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Reticular Electrochemiluminescence Nanoemitters: Structural Design and Enhancement Mechanism

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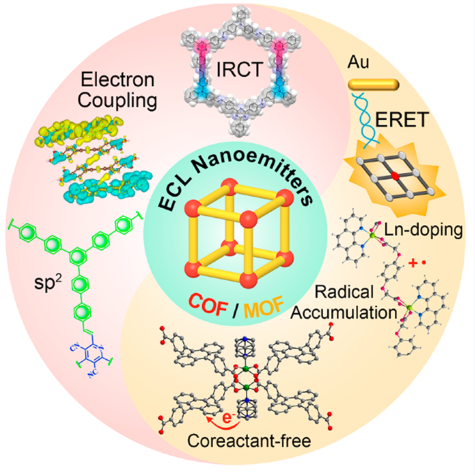

CONSPECTUS: Electrochemiluminescence (ECL) is a powerful transduction technique, which depends critically on the formation of the excited emitter through the charge transfer between the electrochemical reaction intermediates of the emitter and the co-reactant/emitter. The exploration of ECL mechanisms for conventional nanoemitters is limited due to the uncontrollable charge transfer process. With the development of molecular nanocrystals, reticular structures such as metal−organic frameworks (MOFs) and covalent organic frameworks (COFs) have been utilized as atomically precise semiconducting materials. The long-range order in crystalline frameworks and the tunable coupling among building blocks promote the quick development of electrically conductive frameworks. Especially, the reticular charge transfer can be regulated by both interlayer electron coupling and intralayer topology-templated conjugation. By modulating intramolecular or intermolecular charge mobility, reticular structures could serve as promising candidates for enhancing ECL. Thus, reticular crystalline nanoemitters with different topologies provide a confined platform to understand ECL fundamentals for designing next-generation ECL devices.

Aiming at exploring the mechanism of ECL emission, our group has developed a series of ECL nanoemitters as well as enhancement strategies of ECL emission in the past 20 years. A series of water-soluble ligand-capped quantum dots were introduced as ECL nanoemitters to create sensitive analytical methods for detecting and tracing biomarkers. The functionalized polymer dots were also designed as ECL nanoemitters for imaging of membrane proteins with signal transduction strategies of dual resonance energy transfer and dual intramolecular electron transfer. To decode the ECL fundamental and enhancement mechanisms, an electroactive MOF with accurate molecular structure was first constructed with two redox ligands as a highly crystallized ECL nanoemitter in aqueous medium. Through the mixed-ligand approach, luminophores and co-reactants were integrated into one MOF structure for self-enhanced ECL. Furthermore, several donor−acceptor COFs were developed as efficient ECL nanoemitters with tunable intrareticular charge transfer. The atomically precise structure of conductive frameworks established clear correlations between the structure and charge transport in these materials. Therefore, reticular materials as crystalline ECL nanoemitters have demonstrated both proof of concept and mechanistic innovation.

In this Account, taking advantage of reticular materials with accurate molecular structure, we survey the design of the electroactive reticular materials including MOFs and COFs as crystalline ECL nanoemitters at the molecular level. The enhancement mechanisms of ECL emission of various topology frameworks are discussed via the regulation of reticular energy transfer and charge transfer and the accumulation of anion/cation radicals. Our perspective on the reticular ECL nanoemitters is also discussed. This Account provides a new avenue for designing molecular crystalline ECL nanoemitters and decoding the fundamentals of ECL detection methods.

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INTRODUCTION

Electrochemiluminescence (ECL) is a light-emitting process via charge transfer between the electrochemical reaction intermediates of the emitter and the co-reactant/emitter.[5,6] Since silicon nanocrystals were reported as ECL nanoemitters by Bard's group in 2002,[7] many ECL nanoemitters such as quantum dots, polymer dots (Pdots), and metal nanoclusters have been designed, which emit the ECL through either band gap or surface-state emission mechanisms.[8,9] To reduce the applied potential, a low-oxidation-potential route is introduced based on the direct oxidation of co-reactant, which generates a cation radical and subsequently reacts with the luminophore to form excited states for emitting light.[10,11] A self-enhanced ECL mechanism is established to drastically enhance the ECL emission by covalently attaching the co-reactant *N*,*N*-diethylethylenediamine onto Au clusters.[12] However, due to the unpredictable nanostructures in the conventional nanoemitters, fundamental mechanistic studies of ECL generation are rarely explored at the molecular level.

Reticular materials involving metal−organic frameworks (MOFs) and covalent organic frameworks (COFs) are molecular crystalline materials constructed by the staggered arrangement of organic ligands and/or metal atoms.[13] With the development of conductive reticular structures, they have already been used in electrochemical fields such as ECL, photoelectrochemistry, and electrochemical detection. Moreover, due to the predesignable nature of reticular materials, their charge transfer capacity can be modulated by integrating functional building blocks into the long-range ordered frameworks.[14] Typically, the conductivity of a fully π-conjugated sp^{2}c-COF semiconductor is enhanced by 12 orders of magnitude via the chemical oxidization.[15] The enhanced intramolecular or intermolecular charge transfer enables reticular structures as efficient ECL nanoemitters. Additionally, the generation process of excited species can be precisely revealed, thereby offering a potential platform to elucidate the correlation between the reticular structure and the ECL mechanism. Thus, taking advantage of reticular materials such as atomically precise molecular structure, functional designability, and high stability, we recently designed a series of reticular ECL nanoemitters with different topologies and high charge carrier migration via the accurate assembly of organic monomers at the molecular level. Mechanisms of framework-regulated ECL emission are also proposed for enhancing ECL emission. In this Account, we deeply explore the relationship between reticular structure and ECL mechanism (Figure 1), providing a blueprint for a well-guided approach toward the design and development of ECL nanoemitters.

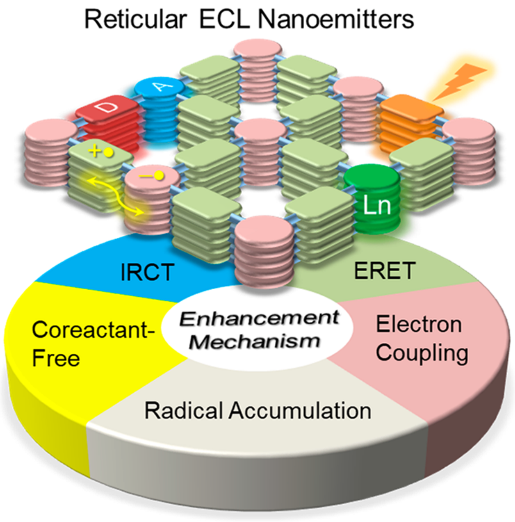

Figure 1. Schematic illustration of the structural design and enhancement mechanism of reticular ECL nanoemitters.

STRUCTURAL DESIGN OF RETICULAR ECL NANOEMITTERS

Compared with conventional luminophores, reticular structures exhibit efficient confinement effect to accelerate the reactivity within pore channels and thus enhance the ECL behaviors. However, the poor electrical conductivity always prevents the use of these materials as efficient ECL emitters. To realize ECL emission of reticular materials, three types of methods have been developed for designing electroactive reticular nanoemitters: integrating electroactive luminophore ligands, doping transition metal elements, and assembling periodic reticular arrays with nonemitting monomers.

Design with Electroactive Luminophore Ligands

By integrating electroactive luminophores such as porphyrin, boron dipyrromethene, and pyrene in the frameworks, the resulting reticular nanoemitters exhibit high charge delocalization and mobility within the frameworks, and restrict intramolecular rotations,[16] thereby remarkably improving the ECL efficiency. Typically, tetrakis(4-carboxyphenyl) porphyrin with strong optical absorption and emission and distinctive electrochemical properties can be integrated into the framework to form porphyrin-based Zr-MOFs, which can overcome the aggregation-caused quenching effect and thus show great

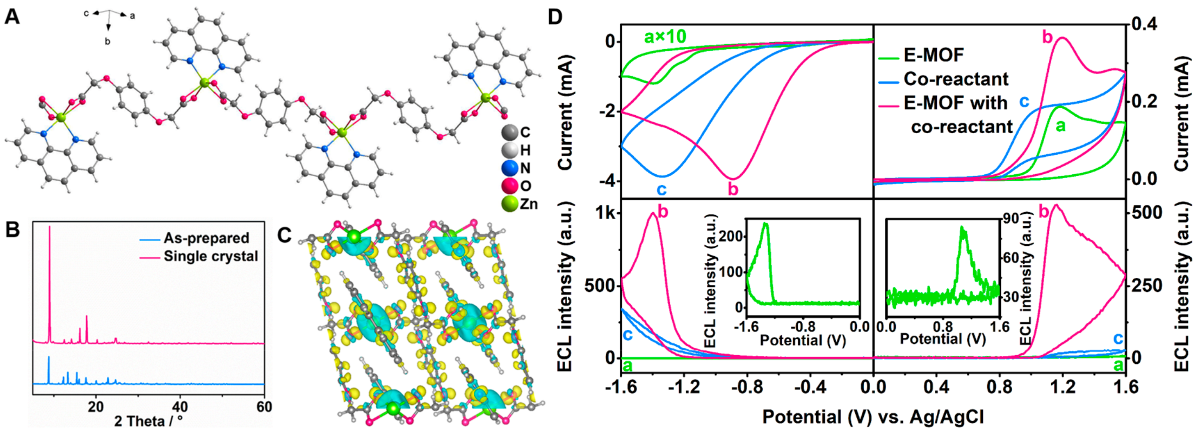

Figure 2. (A) Crystal structure of the mixed ligand E-MOF. (B) Experimental and simulated PXRD patterns of E-MOF. (C) Deformation charge density of E-MOF. (D) Cathodic (left) and anodic (right) cyclic voltammetry and ECL of E-MOF/GCE in the absence (a) and presence (b) of co-reactant, and bare GCE (c) in the presence of co-reactant. Reproduced with permission from ref 3. Copyright 2020 Wiley.

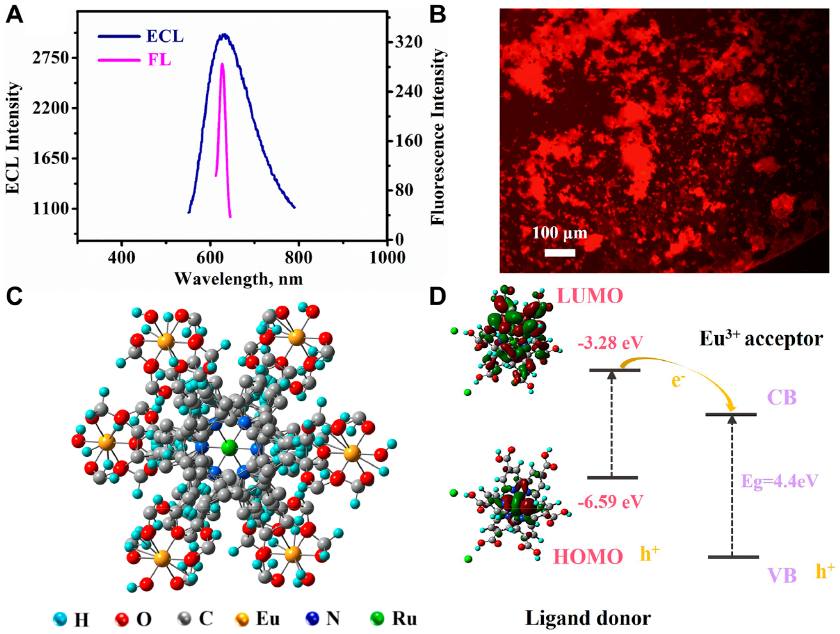

Figure 3. (A) ECL and fluorescence emission spectrum and (B) fluorescence microscopic image of Ln MOFs. Reproduced with permission from ref 25. Copyright 2021 ACS Publications. (C) Ball-and-stick model of $Eu_2[Ru(dcbpy)_3]_3$. (D) Mechanism of resonance energy transfer from $Ru(bpy)_3$-based ligands to Eu^{3+} with frontier molecular orbitals. Reproduced with permission from ref 26. Copyright 2022 Elsevier Inc.

potential in ECL biosensing.[17] Considering the high fluorescence intensity and narrow absorption/emission peaks, the integration of boron dipyrromethene (BDP) into frameworks can separate the aggregated BDP molecules, and thus 24-fold enhancement of ECL intensity is obtained due to the suppressed nonradiative energy dissipation.[18] Furthermore, using hydroquinone and phenanthroline as redox couples, an electroactive MOF (E-MOF) with a one-dimensional zigzag chain is designed as an efficient crystalline ECL emitter in an aqueous medium (Figure 2A). The mixed-ligand E-MOF shows consistency in experimental and simulated powder X-ray diffraction (PXRD) (Figure 2B), suggesting its flawless crystal structure. And the deformation charge density of E-MOF presents two positive charges on the center Zn, indicating the electron flow tendency from Zn centers to ligands (Figure 2C). Benefiting from the electroactive hydroquinone and phenanthroline units, the E-MOF shows good redox activity. In the cathodic system, an E-MOF modifying a glassy carbon electrode (GCE) can be reduced to E-MOF$^{-•}$ at an electrochemical peak potential of −1.4 V, while the E-MOF$^{+•}$ is produced via a strong electrocatalysis toward $S_2O_8^{2-}$ reduction (Figure 2D). The excited state E-MOF* could be generated through the charge transport between E-MOF$^{+•}$ and E-MOF$^{-•}$ and produce the ECL emission through a surface state model in both co-reactant and annihilation ECL.[3] In the anodic system, the E-MOF can be electrochemically oxidized to E-MOF$^{+•}$ by removing electrons from the HOMO, while E-MOF$^{-•}$ is generated by the reduction of E-MOF by electrochemically produced tripropylamine radical (TPrA$^•$). Therefore, an anodic co-reactant ECL can be observed at an onset potential of +0.9 V with a maximum

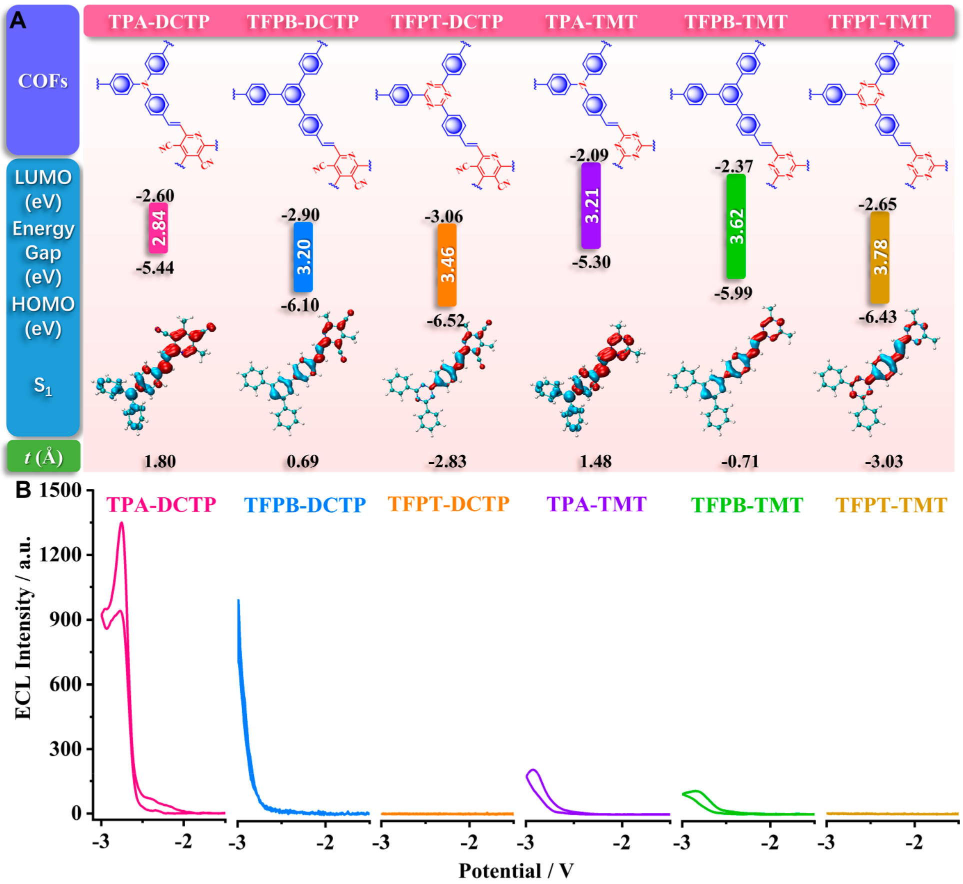

Figure 4. (A) Density functional theory (DFT) calculations with the values of HOMOs, LUMOs, energy gaps, and distribution of hole (blue) and electron (red) for building blocks of COFs. (B) ECL intensities of different COFs at the applied potentials between 0 and −3.0 V. Reproduced with permission from ref 28. Copyright 2021 Nature Publishing Group.

emission at +1.16 V. The mixed-ligand E-MOFs provide a new platform to design molecular crystalline emitters.

Alternatively, by using the aggregation-induced emission (AIE) luminogen as a ligand to build MOFs, enhanced ECL emission can be obtained from the effective restriction of intramolecular motions. For example, using the AIE-active 1,1,2,2-tetra(4-carboxylbiphenyl)ethylene molecule as a bridging ligand, a dumbbell plate-shaped MOF was synthesized, which was used as an ECL tag to achieve higher ECL emission efficiency compared with the monomer and its aggregates.[19] Due to limitation of the intramolecular free rotation of the phenyl rings, the tetraphenylethylene-based Hf-MOF achieves remarkable enhancement of the ECL intensity.[20]

Transition Metal Element Doped Self-Luminescent Nanoemitters

The doping of transition metal elements is an alternative way to address the natively poor electrical conductivity of MOFs in ECL performance. A typical ECL luminophore, carboxyl-rich tris(4,4′-dicarboxylic acid-2,2′-bipyridyl) ruthenium(II), with good water solubility can be incorporated into the backbone of MOFs as an excellent ECL emitter,[21] which can be expanded to the other luminous transition metals. Atomic dispersion of Ru in NiRu MOFs produced by an ion-exchange method leads to the significantly higher ECL luminous efficiency than pure Ni-MOFs.[22] Furthermore, a chemical fixation strategy to *in situ* form a $[Ru(bpy)_3]^{2+}$ luminophore, has been applied to construct a single atom-anchored MOF for solid-state ECL,[23] which can be extended to the anchoring of other luminophores with the different coordination groups.

Based on the long lifetime excited states of lanthanide cations, lanthanide MOFs are promising candidates as ECL luminophores without an extra luminophore.[24] The lanthanide MOFs as ECL signal emitters composed of a Eu(III) ion and 5-boronoisophthalic acid have uniform spherical shape with a 45 nm particle size. The aromatic chromophore of the ligands can absorb ultraviolet radiation to generate a triplet-state, which then triggers Eu(III) ion red emission.[25] The ECL spectrum peaking at 631 nm matches with the fluorescence spectrum (Figure 3A), suggesting a similar emission process of the ECL and fluorescence of MOFs. The fluorescence emission performance of the europium MOFs has been verified by confocal laser scanning microscopy with bright red luminescence (Figure 3B). Furthermore, through the energy transfer from the ligand to the luminescent center Eu^{3+} (Figure 3C), a near-infrared luminescent Eu-MOF can be synthesized to realize annihilation ECL luminescence without extra co-reactant.[26] As shown in Figure 3D, the $Ru(bpy)_3$-based ligand is excited to its S_1 with an excitation energy of 17171.54 cm^{-1}, while the electron transfers to the triplet state through intersystem crossing and then sensitizes Eu^{3+} by nonradiative energy transmission via T_1 for enhancing the Eu-MOF luminescence.

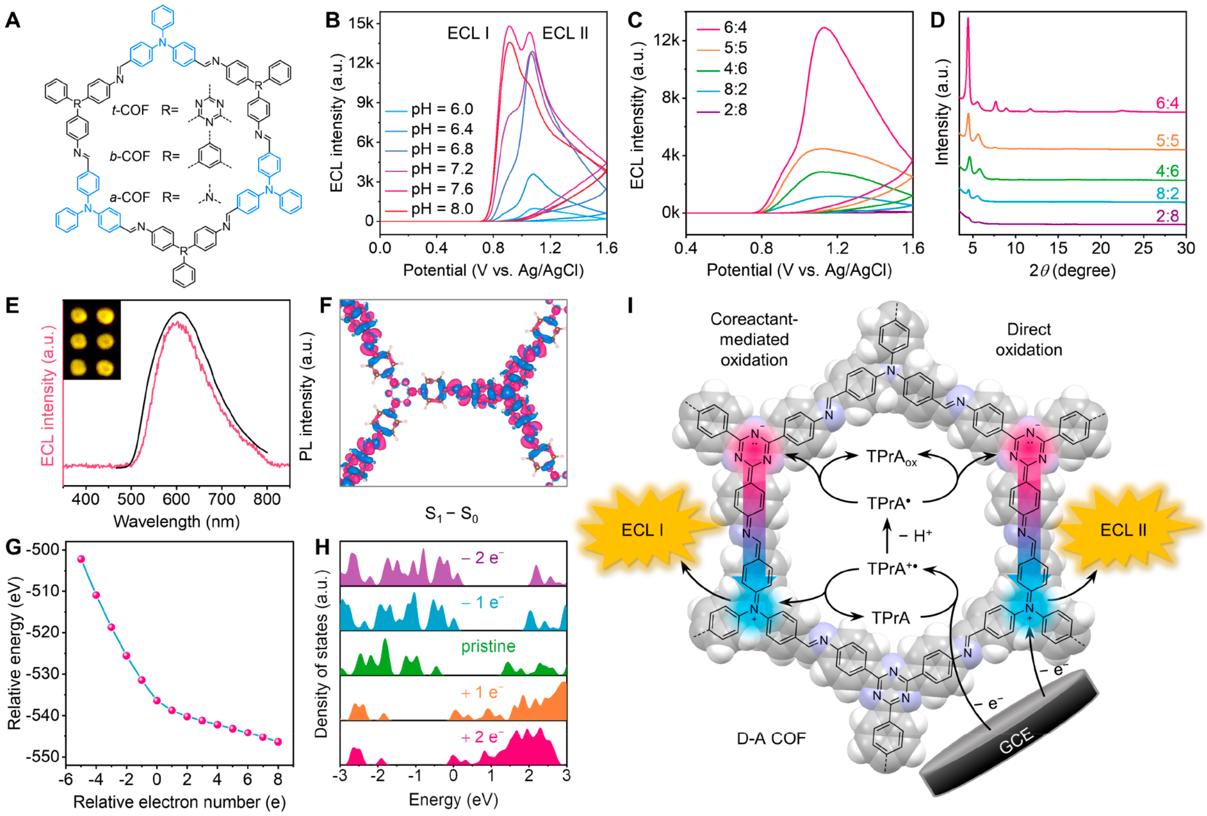

Figure 5. (A) Structure of three TFPA-based COFs. (B) Dual-peaked ECL patterns containing 20 mM tripropylamine (TPrA) of *t*-COF-modified GCEs at different pH values. (C) Crystallinity-dependent ECL and (D) PXRD spectra of *t*-COFs synthesized with various solvent ratios. (E) Fluorescence and ECL spectra of *t*-COF. (F) Charge density difference between S_1 and S_0 for *t*-COF. (G) Relative energy and (H) density of states of the charged *t*-COF. (I) ECL I and II generation mechanism via IRCT. Reproduced with permission from ref 2. Copyright 2021 Nature Publishing Group.

ECL Generation from Non-emitting Monomers

The emergence of COFs may bring an unprecedented opportunity to design ECL nanoemitters due to interlayer stacking and intermolecular synergism. COFs not only allow organic building blocks to be accurately integrated into a long-range ordered structure but also avoid the quenching effect of metal nodes in the framework. In particular, the intramolecular charge-transfer states produced by the separation of electron donors and acceptors within the periodic reticular arrays of COF skeletons can activate ECL behaviors from the nonemitting monomers. Typically, by conjugating a 2,4,6-trimethylbenzene-1,3,5-tricarbonitrile electron acceptor with different electron donors, a series of olefin-linked crystalline COFs have been constructed. By this means, a tunable ECL with maximum efficiency of 32.1% is realized from non-ECL molecules using dissolved oxygen as an inner co-reactant.[27] To address the low conductivity of COFs, a series of electron-donors, tris(4-formylphenyl)amine (TPA), 1,3,5-tris(4-formylphenyl)benzene (TFPB), and 2,4,6-tris(4-formylphenyl)-1,3,5-triazine (TFPT), are paired with the C_{2v} and C_{3v} symmetrical acceptor subunits 2,4,6-trimethylpyridine-3,5-dicarbonitrile and 2,4,6-trimethyl-1,3,5-triazine.[28] According to the reduced overlap of S_1 molecular orbitals (Figure 4A), electrons and holes are effectively separated at the acceptor and donor units during ECL generation, respectively. It can be seen that the TPA-COFs with stronger electron-donating ability possess smaller band gaps and show around 1.4-fold stronger ECL intensities than TFPB-COFs (Figure 4B), indicating that intramolecular charge transfer can effectively activate the ECL signals of COFs. Further, a fully conjugated COF synthesized with trithiophene units shows high ECL efficiency up to 62.2% in aqueous solution, even without exogenous co-reactant.[29]

MECHANISMS OF ECL ENHANCEMENT

To realize high ECL efficiency, it is important to improve the charge transfer rate in reticular frameworks[14] and stabilize the electrochemically generated luminophore radicals. In the case of charge transfer, it can be achieved by designing large conjugation networks for improving intramolecular charge transport[2,28] and interlayer electron coupling pathways and integrating both luminophore and co-reactant units into one framework. Considering the key reaction between cation and anion radicals during ECL emission, radical stabilization may promote excited state generation. Finally, the electrochemiluminescence resonance energy transfer (ERET) approach is involved in the mechanism of ECL enhancement.

Improving Intramolecular Charge Transport

By leveraging the tunability of reticular structures, we can construct efficient ECL nanoemitters with rapid intramolecular charge transport. Typically, intrareticular charge transfer (IRCT) in frameworks encompasses both intermolecular and intramolecular charge transport. For intramolecular charge transport, the integration of donor and acceptor (D−A) units and improving the degree of conjugation can enhance charge mobility. For example, a D−A pair like triphenylamine−

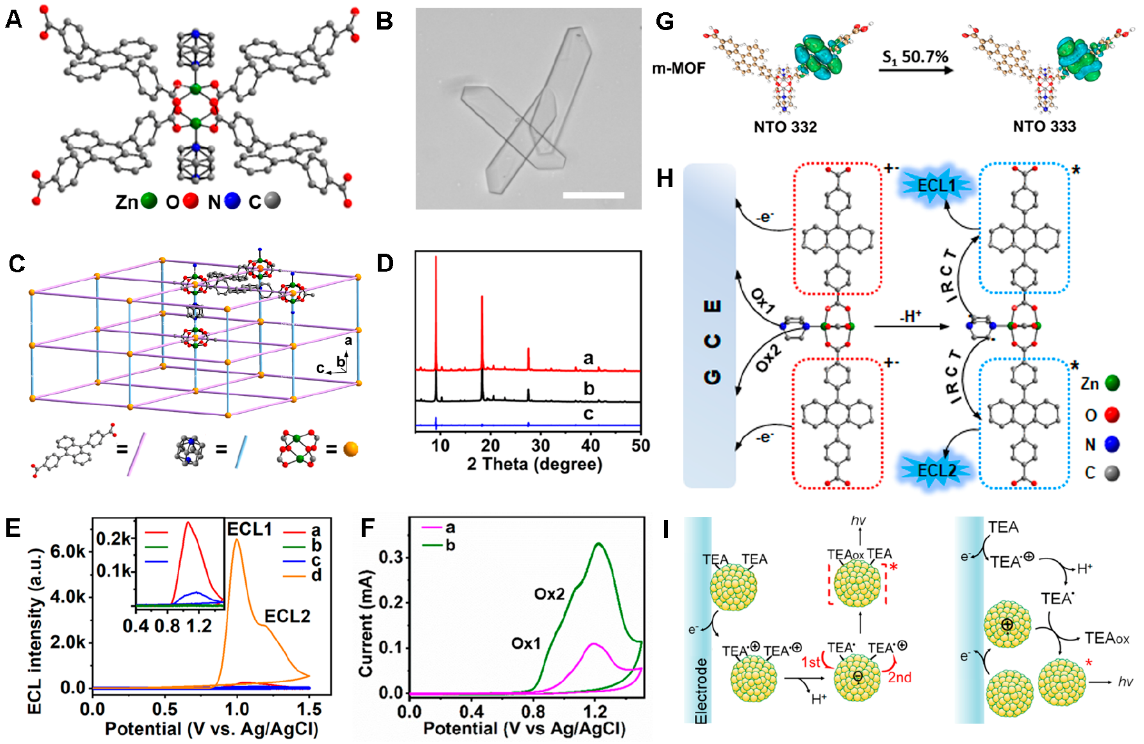

Figure 6. (A) Paddlewheel unit, (B) crystal photograph, and (C) crystal structure of m-MOF. (D) Simulated (a) and experimental (b) PXRD patterns of m-MOF and their difference (c). (E) ECL curves of DPA-modified GCEs with (a) and without (b) 5 mM D-H_2, of s-MOF (c) and m-MOF (d) modified GCEs without co-reactant. (F) Cyclic voltammetry at s-MOF (a) and m-MOF (b) modified GCEs without co-reactant. (G) NTO isodensity surfaces in the S_1 state of m-MOF clusters. (H) Stepwise ECL mechanism via dual intrareticular oxidation. Reproduced with permission from ref 1. Copyright 2021 ACS Publications. (I) Schematic illustration of intramolecular electron transfer (left) and intermolecular electron transfer between nanoemitters and co-reactant (right). Reproduced with permission from ref 4. Copyright 2021 Wiley.

triazine can serve as building blocks for synthesizing ECL nanoemitters (Figure 5A).[2] When the protonation degree decreased, dual ECL peaks were observed at +0.92 V and +1.05 V (Figure 5B), which depended on the oxidation of TPrA and the COF at the electrode surface. Intriguingly, *t*-COFs, synthesized with varying solvent ratios, with higher crystallinity exhibited a stronger ECL signal (Figure 5C,D). The consistency of ECL with fluorescence spectra suggested the same excited states via the band gap ECL model (Figure 5E). Moreover, the charge distribution change in the COF cell fragment revealed the intramolecular charge transfer from triazine units to triphenylamine units (Figure 5F). Compared to cation radicals at triphenylamine units, the anion radicals at triazine units of *t*-COFs demonstrated relatively high stability (Figure 5G). Additionally, upon doping with holes/electrons, the density of states displayed distribution around the Fermi level, suggesting enhanced charge mobility in the corresponding charged *t*-COFs (Figure 5H). Collectively, triazine units were reduced to $COF^{-\bullet}$ by $TPrA^{\bullet}$, whereas the triphenylamine units were oxidized to *t*-$COF^{+\bullet}$ by either $TPrA^{+\bullet}$ (Figure 5I, left) or an electrode (Figure 5I, right). Ultimately, ECL excited states were produced via intramolecular charge transport between *t*-$COF^{+\bullet}$ and *t*-$COF^{-\bullet}$, leading to a competitive oxidation mechanism at two different potentials.

To obtain strong and stable ECL generation, the sp^2 carbon-conjugated COF was selected as an efficient ECL nanoemitter, while high contrast donor−acceptor COFs were designed as ECL emitters with long-range ordered arrangement, effectively facilitating intramolecular charge transfer to enhance excited-state generation. A pyrene-based sp^2 carbon-conjugated COF nanosheet exhibited higher ECL efficiency than those of the ligands, because the porous ultrathin structure of the COF nanosheet not only increased the amount of luminophore immobilization but also effectively shortened transport distances of the electron and co-reactant,[30] opening a new horizon for developing highly efficient ECL nanoemitters.

Integrating Luminophore and Co-reactant Units into a Framework

Inspired by the molecular approach enhanced ECL systems,[31−33] integrating luminophore and co-reactant units into a framework can significantly accelerate the mass transfer, reduce the charge transfer distance, and decrease the energy loss during the electrochemical reaction. Significantly enhanced ECL could be achieved in the reticular structure coupling with the co-coordination of luminophores and co-reactants. Typically, to develop a co-reactant-free ECL nanoemitter, 9,10-di(*p*-carboxyphenyl)anthracene (DPA) and 1,4-diazabicyclo[2.2.2]octane (D-H_2) ligands were integrated into a mixed-ligand framework (m-MOF) as the luminophore and co-reactant, respectively (Figure 6A).[1] The resulting m-MOF exhibited flakelike crystals with the orthorhombic space group *Fmmm* (Figure 6B). The D-H_2 ligands axially coordinate with the zinc ion and interconnect Zn−DPA layers in the m-MOF crystal, as determined by the single-crystal and powder XRD pattern (Figure 6C,D). Compared with the mixture of DPA and D-H_2, the m-MOF displays a 26.5-fold enhancement in ECL intensity (Figure 6E), suggesting that the D-H_2 linker serves as an efficient co-reactant in the ECL process. Moreover, two ECL peaks denoted as ECL1 and ECL2 are observed at peak potentials of 1.0 and 1.2 V, respectively, which correspond to the stepwise oxidation of the DPA unit (Figure 6F). From the natural transition orbital (NTO) analysis, the $\pi-\pi^*$ excitation dominantly localizes at the DPA unit in ECL generation (Figure 6G). Overall, both DPA and D-H_2 could be oxidized in the framework, generating cation radicals $DPA^{+\bullet}$ and D-$H_2^{+\bullet}$, respectively. After deprotonation, the neutral species (D-$H^\bullet$) can be obtained and then annihilated with $DPA^{+\bullet}$ via IRCT, leading to excited DPA* for ECL emission without exogenous co-reactant (Figure 6H). Furthermore, based on the large conjugated superstructure embedded with co-reactant, a dual intramolecular electron transfer induced ECL emission was developed, which was 132-fold stronger than those from the mixture of nanoemitters and co-reactants (Figure 6I). This system realized the visual analysis of a membrane protein near the electrode surface, where it is difficult for external co-reactant to reach without additional permeabilization treatment for transporting.[4] Subsequently, the D-H_2 co-reactants were integrated with the 1,1,2,2-tetra(4-carboxylbiphenyl)ethylene luminophore to obtain a mixed-ligand MOF, which revealed 3.5 times higher ECL emission in comparison with that of single-ligand MOF even with the addition of exogenous D-H_2.[34]

A self-enhanced ECL emitter was synthesized in one-pot by integrating DPA and *N*,*N*-diethylethylenediamine (DEAEA) ligand with zinc ions to form the Zn-DPA/DEAEA system.[35] Furthermore, with introduction of the abundant DEAEA on the surface of Zn-MOFs by the hybridization chain reaction, a co-reactant-free ratiometric ECL strategy was established for sensitive detection of miRNA-133a, which did not require a pre-embedded co-reactant in the framework during the synthesis.[36]

Intrareticular Electron Coupling Pathway

Alternatively, high $\pi-\pi$ interaction propensity in reticular structures could facilitate the delocalization of orbitals and π electrons and promote electron injection during electrochemical excitation, signifying the effect known as intrareticular electron coupling (IREC). Notably, the large electronic coupling at closely spaced exciton sites leads to the formation of significant dipoles with orientations favorable for inter-exciton resonance,[37] which boosts long-range charge transfer and thereby expedites ECL generation. Typically, triazinyl-based hydrogen bond organic frameworks (HOFs) prepared by N···H hydrogen bond self-assembly aggregation demonstrate 21.3% ECL efficiency due to accelerated charge transfer.[38] Because the pyrene unit is stacked in a slipped face-to-face mode to form a J-aggregate, a superb and stable ECL intensity is obtained through the facilitated migration of ions, electrons, and co-reactant.[39]

Designing densely stacked ECL emitters with tunable charge transfer pathways is essential to uncovering the mechanism of ECL generation. Using 1,3,6,8-tetra(4-carboxylphenyl)pyrene (TCPPY) molecules, HOF-101 was synthesized through multiple H-bonds and π-interactions with the eclipse-stacked structure (Figure 7A). Compared with TCPPY, HOF-101 shows a significant increase in ECL intensity, attributed to the IREC effect within its unique framework structure. The relaxed stacking morphology of Mg-MOFs markedly diminished the IREC pathway, leading to only 2.0 times higher relative ECL efficiency compared to TCPPY (Figure 7B). When one electron and one hole were injected into the top and bottom layers, respectively, the neutral charge density difference revealed mutual electron density depletion and accumulation within vertical stacking units (Figure 7C).[40] The electron transfer from the anion radical to the cation radical within HOF-101 facilitated ECL emission via the IREC pathway (Figure 7D). Moreover, the unique properties of HOFs enable *in situ* self-repairing ECL ability, providing a new proof of concept for designing an efficient ECL system.

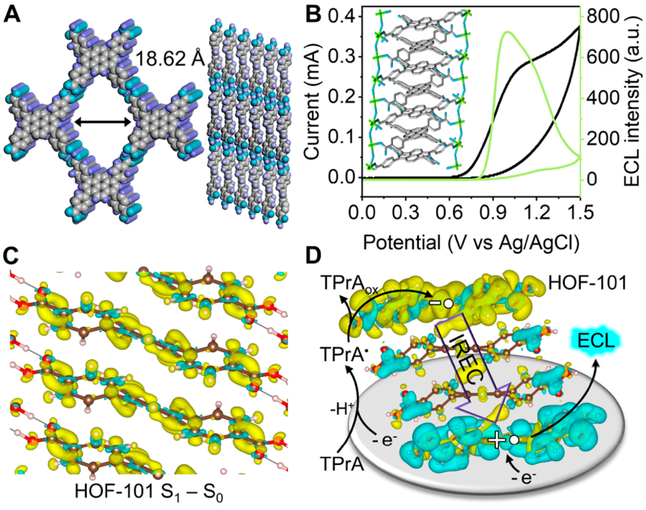

Figure 7. (A) Channel structure and interlayer stacking of HOF-101. (B) Cyclic voltammetry and ECL curves of Mg-MOF with an interlayer stacking morphology in 0.1 M PBS with 20 mM TPrA. (C) Charge density difference between S_1 and S_0 for HOF-101 in side view. (D) IREC mediated the ECL mechanism for HOF-101. Reproduced with permission from ref 40. Copyright 2022 Royal Society of Chemistry.

Accumulation of Anion/Cation Radicals

Since porous networks can serve as carriers to stabilize electrons/holes, the ECL intensity of the reticular system is enhanced via the accumulation of anion/cation radicals upon pre-reduction or -oxidation electrolysis. A fascinating 3D porous framework composed of a tetrachloroperylene anhydride-based ligand and Zr clusters (Zr-PDI) can serve as cage to trap electron donors to furnish anion radicals (Zr-$PDI^{\bullet -}$) with one-month stability, which provides abundant radical intermediates for annihilation between anion and cation radicals.[41] Stable and self-enhanced ECL emission was achieved by the accumulation of MOF cation radicals via pre-reduction electrolysis. Compared to a bare GCE, the cathodic ECL intensity showed 3-fold enhancement with a knife-like ECL peak shape at the fifth pulse (Figure 8A). Upon pre-reduction at −0.8 V, the ECL intensity centered at the 610 nm emission peak was enhanced 17-fold with high stability owing to the stable E-$MOF^{+\bullet}$ species (Figure 8B). These results indicate that the self-enhanced ECL was due to the accumulation of E-$MOF^{+\bullet}$ during the step pulse process (Figure 8C), providing a promising approach and platform for strong ECL emission.

Interestingly, the long-range arrays of extended planar frameworks in COFs not only possess excellent electrical conductivity to speed up charge transport but also lead to extra stability of cation radicals against external stresses.[42] A fully π-conjugated pyrazine-linked conductive COF was synthesized with 2,3,6,7,10,11-hexaaminotriphenylene and highly planar 2,3,6,7,10,11-hexahydroxytriphenylene ligands to exhibit superior electronic conductivity and strong ECL emission (Figure

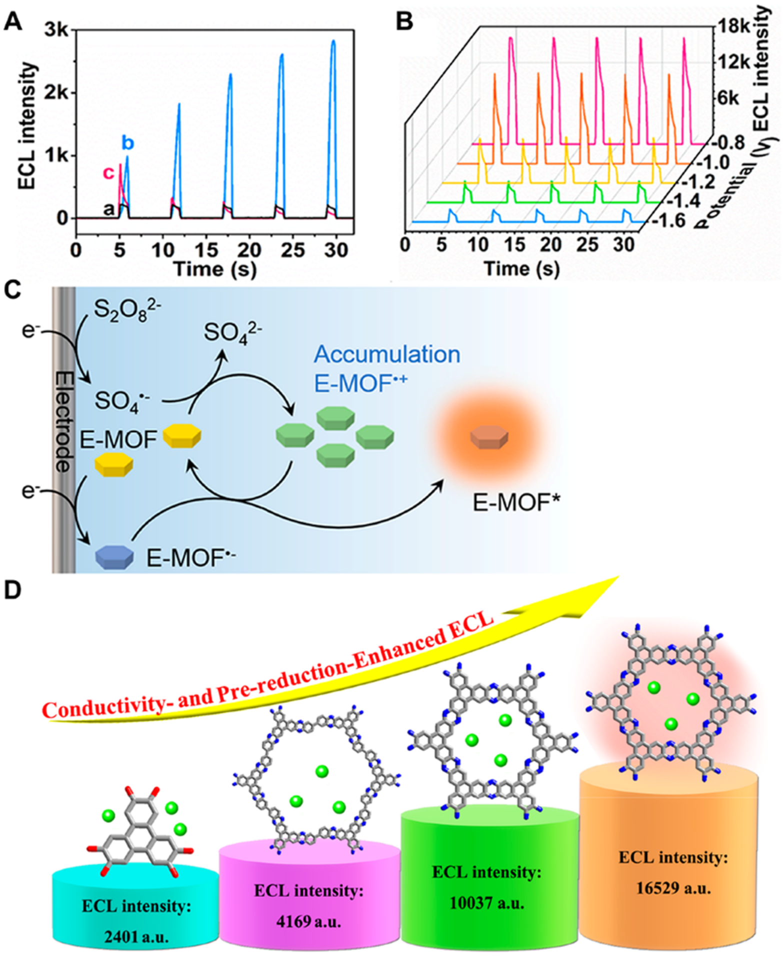

Figure 8. (A) Cathodic stepping pulse from 0 to −1.4 V at (a) bare GCE and (b) E-MOF/GCE with co-reactant $K_2S_2O_8$, and (c) anodic stepping pulse from 0 to + 1.2 V at E-MOF/GCE with co-reactant TPrA. (B) ECL transients of E-MOF/GCE with pre-reduction at different potentials for 60 s followed by stepping potential in 0.1 M $K_2S_2O_8$. (C) Self-enhanced ECL mechanism. Reproduced with permission from ref 3. Copyright 2020 Wiley. (D) Illustration of conductivity- and pre-reduction-enhanced ECL of COFs. Reproduced with permission from ref 43. Copyright 2022 ACS Publications.

8D). Upon pre-reduction electrolysis, the ECL intensity of the COF/$S_2O_8^{2-}$ system can further increase because of the accumulation of $COF^{+•}$.[43] Anion or cation radical accumulation might be achieved through the rational introduction of donor−acceptor pairs or reversible transformation groups.

Electrochemiluminescence Resonance Energy Transfer

In principle, the ERET process is caused by energy transfer between the ECL emission donor and the acceptor.[44] Coupling framework donors with different energy acceptors, ERET systems can be constructed with the enhanced ECL performance without an additional co-reactant. Inspired by this, a multiple convertible ERET system was established using a DNA structure that regulated the distance between the tetraphenylethylene-functionalized MOF donor and gold nanoparticle/adriamycin acceptors.[45] Based on the aggregation-induced ECL emission of ligands and silver-catalysis toward $S_2O_8^{2-}$, an ERET biosensor with a AgMOF donor and black hole quencher-2 acceptor was assembled for miRNA-107 detection.[46] Furthermore, utilizing 6-carboxy-4′,5′-dichloro-2′,7′-dimethoxyfluorescein as the receptor, an ERET biosensor was constructed based on a mixed ligand MOF donor composed of the luminophore and DEAEA co-reactant for sensitive detection of miR-21 without additional co-reactant.[35]

In addition, due to the surface plasmon resonance effect of Au−Pt nanorods, a high performance ECL platform composed of a Eu-MOF as luminophore and Au−Pt bimetallic nanorods as plasma source exhibits 2.6-fold enhancement compared to free Eu-MOF.[47]

■ SUMMARY AND OUTLOOK

Compared with conventional luminophores, reticular nanoemitters with different topologies demonstrate high mass transfer ability for accelerating the reactivity in pore channels, which are conducive to achieving significant confinement-enhanced ECL. Moreover, by integrating luminophores into frameworks, the luminescence properties are significantly improved due to the arrangement of molecules and intermolecular electron transfer. The possible reasons for the intense ECL emission in the frameworks should be attributed to the following four points: (1) The superior electronic conductivity of reticular nanoemitters is beneficial to the electron transfer in the whole framework, especially for fully charge-delocalized structures, which accelerates the annihilation between anion and cation radicals to produce the excited state for strong ECL emission. (2) The porous frameworks allow the co-reactant in the electrolyte to diffuse into the internal cavities of the framework, achieving significant confinement-enhanced ECL.[48−50] (3) The organic monomers as luminophores are directly connected to the metal, which makes ECL luminophores easy to electrochemically activate, thus leading to a low potential ECL emission. (4) The immobilized luminophores in the conductive frameworks significantly limit the spin motion of luminophores to suppress nonradiative energy loss, realizing the improvement of ECL signal.

The elaborated structure−conductivity relationships provide a well-guided approach toward the design and development of ECL nanoemitters. By taking advantage of the synthetic tunability and structural regularity, we highlight some of the grand challenges in designing and unveiling the pristine ECL properties of reticular nanoemitters: (1) Multivariate MOFs containing mixed metal combinations can accelerate the electrochemical activation of luminophores and improve the utilization ratio of ECL luminophores, thereby achieving an intensive ECL emission.[51] (2) The electronic structure of MOFs can be modified by incorporating missing linkers into the frameworks, which results in defects to tune well the ECL properties.[52] (3) The radical-stabilized frameworks can accelerate the annihilation between anion and cation radicals to produce the excited state for strong ECL emission. (4) The 3D sp^2 carbon-conjugated COFs have a largely conjugated electron structure and accelerate the charge transfer in the whole frameworks, leading to the splendid ECL intensity even from nonemitting monomers. (5) Due to the flexibility of H-bonds and being free of heavy metal ions, HOFs exhibit remarkable *in situ* self-repairing capability for biocompatible ECL biosensors.[53] (6) The mixed ligand frameworks allow us to directly construct multicolor ECL nanoemitters, which benefit development of high-throughput analytical platforms. (7) The introduction of lanthanide elements such as Eu and La endows the frameworks with the characteristics of self-luminescence, which can be utilized as ECL signal nanoemitters without extra luminophores. (8) By utilizing the pore size effect, functionalized recognition groups in the pore, and the electrostatic environment of the cavity surface, reticular ECL emitters can be applied for specific chemical sensing.[54] Overall, the atomically precise reticular nanoemitters not only provide a molecular structure for decoding ECL fundamentals but also open a new avenue for design of enhanced ECL methodology in the next generation of ECL devices.

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Notes

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