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Chiral covalent–organic frameworks as a new class of circularly polarized luminescent materials

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Chiral covalent organic frameworks (COFs) have emerged as a promising class of circularly polarized luminescent (CPL) materials. This review systematically summarizes the synthesis and CPL activity of chiral COFs, including synthetic strategies, chirality–luminophore integration approaches, and film fabrication techniques for potential applications as well as mechanistic insights for chiroptical properties. Moreover, this review provides perspectives on future efforts for optimizing CPL performance, exploring diversified frameworks, and elucidating chirality transfer kinetics to unlock applications in optical encryption and biomedicine.

1. Introduction

Circularly polarized light refers to an optical phenomenon where the electric field vector undergoes a helical rotation about the propagation axis as the wave travels.^{1–3} Due to its peculiar photophysical properties, circularly polarized light has found wide applications in optoelectronic devices, selective recognition, biomedicine, security, and other fields.^{3–5} Depending on the rotation direction, it is classified as either left-handed circularly polarized light (I_L) or right-handed circularly polarized light (I_R).⁶ Conventional methods for generating circularly polarized light involve passing unpolarized light successively through a linear polarizer and a quarter-wave plate.⁷ However, this approach leads to loss of both energy and information. In order to avoid these losses, circularly polarized luminescence (CPL) has attracted considerable attention from researchers. CPL refers to the phenomenon where chiral luminescent materials emit left- or right-handed circularly polarized light. In recent years, materials exhibiting this phenomenon have been intensively researched.^{7,8} To date, diverse CPL materials systems have been developed, including metal complexes,^{3,9,10} organic molecules,^{11–13} supramolecular assemblies,^{14–16} and liquid crystal^{17–19} and reticular frameworks.^{20–22} Research studies of CPL materials are based on asymmetric chemistry. Early research on CPL-active materials mainly focused on chiral small molecules with organic luminophores.²³ After that, CPL-active materials based on

lanthanide complexes¹⁰ and chiral polymers^{24,25} have witnessed significant progress and emerged as a mainstream solution in practical applications. However, the forbidden nature of the f–f transitions²⁶ in lanthanides and similar systems implies that these complexes typically exhibit poor photoluminescence quantum yields (PLQYs). In recent years, supramolecular chemistry and non-covalent interactions have become a popular strategy to enhance CPL. The potential of these materials lies in the interaction of guest species with the host framework,²⁷ which can enable richer functionality. Selecting appropriate host materials and guest species to construct a Förster resonance energy transfer (FRET) platform can realize chirality transfer from the chiral environment to achiral fluorescent molecules, which enable simultaneously fulfilling both the luminescence and polarization requirements of CPL.^{28,29} Multi-component systems including supramolecular assemblies, liquid crystals, and helical polymers have been achieved advances.^{30–32} Nevertheless, the chiral structures of these multi-component systems materials are unstable and prone to deformation.^{27,33}

Covalent organic frameworks (COFs) are crystalline porous materials composed of organic building blocks linked by covalent bonds, which allow the atomically precise integration of organic units into extended structures with highly tunability of structure and functionalities.³⁴ They are comprised of light elements like C, H, O, and N, which exhibit biocompatibility with no biological toxicity.^{35,36} COFs stitch organic molecules together through strong covalent bonds, which ensure the long-range orderliness and robustness so that COFs retain their crystallinity during chemical processes.³⁷ Due to these advantages, COFs have shown outstanding potential in various fields, including gas storage,^{38–40} environmental remediation,^{41–43} catalysis,^{44–46} drug delivery,^{47–49} optoelectronics.^{49–51}

Chiral COFs are frameworks possessing chiral features, including chiral ligands, chiral guests, or large-scale chiral

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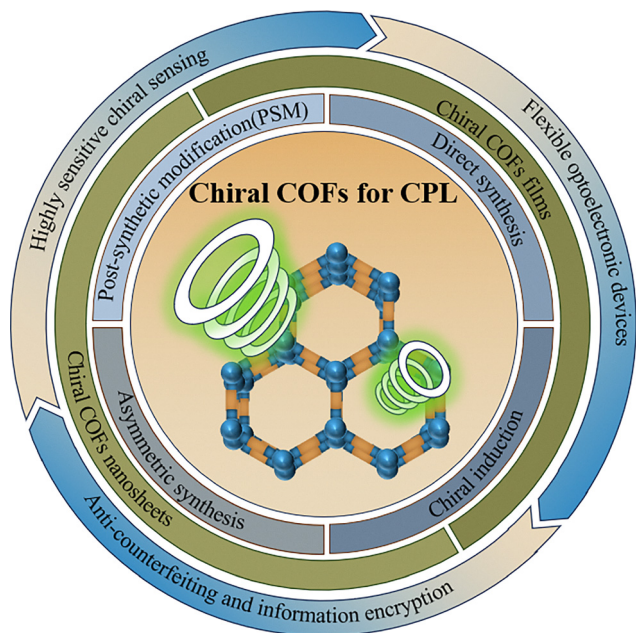


Fig. 1 Chiral COFs for CPL, the summary of preparation methods, forms, and applications.

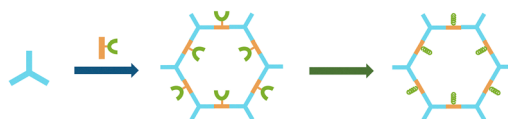
topologies such as helical chains.^{52,53} The interaction of optics with chiral COFs gives rise to interesting photonics,^{54–56} especially chiral and nonlinear optics (Fig. 1). The chiral COFs' special topological confinement of the framework can provide chiral environment, which is a key condition for chirality transfer. Despite the currently limited reports on CPL-active COFs,^{54,57–61} this field holds significant potential.

2. Preparation of chiral COFs

COFs are composed entirely of two distinct components: knots (building units) and linkages (bonds formed between those units upon reticulation). To date, there are several kinds of synthetic strategies to prepare chiral COFs:⁵² post-synthetic modification, direct synthesis, asymmetric synthesis, and chiral induction (Fig. 2).

Post-synthetic modification (PSM) stands as one of the primary strategies for fabricating chiral COFs.⁶² This approach utilizes specific functional group reactions to anchor chiral moieties onto the pre-constructed achiral COF backbone. The modification process typically involves condensation reactions or click chemistry, necessitating the presence of non-coordinating functional groups (e.g., $-\text{COOH}$, $-\text{NH}_2$) in the pristine achiral COFs. By employing inexpensive and readily available achiral materials as precursors, diverse chiral functional groups can be introduced to modulate the material's structure and functionality. This significantly reduces production costs while substantially enhancing the material's versatility and diversity. However, PSM conditions must be judiciously selected to avoid compromising the structural integrity of the material and to prevent racemization of the incorporated chiral moieties. Additionally, precise spatial control over the

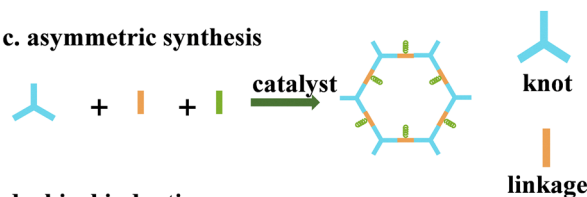
a. post-synthetic modification



b. direct synthesis



c. asymmetric synthesis



d. chiral induction

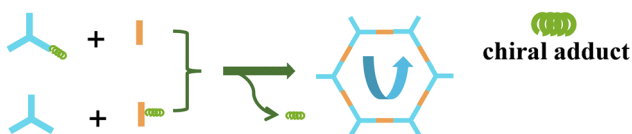


Fig. 2 Synthetic strategies for chiral COFs: (a) post-synthetic modification (PSM), (b) direct synthesis, (c) asymmetric synthesis, and (d) chiral induction.

distribution of chiral functional groups within the framework remains challenging.

Direct synthesis using chiral precursors represents a streamlined approach for preparing chiral COFs. Chiral building blocks are categorized into two types: ligands with stereogenic centers and ligands exhibiting axial chirality.^{63,64} The critical aspect of this synthetic strategy lies in selecting appropriate chiral ligands, where naturally occurring chiral molecules are frequently employed either as direct ligands or as subunits for constructing larger ligands. Chiral COFs synthesized *via* this method accurately replicate the initial design while ensuring uniform distribution of chiral units throughout the framework.^{65,66} It's also a reliable way to synthesize both homochiral and racemic 2D COFs from enantiopure and racemic helicene derivatives by introducing helical chirality into the backbone of all-organic homochiral 2D COFs.⁶⁷

Asymmetric synthesis remains relatively underexplored for constructing chiral COFs. In current reports, catalytic asymmetric polymerization has been demonstrated to produce chiral COFs from prochiral monomers.^{53,68} The reaction conditions in this particular case prove milder than alternative methods. Drawing on its extensive experience in other organic domains, the selection of appropriate chiral catalysts emerges as the key factor for successful asymmetric synthesis in COF fabrication. Schiff-base condensation plays a significant role in the asymmetric catalytic synthesis of chiral COFs involving aldehydes and primary amines. Compared to traditional acid catalysis, the improved method using amino catalysis for Schiff



base condensation to synthesize chiral COFs is a greener synthetic approach and is widely adopted by researchers.⁶⁹

The periodic structure of COFs enables the asymmetric spatial arrangement of achiral building blocks under chiral induction environments. Chiral induction strategies are categorized into linker exchange chiral induction⁷⁰ and linker decomposition chiral induction.⁵⁶ During synthesis, the addition of chiral agents to the solution can induce the assembly of achiral components into chiral COFs with helical morphology. Both additive-dependent strategies (employing chiral catalysts or forming chiral precursors as templates) and additive-free templating approaches utilizing natural chiral sources have been documented.

Overall, post-synthetic modification achieves functionalization flexibility by introducing chiral groups onto pre-synthesized achiral COFs. Direct synthesis utilizes chiral monomers as building blocks to assemble chiral COFs in one step, this method ensures uniform distribution of chiral units within the lattice, high crystallinity, and a well-defined structure. The asymmetric synthesis strategy introduces an asymmetric catalytic environment during the COF formation process, enabling precise control over individual stereocenters to prepare enantiopure compounds. Chiral induction employs chiral sources to induce the assembly of achiral precursors into chiral COFs, offering a relatively straightforward synthetic approach with promising potential for large-scale production.

3. Chiral COFs for CPL

Typically, the different emission intensities of left- and right-handed circularly polarized luminescence is quantified by the dissymmetry factor, g_{lum} .^{26,71}

$$g_{\text{lum}} = \frac{2(I_{\text{L}} - I_{\text{R}})}{I_{\text{L}} + I_{\text{R}}}$$

From this equation, it is evident that the magnitude of g_{lum} lies within the range of $[-2, +2]$. A value of $g_{\text{lum}} = \pm 2$ corresponds to exclusively left- and right-handed CPL emission and a g_{lum} value of 0 indicates non-polarized emission from the material.

From a microscopic perspective, g_{lum} can be expressed in terms of the total electric, μ , and magnetic transition dipole moments including contributions from all luminescent molecules, m , and the angles of μ and m , θ .⁷²

$$g_{\text{lum}} = 4 \frac{|\mu||m| \cos \theta}{|\mu|^2 + |m|^2}$$

This expression demonstrates that larger g_{lum} values can be achieved by employing chiral luminophores where the m is comparable in magnitude to μ .

This principle aligns with the favorable experimental performance of lanthanide complexes in CPL materials design, which are known to achieve relatively large values due to their significant magnetic dipole transitions.^{73,74} The other key parameter for characterizing the properties of CPL materials is photoluminescence quantum yields (PLQYs), which refers to the ratio of the emitted photon number to the absorbed photon

number and is used to describe the light emitting ability of the material.^{75,76} Herein lies the current challenge in designing powerful CPL-active materials: attaining a large g_{lum} without compromising the PLQY.⁷⁷

Most chiral units are non-emissive and most luminophores are achiral.⁵⁵ Meanwhile, the variations of dimensional morphologies and sizes affect the properties of CPL materials since the microscopic packing modes will affect the luminescence processes and chirality transfer processes.⁷⁸ For the purpose of expanding structural diversity, a class of CPL-active materials has been developed, wherein chiral frameworks enable chirality transfer through provision of chiral environments, consequently imparting CPL properties to achiral luminophores. As another vital component of reticular chemistry research, chiral MOFs have achieved notable progress in developing CPL-active materials (Fig. 3).^{22,79–81} Sharing structural and synthetic similarities with chiral MOFs, chiral COFs have evolved synergistically with them, with mutual guidance driving advancements in both fields. Simultaneously, chiral COFs exhibit enhanced stability in acid–base solution⁸² and superior biocompatibility. Consequently, chiral COF-based CPL materials demonstrate promising potential for specific recognition and sensing applications. Representative examples of reported chiral COF CPL systems (including chiral COF nanosheets and chiral COF films) are summarized in Table 1.

Notably, all currently reported CPL-active COFs predominantly adopt a hexagonal topology. From a geometric perspective, this rigid framework suppresses fluorescence quenching caused by molecular vibrations,³⁶ thereby enhancing the PLQY. To date, considering the role of conjugated systems in fluorescence emission, only sp^2 -C-COFs, imine-linked COFs, and amination-linked COFs have been used to construct CPL-active COF skeletons. Researchers must construct COFs linked by partially π -conjugated linkages or fully π -conjugated linkages. In 2021, Du *et al.* fabricated the first CPL-active COF nanosheets *via* a Knoevenagel condensation reaction. They used 1,3,5-benzenetriacetonitrile (C3-CN) as a knot and introduced cyano-substituted olefinic linkages, which endowed the chiral COFs with stacking-induced emission enhancement, so guaranteeing their solid-state luminescence properties. Base-catalyzed aldol condensation of 2,4,6-trimethyl-1,3,5-triazine (TMT), as a knot, and terephthalaldehyde (DFB), as a linker, is also a reported way to synthesize sp^2 -C-COFs.⁵⁵ For the first time, they synthesized COF materials with CPL properties using axially chiral luminophores. It demonstrates that a rational COF design can retain the photophysical properties of the building blocks, proposing the most straightforward strategy for synthesizing CPL-COFs. However, owing to the low reversibility of a C=C-bond-formation reaction, the resulting frameworks usually have low crystallinity and porosity.³⁶ Jing *et al.* developed a scalable and facile bottom-up approach to fabricate 2D imine-linked ultrathin chiral fluorescent COF NS *via* a chiral-induced synthesis strategy. 1,3,5-Triformylphloroglucinol (Tp), as a knot, 2,2'-bipyridine-5,5'-diamine (Bpy), as a linker, and chiral inducers were mixed into the reaction system under solvothermal conditions to obtain



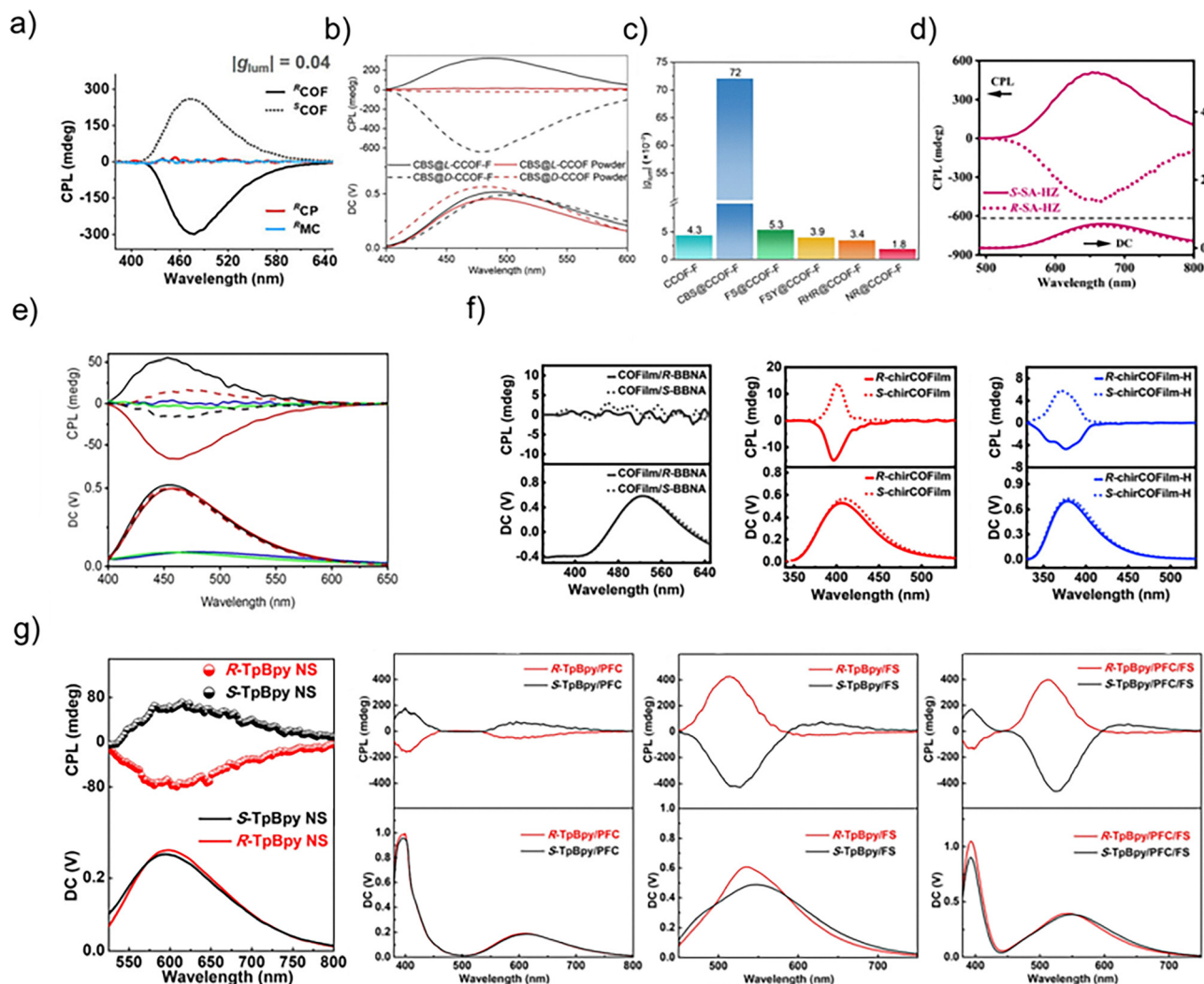


Fig. 3 CPL spectra of CPL-active COFs. (a) CPL spectra of COF, CP, MC⁵⁵ (b) CPL and DC spectra of CBS@CCOF-F and CBS@CCOF powder.⁵⁹ (c) $|g_{lum}|$ values of CCOF-F, CBS@CCOF-F, FS@CCOF-F, FSY@CCOF-F, RHR@CCOF-F and NR@CCOF-F⁵⁹ (d) R/S-SA-HZ in the solid-state⁶⁰ (e) CPL and DC spectra of L-PDC-TZ COF@CBS (black), D-PDC-TZ COF@CBS (red), L-PDC-TZ COF (blue) and D-PDC-TZ COF (green) dispersed in water⁸³ (f) COFilm/R- and S-BBNA, R- and S-chirCOFilm, and R- and S-chirCOFilm-H excited by 365 nm⁵⁸ (g) R- and S-TpBpy NS, R- and S-TpBpy/PFC, R-TpBpy/FS, R-TpBpy/PFC/FS.⁵⁴

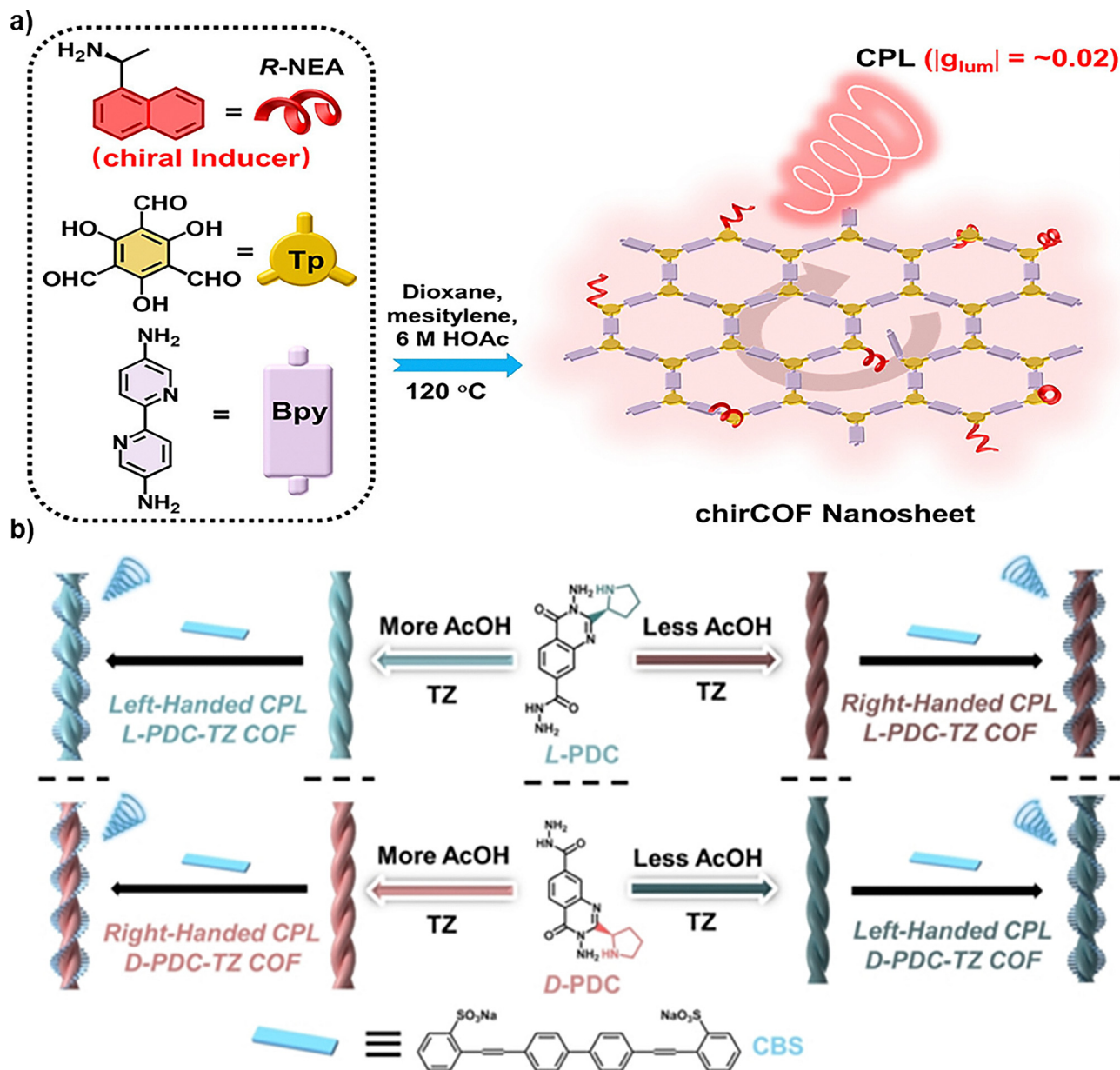
Table 1 COFs demonstrating CPL

COF	$g_{lum} (\times 10^{-3})$	PLQY (%)	Topology	Synthesis method	Ref.
BC-COF	40	20	[C3 + C2]	Direct synthesis	55
R-/S-TpBpy	−23/22	—	[C3 + C2]	Chiral induction	54
R-/S-TpBpy/PFC	28	8.3	—	—	54
R-/S-TpBpy/FS	7	—	—	—	54
R-/S-TpBpy/PFC/FS	100	19.4	—	—	54
L-/D-PDC-TZCOF@CBS	6.8/9.5	—	[C3 + C2]	Chiral induction	83
COFilm/R-/S-BBNA	−2.16/1.78	—	[C3 + C2 + C2]	Post-synthetic modification	58
L-/D-CCOF-F	4.3	—	[C3 + C2]	Chiral induction	59
Dye@CCOF-Fs	72	—	—	—	59
S-SA-HZ	55	4.79	[C3 + C2]	Chiral induction	60

chiral COF NS.⁵⁴ Tang *et al.* utilized (1,3,5-triazine-2,4,6-triyl)tribenzaldehyde (TZ) as a knot, involving aminated linkage and hydrazone linkage.⁵⁶

It's a challenge of simultaneously introducing chirality and chromophore. Using chiral organic luminophores represents the most straightforward solution.





The formyl-functionalized 2,2'-bis(diphenylphosphino)-1,1'-binaphthalene (BINAPO) was utilized as axially chiral linkers to direct synthesis⁵⁵ (Fig. 4). However, due to the scarcity of groups possessing these specific characteristics and the potential compromise of their properties during the reaction process, direct synthesis is not a readily scalable approach. Chiral induction represents a reliable strategy for imparting CPL activity to COF skeletons integrated with fluorescent moieties (Fig. 4). Encapsulating guest emitters in the host matrix to form a host-guest system has attracted considerable interest. Various guest emitters (such as lanthanide ions and fluorescent dyes) can be encapsulated within chiral COFs enables the construction of guest-centered and guest-sensitized luminescent materials.²⁷ Gu *et al.*⁵⁴ incorporated dyes into

CPL-COFs and discovered that the constructed host-guest encapsulation system enables efficient energy and chirality transfer. This finding proposes a new direction for fabricating CPL-COFs with larger g_{lum} values, significantly expanding their potential. Loading non-luminescent chiral COFs by achiral fluorescent dyes enriches preparation alternatives.⁵⁸ The introduction of reaction groups similar to the linker in chiral inducer cause coordination defects in the COFs, facilitating the chirality. Dye groups are impregnated into the framework, and combined with chiral COFs through hydrogen bonds, obviating the need for exfoliation and covalent attachment of chromophores. Incorporating aggregation-induced emission (AIE) units (salicylaldehyde azine) into the COF skeleton significantly enhances its solid-state fluorescence activity.⁶⁰ Using COFs



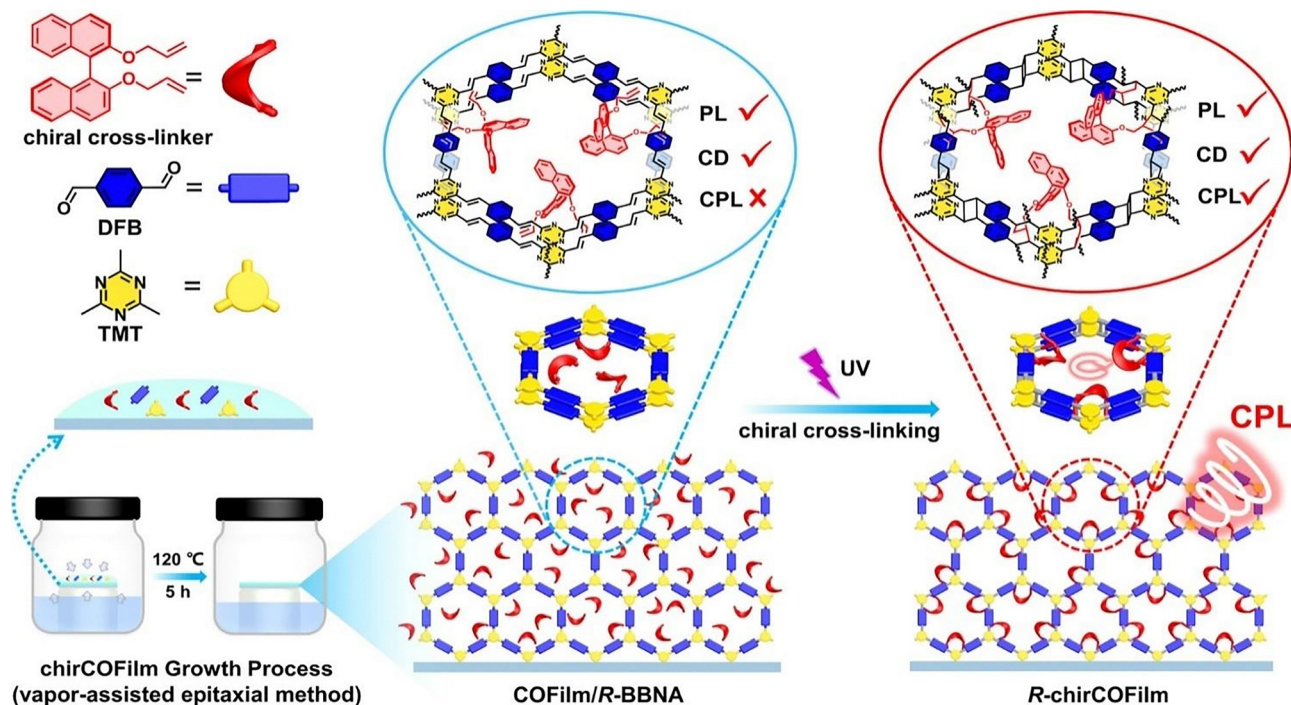


Fig. 5 Imparting CPL to COF films via photo-addition.⁵⁸

with mesoscopic helical morphology can induce chirality to physisorbed fluorescent molecules. Utilizing chiral cross-linking reaction *via* photo addition⁵⁸ can also introduce chirality into CPL-active COFs (Fig. 5). Zuo *et al.* present a facile strategy for constructing solid-state CPL-active Chiral COFs solely from achiral building blocks by chiral inducer, demonstrate a rare example of solid-state CPL-active Chiral COFs with stimuli responsiveness derived entirely from achiral monomers.⁶⁰ This two strategies were used to fabricate CPL-active COF films. Both dispersing CPL-active NS into flexible substrates⁵⁴ and assembling self-standing films⁵⁹ are established methods for obtaining CPL-active chiral COF films (chirCOFilm) (Fig. 6). A chirCOFilm supported on exogenous substrates exhibit superior mechanical strength and flexibility,⁵⁴ whereas a self-standing chirCOFilm prepared *via* the polymerization–dispersion–filtration strategy⁵⁹ mitigate CPL signal attenuation caused by dilution.

Subsequent growth of pre-formed self-standing films on flexible substrates⁵⁸ can synergistically combine these advantages. Jing *et al.* fabricated chirCOFilm using vapor-assisted epitaxial growth, preserving functional group integrity. Leveraging interlayer [2+2] photocycloaddition reactions in sp²-C-COFs enabled sensitive photochromic effects. Further growth of these films on PDMS substrates yielded COF/PDMS composites demonstrating exceptional transparency, stability, and ease of handling, showcasing significant potential for optical sensor applications.⁵⁸ The roughness, area, and thickness of those films can be easily customized.

Despite extensive research on the chiral transfer mechanism and luminescence properties of CPL-active COFs, current evidence suggests these critical questions remain unresolved. By

comparing with the CPL-silent model compound (MC) and chiral polymers (PC) synthesized from the same starting units, Liu, Zhu *et al.* demonstrated that dual confinement of reticular frames and interlayer stacking significantly amplifies chiroptical properties.⁵⁵ They believe that a COF skeleton offers a confined reticular frame to efficient chirality transfer from linkers to chiroptical properties, and stacking of the reticular frame further enabled amplification of the chiroptical properties of the chiral COFs due to the interlayer confinement. The columnar π -arrays in 2D COFs provide predesigned pathways for ideal charge carrier transport;³⁶ however, interlayer π - π stacking inevitably causes fluorescence quenching.⁵⁴ To mitigate this effect, all reported CPL-COFs adopt hexagonal topology—the configuration with minimal π -orbital density.³⁶ Introducing hydrophobic modifiers during COF synthesis also serves as a viable strategy to suppress π - π interactions. Liu, Cai *et al.*⁵⁶ synthesized a nanofibrillar COF featuring tunable helicity in homochiral double-helical strands, observing inversion of its CPL signal upon helicity reversal. Additionally, frameworks with relatively large HOMO–LUMO gaps contribute to enhanced fluorescence.^{60,84} In dye-loaded CPL-active COF materials, the contribution of dyes to CPL can be explained through energy transfer between the host and guest. FRET and Dexter energy transfer (DET) serve as mechanisms to enhance the CPL effect.²⁸ Chiral confined spaces can impart chirality to guest molecules incorporated within them.¹⁶ And encapsulating specific guest molecules can significantly amplify the chiral-induced spin selectivity in helical covalent organic frameworks.⁸⁵ Therefore, inducing CPL from achiral luminescent guests through chirality induction is an important method for preparing CPL materials. The process of chiral transfer is



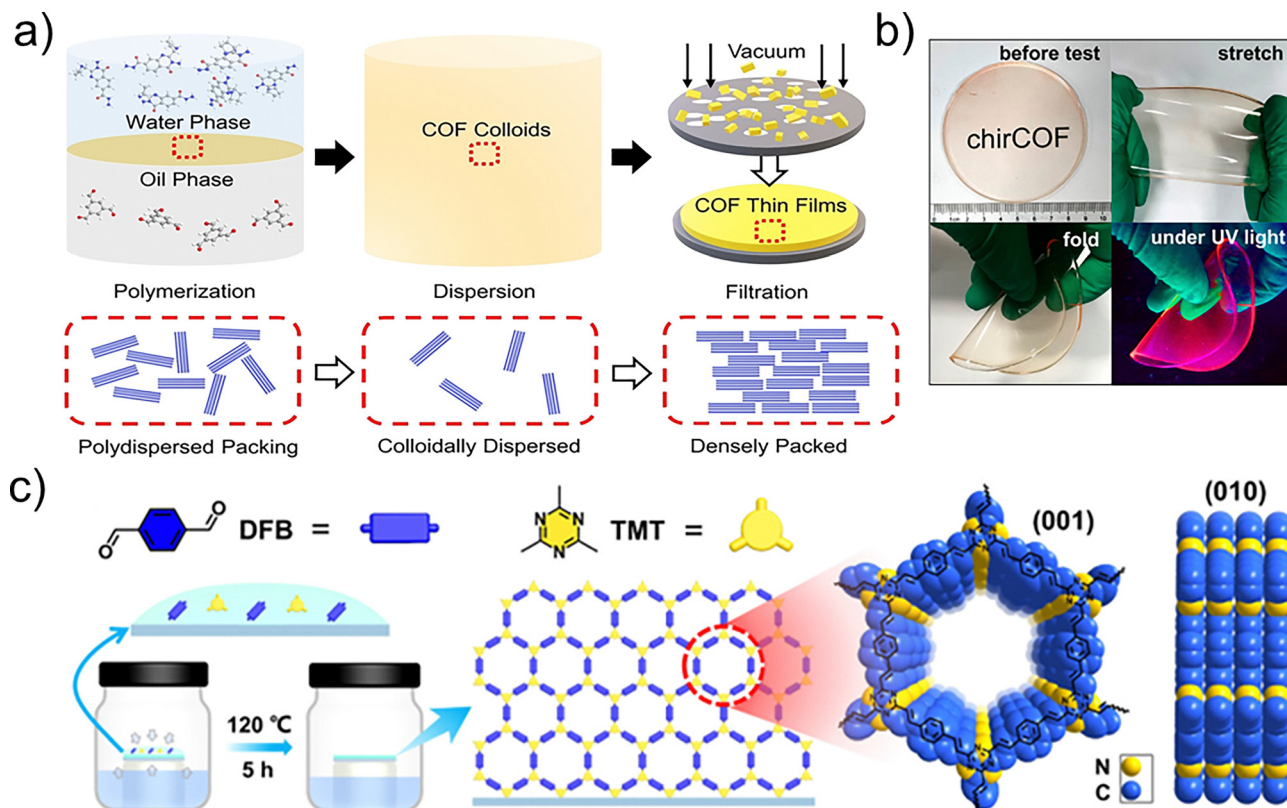


Fig. 6 Preparation methods for COF films. (a) Schematic illustration of the fabrication of self-standing chiral COF Films via a polymerization–dispersion–filtration sequence.⁵⁹ (b) Dispersed COF NS into polydimethylsiloxane (PDMS) matrix to obtain highly transparent, large size, and flexible films.⁵⁴ (c) Preparation of COF films via vapor-assisted epitaxial methods.⁵⁸

primarily influenced *via* host–guest interactions, chiral micro-environments, and host–guest coordination bonds. Constructing chiral host–guest systems by encapsulating achiral dyes into CPL-COF materials enables the achiral dyes to acquire CPL properties through chirality induction and chiral transfer mechanisms from chiral donors to achiral acceptors.²⁸ The FRET process facilitates continuous and efficient chiral transmission and CPL amplification in co-assembled systems, resulting in a higher g_{lum} value for the dye-loaded CPL-COF materials. Since the luminescence originates from achiral guest dye molecules, this demonstrates physical adsorption-mediated chiral transfer from the framework to the luminophores.

Although the mechanism of axial-to-central chirality conversion during cyclization is well-established,⁸⁶ a deep relationship between the assembly morphology and CPL chirality still needs to be explored.⁵⁵

4. Applications and prospects of CPL-COFs

CPL materials have been demonstrated the powerful potential in display technology, information communication, chiral optoelectronics, recognition and other fields.²⁵ As a branch of

CPL materials, CPL-COFs have now found applications in chiral recognition, anti-counterfeiting, and chiral optical response (Fig. 7). CPL offers excited-state information for chiral luminescent systems, which provide a highly sensitive way to determine the conformation of chiral enantiomers and detect their activities. Comparing to traditional fluorescent probes, CPL probes can filter out false-positive result achiral interferents, promising a superior signal-to-noise ratio.

The operation of a chiral sensor relying on the CPL response involves switching the signal on or off, raising or lowering its intensity, or reversing its direction. Left-handed and right-handed circularly polarized light are absorbed to different extents by different enantiomers, leading to differences in excited-state population, which in turn affects the CPL signal.^{72,87} When CPL-COF complexes with certain chiral molecules, the different configurations of the chiral molecules directly influence the extent of weakening of the CPL signal, demonstrating enantioselectivity. This provides theoretical support for using CPL-COF to study and distinguish between enantiomers. Jing *et al.* utilized their synthesized chirCOFfilm to achieve highly sensitive CPL detection of *R/S*-phenyl-ethanol enantiomers (PE), successfully identifying enantiomers at concentrations as low as 5%, which is a feat unattainable value by conventional fluorescence detection.⁵⁸ Zuo *et al.* investigated the interaction between their synthesized



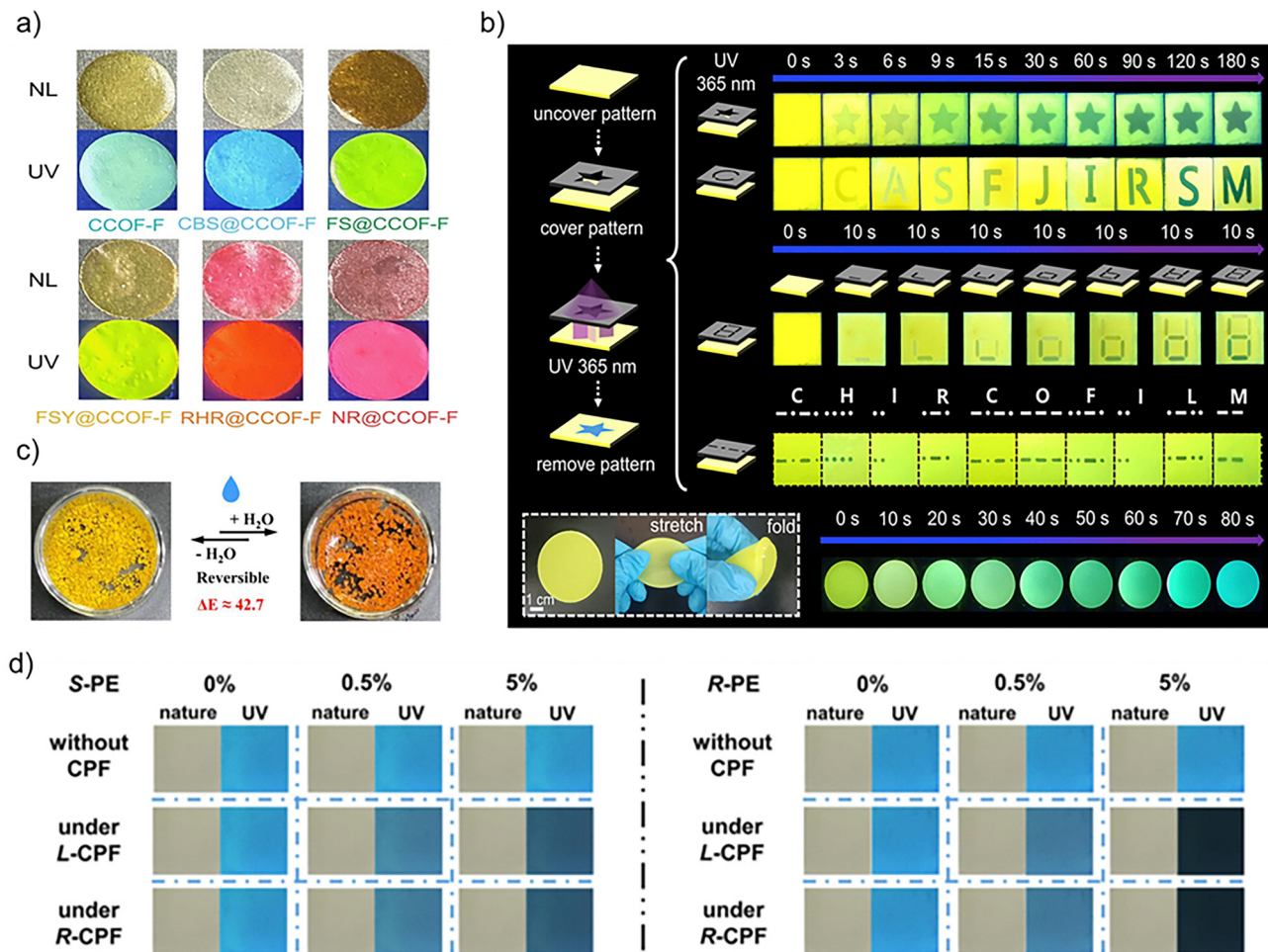


Fig. 7 Applications of CPL-active COFs. (a) Full-color tunable CPL-active COF films.²⁹ (b) CPL-active COF for anti-counterfeit. Exposing the ChirCOFilm to 365 nm UV light resulted in the covered areas maintaining yellow fluorescence, while the uncovered regions underwent a photochromic reaction. By precisely controlling the duration and position of 365 nm UV exposure, a gradient optical pattern transitioning from yellow to blue was achieved.⁵⁸ (c) Hydrochromism of S-SA-HZ.⁶⁰ (d) ChirCOFilm for highly sensitive detection of *R/S*-PE. modifiable channels,⁸⁸ allowing for further functional modifications.⁵⁸

S-SA-HZ and typical chiral molecules containing amino/hydroxy groups (2-aminocyclohexanol and *N,N'*-dimethylcyclohexane-1,2-diamine), revealing distinguishable binding affinity toward both enantiomers.⁶⁰ This demonstrates the significant application potential of CPL-active COFs in effectively differentiating and recognizing amine- and hydroxy-containing chiral molecules within pharmaceutical intermediates and bioactive compounds. Furthermore, leveraging the intrinsic structural properties of COFs enables photochromic⁵⁸ and hydrochromic⁶⁰ responses, positioning them as promising materials for anti-counterfeiting and multifunctional smart material development. Additionally, dye-doped CPL-active COF materials enable full-color-tunable²⁹ CPL, offering potential for optical imaging applications (Fig. 7). Currently, novel CPL materials have not yet been widely adopted in practical applications. Nevertheless, they hold significant promise and are expected to find their distinct advantages in specific niches. Compared to other CPL materials, CPL-COF materials exhibit remarkable stability in complex environments

and possess biological affinity, making them potentially valuable across various fields.

5. Conclusions

Based on current literature reports, we concisely summarize key strategies for developing CPL-active COF materials, encompassing (i) framework synthesis protocols, (ii) chirality-luminophore incorporation approaches, (iii) thin-film fabrication methodologies, and (iv) mechanistic insights into CPL generation.

From a synthetic standpoint, both direct synthesis using chiral monomers and post-synthetic modification offer viable routes to chiral COFs. Condensation polymerization enables the construction of C=C- and nitrogen-linked COF backbones. Notably, fully π -conjugated linkages yield COFs with compromised crystallinity that detrimentally impacts CPL performance. However, C=C bonds offer greater post-synthetic flexibility exploitable, through [2+2] photocycloaddition reactions to develop photoresponsive functionalities



(e.g., photochromism). In contrast, partially π -conjugated frameworks demonstrate superior crystallinity and stability, exhibiting enhanced CPL characteristics compared to sp^2 -C-COF architectures.

Chirality is typically introduced during framework synthesis *via* axially chiral linkers or imparted post-synthetically through strategic linker selection enabling chiral cross-linking reaction. Asymmetric synthesis and chiral induction strategies, provide alternative pathways to access enantioenriched frameworks from achiral precursors, highlighting the versatility of chiral COF chemistry. Both chiral chromophores covalently integrated within the COF skeleton and achiral fluorophores physically adsorbed within COF nanochannels exhibit CPL activity, demonstrating the framework's efficacy as a chiral inducer. Fluorescent dyes loading significantly amplifies CPL performance. ChirCOFs fabricated from CPL-active COFs exhibit robust structural/chemical properties suitable for enantioselective sensing applications.

Mechanistically, the confined environment within COF pores facilitates efficient chirality transfer from the framework to guest molecules, while the periodic stacking of layers can amplify chiroptical signals through supramolecular interactions. However, a detailed understanding of how molecular-level chirality translates into macroscopic CPL output remains incomplete. The interplay between π -conjugation, interlayer stacking, and chiral configuration necessitates further theoretical and experimental investigation.

The reticular frame was indispensable for CPL generation *via* confined chirality transfer. While many efforts have been devoted to elucidating the chiral transfer and luminescent properties of CPL-active COFs, consensus on the operative mechanisms has yet to emerge.

Current research on CPL-active COFs remains in its nascent stages. Leveraging the inherent designability of COF architectures, these materials possess a substantial amount of untapped potential for future development. From a materials engineering perspective, key priorities include synthesizing CPL-COFs with enhanced dissymmetry factors g_{lum} , broader emission color gamuts, and higher PLQYs. Concurrently, elucidating chiral transfer mechanisms through fundamental studies will provide critical theoretical guidance for resolving the dual challenges of chirality–luminescence synergy and stable structure construction.

For practical implementation, identifying unique competitive advantages is paramount. While CPL-active COFs have demonstrated exceptional sensitivity in phenylethanol enantiomer, 2-aminocyclohexanol, and N,N' -dimethylcyclohexane-1,2-diamine discrimination—highlighting their potential in fluorescence-based detection—they have yet to establish a definitive performance edge over competing CPL materials across diverse substrates. This limitation precludes their irreplaceable deployment in conventional nonlinear optical applications. These considerations merit further examination to engineer CPL-active COFs with distinctive application value. Utilizing computational chemistry research and high-throughput screening to explore potential CPL-COF material

structures is a future direction for development. Furthermore, while current studies have enhanced CPL effects through dye loading, a wider range of host–guest encapsulation architectures remains to be explored, to solve the problem of quenching of CPL, which is influenced by aggregation-caused quenching (ACQ) and twisted intramolecular charge transfer (TICT) processes.⁸⁷ Additionally, the chiral stability of CPL-COFs warrants more in-depth investigations to facilitate their application in complex environments. Bella *et al.*⁸⁹ employed computational chemistry methods, combining DFT benchmarking, excited-state Born–Oppenheimer molecular dynamics, and TD-DFT analysis, to investigate the effects of dimensionality, network structure, and chirality transfer mechanisms on CPL spectral bands. They established a theoretical simulation protocol for CPL in COFs, providing a transferable computational framework for the design of subsequent chiral luminescent materials and guiding the efficient screening in future research.

Furthermore, the standardization of CPL characterization should be noted by researchers. Recently, a guideline for standardizing CPL characterization of chiral materials has been proposed.⁹⁰ This guideline systematically organizes the measurement procedures and common experimental pitfalls, helping to address challenges arising from non-standardization and inconsistent measurements. We recommend that subsequent research studies should refer to this guideline for testing, which will accelerate progress in the field.

In conclusion, while chiral COFs represent a promising platform for CPL materials, their full potential remains untapped. Interdisciplinary collaborations involving synthetic chemistry, materials science, and photophysics will be essential to overcome current limitations and realize the practical applications of these versatile materials.

Conflicts of interest

There are no conflicts to declare.

Data availability

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

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