

Polymer-integrated Covalent Organic Frameworks (PolyCOFs): Covalent Organic Frameworks (COFs) Covalently Integrating Polymer for Advanced Applications

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Abstract Polymer-integrated covalent organic frameworks (polyCOFs) are a promising class of hybrid materials. They combine the well-ordered crystalline architectures and high porosity of conventional covalent organic frameworks (COFs) with the flexibility, processability, and mechanical robustness of the polymers. These hybrid materials are crafted by integrating polymer chains into COFs using a variety of approaches, including pre-synthetic, post-synthetic, and in-framework polymerization techniques. Such integration not only bolsters the structural stability of COFs, but also facilitates their dimensional expansion, thereby paving the way for their utilization across a broad spectrum of domains, including catalysis, energy storage, sensing, and biomedical applications. This feature article provides a comprehensive overview of the latest advancements in polyCOF synthesis, their inherent properties, and rapidly expanding applications, while also offering valuable insights into prospective avenues for further advancement of polyCOF materials.

Keywords Covalent organic frameworks (COFs); Polymers; Polymer-integrated covalent organic frameworks (polyCOFs)

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INTRODUCTION

Covalent organic frameworks (COFs), a newly emerging category of crystalline porous materials, were first documented by Côté *et al.* in 2005.^[1] Organic building units (such as monomers incorporating boronic acid, aldehyde, or amino groups) undergo conditional self-assembly through robust chemical bonds (including boronate esters, imines, hydrazones, and sp² carbon linkages) to form two-dimensional (2D) or three-dimensional (3D) ordered structures, known as COFs.^[2–5] Over the past two decades, COFs have garnered increasing interest compared with traditional porous materials owing to their distinctive structural and physicochemical attributes.^[6,7] These characteristics stem from the strong covalent bonding of lightweight elements (*e.g.*, H, B, O, N, and C), which endows COFs with well-ordered frameworks, adjustable pore dimensions, exceptional chemical stability, expansive surface areas, high porosity, and

superior crystallinity.^[8–11] As a result, COFs have exhibited considerable promise in tackling the challenges associated with environmental remediation and sensing,^[12–15] while also facilitating applications in catalysis,^[16,17] gas storage,^[18] energy conversion,^[19] drug delivery,^[20,21] and enzyme immobilization.^[22,23] Despite extensive research on the synthesis and diverse applications of COFs, their practical utility remains hindered by inherent limitations. Specifically, COFs are commonly synthesized as nano- or micro-scale crystalline powders, primarily because structural defects within their frameworks impede the growth of large single crystals or the formation of continuous films. Furthermore, conventional COFs typically demonstrate poor processability owing to their insolubility in common solvents and their inherent brittleness.^[24,25] Therefore, there is a pressing need to devise innovative strategies for functionalizing COFs and introducing additional synergistic properties to expand their practical applications.

In recent years, flexible and impermeable polymers have garnered growing interest owing to their outstanding thermal,^[26,27] electrical,^[28] and mechanical characteristics,^[29] making them promising for a wide range of applications.^[30–32] Consequently, the integration of polymers with COFs has been proposed as a potent tactic to overcome the inherent constraints of pristine COFs. Traditionally, the most prevalent

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method involves the direct blending of COF powders with polymers.^[33,34] However, this method is prone to inducing phase separation between COF particles and the polymer phase, which can compromise the structural integrity of COFs.^[35,36] Overall, this method fails to simultaneously achieve the high crystallinity and porosity of COFs along with the flexibility and processability necessary for macroscopic materials, frequently resulting in a compromise between the structural order and mechanical performance.^[37,38] Therefore, developing synthetic strategies for the direct fabrication of mechanically robust macroscopic COF materials remains a pivotal challenge in this field. These strategies must preserve the inherent porous structures of the COFs while improving their mechanical properties. To address these challenges, a novel material design strategy, polymer-integrated covalent organic frameworks (polyCOFs), has recently emerged.^[39] In this strategy, flexible polymer chains are covalently incorporated into the crystalline COF backbones to construct hybrid materials. These polyCOFs retained the intrinsic properties of COFs, including high crystallinity, large surface area, and ad-

justable pore sizes. Meanwhile, they exhibit polymer-derived advantages, such as flexibility, solution processability, and enhanced fracture toughness. These hybrid crystalline materials are referred to as polyCOFs. This synergistic integration marks a significant advancement in the realm of COF materials, enabling the creation of COFs that combine high mechanical strength and flexibility (Fig. 1). As a result, polyCOFs have demonstrated promising potential in applications such as precision separation, drug delivery, and flexible electronic devices, thereby substantially broadening the application horizon of COF-based materials.

STRUCTURAL CLASSIFICATION OF POLYCOFS

The incorporation of polymer chains into COFs has proven to be an effective approach for structural engineering.^[40,41] In this approach, polymer chains are introduced as flexible or semi-rigid linkers that covalently connect discrete COF building blocks, thereby converting the isolated domains into structurally continuous networks (Fig. 2). This design concept offers multiple

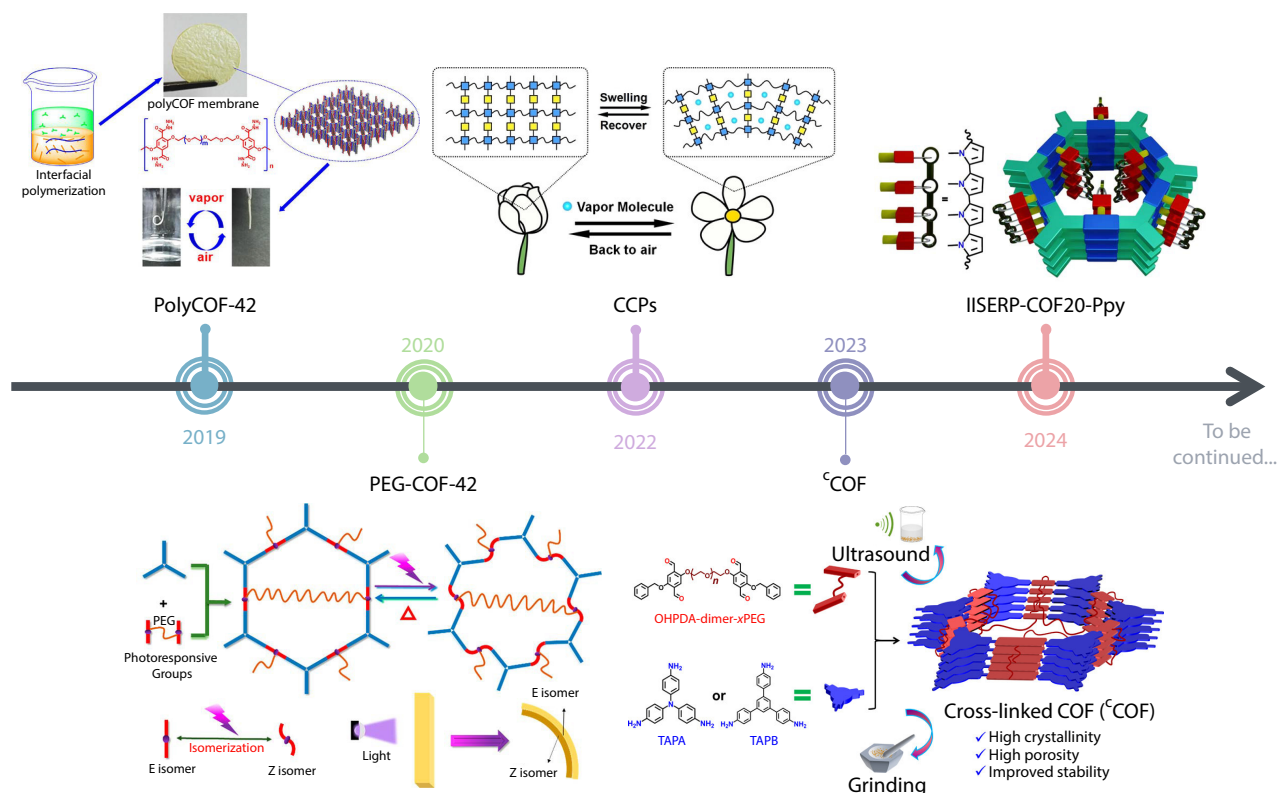


Fig. 1 Timeline for the development of representative polyCOFs.

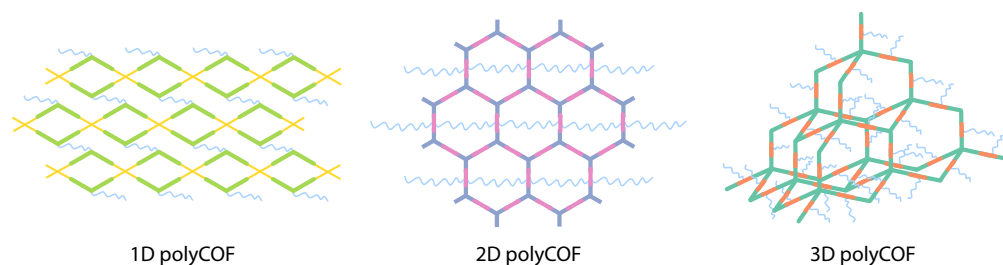


Fig. 2 Illustration of polyCOF with different dimensions.

benefits, including improved framework connectivity,^[42] adjustable mechanical flexibility or rigidity,^[43] and controlled modulation of the pore size,^[44] channel architecture,^[45] and interlayer interactions.^[46] Notably, polymer bridging promotes the dimensional expansion of COFs, facilitating the transition from lower-dimensional structures to multidimensional networks, while maintaining crystallinity and overall structural integrity. When polymer integration is considered in this context, a systematic design strategy can be developed to guide the creation of polyCOFs with customized mechanical, chemical, and multifunctional properties.

One-dimensional COF Backbones Linked with Polymers

One-dimensional covalent organic frameworks (1D COFs) are constructed from linear chain-like backbones formed *via* directional covalent coupling of monomeric building blocks.^[47,48] Such architectures exhibit pronounced structural anisotropy and are characterized by limited lateral connectivity. Although these ordered linear architectures can promote directional charge and mass transport, their practical application is typically constrained by weak interchain interactions, insufficient mechanical stability, and high susceptibility to structural degradation. To address these limitations, polymer chains can be incorporated to covalently bridge adjacent 1D COF backbones, thereby converting discrete chains into laterally interconnected networks. Such bridging can be achieved through covalent side-chain grafting, interchain crosslinking, or integration of conjugated polymer segments within the framework. Through lateral polymer crosslinking, quasi-two-dimensional architectures can be generated, resulting in significantly enhanced interchain cohesion. The incorporation of flexible polymers such as poly(ethylene glycol) (PEG) can enhance elasticity and improve processability.

Our group has introduced a new category of rigid-flexible coupling crystalline crosslinked polymers (CCPs), synthesized *via* an interfacial condensation reaction involving linear polymers (Fig. 3).^[49] This synthesis employed C_2 -symmetric 2,5-diethoxyterephthalohydrazide (DTH) as rigid segments and PEG as flexible linkers, along with rigid dialdehyde

monomers. Using this approach, freestanding membranes are directly produced at room temperature, in which rigid π - π stacked chain arrays are covalently interconnected by flexible linkers, resulting in an ordered, elastic, two-dimensional network structure derived from one-dimensional chain-like COFs. Significantly, this study marks an inaugural instance of crosslinked polymers demonstrating both high crystallinity and intrinsic porosity, thereby pioneering a novel synthetic paradigm.

Two-dimensional COF Backbones Linked with Polymers

Two-dimensional covalent organic frameworks (2D COFs) were constructed from extended planar sheets assembled *via* reticular chemistry. These sheets are generally stacked together *via* π - π interactions or van der Waals forces, resulting in layered architectures with precisely defined in-plane porosities.^[47,48] Although 2D COFs often exhibit high crystallinity and well-defined channels, their interlayer interactions are relatively weak, making them prone to delamination, interlayer slippage, and mechanical fragility.^[50,51] Polymer integration within 2D COFs can be accomplished using various rational design strategies. Covalent interlayer locking can be achieved by introducing reactive functional groups that promote the formation of polymers between adjacent layers. Alternatively, polymer chains can be polymerized within pore channels or covalently grafted onto the surface or edge sites, thereby enhancing both in-plane and out-of-plane structural connectivity.

Our group has previously reported the synthesis of layer-interlocked COFs (designated as ^{c} COFs) using a bottom-up condensation strategy.^[52] To execute this strategy, tetratopic aldehyde dimers linked with flexible PEG units of varying lengths were designed and synthesized as crosslinking monomers to react with 1,3,5-tris(4-aminophenyl)benzene (TAPB), yielding a series of crosslinked COFs named ^{c} COF-xPEG. This approach enabled, for the first time, the covalent interconnection of 2D COF layers into a quasi-three-dimensional integrated architecture. The resulting material maintained high crystallinity and permanent porosity, while displaying significantly improved structural stability, as demon-

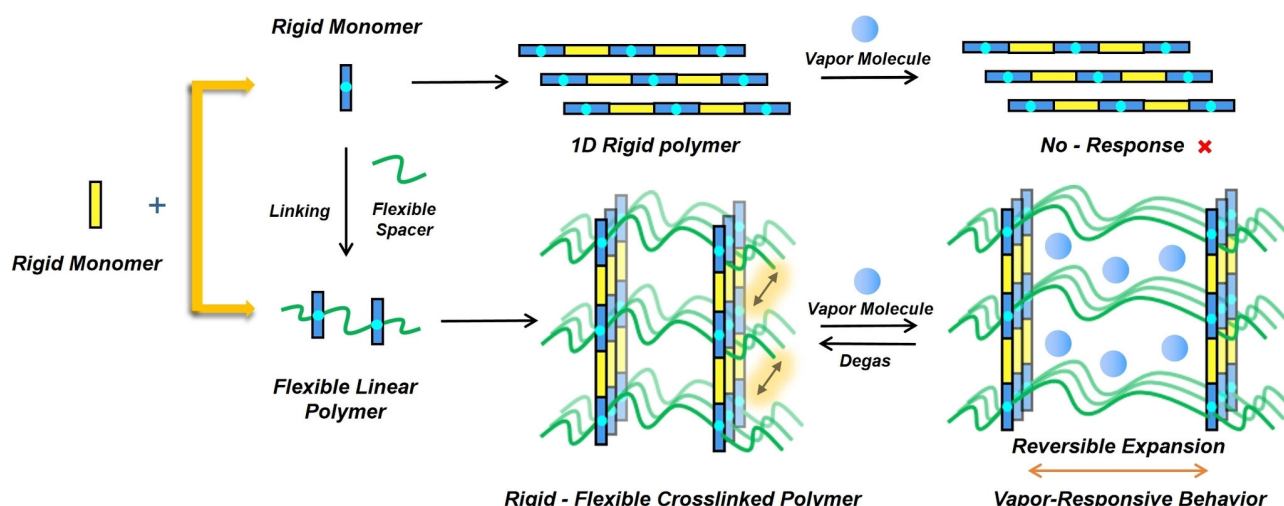


Fig. 3 Illustration of the strategy to construct crystalline crosslinked polymers (Reproduced with permission from Ref. [49]; Copyright (2022), Wiley-VCH GmbH).

strated by its resistance to exfoliation into nanosheets under ultrasonic treatment or mechanical grinding.

Three-dimensional COF Backbones Linked with Polymers

Three-dimensional covalent organic frameworks (3D COFs) are assembled from multivalent monomeric units covalently linked in all three spatial dimensions, creating fully extended network architectures.^[53,54] These structures typically demonstrate high structural rigidity, permanent porosity, and interconnected pore channels, which are advantageous for mass transfer and host-guest interactions.^[55,56] Despite these benefits, 3D COFs also have several inherent limitations. They are typically characterized by robust covalent backbones, and their high structural rigidity and densely crosslinked network morphology commonly results in poor processability and restricted structural tunability.^[57,58] Additionally, the lack of flexible components within the framework can result in brittleness and reduced adaptability to external stimuli, thereby restricting their practical use in dynamic or soft-material systems.^[59] The integration of polymer chains into 3D COFs has mainly been explored using post-synthetic grafting methods. In the currently reported systems, polymer chains are covalently attached to the surface or internal pore walls of pre-existing 3D COFs, allowing the introduction of additional functional groups without disrupting the crystalline structure.^[60] However, compared with their 1D and 2D counterparts, strategies for incorporating polymers into 3D COFs remain relatively limited. More diverse strategies, such as *in situ* polymerization within 3D frameworks or direct polymer participation during COF crystallization, remain largely unexplored. These strategies warrant further investigation to expand the possibilities of designing polyCOFs. The incorporation of polymers into 3D COFs is expected to offer several advantages. Specifically, the introduction of flexible polymers, such as PEG, can enhance dispersibility, improve biocompatibility, and impart surface functionality, which is particularly advantageous for biomedical applications.^[61,62] Furthermore, polymer grafting can improve interfacial compatibility with external environments and facilitate functional integration, thereby expanding the application range of 3D COFs. Although current research primarily focuses on PEG-based modifications, future efforts to incorporate a variety of functional polymers may unlock additional properties, including stimulus responsiveness, enhanced mechanical adaptability, and multifunctionality.

Across 1D, 2D, and 3D COF systems, polymer participation provides several overarching benefits.^[63–65] Mechanical robustness is significantly enhanced as brittle crystalline frameworks are transformed into resilient interconnected structures capable of withstanding mechanical deformation and repeated stress. Structural integrity is substantially reinforced, with polymer crosslinking reducing defect propagation and enhancing the resistance to solvent-induced degradation.^[66] Transport properties can also be precisely adjusted, as polymer incorporation allows for fine control over the pore size, channel continuity, and interfacial compatibility with guest species. Moreover, multifunctionality can be integrated into a single architecture by rationally selecting polymers with specific electronic, ionic, or catalytic functionalities, thereby simultaneously optimizing multiple performance metrics.^[67]

Future research on polyCOFs is expected to advance toward increasingly multidimensional hierarchically interconnected architectures. Rather than merely reinforcing existing frameworks, polymer engineering can be strategically employed to construct fully covalently locked multidimensional networks derived from lower-dimensional COF precursors.

SYNTHETIC STRATEGIES OF POLYCOFS

Based on the timing of polymer integration and covalent bond formation, chemically bonded polymer-COF systems can be generally categorized into three types: (i) pre-synthetic approaches, where linear polymers with reactive functional groups are pre-synthesized and directly incorporated into COF formation; (ii) post-synthetic approaches, involving the grafting of polymers onto pre-existing COF frameworks; and (iii) in-framework polymerization, which entails initiating topochemical polymerization of polymerizable units pre-installed on neighboring building blocks within layered COF structures.

Pre-synthetic Strategy

Using polymers as building blocks for COFs

Presynthetic strategies encompass the deliberate design and synthesis of linear polymers featuring reactive functional groups, such as aldehydes or amine groups, capable of reacting with COF precursors. These polymers serve as structural building blocks that directly engage in the covalent assembly of the COF framework, thereby facilitating the uniform integration of polymers during the crystallization process.^[68,69]

In 2019, our team pioneered the development of a novel class of freestanding flexible polyCOF membranes (Fig. 4a).^[39] We synthesized a PEGylated linear polymer incorporating DTH moieties within its backbone. The polymer was then subjected to a three-component condensation reaction with 1,3,5-triformylbenzene (TB) and DTH through interfacial polymerization at room temperature. The integration of PEG chains into the framework endowed the resulting polyCOF membranes with both the high crystallinity and porosity characteristics of COFs as well as the processability and mechanical properties of linear polymers. Subsequently, our team further refined the approach by employing a more feasible and straightforward method utilizing PEG-bridged DTH-dimers as the building blocks for COF-42 (Fig. 4b).^[70] In contrast to polyCOF-42, freestanding and uniform PEG-COF-42 membranes with excellent crystallinity were obtained through a two-component condensation reaction between the DTH dimer and TB, eliminating the need for a DTH monomer. Later, employing a similar methodology, Liu *et al.* designed and synthesized elastic porphyrin-based polyCOFs (designated as PP-PEG) through a reaction between pyrrole and dialdehyde precursors containing PEG chains. These membranes were subsequently utilized as solar evaporators in three-dimensional foams for solar steam generation (Fig. 4c).^[71] The incorporation of PEG chains effectively mitigated porphyrin aggregation and self-quenching, thereby enhancing photothermal conversion efficiency. By optimizing material hydrophilicity, PEG chain length, and reflector design, an impressive evaporation rate of up to 18.88 kg·m⁻²·h⁻¹ was achieved, offering a promising strategy for high-efficiency solar desalination.

Post-synthesis Strategy

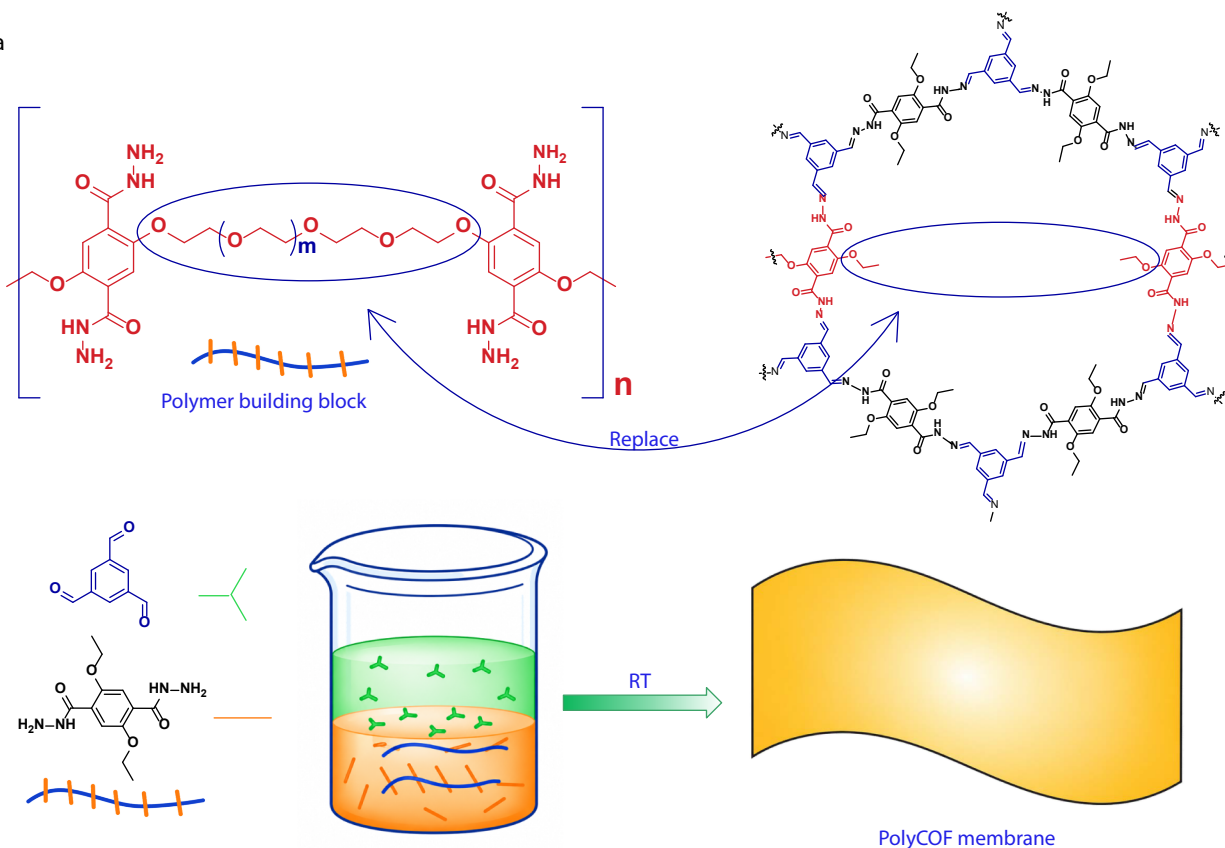
Grafting polymers onto existing COFs

In post-synthetic modification strategies, active sites are introduced onto pre-fabricated COFs, which possess well-ordered porous structures, *via* surface or pore-channel functionalization. Subsequently, polymer chains can be grafted onto the COF skeleton using reactions such as click chemistry or atom transfer radical polymerization.^[72,73] By varying the lengths of the grafted polymer chains, precise control over the pore size, surface chemistry, and interfacial interactions can be achieved, thereby optimizing the performance of the COFs for a wide

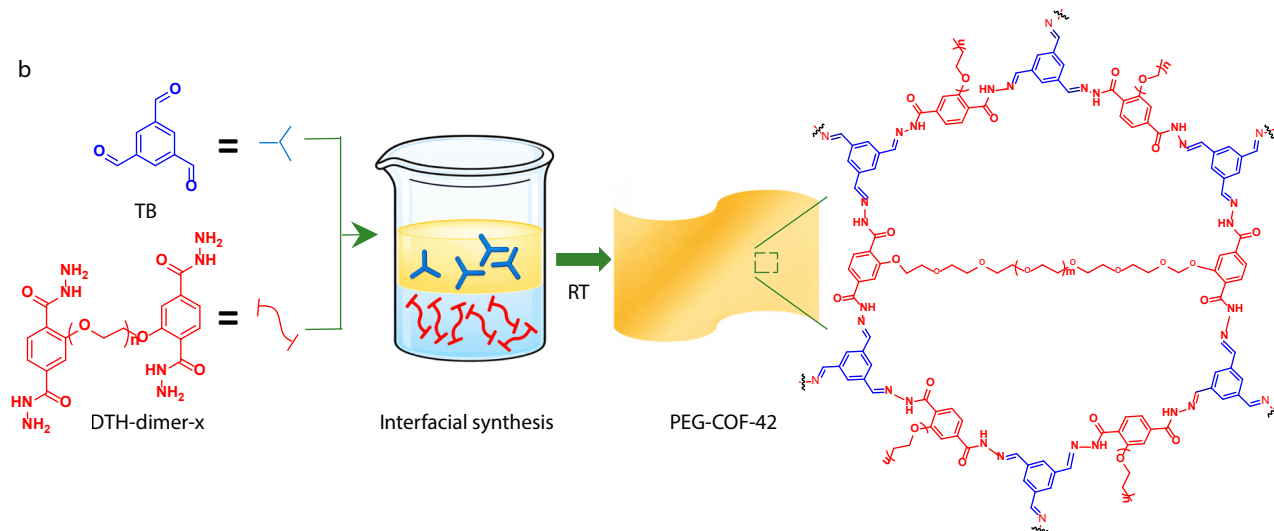
range of applications.^[74,75]

Ma *et al.* fabricated heterostructures using the asymmetrical monomer exchange (AME) approach applied to hollow COF nanoparticles (h-COF) (Fig. 5a).^[76] Initially, PEG and poly(*N*-isopropylacrylamide) (PNIPAM) were functionalized *via* grafting reactions involving amine or aldehyde groups, yielding methoxy polyethylene amine (mPEG-NH₂), methoxy polyethylene aldehyde (mPEG-CHO), and poly(NIPAM-DMEAm-Ald). Subsequently, the residual aldehyde or amine groups on the h-COF edges react with these amino- or aldehyde-functionalized polymers. The resulting hybrids exhibit-

a



b



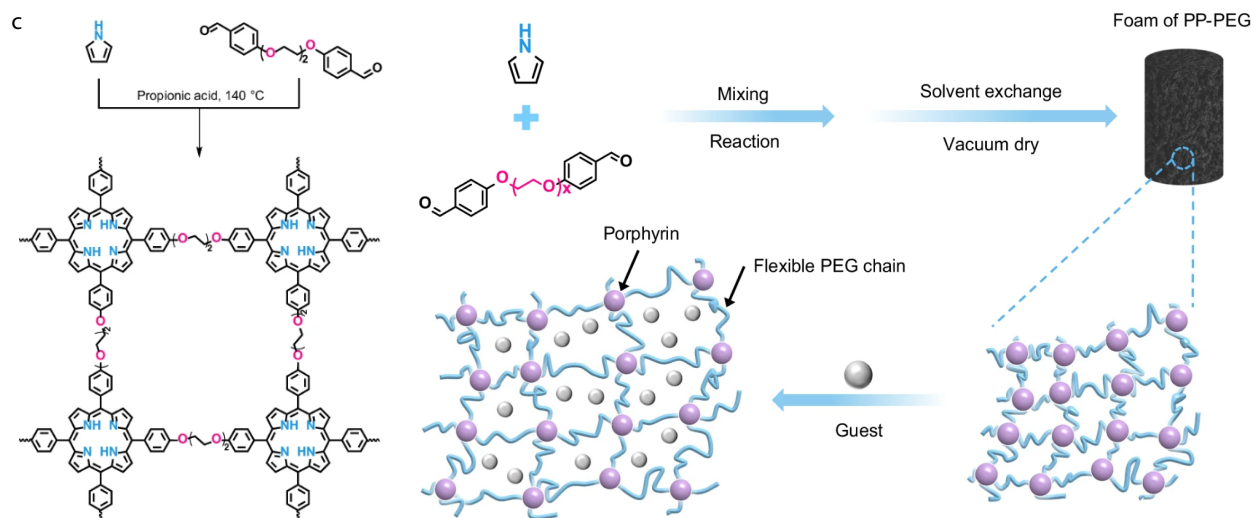
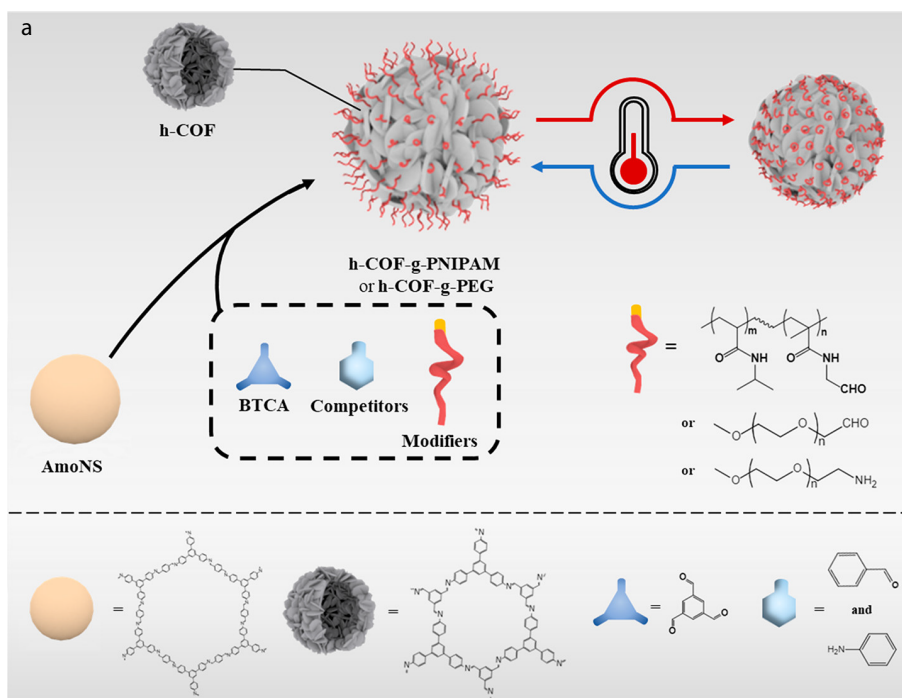


Fig. 4 (a) Illustration of the incorporation of polymer segments containing DTH into the COF skeleton, and of the resulting freestanding, flexible polyCOF membranes (Reproduced with permission from Ref. [39]; Copyright (2019), American Chemical Society); (b) Illustration of the formation of a PEG-COF-42 membrane *via* room-temperature interfacial polymerization (two-component condensation) between a PEG-bridged DTH dimer and TB (Reproduced with permission from Ref. [70]; Copyright (2020), American Chemical Society); (c) Illustration of the synthesis of PP-PEG foam *via* the reaction of pyrrole with a dialdehyde precursor containing PEG chains (Reproduced with permission from Ref. [71]; Copyright (2024), Open access).

ed excellent water dispersibility, rapid thermal responsiveness, and high capacity. Liu *et al.* synthesized PEGylated copper-porphyrin COF (PEG-CuP-COF) nanocatalysts by grafting flexible PEG chains onto CuP-COF through an amidation reaction (Fig. 5b).^[77] This modification significantly enhanced the stability of COFs under varying pH conditions and improved their functionality for tumor-targeting applications. PEGylation not only improved the biocompatibility and *in vivo* stability of the COFs but also facilitated better targeting to tumor sites when combined with Salmonella-mediated delivery. Ren *et al.* synthesized dual-fluorophore 3D COFs through a Schiff

base reaction between an amino-terminated Ru complex and 4,4',4'',4'''-(ethene-1,1,2,2-tetrayl)tetrabenzaldehyde (TPE-4CHO) in methanol (Fig. 5c).^[60] Tris(4,4'-diamino-2,2'-bipyridine) ruthenium(II) dichloride (RuR₃), featuring an octahedral structure, was synthesized as the vertex of the framework by coordinating dichloro(*p*-cymene)ruthenium(II) dimer with 4,4'-diamino-2,2'-bipyridine. PEGylation of the 3D-COFs was then performed using benzaldehyde-terminated mPEG-CHO (Mw about 2000 Da) *via* imine linkage with residual amino groups on the 3D-COFs, resulting in PEG-3D-COFs. The PEGylated COFs exhibited amphiphilicity and enhanced water dis-



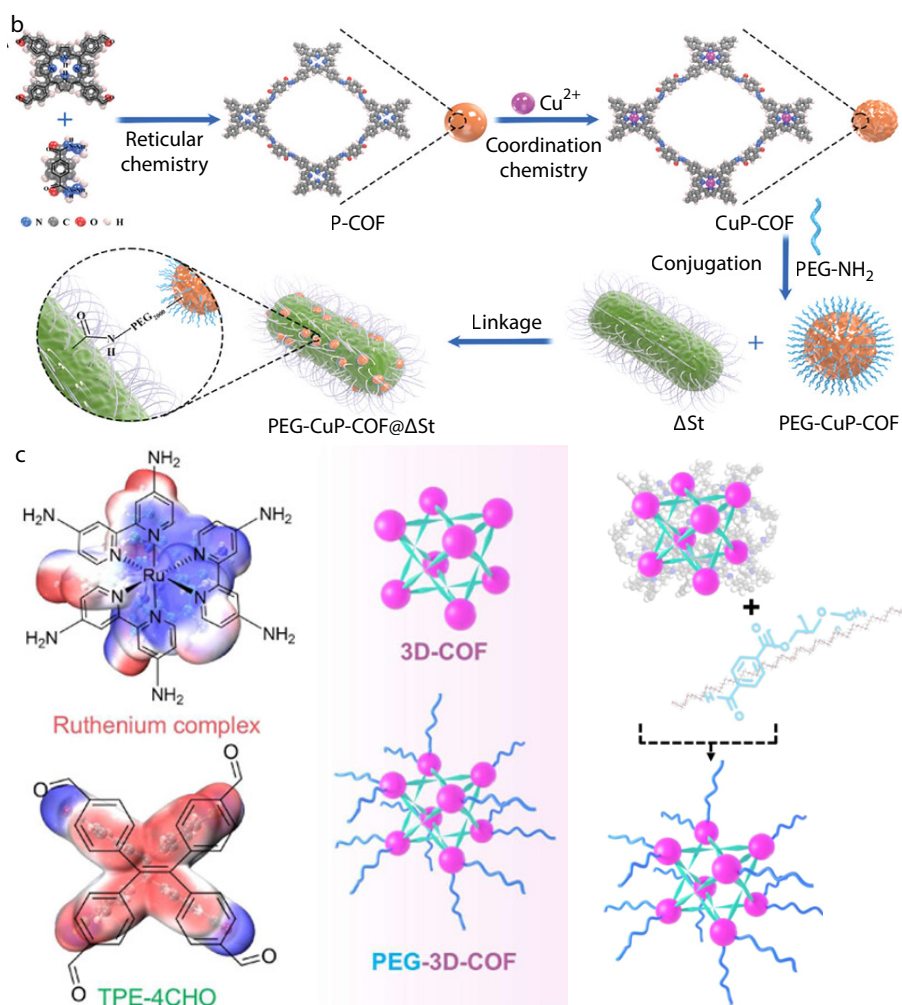


Fig. 5 (a) Illustration of the Transformation of Amorphous Nanoparticles (AmonS) to h-COF-g-PEG or h-COF-g PNIPAM with Temperature Responsiveness (Reproduced with permission from Ref. [76]; Copyright (2022), American Chemical Society); (b) Illustration of the synthesis of PEG-CuP-COF and PEG-CuP-COF@ΔSt (Reproduced with permission from Ref. [77]; Copyright (2024), Wiley-VCH GmbH); (c) Illustration of the synthesis and secondary assembly of PEGylated 3D-COFs (Reproduced with permission from Ref. [60]; Copyright (2025), American Chemical Society).

persion. This PEGylation not only facilitated the formation of submicrometer-sized superstructures but also enabled the COFs to display concentration-dependent morphology and photoluminescence properties.

In-framework Polymerization

In-framework polymerization strategies involve the strategic placement of pre-arranged polymerizable groups, either between or within the COF layers. When subjected to external stimuli, such as light or heat, topochemical polymerization is initiated, leading to the transformation of the original 2D COF architecture into a 3D crosslinked polymer network.^[78,79] This process facilitates the structural transition from an ordered crystalline framework to a continuous polymeric network.

To achieve a widespread and well-defined 2D-to-3D structural transformation of COFs through "molecular weaving" and obtain precise structural information, careful design of COF building units is of paramount importance. Jain *et al.* utilized polypyrrole (Ppy) chains as covalent "weaving threads" to crosslink adjacent 2D COF layers, thereby constructing a quasi-3D conductive framework (Fig. 6a).^[80] Initially, they synthesized a (3+2) nitro-functionalized framework, designated

COF20-NO₂, through a Schiff base condensation reaction between 2,4,6-triformylresorcinol and 2-nitro-1,4-phenylenediamine under solvothermal conditions. Starting with these nitro-functionalized COFs, they carried out a post-synthetic modification process that involved reduction to amine, followed by Clauson-Kaas pyrrole modification using dimethoxytetrahydrofuran (dimethoxy-THF), culminating in oxidative polymerization with iodine as the catalyst to produce COF20-Ppy.

Subsequently, Huang *et al.* developed a thiophene-porphyrin-based COF photocatalytic system comprising a COF with thiophene-modified pore walls and a quasi-3D COF (Fig. 6b).^[81] Initially, 2,5-di(thiophen-3-yl)benzene-1,4-dicarbaldehyde (DTBDA), which contains thiophene units at the pore walls, and 5,10,15,20-tetrakis(4-aminophenyl)-porphyrinato copper (Cu(TAP)) were used as building blocks. These were used to form COF-Th via Schiff base condensation under solvothermal conditions, followed by iodine-catalyzed oxidative polymerization to prepare COF-PTH. The integration of 2D COFs layers with conjugated polythiophene units not only enhanced the light absorption capability of the 3D COFs

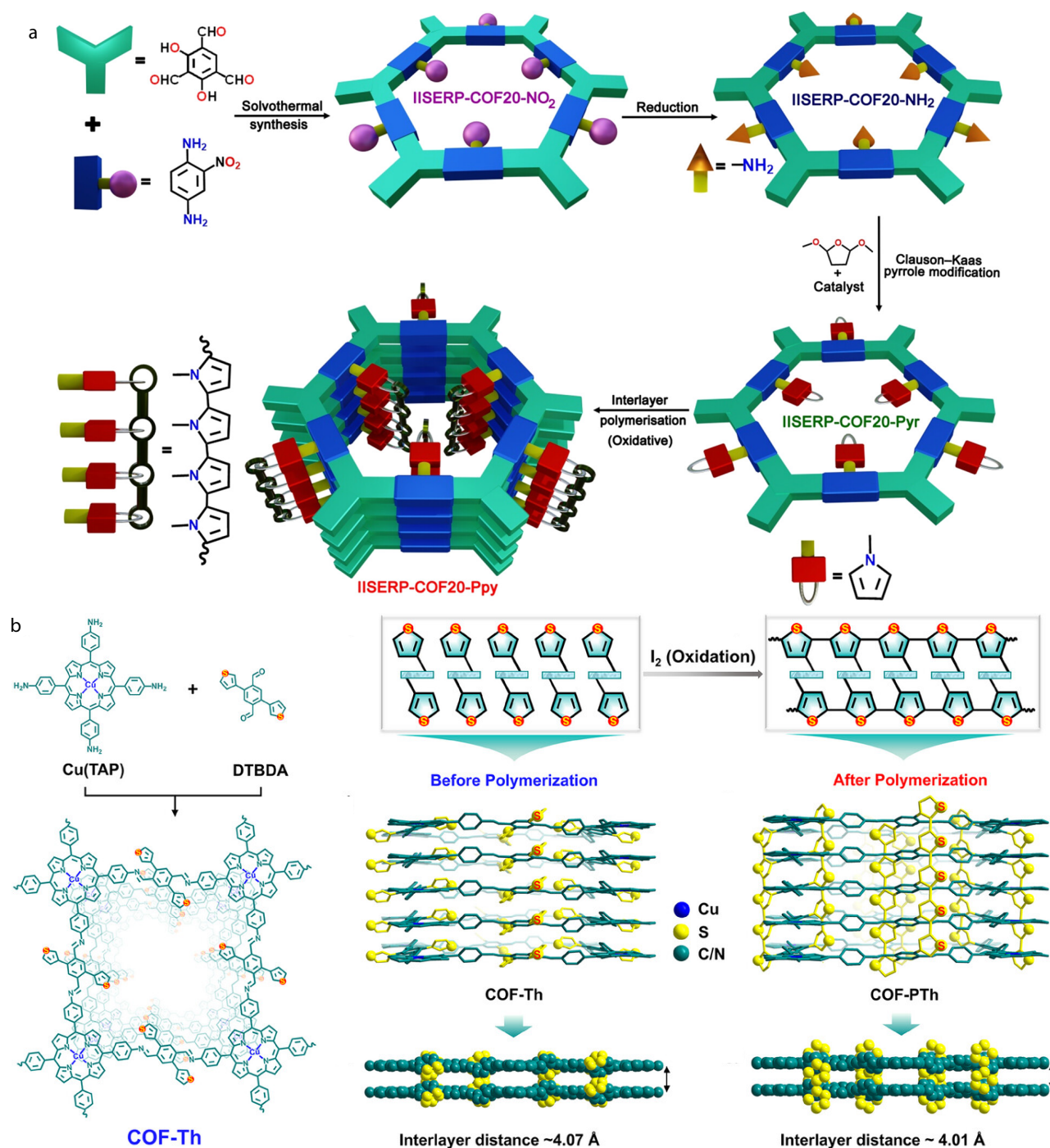


Fig. 6 (a) Illustration of the synthesis process and structural schematic of the COF in which polypyrrole chains are formed *via* reaction (Reproduced with permission from Ref. [80]; Copyright (2023), American Chemical Society); (b) Illustration of the synthesis and structural schematic of the COF formed *via in situ* generation of polythiophene chains (Reproduced with permission from Ref. [81]; Copyright (2025), Wiley-VCH GmbH).

but also increased their conductivity by four orders of magnitude. The combined structural and functional advantages of these 3D COFs result in exceptional performance in quinazolinone photosynthesis, demonstrating the double selectivity of their 2D counterparts.

APPLICATION OF POLYCOFS

By leveraging the structural benefits of a "rigid framework com-

bined with flexible functional chains," polyCOFs exhibit significant core values across multiple domains. Smart actuators demonstrate reversible deformation and energy conversion in response to stimuli, such as vapor, light, and humidity, making them ideal for applications in soft robotics and intelligent switches.^[74,82] In terms of energy storage and conversion, structural optimization improves conductivity and photothermal performance, facilitating applications such as supercapacitor energy storage, photocatalysis, and solar-powered desalination.

In the biomedical field, polyCOFs excel in targeted tumor therapy, precise biocatalysis, and non-invasive imaging diagnosis, achieving harmonious integration of diagnostic/therapeutic functions with green synthesis. Table 1 provides an overview of the applications of polyCOFs in these fields.

Smart Actuators

A key benefit of polyCOFs is their capacity to address the inherent brittleness of conventional COF materials, facilitating film formation and enabling stretchable processing.^[85,86] As responsive materials, polyCOFs can swiftly and reversibly alter their shapes in response to specific stimuli including light, electricity, heat, chemical vapors, and pH levels. This characteristic endows them with significant potential for application in sensors, artificial muscles, soft robotics, and intelligent switches. By integrating PEG segments into the COF framework, polyCOF membranes exhibited rapid, reversible bending upon exposure to various organic vapors, including ethanol, acetone, dichloromethane, and tetrahydrofuran.^[39] These actuators exhibit outstanding performance, featuring a high bending curvature, rapid response times (forming a closed loop within approximately 4 s upon exposure to ethanol vapor), and excellent cyclic stability (withstanding over 20 cycles without fatigue). Practical demonstrations include their use as "artificial arms" capable of lifting objects up to 8.0 mm in height and enabling "sit-up" motions in assembled dolls, highlighting their potential in soft robotics and intelligent manipulators (Fig. 7a). PolyCOFs have also been innovatively developed into photoresponsive artificial muscles by incorporating photochromic acylhydrazone groups into COF skeletons.^[70] These actuators respond quickly to UV light (370 nm), bend within 20 s to achieve a bending angle (θ) of 30°, and exhibit reversible recovery upon exposure to

blue light (440 nm) or heating (100 °C). Additionally, these materials retain their vapor-responsive properties, enabling multi-stimulus responsiveness (light + vapor) (Fig. 7b). Advanced polyCOF systems have been further extended to humidity-responsive actuation. Through a rigid-flexible coupling design that uses COFs as a rigid skeleton and PEG as a flexible, humidity-sensitive component, the resulting membranes can detect subtle humidity fluctuations (e.g., fingertip moisture) with a response time of 3 s and undergo reversible bending.^[82] Notably, these actuators exhibited autonomous self-oscillation behavior above the water surface, driven by spatial humidity gradients (Fig. 7c). When paired with piezoelectric films (e.g., PVDF), the self-oscillating motion can convert mechanical energy into electrical energy, achieving continuous power output for over 48 h with a peak voltage of 0.61 V, thus providing a novel approach for self-sustained energy transduction.

Energy Storage and Conversion

PolyCOFs have recently emerged as highly promising platforms for energy-related applications, effectively overcoming the inherent limitations of conventional 2D COFs, notably, their poor interlayer charge transport and restricted conductivity.^[87] The quasi-3D polyCOFs, crafted by covalently knitting 2D COF layers with Ppy chains, demonstrate a remarkable increase in conductivity, from 10^{-9} S·m⁻¹ to 10^{-2} S·m⁻¹.^[80] This enhancement was attributed to the formation of polaron states and the creation of extended conjugation bridges. This innovative structural engineering approach enables the material to achieve a significantly enhanced areal capacitance in symmetric solid-state supercapacitors, which is approximately six times higher than that of the original 2D COF, while maintaining excellent electrochemical durability, as evidenced by a 75% capacitance retention af-

Table 1 Applications of polyCOFs.

Application	PolyCOFs	Synthesis method	Research fields	Key performance indicators	Ref.
Smart actuators	polyCOF-42	Pre-synthesis (hydrazone-linked)	Soft robotics and intelligent manipulators	Ethanol vapor response time: about 4 s; cyclic stability: >20 cycles; lifting height: 8.0 mm	[39]
	PEG-COF-42	Presynthesis (hydrazone-linked)	Photoresponsive artificial muscle	UV response: 20 s; bending angle: 30°; reversible recovery (440 nm light/100 °C heating)	[70]
	PEG-COF-x	Pre-synthesis (hydrazone-linked)	Lifting robot, smart electricity switch and self-oscillating actuators	Humidity response: 3 s; reversible bending; continuous output: >48 h; peak voltage: 0.61 V	[82]
Energy storage and conversion	IISERP-COF20-Ppy	In-framework polymerization (imine-linked)	Supercapacitor	Conductivity increased from 10^{-9} S·m ⁻¹ to 10^{-2} S·m ⁻¹ ; areal capacitance: about 6 times higher; 75% retention after 5000 cycles	[80]
	COF-PTH	In-framework polymerization (imine-linked)	Photocatalysts	Conductivity enhanced by 4 orders of magnitude; 2× selectivity in quinazolinone photosynthesis	[81]
	PP-PEG	Pre-synthesis (imine-linked)	Highly efficient solar steam evaporation	Solar absorption: >98%; evaporation rate: 4.89 kg·m ⁻² ·h ⁻¹ (1 sun); 18.88 kg·m ⁻² ·h ⁻¹ with reflector	[71]
Catalysis	iCOFcap-1/2	Pre-synthesis (hydrazone-linked)	Photoenzymatic reduction of CO ₂	Multienzyme immobilization; high enzyme retention; excellent recyclability	[83]
	COFcap-2	Pre-synthesis (hydrazone-linked)	Nitrogen fixation and conversion to chiral amines	Tandem N ₂ fixation/chiral amine synthesis; enantiomeric excess: >99%; recyclable catalyst	[84]
Biomedical field	PEG-CuP-COF	Post-synthesis (hydrazone-linked)	Tumor therapy	pH stability enhancement; improved <i>in vivo</i> biostability	[77]
	PEG-3D-COF	Post-synthesis (imine-linked)	Biomedical imaging	<i>In vivo</i> fluorescence visualization; strain-responsive sensing	[60]

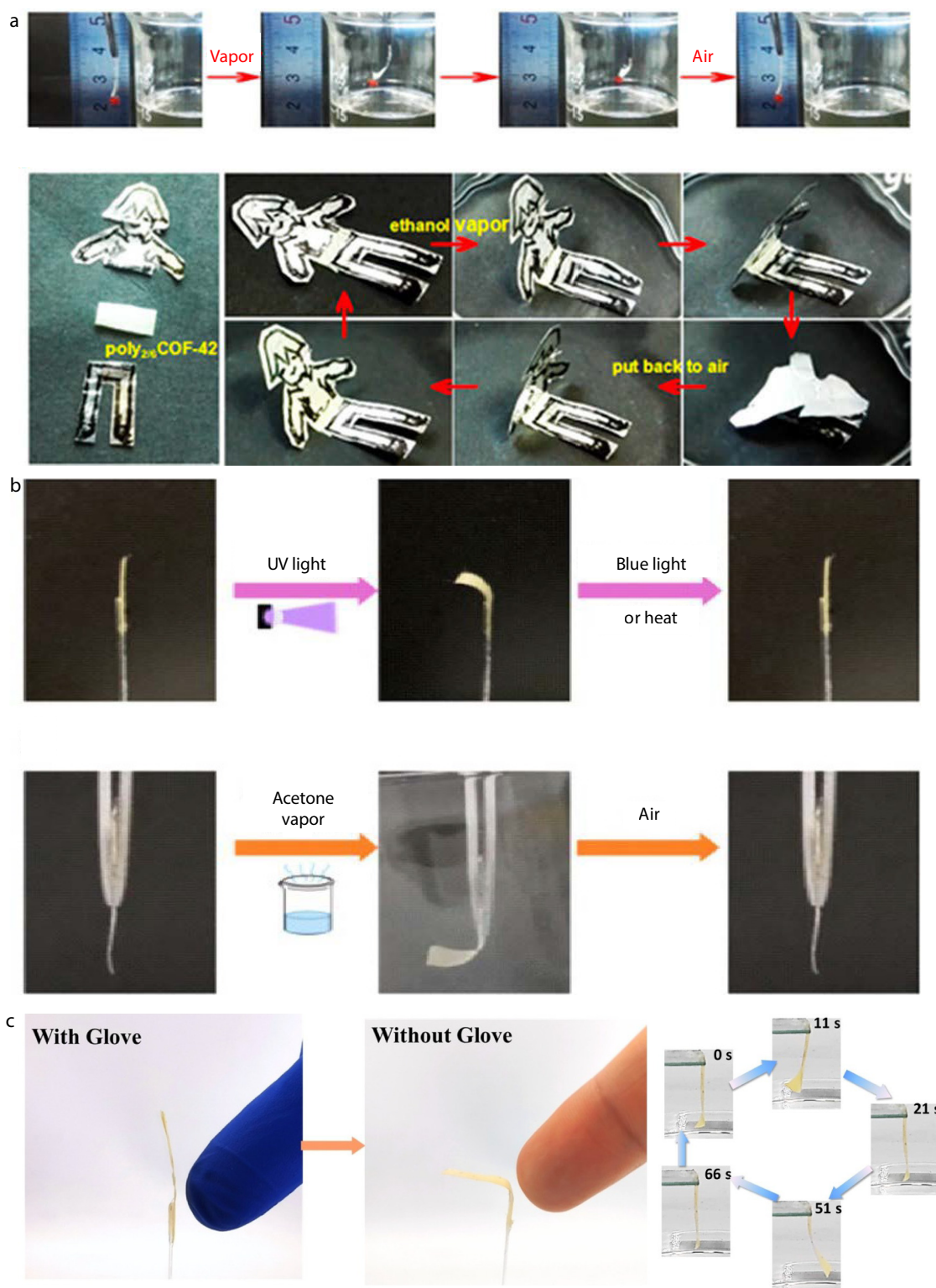


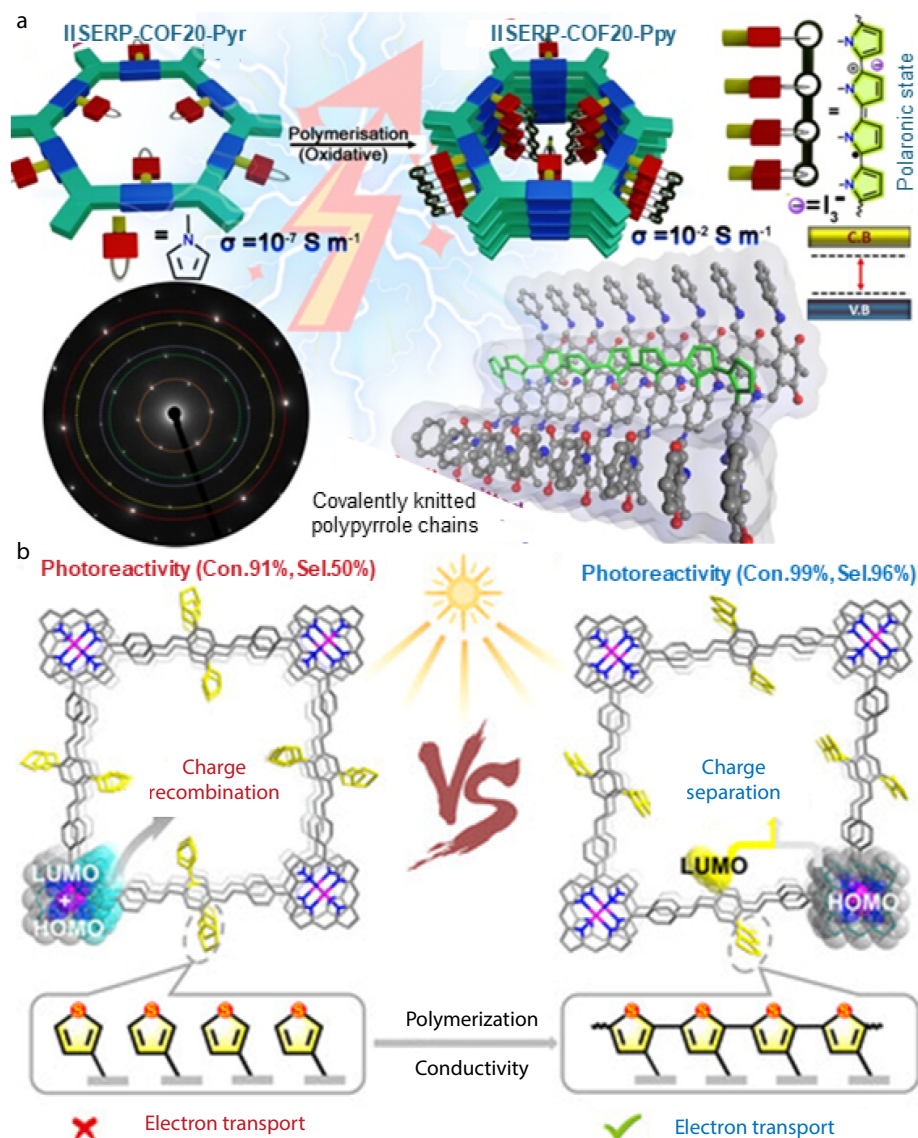
Fig. 7 (a) Optical images of the $\text{poly}_{2/6}\text{COF-42}$ membrane used as an artificial arm and demonstration that the doll made from the polyCOF-42 membrane can perform a series of complicated movements (e.g., sit-ups) (Reproduced with permission from Ref. [39]; Copyright (2019), American Chemical Society); (b) Photoresponsive bending behavior via UV irradiation and heating of $\text{PEG}_{400}\text{-COF-42}$ (Reproduced with permission from Ref. [70]; Copyright (2020), American Chemical Society); (c) A comprehensive visualization of the humidity-responsive applications and self-oscillation performance of PEG-COF-based actuators (Reproduced with permission from Ref. [82]; Copyright (2022), Wiley-VCH GmbH).

ter 5000 charge-discharge cycles (Fig. 8a). Additionally, a thiophene porphyrin-based COF photocatalytic system was developed by covalently knitting COF layers through oxidative polymerization, resulting in a quasi-3D polyCOF system with built-in molecular wires.^[81] The conductive interlayer bridges formed in this system increased the electrical conductivity by several orders of magnitude, narrowing the bandgap and enhancing the spin density. The interlayer covalent linkages of thiophene can effectively manipulate the density of the active sites and charge mobility, thereby improving the photocatalytic efficiency. The polythiophene chains acted as conjugated bridges, further narrowing the bandgap and creating additional pathways for electron transport. This breakthrough pioneered a new paradigm for enhancing the photocatalytic activity through an interlayer conductive weaving strategy within COF architectures (Fig. 8b). In addition to electrochemical energy storage and chemical energy conversion, polyCOFs have also made strides in solar-to-thermal energy utilization for water purification. Elastic porphyrin-based polyCOFs integrated with PEG chains form 3D foams that exhibit full solar spectrum absorbance (>98%) and superior photothermal conversion capabilities.^[71] Through opti-

mized thermal management and hydrophilicity regulation, these foams achieve a solar evaporation rate of $4.89 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ under 1 sun illumination. When coupled with a truncated cone reflector, the evaporation rate further soars to $18.88 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, surpassing all reported solar steam evaporators. This application enables efficient conversion of solar energy into thermal energy for seawater desalination and wastewater treatment. The PEG chains prevented porphyrin aggregation and enhanced mechanical elasticity, whereas the 3D structure facilitated environmental energy input and minimized heat loss (Fig. 8c). Collectively, these studies indicate that integrating conjugated polymer chains into COF architectures is an effective strategy for engineering charge-transport pathways, regulating electronic structures, and unlocking the full potential of poly-COFs for advanced applications in energy storage, energy conversion, and solar-to-thermal utilization.

Catalysis Applications

PolyCOFs, as multifunctional and biocompatible COF materials integrated with functional polymers, have emerged as pivotal platforms for carrier and reactor construction in the field of bio-



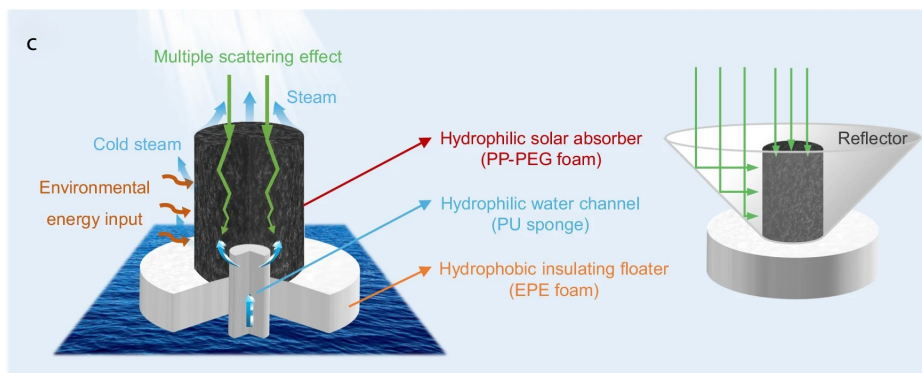


Fig. 8 (a) Schematic illustration Interlayer covalent weaving of polypyrrole chains converts a 2D COF into a quasi-3D conductive architecture (Reproduced with permission from Ref. [80]; Copyright (2023), American Chemical Society); (b) Schematic illustration of charge carrier dynamics for unpolymerized thiophene-based COFs and conductive polythiophene-interwoven COFs (Reproduced with permission from Ref. [81]; Copyright (2025), Wiley-VCH GmbH); (c) Schematic illustration of the efficient solar steam evaporation system based on PP-PEG solar evaporators (Reproduced with permission from Ref. [71]; Copyright (2024), Open access).

catalysis. Their core applications are centered on efficient enzyme immobilization, co-loading of multiple catalysts, and construction of cascade catalytic systems. COFcap-2 functioned as a recyclable tandem reactor for nitrogen fixation and subsequent

conversion to chiral amines, achieving an impressive enantiomeric excess of over 99% under ambient conditions (Fig. 9a).^[84] This offers a green and sustainable pathway for the synthesis of pharmaceutical intermediates (Fig. 9b). In precision

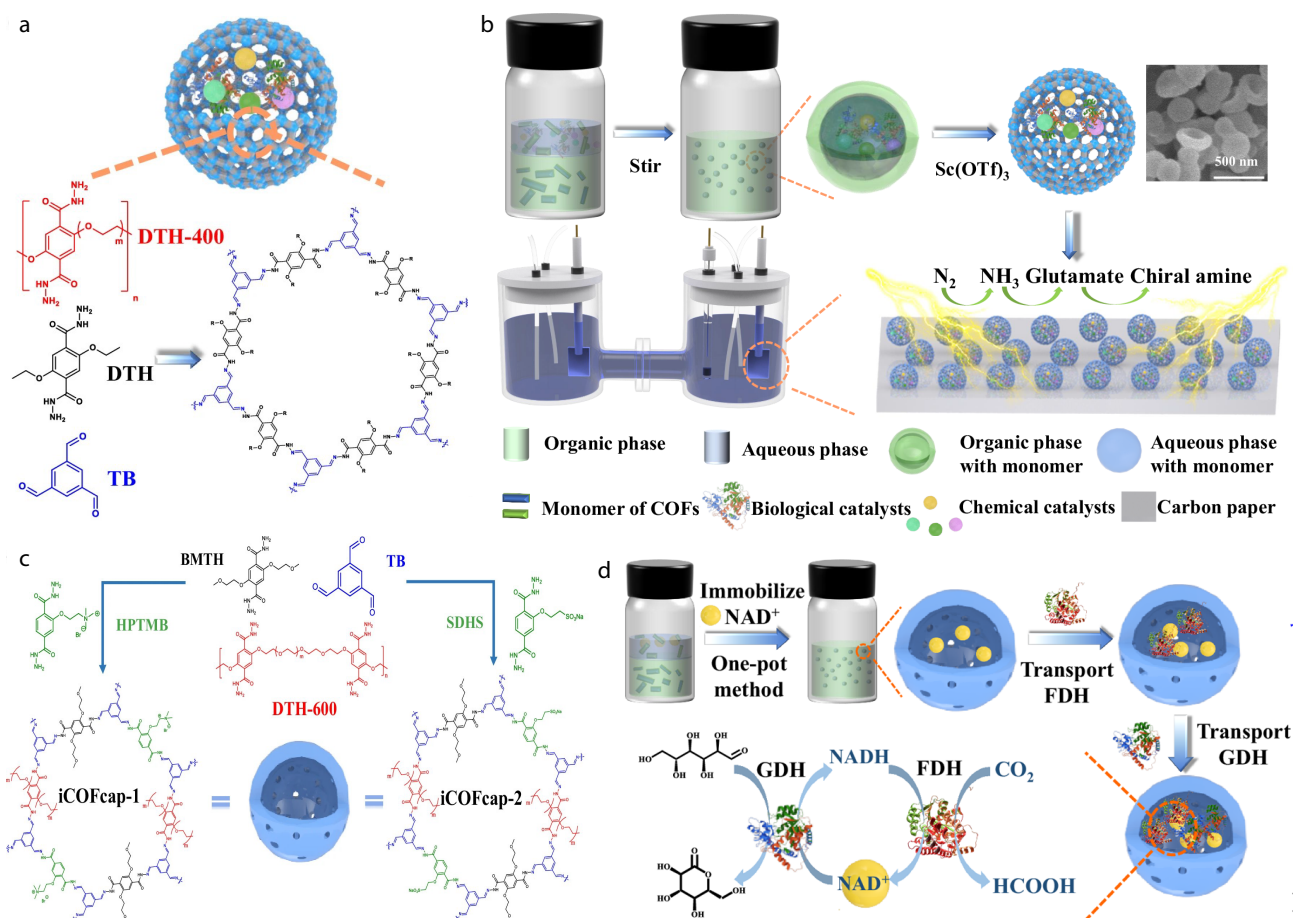


Fig. 9 (a) Synthesis of COFcap-2; (b) Schematic illustrations of COFcap-2 fabrication. The PEG-driven emulsion templating approach to prepare COFcap-2 enabled immobilization of multiple catalysts and subsequent conversion of N_2 to chiral amines. SEM image of COFcap-2 on the upper right (Reproduced with permission from Ref. [84]; Copyright (2025), Open access); (c) Synthesis route of iCOFcap-1; (d) The illustration of the synthesis of FDH&GDH&NAD⁺@iCOFcap-1 and cascade biocatalysis of CO_2 to formic acid (Reproduced with permission from Ref. [83]; Copyright (2025), Open access).

biocatalysis, ionic polyCOF capsules (iCOFcap) featuring swellable PEG chains ingeniously mimic the cellular transmembrane transport mechanisms (Fig. 9c).^[83] This enables the co-immobilization of multiple enzymes and chemocatalysts, leading to efficient photoenzymatic reduction of CO₂ to formic acid. Notably, this process resulted in high enzyme activity retention and excellent recyclability (Fig. 9d). Capsule-like and membrane-like heterogeneous bioreactors prepared based on polyCOFs can be efficiently recovered through simple water washing. This addresses the separation challenges associated with traditional homogeneous enzyme catalysis and paves the way for greening, scaling-up, and sustainability of biomanufacturing processes.

Biomedical Applications

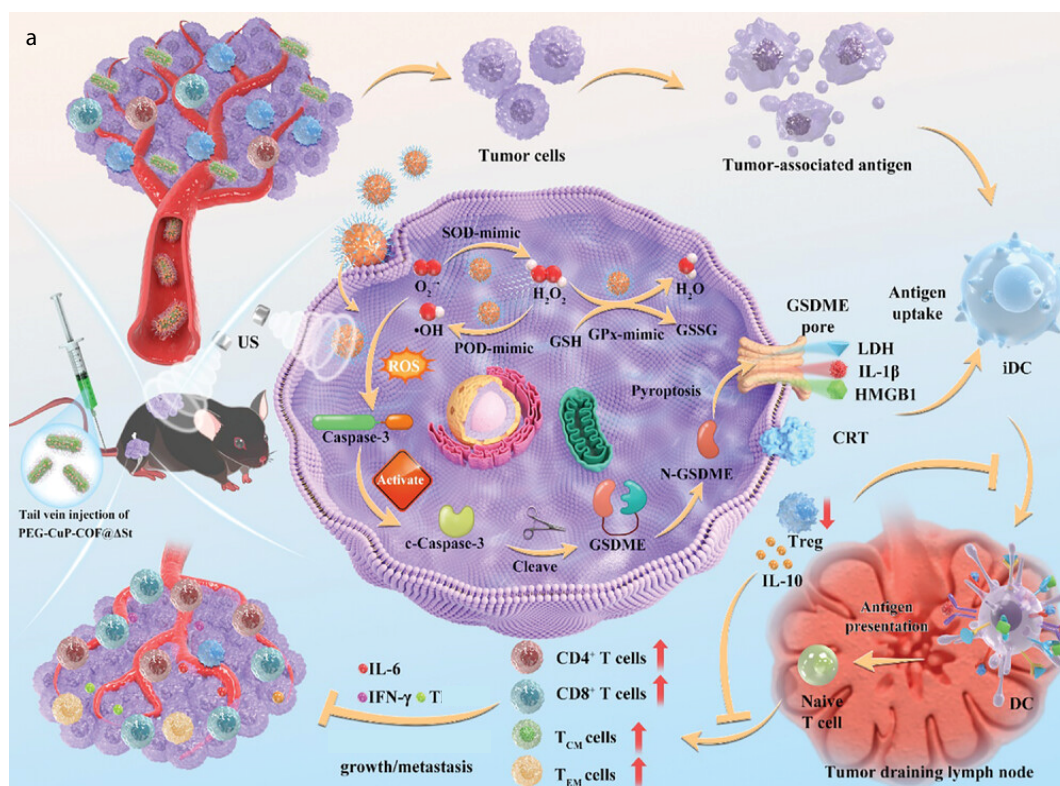
PolyCOFs, intelligent and responsive COF materials modified with PEG, have emerged as exceptionally promising functional platforms for both biomedical therapy and biomedical imaging.^[88] In tumor therapy, the bacteria-mediated PEG-CuP-COF@ΔSt nanosystem facilitates the targeted delivery of multi-enzyme-mimicking polyCOFs to hypoxic microenvironments within tumors.^[77] Here, ultrasound activation triggers the production of reactive oxygen species (ROS), subsequently inducing caspase-3/gasdermin E (GSDME)-dependent pyroptosis. This process initiates robust antitumor immune responses that not only inhibit primary tumors, but also suppress distant metastases and prevent bone metastasis by forming immune memory (Fig. 10a). In biomedical imaging, PEGylated dual-fluorophore 3D-polyCOFs enable real-time *in vivo* fluorescence visualization of the cerebral blood flow velocity.^[60] This provides a non-invasive tool for diagnosing ischemic stroke and monitoring reperfusion therapy. Moreover, their strain-responsive prop-

erties open up potential applications for the development of biosensors for physiological force detection (Fig. 10b). The biocompatibility and structural tunability of polyCOFs effectively address the key challenges of poor targeting in traditional tumor therapy and low precision in conventional sensing, thereby offering innovative strategies for advancing precision medicine and intelligent detection technologies.

CONCLUSIONS AND PERSPECTIVES

PolyCOFs have emerged as a promising class of hybrid materials that combine the ordered porous structures of COFs with their flexibility, processability, and mechanical robustness. In this review, we summarize recent advances in the design strategies, structural characteristics, and multifunctional applications of polyCOFs, including their roles in catalysis, energy storage and conversion, environmental remediation, sensing, and biomedicine. Through rational incorporation of polymer components, polyCOFs provide new opportunities to overcome the intrinsic limitations of conventional COFs, such as poor mechanical stability, limited processability, and insufficient functional adaptability.

Although substantial progress has been made in the development of polyCOFs, multiple critical challenges remain to be addressed. Owing to the structural complexity arising from the integration of crystalline COF frameworks and polymer chains, precise control over the polymer architectures within polyCOFs remains a core bottleneck. The polymer chain length, grafting density, and spatial distribution within COF frameworks strongly influence the crystallinity, porosity, mechanical properties, and functional performance of polyCOFs. However, current synthetic strategies often lack sufficient



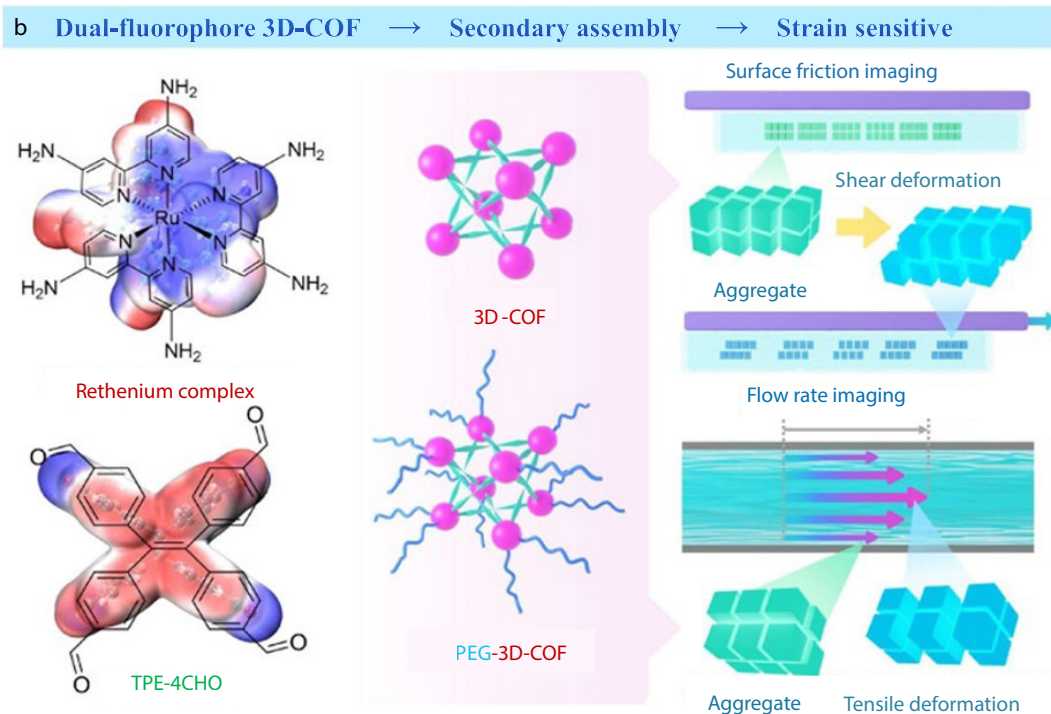


Fig. 10 (a) Schematic illustration of PEG-CuP-COF@ Δ St nanosystem promoting pyroptosis for combinatorial sono-catalytic immunotherapy (Reproduced with permission from Ref. [77]; Copyright (2024), Wiley-VCH GmbH); (b) Characterization and imaging results of PEG-3D-COFs for *in vivo* mapping of cerebral blood flow rate (Reproduced with permission from Ref. [60]; Copyright (2025), American Chemical Society).

control over these parameters, which may result in structural heterogeneity and performance variation. Therefore, future research should prioritize the development of more precise polymer integration strategies, such as sequence-controlled polymerization, DNA-templated polymer organization, and molecularly programmed grafting approaches, to achieve accurate regulation of polymer architectures and establish clear structure–property relationships.

In addition to molecular-level structural regulation, the scalable fabrication and practical implementation of polyCOFs remain important challenges. Many reported polyCOFs have been synthesized *via* complex multistep synthesis or post-synthetic modification processes, which may limit their large-scale production and reproducibility. Therefore, the development of facile, scalable, and environment-compatible fabrication methods is highly desirable. Meanwhile, the transformation of polyCOFs into practical devices requires further consideration of the application-specific requirements. For example, in flexible electronic devices, the integration of polyCOFs with electrodes and other functional components is often compromised by the interfacial impedance, poor electrical contact, mechanical degradation under repeated bending, and insufficient long-term operational stability. Addressing these issues will require coordinated optimization of polymer chemistry, COF structure, interface engineering, and device fabrication processes.

Beyond improving the structural stability and device compatibility, future research should further explore the development of adaptive and sustainable polyCOF systems. The incorporation of conductive, stimuli-responsive, and dynamic covalent polymers provides opportunities for constructing

multifunctional materials with tunable responses. The design of degradable or dynamically reconfigurable polyCOFs may offer new possibilities for recyclable, self-healing, and stimuli-responsive materials. Dynamic covalent interactions can enable reversible structural transformations while preserving the framework integrity, thereby extending the application of polyCOFs to sustainable and intelligent material systems. Furthermore, the integration of new polymerization strategies, advanced characterization techniques, and computational modeling is critical for guiding the rational design of next-generation polyCOFs. Despite these challenges, continued efforts in molecular design, scalable synthesis, and application-oriented engineering are expected to accelerate the transition of polyCOFs from emerging laboratory materials to practical platforms for advanced technologies.

BIOGRAPHIES

Hong-Xia Ren received her Ph.D. degree from Northwest Normal University in 2004. She was appointed as a lecturer at Nankai University in 2004. She has currently joined the team led by Professor Zhenjie Zhang.

Zhen-Jie Zhang received his Ph.D. degree from the University of South Florida in the field of metal-organic frameworks in 2014. He did his postdoctoral research with Professor Seth M. Cohen at UC San Diego (2014–2016) and then began his independent research career as a professor at the College of Chemistry, Nankai University. Zhang group is currently focused on developing new crystal materials (such as MOF, COF, MOP) for value-added product purification (such as light hydrocarbon separation), membrane manufacturing, and manufacturing intelligent actuators or robots.

Conflict of Interests

The authors declare no interest conflict.

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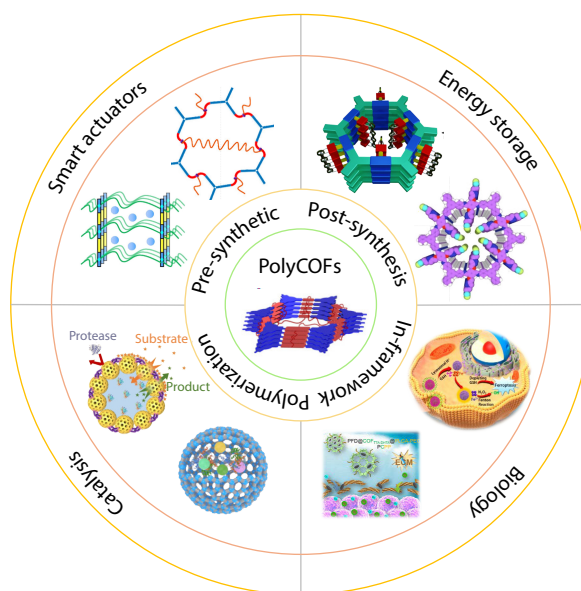
Graphical Abstract

Polymer-integrated Covalent Organic Frameworks (PolyCOFs): Covalent Organic Frameworks (COFs) Covalently Integrating Polymer for Advanced Applications

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Chemical Research Co., LTD.

Polymer-integrated covalent organic frameworks (poly-COFs) combine the ordered porosity of COFs with the flexibility and functionality of polymers, thereby enabling advanced applications in catalysis, energy, sensing, and biomedicine. This review highlights the design strategies, structural regulations, multifunctional properties, and future challenges of polyCOFs.



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