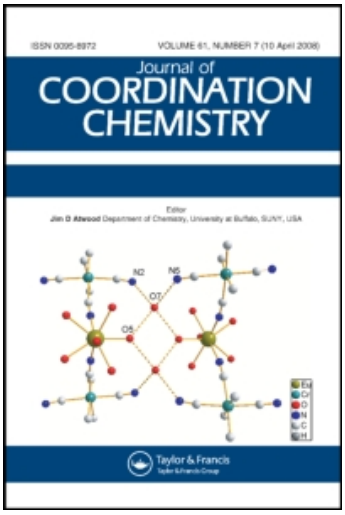

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Synthesis, characterization and properties of some metallophthalocyanine complexes substituted by N-piperidineethanol

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Synthesis, characterization and properties of some metallophthalocyanine complexes substituted by *N*-piperidineethanol

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The preparation of eight metallophthalocyanine complexes substituted by *N*-piperidineethanol was achieved by tetramerization of 3-[2-(piperidin-1-yl)ethoxyl] phthalonitrile and 4-[2-(piperidin-1-yl)ethoxyl]phthalonitrile in the presence of a metal salt with *n*-pentanol as solvent and DBU as catalyst, respectively. These complexes were characterized by IR, elemental analysis, ^{1}H NMR and mass spectra. Some properties such as UV/visible absorption spectra, rate of singlet oxygen yields, fluorescence spectra and quantum yields were examined and discussed.

Keywords: Phthalocyanine; *N*-piperidineethanol; Synthesis; Property

1. Introduction

Phthalocyanine (Pc) complexes have been widely used as organic pigments and dyestuffs for many years [1–3]. Besides the application in such traditional areas, phthalocyanines (Pcs) have been extensively studied due to their chemical, physical and biological characteristics. From the viewpoint of metallophthalocyanine complexes (MPcs) to be used as photosensitizers for photodynamic therapy (PDT) in the treatment of cancer, zinc and aluminum derivatives are the most studied [5–8]. In order to enhance their solubility, some polar derivatives such as sulfonated, amino and hydroxyl derivatives have received attention [9–11]. Upon substitution by alkoxyl groups with electron withdrawing effect containing aza-substituents, the MPcs may be easily dissolved even in organic polar solvents so that their photosensitive characteristics can be improved. Moreover, interest in Pcs substituted by piperidine was aroused by the consideration that with substitution of piperidine to Pc ring, the Pc molecule so formed will contain the unit of structure with N–C–C–O–C–C, which was known to be used as

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an agonist to M-choline acceptor in biological systems [12–15]. Therefore, using photosensitizers of this kind may have certain additional effects to be explored.

In this paper, we have designed and synthesized several phthalocyanines substituted by *N*-piperidineethanol in order to find new properties and better photosensitive activities to be employed for certain fields. Synthetic routes to metal phthalocyanine complexes involve initial synthesis of phthalonitrile precursors, followed by cyclization in the presence of metal salt so as to form the phthalocyanine. Eight new piperidine derivatives of metal (Zn, Co, Ni, Cu) phthalocyanine complexes both in α-position and β-position are synthesized and characterized. The results show that these complexes possess good solubility in polar organic solvents, and the UV/visible absorption spectra, rate of singlet oxygen yield, fluorescence spectra and quantum yields were examined.

2. Experimental

2.1. *Materials*

N,N′-dimethylformamide (DMF) was freshly distilled under vacuum after pretreatment with 4A molecular sieves for 24 h; *n*-pentanol was filtered after being dipped in K_2CO_3 for 24 h. Anhydrous potassium carbonate, anhydrous zinc acetate and cuprous chloride were dried at 103°C for 12 h. Anhydrous nickel chloride and anhydrous cobalt chloride were prepared as described [16]. All reagents were purchased from Sinopharm Chemical Reagent Co. Ltd., except *N*-piperidineethanol (PDE) and 1,3-diphenylbenzoisofuran (DPBF) were purchased from Alfa Aesar, 100–120 mesh ZCX-II type column chromatography silica gel was purchased from Qingdao Haiyang Chemical Co. Ltd., 1,8-diaza-bicyclo[5,4,0]undec-7-ene (DBU) was purchased from Aldrich, and Cremophor EL, a castor oil derivative, was purchased from Sigma; all are used without further purification.

2.2. *Equipment*

Infrared spectra were recorded on a Perkin-Elmer FT-IR spectrometer using potassium bromide pellets. ^{1}H NMR spectra with DMSO-d6 as solvent and TMS (tetramethylsilane) as the internal standard were recorded on a Varian Unity 500 NMR. Mass spectra were recorded on a Finnigan LCQ Deca Xp Max, Thermo Electron Corporation. Elemental analyses were carried out on a Vario EL III Elementar. UV/Visible spectra were recorded on a Perkin Elmer Lambda 800 UV/Vis spectrometer. Melting points were measured by a YRT-3 melting point meter made in P.I.T. Tianjin University. 670 nm laser was generated from a PDT 670 nm laser meter. Fluorescence emission spectra and quantum yield were recorded on a FL/FS920 TCSPC Lifetime spectrometer and spectrofluorimeter.

2.3. *Syntheses of phthalocyanine precursors*

2.3.1. Synthesis of 3-[2-(piperidin-1-yl)ethoxyl]phthalonitrile (3). PDE (1.33 mL, 10 mmol) was added to a mixture of 3-nitro-phthalonitrile (850 mg, 5.0 mmol),

anhydrous potassium carbonate (2.78 g, 20 mmol) and 50 ml DMF at room temperature under nitrogen. The reaction mixture was stirred at 80°C for 24 h and then distilled to remove DMF under reduced pressure; 60 mL CH_3OH was added to dissolve mixture and the insoluble precipitate was removed by a membrane filter. Then the solution was distilled to remove CH_3OH and the residue was dried at 70°C for 24 h. After ethyl acetate (60 mL) was added to dissolve the residue, the solution was purified by column chromatography on silica gel with ethyl acetate as eluant, giving a light yellow solid after distillation to remove ethyl acetate and drying at 70°C for 12 h. The reaction is shown in figure 1. **3**, yield 67%, m.p. 170.2–171.5°C. Anal. Calcd for $C_{15}H_{17}N_3O$ (%): C, 70.56; N, 16.46; H, 6.71. Found: C, 69.87; N, 16.32; H, 6.66. IR (KBr, ν/cm^{-1}): 3045(Ar–H), 2243(C≡N), 1586(Ar skeleton), 1467(CH_2), 1314(C–N), 1280, 975(Ar–O–C). ^1H NMR (DMSO-d_6 δ/ppm): 1.44(2H, CH_2), 1.55(4H, CH_2), 3.71(2H, CH_2), 7.51(1H, Ar–H_4), 7.69(1H, Ar–H_5), 7.36(1H, Ar–H_6). MS(m/z): 255(M^+).

2.3.2. Synthesis of 4-[2-(piperidin-1-yl)ethoxyl] phthalonitrile (4). PDE (1.00 mL, 7.5 mmol) was added to a mixture of 4-nitro-phthalonitrile (850 mg, 5.0 mmol), anhydrous potassium carbonate (2.78 g, 20 mmol) and 50 mL DMF at room temperature under nitrogen. The reaction mixture was stirred at 50°C for 72 h and then distilled under reduced pressure to remove DMF; 60 mL CH_3OH was added to dissolve the mixture and the insoluble precipitate was removed by membrane filter. Then the solution was distilled to remove CH_3OH and the residue was dried at 70°C for 24 h. After acetone (60 mL) was added to dissolve the residue, the solution was purified by column chromatography on silica gel with acetone as eluant, giving a light yellow solid after distillation to remove acetone and drying at 70°C for 12 h; the reaction is shown in figure 1. **4**, yield 41%, m.p. 191.5–193.0°C. Anal. Calcd for $C_{15}H_{17}N_3O$ (%): C, 70.56; N, 16.46; H, 6.71. Found: C, 69.95; N, 16.42; H, 6.62. IR (KBr, ν/cm^{-1}): 3045(Ar–H), 2243(C≡N), 1567(Ar skeleton), 1462(CH_2), 1312(C–N), 1227, 964(Ar–O–C). ^1H NMR (DMSO-d6 δ/ppm): 1.43(2H, CH_2), 1.54(4H, CH_2), 3.71(2H, CH_2), 7.40(1H, Ar–H_3), 7.20(1H, Ar–H_5), 7.91(1H, Ar–H_6). MS(m/z): 256($[M+H]^+$).

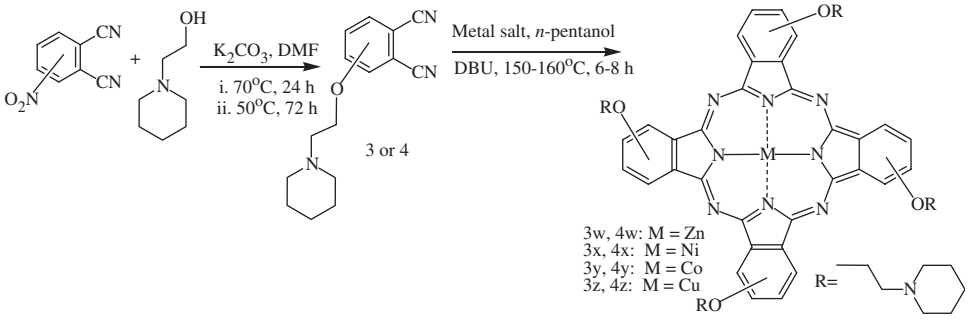

Figure 1. Synthetic approach of the phthalocyanine complexes.

2.4. *Syntheses of metallophthalocyanine complexes*

2.4.1. 1,8(11),15(18),22(25)-tetra-[2-(piperidin-*N*-)ethyoxyl]phthalocyanine zinc (3w). A mixture of **3** (128 mg, 0.50 mmol) and 10.0 mL *n*-pentanol as solvent was heated to 100°C under nitrogen, then 0.20 mL DBU as catalyst and anhydrous zinc acetate (50 mg, >0.125 mmol) were added. The mixture was heated to 150°C quickly with stirring and refluxed at 150°C for 6–8 h; the mixture eventually transformed to dark green. Next, *n*-pentanol was evaporated in a vacuum system, 50 mL DMF was added to dissolve the product, the solution was filtered after 30 min of stirring and 20 mL concentrated solution was obtained by evaporative concentration. The solution was purified by column chromatography on silica gel with DMF as eluant (1), giving a green solid by distillation to remove solvent and drying at 110°C for 12 h. Then 25 mL DMF was added to dissolve the green solid and the solution was purified by column chromatography on silica gel with DMF : $CH_3CH_2OH = 1:1$ (v/v) as eluant (2), giving **3w** by distillation to remove the solvent and drying at 110°C for 24 h. **3w**, yield 23.4%. Anal. Calcd for $C_{60}H_{68}N_{12}O_4Zn$ (%): C, 66.32; N, 15.47; H, 6.31. Found: C, 65.38; N, 15.02; H, 6.38. IR(KBr, ν_{max}/cm^{-1}): 2923(Pc–H), 1599, 1091(Pc ring), 1471(CH_2), 1250, 1036(Ar–O–C), 743(Zn–N). MS (*m*/*z*): 1084($[M-H]^+$).

2.4.2. 2,9(10),16(17),23(24)-tetra-[2-(piperidin-*N*-)ethyoxyl]phthalocyanine zinc (4w). The synthesis of **4w** was similar to **3w** in the presence of zinc acetate as metal salt, DMF as eluant (1) and DMF : $CH_3OH = 1:1$ (v/v) as eluant (2) in purification. **4w**, yield 19.6%. Anal. Calcd for $C_{60}H_{68}N_{12}O_4Zn$ (%): C, 66.32; N, 15.47; H, 6.31. Found: C, 65.02; N, 14.68; H, 6.57. IR(KBr, ν_{max}/cm^{-1}): 2927(Pc–H), 1608, 1088(Pc ring), 1485(CH_2), 1221, 1047(Ar–O–C), 747(Zn–N). MS (*m*/*z*): 1086($[M+H]^+$).

2.4.3. 1,8(11),15(18),22(25)-tetra-[2-(piperidin-*N*-)ethyoxyl]phthalocyanine nickel (3x). The synthesis of **3x** was similar to **3w** in the presence of anhydrous $NiCl_2$ as metal salt, DMF as eluant (1) and DMF : $THF = 1:1$ (v/v) as eluant (2) in purification. **3x**, yield 20.2%. Anal. Calcd for $C_{60}H_{68}N_{12}O_4Ni$ (%): C, 66.73; N, 15.56; H, 6.35. Found: C, 65.02; N, 14.68; H, 6.57. IR(KBr, ν_{max}/cm^{-1}): 2929(Pc–H), 1611, 1093(Pc ring), 1485(CH_2), 1276(Ar–O–C), 745(Ni–N). MS (*m*/*z*): 1080($[M-H]^-$).

2.4.4. 2,9(10),16(17),23(24)-tetra-[2-(piperidin-*N*-)ethyoxyl]phthalocyanine nickel (4x). The synthesis of **4x** was similar to **3w** in the presence of anhydrous $NiCl_2$ as metal salt, DMF as eluant (1) and DMF : $CH_3OH = 1:2$ (v/v) as eluant (2) in purification. **4x**, yield 21.2%. Anal. Calcd for $C_{60}H_{68}N_{12}O_4Ni$ (%): C, 66.73; N, 15.56; H, 6.35. Found: C, 64.79; N, 14.52; H, 6.73. IR(KBr, ν_{max}/cm^{-1}): 2927(Pc–H), 1615, 1083(Pc ring), 1489(CH_2), 1261, 977(Ar–O–C), 753(Ni–N). MS (*m*/*z*): 1079($[M]^+$).

2.4.5. 1,8(11),15(18),22(25)-tetra-[2-(piperidin-*N*-)ethyoxyl]phthalocyanine cobalt (3y). The synthesis of **3y** was similar to **3w** in the presence of anhydrous $CoCl_2$ as metal salt, DMF as eluant (1) and DMF : $CH_3OH = 1:2$ (v/v) as eluant (2) in purification. **3y**, yield 23.5%. Anal. Calcd for $C_{60}H_{68}N_{12}O_4Co$ (%): C, 66.32; N, 15.47; H, 6.31. Found: C, 65.02; N, 14.68; H, 6.57. IR(KBr, ν_{max}/cm^{-1}): 2927(Pc–H), 1612, 1059(Pc ring), 1468(CH_2), 1293, 980(Ar–O–C), 749(Co–N). MS (*m*/*z*): 1079($[M]^+$).

2.4.6. 2,9(10),16(17),23(24)-tetra-[2-(piperidin-*N*-)ethyoxyl]phthalocyanine cobalt (4y). The synthesis of **4y** was similar to **3w** in the presence of anhydrous $CoCl_2$ as metal salt, DMF as eluant (1) and DMF : ethyl acetate = 2 : 1 (v/v) as eluant (2) in purification. **4y**, yield 20.4%. Anal. Calcd for $C_{60}H_{68}N_{12}O_4Co$ (%): C, 66.71; N, 15.56; H, 6.35. Found: C, 64.46; N, 15.02; H, 6.52. IR(KBr, ν_{max}/cm^{-1}): 2927(Pc–H), 1600, 1097(Pc ring), 1489(CH_2), 1250(Ar–O–C), 752(Co–N). MS (m/z): 1080($[M+H]^+$).

2.4.7. 1,8(11),15(18),22(25)-tetra-[2-(piperidin-*N*-)ethyoxyl]phthalocyanine copper (3z). The synthesis of **3z** was similar to **3w** in the presence of CuCl as metal salt, DMF as eluant (1) and DMF : THF = 2 : 1 (v/v) as eluant (2) in purification. **3z**, yield 24.3%. Anal. Calcd for $C_{60}H_{68}N_{12}O_4Cu$ (%): C, 66.43; N, 15.49; H, 6.32. Found: C, 65.32; N, 14.95; H, 6.45. IR(KBr, ν_{max}/cm^{-1}): 2927(Pc–H), 1600, 1091(Pc ring), 1485(CH_2), 1250, 1047(Ar–O–C), 748(Cu–N). MS (m/z): 1084($[M]^+$).

2.4.8. 2,9(10),16(17),23(24)-tetra-[2-(piperidin-*N*-)ethyoxyl]phthalocyanine copper (4z). The synthesis of **4z** was similar to **3w** in the presence of CuCl as metal salt, DMF as eluant (1) and DMF : CH_3CH_2OH = 2 : 1 (v/v) as eluant (2) in purification. **4z**, yield 26.1%. Anal. Calcd for $C_{60}H_{68}N_{12}O_4Cu$ (%): C, 66.43; N, 15.49; H, 6.32. Found: C, 65.42; N, 14.09; H, 6.47. IR(KBr, ν_{max}/cm^{-1}): 2935(Pc–H), 1603, 1092(Pc ring), 1483(CH_2), 1245, 1049(Ar–O–C), 748(Cu–N). MS (m/z): 1083($[M-H]^-$).

3. Results and discussion

3.1. *UV/Vis spectra in DMF*

The maximum absorptions (λ_{max}) of UV/Vis spectra and corresponding molar extinction coefficients (ε) for all complexes dissolved in DMF are listed in table 1.

Similar to other phthalocyanine compounds [17–19], the title complexes exhibited two characteristic absorption bands in their UV/Vis spectra, namely Q-band and B-band, the former is in the visible region at ca 600–720 nm, attributed to the π–π^* transition (a_{1u}–e_g) from HOMO to the LUMO of the conjugated Π-bond system of phthalocyanine, and the latter is in the UV region at ca 320–400 nm arising from the deeper π–π^* transitions (a_{2u}–e_g). In addition, the absorptions of the Q-band were observed as a band of high intensity usually accompanying the vibronic band on the

Table 1. Absorption and molar extinction coefficient of the complexes in DMF.

Complexes	**3w**	**3x**	**3y**	**3z**	**4w**	**4x**	**4y**	**4z**
Central ion	Zn^{2+}	Ni^{2+}	Co^{2+}	Cu^{2+}	Zn^{2+}	Ni^{2+}	Co^{2+}	Cu^{2+}
Position of substituent		α-position				β-position		
Q-band absorption (nm)	694	691	687	693	680	680	677	679
ε_Q ($\times 10^5$ L cm^{-1} mol^{-1})	0.81	0.72	0.92	0.80	0.87	1.04	0.96	1.28
B-band absorption (nm)	352	364	352	347	352	350	339	350
ε_B ($\times 10^5$ L cm^{-1} mol^{-1})	0.677	0.302	0.411	0.262	0.408	0.405	0.325	0.398

slightly higher energy side. All complexes possess a high molar extinction coefficient of the Q-band absorption about $10^5\,L\,cm^{-1}\,mol^{-1}$.

3.2. *UV/Vis spectra in aqueous media*

All complexes except **4z** dissolve in 0.5% CEL (Cremophor EL) solution after concentrated solution was prepared in DMF at first. Absorption spectra of **4y** in CEL solution are shown in figure 2. These complexes showed very large molar extinction coefficient in CEL solution as listed in table 2, with a linear relationship between concentration and absorbance. Unexpectedly, **4z** aggregated when 0.5% CEL was added to its concentration solution, but the reason awaits further studies.

3.3. *Effects of peripherally substituted position and central ion on the Q-band*

As for many phthalocyanines bearing alkoxyl substituted moieties on the periphery, the Q-band absorption of the title complexes is shifted to lower energy than that of unsubstituted phthalocyanines (ZnPc). All of the α-position substituted complexes **3w**, **3x**, **3y**, **3z** show similar absorption positions of the Q-band at 687–694 nm in DMF together with two vibronic bands at 610–635 and 635–670 nm. All of the β-position substituted complexes **4w**, **4x**, **4y**, **4z** show similar absorption positions of the Q-band at

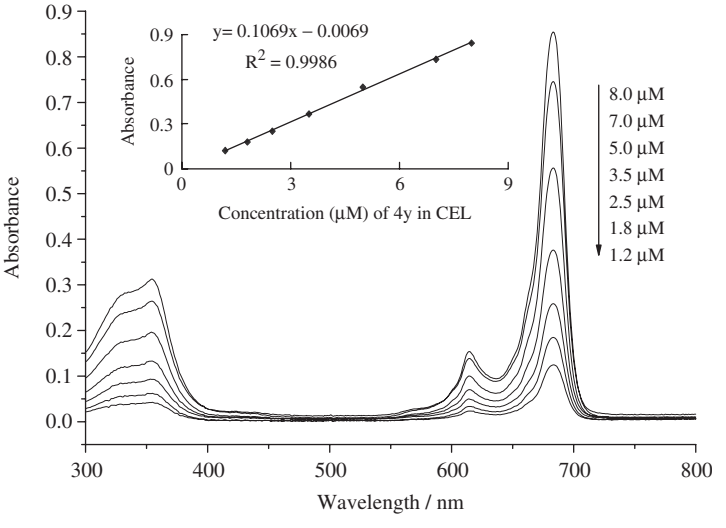

Figure 2. Absorption spectra of **4y** in CEL solution. Inset: Plot of concentration of **4y** in CEL *vs.* absorbance.

Table 2. Absorptions and molar extinction coefficients of the complexes in aqueous media.

Complexes	**3w**	**3x**	**3y**	**3z**	**4w**	**4x**	**4y**	**4z**
Absorption λ_{max} (nm)	694	690	685	693	680	679	677	–
ε ($\times 10^5\,L\,cm^{-1}\,mol^{-1}$)	1.02	0.85	0.65	0.72	0.86	0.92	1.07	–

677–680 nm in DMF together with two vibronic bands at 605–635 and 635–670 nm. The red shift of α-substituted is bigger than β, as expected [20–22].

The red shift of the Q-band in both α- and β-substituted complexes has a similar order with different central ions as $Zn^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+}$, which obviously is caused by the difference of 3d electrons in the LUMO, and the energy level of LUMO decreases when 3d electrons increase [23, 24].

3.4. *Fluorescence emission spectra and quantum yields*

Fluorescence emission spectra and quantum yields were determined using ZnPc ($\Phi_F = 0.32$ in DMF [25]) as standard; 610 nm was chosen for excitation of the complexes. Quantum yields of all complexes are shown in table 3. Calculation of fluorescence quantum yield is performed by equation (1):

$$\phi_f = 0.32 \cdot \frac{A_{Znpc}}{S_{Znpc}} \cdot \frac{S}{A} \tag{1}$$

where Φ_f represents the fluorescence quantum yield of the complexes, A_{ZnPc} represents the absorbance of ZnPc at 610 nm, S_{ZnPc} represents emission area of ZnPc, A represents the absorbance of the complexes and S represents emission area of the complexes.

The excited singlet energy (*Es*) is calculated by equation (2):

$$Es = \frac{1}{2}(E^{abs} + E^{fl}) \tag{2}$$

where E^{abs} represents the energy of maximum absorption of the Q-band and E^{fl} represents the energy of maximum emission of fluorescence spectra upon excitation at 610 nm.

It can be seen that upon excitation at 610 nm (table 3) for the β-substituted complexes only **4w** showed a strong fluorescence emission at ca 688 nm with a Stock's shift of 8 nm and a fluorescence quantum yield (Φ_f) of 0.11; for the α-substituted complexes, only complex **3w** showed a strong fluorescence emission at 705 nm with a Stock's shift of 11 nm and a fluorescence quantum yield (Φ_f) of 0.07, indicating that complexes with closed shell electronic structure such as Zn^{2+} is beneficial to producing fluorescence emission, while complexes with open shell electronic structure such as Cu^{2+}, Ni^{2+} and Co^{2+} do not fluoresce because those electronic structures easily quench the singlet state of metallophthalocyanine with nonfluorescent radiation [26–28]. In addition, the excitation spectra were similar to absorption spectra and both were mirror images of the

Table 3. Quantum yields of the complexes.

Product	**3w**	**3x**	**3y**	**3z**	**4w**	**4x**	**4y**	**4z**
Maximum λ_{abs} (nm)	694	691	687	693	680	680	677	679
Maximum λ_{flu} (nm)	705	–	–	–	688	–	–	–
Stokes' shift (nm)	11	–	–	–	8	–	–	–
E_s (KJ mol^{-1})	171.3	–	–	–	175.2	–	–	–
τ (ns)	2.9	–	–	–	3.0	–	–	–
Φ_f	0.07	≈0	≈0	≈0	0.11	≈0	≈0	≈0

fluorescent spectra in DMSO for **3w** and **4w**. The proximity of the wavelength of each component of the Q-band absorption to the Q-band maxima of the excitation spectra for two complexes suggests that the electronic configurations of the ground and excited states are similar and not affected by excitation in DMSO. The observed Stokes shifts were typical of MPc complexes in DMSO [29–32].

3.5. *Rate of singlet oxygen yields*

The procedure for determination of singlet oxygen yield under irradiation was as follows: DMSO solutions containing phthalocyanine complexes (2.5×10^{-5} mol L^{-1}) and 1,3-diphenyl-benzoisofuran (DPBF, 2.4×10^{-5} mol L^{-1}) were prepared in the dark. 2.0 mL such solution in cuvette was bubbled by oxygen gas continuously and irradiated by 670 nm dot-state laser concurrently. Under irradiation, the phthalocyanine complexes produce singlet oxygen, then DPBF captures singlet oxygen and decomposes. The characteristic absorption at 417 nm of DPBF decreases, the concentration of DPBF was calculated using the Lambert-Beer Law. The time decay of absorbance at 417 nm for each phthalocyanine complex is first-order. The rate constants of singlet oxygen yields are listed in table 4, calculated by equation (3):

$$\ln \frac{[\mathrm{DPBF}]_0}{[\mathrm{DPBF}]_t} = kt \tag{3}$$

where $[\mathrm{DPBF}]_0$ and $[\mathrm{DPBF}]_t$ in mol L^{-1} are the concentrations of DPBF after and prior to irradiation, respectively. Values of k were the rate constants of singlet oxygen yields, t is the time of irradiation.

The quantum yield of singlet oxygen (Φ_Δ) is listed in table 4, which is calculated by equation (4) [33, 34]:

$$\frac{1}{\Phi_{\mathrm{DPBF}}} = \frac{1}{\Phi_\Delta} + \frac{1}{\Phi_\Delta}\frac{k_\mathrm{d}}{k_\mathrm{a}}\frac{1}{[\mathrm{DPBF}]} \tag{4}$$

where k_d is the decay rate constant of singlet oxygen in the respective solvent and k_a is the rate constant of the reaction of DPBF with $^1O_2$. The value $1/\Phi_\Delta$ is the intercept obtained from the Stern–Volmer plot ($1/\Phi_{\mathrm{DPBF}}$ *vs.* $1/[\mathrm{DPBF}]$).

It can be seen from table 4 that the complexes with zinc as central ion have the largest rate of singlet oxygen yields and quantum yield while the singlet oxygen yield of complexes with other central ions is less. Thus, complexes of central ion with closed shell electronic structure are beneficial to singlet oxygen production, while those with open shell electronic structure lead to less singlet oxygen production because the open shell electronic structure has increasing spin orbital coupling, enhancing intersystem

Table 4. Rate constants of singlet oxygen yields of all complexes.

Product	**3w**	**3x**	**3y**	**3z**	**4w**	**4x**	**4y**	**4z**
Central ion	Zn^{2+}	Ni^{2+}	Co^{2+}	Cu^{2+}	Zn^{2+}	Ni^{2+}	Co^{2+}	Cu^{2+}
Electronic configuration	$3d^{10}$	$3d^8$	$3d^7$	$3d^9$	$3d^{10}$	$3d^8$	$3d^7$	$3d^9$
k (min^{-1})	0.82	0.56	0.73	0.45	1.34	0.63	0.57	0.76
Φ_Δ	1.12	0.71	0.95	0.63	1.78	0.82	0.75	0.98

crossing [35–37]. There was no change in the Q band intensity during the Φ_{Δ} determinations, confirming that complexes are not degraded during singlet oxygen studies.

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References

[1] N.B. McKeown. *Phthalocyanine Materials Synthesis, Structure and Function*, Cambridge University Press, London (1998).
[2] N. Kobayashi. *Current Opinion in Solid State and Materials Science*, **4**, 345 (1999).
[3] C.C. Leznoff, A.B.P. Lever. *Phthalocyanines: Properties and Applications*, VCH, New York (1989).
[4] G. Antoon, D. Annelies, M. Ludwig, D.V. Dirk, H. Jorg, E. Alex, D.W. Peter. *Canada Int. J. Cancer*, **101**, 78 (2002).
[5] Y.S. Li, E.M. Kenney. *US Patent No*. 5763602 (1998).
[6] J.L. Huang, N.S. Chen, E.S. Liu, Z.F. Dai, J.D. Huang, S.L. Yang, H.Q. Chen. *Invention Patents of China*, ZL96117137.5 (1996).
[7] S.L. Marcus. *Proceedings of the IEEE*, **80**(6), 869 (1992).
[8] J. He, M.L. Agarwal, H.E. Larkin, L.R. Friedman, L.Y. Xue, N.L. Oleinick. *Photochem. Photobiol.*, **65**, 581 (1997).
[9] J.-P. Daziano, L. Humeau, M. Henry, M. Patrice, C. Michel, C. Christian. *Photochem. Photobiol. B: Biol.*, **43**, 128 (1998).
[10] A. Segalla, C.D. Borsarelli, S.E. Braslavsky, J.D. Spikes, G. Roncucci, D. Dei, G. Chiti, G. Jori, E. Reddi. *Photochem. Photobiol. Sci.*, **1**, 641 (2002).
[11] G. Ferraudi, J.C. Canales, B. Kharisov, J. Costamagna, J.G. Zagal, G. Cardenas-Jirón, M. Paez. *J. Coord. Chem.*, **58**(1), 89 (2005).
[12] Q.D. You. *Medicinal Chemistry (In Chinese)*, Chemical Industry Press, Beijing (2004).
[13] S.Z. Xia, G.L. Li. *Chin. J. Zoonoses.*, **3**, 233 (2004).
[14] S. Elz, A. Keller. *Pub. Med.*, **328**(7-8), 585 (1995).
[15] M.A. Farajzadeh, M. Ebrahimi, A. Ranji, E. Feyz, V. Bejani1, R. Maleki. *Microchim. Acta*, **150**, 173 (2005).
[16] Y. Shi. Edn. In *The Purifying Method of Chemicals for Laboratory*, 2nd Edn, D.D. Perrin, W.L.F. Arovego, D.R. Perrin (Eds.), Chemical Industry Press, Beijing (1997).
[17] O. Abimbola, M. David, N. Tebello. *J. Mol. Struct.*, **650**, 131 (2003).
[18] M. Willem. *J. Photochem Photobiol. B: Biol.*, **28**, 101 (1995).
[19] I.S. Mokhosi, N. Kuznetsova, T. Nyokong. *J. Photochem. Photobiol., A: Chem.*, **140**, 215 (2001).
[20] T. Nyokong. *Coord. Chem. Rev.*, **251**, 1707 (2007).
[21] J.D. Huang, E.S. Liu, S.L. Yang, N.S. Chen, J.L. Huang, J.P. Duan, Y. Chen. *Chin. Spectroscopy and Spectral Anal.*, **20**(1), 95 (2000).
[22] M. Durmus, T. Nyokong. *Polyhedron*, **26**, 3323 (2007).
[23] C. Marti, S. Nonell, M. Nicolau, T. Torres. *Photochem. Photobiol.*, **71**(1), 53 (2000).
[24] V. Chauke, M. Durmus, T. Nyokong. *J. Photochem. Photobiol., A*: *Chem*. (2007). Available online at www.sciencedirect.com
[25] X.F. Zhang, H.J. Xu. *J. Chem. Soc., Faraday Trans.*, **89**(18), 3347 (1993).
[26] M. Durmus, T. Nyokong. *Spectrochim. Acta, Part A* (2007). Available online at www.sciencedirect.com
[27] J.P. Xue, H.M. Hong, S.L. Cai, H. Liu, N.S. Chen, J.L. Huang. *Chin. J. Inorg. Chem.*, **21**(6), 810 (2005).
[28] J.D. Huang, E.S. Liu, S.L. Yang, D.F. Wu, N.S. Chen, J.L. Huang, R.Z. Ou-Yang. *Chin. J. Xiamen University (Natural Sci.)*, **36**(3), 399 (1997).
[29] P. Tau, A.O. Ogunsipe, S. Maree, M.D. Maree, T. Nyokong. *J. Porphyrins Phthalocyanines*, **7**(6), 439 (2003).
[30] D.P. Zoran, M.I. Khan, A.-M. Hor, L.G. Joshua, F.G. John. *J. Phys. Chem. B*, **106**, 8625 (2002).
[31] A. Ogunsipe, D. Maree, T. Nyokong. *J. Mol. Struct.*, **650**, 131 (2003).

[32] A. Ruck, G. Beck, R. Bachor, N. Akgun, M.H. Gschwend, R. Steiner. *J. Photochem. Photobiol. B: Biol.*, **36**, 127 (1996).
[33] W. Spiller, H. Kliesch, D. Wöhrle, S. Hackbarth, B. Röder, G. Schnurpfeil. *J. Porphyrins Phthalocyanines*, **2**, 145 (1998).
[34] H. Tayyaba, C.E.M. Anne, O. Bernard. In *Cancer medicine*, C.B. Robert, W.K. Donald, E.P. Raphael (Eds.), BC Decker Inc., London (2000).
[35] H. Shinohara, O. Tsaryova, G. Schnurpfeil, H. Nishide, D. Wöhrle. *J. Photochem. Photobiol., A: Chem.*, **184**, 50 (2006).
[36] Y.Q. Wu, X. Zuo, R.Z. Ou-Yang, E.S. Liu, S.L. Yang, N.S. Chen, J.L. Huang. *Chin. J. Chem. Phys.*, **12**(1), 93 (1999).
[37] Z.Y. Sheng, X.D. Ye, Z.X. Zheng, S.Q. Yu, N.G. Kee, P. Dennis, T. Ngai, C. Wu. *Macromolecules*, **35**, 3681 (2002).