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Meso 位单取代卟啉及其配合物的合成、表征和光谱性质

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摘要：设计合成了一系列新型的 *meso* 位 *N*,*N*-二甲氨基苯基或 *N*-苯基咔唑基单取代卟啉(**5a~c**)及其锌配合物(**6a~c**),用高分辨质谱、^{1}H NMR、紫外–可见光谱及 X 射线单晶衍射方法等对结构进行了表征;研究了卟啉化合物及其配合物的热稳定性及荧光性质。结果表明，这些卟啉化合物及其锌配合物在 400~410 nm 之间具有强的吸收且具有很好的热稳定性，荧光量子产率在 0.05~0.09;另外还分析了 *meso* 位不同取代基对光谱性质的影响。

关键词：卟啉；配合物；合成；晶体结构；荧光

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Syntheses, Characterizations, Spectroscopic Properties of *Meso*-mono-substituted Porphyrins and Their Metal Complexes

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Abstract: A series of novel asymmetrical meso-mono-substituted porphyrin derivatives and their zinc complexes with *N*,*N*-dimethylphenylamine phenyl and *N*-phenyl-carbazole were synthesized. Their structures and photophysical properties were characterized by MS, ^{1}H NMR, single Crystal X-ray diffraction analysis, thermogravimetric analysis (TGA), UV-Vis absorption spectroscopy, and photoluminescence spectroscopy. The results showed that free base porphyrins (**5a~c**) and their zinc porphyrins (**6a~c**) exhibited a strong absorption in the range of 400~450 nm with molar absorptivity of ~10^5 L·mol^{-1}·cm^{-1}. Their emission were characterized in solution by large Stokes shifts (80~290 nm) and the fluorescence quantum yields ranged from 0.05 to 0.09. The compounds had also shown high thermal stability. In addition, the effect of the different substituent groups of the meso positions on the photophysical properties was studied. CCDC: 1450675, **5a**; 1471067, **6a**.

Keywords: porphyrins; complex; synthesis; crystal structure; photoluminescence

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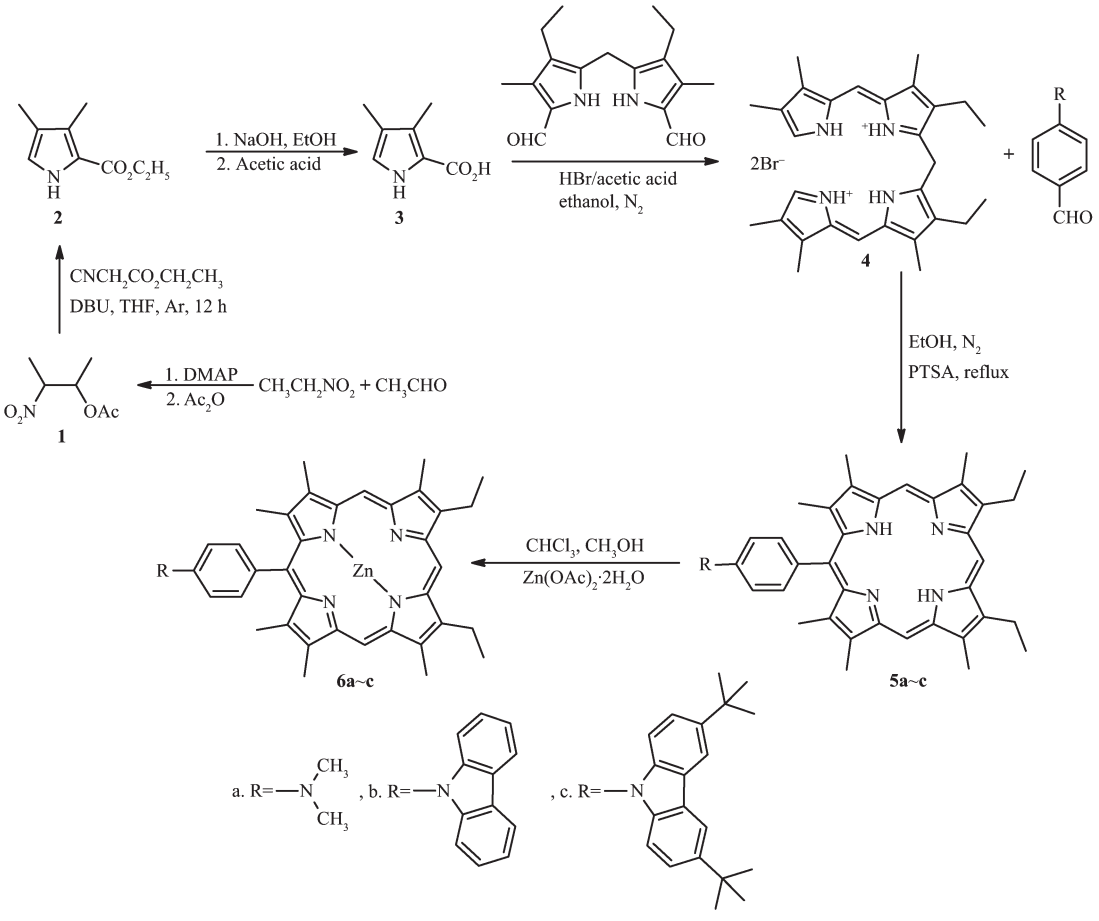
0 Introduction

Porphyrin and porphyrin derivatives have received great attention and study for many years due to their unique chemical and optical properties, such as good photostability, rigid molecular structures and many reaction sites. They play important roles in many fields and show a wide range of perspective applications in molecular electronic devices[1], photodynamic therapy[2-3], catalytic reactions[4-5], solar energy transduction[6-9], mimicking enzymes[10-11], and sensors[12-13]. The diversity in functions has a great impetus on the extensive development of the design and synthesis of novel porphyrin derivatives. Among *meso*-substituted porphyrins, symmetrical porphyrins are usually more easily synthesized than unsymmetrical porphyrins[14-15]. However, to the best of our knowledge, only a few of *meso*-mono-substituted porphyrin derivatives have been synthesized[16-19]. The nature and propensity of *meso*-substituents are mainly responsible for tuning the electronic, chemical and thermal properties of porphyrin derivatives[20-22]. *N*,*N*-dimethylphenylamine phenyl and *N*-phenyl-carbazole groups with the strong electron ability by introducing the meso position of porphyrin ring can be used for tuning their optical, electrochemical, and photophysical properties[21-24]. However, *meso*-mono-substituted porphyrin derivatives with *N*, *N*-dimethylphenylamine phenyl or *N*-phenyl-carbazole groups could not be characterized up to now probably due to the poor reactivity of 4-(dimethylamino) benzaldehyde or 4-(carbazol-9-yl)benzaldehyde under normal Lindsey porphyrin condensation. Therefore, we herein report the synthesis, characterization, and spectroscopic property studies of a series of new mono-substituted porphyrin derivatives (**5a~c**) and their zinc complexes (**6a ~c**) with *N*,*N*-dimethylphenylamine phenyl or *N*-phenyl-carbazole groups (Scheme 1).



Scheme 1

1 Experimental

1.1 Instruments

Column chromatography and TLC were performed on C-200 (Wakogel) and Kieselgel 60 F254 (Merck), respectively. ^{1}H NMR spectra were recorded on a Bruker DRX-600 AVANCE Ⅲ spectrometer. Chemical shifts for ^{1}H NMR spectra were expressed using $CDCl_3$ (δ=7.26) as the internal standard. The mass spectra data were obtained on a LTQ Orbitrap XL spectrometer in ESI mode. UV-Vis spectra were carried out on a Shimadzu UV-3100 spectrophotometer. All the emission spectra were measured in FluoroLog-3-TCSPC (HORIBA Scientific, Edison) equipped with a 450 W CW xenon lamp and an Open-Electrode TE-Cooled CCD Detector (Syncerity). Thermogravimetric analysis (TGA) measurements were performed on a Netzsch TG 209 analyzer under nitrogen at a scan rate of 10 ℃·min^{-1}.

1.2 Materials

Unless otherwise noted, all chemicals and solvents were of analytical reagent grade and used directly as received. Dry dichloromethane was freshly distilled over CaH_2 under nitrogen. Dry tetrahydrofuran (THF) was distilled from sodium/benzophenone under nitrogen. 2-Acetoxy-3-nitrobutane[25], 3,3′-diethyl-5,5′-diformyl-4, 4′-dimethyl-2, 2′-dipyrrylmethane[26], 4-(carbazol-9-yl)benzaldehyde[27] were prepared according to the related literature method, respectively. In addition, the introduction of *tert*-butyl group into the 3- and 6-positions of carbazole could readily lead to the good solubility and 4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-benzaldehyde was synthesized according to the similar procedure of 4-(carbazol-9-yl)benzaldehyde.

1.3 Synthesis

The porphyrins and their complexes were synthesized as shown in Scheme 1.

1.3.1 Synthesis of ethyl 3,4-dimethyl-1*H*-pyrrole-2-carboxylate (**2**)

Ethyl isocyanoacetate (7.6 mL, 69.4 mmol) and 2-Acetoxy-3-nitrobutane (11.7 g, 61.8 mmol) were dissolved in dry THF (160 mL) under an Ar atmosphere and cooled with an ice bath. DBU (21.6 mL, 144.7 mmol) was slowly added and the solution was stirred. After dropping, the reaction mixture was stirred for another 12 h. Hydrochloric acid (1 mol·L^{-1}) was added until the pH value of the solution became 7. The solution was diluted with water (50 mL). The organic materials were extracted with $CHCl_3$ (3×100 mL), and the combined organic layer was washed by water and brine, then dried with anhydrous sodium sulfate and the solvent was evaporated to get crude product which was further purified by column chromatography on silica gel with 60% (*V*/*V*) CH_2Cl_2-heptane as eluent. The white solid was obtained. Yield: 8.4 g, 81.1%. ^{1}H NMR ($CDCl_3$): δ 8.68 (s, 1 H), 6.66 (s, 1 H), 4.31(q, 2 H), 2.27 (s, 3 H), 2.01(s, 3 H), 1.35 (t, 3 H).

1.3.2 Synthesis of 3, 4-dimethyl-1*H*-pyrrole-2-carboxylic acid (**3**)

Compound **2** (9.35 g, 57.4 mmol) was dissolved in degassed absolute ethanol (150 mL) and the mixture was heated to reflux. A solution of sodium hydroxide (10.4 g, in 20 mL of water) was added dropwise and the reaction mixture was refluxed for 4 h. The mixture was then poured into ice, and diluted with water. After 10 min, acetic acid was added until pH=4. The solid was filtered using a sintered funnel and washed with water, dried in vacuo to afford compound **3** (5.98 g, 75%) as a white solid. ^{1}H NMR (DMSO-d_6): δ 10.96 (s, 1 H), 6.64 (s, 1 H), 2.15 (s, 3 H), 1.91 (s, 3 H).

1.3.3 Synthesis of 1,19-dideoxy-8,12-diethyl-2,3,7,13,17,18-hexamethyl-*a*,*c*-biladiene dibromide (**4**)

Compound **3** (3.91 g, 28.10 mmol) and 3,3′-dicarboxy-5, 5′-diformyl-4, 4′-dimethyl-dipyrryl methane (4.02 g, 14 mmol) were mixed and degassed ethanol (200 mL) was added and the mixture was heated to reflux for 10 min. Hydrobromic acid/acetic acid solution (33%, *V*/*V*, 20 mL) was added to the reaction mixture, which was checked by UV-Visible spectra, and the reaction was stopped after 5 min (the reaction should be stopped as soon as possible). The reaction mixture was cooled using dry ice bath, then added to cold diethyl ether (−20 ℃) (300 mL), followed by

filtration in sintered funnel and washing with cold ether. After drying in a desiccator, compound **4** (6.50 g, 77%) was acquired and used directly in the next step without any further purification.

1.3.4 Synthesis of 5-(4-*N*,*N*-dimethylamino phenyl)-13,17-diethyl-2,3,7,8,12,18-hexamethyl-porphyrin (**5a**)

A solution of 4-(dimethylamino)benzaldehyde (149.1 mg, 1.0 mmol) and compound **4** (602.0 mg, 1.0 mmol) in ethanol (150 mL) was heated to reflux, and nitrogen was bubbled through the system. Then, 10.0 mL of a solution of para-toluene sulfonic acid (PTSA, 2.50 g) in ethanol was slowly added during 18 h. The deep red solution was refluxed for 48 h under N_2. The organic solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2, washed with saturated $NaHCO_3$ solution. The organic solution was separated by use of a separatory funnel. The solvent was removed under vacuum and the remaining residue was purified by repeated column chromatography on silica gel with CH_2Cl_2-petroleum ether as eluents. The bright red band eluted was collected and dried. Recrystallization from CH_2Cl_2/methanol afforded compound **5a**. Yield: (251.1 mg, 44.1%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.15 (2H, s, *meso-H*), 9.93(1H, s, *meso-H*), 7.79 (2H, m, Ar-*H*), 7.04 (2H, m, Ar-*H*), 4.04 (4H, q, pyrro-CH_2CH$_3$), 3.64 (6H, s, pyrro-CH_3), 3.53(6H, s, pyrro-CH_3), 3.22(6 H, s, -N(CH_3)$_2$), 2.54(6 H, s, pyrro-CH_3), 1.88(6 H, t, CH$_2$CH_3), −3.16(1 H, s, N*H*), −3.27 (1 H, s, N*H*); HRMS (ESI): Calcd. for $C_{38}H_{44}N_5$(M+H$^+$): 570.359 1, Found: 570.358 5; UV-Vis (CH_2Cl_2): λ_{max} / nm (ε/(L·mol^{-1}·cm^{-1})): 403(2.143×10^5), 500 (4.77×10^4), 535 (1.69×10^4), 573 (1.49×10^4), 637 (1.28×10^4).

1.3.5 Synthesis of 5-(4-*N*-carbazolylphenyl)-13,17-diethyl-2,3,7,8,12,18-hexamethyl-porphyrin (**5b**)

This compound was prepared in 31.5% yield (217.9 mg), as described for **5a**, starting from 4-(carbazol-9-yl)benzaldehyde (271.3 mg, 1 mmol). ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.20 (2H, s, *meso-H*), 9.98 (1H, s, *meso-H*), 8.29 (4 H, m, Ar-*H*), 7.93 (2 H, d, Ar-*H*), 7.75(2 H, d, Ar-*H*), 7.62(2 H, m, Ar-*H*), 7.43(2 H, m, Ar-*H*), 4.08 (4 H, q, pyrro-CH_2CH$_3$), 3.66 (6 H, s, pyrro-CH_3), 3.59 (6 H, s, pyrro-CH_3), 2.70 (6 H, s, pyrro-CH_3), 1.89(6 H, t, CH$_2$CH_3), −3.14(1 H, s, N*H*), −3.28(1 H, s, N*H*); HRMS (ESI): Calcd. for $C_{48}H_{46}N_5$ (M+H$^+$): 692.374 8, Found: 692.375 4; UV-Vis (CH_2Cl_2): λ_{max} / nm (ε/(L·mol^{-1}·cm^{-1})): 293(4.38×10^4), 403(2.937×10^5), 500(1.99×10^4), 535(1.04×10^4), 570(1.34×10^4), 625(2.69×10^3).

1.3.6 Synthesis of 5-(4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)-13,17-diethyl-2,3,7,8,12,18-hexamethyl-porphyrin (**5c**)

This compound was prepared in 32.9% yield (265 mg), as described for **5a**, starting from 4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)benzaldehyde (383.5 mg, 1 mmol). ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.19 (2H, s, *meso-H*), 9.97 (1H, s, *meso-H*), 8.30 (2 H, s, Ar-*H*), 8.17(2 H, d, Ar-*H*), 7.87(2 H, d, Ar-*H*), 7.70(4 H, d, Ar-*H*), 4.08 (4 H, q, pyrro-CH_2CH$_3$), 3.65 (6 H, s, pyrro-CH_3), 3.57(6 H, s, pyrro-CH_3), 2.64(6 H, s, pyrro-CH_3), 1.90(6 H, t, CH$_2$CH_3), 1.59(18 H, s, -C(CH_3)$_3$), −3.16 (1 H, s, N*H*), −3.28 (1 H, s, N*H*); HRMS(ESI): Calcd. for $C_{56}H_{62}N_5$(M+H$^+$): 804.500 0, Found: 804.501 3; UV-Vis (CH_2Cl_2): λ_{max} / nm (ε/(L·mol^{-1}·cm^{-1})): 297(5.25×10^4), 403(2.893×10^5), 501(2.37×10^4), 536(1.22×10^4), 570(1.85×10^4), 622 (5.53×10^3).

1.3.7 Synthesis of zinc 5-(4-*N*,*N*-dimethylamino phenyl)-13,17-diethyl-2,3,7,8,12,18-hexamethyl-porphyrin (**6a**)

To a solution of porphyrin **5a** (60 mg) in $CHCl_3$ (30 mL) was added with a saturated solution of $Zn(OAc)_2$·4H_2O in MeOH (5 mL) and the mixture was stirred overnight at room temperature. The reaction was checked by TLC. The reaction mixture was diluted with chloroform, washed with water two times, dried by $MgSO_4$ and concentrated to dryness *in vacuo*. The residue was purified by column chromatography (silica gel, 50% (*V*/*V*) heptance-CH_2Cl_2) and recrystallized from $CHCl_3$-methanol to afford the pure zinc complex 6a as a red solid (63 mg, Yield: 95%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.07 (2 H, s, *meso-H*), 9.91 (1 H, s, *meso-H*), 7.82(2 H, d, Ar-*H*), 7.10(2 H, d, Ar-*H*), 4.03 (4 H, q, pyrro-CH_2CH$_3$), 3.59(6 H, s, pyrro-CH_3), 3.52 (6 H, s, pyrro-CH_3), 3.24(6 H, s, -N(CH_3)$_2$), 2.55(6 H, s,

pyrro-CH_3), 1.86(6 H, t, CH_2CH_3); HRMS(ESI): Calcd. for $C_{38}H_{42}N_5Zn$(M+ H^+): 632.272 6, Found: 632.271 3; UV-Vis (CH_2Cl_2): λ_{max} / nm (ε/(L·mol^{-1}·cm^{-1})): 405(1.632×10^5), 534(1.22×10^5), 570(1.08×10^5).

1.3.8 Synthesis of zinc 5-(4-*N*-carbazolylphenyl)-13,17-diethyl-2,3,7,8,12,18-hexamethyl-porphyrin (**6b**)

Compound **6b** was prepared as a red solid in a similar way to the synthesis of **6a**. Yield: 98%, 70 mg. ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.19 (2H, s, *meso-H*), 10.08 (1H, s, *meso-H*), 8.32(2 H, d, Ar-*H*), 8.29 (2 H, d, Ar-*H*), 7.94(2 H, d, Ar-*H*), 7.77(2 H, d, Ar-*H*), 7.62 (2 H, m, Ar-*H*), 7.43(2 H, m, Ar-*H*), 4.12(4 H, q, pyrro-CH_2CH$_3$), 3.66(6 H, s, pyrro-CH_3), 3.59(6 H, s, pyrro-CH_3), 2.71(6 H, s, pyrro-CH_3), 1.91(6 H, t, CH_2CH_3); HRMS (ESI): Calcd. for $C_{48}H_{43}N_5Zn$ (M^+)$^·$: 753.281 0, Found: 753.280 6; UV-Vis (CH_2Cl_2): λ_{max} / nm (ε/(L·mol^{-1}·cm^{-1}): 293 (3.68×10^4), 405 (1.726×10^5), 535 (1.05×10^4), 573(8.71×10^3).

1.3.9 Synthesis of zinc 5-(4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)-13,17-diethyl-2,3,7,8,12,18-hexamethyl-porphyrin (**6c**)

Compound **6c** was prepared as a red solid quantitatively in a similar way to the synthesis of **6a**. ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.12(2H, s, *meso-H*), 9.98(1H, s, *meso-H*), 8.29(2 H, s, Ar-*H*), 8.24(2 H, m, Ar-*H*), 7.92(2 H, d, Ar-*H*), 7.72(2 H, d, Ar-*H*), 7.69(2 H, m, Ar-*H*), 4.06(4 H, q, pyrro-CH_2CH$_3$), 3.62(6 H, s, pyrro-CH_3), 3.56(6 H, s, pyrro-CH_3), 2.66(6 H, s, pyrro-CH_3), 1.89(6 H, t, CH_2CH_3), 1.57(18 H, s, -C(CH_3)$_3$); HRMS (ESI): Calcd. for $C_{56}H_{60}N_5Zn$ (M^+): 865.406 2, Found: 865.406 4; UV-Vis (CH_2Cl_2): λ_{max} / nm (ε/(L·mol^{-1}·cm^{-1})): 298(2.57×10^4), 405(2.10×10^5), 536(1.08×10^4), 571(1.23×10^4), 633(1.81×10^3).

1.4 Crystal structure determination

Single crystal diffraction data of **5a** and **6a** at 296 K was collected on a Bruker SMART APEX Ⅱ CCD area-detector diffractometer using a graphite-monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm). The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques using SHELXL-97[28]. All of the non-hydrogen atoms were refined by anisotropic thermal parameters, and hydrogen atoms bonded to the carbon and nitrogen atoms were generated geometrically and refined isotropically with the riding mode. The crystal data and structure refinement of **5a** and **6a** are summarized in Table 1.

CCDC: 1450675, **5a**; 1471067, **6a**.

Table 1　Crystal data and structure and refinement for compounds 5a and 6a

Compound	**5a**	**6a**
Empirical formula	$C_{77}H_{87}Cl_3N_{10}$	$C_{38}H_{41}N_5Zn$
Formula weigh	1 258.92	633.13
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a / nm	1.260 7(2)	1.171 2(3)
b / nm	1.309 5(3)	1.244 0(3)
c / nm	1.337 0(4)	1.359 3(3)
α / (°)	117.632(9)	112.167(2)
β / (°)	110.833(6)	107.846(2)
γ / (°)	90.306(6)	102.607(3)
Z	1	2
D_c / (g·cm^{-3})	1.169	1.301
μ / mm^{-1}	0.177	0.795
F(000)	670	668
Index ranges	$-14 \leqslant h \leqslant 14, -12 \leqslant k \leqslant 15, -15 \leqslant l \leqslant 15$	$-13 \leqslant h \leqslant 13, -14 \leqslant k \leqslant 14, -16 \leqslant l \leqslant 15$
Reflections collected, unique	12 505, 6 140 (R_{int}=0.027 4)	11 254, 5 613 (R_{int}=0.052 4)
Data, restraints, parameters	6 140, 167, 464	5 613, 0, 407

Continued Table 1

Goodness-of-fit on F^2	1.122	0.970
R_1, wR_2 ($I>2\sigma(I)$)	0.082 8, 0.220 9	0.052 9, 0.120 2
R_1, wR_2 for all	0.136 0, 0.247 3	0.099 8, 0.137 5
Largest diff. peak and hole / ($e\cdot nm^{-3}$)	404 and −310	267 and −424

2 Results and discussion

2.1 Synthesis

The synthesis of *meso*-mono-substituted porphyrins **5a~c** and their metal complexes **6a~c** involved a multistep approach as shown in Scheme 1. Briefly, the porphyrin derivatives **5a~c** were prepared by the condensation of **4** and different aromatic aldehyde in the presence of catalytic para-toluenesulfonic acid (PTSA) in higher yields of 44.1%, 31.5% and 32.9%, respectively, compared with the convenient synthesis of the AB_3-symmetric porphyrin[29]. Their corresponding zinc complexes **6a~c** were prepared in excellent yields (>90%) by starting from **5a~c** and using Zn $(OAc)_2\cdot 2H_2O$ in a methanol/chloroform mixture by use of the standard procedure. Their structures were characterized by ^{1}H NMR, ESI-HRMS and UV-Vis spectroscopy.

2.2 Spectroscopic characterization

The proton NMR spectrum of **5a** in $CDCl_3$ is shown in Fig.1. Peak assignments were made on the basis of chemical shifts, multiplicity, integrations, and spectral intercomparisons. As could be seen, signals at δ 10.14 and 9.13 could be assigned to the meso protons. The two doublets at δ 7.79 and 7.04 corresponded to the protons of phenyl ring. In the aliphatic region, the quadruplet at δ 4.05~4.09 was attributed to the resonances of the -CH_2 protons. The signals observed at δ 3.64, 3.53 and 2.54 were attributed to the three types of methyl protons of the β position of porphyrin respectively, and the signal of methyl protons which closest to the phenyl subunit lay relatively upfield due to the shielding effect of the phenyl rings. The chemical shift of the methyl protons of -$N(CH_3)_2$ appeared at δ 3.22. The triplet signals at δ 1.87~1.90 were ascribed to the -CH_2CH_3 methyl protons. In addition, the two singlets at δ −3.16 and −3.27 for two protons were assigned to the internal NH for the porphyrin ring. The structure was also supported by high resolution mass spectrometry, which gave the expected $(M+H)^+$ peak at m/z=570.358 5. Similarly, porphyrin derivatives **5b~c** and their corresponding zinc complexes **6a~c** were characterized and their spectra data were in accordance with their proposed structures.

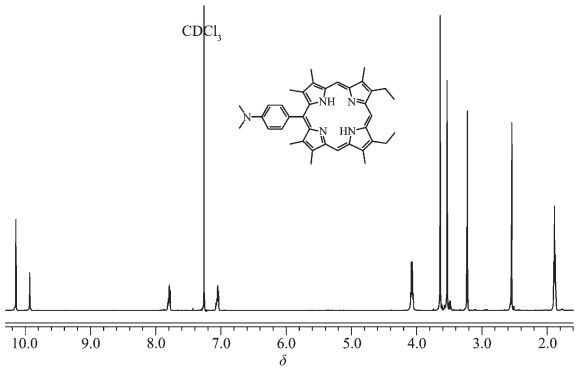
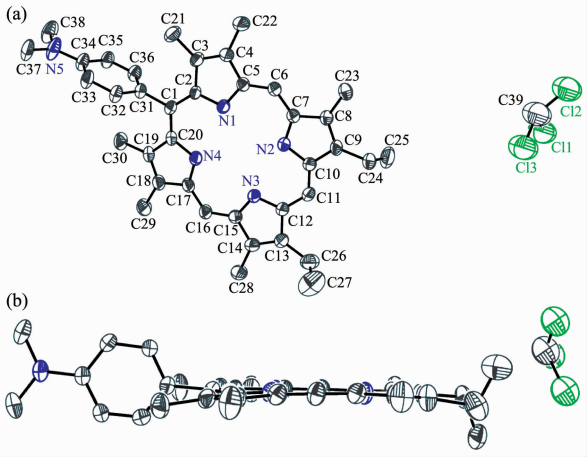


Fig.1 Partial ^{1}H NMR spectrum (600 MHz) of **5a** in $CDCl_3$

2.3 X-ray crystal structure

X-ray crystallography analysis for **5a** and **6a** further supported the structure of porphyrin derivatives. Single crystals of **5a** and **6a** suitable for X-ray crystallographic characterization were obtained by slow diffusion of methanol into the solution of **5a** and **6a** in chloroform. The compounds crystallized in the triclinic crystal system with space group $P\bar{1}$. The resulting structures of **5a** are shown in Fig.2, which confirms the asymmetric units consists of one porphyrin molecule and half chloroform molecule (Fig. 2). The porphyrin structure exhibits a planar macrocycle and is very similar to that of previously reported porphyrins[30]. The bond angles and bond distances are very similar to those found in the X-ray crystal structure of porphyrin derivatives[30]. The substituted Cm position C1 exhibits Ca-Cm-Ca angle of 124.6(3)°, while the average Ca-Cm-Ca angles for C6, C11 and C16 is 128.9(3)°. With respect to the

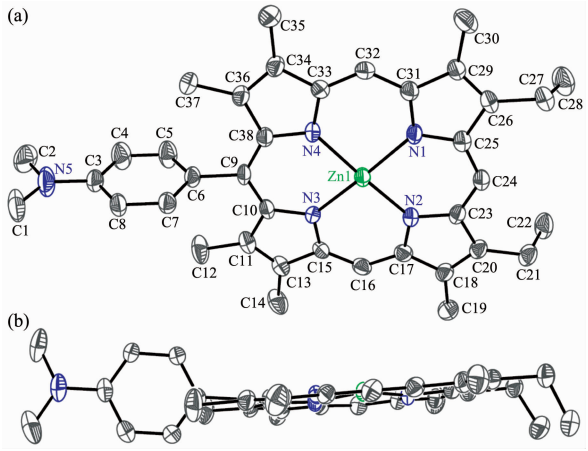
porphyrin (N4) plane, two ethyl groups are oriented above and below the N4 plane, respectively. The phenyl rings are almost orthogonal to the N4 plane and make an angle of 83.01(13)° due to the steric repulsion from the two methyl substituents at the pyrrole β-positions (C…Ph 0.293 1~0.296 2 nm).



Thermal ellipsoids are set at the 30% probability level, and hydrogen atoms have been omitted for clarity

Fig.2　X-ray crystal structure of **5a** (a) showing the side view (b)

The structure of the corresponding zinc porphyrin **6a** is shown in Fig.3 and exhibits very similar conformations and structural parameters. Its 24-atom porphyrin ring system is also nearly planar similar to **5a**, exhibiting a mean deviation of 0.006 87 nm and a maximum of 0.015 7 nm. N1…N3 distance is 0.407 5 nm and N2…N4 distance is 0.405 5 nm. The phenyl ring is virtually perpendicular to the porphyrin plane with a dihedral angle of 86.15° which is in agreement with the result observed in **5a**. The zinc atom located on an inversion center with small mean plane



Thermal ellipsoids are set at the 30% probability level, and hydrogen atoms have been omitted for clarity

Fig.3　X-ray crystal structure of **6a** (a) showing the side view (b)

deviations (0.007 11 nm). Zn-N bond distances are between 0.202 8 and 0.204 2 nm, which are similar to the reported zinc porphyrin derivatives[31]. Two ethyl groups point to the same direction different from **5a**. In addition, the plane defined by C1, N5 and C2 atoms is almost coplanar to the phenyl ring with a dihedral angle of 5.17(94)°.

2.4　Absorption spectra

The absorption peaks of porphyrin derivatives **5a~c** and **6a~c** are presented in Table 1. The UV-Vis spectra of free base porphyrins **5a~c** are shown in Fig.4a and exhibit typical intense Soret band at 403 nm and four weaker Q bands at ~500, 535, 570 and 637 nm, which are similar to that of *meso*-mono-substituted porphyrins such as 13,17-diethyl-2,3,7,8,12,18-hexamethyl-5-phenylporphyrin[16] and 2-(13,17-diethyl-2,3,7,8,12,18-hexamethylporphyrin-5-yl)-5, 5′,

Table 1　Electronic absorption and emission data for the porphyrin derivatives 5a~c and 6a~c

Compound	Absorption[a] (λ_{max} / nm)	Fluorescence[b] (λ_{em} / nm)	Φ_f[c]
5a	403, 500, 535, 573, 637	633, 698	5.21
5b	293, 403, 500, 535, 570, 625	636, 698	5.91
5c	297, 403, 501, 536, 570, 622	636, 699	6.65
6a	405, 534, 570	588, 636	6.72
6b	293, 405, 535, 573	589, 635	7.41
6c	298, 405, 536, 571	586, 634	9.89

[a] Absorption data were taken for CH_2Cl_2 solution of porphyrins; [b] emission data were taken in toluene containing 1% (*w*/*w*) pyridine; [c] Quantum yields relative to the zinc phthalocyanine used as the reference for calculating photoluminescence quantum yield (Φ_{PL}=0.30) and the excitation wavelength is 400 nm.

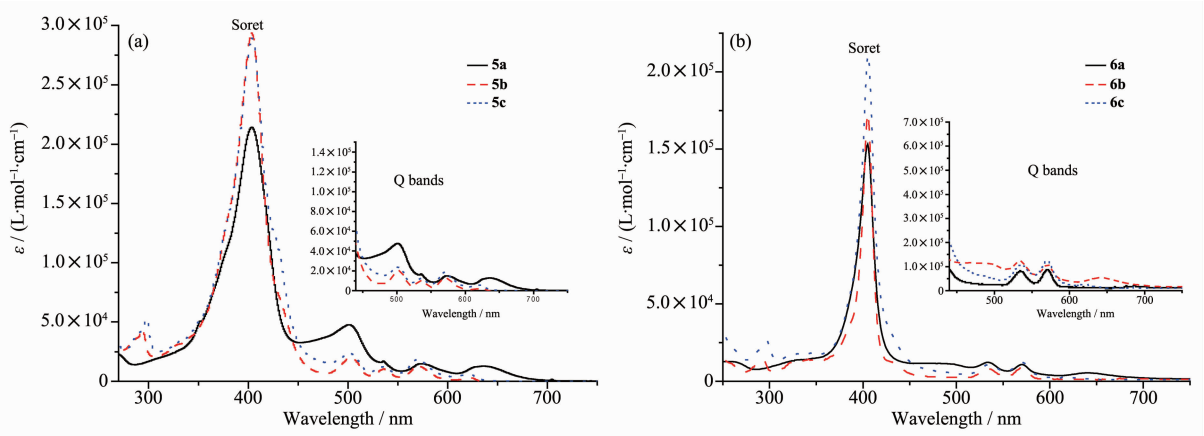


Fig.4 Absorption spectra of porphyrins **5a~c** (a) and **6a~c** (b) in CH_2Cl_2

10, 10′, 15, 15′-hexahexyltruxene[17]. However, these bands slightly blue-shift compared to the tetrakis(4-*N*,*N*-dimethylaminophenyl)porphyrin[32]. Besides, the Soret and Q bands in porphyrins **5b** and **5c** are different from **5a** with an additional absorption peak originating from the presence of carbazolyl units at ~293 nm. Therefore, the absorption spectra of the two compounds **5b** and **5c** show the features of both porphyrin and carbazolyl subunits and suggest that there are no substantial interaction between the attached moiety and the porphyrin ring in the ground state. The electronic absorption spectra of the metalloporphyrins **6a~c** are shown in Fig.4b. The compounds **6a~c** show an intense absorption peak for the Soret bands at 405 nm and small absorption peaks for the Q-bands at ~535 and ~671 nm, which are almost equal to that of 13,17-diethyl-2,3,7,8,12,18-hexamethyl-5-(4-(dipheny-lamino)phenyl) porphyrinatozinc[18]. Their Soret bands were found to red-shift by 2 nm in comparison to their corresponding free base porphyrin derivatives. In addition, comparing the absorption spectra data of **5a~c** and **6a~c** with that of the literature[18], the results show that different *meso*-substituents of porphyrins have little impact on the electronic absorption region. The main reason could be the presence of the strong steric hindrance between the *β*-methyl of the pyrrole ring and the meso aromatic rings which leaded to the lack of the substantial conjugation interaction between the meso aryl and the porphyrin ring. The results have also been proved by their crystal structures.

2.5 Emission spectroscopy

The fluorescence spectra of compounds **5a~c** and **6a ~c** in 1% pyridine-toluene solution at excitation wavelength of 400 nm are shown in Fig.5. The porphyrins **5a ~c** show emission bands at ~633 nm and a shoulder at ~698 nm with almost equal intensities, and the porphyrins **6a ~c** show emission bands at ~588 nm and a shoulder at ~635 nm. The

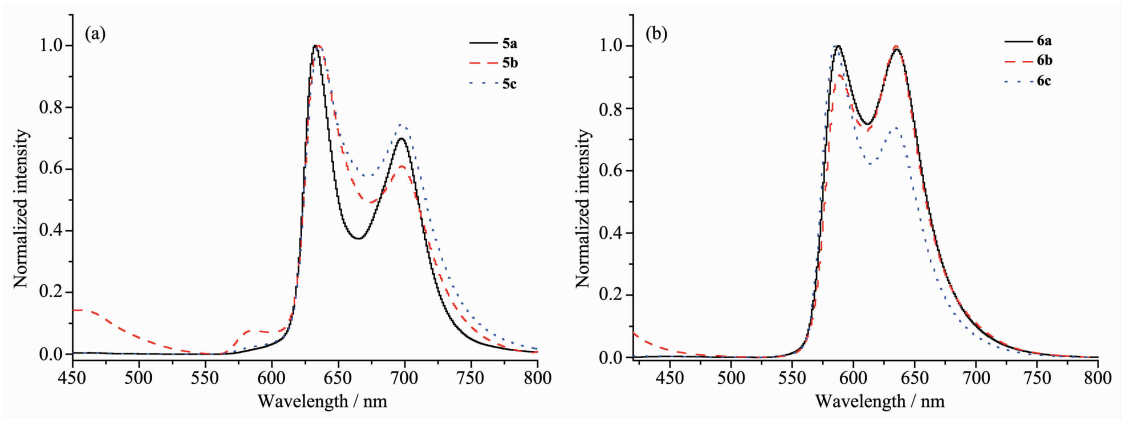


Fig.5 Emission spectra of **5a~c** (a) and **6a~c** (b) in 1% pyridine-toluene solution

fluorescence bands of **6a~c** blue-shift by 45~63 nm with respect to their corresponding ligands **5a~c**. On excitation at 400 nm, the fluorescence bands of all the compounds blue-shift by ~20 nm in contrast to TPP and Zn-TPP, respectively.

2.6 Fluorescence quantum yields

The fluorescence quantum yields of these compounds were determined by comparing with a calibration standard of zinc phthalocyanine in toluene solution containing 1% pyridine presenting a fluorescence quantum yield of 0.3. The Fluorescence quantum yields were calculated according to the following equation:

$$\Phi_x=\Phi_{std}\frac{I_x}{I_{std}}\frac{A_{std}}{A_x}\left(\frac{\eta_x}{\eta_{std}}\right)$$

where the 'x' and 'std' subscripts refer to sample and standard (the reference), respectively, Φ is the photoluminescence quantum yield, I is the integrated intensity of emission spectra, A stands for the absorbance at the excitation wavelength, and η is the refractive index of the solvent used in the measurement.

Values of quantum yields of the free base porphyrin derivatives and their metal complexes are reported in Table 1. The quantum yields of **6a** and **6c** are slightly higher than their parent compound **5a** and **5c**, but **6b** is almost equivalent to **5b**. These observations may be explained by the non-conjugation interaction between the *meso*-aryl group and porphyrin ring. Further photophysical studies are currently under investigation.

2.7 Thermal analysis

The thermal properties of the porphyrin derivatives have been investigated by TGA. The results are shown in Fig.6. Two stages of thermal decomposition were observed for **5a**. The first began at 143 ℃ and ended at 180 ℃ with a small loss of 4%. The second stage of decomposition began at 350 ℃ and continued up to a temperature of 700 ℃, at which complete decomposition of the material had not occurred. All other porphyrin derivatives only showed one major thermal events at approximately 403 ℃ and complete decomposition had not been observed up to 700 ℃ similar to **5a**. In addition, the decomposition temperature of zinc complexes **6a** and **6c** increases by approximately 10 ℃ relative to their corresponding free base porphyrin **5a** and **5c**, indicating an increase in the thermal stability of the zinc complexes. These results show that all the porphyrin derivatives feature good thermal stability.

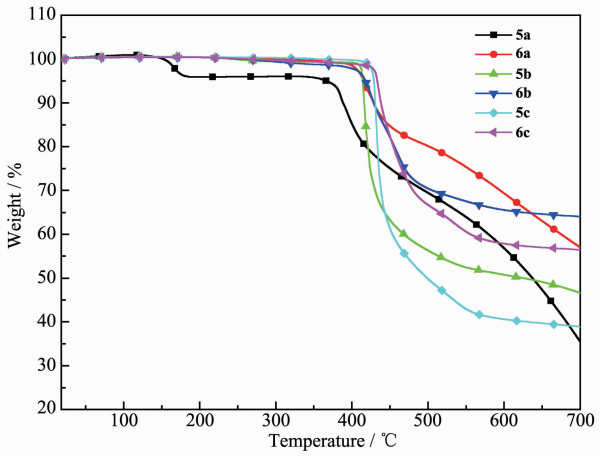


Fig.6　Thermogravimetric curves for **5a~c** and **6a~c**

3 Conclusions

In summary, three new *meso*-mono substituted porphyrin derivatives have been successfully synthesized and characterized. Their corresponding zinc complexes were prepared in high yield. These porphyrin derivatives can emit essentially red light after 400 nm irradiation. Different substituents of *meso*-position have no remarkable effect on the spectra properties, which can be attributed to the possible steric hindrance between the meso phenyl substituents and β methyl group. In addition, they present good thermal stability. Accordingly, these porphyrin derivatives might be promising candidates for luminescent materials.

Supporting information is available at http://www.wjhxxb.cn

References:

[1] Jurow M, Schuckman A E, Batteas J D, et al. *Coord. Chem. Rev.*, **2010**,**254**(19/20):2297-2310

[2] Rangasamy S, Ju H, Um S, et al. *J. Med. Chem.*, **2015**,**58**(17):68646874

[3] WANG Ling-Yun(汪凌云), CAO De-Rong(曹德榕). *Chin. J.*

Org. Chem.(有机化学), **2012**,**32**(12):2248-2264

[4] REN Qi-Zhi(任奇志), LIU Shuang-Yan(刘双艳), WANG Ai-Qin(王爱琴), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2008**,**24**(9):1438-1443

[5] Chan K, Guan X, Lo V, et al. *Angew. Chem. Int. Ed.*, **2014**, **53**(11):2982-2987

[6] WU Di(吴迪), SHEN Zhen(沈珍), XUE Zhao-Li(薛兆历), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2007**,**23**(1): 1-14

[7] Rawson J, Stuart A C, You W, et al. *J. Am. Chem. Soc.*, **2014**,**136**(50):17561-17569

[8] Lu J, Li H, Liu S, et al. *Phys. Chem. Chem. Phys.*, **2016**,**18** (9):6885-6892

[9] Arrechea S, Clifford J, Pellejà L, et al. *Dyes Pigm.*, **2016**,**126**: 147-153

[10]Xu J, Wu J, Zong C, et al. *Anal. Chem.*, **2013**,**85**(6):3374-3379

[11]Hessenauer-Ilicheva N, Franke A, Meyer D, et al. *Chem. Eur. J.*, **2009**,**15**(12):2941-2959

[12]Cheng F, Wu X, Liu M, et al. *Sens. Actuators B*, **2016**,**228**: 673-678

[13]Liu X, Liu X, Tao M, et al. *J. Mater. Chem. A*, **2015**,**3**(25): 13254-13262

[14]Kral V, Kralova J, Kaplanek R, et al. *Physiol. Res*., **2006**,**55** (Suppl.2):S3-S26

[15]Mahmood M, Liu H, Wang H, et al. *Tetrahedron Lett.*, **2013**, **54**(44):5853-5856

[16]Kolodina E, Syrbu S, Semeikin A, et al. *Russ. J. Org. Chem.*, **2010**,**46**(1):138-143

[17]Xu H, Du B, Gros C, et al. *J. Porphyrins Phthalocyanines*, **2013**,**17**(1/2):44-55

[18]Takai A, Gros C, Barbe J, et al. *Chem. Eur. J.*, **2011**,**17**(12): 3420-3428

[19]Senge M, Kalisch W, Bichoff I. *Chem. Eur. J.*, **2000**,**6**(15): 2721-2738

[20]Lee M, Seo K, Song H, et al. *Tetrahedron Lett.*, **2011**,**52** (30):3879-3882

[21]Nowak-Król A, Gryko D, Gryko D T. *Chem. Asian J.*, **2010**, **5**(4):904-909

[22]Ormond A, Freeman H. *Dyes Pigm.*, **2013**,**96**:440-448

[21]Goldberg P, Pundsack T, Splan K. *J. Phys. Chem. A*, **2011**, **115**(38):10452-10460

[22]Panda M, Sharma G, Thomas K, et al. *J. Mater. Chem.*, **2012**, **22**(16):8092-8102

[23]Loiseau F, Campagna S, Hameurlaine A, et al. *J. Am. Chem. Soc.*, **2005**,**127**(32):11352-11363

[24]Xu T, Lu R, Liu X , et al. *J. Org. Chem.*, **2008**,**73**(5):1809-1817

[25]Matsuo T, Hayashi A, Abe M, et al. *J. Am. Chem. Soc.*, **2009**,**131**(42):15124-15125

[26]Juillard S, Simonneaux G. *Synlett*, **2006**(17):2818-2820

[27]Sun T, Pan Y, Wu J, et al. *Transition Met. Chem.*, **2007**,**32** (4):449-455

[28]Sheldrick G M. *Acta Crystallogr. A*, **2008**,**A64**:112-122

[29]Ballatore M, Spesia M, Milanesio M, et al. *Eur. J. Med. Chem.*, **2014**,**83**:685-694

[30]Luguya R, Jaquinod L, Fronczek F, et al. *Tetrahedron*, **2004**, **60**(12):2757-2763

[31]Byrn M, Curtis C, Hsiou Y, et al. *J. Am. Chem. Soc.*, **1993**, **115**(21):9480-9497

[32]SUN Zhe(孙哲), JIA Li-Xia(贾立夏), LI Yan-Rong(李艳荣), et al. *Chin. J. Org. Chem.*(有机化学), **2010**,**30**(4):546-550