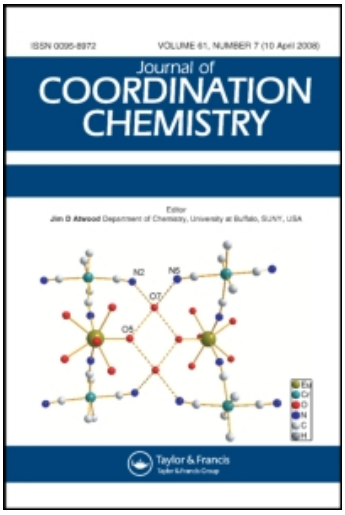

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Synthesis and characterization of soluble *seco*-porphyrazines with bulky substituents

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By cyclotetramerization of 3,4-*bis*(4-*tert*-butylphenyl)pyrroline-2,5-diimine in the presence of magnesium butanolate, magnesium porphyrazinate with eight (4-*tert*-butylphenyl) units on the periphery has been synthesized. Its demetalation by the treatment with trifluoroacetic acid resulted in a partially oxidized product, namely, octakis(4-*tert*-butylphenyl)-2-*seco*-porphyrazine-2,3-dione. Further reaction of this product with copper(II) acetate, zinc(II) acetate, and cobalt(II) acetate led to the metallo derivatives, [octakis(4-*tert*-butylphenyl)-2-*seco*-2, 3-dioxoporphyrazinato]M(II) (M = Cu, Zn, Co). These soluble complexes have been characterized by elemental analysis, FT-IR, ^{1}H NMR, UV-Vis, and mass spectral data.

Keywords: *Seco*-porphyrazine; 4-*Tert*-butylphenyl; Pyrroline; Copper; Zinc

1. Introduction

Tetrapyrrole complexes with different substituents have catalytic properties, high electron delocalization, high synthetic possibilities, numerous technological applications, and biological importance [1–6]. However, porphyrazines have received less interest than porphyrins and phthalocyanines. Peripheral heteroatom functionalization of the macrocycle results in important modulation of their physical and electronic properties [7–9]. In spite of the fact that the number of metal ions capable of taking part in the inner core of tetrapyrrole derivatives reaches 80, derivatization of porphyrazines has generally been achieved by addition of various substituents (e.g., naphthyl-, anthracenyl-, tolyl-, alkyl-, aryl-, ether-, sulfanyl-, amino-, quaternized amino-groups, etc.) to the peripheral positions [10–13]. These substituents enhance the solubility of the products and provide additional functionalities for interaction with alkali or transition metal ions, mesophase formation, etc. [14–18].

Our group has been interested in preparation of new soluble phthalocyanine and porphyrazine derivatives. Among these are phthalocyanines fused to, or attached through bridges to, macrocyclic structures and porphyrazines with long chains or functional units such as quaternizable amino groups [19], crown ethers [20],

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ferrocenes [21], triphenylphosphine [22], 4-*tert*-butylphenylthio [23], and tosylaminoethylthio [24]. Recently, we synthesized porphyrazines with bulky electron-rich substituents such as (1-naphthylmethylthio) [25] and (9-anthracenylmethylthio) [26]. We have also reported *seco*-porphyrazines substituted with (1-naphthyl) [27] or (4-biphenyl) units [28] on peripheral positions as Garrido Montalban *et al*. have with peripheral amino porphyrazine derivatives [29].

In this study, we report soluble *seco*-porphyrazines with eight (4-*tert*-butylphenyl) substituents appended to the periphery. By cyclotetramerization of 3,4-*bis*(4-*tert*-butylphenyl)pyrroline-2,5-diimine in the presence of magnesium butanolate, magnesium porphyrazinate with eight (4-*tert*-butylphenyl) units has been synthesized. Its demetalation by treatment with trifluoroacetic acid resulted in partially oxidized product, octakis(4-*tert*-butylphenyl)-2-*seco*-porphyrazine-2,3-dione. Further reaction of this product with copper(II) acetate, zinc(II) acetate, and cobalt(II) acetate led to metallo derivatives, [octakis(4-*tert*-butylphenyl)-2-*seco*-2,3-dioxoporphyrazinato]M(II) (M = Cu, Zn, Co). These new soluble complexes have been characterized by elemental analysis, FT-IR, ^{1}H NMR, UV-Vis, and mass spectra.

2. Experimental

IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer and electronic spectra on a Unicam UV2 spectrophotometer. Elemental analyses were recorded on a Thermo Finnigan Flash EA 1112 instrument. Proton NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer using TMS and d-chloroform as the reference and solvent, respectively. Mass spectra were recorded on a Bruker Daltonics MicrOTOF LC–MS spectrometer using the electro spray ionization (ESI) method. The instrument was operated in positive ion mode. All reagents and solvents were of reagent grade that obtained from commercial suppliers. Homogeneity of the products was tested in each step by TLC. Chemicals were of the highest grade available. Unless specified otherwise, reagent grade reactants and solvents were used as received from chemical suppliers. The solvents were stored over molecular sieves.

3,4-*bis*(4-*tert*-butylphenyl)pyrroline-2,5-diimine (**1**) was prepared according to previously reported procedure [30].

[2, 3, 7, 8, 12, 13, 17, 18-Octakis(4-*tert*-butylphenyl) porphyrazinato]Mg(II) (2): Mg turnings (6.0 mg, 0.25 mmol) and a small I_2 crystal were refluxed in *n*-BuOH (20 mL) for 8 h to obtain $Mg(BuO)_2$. 3,4-*Bis*(4-*tert*-butylphenyl)pyrroline-2,5-diimine (**1**) (180 mg, 0.50 mmol) was added to this solution and the mixture was refluxed for 12 h. The blue-green product was filtered, washed with ethanol and water, and dried *in vacuo*. The crude product was dissolved in chloroform and filtered. The chloroform solution was dried over anhydrous Na_2SO_4. When the solvent was evaporated, blue-green product was obtained. Finally, pure porphyrazine was obtained by column chromatography (SiO_2, CH_3OH : $CHCl_3$, 1 : 20 v/v). The product **2** was highly soluble in chloroform, soluble in dichloromethane and acetone, but insoluble in EtOH. Yield: 119 mg, 68%. FT-IR, ν_{max} (cm^{-1}): 3055–3035 (CH, aromatic), 2975–2865 (CH, aliphatic), 1610 (C=C, aromatic), 1494, 1410, 1215, 1144, 1015, 835, 761, and 703.

^{1}H NMR (d-chloroform, 500 MHz): δ (ppm) 7.35–7.12 (m, 32H, Ar–H), 1.35 (s, 72H, $(CH_3)_3$–C). MS (ESI): (m/z): 1394.6 $[M]^+$.

[2, 3, 7, 8, 12, 13, 17, 18-Octakis(4-*tert*-butylphenyl)-2-*seco*-porphyrazine-2, 3-dione] (3): Compound **2** (139 mg, 0.100 mmol) was dissolved in the minimum amount of trifluoroacetic acid (~4.00 mL) and stirred for 4 h at room temperature. When the reaction mixture was added to ice drop by drop and neutralized with 25% ammonia solution, precipitation occurred and was collected by filtration. The precipitate was extracted into chloroform and the chloroform solution was extracted with water twice. After drying over anhydrous Na_2SO_4, the solvent was evaporated to obtain the green metal-free porphyrazine. Compound **3** was purified by column chromatography (SiO_2, $CH_3OH : CHCl_3$, 1 : 50 v/v). The product was soluble in chloroform, dichloromethane, and acetone, but insoluble in EtOH. Yield: 79 mg (56%). FT-IR, ν_{max} (cm^{-1}): 3330 (N–H), 3050–3030 (CH, aromatic), 2970–2862 (CH, aliphatic), 1718 (C=O), 1612 (C=C, aromatic), 1499, 1413, 1218, 1145, 1018, 838, 763, and 705. ^{1}H NMR (d-chloroform, 500 MHz): δ (ppm) 7.38–7.36 (d, 12H, Ar–H), 7.31–7.28 (d, 12H, Ar–H), 7.25–7.22 (d, 4H, Ar–H), 7.18–7.16 (d, 4H, Ar–H), 1.33 (s, 54H, $(CH_3)_3$–C), 1.24 (s, 18H, $(CH_3)_3$–C), −1.20 (br s, 2H, N–H). MS (ESI): (m/z): 1403.5 $[M]^+$.

2.1. *General procedure for metallo* seco-*porphyrazines, 4–6*

Compound **3** (140 mg, 0.100 mmol) in $CHCl_3$ (15.0 mL) was stirred with the metal salt [$Cu(OAc)_2$ (182 mg, 1.00 mmol), $Zn(OAc)_2$ (183 mg, 1.00 mmol), or $Co(OAc)_2$ (177 mg, 1.00 mmol)] in ethanol (15.0 mL) and refluxed under nitrogen for 6 h. The precipitate composed of the crude product and excess metal salt was collected, treated with chloroform, and the insoluble metal salts removed by filtration. The filtrate was reduced to the minimum volume under reduced pressure and then added into *n*-hexane (150 mL) drop by drop to realize precipitation. Finally, pure porphyrazine was obtained by column chromatography (SiO_2, $CH_3OH : CHCl_3$, 1 : 30 v/v). Compounds **4**–**6** were highly soluble in chloroform, acetone, and dichloromethane.

[2, 3, 7, 8, 12, 13, 17, 18-Octakis(4-*tert*-butylphenyl)-2-*seco*-2, 3-dioxoporphyrazinato] Cu(II) (4): Yield: 66 mg (45%). FT-IR, ν_{max} (cm^{-1}): 3048–3032 (CH, aromatic), 2972–2865 (CH, aliphatic), 1720 (C=O), 1615 (C=C, aromatic), 1485, 1410, 1212, 1141, 1013, 836, 761, and 704. MS (ESI): (m/z): 1465.8 $[M]^+$.

[2, 3, 7, 8, 12, 13, 17, 18-Octakis(4-*tert*-butylphenyl)-2-*seco*-2, 3-dioxoporphyrazinato] Zn(II) (5): Yield: 78 mg (53%). FT-IR, ν_{max} (cm^{-1}): 3052–3033 (CH, aromatic), 2974–2861 (CH, aliphatic), 1721 (C=O), 1614 (C=C, aromatic), 1489, 1411, 1214, 1148, 1014, 833, 768, and 707. ^{1}H NMR (d-chloroform, 500 MHz): δ(ppm) 7.33–7.31 (d, 12H, Ar–H), 7.27–7.25 (d, 12H, Ar–H), 7.20–7.17 (d, 4H, Ar–H), 7.12–7.10 (d, 4H, Ar–H), 1.37 (s, 54H, $(CH_3)_3$–C), 1.27 (s, 18H, $(CH_3)_3$–C). MS (ESI): (m/z): 1467.8 $[M]^+$.

[2, 3, 7, 8, 12, 13, 17, 18-Octakis(4-*tert*-butylphenyl)-2-*seco*-2, 3-dioxoporphyrazinato] Co(II) (6): Yield: 70 mg (48%). FT-IR, ν_{max} (cm^{-1}): 3045–3025 (CH, aromatic), 2974–2860 (CH, aliphatic), 1715 (C=O), 1608 (C=C, aromatic), 1485, 1416, 1217, 1143, 1014, 835, 765, and 701. MS (ESI): (m/z): 1460.3 $[M]^+$.

3. Results and discussion

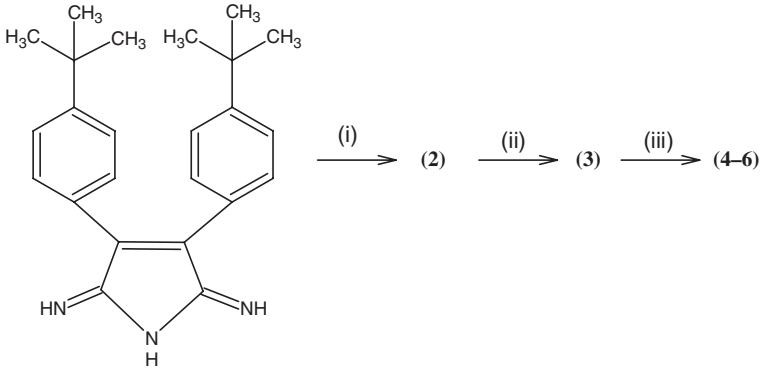
Conversion of 3,4-*bis*(4-*tert*-butylphenyl)pyrroline-2,5-diimine (**1**) into magnesium porphyrazine (**2**) was achieved by the template effect of magnesium butanolate (scheme 1). Cyclotetramerization gave the blue-green octakis(4-*tert*-butylphenyl)-porphyrazinatomagnesium (**2**) (figure 1) in 68% yield.

In conversion of compound **2** to **3** (figure 2) by treatment with trifluoroacetic acid, a *seco*-porphyrazine macrocycle in which one of the four pyrrole rings has been oxidized is the main product. Steric tension due to the presence of eight bulky (4-*tert*-butylphenyl) units around the core might be the reason for cleavage of one pyrrole ring. 4-*Tert*-butylphenyl units are not comparable with dimethylamino groups [29, 31, 32], but with naphthyl groups as electron donors to the 18-π electron system of the inner core [31]. In the present case, the tendency of (4-*tert*-butylphenyl) substituted porphyrazine to oxidize to the *seco*-porphyrazine should be higher than dimethylamino substituted ones because the reactions were carried out under inert atmospheres during these experiments, but still no product corresponding to the metal-free derivative of compound **2** could be isolated. The mass spectral results clearly indicate the change of structure from magnesium porphyrazinate (**2**) to the demetalated *seco*-porphyrazine (**3**). In addition to the mass spectral results, intense C=O absorption clearly differentiates oxidized products from the symmetrically octakis(4-*tert*-butylphenyl) substituted magnesium porphyrazinate. Insertion of metal ions into the demetalated *seco*-porphyrazine (**3**) with metal(II) acetates (M = Cu, Co, Zn) at reflux in ethanol afforded an approximately quantitative yield for compounds **4**–**6** (scheme 1).

All new compounds were identified through the spectroscopic techniques ^{1}H NMR, FT-IR, UV–Vis, mass and elemental analysis. The spectroscopic data are in accord with the assigned structures.

Elemental analyses correspond closely with calculated values for compounds **2**–**6** (table 1).

In the FT-IR spectrum of **2**, the aromatic C–H peaks are 3035–3055 cm^{-1}, the aliphatic C–H peaks 2865–2975 cm^{-1}, and the aromatic C=C peak at 1610 cm^{-1}, as expected [25–28]. After conversion of **1** to magnesium porphyrazine (**2**), the N–H vibration at 3315 cm^{-1} disappeared. The N–H stretching absorption of the inner core of **3** was at 3330 cm^{-1}, and peripheral oxidation of one pyrrole ring was indicated with an



Scheme 1. (i) Mg turnings, I_2, *n*-BuOH; (ii) CF_3CO_2H; (iii) EtOH and $Cu(OAc)_2$, $Zn(OAc)_2$, or $Co(OAc)_2$.

intense absorption at 1718 cm^{-1} [29, 32]. The FT-IR spectra of all porphyrazine derivatives (**2**–**6**) showed aromatic C–H peaks at 3025–3055 cm^{-1}, aliphatic C–H peaks at 2860–2975 cm^{-1}, characteristic C=C aromatic peaks at 1608–1615 cm^{-1}, and characteristic *para*-substituted phenyl C–H bends at 833–838 cm^{-1} [23, 25–27], indicating the presence of (4-*tert*-butylphenyl) substituents with the *seco*-porphyrazine derivatives.

In the ^1H NMR spectra of diamagnetic porphyrazines (**2**, **3**, **5**), several types of protons are observed, sets of doublets around 7.10–7.38 ppm for phenyl-protons [23, 25–28] and a singlet at 1.35 ppm in **2**, 1.33 and 1.24 ppm in **3**, or 1.37 and 1.27 ppm in **5** corresponding to *tert*-butyl groups. Inner core N–H protons of metal-free porphyrazine (**3**) appear as a broad singlet peak at −1.20 ppm indicating the typical shielding of inner core protons, common for metal-free porphyrazines [11, 20, 21].

Electronic spectra of metallo-porphyrazines exhibit a strong absorption at 676 nm, due to a $\pi \rightarrow \pi^*$ transition (the Q band) and a second intense and broad $\pi \rightarrow \pi^*$ transition in the near UV region at 348 nm (Soret or B-band) [10, 11]. UV-Vis spectra of **2**–**6** exhibit an intense single Q band absorption at 674–680 nm and B bands at 340–356 nm (table 2). As expected, the metal-free derivative (**3**) shows a split Q band at 654 and 710 nm as a consequence of the lowering of the symmetry of porphyrazine core. UV-Vis spectra of **2** and **3** in chloroform are shown in figure 3. An absorbance

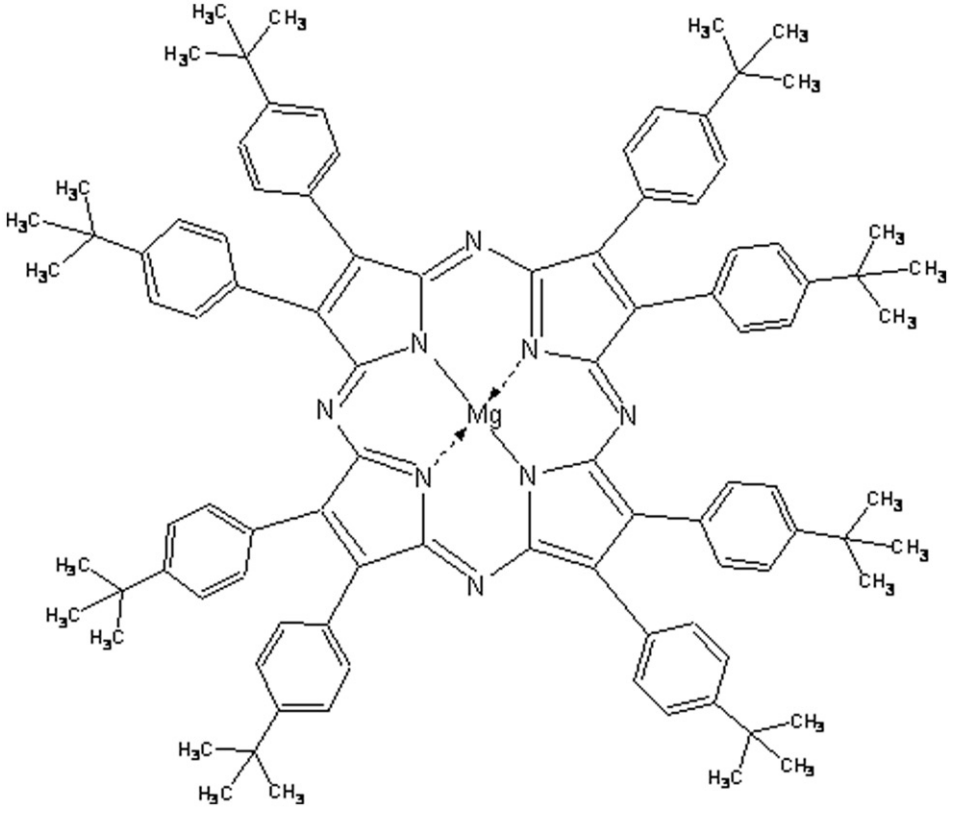


Figure 1. [2, 3, 7, 8, 12, 13, 17, 18-Octakis(4-*tert*-butylphenyl)porphyrazinato]Mg(II) (**2**).

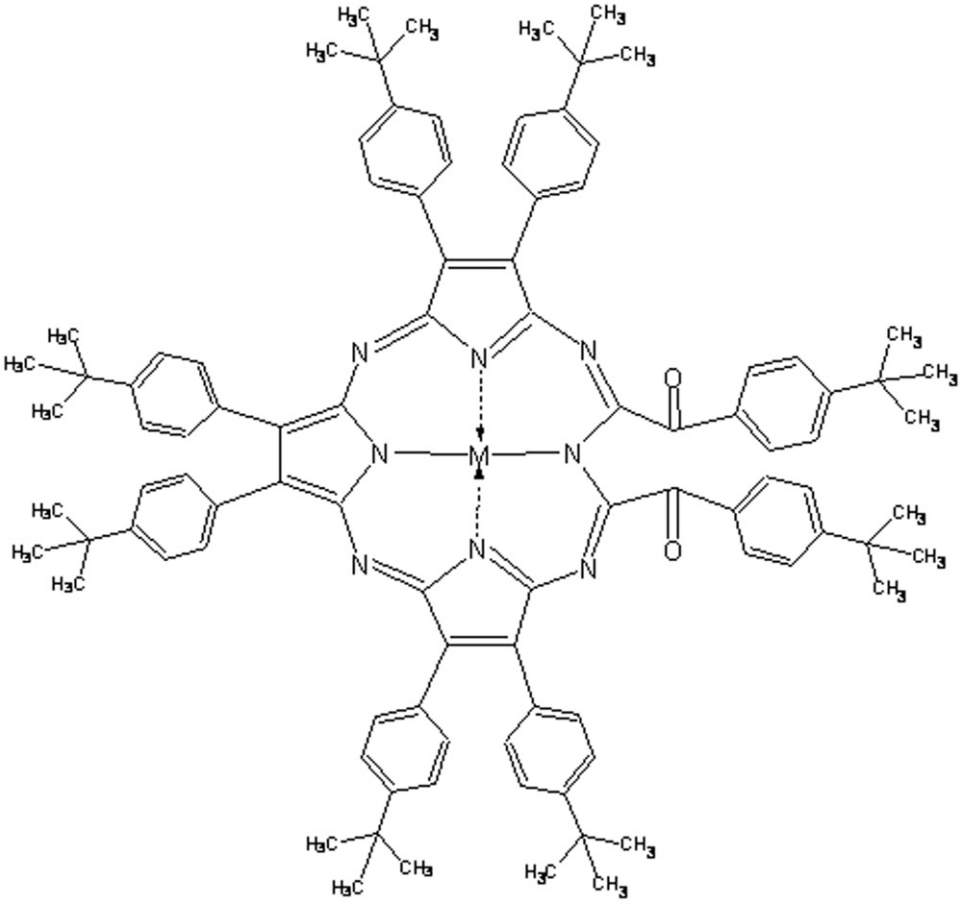


Figure 2. [2, 3, 7, 8, 12, 13, 17, 18-Octakis(4-*tert*-butylphenyl)-2-*seco*-porphyrazine-2, 3-dione] and metal derivatives {M = 2H, Cu(II), Zn(II), or Co(II)}.

Table 1. Elemental analyses results of compounds **2**–**6**.*

Compound	C	H	N
2	82.59 (82.70)	7.64 (7.52)	8.16 (8.04)
3	83.28 (83.13)	7.75 (7.61)	7.86 (7.98)
4	78.80 (78.68)	7.07 (7.15)	7.53 (7.65)
5	78.71 (78.58)	7.06 (7.14)	7.75 (7.64)
6	78.81 (78.94)	7.29 (7.18)	7.79 (7.67)

*Required values are given in parentheses.

versus concentration study showed that due to the bulky (4-*tert*-butylphenyl) substituents, no aggregation occurred either for **2** or **3**.

In conclusion, we report the synthesis, characterization, and spectral properties of a soluble *seco*-porphyrazine with bulky (4-*tert*-butylphenyl) units on the periphery; steric requirements of the eight bulky (4-*tert*-butylphenyl) substituents lead to oxidized *seco*-porphyrazines. The presence of bulky (4-*tert*-butylphenyl) substituents hindered aggregation at higher concentrations.

Table 2. UV-Vis data for the porphyrazines in chloroform.

Compound	λ (nm) ($\log \varepsilon$ ($dm^3\,mol^{-1}\,cm^{-1}$)		
2	340 (4.71)	680 (4.75)	
3	336 (4.65)	654 (4.45)	710 (4.48)
4	348 (4.76)	674 (4.72)	
5	352 (4.80)	678 (4.66)	
6	356 (4.84)	676 (4.76)	

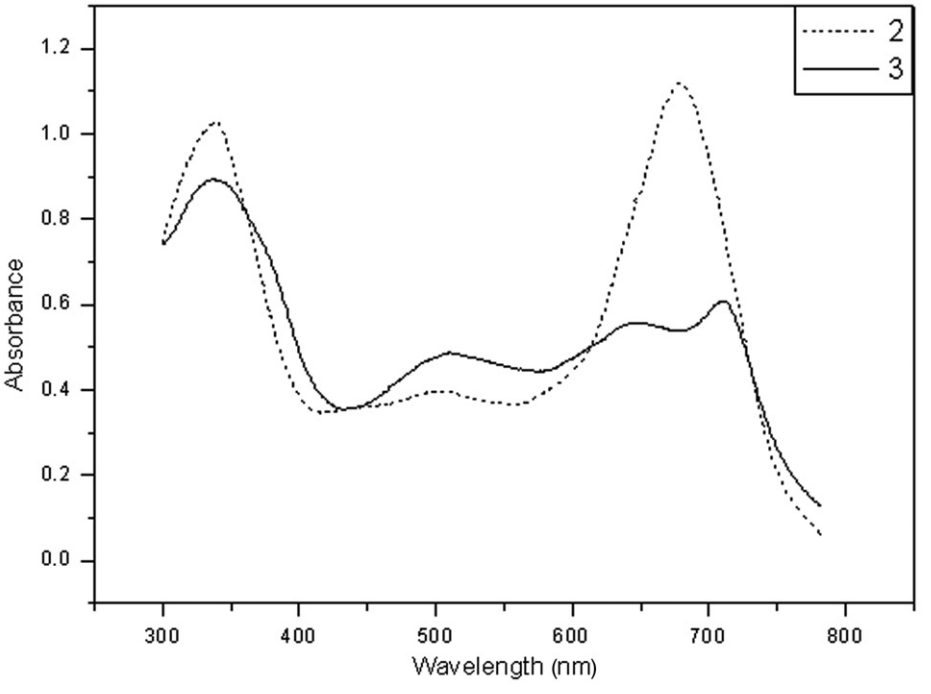


Figure 3. UV-Vis spectra of **2** and **3** in chloroform.

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