

**Supporting Information**

**for**

**Dehydrogenation of Formic Acid using Molecular Rh and Ir Catalysts  
Immobilized on Bipyridine-based Covalent Triazine Frameworks**

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## General experimental methods

### Materials

All chemicals and reagents were purchased from commercial supplies and used as received unless otherwise mentioned: Nickel chloride hexahydrate, anhydrous dimethyl formamide, lithium chloride, zinc dust, iodine, zinc chloride, anhydrous methanol and chloroform, triethylamine were purchased from Sigma Aldrich. Iridium chloride hydrate, 1,2,3,4,5-pentamethyl cyclopentadiene were purchased from T.C.I. chemicals. 2-bromo-5-cyanopyridine was obtained from AK Scientific Inc. and purified by column chromatography using methylene chloride. CO<sub>2</sub> (99.99%) and H<sub>2</sub> (99.99%) were purchased from Sinyang gas industries. Complexes [bpyIrCp\*Cl]Cl, [bpyRhCp\*Cl]Cl, [IrCp\*Cl<sub>2</sub>]<sub>2</sub> and [RhCp\*Cl<sub>2</sub>]<sub>2</sub>, DCBPY were synthesized according to the previously reported methods.<sup>[1-5]</sup>

### Instrumentations

Fourier transform infrared spectroscopy (FT-IR) measurements were carried out on a Nicolet iS 50 (Thermo Fisher Scientific). Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS) measurements were performed using JEOL LTD (JAPAN) JEM-7610F operating at an accelerating voltage of 20.0 kV. X-ray photoelectron Spectroscopy (XPS) measurements were recorded on an ESCA 2000 (VG microtech) at a pressure of  $\sim 3 \times 10^{-9}$  mbar using Al-K $\alpha$  as the excitation source ( $h\nu=1486.6$  eV) with concentric hemispherical analyzer. Metal content in the complexes were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (iCAP-Q, Thermo fisher scientific) using microwave assisted acid digestion system (MARS6, CEM/U.S.A). Sorption measurements were conducted at 77 K using an automated gas sorption system (Belsorp II mini, BEL Japan, Inc.). Gas chromatography was measured on Younglin instrument, Korea, equipped with a FID detector and a capillary column (RT@Msieve 5A).

HPLC was measured on Waters Alliance 2695 (Waters Corporation) system equipped with an online degasser, an auto plate-sampler, a binary pump, and a thermostatically controlled column compartment and an RI detector. An Aminex HPX-87H column was used to carried out the separation using 5.00 mM H<sub>2</sub>SO<sub>4</sub> solution (0.6 mL/min) at 50 °C with a run time of 30 min. The sample volume injection was 10  $\mu$ L (each samples were analyzed thrice for better understanding). A series of formic acid/formate salt solution used (0.025 to 4 M) to generate a calibration curve with a R<sup>2</sup> of 0.999.

### Synthesis of bpy-CTF400 and bpy-CTF500

In a glove box, DCBPY (0.10 g, 0.04 mmol) and zinc chloride (0.33 g, 2.4 mmol) were taken in a 1 mL ampule (10 numbers) and closed with vacuum adapters. The ampules were taken out from glove box and sealed under vacuum by flame and heated to 400 or 500 °C in a furnace with heating rate of 60 °C/h. After 48 h of maintenance, the furnace was cooled to 200 °C with cooling rate of 10 °C/h. The crude monolith was ground well and stirred with 250 mL of water for 3 h. The filtered black solid was washed with water (500 mL) and acetone (500 mL). It is then refluxed in 1M HCl (250 mL) for overnight and filtered, washed with 1M HCl (3X100 mL), H<sub>2</sub>O (3X100 mL), THF (3X100 mL) and acetone (3X100 mL). The obtained black solid was dried under vacuum at 200 °C for 12 h.

#### **Synthesis of complexes Ir<sub>4.7</sub>@bpy-CTF400 and Rh<sub>1.7</sub>@bpy-CTF400**

In an oven-dried multi neck round bottom flask equipped with a condenser, bpy-CTF400 (0.15 g) and 1:1 mixture of methanol/chloroform were added under N<sub>2</sub> atmosphere. To the resulting black suspension, metal precursor ([IrCp\*Cl<sub>2</sub>]<sub>2</sub> or [RhCp\*Cl<sub>2</sub>]<sub>2</sub>) (0.10 g, 0.01 mmol) was added and refluxed under N<sub>2</sub> atmosphere for 24 h. After cooling to room temperature, the black solid was filtered, washed with dichloromethane (2x 250 mL) and acetone (2x 250 mL), and dried under vacuum at room temperature for 12 h.

#### **Synthesis of complex Ir<sub>11.3</sub>@bpy-CTF500**

The synthetic procedure was similar to that of complex Ir<sub>4.7</sub>@bpy-CTF400 except that bpy-CTF500 was used instead of bpy-CTF400.

#### **Synthesis of complexes Ir<sub>1.4</sub>@bpy-CTF400 and Ir<sub>4.1</sub>@bpy-CTF400**

The synthetic procedure was similar to that of complex Ir<sub>4.7</sub>@bpy-CTF400 except that varied amounts of [IrCp\*Cl<sub>2</sub>]<sub>2</sub> (0.03 and 0.07 g) were employed to synthesize complexes Ir<sub>1.4</sub>@bpy-CTF400, and Ir<sub>4.1</sub>@bpy-CTF400, respectively.

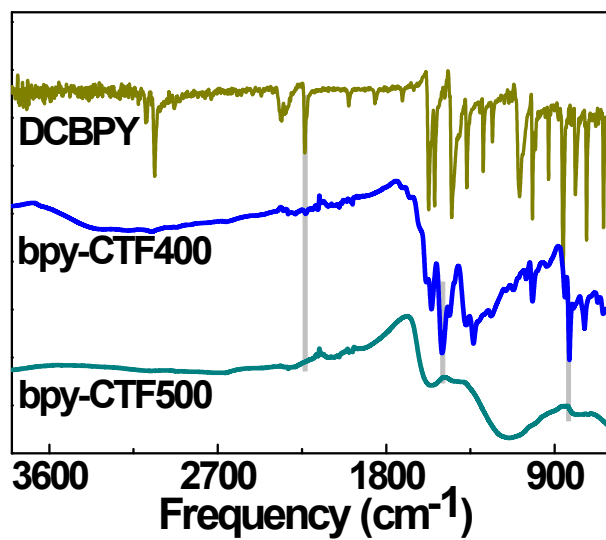
#### **Representative procedure for the dehydrogenation of formic acid into CO<sub>2</sub>/H<sub>2</sub>**

All reactions were performed in a reaction vessel (50 mL) using oil bath under steady magnetic stirring (350 rpm) at given temperature (50–90 °C) with a reflux condenser. To a pre-heated solution of 1.0 M aqueous formic acid (20.0 mL), the catalyst with a metal concentration of 0.244 mM (Ir<sub>1.4</sub>@bpy-CTF400 = 67.0 mg; Ir<sub>4.1</sub>@bpy-CTF400 = 23 mg; Ir<sub>4.7</sub>@bpy-CTF400 = 20.0 mg; Ir<sub>11.3</sub>@bpy-CTF500 = 8.32 mg, and Rh<sub>1.7</sub>@bpy-CTF400 = 29.6 mg) was added and this point was considered to have started the reaction. After 10 min, an aliquot of the reaction mixture was filtered through 0.2 µm filter and analyzed by HPLC to examine the decrement of formic acid concentration.

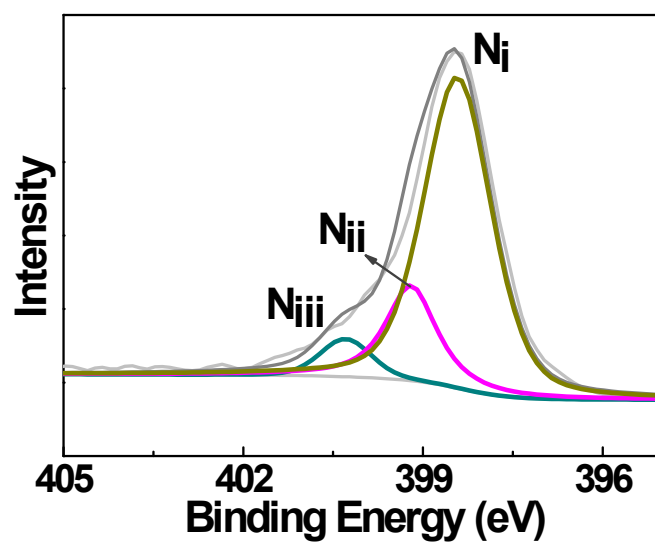
TON was calculated as molar ratio of formic acid conversion and amount of metal (Rh or Ir) used in the experiment. Initial TOF = TON/h.

In the recycling experiment, the catalyst was recovered by filtration, washed with water (25.0 mL) and acetone (25.0 mL) and dried under vacuum for 12 h. The collected solid was used for the next cycle with a fresh formic acid solution by following the above procedure.

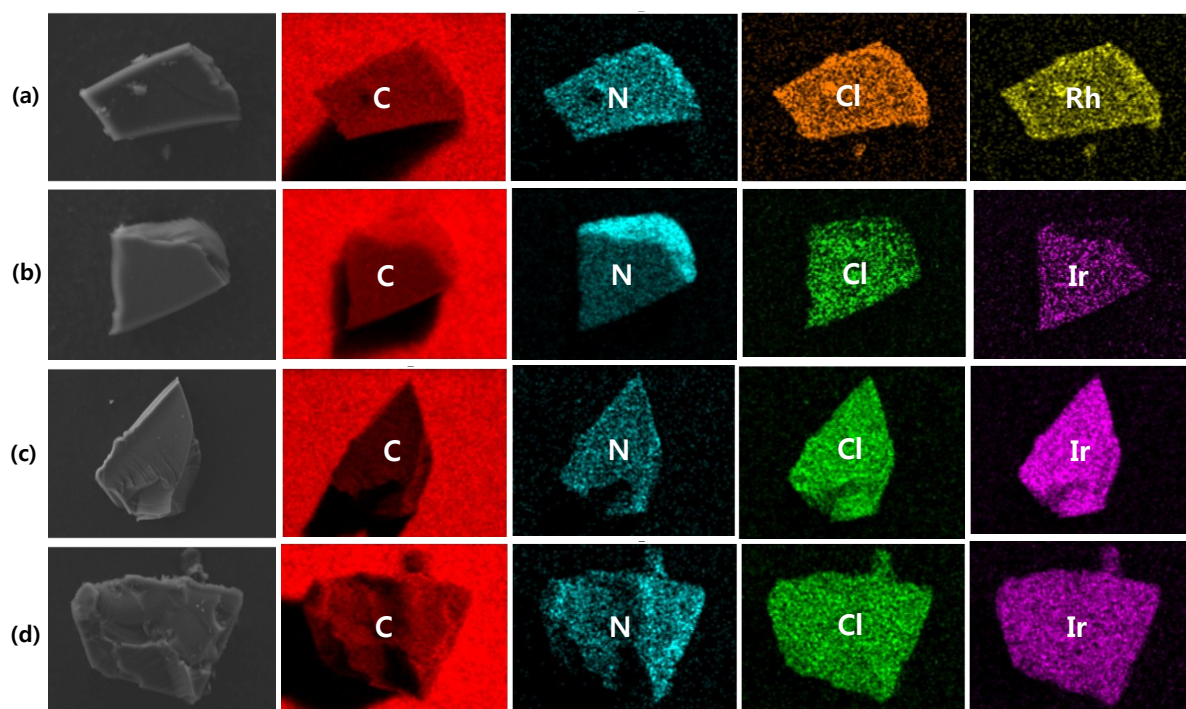
**Figure S1:** IR spectra of bpy-CTFs with DCBPY



**Figure S2:** XPS of bpy-CTF500

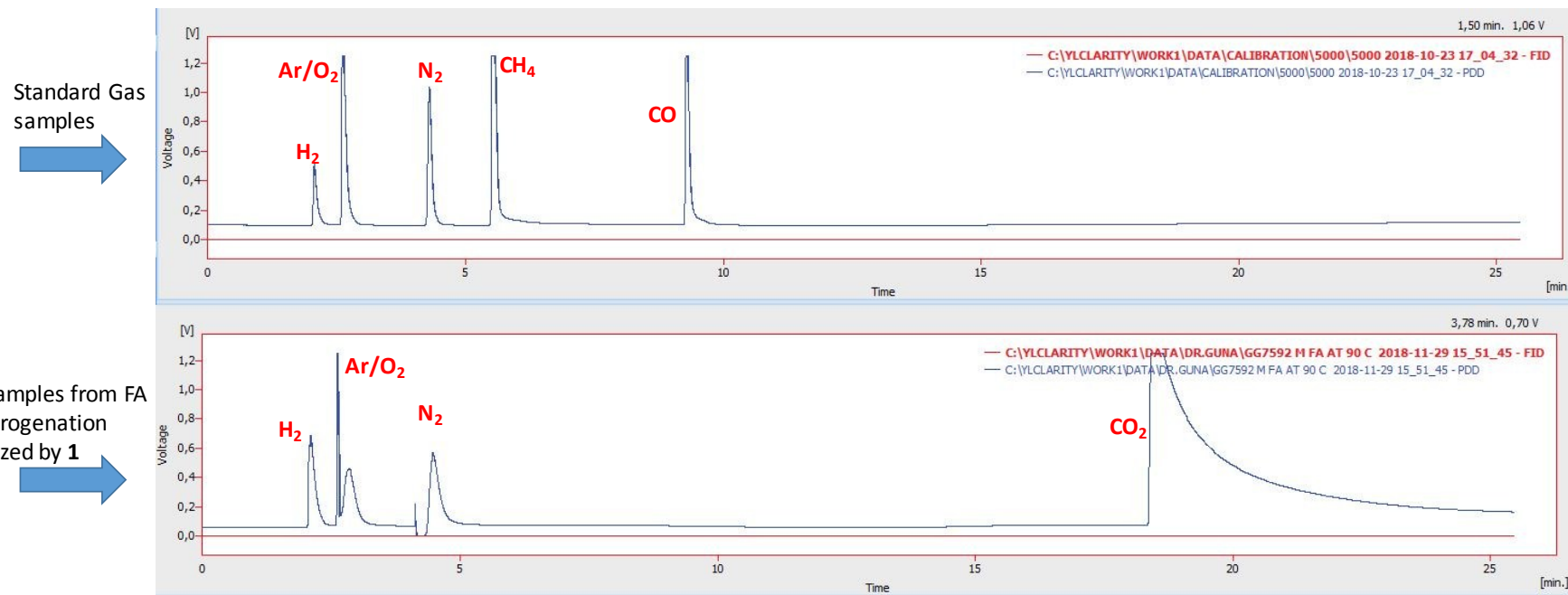


**Figure S3:** SEM-EDS mapping of the prepared catalysts



(a) =  $\text{Rh}_{1.7}@\text{bpy-CTF400}$ ; (b) =  $\text{Ir}_{1.4}@\text{bpy-CTF400}$ ; (c) =  $\text{Ir}_{4.1}@\text{bpy-CTF400}$ ; (d) =  $\text{Ir}_{11.3}@\text{bpy-CTF500}$ .

Figure S4: Results of gas samples analyzed by Gas Chromatography





**Table S1.** Elemental analysis of bpy-CTFs

Sample	C	N	H	C/N ratio
bpy-CTF400	58.27	19.18	3.78	3.03
bpy-CTF500	46.91	11.34	3.41	4.13

**Table S2:** N<sub>2</sub> adsorption-desorption analysis of prepared samples at 77K

Entry	Compound	Surface area (m <sup>2</sup> /g)	Total pore volume (cm <sup>3</sup> /g)	Average pore size (nm)
1	bpy-CTF400	684	0.40	2.35
2	bpy-CTF500	1566	0.87	2.23
3	Ir <sub>4.7</sub> @bpy-CTF400	170	0.09	2.24
4	Ir <sub>4.1</sub> @bpy-CTF400	257	0.30	4.7
5	Ir <sub>1.4</sub> @bpy-CTF400	479	0.28	2.38
6	Rh <sub>1.7</sub> @bpy-CTF400	151	0.12	3.32
7	Ir <sub>11.3</sub> @bpy-CTF500	686	0.38	2.23

**Table S3:** Atomic composition of presented CTFs by SEM-EDS analysis

Element	Rh <sub>1.7</sub> @bpy- CTF400	Ir <sub>11.3</sub> @bpy- CTF500	Ir <sub>1.4</sub> @bpy- CTF400	Ir <sub>4.1</sub> @bpy- CTF400
C	81.33	80.14	80.00	81.16
N	15.85	16.42	18.11	14.11
Cl	1.78	2.37	0.93	3.08
Ir	-	1.06	0.44	1.65
Rh	0.94	-	-	-

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