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Review

## Porphyrin-based compounds and their applications in materials and medicine

Yingyan Shi<sup>a,b,\*</sup>, Fuming Zhang<sup>c</sup>, Robert J. Linhardt<sup>b,c,d,\*\*</sup><sup>a</sup> Department of the Chemistry, School of Basic Science, Jilin Jianzhu University, Changchun, 130118, China<sup>b</sup> Department of Chemistry and Chemical Biology, Center for Biotechnology and Interdisciplinary Studies, Rensselaer Polytechnic Institute, Troy, NY, 12180, USA<sup>c</sup> Department of Chemical and Biological Engineering, Center for Biotechnology and Interdisciplinary Studies, Rensselaer Polytechnic Institute, Troy, NY, 12180, USA<sup>d</sup> Department of Biological Science and Biomedical Engineering, Center for Biotechnology and Interdisciplinary Studies, Rensselaer Polytechnic Institute, Troy, NY, 12180, USA

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## ABSTRACT

Porphyrin-based compounds has been the subject of recent investigations for their chemical and biological properties. A variety of chemical modifications have been introduced in the porphyrin skeleton to improve the diversity, stability, and selectivity for porphyrin-based compounds. This review provides an update on a variety of porphyrin-based compounds and highlights new developments in porphyrin-based structural modification, with a specific emphasis on their recent roles in organic solar cells, porphyrin-based functional devices, and for cancer treatment.

### 1. Introduction

Porphyrins are molecules with four pyrrole units linked by four methine bridges having a square planar conformation [1–4]. The porphyrin macrocycle contains 18 delocalized  $\pi$ -electrons, that are in accord with Hückel's rule of aromaticity with the  $(4n + 2)$   $\pi$ -electrons of the porphyrin corresponding to an aromatic system. An unsubstituted porphyrin, known as porphin, represents the simplest porphyrin. Numerous functional groups can be substituted onto porphin macrocycles at the meso-position or the  $\beta$ -position [5] producing a wide variety of porphyrin derivatives. In addition, free-base porphyrins can be coordinated with numerous metal ions at the porphyrin center to form metal complexes, known as metalloporphyrins [6].

Porphyrins and porphyrin derivatives are important functional molecules and a class of organic chromophores. They have been applied in various applications due to their characteristics and versatile functions. Compared to porphyrin monomer, porphyrin-based compounds have notable advantages in that these compounds can remarkably enhance the functionalities of porphyrins extending their applications [7–17].

This review focuses on the properties and applications of porphyrin-based compounds. Recent progress on the applications of porphyrin-

based compounds in organic solar cells, functional devices and in cancer treatment is discussed.

### 2. The synthesis porphyrin and porphyrin-based compounds

#### 2.1. The synthesis of porphyrins

The synthesis of porphyrin was widely reported [18–25]. The classical method for the synthesis of symmetric porphyrins is the condensation of pyrrole with an appropriate aldehyde under acid catalysis followed by the oxidation of protoporphyrins to porphyrins (Scheme 1). This method is simple, mild, practical, and suitable for the preparation of a large number of tetrasymmetric porphyrins [26–29].

The synthesis of these tetrasymmetric porphyrins is not complicated as the single meso-position functional group of porphyrins limits the synthesis of copolymerized porphyrins. Asymmetric porphyrin monomers suitable for preparing porphyrin polymers can be synthesized through the condensation of a mixture of aldehydes and pyrrole (Scheme 2). However, this method has a low product yield and requires a complicated separation process [30,31]. The MacDonald group first proposed the “2 + 2” method (Scheme 3) in 1960 and developed a “3 + 1” synthesis method to solve this problem [32]. These methods can

\* Corresponding author. Department of the Chemistry, School of Basic Science, Jilin Jianzhu University, Changchun, 130118, China.

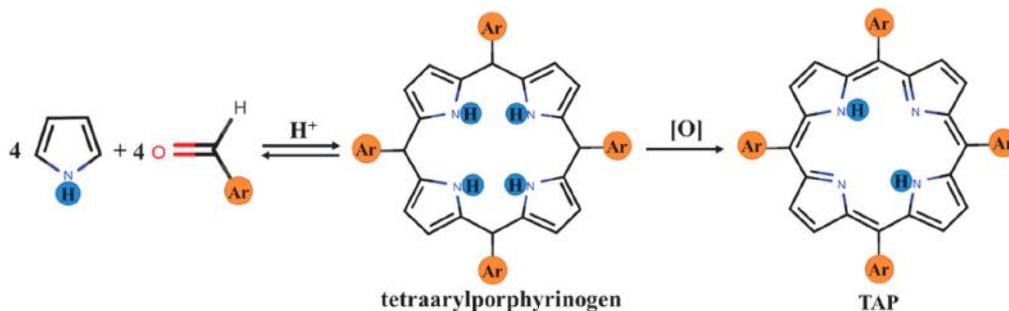
\*\* Corresponding author. Department of Chemical and Biological Engineering, Center for Biotechnology and Interdisciplinary Studies, Rensselaer Polytechnic Institute, Troy, NY, 12180, USA.

E-mail addresses: [shiyinyan73@hotmail.com](mailto:shiyinyan73@hotmail.com) (Y. Shi), [linhar@rpi.edu](mailto:linhar@rpi.edu) (R.J. Linhardt).

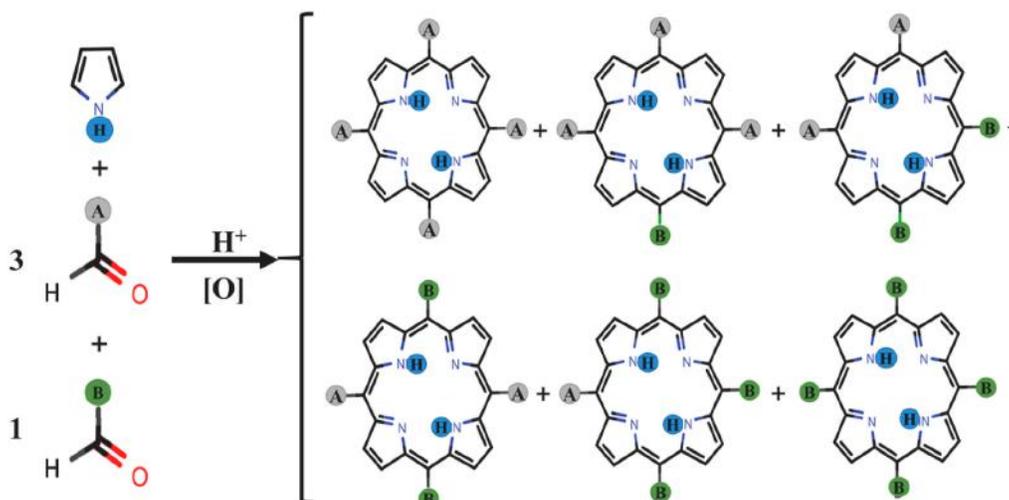
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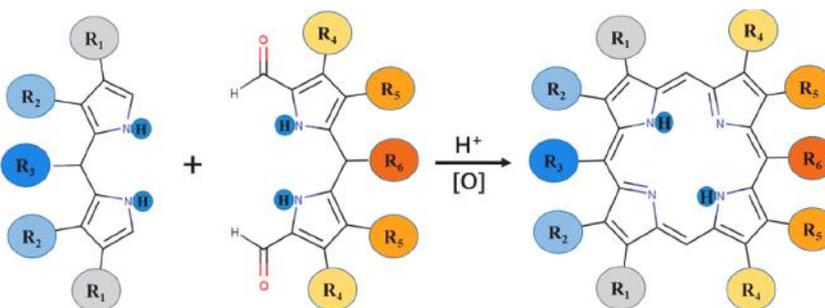
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Scheme 1. Condensation of pyrrole and arylaldehydes to form tetrasymmetric porphyrins (TAPs).



Scheme 2. Mixed aldehyde condensation results in a mixture of products.



Scheme 3. A 2 + 2 condensation of dipyrromethanes, the MacDonald method.

provide various porphyrin molecules for the synthesis of porphyrin-based compounds.

## 2.2. Synthesis of porphyrin-based compounds

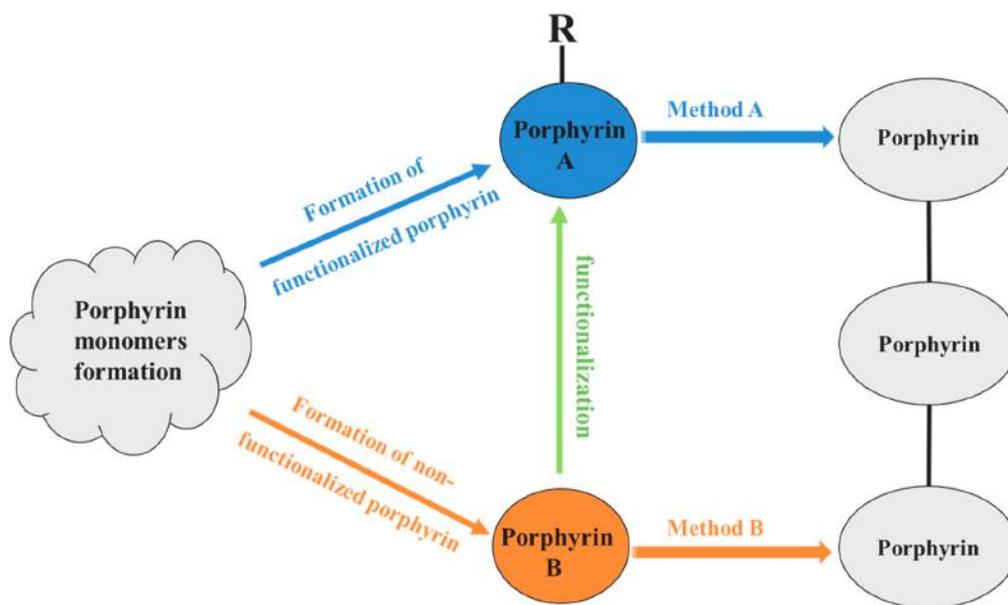
### 2.2.1. Two basic methods for the synthesis of porphyrin-based compounds

The key point of the first method (Method A, Scheme 4) is the introduction of ideal functional groups around the porphyrin molecules to realize porphyrin polymerization through a bridging agent.

The second method (Method B, Scheme 4) is widely used and involves the direct coupling of porphyrin monomer with other molecules.

### 2.2.2. Synthesis of metalloporphyrins

Tsutsui and coworkers [33–36] introduced and thoroughly developed the classical method for the synthesis of metalloporphyrins, which uses metal carbonyls to afford metalloporphyrins. This method inserts metal ions into nearly all classes of porphyrins. When metalloporphyrin complexes are synthesized, factors including the solubility of the porphyrin and salt in the selected solvent, the basicity of the solvent, the propensity of the salt for solvation and re-solvation during activation, and the stability of the metalloporphyrin under the conditions of its formation reaction must be taken into account. *N,N*-dimethylformamide (DMF) is a universal solvent in the reactions for complex formation, when using weakly charged cations by the Adler method, since



Scheme 4. General synthetic scheme for porphyrin array formation.

**Table 1**  
Typical bond types of porphyrin-based compounds.

Bond Type		Bridging Agent	Ref.
Heteroatom	Esters and Amino Compounds	Ester bond	[38]
	Ether	Ether bond	[39]
	Other heteroatom	Azobenzene	[40]
		Heteroatoms on aromatic heterocycle	[41]
Carbon-carbon bonds	Direct bond	Two pyrimidine	[42]
	Alkyl bond	–	[43]
	Olefin bond	Ethane	[44–46]
	Alkynes bond	Vinyl	[47]
		Alkynyl	[48]
		diacetylene	[49–51]
		alkyne group with aromatic rings	[52]
Other bonding	Aromatic hydrocarbon bond	Aromatic ring	[53–55]
	Polycyclic aromatic hydrocarbons linking	Benzo	[56,57],
	Other Aromatic hydrocarbon bond	Phthalocyanine	[58,59],
	Metal- metal bond	M-M	[60–63]
	Metal - ligand bond	M-ligand coordination bonds	[64,65]
	Hydrogen bond	Non-covalent hydrogen bonds	

DMF has a high dielectric constant [37].

### 2.2.3. Polymerization of porphyrin-based compounds

Intricate binding modes enable porphyrins to form molecular cages or framework solids. The polymerization of porphyrin-based polymer molecules can be divided into three categories: (1) non-metallic covalent bond bridging agents (e.g., C–N, C–O, C–C bonds), (2) metal (M) coordination bond bridging agents (e.g., M – O, M – N bonds), and (3) non-covalent bond bridging agents (e.g., hydrogen bonds, electrostatic attraction). These isolate porphyrin molecules from one another, promoting monomer interactions. The properties and position of polymerization have a marked influence on the chemical stability, thermal stability and the solubility of porphyrin polymers. The porphyrin molecules of meso- or pyrrole  $\beta$ -type can achieve polymerization connection. Table 1 shows the different bond types of porphyrin-based compounds.

## 3. Properties of porphyrins and porphyrin-based compounds

### 3.1. Color and solubility

Most porphyrins and porphyrin compounds currently produced are dark purple, reflecting the color of the porphyrins. Transition metal-porphyrin compounds can show different colors and are greatly impacted by their metal ions.

Water-soluble porphyrins dissolve in both water and water-DMF mixtures. Water-insoluble porphyrins generally dissolve in benzene, chloroform, dichloromethane, pyridine, ethanol, dimethyl sulfoxide and DMF. The solubility of porphyrins is determined by their functional groups.

### 3.2. Electron spectra of porphyrins [66]

Porphyrin compounds have very deep color and a fixed absorption wavelength in visible region. Peripheral substitution on the porphyrin

ring generally results in a slight change in absorption wavelength and intensity. The absorption and emission spectra of porphyrin molecules are mainly determined by the  $\pi$ -electrons in the porphyrin ring, while the electrons in the central ions contribute little.

The electronic spectra of porphyrins display two main absorption regions, a strong Soret band in the range of 250–500 nm, and relatively weak bands (Q bands) in the range of 550–700 nm [67,68]. Experimental as well as theoretical interpretations of the electronic transitions, corresponding to these absorption bands, have been reported [69]. [70] According to the four-orbital model theory, the four orbitals are the  $\pi$  orbitals and  $\pi^*$ -antibonding orbitals of a porphyrin. The two highest occupied orbitals (HOMO) have symmetry of  $a_{1u}$  and  $a_{2u}$ , and the two lowest unoccupied orbitals (LUMO) have symmetry of  $eg$ . The two main forms of absorption are the transition coupling between HOMO and LUMO ( $\pi \rightarrow \pi^*$ ). The Q band is the result of the transition dipoles cancelling each other out, so the absorption is weak. The higher energy Soret transition is a linear combination of two transitions, reinforcing the transition dipole and, thus, showing strong absorption.

Compared with the ligand molecules, the molecular symmetry of metalloporphyrin is increased (from  $D_{2h}$  to  $D_{4h}$ ), the degree of molecular orbital division is decreased, the degree of dehydrogenation is increased, and the number of q-band spectral peaks is decreased, but the strength is increased. After the polymer is formed, the spectrum shows a blue shift or red shift depending on the configuration of the product. In general, the redshift and cleavage often occur in the Soret band of one-dimensional dimers, trimers or pentamers, and the greater the number of porphyrin molecules, the greater the cleavage width [71].

### 3.3. Infrared spectra of porphyrins

The infrared spectra of porphyrin were studied in the 1950s [72]. The characteristic absorption peaks in the spectrum determined specific groups in porphyrin molecules, the structure of substituents group on porphyrin rings, and whether porphyrin molecules were metallized. The attribution of infrared spectra of some known porphyrins has been reported in detail [73]. Infrared spectroscopy can be used to determine whether porphyrin molecules contain hydroxyl, alkyl, phenyl, carbonyl, amino, cyanide and other functional groups [74].

### 3.4. Photovoltage spectra of porphyrins

Photovoltage technology was first used to characterize the parameters and surface properties of semiconductor materials. In recent years, it has been widely used in the research of nano-functional materials, organic semiconductors, catalysis and solar energy conversion.

Porphyrins have relatively high chemical and thermal stability, so that they can be purified by physical methods and used to prepare thin films for various applications. The activity of porphyrins can be controlled by changing their central ions and peripheral substituents; thus, porphyrins play an important role in organic semiconductors.

Organic semiconductors have a characteristic photovoltaic effect because of their good light absorption and through their mobile carriers generated by absorption. The photoconductive behavior of organic semiconductors is generally explained by band theory, the bonding  $\pi$ -orbitals form the valence band of the organic solids and antibonding  $\pi^*$ - orbitals form the conduction band of the organic solids. In the  $\pi$  system, photogenic carriers behave as non-localized carriers, and their motion is limited to the energy bands of the system. Specifically, photogenic holes are in the valence band, and photogenic electrons are transferred between molecules in the conduction band. The central metal ions and peripheral substituents of porphyrins can easily influence the electronic transition and excited state life of porphyrins, thus, changing the photovoltaic characteristics of the porphyrin composites.

### 3.5. Nuclear magnetic resonance (NMR) spectroscopy of porphyrins

$^1H$  NMR and  $^{13}C$  NMR have been used to identify the types of hydrogens and carbons in paramagnetic and diamagnetic porphyrin molecules and their positions. NMR can also be used to characterize and determine the molecular structure of porphyrins and is a very accurate and effective means of establishing structure.

### 3.6. The third-order nonlinear optical property of porphyrins

Third-order nonlinear optical effects are associated with large, delocalized  $\pi$ -electron systems, and structure does not necessarily require non-central symmetry. In general, the conjugated molecules with alternating single and double bonds can exhibit macroscopic third-order nonlinear optical properties. Porphyrins are good third-order nonlinear optical materials because they are electronically delocalized systems and the large porphyrin ring is modifiable. Any substituent group can be attached to the outer ring, and the central metal can change or even extend ring size.

### 3.7. Fluorescence spectroscopy of porphyrins

Most organic molecules are singlets (all electrons are paired) in their ground state. When a molecule absorbs radiation, an electron is excited to a higher energy level without changing its spin. This is called the excited singlet state. Fluorescence occurs when the first excited singlet state relaxes back to the ground state. If the initial absorption produces an excited state of higher energy, it will quickly dissipate instead of radiating back to the first excited singlet and then emit fluorescence. When the sample is excited at a fixed wavelength, the emission spectrum is obtained as a function of the relation between the emission intensity and the emission wavelength. An emission wavelength is selected and the emission intensity is taken as a function of the excitation wavelength to obtain an excitation spectrum. Porphyrins are highly fluorescent substances and their molecular structural diversity and modifiability affect the fluorescence properties of porphyrins.

## 4. Applications of porphyrin-based compounds

Porphyrins and porphyrin derivatives are an important class of organic chromophores and have been applied for various applications due to their characteristics and versatile functions.

### 4.1. Organic solar cells

Organic solar cells (OSCs) have been in development for more than 40 years [75]. Dye-sensitized solar cells (DSSCs) are new types of solar cells developed by imitating the principle of photosynthesis. DSSCs are made from low-cost nanometer-sized titanium dioxide particles and photosensitive dyes. These simulate photosynthesis of plants in nature, converting solar energy into electricity. Several conditions must be met to use dyes as photosensitizers: (1) the semiconductor electrode surface of titanium dioxide nanocrystalline structure needs to exhibit good adsorption, quickly reaching an adsorption balance that does not easily fall off; (2) they have a wide absorption band in the visible region; (3) the oxidation state and excited state of dye should have higher stability; (4) the excited state has a sufficiently long life and a high charge transfer efficiency to prolong the electron-hole separation and play a decisive role in the electron injection efficiency; and (5) they have a sufficiently negative excited REDOX potential to ensure that the dye excited electrons are injected into the titanium dioxide conduction band.

Porphyrins are important macrocyclic compounds with sharp and intense Soret bands and broad Q bands. Thus, porphyrins are considered very promising for use in DSSCs mainly owing to their efficient capture of solar energy in the visible region and their high molar extinction coefficients. The structural diversity of porphyrins, with core-, meso-,

and  $\beta$ -modifications, having a role in donating electrons, suggest a way to tune the electronic structures and their properties as dye sensitizers in DSSCs [76]. Porphyrin derivatives have also been widely used as sensitizers in dye-sensitized solar cells (DSSC) [77,78]. Some porphyrins have been used as photosensitizers in  $\text{TiO}_2$  DSSCs. Tetra (4-carboxyphenyl) porphyrin dye (TCPP) [79], 5-(4-carboxyphenyl)-10,15,20-tritolypporphyrin ( $\text{H}_2\text{TC}_1\text{PP}$ ) and 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin ( $\text{H}_2\text{TC}_4\text{PP}$ ) [80] and other porphyrins [70] have been investigated as effectual photosensitizers for solar-energy alteration.

Some researchers have designed and synthesized donor-acceptor (D-A) structured porphyrin sensitizers with different electron-donating groups attached at the meso-position of these porphyrins to improve the electron transfer efficiency [81–83]. Porphyrins containing a strong donor unit exhibit a similar Soret band absorption and a slightly red-shifted Q-band absorption. Porphyrin-containing conjugated polymers, which are among the most promising organic optoelectronic materials have been widely used in solar cells. A conjugated polymer, consisting of the repeat units of a carbazole donor and a porphyrin acceptor with a terthiophene bridge, has been reported [84,85]. A series of D-A conjugated polymers based on quinoxalino [2,3-b'] porphyrin (QP) and diketopyrrolopyrrole (DPP) as acceptor units and oligothiophene as donor units have been synthesized by palladium-catalyzed Stille-coupling polymerization [86]. Tan and co-workers introduced the linker moieties into porphyrin-containing conjugated polymers to obtain donor-linker-acceptors with three parts consisting of a conjugated polymer prepared by Stille coupling reaction, i.e., 5,15-bis(4-bromophenyl)-10,20-bis(4-(octyloxyphenyl) porphyrin, 2, 1, 3-benzothiadiazole and thiophene [87].

#### 4.2. Porphyrin functional devices

With the rapid development of electronic communication and computer technology, the technology to produce large scale integration (LSI) devices on monocrystalline silicon is approaching its limit. The principle of semiconductor operation is also very limited for 100 nm integrated circuits. Therefore, it is necessary to develop new technologies and seek new approaches if electronic information technology is to surpass the present era of microelectronics and realize the revolutionary transformation into the future molecular era. Research to develop electronic devices at the molecular level for high-tech products such as molecular computers to reduce volume, power consumption and improve environmental friendliness. Thus, research on molecular devices is currently a hot topic in the field of molecular electronics. Most developed countries are investing in the development of molecular devices. Molecular conductors, a standard component of such devices, have particularly attracted much attention [88–92].

A molecular wire is a connector between an electron acceptor (A) and an electron donor (D). It conducts electrical signals and impulses across a specified distance between the two. At the molecular scale these electrical signals can be as small as one electron. The structure of porphyrins consists of 20 carbon and 4 nitrogen atoms, which are hybridized as  $sp^2$  and the remaining p-orbital is occupied by single or lone pair electrons, forming the large ring, electron-conjugated delocalization system of the  $4n+2$  type with 26 electrons. Metal porphyrins are formed by the substitution of two protons on the central nitrogen atom by metal ions. The outer ring of porphyrins can be connected with a variety of substituents. The monomer has a large size. The central metal ions can be controlled and the ring size can be extended. The photoelectric properties of porphyrin molecules can be changed by regulating their peripheral substituents and metal ions. Thus, porphyrins are promising model compounds for the preparation of molecular devices [93]. The  $\pi$  structure of porphyrin polymers form large supramolecular chromophores reducing the energy difference between HOMO and LUMO, giving these polymers the better electrical properties required for molecular wires.

For many years, the design and study of functional molecules based on porphyrins has been a hot topic among chemists and materials scientists. In 1986, Colman explored optical and electrical properties of pyrazine-bridged Fe, Ru, Os octaethylporphyrin polymers [94]. At present, the research of porphyrin molecular wires at home and abroad mainly focuses on the synthesis of molecular wires with single porphyrin molecules. The chemical structure and other aspects of the test of molecular wires and their components are also being studied. In 2006, Kawaoa et al. investigated the synthesis and self-assembly of porphyrin molecular wires [95]. In 2008, Atula S. D. Sandanayaka et al. studied the structure and photophysical properties of self-assembled porphyrin complexes constructed using ethylene glycol derivatives [96]. Photophysical properties of zinc porphyrins self-assembled by bidentate diamine ligands were examined by Danger et al., in 2010 [97]. Malvoti et al. studied the content of ruthenium porphyrins assembled into molecular wires by metallic bonds [98]. In 2011, Koepf et al. investigated highly linear molecular wires [99]. In 2012, Conklin et al. studied the electron conduction process in the structure of porphyrin supramolecular gold nanoparticles, Pereira et al. addressed the problem of porphyrin supramolecules, and Lewtaka et al. looked at the effect on the conjugated properties of porphyrin through the interaction between porphyrin molecules [100,101,102,103,104,105]. Solladié et al. undertook research on bis-porphyrins with flexible linkers such as uridine or 2'-deoxyuridin pre-organize in a face-to-face conformation and form stable sandwich complexes with bidentate base such as DABCO [106]. The resulting molecule combined the fullerene-functionalized macrocycle with an axle bearing a porphyrin stopper as a photoactive molecular device in which the porphyrin emission was efficiently quenched by the fullerene moiety [107].

Supramolecular structures of metalloporphyrin derivatives, i.e., Zn, Co, and Ni on a single-walled carbon nanotube (SWNT) surface, were investigated. This provided further understanding of how to build new supramolecular architectures on SWNT surfaces to design novel molecular architectures of porphyrin/SWNTs-based devices [108]. Molecular conductivity calculations in donor-insulator-acceptor (D- $\sigma$ -A) devices using porphyrin, hexaphyrin, and hexathia [26 $\pi$ ] annulene show promise in the field of molecular electronics and memory storage [109]. Single-molecule spin caloritronic devices, which convert heat into electricity by using spin degree of freedom of electron, are attracting attention. These have inspired the utilization of molecules as elementary blocks to shrink electronic components. Molecular-scale spin caloritronic devices were proposed that consisted of a transition metal porphyrin (TM(Pr), TM = V, Mn, Fe, Co) molecule sandwiched between single-walled carbon nanotube (SWCNT) electrodes through carbon atomic chains (CACs) [110].

Molecular electronics based on porphyrin systems show great promise. The molecular design and formation of functional devices has been aided by new fabrication strategies, measurement tools, and theoretical models. For example, the intermolecular interactions between free-base porphyrins are different than the corresponding zinc metalloporphyrins in nanodomains of these molecules in self-assembled mono layers (SAMs). The precise architecture mediated by supramolecular interactions, ranging from interactions to coordination bonds, dictates the electronic communication between the molecules. Thus, having profound effects on the observed molecular electronic properties. In the future, developing better theoretical and experimental probes to determine how both the ensemble and matrix effects molecular electronic properties should facilitate the design of enabling technologies [111,112].

#### 4.3. Cancer treatment

As the population ages, the number of cancer cases and deaths worldwide has been rapidly growing. The treatment strategies for cancer are constantly improving with the continued development of medical science. Photodynamic therapy (PDT) is non-invasive type of

**Table 2**  
The porphyrin-based inorganic nanoparticles (NPs) and application.

Nano particles	Porphyrin	Applications	Ref.
Gold (III)	5-[4-(11-Mercaptoundecyloxy)phenyl]-10,15,20-triphenylporphyrin	Potential PDT applications	[120]
	4-Carboxyphenylporphyrin	PDT treatment	[121]
	Tetraphenylporphyrin	Clinical treatments of PDT	[122]
	Tetraphenylporphyrin	2P-PDT with simultaneous imaging modality	[123]
	Tetraphenylporphyrin	Tumor targeting reagent	[124]
Gold (III)	Hematoporphyrin	Cytotoxic effects and triggered apoptosis (DNA fragmentation)	[125]
Zn	$\beta$ -(Hydroquinon-2-yl)-5,10,15,20-tetra(4-hydroxyphenyl) porphyrins	Promising photosensitizer for PDT	[126]
	Meso-substituted tetra-cationicporphyrins	PDT	[127]
	5,10,15,20-Tetrakis(carboxyl)porphyrin	PDT	[128]
	5, 10, 15, 20-Tetrakis (4-amidinophenyl) porphyrin	PDT	[129]
	$\beta$ -(Hydroquinon-2-yl)-5,10,15,20-tetra(4-hydroxyphenyl) porphyrins	Promising photosensitizer for PDT	[126]
Platinum	Zn-2( $\beta$ -I) Porphin; Mn(py)Br-porphin	PDT	[130]
	Tetraarylporphyrin	Phototoxic antitumor agents	[131]
	5,10,15-Tri( <i>N</i> -methyl-4-pyridiniumyl) porphyrin (TrisMPyP)	High antitumor activity	[132]
	Tetraarylporphyrins of the Ar:Ar' = 3:1-type	Cytotoxic and phototoxic antitumor agents	[133]
	5,10,15,20-Tetra(4-pyridyl) porphyrin	PDT	[134]
	<i>Meta</i> isomers of free-base <i>meso</i> -tetra(pyridyl)porphyrins	PDT	[135]
	5-[4-(Carboxyl)-phenyl]-10,15,20-tri(3,4,5-trimethoxyphenyl) phenylporphyrin	PDT agent	[136]
Ruthenium	Monopyridylporphyrin, Tetrapyrindylporphyrin	PDT	[137]
	Monopyridylporphyrin	Organometallic photosensitizers	[138]
	H <sub>2</sub> - $\beta$ -Ethynyltetraphenyl porphyrin -1,10- phenanthroline;	PDT agent	[139]
	H <sub>2</sub> - $\beta$ -Ethynyltetraphenyl porphyrin (Zn)-1,10-phenanthroline		
Ga	5,10,15,20-Tetra(4-pyridyl)-21 <i>H</i> ,23 <i>H</i> -porphine (H2TPyP)	PDT	[140]
Gd	<i>Meso</i> -tetraphenyl porphyrin	Clinical PET agent	[141]
Indium	Chlorophyll-a	Nonradioactive peripheral benzodiazepine receptor (PBR) binding probes and photosensitizers for use in PDT	[142]
	Tetraphenyl porphyrin	Bifunctional agent	[143]
Magnetic- nanoparticles: Fe <sub>3</sub> O <sub>4</sub>	Tetraphenyl porphyrin tetrasulfonic acid hydrate (TPPS)	<i>In vitro</i> PDT treatment of HepG2 and HeLa cells	[144]
silica- nanoparticles	5-(4-Hydroxyphenyl)-10,15,20-triphenylporphyrin (TPPOH)	<i>In vitro</i> PDT treatment of human colorectal cancer cells (CRC)	[145]

phototherapy that exhibits reduced side effects compared to conventional cancer therapies that exhibit high toxicity in normal tissues [113]. Porphyrins and their derivatives have been widely utilized in biomedical fields, as biosensors, in bioimaging, in cancer therapy, and especially in photodynamic therapy (PDT) [114,115]. Photosensitizers (PS) plays a vital role in PDT processes, and the efficacy of PDT is mainly determined by the nature and status of photosensitizers [116]. Porphyrins are important PS agents in cancer phototherapy due to their structural presence of N-H groups and nitrogen atoms, whereby they can be further functionalized by having either nanoparticles, metal ion chelates or polymers conjugated onto their surfaces [117].

#### 4.3.1. Porphyrin-based inorganic nanoparticles (NPs)

NPs are small in size and range between 1 and 100 nm in diameter and some can contain/carry multiple theranostic agents. Drug delivery systems based on inorganic NPs provide the advantages of a wide surface area conjugation chemistry with versatile surface functionalization. In addition, they bestow great biocompatibility, easy preparation, and excellent physical-chemical properties to enhance therapeutic efficacy [118]. It is important to appreciate that non-biodegradable nanoparticles, including inorganic NPs, have recently attracted considerable research interest in the field of PDT. Multifunctional theranostic carriers are of interest due to their unique optical properties and size, shape, and porosity tunability. Combining porphyrins with metals not only provides additional anti-tumor activity and tumor selectivity, but the bio-distribution of the metal inside and outside the tumor cell can be tracked [119]. Porphyrin-based inorganic nanoparticles (NPs) have been designed for PDT and are summarized in Table 2.

#### 4.3.2. Porphyrin-based polymers

Porphyrin-based polymers, which combine the advantages of

porphyrins and polymers. Therefore, porphyrin-based polymers have important potential applications in photovoltaics, catalysis, biological and biomedical fields. The natural polymers have been widely utilized in biology and biomedicine fields, due to their good biocompatibility. Natural polymers and synthetic biocompatible polymers also have been widely developed for PDT. The porphyrin-based polymers have been widely studied as photosensitizers for PDT [146].

In recent years, metal-organic frameworks, as a new type of hybrid porous coordination polymers assembled from metal ions/secondary building units (SBUs) and organic linkers, have gained increasing attention. The construction of porphyrin-based metal-organic frameworks can be prepared by introducing porphyrin molecules into metal-organic frameworks or using porphyrins as organic linkers to form metal-organic frameworks. These can integrate the unique features of porphyrins and metal-organic frameworks as well as overcome the limitations of porphyrins, facilitating their use in biomedicine. For porphyrin-based metal-organic frameworks, the high porphyrin loading capacity and free diffusion of oxygen and reactive oxygen species allow the highly efficient PDT due to their porous structures. Furthermore, the biocompatible and biodegradable characteristics of metal-organic frameworks result in enhanced biosafety in PDT [147]. Since the first report on porphyrinic metal-organic frameworks for potential tumor PDT by Lin et al., in 2014 [148], numerous porphyrin-based metal-organic frameworks have been designed for PDT until now [147].

#### 5. Conclusions and future perspective

Many different porphyrin-based compounds have been reviewed for a variety of potential applications. Porphyrins are abundantly available and offer important synthesis, fabrication, and structural properties. Applications range from biomaterials to electronics and other industrial

uses. Porphyrins also offer an abundant alternative to porphyrin-based synthetic compounds.

### Declaration of competing interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled, "Porphyrin-based compounds and their applications in materials and medicine".

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