for CO_2 capture and conversion, *Microporous and Mesoporous Materials*, 2022, **329**, 111526, doi: 10.1016/j.micromeso.2021.111526.

[118] W. Dai, Q. Li, J. Long, P. Mao, Y. Xu, L. Yang, J. Zou, X. Luo, Hierarchically mesoporous imidazole-functionalized covalent triazine framework: an efficient metal- and halogen-free heterogeneous catalyst towards the cycloaddition of CO_2 with epoxides, *Journal of CO_2 Utilization*, 2022, **62**, 102101, doi: 10.1016/j.jcou.2022.102101.

[119] J. Yin, T. Zhang, E. Schulman, D. Liu, J. Meng, Hierarchical porous metallized poly-melamine-formaldehyde (PMF) as a low-cost and high-efficiency catalyst for cyclic carbonate synthesis from CO_2 and epoxides, *Journal of Materials Chemistry A*, 2018, **6**, 8441-8448, doi: 10.1039/C8TA00625C.

[120] F. Tang, J. Hou, K. Liang, J. Huang, Y.-N. Liu, Melamine-based metal-chelating porous organic polymers for efficient CO_2

capture and conversion, *European Journal of Inorganic Chemistry*, 2018, **2018**, 4175-4180, doi: 10.1002/ejic.201800764.

[121] P. Puthiaraj, H. S. Kim, K. Yu, W.-S. Ahn, Triphenylamine-based covalent imine framework for CO_2 capture and catalytic conversion into cyclic carbonates, *Microporous and Mesoporous Materials*, 2020, **297**, 110011, doi: 10.1016/j.micromeso.2020.110011.

[122] K. Liu, Z. Xu, H. Huang, Y. Zhang, Y. Liu, Z. Qiu, M. Tong, Z. Long, G. Chen, *In situ*synthesis of pyridinium-based ionic porous organic polymers with hydroxide anions and pyridinyl radicals for halogen-free catalytic fixation of atmospheric CO_2, *Green Chemistry*, 2022, **24**, 136-141, doi: 10.1039/d1gc03465k.

[123] C. Guo, G. Chen, N. Wang, S. Wang, Y. Gao, J. Dong, Q. Lu, F. Gao, Construction of multifunctional histidine-based hypercrosslinked hierarchical porous ionic polymers for efficient CO_2 capture and conversion, *Separation and Purification Technology*, 2023, **312**, 123375, doi: 10.1016/j.seppur.2023.123375.

[124] H. Cai, J. Chen, K. Cai, F. Liu, T. Zhao, N-doped porous polymer with protonated ionic liquid sites for efficient conversion of CO_2 to cyclic carbonates, *Microporous and Mesoporous Materials*, 2023, **350**, 112447, doi: 10.1016/j.micromeso.2023.112447.

[125] H. Huang, C. Meng, Z. Xu, S. Wang, Y. Chang, S. Wang, J. Chen, Z. Long, G. Chen, Construction of silsesquioxane and phosphinum-based ionic porous hypercrosslinked polymers for efficient heterogeneous catalytic CO_2 cycloaddition, *Journal of Polymer Science*, 2024, **62**, 1686-1697, doi: 10.1002/pol.20230335.

[126] Y. Zhang, D. Yang, S. Qiao, B. Han, Synergistic catalysis of ionic liquid-decorated covalent organic frameworks with polyoxometalates for CO_2 cycloaddition reaction under mild conditions, *Langmuir*, 2021, **37**, 10330-10339, doi: 10.1021/acs.langmuir.1c01426.

[127] L. Ma, Z. Su, N. Wang, J. Li, A pyridinium-pyridinium zinc(II) porphyrin ion porous organic polymer as efficient heterogeneous catalyst for cycloaddition of epoxides with CO_2, *European Journal of Inorganic Chemistry*, 2023, **26**, e202200744, doi: 10.1002/ejic.202200744.

[128] D. Wang, L. Ma, D. Wang, R. Wang, N. Wang, J. Li, Zinc(II) porphyrin-based ionic porous organic polymers (iPOPs) having abundant dual-function sites for promoting cycloaddition of CO_2 with epoxides, *Applied Catalysis A: General*, 2023, **665**, 119380, doi: 10.1016/j.apcata.2023.119380.

[129] T. Liu, J. Liang, Y. Huang, R. Cao, A bifunctional cationic porous organic polymer based on a Salen-(Al) metalloligand for the cycloaddition of carbon dioxide to produce cyclic carbonates, *Chemical Communications*, 2016, **52**, 13288-13291, doi: 10.1039/C6CC07662A.

[130] J. Sun, W. Chen, H. Shen, M. Mu, X. Yin, Rational engineering of multifunctional ionic covalent organic frameworks for metal-free and efficient chemical fixation of CO_2 under mild conditions, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2023, **671**, 131554, doi: 10.1016/j.colsurfa.2023.131554.

[131] Y. Liu, S. Li, Y. Chen, T. Hu, M. Pudukudy, L. Shi, S. Shan, Y. Zhi, Modified melamine-based porous organic polymers with imidazolium ionic liquids as efficient heterogeneous catalysts for CO_2 cycloaddition, *Journal of Colloid and Interface Science*, 2023, **652**, 737-748, doi: 10.1016/j.jcis.2023.07.127.

[132] X. Lin, Z. Guo, Y. Wu, J. Yuan, Y. Liao, W. Zhang, Ionic conjugated microporous polymers for cycloaddition of carbon dioxide to epoxides, *Macromolecular Materials and Engineering*, 2024, **309**, 2300218, doi: 10.1002/mame.202300218.

[133] W. Yu, S. Gu, Y. Fu, S. Xiong, C. Pan, Y. Liu, G. Yu, Carbazole-decorated covalent triazine frameworks: Novel nonmetal catalysts for carbon dioxide fixation and oxygen reduction reaction, *Journal of Catalysis*, 2018, **362**, 1-9, doi: 10.1016/j.jcat.2018.03.021.

[134] S. Ravi, P. Puthiaraj, D. W. Park, W. S. Ahn, Cycloaddition of CO_2 and epoxides over a porous covalent triazine-based polymer incorporated with Fe_3O_4, *New Journal of Chemistry*, 2018, **42**, 12429-12436, doi: 10.1039/C8NJ01965G.

[135] S. Sarkar, S. Ghosh, R. Sani, J. Seth, A. Khan, S. M. Islam, Covalent immobilization of quaternary ammonium salts on covalent organic framework: sustainable intensification strategy for the synthesis of cyclic carbonates from CO_2, *ACS Sustainable Chemistry & Engineering*, 2023, **11**, 14422-14434, doi: 10.1021/acssuschemeng.3c03041.

[136] S. Xue, X. Ma, Y. Wang, G. Duan, C. Zhang, K. Liu, S. Jiang, Advanced development of three-dimensional covalent organic frameworks: Valency design, functionalization, and applications, *Coordination Chemistry Reviews*, 2024, **504**, 215659, doi: 10.1016/j.ccr.2024.215659.

[137] H. Wang, L. Shi, Z. Qu, L. Zhang, X. Wang, Y. Wang, S. Liu, H. Ma, Z. Guo, Increasing donor-acceptor interactions and particle dispersibility of covalent triazine frameworks for higher crystallinity and enhanced photocatalytic activity, *ACS Applied Materials & Interfaces*, 2024, **16**, 2296-2308, doi: 10.1021/acsami.3c15536.

[138] X. Hu, Y. Guo, R. Sun, X. Wang, B. Tan, Crystalline covalent triazine frameworks manipulated by aliphatic amine modulator, *Science China Chemistry*, 2023, **66**, 2676-2682, doi: 10.1007/s11426-023-1700-9.

[139] L. Xia, H. Chen, W. Wang, X. Jia, D. Zhang, L. Wang, P. Wu, L. Li, J. Huang, Facet and dual vacancy engineering-boosting BiOBr for enhanced CO_2 and epoxide cycloaddition reaction under mild and cocatalyst-free conditions: Double substrate active sites and activated surface bromine ions synergy, *Journal of Materials Science & Technology*, 2024, **202**, 39-49, doi: 10.1016/j.jmst.2024.03.029.

[140] H. Luo, S. Wang, X. Meng, G. Yuan, X. Song, Z. Liang, A hollow viologen-based porous organic polymer for the catalytic cycloaddition of CO_2, *Materials Chemistry Frontiers*, 2023, **7**, 2277-2285, doi: 10.1039/D3QM00137G.

[141] Y. Zhang, Q. Wang, Q. Chen, X. Li, Y. Li, M. Kang, Q. Li, J. Wang, A new boron modified carbon nitride metal-free catalyst for the cycloaddition of CO_2 and bisepoxides, *Applied Catalysis A: General*, 2024, **675**, 119615, doi: 10.1016/j.apcata.2024.119615.

[142] N. Huang, G. Day, X. Yang, H. Drake, H.-C. Zhou, Engineering porous organic polymers for carbon dioxide capture, *Science China Chemistry*, 2017, **60**, 1007-1014, doi: 10.1007/s11426-017-9084-7.

[143] Z. T. Hlatshwayo, J. G. Doremus, P. L. McGrier, Hydrosilylative reduction of CO_2 to formate and methanol using a cobalt porphyrin-based porous organic polymer, *ChemCatChem*, 2022, **14**, e202200783, doi: 10.1002/cctc.202200783.

[144] Y. Bao, J. Liu, Y. Zhang, L. Zheng, J. Ma, F. Zhang, Y. Xiong, X. Meng, Z. Dai, F. Xiao, Porous organic polymers with diverse quaternary phosphonium units for chemical fixation of CO_2 with low concentration, *Fuel*, 2023, **331**, 125909, doi: 10.1016/j.fuel.2022.125909.

[145] S. Hao, Y. Liu, C. Shang, Z. Liang, J. Yu, CO_2 adsorption and catalytic application of imidazole ionic liquid functionalized porous organic polymers, *Polymer Chemistry*, 2017, **8**, 1833-1839, doi: 10.1039/C6PY02091G.

[146] H. Gao, Q. Li, S. Ren, Progress on CO_2 capture by porous organic polymers, *Current Opinion in Green and Sustainable Chemistry*, 2019, **16**, 33-38, doi: 10.1016/j.cogsc.2018.11.015.

[147] Y. Xie, T.Wang, X. Liu, K. Zou, W. Deng, Capture and conversion of CO_2 at ambient conditions by a conjugated microporous polymer, *Nature Communications*, 2013, **4**, 1960, doi: 10.1038/ncomms2960.

[148] W. He, M. Wen, L. Shi, R. Wang, F. Li, Porous polymeric metalloporphyrin obtained through Sonogashira coupling: Catalytic performance at CO_2 cycloaddition to epoxides, *Journal of Solid State Chemistry*, 2022, **309**, 122965, doi: 10.1016/j.jssc.2022.122965.

[149] L. Ding, B. Yao, W. Wu, Z. Yu, X. Wang, J. Kan, Y. Dong, Metalloporphyrin and ionic liquid-functionalized covalent organic frameworks for catalytic CO_2 cycloaddition *via* visible-light-induced photothermal conversion, *Inorganic Chemistry*, 2021, **60**, 12591-12601, doi: 10.1021/acs.inorgchem.1c01975.

[150] K. S. Song, P. W. Fritz, A. Coskun, Porous organic polymers for CO_2 capture, separation and conversion, *Chemical Society Reviews*, 2022, **51**, 9831-9852, doi: 10.1039/D2CS00727D.

[151] R. Luo, Y. Yang, K. Chen, X. Liu, M. Chen, W. Xu, B. Liu, H. Ji, Y. Fang, Tailored covalent organic frameworks for simultaneously capturing and converting CO_2 into cyclic carbonates, *Journal of Materials Chemistry A*, 2021, **9**, 20941-20956, doi: 10.1039/D1TA05428G.

Open Access