Silver Cluster-Porphyrin-Assembled Materials as Advanced Bioprotective Materials for Combating Superbacteria

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Superbugs are bacteria that have grown resistant to most antibiotics, seriously threatening the health of people. Silver (Ag) nanoparticles are known to exert a wide-spectrum antimicrobial property, yet remain challenging against superbugs. Here, Ag clusters are assembled using porphyrin-based linkers and a novel framework structure ($\text{Ag}_9\text{-AgTPyP}$) is produced, in which nine-nuclearity Ag$_9$ clusters are uniformly separated by Ag-centered porphyrin units ($\text{AgTPyP}$) in two dimensions, demonstrating open permeant porosity. Ag$_9$-AgTPyP eliminates over 99.99999% and 99.999% methicillin-resistant $\textit{Staphylococcus aureus}$ (MRSA) and $\textit{Pseudomonas aeruginosa}$ ($P.$ aeruginosa) within 2 h upon visible-light irradiation, which are superior to a majority of bacteria inactivation photocatalysts. The novel-established long-term charge-transfer states from AgTPyP to adjacent Ag$_9$ cluster that has preferential affinity to $\text{O}_2$ greatly promote reactive oxygen species (ROS) production efficiency; and its unique framework accelerates the ROS transportation. Personal protective equipment (masks and protective suits) incorporating Ag$_9$-AgTPyP film also shows excellent performances against superbugs. This superbugs-killing efficiency is unprecedented among silver complexes and porphyrin derivatives. Utilizing efficient photogenerated electrons and holes between metal cluster and linkers can open up new interests of research in photocatalytic areas.

1. Introduction

More recently, multidrug-resistant pathogenic bacteria, also called “superbacteria” or “superbugs,” featuring strong infectiousness and high mortality, have become one of the most serious threats to global safety.[1] Some superbacteria that release a large amount of toxins could be utilized as bioweapons via an aerosol route of exposure.[2] If these bacteria are delivered successfully in a military context, inevitable soldiers’ casualties and subsequent healthcare delivery system chaos would result. Although personal protective equipment, such as face masks and bioprotective suits could intercept pathogenic bacteria physically, the risk of acquisition of a superbacteria-related infectious disease for soldiers and healthcare workers who take care of the infectious patients are still high due to the sustained activity of captured superpathogens.[3] Silver nanoparticles (AgNPs) as the broad-spectrum antibacterial materials have been widely used in daily life.[4] However, the limited activity...
toward superbacteria[5] and intrinsic toxicity[6] is a knotty problem to be settled for advanced bioprotective equipment. Therefore, developing novel bioprotective materials to efficiently prevent the transmission of super-bacteria-related infectious diseases is of utmost urgency, yet remains a formidable challenge.

Combating bacteria via photocatalysis strategies has attracted increasing attention because of its high biocidal efficiency.[10,7] In particular, photoinduced antimicrobial materials hold great promise for the constructing bioprotective equipment.[10,7a]

Porphyrins and metalloporphyrins with strong visible light-harvesting and oxygen transport abilities are promising photosensitizers for antibacterial photocatalytic therapy via reactive oxygen species (ROS) production, such as peroxide, superoxide, hydroxyl radicals, and singlet oxygen.[9] Nevertheless, they easily aggregate and could result in self-quenching issues.[9] One approach to overcome this issue is to embed porphyrins into metal organic framework scaffolds, which provide good accessibility for ROS generation and transportation due to the well-developed porous structure and isolated sites.[9b,10]

Herein, we use a porphyrin-based linker to assemble Ag clusters, which have well-defined structures and much smaller sizes than Ag nanoparticles, producing a novel framework structures ([Ag₉(BuC≡CPh)(CF₃COO)₃(AgTPyP)]ₙ, Ag₉-AgTPyP), in which nine-nuclearity Ag₉ clusters are uniformly separated by Ag-centered porphyrin units (AgTPyP) in two dimensions. Particularly, Ag₉-AgTPyP integrated light harvesters, silver sites, and high surface areas all in one catalyst with an orderly manner, simultaneously optimizing the photocatalytic kinetics for efficient ROS production and leading to high super-bacterial inactivation efficiency. As a result, Ag₉-AgTPyP showed outstanding photocatalytic inactivation efficiency against super-bacteria methicillin-resistant Staphylococcus aureus (MRSA, >99.99999%) and Pseudomonas aeruginosa (P. aeruginosa, >99.9999%) under visible light within 120 min at a catalyst dose of 50 mg L⁻¹. Theoretical calculations and ultrafast transient absorption (TA) spectroscopy suggested that the porphyrinic unit in Ag₉-AgTPyP behaves as an antenna to harvest visible light, leading to formation of the excited state, which then transfers electrons to the catalytic sites around the Ag₉ cluster, enabling the activation of O₂ to various ROS, including singlet oxygen (¹O₂), superoxide anion (O₂⁻), and hydrogen peroxide (H₂O₂). More importantly, we fabricated Ag₉-AgTPyP film as the bioprotective layer and incorporated into the face masks or bioprotective suits, which displayed intriguing phototoxic antibacterial performance in both aerosol and liquid forms, demonstrating their great potential as bioprotective materials against super-bacteria.

2. Results and Discussion

Ag₉-AgTPyP was synthesized by a one-pot reaction of TPyP, CF₃COOAg, and AgCl·Bu in a mixed solution of dimethylformamide (DMF) and CHCl₃ via a conventional slow solvent evaporation method. Single-crystal X-ray diffraction analysis revealed that Ag₉-AgTPyP crystallizes in the C2/c space group (Table S1, Supporting Information), in which the 4-connected Ag₉ node is linked with μ₁-TPyP ligands to form a 2D framework that adopts an AB stacking mode (Figure 1A.B and Figure S1, Supporting Information). Notably, one Ag atom was spontaneously incorporated into the free-base TPyP ligand to form the metalloligand Ag₉-AgTPyP. Such in situ metallization at the porphyrin core may provide more accessible metal centers to achieve a synergistic enhancement of antimicrobial activity. The phase purity of the bulk Ag₉-AgTPyP product was confirmed by a comparison between the simulated and experimental powder X-ray diffraction (PXRD) patterns (Figure S2, Supporting Information). The core of the Ag₉ cluster is a tower-like structure, capped by six tert-butyl groups with two kinds of mixed σ-type and π-type bonding modes, namely, μ₁-η₁, η₂, σ₁, σ₂ and μ₁-η₃, η₄, η₅, η₆ bonding types (Figures S3 and S4, Supporting Information). The Ag₉ core is further consolidated by numerous inner close Ag(I)--Ag(I) contacts, with distances of 2.8823(16)–3.0901(12) Å (Table S2, Supporting Information). These distances are shorter than the sum of van der Waals radii of two silver ions (3.44 Å), suggesting the presence of argentophilic interactions.[11] Moreover, the chemical composition of the structure was further confirmed by infrared spectroscopy (Figures S5, Supporting Information). Thermogravimetric analysis (TGA) curve indicated that Ag₉-AgTPyP was thermally stable at 117 °C (Figures S6, Supporting Information).

Compared to the isolated silver clusters, the highly assembled materials provide enhanced stability by resisting the attack of various guest species.[12] The crystallinity of Ag₉-AgTPyP was well maintained after immersing the samples in water for 24 h or exposing them to air for 5 months (Figure S2, Supporting Information). Ag₉-AgTPyP is hydrophobic, with a water contact angle of 115.6°, which is attributed to the exposed terminal -CF₃ and -t-Bu groups in the Ag₉ cluster (Figure S7, Supporting Information). Such hydrophobic surfaces could efficiently block the adhesion of bacteria and prevent microbial colonization on the surface.[13] The permeant porosity of Ag₉-AgTPyP was confirmed by nitrogen sorption measurements at 77 K, the Brunauer–Emmett–Teller specific surface area was determined to be 190 m² g⁻¹, which provides good accessibility for O₂ encapsulation and ROS
Figure 2. Band-structure characterization and ROS generation of Ag9-AgTPyP. A) UV-Vis spectra and determined optical energy gap of Ag9-AgTPyP. B) Mott–Schottky plots of Ag9-AgTPyP in a 0.2 m Na2SO4 aqueous solution. C) The band positions of Ag9-AgTPyP with respect to the ROS formation potential. EPR spectra of Ag9-AgTPyP for testing of D) 1O2, E) O2−, and F) ·OH in an air atmosphere under visible light irradiation.

production (Figures S8, Supporting Information). In addition, Ag oxidation states in Ag9-AgTPyP were studied by X-ray photoelectron spectroscopy (XPS). Ag 3d3/2 and 3d5/2 peaks were observed at binding energies of 368.2 and 374.2 eV, respectively, indicating the presence of both Ag(II) and Ag(I) oxidation states in Ag9-AgTPyP (Figure S9, Supporting Information). The +2 oxidation state of Ag originates from the porphyrin macrocycle and is obtained during the in situ insertion process, while the +1 oxidation state mainly exists in the Ag9 cluster.[14]

The UV-Vis diffuse reflectance spectra of Ag9-AgTPyP showed strong absorption over a wide range from 240 to 800 nm due to the light-harvesting porphyrinic macrocycle (Figure 2A). According to the Tauc plot, the band gap energy was estimated to be 1.59 eV (Figure 2A). Furthermore, the conduction band (CB) position of Ag9-AgTPyP was estimated by measuring the flat-band potential via Mott–Schottky measurements, which were performed at frequencies of 1000, 1500, and 2000 Hz (Figure 2B). The positive slopes of the C−2 values versus potential plot indicate that Ag9-AgTPyP is an n-type semiconductor and that most of the carriers are electrons. The CB was determined by fitting to be −0.71 V versus Ag/AgCl (i.e., −0.49 V vs normal hydrogen electrode (NHE)), and the corresponding valence band (VB) was calculated to be 1.10 V versus NHE. Additionally, the VB potential was determined by using valence band X-ray photoelectron spectroscopy (VB-XPS) (Figure S10, Supporting Information), and the result was consistent with the Mott–Schottky result. Accordingly, we illustrated the band structure of Ag9-AgTPyP in Figure 2C. Since the CB was more negative than the oxygen reduction potential of O2/O2− (−0.33 V vs NHE, pH 7) and O2/H2O2 (0.28 V vs NHE, pH 7).[7b,15] Ag9-AgTPyP meets the thermodynamic requirements for the generation of O2− and H2O2 (Figure 2C). In addition, we analyzed the O2 sorption ability of Ag9-AgTPyP, which showed an O2 uptake of 51.69 cm3 g−1 at 77 K (Figure S8, Supporting Information). Considering its wide-range light-harvesting ability, proper band alignment, and high O2 uptake, Ag9-AgTPyP is an ideal candidate for photocatalytic ROS generation.

In our previous study, we demonstrated that the synergistic effect of silver clusters and porphyrin units contributed to the transformation of ground-state oxygen (O2) to 1O2.[12b] Herein, the production of 1O2 in Ag9-AgTPyP was confirmed by using electron paramagnetic resonance (EPR) with 2,2,6,6-tetramethyl-4-piperidinol (TEMP) as a spin probe, and a typical 1:1:1 triplet peak for 4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) was observed upon light illumination (Figure 2D). The ·O2− generation was examined by utilizing trapping reagent 5,5-dimethyl-1-pyrroline N-oxide (DMPO), which displayed the specific quartet signals of DMPO·O2− with an intensity ratio of 1:1:1:1 (Figure 2E). Moreover, the amount of 1O2 and ·O2− production gradually increased as the irradiation time was increased from 0 to 30, 60, and 90 s. The steady-state concentration of 1O2 produced by Ag9-AgTPyP was measured by testing the decay of furfuryl alcohol (FFA) and was determined to be (2.91 ± 10−7) × 10−6 M (Figure S11, Supporting Information). The concentration of steady-state ·O2− was determined to be (1.80 ± 10−7) × 10−6 M by the nitroblue tetrazolium (NBT) reduction method (Figure S12, Supporting Information). Additionally, we investigated the production of ·OH during the photocatalysis process, but no
signals were detected (Figure 2F), which explained the more positive potential of H$_2$O$_2$/OH$^\bullet$ (2.32 V vs NHE, pH 7)\cite{20,21} than of the VB of Ag$_9$-AgTPyP. Moreover, the generation of H$_2$O$_2$ was monitored by using a fluorescent method with N-acetyl-3,7-dihydroxyphenoxazine (Amplex Red) as an indicator, which can be oxidized to luminous resorufin in the presence of horseradish peroxidase (HRP). After 120 min of irradiation, the H$_2$O$_2$ concentration in this system was determined to be 3.40 × 10^{-6} M (Figure S13, Supporting Information). The H$_2$O$_2$ concentration in the Ag$_9$-AgTPyP system was much higher than that of O$_2^-$ and O$_2^-$. Furthermore, the inhibition efficiency reached over 99.9999% (equivalent to −log$_{10}$(C/C$_0$) = 5) for E. coli at 120 min and 99.999999% (equivalent to −log$_{10}$(C/C$_0$) = 7) for S. aureus at 90 min, which are much higher than the results presented in many previous reports on materials such as porphyrin-based coordination polymers\cite{8} and typical semiconductor-based materials\cite{7a-c,16} (Table S3, Supporting Information). The difference in inactivation performance on E. coli and S. aureus was significantly reduced within 120 min, suggesting that Ag$_9$-AgTPyP is an excellent broad-spectrum antimicrobial material. Impressive inhibition efficiency was obtained (99.999% (equivalent to −log$_{10}$(C/C$_0$) = 5) for E. coli at 120 min and 99.999999% (equivalent to −log$_{10}$(C/C$_0$) = 7) for S. aureus at 90 min, which are much higher than the results presented in many previous reports on materials such as porphyrin-based coordination polymers\cite{8} and typical semiconductor-based materials\cite{7a-c,16} (Table S3, Supporting Information). The difference in inactivation performance on E. coli and S. aureus was significantly reduced within 120 min, suggesting that Ag$_9$-AgTPyP is an excellent broad-spectrum antimicrobial material. Impressive inhibition efficiency was obtained (99.999% (equivalent to −log$_{10}$(C/C$_0$) = 5) for E. coli at 120 min and 99.999999% (equivalent to −log$_{10}$(C/C$_0$) = 7) for S. aureus at 90 min, which are much higher than the results presented in many previous reports on materials such as porphyrin-based coordination polymers\cite{8} and typical semiconductor-based materials\cite{7a-c,16} (Table S3, Supporting Information). The difference in inactivation performance on E. coli and S. aureus was significantly reduced within 120 min, suggesting that Ag$_9$-AgTPyP is an excellent broad-spectrum antimicrobial material. Impressive inhibition efficiency was obtained (99.999% (equivalent to −log$_{10}$(C/C$_0$) = 5) for E. coli at 120 min and 99.999999% (equivalent to −log$_{10}$(C/C$_0$) = 7) for S. aureus at 90 min, which are much higher than the results presented in many previous reports on materials such as porphyrin-based coordination polymers\cite{8} and typical semiconductor-based materials\cite{7a-c,16} (Table S3, Supporting Information).
Figure 3. Antibacterial properties of Ag₉–AgTPyP. Comparison of the photocatalytic antibacterial performance of Ag₉–AgTPyP, Ag⁺, TPyP, and AgTPP under both light and dark conditions on A) E. coli and B) S. aureus (**p < 0.01). C) Inactivation efficiency of different amounts of Ag₉–AgTPyP toward the antibiotic-resistant bacteria P. aeruginosa. D) Photos of plate count agars spread with P. aeruginosa before and after photocatalytic disinfection using Ag₉–AgTPyP (0.5 mg). E) Inactivation efficiency of different amounts of Ag₉–AgTPyP toward the antibiotic-resistant bacteria MRSA. F) Photos of plate count agars spread with MRSA before and after photocatalytic disinfection using Ag₉–AgTPyP (0.5 mg). In the graph of inactivation performance, all bars represent group means. Error bars indicate maximum positive deviation and maximum negative deviation of the mean. p-Values were calculated using one-way analysis of variance (ANOVA) (n = 3). The data marked by three zeros (000) on the bar indicate that no live bacteria were detected.

Further insight into the rapid charge separation in Ag₉–AgTPyP was obtained using transient absorption (TA) spectroscopy. In Figure 5A,B, the TA spectra of both AgTPP and Ag₉–AgTPyP at 1 ps showed a new increased excited state absorption at 440 nm compared with that at 0.3 ps, and the kinetic signal corresponding to probe wavelength of 440 nm showed a rising signal, indicating that energy transfer from porphyrin to its central silver was occurred (Figure 5C,D). While, the process is ultrafast with only ≈300 fs, and the energy decay occurs rapidly with a short lifetime (≈2 ps, ≈10 ps). Noting that the TA spectra of Ag₉–AgTPyP showed a bleaching peak centered at 475 nm in the 460–490 nm range (Figure 5B), which can be ascribed to the fast charge transfer from TPyP to the Ag₉ cluster. As shown
Figure 4. Theoretical calculations and charge transfer efficiency for Ag$_9$-AgTPyP. A) The top of the VB and B) the bottom of the CB of Ag$_9$-AgTPyP calculated by VASP. C) Calculated DOS profiles of Ag$_9$-AgTPyP. D) Free-energy diagram of O$_2$ adsorption on active Ag metal sites in AgTPyP (black line) and the Ag$_9$ cluster (blue line). E) Photocurrent responses and F) EIS Nyquist plots for Ag$_9$-AgTPyP and TPyP.

in Figure 5D, the kinetic spectrum at 475 nm indicated that the signal is gradually turning to negative at 4 ps and converges to an asymptote, illustrating that this is a long-lived state generated after the electron transfer from TPyP to Ag$_9$ cluster (with the charge separated state lifetime >8 ns). We speculated that the slow charge recombination process in Ag$_9$-AgTPyP was account for the trapping of electrons in Ag$_9$ cluster, and the holes are remained at TPyP (Figure 5E). Besides, the control experiment of TPyP showed unchanged TA spectral signatures at 430–500 nm, suggesting that there was no energy transfer process (Figure S22, Supporting Information). The above spectroscopic analysis demonstrated that the introduction of Ag$_9$ cluster could facilitate charge separation by suppressing the detrimental electron–hole combination.

Consequently, the generated ROS concentration of Ag$_9$-AgTPyP was much higher than that of the ligand TPyP, as determined by 3,3′,5,5′-tetramethylbenzidine (TMB) oxidation experiments (Figure S23, Supporting Information). Ag$_9$-AgTPyP showed strong UV absorbance for the TMB oxidation product as well as a distinct color change from colorless to blue, which suggests a higher oxidation degree of TMB, whereas TPyP exhibited much less activity and a slight color change. Various scavengers, including carotene, mannite, catalase, and superoxide dismutase (SOD), were introduced into the system to clearly identify the active oxygen species of $^{1}$O$_2$, -OH, H$_2$O$_2$, and $^{·}$O$_2$$^-$. For TPyP, only carotene suppressed the oxidation of TMB, indicating that $^{1}$O$_2$ as the ROS promotes the reaction. In comparison, the TMB oxidation by Ag$_9$-AgTPyP was inhibited by carotene, SOD and catalase, in accordance with our EPR and fluorescence results. The above results are consistent with the fact that Ag$_9$-AgTPyP exhibits a higher disinfection rate than TPyP.

Inspired by above results, we fabricated the Ag$_9$-AgTPyP film through a facile hot-pressing method as bioprotective layer to defeat superbacteria. Considering that nonwoven fabrics was
usually employed as the outermost layer in the personal protective equipment to contact the superbacteria. First, we choose it as substrate to load Ag9-AgTPyP particles (Figure 6A). SEM images and elemental mapping analysis indicated the obtained flexible film coating with uniformly dispersed Ag9-AgTPyP particles, which ranging from 0.5 to 5 μm (Figure 6B and Figure S25, Supporting Information). The loading level was 0.75 mg cm⁻². Moreover, the PXRD patterns of Ag9-AgTPyP film maintained well with pristine Ag9-AgTPyP (Figure 6C). To examine the applicability of Ag9-AgTPyP film in personal protective equipment, Ag9-AgTPyP film was first integrated into the masks serving as the biocidal layer. As shown in Figure 6D-F, no living bacteria were observed on Ag9-AgTPyP film area or its covered area in the mask under 1 h of visible light irradiation when the gram-positive model MRSA aerosols was about 10⁶ CFU. On the contrary, most of the bacteria in control area (outer layers of N95 masks) were survived with a negligible antimicrobial efficiency of 54.85%. When the experiment was conducted in dark conditions, the inferior antibacterial activity (48.29%) is not enough to defeat the bacterial infection, further supporting that photocatalytic is a prerequisite to kill superbacteria for Ag9-AgTPyP film. Similarly, Ag9-AgTPyP film also displayed promising bioprotection against gram-negative model P. aeruginosa in liquid form to the protective suits (Figure 6G-I). Almost no viable bacterial P. aeruginosa colonies were observed within 1 h in the covered area upon treatment with Ag9-AgTPyP film under light illumination. While over 10⁵ CFU of bacteria survived in the control group of commercial protective suit surface under the same conditions. Furthermore, the recycling experiment of Ag9-AgTPyP film was conducted. Results showed that no performance decay was observed after three
Figure 6. Bioprotection performance of Ag$_9$-AgTPyP film. A) Optical photograph of Ag$_9$-AgTPyP film (4 × 4 cm$^2$). B) SEM images of Ag$_9$-AgTPyP film. C) PXRD patterns of Ag$_9$-AgTPyP, nonwoven cloth, and Ag$_9$-AgTPyP film. D) Simulated bacterial aerosols and the interception test by N95 mask. E) Three selected test areas on the mask and F) the relevant CFU count of MRSA, its illustration represents each area of mask washed three times incubated in nutrient agar after 1 h of light irradiation (*$p < 0.05$). G) Photograph showing the protective suit was loaded with Ag$_9$-AgTPyP film. H) Three selected test areas on the protective suit and I) the relevant CFU count of P. aeruginosa, its illustration represents each area of mask washed three times incubated in nutrient agar after 1 h of light irradiation (**$p < 0.01$). All bars represent group means. Error bars indicate maximum positive deviation and maximum negative deviation of the mean. $p$-Values were calculated using two-tailed independent student’s $t$-test method ($n = 3$). The data marked by three zeros (000) on the bar indicate that no live bacteria were detected.

cycles and the PXRD patterns were well maintained, suggesting that the film have great reusability (Figure S26, Supporting Information). Above results strongly supported that Ag$_9$-AgTPyP film showed great potential as a protective layer for combating super-bacteria in various scenarios like individual combat equipment in the war, surgical masks, etc.

3. Conclusion

In summary, we developed a new silver-porphyrinic cluster-assembled material Ag$_9$-AgTPyP, and explored its bioprotection application toward the super-bacteria under visible light. A mechanistic investigation indicated that the co-contribution of silver clusters and porphyrinic units in the framework could efficiently enhance the charge separation ability upon photoexcitation and activate O$_2$ to produce $^{1}$O$_2$, $^{·}$O$_2^-$, and H$_2$O$_2$. To be specific, a novel long-term charge-transfer state from AgTPyP to adjacent Ag$_9$ cluster has been established. We also proved that Ag$_9$ cluster has preferential affinity to O$_2$ which greatly promoted ROS production efficiency. This research provides a deep understanding of combating multidrug-resistant bacteria via photocatalysis in silver-porphyrinic cluster-assembled materials. Utilizing efficient photogenerated electrons and holes between metal cluster and linkers would open up new interests of research.
in photocatalytic areas. Considering the tailorabile optical and electronic structure of silver clusters and the diversity of organic ligands, we expect that there will be more work on regulating the catalytic ability of silver cluster-assembled materials.

4. Experimental Section

Synthesis of Ag9-AgTPyP: AgC≡CBr (0.020 g, 0.106 mmol) and CF3COOAg (0.022 g, 0.1 mmol) were dissolved in DMF (6 mL), and the solution was stirred for 5 min. Then, 1 mL of trichloromethane solution containing TPyP (0.01 g, 0.016 mmol) was added under stirring, and the solution was subsequently filtered. The filtrate was slowly evaporated in air to give dark-purple crystals of Ag9-AgsTPyP (34.55% yield based on TPyP).

−OH and methanol was used for 1O2, and DMPO (100 mg) was used for H2O2, and 5 m Na2S2O3 was used for 1O2, and DMPO (100 mg) was used for H2O2.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.
antibiotic-resistant bacteria, atomically precise silver cluster, charge transfer, photocatalyst, reactive oxygen species (ROS), silver cluster-porphyrin assembled materials