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Dyes and Pigments 73 (2007) 245–250

DYES and PIGMENTS

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# Synthesis, spectroscopic properties and thermal stability of metal(II) tetraazaporphyrin complexes with two strong wavelength absorption

Zhimin Chen [a,b,*], Yiqun Wu [a,b], Xia Zuo [a]

[a] *Lab of Functional Materials, School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, PR China*
[b] *Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, PR China*

Received 14 July 2005; received in revised form 19 October 2005; accepted 14 December 2005
Available online 2 March 2006

## Abstract

Three kinds of metal(II) tetraazaporphyrin complexes with blue-violet and red light wavelength absorption were synthesized by refluxing tetraazaporphyrin ligand and different metal(II) ions, respectively. Their structures were confirmed by elemental analysis, LDI-TOF-MS, FT-IR and UV–Vis. The solubility of metal(II) tetraazaporphyrin complexes in organic solvents and absorption properties of their chloroform solution and films on K9 glass in the region 250–800 nm were measured. The influence on the difference of absorption maximum from metal(II) tetraazaporphyrin complexes to tetraazaporphyrin ligand by different metal(II) ions was studied. In addition, the thermal stability of the complexes was also evaluated.

*Keywords:* Metal(II) tetraazaporphyrin complexes; Synthesis; Absorption spectra; Thermal stability

## 1. Introduction

With an increasing development of blue-laser capable of recording information at a very high-density (over 23 GB on a single layer of a 120-mm-diameter disc), write-once-read-many optical recording media sensitive to blue-laser wavelengths or shorter have been increasingly developed [1,2]. For use in a recording layer of write-once-read-many optical recording media sensitive to blue-laser wavelengths, an organic material must have suitable optical properties and thermal decomposition behavior with respect to light at blue-laser wavelengths. Consequently, intensive efforts have been made to seek new organic storage materials with short wavelength absorption and new preparation approaches to obtain high quality recording films in recent years [3–6]. Metal tetraazaporphyrin complexes can attract much attention because they are more stable than azo and cyanine dyes against light, can provide easier control of the wavelength according to the substituted group and different metal ions, have good thermal stability, and have good solubility in many organic solvents [7]. A few years ago, metal tetraazaporphyrin complexes have been reported for applications in digital versatile disc-recordable (DVD-R) optical recording mediums [8,9]. But these works paid their main attention to the synthesis of the metal tetraazaporphyrin complexes with the maximum absorption wavelength between 550 and 650 nm. In fact, with the appearance of 405 nm blue-ray semiconductor laser, metal tetraazaporphyrin complexes with shorter wavelength, such as blue-violet light wavelength, seem to be very promising organic recording materials for the next generation of high-density digital versatile disc-recordable (HD-DVD-R) systems that use a high numerical aperture of 0.85 at 405 nm wavelength [10]. However, no investigations have been reported on the solubility and thermal properties of metal tetraazaporphyrin complexes, and little study has worked on synthesis and the relationships between the difference ($\Delta\lambda_{max}$) of absorption maximum from metal tetraazaporphyrin complexes to ligand and the structures of the metal tetraazaporphyrin complexes.

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[*] Corresponding author. Tel.: +86 21 69918592; fax: +86 21 69918800.
*E-mail address:* zmchen@siom.ac.cn (Z. Chen).

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doi:10.1016/j.dyepig.2005.12.001

Based upon the consideration of the above requirements, in this work we reported on the synthesis of the tetraazaporphyrin complexes with strong blue-violet and red light wavelength absorption. Their chemical structures are shown in Fig. 1. The relationships between the difference ($\Delta\lambda_{max}$) of absorption maximum from metal(II) tetraazaporphyrin complexes with different metal ions ($Ni^{2+}$, $Pd^{2+}$ and $Pb^{2+}$) to ligand and the structures of the metal(II) tetraazaporphyrin complexes were discussed. It can be expected that the relationships will guide the syntheses of new metal(II) tetraazaporphyrin complexes for the application later. Moreover, we also studied the thermal properties of these metal tetraazaporphyrin complexes and the solubility of these complexes in organic solvents as well as the absorption maximum of their films. All these properties indicate that these complexes have a promising use not only in conventional digital versatile disc-recordable (DVD-R), but also in high-density digital versatile disc-recordable (HD-DVD-R) systems for next generation optical storage.

## 2. Experimental

### 2.1. Materials

The metal-free compound, tetra-(*tert*-butyl)-tetraazaporphyrin (TAP), was purchased from Aldrich Chemicals Ltd. and it was purified by passing through a neutral alumina column and eluting with benzene–petroleum ether (2:1). The other reagents used for synthesis were of synthetic grade and were used without any purification. The other chemicals used for spectroscopic analysis were of analytical reagent grade.

### 2.2. Synthesis of metal(II) tetra-(tert-butyl)-tetraazaporphyrin complexes

A facile route was adopted in the synthesis of three metal(II) tetra-(*tert*-butyl)-tetraazaporphyrin complexes and the structures of complexes are shown in Fig. 1.

#### 2.2.1. Synthesis of nickel(II) tetra-(tert-butyl)-tetraazaporphyrin complex (Ni–TAP)

Metal-free tetraazaporphyrin (TAP) (54 mg, 0.10 mmol), ammonium molybdate (0.1 g) and anhydrous nickel dichloride (0.13 g, 1.0 mmol) were taken in 4 ml 1,2,4-trichlorobenzene and the suspension was heated at 220 °C with continuous stirring under a $N_2$ atmosphere. Within 4 h no metal-free tetraazaporphyrin was present, as shown by UV–visible spectroscopy. After cooling, the resulting deep solution was concentrated by rotary evaporation and the residue was dissolved in benzene (10 ml) for 20 min. The solution was filtered off and then the filtrate was collected within the rough product. The compounds were purified by passage through a 1.4 × 20 cm neutral alumina column, eluting with benzene/petroleum ether (1:1, v/v). The initial minor purple bands with fluorescence were discarded. Subsequently, the eluent was changed to pure benzene and the main purple bands were collected. Solvent was removed at reduced pressure and the residue was finally recrystallized from methanol/petroleum ether mixture. Dryness over anhydrous calcium chloride under vacuum caused purple–black crystals to form. Yield: 55.5 mg (93.4%). mp: >200 °C. Anal. calcd (found) for $C_{32}H_{40}N_8Ni$: C, 64.55 (64.22); H, 6.77 (6.77); N, 18.82 (19.24). Electronic absorption spectrum (UV–vis) in chloroform: $\lambda_{max}$ (nm) ($\log \varepsilon$) = 584 (4.79); 341 (4.61); 314 (4.56). FT-IR spectra (KBr pellets) $\upsilon$: 2954, 2922, 2863, 1457, 1387, 1358, 1252, 1203, 1079, 1013, 843, 772, 540 $cm^{-1}$; LDI-TOF-MS Found (calcd): $m/z = 595.6$ (595.4) [$M^+$].

#### 2.2.2. Synthesis of palladium(II) tetra-(tert-butyl)-tetraazaporphyrin complex (Pd–TAP)

The palladium(II) tetra-(*tert*-butyl)-tetraazaporphyrin complexes was synthesized by a procedure similar to that of the nickel(II) tetra-(*tert*-butyl)-tetraazaporphyrin complex, except that anhydrous palladous chloride (0.17 g, 1.0 mmol) was used and the solution was stirred for over 6 h at same temperature. The product was isolated to give purple–black crystals. Yield: 57.5 mg (89.4%). mp: >200 °C. Anal. calcd (found) for $C_{32}H_{40}N_8Pd$: C, 59.76 (59.34); H, 6.27 (6.27); N, 17.42 (17.77). Electronic absorption spectrum (UV–vis) in chloroform: $\lambda_{max}$ (nm) ($\log \varepsilon$) = 577 (4.77); 529 (4.11); 337 (4.56); 302 (4.42). FT-IR spectra (KBr pellets) $\upsilon$: 2956, 2923, 2863, 1456, 1389, 1359, 1250, 1202, 1071, 1016, 839, 769, 540 447 $cm^{-1}$; LDI-TOF-MS Found (calcd): $m/z = 642.7$ (643.1) [$M^+$].

#### 2.2.3. Synthesis of lead(II) tetra-(tert-butyl)-tetraazaporphyrin complex (Pb–TAP)

The lead(II) tetra-(*tert*-butyl)-tetraazaporphyrin complex was synthesized by a procedure similar to that of the nickel(II)

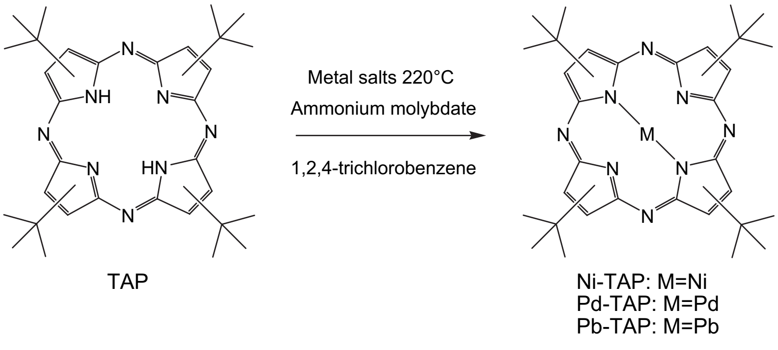

Fig. 1. Synthetical scheme of metal(II) tetra-(*tert*-butyl)-tetraazaporphyrin complexes.

tetra-(*tert*-butyl)-tetraazaporphyrin complex, except that anhydrous lead acetate (0.48 g, 0.15 mmol) was used and the solution was stirred for over 12 h at the same temperature. The product was isolated to give deep green crystals. Yield: 70 mg (94.3%). mp: >200 °C. Anal. calcd (found) for $C_{32}H_{40}N_8Pb$: C, 51.66 (51.13); H, 5.42 (5.44); N, 15.06 (15.83). Electronic absorption spectrum (UV–vis) in chloroform: $\lambda_{max}$ (nm) (log $\varepsilon$) = 622 (4.87); 345 (4.62); 259 (4.26). FT-IR spectra (KBr pellets) $\upsilon$: 2953, 2915, 2863, 1459, 1387, 1358, 1246, 1203, 1070, 991, 843, 771, 529 $cm^{-1}$; LDI-TOF-MS Found (calcd): $m/z$ = 743.0 (743.9) [$M^+$].

### 2.3. Preparation of thin films

The solutions were prepared by dissolving the respective tetra-(*tert*-butyl)-tetraazaporphyrin complexes in toluene to give a concentration of 20 mg/ml. The solutions were filtered with a 0.22 μm Millipore membrane filter to obtain the coating solutions. The K9 glass substrates (diameter: 30 mm) were cleaned in an ultrasonic bath with acetone, ethanol, deionized water several times and dried, successively. The films were prepared with a KW-4A precision spin-coater (Chemat Technology Inc.) using a syringe. A two-step procedure, 800 rpm for the first 5 s and 3000 rpm thereafter for 30 s, is usually used in our laboratory to prepare smooth films. The substrates were kept at room temperature and a relative humidity of 50% throughout the deposition process. The resulting films were then heated at 50 °C for 2–3 h to ensure removal of the solvent.

### 2.4. Instrument and methods

FT-IR spectra were recorded as KBr pellets over the range 4000–400 $cm^{-1}$ using a Perkin–Elmer instruments Spectrum One FT-IR Spectrometer. Elemental analyses were performed with an elemental analyzer (Perkin–Elmer-2400). UV–Vis spectra were measured using a Perkin–Elmer Lambda 9 UV/VIS/NIR spectrophotometer. Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS) was determined using LDI-1700 (Linear Scientific Inc). Thermal properties were analyzed with a Perkin–Elmer Instruction system (TGA-7) at a heating rate of 10 °C/min from 30 to 800 °C under a nitrogen atmosphere.

## 3. Results and discussion

### 3.1. Synthesis and characterization

The synthesis of metal(II) tetra-(*tert*-butyl)-tetraazaporphyrin complexes described above is a significant improvement to the methods in the literature [11,12]. The nickel(II) complex (Ni–TAP) and the palladium(II) complex (Pd–TAP) were prepared readily by the reaction of the free-base tetra-(*tert*-butyl)-tetraazaporphyrin (TAP) with the respective anhydrous metal chloride or metal acetate in 1,2,4-trichlorobenzene using ammonium molybdate as the catalyst at the reflux temperature. However, the lead(II) complex (Pb–TAP) could not be obtained by the anhydrous lead chloride, but could be synthesized by the anhydrous lead acetate under the same reaction conditions. The corresponding anhydrous metal chloride or metal acetate used in the reaction was a large excess (5–15 equiv) over the free-base tetra-(*tert*-butyl)-tetraazaporphyrin (TAP). The metalation process was monitored by UV–vis spectroscopy and stopped when the optical spectrum showed the completion of the reaction. All these resulting complexes were obtained in the solid state in good yields following chromatography due to fewer by-products and better resolution of each band on the column. They are stable in solution as well as in the dry state under ambient conditions. The elemental analytical data, MALDI-TOF mass spectra and FT-IR spectra of the metal(II) complexes agree well with their formulae.

The IR spectra of three meta(II) tetra-(*tert*-butyl)-tetraazaporphyrin complexes are very similar, except some slight shifts of a few vibration bands caused by different centre metals. Of these bands, the absorption at 2953–2956 ($\upsilon_{as}$CH), 2915–2923, 2863 ($\upsilon_s$CH), 1246–1252 (skeleton), and 1202–1203 $cm^{-1}$ are attributed to *tert*-butyl groups, but other remaining bands observed commonly for metal complexes at 769–772, 839–843, 991–1016, 1070–1079, 1358–1359, 1387–1389 and 1456–1459 $cm^{-1}$ would be mostly due to the various skeletal vibrations of tetraazaporphyrin ring [13]. Among these, the bands at 991–1016 $cm^{-1}$ are the strongest, and the bands at 1070–1079 and 1456–1459 $cm^{-1}$ are doublets. To demonstrate that metal(II) tetra-(*tert*-butyl)-tetraazaporphyrin complexes are different from their precursor (TAP), we also measured the IR spectra of the free-base tetra-(*tert*-butyl)-tetraazaporphyrin (TAP). The results shown that metal-free tetraazaporphyrin (TAP) exhibited a series of vibration bands at 3300, 940 and 736 $cm^{-1}$, which are not seen with metallated derivatives (Ni–TAP, Pd–TAP and Pb–TAP). These bands are due to the NH stretching and in-plane and out-plane bending vibration of the inner tetraazaporphyrin core in the metal-free molecule. Furthermore, as seen in the IR spectra of metal-free tetraazaporphyrin (TAP), a group of six strong bands between 1100 and 700 $cm^{-1}$ appears in nearly uniform intensity; however, a band around 1000 $cm^{-1}$ became more prominent vis-a-vis other bands in this region for the metal(II) complexes.

The formation of the metal(II) tetraazaporphyrin complexes was also confirmed by UV–vis spectra. The spectra of the compounds (TAP, Ni–TAP, Pd–TAP and Pb–TAP) in $CHCl_3$ solutions are shown in Fig. 2, respectively, and important data are summarized in Table 1. All of the metal complexes showed typical electronic absorption spectra with two strong absorption regions, one in the UV region at about 340 nm (B-band) and the other in the visible region at 570–630 nm (Q-band) with a weaker satellite band around 520–560 nm [13]. For metal-free tetraazaporphyrin split Q-bands appeared at 622 and 553 nm, while the B-band remained at 336 nm. The electronic absorption spectra of tetraazaporphyrins can be readily interpreted using Gouterman's four-orbital model [14]. Specifically, there are two principle π–π* transitions of the tetraazamacrocycle ring: a lower

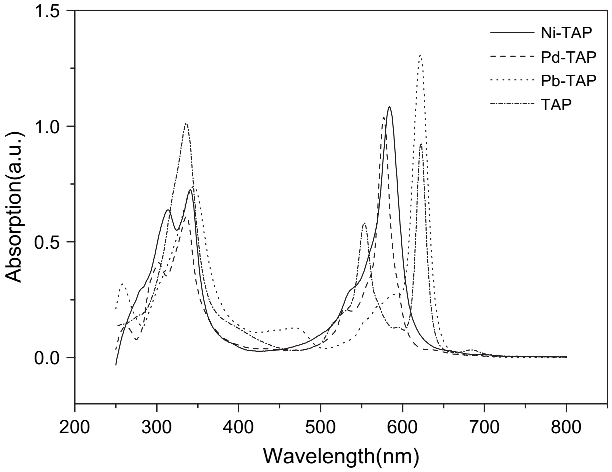

Fig. 2. Absorption spectra of metal(II) tetra-(*tert*-butyl)-tetraazaporphyrins in chloroform.

energy "Q-band" (550–650 nm), attributed to the transition from the highest occupied molecular orbital (HOMO) $a_{1u}$ to the lowest unoccupied molecular orbital (LUMO) $e_g$, and a higher energy "B-band" (250–400 nm), arising from the $a_{2u}$(HOMO-1) → $e_g$(LUMO) transitions (in $D4h$ symmetry). The reduced symmetry from $D4h$ to $D2h$ of the free-base tetraazaporphyrin splits the degenerate $e_g$(LUMO) level and doubles the number of transitions, giving a natural interpretation of the double-peak structure seen experimentally in the Q-band region.

We also study the influence of different metal ions on the $\lambda_{max}$ for the same ligand of TAP. From Fig. 2, it can be seen clearly that the ability of metal ions to make hypsochromic shifts is palladium(II) > nickel(II) > lead(II) and the extent of this shift for B-band is much smaller than that of Q-band. This indicates that the nature of the central metal ions significantly affected the position of the absorption band. According to modern molecular orbital theory [13], any factors that can influence the electronic density of conjugated ring must result in the bathochromic or hypsochromic shifts of absorption bands. Here, in the case of the tetraazaporphyrin with the same substituent the main reason for hypsochromic shifts are generally related with two aspects: the ionic radius ($r^{2+}$) and the electronegativity ($X$) of the central metal ions. The order of the electronegativity of the central metal ions is $Pd^{2+}$ (2.2) > $Ni^{2+}$ (1.91) > $Pb^{2+}$ (1.87) [15]. The larger the electronegativity, the greater the ability of the central metal for attracting the π-electrons in conjugated ring, so the electronic density in conjugated ring is reduced, the energy difference of $\pi \rightarrow \pi^*$ transition is increased and the hypsochromic shift of absorption band is enhanced. As for the radius of metal ions, the order is $Ni^{2+}$ (78 pm) < $Pd^{2+}$ (80 pm) < $Pb^{2+}$ (132 pm) [15]. The bigger the ions radius, the greater the d-electron contribution of the central metal to the π-electron in conjugated ring, so the electronic density is increased with the electronic overlapping and the bathochromic shift occur. The Pd(II) shows that the biggest electronegativity with a moderate ions radius leads to a hypsochromic shift, while the Pb(II) holds that a smallest electronegativity with the biggest ions radius results in a bathochromic shift. Therefore, the consequence of absorption maximum ($\lambda_{max}$) of the synthesized complexes is Pb–TAP > Ni–TAP > Pd–TAP, especially in the Q-band.

### 3.2. Solubility and absorption spectra of metal(II) complexes' thin films

The solubility of tetraazaporphyrins was investigated and the result shown in Table 1. In contrast with unsubstituted tetraazaporphyrins, which is only low soluble in aprotic solvents like DMF, DMSO [7], the synthesized complexes 2, 3and 4 can also be easily dissolved in many weakly and medium polar organic solvents such as benzene, toluene, chloroform, ethyl acetate and tetrahydrofuran (THF). The increased high solubility might be due to the four substituted *tert*-butyl groups on the tetraazaporphyrin ring which increase the repulsion force and reduce the aggregation of tetraazaporphyrin molecules, so improving the solubility of complexes. But their solubility decreases in strongly polar solvents such as methanol, ethanol, acetonitrile and water, because *tert*-butyl groups are weakly polar and lipophilic. In addition, the solubility of the three complexes has not much difference in the same solvent. This indicates that central metals have a small influence on the solubility of the title compounds. Since the recording layer is applied on a polycarbonate substrate by the spin-coating method, the recording dye must be soluble in specific organic solvents which do not attack polycarbonate (PC) resins commonly used as the substrate material for optical recording media [3]. In

Table 1
Summary of physical and optical properties for metal(II) tetra-(*tert*-butyl)-tetraazaporphyrin complexes

| Product | Solution (nm)[a] | | Film (nm)[b] | | Abs.[b] at 650 nm | Abs.[b] at 405 nm | Solubility[c] | Td/°C[d] |
|---|---|---|---|---|---|---|---|---|
| | Q-band $\lambda_{max}$/log $\varepsilon$ | B-band $\lambda_{max}$/log $\varepsilon$ | Q-band Abs./$\lambda_{max}$ | B-band Abs./$\lambda_{max}$ | | | | |
| TAP | 622, 553 | 336 | – | – | – | – | O | – |
| Ni–TAP | 584/4.79 | 341/4.61 | 586/0.90 | 341/0.81 | 0.09 | 0.10 | O | 349 |
| Pd–TAP | 577/4.77 | 337/4.56 | 583/0.80 | 339/0.62 | 0.10 | 0.12 | O | 359 |
| Pb–TAP | 622/4.87 | 345/4.62 | 623/0.65 | 343/0.53 | 0.26 | 0.14 | O | 338 |

[a] In chloroform solvent.

[b] On K9 substrate.

[c] In chloroform, toluene, solvent or THF (O: >2 wt%).

[d] 10 °C/min under $N_2$ gas.

general, more than 2.0 wt% solubility is necessary. The synthesized metal(II) complexes are well soluble, a coating solution of such concentration can be easily prepared.

The absorption spectra of metal(II) complexes' thin films are shown in Fig. 3 and important data are summarized in Table 1. The thin films show similar absorption bands compared with those in the chloroform solution. But the obvious broadening of absorption bands is also observed. Meanwhile, the Q-bands show a slightly bathochromic shift, while the B-band remains almost the same as in the case of the chloroform solution. The broadening effect and bathochromic shift originate from extensive excitation coupling between adjacent conjugated macrocycles, and the extent of the broadening strongly correlates with the degree of coupling, which depends on several factors, such as the closeness of adjacent macrocycles, the tilting angle, the overlap position, the substituted groups, and the extinction coefficients of the transition bands involved [16]. All of the metal(II) complexes' films showed typical electronic absorption spectra with two wavelength absorption regions, one in the UV region at about 340 nm (B-band) and the other in the visible region at 570–630 nm (Q-band). They have sharp tails in the longer wavelength region and a small absorbance at the 405 and 650 nm side. These characteristics indicate that it would be easy to obtain high refractive index and reflectivity based on their thin films, and the high refractive index results in a high-modulated amplitude of the recording signal [17,18]. Therefore, these metal(II) complexes have potential application for high-density optical recording media which can be recorded and read at two wavelengths, a conventional red laser of 650 nm and a short wavelength laser (blue-laser) of 405 nm.

### 3.3. Thermal properties of the metal(II) complexes

The thermal stability of metal(II) complexes was investigated by thermogravimetric analysis. Fig. 4 presents the recorded curves of weight loss for three metal(II) complexes in nitrogen atmosphere. It can be seen that the TGA curves of the Ni–TAP and Pd–TAP complexes show no weight loss up to 100 °C, while for the Pb–TAP complexes, the loss does not appear until 230 °C. As the temperature is increased, the TGA curves of three complexes exhibit a progressive weight loss below ∼260 °C. This process can be readily interpreted as sublimation of the complexes, because it is also observed by microscope melting point instrument. And then a sharp decomposition with high weight loss rate occurs at temperatures between 280 and 360 °C, especially in Ni–TAP complex. These data show that the Ni–TAP complex possesses better thermal properties than Pd–TAP and Pb–TAP complexes and is possible to fabricate a small and sharp recording mark edge due to its higher and sharper thermal decomposition threshold.

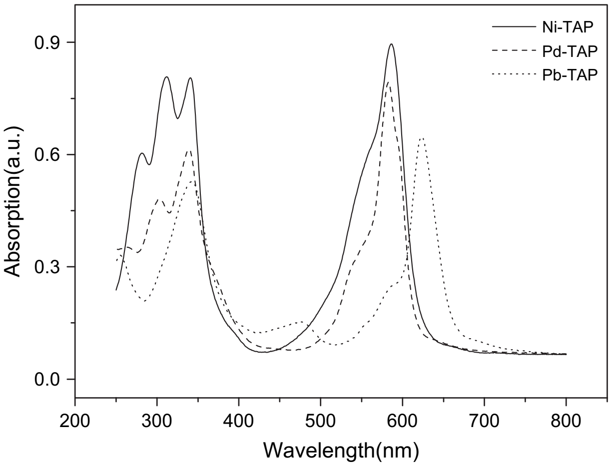

Fig. 3. Absorption spectra of metal(II) tetra-(*tert*-butyl)-tetraazaporphyrin complexes' films.

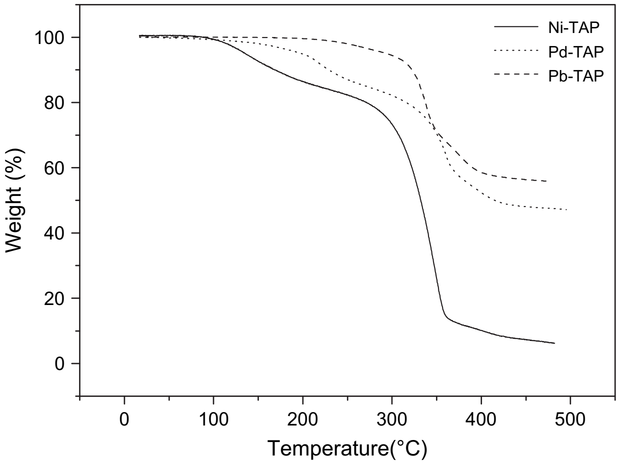

Fig. 4. TGA curves of metal(II) tetra-(*tert*-butyl)-tetraazaporphyrin complexes.

## 4. Conclusion

In conclusion, we have described the synthesis and some spectroscopic and thermal properties of three metal(II) tetraazaporphyrin complexes with strong blue-violet and red light wavelength absorption. It is found that the metal(II) tetraazaporphyrin complexes have potential application for high-density optical recording at two wavelengths due to their good solubility in organic solvents and suitable absorption spectra in thin films, and the Ni–TAP complex would be suitable for high-density optical recording medium because of its higher thermal stability and sharper thermal decomposition threshold with a high weight loss rate.

## Acknowledgements

Financial support from the National Natural Science Foundation of China (No. 20141001) the Key Science and Technology Project of Heilongjiang Province (No. GC01A217) is gratefully acknowledged.

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