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Synthesis and spectroscopic properties of a series of metal-free and metallo-phthalocyanines substituted with 8-quinolinoxy moieties

Wei-Li Li, Ji-Cheng Ma, Wen-Ju Li, Qiang Fu* and Kun Wang

Faculty of Chemistry; N,ortheast Normal University, Changchun 130024, P. R. China

Peripherally tetraquinolinoxy-substituted, metal-free phthalocyanines and metallo-phthalocyanines **1c–f, 2c–f** have been synthesised by reaction of an inorganic salt with phthalonitriles substituted with 5-(phenylamino)methyl-8-quinolinoxy and 5-[(4-chlorophenylamino)methyl]-8-quinolinoxy groups, respectively. The effects of metal ions [Zn(II), Cu(II), Co(II); N,i(II)], substituent, solvent and concentration on the UV-Vis spectra of these new complexes and their fluorescent properties are also described. The diamagnetic Zn(II) and Ni(II) complexes display intense fluorescence.

Keywords: phthalocyanines, synthesis, 8-quinolinoxy, UV–Vis, fluorescence

Phthalocyanines (Pcs), which are capable of including more than 70 metallic and non-metallic ions in the ring cavity,[1] have attracted considerable interest for many decades because of their remarkable electronic and optical properties. These properties make them suitable for a wide range of applications. Phthalocyanines are used not only as classical dyes in practical use but also as modern functional materials in scientific research.[2,3] Current research on phthalocyanines has expanded into several new applied fields including photovoltaics, electrochromism, optical data storage, laser dyes and liquid crystals, as well as chemical sensors and photosensitisers for photodynamic therapy.[4–9] However, due to the intermolecular interactions between the macrocycles, peripherally unsubstituted metal Pcs are practically insoluble in common organic solvents, thereby minimising their applications. The synthesis of soluble Pcs derivatives is important for solving this problem. Several synthetic strategies have been designed: one of the principal strategies for the molecular design and control of properties of phthalocyanines involves ring substitution on the peripheral and non-peripheral positions of the phthalocyanine ring, the other way is to introduce a different kind of transition metal to the central cavity.[10,11] In such a system, the metal in the central macrocyclic cavity and periphery can be chosen independently and special physical properties are introduced that are not observed in the phthalocyanine or metal fragment alone. So far, many novel substituted metal phthalocyanines have been synthesised using these strategies.[12–17] The family of reactive phthalocyanine molecules has been an interesting target for the development of further chemical reactions with phthalocyanine complexes.[18] Designed peripheral moieties on the phthalocyanines bearing heteroatoms (N, O, S) are used to confer solubility.[19–22] Notably, 8-quinolinol (8-QH) groups are especially useful to achieve solubility in most common solvents.[23,24] In addition, 8-QH is an electroluminescent material, thus the periphery of a phthalocyanine subsituted by 8-QH should show better optical properties.

Phthalocyanines are usually prepared by a high-temperature cyclotetramerisation processes of either phthalonitrile (liquid state method), phthalic anhydride (solid state method) and microwave-assisted methods,[25–27] in which the template effect afforded by a suitable metal cation is required. The reactions can be carried out in variety of solvents in the liquid state as well as under solvent-free conditions, but the second processes require temperature above 200 °C and difficult purification procedures.[28] The microwave-assisted method is a new synthetic method with short time and high yield characteristics, but is not conducive to mass production and lacks controllability, reproducibility and safety aspects. We now describe the synthesis of a series of new phthalocyanine compounds containing 5-(phenylamino)methyl-8-quinolinoxy or 5-[(4-chlorophenylamino)methyl]-8-quinolinoxy groups on the periphery positions using a liquid state method, and investigated their properties.

Experimental

5-(Phenylamino)methyl-8-quinolinol and 5-[(4-chlorophenylamino) methyl]-8 -quinolinol were prepared according to the literature.[29] All other reagents and solvents were commercially available and used without further purification. IR spectra were recorded on a Magna 560 FT-IR spectrophotometer using KBr pellets. The UV spectra were performed on a Cary 500 UV-Vis–NIR spectrophotometer. MS spectra were recorded on an LDI-1700 MALDI-TOF mass spectrometer. ^{1}H NMR spectra were recorded on a Varian XL-500 NMR spectrometer in DMSO-d_6. Elemental analyses were determined on a Perkin-Elmer 2400 CHN elemental analyser. Fluorescent spectra were measured on a Cary Eclipse fluorimeter.

4-(5-(Phenylamino)methyl-8-quinolinoxy)phthalonitrile (**1a**): Compounds **1a** and **2a** were prepared in the same way; **1a** is taken as example. 5-Phenylaminomethyl-8-quinolinol (0.01 mol, 2.50 g) and 4-nitrophthalonitrile (0.01 mol, 1.73 g) were dissolved in DMSO (30 mL). After stirring for 15 min, finely powdered LiOH (0.02 mol, 0.38 g) was added in portions during 2 h with efficient stirring. The reaction mixture was stirred at room temperature for 3 days, then the solution was poured into cool water (400 mL). The resulting precipitate was collected by filtration and washed by water, dried and recrystallised from ethanol to give a brick red solid **1a**. Yield: 90%. m.p. > 250 °C; IR (KBr), υ /cm^{-1}: 3043 (ArH), 2231 (C≡N), 1249 (C–O–C). ^{1}H NMR (500 MHz, DMSO-d_6) (δ: ppm): 8.83–8.69 (m, 2H, ArH), 8.00–6.27 (m, 11H, ArH), 4.74–4.76 (d, 2H, *J* = 5.0, –CH$_2$), 4.57 (m, 1H; N,–H). Elemental anal. Calcd for $C_{24}H_{16}N_4O$ (M = 376.13): C, 76.58; H, 4.28; N, 14.88. Found: C, 76.43; H, 4.25; N, 14.96%.

4-(5-[(4-chlorophenylamino)methyl]-8-quinolinoxy)phthalonitrile (**2a**): Yield: 86%. m.p. > 250 °C; IR (KBr), υ /cm^{-1}: 3041 (ArH), 2229 (C≡N), 1247 (C–O–C). ^{1}H NMR (500 MHz, DMSO-d_6) (δ: ppm): 8.86–8.87 (dd, 2H, *J* = 1.5, *J* = 1.5, ArH), 7.71–6.50 (m, 10H, ArH), 5.23 (t, 1H; N,–H), 4.76–4.75 (d, 2H, *J* = 5.0, –CH$_2$); Elemental anal. Calcd for $C_{24}H_{15}ClN_4O$ (M = 410.09): C, 70.16; H, 3.68; N, 13.64. Found: C, 70.33; H, 3.58; N, 13.55%.

Syntheses of 2,9,16,23-tetrakis(5-(phenylamino)methyl-8-quinolinoxy)-phthalocyanine (**1b**): Lithium metal (10 mmol, 0.08 g) was dissolved in 1-pentanol (30 mL) at 80 °C and then compound **1a** (1.8 mmol, 0.32 g) was added. The reaction mixture was heated to 135 °C and refluxed under N$_2$ for 5 h then the dark blue solution was allowed to cool to room temperature. A mixture of ethanol (20 mL) and glacial acetic acid (20 mL) was added. The resulting suspension was allowed to stand for 12 h, then the dark green product was filtered off and washed several times with ethanol to dissolve any unreacted precursor. The green product (**1b**) was dried under vacuum and purified by column chromatography (silica gel, CHCl$_3$), Compound **1b**: Yield: 49%. m.p. > 250 °C; IR (KBr), υ /cm^{-1}: 3406 (–NH), 2926 (alkyl CH$_2$), 1324 (C–N), 1250, 1088 (C–O–C). ^{1}H NMR (500 MHz, DMSO-d_6), (δ: ppm): 8.98–8.50 (m, 8H, ArH), 7.81–6.29 (m, 46H, ArH), 4.79–4.84 (m, 4H, –NH–CH$_2$), 4.73 (d, 8H, –CH$_2$); UV-Vis λ_{max} (nm) in DMF: 612, 680; Elemental anal. Calcd for $C_{96}H_{66}N_{16}O_4$

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* Correspondent. E-mail: fqiang@nenu.edu.cn

(M = 1506.55): C, 76.48; H, 4.41; N, 14.86. Found: C, 76.43; H, 4.46; N, 14.93%.

Syntheses of 2,9,16,23-tetrakis (5-[(4-chlorophenylamino)methyl]-8-quinolinoxy)-phthalocyanine (**2b**): The preparation of compound **2b** was similar to that of compound **1b**, but in which compound **2a** (1.80 mmol, 0.33 g) was the reactant. Compound **2b**: Yield: 52%. m.p. > 250 °C; IR (KBr), υ /cm^{-1}: 3387 (–NH), 2959–2863 (alkyl-CH$_2$), 1299 (C–N), 1252, 1093 (C–O–C). ^{1}H NMR (500 MHz, DMSO-d$_6$) (δ: ppm): 8.82–7.94 (m, 8H, ArH), 7.60–6.46 (m, 42H, ArH), 5.30 (m, 4H, CH$_2$N–H), 4.70 (d, 8H, –CH$_2$); UV-Vis λ_{max} (nm) in DMF: 672, 704; MS (MALDI-TOF): *m/z* 1647.8 [M+2H]$^+$. Elemental anal. Calcd for $C_{96}H_{62}Cl_4N_{16}O_4$ (M = 1645.44): C, 70.07; H, 3.80; N, 13.62. Found: C, 70.10; H, 3.72; N, 13.56%.

Syntheses of 2,9,16,23-tetrakis(5-(phenylamino)methyl-8-quinolinoxy)-phthalocyaninatozinc(II) (**1c**) *and 2,9,16,23-tetrakis (5-[(4-chlorophenylamino)methyl]-8-quinolinoxy)-phthalocyaninatozinc(II)* (**2c**): A mixture of compound **1a** (1.80 mmol, 0.32 g), $Zn(CH_3COO)_2$• $2H_2O$ (0.30 mmol, 0.066 g) and 1, 8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.75 mL) was heated at 135 °C in dry 1-pentanol (20 mL) with stirring under N$_2$ for 8 h. After cooling to room temperature, the reaction mixture was treated with ethanol and then filtered off and washed with water to remove unreacted $Zn(CH_3COO)_2$•$2H_2O$. The obtained product was purified by column chromatography (silica gel, CHCl$_3$–MeOH, 95:5). The green product (**1c**) was collected, then dried under vacuum. The preparation of compound **2c** was similar to that of compound **1c**.

1c: Yield: 52%. m.p. > 250 °C; IR (KBr), υ /cm^{-1}: 3645 (–NH), 2924–2850 (alkyl CH$_2$), 1251, 1088 (C–O–C), 1317 (C–N), 749 (M–N). ^{1}H NMR (500 MHz, DMSO-d$_6$) (δ: ppm): 8.88–8.61 (m, 8H, ArH), 7.84–6.26 (m, 44H, ArH), 4.36 (d, 8H, –CH$_2$), 4.71–4.54 (m, 4H, –NH–CH$_2$); UV-Vis, λ_{max} (nm) in DMF: 352, 613, 683. MS (MALDI-TOF), *m/z*: 1569.5 [M+H$^+$]. Elemental anal. Calcd for $C_{96}H_{64}N_{16}O_4Zn$ (M = 1568.46): C, 73.39; H, 4.11; N, 14.26. Found: C, 73.37; H, 4.15; N, 14.35%.

2c: Yield: 50%. m.p. > 250 °C; IR (KBr), υ /cm^{-1}: 2926 (alkyl CH$_2$), 1249, 1091 (C–O–C), 726 (M–N) cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d$_6$) (δ:ppm): 8.90–8.63 (m, 8H, ArH), 7.86–6.43 (m, 40H, ArH), 4.69 (d, 8H, –CH$_2$), 4.78 (m, 4H, –NH–CH$_2$); UV-Vis λ_{max} (nm) in DMF: 355, 613, 683. MS (MALDI-TOF), *m/z*: 1708 (M+4H$^+$). Elemental anal. Calcd for $C_{96}H_{60}N_{16}Cl_4O_4Zn$ (M = 1704.3): C, 67.48; H, 3.54; N, 13.11. Found: C, 67.43; H, 3.58; N, 13.15%.

Syntheses of 2,9,16,23-tetrakis(5-(phenylamino)methyl-8-quinolinoxy)-phthalocyaninatocopper(II) (**1d**) *and 2,9,16,23-tetrakis (5-[(4-chlorophenylamino)methyl]-8-quinolinoxy)-phthalocyaninatocopper(II)* (**2d**): The preparation of compound **1d** was similar to that of compound **1c**, in which compound **1a** (1.90 mmol, 0.40 g), anhydrous CuCl$_2$•2H$_2$O (0.60 mmol, 0.10 g) and DBU (0.75 mL) were the reactants. The preparation of compound **2d** was similar to that of compound **1d**, in which compound **2a** (1.80 mmol, 0.33 g) was reactant.

1d: Yield: 59%. m.p. > 250 °C; IR (KBr), υ /cm^{-1}: 3033–2856 (alkyl CH$_2$), 1251 (C–O–C), 1367 (C–N), 734 (M–N). UV-Vis λ_{max} (nm) in DMF: 678. Elemental anal. Calcd for $C_{96}H_{64}N_{16}O_4Cu$ (M = 1567.46): C, 73.48; H, 4.11; N, 14.28. Found: C, 73.69; H, 4.13; N, 14.36%.

2d: Yield: 59%. m.p. > 250 °C; IR (KBr), υ /cm^{-1}: 2924–2853 (alkyl CH$_2$), 1248, 1084 (C–O–C), 1370 (C–N), 790 (M–N). UV-Vis λ_{max} (nm) in DMF: 350, 620, 683. Elemental anal. Calcd for $C_{96}H_{60}N_{16}Cl_4O_4Cu$ (M = 1703.3): C, 67.55; H, 3.54; N, 13.13. Found: C, 67.59; H, 3.51; N, 13.24%.

Synthesis of 2,9,16,23-tetrakis(5-(phenylamino)methyl-8-quinolinoxy)-phthalocyaninatocobalt(II) (**1e**) *and 2,9,16,23-tetrakis(5-[(4-chlorophenylamino)methyl]-8-quinolinoxy)-phthalocyaninatocobalt (II)* (**2e**)

The preparation of compound **1e** was similar to that of **1c**, in which compound **1a** (1.80 mmol, 0.32 g), CoCl$_2$•6H$_2$O (0.60 mmol, 0.15 g) and DBU (0.75 mL) were selected as the reactants. The preparation of compound **2e** was similar to that of compound **1e**, in which compound **2a** (1.80 mmol, 0.33 g) was the reactant.

1e: Yield: 53%. m.p. > 250 °C; IR (KBr), υ /cm^{-1}: 2925–2856 (alkyl CH$_2$), 1373 (C–N), 1252 (C–O–C), 750 (M–N). UV-Vis λ_{max} (nm) in DMF: 672. Elemental anal. Calcd for $C_{96}H_{64}N_{16}O_4Co$ (M = 1563.46): C, 73.70; H, 4.12; N, 14.32. Found: C, 73.73; H, 4.11; N, 14.35%.

2e: Yield: 56%. m.p. > 250 °C; IR (KBr), υ /cm^{-1}: 2929–2858 (alkyl CH$_2$), 1252, 1074 (C–O–C), 1369 (C–N), 789 (M–N). UV-Vis λ_{max} (nm) in DMF: 669. Elemental anal. Calcd for $C_{96}H_{60}N_{16}Cl_4O_4Co$ (M = 1699.31): C, 67.73; H, 3.55; N, 13.16. Found: C, 67.75; H, 3.58; N, 13.23%.

Synthesis of 2,9,16,23-tetrakis(5-(phenylamino)methyl-8-quinolinoxy)-phthalocyaninatonickel(II) (**1f**) *and 2,9,16,23-tetrakis(5-[(4-chlorophenylamino)methyl]-8-quinolinoxy)-phthalocyaninatonickel (II)*(**2f**)

The preparation of compound **1f** was similar to that of compound **1c**, in which compound **1a** (1.80 mmol, 0.32 g); NiCl$_2$•6H$_2$O (0.60 mmol, 0.15 g) and DBU (0.55 mL) were selected as the reactants. The preparation of compound **2f** was similar to that of compound **1f**, in which compound **2a** (1.81 mmol, 0.33 g) was the reactant.

1f: Yield: 51%. m.p. > 250 °C; IR (KBr), υ /cm^{-1}: 2927–2856 (alkyl CH$_2$), 1252 (C–O–C), 1360 (C–N), 741 (M–N). UV-Vis λ_{max} (nm) in DMF: 676. Elemental anal. Calcd for $C_{96}H_{64}N_{16}NiO_4$ (M = 1562.46): C, 73.71; H, 4.12; N, 14.33. Found: C, 73.75; H, 4.15; N, 14.30%.

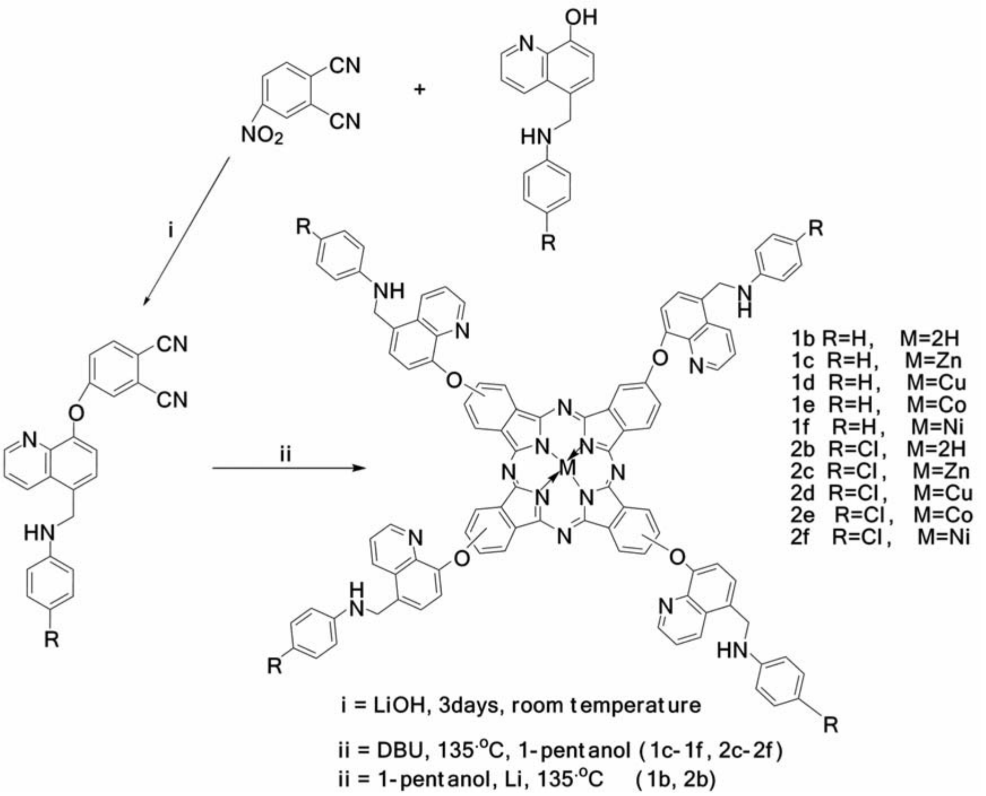
2f: Yield: 49%. m.p. > 250 °C; IR (KBr), υ /cm^{-1}: 2923–2854 (alkyl CH$_2$), 1254 (C–O–C), 748 (M–N) cm^{-1}. UV-Vis λ_{max} (nm) in DMF: 640, 674. Elemental anal. Calcd for $C_{96}H_{60}Cl_4N_{16}NiO_4$ (M = 1698.31): C, 67.74; H, 3.55; N, 13.17. Found: C, 67.77; H, 3.59; N, 13.20%.

Results and discussion

The synthetic route in this work is shown in Scheme 1. Compounds **1a** and **2a** were prepared by the base-catalysed nucleophilic aromatic nitro-displacement of 4-nitrophthalonitrile in the presence of 5-(phenylamino)methyl-8-quinolinol and 5-[(4-chlorophenylamino) methyl]-8-quinolinol. The reaction was carried out in a single step synthesis by using the LiOH as the nitro-displacing base at room temperature in DMSO.[30,31] the Pcs was prepared by cyclotetramerisation of the phthalonitrile derivatives **1a** and **2a** in 1-pentanol at refluxing temperature under N$_2$ in the presence of DBU or lithium metal catalyst.[32] A similar reaction has been effectively used in the preparation of a variety of ether-or thioether-substituted phthalonitrile derivatives.[2,33–35] The precursors **1a** and **2a** were purified by recrystallisation, while phthalocyanines required column chromatography. The yields of tetra-substituted Pcs were satisfactory. The characterisations of the products included elemental analysis, mass spectrum, IR, ^{1}H NMR, UV-Vis and fluorescent spectra.

IR, MS, ^{1}H NMR and elemental analysis

Spectral investigations of the newly synthesised intermediates and phthalocyanines are in accordance with the proposed structures. Comparison of the IR spectra of each step offer some information as to the nature of the products. It is found that the sharp peak for the C≡N vibrations around 2230 cm^{-1} are associated with nitrile groups, which disappeared after phthalocyanine formation. The appearance of new absorption bands at about 1254 cm^{-1} and 1092 cm^{-1} (Ar–O–Ar) for **1b–f** and **2b–f** clearly indicates that substituents have connected to the phthalocyanine ring. In order to further confirm the proposed structures of Pcs, the mass spectrum of representatives **1c**, **2b** and **2c** were measured. Molecular ion peaks of **1c**, **2b** and **2c** at 1569, 1647.8 and 1707 are observed, respectively, consistent with the proposed structures. In addition, the ^{1}H NMR spectra of **1a–c** and **2a–c** display the characteristic resonances for precursors and Pc; the ^{1}H NMR spectra of **1a** and **2a** are almost identical except for a small shift. Taking compound **1a** for example, in its ^{1}H NMR spectrum, the peak at 8.83 can be attributed to the quinoline ring CH=N proton absorption peak, while the multiple absorption peaks of protons on the benzene ring are between 8.00 ppm and 6.27 ppm. Furthermore, absorption peaks at 4.76–4.74 ppm and 4.57 ppm are assigned to methylene and –NH protons, respectively. ^{1}H NMR spectra of H$_2$Pc and MPc derivatives in DMSO show that all the substituent and Pc ring protons are observed in their respective regions. A singlet, assigned to quinoline ring protons, appears in the range of 8.98–8.50 (integrating for 8 protons) in the ^{1}H NMR spectra of **1b–2b** and **1c–2c**. A multiplet, assigned to Pc aromatic ring protons, appears in the range of 7.81–6.29 (integrating for 42 protons) in the ^{1}H NMR spectra of **1b–2b** and **1c–2c**. Comparing the ^{1}H NMR spectra of **1c** with **1a**, the hydrogens around the Pc ring show similar, poorly resolved wide peaks with the same chemical shift order. These peaks become wide, which is one of the characteristics of Pc compounds with an M(II) ion at the center of the Pc ring, and the poor peak split may be ascribed to the limited solubility of **1c**. In addition, the elemental analytical results of the starting materials



Scheme 1 Synthesis of **1b–f, 2b–f**.

and phthalocyanines also show good agreement with the calculated values.

UV-Vis analysis

The Pcs (**1b–f** and **2b–f**) shows two characteristic absorption regions: one of them is in the UV region at about 300–400 nm (B band) and the other is in the visible part of the spectra around 600–800 nm (Q band). In this study, we mainly discuss the impacts of concentration, solvent, central metal ion and peripheral group on the Q band.

The UV-Vis spectra of **1c** and **2c** show similar phenomena in their solutions in DMF at different concentrations, and the UV-Vis spectra of **1c** should give much information. Thus the UV-Vis spectrum of **1c** is selected to account for the impacts of concentration on UV-Vis absorbance. As shown in Fig. 1, the concentration significantly influences UV-Vis absorbance intensity, and at Q-band, the relationship of λ_{max} intensity and concentration is generally consistent with the Beer-Lambert law. The concentration dependence of the UV-Vis spectra of these derivatives is further assessed in order to prove the absence of aggregation. Although the position of the Q-band of **1c** at 683 nm and 612 nm is constant with increasing the concentration, the aggregate absorption peak becomes stronger with increasing the concentration.

A obvious difference of λ_{max} is observed when the MPc dissolve in different solvents. As shown in Fig. 2, the λ_{max} of Q band is located at 701 and 688 nm when **2c** is dissolved in DMF and $CHCl_3$, respectively. It is suggested that there is interaction between MPc and solvent. On the one hand, the polar of solvents plays an important role for ground state and excited states of Pc complexes, this may result in a smaller π–π* energy gap, corresponding to a red shift of λ_{max}. On the

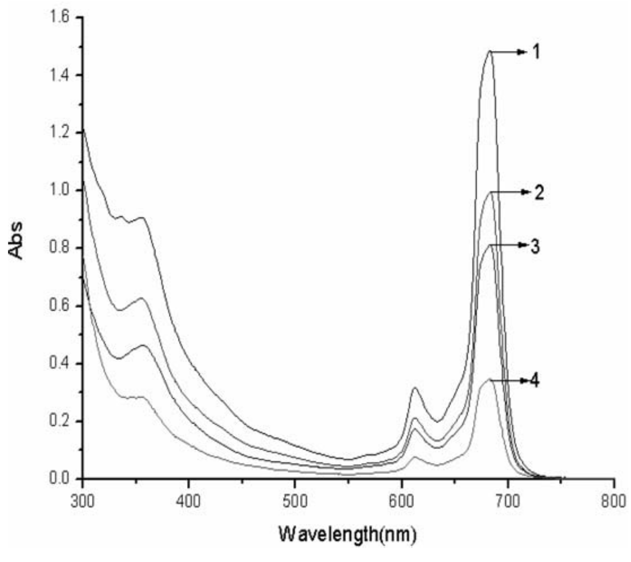


Fig. 1 UV-Vis spectra of **1c** in DMF at various concentration: 1 = 5 × 10^{-5} mol L^{-1}, 2 = 2.5 × 10^{-5} mol L^{-1}, 3 = 1 × 10^{-5} mol L^{-1}, 4 = 0.2 × 10^{-5} mol L^{-1}.

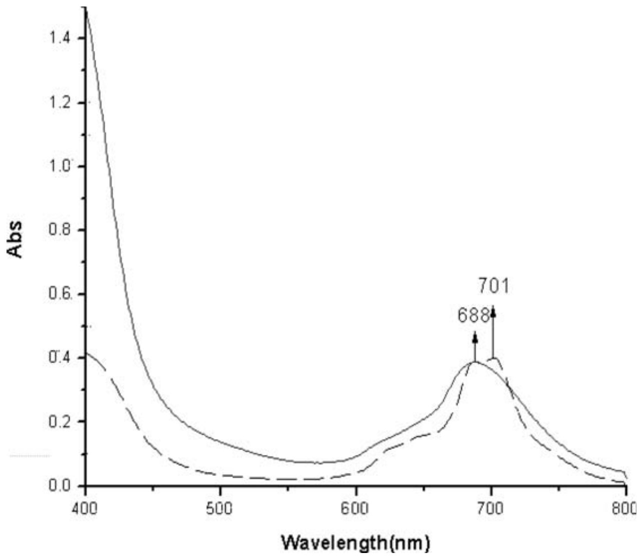


Fig. 2 UV-Vis spectra of **2c** in DMF (dash line) and $CHCl_3$ (solid line) Concentration = 1 ×10^{-5} mol L^{-1}.

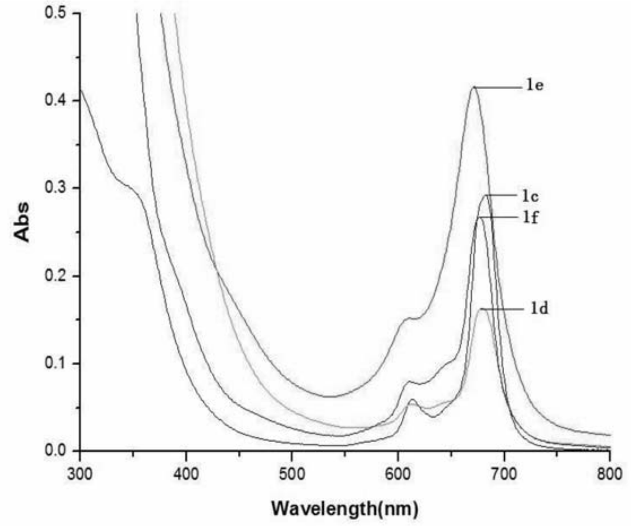


Fig. 3 UV-Vis spectra of **1c–f** in DMF concentration = 5 × 10^{-6} mol L^{-1}.

other hand, the coordinating groups of solvent can stabilise the phthalocyanine ground state, thus resulting in λ_{max} blue shift. Usually, these two factors tend to be mixed for polar solvents containing O-or N-donor groups.[36] DMF is a typical strong polarity solvent, which obviously can cause a λ_{max} red shift; but the weakly coordinated effect of the DMF molecule through its oxygen atom can only result in inappreciable blue shift. Thus the mixed effects result in a λ_{max} red shift to 701 nm. The polarity of $CHCl_3$ is weaker than that of DMF, corresponding to slight red shift for λ_{max}.

The UV-Vis spectra of **1c–f** are selected to monitor the impact of the central metal ion on the Q band as shown in Fig. 3. The strong absorption regions ranging from 672 to 684 nm (Q band) are associated with the excitation between the HOMO-A_{1g} ground state [$(a^2_{1u})(\pi)$] and the degenerate LUMO-[$e_g(\pi^*)$]. The first excited singlet state has E_u symmetry from the $(a^1_{1u}e^1_g)$ configuration. Clearly, when the Pcs possess the same substituted group [5-(phenylamino)methyl-8-quinolinoxy], the Q band of the corresponding Pcs varies with the central metal ion. The peak shift may be attributed to the different polarisation of central metal ions.[37] In general, as the atomic number of the metal ion increases, a red shift of the absorption peak is observed, and the order of red shift is Co(II)<Ni(II)<Cu(II)<Zn(II). The UV-Vis spectra of **2c–f** in DMF also show similar phenomena.

Generally, the substituting groups of Pcs can affect the location of the Q band to some extent, compared with the unsubstituted ones. In order to investigate the influence of different substituent groups on the Q band, the UV-Vis spectra of **1c** and **2c** are summarised in Fig. 4. The results show that an obvious difference of Q band is observed between **1c** and **2c** when the peripheral groups are replaced by 5-(phenylamino)methyl-8-quinolinoxy and 5-[(4-chlorophenylamino) methyl]-8-quinolinoxy, respectively. A possible reason is that the chlorine atoms attract the electron cloud of the conjugated phthalocyanine ring, when the hydrogen atoms on the benzene ring are substituted by chlorine atoms. The π–π* of the energy gap becomes narrow with changing the distribution of electron cloud density to induce the red-shift of Q band.[38]

Fluorescent characterisation

The emission spectra of **1b–f** and **2b–f** in DMF were recorded at room temperature after correcting for self-absorption. The spectra of **2b–f** in DMF show similar phenomena as **1b–f**. As shown in Fig. 5. The metal-free phthalocyanine **1b** exhibits two strong emission peaks located at 475 and 719 nm. The metallo-phthalocyanines **1c–f** show various fluorescent emissions, which can be attributed to two categories. The fluorescent emissions of **1d** and **1e**, containing the paramagnetic Cu(II) and Co(II) atoms, are relatively weak. In contrast, **1c** and **1f**, containing the diamagnetic Zn(II) and Ni(II), display intense fluorescence emission. In particular, **1c** presents strong fluorescent emissions located at 715 and 754 nm. The reason is that no single electron occupies the central metal ion with a closed-shell electronic structure, which greatly reduces the role of spin-orbit coupling. Then, intersystem crossing probability is reduced. As a result, the probability of fluorescence emission is improved.[39] This phenomenon is in good agreement with reported results.[40, 41]

Solubility

The substitution of Pcs decreases intermolecular interactions, which prohibits them forming dimers. Thus, substituents on the periphery of a Pc significantly enhances its solubility in organic solvents, such as in pyridine, chloroform, acetone and DMF. On the other hand, based on our experimental results, the solubility of MPc is also central metal ion dependent. It is found that H_2Pc and ZnPc have better solubility than the other systems.

Conclusion

In conclusion, a series of novel soluble Pcs, modified by four 8-HQ derivative moieties, has been successfully prepared and characterised. The UV-Vis spectra of **1–4** reveal some special properties in terms of the impact of concentration, organic solvent, metal ion and substituent on the Q-bands. It is found that concentration has a significant influence on the UV-Vis absorbance intensity without position changes; oxygen-containing groups of solvent and phthalocyanine favour coordination, resulting in λ_{max} red shifts. The red shift of the absorption peak

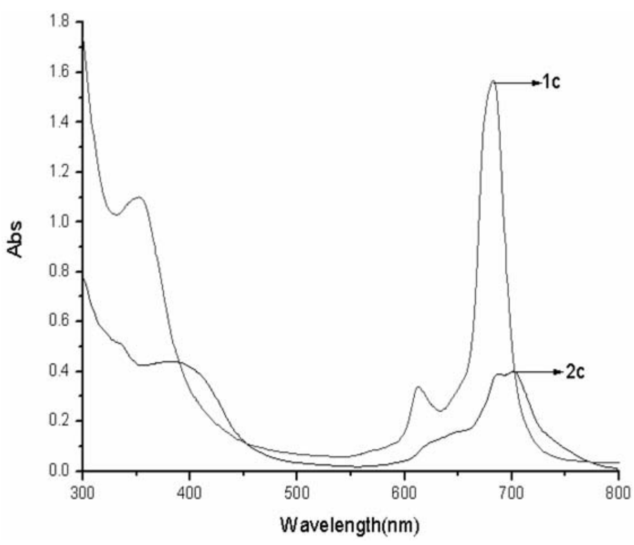


Fig. 4 UV-Vis spectra of **1c** and **2c** in DMF Concentration = 1 × 10^{-5} mol L^{-1}.

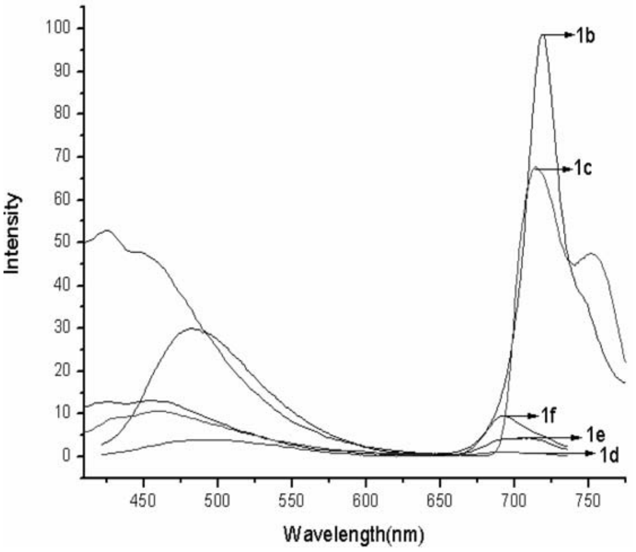


Fig. 5 Fluorescent emission spectra of **1b–f** in DMF with concentration = 1 × 10^{-5} mol L^{-1} and λ_{ex} = 380 nm.

is central metal dependent, the order of red shift is Co(II)< Ni(II)<Cu(II)<Zn(II). Moreover, the substituent groups of Pcs can affect the location of the Q band to some extent. The central metal ions of Pcs significantly influence fluorescent intensity.

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