Supporting Information Enabling the Terpyridine Ligand Motif for Ir-based Solid Molecular Catalysts

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Table of Contents

1	Expe	rimental Methods	.3
	1.1	Batch Experiments	.3
	1.2	Continuous stirred tank reactor experiments	.3
	1.3	Characterization	.4
	1.3.1	Solid State NMR	.4
	1.3.2	N2 physisorption	.5
	1.3.3	HAADF-STEM and HAADF-STEM-EDX	.5
	1.3.4	XRD	.5
	1.3.5	Batch catalytic experiments	.5
	1.3.6	Thermogravimetric Analysis	.5
	1.3.7	DRIFTS-IR	.5
2	Synth	nesis and characterization of Monomers	.5
	2.1	Synthesis of tetravalent linker	.5
	2.2	General Terpyridine Monomer Synthesis	.6
	Synth	nesis and Characterisation of M1	.6
	Syntl	nesis and Characterisation of M2	.6
	Syntl	nesis and Characterisation of M3	.7
	Synth	nesis and Characterisation of M4	.7
3	Synth	nesis and characterization of Polymers	.7
	3.1	General Polymer Synthesis	.7
	Synth	nesis and Characterisation of P1	.8
	Synth	nesis and Characterisation of P2	.9
	Synth	nesis and Characterisation of P3	10
	Synth	nesis and Characterisation of P4	12

4	Addit	ional Characterization14	4
	4.1	Metal uptake determined by ICP-MS14	4
	4.2	XPS Analysis14	4
	4.3	HAADF-STEM	6
	4.4	DRIFTS-IR	7
	4.5	EXAFS/XANES and plot parameters	3
	4.6	Precursor / Nanoparticle Catalytic Results	9
	4.7	Variation of macroligand amount19	9
	4.8	Solvent exchange recycling)
5	Value	es for Reproduction of bar graphs22	1
	5.1	Figure 322	1
	5.2	Figure 4	2
6	Refe	ences22	2

1 Experimental Methods

All terpyridine monomers and the C4-linker were synthesized according to the methods described herein from commercially purchased chemicals. All purchased chemicals were stored correctly and used as received.

1.1 Batch Experiments

In a typical experiment, a 15 mL finger autoclave with digital pressure recorder was charged with a magnetic stirrer and 6 mL of 10 wt% aqueous FA solution and 20 mg of catalyst. The atmosphere in the autoclave was replaced three times with 40 bars of hydrogen and afterwards depressurized. Next, the autoclave was placed in a preheated metal block and the FADH commenced at the appropriate temperature while stirred at 750 rpm. The pressure and temperature were recorded digitally, while the gas phase was captured and analyzed after the reaction using gas sampling bags. The remaining reaction solution was filtered and collected for HPLC analysis.

1.2 Continuous stirred tank reactor experiments

Continuous formic acid decomposition reactions were carried out in a modified Hastelloy 120 mL Parr 4590 CSTR. To measure the fill level of the reactor and to automate its refilling, the CSTR entails a rising pipe equipped with ultrasonic level meters at 66% and 100% fill volume. In a typical reaction, 100 mg of catalyst (0.1 wt% Ir@P2, 0.0005 mmol Ir) was placed into the reactor and aq. formic acid solution (10 wt. %, 90.97 g) was added from a reservoir via a HPLC pump. To start the reaction, a hydrogen flow of 30 mL/min was set using a mass flow controller (MFC) to regulate the pressure of the system to 10 bar using a back pressure regulator (BPR) and the reactor heated to 160°C while stirring at 750 rpm. The reactor pressure, temperature, HPLC pump pressure and flow as well as the reactor fill level were continuously monitored using a connected LabVIEW program during the reaction. As soon as the fill level decreased below the maximum fill level as determined by the ultrasonic level meters, conc. formic acid was added automatically until the maximum fill level was reached again. TONs were calculated by gravimetric determination of the decomposed formic acid.



Figure S1. Schematic drawing of the CSTR.

Calculation of Catalyst Selectivity

Selectivity was calculated using GC analysis. The volume V_{co} , in the GC injection is calculated from the CO peak area A_{co} obtained during the measurement in accordance to equation 1. According to equation 2, the share of V_{co} of the total injection volume $V_{injection}$ is used to calculate the CO impurity in ppm.

$$V_{CO} = \frac{A_{CO}}{252.7}$$
(Eq. 1)

$$CO_{PPM} = \frac{V_{CO}}{V_{injection}} \cdot 1\ 000\ 000 \tag{Eq. 2}$$

The TOFs of catalysts were calculated assuming very high selectivity, near full conversion and ideal gases. According to equation 3, the TOF is the ratio of the amount of formic acid decomposed, $n(FA)_{decomposed}$, over a period of time Δt per molar amount of iridium n(Ir). The result is multiplied by 3 600 to receive the TOF as an hourly rate.

$$TOF = \frac{n(FA)_{decomposed}}{\Delta t \cdot n(Ir)} \cdot 3600$$
(Eq. 3)

In turn, $n(FA)_{decomposed}$ is calculated using the pressure-time profile of the reaction. As shown in equation 4, the calculation is based on the ideal gas law. The pressure difference Δp is between the pressures recorded in the dehydrogenation reaction and a parallel blind reaction under identical conditions. This is intended to remove pressure increases from heating from the equation. The factor two accounts for the fact that one molecule of formic acid decomposes to two molecules of gas.

$$n(FA)_{decomposed} = \frac{\Delta p \cdot V}{2 \cdot R \cdot T}$$
(Eq. 4)

Calculation of TON

The TON for batch experiments was calculated based on the amount of formic acid decomposed $n(FA)_{decomposed}$ per molar amount of iridium n(lr).

$$TON = \frac{n(FA)_{decomposed}}{n(Ir)}$$
(Eq. 5)

For continuous experiments, the amount of decomposed FA was measures gravimetrically by comparing the weight of the FA container before and after the CSTR experiment concluded.

Calculation of Conversion

Conversion was calculated using HPLC analysis of the reaction solution after the FADH, based on the remaining concentration $c(FA)_{post-reaction}$ of FA.

$$Conversion = 1 - \frac{c(FA)_{post-reaction}}{c_0(FA)}$$
(Eq. 6)

Calculation of Leaching

Leaching was calculated using ICP analysis of the reaction solution after the FADH, based on the mass concentration of iridium c(Ir) in the reaction mixture and the total amount of iridium added *via* SMC.

$$Leaching = 1 - \frac{c(lr) \cdot V_{reaction}}{n(lr) \cdot M(lr)}$$
(Eq. 7)

1.3 Characterization

1.3.1 Solid State NMR

¹³C-SS-MAS-NMR (cross polarization with spinal ¹H decoupling) spectra were obtained on a Bruker Avance III 500 instrument (4 mm zirconia MAS rotor, 7-11 kHz spinning frequencies, 125 MHz).

1.3.2 N2 physisorption

Nitrogen physisorption measurements were conducted using a Quadrasorb SI (3P Instruments). Before the measurement, all samples were degassed in a FloVac degasser at 120 °C under vacuum for 12 h. The measurements were conducted at -196 °C and the obtained data was evaluated using the software QuadraWin provided by 3P Instruments. For the determination of the specific surface area S_{BET} , the BET model was used in the range $0.05 \le p/p_0 \le 0.2$. The total pore volume V_{total} was analyzed from the highest relative pressure point, $p/p_0 = 0.95-0.98$.

1.3.3 HAADF-STEM and HAADF-STEM-EDX

Characterisation of the samples by high angle annular darkfield (HAADF) scanning transmission electron microscopy (STEM) were conducted with а FEI Titan G2 80-200 CREWLEY7, а FEI Tecnai F20 and а JEOL JEM-F200 transmission electron microscope. All investigations were performed at an accelerating voltage of 200 kV.

The High Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM) and STEM Energy Dispersice X-Ray spectroscopy (STEM-EDX) was carried out on an FEI Titan 80–200 probe Cs-corrected electron microscopes operated at 200kV and equipped with SuperX EDX detector.

1.3.4 XRD

Powder X-ray diffraction (XRD) pattern were recorded on a Siemens D5000 instrument with a Cu K α radiation (λ = 0.154 nm). The scanning range was set from 10° to 90° 2 Θ with 0.02° intervals and a collection time of 1 s per step.

1.3.5 Batch catalytic experiments

All batch catalytic experiments were carried out under hydrogen atmosphere with exclusion of air. Autoclave reactions were run until no change in internal pressure was observed or until time constraints occurred. Gas samples were taken directly from the autoclaves using gas sampling bags and analyzed by GC. Liquid samples were taken from the autoclaves and filtered to remove catalyst. Conversion was analyzed using HPLC, while catalyst loading and metal leaching was determined using ICP. If spent catalyst was needed for analysis, the used reaction mixture was instead filtered and dried under argon.

1.3.6 Thermogravimetric Analysis

Analysis of thermal stability was performed by thermogravimetric measurements. These were conducted on a Netzsch Simultaneous Thermal Analyzer (Type STA449G) in nitrogen gas and at a heating rate of 10 °C min⁻¹.

1.3.7 DRIFTS-IR

IR spectra of SMCs were collected using a *Bruker VERTEX 70* spectrometer with a *Harrick* praying mantis DRIFTS cell at atmospheric pressure and ambient temperature.

2 Synthesis and characterization of Monomers 2.1 Synthesis of tetravalent linker



Tetrakis(4-Bromophenyl) methane (5g, 7.86 mmol, 1 eq, 95%, TCI), Bis(pinacolato) diboron (8.78 g, 34.59 mmol, 4.4 eq, 98%, CARL ROTH), and KOAc (9.26 g, 99%, CARL ROTH) were dissolved in 150 ml DMSO under inert atmosphere. To this solution, 575 mg of Pd(dppf)Cl₂ (0.1 eq, 99%, J&K) was added. The mixture was stirred at 100 °C for 16 h. After cooling, the reaction mixture was quickly poured into 500 ml of acetone and filtered. The acetone was removed and the resulting solid suspended in DCM. After vigorous stirring, the mixture was again filtered to remove the remaining solid and excess solvent removed. The resulting light gray powder was then purified by column chromatography using silica gel and 5% MeOH in DCM as eluent to yield a white solid (3.95 g, 61 % yield).

¹H-NMR: (300 MHz, Chloroform-d) δ 7.65 (d, 8H), 7.27 (d, 8H), 1.30 (s, 48H).

2.2 General Terpyridine Monomer Synthesis



The M1-4 modified procedure.^[1] synthesis of monomers was based literature on а 2-Acetyl-6-bromopyridine (1 eq), an aromatic aldehyde (0.5 eq., 99%) and KOH (1.18 eq) were dissolved in EtOH and 25% ammonia solution (HONEYWELL) and stirred at room temperature for 72 h. The reaction solution guickly turned to bright red. After 24 h, a precipitation was observed. After conclusion of the reaction, the precipitate was filtered and washed with cold water and EtOH and dried in vacuo.

Synthesis and Characterisation of M1

2-Acetyl-6-bromopyridine (1.00g, 4.99 mmol, 1 eq., 98%, TCl), benzaldehyde (255 μ l, 2.5 mmol, 0.5 eq., 99%, SIGMA ALDRICH) and KOH (331 mg, 5.9 mmol, 1.18 eq, 85%, CHEMSOLUTE) were dissolved in 20 ml of EtOH and 13 ml of 25% ammonia solution (HONEYWELL) and stirred at room temperature for 72 h. The reaction solution quickly turned to bright red. After 24 h, a precipitation was observed. After conclusion of the reaction, the precipitate was filtered and washed with cold water and EtOH and dried *in vacuo*. **M1** was received as a mint-colored powder (0.951 g, 81%).

¹**H-NMR**: (300 MHz, Chloroform-d) δ 8.70 (s, 2H), 8.60 (d, J = 7.7 Hz, 2H), 7.88 (d, 2H), 7.73 (t, J = 7.8 Hz, 2H), 7.58 – 7.47 (m, 5H).

 13 C-NMR: (400 MHz, Chloroform-d) δ 157.5,154.7, 142.2, 139.7, 129.8, 129.5, 128.8, 128.0, 120.6, 120.5.

Synthesis and Characterisation of M2

2-Acetyl-6-bromopyridine (1.00g, 4.99 mmol, 1 eq., 98%, TCI), pyrrole-2-carboxaldehyde (238 mg, 2.5 mmol, 0.5 eq., 98%, SIGMA ALDRICH) and KOH (331 mg, 5.9 mmol, 1.18 eq, 85%, CHEMSOLUTE) were dissolved in 20 ml of EtOH and 13 ml of 25% ammonia solution (HONEYWELL) and stirred at room temperature for 72 h. The reaction solution quickly turned to bright red. After 24 h, a precipitation was observed. After conclusion of the reaction, the precipitate was filtered and washed with cold water and EtOH and dried *in vacuo*. **M2** was received as a pale yellow powder (0.425 g, 37%).

¹**H-NMR**: (300 MHz, Chloroform-d) δ 9.13 (s, 1H), 8.54 (s, 2H), 8.47 (s, 2H), 7.71 (s, 2H), 7.54 (s, 2H), 7.01 (s, 2H), 6.43 – 6.32 (m, 1H).

¹³C-NMR: (400 MHz, Chloroform-d) δ 131.38, 131.35, 131.2, 130.9, 129.21, 129.18, 129.0, 128.6, 127.7, 126.6.

Synthesis and Characterisation of M3

2-Acetyl-6-bromopyridine (2.68 g, 13.4 mmol, 1 eq., 98%, TCI), 4-Dimethylamino benzaldehyde (1 g, 6.7 mmol, 0.5 eq., 99%, SIGMA ALDRICH) and KOH (888 mg, 15.8 mmol, 1.18 eq, 85%, CHEMSOLUTE) were dissolved in 60 ml of EtOH and 40 ml of 25% ammonia solution (HONEYWELL) and stirred at room temperature for 72 h. The reaction solution quickly turned to bright red. After 24 h, a precipitation was observed. After conclusion of the reaction, the precipitate was filtered and washed with cold water and EtOH and dried *in vacuo*. The resulting orange solid was then purified by column chromatography using silica gel and 5% MeOH in DCM as eluent to yield a yellow powder (2.12 g, 62 % yield).

¹H-NMR: (300 MHz, Chloroform-d) δ 8.65 (s, 2H), 8.57 (d, 2H), 7.86 (d, 2H), 7.71 (m, 3H), 7.52 (m, 3H), 3.09 (s, 6H).

Solubility was too low to obtain a ¹³C-NMR spectrum.

Synthesis and Characterisation of M4

2-Acetyl-6-bromopyridine (1.53 g, 7.7 mmol, 1 eq., 98%, TCI), 4-[N,N-Bis(2-hydroxyethyl)amino] benzaldehyde (0.8 g, 3.8 mmol, 0.5 eq., 95%, SIGMA ALDRICH) and KOH (506 mg, 9.02 mmol, 1.18 eq, 85%, CHEMSOLUTE) were dissolved in 30 ml of EtOH and 20 ml of 25% ammonia solution (HONEYWELL) and stirred at room temperature for 72 h. The reaction solution quickly turned to bright red. After 24 h, a precipitation was observed. After conclusion of the reaction, the precipitate was filtered and washed with cold water and EtOH and dried *in vacuo* to yield a yellow powder (860 mg, 40 % yield).

¹H-NMR: (400 MHz, DMSO-d6) δ 8.63 (d, 2H), 8.48 (s, 2H), 7.97 (t, 2H), 7.76 (m, 4H), 3.60 (m, 4H), 3.52 (m, 4H).

¹³**C-NMR**: (400 MHz, DMSO-d6) δ 156.8, 154.2, 150.1, 149.7, 141.4, 141.0, 128.9, 128.1, 123.0, 120.6, 117.1, 112.2, 58.5, 56.5.

3 Synthesis and characterization of Polymers 3.1 General Polymer Synthesis



А nitrogen atmosphere was maintained at all times during polymerization until filtration.[2] А 100 ml round bottom flask was charged with M1-4 (1 eq.), Tetrakis(4-phenylboronic acid pinacol ester)methane (0.5 eq) and dry toluene. To this 2M K₂CO₃ solution (99%, SIGMA ALDRICH), two spatula tips of Aliquat 336 (SIGMA ALDRICH) and Pd(PPh₃)₄ (0.05 eq, 98%, FLUOROCHEM) were added and the solution refluxed at 100 °C under constant stirring. A precipitate was observed. After 24 h, the reaction mixture was allowed to cool down and bromobenzene (0.68 eq, 99%, SIGMA ALDRICH) was added in dry toluene with a syringe. The mixture was refluxed at 100 °C again for 24 h. The solution was allowed to cool down and benzyl boronic acid pinacol ester (0.84 eq., 96%, ABCR) was added in 2 ml of dry toluene with a syringe. After 24 h of reflux at 100 °C, the mixture was allowed to cool down. The precipitate was filtered off and washed with 3x30 ml of water, MeOH, and Et₂O in that order. The precipitate was stirred in an aqueous solution of 5 vol% H₂O₂ and 7 vol% HCl for 45 min to remove excess palladium. It was washed with 3x30 ml of water, MeOH, and Et₂O in that order and then collected and dried in vacuo.

Synthesis and Characterisation of **P1** Synthesis of **P1** was realised using the general procedure and monomer **M1**. **P1** was received in quantitative yield as a

pale powder.



Figure S2. Solid state MAS 13C NMR spectrum of polymer P1.



Figure S3. Thermogravimetric analysis of polymer P1.



Figure S4. XRD spectrum of P1

Synthesis and Characterisation of P2 Synthesis of P2 was realised using the general procedure and monomer M2. P2 was received in quantitative yield as a

yellow powder.



Figure S5. Solid state MAS 13C NMR spectrum of polymer P2.



Figure S6. Thermogravimetric analysis of polymer P2.



Figure S7. XRD spectrum of P2.

Synthesis and Characterisation of P3 Synthesis of P3 was realised using the general procedure and monomer M3. P3 was received in quantitative yield as an

orange powder.



Figure S8. Solid state MAS 13C NMR spectrum of polymer P3.



Figure S9. Thermogravimetric analysis of polymer P3.



Figure S10. XRD spectrum of P3.

Synthesis and Characterisation of P4 Synthesis of P4 was realised using the general procedure and monomer M4. P4 was received in quantitative yield as a

yellow powder.







Figure S12. Thermogravimetric analysis of polymer P4.



Figure S13. XRD spectrum of P4.

4 Additional Characterization

4.1 Metal uptake determined by ICP-MS

Table S1.: Measured Ir uptake by ICP-MS after immobilization of IrCl₃ on polymers P1-P4.

Polymer	Ir uptake
lr@P1	79,0 %
lr@ P2	88,0 %
0.1 wt% Ir@ P2	96,8 %
lr@ P3	97,4 %
lr@ P4	99,7 %

4.2 XPS Analysis

XPS analysis was performed on a Phi5000 VersaProbell by ULVAC-Phi Inc., USA. A monochromatic Al K-alpha source was used (1.486 keV). X-Ray settings were 50 W, 15 kV and 200 µm spot. Survey spectra were recorded at 187.5 eV pass energy, 0.8 eV steps and 100 ms/step. Fine spectra were recorded at 23.5 eV pass energy, 0.1 eV steps and 100 ms/step. Charge correction was done by setting the main component of the C1s spectrum to 285 eV.



Figure S14. XPS survey spectrum of polymer P1.



Figure S15. XPS survey spectrum of SMC Ir@P2.



Figure S16. XPS Ir high resolution spectrum of SMC Ir@P2.

4.3 HAADF-STEM



Figure S17. HAADF-STEM images of polymer P2.



Figure S18. HAADF-STEM images of catalyst Ir@P2.

4.4 DRIFTS-IR



Figure S19. DRIFTS-IR of catalyst Ir@P2 and spent catalyst Ir@P2, normalized to highest peak.

DRIFTS-IR shows the following changes from the fresh to the spent SMC: A broad signal around 3300 cm⁻¹ corresponding to adsorbed water. A sharp signal at 2900 cm⁻¹ corresponding to a partial hydrogenation of the aromatic macroligand. Two signals at 2800 and 2650 as well as at 1100 and 1300 cm⁻¹ corresponding to adsorbed formic acid.

4.5 **EXAFS/XANES** and plot parameters

L-edge extended X-ray absorption fine structure spectra (EXAFS) of IR were obtained at the B18 beamline of Diamond Light Source (DLS), Oxford, Great Britain) using a Si(311) crystal monochromator. The storage ring was operated at 3.0 GeV with injection currents of 300 mA. The EXAFS data was analyzed using the Demeter software package. All spectra except IrCl₃ were referenced using the reference Pt foil at E_0 =11560.25 eV. IrCl₃ was referenced using literature values at E_0 =11211.8 eV.

Sample ID	Rbkg	k-weight	Lower k	Upper k	E ₀ /eV	Pre-edge lower	Pre-edge upper	Norm. range lower	Norm. range upper
lr@ P2	1	3	3.126	12.144	11212.7	-160.2	-67.3	150	773.8
Ir@ P2 15 min	1	3	3.153	11.533	11213.9	-150	-58.2	150	776.0
Ir@ P2 spent	1	3	3.188	11.597	11213.7	-201.9	-67.4	150	831.7
lr(tpy)Cl₃	1	3	3.181	13.475	11214.1	-160.2	-47.1	150	773.8
IrCl ₃	1	3	3.209	13.475	11211.8	-197.56	-168.9	150	789.0

Table S2. EXAFS/XANES plot parameters.



Figure S20. k³-weighted Iridium L_{III}-edge FT-EXAFS of reference samples IrCl₃ and Ir(tpy)Cl₃.

4.6 **Precursor / Nanoparticle Catalytic Results** Ir nanoparticles were synthesized according to a literature procedure.^[3] The received nanoparticle solution was washed

and centrifuged with MeOH three times before impregnation of P2.

Table S3. Activity in the base-free FADH employing Ir precursor and nanoparticular catalyst IrNP@P2.

Catalyst	TOF / h ⁻¹	Time (h)	Conv. (%)	CO (ppm)
IrCl ₃ ª	-	4	6.7	n.d.
IrNP@ P2 ⁵	12 500	1	n.d.	n.d.

Conditions: 6 ml of 10 wt% FA solution, 160 °C. [a] Equivalent amounts of molecular Ir precursor to 20 mg of SMC. [b] 20 mg of 1 wt% IrNPloaded polymer (SMC).

4.7 Variation of macroligand amount

Table S4. Variation of macroligand amount and resulting TOF.

Amount Ir@ P2 / mg	TOF / h ⁻¹	Standard Deviation / h ⁻¹
7	175 000	7070
15	70 000	2830
20	65 500	6800
25	78 250	3182

4.8 Solvent exchange recycling

To verify that no leached species was responsible for the observed catalytic activities, a solvent exchange recycling was carried out. To this end, batch autoclave experiments were performed and the reaction solution filtrated after their conclusion while still warm. The catalyst was dried and then transferred back to the autoclave with fresh 10 wt% formic acid solution.



Figure S21. Solvent exchange recycling experiments of Ir@**P2** in the FADH at 160 °C. Conditions: 6 ml of 10 wt% FA solution. 20 mg of 1 wt% Ir@**P2**.. SMC was filtered off and dried between runs. Fresh FA solution and dried SMC were added to the autoclave after the completion of each reaction cycle. FA conversion was above 95% in each run.

5 Values for Reproduction of bar graphs 5.1 Figure 3

Table S5. Data for reproduction of first bar graph.

ID	TOF / h/1	CO / ppm	Conversion / %	Ir leach / %
lr@ P1	10000	778	99.3	0.42
	13000	596	95.4	0.03
Ir@ ₽ 2	61000	144	97.9	0.03
n⊚r2	70000	239	99.9	0.15
Ir@ ₽3	12000	578	99.9	0.02
n⊚rJ	11800	712	99.9	0.04
Ir@ ₽ 4	50000	194	99.3	0.79
II ≝ F4	49000	313	99.9	0.72

5.2 Figure 4

 Table S6. Data for reproduction of second bar graph.

Run	TOF / h/1	CO / ppm	Conversion / %	Ir leach / %
1	2100	277	-	
ľ	2200	259		
2	2600	210	-	
L	2750	202	-	
3	2300	310	-	
Ŭ	2600	Not detected	-	
4	2200	428	-	
	2500	434		-
5	1800	471	99.9	1.4
č	2000	634	n.d.	1.9

6 References

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