Supplementary Information

for

Molecular Rh(III) and Ir(III) Catalysts Immobilized on Bipyridine-based Covalent Triazine Frameworks for the Hydrogenation of CO_2 to Formate

Gunniya Hariyanandam Gunasekar [1,2], Kwangho Park [1], Hyeonseok Jeong [1], Kwang-Deog Jung [2], Kiyoung Park [3], and Sungho Yoon [1,*]

[1]Department of Applied Chemistry, Kookmin University, 861-1 Jeongneung-dong, Seongbuk-gu, Seoul 136-702, Republic of Korea.

[2]Clean Energy Research Center, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 136-791, Republic of Korea.

[3]Department of Chemistry, Korea Advanced Institute of Science and Technology, Daejeon 34141, Republic of Korea.

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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_2 (99.99%) and H_2 (99.99%) were purchased from Sinyang gas industries. Complexes [bpyIrCp*Cl]Cl, [bpyRhCp*Cl]Cl, $[IrCp^*Cl_2]_2$ and $[RhCp^*Cl_2]_2$ were synthesized according to the previously reported methods [1-4]

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 ~3 x 10^{-9} mbar using Al-Ka as the excitation source (hγ=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.).

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_2SO_4 solution (0.6 mL/min) at 50 °C with a run time of 30 min. The sample volume injection was 10 µL (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^2 of 0.999.

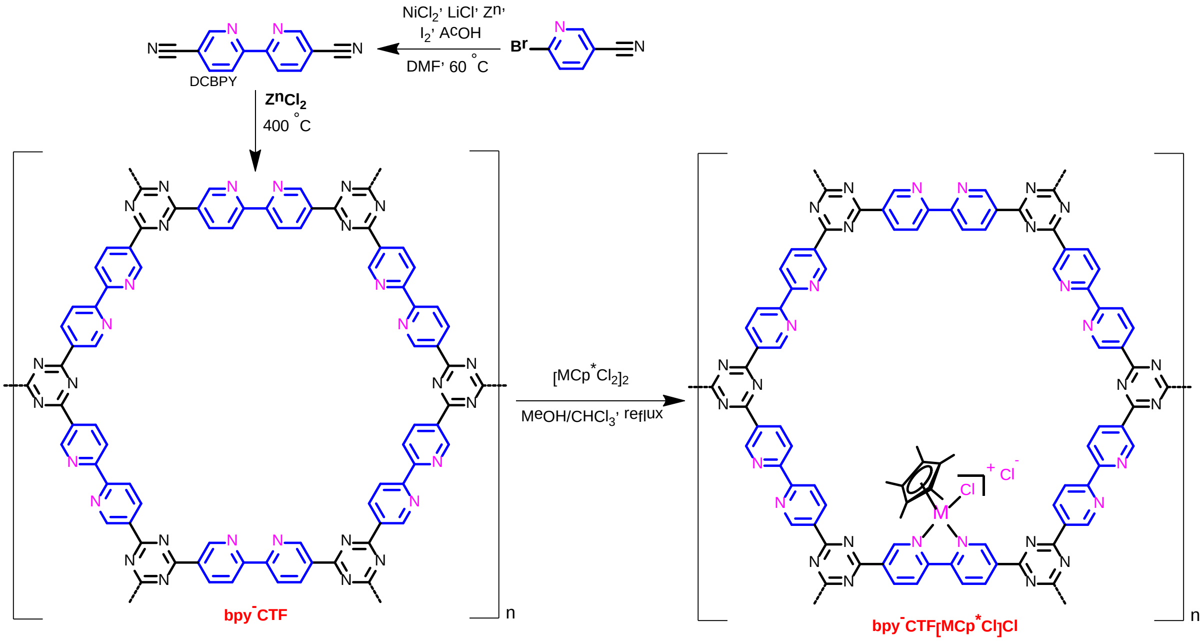
Computational Methods

All computations were performed by using the Gaussian 09 (g09) package [5] with the Becke-Perdew86 (BP86) functional [6,7] and the LANL2DZ basis set/ECP combination [8-10] for geometry optimizations and frequency calculations. For single point calculations, the LANL2TZ basis set was used for the Ru center. [8-10] The potential energy surfaces for the Ru-H formation were constructed in two dimensions along the Ru-O (of acac or bicarbonate) bond and Ru-H_2 distances, while that for the formate formation was constructed in one dimension along the hydride-CO_2 distance. From the saddle points, transition states were searched and validated using g09 intrinsic reaction coordinate calculations [11,12].

Hydrogenation Reactor Design

Hydrogenation was carried out in a homemade stainless steel 100 mL autoclave equipped with heaters (temperature of up to 300°C can be used), pressure and temperature sensors. The reactor is equipped with a burst disc which hold the pressure of up to 300 bar. CO_2 was supplied using HPLC pump (if required) and H_2 was supplied using Mass Flow Controller (MFC) at a rate of 200 mL/min.

Reaction Scheme for the synthesis of Complexes Ir@bpy-CTF400 and Rh@bpy-CTF400



Synthesis of 5,5'-dicyano-2,2'-bipyridine (DCBPY)[5]

In a 250 mL round bottom flask, $NiCl_2{\cdot}6H_2O$ (0.12 g, 0.5 mmol), 2-bromo-5-cyanopyridine (10.0 mmol) and anhydrous LiCl (0.43 g, 10.0 mmol) were taken and dried under vacuum at room temperature for 10 h. After releasing the vacuum using N_2, anhydrous DMF (20 mL) was added and heated to 45 °C under N_2 atmosphere. In another round bottom flask, Zn dust (0.78 g, 12.0 mmol) was taken and dried under vacuum at room temperature for 10 h. To this dried Zn dust, anhydrous

DMF (20 mL) was added under N_2 atmosphere and the resulting suspension was transferred to the above greenish blue $NiCl_2$ solution at 45 °C. To the resulting blue suspension, a pinch of I_2 and two drops of acetic acid were added and stirred at 55 °C for 5h. Cooled the greenish blue suspension to room temperature and acidified with 15 mL of 1M HCl and then 25 % ammonia solution (excess) was added and extracted with CH_2Cl_2. The organic layers were collected and dried over Na_2SO_4 and concentrated, and the crude material was purified by column chromatography using methylene chloride and obtained DCBPY as a white solid. Yield – 70 %): ^1H NMR (400 MHz, $CDCl_3$, 25˚C, TMS): δ= 8.97 (dd, J=2.1 Hz, J=0.8 Hz, 2H), 8.64 (dd, J=8.3 Hz, J=0.8 Hz, 2H), 8.14 (dd, J=8.3 Hz, J=2.1 Hz, 2H).

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 1 M HCl (3X100 mL), H_2O (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 $Ir_{4.7}$@bpy-CTF400 and $Rh_{1.7}$@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_2 atmosphere. To the resulting black suspension, metal precursor ($[IrCp^*Cl_2]_2$ or $[RhCp^*Cl_2]_2$) (0.10 g, 0.01 mmol) was added and refluxed under N_2 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 $Ir_{11.3}$@bpy-CTF500

The synthetic procedure was similar to that of complex $Ir_{4.7}$@bpy-CTF400 except that bpy-CTF500 was used instead of bpy-CTF400.

Synthesis of complexes $Ir_{1.4}$@bpy-CTF400, $Ir_{4.1}$@bpy-CTF400, and $Ir_{10.6}$@bpy-CTF400

The synthetic procedure was similar to that of complex $Ir_{4.7}$@bpy-CTF400 except that varied amounts of $[IrCp^*Cl_2]_2$ (0.03, 0.07 and 1.0 g) were employed to synthesize complexes $Ir_{1.4}$@bpy-

CTF400, $Ir_{4.1}$@bpy-CTF400, and $Ir_{10.6}$@bpy-CTF400, respectively.

Representative procedure for the hydrogenation of CO_2 to formate

Hydrogenation was carried out in a batch mode with pre-determined time duration. In a typical run, the catalyst (0.122 mM of metal concentration; $Ir_{1.4}$@bpy-CTF400 = 33.5 mg; $Ir_{4.1}$@bpy-CTF400 = 11.5 mg; $Ir_{4.7}$@bpy-CTF400 = 10.0 mg; $Ir_{10.6}$@bpy-CTF400 = 4.45 mg; $Ir_{11.3}$@bpy-CTF500 = 4.16 mg, and $Rh_{1.7}$@bpy-CTF400 = 14.8 mg) was added to a CO_2 saturated aqueous triethylamine solution (20.0 mL) and kept inside the reactor. After flushing with CO_2 for three times, the reactor was pressurized first with CO_2 up to 4 MPa and then with H_2 (1:1) to the 8 MPa pressure at room temperature and heated to the desired temperature (80-120 °C). The reaction was cooled to room temperature after pre-determined time and slowly released the pressure. An aliquot of the reaction mixture from autoclave was analyzed by HPLC using 0.005 M of H_2SO_4 as an eluent. TON was calculated as molar ratio of formate produced and amount of metal (Rh or Ir) used in the experiment. Initial TOF = TON/h. The time dependent formic acid production/consumption experiments were carried out for a pre-determined time.

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 at room temperature for 12 h. The collected solid was used for the next cycle by following the above procedure.

Figure S1: SEM-EDS mapping of catalyst $Rh_{1.7}$@bpy-CTF400

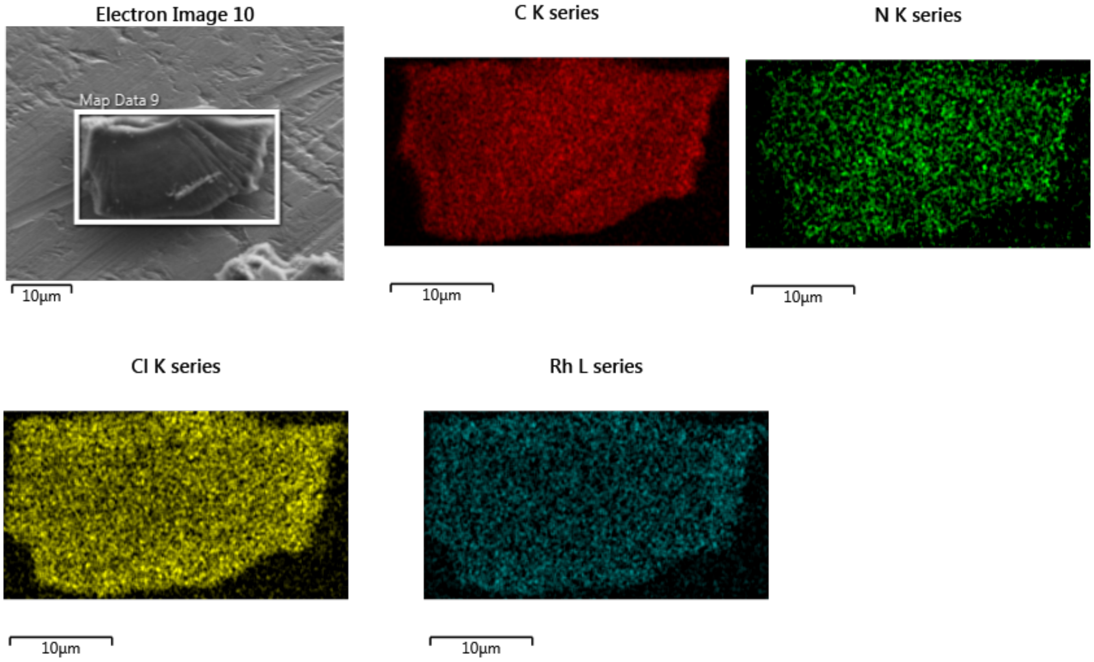


Figure S2: SEM-EDS mapping of catalyst $Ir_{11.3}$@bpy-CTF500

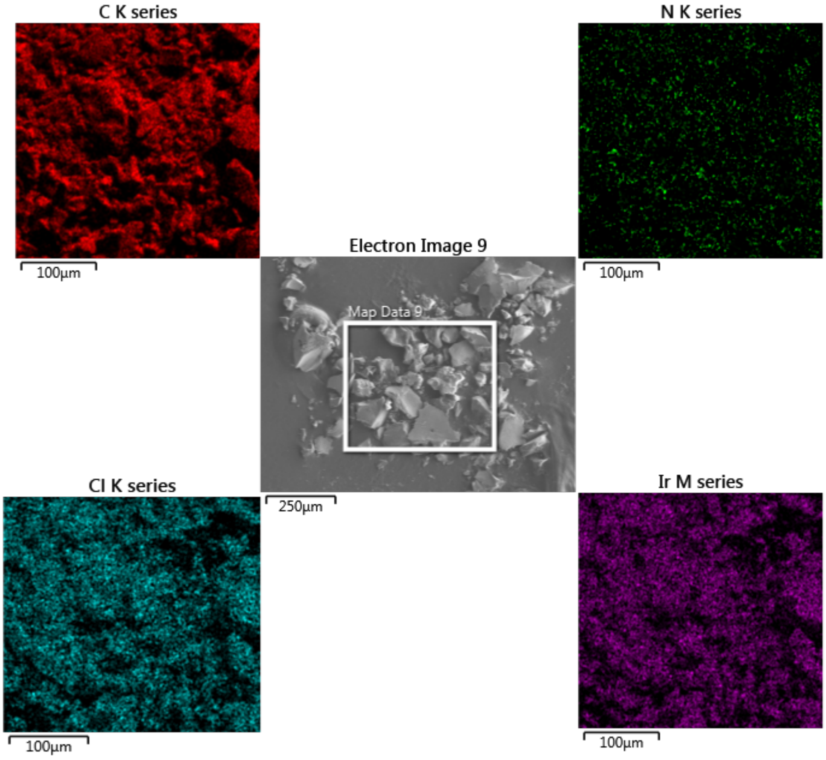


Figure S3: SEM-EDS mapping of catalyst Ir$_{1.4}$@bpy-CTF400

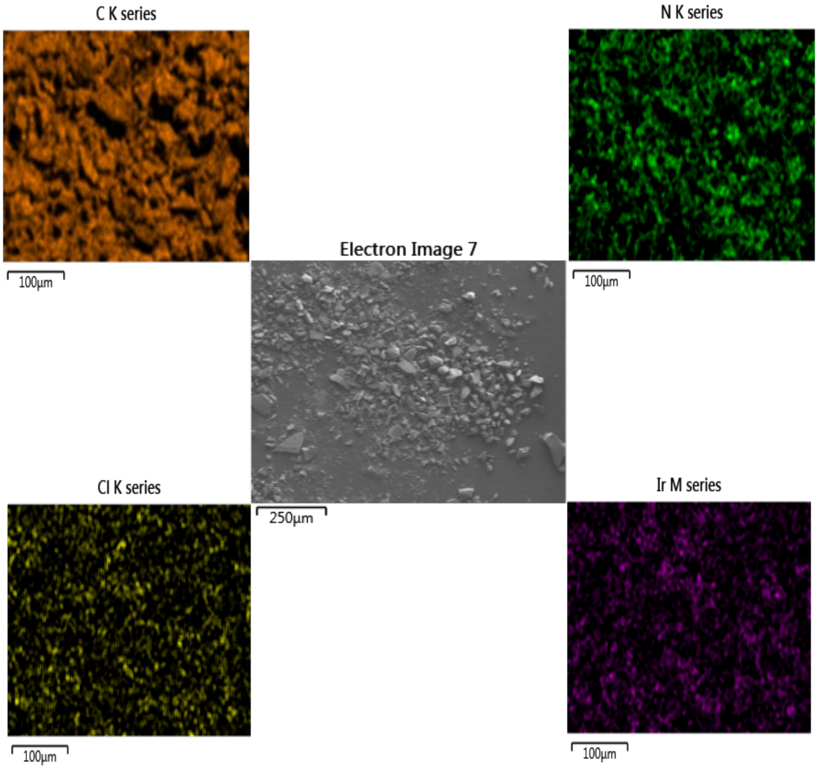


Figure S4: SEM-EDS mapping of catalyst Ir$_{4.1}$@bpy-CTF400

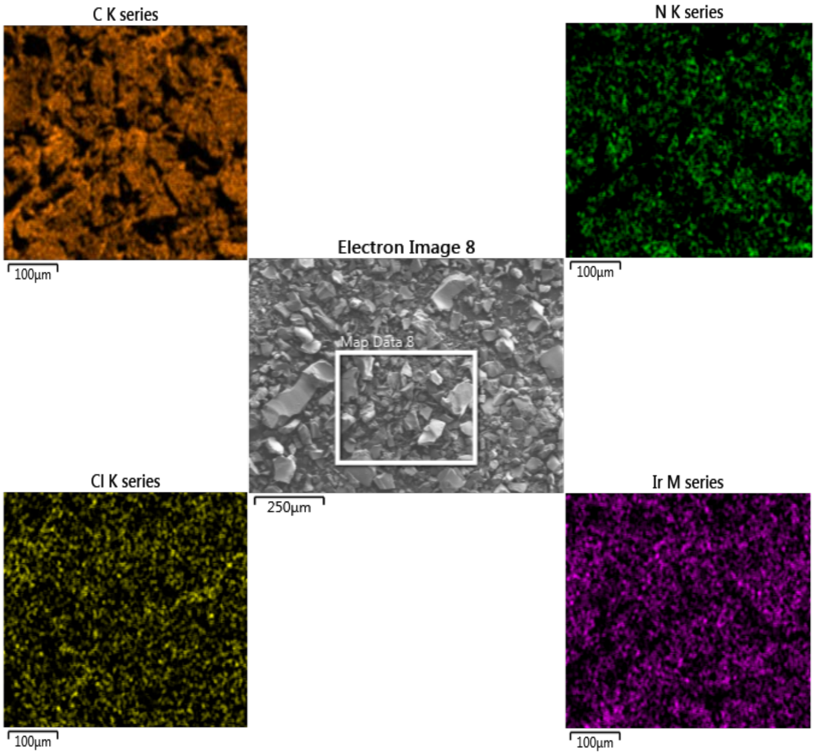


Figure S5: SEM-EDS mapping of catalyst $Ir_{10.6}$@bpy-CTF400

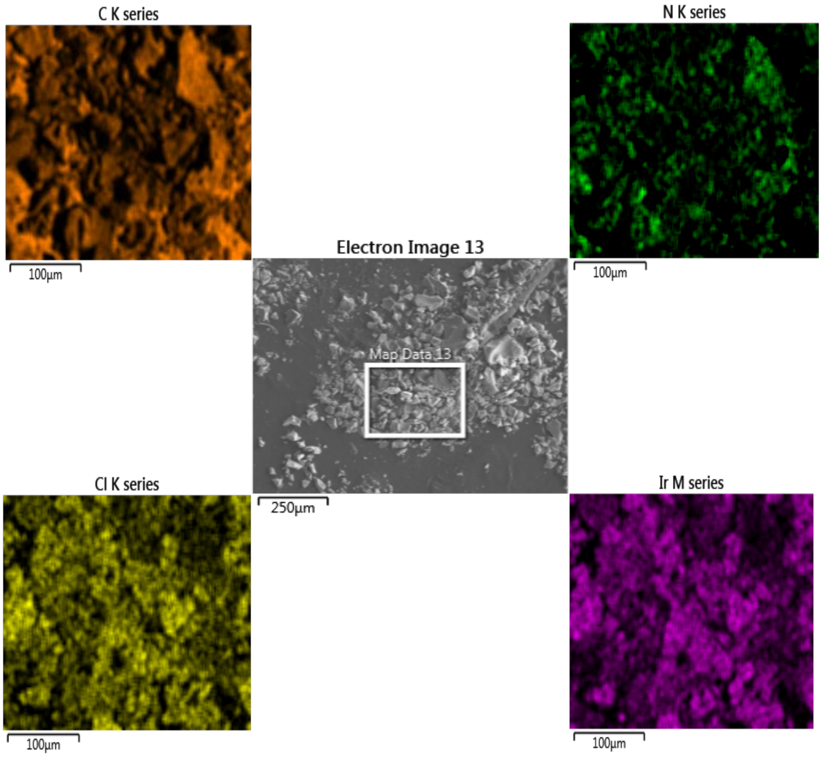


Figure S6: Recyclability of Rh$_{1.7}$@bpy-CTF400 and Ir$_{4.7}$@bpy-CTF400

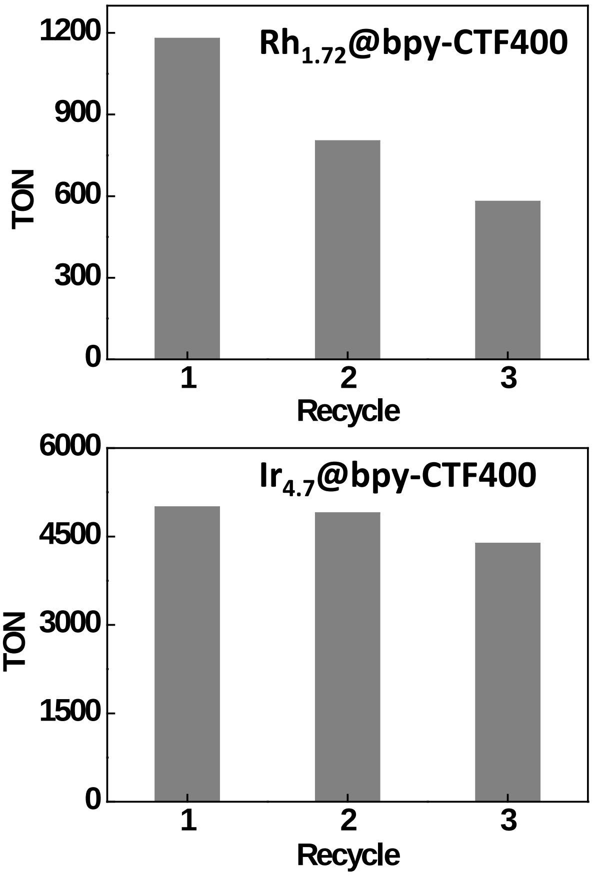


Figure S7. XPS of recovered Ir catalyst $Ir_{4.7}$@bpy-CTF400

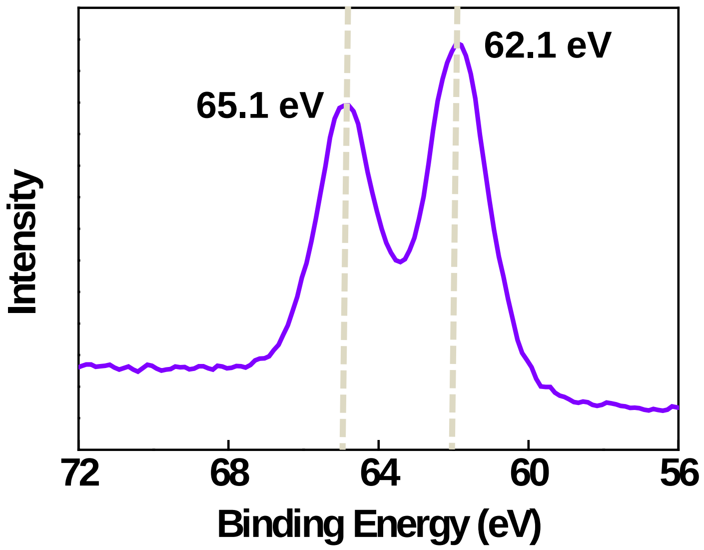


Table S1: Atomic composition of presented CTFs by SEM-EDS analysis

Element	$Rh_{1.7}$@bpy-CTF400	$Ir_{11.3}$@bpy-CTF500	$Ir_{1.4}$@bpy-CTF400	$Ir_{4.1}$@bpy-CTF400	$Ir_{10.6}$@bpy-CTF400
C	81.33	80.14	80.00	81.16	81.33
N	15.85	16.42	18.11	14.11	15.58
Cl	1.78	2.37	0.93	3.08	1.90
Ir	-	1.06	0.44	1.65	1.17
Rh	0.94	-	-	-	-

Table S2: N_2 adsorption-desorption analysis of prepared samples at 77K

Entry	Compound	Surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore size (nm)
1	bpy-CTF400	684	0.40	2.35
2	bpy-CTF500	1566	0.87	2.23
3	$Ir_{4.7}$@bpy-CTF400	170	0.09	2.24
4	$Rh_{1.7}$@bpy-CTF400	151	0.12	3.32
5	$Ir_{11.3}$@bpy-CTF500	686	0.38	2.23
6	$Ir_{1.4}$@bpy-CTF400	479	0.28	2.38
7	$Ir_{4.1}$@bpy-CTF400	257	0.30	4.7
8	$Ir_{10.6}$@bpy-CTF400	10	0.01	7.68

Table S3. 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 S4: Base concentration vs Formate concentration at different intervals of time[a]

Catalyst amount (mg)	Base – TEA (M)	Time (h)	FA conc. (M)	TON
10	1	0.25	0.15	1300 (Initial TOF -5300 h^{-1})
10	1	0.5	0.24	2000
10	1	2	0.6	5000
10	2	2	0.79	6475
10	2	3	1.01	8278
10	2	5	1.13	8852
10	2	7	1.18	9010
10	3	2	0.84	6885
10	3	3	0.98	8032
10	3	5	1.34	11050
10	3	7	1.67	13713
10	3	10	1.80	14885
100	3	4	1.79	1467

a. Reactions were performed at 120 ˚C under 8 MPa total pressures using $Ir_{4.7}$@bpy-CTF400

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