

Efficient and Recyclable Phthalocyanine-Based Sensitizers for Photooxygenation Reactions

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Abstract: Treatment of 4,5-bis(4-methoxycarbonylphenoxy)phthalonitrile with $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and 1,8-diazabicyclo[5.4.0]undec-7-ene in octan-1-ol or dodecan-1-ol led to base-promoted cyclotetramerization. Under these conditions, transesterification also occurred to give the corresponding zinc(II) octakis(4-alkoxycarbonylphenoxy)phthalocyanines. These two macrocycles, together with another two pegylated silicon(IV) phthalocyanines, were found to be highly efficient sensitizers for the photooxygenation of a series of alkenes and 1-naphthol. In general, the zinc(II) analogues exhibit a higher photostability and can be recycled at least four times without a significant loss of activity.

Key words: phthalocyanines, sensitizers, photooxygenation reactions, singlet oxygen

Singlet oxygen is the lowest excited electronic state of molecular oxygen. It is a highly reactive species, which has great environmental and biomedical significance.² It is also a highly versatile oxidant for a variety of organic transformations including the ene reactions, [4+2] cycloaddition reactions, and oxidation of electron-rich aromatic compounds.^{3a-c} Some of these reactions have been employed as key steps in synthesis of some important natural products and pharmaceuticals.^{3d-f} This short-lived species can be generated through heterolytic disproportionation of hydrogen peroxide catalyzed by molybdate⁴ and lanthanide salts.⁵ Another common approach involves dye-sensitized photoexcitation of ground-state triplet oxygen using sensitizers such as methylene blue,⁶ rose bengal,^{3d,e,7} porphyrins,^{6a,f,8} *seco*-porphyrazines,⁹ squaraines,¹⁰ and fullerenes.¹¹ To facilitate the recovery of photosensitizers, various approaches have been employed which include conjugation with polymers,^{8c,f,9b,11a} immobilization on solid supports,^{11c,d,12} and the use of perfluorinated photosensitizers.^{8a,e}

Phthalocyanines represent an important class of functional dyes which have found a wide range of applications.¹³ Although it has been well documented that, upon interaction with molecular oxygen, these macrocyclic compounds can generate reactive oxygen species leading to a number of biomedical¹⁴ and environmental applications,¹⁵ catalytic application of these compounds in organic synthesis has been little studied. Only a few types of reactions

employing phthalocyanines as catalysts have been sporadically reported. Some examples include the oxidation of thiols to disulfides,¹⁶ oxidation of alkanes to alcohols,¹⁷ epoxidation of alkenes,¹⁸ hydroxylation of benzene,¹⁹ oxidation of alkynes to α,β -acetylenic ketones,²⁰ oxidative C–P bond formation,²¹ and Diels–Alder reactions.²²

Over the past few years, we have been exploring phthalocyanine-based photosensitizers for photodynamic therapy (PDT).²³ Some of these macrocycles are highly efficient singlet-oxygen generators which should also function well as sensitizers for photooxygenation reactions. We report herein the synthesis of several specially designed phthalocyanines and the first use of these compounds as efficient and recyclable photosensitizers for oxidation of a series of alkenes and 1-naphthol.

Zinc(II) phthalocyanines **2** and **3** were first prepared by cyclotetramerization of phthalonitrile **1** in the presence of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in octan-1-ol or dodecan-1-ol (Scheme 1). Under these conditions, the methoxycarbonyl groups underwent in situ transesterification with the alcohols to give the corresponding alkoxycarbonylphthalocyanines. This one-pot cyclization–transesterification procedure was reported by us previously,²⁴ and is a facile route to preparing various ester-containing phthalocyanines. Zinc(II) ion was selected as the metal center because of the general robustness and the desirable photophysical properties of these metallophthalocyanines.²⁵ The long alkyl chains were introduced to facilitate the recovery of these compounds by precipitation after photooxygenation. Both compounds could be purified readily by column chromatography and characterized with various spectroscopic methods.

In addition to these two compounds, we also selected two additional silicon(IV) phthalocyanines **4** and **5** to evaluate their photocatalytic activities (Figure 1). Both compounds were prepared by us previously and used as efficient photosensitizers for PDT.²⁶ The two long polyethylene glycol chains (each with an average molecular weight of 550 or 750) in these compounds again should facilitate the recovery process, while the eight chloro groups in **5** are expected to enhance the intersystem crossing by the heavy atom effect, thereby promoting the formation of singlet oxygen.^{26,27}

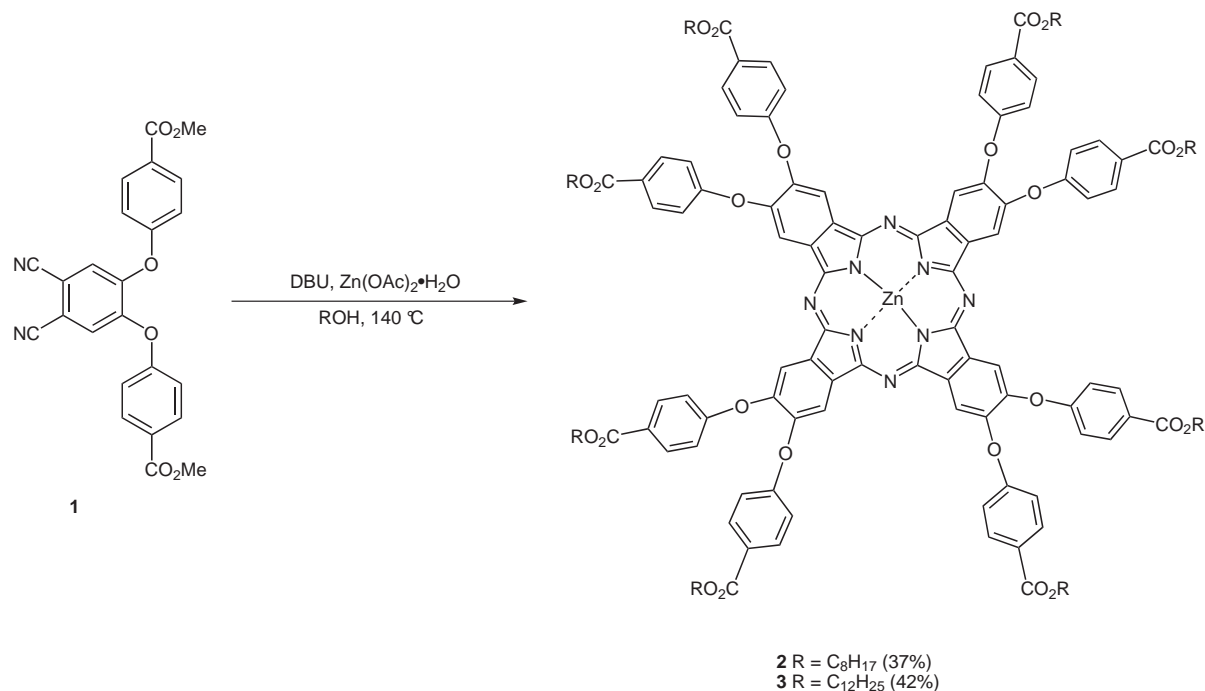
To find out the optimized conditions for the photooxygenation reactions, photooxygenation of 2-furoic acid (**6**)²⁸ using phthalocyanine **5** (0.1–0.3 mol%) as the sensitizer

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Scheme 1

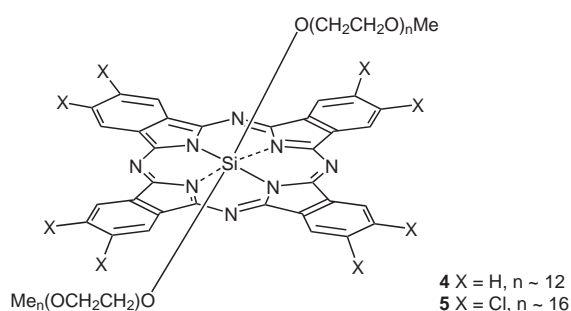
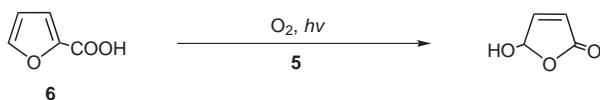


Figure 1

was first examined at 0 °C (Scheme 2). The solvent effect was investigated using a series of solvents and the results are summarized in Table 1. Here, the conversion is defined as the percentage of starting material consumed, and the yield is referred to as the percentage of product actually obtained based on the consumed starting material. As shown in this table, chloroform is the most preferable solvent, which leads to 92% conversion with a quantitative yield (entry 1). Although a quantitative yield was also obtained by using tetrahydrofuran, benzene, or dichloromethane as solvent, the relatively low conversion was a general problem (entries 4–6). When methanol was used as the reaction medium, no product could be detected by ¹H NMR spectroscopy (entry 7).



Scheme 2

Table 1 Solvent Effect for Photooxygenation of 2-Furoic Acid (**6**) with Phthalocyanine **5** as the Sensitizer^a

Entry	Solvent	Conv (%)	Yield (%)
1	CHCl ₃	92	100
2	acetone	25	93
3	MeCN	39	84
4	THF	80	99
5	benzene	32	100
6	CH ₂ Cl ₂	65	100
7 ^b	MeOH	–	–

^aThe mixtures (with 0.1–0.3 mol% of **5**) were irradiated with a 500 W halogen lamp equipped with a color glass filter (cut-on 610 nm) for 40 min at 0 °C. The reported yields and conversions were determined by ¹H NMR spectroscopy using 2,5-dimethylfuran as an internal standard.

^bThe expected product could not be detected by ¹H NMR spectroscopy.

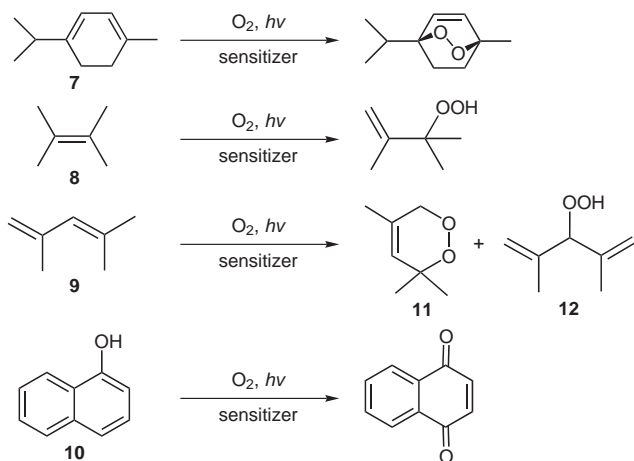
The same reaction was also performed at different temperatures to study the temperature effect, using chloroform as the reaction medium as it gave the best result as demonstrated above. The results are listed in Table 2. It can be seen that both the conversion and yield are not changed significantly with temperature in the range from 0 °C to 25 °C. It indicates that temperature does not have a significant effect on this photooxygenation reaction. As a result, all the subsequent studies were carried out at 0 °C, which could be attained readily by simply immersing the reaction tube in an ice-bath, even upon illumination with a high-power halogen lamp.

Table 2 Temperature Effect for Photooxygenation of 2-Furoic Acid (**6**) with Phthalocyanine **5** as the Sensitizer^a

Entry	Temp (°C)	Conv (%)	Yield (%)
1	0	67	85
2	10	77	88
3	15	75	93
4	20	72	84
5	25	77	94

^aThe mixtures (in CHCl₃ with 0.1–0.3 mol% of **5**) were irradiated with a 500 W halogen lamp equipped with a color glass filter (cut-on 610 nm) for 30 min. The reported yields and conversions were determined by ¹H NMR spectroscopy using 2,5-dimethylfuran as an internal standard.

Apart from the substrate **6**, the photooxygenation reactions of alkenes **7–9** as well as 1-naphthol (**10**) were also studied (Scheme 3). These are representative types of reactions for singlet oxygen, namely the [4+2] cycloaddition reaction, the ene reaction, and the oxidation of phenols. All of the reactions gave the expected products. Under the conditions chosen, photooxygenation of 2,4-dimethylpenta-1,3-diene (**9**) gave a mixture of the endoperoxide **11** (the cycloaddition product) and the allylic hydroperoxide **12** (the ene reaction product).²⁹

**Scheme 3**

The photooxygenation reactions of these substrates (**6–10**) were performed in a mixed-solvent system (chloroform–methanol, 9:1) at 0 °C using the zinc(II) phthalocyanines **2** and **3** as well as the pegylated silicon(IV) phthalocyanines **4** and **5** as the photosensitizers. The course of the reaction was monitored by thin-layer chromatography. As shown in Table 3, all of the substrates could be smoothly converted into the corresponding oxidation products in high yields. For the oxidation of 2-furoic acid (**6**), the reaction was relatively slow under illumination with a 250 W halogen lamp. The color glass filter was therefore removed to increase the light intensity and accelerate the reaction. Photooxygenation of diene **9**

gave the endoperoxide **11** as the major product as found for other photosensitizing systems.²⁹ For the oxidation of 1-naphthol (**10**), the silicon(IV) phthalocyanines **4** and **5** were less effective than the zinc(II) analogues **2** and **3**, giving a significantly lower conversion (ca. 50% vs. > 84%). Owing to the absence of distinct ¹H NMR signals for the oxidation product, the percentage yield and conversion were calculated based on the isolated product and starting material recovered. In general, all of these phthalocyanines are highly efficient sensitizers for these photooxygenation reactions. The photocatalytic activities are comparable with those of *seco*-porphyrazines⁹ and fullerenes.^{11a,d}

Table 3 Photooxygenation of **6–10** Sensitized by Phthalocyanines **2–5**^a

Sensitizer	Substrate	Time (min)	Conv (%)	Yield (%)
2	6 ^b	120	98	97
	7	40	100	97
	8	80	90	96
	9	30	100	92 (for 11) 8 (for 12)
	10 ^c	100	84	93
3	6 ^b	120	100	97
	7	40	100	97
	8	80	92	96
	9	35	100	91 (for 11) 9 (for 12)
	10 ^c	100	93	93
4	6 ^b	120	99	98
	7	45	100	95
	8	60	100	93
	9	25	100	92 (for 11) 8 (for 12)
	10 ^c	100	50	93
5	6 ^b	120	98	96
	7	45	100	94
	8	80	93	98
	9	25	100	92 (for 11) 8 (for 12)
	10 ^c	100	45	93

^aThe mixtures [(in CHCl₃–MeOH, 9:1) with 0.1–0.3 mol% of the sensitizers] were irradiated with a 250 W halogen lamp equipped with a color glass filter (cut-on 610 nm) at 0 °C, and the reported yields and conversions were determined by ¹H NMR spectroscopy using 2,5-dimethylfuran as an internal standard unless otherwise stated.

^bThe filter was removed to accelerate the reaction.

^cIsolated yields and conversions.

The recyclability of these photosensitizers in the photooxygenation of 2-furoic acid (**6**) and α -terpinene (**7**) was also investigated. Due to the presence of long alkyl chains and the eight chloro groups (for **5**), phthalocyanines **2**, **3** and **5** could be recovered readily by precipitation upon addition of methanol. The resulting solid was collected by filtration and then used again in another run of photooxygenation reactions. Compound **4**, however, could not be recovered by this simple method. The results for this study are collected in Table 4. For all the reactions, the percentage conversion was very close to unity. When α -terpinene (**7**) was used as the substrate, all of the three photosensitizers could be recycled four times without significantly lowering the reaction yields. However, for the reaction sensitized by **5**, a slightly longer reaction time was required for subsequent runs (from 45 to 60 minutes), showing that there was a loss of the sensitizer after recovery. For the photooxygenation of 2-furoic acid (**6**), which required a longer reaction time, the silicon(IV) phthalocyanine **5** could only be repeatedly used twice. In the third run, no complete conversion was obtained due to the severe photobleaching of **5**. In contrast, photosensitizers **2** and **3** could be successfully reused at least four times under the same conditions without a significant loss of their photocatalytic activity. In fact, as shown by absorption spectroscopy, less than 10% of **2** and **3** was degraded after the fourth cycle of these reactions, while for **5**, about 90% and 40% of material was lost after the second (for **6**) and fourth cycle (for **7**), respectively. These results indicated that zinc(II) phthalocyanines **2** and **3** have a higher photostability than the silicon(IV) analogue **5**, and therefore serve as better sensitizers for these photooxygenation reactions.

Table 4 Recycling of Sensitizers **2**, **3**, and **5** in Photooxygenation of **6** and **7**^a

Substrate	Sensitizer	Time (min)	Cycle, yield (%)			
			1	2	3	4
6	2	120	96	95	95	93
	3	110	93	92	92	91
	5	120	96	93	–	–
7	2	40	97	95	95	93
	3	25	97	97	95	94
	5	45–60 ^b	96	94	94	92

^a The mixtures [(in CHCl₃–MeOH, 9:1) with 0.1–0.3 mol% of the sensitizers] were irradiated with a 250 W halogen lamp equipped with a color glass filter (cut-on 610 nm) at 0 °C. The reported yields and conversions were determined by ¹H NMR spectroscopy using 2,5-dimethylfuran as an internal standard.

^b The reaction time increased from 45 to 60 min during the recycling experiments.

In summary, two zinc(II) phthalocyanines (**2** and **3**) have been prepared by a facile cyclization–transesterification procedure. These compounds together with the pegylated silicon(IV) analogues **4** and **5** are highly efficient sensitizers for photooxygenation of various alkenes and 1-naphthol. Some of these phthalocyanines can also be recovered

simply by precipitation and reused without a significant loss of activity. The zinc(II) analogues **2** and **3** are particularly attractive for this practical application due to their relatively high photostability, recyclability, and sensitizing activity.

n-Octanol and *n*-dodecanol were distilled from sodium. Chromatographic purifications were performed on silica gel columns (Macherey–Nagel, 230–400 mesh) with the indicated eluents. Hexane used in chromatography was distilled from anhyd CaCl₂. α -Terpinene (**7**) (from Aldrich) was purified by vacuum distillation. 1-Naphthol (**10**) (from BDH) was purified by recrystallization from benzene. All other reagents and solvents were of reagent grade and used as received. Compounds **1**,³⁰ **4**,²⁶ and **5**²⁶ were prepared as described. ¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker DPX 300 spectrometer (¹H, 300; ¹³C, 75.4 MHz). Chemical shifts were relative to internal TMS ($\delta = 0$ ppm). MALDI-TOF mass spectra were obtained on a Bruker Bench TOF mass spectrometer equipped with a standard UV-laser desorption source, using α -cyano-4-hydroxycinnamic acid as a matrix. UV/Vis spectra were taken with a Cary 5G UV/Vis/NIR spectrophotometer. Elemental analysis was performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

[2,3,9,10,16,17,23,24-Octakis(4-octoxycarbonylphenoxy)phthalocyaninato]zinc(II) (2)

A mixture of 4,5-bis(4-methoxycarbonylphenoxy)phthalonitrile (**1**) (200 mg, 0.47 mmol) and Zn(OAc)₂·2H₂O (36 mg, 0.16 mmol) in octan-1-ol (4 mL) was heated with stirring to 100 °C. DBU (10 drops) was then added and the resulting mixture was stirred at 140 °C overnight under N₂. The solvent was removed in vacuo, then the deep green residue was purified by column chromatography (EtOAc–hexane, 1:3). The green band was collected and rotary evaporated to give a deep green oily solid (111 mg; 37%).

$R_f = 0.74$ (EtOAc–hexane, 1:3).

¹H NMR (CDCl₃–DMSO-*d*₆, 7:1): $\delta = 8.73$ (br s, 8 H, Pc-H_a), 7.99 (d, $J = 7.8$ Hz, 16 H, ArH), 7.20 (d, $J = 7.8$ Hz, 16 H, ArH), 4.28 (t, $J = 7.5$ Hz, 16 H, CO₂CH₂), 1.72–1.81 (m, 16 H, CH₂), 1.24–1.48 (m, 80 H, CH₂), 0.86 (t, $J = 7.5$ Hz, 24 H, Me).

¹³C{¹H} NMR (CDCl₃): $\delta = 166.4, 161.5, 153.4, 149.3, 136.3, 131.8, 125.4, 117.0, 65.6, 32.3, 29.8, 29.7, 29.1, 26.5, 23.2, 14.7$.

MS (MALDI-TOF): $m/z = 2561.2$ [M⁺].

UV/Vis (THF): λ_{\max} (log ϵ) = 357 (5.07), 608 (4.69), 647 (4.66), 673 nm (5.49).

Anal. Calcd for C₁₅₂H₁₇₆N₈O₂₄Zn: C, 71.19; H, 6.92; N, 4.37. Found: C, 70.27; H, 6.78; N, 3.82.

[2,3,9,10,16,17,23,24-Octakis(4-dodecoxycarbonylphenoxy)phthalocyaninato]zinc(II) (3)

By using the above procedure, a mixture of 4,5-bis(4-methoxycarbonylphenoxy)phthalonitrile (**1**) (200 mg, 0.47 mmol) and Zn(OAc)₂·2H₂O (36 mg, 0.16 mmol) was treated with DBU (10 drops) in dodecan-1-ol (4 mL) to yield a deep green sticky solid (148 mg; 42%).

$R_f = 0.60$ (EtOAc–hexane, 1:3).

¹H NMR (CDCl₃–DMSO-*d*₆, 7:1): $\delta = 8.81$ (br s, 8 H, Pc-H_a), 8.01 (br s, 16 H, ArH), 7.21 (br s, 16 H, ArH), 4.29 (br s, 16 H, CO₂CH₂), 1.77 (br s, 16 H, CH₂), 1.26 (br s, 144 H, CH₂), 0.86 (br s, 24 H, Me).

¹³C{¹H} NMR (CDCl₃): $\delta = 166.4, 161.8, 153.3, 149.2, 136.3, 132.1, 125.7, 117.1, 65.7, 32.5, 30.2, 29.9, 29.3, 26.6, 23.2, 14.7$ (some of the CH₂ signals are overlapped).

MS (MALDI-TOF): $m/z = 3009.7$ [M⁺].

UV/Vis (THF): λ_{\max} (log ϵ) = 357 (4.98), 608 (4.59), 645 (4.54), 674 nm (5.40).

Photooxygenation Reactions: General Procedure

All of the reactions were carried out in a test tube with an oxygen-inlet apparatus at 0 °C. The concentration of all the substrates was fixed at 0.1 M with 0.1–0.3 mol% of the sensitizers. A mixture (CHCl₃–MeOH, 9:1) was used as the solvent unless otherwise stated. The mixtures were stirred with the bubbling of oxygen and were irradiated with a halogen lamp (250 W or 500 W) placed at ca. 10 cm from the reactor. A glass filter was used to cut off the light ($\lambda < 610$ nm) unless otherwise stated. The reactions were monitored by TLC. The isolated yields and conversions were based on the starting material and product isolated by column chromatography. The NMR yields and conversions were determined with reference to the signals of the products^{28,29,31} using 2,5-dimethylfuran as an internal standard.

Recycling of Sensitizers: General Procedure

To a solution of **6** (60 mg, 0.54 mmol) or **7** (0.11 mL, 0.68 mmol) in CHCl₃–MeOH (9:1) was added the sensitizer **2**, **3**, or **5** (0.1–0.3 mol%). The concentration of the substrate was fixed at 0.1 M. The reaction was monitored by TLC. After all the starting material had been consumed, an appropriate amount of MeOH was added to induce precipitation of the sensitizer. The recovered sensitizer was collected by filtration and used in another run of photooxygenation.

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