

## A metal-catalyzed thermal polymerization strategy for the synthesis of atomically dispersed catalysts

Lin-Wei Chen,<sup>‡a</sup> Zhen-Yu Wu,<sup>‡a</sup> Hang Nan,<sup>a</sup> Lei Wang,<sup>a</sup> Sheng-Qi Chu,<sup>b</sup> and Hai-Wei Liang<sup>\*a</sup>

<sup>a</sup>Hefei National Laboratory for Physical Sciences at the Microscale, Department of Chemistry, University of Science and Technology of China, Hefei, 230026, China. E-mail: hwliang@ustc.edu.cn

<sup>b</sup>Institute of High Energy Physics, Chinese Academy of Sciences, Beijing, 100049, China.

### Materials and Instrumentation

All chemicals were from commercial sources and used without further purification. 3,8-dibromo-1,10-phenanthroline was purchased from Kangyu Chem Co. LTD (Shanghai, China). Fumed silica (S5130) was purchased from Sigma-Aldrich. Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, ethanol (AR), ethylbenzene (AR), acetophenone (AR), benzoic acidethyl (AR), benzaldehyde (AR), acetate (AR), anisole (AR), and tert-Butyl hydroperoxide (t-BHP, 70%, AR) were purchased from Sinopharm Chemical Reagent Co. LTD. 1-ethyl-4-methoxybenzene, 1-(4-methoxyphenyl)ethan-1-one, 1-ethyl-4-nitrobenzene, 1-(4-nitrophenyl)ethan-1-one, propylbenzene, propiophenone, isobutylbenzene, 2-methyl-1-phenylpropan-1-one, 9H-fluorene, 9H-fluoren-9-one, diphenylmethane, and benzophenone were purchased from Energy Chemical (Shanghai, China).

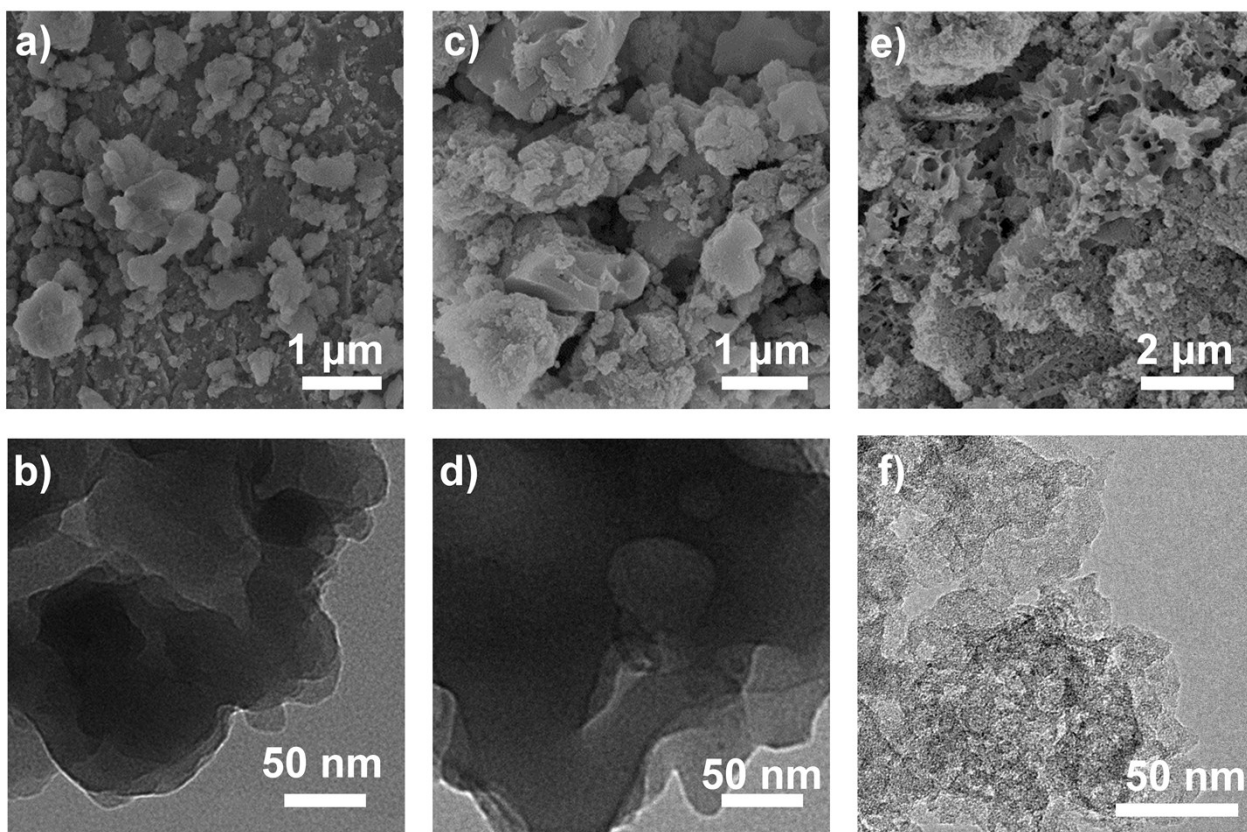
SEM images were captured on a Zeiss Supra 40 scanning electron microscope at an acceleration voltage of 5 kV. TEM was carried out using a Hitachi H7700 transmission electron microscope with a charge-coupled device imaging system and an accelerating voltage of 100 kV. HRTEM was performed on JEOL-2100F with an acceleration voltage of 200 kV. Aberration-corrected HAADF-STEM was collected on a JEOL ARM-200F field-emission transmission electron microscope operating at 200 kV accelerating voltage. STEM-EDS element mapping was carried out on a JEOL-2100F equipped with Oxford Inca. XRD data were recorded on a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite monochromatic Cu K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). XPS were acquired on an x-ray photoelectron spectrometer (ESCALAB MKII) with an excitation source of Mg

K $\alpha$  radiation (1253.6 eV). Solid UV-Vis absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer (Kyoto, Japan).  $^{13}\text{C}$  MAS NMR spectra were recorded on a Bruker AVANCE 400WB NMR spectrometer (400 MHz). X-ray absorption fine structure (XAFS) spectra at Co, Fe and Ni K-edge was obtained on the 1W1B beamline of Beijing Synchrotron Radiation Facility (BSRF) operated at 2.5 GeV and 250 mA and on the BL14W1 beam line of Shanghai Synchrotron Radiation Facility (SSRF) operated at 3.5 GeV and 220 mA. Athena and Artemis packages were used to normalize the data for the EXAFS profiles. The Fourier transformed (FT) data of Co, Fe and Ni K-edge spectra were analyzed. TGA was measured by a TGA Q5000IR analyzer under  $\text{N}_2$  flow with a temperature ramp of  $10^\circ\text{C min}^{-1}$ .  $\text{N}_2$  adsorption-desorption analysis was conducted using an ASAP 2020 accelerated surface area and porosimetry instrument (Micromeritics), equipped with automated surface area, at 77 K using BET calculations for the surface area. The quenched solid density functional theory (QSDFT) method was applied to reveal the pore size and volume distributions of the catalysts in the micropore and mesopore ranges.

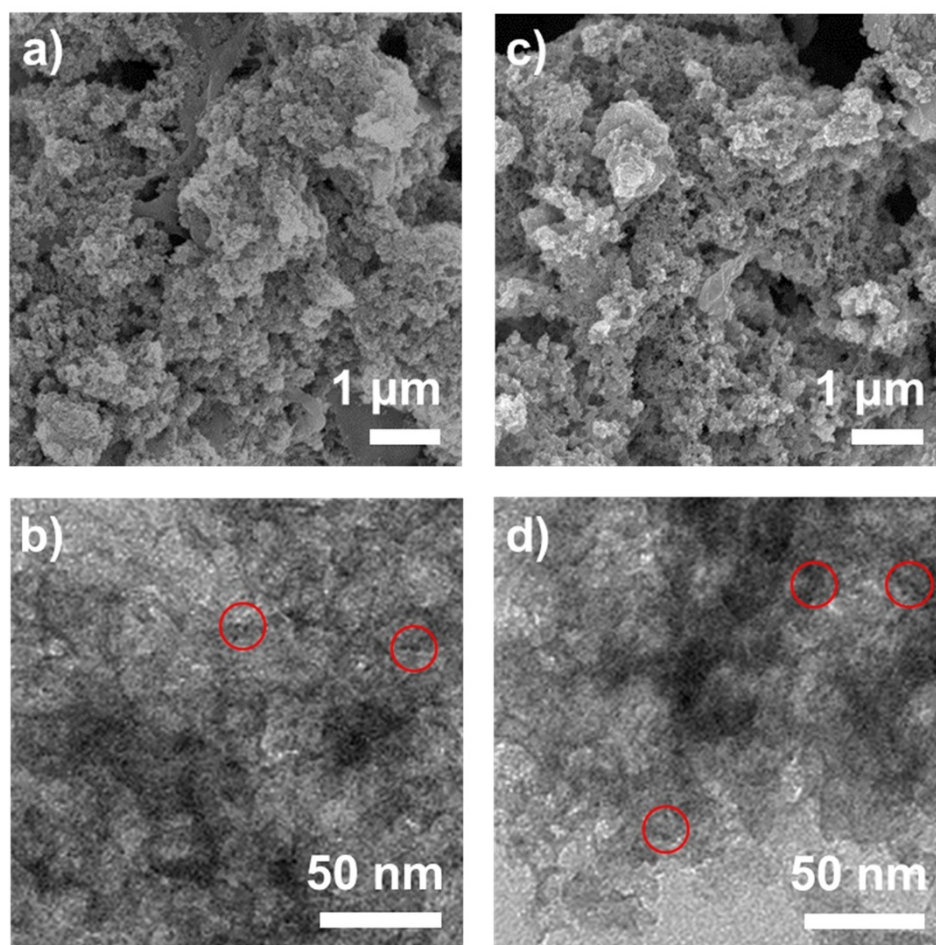
## Experimental section

**Synthesis of Co-PPhen-X.** 200 mg 3,8-dibromo-1,10-phenanthroline and 100 mg  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were first dissolved in 60 ml ethanol before 200 mg fumed silica was added under stirring to form a homogeneous dispersion. Then the mixture was dried by a rotary evaporator. The dried fine power was put into tube furnace and underwent the heat-treatment at  $300\text{-}700^\circ\text{C}$  ( $5^\circ\text{C min}^{-1}$ ) under  $\text{N}_2$  atmosphere for 2 hours. Afterwards, the products were etched in 2 M NaOH for 3 days followed in 0.5 M  $\text{H}_2\text{SO}_4$  for 10 hours at  $90^\circ\text{C}$  to remove  $\text{SiO}_2$  templates and cobalt particles, respectively.

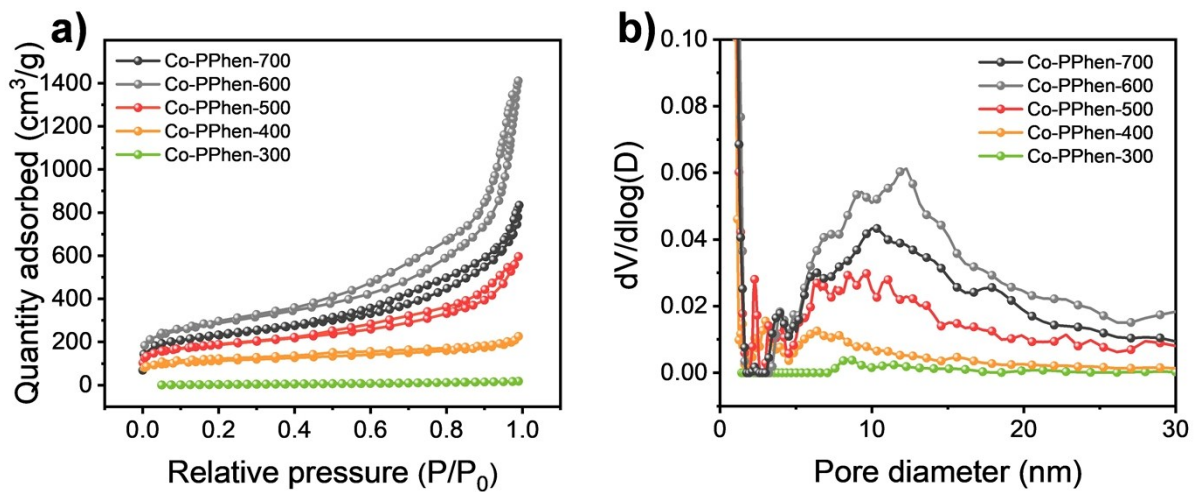
**Selectively catalytic oxidation of ethylbenzene.** In a typical catalytic reaction, 10 mg catalyst, ethylbenzene (0.5 mmol),  $\text{H}_2\text{O}$  (1 ml), and t-BHP (70% solution in water, 500  $\mu\text{l}$ ) were added into a 15 ml quartz glass vessel. The reaction vessel was then heated at  $80^\circ\text{C}$  for 6 h with magnetic stirring at 1500 rpm. Afterwards, 77  $\mu\text{l}$  anisole was added into the reaction system and used as internal standard. 10 ml ethyl acetate was used to extract the organic compounds in the reaction system. Finally, the reaction products were analyzed by using a Shimadzu gas chromatograph with an FID detector (GC-FID) and high purity nitrogen as the carrier gas. For stability tests, the used catalyst was recovered by centrifugation under 9000 rpm for 12 min, thoroughly washed with ethanol and water, and dried under vacuum at  $60^\circ\text{C}$  overnight.



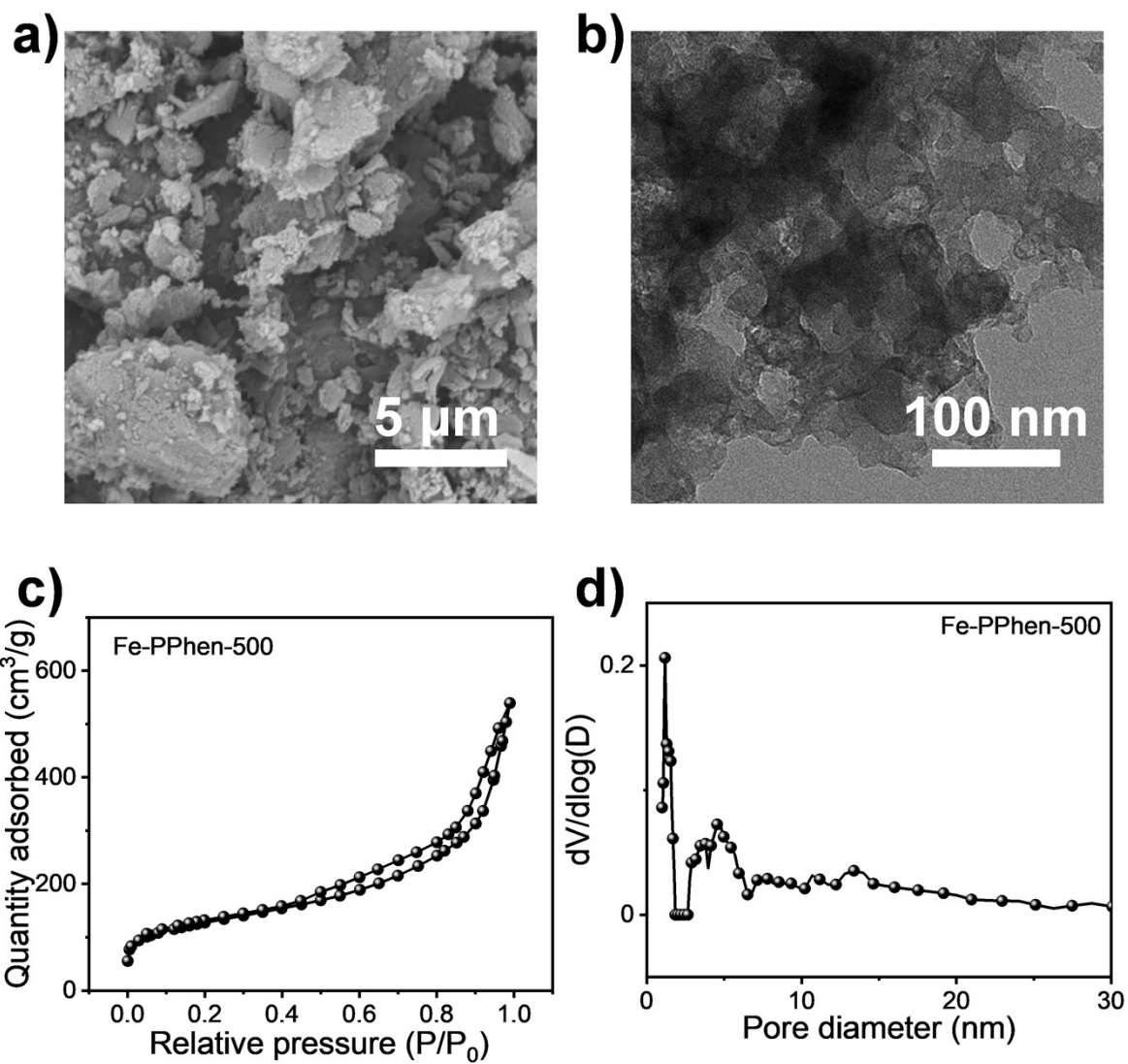
**Figure S1.** SEM and TEM images of Co-PPhen-300 (a, b) and Co-PPhen-400 (c, d), and SEM and HRTEM images of Co-PPhen-500 (e, f).



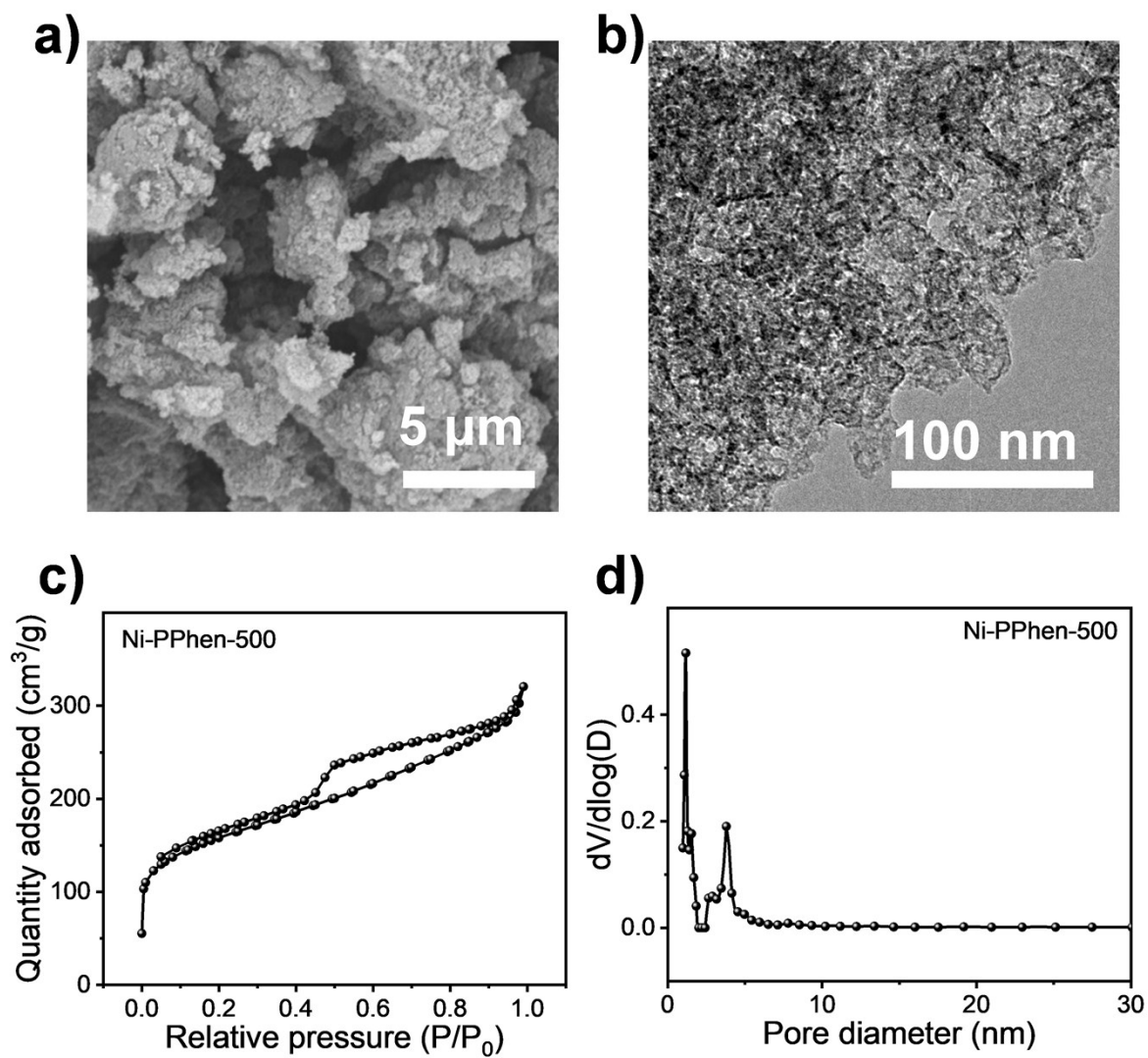
**Figure S2.** SEM and TEM images of Co-PPhen-600 (a, b) and Co-PPhen-700 (c, d). The red circles indicate the metal-containing particles.



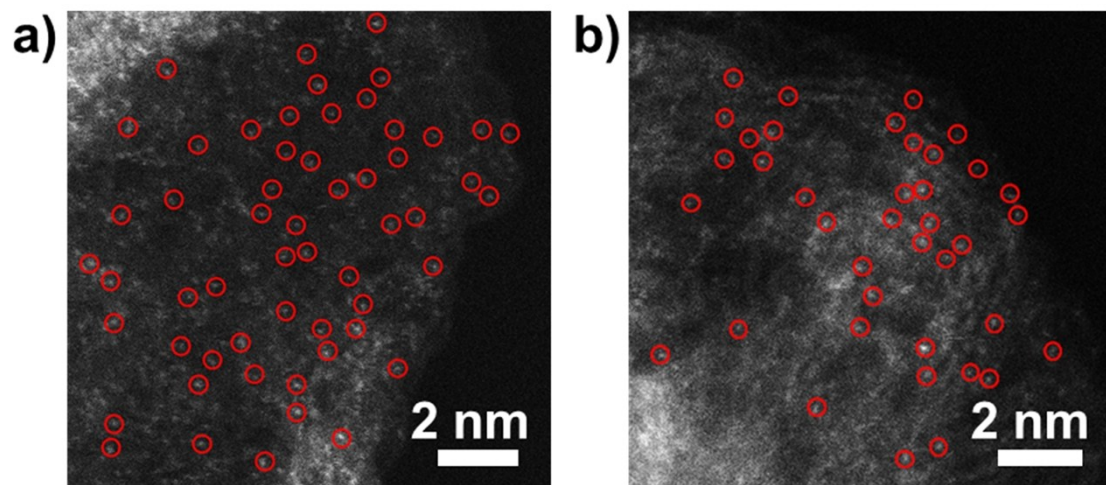
**Figure S3.** (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of the Co-PPhen-X catalysts.



**Figure S4.** (a) SEM, (b) TEM, (c) nitrogen adsorption-desorption isotherms, and (d) pore size distribution of Fe-PPhen-500, respectively.

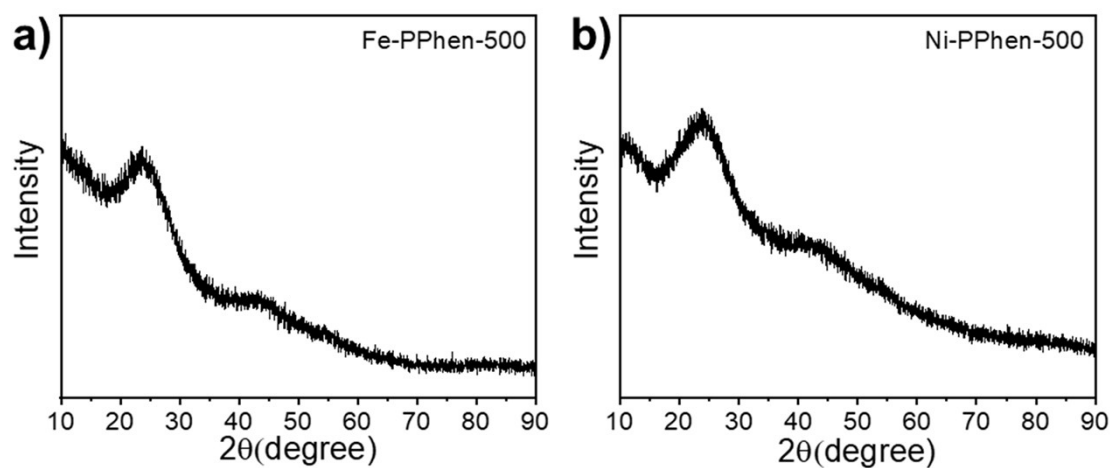


**Figure S5.** (a) SEM, (b) TEM, (c) nitrogen adsorption-desorption isotherms, and (d) pore size distribution of Ni-PPhen-500, respectively.

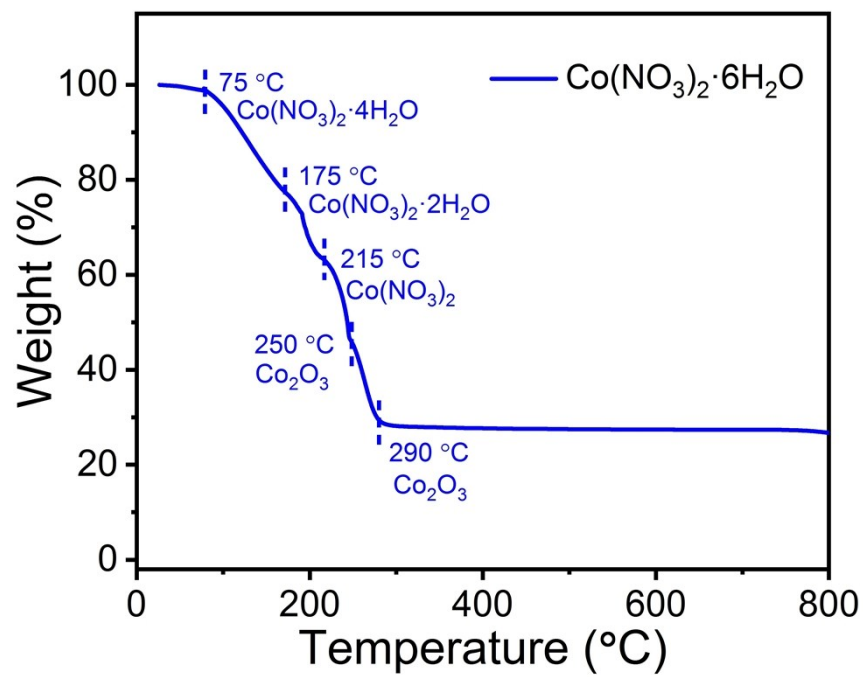


**Figure S6.** HAADF-STEM images of Fe-PPhen-500 (a) and Ni-PPhen-500 (b).

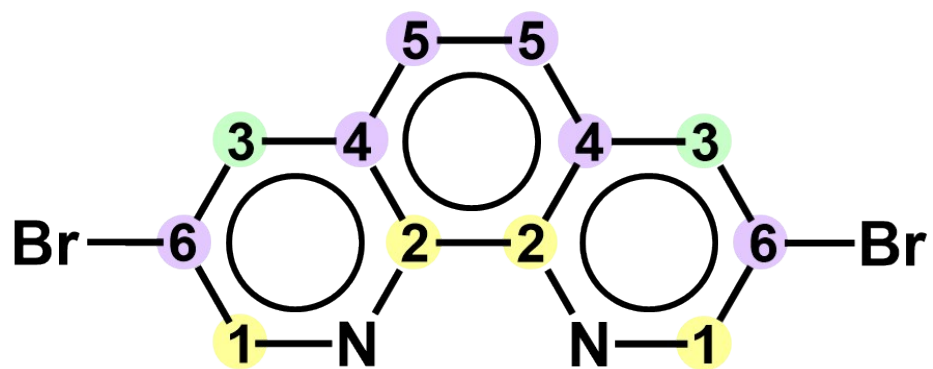




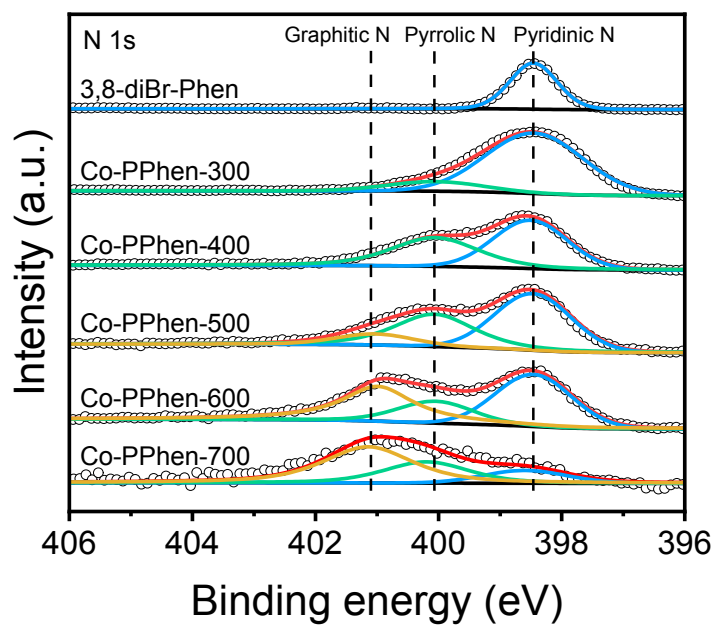
**Figure S7.** XRD patterns of Fe-PPhen-500 (a) and Ni-PPhen-500 (b).



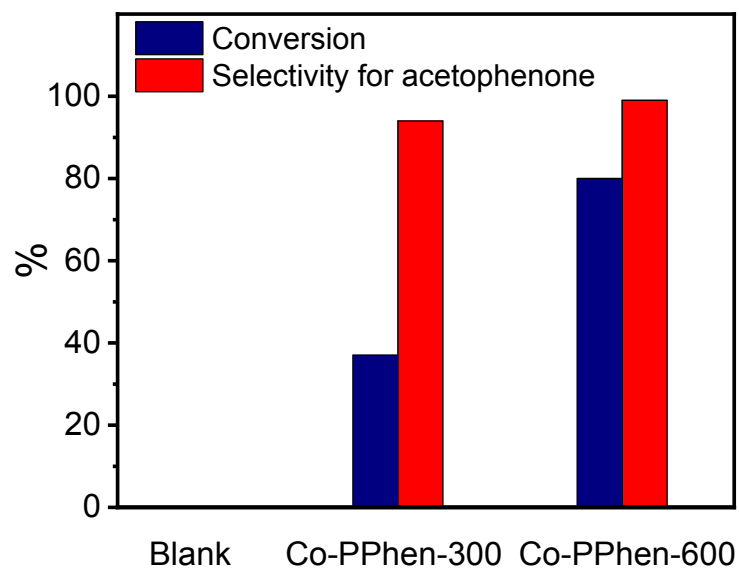
**Figure S8.** TGA curve of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in air atmosphere.



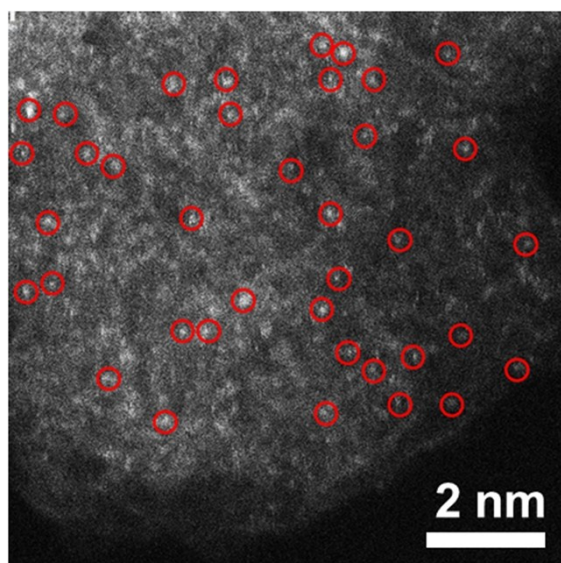
**Figure S9.** Diagrammatic drawing of six kinds of environmental carbon atoms in 3,8-diBr-Phen.



**Figure S10.** High-resolution XPS spectra for the N 1s region of the 3,8-diBr-Phen precursor and the Co-PPhen-X catalysts.



**Figure S11.** Catalytic performance for ethylbenzene oxidation of Co-PPhen-X.



**Figure S12.** HAADF-STEM image of Co-PPhen-500 after four catalytic runs.

**Table S1.** Specific surface area and pore volume of the Co-PPhen catalysts.

Catalyst	Specific surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)
Co-PPhen-300	18	0.034
Co-PPhen-400	411	0.309
Co-PPhen-500	669	0.962
Co-PPhen -600	835	2.280
Co-PPhen-700	771	1.130

**Table S2.** Elemental compositions of the catalysts based on the EA, XPS, and ICP measurements.

Catalyst	EA content (wt%)			XPS content (at%)		Metal content (wt%)
	C	H	N	C	N	
Co-PPhen-300	47.65	2.46	10.01	72.13	11.59	3.50
Co-PPhen-400	65.24	3.12	13.33	75.49	11.80	3.14
Co-PPhen-500	69.51	2.88	11.62	80.48	10.34	2.29
Co-PPhen-600	72.02	2.40	8.92	83.21	7.99	2.18
Co-PPhen-700	75.62	2.27	7.42	85.53	3.86	2.06



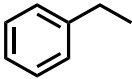
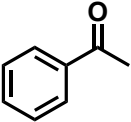
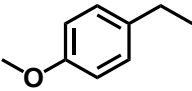
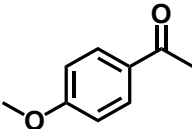
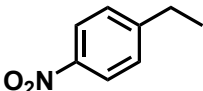
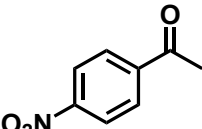
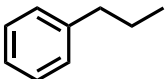
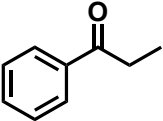
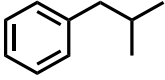
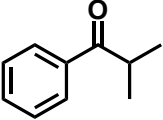
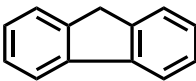
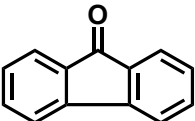
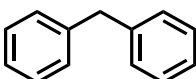
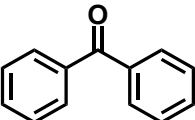
**Table S3.** Fitting results of N 1s XPS spectra.

Catalyst	XPS content (at%)		
	Graphitic N	Pyrrolic N	Pyridinic N
3,8-diBr-Phen	0	0	100
Co-PPhen-300	0	13.68	86.32
Co-PPhen-400	0	45.54	54.46
Co-PPhen-500	11.20	38.35	50.45
Co-PPhen-600	39.44	21.06	39.50
Co-PPhen-700	63.21	20.31	16.48

**Table S4.** Comparison of catalytic performances for selective oxidation of ethylbenzene with t-BHP in the aqueous phase by various catalysts.

Catalyst	Amount (mmol %)	t-BHP (ml)	Temp (°C)	Time (h)	Conv. (%)	AP Sel. (%)	Reference
Co-ISA/CNB	0.04	1.0	RT	48	98	99	<i>Adv. Funct. Mater.</i> , 2018, 28, 1802167.
Fe-N-C	0.57	0.5	RT	7	99	99	<i>J. Am. Chem. Soc.</i> , 2017, 139, 10790.
Mn-Ti/SBA-15	-	0.7	80	2	82	87	<i>Catal. Sci. Technol.</i> , 2013, 3, 2340.
N/Carbon	-	0.4	80	12	63	84	<i>Chem. Commun.</i> , 2014, 50, 9182.
Co/oxide	1.12	4.2	120	12	69	80	<i>Catal. Sci. Technol.</i> , 2015, 5, 540.
Au/LDH	0.002	0.2	140	16	39	91	<i>Nat. Commun.</i> , 2015, 6, 6957.
Co/AC	0.76	0.6	80	4	48	83	<i>Phys. Chem. Chem. Phys.</i> , 2017, 19, 4967.
Ag/SBA-15	1.83	0.4	90	5	92	99	<i>Catal. Commun.</i> , 2012, 23, 5.
<b>Co-PPhen-500</b>	<b>0.78</b>	<b>0.5</b>	<b>80</b>	<b>6</b>	<b>92</b>	<b>99</b>	<b>This work</b>

**Table S5.** Selective oxidation of hydrocarbons with Co-PPhen-500.\*

Entry	Substrate	Product	Conv. (%)	Sel. (%)
1 <sup>[a]</sup>			92	>99
2 <sup>[b]</sup>			99	98
3 <sup>[b]</sup>			99	>99
4 <sup>[b]</sup>			88	87
5 <sup>[b]</sup>			99	65
6 <sup>[a]</sup>			99	>99
7 <sup>[a]</sup>			99	>99

\*Reaction conditions: 0.5mmol substrate; [a] T=80 °C, 6 h, 5 mg catalyst, 1 ml H<sub>2</sub>O, 0.5 ml t-BHP; [b] T=100 °C, 12 h, 10 mg catalyst, 2 ml t-BHP.