Photosensitizers

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Metallophthalocyanine-Based Conjugated Microporous Polymers as Highly Efficient Photosensitizers for Singlet Oxygen Generation**

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Abstract: *Singlet oxygen ($^1O_2$) is of great interest because of its potential applications in photodynamic therapy, photooxidation of toxic molecules, and photochemical synthesis. Herein, we report novel metallophthalocyanine (MPc) based conjugated microporous polymers (MPc-CMPs) as photosensitizers for the generation of $^1O_2$. The rigid microporous structure efficiently improves the exposure of the majority of the MPc units to oxygen. The MPc-CMPs also exhibit an enhanced light-harvesting capability in the far-red region through their extended π-conjugation systems. Their microporous structure and excellent absorption capability for long-wavelength photons result in the MPc-CMPs showing high efficiency for $^1O_2$ generation upon irradiation with 700 nm light, as evident by using 1,3-diphenylisobenzofuran as an $^1O_2$ trap. These results indicate that MPc-CMPs can be considered as promising photosensitizers for the generation of $^1O_2$.*

Singlet oxygen ($^1O_2$), a reactive oxygen species, is highly desired for use in photodynamic therapy (PDT) because of its high oxidative ability.[1] A photosensitizer is necessary to produce singlet oxygen because direct excitation from triplet molecular oxygen ($^3O_2$) to $^1O_2$ is forbidden.[2] The photosensitizer in the lowest excited singlet state (S1), produced by the absorption of light, is converted into the lowest excited triplet state (T1), and then $^1O_2$ is generated by energy transfer from the T1 state of the photosensitizer to $^3O_2$. A large number of photosensitizers have been investigated for the generation of singlet oxygen, such as fluorescein, rose bengal, and porphyrin.[2a] The porphyrin derivatives are the most widely used photosensitizers because of their high singlet oxygen quantum yield and light absorption capability, and have already been developed into commercial products for PDT, such as Photofrin,[3a] Visudyne,[3b] Foscan,[3c] and Laserphyrin.[3d] However, it is still a big challenge to produce ideal $^1O_2$ photosensitizers for PDT with much higher efficiency and light-capture capability in the long wavelength region.

Metallophthalocyanines (MPcs), which are macrocyclic molecules with a planar conjugated array of 18-π electrons, have been extensively explored as new generation photosensitizers as a result of their outstanding absorption capability in the long-wavelength visible region.[4] However, strong π–π stacking interactions arising from their large π-conjugated systems make MPcs prone to form aggregates, which limits their $^1O_2$ generation efficiency through insufficient contact with the oxygen molecules.

Over the past decade, interest in the field of microporous materials derived from organic precursors has grown tremendously because of their outstanding performance and broad applications.[5,6] In particular, conjugated microporous polymers (CMPs), a class of cross-linked porous polymers that combine porosity with π conjugation, have promising properties for applications in gas adsorption,[7] superabsorption,[8] catalysis,[9] light emission,[10] light harvesting,[11] sensing,[12] and energy storage.[13]

Herein, we report a series of novel CMPs (MPc-CMPs, M = Co, Ni, Cu, Zn) based on MPc units (Figure 1a). These

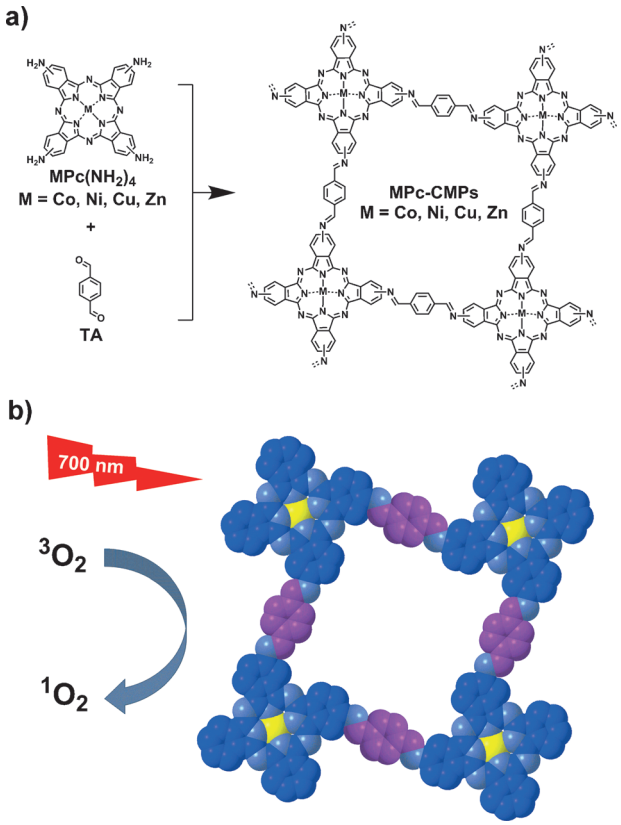

Figure 1. a) Synthesis of MPc-CMPs. b) Schematic description of the process that generates singlet oxygen.

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materials are microporous, and their rigid porous structures can efficiently prevent aggregation of the MPc units and thus increase the chances for contact with O_2. The extended π-conjugation systems in these materials enhance their light-harvesting capability even in the far-red region. In accord with our expectation, the MPc-CMPs exhibit high activities as photosensitizers for the generation of singlet oxygen (Figure 1b).

We designed and successfully synthesized the MPc-CMPs by Schiff base chemistry. Typically, a tetraaminometallophthalocyanine ($MPc(NH_2)_4$) was utilized in a polycondensation reaction with terephthalaldehyde (TA) under solvothermal conditions (*N*,*N*-dimethylacetamide (DMAc), 150 °C, 72 h) to form the four imine-linked MPc-CMPs (M = Co, Ni, Cu, Zn) as dark green powders, which were isolated in yields of 66–79 %. No changes were observed in these materials upon exposure of the insoluble powders to air, humidity, or organic solvents. Thermogravimetric analysis (TGA) of the MPc-CMPs showed high thermally stabilities with decomposition not occurring below 450 °C (see Figure S1 in the Supporting Information).

High conversion of the functional groups initially existing in the monomers was confirmed by Fourier transform infrared (FTIR) spectroscopic analysis of all four CMPs (see Figure S2 in the Supporting Information). The vibration bands centered at 2864 (C-H stretching) and 1692 cm^{-1} (C=O stretching) corresponding to the carbonyl moieties of the aldehydes are strongly attenuated in the spectra of all the MPc-CMPs. Peaks in the range 3200–3500 cm^{-1} can be attributed to the stretching of residual NH_2 groups, which is a general phenomenon in imine-linked porous polymers as a result of the existence of edge units after polymerization.[14] The C=N stretching vibration peak attributed to imine linkages appears around 1600 cm^{-1}, which is identical to the position of the NH_2 deformation peak. The solid-state ^{13}C CP/MAS NMR spectrum of ZnPc-CMP shows three signals at $\delta = 151$, 145, and 130 ppm, which can be assigned to carbon atoms of the phthalocyanine and phenyl groups (see Figure S3 in the Supporting Information). The elemental analysis results confirm the C, H, N, and M contents (M = Co, Ni, Cu, Zn), which are close to the theoretical values of the MPc-CMPs (see the Supporting Information).

Powder X-ray diffraction measurements (PXRD) reveal that the MPc-CMPs are amorphous, with no definite peaks evident (see Figure S4 in the Supporting Information). Although the reaction types and conditions are similar to those used for the preparation of crystalline imine-linked covalent organic frameworks (COFs), the MPc-CMPs exhibit no regular stacking structure because of the existence of less symmetric isomers in $MPc(NH_2)_4$. Irregular schistose morphologies were observed by field-emission scanning electron microscopy (FE-SEM) measurements (see Figure S5 in the Supporting Information). High-resolution transmission electron microscopy (HRTEM) reveals the presence of micropores that originated from the highly cross-linked molecular skeletons (see Figure S6 in the Supporting Information).

The porosity of the MPc-CMPs was investigated by nitrogen sorption isotherm measurements at 77 K. The sorption isotherms have type I and IV characters (Figure 2a),

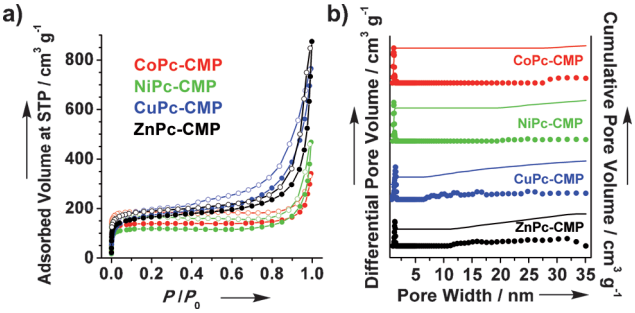

Figure 2. a) Nitrogen sorption isotherms measured at 77 K and b) pore size distribution profiles of MPc-CMPs calculated using the NLDFT method.

and show clear uptakes at low relative pressure ($P/P_0 = 0.1$), thus demonstrating the microporous characters of the materials. A slight sorption hysteresis can be observed over the whole range of relative pressure, which can be interpreted as the network swelling or the restricted access of adsorbate molecules through a narrow pore opening.[15] Moreover, the apparent rise at high relative pressure suggests their macroporosity as a result of the loose stacking of nanoparticles. The Brunauer–Emmett–Teller (BET) surface areas are evaluated to be 540, 510, 600, and 610 $m^2 g^{-1}$ for CoPc-CMP, NiPc-CMP, CuPc-CMP, and ZnPc-CMP, respectively (see Figure S7 in the Supporting Information). These values are comparable with other phthalocyanine-based porous organic polymers,[16] such as Pc-PBBA COF (PBBA = phenylenebis(boronic acid), 450 $m^2 g^{-1}$),[16a] NiPc-COF (624 $m^2 g^{-1}$),[16b] and CoPc20 network-PIM (PIM = polymer of intrinsic microporosity, 610 $m^2 g^{-1}$).[16g] The total pore volume is calculated to be 0.53–0.86 $cm^3 g^{-1}$ according to single point adsorption at $P/P_0 = 0.99$ (see Table S1 in the Supporting Information). The pore size distribution profiles based on the nonlocal density function theory (NLDFT) method reveal that the pore size of all these MPc-CMPs distributes around 1.2–1.5 nm, whereas small fluctuations can be observed in the mesoporous regions (Figure 2b). These results on the porosity suggest that MPc-CMPs are microporous materials.

The capability for light absorption was evaluated by spectroscopic measurements (Figure 3). For all the MPc-CMPs, although only a slight red-shift in the main peak of the Q-band occurs, their UV/Vis spectra become significantly broad in the long-wavelength region compared with their monomers. A narrowing of the band gap originating from their extended π-conjugation networks indicates their exceptional light-harvesting capability in the long-wavelength visible, even far-red, region.

MPc-CMPs are promising candidates for $^1O_2$ generation because of their excellent photon absorption capability and microporous structure (see Figure S8 in the Supporting Information). The photocatalytic properties of the MPc-CMPs to generate singlet oxygen upon irradiation at 700 nm with a xenon lamp was investigated by using 1,3-diphenylisobenzofuran (DPBF) as a trap and monitored by time-dependent electronic absorption spectroscopy.[17] As a control experiment, DPBF (50 μM) was irradiated in dimethylformamide (DMF) without MPc-CMPs. Only a negligible decrease

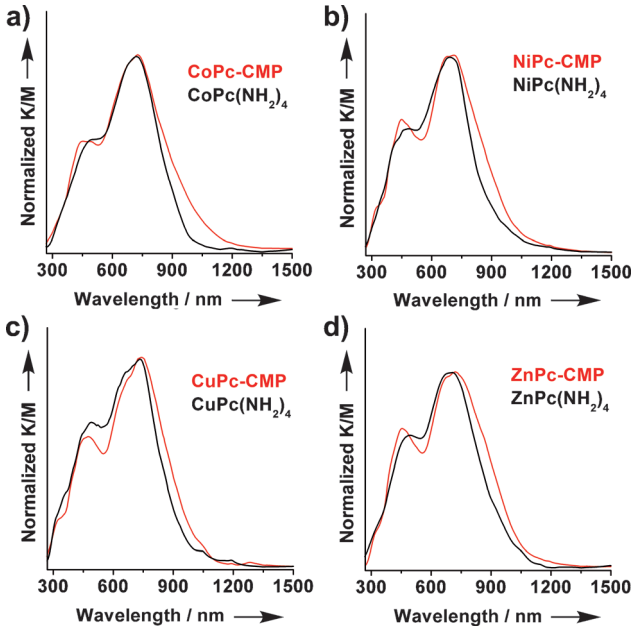

Figure 3. Absorption spectra of MPc-CMPs compared with their monomers. a) CoPc-CMPs and $CoPc(NH_2)_4$; b) NiPc-CMPs and $NiPc(NH_2)_4$; c) CuPc-CMPs and $CuPc(NH_2)_4$; d) ZnPc-CMPs and $ZnPc(NH_2)_4$. K/M is the Kubelka–Munk absorption.

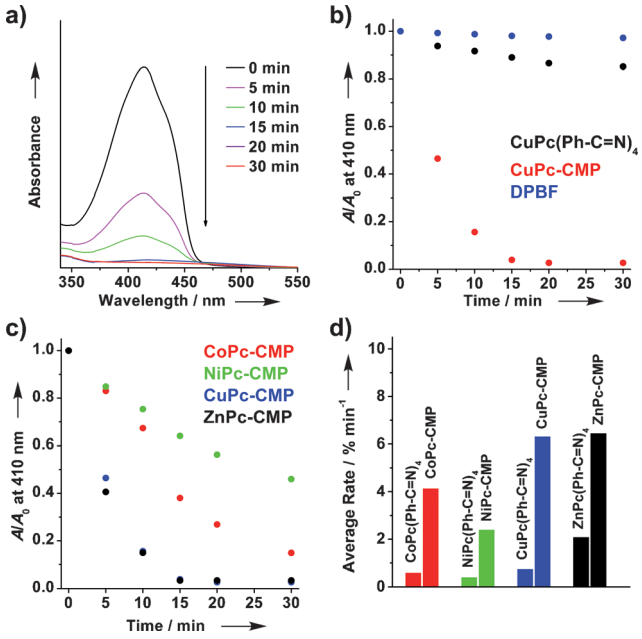

Figure 4. a) Time-dependent absorption spectra of DPBF (in DMF) upon irradiation at 700 nm in the presence of CuPc-CMP. b) Comparison of the decay rate of DPBF (blue) alone, and in the presence of CuPc-CMP (red) and $CuPc(Ph\text{-}C{=}N)_4$ (black), respectively. c) Comparison of the decay rate of DPBF in the presence of MPc-CMPs. d) Comparison of the average decay rate of DPBF in the presence of MPc-CMPs and $MPc(Ph\text{-}C{=}N)_4$ within 15 min.

in the absorbance of DPBF was found, which reveals that DPBF is stable under these experimental conditions (see Figure S9a in the Supporting Information). Irradiation of an oxygen-saturated solution of DPBF (50 μM) in DMF (2.5 mL) with light in the presence of CuPc-CMP (0.1 mg) causes a steady generation of singlet oxygen, as evident by the absorption band of DPBF at 410 nm decreasing upon oxidative degradation by $^1O_2$ (Figure 4a). In sharp contrast, the small molecule $CuPc(Ph\text{-}C{=}N)_4$ exhibits only small spectral changes as a result of its much lower activity under the same conditions (see Figure S9b in the Supporting Information). A time-dependent plot of the DPBF absorbance at 410 nm (Figure 4b) reveals that the DPBF is consumed rapidly and almost completely within 15 min in the presence of CuPc-CMP, whereas $CuPc(Ph\text{-}C{=}N)_4$ shows low photoactivity, with a conversion of less than 20% even after a long reaction period. The experiments in the presence of CoPc-CMP, NiPc-CMP, and ZnPc-CMP show the same tendencies (see Figure S9 in the Supporting Information). We also notice differences in the photocatalysis capability of these MPc-CMPs (Figure 4c,d). For example, high decay rates of DPBF upon irradiation with light are found in the presence of CuPc-CMP and ZnPc-CMP (the absorption band of DPBF at 410 nm completely disappeared within 15 min), whereas NiPc-CMP exhibits a lower reaction activity than the others (see Figure S10 in the Supporting Information). These phenomena indicate that the central metal species in the MPcs probably influence the triplet states that play important roles in triggering the activation of molecular oxygen.[4a,18] For example, phthalocyanines with metal ions having open-shell configurations show lower activities for the generation of $^1O_2$ because of the influences of the d electrons on their triplet states, whereas ZnPc-CMP shows a high capability to generate $^1O_2$ because of the d^{10} configuration of the central Zn^{2+} ion. Remarkably, the catalytic activities of the MPc-CMPs for the generation of singlet oxygen are nearly one order of magnitude higher than those of the reported organic porous materials, as well as requiring shorter reaction times and affording higher conversion.[17a] In addition, the excitation of the MPc-CMPs using long-wavelength photons (700 nm) for the generation of $^1O_2$ is another advantage over other porous materials that need high-energy light (400–500 nm) to irradiate their porphyrin photosensitizer units.[17]

In summary, we have designed and synthesized novel CMPs with excellent chemical and thermal stabilities by Schiff base chemistry using MPcs as building blocks. Their microporous nature and remarkable light-harvesting capability for long-wavelength photons even in the far-red region result in MPc-CMPs, especially ZnPc-CMP and CuPc-CMP, showing remarkable efficiency for the generation of $^1O_2$ and displaying apparent superiority over other reported organic porous materials by using lower energy excitation light. These results reveal that MPc-CMPs are promising candidates as photosensitizers to generate $^1O_2$, and further extend the research perspectives of CMPs in novel application fields such as photodynamic therapy.

Keywords: energy transfer · metallophthalocyanines · photosensitizers · polymers · singlet oxygen

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