Supporting Information

Iridium Complexes Supported on Cross-linked Polyacrylic Acid as Release-and-Catch Catalysts for Continuous Formic Acid Dehydrogenation

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General Procedures

All commercially available chemicals were used received. $[Cp*Ir(H_2O)_3]SO_4$ was purchased from FURUYA METAL Co. Ltd., 4,4'-dichloro-2,2'-bpyridine, Acrylic acid, *N,N'*-Methylenebisacrylamide (MBA), and 2,2'-Azobisisobutyronitrile (AIBN) was purchased form Fujifilm Wako Chemicals Co. Ltd. Formic acid (>99%) was purchased from Kishida Chemical Co. Ltd..

α-Al₂O₃ with a purity of 99.99% was purchased from Kojundo Chemical Laboratory Co. Ltd. The ion exchange resin (cation), DiaionTM CR20, was purchased from Mitsubishi Chemical Corporation. Strongly acidic cation exchange resin No. 6 (8% crosslinked, 200-400 mesh, H-type) purchased from Fujifilm Wako Chemicals Co. Ltd. was used as the ion exchange resin (anion). It was carefully washed with water before use. Activated carbon was purchased from Fujifilm Wako Chemicals Co. Ltd.

Solution NMR spectra were recorded on a 600 MHz spectrometer (Bruker Corp., AVANCE III HD 600 spectrometer) at room temperature. Chemical shift were given in ppm relative residual solvent in D₂O ($^{1}H=4.65$ ppm) or tetramethylsilan (TMS, $^{1}H=0$ ppm).

Solid-state ¹³C CP/MAS NMR spectra were recorded on a Bruker AVANCE II+ 400 spectrometer using a 4 mm diameter ZrO₂ rotor, and the rotation frequency was set to 12.5 kHz. Standard ramp cross-polarization (CP) was used to transfer polarization from the ¹H nuclei to the nucleus of interest ¹³C, and the CP contact time was set to 0.2 ms. The Recycle delay was set as 2 s for CP/MAS measurement. SPINAL-64 ¹H heteronuclear decoupling was applied during acquisition for CPMAS measurement. ¹³C chemical shifts were referenced to TMS at 0 ppm using adamantane as an external standard (38.52 ppm).

FT-IR spectra were measured directly by ATR methods using FT/IR-6100 (JASCO) UV-Vis spectra were taken with Cary 60 UV-Vis spectrometer (Agilent Technology Inc.) with a fiber probe.

Elemental analysis was performed using ICP-AES (HORIBA ULTIMA2). The calibration curve for Ir was created using an Ir standard solution purchased from Fujifilm Wako Chemicals CO. Ltd., and quantitative analysis of the Ir content in the catalyst was

carried out. The ICP samples were prepared by heating in a solution of nitric acid and sulfuric acid at a 1:1 ratio at 100 °C, followed by dilution with water. The mass analysis was performed using 6230 ESI-TOF-MS system (Agilent Technology Inc.) and ESI-Qq-TOF MS compact (Bruker).

For SEM-EDS analysis, samples were pre-coated with gold for charge suppression. JEOL, JSM-7100F was used for the measurements.

Catalysts Synthesis

Cp*Ir-HMDAbpy@PAA was synthesized following route as shown in Figure S1.



Figure S1. Synthesis of Cp*Ir-HMDAbpy@PAA.

Synthesis of *N*,*N*'-([2,2'-bipyridine]-4,4'-diyl)bis(hexane-1,6-diamine) (4-hmdabpy)

4,4'-dichloro-2,2'-bipyridine (445 mg, 1.98 mmol) and a large excess of hexamethylenediamine (7.0 g, 0.06 mol) were heated and stirred in a stainless-steel autoclave under neat conditions at 130 °C for 24 h. Water was added to the resulting mixture and a white precipitate was obtained. The mixture was carefully washed with deionized water 3 times and collected by centrifugation. The mixture was then vacuum dried overnight at 55 °C to obtain a white solid as N,N'-([2,2'-bipyridine]-4,4'-diyl)bis(hexane-1,6-diamine) (4-hmdabpy, 710 mg, 1.85 mmol, 93% yield).

¹H NMR(600 MHz, MeOH- d_4): δ 8.05 (d, J = 5.91 Hz, 2H), 7.19 (d, J = 2.37, 2H) 6.55 (dd, J = 2.44, 5.98, 2H), 3.22 (t, 7.16, 4H), 2.63 (t, 7.20 Hz, 4H), 1.70-1.65 (m, 4H), 1.52-1.38 (m, 12H). ¹³C NMR (150 MHz, MeOH- d_4 , ppm) δ 155.9, 156.9, 149.6, 108.2, 106.1, 43.3, 42.4, 33.4, 30.0, 28.0, 27.8. ESI-TOF-MS (m/z): [N,N'-([2,2'-bipyridine]-4,4'-diyl)bis(hexane-1,6-diamine)] calculated for C₂₂H₃₇N₆²⁺ [M+2H], 193.1573; found,193.1576.

Synthesis of Cp*Ir-HMDAbpy

N,N'-([2,2'-bipyridine]-4,4'-diyl)bis(hexane-1,6-diamine) (4-hmdabpy, 140 mg, 0.36 mmol) and [Cp*Ir(H₂O)₃]SO₄ (173.8 mg, 0.36 mmol) were dissolved in deionized water and stirred for 24 h under N₂ at room temperature. Water was removed by freeze-dry at -196 °C to obtain the pale-yellow solid as Cp*Ir-HMDAbpy (256 mg, 0.30 mmol, 84% yield).

¹H NMR(600 MHz, D₂O+CH₃COOH, ppm) $\delta = 8.38$ (d, J = 5.76 Hz, 2H), 7.21 (s, 2H), 6.73 (dd, J = 2.48, 6.69, 2H), 3.26 (t, J = 6.99Hz, 4H), 2.95 (t, J = 7.71 Hz, 4H), 1.68-1.59 (m, 8H), 1.55 (s, 15H), 1.42-1.35 (m, 8H). ¹³C NMR (150 MHz, D₂O + CH₃COOH, ppm) $\delta = 155.7$, 155.5, 150.3, 107.5, 105.9, 86.6, 42.0, 39.4, 27.6, 26.6, 25.6, 25.3, 7.72. ESI-TOF-MS (m/z): [Cp*Ir-HMDAbpy-OCOH]⁺ calcd for C₃₃H₅₂IrN₆O₂, 757.38; found, 757.38 .

Synthesis of PAA

Acrylic acid (30.92 ml, 0.408 mol) and N,N'-methylenebisacrylamide (MBA, 12.25 g 0.0794 mol) were degassed at 80 °C for 30 min by N₂ bubbling in a water. Then, 2,2'- azobis-2-methylpropionitrille (AIBN, 217 mg, 1.28 mmol in MeOH) was added to the acrylic acid solution and polymerized at 80 °C under N₂ atmosphere for 1 h. The resulting white gel was milled and washed carefully with MeOH and deionized water. The white gel was freeze-dried at -196 °C and used as a cross-linked polyacrylic acid (PAA, 37.95g, 87% weight yield).

Synthesis of HMDAbpy@PAA

Cross-linked polyacrylic acid (PAA) (860 mg) and HMDAbpy (70 mg, 0.182 mmol) were dissolved in dry CH_2Cl_2 and stirred for 15 h at room temperature under N_2 atmosphere. The resulting white powder was filtered, washed with deionized water and freeze-dried at -196 °C to give a white solid as HMDAbpy@PAA (909 mg, 97% by weight yield). Catalysts with other substituents were synthesized in a similar method.

Synthesis of Cp*Ir-HMDAbpy@PAA

HMDAbpy@PAA (216 mg) was stirred with $[Cp*Ir(H_2O)_3]SO_4$ (7.7 mg, 0.016 mmol) in water for 12 hours. As soon as stirring started, the yellow solution became clear and PAA changed to yellow by absorption of Cp*Ir complex. The yellow solid was filtered, carefully washed with deionized water and freeze-dried at -196°C. Finally, a pale-yellow solid was obtained as Cp*Ir-HMDAbpy@PAA (205 mg, 95 % yield).

Synthesis of pre-Cp*Ir-HMEDBP@PAA

PAA (900 mg) was stirred with [Cp*Ir-HMDAbpy]SO₄ (41.25 mg, 0.050 mol) in water for 12 hours. As soon as stirring started, the yellow solution became clear and PAA changed to yellow by absorption of Cp*Ir complex. The yellow solid was filtered, then carefully washed with deionized water and freeze-dried at -196°C. Finally, 938 mg (99% by weight yield) of a pale-yellow solid was obtained as pre-Cp*Ir-HMEDBP@PAA.

Synthesis of Cp*Ir complex 7, [Cp*Ir(4,4'-dichloro-2,2'-bpy)H₂O]SO₄

 $[Cp*Ir(H_2O)_3]SO_4$ (247 mg, 0.50 mmol) and 4,4'-dichloro-2,2'-bipyridyl (0.113 g, 0.50 mmol) were dispersed in deionized water (10 mL) and stirred at room temperature under atmospheric conditions for 1 day. The resulting yellow solution was filtered, and the filtrate was freeze-dried for 1 day. Yellow particles, identified as $[Cp*Ir(4,4'-dicloro-2,2'-bipyridine)H_2O]SO_4$ (0.324 g, 0.476 mmol), were obtained, corresponding to a yield of 95.1% based on the isolated product.

¹H NMR (600 MHz, MeOH-d₄) δ 9.07 (d, J = 6.12 Hz, 2H), 8.76 (d, J = 2.16 Hz, 2H), 7.90 (dd, J = 2.28, 2.22, 2H), 1.67 (s, 15H). ¹³C NMR (150 MHz, MeOH-d₄) δ 158.4, 154.1, 149.8, 130.2, 125.9, 90.0, 8.53. ESI-TOF-MS (m/z): [(Cp*Ir(4,4'-dichloro-2,2'bpy) (H₂O)]SO₄) – (H₂O+SO₄)]²⁺ calcd for C₂₀H₂₁Cl₂IrN₂, 276.0343; found, 276.0364.



Figure S2. ¹H NMR spectra of *N*,*N*'-([2,2'-bipyridine]-4,4'-diyl)bis(hexane-1,6-diamine) (4-hmdaAbpy)



Figure S3. ¹³C NMR spectra of *N*,*N*'-([2,2'-bipyridine]-4,4'-diyl)bis(hexane-1,6-diamine) (4-hmdabpy)



Figure S4. ESI-TOF-MS NMR spectra of HMDAbpy dissolved in methanol.



Figure S5. ¹H NMR spectra of Cp*Ir-HMDAbpy in D₂O with acetic acid.



Figure S6. ¹³C NMR spectra of Cp*Ir-HMDAbpy in D₂O with acetic acid.



Figure S7. ESI-TOF-MS spectra of Cp*Ir(N,N'-([2,2'-bipyridine]-4,4'-diyl)bis(hexane-1,6-diamine))SO₄ (Cp*Ir-HMDAbpy) in MeOH with FA.



Figure S8 ¹H NMR spectra of $[Cp*Ir(4,4)-dichloro-2,2)+Dy(H_2O]SO_4$ in D₂O.





Figure S10 ESI-TOF-MS spectra of [Cp*Ir(4,4'-dichloro-2,2'-bipyridine)H₂O]SO₄ in H₂O. The red spectrum is the observed spectrum, and the green spectrum is the calculated spectrum.

Formic acid dehydrogenation

1.1 General formic acid dehydrogenation



FA aqueous solution $(1 \sim 20 \text{ M}, 20 \text{ ml})$ was placed in a 50 mL round-bottom flask and preheated to 80.0 °C (±0.07°C) using water bath (EYELA, NTT-2000). Subsequently, Cp*Ir-HMDAbpy@PAA (containing 0.28 to 2 µmol of Ir) was added and stirred in the FA aqueous solution. The generated gas was monitored every 2 seconds using gas meter (Shinagawa Co. Ltd., W-NK-0.5A, Japan Flow controls Co. Ltd, MGC-1). The generated gas was collected using an aluminum bag connected directly to the gas meter. Gas composition analysis was performed using a gas chromatography. The analysis H₂ and CO₂ was conducted using a GC-TCD (Inficon, Micro GC fusion, Cp-COX column and MS-5A column). Gas volume were converted to standard temperature and pressure values using the ideal gas low.

The investigation of residual FA after the reaction were conducted by carefully filtering the reaction solution and measuring the formate anion content using ion chromatography (Metrohm, Eco IC).

1.2 Catalyst recycling test

The reaction was started by introducing Cp*Ir-HMDAbpy@PAA (containing 2 µmol Ir) into 20 mL of 1 mol/L FA solution preheated to 80°C. After the reaction, the reaction mixture was filtered, carefully washed with water, and dried under vacuum at 55 °C. The recovered catalyst was used for the next reaction under same conditions.

The reaction was repeated a total five times using the same procedure with the recovered catalyst, and the TOF value was calculated based on the amount of catalyst recovered each time.

1.3 Large scale FA dehydrogenation experiment.

The reaction was started by introducing Cp*Ir-HMDAbpy@PAA (containing 2 µmol of Ir) into 193 ml of 4.2 mol/L FA solution preheated to 80°C. After completing the 1st FA dehydrogenation, an additional 38 ml of FA was added to repeat the reaction. FA was added a total of 4 times with a total added amount of 150 ml.

1.4 Monitoring the amount of catalyst in solution during FA dehydrogenation.

Cp*Ir-HMDAbpy@PAA (1 μ mol Ir cont.) was placed in 1 mol/L of 10 mL FA aqueous solution. 8 samples were prepared and heated to 80 °C simultaneously to initiate the reaction. After 1 min to 1 h respectively, the samples were cooled to 0 °C by ice to quench the reaction. After cooling, the supernatant was quickly removed and measured by UV-Vis spectrometer.

1.5 FA dehydrogenation by flow operation.



A flow-type reaction was performed using the apparatus shown in Figure 11. A mixture of Cp*Ir-HMEDBP@PAA (8.8 µmol Ir content) and Celite (2 g) was introduced into a column reactor (a diameter: 10 cm, a length: 3 cm). Before the reaction the column reactor was flowed with 20 mL deionized water 8 times.

To initiate FA dehydrogenation, 10 ml of a 1.5 mol/L FA aqueous solution, preheated to 80°C, was carefully injected at 1 mL/min into the column reactor using a syringe pump (a yellow solution dissolved Cp*Ir-HMDAbpy was introduced into the 50 mL of grass

reactor). An additional 5 mL of deionized water was injected into the column reactor to transfer any residual FA to the glass reactor. The glass reactor was heated in a water bath at 80°C, and the amount of produced gases was monitored with a gas meter. After the completion of FA dehydrogenation, the reaction solution in the glass reactor was slowly drawn through the catalyst column using a diaphragm pump, and the solution was collected. The collected solution was analyzed by UV-VIS, ICP-AES, and ion chromatography.

1.6 Turnover frequency (TOF) and turnover number (TON)

TOF and TON values of FA dehydrogenation were calculated from gas flow rate (v) and the total gas volume (V), respectively, using the ideal gas low as follows:

$$TON = \frac{p \cdot V}{2 \cdot R \cdot T \cdot n \ cat}$$
$$TOF = \frac{p \cdot v}{2 \cdot R \cdot T \cdot n \ cat}$$

Where p, T and R represent the atmospheric pressure, room temperature and the gas content, respectively. n_{cat} is denotes the number of initial moles of Ir. The generated gas consisted of H₂ and CO₂ in 1 : 1 ratio.



Figure S11. SEM-EDX analysis of Cp*Ir-HMDAbpy@PAA as prepared.





Figure S12. SEM images of Cp*Ir-HMDAbpy@PAA as prepared.



Figure S13. SEM images of Cp*Ir-HMDAbpy@PAA after FA dehydrogenation.

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Figure S14. SEM-EDX analysis of Cp*Ir-HMDAbpy@PAA after FA dehydrogenation.

JED-2300 AnalysisStation



Figure S15. FT-IR spectrum of a) cross-linked PAA, b) HMDAbpy@PAA, c) Cp*Ir-HMDAbpy@PAA, d) HMDAbpy, and e) Cp*Ir-HMDAbpy.





Figure S17. ¹H solid state NMR spectrum of PAA (blue line), HMDAbpy@PAA (red line), and Cp*Ir-HMDAbpy@PAA (yellow line).



Figure S18. ESI-TOF-MS spectrum for the [Cp*Ir(HMDAbpy)(H₂O)]SO₄.



Figure S19. Gas composition analysis of generated gas from FA dehydrogenation (red line) and the reference gases (H_2 :CO₂ = 1:1) (black line).



Figure S20. Comparison of catalytic activities (TOFs) of Cp*Ir-HMDAbpy homogeneous catalyst, pre-Cp*Ir-HMDAbpy@PAA, and Cp*Ir-HMDAbpy@PA for release-and-catch catalytic system: Reaction conditions; Ir in catalysts = 2μ mol, 20ml, 1 mol/L FA, and 80 °C.



Figure S21. UV-Vis absorption spectrum of Cp*Ir-HMDAbpy in aqueous solution (20 mL, 0.1 mmol/L). Red line shows the Cp*Ir-HMDAbpy solution before addition of CR-20 (500 mg), and blue line shows the that after the addition of CR-20 after 3 hours.



Figure S22a. The dependence of FA concentration for TOF. Reaction condition: $Ir = 2 \mu mol$, 20ml of 1, 3, 5, 7, 10, 20 mol/L of FA aq., and 80 °C.



Figure S22b. Time course of TON values for FA dehydrogenation using Cp*Ir-HMDAbpy@PAA. Reaction condition; Ir content = 0.28 μ mol, 20 mL of 5mol/L FA aq., temp. = 80 °C. The maximum TOF value was TOF=110,500 h⁻¹.

Initial FA conc. / mol/L	Initial TOF / 10 min	Catalyst conc. / ppm
1	52000	N.D.
3	97000	N.D.
5	108000	N.D.
7	107000	N.D.
10	87000	0.015
20	58000	N/A

Table S1. ICP-AES analysis after FA dehydrogenation using aqueous FA solutions (1~10 mol/L).



Figure S23. Time course of FA dehydrogenation versus the concentration of FA. Reaction conditions: Ir = 2μ mol, 20ml of 1, 3, 5, 7, 10, 20 mol/L of FA aq., and 80 °C.



Figure S24. Temperature dependance on the FA dehydrogenation rate with 20 mL of FA (1 mol/L) using Cp*Ir-HMDAbpy@PAA as the "<u>release-and-catch</u>" catalyst.



Figure S25. Arrhenius plot on the FA dehydrogenation catalyzed by Cp*Ir-HMDAbpy@PAA ("<u>release-and-catch</u>" catalyst).



Figure S26. Temperature dependance on the FA dehydrogenation rate with 20 mL of FA (1 mol/L) using [Cp*Ir(HMDAbpy)(H₂O)]SO₄ as a homogeneous catalyst.



Figure S27. Arrhenius plot on the FA dehydrogenation catalyzed by [Cp*Ir(HMDAbpy)(H₂O)]SO₄ as a homogeneous catalyst.



Figure S28. Kinetic Isotope Effects for FA dehydrogenation using <u>Cp*Ir-HMDAbpy@PAA (catch-and-release immobilized catalyst)</u>.

Table S2.	Kinetic Isotope	Effects	for FA	dehydroge	enation. ^{[a],[b]}
				J ()	

Run	Solvent	FA	TOF ^[b] / h ⁻¹	KIE ^[b]
1	H ₂ O	НСООН	$49,500 \pm 1,500$	-
2	H_2O	DCOOD	$23,000 \pm 1,000$	2.15 ± 0.01
3	D_2O	НСООН	$35,500 \pm 1,500$	1.40 ± 0.05
4	D_2O	DCOOD	$18,000 \pm 1,000$	2.77 ± 0.12

[a] Reaction conditions: reaction temp.: 80 °C, FA: 1 mol/L, 20 mL, Cp*Ir-

<u>HMDAbpy@PAA</u>: 35 mg (including 2 µmol Ir). The KIE value was calculated from the gas volume after 10 minutes. [b] The experiments were conducted twice, and the TOF and KIE values represent the averages of these data.



Figure S29 Kinetic Isotope Effects for FA dehydrogenation using <u>Cp*Ir-HMDAbpy</u> (homogeneous catalyst).

Run	Solvent	FA	TOF ^[b] / h ⁻¹	KIE ^[b]
1	H ₂ O	НСООН	$51,000 \pm 1,500$	-
2	H_2O	DCOOD	$24,000 \pm 1,000$	2.15 ± 0.04
3	D_2O	НСООН	$34,000 \pm 1,500$	1.40 ± 0.04
4	D_2O	DCOOD	$17,000 \pm 1,000$	3.00 ± 0.04

 Table S3.
 Kinetic Isotope Effects for FA dehydrogenation.^{[a],[b]}

[a] Reaction conditions: reaction temp.: 80 °C, FA: 1 mol/L, 20 mL, <u>Cp*Ir-HMDAbpy</u>: 2 μ mol. The KIE value was calculated from the gas volume after 10 minutes. [b] The experiments were conducted twice, and the TOF and KIE values represent the averages of these data.



Figure S30. ESI-TOF-MS spectrum of $[Cp*Ir-HMDAbpy-OCOH]^+$, found (calcd) for $[C_{33}H_{52}IrN_6O_2]^+$ m/z 757.3807 (757.37809) in the FA dehydrogenation solution by released-and-catch catalytic system. The spectrum was recorded using an electrospray ionization mass spectrometer (Agilent Technologies, 6224 TOF MS system) in a positive ion mode.



Figure S31. UV-Vis spectra of solutions during FA dehydrogenation using Cp*Ir-HMDAbpy@polystylene sulfonic acid as catalyst supports. No catalyst release has been observed at all.



Figure S32. Recovery rate of Cp*Ir-HMDAbpy with UV-Vis absorption spectrum. 100 mg of each solid (activated carbon, PAA, α -Al₂O₃, and CR-20) was immersed in 20ml of 0.1 mmol/L Cp*Ir-HMDAbpy aquesou solution and stirred for 1 h at 80 °C. Then, UV-Vis was measured, and recovery rate was calculated from UV-Vis absorption at 350 nm; Active carbon = 98.2 %, PAA = 98.3%, CR-20 = 1.7%, α -Al₂O₃ = 0%)



Figure S33. Calibration curve of UV-Vis spectra for Cp*Ir-HMDAbpy in deionized water (0.05, 0.025, 0.0125, 0.0075 mol/L).



Figure S34. UV-Vis absorption spectra of Cp*Ir complex 1 (0.1 mmol/L, 20mL) before immersion of 100 mg of PAA and after the immersion of PAA for 1 hour.



Figure S35. UV-Vis absorption spectra of Cp*Ir complex **2** (0.1 mmol/L, 20mL) before immersion of 100 mg of PAA and after the immersion of PAA for 1 hour.



Figure S36. UV-Vis absorption spectra of Cp*Ir complex **3** (0.1 mmol/L, 20mL) before immersion of 100 mg of PAA and after the immersion of PAA for 1 hour.



Figure S37. UV-Vis absorption spectra of Cp*Ir complex **4** (0.1 mmol/L, 20mL) before immersion of 100 mg of PAA and after the immersion of PAA for 1 hour.



Figure S38. UV-Vis absorption spectra of Cp*Ir complex **5** (0.1 mmol/L, 20mL) before immersion of 100 mg of PAA and after the immersion of PAA for 1 hour.



Figure S39. UV-Vis absorption spectra of Cp*Ir complex **6** (0.1 mmol/L, 20mL) before immersion of 100 mg of PAA and after the immersion of PAA for 1 hour.



Figure S40. UV-Vis absorption spectra of Cp*Ir complex 7 (0.1 mmol/L, 20mL) before immersion of 100 mg of PAA and after the immersion of PAA for 1 hour.



Figure S41. Time course of TON values of FA dehydrogenation by batchwise operation catalyzed by various <u>"release-and-catch"</u> catalysts with various Cp*Ir catalysts (1 - 7) immobilized on PAA support.



Figure S42. TOF values of FA dehydrogenation by various <u>"release-and-catch catalysts"</u> with Cp*Ir catalysts (1 - 7) immobilized on PAA. Reaction conditions: Ir = 2µmol, FA: 20ml, 1 mol/L, reaction temp. 80 °C.



Figure S43 Time course of TON values of FA dehydrogenation by batchwise operation catalyzed by Cp*Ir catalysts (1 - 7) of <u>homogeneous catalysts</u>. Reaction conditions: Ir = 2µmol, FA: 20ml, 1 mol/L, reaction temp. 80 °C.



Figure S44 TOF values of FA dehydrogenation by using Cp*Ir catalysts (1 - 7) of <u>homogeneous catalysts</u>. Reaction conditions: Ir = 2µmol, FA: 20ml, 1 mol/L, reaction temp. 80 °C.



Figure S45 Hammett plot for the rate of FA dehydrogenation catalyzed by a) release-andcatch catalysts with Cp*Ir complexes (slope is -1.3) and b) homogeneous Cp*Ir complexes (slope is -1.5) with para-substituted bipyridine ligands such as hexamethylene diamine (-HMDA), dimethyl amine (-NMe₂), amine (-NH₂), hydroxy (-OH), methoxy (-OMe), methyl (-Me), hydrogen (-H), and chloride (-Cl).

Table S4.Leaching amount of Ir (ppm) from each Cp*Ir complex after FAdehydrogenation by release-and-catch catalytic system. Each Ir leaching amount wasmeasured by ICP-AES.

Cp*Ir complex	TOF / h ⁻¹	Conversion / %	Ir leaching / ppm
1. $R = -NH(CH_2)_6NH_2$	62,000	99.9	N.D.
2. $R = -NMe_2$	53,000	99.9	N.D.
3. $R = -NH_2$	41,000	99.9	N.D.
4. $R = -OH$	10,200	99.8	N.D.
5. $R = -OMe$	4800	99.5	0.017 ± 0.001
$6. \mathbf{R} = -\mathbf{M}\mathbf{e}$	2600	94.5	1.79 ± 0.003
7. $R = C1$	130	<1	8.8 ± 0.12



Figure S46. ¹³C CP/MAS NMR spectrum of Cp*Ir-HMDAbpy@PAA after FA dehydrogenation.



Figure S47. ¹³C CP/MAS NMR spectrum of Cp*Ir-HMDAbpy@PAA after leaching Cp*Ir-HMDAbpy by FA solution.



Figure S48. ¹³C CP/MAS NMR spectrum of pre-Cp*Ir-HMDAbpy@PAA.

Table S5. Results of ICP-AES analysis of the solution after FA dehydrogenation using the release-and-catch catalytic system with flow-type operation. Each sample was analyzed three times to confirm the data.

runs	Ir conc. / ppm ^[a]	runs	Ir conc. / ppm ^[a]
1 st	N.D.	7 th	N.D.
	N.D.		N.D.
	N.D.	_	N.D.
3 rd	N.D.	10 th	N.D.
	N.D.		N.D.
	N.D.		N.D.

[a] N.D. = no detection (<0.001 ppm)



Figure S49 Full-width XPS spectra (0 to 1200 eV) of 1) Cp*Ir complex ([Cp*Ir(HMDAbpy)H₂O]SO₄, black line), 2) Cp*Ir(HMDAbpy) complex immobilized PAA after the 1 cycle reaction, blue line, and 3) Cp*Ir(HMDAbpy) complex immobilized PAA after the 5 cycle reaction, red line.



Figure S50 Narrow-width XPS spectra (50 to 70 eV) of 1) Cp*Ir complex ([Cp*Ir(HMDAbpy)H₂O]SO₄, black line), 2) Cp*Ir(HMDAbpy) complex immobilized PAA after the 1 cycle reaction, blue line, and 3) Cp*Ir(HMDAbpy) complex immobilized PAA after the 5 cycle reaction, red line.



Figure S51. FA dehydrogenation Flow reaction at the initial stage with Cp*Ir complex releasing.



Figure S52. FA dehydrogenation flow reaction after FA dehydrogenation with Cp*Ir complex catching.