Supporting Information for

4-Pyridyl-substituted azacycloalkanes with multiple donor sites prepared via a solvent-free, one-pot method for use in electrocatalysts

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Experimental

Reagents: All reagents were purchased from TCI (Tokyo, Japan) and used without further purification. Solvents were purchased from Wako and used without further purification. Triruthenium clusters used in this study were prepared as previously reported.

Analytical Methods: ^{1}H NMR spectra were recorded on a Bruker AV500 and referenced to internal tetramethylsilane. Mass spectra were acquired on a Waters Xevo G2 Q-TOF spectrometer equipped with an electrospray ionization (ESI) probe. Cyclic voltammetry was performed using an ALS/HCH Model 620D Electrochemical Analyzer with a glassy carbon working electrode, Ag/Ag^+ reference electrode, and a Pt-wire auxiliary electrode. The supporting electrolyte was 0.1 M ^{n}Bu$_4$N(PF$_6$) in CH_3CN, and scan rate was 100 mV/s. Concentrations of samples were 1 mM for [{Ru$_3$}$_2$**L1**](PF$_6$)$_2$ and 0.05 mM for [{Ru$_3$}$_4$**L2**](PF$_6$)$_4$, which was due to its lower solubility. For the CO_2 experiment, dry CO_2 was slowly bubbled into the solution for 10 min, which should be enough to saturate the solution.

For X-ray single crystal structure analysis, single crystals of the compounds were mounted on a glass loop rod with Paratone-N (Hampton Research). Data collection was performed on a Rigaku Varimax diffractometer equipped with a Saturn724 CCD detector using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) in a N_2 stream. An empirical absorption correction based on azimuthal scans of several reflections was applied. The data were corrected for Lorentz and polarization effects. All non-hydrogen atoms were refined anisotropically using a least-squares method, and hydrogen atoms were fixed at calculated positions and refined using a riding model. SHELXTL was used for structure refinement. Full-matrix least-square refinement of F^2 using unique reflections with unweighted and weighted agreement factors of $R = ||F_o|- |F_c||/|F_o|$ ($I > 2.00\sigma(I)$) and wR = $[w(F_o^2 - F_c^2)^2/w(F_o^2)^2]^{1/2}$.

In the checkcif file for **L1**, the Level A and B errors are due to disorder in the solvent molecules as well as the disordered unsubstituted aza N atoms. Since we make no quantitative arguments using the atoms involved, we believe that these errors can be ignored, and the structure is useable in qualitative arguments and discussion.

Synthesis of 1,7-tetra(4-pyridyl)-1,4,7,10-tetraazacyclododecane (L1): To a Schlenk tube were added 1,4,7,10-tetraazacyclododecane tetrahydrochloride (1.0 g, 3.1 mmol) and 1-(4-pyridyl)pyridinium chloride hydrochloride hydrate (>3 equiv.) and the two solids were mixed with a spatula. The tube was degassed by repeated cycles of evacuation and refilling with N_2. The Schlenk tube was then placed into an oil bath at 170 °C for 3 h, during which time the pyridinium salt melted. The tube was allowed to cool, and the pH was adjusted to >11 by adding 6 M aqueous NaOH. A reflux condenser was attached to the Schlenk tube, and the solution was refluxed for 2 h. The solution was extracted four times with $CHCl_3$ (100 mL), and the extracts were dried over Na_2SO_4. The solvent was removed on a rotary evaporator, and the residue was purified by recrystallization from CH_2Cl_2/hexane. Yield: 196 mg (19.3%). ^{1}H NMR ($CDCl_3$): δ 8.18 (m, 4H, H ortho to N_{py}), 6.41 (m, 4H, H meta to N_{py}), 3.54 (m, 8H, C$\underline{H}_2$ next to N_{aza}py), 2.88 (m, 8H, C$\underline{H}_2$ next to N_{aza}). ^{13}C NMR ($CDCl_3$): δ 152.78, 149.91, 107.20, 54.33, 48.97. ESI-MS: *m/z* = 327.2042 ($[M+H]^+$). Elemental Anal. Calcd. for $C_{18}H_{26}N_6 \cdot 1/2H_2O \cdot 1/4CH_2Cl_2$: C, 61.63; H, 7.93; N, 23.80%; Found: H, 61.45; H, 7.77; N, 23.56%.

Synthesis of 1,4,7,10-tetra(4-pyridyl)-1,4,7,10-tetraazacyclododecane (L2): L2 was prepared using the same method. However, a larger excess of the pyridinium salt (~6 equiv) was mixed with 1,4,7,10-tetraazacyclododecane tetrahydrochloride (1.0 g, 3.1 mmol). Yield: 95 mg (9.4%). ^{1}H NMR ($CDCl_3$): δ 8.34 (m, 8H, H ortho to N_{py}), 6.49 (m, 8H, H meta to N_{py}), 3.50 (m, 16H, C$\underline{H}_2$). ^{13}C NMR (CD_3OD): δ 156.02, 150.51, 109.93, 52.88. ESI-MS: *m/z* = 481.31 ($[M+H]^+$). Elemental Anal. Calcd. for $C_{28}H_{32}N_8 \cdot 1/4CH_2Cl_2 \cdot 1/4H_2O$: C, 64.330; H, 6.440; N, 21.060%; Found: H, 64.085; H, 6.331; N, 21.010%.

Synthesis of 1,4-di(4-pyridyl)-1,4,7-triazacyclononane (L3) and 1,4,7-tri(4-pyridyl)-1,4,7-triazacyclononane (L4): Both **L3** and **L4** were synthesized using the same method as that for **L1** except that 4 equiv. of the pyridinium was used 1,4,7-triazacyclononane trihydrochloride (1.0 g, 4.2 mmol). In addition, the obtained mixture of **L3** and **L4** were purified by fractional crystallization from CH_2Cl_2/hexane.

L3: Yield: 220 mg (18.5%). ^{1}H NMR ($CDCl_3$): δ 8.24 (m, 4H, H ortho to N_{py}), 6.49 (m, 4H, H meta to N_{py}), 3.74 (s, 12H, C$\underline{H}_2$ between N_{aza}py), 3.38 (m, 4H, C$\underline{H}_2$), 2.95 (m, 4H, C$\underline{H}_2$ next to N_{aza}H). ^{13}C NMR ($CDCl_3$): δ 152.62, 150.11, 107.16, 53.99, 50.49, 46.95. ESI-MS: *m/z* = 284.1873 ($[M+H]^+$); calcd *m/z* = 284.1875. Elemental Anal. Calcd. for $C_{16}H_{21}N_5$: C, 67.86; H, 7.47; N, 24.71%; Found: H, 67.71; H, 7.50; N, 24.38%.
L4: Yield: 240 mg (15.9%). ^{1}H NMR ($CDCl_3$): δ 8.21 (m, 6H, H ortho to N_{py}), 6.39 (m, 6H, H meta to N_{py}), 3.61 (s, 12H, C$\underline{H}_2$). ^{13}C NMR ($CDCl_3$): δ 152.56, 150.40, 107.45, 50.22. ESI-MS: *m/z* = 361.2138 ($[M+H]^+$). Elemental Anal. Calcd. for $C_{21}H_{24}N_6 \cdot 2.6H_2O$: C, 61.93; H, 7.23; N, 20.63%; Found: H, 61.70; H, 7.14; N, 20.61%.

Preparation of $[\{Ru_3\}_2L1](PF_6)_2$ and $[\{Ru_3\}_4L2](PF_6)_4$: Both complexes were prepared by adding a solution of the respective linker (40 mg in both cases) in CH_2Cl_2 (5 mL) to a solution of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}O_2CCH_3)_6(dmap)_2(CH_3OH)](PF_6)$ (**L1**: 291.5 mg, 0.268 mmol; **L2**: (378.2 mg, 0.35 mmol) (dmap = N,N-dimethylaminopyridine). The solutions were allowed to stir for 18 and 48 h, respectively, and then the solvent was removed on a rotary evaporator. The complexes were recrystallized from CH_2Cl_2/hexane and then purified using size-exclusion column chromatography over BioBeads S-X1 with CH_2Cl_2 as the eluent.
$[\{Ru_3\}_2L1](PF_6)_2$: Yield: 180 mg (59.8%). ESI-MS: *m/z* 1081.57 ($[M]^{2+}$). Elem. Anal. Calcd for $Ru_6C_{70}H_{102}F_{12}N_{14}O_{26}P_2$: C, 34.29; H, 4.19; N, 8.00%; Found: C, 34.43; H, 4.52; N, 7.8%.
$[\{Ru_3\}_4L2](PF_6)_4$: Yield: 159 mg (40.3%). ESI-MS: *m/z* = 1038.0278 ($[M]^{4+}$); calcd *m/z* = 1038.0281.

ESI-MS detection of Ag(I) complex of $[\{Ru_3\}_4L2]^{4+}$: To a solution of **$[\{Ru_3\}_4L2](PF_6)_4$** (4 mg, mmol) in CH_3CN (10 mL) was added $AgNO_3$ (1 mg, mmol). As soon as the $AgNO_3$ completely dissolved, 1 mL of the solution was diluted 20-fold, and the dilute solution was injected into ESI mass spectrometer. A peak envelope was observed centered at *m/z* 859.14 with five peaks per mass unit, which indicates that the molecule has a +5 charge (see Figure S6).

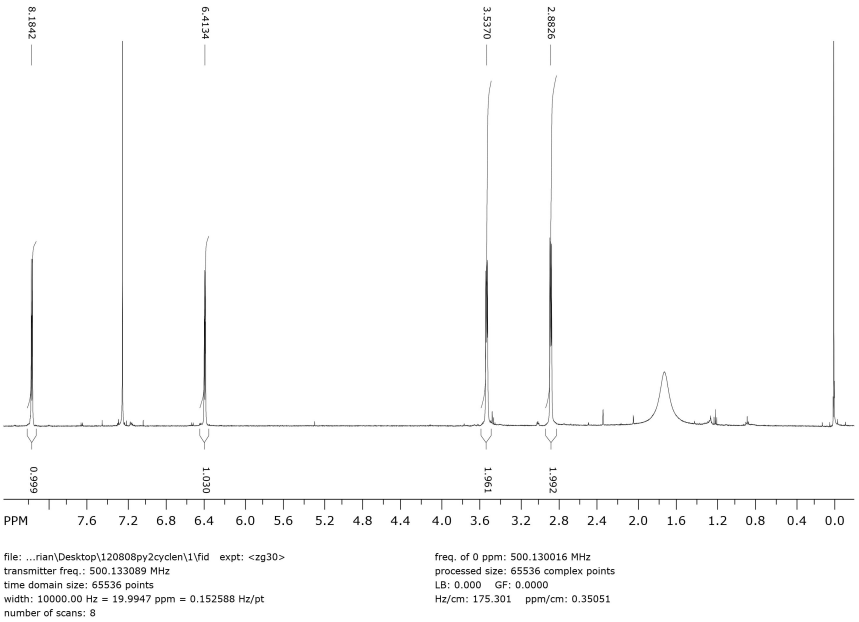

Figure S1. ^{1}H NMR spectrum of **L1** in $CDCl_3$. Spectrum was referenced to TMS.

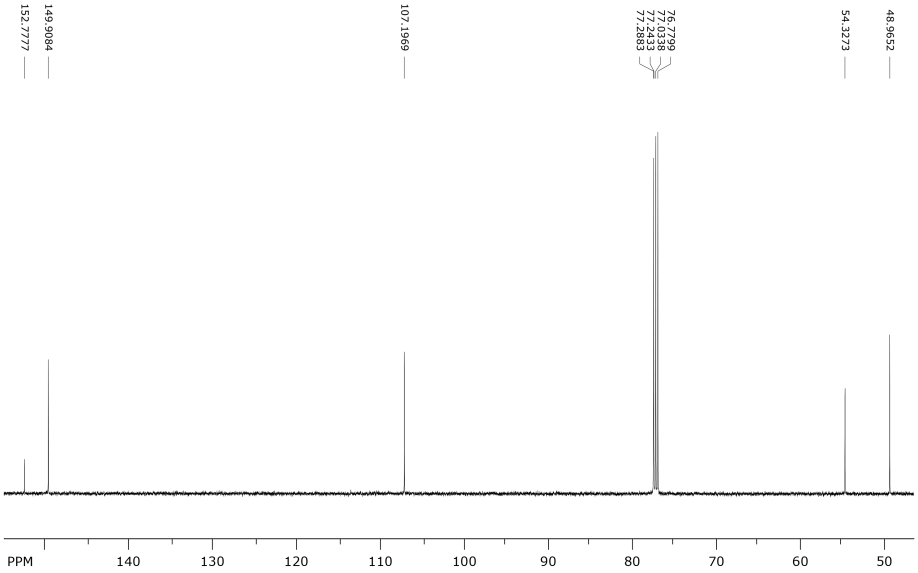

Figure S2. ^{13}C NMR spectrum of **L1** in $CDCl_3$.

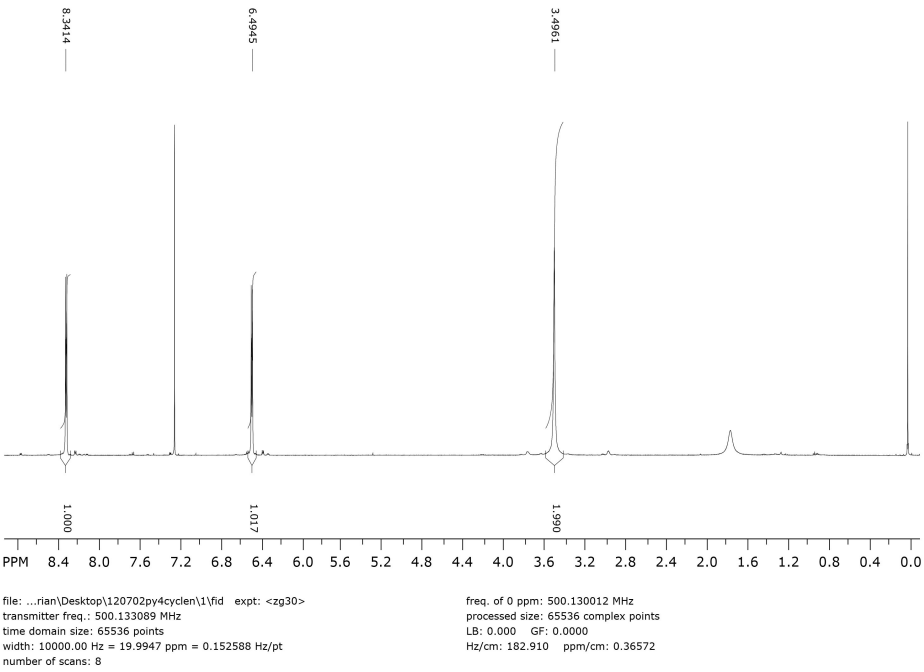

Figure S3. ^{1}H NMR spectrum of **L2** in $CDCl_3$. Spectrum was referenced to TMS.

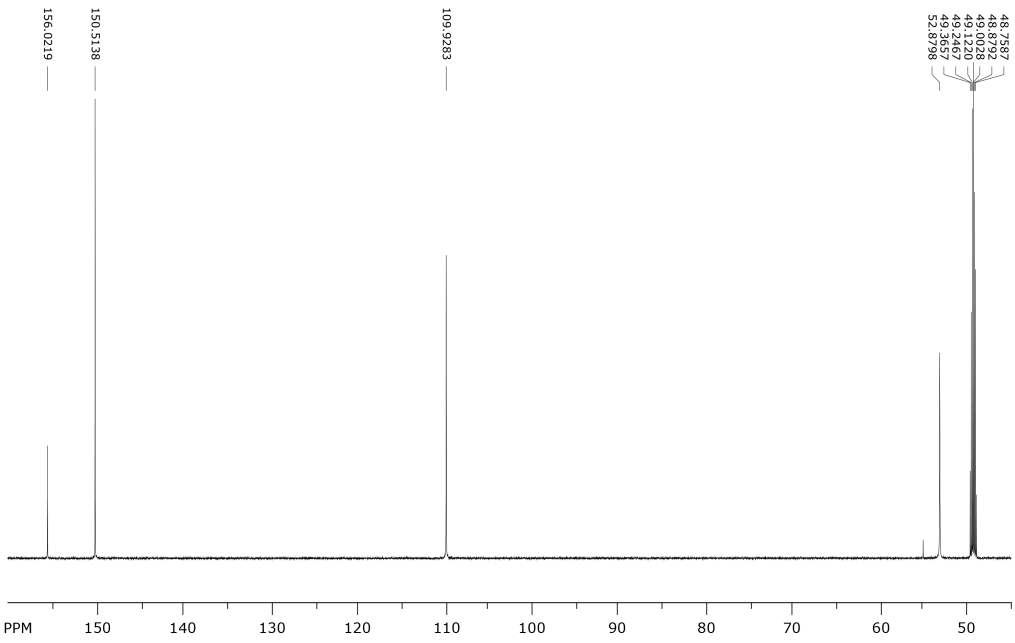

Figure S4. ^{13}C NMR spectrum of **L2** in CD_3OD.

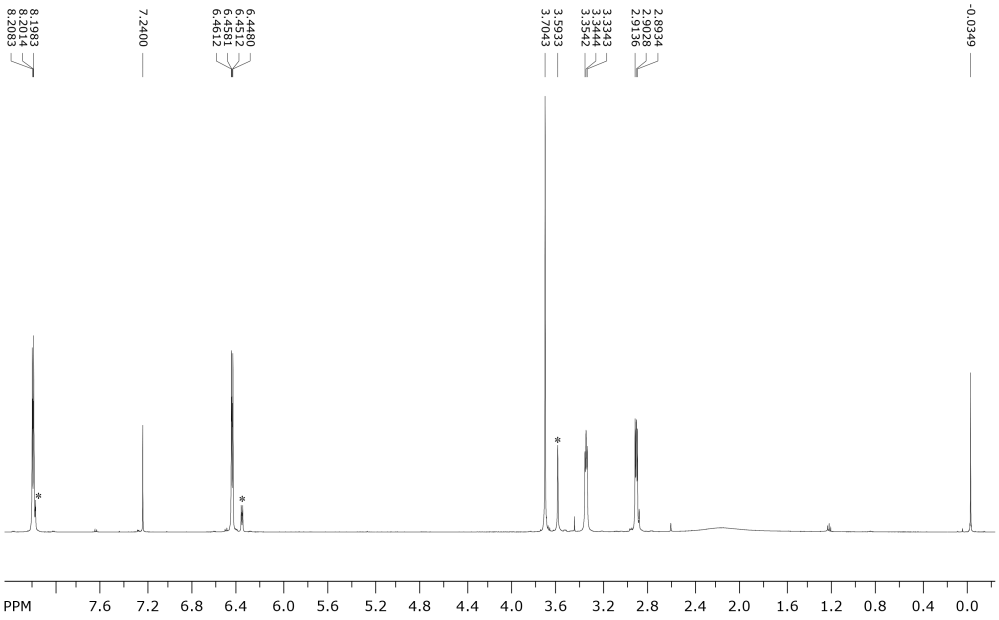

Figure S5. ^{1}H NMR spectrum of **L3** in $CDCl_3$. Spectrum was referenced to TMS. Peaks marked with (*) correspond to a small amount of **L4**.

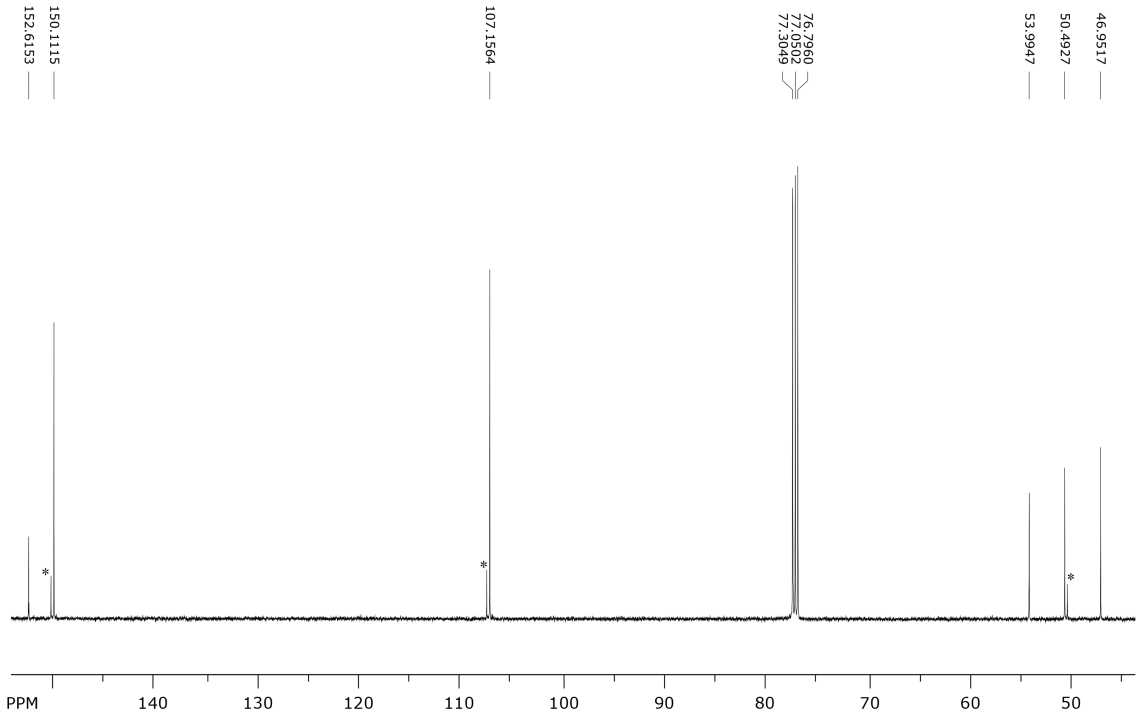

Figure S6. ^{13}C NMR spectrum of **L3** in $CDCl_3$. Peaks labeled with * correspond to a small amount of **L4**.

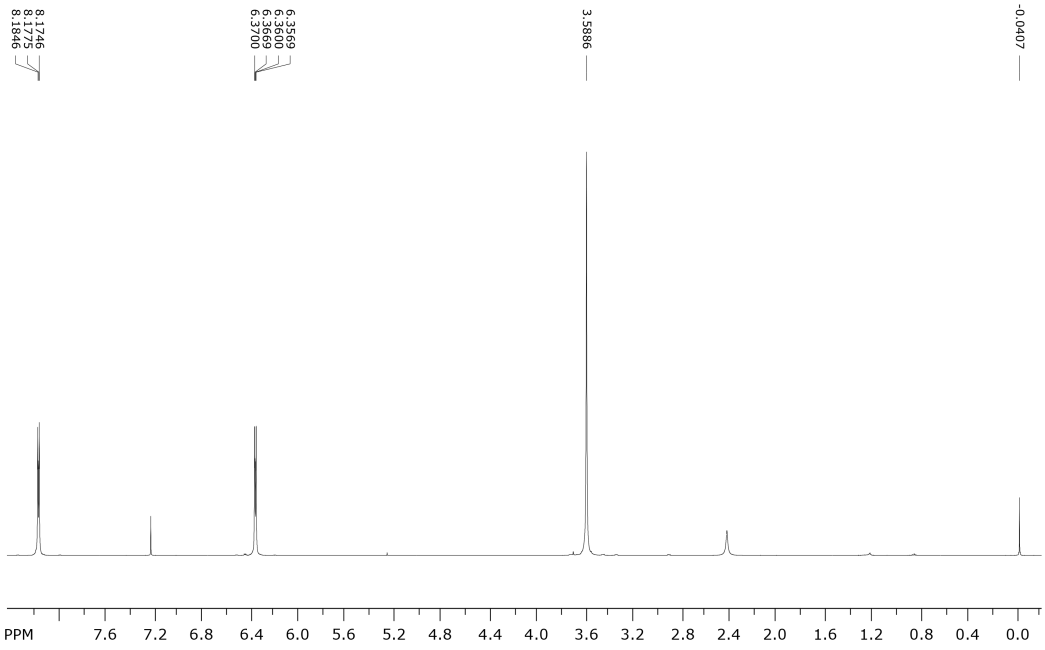

Figure S7. ^{1}H NMR spectrum of **L4** in $CDCl_3$. Spectrum was referenced to TMS.

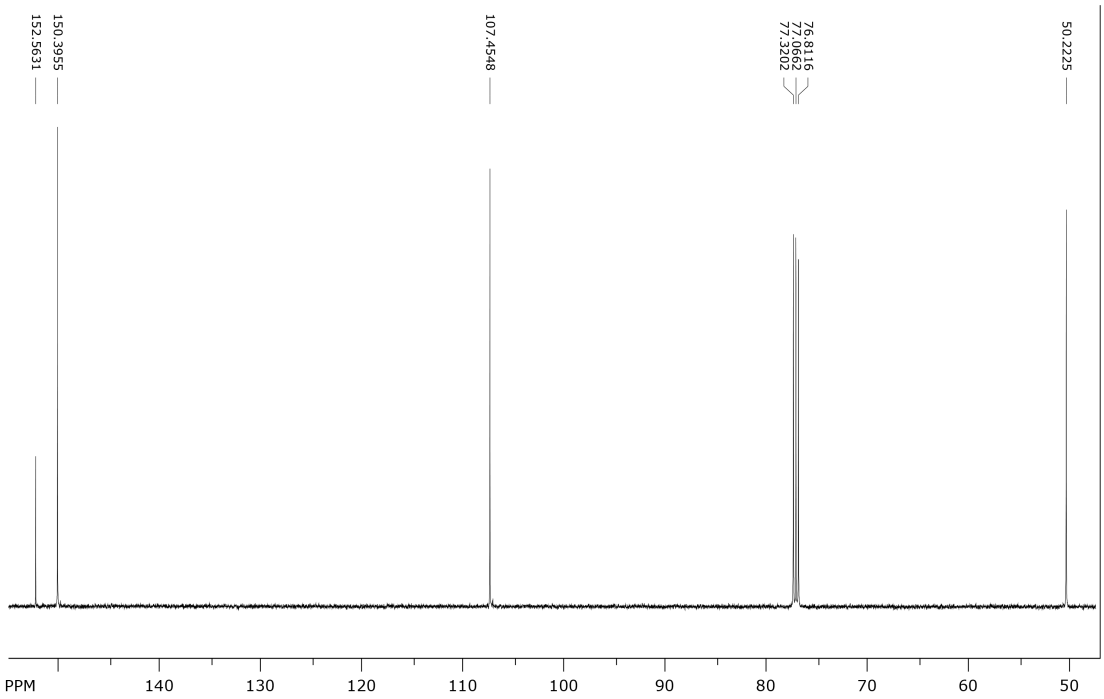

Figure S8. ^{13}C NMR spectrum of **L4** in $CDCl_3$.

Table S1. Crystal Data for **L1**–**L4**.

	L1	**L2**	**L3**	**L4**
Formula	$C_{54}H_{94}N_{18}O_8$	$C_{28}H_{32}N_8$	$C_{16}H_{20}N_5$	$C_{21}H_{26}N_6O$
*M*r	1123.47	480.62	282.37	378.46
Crystal system	triclinic	monoclinic	monoclinic	orthorhombic
Space group	$P\bar{1}$	$P2_1/a$	$P2_1/c$	*Pbca*
Temperature (K)	93	103	293	293
a (Å)	8.923(2)	8.456(3)	6.906(4)	10.277(5)
b (Å)	12.881(3)	15.508(5)	7.641(4)	14.718(5)
c (Å)	13.548(3)	9.731(3)	26.901(14)	25.634(5)
α (deg)	78.191(9)			
β (deg)	79.149(8)	108.424(4)	79.149(8)	90
γ (deg)	75.802(8)			
V (Å^3)	1461.9(6)	1210.7(6)	1419.5(13)	3877(2)
Z	1	2	4	8
ρ_{calcd} (g cm^{-3})	1.276	1.318	1.321	1.290
Reflections collected	10377	9543	10842	20253
Unique reflections	5502	2699	3140	2491
Reflections with $F^2 > 2\sigma(F^2)$	4172	2235	2065	2150
R_1 ($F^2 > 2\sigma(F^2)$)	0.0637	0.0395	0.0500	0.0264
wR_2 (all data)	0.1916	0.1126	0.1669	0.0694
GOF	1.104	1.095	0.978	1.025
CCDC	960768	960767	960765	960766

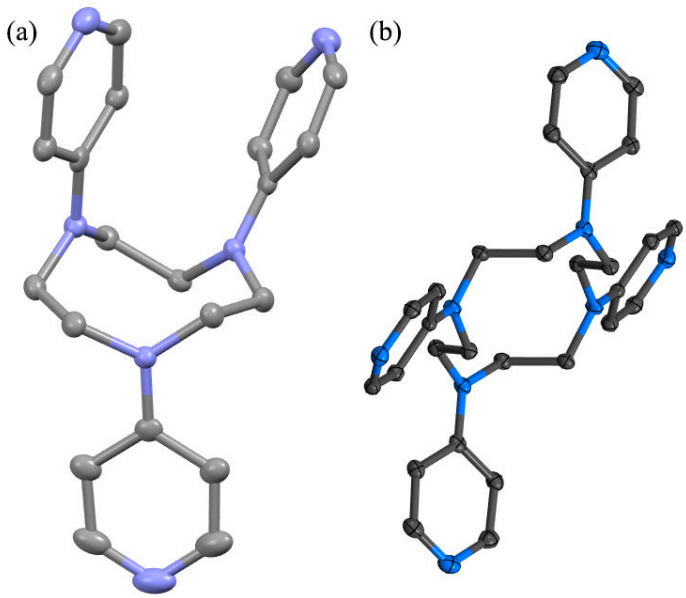

Figure S9. ORTEP diagrams of (a) **L4** and (b) **L2**. N atoms are in blue, and C atoms in grey.

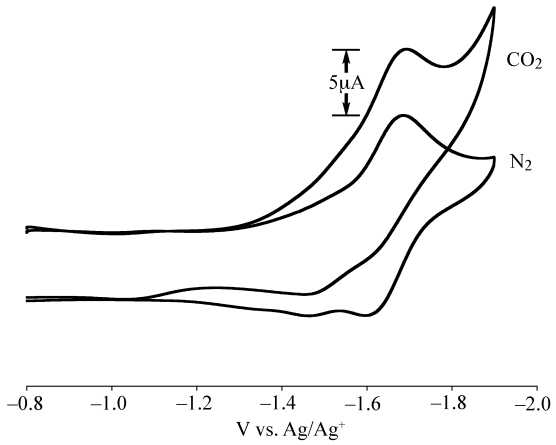

Figure S10. Cyclic voltammograms of $[\{Ru_3\}_4\mathbf{L2}]^{4+}$ and Ni(II) ions under N_2 and CO_2. Working electrode: glassy carbon; reference electrode: Ag/Ag+; auxiliary electrode: Pt wire; 0.1 M nBu_4NPF_6; scan rate, 100 mV/s.

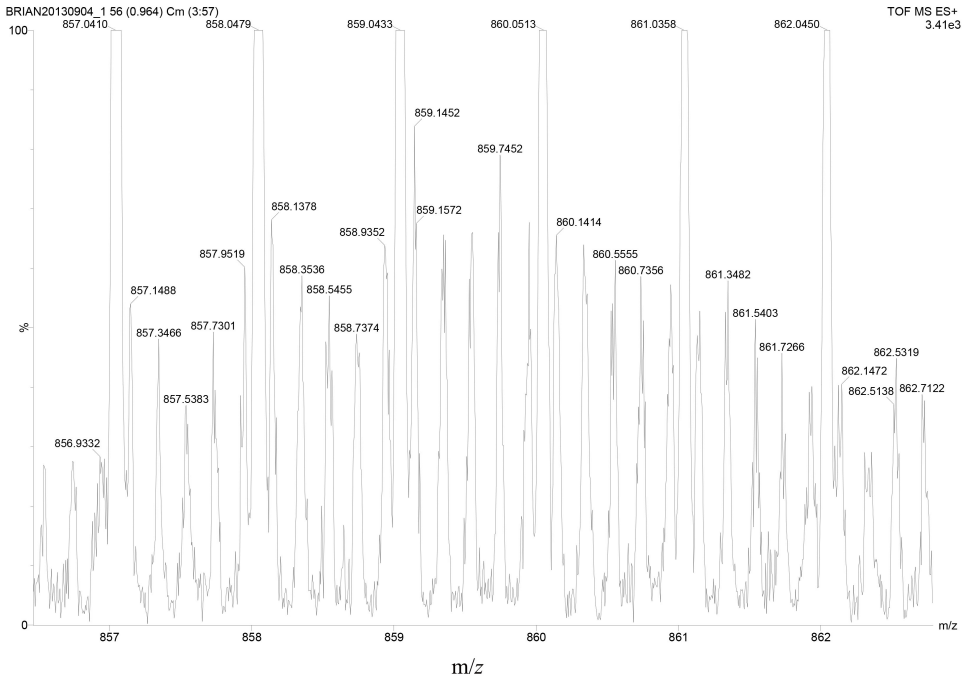

Figure S11. ESI mass spectrum of $\mathbf{[\{Ru_3\}_4L2Ag(CH_3CN)]^{5+}}$.