



# Preparation and photoactivity of a novel water-soluble, polymerizable zinc phthalocyanine

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## ABSTRACT

A novel water-soluble and polymerizable photosensitizer, zinc tetra(*N*-carbonylacrylic)aminophthalocyanine (Zn-MPc), was synthesized by the ornament of zinc tetraaminophthalocyanine (Zn-APc) with maleic anhydride and characterized by <sup>1</sup>H NMR, FT-IR, and MALDI-TOF mass spectra. The photoactivity of Zn-MPc was determined by tracking the degradation of 1,3-diphenylisobenzofuran (DPBF). The results indicated that Zn-MPc is an efficient photosensitizer and has a high photostability. The apparent rate constant, *k<sub>a</sub>*, of DPBF photodegradation increased with the increase of the Zn-MPc concentration or light intensity, but declined with the increase of the initial concentration of DPBF. Furthermore, the kinetics equation was deduced as  $R_d = 1.12 \times 10^{-5} [DPBF]^{0.51} [Zn-MPc]^{0.54} E^{1.35}$ . The results in this work provide a basis for the further development of more desirable photosensitizers and their applications in photodynamic therapy (PDT) of cancer.

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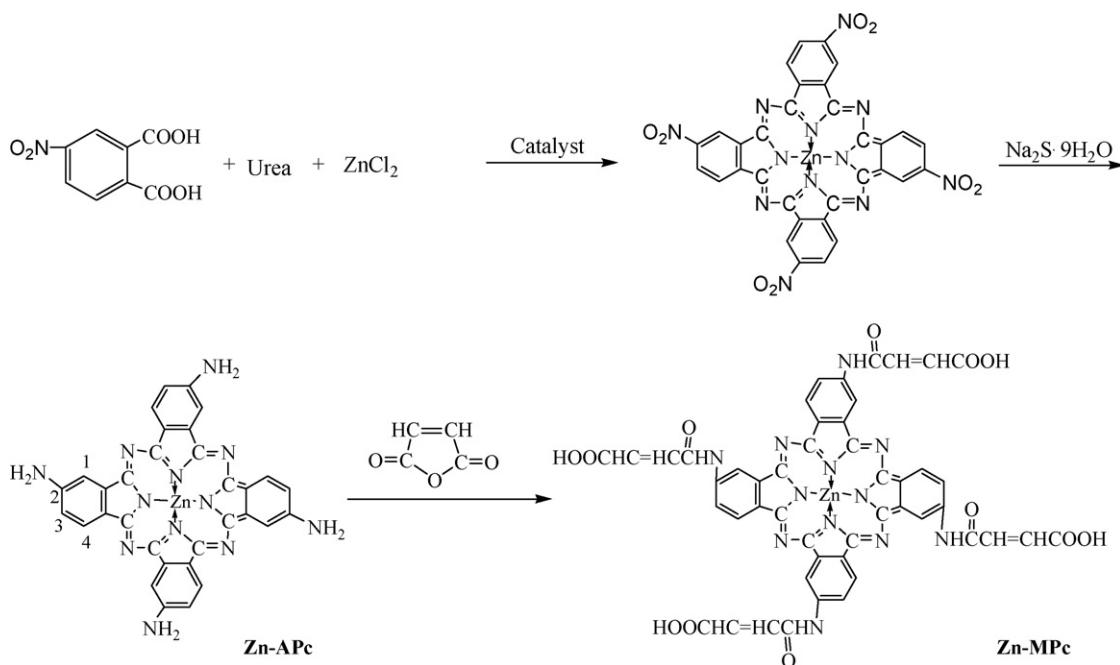
## 1. Introduction

Zinc phthalocyanines (Zn-Pcs) as one class of efficient photosensitizers have attracted considerable interest, which can be used in the photodynamic therapy of cancer (PDT) [1,2], water treatment [3–5], and fine chemical synthesis [6–8], etc. Among these applications, PDT is currently the object of intense investigation due to their high efficiency to generate singlet oxygen, intense absorption in the optimally tissue-penetrating spectral region (630–800 nm) and lack of dark toxicity [9,2]. However, this application is greatly limited by their insolubility in water, which strongly influences the bioavailability and *in vivo* distribution [10]. Therefore, the enhancement of their water solubility is the important aim of studies on the chemistry of Zn-Pcs. Several aqueous soluble Zn-Pcs, such as tetrasulfonated Zn-Pc [11], tetra- and octa-triethyleneoxysulfonyl substituted Zn-Pc [12], [1,2,3,4-tetrakis(α/β-D-galactopyranos-6-yl)-phthalocyaninato] zinc [13], Zn-Pc containing four carboxyphenoxy substituents (p-HPcZn) [14], have been successfully prepared. However, they tend to aggregate at relatively low concentrations in aqueous media. These aggregates provide a facile nonradiative energy relaxation pathway and negatively result in the significant reduce of the photoactiv-

ity [15–17]. The effective strategies to prevent such aggregation involve the introduction of polymeric substituents to the peripheral benzene rings [18] and conjugation with polymers [19–21]. Furthermore, via adjusting the size of the polymeric substituents and polymers or incorporating site-selective moieties, the biodistribution of the photosensitizers can be improved, and these systems may be used for targeted delivery and release of photosensitizers [18,22]. Whereas, most of the water-soluble Zn-Pcs reported, including those mentioned above, are lack of functional groups for further design of photosensitizers to satisfy various requirements, thus the exploration of Zn-Pcs which have high aqueous solubility and are facile to chemical modification is particularly attractive.

Herein, we reported a novel water-soluble Zn-Pc with unsaturated double bonds, zinc tetra(*N*-carbonylacrylic)aminophthalocyanine (Zn-MPc). Moreover, the special molecular structure of Zn-MPc supplies extensive space for the further design of flexible molecular, effectively preventing the aggregation of Zn-Pcs and exhibiting desirable photoactivity. Since PDT activity is mainly based on singlet oxygen [23], 1,3-diphenyl isobenzofuran (DPBF) as a specific scavenger of this toxic species [24–26] is chosen to evaluate the photoactivity of Zn-MPc, and the kinetics of DPBF degradation is investigated. A thermosensitive macromolecular photosensitizer with desirable photoactivity and PDT selectivity based on Zn-MPc is currently being explored in our labs and will be reported soon.

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**Scheme 1.** Synthesis of Zn-MPc.

## 2. Experimental

### 2.1. Preparation of Zn-MPc

The synthetic methodology was shown in [Scheme 1](#). Finely ground zinc tetraaminophthalocyanine (Zn-APc, prepared according to the literature method [27]) (3.0 g) was dissolved in 150 ml DMF, and then maleic anhydride (1.32 g) was added. After stirring at 60 °C for 3 h, the solution was poured into 1000 ml H<sub>2</sub>O and a dark cyan floccule was obtained. The mixture was centrifugated and the precipitate was collected. The crude product was then dissolved in sodium hydroxide solution (0.1 M) and filtrated through a glass funnel. The filtrate pH was adjusted to 2. When much dark cyan floccule appeared, centrifugated it again. This procedure was repeated three times. After washing with water, ethanol and ether, the final product (Zn-MPc) was dried in vacuo for 24 h.

### 2.2. Characterization

FT-IR spectra was determined on a Bruker vector 22 spectrophotometer using KBr pellets. <sup>1</sup>H NMR spectra was recorded on a Bruker-400 spectrophotometer (400 MHz) in deuterated dimethylsulfoxide (DMSO-d<sub>6</sub>), using TMS as internal reference. MALDI-TOF mass spectra was taken on a MALDI-TOF 4700 proteomics Analyzer, and the sample was dissolved in a 10:90 mixture of DMF:H<sub>2</sub>O.

### 2.3. Solubility test

0.01 g Zn-Pcs were placed into 50 ml of solvent (THF, acetone, ethanol, toluene, DMF, H<sub>2</sub>O and CHCl<sub>3</sub>) and vibrated at 25 °C for 24 h in a thermostatic vibrator. The solution was filtered and the insoluble substrate was collected, dried and weighed (*m*). The formula of dissolution rate ( $\eta$ ) can be expressed as follows:

$$\eta = \frac{0.01 - m}{0.01} \times 100\%$$

$\eta < 0.1\%$ , insoluble;  $0.1\% \leq \eta < 1\%$ , slightly soluble;  $\eta \geq 1\%$ , soluble.

### 2.4. Photoactivity studies

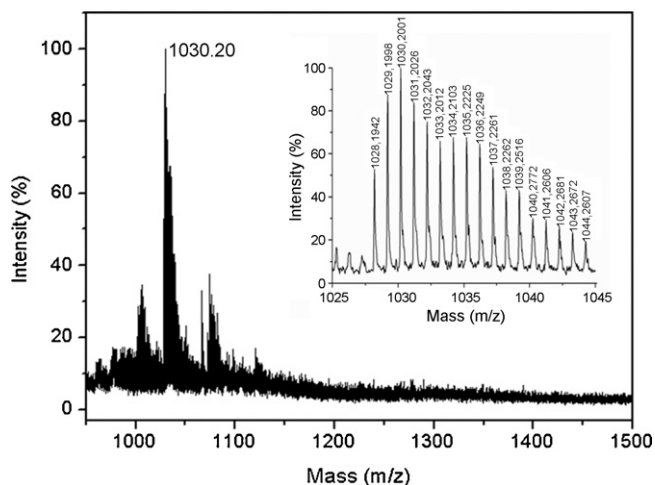
All experiments were carried out in oxygen-saturated DMF at 25 °C, using 1,3-diphenylisobenzofuran (DPBF, Acros Organics) as chemical quencher. Electronic energy-saving lamps (15, 11, 8, and 5 W, Philips, Shanghai) were used as the irradiation source. A 550 nm glass cut off filter (CB550, Shanghai Seagull Coloured Optical Glass Co., Ltd., China) was used to filter off ultraviolet light, so that only the phthalocyanine Q band was irradiated, avoiding direct photodegradation of DPBF under UV light irradiation. The light intensity was measured by a luminometer (TES-1339, TES Electrical Electronic Corp., Taipei). After irradiation for certain interval, the sample was monitored by a Hitachi UV-3010 spectrophotometer. For the study on photodegradation kinetics of DPBF, experiments were performed where one of the initial concentration of DPBF, Zn-MPc concentration and light intensity changed while the other two factors were restrained.

## 3. Results and discussion

### 3.1. Characterization of Zn-MPc

In the FT-IR spectra ([Fig. S1](#), see supporting information), for Zn-MPc, the absorption peaks at 1167, 1085, 1045, 840 and 745 cm<sup>-1</sup> were assigned to phthalocyanine skeleton [28]. Peak around 1706 cm<sup>-1</sup> indicated the presence of C=O group, and the band at 3000–3500 cm<sup>-1</sup> corresponded to OH of the COOH group; and for Zn-APc, the absorption peaks at 1136, 1095, 1059, 822 and 751 cm<sup>-1</sup> were also assigned to phthalocyanine skeleton. The strong absorption bands around 3300 cm<sup>-1</sup> were due to the NH<sub>2</sub> group on the ring of phthalocyanine, which was diminished in the spectra of Zn-MPc. It can be concluded that the nucleophilic reaction had taken place between Zn-APc and maleic anhydride.

The <sup>1</sup>H NMR spectra of Zn-APc and Zn-MPc ([Fig. S2](#)) are consistent with the results from FT-IR analysis. In the <sup>1</sup>H NMR spectra of Zn-APc, the 3-H ([Scheme 1](#)) of phthalocyanine ring had the maximum chemical shift because of the effect of Zn(II) through the phthalocyanine ring and the easiest solvation, appearing as a



**Fig. 1.** MALDI-TOF mass spectra of Zn-MPc. The inset shows the isotopic distribution patterns of this molecule.

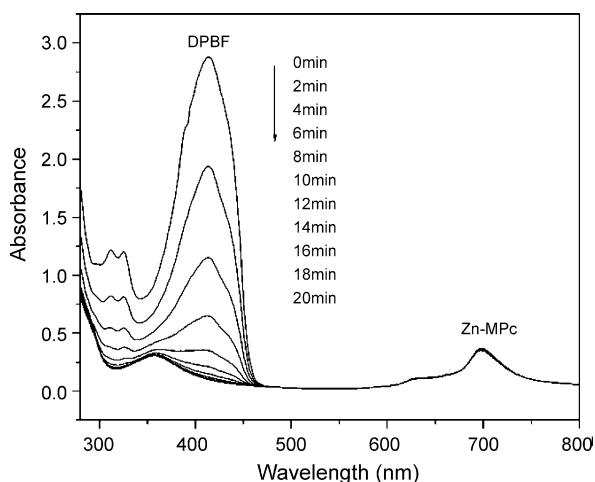
quartet at 8.90–8.96 ppm, the 4-H (Scheme 1) had a smaller chemical shift at 8.41–8.45 ppm because of the relatively disadvantageous position, the 1-H (Scheme 1) had the smallest chemical shift at 7.38–7.42 ppm for the most difficult solvation and the  $-\text{NH}_2$  protons appeared as a typical broad singlet at 6.23 ppm. While in the  $^1\text{H}$  NMR spectra of Zn-MPc, the broad singlet at 6.23 ppm for  $-\text{NH}_2$  protons disappeared and a new singlet at 11.30 ppm for  $-\text{COOH}$  proton emerged, indicating the successful preparation of Zn-MPc. Meanwhile, the introduction of functional group ( $-\text{COCH}=\text{CHCOOH}$ ) influences the electron cloud of the protons of phthalocyanine ring and makes the space conformation complicated, hence causing the spectral broadening.

For the further certification of the structure of Zn-MPc, the MALDI-TOF mass spectra of the compound were tested. In Fig. 1, the intense molecular ion peak at  $m/z$  1030.20 provided a definitive

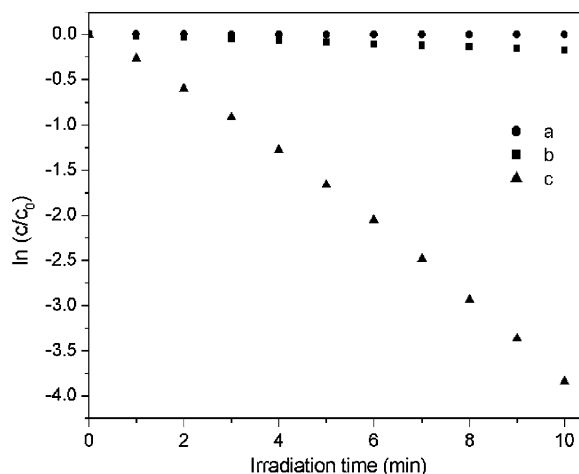
**Table 1**  
Solubility test of Zn-APc and Zn-MPc<sup>a</sup>.

Sample	DMF	$\text{CHCl}_3$	Toluene	Ethanol	THF	$\text{H}_2\text{O}$ (pH > 7)	Acetone
Zn-APc	+	–	–	–	–	–	–
Zn-MPc	+	–	–	–	±	+	–

<sup>a</sup> (+) soluble; (±) partially soluble; (–) insoluble.



**Fig. 2.** Time evolution of the UV-vis spectrum of a DPBF ( $1.0 \times 10^{-4} \text{ mol l}^{-1}$ ) and Zn-MPc ( $5.0 \times 10^{-6} \text{ mol l}^{-1}$ ) in DMF solution.



**Fig. 3.** Control experiments: (a) Zn-MPc:  $5.0 \times 10^{-6} \text{ mol l}^{-1}$ , DPBF:  $5.0 \times 10^{-5} \text{ mol l}^{-1}$ , dark; (b) DPBF:  $5.0 \times 10^{-5} \text{ mol l}^{-1}$ , irradiation resource: 8 W, no Zn-MPc; (c) Zn-MPc:  $5.0 \times 10^{-6} \text{ mol l}^{-1}$ , DPBF:  $5.0 \times 10^{-5} \text{ mol l}^{-1}$ , irradiation resource: 8 W.

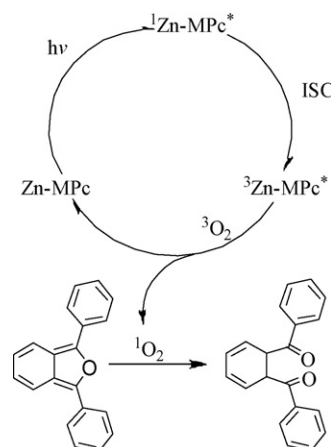
proof for the proposed structure of Zn-MPc (calculated for  $[\text{C}_{48}\text{H}_{28}\text{N}_{12}\text{O}_{12}\text{Zn}]$ : 1030.19). As expected, complex isotopic distributions were observed around 1030.20. In addition, a specie with a  $M_w$  of 1066.15 was observed, which seemed to be Zn-MPc conjugated with two  $\text{H}_2\text{O}$  (+36) in the Zn(II) coordination center. Another molecular ion peak at  $m/z$  1005.24 may correspond to Zn-MPc (+2  $\text{H}_2\text{O}$ - $\text{CO}_2$ -OH: +36-44-17), created by the excess laser power.

### 3.2. Solubility test

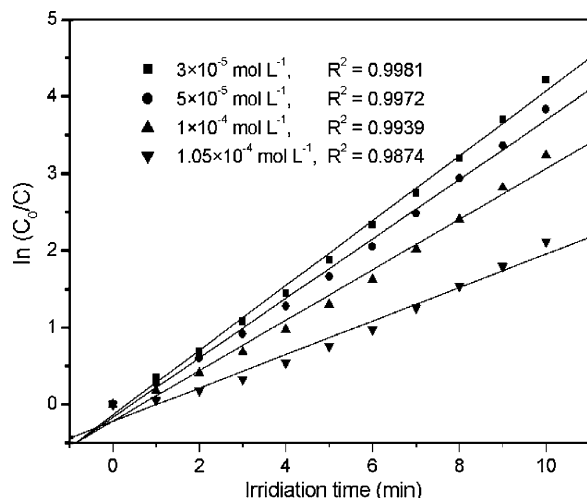
As shown in Table 1, compared with Zn-APc, which was only soluble in aprotic polar solvents like DMF, Zn-MPc can also be dissolved in basic solution since the dissociated carboxyl groups on the phthalocyanine rings increase the electrostatic repulsion and reduce the aggregation of phthalocyanine molecules, improving its solubility. Moreover, Zn-MPc was partially soluble in THF due to the enhancement of the solubility by substituting of the functional groups on the phthalocyanine ring.

### 3.3. Photoactivity studies

As a specific singlet oxygen quencher, DPBF is known to form an endoperoxide upon cycloaddition with singlet oxygen, resulting in



**Scheme 2.** The proposed mechanism of DPBF decomposition.



**Fig. 4.** Effect of the initial concentration of DPBF on the photodegradation rate of DPBF. All the reactions were performed in DMF; Zn-MPc:  $5.0 \times 10^{-6} \text{ mol l}^{-1}$ ; irradiation resource: 8 W.

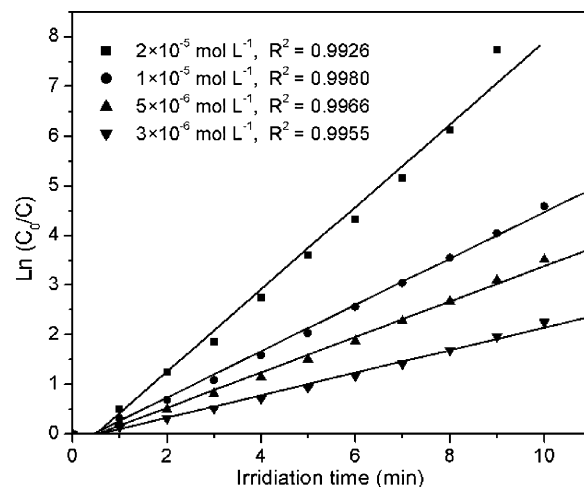
the complete disappearance of its characteristic absorption band at 415 nm [24]. Fig. 2 shows a family of spectra obtained for the photodegradation of DPBF in DMF. It can be seen that the absorption of DPBF (415 nm) decreased significantly and disappeared after 20 min, while the Zn-MPc absorption (698 nm) seldom changed during the whole process, indicating that Zn-MPc is an efficient photosensitizer with high photoactivity and photostability.

The concentration change of DPBF under various conditions (Fig. 3) was investigated. The result indicated that light and Zn-MPc were essential for the efficient degradation of DPBF (Fig. 3c), while DPBF was hardly degraded in dark (Fig. 3a) or decomposed very slowly under irradiation without Zn-MPc (Fig. 3b). According to the well known Type II mechanism [7,29], the excited triplet state sensitizer  $^3\text{MPc}^*$  was obtained by irradiation and intersystem crossing (ISC), which then interacted with the ground state triplet oxygen ( $^3\text{O}_2$ ) to generate the highly active singlet oxygen ( $^1\text{O}_2$ ), inducing the immediate decomposition of DPBF (Scheme 2). Without irradiation, no  $^1\text{O}_2$  was formed, thus there was no degradation in dark (Fig. 3a). However, trace singlet oxygen may be spontaneously produced in solvent under the illuminance of visible light even without Zn-MPc, resulting in the slight decomposition of DPBF.

Based on the reaction kinetics shown in Fig. 4, which was fitted well into the first-order kinetic equation  $\ln(C_0/C) = k_a t$ , the apparent rate constant,  $k_a$ , of DPBF photodegradation decreased from 0.4205 to  $0.2173 \text{ min}^{-1}$  as the initial concentration of DPBF increased from  $3 \times 10^{-5}$  to  $1.05 \times 10^{-4} \text{ mol l}^{-1}$  (Table 2). The reason is that the rate

**Table 2**  
Initial rate ( $R_d$ ) and the apparent rate constant ( $k_a$ ) of DPBF photodegradation.

E (lux)	Initial concentration ( $\times 10^{-5} \text{ mol l}^{-1}$ )		Initial rate ( $R_d$ ) ( $\times 10^{-5} \text{ mol l}^{-1} \text{ min}^{-1}$ )	$k_a$ ( $\text{min}^{-1}$ )
	DPBF	Zn-MPc		
6350	10.5	0.5	1.68	0.2173
6350	10.0	0.5	1.58	0.3277
6350	5.0	0.5	1.28	0.3861
6350	3.0	0.5	0.88	0.4205
6350	8.0	2.0	3.27	0.8297
6350	8.0	1.0	2.11	0.4671
6350	8.0	0.5	1.62	0.3566
6350	8.0	0.3	1.12	0.2267
9850	5.0	0.5	2.07	0.6841
7900	5.0	0.5	1.72	0.4736
2100	5.0	0.5	0.27	0.05418



**Fig. 5.** Effect of Zn-MPc concentration on the photodegradation rate of DPBF. All the reactions were performed in DMF; DPBF:  $5.0 \times 10^{-5} \text{ mol l}^{-1}$ ; irradiation resource: 8 W.

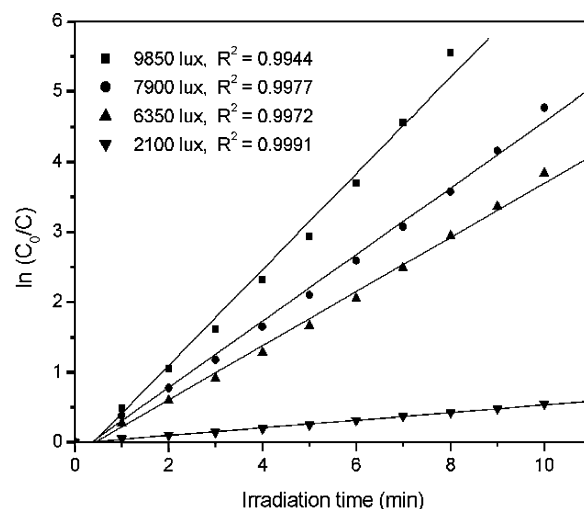
of  $^1\text{O}_2$  generation was almost changeless when the light intensity and the Zn-MPc concentration were fixed. Although the subtle amount of DPBF degradation increased with the increase of initial concentration, contrarily,  $k_a$ , depending on  $C_0/C$  decreased.

The effect of the amount of catalyst added on the photodegradation rate of DPBF was shown in Fig. 5. As the concentration of Zn-MPc increased from  $3 \times 10^{-6}$  to  $2 \times 10^{-5} \text{ mol l}^{-1}$ , the relevant value of  $k_a$  increased from 0.2267 to  $0.8297 \text{ min}^{-1}$  (Table 2). This could be explained by the fact that increasing amount of catalyst led to the increasing rate of singlet oxygen generation.

The light intensity is another factor which influences the rate of photodegradation (Fig. 6). As the illumination increased from 2100 to 9850 lux, the relevant value of  $k_a$  increased from 0.05418 to  $0.6841 \text{ min}^{-1}$  (Table 2), which was consistent with the Type II mechanism. Because higher light intensity brings more incident photons, which will excited more Zn-MPc.

In order to determine the influences of the initial concentration of DPBF, Zn-MPc concentration and light intensity on the initial photodegradation rate of DPBF ( $R_d$ ) in detail, a dynamics equation was assumed as follows:

$$R_d = k[\text{DPBF}]^a[\text{Zn-MPc}]^b E^c$$



**Fig. 6.** Effect of light intensity on the photodegradation rate of DPBF. All the reactions were performed in DMF; DPBF:  $5.0 \times 10^{-5} \text{ mol l}^{-1}$ ; Zn-MPc:  $5.0 \times 10^{-6} \text{ mol l}^{-1}$ .

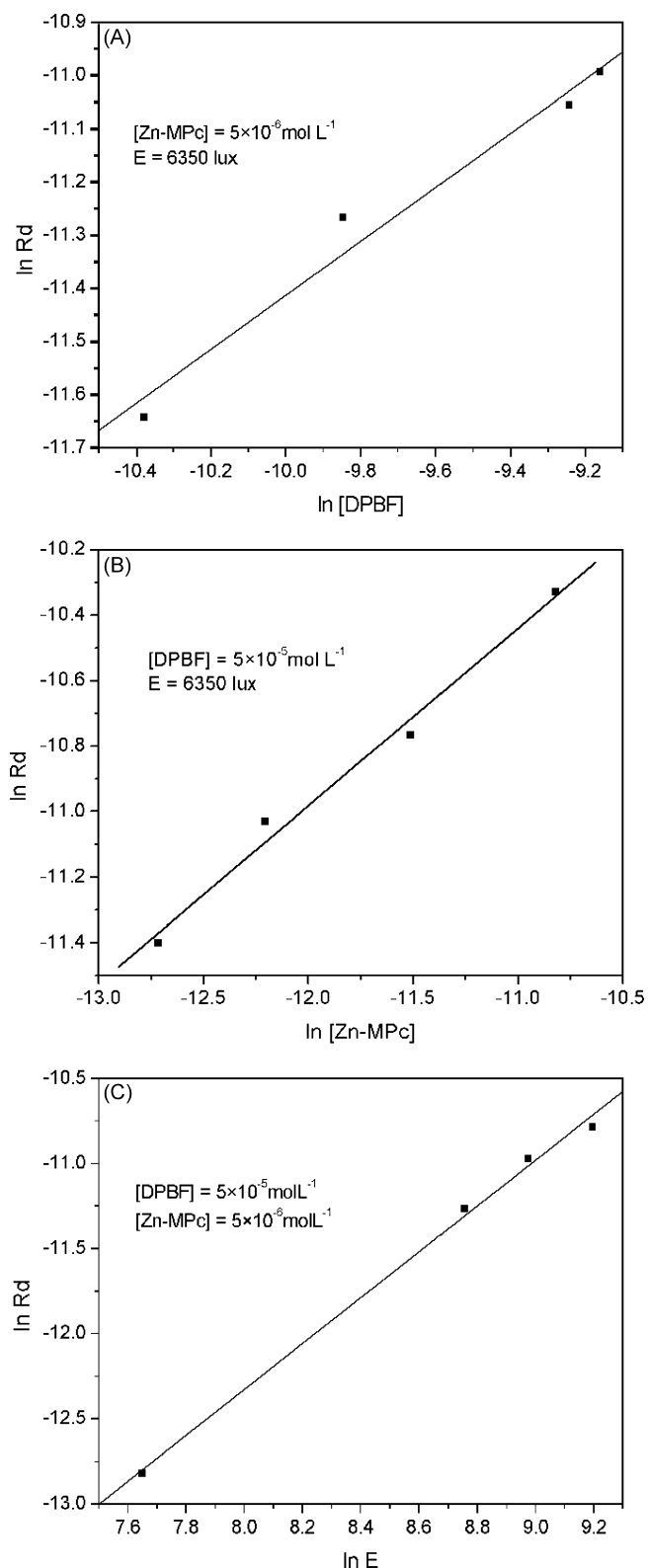


Fig. 7. Regression lines of  $\ln R_d \sim \ln [\text{DPBF}]$  (A),  $\ln R_d \sim \ln [\text{Zn-MPc}]$  (B) and  $\ln R_d \sim \ln E$  (C).

**Table 3**  
Orders with respect to the reactants and rate constants of DPBF degradation.

Variable	$R^2$	Order	Rate constant ( $k$ ) ( $\text{mol l}^{-1}$ ) <sup>-0.05</sup> (lux) <sup>-1.35</sup> min <sup>-1</sup>
DPBF	0.9863	0.51	$1.31 \times 10^{-5}$
Zn-MPc	0.9940	0.54	$1.00 \times 10^{-5}$
$E$	0.9983	1.35	$1.05 \times 10^{-5}$

where  $a$ ,  $b$  and  $c$  were the reaction orders of DPBF concentration, Zn-MPc concentration and light intensity, respectively,  $k$  the rate constant of the photodegradation of DPBF,  $E$  the illuminance of irradiation source. The initial degradation rate of DPBF,  $R_d$  (Table 2), was calculated from the decreased concentration at initial 1 min of irradiation according to the reported method [5,30]. When two of [DPBF], [Zn-MPc] and  $E$  were fixed, using a plot of  $\ln R_d$  versus  $\ln [\text{DPBF}]$ ,  $\ln R_d \sim \ln [\text{Zn-MPc}]$  and  $\ln R_d \sim \ln E$ , the values of  $a$ ,  $b$ ,  $c$  and  $k$  could be obtained from the slope and intercept, respectively (Fig. 7). As shown in Table 3, the results of linear fitting were fine ( $R^2 > 0.98$ ) and the three constants of  $k$  varied slightly from each other, which indicated that the assumed dynamics model was reasonable. The final equation was obtained as follows:

$$R_d = 1.12 \times 10^{-5} [\text{DPBF}]^{0.51} [\text{Zn-MPc}]^{0.54} E^{1.35}$$

in which the unit of  $E$  is lux.

This equation shows that the light intensity is the most important influencing factor to the photosensitizing efficiency. The results also shed some light on the understanding of the action of light irradiation, and on the design of highly efficient photosensitizers for the potential utility in PDT. Moreover, DPBF is a singlet oxygen trapper extensively used in research of photoactivity of various photosensitizers, and to the best of our knowledge, no similar dynamic equations have been reported.

#### 4. Conclusion

A novel aqueous soluble polymerizable phthalocyanine, Zn-MPc, with high photoactivity and photostability, was successfully synthesized and characterized. The increase of the Zn-MPc concentration or light intensity resulted in an increased efficiency of photosensitivity, while the increase of the initial concentration of substrate decreased it. The kinetics equation of the initial degradation rate of DPBF is  $R_d = 1.12 \times 10^{-5} [\text{DPBF}]^{0.51} [\text{Zn-MPc}]^{0.54} E^{1.35}$ , which can provide a novel thought for the potential application of photosensitizers in PDT and the further design of highly efficient photosensitizers.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2008.09.023.

#### References

- [1] J.W. Hofman, F. van Zeeland, S. Turker, H. Talsma, S.A.G. Lambrechts, D.V. Sakharov, W.E. Hennink, C.F. van Nostrum, J. Med. Chem. 50 (2007) 1485–1494.
- [2] C. Fabris, M. Soncin, G. Miotto, L. Fantetti, G. Chiti, D. Dei, G. Roncucci, G. Jori, J. Photochem. Photobiol. B: Biol. 83 (2006) 48–54.
- [3] M.C. DeRosa, R.J. Crutchley, Coord. Chem. Rev. 233–234 (2002) 351–371.

- [4] E. Marais, R. Klein, E. Antunes, T. Nyokong, *J. Mol. Catal. A: Chem.* 261 (2007) 36–42.
- [5] L. Wu, A. Li, G. Gao, Z. Fei, S. Xu, Q. Zhang, *J. Mol. Catal. A: Chem.* 269 (2007) 183–189.
- [6] N. Sehlootho, T. Nyokong, *J. Mol. Catal. A: Chem.* 219 (2004) 201–207.
- [7] P. Tau, T. Nyokong, *J. Mol. Catal. A: Chem.* 273 (2007) 149–155.
- [8] A. Maldotti, A. Molinari, R. Amadelli, *Chem. Rev.* 102 (2002) 3811–3836.
- [9] M. Magaraggia, A. Visoná, A. Furlan, A. Pagnan, G. Miotto, G. Tognon, G. Jori, *J. Photochem. Photobiol. B: Biol.* 82 (2006) 53–58.
- [10] K. Sakamoto, T. Kato, E. Ohno-Okumura, M. Watanabe, M.J. Cook, *Dyes Pigments* 64 (2005) 63–71.
- [11] S. Dhami, D. Phillips, *J. Photochem. Photobiol. A* 100 (1996) 77–84.
- [12] D. Atilla, N. Saydan, M. Durmuş, A.G. Gürek, T. Khan, A. Rück, H. Walt, T. Nyokong, V. Ahsen, *J. Photochem. Photobiol. A: Chem.* 186 (2007) 298–307.
- [13] A.O. Ribeiro, J.P.C. Tomé, M.G.P.M.S. Neves, A.C. Tomé, J.A.S. Cavaleiro, Y. Iamamoto, T. Torres, *Tetrahedron Lett.* 47 (2006) 9177–9180.
- [14] Y. Yan, S. Lu, B. Li, R. Zhu, J. Zhou, S. Wei, S. Qian, *J. Phys. Chem. A* 110 (2006) 10757–10762.
- [15] L. Howe, J.Z.J. Zhang, *Phys. Chem. A* 101 (1997) 3207–3213.
- [16] V. Iliev, V. Alexiev, L. Bilyarska, *J. Mol. Catal. A: Chem.* 137 (1999) 15–22.
- [17] V. Iliev, A. Ileva, *J. Mol. Catal. A: Chem.* 103 (1995) 147–153.
- [18] D. Atilla, M. Durmuş, Ö. Yılmaz, A.G. Gürek, V. Ahsen, T. Nyokong, *Eur. J. Inorg. Chem.* 22 (2007) 3573–3581.
- [19] P.P.S. Lee, T. Ngai, J.-D. Huang, C. Wu, W.-P. Fong, D.K.P. Ng, *Macromolecules* 36 (2003) 7527–7533.
- [20] J. Fu, X. Li, D.K.P. Ng, C. Wu, *Langmuir* 18 (2002) 3843–3847.
- [21] W. Chen, B. Zhao, Y. Pan, Y. Yao, S. Lu, S. Chen, L. Du, *J. Colloid Interface Sci.* 300 (2006) 626–632.
- [22] S.O. McDonnell, M.J. Hall, L.T. Allen, A. Byrne, W.M. Gallagher, D.F. O'Shea, *J. Am. Chem. Soc.* 127 (2005) 16360–16361.
- [23] D.E.J.G.J. Dolmans, D. Fukumura, R.K. Jain, *Nat. Rev. Cancer* 3 (2003) 380–387 (review).
- [24] T. Wilson, *J. Am. Chem. Soc.* 88 (1966) 2898–2902.
- [25] B. Luca, A. Alessandro, L. Mirko, C. Michele, T. Riccardo, M. Francesco, B. Silvia, A. Giorgio, *Org. Lett.* 7 (2005) 4257–4260.
- [26] M. Kostka, P. Zimcik, M. Miletin, P. Klemra, K. Kopecky, Z. Musil, *J. Photochem. Photobiol. A: Chem.* 178 (2006) 16–25.
- [27] W. Chen, S. Chen, S. Lu, Y. Yao, M. Xu, *Sci. China Ser. B: Chem.* 50 (2007) 379–384.
- [28] J. Mack, M.J. Stillman, *Coord. Chem. Rev.* 219 (2001) 993–1032.
- [29] R. Bonnett, *Chem. Soc. Rev.* 24 (1995) 19–33.
- [30] Z. Xiong, Y. Xu, L. Zhu, J. Zhao, *Langmuir* 21 (2005) 10602–10607.