Review of porphyrin-based photodynamic therapy materials

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Abstract

Photodynamic therapy (PDT) has emerged as a promising and non-invasive modality for cancer treatments. Photosensitizers, as one of the essential elements in PDT, play a crucial role in the practical applications of PDT. Exposure to suitable light irradiation leads these photosensitizers to absorb the energy and move to excited state. Eventually, they transfer the energy to surrounding molecules and produce reactive oxygen species (ROS), particularly the singlet oxygen ($^1\text{O}_2$). Porphyrins, consisting of tetrapyrrole bridged with four methylene groups, are the classical and typical photosensitizers. However, the poor water-solubility, low biostability and non-specific tumor-targeting properties of porphyrins limit the PDT efficiency and their clinical applications. Thus, in order to promote the PDT efficiency of porphyrins, a variety of modification and functionalization strategies have been developed to construct multi-dimensional porphyrin-based functional materials. Herein, we summarize the recent advances of porphyrin-based functional materials from the following aspects: (1) the porphyrinic amphiphiles, (2) physical encapsulation of porphyrins by nanoparticles, (3) the construction of porphyrin-based polymers including block copolymers with covalent bonding and supramolecular polymers with non-covalent bonding, and (4) porphyrin-based organic frameworks. We believe that the development of porphyrin-based functional materials provide more fascinating superiorities in PDT and dramatically expand the potentials and possibilities in cancer treatments.

1. Introduction

1.1. Porphyrins

Porphyrins are a class of tetrapyrrole compounds, which consist of a planar porphyrin core surrounded by substituent groups [1-3]. It is undoubted and well documented that porphyrins are one of invaluable and ubiquitous molecular species, which play critical roles in living systems including photosynthesis [4-7]. The stable macrocyclic arrangement of porphyrin core forms an ideal anchoring site for metal atoms complexation [8]. In addition, various derivatives can be obtained via introducing different substituents at pyrrolic meso- or b-positions. Although the structure of porphyrins was suggested more than one hundred years ago, the studies of their synthesis, assemblies and applications have always been of great interest in the scientific community [9].

Due to the high absorption coefficient and superior capabilities of energy-, hydrogen- and electron-transfer, porphyrins present diverse outstanding photophysical and photochemical properties. These intrinsic superior properties of porphyrin render their extravagant studies in solar cells, [10-12] catalysis, [13] imaging, [14] molecular electronics [15] and biomedicines [16]. Considering the several reviews, summarizing the synthesis, self-assembly, and applications of porphyrins in solar cells, catalysis, imaging and drug delivery, the aim of this review is to specifically focus the porphyrin-based materials for photodynamic therapy in the last five years.

1.2. Photodynamic therapy

Photodynamic therapy (PDT) refers to the administration of photosensitizers, light and oxygen molecules to generate cytotoxic reactive oxygen species (ROS), particularly singlet oxygen ($^1\text{O}_2$) [17,18]. PDT is a site-specific and non-invasive treatment, and has arisen intensive interest in chemistry, materials and biology [19,20]. Among the three elements (photosensitizers, light and oxygen molecules), photosensitizers are the essential parameter in PDT, which directly affect the PDT efficiency [21,22].

As presented in Fig. 1, the modified Jablonski diagram illustrates the main photochemical reactions occurring in PDT process [17]. Upon the light irradiation of suitable wavelength, photosensitizers can be transformed from the ground state (S_0) to excited singlet state (S_1). These excited photosensitizers can then either relax back to S_0 state accompanying with a fluorescence photon emission or can be transformed to excited triplet state (T_1) by intersystem crossing. Furthermore, the energy of photosensitizers in T_1 state can either be relaxed by a phosphorescent photon exhibiting phosphorescence or can be transferred to ambient molecules by photochemical reaction by type-I and type-II paths. In type-I path, photosensitizers in T_1 state undergo an electron- or hydrogen transfer process to produce free radicals, which further interact with water or oxygen molecules leading to the production of

hydroxyl radicals ($\text{OH}^\bullet$) or superoxide anions ($\text{O}_2^\bullet$) [23]. It is worth noting that the type-I PDT can undergo in hypoxic condition, particularly in hypoxic tumor microenvironment of deep-seated tumors. On the other hands, in well-oxygenated condition, photosensitizers in T_1 state participate an energy-transfer process with localized $^3\text{O}_2$ resulting in the formation of highly cytotoxic singlet oxygen ($^1\text{O}_2$). [24] which is known as type-II PDT. It has been reported that type-II path generally dominates PDT process. However, the high concentration of photosensitizers and hypoxic condition can lead the type-I PDT pathway dominantly. PDT as a whole has been recognized as a promising anticancer strategy with the merits of non-invasiveness and spatiotemporal control [25-27].

Besides photosensitizers, the light source is another critical parameter for the PDT process. Since living tissues can largely reflect and decay the light, the limited tissue penetration depth and delivery efficiency of light are the essential barriers in PDT especially for deep tumor treatments. The light penetration depth in tissues during PDT is affected by several factors including wavelength and intensity of light as well as tissue physiology. There is strong absorption in the visible spectrum

below 650 nm by the endogenous fluorophores. In addition, near-infrared (NIR) light with wavelength longer than 900 nm is probably not strong enough to activate the photosensitizers [28]. Thus, the light source generally used in a PDT process ranges from 650 to 850 nm.

[17,20,29] Furthermore, the optimization of specific light intensity to get effective therapeutic efficacy and reduce photodamage to normal tissues dragged much effort [30].

Singlet oxygen generation efficiency is another crucial criterion to evaluate PDT efficiency [22,31]. Several dyes have been used as photo probes for detecting the generation of singlet oxygen. For example, the absorbance of 1,3-diphenylisobenzofuran (DPBF) is monitored as the function of light irradiation dosage to indicate the extracellular generation of $^1\text{O}_2$ for photosensitizers. The reaction between DPBF and $^1\text{O}_2$ can induce an absorbance loss of DPBF [32,33]. Similarly the fluorescence enhancement of singlet oxygen sensor green (SOSG) can be employed to quantify singlet oxygen generation [34,35]. The intracellular $^1\text{O}_2$ generation can also be estimated by using 2,7-dichlorofluorescein diacetate (DCFH-DA) as an indicator because DCFH-DA can be oxidized by $^1\text{O}_2$ to dichlorofluorescein (DCF) yielding green fluorescence [36,37].

2. Porphyrin and its derivatives in PDT

Porphyrin and its derivatives including chlorins and bacteriochlorins are one of the most typical and useful photosensitizers in PDT [38,39]. The longest absorption of porphyrins is in red light portion, allowing the light penetration to deep tissues which helps in deep tumor treatments. The chemical structures of porphyrins and their derivatives commonly used in PDT are presented in Fig. 2. So far, the most universal studied and used photosensitizer is Photofrin, which is isolated from the hematoporphyrin mixtures [40]. However, owing to the accumulation in the skin, the compli-

Fig. 1. Modified Jablonski diagram showing the formation of reactive oxygen radicals in type-I and type-II PDT.

cation of severe skin photosensitizations generally accompanies the treatment of Photofrin. In addition, the limited watersolubility, low circulation half-life and low tumor-specificity of traditional porphyrins lead to their limited PDT efficiency. Therefore, a variety of chemical functionalization and physical encapsulation strategies have applied to overcome the shortcomings and enhance the PDT efficiency of porphyrins [41,42].

2.1. Porphyrinic amphiphiles

On the basis of chemical coupling reactions and self-assembly, hydrophilic or amphiphilic molecules including peptides, saccharide, lipids and surfactants can be coupled with porphyrins. These

Fig. 2. Structures of porphyrins and their derivatives commonly used in photodynamic therapy.

adopted strategies as well as introduced functionalities produce functionalized porphyrinic amphiphiles with improved watersolubility and retained intrinsic properties of porphyrin [43–45]. Additionally, the amphiphilic porphyrinic photosensitizers can further self-assemble into nano-sized particles to passively accumulate at tumor sites via enhanced permeability and retention (EPR) effect.

To introduce good biocompatibility, biodegradability and nonimmunogenicity in the functionalized porphyrins, peptides being the basic units for proteins are the ideal candidates [46,47]. A variety of substructures and functionalities can be obtained from the amount and different sequences of amino acid in peptides. Thus, peptides in general have been recognized as a promising candidate for biomedical application [48,49]. For example, it has been reported that porphyrinated nanofibers were constructed on tumor site from the peptide-porphyrin conjugates. It was achieved by conjugating tumor-targeting ligand and a responsive linker by the standard solid-phase peptide synthesis techniques (Fig. 3) [50]. The nanofibers presented aggregation-induced retention effect, leading to significant improvement in photoacoustic (PA) imaging signals and PDT efficacy. In addition, the peptideporphyrin conjugates also self-assembled to “sandwich” dimeric structure by the consociation between chlorins and Cu^{2+} [48]. Similarly, the peptide-chlorophyll-based dimer with terminal mannose units triggered the targeting property to macrophage and eliminated intracellular bacterial infections by PDT.

Recently, Yan and coworkers pioneered several research works on the peptide-tuned porphyrin-based self-assemblies for anticancer photodynamic and photothermal therapy [52–54]. For example, a common short peptide, L-phenylalanine-L-phenylalanine (FF), was self-assembled with tetraphenyl porphyrin (TPP) and zinc ions to construct spherical nanoparticles by multicomponent coordination self-assembly strategy (Fig. 4) [51]. These well-defined metalloporphyrin nanodrugs exhibited high loading rate of porphyrins, sensitive redox- and pH-dualresponsiveness which eventually enhanced its PDT efficacy. In addition, photothermal nanodots were synthesized in an effort to couple tetraphenyl porphyrin with FF to obtain peptideporphyrin conjugates (TPP-G-FF) [55]. The conjugates selfassembled into well-defined uniform nanodots with controllable sizes ranging from 20 to 100 nm. Porphyrins arranged to regular J-aggregation substructures in nanodots, leading to the high local heating production along with high generation of singlet oxygen and fluorescence emission.

Similarly, liposomes, closed bilayer lipid systems, have emerged as interesting nanocarriers for varieties of drugs to provide better therapeutic efficacy against drug-resistant tumors with lower cardiotoxicity [56,57]. Several research groups have reported the construction and biomedical applications of porphyrin-liposomes by the functionalization of porphyrins with lipids via esterification or amidation reactions. It is a well established fact that porphyrins generally conjugate with amphiphilic lipids with a high loading content [58–61]. Because of the amphiphilicity of porphyrin lipids, they could directly self-assemble into porphyrin liposomes in physiological condition with the porphyrin motifs at the walls. Such smart self-arrangement induced the fascinating merits of porphyrin-liposomes adducts including the remarkable bioimaging, [14] photodynamic [62] and photothermal effects [58]. To support this hypothesis, TPP was grafted onto the lipid at the junction point to obtain lipid-porphyrin conjugates which further encapsulated the DOX and cholesterol. This encapsulation resulted into self-assembled nanoparticles which could well perform the fluorescence imaging-guided synergistic chemo-photodynamic therapy (Fig. 5) [63].

Thus, the functionalization of porphyrins with hydrophilic or amphiphilic molecules by chemical modification and coupling reactions can significantly improve the water-solubility and biocompatibility of porphyrins. More importantly, they can selfassemble into porphyrin-based micelles, liposomes, nanodots with high porphyrin loading content. The dense packing of porphyrin motif results in the promising photophysical and chemical properties, which is beneficial to the PDT application.

2.2. Porphyrin-loaded nanoparticles

Despite of the chemical functionalization of porphyrins, physical encapsulation is recognized as another commonly used strategy to enhance the water-solubility and biocompatibility of por-

Fig. 3. (a) Schematic illustration of the structure of peptide-porphyrin conjugates (Compound 1). (b) The assembly induced retention effect of peptide-porphyrin conjugates in tumor site. (c) Assembly and monomer content/proportion of peptide-porphyrin conjugates in tumor site. (d) Time-dependent U87-xenografted tumor volumes changes of different treatments. (e) Representative photos of the tumor size of four group mice before and after 23 days treatments and the images of H&E staining of tumor tissue after treatment. Reprinted with permission of Ref. [50]. Copyright 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

porphyrins. A large number of inorganic/organic nanoparticles have been constructed for the loading and delivery of genes and various hydrophobic drugs including porphyrins [64–69]. The nanoscale size of obtained nanoparticles leads to the significant EPR effect for their passive accumulation at tumor sites. For example, gold nanoparticles, possessing a range of excellent properties including facile preparation, tunable functionalization, nontoxic and bioinert properties, have been recognized as an attractive nanocarrier for PDT applications [70,71].

Similarly, mesoporous nanoparticles have provided promising superiorities for the encapsulation of hydrophobic photosensitizers because of their high porous volume and large surface area [72]. Mesopores supply a protected physiological environment, passive tumor-targeting, and sustained photosensitizer release [73,74]. Shi et al. reported a variety of research works focusing on the biomedical applications of mesoporous silica nanoparticles. For example, porphyrin-loaded core-shell functional nanoparticles were constructed by a gadolinium-doped upconversion nanoparticle (UCNP) core and mesoporous silica shell (Fig. 6) [75]. Porphyrins chelated with manganese (Mn) ions were then grafted onto the mesoporosity of these core-shell nanoparticles by an amidation reaction, which showed high magnetic resonance imaging

Fig. 4. Schematic illustration of metalloporphyrins by coordination for efficient antitumor PDT. (b) The self-assembly of small peptides and photosensitizers in the presence of zinc ions through cooperative coordination to construct metalloporphyrin nanodrugs. (c) Schematic molecular organization pattern of a metal-binding peptide and Zn²⁺. (d) Accumulation in tumors by EPR effect. (e) Cellular internalization of metalloporphyrin nanoparticles and efficient PDT. Reprinted with permission of Ref. [51]. Copyright 2018, American Chemical Society.

(MRI) performance and singlet oxygen generation via sonodynamic therapy. Since the low tissue-penetrating depth of light limited the antitumor efficacy of PDT, sonodynamic therapy by ultrasound waves presented superiority to the tumor tissue in deep site, particularly to the hypoxic tumor tissue.

However, the recent studies showed that the inorganic nanoparticles used in nanomedicine possess important issue of metabolism [76]. The toxicity and unwanted stability of the nanoparticles bear deep concerns in translating the scientific innovation into clinical applications [77,78]. Several studies have been explored that various physicochemical properties including the particle size, chemical composition, surface charge, surface modification, and surface roughness of nanoparticles play crucial roles in their toxicity and long term stability [79,80]. Thus, some cleavable units including disulfide [81] and iron [82], which can be broken under the distinctive tumor microenvironment, were introduced into inorganic nanoparticles to acquire stimuli-responsive biodegradability.

Besides, based on the good dispersity and self-assembly of surfactants, Fan and co-workers constructed porphyrin-based nanodisks, nanowires, [83] nanocubes, [84] and nanorods [85] using the noncovalent interaction between ZnTPP and surfactants. These constructs promoted energy transfer between porphyrin molecules, leading to a red shift in absorption for enhanced photocatalytic and PDT performance.

More recently, organic nanocarriers have attracted wide interests because of their facile molecular design, tunable function modification and good biocompatibility. A variety of organic nanoparticles, vesicles, nanocapsules have been fabricated to load porphyrinic photosensitizers [86–89]. For example, our group reported the construction of porphyrin-loaded hollow nanocapsules to control the release of photosensitizers triggered by the over expressed glutathione (GSH) in tumor microenvironment [90]. Although diverse porphyrin-based nanoparticles with various functions have been studied, the possible leakage release of porphyrins and poor reproducibility are the main drawbacks for their potential applications.

Fig. 5. (a) Illustration of the synthesis of porphyrin-liposomes loading with DOX and cholesterol. (b) Size distribution and (c) TEM image DOX-loaded porphyrin-liposomes. Reprinted with permission of Ref. [63]. Copyright 2018, Ivyspring international publisher.

3. Porphyrin-based polymers in PDT

During the past decades, porphyrin-based polymers have emerged and presented attractive merits in chemical structure design, self-assembly and biomedical applications. Presence of intrinsic functional groups in porphyrin molecules, induces ease of functionalization rendering variety of customised derivatives to work as the initiator, monomers, chain transfer agents for polymerization, and coupling agents for post polymerization modifications [91,92]. A variety of porphyrin-based block copolymers and supramolecular polymers have been constructed with aim to utilize in biomedicines, particularly, for PDT [93].

3.1. Porphyrin-based block polymers in PDT

Due to the development of control/living radical polymerization, the synthesis and self-assembly of block copolymers have attracted extensive interests [94,95]. Among these, the study of photo-responsive functional block copolymers owing to their significant physical and chemical properties is a quite interesting yet challenging research topic [96–99]. As a typical photoresponsive functional unit, porphyrin-based block copolymers have been well studied and used in applications including solar cells, catalysis, light harvesting, and biomedicines [100–103]. Similarly, a good number of studies on porphyrin-based block copolymers have been conducted especially to utilize them in PDT itself and PDT involved therapies [104,105]. According to the previous works, [91,93] there are two major points in the construction of porphyrin-based block copolymers for their usage in PDT: (I) hydrophilic modification is needed for biostability improvement, such as PEGlated coupling and the polymerization of hydrophilic block; (II) Stimuli-responsive functionalization can endow specific adaptability of porphyrin-based block copolymers for the blood circulation and for the particular tumor micro-environment.

In the first strategy, PEG block can be constructed by both coupling of polyethylene glycol (PEG) chains and polymerization of oligo(ethylene-glycol) methyl ether methacrylate. For example, Zhang and co-workers pioneered a research of PEG-block-peptide conjugated with porphyrin units (PPK). This porphyrinic conjugate was self-assembled into uniform nanoparticles and used as mitochondria-targeted self-delivery system with long-term dualstage-light-guided PDT (Fig. 7) [106]. Consequently, a short irradiation (5 min) led to the photochemical internalization, while, the long-time irradiation (15 min) resulted in photodynamic therapy. The proapoptosis peptide motif endowed the porphyrin-based nanoparticles with the mitochondria-targeting functionality. After the treatment of light irradiation, the tumor growth was significantly inhibited on the 5th day. The results of tumor weights, tumor images and H&E staining images confirmed the good in vivo synergistic efficacy of the PPK nanoparticles.

As the second strategy, our group have pioneered systematic research focusing on the synthesis, self-assembly, and biomedical applications of stimuli-responsive porphyrin-based telechelics, [107,108] dendrimers, [109,110] block copolymers, [111–113] and supramolecular polymers [114,115]. However, compared with the possible leakage release of physical encapsulated porphyrin molecules, these could be functionalized as the motifs of polymers by stimuli-responsive covalent bonds in porphyrin-based polymers. For example, TPP units were coupled at the terminal of PEG-b-PCL via a pH-responsive acetal linker to construct porphyrin-based telechelics [107]. More recently, we also used the combination of reversible addition-fragmentation chain transfer (RAFT) polymerization, “click” reactions and coupling reactions to construct the stimuli-responsive porphyrin-based block copolymers. It is obvious that the photophysical and photochemical properties of porphyrins could be significantly improved by the introduction of a hydrophilic block and unique stimuli-responsiveness at tumor sites.

A porphyrin-based block copolymer with upper critical solution temperature (UCST) behavior was synthesized by RAFT polymerization and grafted onto gold nanorods (AuNRs) to construct a polymer/AuNRs hybrid photosensitizer (Fig. 8) [116]. The UCST of hybrid photosensitizers can be modulated around 42 °C with the help of feeding ratio of acrylamide (AAm) and acrylonitrile (AN) during reversible addition-fragmentation chain transfer (RAFT)

Fig. 6. Illustration of the synthesis, sonodynamic effect and MRI imaging of Mn-porphyrin-modified UCNP-mesoporous silica core-shell nanoparticles. Reprinted with permission of Ref. [75]. Copyright 2017, American Chemical Society.

polymerization. In physiological environment, these porphyrin motifs aggregated together with the collapsed UCST polymers on the surface of AuNRs. In this case the PDT was in “off” state during blood circulation protecting the patients away from sensitive reactions. Upon EPR effect, the hybrid photosensitizers passively accumulated in tumor sites. With the exposure of 808 nm light irradiation, the local heating produced by AuNRs led to the increasing temperature and eventually resulted in the phase transition of UCST polymers. Simultaneously, the porphyrin motifs were separated by the extended UCST polymer chains and upon the irradiation of 650 nm light, the PDT of porphyrin motifs were turned “on” in tumor sites and efficiently killed the cancer cells. The research work integrated photothermal and photodynamic therapy, which could provide a path to overcome the sensitive reactions of PDT.

Recently, our group constructed a unique block copolymer with a polyhedral oligomeric silsesquioxane (POSS)/porphyrin alternating structure for enhanced PDT (Fig. 9) [117]. Porphyrin units modified with styrene derivative and POSS units coupled with maleimide were used as the monomers for RAFT copolymerization. It was noted that the reactivity ratios of styrene and maleic derivatives in polymerization were similar, which led to the copolymer of styrene and maleic derivatives in

Fig. 7. Schematic diagram of the chemical structure of porphyrin-based PEG-block-peptide and mitochondria-targeted self-delivering process: A) passive target to tumor cells and PCI effect enhanced cellular internalization; B) mitochondrial targeting; C) PDT and pro-apoptosis peptide induced mitochondrial destruction and cell death. Reprinted with permission of Ref. [106]. Copyright 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

alternating fashion. Thus, the POSS and porphyrin modified monomers alternatively bonded in the backbone of polymers. In this scenario, the POSS units owing to the steric hindrance of their nanocage structure could automatically separate the adjacent porphyrins. Hence, the singlet oxygen quantum yield of the alternating porphyrins was higher than that of free TPP. In vivo experiments also confirmed that the anticancer effect of POSS/porphyrin alternating polymers was significantly higher than that of porphyrin-based block copolymers without POSS units.

Porphyrin-based block copolymers can be used not only in PDT but also in PDT combined therapies. Recently, a porphyrin-based Janus macromolecular brush was constructed for combinational photo-chemotherapy of cancer (Fig. 10) [118]. A pH-responsive side chain and a porphyrin unit were grafted from the same repeat unit in the polymer backbone. The Janus macromolecular brushes self-assembled into a vesicle and further reorganized to another vesicle with a thin wall and small in size in weak acidic condition. Uniform nanoparticles were obtained by the co-assembly of these Janus macromolecular brushes and DOX. Upon the pH-responsiveness of Poly(2-(diisopropylamino)ethyl methacrylate) (PDPA) side chains, PDT could be suppressed during blood circulation and a small amount of singlet oxygen could be produced to help the nanoparticles escape from endosomes. The acidic microenvironment in tumor resulted in the extension and protonation of PDPA chains. Consequently, the nanoparticles dissociated accompanying with DOX release. The separated porphyrins could generate much more $^1\text{O}_2$, presenting cascade-amplified PDT. Furthermore, due to the strong interaction between DOX, porphyrin units and PDPA side chains, the drug leakage could be efficiently avoided in physiological media. Additionally, the high coupling ratio of porphyrin units in the well-defined Janus macromolecular brush gave rise to the enhanced DOX loading capability by the π - π stacking between porphyrin units and DOX. The synergistic cascade-amplified PDT and enhanced chemotherapy of Janus macromolecular brushes endowed the high phototoxicity and antitumor efficacy, as confirmed by in vitro and in vivo studies.

Despite pH-responsive porphyrin-based block copolymers, our group also developed a ROS-responsive porphyrin-based block copolymers for in situ internalization and self-amplified PDT applications (Fig. 11) [119]. The $^1\text{O}_2$ -cleavable linker of vinylthioether was introduced between pyropheophorbide-a (PheoA) and methacrylate by esterification reactions. A short duration of light irradiation could regulate the trigger of $^1\text{O}_2$, which could further break the $^1\text{O}_2$ -cleavable linker and activate the controlled release of PheoA. Moreover, upon the chelation of ^{64}Cu , the quantitative accumulation kinetics of the block copolymer nanoparticles could be monitored by positron emission tomography (PET)-imaging. A sequential long duration of light irradiation led to the photosensitization and self-amplified PDT. The $^1\text{O}_2$ -responsive block copolymer could provide a new path for the precise manipulation of PDT.

Thus, the construction of porphyrin-based block copolymers can merge the photochemical and photophysical merits of porphyrin units with facile and versatile structural design of polymers. More importantly, because of the unique separation of copolymerized motifs, the expected aggregation-caused quenching of porphyrins could remarkably be suppressed. The PEGylation and the introduction of other hydrophilic blocks can improve the watersolubility and biocompatibility as well. In addition, diverse stimuli-responsive nanocarriers can be fabricated from the porphyrin-based block copolymers for their well demanding application in pristine PDT as well as for combination of PDT and chemotherapy.

Fig. 8. Illustration of the chemical structure of porphyrin-based block copolymers with upper critical solution temperature (UCST) behavior and AuNRs hybrid photosensitizers, and the "off/on" manipulation of PDT. Reprinted with permission of Ref. [116]. Copyright 2019, American Chemical Society.

Fig. 9. Illustration of the self-assembly and photophysical property of porphyrin-based block copolymers with porphyrin/POSS alternating structure. Reprinted with permission of Ref. [117]. Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

3.2. Porphyrin-based supramolecular polymers in PDT

Supramolecular chemistry refers to the utilization of noncovalent interactions such as van der Waals force, electrostatic interaction, hydrogen interaction, π - π stacking and hydrophobic interaction to construct supramolecular materials [120,121]. Since the Nobel prize was awarded to Lehn, Cram and Pedersen in 1987 for their investigation of the host-guest chemistry, extensive efforts have been attracted to develop a variety of host-guest systems and to study their applications in solar

cells, sensors, catalysis and nanomedicines [122–124]. Many macrocycles such as cyclodextrins (CD), pillararenes, cucurbiturils, calixarenes and crown ethers, have been employed as the host molecules. [125–127] Zhang and coworkers reported the pioneering research work of supramolecular photosensitizers in the enhanced antibacterial PDT. [128,129] Porphyrins with four positive charges were selected as the photosensitizer and were used as the building block for the construction of supramolecular photosensitizers with cucurbit[7]uril (CB[7]). The positively charged porphyrins benefited the adsorption of photosensitizers onto the negatively charged surface of bacteria via electrostatic attraction. Due to the host–guest interaction, the distance between porphyrins was largely increased. A low porphyrin concentration and short time of light irradiation

Fig. 10. Schematic illustration of porphyrin-based Janus macromolecular brushes and the co-assembly with DOX, and the process of cascade-amplified photodynamic therapy and enhanced chemotherapy. Reprinted with permission of Ref. [118]. Copyright 2020 Elsevier B.V. resulted in the improved antibacterial PDT efficacy. Importantly, the strategy was found advantageous due to its simplicity, operational ease, environment friendly as well as facile nature.

Supramolecular polymers integrate the intrinsic properties of individual supramolecular chemistry and polymers, which exhibit the stimuli-responsiveness, high reversibility and dynamic properties. [130–133] In this context, diverse supramolecular polymers have been constructed for the utilization in PDT. [134,135] Porphyrins can be coupled with the host or guest molecules and complexed with the complementary motifs. [136] Therefore, a variety of porphyrin-based supramolecular polymers have been fabricated including supramolecular telechelics, block copolymers, comb polymers and star polymers. [137,138] In general, these porphyrin-based host–guest complexes can act as building blocks in porphyrin-based supramolecular polymers either as the coupling junctions in backbones or as conjugates in side chains.

Our group reported the exciting research works of porphyrin-based supramolecular telechelics with b-CD [139] and pillararene [140] as the host motifs in the PDT application (Fig. 12). By esterification and amidation reactions, mono-functionalized porphyrin was coupled with disulfide-linked adamantane as the guest motif, and a hydrophilic PEG chain was grafted onto b-CD as the host motif. Upon the host–guest interaction, porphyrin-based telechelics were constructed and further self-assembled into micelles with the size about 85 nm, which could passively accumulate in tumor sites via EPR effect. Particularly, the steric hindrance and natural cavity of b-CD separated the porphyrin units and hence improved the PDT efficiency. It was also found that the GSH-responsiveness of porphyrin-based supramolecular polymers would be activated by the high concentration of GSH in tumor cells after endocytosis.

On the other hand, porphyrins also could be coupled with macrocycles for example pillar[5]arenes (P[5]), to obtain the host motifs (Fig. 13). [140] The complementary pyridine unit could be coupled with a hydrophilic PEG chain of the amphiphile, as a terminal. An amphiphilic supramolecular polymer was obtained by mixing the two parts. Compared with free TPP, an enhanced PDT efficiency of porphyrin-based supramolecular P[5]/pyridine polymers was confirmed by singlet oxygen production by 1,3-diphenylisobenzofuran (DPBF) and the cell viability by 3-(4,5-dimethylthiazol-2-yl)-2,5-di-phenyltetrazolium bromide (MTT) assay.

Moreover, the porphyrin-based host–guest complex also can play the role of monomers in construction of supramolecular polymers. Ji and co-workers constructed the reduction-triggered supramolecular nanocarriers for PDT by the host–guest interaction of CD-modified porphyrin and adamantane-contained zwitterionic polymers (Fig. 14). [141] CD-modified porphyrin was synthesized through carbodiimide reaction. The disulfide bond between the CD and porphyrin could be broken by the high GSH concentration at tumor sites, leading to the reduction-responsive release and activation of porphyrin.

It is worth noting that, because of the intrinsic hypoxic environment and low light penetration in deep tumor sites, PDT efficiency is very low, that bears the drawback of surviving in-depth cancer cells resulting in tumor recurrence and metastasis. Therefore, the combination of PDT and other therapies including chemotherapy, photothermal therapy, gene therapy and immunotherapy would

Fig. 11. (a) Schematic illustration of the structure of 1O_2 -cleavable porphyrin-based block copolymers, the mechanism of the 1O_2 -responsive release and self-amplified PDT. (b) In vivo fluorescence imaging and (c) PET imaging of B16F10 tumor-bearing mice after injecting porphyrin-based block copolymer nanoparticles without (OCP) or with 1O_2 -cleavable linkers (VSP) upon different time points. Reprinted with permission of Ref. [119]. Copyright 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

significantly enhance the antitumor efficacy. The facile and versatile construction of supramolecular polymers render porphyrinbased supramolecular polymers with a promising candidate as the nanocarrier for combined therapies. [36]

4. Porphyrin-based metal-organic frameworks in PDT

Metal-organic frameworks (MOFs) are a promising porous crystalline material based on organic ligands and metal containing

Fig. 12. Scheme of porphyrin-based telechelics with b-CD-adamantane interaction and the GSH-responsiveness. Reprinted with permission of Ref. [139]. Copyright 2015 Royal Society of Chemistry.

Fig. 13. Schematic Illustration of porphyrin-based telechelics with P[5]-pyridine interaction and the GSH-responsiveness. Reprinted with permission of Ref. [140]. Copyright 2016 Royal Society of Chemistry.

Fig. 14. Schematic Illustration of the construction and GSH-Triggered activation of porphyrin-conjugated supramolecular nanocarriers. Reprinted with permission of Ref. [141]. Copyright 2019, American Chemical Society.

node. [142,143] Nanoscaled MOFs have attracted extensive popu- and fuctionalization of nanoscaled MOFs expanded their applicability because of their tunable pore structures and sizes, large sur- tions in catalysis, [145,146] biomedicine, [147] and chemical face areas, and good biocompatibility. [144] The facile synthesis adsorption. [148] So far, many MOFs have been developed as drug

Fig. 15. (a) Schematic Description of PDT process, (b) TEM image and (c) immunofluorescence microscopy of calreticulin expression on the cell surface of CT26 cells treated with Hf-chlorin MOF and (d) PBS upon irradiation (90 J/cm^2). Blue: DAPI-stained nuclei. Green: Alexa Fluor 488 CRT antibody. Scale bars = 20 nm. Reprinted with permission of Ref. [154]. Copyright 2015, American Chemical Society.

Fig. 16. Scheme of the cancer cell membrane camouflaged nanosized Zr-porphyrin MOFs for cancer targeting synergistic starvation and PDT. Reprinted with permission of Ref. [155]. Copyright 2017, American Chemical Society.

delivery systems. However, since drug delivery inevitably encounters the serious side effects and drug resistance in chemotherapy, the shortcomings of classic drug delivery systems. [149,150] The porphyrin-based MOFs can provide the opportunities as a porphyrinic molecules as the building blocks were directly incorporated into the MOF structures, leading to the high loading efficiency, avoidable self-quenching and facile diffusion of ROS. [151,152]

Lin and co-workers pioneered an early example of Hafnium(Hf)porphyrin MOF as an effective photosensitizer for PDT. [153,154] Hf-porphyrin MOFs exhibited a UiO-type structure and a nanoplate morphology with about 10 nm in thickness and 100 nm in diameter. The well-defined framework structure efficiently isolated porphyrins to suppress the self-quenching of porphyrins. Furthermore, the strong Hf coordination enhanced the ROS generation by promoting intersystem crossing. [153] In vivo PDT studies illustrated that the porphyrinic UiO MOF exhibited a high tumor eradication to resistant head and neck cancer. Recently, they also reported the construction of the first example of chlorin-based MOF in nanoscale range for PDT of colon cancers (Fig. 15). [154] The chlorin-based MOF demonstrated significant increase in the absorption of Q-band and a 13 nm bathochromic shift, which induced a deeper light penetration and higher PDT efficiency.

Generally, tetracarboxyl substituted porphyrins could cooperate with Zr_6 clusters to construct nanosized Zr-MOF of coordination network-224 (PCN-224). On the basis of the well-defined PCN-224 structure, the Zr-porphyrin MOF can serve as a nanocarrier of both chemotherapeutic drugs and photosensitizers. Recently, the Zr-porphyrin MOFs were employed to embed enzymes including catalase and glucose oxidase to produce synergistic starvation and robust PDT (Fig. 16). [155] The combination of glucose oxidase and catalase could speed up glucose decomposition to reduce the nutrient supply in tumor site and increase the intracellular oxygen content by catalyzing endogenous H_2O_2 to oxygen, which is highly beneficial particularly in the hypoxic in-depth tumor. Additionally, the cancer cell membrane could be camouflaged on the surface of enzyme-loaded porphyrin-based MOFs to target homotypic and improve the retention abilities due to immune escape. Thus, the fabricated nanosystem played as a cascade bioreactor with enhanced anticancer efficacy by the synergistic starvation therapy and PDT. It presented a promising example of complementary modes in complicated tumor microenvironments.

The unique and versatile functionalities of porphyrin-based MOFs make them the promising nanocarriers for cytotoxic drugs and efficient mediator for PDT, and even the bioimaging agent. However, there are still some drawbacks to overcome before translational step and clinical applications of porphyrin-based MOFs. For example, the weak coordination interactions between metal ions and organic porphyrinic ligands in MOFs led to their dissociation at low pH conditions. In addition, the degradation mechanisms and systemic toxicity of MOFs still demand better and

Fig. 17. Illustration of the synthesis of porphyrin-based COFs (COF-366) and the photoacoustic imaging-guided combined PDT and PTT therapy. Reprinted with permission of Ref. [169]. Copyright 2019 Elsevier B.V.

Fig. 18. (a) Illustration of the synthesis route of fluorinated porphyrin-based COFs. (b) Illustration of in vivo tumor oxygenation process. Reprinted with permission of Ref. [171]. Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

more comprehensive studies. Although the surface coating of PEG, silica, DNA and proteins has been used to achieve the targeted results with reduced side effects, it is anticipated that more efforts are required for the biosafety, metabolism and excretion of MOFs being used in PDT.

5. Porphyrin-based covalent-organic frameworks in PDT

Similar with MOFs, the porous crystalline materials with organic building motifs connected by covalent bonds are defined as covalent organic frameworks (COFs). [156–158] Triazine, boronate ester, boroxine and imine bonds are generally utilized as the reversible connections for the construction of COFs. [159,160] Because of the planar geometry and rigidity of porphyrins, porphyrinic COFs have attracted much interest in gas adsorption, catalysis, energy harvest, sensing and photochemical applications. [161–163] The groups of Yaghi, [164] Jiang [165] and Banerjee [166] have reported several studies detailing the fabrication and applications porphyrin-based COFs for catalysis, optoelectronics, and CO₂ reduction.

Recently, porphyrin-based COFs has emerged as an efficient nanomedicine in the biomedical application as well and have dragged increasing research efforts. [164,167] The large inner pores and orderly spatial arrangements of building blocks made them promising candidates for drug release and photodynamic therapy. Lang and co-workers reported an initial study of porphyrinic COFs bearing a 3D diamond-like structure via Schiffbase reaction for the photodynamic antibacterial effect. [168] The 3D porphyrinic COFs possessed not only high local loading concentration of porphyrin, but also the high singlet oxygen yield similar with the TPP molecules in good solvents. More recently, several efforts have been made to synthesis and use the porphyrin-based COFs in antitumor applications. Unfortunately, the size of porphyrin-based COFs is generally too big to be utilized in living organisms. Thus, it is necessary to synthesize the nanosized porphyrin-based COFs for these applications. Chen's group synthesized porphyrin-based COFs (COF-366) with a size of about 100 nm and used as photoactive agents for photoacoustic (PA)

imaging-guided PDT and PTT combined therapy (Fig. 17). [169] The dynamic reversible and metal-free imine bond endowed porphyrin-based COFs with the degradation capability and enhanced biosafety. The PA-imaging could be used for precise in vivo antitumor treatment. It was evidenced that only single wavelength light irradiation was needed due to the broad absorption of porphyrin-based COFs resulted from their orderly conjugated structure. These porphyrin-based COFs significantly decreased the self-aggregation and hence the quenching of porphyrin resulting in the enhanced PDT efficacy.

In order to deal with the metabolism problem of COFs, Qu and co-workers reported the construction of porphyrin-based COF nanodots with a renal-clearable ultra-small size and their usage in PDT for antitumor. [170] The imine linkage was used to connect the building blocks, followed by utilizing a liquid exfoliation strategy for the construction of well-dispersed ultra-small porphyrin-based COF nanodots. PEG coating was further used to enhance the biocompatibility and biostability. The COF nanodots possessed good photodynamic efficiency both in cancer cells treatment and in vivo tumor inhibition because of the high stability, effective tumor accumulation and improved metabolism.

Furthermore, fluorinated porphyrin can also be used as the building blocks in the construction of COFs for the enhanced PDT in the deep tumor hypoxia condition (Fig. 18). [171] One-pot esterification was utilized between perfluorosebacic acid and tetrahydroxylporphyrin to construct fluorinated COFs which could efficiently load perfluoro-15-crown-5-ether and molecular oxygen to improve the tumor oxygenation and the efficiency of PDT antitumor treatment. Efficient tumor accumulation was observed by single-photon emission computed tomography imaging after intravenous injection of a radio-isotope ^{99m}Tc chelated fluorinated porphyrin-based COFs.

6. Summary and perspectives

In this review, we provide an overview of recent advances of porphyrin-based functional materials in PDT. We detailed here the PDT applications of different derivatives of porphyrin in association with variety of materials ranging from amphiphiles to polymers, supramolecular polymers and even 3D nanoparticles to organic frameworks via covalent bonding, reversible dynamic supramolecular interactions and physical encapsulation. The functionalizations significantly improve the water-solubility and biocompatibility of porphyrins. Similarly, the high loading concentration of porphyrins and enhanced PDT efficiency can be achieved from diverse porphyrin-based functional materials.

However, several issues for utilization of porphyrin-based functional materials to their full capacities, need to be addressed in near future. Firstly, the absorption and emission of porphyrin-based materials need to be extended to the longer wavelengths for deeper tissue penetration. Secondly, even with the diverse organic, inorganic or hybrid porphyrin-based materials reported, it is highly desirable to develop more 'intelligent' combined or synergistic therapies to rationally arrange the multiple functions against the specific tumor environment and overcome the inherent limitations of PDT. Thirdly, most of the published research works of porphyrin-based materials mainly focus on basic scientific and fundamental research so far. Hence, Porphyrin-based materials activated by NIR light with good biocompatibility and biodegradability, high photocytotoxicity, excellent delivery efficiency in the body and effective tumor targeting with negligible side effects are needed for the translational and clinical PDT practice. We believe that a variety of unique porphyrin-based functional materials would provide more fascinating superiorities in PDT and dramatically expand the potentials and options in cancer treatments. Thus, there is still a long way to go from lab to the patient translation of the findings.

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.

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