Intermolecular forces and assembly strategies in porphyrin-based electrochemiluminescence: Mechanisms and future prospects

Yi-Xuan Li, Yu-Xuan Dai, Jérôme Chauvin, Xue-Ji Zhang, Serge Cosnier, Dan Shan

To cite this version:

Yi-Xuan Li, Yu-Xuan Dai, Jérôme Chauvin, Xue-Ji Zhang, Serge Cosnier, et al.. Intermolecular forces and assembly strategies in porphyrin-based electrochemiluminescence: Mechanisms and future prospects. Trends in Analytical Chemistry, 2024, 180, pp.117969. 10.1016/j.trac.2024.117969 . hal-04751850

HAL Id: hal-04751850

https://hal.univ-grenoble-alpes.fr/hal-04751850v1

Submitted on 24 Oct 2024

Trends in Analytical Chemistry 180 (2024) 117969

Intermolecular forces and assembly strategies in porphyrin-based electrochemiluminescence: Mechanisms and future prospects

Yi-Xuan Li a,b, Yu-Xuan Dai a,b, J´erˆome Chauvin c, Xue-Ji Zhang d, Serge Cosnier c, Dan Shan a,*
a School of Environmental and Biological Engineering, Nanjing University of Science and Technology, Nanjing, 210094, PR China
b College of Chemical and Material Engineering, Quzhou University, Quzhou, Zhejiang, 324000, PR China
c University of Grenoble Alpes-CNRS, DCM UMR 5250, F-38000, Grenoble, France
d School of Biomedical Engineering, Health Science Centre, Shenzhen University, Shenzhen, 518060, PR China

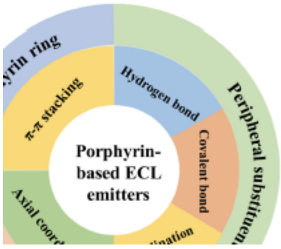
he exploration of innovative luminophores is critical for enhancing the efficiency and stability of electro-chemiluminescence (ECL). Porphyrins, with their superior optical and electrical properties, have emerged as promising organic ECL emitters. The tunable functional groups of the porphyrins facilitate their assembly into ordered structures, thereby reducing aggregation-caused quenching (ACQ) and achieving desirable photo-physical properties. This review introduces the effect of central metal and peripheral substituents of porphyrins on their ECL properties. It then summarizes various assembly strategies for developing enhanced porphyrin- based ECL emitters, focusing on the intermolecular forces introduced by the porphyrin ring, the central metal and peripheral substituents. By correlating characterization and ECL results, the structure-activity relationship between porphyrin assembly structure and ECL performance is analyzed, providing significant reference and guidance for the future design of organic ECL emitters. Finally, current challenges and future perspectives for the construction of porphyrin-based ECL emitters are discussed

Electrochemiluminescence (ECL) is an electrochemically triggered chemiluminescence (CL) reaction in which the excited state is generated by electron transfer between highly reactive radical species formed during the electrochemical process [1,2]. The combination of CL and electrochemistry provides ECL technology with unique advantages, such as the elimination of the need for additional light sources, spatio-temporal controllability, and extremely high signal-to-noise ra-tios, leading to a wide range of applications in biomedical and diagnostic fields [3–8]. Exploring innovative luminophores is critical for enhancing ECL efficiency and stability. In designing novel ECL emitters, scientists often draw inspiration for natural phenomena. A typical example is the bioluminescence of fireflies, where luciferase catalyzes the reaction between luciferin and oxygen to emit light. Inspired by such natural light emission processes, suitable organic compounds are considered promising candidates for achieving efficient and environmentally friendly light emission through specific chemical reactions [9,10].

Porphyrins are a class of macromolecular heterocyclic compounds with a rigid planar structure comprising the α-carbon atoms of four organisms, porphyrins and their derivatives play key roles in photo-synthesis and hemoglobin, demonstrating their natural advantages in light absorption and conversion processes [12,13]. Due to their wide spectral response, structural stability, ease of preparation and func-tionalization, and high luminescence efficiency, porphyrin-based mol-ecules are ideal candidates for the design of novel ECL emitters [14–17]. However, the ECL emission efficiency of most organic emitters, including porphyrins, is often hindered by aggregation-induced quenching (ACQ). The diverse intermolecular forces associated with the porphyrin ring, central metal, and peripheral substituents enable porphyrins to assemble into various structures, effectively mitigating ACQ and achieving desirable photophysical properties. From a molec-ular perspective, the structure of porphyrins and their derivatives acid several remarkable advantages for the assembly of novel ECL emitters: (1) The planar macrocyclic structure enhances the structural stability of the porphyrins and facilitates their assembly on the conducting and catalytic materials via π-π stacking [18]. (2) Porphyrin molecules can coordinate with various metal ions to form metalloporphyrins, with the central metal tunability providing different optical and electrical properties [19]. Moreover, the linking ability of the metal center allows porphyrins to be assembled into ordered structures. (3) The porphyrin macrocycle can be substituted with numerous functional groups at the mid- or β-position, allowing tailored properties through molecular en-gineering, including improved solubility and tuned electronic proper-ties, and assembly into ordered structures to reduce aggregation-caused quenching (ACQ) [20–22].

This review first focused on the effect of central metal and peripheral substituents of porphyrins on their ECL properties. It then details the design strategies for enhanced porphyrin-based ECL emitters based on different intermolecular forces introduced by the porphyrin ring, central metal, and peripheral substituents (Scheme 1). Finally, the future perspectives for the construction of porphyrin-based ECL emitters are discussed.

Porphyrins, as a class of macromolecular heterocyclic compounds with rigid planar structures, naturally exhibit π-π stacking forces, enabling them to spontaneously form ordered aggregates [18]. M. R. Wasielewski's group synthesized the monodisperse aggregates consisting of five molecules arranged in a columnar stack through the self-assembly of zinc tetraphenylporphyrin with four bisimide perylene groups, utilizing intermolecular π-π interaction [23]. Besides self-assembly, π-π stacking allows porphyrins to be assembled on con-ducting or catalytic materials, thereby increasing the electron transfer rate in the ECL process. Shan's group has constructed an efficient bio-mimetic catalyst (CoPPIX@C3N4), assembled from ultrathin carbon nitride nanosheets (C3N4) and cobalt porphyrin, through partial π-π stacking between pyrrole subunits of porphyrin and heptazine of C3N4. This catalyst exhibits excellent electrocatalytic capabilities comparable to those of conventional peroxidases (Fig. 1) [24]. Similarly, Mao's group enhanced ECL intensity by compositing zinc-metal organic frameworks (Zn-MOF) with graphene oxide (GO), which accelerates the electron transfer rate [25].



3. Central metal-based assembly strategy

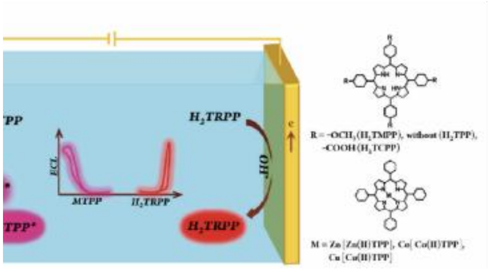
3.1. Effect of central metal on ECL reaction

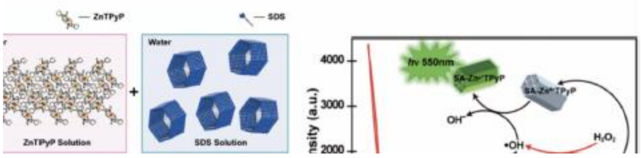
Porphyrins can coordinate with various cations, including most transition metals, forming a square-planar structure. Porphyrins lacking metal cations are referred to as free-base porphyrins. Among metal-loporphyrins, iron porphyrin, cobalt porphyrin, and manganese porphyrin serve as electrocatalysts for numerous small molecules involved in biological processes [26]. However, their luminescence ca-pacity is insufficient. In contrast, free-base porphyrins and zinc por-phyrins are excellent candidates for ECL luminophores due to their reversible redox ability and superior photoelectrochemical properties [27,28]. Various researchers have investigated the ECL performance and mechanism of free-base porphyrins and different metalloporphyrins.

Shan’s group was the first to explore the cathodic ECL mechanism of singlet oxygen (1O2) induced by the electroactive zinc porphyrin in an aqueous medium. They propose that only the electroactive intermediate Zn•+TCPP•⍰ , and not TCPP•- or TCPP2⍰ , can oxidize O2·⍰ to produce 1O2, attributed to the intermediate valence state Zn·+ coordinated to porphyrin ring [29]. Lu’s group systematically investigated the oxygen-involved ECL mechanism of metal porphyrins and metal-free porphyrins. For metal-free porphyrins, the anodic ECL emission arises from the collision between OH· and porphyrin radical anions. For metal porphyrins, the generated O·2⁻ cannot be further converted into H2O due to the absence of proton in the porphyrin ring. Therefore, O2·⍰ reacts directly with the porphyrin radical anion, resulting in cathodic ECL emission (Fig. 2A) [30]. The influence of the central metal on the porphyrin extends beyond the oxygen-involved ECL process. Coordi-nated metal ions can increase the conformational rigidity of porphyrin molecules and reduce the energy loss via bond vibration. Among tran-sition metals, Zn2+ with a d10 orbital is particularly suitable as a porphyrin center metal for ECL reactions, whereas other metal ions with a single electron in the eg orbital tend to quench the ECL spectra. Cui’s group discovered that post-synthesis modification with Zn2+ on nonmetal porphyrin-based MOFs resulted in a staggering amplification of ECL intensity by approximately 19–50 fold when using potassium persulfate as a coreactant (Fig. 2B) [31].

3.2. Central metal dominated assembly structure

Various zinc porphyrin-based ECL luminophores have been devel-oped due to their excellent ECL performance. More importantly, the linking ability of the metal center allows porphyrins to be assembled into ordered structures. Shan’s group reported the construction of one-dimensional nanostructures (SA-ZnTPyP) formed by the self-assembly of zinc tetra (4-pyridyl) porphine (ZnTPyP), where the dominant force was changed from π-π staking to Zn–N axial coordination with the assistance of surfactant. In the ZnTPyP-H2O2 ECL system, the existence of Zn•+/Zn0 transition and •OH groups, which are produced by Zn2+/ Zn•+ transition, plays an essential role. When π-π staking is the dominant force, the active sites (Zn2+) cannot have full access to the co-reactant H2O2, leading to weak ECL emission. When Zn–N axial coordination is the dominant force, the coexisting bonding forces result in more active sites exposed and the facilitated mass transfer, thereby reducing the ACQ effect and improving the ECL performance (Fig. 3A) [32]. Addi-tionally, the central metal linkage enables stable grafting onto carrier material to mitigate the ACQ effect. Deng’s group encapsulated zinc porphyrin within a pyridine-bribed β-cyclodextrin dimer (Py(CD)2), utilizing the axial ligation between the pyridyl N and Zn2+ in porphyrin ring. This configuration exhibits significantly enhanced ECL activity compared to the zinc porphyrin alone (Fig. 3B) [33]. Moreover, they employed a pyrrolidinyl C60 imidazolyl artefact as a congruent nano-center to converge three zinc porphyrins onto its monopole through the axial attachment of imidazole N of C60 derivatives and the central metal of the porphyrin ring [34].





ig. 3. (A) Schematic illustrations for the construction and possible ECL mechanism of SA-ZnTPyP [32]. (B) Enhanced ECL of the supramolecular complex ZnTSPP@Py(CD

ehavior of porphyrins by altering their molecular space structure and electron density distribution [36]. Lu’s group elucidated the effect of substituents on the oxygen-involved ECL of porphyrins by comparing the ECL performance of H2TMPP (containing an electron-donating group) and H2TCPP (containing an electron-withdrawing group) (Fig. 4A) [30]. For porphyrins substituted with electron-withdrawing groups, the space for the motion of the delocalized electrons extends to the benzene ring, and the electron density around the proton on the porphyrin ring is significantly reduced, making it more favorable for protons to attack O•2– (Fig. 4B). Due to this stretched molecular structure and reduced electron density around the proton, porphyrins substituted with electron-withdrawing groups exhibit enhanced ECL signals (Fig. 4C).

4.2. Peripheral substituent dominated assembly structure

Tunable peripheral substituents of porphyrins provide them with different dominant forces, allowing them to assemble into various or-dered structures. Depending on the nature and the linkage mode of the porphyrin peripheral substituents, diverse assembly strategies

aqueous solution.

4.2.1. Hydrogen bond

Porphyrins with substituents such as hydroxyl and carboxyl groups can form assemblies through hydrogen bonding. By regulating the dominant forces during the assembly process from π-π interactions to van der Waals forces or hydrogen bonding, the assembled structure of porphyrins can change from H-type aggregates (face-to-face) to J-type aggregates (edge-to-edge) [18]. Compared to the monomer and H-ag-gregates, the absorption spectra of the J-aggregates are red-shifted, corresponding to the reduced energy gap (Eg) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied mo-lecular orbital (LUMO) (Fig. 5A1). The lower LUMO-HOMO bandgap facilitates electron transfer and recombination of electron–hole pairs, resulting in stronger ECL emission. Fu's group constructed J-aggregated porphyrins as robust organic luminophores with the assistance of an anionic surfactant sodium dodecyl sulfate (SDS). In this ECL system, the TCPP aggregate is the primary luminophore, and the ZnO@Cys NFs can be used as a new energy donor and coreactant accelerator. In the pres-ence of ZnO@Cys NFs, the coreactant S2O82⍰ can oxidize TCPP·⍰ to produce the excited state TCPP* (Fig. 5A2) [37].

Moreover, porphyrins can be loaded or anchored on host materials through hydrogen bonding to attenuate the ACQ effect. β-cyclodextrin (β-CD) has a hollow conical structure with a lipophilic cavity and a hydrophilic outer surface containing hydroxyl groups [38,39]. Lu's group reported a novel depolymerization-induced ECL (DIECL) strategy achieved through the self-assembly of THPP and β-CD via hydrogen bonding of hydroxyl groups [40]. By grafting THPP onto the hydrophilic outer surface of β-CD, the insolubility and aggregation of THPP in aqueous solution were greatly improved, resulting in bright depolymerization-induced ECL emission (Fig. 5B).

4.2.2. Covalent bond

Beyond hydrogen bonding, porphyrin derivatives can be modified with other functional materials via condensation reactions to obtain desirable electrochemical and optical properties. For example, porphy-rins can be linked via peripheral substituents to luminophores whose emission spectra overlap with the porphyrin absorption spectrum, thus improving ECL emission efficiency through efficient energy resonance transfer [41,42]. Additionally, by linking porphyrins to electron-donating or electron-withdrawing molecules, the HOMO and LUMO energy levels of porphyrin-based complexes can be tuned, affecting the electron transfer and recombination of processes in the ECL reaction [43,44]. Lu's group decorated an aggregation-induced emission (AIE)-active chromophore, tetraphenylethene, (TPE), on porphyrin (ATPP) with ACQ properties via a simple Schiff base reaction synthesis method [45]. The non-planar structure between the ATPP core and the TPE peripheral molecules dramatically eliminated the detrimental π-π stacking of ATPP to eliminate the ACQ effect. In the ECL process, ATPP-TPE and K2S2O8 is reduced to ATPP-TPE·⍰ and SO4·⍰ . Subsequently, an electron transfer reaction between ATPP-TPE·⍰ and SO4·⍰ occurs in the vicinity of the electrode to generate ATPP-TPE* (Fig. 6A1). More importantly, the efficient resonance energy transfer from the aggregated TPE molecule to the ATPP imparted AIE-active behavior to reduced HOMO-LUMO gap compared to ATPP, which is conducive to electron-transfer reactions on the electrode (Fig. 6A3).

Considering that ECL is an electrochemically triggered chem-iluminescence reaction, the generation efficiency of reactive in-termediates is one of primary factors limiting the coreactant ECL reaction. Covalently linking the porphyrin to materials with electro-catalytic capability can effectively enhance the catalytic efficiency from the coreactants to the active intermediates. The abundance of linkable groups on metal-organic framework (MOF) materials allows porphyrins to be covalently linked via peripheral substituents, preventing ACQ in the aqueous phase. The porous structures and electrocatalytic capability of MOFs can enrich coreactants and promote electron transfer in ECL reaction [46,47]. Feng's group attached zinc protoporphyrin IX (ZnP) to an aminated ZIF-8 (ZnP–NH-ZIF-8) utilizing an amide condensation reaction. Benefiting from the enhanced oxygen affinity of ZIF-8, the ECL signal of ZnP–NH-ZIF-8 exhibited a 153-fold enhancement (Fig. 7A) [48]. Building on this, they used pyridine-containing zinc-based MOFs (Zn-Bp-MOFs) as effective carriers, where zinc porphyrin (Zn-TP) was assembled via sulfonamide bonds. Zn-Bp-MOFs, with conjugated bipyridine and ordered assembly structures, demonstrate high electro-catalytic performance towards the coreactant (K2S2O8) and increased photoelectrons on the Zn-TP, resulting in boosted ECL efficiency (Fig. 7B) [49].

4.2.3. Coordination bond

A coordination bond is a special type of covalent bond where the shared electron pair is supplied by one of the atoms alone. Assembling metals and luminophores into ordered MOFs by coordination bond is an effective strategy to construct robust and efficient ECL emitters. Intro-ducing porphyrins as ligands into MOFs not only prevents their aggre-gation in the aqueous phase, but also maximizes the integration of functional units, reducing the percentage of inactive components [50, 51].

luminophores to be fully exposed and the coreactants to be enriched in the pores and channels [52–54]. More importantly, due to the tunability of the central metal and ligand, MOFs can integrate coreaction accel-erators and luminophores, thereby reducing the energy loss during the ECL reaction and obtaining enhanced ECL emission [55]. ategy by introducing TCPP as a ligand into the framework (PCN-224), resulting in ECL and photoluminescence (PL) efficiencies that was 8.2 and 6.5 times higher than those of TCPP alone, respectively [56]. Based on the enrichment of coreactants in the channels of MOFs, Shan's group

developed a stable microporous zirconium zinc porphyrin MOF (MOF-525-Zn) as a three-in-one platform comprising of oxygen nanoc-ages, electronic mediators, and bonding sites for ECL protein kinase activity assays (Fig. 8A) [57]. By utilizing on the enrichment of oxygen through the porous and multi-channel structure of MOFs, the electro-active center ZnTCPP can effectively react with the oxygen molecules to generate singlet oxygen and produce enhanced ECL signal.

The specific surface areas, pore sizes, structures, and surface charge states of MOFs can be adjusted by simply changing the reaction time. By optimizing the condition of the hydrothermal reaction, Liu's group ac-quired PCN-222 with a large surface area, abundant micropores, good conductivity, and positively charged surfaces, which are favorable for boosting ECL performance (Fig. 8B) [58].

Compared to 3D MOF crystals, 2D MOF nanosheets with larger sur-face areas and highly exposed active sites have emerged as promising candidates for ECL emitters. However, due to the π-π stacking effect, 2D porphyrin-based MOFs are prone to stacking, which leads to aggregate formation [27,59]. To modulate the assembly process of MOFs, suitable surfactants or small molecules have been introduced to regulate the morphology of 2D MOFs, reduce the interlayer aggregation, induce the anisotropic growth of MOF sheets, and expose more active sites, thereby improving ECL performance. For surfactant-induced depolymerization, Zhang's group synthesized 2D porphyrinic MOF nanosheets with the assistance of surfactant polyvinylpyrrolidone (PVP), displaying cathodic ECL derived from singlet oxygen [60]. For small molecules regulation, Shan’s group obtained nanosized TCPP-Zn-BPS by introducing the capping agent bath-ophenanthrolinedisulfonic acid disodium salt (BPS) and adjusting the solvent (DMF/H2O) ratio to limit the crystal growth of Zn-TCPP (Fig. 9A) [61]. Moreover, Zhu’s team investigated the effects of different small molecule ligands on the morphology, structure, and ECL properties of 2D MOFs. The height of 2D Zn-TCPP MOFs was signifi-cantly reduced upon the addition of benzoic acid (BA) and 4,4′ -biphenyldicarboxylic acid (BPDC) as regulators, with the ECL signals being negatively correlated to the height of the MOFs (Fig. 9B) [62].

Additionally, MOFs are suitable platforms for assembling donor- acceptor pairs in ordered arrays to shorten the energy transfer dis-tance, resulting in efficient ECL resonance energy transfer (ECL-RET) [63]. This system enables the energy from multiple donors to be concentrated on a single acceptor, amplifying the luminescence of the acceptor. The ECL-RET system can be divided into ligand-ligand energy transfer and metal-ligand energy transfer. In constructing an ECL-RET system between ligands, Shan’s group reported a novel ECL amplifica-tion system (ZIF-9-ZnTCPP) based on ECL-RET between benzimidazole (BIM) and ZnTCPP (Fig. 10A1) [64]. The abundant BIM structure sur-rounding ZnTCPP allows the energy from multiple BIM donors to be concentrated on a single ZnTCPP acceptor, thus amplifying the ECL emission of the acceptor. Specifically, ZnTCPP undergoes two reduction processes to produce ZnTCPP2⍰ •, while BIM undergoes redox and annihilation reaction to produce BIM*. In the ECL-RET amplification.

contacted ZnTCPP2⍰ • during the return process of the excited state, causing the decay of the ZIF-9 emission and the amplification of ZnTCPP emission (Fig. 10A2).

Selecting lanthanide ions (Ln3+) with optical properties as MOFs center metals allows the construction of an ECL-RET system between the metal and the ligand. Due to the high coordination number, high con-nectivity, and diverse coordination modes, Ln3+ ions have great po-tential for the construction of various MOFs [65,66]. According to the hard–soft acid–base theory, Ln3+ ions have an affinity for relatively hard oxygenated linkers, enabling them to coordinate with carboxyporphyr-ins to form stable MOF structures [67]. Fu’s group synthesized europium-chelated porphyrin coordination polymers (Eu-PCP) via a simple and reliable solvothermal method (Fig. 10B) [68]. Eu-PCP ach-ieved high and stable ECL emission (673 nm) at low potential (⍰ 1.1 V vs Ag/AgCl) with peroxydisulfate (S2O ⍰) solution as coreactant.

The above-mentioned strategies primarily improve the optical properties of ECL emitters through depolymerization-induced ECL and ECL-RET techniques. However, the electrocatalytic capability is also a critical factor limiting ECL performance. If active intermediates are solely catalyzed from coreactants by applying a voltage at the electrode surface, issues such as slow electron transfer and low efficiency arise. Coreactant accelerators act as catalyst that convert coreactants into active intermediates, significantly enhancing the generation efficiency of these intermediates when introduced into the ECL system [69,70]. This provides a simple, efficient, and low-cost method for signal amplification. MOFs are suitable platforms for integrating co-reactant accelerators and luminophores, effectively increasing the generation rate of reactive intermediates and shortening the distance between radicals and luminophores. Shan’s group synthesized a composite material (Co-2-MI-ZnTCPP) integrating co-reactant accelerators (Co–N) and luminophores groups via a simple ligand exchange strategy oreatants (H2O2), reactive intermediates can be in situ generated and accumulated in situ, which then react with porphyrin anion radicals to achieve self-enhanced ECL emission.

In self-enhanced ECL systems, the catalytic ability of the coreactant accelerators is critical for the amplification of the ECL signal. Intro-ducing competitive ligands during the formation process of MOFs can modulate the coordination environment of the metal centers, further enhancing the catalytic ability of the coreactant accelerators towards the coreactants [72,73]. Shan’s group synthesized a 2D Zn-porphyrinic Co (II)-MOF (MOF 1) with 2-methylimidazole (MeIm) sitting axially on the paddle–wheel units as an enhanced ECL emitter (Fig. 11 B1) [74]. The axially coordinated MeIm ligand on paddle–wheel units facilitates electron transfer between Co(II) ions and oxygen and adjusts the 2D MOF 1 for easy oxygen entry and exposure of ZnTCPP (Fig. 11 B2).

Therefore, in the ECL process, O2 is reduced to O•2-, while the low- spin Co(II) ion is oxidized to Co(III) ion, which is immediately electro-reduced to Co(II). Under the above cyclic amplification process, large amounts of O•2- species is generated, which collides with the ZnTCPP•- from the electrochemical reduction of ZnTCPP to produce 1O2, resulting in enhanced ECL emission (Fig. 11

Conclusion and future perspective

In this review, we summarize various assembly strategies based on different intermolecular forces brought by the porphyrin ring, the cen-tral metal and the peripheral substituents. (1) Natural π-π stacking forces: Utilizing the natural π-π stacking forces of the porphyrin ring, porphyrins can be assembled on conducting or catalytic materials to enhance electron transfer rates in the ECL process. (2) Open axial co-ordination sites: The open axial coordination sites of central metal allow porphyrins to be assembled into ordered structures, thereby attenuating tituents of porphyrins provide different dominant forces (hydrogen bond, covalent bond and coordination bond) to assemble into various ordered structures. These substituents can be modified with functional materials to achieve desirable electrochemical and optical properties.

Based on the excellent optical and electrical properties of porphyrins achieved through these assembly strategies, combined with emerging molecular engineering, nanotechnology and electrochemical analytical techniques, porphyrin-based ECL emitters are poised for applications in biomedical imaging, multi-mode detection, and environmental monitoring. However, several key challenges must be addressed to realize prac-tical applications. (1) The possible aggregation caused by water insol-ubility of porphyrin, which will restrict its application in biological systems. (2) The exploration of designing ECL luminophores with spe-cific emission wavelengths and efficient emission efficiencies is still insufficient, which is a bottleneck for the application of porphyrin-based ECL luminophores in a variety of fields. In order to solve the above challenges, some relevant strategies are provided for reference. (1) Improving water solubility and biocompati-bility: Introducing water-soluble functional groups or complexing with biomolecules such as proteins and nucleic acids can significantly enhance their potential for use in biological systems. (2) Designing ECL emitters with specific emission wavelengths: ECL-RET is an ingenious strategy for constructing wavelength-tunable enhanced ECL emitters, which can expand its application for non-destructive imaging of living cells and tracking the dynamics of biomolecules at the single-molecule level. This strategy can not only adjust the ECL emission wavelength, but also amplify the emission of the acceptor by integrating the energy of multiple donors to single acceptor. (3) Systematic study of the amplification mechanism to design effective ECL emitters: Scanning electrochemical microscopy (SECM) and ECL microscopy (ECLM) are powerful tools to study electron transfer kinetics and mass transport processes, which are the important factor in ECL amplification mechanism.

CRediT authorship contribution statement

Yi-Xuan Li: Writing – review & editing, Writing – original draft, Methodology, Investigation, Conceptualization. Yu-Xuan Dai: Writing – review & editing, Validation, Methodology, Investigation. J´erˆome Chauvin: Writing – review & editing, Supervision, Resources. Xue-Ji Zhang: Writing – review & editing, Resources, Project administration. Serge Cosnier: Writing – review & editing, Supervision, Project administration. Dan Shan: Writing – review & editing, Validation, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

[1] W. Miao, Electrogenerated chemiluminescence and its biorelated applications, Chem. Rev. 108 (2008) 2506–2553, https://doi.org/10.1021/cr068083a.

[2] L. Hu, G. Xu, Applications and trends in electrochemiluminescence, Chem. Soc. Rev. 39 (2010) 3275–3304, https://doi.org/10.1039/b923679c.

[3] H. Qi, C. Zhang, Electrogenerated chemiluminescence biosensing, Anal. Chem. 92 (2020) 524–534, https://doi.org/10.1021/acs.analchem.9b03425.

[4] S. Li, Y. Liu, Q. Ma, Nanoparticle-based electrochemiluminescence cytosensors for single cell level detection, TrAC-Trend. Anal. Chem. 110 (2019) 277–292, https://doi.org/10.1016/j.trac.2018.11.019.

[5] C. Ding, W. Zhang, W. Wang, Y. Chen, X. Li, Amplification strategies using electrochemiluminescence biosensors for the detection of DNA, bioactive molecules and cancer biomarkers, TrAC-Trend. Anal. Chem. 65 (2015) 137–150, https://doi.org/10.1016/j.trac.2014.10.015.

[6] L. Peng, P. Li, J. Chen, A. Deng, J. Li, Recent progress in assembly strategies of nanomaterials-based ultrasensitive electrochemiluminescence biosensors for food safety and disease diagnosis, Talanta 253 (2023) 123906, https://doi.org/10.1016/j.talanta.2022.123906.

[7] Y. Jia, M. Zhu, X. Zhang, D. Jia, T. Tian, B. Shi, Z. Ru, H. Ma, Y. Wan, Q. Wei, Nanobody-based microfluidic immunosensor chip using tetraphenylethylene- derived covalent organic frameworks as aggregation-induced electrochemiluminescence emitters for the detection of thymic stromal lymphopoietin, Anal. Chem. 96 (2024) 10116–10120, https://doi.org/10.1021/ acs.analchem.4c02347.

[8] Y. Jia, X. Zhang, X. Kuang, D. Fan, X. Sun, X. Ren, H. Ma, D. Wu, Q. Wei, 1,1,2,2- Tetra(4-carboxylphenyl)ethylene-Based metal-organic gel as aggregation-induced electrochemiluminescence emitter for the detection of aflatoxin B1 based on nanosurface energy transfer, Anal. Chem. 96 (2024) 12593–12597, https://doi.org/10.1021/acs.analchem.4c02574.

[9] J. Suk, P. Natarajan, J.N. Moorthy, A.J. Bard, Electrochemistry and electrogenerated chemiluminescence of twisted anthracene-functionalized bimesitylenes, J. Am. Chem. Soc. 134 (2012) 3451–3460, https://doi.org/ 10.1021/ja209894q.

[10] K. Wu, Y. Zheng, R. Chen, Z. Zhou, S. Liu, Y. Shen, Y. Zhang, Advances in electrochemiluminescence luminophores based on small organic molecules for biosensing, Biosens. Bioelectron. 223 (2023) 115031, https://doi.org/10.1016/j. bios.2022.115031.

[11] J.S. Lindsey, Synthetic routes to meso-patterned porphyrins, Acc. Chem. Res. 43 (2010) 300–311, https://doi.org/10.1021/ar900212t.

[12] J. Barber, Photosynthetic energy conversion: natural and artificial, Chem. Soc. Rev. 38 (2008) 185–196, https://doi.org/10.1039/b802262n.

[13] A. Magnuson, M. Anderlund, O. Johansson, P. Lindblad, R. Lomoth, T. Polivka, S. Ott, K. Stensj¨o, S. Styring, V. Sundstr¨om, L. Hammarstr¨om, Biomimetic and microbial approaches to solar fuel generation, Acc. Chem. Res. 42 (2009) 1899–1909, https://doi.org/10.1021/ar900127h.

[14] X. Xie, X. Zhang, M. Xie, L. Xiong, H. Sun, Y. Lu, Q. Mu, M.H. Rummeli, J. Xu, S. Li, J. Zhong, Z. Deng, B. Ma, T. Cheng, W.A. Goddard, Y. Peng, Au-activated N motifs in non-coherent cupric porphyrin metal organic frameworks for promoting and stabilizing ethylene production, Nat. Commun. 13 (2022) 63, https://doi.org/ 10.1038/s41467-021-27768-6.

[15] S.-W. Ke, W. Li, Y. Gu, J. Su, Y. Liu, S. Yuan, J.-L. Zuo, J. Ma, P. He, Covalent organic frameworks with Ni-Bis(dithiolene) and Co-porphyrin units as bifunctional catalysts for LiO2 batteries, Sci. Adv. 9 (2023) eadf2398, https://doi.org/10.1126/ sciadv.adf2398.

[16] J. Luo, S. Lee, M. Son, B. Zheng, K.W. Huang, Q. Qi, W. Zeng, G. Li, D. Kim, J. Wu, N-annulated perylene-substituted and fused porphyrin dimers with intense near-infrared one-photon and two-photon absorption, Chem. Eur J. 21 (2015) 3708–3715, https://doi.org/10.1002/chem.201405574.

[17] S. Saito, A. Osuka, Expanded porphyrins: intriguing structures, electronic properties, and reactivities, Angew. Chem., Int. Ed. Engl. 50 (2011) 4342–4373, https://doi.org/10.1002/anie.201003909.

[18] K. Cai, J. Xie, D. Zhang, W. Shi, Q. Yan, D. Zhao, Concurrent cooperative J- aggregates and anticooperative H-aggregates, J. Am. Chem. Soc. 140 (2018) 5764–5773, https://doi.org/10.1021/jacs.8b01463.

[19] S. Ishihara, J. Labuta, W. Van Rossom, D. Ishikawa, K. Minami, J.P. Hill, K. Ariga, Porphyrin-based sensor nanoarchitectonics in diverse physical detection modes, Phys. Chem. Chem. Phys. 16 (2014) 9713–9746, https://doi.org/10.1039/ c3cp55431g.

[20] X. Yan, Y. Song, J. Liu, N. Zhou, C. Zhang, L. He, Z. Zhang, Z. Liu, Two-dimensional porphyrin-based covalent organic framework: a novel platform for sensitive epidermal growth factor receptor and living cancer cell detection, Biosens. Bioelectron. 126 (2019) 734–742, https://doi.org/10.1016/j.bios.2018.11.047.

[21] X. Ma, C. Pang, S. Li, Y. Xiong, J. Li, J. Luo, Y. Yang, Synthesis of Zr-coordinated amide porphyrin-based two-dimensional covalent organic framework at liquid- liquid interface for electrochemical sensing of tetracycline, Biosens. Bioelect

Hong, K. Ma, Y. Wan, X. Zhang, Y. Huang, K. Kang, M. Yang, J. Chen, S. Deng, Porphyrin trio-pendant fullerene guest as an in situ universal probe of high ECL efficiency for sensitive miRNA detection, Biosens. Bioelectron. 150 (2020) 111963, https://doi.org/10.1016/j.bios.2019.111963.

[22] B. Hu, P. Wu, Facile synthesis of large-area ultrathin two-dimensional supramolecular nanosheets in water, Nano Res. 13 (2020) 868–874, https://doi. org/10.1007/s12274-020-2709-9.

[23] M.J. Ahrens, R.F. Kelley, Z.E. Dance, M.R. Wasielewski, Photoinduced charge separation in self-assembled cofacial pentamers of zinc-5,10,15,20-tetrakis (perylenediimide)porphyrin, Phys. Chem. Chem. Phys. 9 (2007) 1469–1478, https://doi.org/10.1039/b617876f.

[24] S. Deng, P. Yuan, X. Ji, D. Shan, X. Zhang, Carbon nitride nanosheet-supported porphyrin: a new biomimetic catalyst for highly efficient bioanalysis, ACS Appl. Mater. Interfaces 7 (2015) 543–552, https://doi.org/10.1021/am506645h.

[25] Y.P. Wei, Y.W. Zhang, J.S. Chen, C.J. Mao, B.K. Jin, An electrochemiluminescence biosensor for p53 antibody based on Zn-MOF/GO nanocomposite and Ag+-DNA amplification, Mikrochim. Acta 187 (2020) 455, https://doi.org/10.1007/s00604-
020- 04425-1.

[26] P. Li, X. Zhang, C. Hou, Y. Chen, T. He, Highly efficient visible-light driven solar- fuel production over tetra(4-carboxyphenyl)porphyrin iron(III) chloride using CdS/Bi2S3 heterostructure as photosensitizer, Appl. Catal. B Environ. 238 (2018) 656–663, https://doi.org/10.1016/j.apcatb.2018.07.066.

[27] G. Ding, Y. Wang, G. Zhang, K. Zhou, K. Zeng, Z. Li, Y. Zhou, C. Zhang, X. Chen, S.
T. Han, 2D metal–organic framework nanosheets with time-dependent and multilevel memristive switching, Adv. Funct. Mater. 29 (2018) 1806637, https://doi.org/10.1002/adfm.201806637.

[28] S. Goswami, M. Chen, M.R. Wasielewski, O.K. Farha, J.T. Hupp, Boosting transport distances for molecular excitons within photoexcited metal-organic framework films, ACS Appl. Mater. Interfaces 10 (2018) 34409–34417, https://doi.org/ 10.1021/acsami.8b14977.

[29] G.-Y. Zhang, S.-Y. Deng, X.-J. Zhang, D. Shan, Cathodic electrochemiluminescence of singlet oxygen induced by the electroactive zinc porphyrin in aqueous media, Electrochim. Acta 190 (2016) 64–68, https://doi.org/10.1016/j.
electacta.2015.12.228.

[30] G. Pu, Z. Yang, Y. Wu, Z. Wang, Y. Deng, Y. Gao, Z. Zhang, X. Lu, Investigation into the oxygen-involved electrochemiluminescence of porphyrins and its regulation by peripheral substituents/central metals, Anal. Chem. 91 (2019) 2319–2328, https://doi.org/10.1021/acs.analchem.8b05027.

[31] Y. Wang, J. Shu, A. Lyu, M. Wang, C. Hu, H. Cui, Zn2+-modified nonmetal porphyrin-based metal–organic frameworks with improved electrochemiluminescence for nanoscale exosome detection, ACS Appl. Nano Mater. 6 (2023) 4214–4223, https://doi.org/10.1021/acsanm.2c05273.

[32] W.R. Cai, G.Y. Zhang, K.K. Lu, H.B. Zeng, S. Cosnier, X.J. Zhang, D. Shan, Enhanced electrochemiluminescence of one-dimensional self-assembled porphyrin hexagonal nanoprisms, ACS Appl. Mater. Interfaces 9 (2017) 20904–20912, https://doi.org/10.1021/acsami.7b05188.

[33] C. Zheng, Y. Sheng, Y. Liu, Y. Wan, G. Liu, X. Zhang, M. Yang, K. Kang, J. Liu,
K. Ma, S. Deng, Enhanced electrochemiluminescent brightness and stability of porphyrins by supramolecular pinning and pinching for sensitive zinc detection,

[35] M. Luciano, C. Bruckner, Modifications of porphyrins and hydroporphyrins for their solubilization in aqueous media, Molecules 22 (2017) 980, https://doi.org/10.3390/molecules22060980.

[36] F. Rizzo, F. Polo, G. Bottaro, S. Fantacci, S. Antonello, L. Armelao, S. Quici,

F. Maran, From blue to green: fine-tuning of photoluminescence and electrochemiluminescence in bifunctional organic dyes, J. Am. Chem. Soc. 139 (2017) 2060–2069, https://doi.org/10.1021/jacs.6b12247.

[37] Q. Han, C. Wang, Z. Li, J. Wu, P.K. Liu, F. Mo, Y. Fu, Multifunctional zinc oxide promotes electrochemiluminescence of porphyrin aggregates for ultrasensitive detection of copper ion, Anal. Chem. 92 (2020) 3324–3331, https://doi.org/ 10.1021/acs.analchem.9b05262.

[38] L. Xiao, Y. Ling, A. Alsbaiee, C. Li, D.E. Helbling, W.R. Dichtel, β-Cyclodextrin polymer network sequesters perfluorooctanoic acid at environmentally relevant concentrations, J. Am. Chem. Soc. 139 (2017) 7689–7692, https://doi.org/ 10.1021/jacs.7b02381.

[39] D.M. Alzate-S´anchez, B.J. Smith, A. Alsbaiee, J.P. Hinestroza, W.R. Dichtel, Cotton fabric functionalized with a β-cyclodextrin polymer captures organic pollutants from contaminated air and water, Chem. Mater. 28 (2016) 8340–8346, https://doi. org/10.1021/acs.chemmater.6b03624.

[40] Y. Wu, Z. Han, L. Wei, H. Sun, T. Wang, J. Chen, R. Zhang, X. Lu, Depolymerization-Induced Electrochemiluminescence of insoluble porphyrin in aqueous phase, Anal. Chem. 92 (2020) 5464–5472, https://doi.org/10.1021/acs. analchem.0c00208.

[41] R. Sinha, O.S. Jaykishan, P. Purkayastha, A curated graphene quantum dot- porphyrin-based photosensitizer for effective singlet oxygen generation through energy transfer, Langmuir 39 (2023) 11108–11118, https://doi.org/10.1021/acs. langmuir.3c01466.

[42] M. Durmus, J.Y. Chen, Z.X. Zhao, T. Nyokong, Energy transfer in zinc porphyrin-phthalocyanine heterotrimer and heterononamer studied by fluorescence resonance energy transfer (FRET), Spectrochim. Acta 70 (2008) 42–49, https://doi. org/10.1016/j.saa.2007.07.010.

[43] S.H. Kang, I.T. Choi, M.S. Kang, Y.K. Eom, M.J. Ju, J.Y. Hong, H.S. Kang, H.K. Kim, Novel D–π–A structured porphyrin dyes with diphenylamine derived electron- donating substituents for highly efficient dye-sensitized solar cells, J. Mater. Chem. A 1 (2013) 3977–3982, https://doi.org/10.1039/c3ta01128c.

[44] S. Suleman, Y. Zhang, Y. Qian, J. Zhang, Z. Lin, O. Metin, Z. Meng, H.L. Jiang, Turning on singlet oxygen generation by outer-sphere microenvironment modulation in porphyrinic covalent organic frameworks for photocatalytic oxidation, Angew. Chem., Int. Ed. Engl. 63 (2024) e202314988, https://doi.org/ 10.1002/anie.202314988.

[45] Y. Zhang, Y. Zhao, Z. Han, R. Zhang, P. Du, Y. Wu, X. Lu, Switching the photoluminescence and electrochemiluminescence of liposoluble porphyrin in aqueous phase by molecular regulation, Angew. Chem., Int. Ed. Engl. 59 (2020) 23261–23267, https://doi.org/10.1002/anie.202010216.

[46] I.M. Honicke, I. Senkovska, V. Bon, I.A. Baburin, N. Bonisch, S. Raschke, J. D. Evans, S. Kaskel, Balancing mechanical stability and ultrahigh porosity in crystalline framework materials, Angew. Chem., Int. Ed. Engl. 57 (2018) 13780–13783, https://doi.org/10.1002/anie.201808240.

[47] J. Chakraborty, I. Nath, F. Verpoort, Snapshots of encapsulated porphyrins and heme enzymes in metal-organic materials: a prevailing paradigm of heme mimicry, Coord. Chem. Rev. 326 (2016) 135–163, https://doi.org/10.1016/j. ccr.2016.08.006.

[48] Y. Fang, H.M. Wang, Y.X. Gu, L. Yu, A.J. Wang, P.X. Yuan, J.J. Feng, Highly enhanced electrochemiluminescence luminophore generated by zeolitic imidazole framework-8-linked

porphyrin and its application for thrombin detection, Anal. Chem. 92 (2020) 3206–3212, https://doi.org/10.1021/acs.analchem.9b04938.

[49] L.-Y. Huang, X. Hu, H.-Y. Shan, L. Yu, Y.-X. Gu, A.-J. Wang, D. Shan, P.-X. Yuan, J.-J. Feng, High-performance electrochemiluminescence emitter of metal organic framework linked with porphyrin and its application for ultrasensitive detection of biomarker mucin-1, Sensor. Actuat. B-Chem. 344 (2021) 130300, https://doi.org/10.1016/j.snb.2021.130300.

[50] S. Huh, S.-J. Kim, Y. Kim, Porphyrinic metal–organic frameworks from custom-designed porphyrins, CrystEngComm 18 (2016) 345–368, https://doi.org/10.1039/c5ce02106e.

[51] W.Y. Gao, M. Chrzanowski, S. Ma, Metal-metalloporphyrin frameworks: a resurging class of functional materials, Chem. Soc. Rev. 43 (2014) 5841–5866, https://doi.org/10.1039/c4cs00001c.

[52] Z. Guo, D. Yan, H. Wang, D. Tesfagaber, X. Li, Y. Chen, W. Huang, B. Chen, A three-dimensional microporous metal-metalloporphyrin framework, Inorg. Chem. 54 (2015) 200–204, https://doi.org/10.1021/ic502116k.

[53] K. Wang, D. Feng, T.F. Liu, J. Su, S. Yuan, Y.P. Chen, M. Bosch, X. Zou, H.C. Zhou, A series of highly stable mesoporous metalloporphyrin Fe-MOFs, J. Am. Chem. Soc. 136 (2014) 13983–13986, https://doi.org/10.1021/ja507269n.

[54] H. Cui, Y. Wang, Y. Wang, Y.-Z. Fan, L. Zhang, C.-Y. Su, A stable and porous iridium(III)-porphyrin metal–organic framework: synthesis, structure and catalysis, CrystEngComm 18 (2016) 2203–2209, https://doi.org/10.1039/c6ce00358c.

[55] Y.X. Li, Y.X. Dai, J.Z. Wang, J. Chauvin, X.J. Zhang, S. Cosnier, R.S. Marks, D. Shan, Fine tuning of porphyrin based-paddlewheel framework by imidazole derivative to boost electrochemiluminescence performance, Talanta 272 (2024) 125779, https://doi.org/10.1016/j.talanta.2024.125779.

[56] Y. Zhao, A. Zhao, Z. Wang, Y. Xu, Y. Feng, Y. Lan, Z. Han, X. Lu, Enhancing the electrochemiluminescence of porphyrin via crystalline networks of metal-organic frameworks for sensitive detection of cardiac troponin I, Anal. Chem. 95 (2023) 11687–11694, https://doi.org/10.1021/acs.analchem.3c01647.

[57] G.Y. Zhang, C. Cai, S. Cosnier, H.B. Zeng, X.J. Zhang, D. Shan, Zirconium-metalloporphyrin frameworks as a three-in-one platform possessing oxygen nanocage, electron media, and bonding site for electrochemiluminescence protein kinase activity assay, Nanoscale 8 (2016) 11649–11657, https://doi.org/10.1039/ c6nr01206j.

[58] P. Li, L. Luo, D. Cheng, Y. Sun, Y. Zhang, M. Liu, S. Yao, Regulation of the structure of zirconium-based porphyrinic metal-organic framework as highly electrochemiluminescence sensing platform for thrombin, Anal. Chem. 94 (2022) 5707–5714, https://doi.org/10.1021/acs.analchem.2c00737.

[59] Y. Zhao, Y. Kuang, M. Liu, J. Wang, R. Pei, Synthesis of metal–organic framework nanosheets with high relaxation rate and singlet oxygen yield, Chem. Mater. 30 (2018) 7511–7520, https://doi.org/10.1021/acs.chemmater.8b02467.

[60] G. Zhang, M. Li, K. Yu, H. Chai, S. Xu, T. Xu, L. Qu, X. Zhang, Two-dimensional metalloporphyrinic framework nanosheet-based dual-mechanism-driven

[61] W.R. Cai, H.B. Zeng, H.G. Xue, R.S. Marks, S. Cosnier, X.J. Zhang, D. Shan, Enhanced electrochemiluminescence of porphyrin-based metal-organic frameworks controlled via coordination modulation, Anal. Chem. 92 (2020) 1916–1924, https://doi.org/10.1021/acs.analchem.9b04104.

[62] Y. Zhao, J. Wang, R. Pei, Micron-sized ultrathin metal-organic framework sheet,
J. Am. Chem. Soc. 142 (2020) 10331–10336, https://doi.org/10.1021/
jacs.0c04442.
[63] Y. Yang, L.Y. Yao, W.B. Liang, W. Huang, Y.J. Zhang, J.L. Zhang, R. Yuan, D.
R. Xiao, Highly efficient electrochemiluminescence resonance energy transfer material constructed from an AIEgen-based 2D ultrathin metal-organic layer for thrombin detection, Chem. Commun. 57 (2021) 4323–4326, https://doi.org/ 10.1039/d1cc00364j.
[64] Y.X. Li, J. Li, H.B. Zeng, X.J. Zhang, S. Cosnier, D. Shan, Artificial light-harvesting system based on zinc porphyrin and benzimidazole: construction, resonance energy transfer, and amplification strategy for electrochemiluminescence, Anal. Chem. 95 (2023) 3493–3498, https://doi.org/10.1021/acs.analchem.2c05559.
[65] Y. Wang, G. Zhao, H. Chi, S. Yang, Q. Niu, D. Wu, W. Cao, T. Li, H. Ma, Q. Wei, Self-luminescent lanthanide metal-organic frameworks as signal probes in electrochemiluminescence immunoassay, J. Am. Chem. Soc. 143 (2021) 504–512, https://doi.org/10.1021/jacs.0c12449.
[66] L. Zhao, X. Song, X. Ren, H. Wang, D. Fan, D. Wu, Q. Wei, Ultrasensitive near- infrared electrochemiluminescence biosensor derived from Eu-MOF with antenna effect and high efficiency catalysis of specific CoS2 hollow triple shelled nanoboxes for procalcitonin, Biosens. Bioelectron. 191 (2021) 113409, https://doi.org/ 10.1016/j.bios.2021.113409.
[67] J. Wang, M. Xia, J. Wei, T. Jiao, Q. Chen, Q. Chen, X. Chen, Dual-signal amplified cathodic electrochemiluminescence aptsensor based on a europium-porphyrin coordination polymer for the ultrasensitive detection of zearalenone in maize, Sensor. Actuat. B-Chem. 382 (2023) 133532, https://doi.org/10.1016/j.
snb.2023.133532.
[68] Q. Han, C. Wang, P. Liu, G. Zhang, L. Song, Y. Fu, Functionalized europium- porphyrin coordination polymer: rational design of high performance electrochemiluminescence emitter for mucin 1 sensing, Biosens. Bioelectron. 191 (2021) 113422, https://doi.org/10.1016/j.bios.2021.113422.
[69] M.N. Ma, Y. Zhuo, R. Yuan, Y.Q. Chai, New signal amplification strategy using semicarbazide as co-reaction accelerator for highly sensitive electrochemiluminescent aptasensor construction, Anal. Chem. 87 (2015) 11389–11397, https://doi.org/10.1021/acs.analchem.5b02848.
[70] Y.Q. Yu, H.Y. Zhang, Y.Q. Chai, R. Yuan, Y. Zhuo, A sensitive electrochemiluminescent aptasensor based on perylene derivatives as a novel co- reaction accelerator for signal amplification, Biosens. Bioelectron. 85 (2016) 8–15, https://doi.org/10.1016/j.bios.2016.04.088.
[71] Y.X. Li, J. Li, W.R. Cai, W.L. Xin, R.S. Marks, H.B. Zeng, S. Cosnier, X. Zhang,
D. Shan, Postsynthesis ligand exchange induced porphyrin hybrid crystalloid reconstruction for self-enhanced electrochemiluminescence, Anal. Chem. 92 (2020) 15270–15274, https://doi.org/10.1021/acs.analchem.0c03391.
[72] I. Liberman, R. Shimoni, R. Ifraemov, I. Rozenberg, C. Singh, I. Hod, Active-site modulation in an Fe-porphyrin-based metal-organic framework through ligand axial coordination: accelerating electrocatalysis and charge-transport kinetics,
J. Am. Chem. Soc. 142 (2020) 1933–1940, https://doi.org/10.1021/jacs.9b11355.
[73] J. Han, P. An, S. Liu, X. Zhang, D. Wang, Y. Yuan, J. Guo, X. Qiu, K. Hou, L. Shi,

Y. Zhang, S. Zhao, C. Long, Z. Tang, Reordering d orbital energies of single-site catalysts for CO2 electroreduction, Angew. Chem., Int. Ed. Engl. 58 (2019) 12711–12716, https://doi.org/10.1002/anie.201907399.

[74] Y.X. Li, J. Li, D. Zhu, J.Z. Wang, G.F. Shu, J. Li, S.L. Zhang, X.J. Zhang, S. Cosnier, H.B. Zeng, D. Shan, 2D Zn-porphyrin-based Co(II)-MOF with 2-methylimidazole sitting axially on the paddle-wheel units: an efficient electrochemiluminescence bioassay for SARS-CoV-2, Adv. Funct. Mater. 32 (2022) 2209743, https://doi.org/ 10.1002/adfm.202209743.