

Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

A novel bimetallic MOF derived N-doped carbon supported Ru nanoparticles for efficient reduction nitro aromatic compounds and rhodamine B

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Characterization

Thermogravimetric Analysis (TGA) was conducted in flowing N₂ on a Rigaku TG-DTA8122 and the samples were heated from 30 to 1000 °C with a heating rate of 10 °C/min. The single-crystal X-ray diffraction study was performed on a Rigaku XtalAB PRO MM007DW instrument with Mo K α radiation ($\lambda=0.71073$ Å). The data were collected at 100 K. The structure was solved by direct methods and refined by full-matrix least-square methods on all F^2 data with the program Olex2. Powder X-ray diffraction (PXRD) patterns were collected using a Rigaku SmartLab X-ray diffractometer at 40 kV, 150 mA (6000 W) using Cu K α radiation ($\lambda=1.54056$ Å). UV absorption spectra were recorded at room temperature using a Agilent Cary 100 UV-vis-NIR spectrophotometer. NMR spectra were acquired on a Bruker AVANCE III 400MHz spectrometer and chemical shifts were recorded in delta (δ) units and expressed as ppm values relatively to the internal standard TMS. The morphology of catalytic materials was obtained by scanning electron microscopy (SEM: Phenom XL) and high resolution transmission electron microscopy (HRTEM: FEI Talos F200X G2 AEMC) at 200 kV. X-ray photoelectron spectra (XPS) were recorded on a Thermo Scientific K-Alpha and all XPS spectra were recorded using the Al K α line. The BET specific surface area and pore size distribution were measured by a ASAP 2460 instrument under liquid N₂ at 77 K. The content of metallic ruthenium in the solution after reaction was measured by ICP-OES technique on a Thermo Fisher iCAP PRO instrument.

Catalysts preparation

1. Synthesis of *mcptpy*

The *mcptpy* was synthesized according to a modified procedure [59]. Physically mix 4-methoxycarbonylbenzaldehyde (6.82 g, 42 mmol), 2-acetylpyridine (9.2 mL, 82 mmol) and potassium hydroxide (2.5 g, 44 mmol) and thoroughly grind them to obtain a yellow viscous solid. The solid was left standing for half an hour and ground into powder. The powder was washed with water and dispersed into an ethanol (125 mL) suspension containing ammonium acetate (16.0 g, 208 mmol). The suspension was then heated and refluxed for 24 h. After cooled to room temperature, the solid product was filtered and recrystallized twice with hot ethanol to obtain *mcptpy* (methyl 4-((2,2':6',2''-terpyridine)-4'-yl)benzoate) as a light yellow fibrous solid. (2.89 g, 7.6 mmol, 19%); $\delta_{\text{H}}/\text{ppm}$ (400 MHz, CDCl_3): 8.81 (2H, s), 8.76 (2H, d, $J = 4.8$ Hz), 8.71 (2H, d, $J = 8.0$ Hz), 8.19 (2H, d, $J = 8.0$ Hz), 8.00 (2H, d, $J = 8.4$ Hz), 7.92 (2H, dt, $J = 1.7, 7.7$ Hz), 7.40 (2H, ddd, $J = 1.0, 4.8, 7.4$ Hz), 3.98 (3H, s).

2. Synthesis of $\text{Ru}(\text{cptpy})_2(\text{PF}_6)_2$

Synthesis of the $\text{Ru}(\text{cptpy})_2(\text{PF}_6)_2$ was performed according to the literature with a slight modification [60]. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (130 mg, 0.5 mmol) and *mcptpy* (367 mg, 1.0 mmol) were added into a round-bottom flask. The above system was degassed thoroughly and then filled with argon. Then a mixture of ethanol (10 mL) and water (10 mL) was added into the flask with a syringe. The solution was refluxed 12 h under an argon atmosphere, then one aqueous solution containing 190 mg of KOH (5 mL) was added and the obtained mixture was continued to reflux for 2 h. The solvents were evaporated, after cooling at room temperature. The crude product was washed with acetone and dissolved in few milliliters of DMF, and then ammonium hexafluorophosphate solution (1 M, 5 mL) was added followed by HPF_6 solution (70 wt%, 1 mL). The solid product was collected by vacuum suction filtration and washed

by distilled water. After drying at 70 °C for 1 h, the dark red solid product was obtained. Yield: 502.2 mg, 92%. $\delta_{\text{H}}/\text{ppm}$ (400 MHz, DMSO- d_6): 9.58 (4H, s), 9.16 (4H, d, $J = 8.0$ Hz), 8.58 (4H, d, $J = 8.4$ Hz), 8.31 (4H, d, $J = 8.0$ Hz), 8.09 (4H, dt, $J = 0.9, 7.7$ Hz), 7.59 (4H, d, $J = 5.2$ Hz), 7.30 (4H, t, $J = 6.2$ Hz).

3. Synthesis of Zn-MOF-Ru(cptpy)₂

Zn(NO₃)₂·6H₂O (30.0 mg, 0.1 mmol), Ru(cptpy)₂(PF₆)₂ (11.0 mg, 0.01 mmol), malonic acid (150 mg, 1.44 mmol), and DMF (3 mL) was sealed in a 20 mL Teflon-lined autoclave, and sonicated for 20 min, then heated to 120 °C for 48 h in a preheated oven. After cooling down to room temperature, the red block-shaped crystals were obtained. The solid product was washed 3 times with DMF and dried at 70 °C for 1 h to obtain the Zn-MOF-Ru(cptpy)₂ (yield 59% based on Ru(cptpy)₂).

4. Synthesis of Ru-NC

The as-synthesized Zn-MOF-Ru(cptpy)₂ precursor (200 mg) was physically mixed with dicyandiamide (2.0 g) and ground together. With a heating rate of 5 °C/min, the mixture was calcined at 900 °C for 3 h in a tubular furnace in the N₂ atmosphere. After cooling down at room temperature, the obtained solid was washed for 1 h with 1 M diluted hydrochloric acid and water. After drying at 70 °C for 1 h, the MOF-derived catalyst, namely N-doped carbon supported Ru nanoparticles was obtained, denoted as Ru-NC-10. Afterwards, under the same calcined conditions, the adding amount of dicyandiamide was tuned to different target mass ratio (1:1, 1:5, 1:15). The obtained materials are denoted as Ru-NC-1, Ru-NC-5, and Ru-NC-15, respectively. At the same conditions, the product obtained by calcining the precursor without dicyandiamide was labeled as Ru-NC-0.

Catalytic reduction of nitro aromatic compounds

Tests for the catalytic reduction of nitro aromatic compounds were carried out in a standard quartz cell with a path length of 1 cm under room temperature. The freshly prepared NaBH₄ aqueous solution was employed as reducing agent. In general, 3.0 mL of deionized water, 20 μL of 4-NP solution (13.5 mM), 10 μL of fresh NaBH₄ solution (3.0 M) were added into a cuvette in turn, followed by the addition of 0.2 mg

catalyst (2.0 mg/mL, 100 μ L) to the solution. The suspension was oscillated uniformly and immediately subjected to UV-vis test at a scan rate of 600 nm/min in the range of 250-500 nm (Cary 100).

The reusability of the catalyst was investigated by five successive repeated cycle tests. Because the mass of catalyst added to the reaction system is too small and difficult to recycle, it can only be left in the reaction system. Then the same amount of substrate and reducing agent can be added into the original reaction system for the next round of test directly.

With NaBH₄ as the reducing agent, the catalytic activities of the as-synthesized catalysts towards different nitro aromatic compounds were investigated. Typically, 0.2 mg of catalysts were added into the solutions of 2-NP, 4-NA, 2-NA, 4-NBA and 2-NBA, respectively. Other reaction conditions were similar to 4-NP, except UV-vis measurement of 4-NBA and 2-NBA ranging from 200 to 400 nm.

Catalytic reduction of rhodamine B

Tests for the catalytic reduction of rhodamine B were carried out in a standard quartz cell with a path length of 1 cm under room temperature. The freshly prepared NaBH₄ aqueous solution was employed as reducing agent. In general, 3.0 mL of deionized water, 20 μ L of RhB solution (5.0 mM), 40 μ L of fresh NaBH₄ solution (3.0 M) were added to a cuvette in turn, followed by the addition of 0.4 mg catalyst (2.0 mg/mL, 200 μ L) to the solution. The suspension was oscillated uniformly and immediately subjected to UV-vis test at a scan rate of 600 nm/min in the range of 400-650 nm (Cary 100).

The reusability of the catalyst was investigated by five successive repeated cycle tests. Because the mass of catalyst added to the reaction system is too small and difficult to recycle, it can only be left in the reaction system. Then the same amount of substrate and reducing agent can be added into the original reaction system for the next round of test directly.

Table S1Crystal data and structure refinement for Zn-MOF-Ru(cptpy)₂.

Compound	Zn-MOF-Ru(cptpy) ₂
Empirical formula	C ₄₅ H ₂₈ N ₆ O ₆ RuZn
Formula weight	915.19
Temperature/K	100.00(10)
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	17.0019(6)
<i>b</i> /Å	16.1026(11)
<i>c</i> /Å	17.2680(8)
α /°	90
β /°	99.589(4)
γ /°	90
Volume/Å ³	4661.5(4)
<i>Z</i>	4
ρ_{calc} /g/cm ³	1.408
μ /mm ⁻¹	0.896
F(000)	2008.0
Crystal size/mm ³	0.14 × 0.11 × 0.09
Radiation	Mo K α (λ = 0.71073 Å)
2 θ range for data collection/°	6.966 to 59.938
Index ranges	-22 ≤ <i>h</i> ≤ 18, -22 ≤ <i>k</i> ≤ 17, -24 ≤ <i>l</i> ≤ 21
Reflections collected	28825
Independent reflections	11174 [<i>R</i> _{int} = 0.0751, <i>R</i> _{sigma} = 0.1335]
Data/restraints/parameters	11174/6/532
Goodness-of-fit on <i>F</i> ²	1.061
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0970, <i>wR</i> ₂ = 0.1878
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1531, <i>wR</i> ₂ = 0.2081
Largest diff. peak/hole / e Å ⁻³	0.97/-0.68

$${}^a R_1 = \sum ||F_o| - |F_c|| / |F_o|, {}^b wR_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2]^{1/2}.$$

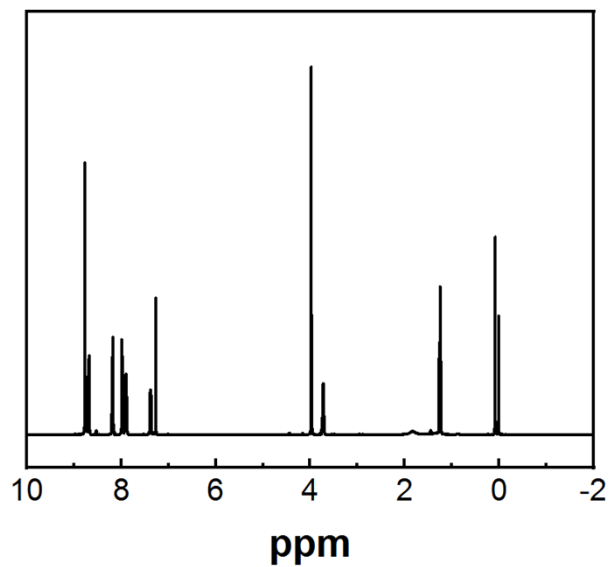


Figure S1: ^1H NMR of mcptpy in CDCl_3 at 400 MHz.

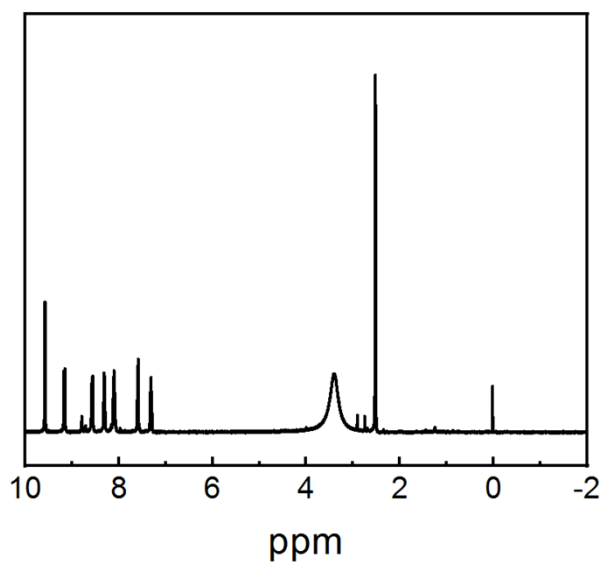


Figure S2: ^1H NMR of $\text{Ru}(\text{cptpy})_2(\text{PF}_6)_2$ in $\text{d}_6\text{-DMSO}$ at 400 MHz.