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Synthesis and catalytic performance of a soluble asymmetric zinc phthalocyanine

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The soluble asymmetric phthalocyanine (ZnPc-OH) was synthesized and used as a photosensitizer to degrade water pollutants. The catalytic ability of zinc phthalocyanine was proved by degrading Rhodamine B (RhB). In addition, ZnPc-OH, which has good solubility, can also be used in photodynamic therapy.

Keywords: Zinc phthalocyanine; Photosensitizer; Soluble; Asymmetric; Catalytic

Graphical abstract



1. Introduction

Photosensitizers (PS), which were used in fields such as photodynamic therapy (PDT) [1-4] and catalysis [5, 6], have attracted much attention. Metal complexes can be applied in many fields

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because of their special properties [7-16]. Metal porphyrin and metal phthalocyanine derivatives are the major types of photosensitizers. Phthalocyanine (Pc) is best as second generation of photosensitizers which has been applied as nonlinear optical [17], sensor [18], PDT [19-23] and catalytic [24-27]. However, the solubility of Pc limits its applications [28].

We are making efforts to develop new Pc derivatives to solve its solubility problem. In order to solve the solubility purification problem, we modified the precursor of Pc by increasing its carbon chain. In the design of the Pc structure, we considered the derivatives using a structure that only left a single reaction site. The introduction of terminal hydroxyl groups led to increase of polarity of molecule, thus increasing its solubility in water. This asymmetrical structure of Pc has rarely been reported in comparison with symmetric ones. This study describes the preparation of a soluble asymmetric Pc and studies its ability to degrade RhB.

2. Experimental

2.1. Materials and instrumentation

Dimethyl formamide (DMF) and dichloromethane (DCM) were dried over calcium hydride before use. THF was refluxed with sodium chips under N₂ before use. All other chemical reagents were analytic grade and used without purification. ¹H NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer using DMSO- d_6 as solvent at ambient temperature. FT-NIR measurements were performed as KBr pellets on a Shimadzu-8400S IR spectrometer. UV-Vis spectra of the samples were recorded over different irradiation time intervals using a Thermo Scientific Evolution 220 spectrophotometer.

2.2. Synthesis of 4-decyloxy phthalonitrile

4-Hydroxyphthalonitrile (1.15 g, 8.0 mmol), 1-bromodecane (1.94 g, 8.8 mmol) and K₂CO₃ (4.14 g, 30 mmol) were added to a flask charged with DMF (20 mL) under nitrogen, and the mixture was stirred at 90 °C for 3 h. After cooling to room temperature, the product was resolved in DCM and washed by H₂O, drying over anhydrous MgSO₄. After DCM was removed by rotary evaporation, the crude product was purified by column chromatography SiO₂. The product was 1.59 g. Yield: 70.0%. Anal. Calcd. for C₁₈H2₄N₂O (Mr = 284.4): C, 76.02; H, 8.51; N, 9.85. Found: C, 76.50; H, 8.17; N, 9.89. FT-NIR (KBr, cm⁻¹): 2230 (vC=N), 1600, 1460 (vAr-C-C-). ¹H NMR (500 MHz, DMSO-*d*₆), δ ppm: 8.04 (d, *J* = 8.8 Hz, 1H,

Ar-*H*), 7.76 (d, J = 2.6 Hz, 1H, Ar-*H*), 7.45 (dd, J = 8.8 Hz, J = 2.6 Hz, 1H, Ar-*H*), 4.13 (t, J = 6.6 Hz, 2H, -OCH₂-), 1.72 (p, J = 7.0 Hz, 2H, -CH₂-), 1.32 (m, 14H, -CH₂-), 0.85 (t, J = 6.9 Hz, 3H, -CH₃) (figure S1). ¹³C NMR (125 MHz, DMSO-d₆): 162.62, 135.56, 119.91, 119.71, 117.76, 116.16, 115.72, 107.31, 69.71, 32.25, 29.87, 29.67, 29.61, 29.11, 26.18, 23.05, 14.50.

2.3. Synthesis of 4-[2-(2-bromoethoxy-pyran)] phthalonitrile

2-(2-Bromoethoxy)-pyran was synthetized according to the literature [29]. A mixture of 2-(2-bromoethoxy)-pyran (2.0 g, 9.6 mmol), 4-hydroxyphthalonitrile (1.325 g, 9.2 mmol) and K₂CO₃ (4.14 g, 30.0 mmol) in DMF (50 mL) was stirred at 60 °C for 8 h. Then the product was cooled to room temperature adding DCM (50 mL) and washed by water. After removing DCM, the product was purified by chromatography, finally getting 0.8 g white solid. Yield: 30.0%. FT-NIR (KBr, cm⁻¹): 2224 (vC=N), 1600, 1560, 1460 (vAr-C-C), 1260, 1120 (vC-O-C). ¹H NMR (500 MHz, DMSO-*d*₆), δ ppm: 8.05 (d, *J* = 8.8 Hz, 1H, Ar-*H*), 7.82 (d, *J* = 8.8 Hz, 1H, Ar-*H*), 7.50 (dd, *J* = 8.9 Hz, *J* = 2.7 Hz, 1H, Ar-*H*), 4.65 (t, *J* = 3.5 Hz, 1H, -C*H*-), 4.33 (m, 2H, -C*H*₂-), 3.93, 3.45 (m, 2H, -C*H*₂-), 3.75 (m, 2H, -C*H*₂-), 1.46-1.65 (m, 6H, -C*H*₂-) (figure S2).

2.4. Synthesis of 3-ethoxyhydroxy-9(10),16(17),23(24)-tris decyloxy phthalocyanine zinc(II) (ZnPc-OH)

4-Decyloxy phthalonitrile (568 mg, 2.0 mmol) and 4-[2-(2-bromoethoxy-pyran)] phthalonitrile (182 mg, 0.67 mmol) in the presence of $Zn(CH_3CO_2)_2$ (240 mg, 1.10 mmol), 1-pentanol (10 mL) and 0.75 mL DBU were refluxed for 48 h under nitrogen. Methanol (50 mL) was added after the reaction completed. The residue was treated with p-toluenesulfonic acid (0.30 g, 1.70 mmol) in a mixture of methanol and dichloromethane (10 mL, 1:2 v/v) to remove the tetrahydropyran protecting group. The solvent was removed by rotary evaporation and the residue was washed with methanol. The crude product was purified, getting asymmetrical phthalocyanine 72.41 mg. Yield: 10%. Anal. Calcd. for $C_{64}H_{80}N_8O_5Zn$ (%): C, 69.45; H, 7.29; N, 10.12. Found: C, 69.30; H, 7.32; N, 10.24. HRMS (m/z): calcd for $C_{64}H_{80}N_8O_5Zn$: 1104.55; Found: 1104.50 [M + H]+. FT-NIR (KBr, cm⁻¹): 3404 (vOH), 2953 (vCH₃), 2853 (vCH₂), 1605 (vC=C), 1341 (vC-N). ¹H NMR (500 MHz,

DMSO-*d*₆), δ ppm: 9.06 (4H, Ar-*H*), 8.68 (4H, Ar-*H*), 7.69 (4H, Ar-*H*), 5.19 (1H, -O*H*), 4.27 (10H, -OC*H*₂-), 1.31-2.04 (48H, -C*H*₂-), 0.91 (9H, -CH₃).

3. Results and discussion

3.1. Preparation and characterization

The soluble asymmetric phthalocyanine (ZnPc-OH) (figure 1) was prepared by separating the synthesized products of 4-decyloxy phthalonitrile and 4-[2-(2-bromoethoxy-pyran)] phthalonitrile by column chromatography. As shown in figure 2, 4-decyloxy phthalonitrile was synthesized from reaction of 4-hydroxyphthalonitrile and 1-bromodecane in DMF with K₂CO₃ at 90 °C under a nitrogen atmosphere for 6 h. The crude product was purified by column chromatography. The ¹H NMR spectrum of 4-decyloxy phthalonitrile is shown in figure S1. Proton peaks at 8.04 ppm, 7.76 ppm and 7.45 ppm were assigned to the phenyl protons, and 4.13 ppm, 1.72 ppm, 1.32 ppm corresponded to the peaks of methylene groups at different positions. The methyl peak was at 0.85 ppm. The result above proved that the 4-decyloxy phthalonitrile was synthesized. 2-(2-Bromoethoxy)-pyran was synthetized according to the literature [29] and then transformed to 4-[2-(2-bromoethoxy-pyran)] phthalonitrile by reacting with 4-hydroxyphthalonitrile in the presence of K_2CO_3 with DMF as solvent at room temperature for 9 h. The ¹H NMR spectrum of 4-[2-(2-bromoethoxy-pyran)] phthalonitrile is shown in figure S2. The peaks of phenyl protons were at 8.05 ppm, 7.82 ppm and 7.50 ppm. The peaks of methylene groups at different positions were clearly identified in the ¹H NMR spectrum, indicating that 4-[2-(2-bromoethoxy-pyran)] phthalonitrile was synthesized.

To synthesize ZnPC-OH we used statistical methods; 4-[2-(2-bromoethoxy-pyran)] phthalonitrile and 4-decyloxy phthalonitrile were fed at a ratio of 1:3 with DBU as a catalyst in 1-pentanol solution with $Zn(CH_3CO_2)_2$ under N₂ at 150 °C for 48 h. After that the protecting group was removed and the crude product separated and purified. The ¹H NMR spectrum of ZnPc-OH is shown in figure 3 and the IR spectra of ZnPc-OH and precursor are shown in figure 4. As shown in figure 3, the proton peaks at 9.06 ppm, 8.68 ppm and 7.69 ppm were assigned to phthalocyanine ring protons. The peak at 0.91 ppm was assigned to the protons of methyl group. It can be clearly seen that the band at 2230 cm⁻¹ (vC=N) disappeared and the other peaks were consistent with the precursors from figure 4c. The results indicated that ZnPc-OH

was synthesized. The Q band of ZnPc-OH was at 685 nm (figure 5). All the results proved that we synthesized the soluble asymmetric phthalocyanine.

3.2. Degradation of Rhodamine B

RhB threatens health as an organic dye contaminant that is carcinogenic to humans. Recently, degradation of RhB has received attention [30-33]. RhB has a characteristic absorption at 554 nm and is often chosen as a representative hazardous organic dye to research the photocatalytic activity of catalysts under visible light [34]. The degradation ability of photosensitizers could be reflected by the degradation of RhB. H_2O_2 is usually used to enhance organic pollutant degradation in photocatalytic reaction. In order to determine the effects of H_2O_2 , we test the photocatalytic efficiency of blank (only RhB), H_2O_2 , ZnPc-OH and ZnPc-OH/ H_2O_2 , respectively. If only ZnPc-OH or H_2O_2 is added into the system, the photocatalytic efficiency of RhB under visible light irradiation for 180 min reaches 45% and 69%, respectively (figure 6). However, it is clear from figure 7 that 85% of RhB was degraded during 180 min with ZnPc-OH/ H_2O_2 , indicating that ZnPC-OH/ H_2O_2 has ability for degradation.

The mechanism of H_2O_2 decomposition was proposed according to references [35, 36]. H_2O_2 decomposition produces hydroxyl radicals (HO•). The Pc could turn oxygen into singlet oxygen (1O_2) [37] and superoxide radical anions ($^{\bullet}O_2$) [22] under light. It has been widely acknowledged that $^{\bullet}O_2$ and $^{\bullet}OH$ are the major factors for photocatalytic oxidation [30]. According to the literature [38], the schematic diagram of the mechanism for RhB degradation is shown in figure 8.

4. Conclusion

Modification of the precursor was used to improve the solubility of phthalocyanine. A soluble asymmetric phthalocyanine was synthesized by statistical methods and verified to have good solubility in DMF and dichloromethane. The degradation of RhB showed that ZnPc-OH could be used in catalysis and has good degradation. The solubility of ZnPc-OH makes it easy to modify to use in PDT and catalysis. The ZnPc-OH is a potential photosensitizer.

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Figure 1. Chemical structure of soluble asymmetric phthalocyanine (ZnPc-OH).

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Figure 2. The synthesis of soluble asymmetric phthalocyanine (ZnPc-OH).

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Figure 3. ¹H NMR spectrum of ZnPc-OH in DMSO- d_6 at room temperature.

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Figure 4. IR spectrum of 4-decyloxy phthalonitrile (a), 4-[2-(2-bromoethoxy-pyran)] phthalonitrile (b) and ZnPc-OH (c).

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Figure 6. The UV-vis absorbance spectra changes of RhB upon visible light irradiation: (a) only RhB, (b) ZnPc-OH, (c) H_2O_2 .





Figure 7. (a) Comparison of the decay rate of RhB (black) alone and in the presence of H_2O_2 (red), ZnPc-OH (blue) and ZnPc-OH/ H_2O_2 (green) under visible light irradiation in water at room temperature. (b) The UV-vis absorbance spectra of RhB upon visible light irradiation in the presence of ZnPc-OH/ H_2O_2 in water at room temperature.

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Figure 8. The mechanism for degradation of RhB in the presence of radicals.