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SYNTHESES AND CATALYTIC PROPERTIES OF 1-NAPHTHOATE-COPPER-BIPY COMPLEX

Yi Zhu,* Wenjuan Zhu, Chibin Liu, Yanxin Wei, Mingjing Xia, and Xi Wang

Department of Chemical and Pharmaceutical Engineering, Hefei Normal University, 230601, e-mail: zhuyi069@hfnu.edu.cn

Abstract – In this paper, 1-naphthoic acid, 2,2-dipyridyl (Bipy) and cupric nitrate are used to synthesize a novel complex by hydrothermal method. The complex is characterized by means of IR and X-ray diffraction. The complex is applied in the hydroxylation of phenol and the degradation of Congo Red as catalysts. The influence of dosage of catalyst, reaction time, temperature, etc. is studied in both hydroxylation of phenol and the degradation of Congo Red. The best results of the phenol hydroxylation reaction are obtained by reacting 0.2 g phenol with 0.30 mL hydrogen peroxide (30%) at 80 °C for 180 min under the catalysis of 8 mg complex. The yield of benzenediol is 81.45%. The optimum degradation of Congo Red reaction is achieved by mixing 0.75 mg Congo Red with 4 mg complex, 0.30 mL hydrogen peroxide and reacting at 45 °C, for 30 min.

Catechol (CAT) and hydroquinone (HQ) are important organic intermediates and chemical materials which are utilized to synthesize the compound drugs, pharmaceuticals, dye, and so on.^{1,2} Based on the Green Chemistry principles, hydroxylation of phenol with hydrogen peroxide as the oxidant becomes the most general way to obtain diphenols, owing to its environmental acceptability (water is the only by-production of oxidant). In the early stage, the free radical mechanism of the transition metals being as the active sites have been applied in the phenol hydroxylation,³⁻⁹ but these homogeneous catalysts are difficult to be separated and recovered from the reaction mixture, which prevents their practical utilization in phenol hydroxylation. Therefore, heterogeneous catalysis over various metal oxides and complexes, such as metal complex oxides,^{10,11} and zeolite-encapsulated metal complexes,¹² has been of great interest to many researchers for a long time.

In recent years, there was an explosive growth of interest in metal-organic frameworks (MOFs) for their potential applications in gas storage, catalysis, separations, sensors and purification purpose.¹³⁻¹⁸ MOFs

with unsaturated coordinated metal sites, like copper, and aromatic ligands have been successfully constructed and applied to catalyze some oxidation reactions.¹⁹⁻²² Meantime many synthetic dyes such as Congo Red, which endanger the human health and the other living things due to their toxic substances, can be oxidized and degraded by catalyzed decomposition of hydrogen peroxide.²³⁻²⁵

In this paper, the synthesis of a novel metal complex $C_{64}H_{42}Cu_2N_4O_8$ by hydrothermal reaction of 1-naphthoic acid, 2,2-dipyridyl (Bipy) and cupric nitrate is reported. 1-Naphthoic acid (0.086 g, 0.5 mmol), cupric nitrate (0.094 g, 0.5 mmol), 2,2-dipyridyl (Bipy) (0.031 g, 0.2 mmol) and deionized water (25 mL) were added to a 50 mL Teflon-lined stainless steel vessel. The mixture was sealed and reacted at 130 °C for 4 h (Figure 1). After cooling to 30 °C, blue oblate crystals were obtained. The product was collected by filtration and washed with distilled water.

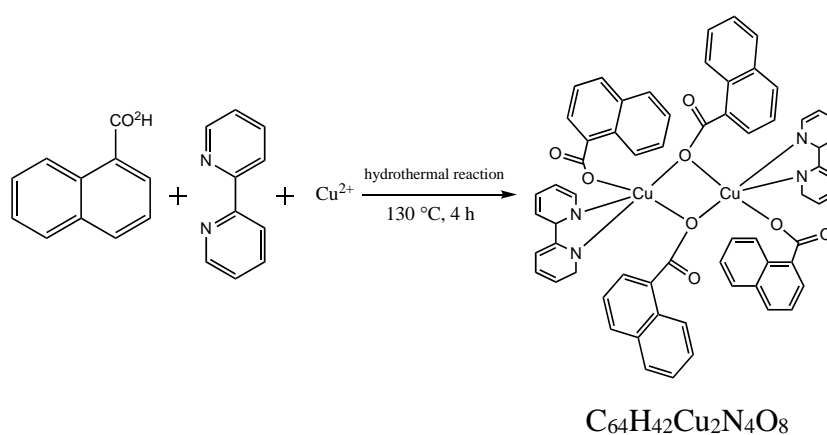


Figure 1. Illustration of the synthesis of the complex process

The complex is characterized by IR and X-ray diffraction analysis. The application of this complex as a catalyst for hydroxylation of phenol and the degradation of Congo Red has been explored.

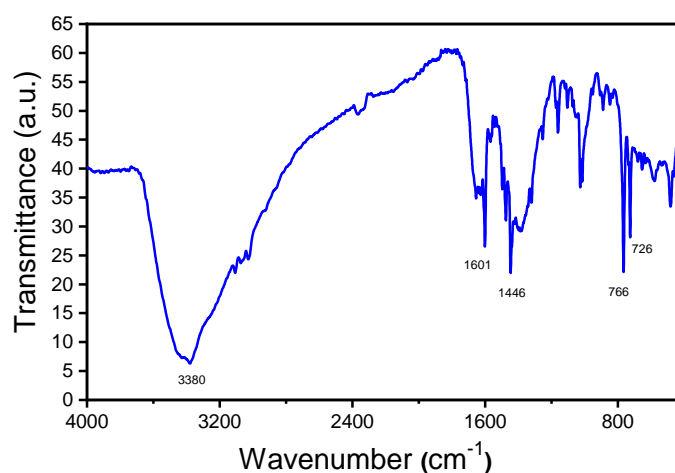


Figure 2. Infrared spectrogram of the complex

The complex was characterized with IR (Figure 2). The broad absorption peak at 3380 cm^{-1} was assigned to the stretching vibration of OH. The absorption peak at 1601 cm^{-1} was attributed to the C=O stretching vibration of the ligand. The broad absorption peaks at 1475 and 1446 cm^{-1} were assigned to the vibrations of the naphthalene ring. The 766 and 726 cm^{-1} peaks corresponded to $\delta^{\text{C-H}}$ in pyridine.

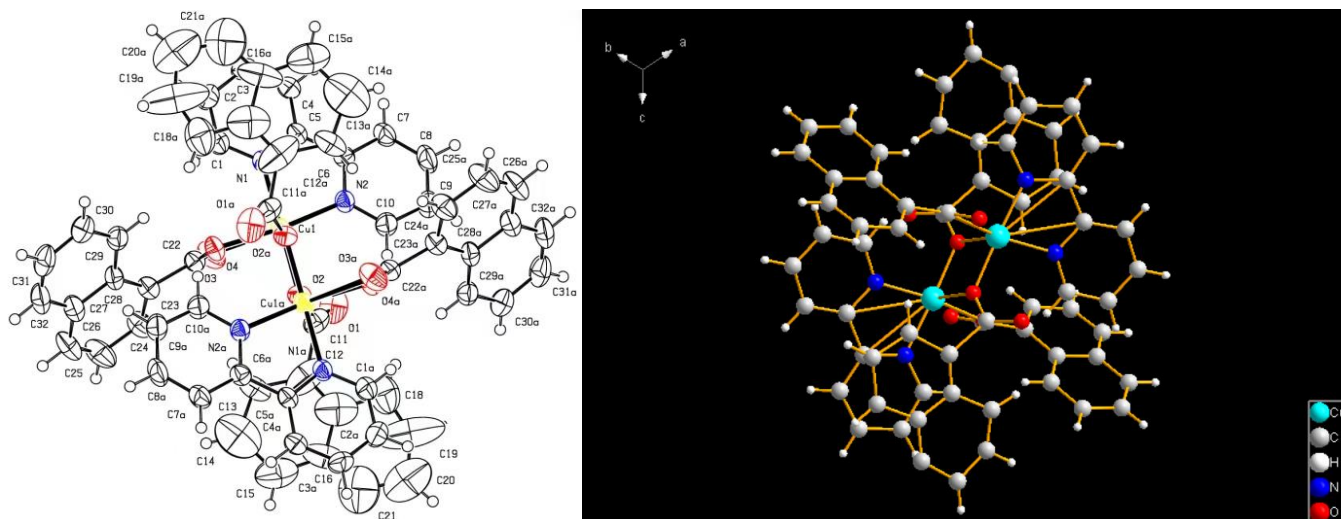


Figure 3. View of crystal structure of complex

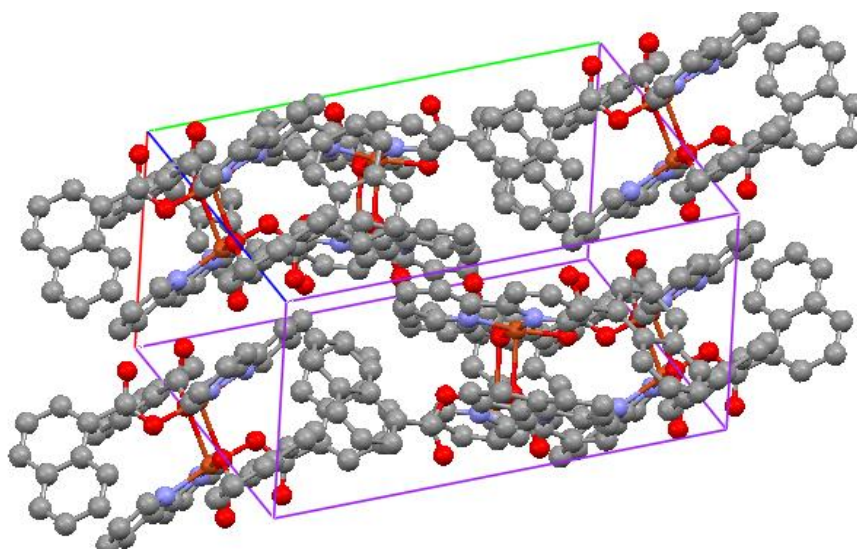
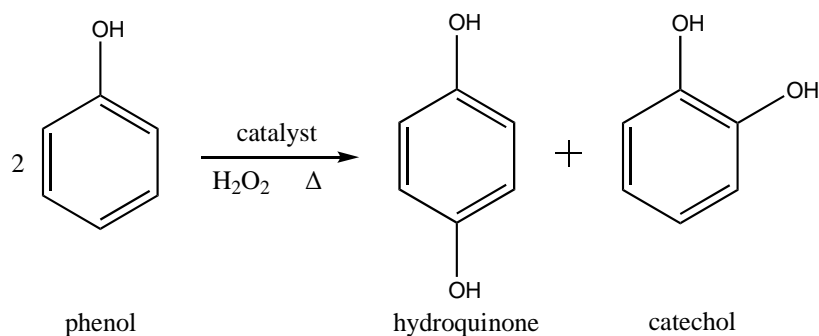


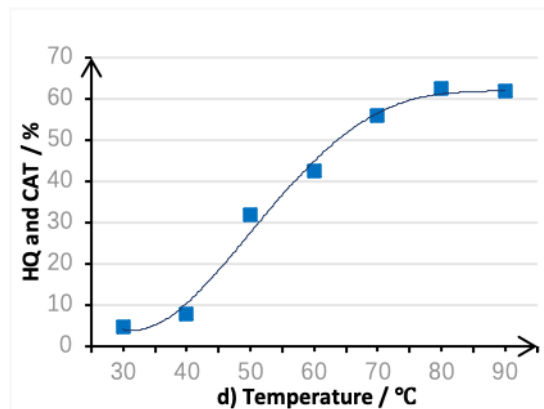
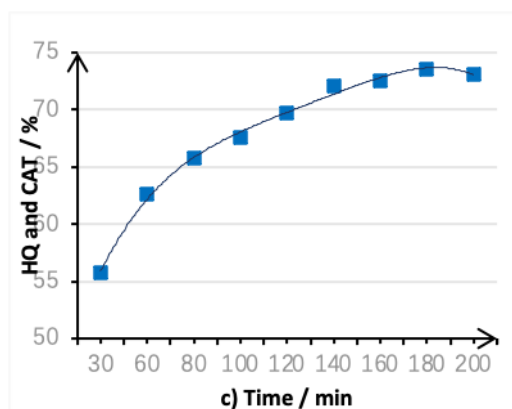
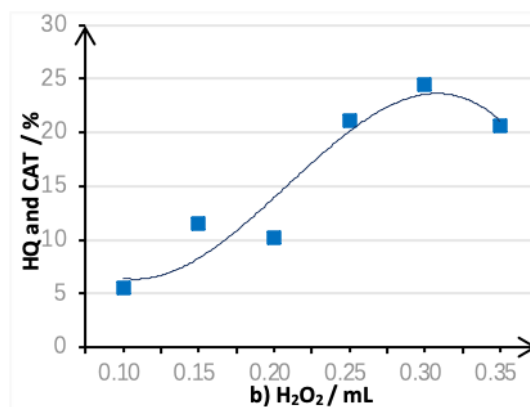
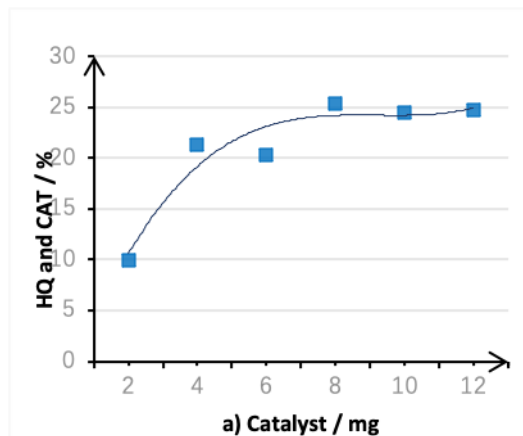
Figure 4. View of molecular cell accumulation of complex

This complex belonged to monoclinic crystal system. It was constituted by two cupric ions (Cu^{2+}), two 2,2-dipyridyl molecules and two 1-naphthoic acid molecules (Figure 3 and Figure 4).

The products of the catalytic actions are primarily HQ and CAT (Scheme 1), total of two products represent the percentage conversion of phenol. The effect of reaction temperature, reaction time, amount of H_2O_2 , amount of catalyst and the reaction media were investigated to acquire the optimum conditions.

Scheme 1. Catalytic phenol hydroxylation by H₂O₂

For investigating the effect of one influencing factor, keeping the other experimental conditions unchanged. For example, when other reaction conditions (30 mL distilled water as reaction medium, 0.2 mL H₂O₂, 50 °C reaction temperature, 60 min reaction time) were fixed, the yield of the reaction was tested with 2 mg, 4 mg, 6 mg, 8 mg, 10 mg and 12 mg catalyst respectively. Figure 5a showed the yield of phenol increased with the increase of catalyst until the amount of catalyst reached 8 mg, when the yield of phenol reached the maximum. Then with the continuous increase of catalyst amount, the yield of phenol no longer increased, so 8 mg is selected as the best catalyst dosage.



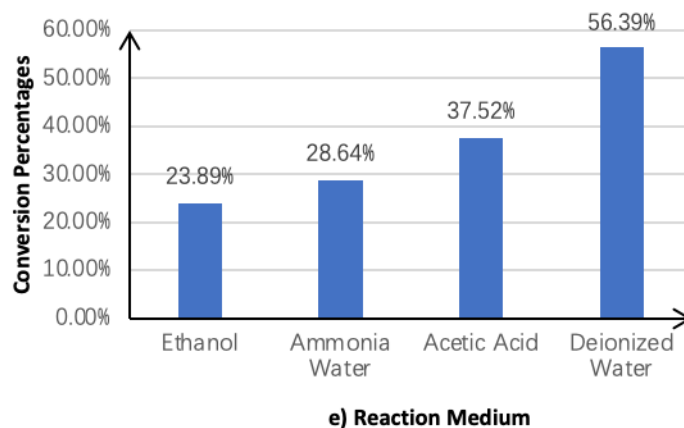


Figure 5. The experiment of condition of a) amount of catalyst, b) amount of H₂O₂, c) reaction time, d) reaction temperature and e) reaction medium.

According to the investigation of different influencing factors in a series of experiments, the best conditions for catalyzing phenol hydroxylation reaction of catalysts are obtained: deionized water as the reaction medium, 8 mg catalyst, 0.30 mL hydrogen peroxide, reaction 180 min at a temperature of 80 °C (Figure 5), which could achieve the maximum yield of the reaction, 81.45%. To compare the catalytic activity, copper nitrate was also used as catalyst in the same condition, and a much lower phenol conversion at 60.32% is observed than that over the complex at 81.45%, which indicates that the catalytic activity of Cu²⁺ is improved by the introduction of Cu²⁺ into structure of the complex.

In three 25 mL small beakers numbered 1, 2 and 3 were added 15 mL (50 mg/L) of Congo Red solution respectively, then 0.20 mL 30% H₂O₂ was added to the No. 2 and No. 3 beakers, and 3 mg of the catalyst was added to the No. 3 beaker. All of the three beakers were controlled at 40 °C and stirred for 30 min. After cooling, resting and centrifugation, the upper layer of the liquid was scanned in the range of 320-800 nm UV absorption spectrum, with distilled water as a reference.

Figure 6 shows that the catalyst improved the degradation rate of Congo Red obviously, and the degraded Congolese red solution was almost non-absorbent, which illustrate the excellent catalytic degradation activity.

To acquire the optimum reaction condition of degradation of Congo Red, the effect of reaction time, temperature, the amount of catalyst and H₂O₂ were investigated as influencing factors. For investigating one influencing factor, the others were maintained in the described experiment condition. The results were shown in Figure 7, in which we got the optimum degradation reaction condition as follows: The mixture of Congo Red (0.75 mg) and the complex (4 mg) was heated to 45 °C with stirring in 30 mL distilled water, and hydrogen peroxide (0.30 mL, 30%, w/v) was added dropwise into the solution with stirring for 30 min.

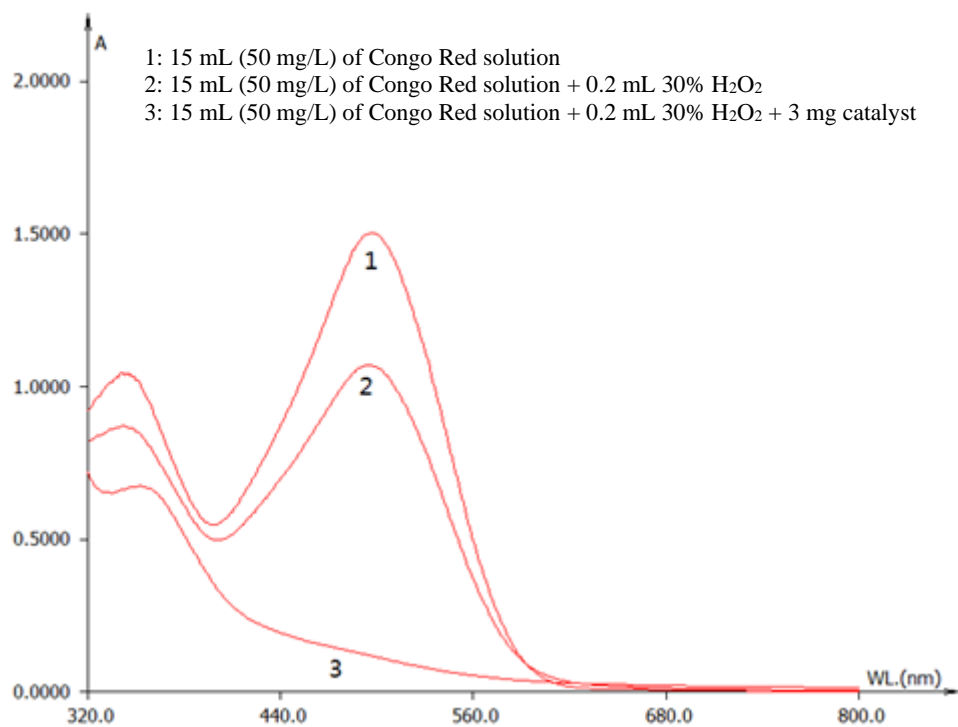


Figure 6. The contrast experiment of the degradation of Congo Red

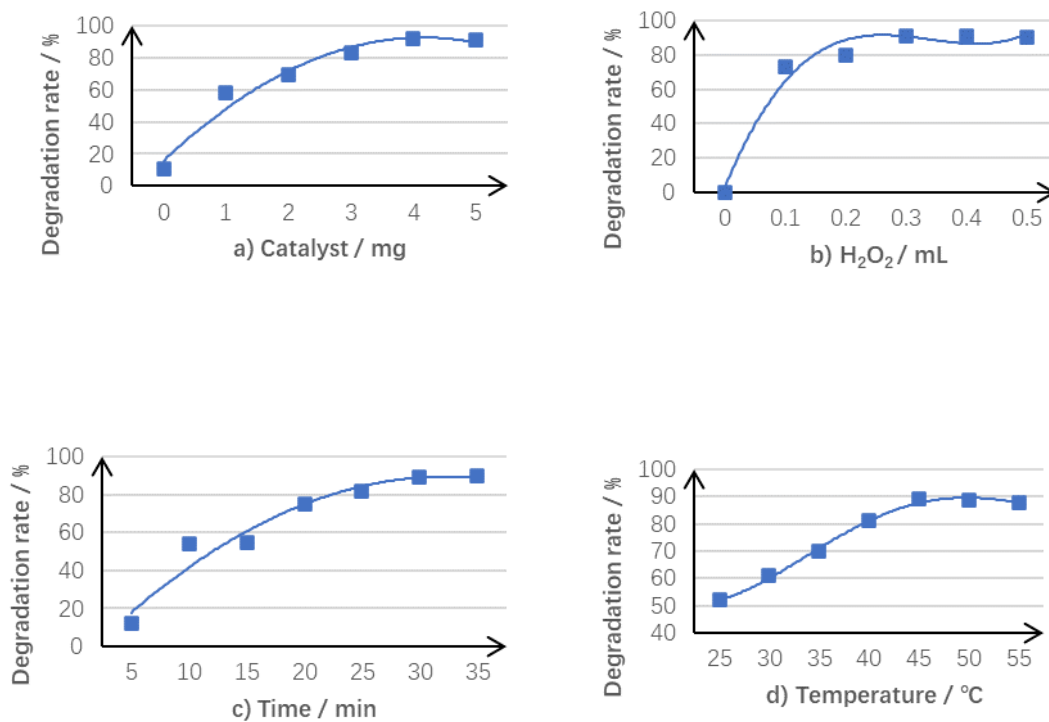


Figure 7. The experiment of condition of a) amount of catalyst, b) amount of H₂O₂, c) reaction time and d) reaction temperature

In conclusion, a transition metal complex containing bridging formation was synthesized. The complex as a catalyst has been investigated in the oxidation of phenols and the degradation of Congo Red, with H₂O₂ as an oxidant in both reactions. The effects of reaction time, amount of catalyst, and reaction medium were investigated. The complex was found to be an effective heterogeneous catalyst.

EXPERIMENTAL

Materials and Physical Measurements. All commercially available chemicals were reagent grade and used as received without further purification. IR spectra were recorded using a WGH-30 spectrophotometer in the range of 4000-400 cm⁻¹ using the KBr disk method. Crystallographic X-ray diffraction (XRD) data were collected by Siemens SMART CCD area detector diffractometer equipped with graphite-monochromatic MoK α radiation ($\lambda=0.71073\text{\AA}$). The data were collected by SMART and reduced by the program SAINT. The structure was solved by the direct method and refined by full-matrix least squares fitting on 'F²_{obs}' by SHELXTL-PC. All non-hydrogen atoms were refined by anisotropic thermal parameters. The O-H hydrogen atoms were localized by difference Fourier maps and refined by fixing the bond lengths to 0.840(1) \AA . The diffraction intensities of 0.26 \times 0.21 \times 0.17 mm blue oblong columnar crystals of the complex were measured at 296K. The reflections were collected over the angle range 2.54 $^\circ$ < θ < 24.990 $^\circ$. Corrections for Lp effects and empirical absorption were applied. Table 1 listed Crystallographic Data and Refinement Parameters for complex.

The products of the catalytic phenol hydroxylation reaction were analyzed by an LC-1000 liquid chromatograph under following conditions: chromatography column: Hypersil ODS2 4.5 \times 250 mm, 5 μ m;

Table 1. Crystallographic Data and Refinement Parameters for complex

| Crystal parameter items | Crystal parameters |
|--------------------------------------|--|
| Empirical formula | C ₆₄ H ₄₂ Cu ₂ N ₄ O ₈ |
| Formula weight | 1122.12 |
| Crystal system, space group | monoclinic crystal system, P2(1)/n |
| Unit cell dimensions | a = 10.229(3) \AA α = 90 $^\circ$ b = 17.524(5) \AA β = 103.045(6) $^\circ$ c = 14.788(5) \AA γ = 90 $^\circ$ |
| Z, Calculated density | 2, 1.443g/cm ⁻³ |
| Absorption coefficient | 0.89 mm ⁻¹ |
| Reflections collected / unique | 3884 / 44995 [R(int) = 0.0341] |
| Max. and min. transmission | 0.799 and 0.860 |
| Goodness-of-fit on F ² | 1.063 |
| Final R indices [I > 2 σ (I)] | R1 = 0.0599(3400), wR2 = 0.1784(4537) |

mobile phase, MeOH:H₂O (40:60, v/v); Flow rate: 1.0 mL/min and wavelength of ultraviolet detector: 277 nm; temperature: room temperature.

Hydroxylation of phenols. The catalytic activities of the complex for the hydroxylation of phenols were studied. After adding the 0.2 g phenol and 30 mL solvent, the solution was heated to 80 °C with stirring in a 100 mL water-cooled flask. Then hydrogen peroxide (30%, w/v) was added dropwise (over 30 min) into the solution with stirring at desired conditions. The course of the reaction was monitored by periodically analyzing a small sample (20 µL) of the reaction product with liquid chromatography.

Catalytic Degradation Experiments. The catalytic activities of the complex for the degradation of Congo Red were investigated. To a 25 mL beaker was added Congo Red (15 mL, 50 mg/L) and the catalyst (3 mg). The mixture was heated to 40 °C with stirring. Hydrogen peroxide (30%, w/v) was added dropwise (over 30 min) at desired conditions. The reaction was monitored by periodically analyzing a small sample (20 µL) of the reaction product with UV-Visible Spectrophotometer.

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