A New Method for the Synthesis of Cobalt Complex of Tetra-2,3-(5-tert-butyl-pyrazino) porphyrazine

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Abstract. A two-step synthesis of cobalt complex of tetra-2,3-(5-tert-butyl-pyrazino) porphyrazine as porphyrazine derivatives carrying six-membered pyrazine rings annulated at the periphery of the tetrapyrrolic macrocycle was described starting from 3,3-dimethyl-2-butanone, selenium dioxide, 2,3-diaminomaleonitrile, metal salts, and urea. In comparison with the previously reported multistep procedure, this new multicomponent protocol for the preparation of synthetically, biologically, and technologically relevant tetra-2,3-(5-tert-butyl-pyrazino) porphyrazine includes some important aspects like the fast and simple reaction, easy workup procedure, and high atom economy.

1. INTRODUCTION

Tetrapyrazinoporphyrazine and its metal derivatives (TPyzPzs) are the most widely studied class of azaanalogues of phthalocyanines (Pcs) [1](see Figure 1). The TPyzPzs were the first briefly reported by Linstead and his colleagues in 1937 [2], however, the systematic researches only began in the late 1960s, mainly by Lukyanets [3-5] and Korzhenevskii [6-8] in the former Soviet Union, then became active in the past two decades.

Pc  TPyzPzH₂

Figure 1 Structure of Pc and TPyzPzH₂

Ever since TPyzPzs were discovered, they had been attracted significant attention due to their industrial applications in different fields. Many patents have described the use of different types of
TPyzPz macrocycles, especially as materials for various electronic devices (optical information recording [9], electrophotographic photoreceptors and photoconductors [10, 11], organic transistors [12], liquid-crystalline films [13, 14]), components of electroluminescent [15] and electrochemical devices [16], pigments and dyestuffs in printing inks [17, 18] and toner colorants [19], preservatives for cut flowers [20], heat stabilizers for polymers [21, 22], photoactivators of singlet oxygen production for photodynamic therapy [23-25] and quenchers of fluorescence for detection of DNA [26].

Initially, the main focus was on the most readily available unsubstituted metal-free tetrapyrazinoporphyrine [TPyzPzH2] and its metal complexes [TPyzPzM]. However, the extremely low solubility of unsubstituted TPyzPzs greatly limits its potential for practical applications. Not surprisingly, most recent publications are devoted to the synthesis and research of substituted nonmetals with various functions at peripheral locations and metallized TPyzPzs. Peripheral substituents make TPyzPzs not only soluble in organic or aqueous solvents, but also can fine-tune the spectrum and other physical and chemical properties and biological activities.

![Synthetic route of TPyzPzM](image)

**Figure 2** The synthetic route of TPyzPzM reported in the literature

There are few reports on the synthesis of tBu-TPyzPzM (The peripheral substituents are tert-butyls) under mild and effective conditions. In the literature [4], a synthesis method is described, as shown in **Figure 2**. The process is complicated to operate, waste of raw materials and environmental pollution. On the other hand, attempts to directly synthesize Pzs with unprotected vicinal NH2 groups from 2,3-diaminomaleodinitrile were unsuccessful [27-29]. Due to the importance of these macrocycles, it is essential to introduce new, efficient, and inexpensive protocols for this purpose.

In the following sections, the cobalt complex of tetra-2,3-(5-tert-butyl-pyrazino) porphyrin [tBu-TPyzPzCo] (**Figure 3**) will be considered, focusing on the synthesis and structural aspects. We hope to study the synthesis of tBu-TPyzPzCo through a two-step method under nonspecific conditions.
2. EXPERIMENTAL

2.1 Materials and Equipment
All solvents, chemicals, and reagents are of AR grade, purchased from Sinopharm Chemical Reagent Company, China, and used as they are. The UV-Vis spectrum of the sample was recorded on a TU-1901 spectrophotometer (Pgeneral, China), the scanning range was 300 nm-800 nm. XRD was performed on the X’pert PRO X-ray diffractometer, whose Cu Kα monochromatized radiation (λ = 1.54 Å) was run at 45 kV and 40 mA. The scan rate is 8°/min, and the 2θ scan range is 0° to 70°. The morphological information was collected on the FEI Quanta200 scanning electron microscope (SEM) instrument. The FT-IR spectrum was scanned 32 times in the range of 4000-400 cm$^{-1}$ on a Nexus spectrometer (Nicolet, USA), and the samples were prepared as KBr particles.

2.2 Synthesis of 3,3-dimethyl-2-oxobutanal
As shown in Figure 4, according to the general procedure of Riley, Morley and Friend [30], 3,3-dimethyl-2-butane (2) was synthesized by oxidation with selenium dioxide and 3,3-dimethyl-2-oxobutanal (1). In the initial stage of the reaction exotherm, carefully reflux selenium dioxide (0.11 mol) and 2 (0.1 mol) for 3-4 hours. The yellow liquid product was decanted, the black residue was washed with 2, and the entire liquid was fractionated. The light-yellow distillate, b. p. 105 ℃, is an azeotropic mixture of water and 2, which contains truly little 1, and can be conveniently used as a raw material for further preparation of 1. The mixture was recovered to 115 ℃, and the remaining liquid was fractionated under reduced pressure. This fraction condensed into a bright yellow fluid liquid, which gradually turns into white crystal at room temperature. That is 3,3-dimethyl-2-oxobutanal. The yield is greater than 10 g (Found: C: 63.08 %; H: 8.75 %. Calculated: C: 63.16 %; H: 8.77 %.)

$$\text{3,3-Dimethyl-2-butane} + \text{SeO}_2 \xrightarrow{55 \degree \text{C, reflux, 4 h}} \text{3,3-Dimethyl-2-oxobutanal}$$

Figure 4 Synthesis route of 3,3-dimethyl-2-oxobutanal

2.3 Procedure for the preparation of tBu-TPyzPzCo
In a typical experiment (Figure 5), 3,3-dimethyl-2-oxobutanal 1 (0.02 mol) with 2,3-diaminomaleonitrile 3 (0.02 mol), urea 4 (0.08 mol), and cobalt chloride hydrate 5 (0.01 mol) are mixed to synthesize tBu-TPyzPzCo. under heating conditions. In this step, raw materials of various molar ratios are used to optimize the reaction conditions. It was found that, the molar ratio of 1 : 1 : 4 : 0.5 was 1 : 2 : 4 : CoCl$_2$·6H$_2$O obtained the best result. After fully mixing, put the raw materials into a round-
bottomed flask, and then slowly heat to 140°C while stirring in an oil bath under reflux. Currently, the urea melts and forms a dark blue slurry. After the urea was completely melted, the reaction mixture was continued to be heated to 200°C and kept at 200°C for 2 hours under constant stirring until the product became solid.

The crude product was cooled to room temperature and thoroughly ground, then washed with water and filtered off, and the solid residue was further purified by washing with boiling alcohol. The two methods were operated alternately several times to obtain pure tBu-TPyzPzCo with a yield of 81.6%. The product was dried in an oven for 12 h to obtain a navy blue solid. (Found: C: 59.78 %; H: 4.98 %, N: 27.9%. Calculated: C: 59.12 %; H: 5.08 %, N: 27.54 %.)

\[
\begin{align*}
3,3\text{-Dimethyl-2-oxobutanal} & + 
2,3\text{-Diamino-2-butenedinitrile} & + 
\text{Urea} & \rightarrow 
\text{tBu-TPyzPzCo} \\
& & & \text{190 }^\circ \text{C} \\
& & & \text{2 h}
\end{align*}
\]

Figure 5 The synthetic route of this research

3. RESULTS AND DISCUSSION

3.1 UV-visible absorption spectrum
The UV-visible spectrophotometer is an excellent tool for phthalocyanine research and characterization. The spectra of phthalocyanine and its derivatives show characteristic Q and B bands [31-33]. Figure 6 shows the UV-visible absorption spectra of tBu-TPyzPzCo and unsubstituted TPyzPzCo, using DMF as a solvent in the range of 300-800 nm. The compound showed two obvious absorption bands at 330nm, 308nm, 615.5nm, and 633.5nm, which corresponded to the B band and Q band of the phthalocyanine analog. At the same time, comparing the two spectra, the absorption peak of tBu-TPyzPzCo shows a red shift in the UV region and a blue shift in the visible region, which may be due to the larger π structure. In addition, there are several weak peaks near the Q-band in the unsubstituted TpyzPzCo spectrum, which are stronger than tBu-TpyzPzCo. The peaks are attributed to the dimer produced by the polymerization reaction [34], which will affect the performance of the compounds. This explains that the presence of peripheral substituents may inhibit the production of dimers.

3.2 X-ray diffraction.
The structural features of the compound were checked by XRD measurements in Figure 7. The metal phthalocyanine complexes have very obvious characteristic diffraction peaks in the range of 2θ = 10~30° [35](2θ=12.95°, 14.88°, 15.49°, 17.77°, 19.73°, 21.52°, 27.45° and 28.82°).
3.3 FT-IR spectroscopy
The FT-IR spectrum of tBu-TPyzPzCo is shown in Figure 8, recorded in a basic area of 400-4,000 cm\(^{-1}\), and KBr disk technology is used. The spectra show absorption peaks near 769, 964, 1122 and 1329 cm\(^{-1}\), which may be related to the phthalocyanine skeletal vibrations [36]. Due to the presence of tert-butyls, the spectrum also shows an absorption peak near 1375 cm\(^{-1}\). Specifically, we can see that two peaks are displayed at 1371 cm\(^{-1}\) and 1386 cm\(^{-1}\). The intensity of the former is approximately twice that of the latter. In addition, there are two absorption peaks near 1456 cm\(^{-1}\) and 1682 cm\(^{-1}\), which are attributed to the C=C bond and C=N bond extending the vibration of the pyrazine macrocycle.

3.4 Scanning electron microscope
Figure 9 shows the morphology of tBu-TPyzPzCo. The SEM image shows the random pore size distribution and interconnected pore system in the compound. We can see that it has a sheet-like structure with a thickness of about 1 \(\mu\)m.

In order to explore the scope and limitations of the reaction, the optimization scheme was applied to other substrates. The program has been extended to different metal salts such as CuCl\(_2\) \(\cdot\) 2H\(_2\)O, FeCl\(_2\) \(\cdot\) 4H\(_2\)O, and ZnCl\(_2\). It can be seen from Table 1 that different starting materials were converted into tBu-TPyzPzM with good yields, and it was confirmed that their UV-visible spectra conformed to the characteristic absorption band of phthalocyanine.
4. CONCLUSION

Compared with previously reported multi-step procedures [4], this new multi-component protocol for the synthesis, biological and technical preparation of tBu-TPyzPzM includes some important aspects, such as fast and simple reactions, simplicity Post-processing procedures and high atomic economy. In addition, our agreement does not require any protection/unprotection of functional groups.

| Products     | Metal Salts | B bands (nm) | Q bands (nm) | Yield (%) |
|--------------|-------------|--------------|--------------|-----------|
| tBu-TPyzPzCu | CuCl$_2$ : 2H$_2$O | 340          | 631          | 82.7      |
| tBu-TPyzPzFe | FeCl$_2$ : 4H$_2$O | 340          | 645          | 76.5      |
| tBu-TPyzPzs  | ZnCl$_2$     | 337          | 642          | 77.2      |

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