

Facile synthesis, characterization and property comparisons of tetraaminometallophthalocyanines with and without intramolecular hydrogen bonds

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Abstract

Tetraaminometallophthalocyanines (TAMPcs) **3a₁–3a₄** and **3b₁–3b₄** were prepared, in two steps, from 3-nitro-phthalic anhydride and 4-nitro-*o*-phenyleneimine, respectively. Although simple methods were employed without using chromatographic fractionation, purer products with higher yields were obtained. Synthesized compounds were characterized by MS, ¹H NMR, UV–VIS and IR. Characterization results showed that **3a₁–3a₄** contained intramolecular hydrogen bonds, while **3b₁–3b₄** did not contain intramolecular hydrogen bonds. Property comparisons between **3a₁–3a₄** and **3b₁–3b₄** are presented in this paper.

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Keywords: Tetraaminometallophthalocyanine; Synthesis; Characterization; Intramolecular hydrogen bond

1. Introduction

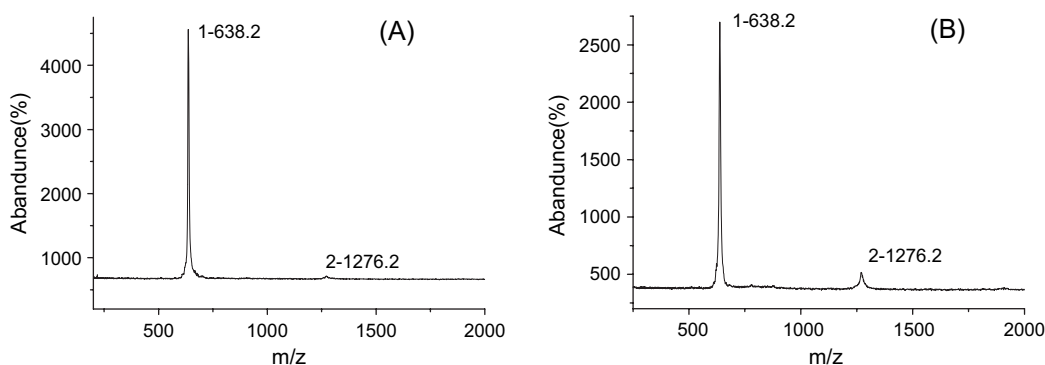
Phthalocyanine (Pc) and its derivatives have received much attention for their potential applications in a variety of fields such as catalysis [1], photochemistry [2], electrochemistry [3], nonlinear optics [4], information storage [5] and photodynamic therapy [6,7], etc. But the difficulty of Pc dissolution limits its application to a certain extent [8], so soluble Pcs have been synthesized and used to prepare their derivatives [9–11]. For example, amino Pc (APc) is the desired compound both in dissolution and in derivation from its amino-groups. There has been a considerable effort to synthesize APcs. APcs could not be synthesized through self-congregation of the substrate containing amino-groups because of the interference of amino-groups. To solve the problem, two methods were usually employed. One

approach was that nitro-Pc was prepared in the first place and then reduced to APc; the other one was that the amino-group in substrate was firstly protected by acyl before the substrate was self-congregated to Pc, which was then hydrolyzed to APc. The former method needs relatively fewer reaction steps, so it was usually employed.

In comparison with our method, previous APcs synthesis approach needed relatively longer reaction time, gave lower yield and had difficulty in the separation of APcs from the reaction mixture. No perfect MS or ¹H NMR spectra were given in previous literature; maybe pure APcs were difficult to acquire, hence few derivatives from APcs, to date, have been presented by previous researchers [12–15]. In the reference to previous literature, we created a more facile approach to prepare peripherally substituted TAMPcs **3b₁–3b₄** and non-peripherally substituted TAMPcs **3a₁–3a₄** in both higher yield and purity. Furthermore, we present necessary spectra and performed comparisons between the two series of TAMPcs.

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Fig. 1. MS of **3a₁** (A) and **3b₁** (B).

2. Results and discussions

2.1. Synthesis of **3a₁–3a₄** (**3b₁–3b₄**)

Many compounds, such as 3(or 4)-nitro-*o*-phthalic acid, 3(or 4)-nitro-phthalic anhydride, 3(or 4)-nitro-phthalic amide, 3(or 4)-nitro-phthalimide, 3(or 4)-nitro-phthalic nitrile or 4(or 5)-nitro-1,3-diiminoisoindoline, can be used as substrates to synthesize teranitro-phthalocyanines. However, considering the purity of the precursors above, we selected 3-nitro-phthalic anhydride **1a** as the substrate to synthesize **2a₁–2a₄** and 4-nitro-phthalimide **1b** as the substrate to prepare **2b₁–2b₄**.

In addition to **2a₁–2a₄** (**2b₁–2b₄**), other compounds in reaction mixture dissolve readily in heat hydrochloric acid (1mol/L) or heat sodium hydroxide (1mol/L). We just make use of the hard dissolution of **2a₁–2a₄** (**2b₁–2b₄**) in the heat hydrochloric acid or heat sodium hydroxide to boil the reaction mixture, just like the operations described in Section 3. Thus, **2a₁–2a₄** (**2b₁–2b₄**) can be purified conveniently and thoroughly.

DMF is selected as the solvent because both **2a₁–2a₄** (**2b₁–2b₄**) and reductive sodium sulfide nonahydrate can be readily solved in it. Reaction temperature is maintained at 60 °C for 1 h, which is the optimal temperature for this reductive reaction. The reaction time of this method was shorter than those reported previously [12–15]. From MS (Fig. 1), we can see that reaction efficiency that nitro-groups of tetranitrometalloPcs are

reduced to amino-groups is almost 100%, because no nitro-Pc peak is observed in the MS spectra. In the reaction mixture, only TAMPC is nonsoluble in water, so we choose to dump the reaction mixture into water, thus TAMPC is readily filtered out and cleaned by using water. As a result, without using chromatogram fraction operation [12], we are able to obtain purer target products, moreover, the yields were over 90%.

2.2. MS analysis, dimers and anti-oxidation of amino-group

For the ready dissolution of TAMPCs in DMF, DMSO and THF, they were conveniently characterized. The results of MS (Table 1) showed that observed values of TAMPC monomers and their dimers were consistent with the calculated values. For example, we can obviously find peaks of monomers and dimers from the MS spectra of **3a₁** and **3b₁** (Fig. 1). Dimers formed through part-overlap of intermolecular conjugated π orbits. In this case, dimers are few because the intermolecular action is weak. Trimers and polymers are almost nonexistent, because their peaks cannot be found in the MS spectra. All the TAMPC MS characterizations were repeated after they had been placed in air for 2 months and no MS spectrum change was found. This indicates that amino groups in TAMPCs have strong anti-oxidation, which is seldom found in the aryl amine compounds whose molecules are relatively

Table 1
Synthesis of TAMPCs

No.	Yield (%)	MS (required)		IR (KBr) ν (NH ₂) (cm ⁻¹)	Found (required)		
		Monomer	Dimer		C	H	N
3a₁	91	638.2 (638.0)	1276.2 (1275.9)	3434.70 2923.25 1613.34	60.21 (60.25)	2.89 (3.16)	26.12 (26.35)
3b₁	92	638.2 (638.0)	1276.2 (1275.9)	3431.08 3204.19 1607.50	59.19 (60.25)	3.01 (3.16)	26.40 (26.35)
3a₂	96	636.0 (636.1)	1271.9 (1272.3)	3428.38 3093.56 1609.77	59.48 (60.42)	3.02 (3.17)	26.00 (26.42)
3b₂	98	636.0 (636.1)	1271.9 (1272.3)	3351.65 3194.54 1608.47	60.21 (60.42)	3.13 (3.17)	26.39 (26.42)
3a₃	95	631.2 (631.3)	1261.5 (1262.4)	3445.95 3065.82 1622.69	59.85 (60.88)	3.09 (3.20)	25.86 (26.62)
3b₃	97	631.2 (631.3)	1261.5 (1262.4)	3360.77 3219.78 1612.73	60.20 (60.88)	3.37 (3.20)	25.78 (26.62)
3a₄	79	631.4 (631.5)	1263.4 (1263.0)	3437.95 2931.43 1621.56	60.02 (60.86)	2.75 (3.20)	25.78 (26.62)
3b₄	80	631.4 (631.5)	1263.4 (1263.0)	3434.09 3361.33 1612.56	60.00 (60.86)	3.37 (3.20)	26.00 (26.62)

Table 2
UV–VIS spectra of TAMPcs

λ (nm)	3a₁ (3b₁)	3a₂ (3b₂)	3a₃ (3b₃)	3a₄ (3b₄)
B	200.0 335.0 (300.0 354.0)	272.0 332.279 (305.0 338.0)	311.0 (304.504 320.058)	264.508 330.057 (321.169)
Q	766.0 (716.0)	775.568 (723.000)	771.000 (721.129)	751.126 (707.797)
Q _a –Q _b	50.0	52.568	49.871	43.329
T	478.070 (424.610)	436.539 (430.796)	487.348 (433.796)	463.932 (421.518)

smaller, such as aniline. It is possible that conjugation effect between amino-groups and Pc ring could account for the strong anti-oxidation of amino-groups. Specifically, electronic cloud density of N atoms in amino-group is decreased because of the conjugation effect between amino-groups and Pc ring, so amino-groups in TAPM are not readily oxidated.

2.3. UV–VIS analysis, red shift and intramolecular hydrogen bond

There is a weak peak (T, shown in Table 2) between 400.0 and 500.0 nm in the UV–VIS spectrum of each TAMPc, which can be clearly seen in the spectra (such as Fig. 2). The T peak disappeared immediately when one drip of hydrochloric acid (1 mol/L) was dropped into DMF solution of TAMPc. This may indicate that the peak was caused by the electron transfer from amino-groups to center M(II) through Pc ring. After hydrochloric acid (1 mol/L) was added into the solution, the amino-group was transformed from electron-donating group ($-\text{NH}_2$) to electron-withdrawing group ($-\text{NH}_3^+$), so T peak cannot be observed.

In Table 2, we find that the Q bands of **3a₁–3a₄** comparing with those of **3b₁–3b₄** are red-shifted ($Q_a - Q_b \approx 50$ nm). In the comparison with **3b₁–3b₄**, one H atom in amino-group of **3a₁–3a₄** can form intramolecular hydrogen bond with the adjacent N atom in Pc ring. Intramolecular hydrogen bond cannot form in **3b₁–3b₄** because the amino-group lies in the

molecular peripheral moiety. Intramolecular hydrogen bonds make the conjugation of amino-group with Pc ring stronger and cause the electron transfer from amino-group to M(II) more readily, which, to some extent, results in the enlargement of π conjugation system of **3a₁–3a₄**. As we all know, extended conjugation can make Q band red-shifted [16,17]. Just because of the formation of intramolecular hydrogen bonds, the dissolution of **3a₁–3a₄** in DMF is not as good as that of **3b₁–3b₄**. Owing to the relative red shift of Q-band, DMF solutions of **3a₁–3a₄** present brown yellow color and those of **3b₁–3b₄** display black green color.

The Q-band wavelength of **3a₁–3a₄** or **3b₁–3b₄** follows the rule of $\text{Zn(II)} < \text{Cu(II)} > \text{Ni(II)} > \text{Co(II)}$. We believe that it is just M(II) that brings out this order, which is the same as the order of coordination capability of transition M(II) in an octahedral field. Due to the coordination with DMF in axis direction, M(II) of TAMPc in DMF solution can be imagined in an octahedral field, so coordination capability of M(II) gives rise to this order.

An interesting phenomenon is found in the UV–VIS spectra of **3a₂** (Fig. 3). When it was freshly prepared, there were two peaks at 725.0 nm and 775.0 nm. Nevertheless, the peak at 725.0 nm disappeared 3 weeks later and only the peak at 775.0 nm can be found in the UV–VIS spectrum of **3a₂**. The phenomenon is not found in spectra of other TAMPcs synthesized by us, which needs to be further investigated. The peak at

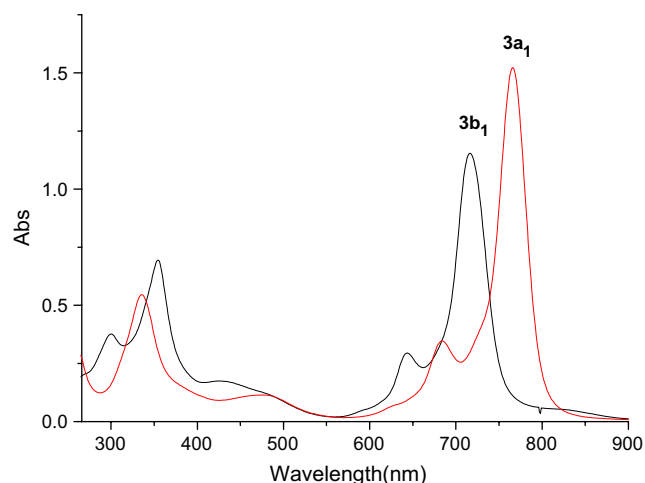


Fig. 2. UV–VIS spectra of **3a₁** and **3b₁** (DMF, 25 °C).

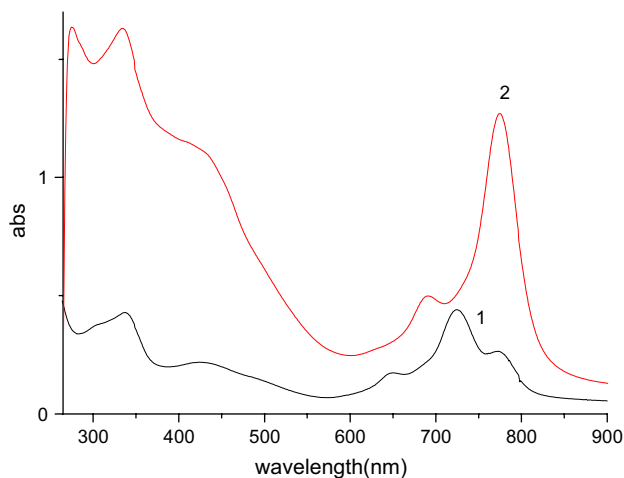


Fig. 3. UV–VIS spectra of **3a₂** (1, the spectra of **3a₂** freshly prepared; 2, that of **3a₂** 3 weeks later).

725.0 nm is possibly the result of amino-group rotation state and the peak at 775.0 nm maybe is caused by the amino-group conjugation state, in which intramolecular hydrogen bonds are formed. The former state converted gradually to the latter state during the 3 weeks and completely transformed the latter state in the end.

2.4. ^1H NMR analysis, magnetism and thermodynamic state of the amino-group

For showing wide spectra bands, ^1H NMR spectra of **3a₂–3a₄** and **3b₂–3b₄** are difficult to analyze. This is because they are paramagnetic compounds, d electron number of M(II) (Cu(II) , Ni(II) and Co(II)) is less than 10.

However, because **3a₁** and **3b₁** were diamagnetic compounds, due to Zn(II) having ten d electrons, their ^1H NMR spectra (Fig. 4) are clean and clear, which indicate that the isomers and dimers of **3a₁** and **3b₁** are few (Scheme 1).

Three kinds of protons of **3a₁** tagged by 2, 3 and 4 can be seen in Scheme 1. Not all of them follow $\Delta\delta/J \geq 6$. The chemical shift values are in the following: δ 7.660(s, 1H), 8.570(m, 1H), 7.906(s, 1H), 7.429(s, 1H of N–H...), 7.286(s, 1H of N–H); Three kinds of protons of **3b₁** tagged by 1, 2 and 4 are shown in Scheme

1 and all of them follow $\Delta\delta/J \geq 6$, their chemical shifts δ are as follow: 7.3705(d, 1H), 8.913(t, 1H), 8.415(d, 1H), 6.230(s, 2H of $-\text{NH}_2$), J 15.6(3–4), 7.6(3–1).

Protons in **3a₁** and **3b₁** have larger chemical shifts comparing to those of ordinary aryl amine compounds, which are the result of π bond electron transfer to Zn(II) and solvent effect. The differences of chemical shifts among protons in **3a₁** or **3b₁** are mainly because their different locations around the Pc ring make them have different solvent effects in DMSO. Because the steric hindrance of 1-H (or 2-H), 4-H and 3-H increase in succession, their solvent effect in DMSO and chemical shift augment accordingly in the same order.

As the result of intramolecular hydrogen bonds in **3a₁**, extended conjugation structure makes various protons have analogous chemical shifts, which are against $\Delta\delta/J \geq 6$. 3-H presents a multiply speak due to its coupling with 2-H, 4-H, N–H and N–H.... 2-H and 4-H display a single peak, respectively. Different chemical circumstance makes N–H and N–H... have different chemical shift (Fig. 4, **3a₁**).

Nevertheless, in Fig. 4, **3b₁**, the two protons of amino-group show a wilder single peak at 6.230 comparing with other protons. This accords with the NMR peak feature of N–H and suggests that the amino-groups of **3b₁** are in

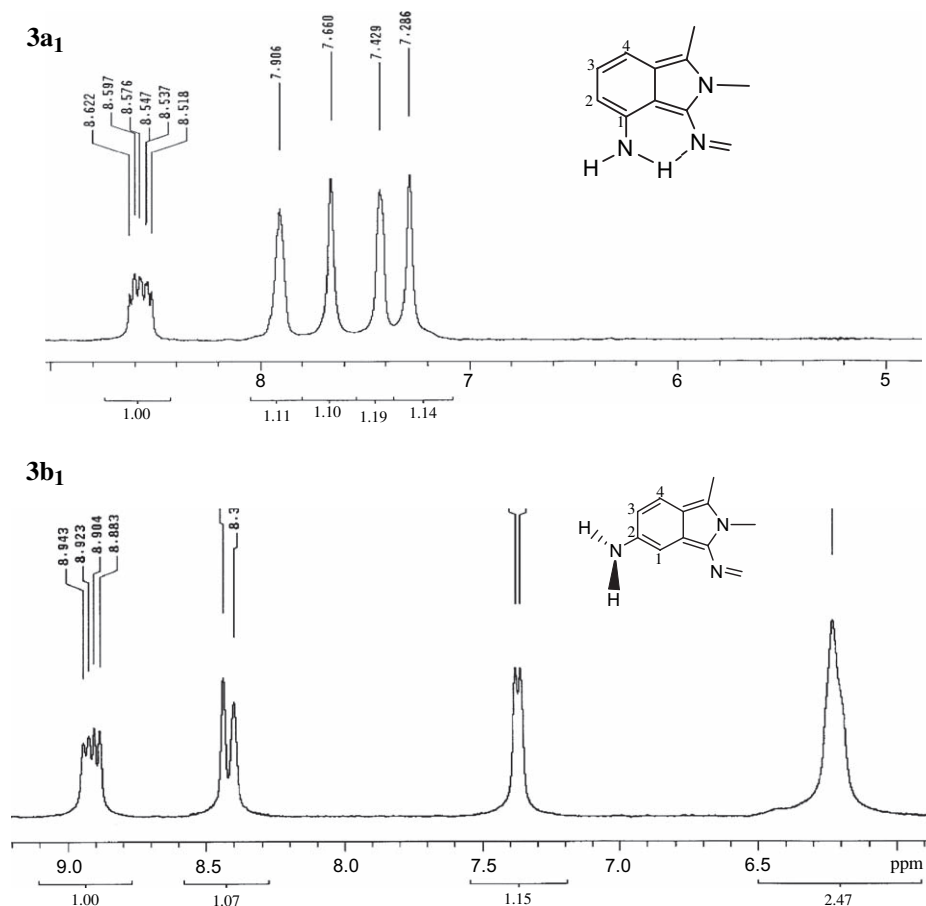
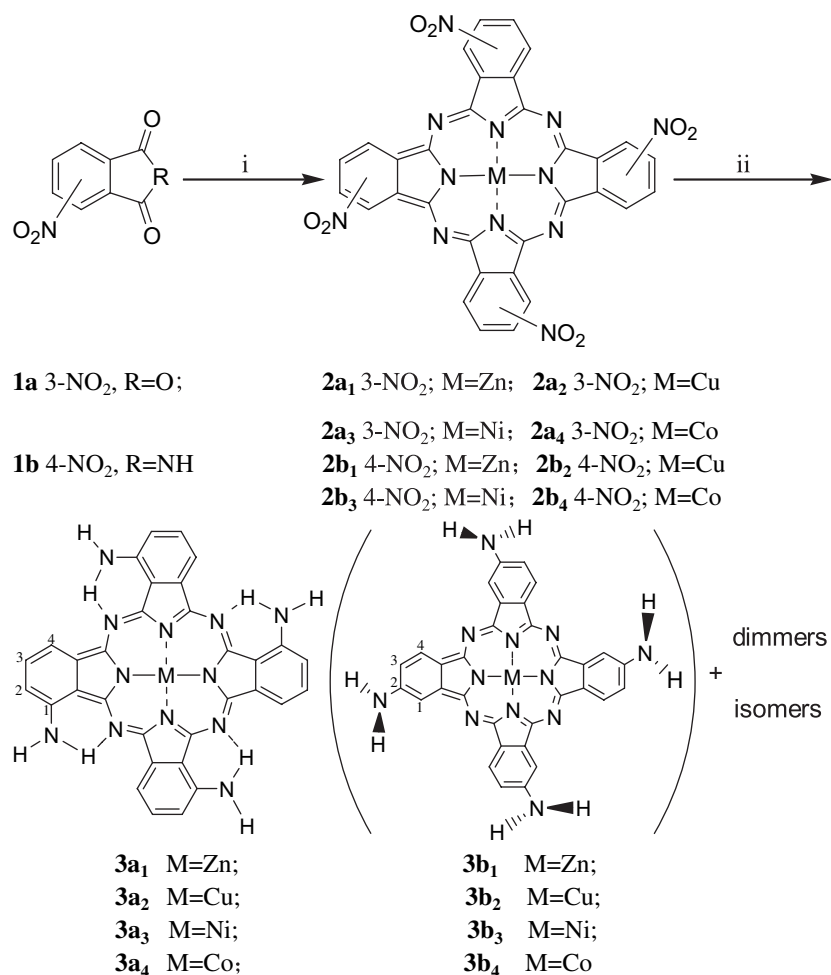


Fig. 4. ^1H NMR spectra of **3a₁** and **3b₁**.



Scheme 1. Reagents and conditions: (i) urea, ammonium molybdate, 160 °C (Zn) or 190 °C (Ni, Cu, Co); (ii) sodium sulfide nonahydrate in DMF, 60 °C, 1 h.

the thermodynamic rotation state because the two N—Hs only display one peak in NMR spectrum of **3b₁**. A smaller protuberance exists on the left of the peak at 6.230, this is possibly because amino-group rotation is hindered by the strong conjugation effect between amino-group and π bond.

In IR spectra, $\nu_{\text{as(N-H)}}$ values of amino groups in **3a₁–3a₄**, comparing to those of amino-groups in **3b₁–3b₄**, shift toward longer wavelength and $\nu_{\text{s(N-H)}}$

values shift toward shorter wavelength (Table 3), which are the evidence that intra-molecular hydrogen bonds exist in **3a₁–3a₄**.

3. Experimental

4-Nitro-*o*-phenyleneiine (>98%) (**1a**) was prepared according to the literature [18]. 3-Nitro-phthalic

Table 3
Synthesis of TNMPs

Metal salt, temperature	No.	Yield (%)	MS (required)	IR (KBr) ν (NO ₂) (cm ⁻¹)	Found (required)		
					C	H	N
ZnAc ₂ ·2H ₂ O 1.1g, 160 °C	2a₁	59.7	757.8 (757.9)	1533.31 1394.01	50.00 (50.64)	1.46 (1.60)	21.31 (22.14)
	2b₁	65.0	757.8 (757.9)	1523.46 1339.27	50.05 (50.64)	1.51 (1.60)	21.29 (22.14)
CuCl ₂ ·2H ₂ O 0.85g, 190 °C	2a₂	90.0	756.0 (756.1)	1537.51 1351.92	50.10 (50.83)	1.45 (1.60)	21.19 (22.23)
	2b₂	96.0	756.0 (756.1)	1519.95 1331.39	50.02 (50.83)	1.44 (1.60)	22.00 (22.23)
NiCl ₂ ·6H ₂ O 1.19g, 190 °C	2a₃	73.1	751.0 (751.2)	1533.47 1353.23	51.25 (51.17)	1.50 (1.61)	21.38 (22.37)
	2b₃	83.4	751.0 (751.2)	1526.05 1338.82	50.12 (51.17)	1.48 (1.61)	22.04 (22.37)
CoCl ₂ ·6H ₂ O 1.19g, 190 °C	2a₄	82.0	751.4 (751.5)	1536.47 1362.20	51.22 (51.14)	1.48 (1.61)	21.32 (22.37)
	2b₄	86.2	751.4 (751.5)	1523.51 1335.96	50.28 (51.14)	1.52 (1.61)	22.00 (22.37)

anhydride was purchased from England. Mass spectra were obtained on a LDI-1700 MALDI-TOF MS spectrometer. Microanalysis for C, H and N were performed on a Perkin-Elmer 2400 elemental analyzer. ^1H NMR spectra were obtained on a Unity-400 NMR spectrometer. UV–VIS spectra were recorded on a Cary 500 UV–VIS-NIR spectrophotometer. IR spectra were recorded on a Alpha-Centaur FT-IR spectrometer (KBr).

3.1. Synthesis of $2\mathbf{a}_1$ – $2\mathbf{a}_4$

3-Nitro-phthalic anhydride (3.86 g, 0.02 mol), urea (10 g), ammonium molybdate (0.05 g) and metal salt (0.005 mol) were finely ground and mixed. The mixture was put into a 250 mL beaker whose mouth was covered with a watch glass. The mixture was heated at a certain temperature, blue violet solid substance and bubbles then appeared slowly in the brown melting phase. After bubbling phenomenon disappeared completely, cooled the reaction mixture and then boiled it in hydrochloric acid (300 mL, 1 mol/L) and sodium hydroxide (300 mL, 1 mol/L) for 1 h, respectively. After the boil operations were repeated twice, solid substance was filtered out and washed with water to neutrality. The product was dried in air to afford blue violet $2\mathbf{a}_1$ – $2\mathbf{a}_4$ (Table 1).

3.2. Synthesis of $2\mathbf{b}_1$ – $2\mathbf{b}_4$

4-Nitro-*o*-phenyleneimine $\mathbf{1a}$ (3.84 g, 0.02 mol), urea (10 g) and ammonium molybdate (0.05 g) were mixed and heated to melt. Ground metal salt (0.005 mol) was then added to the reaction mixture and stirred with a glass stick. Other operations were the same as those in Section 3.1. Blue violet $2\mathbf{b}_1$ – $2\mathbf{b}_4$ were obtained (Table 1).

3.3. Synthesis of $3\mathbf{a}_1$ – $3\mathbf{a}_4$ ($3\mathbf{b}_1$ – $3\mathbf{b}_4$)

Powders of $2\mathbf{a}_1$ – $2\mathbf{a}_4$ ($2\mathbf{b}_1$ – $2\mathbf{b}_4$) (1 mmol) and sodium sulfide nonahydrate (2.88 g, 12 mmol) were put into a 50 mL tri-neck flask equipped with a thermometer, stirrer and condenser, DMF (15 mL) was then added. Heated and stirred the mixture slowly, when the temperature raised to 60 °C, quicker stir was given for 1 h at 60 °C. Reaction mixture was then dumped into 150 mL of water, filtered, washed with water to neutrality and dried in air to afford black green solid $3\mathbf{a}_1$ – $3\mathbf{a}_4$ ($3\mathbf{b}_1$ – $3\mathbf{b}_4$) (Table 3).

4. Conclusion

We find general characters of $3\mathbf{a}_1$ – $3\mathbf{a}_4$ and $3\mathbf{b}_1$ – $3\mathbf{b}_4$: (1) there are dimmers in their DMF solutions;

(2) amino-groups display strong anti-oxy properties; (3) wavelengths of Q bands in their UV–VIS spectra are related to the center M(II) and have the order $\text{Zn(II)} < \text{Cu(II)} > \text{Ni(II)} > \text{Co(II)}$. The differences between $3\mathbf{a}_1$ – $3\mathbf{a}_4$ and $3\mathbf{b}_1$ – $3\mathbf{b}_4$ are also found. Intra-molecular hydrogen bonds in $3\mathbf{a}_1$ – $3\mathbf{a}_4$ form due to their proper molecular structure, which makes electron transfer from amino-groups to center M(II) more readily than that in $3\mathbf{b}_1$ – $3\mathbf{b}_4$. $3\mathbf{a}_2$ – $3\mathbf{a}_4$ ($3\mathbf{b}_2$ – $3\mathbf{b}_4$) display paramagnetism and $3\mathbf{a}_1$ ($3\mathbf{b}_1$) displays diamagnetism. ^1H NMR of $3\mathbf{a}_1$ goes against $\Delta\delta/J \geq 6$ and ^1H NMR of $3\mathbf{b}_1$ follows $\Delta\delta/J \geq 6$. All of them above will direct us to investigate the synthesis and properties of TAMPc derivatives in the future.

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