Supporting Information

Modulation of the CO_2-Fixation in Dinickel-Azacryptands

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General synthetic procedure for $[Ni_2L_A^R(HCO_3)]$: $\mathbf{L_A^R}$ (0.062 mmol) was dissolved in 2 mL MeCN/MeOH or MeCN/EtOH 4:1. A solution of $Ni(ClO_4)_2{\cdot}6H_2O$ (0.12 mmol) in MeCN/EtOH 4:1 was added to the solution. CO_2 was streamed through the solution for 10 min. The mixture was stirred over night. The solvent was removed under reduced pressure and the residue was precipitated from MeCN/Et_2O, MeCN/hexane or by slow evaporation of the solvent.

$[Ni_2L_A^{Me}(HCO_3)](ClO_4)_3$: blue solid, 93 %. ESI-MS calc. for $[C_{40}H_{60}ClN_8Ni_2O_7]^+$: *m/z* = 915.30. Found: *m/z* = 914.9. IR (KBr, cm^{-1}): 3345, 2917, 2774, 1654, 1612, 1464, 1440, 1093, 714, 626.

$[Ni_2L_A^F(HCO_3)](ClO_4)_3$: red solid, 89 %. ESI-MS calc. for $[C_{37}H_{51}ClF_3N_8Ni_2O_7]^+$: *m/z* = 927.22. Found: *m/z* = 927.9. IR (KBr, cm^{-1}): 3447, 3270, 2963, 2925, 2856, 1738, 1676, 1634, 1603, 1460, 1304, 1150, 1099, 982, 884, 841, 799, 708, 628.

$[Ni_2L_A^{OMe}(HCO_3)](ClO_4)_3$: blue solid, 98 %. ESI-MS calc. for $[C_{40}H_{60}ClN_8Ni_2O_{10}]^+$: *m/z* = 963.28. Found: *m/z* = 963.9. IR (KBr, cm^{-1}): 3419, 2910, 2781, 1620, 1467, 1340, 1302, 1145, 1113, 1087, 629.

$[Ni_2L_A^{Fur}(HCO_3)](ClO_4)_3$: green solid, 96 %. ESI-MS calc. for $[C_{31}H_{48}ClN_8Ni_2O_{10}]^+$: *m/z* = 842.19. Found: *m/z* = 842.8. IR (KBr, cm^{-1}): 3444, 3304, 2926, 2858, 1637, 1521, 1454, 1088, 1016, 975, 926, 803, 626.

General synthetic procedure for $[Ni_2L_A^R(H^{13}CO_3)]$: $\mathbf{L_A^R}$ (0.062 mmol) and $Ni(ClO_4)_2{\cdot}6H_2O$ (0.12 mmol) were dissolved in 5 mL degassed MeCN/MeOH 4:1 and stirred under N_2. $^{13}CO_2$ was streamed through the solution. The mixture was stirred over night. The solvent was removed under reduced pressure and dried in vacuum.

$[Ni_2L_A^{Me}(H^{13}CO_3)](ClO_4)_3$: blue solid, 42 %. ESI-MS calc. for $[^{12}C_{39}{}^{13}CH_{60}ClN_8Ni_2O_7]^+$: *m/z* = 918.23. Found: *m/z* = 918.00. IR (KBr, cm^{-1}): 3510, 3267, 2953, 2878, 1645, 1620, 1450, 1379, 1261, 1093, 324, 802, 625.

$[Ni_2L_A^F(H^{13}CO_3)](ClO_4)_3$: red solid, 52 %. ESI-MS calc. for $[^{12}C_{36}{}^{13}CH_{53}ClF_3N_8Ni_2O_7]^+$: *m/z* = 930.24. Found: *m/z* = 930.00. IR (KBr, cm^{-1}): 3531, 3277, 3072, 2941, 2881, 1697, 1626, 1602, 1456, 1304, 1103, 986, 878, 709, 627.

$[Ni_2L_A^{OMe}(H^{13}CO_3)](ClO_4)_3$: blue solid, 38 %. ESI-MS calc. for $[^{12}C_{39}{}^{13}CH_{61}ClN_8Ni_2O_{10}]^+$: *m/z* = 965.29. Found: *m/z* = 965.80. IR (KBr, cm^{-1}): 3537, 3265, 2949, 2872, 2853, 1636, 1605, 1464, 1337, 1304, 1092, 843, 625.

$[Ni_2L_A^{Fur}(H^{13}CO_3)](ClO_4)_3$: green solid, 79 %. ESI-MS calc. for $[^{12}C_{30}{}^{13}CH_{49}ClN_8Ni_2O_{10}]^+$: *m/z* = 845.20. Found: *m/z* = 845.8. IR (KBr, cm^{-1}): 3528, 3273, 2930, 2864, 1623, 1483, 1448, 1379, 1099, 1016, 982, 926, 804, 625.

General synthetic procedure for $[Ni_2L_A^R(N_3)](ClO_4)_3$: $\mathbf{L_A^R}$ (0.038 mmol) was dissolved in MeCN/MeOH or MeCN/EtOH 4:1. A solution of $Ni(ClO_4)_2{\cdot}6H_2O$ (0.076 mmol) in MeCN/EtOH 4:1 was added to the solution. After 30 min NaN_3 (0.038 mmol), dissolved in EtOH/H_2O (1:1), was added to the solution. The mixture was stirred overnight. The solvent was removed under reduced pressure and the residue was precipitated from MeCN/Et_2O or by slow evaporation of the solvent.

$[Ni_2L_A^F(N_3)](ClO_4)_3$: crystallization from MeCN/EtOH, green crystals, 89 %. ESI-MS calc. for $[C_{36}H_{51}F_3N_{11}Ni_2]^+$: *m/z* = 810.30. Found: *m/z* = 809.6. IR (KBr, cm^{-1}): 3447, 3019, 2925, 2872, 2197, 2114, 2048, 1627, 1598, 1457, 1299, 1146, 1114, 1083, 629.

$[Ni_2L_A^{Me}(N_3)](ClO_4)_3$: blue-green solid, 92 %. ESI-MS calc. for $[C_{39}H_{60}N_{11}Ni_2 + 2\ ClO_4]^+$: *m/z* = 996.27. Found: *m/z* = 997.73. IR (KBr, cm^{-1}): 3421, 2922, 2872, 2781, 2194, 2118, 2058, 1616, 1445, 1146, 1085, 629.

$[Ni_2L_A^{Py}(N_3)](ClO_4)_3$: violett solid, 67 %. ESI-MS calc. for $[C_{33}H_{45}Cl_2N_{14}Ni_2 + 2\ ClO_4]^+$: *m/z* = 951.16. Found: m/z = 951.78. IR (KBr, cm^{-1}): 3429, 2931, 2119, 2065, 1610, 1458, 1145, 1086, 630.

$[Ni_2L_A^{Fur}(N_3)](ClO_4)_3$: green solid, 65 %. ESI-MS calc. for $[C_{30}H_{42}N_{11}Ni_2O_3 + + 2\ CH_3OH + 2\ ClO_4]^+$: *m/z* = 982.17 IR (KBr, cm^{-1}): 3418, 2876, 2176, 2067, 1636, 1452, 1145, 1085, 1020, 630.

$[Ni_2L_A^{OMe}(N_3)](ClO_4)_3$: green solid, 91 %. ESI-MS calc. for $[C_{39}H_{60}N_{11}Ni_2O_3 + ClO_4]^+$: m/z = 1044.26. Found: *m/z* = 1046.30. IR (KBr, cm^{-1}): 3420, 2937, 2878, 2193, 2122, 1599, 1469, 1441, 139, 1301, 1146, 1114, 1086, 842, 711, 627.

$[Ni_2L_A^{Thio}(N_3)](ClO_4)_3$: green solid, 87 %. IR (KBr, cm^{-1}): 3554, 3478, 3416, 3247, 2926, 2855, 2191, 2105, 2056, 1622, 1442, 1087, 808. 629.

[$Ni_2L_A^{OH}(N_3)$](ClO_4)$_3$: dark green solid, 93 %. ESI-MS calc. for [$C_{36}H_{55}N_{11}Ni_2O_3$ + 2 ClO_4]$^+$: *m/z* = 1003.21. Found: *m/z* = 1003.85. IR ((KBr, cm^{-1}): 3556, 3417 (br), 1326, 2931, 2871, 2189, 2116, 1603, 1461, 1310, 1144, 1114, 1084, 841, 629.

Synthesis of [(Tren)Ni(CH_3CN)$_2$](ClO_4)$_2$: **L_I^{tBu}** or **L_I^H** (0.066 mmol) was dissolved in 3 mL MeCN/MeOH (4:1) and Ni(ClO_4)$_2$·6H_2O was added. The solution was stirred for 1d at RT. The solvent was removed under reduced pressure and the violet solid was crystallized by slow diffusion of Et_2O into a solution of the compound, dissolved in MeCN/EtOH. Violet crystals were isolated with 33% (0.022 mmol) yield. ESI-MS calc. for [$C_6H_{20}N_4NaNi$ + 2 CH_3CN + 4 ClO_4]$^+$: *m/z* = 706.93. Found: *m/z* = 706.9. IR (KBr, cm^{-1}): 2494, 3350, 3299, 2934, 2898, 1602, 1476, 1143, 1089, 984, 828, 628.

Synthesis of [$Ni_2L_A^{H,para}$(CN)]: $L_A^{H,para}$ (0.084 mmol) was dissolved in MeCN (3 mL) and Ni(ClO_4)$_2$·6H_2O (0.167 mmol) was added. The solution was stirred for 2d at RT. The solvent was removed under reduced pressure to give a violet solid with 96 % (0.081 mmol). ESI-MS calc. for [$C_{38}H_{58}N_9Ni_2$]: *m/z* = 756.34. Found: *m/z* = 756.37. IR (KBr, cm^{-1}): 3442, 3262, 2938, 2883, 2310, 2287, 2022, 1636, 1454, 1089, 807, 627.

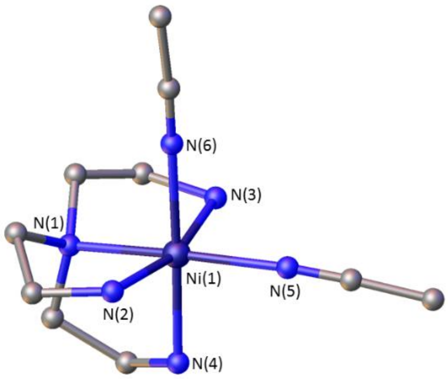

Figure S1. Molecular structure of **[(Tren)Ni(CH_3CN)$_2$](ClO_4)$_2$**. Hydrogen atoms and counter ions omitted for clarity.

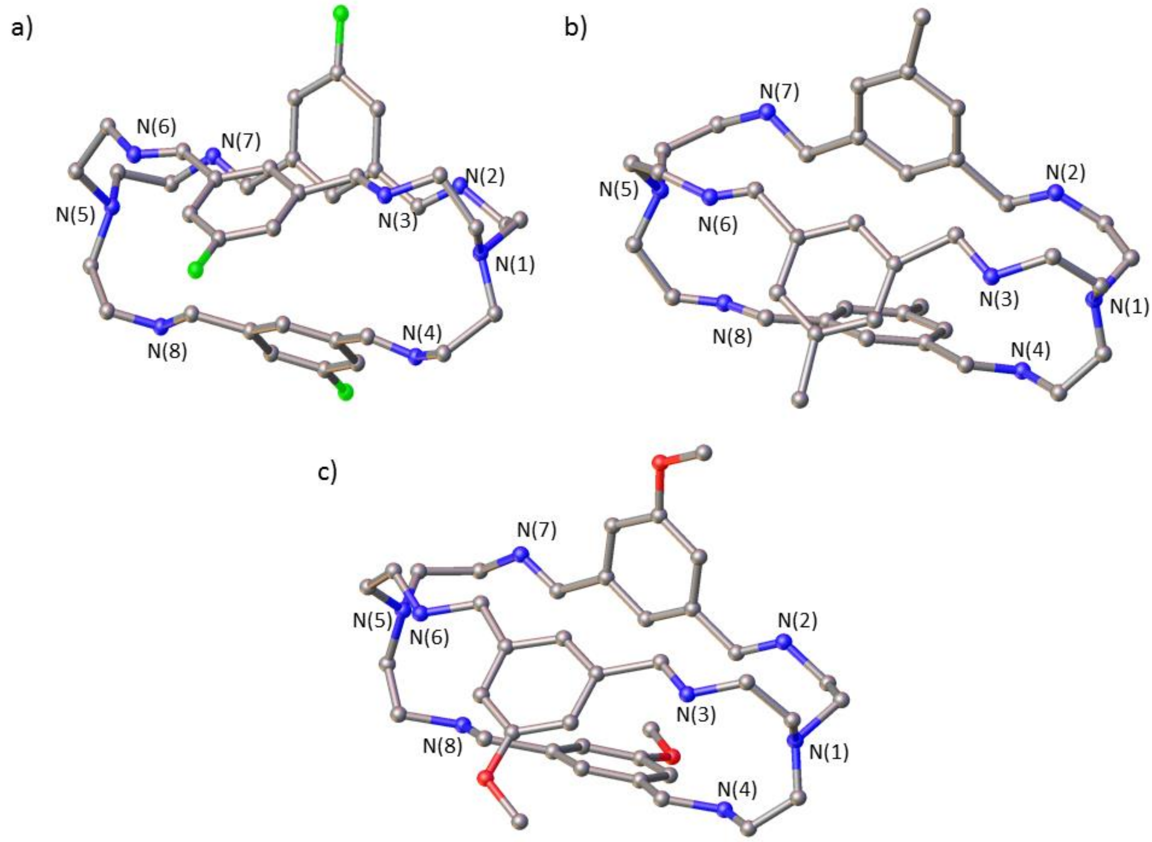

Figure S2. Molecular structures of a) $\mathbf{L_I^F}$, b) $\mathbf{L_I^{Me}}$ and c) $\mathbf{L_I^{OMe}}$. Hydrogen atoms omitted for clarity.

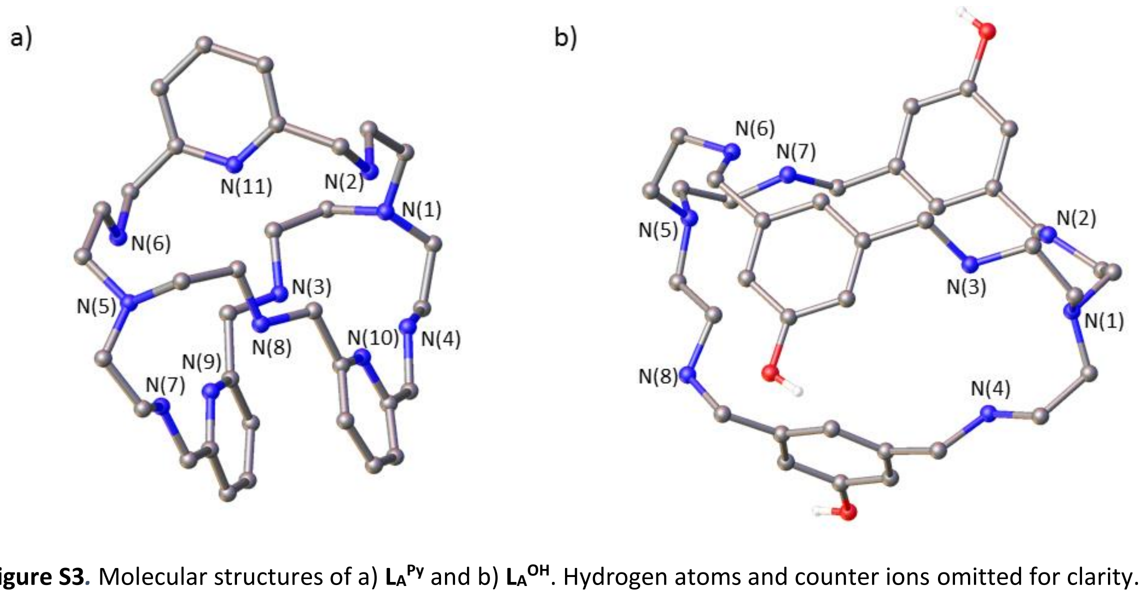

Figure S3. Molecular structures of a) $\mathbf{L_A^{Py}}$ and b) $\mathbf{L_A^{OH}}$. Hydrogen atoms and counter ions omitted for clarity.

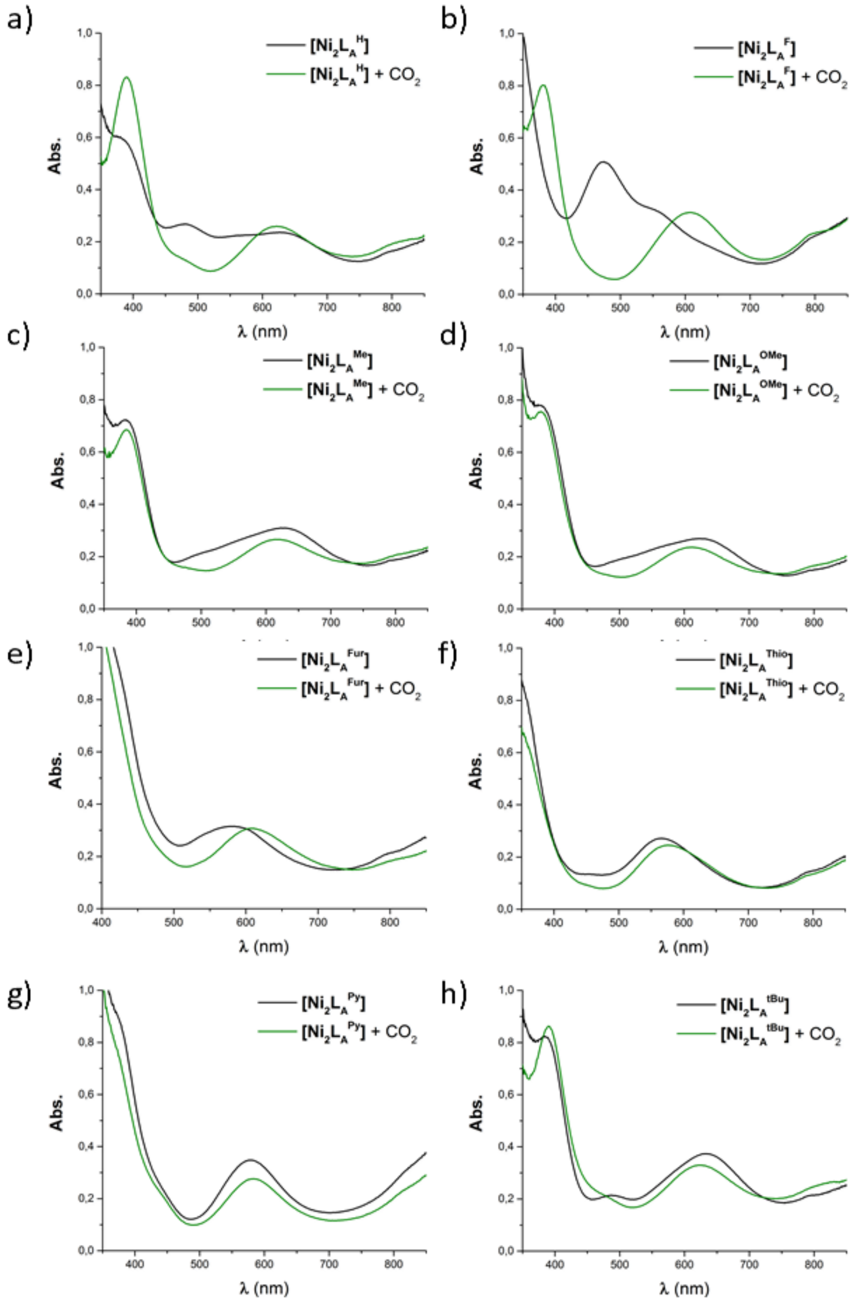

Figure S4. UV-vis spectra (MeCN/MeOH 20%, RT) of a) **$[Ni_2L_A^{H}]$**, b) **$[Ni_2L_A^{F}]$**, c) **$[Ni_2L_A^{Me}]$**, d) **$[Ni_2L_A^{OMe}]$**, e) **$[Ni_2L_A^{Fur}]$**, f) **$[Ni_2L_A^{Thio}]$**, g) **$[Ni_2L_A^{Py}]$**, h) **$[Ni_2L_A^{tBu}]$** (black) and after CO_2-purging (green).

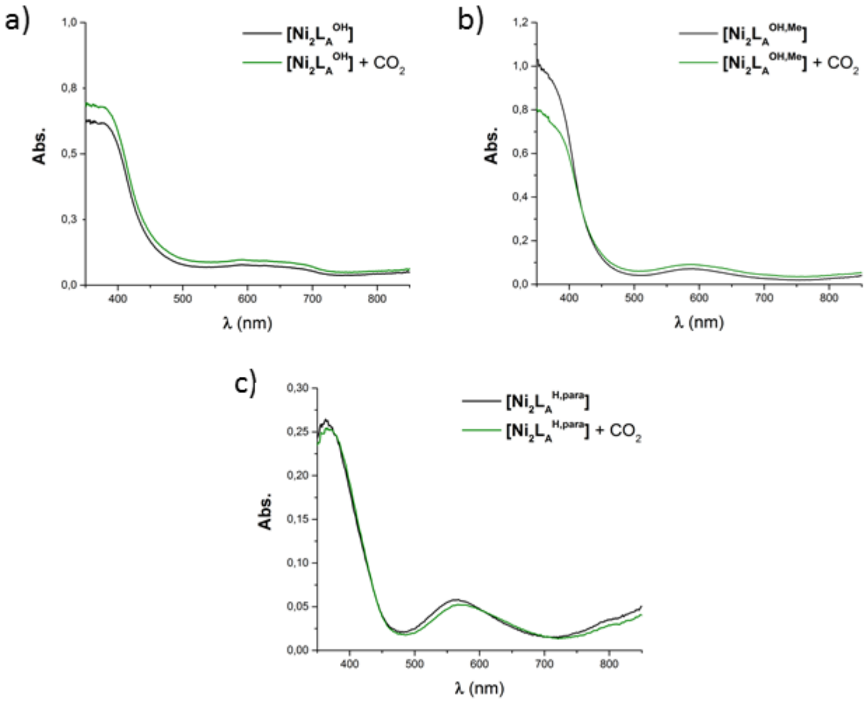

Figure S5. UV-vis spectra (MeCN/MeOH 20%, RT) of a) **[$Ni_2L_A^{OH}$]**, b) **[$Ni_2L_A^{OH,Me}$]** and c) **[$Ni_2L_A^{H,para}$]** (black) and after CO_2-purging (green).

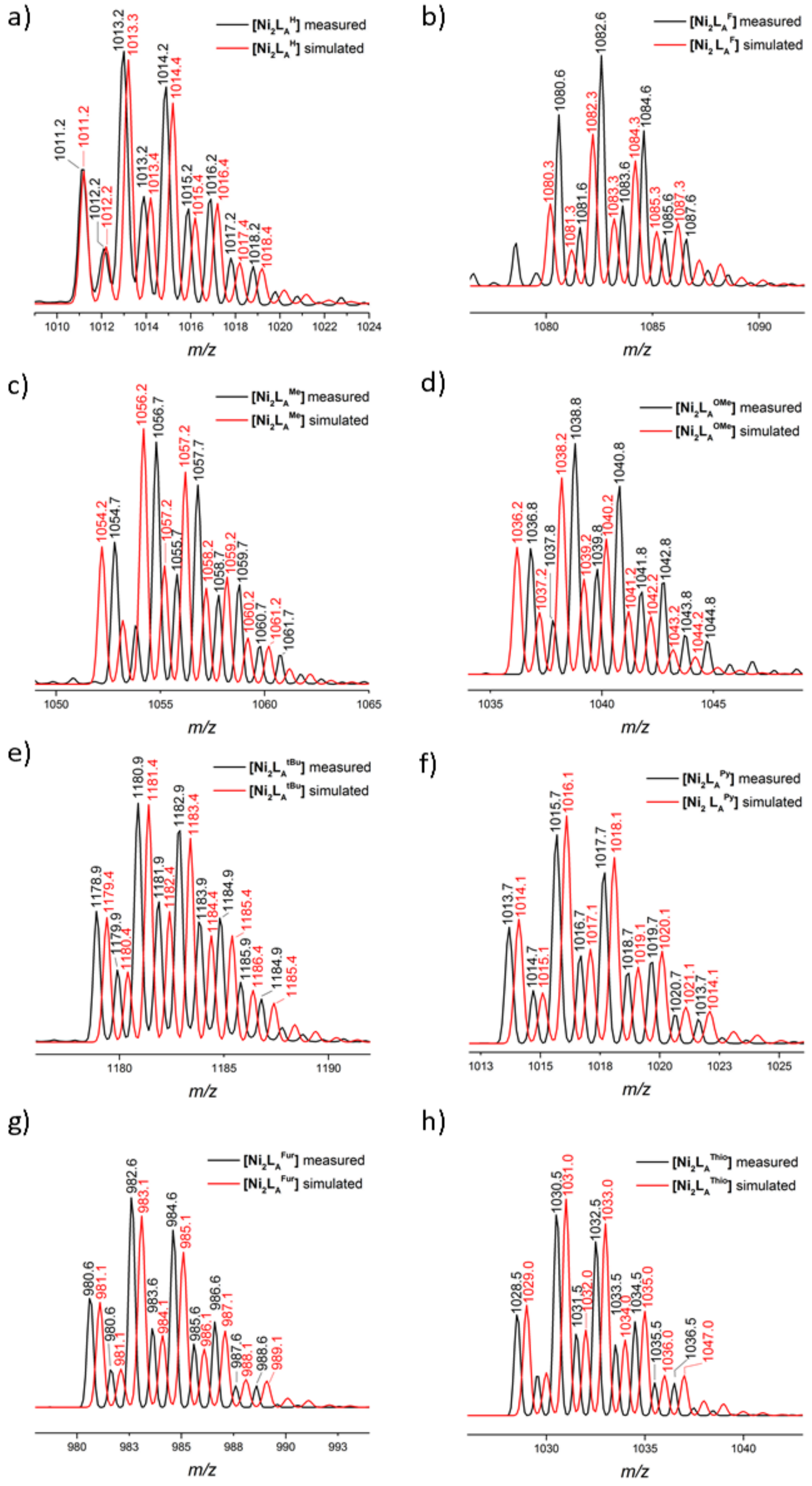

Figure S6. ESI spectra of the mass-peak **[$Ni_2L_A^R$](ClO_4)$_3$** (black: measured, red: simulated) of a) **[$Ni_2L_A^H$]**, b) **[$Ni_2L_A^F$]**, c) **[$Ni_2L_A^{Me}$]**, d) **[$Ni_2L_A^{OMe}$]**, e) **[$Ni_2L_A^{tBu}$]**, f) **[$Ni_2L_A^{Py}$]**, g) **[$Ni_2L_A^{Fur}$]** and h) **[$Ni_2L_A^{Thio}$]**.

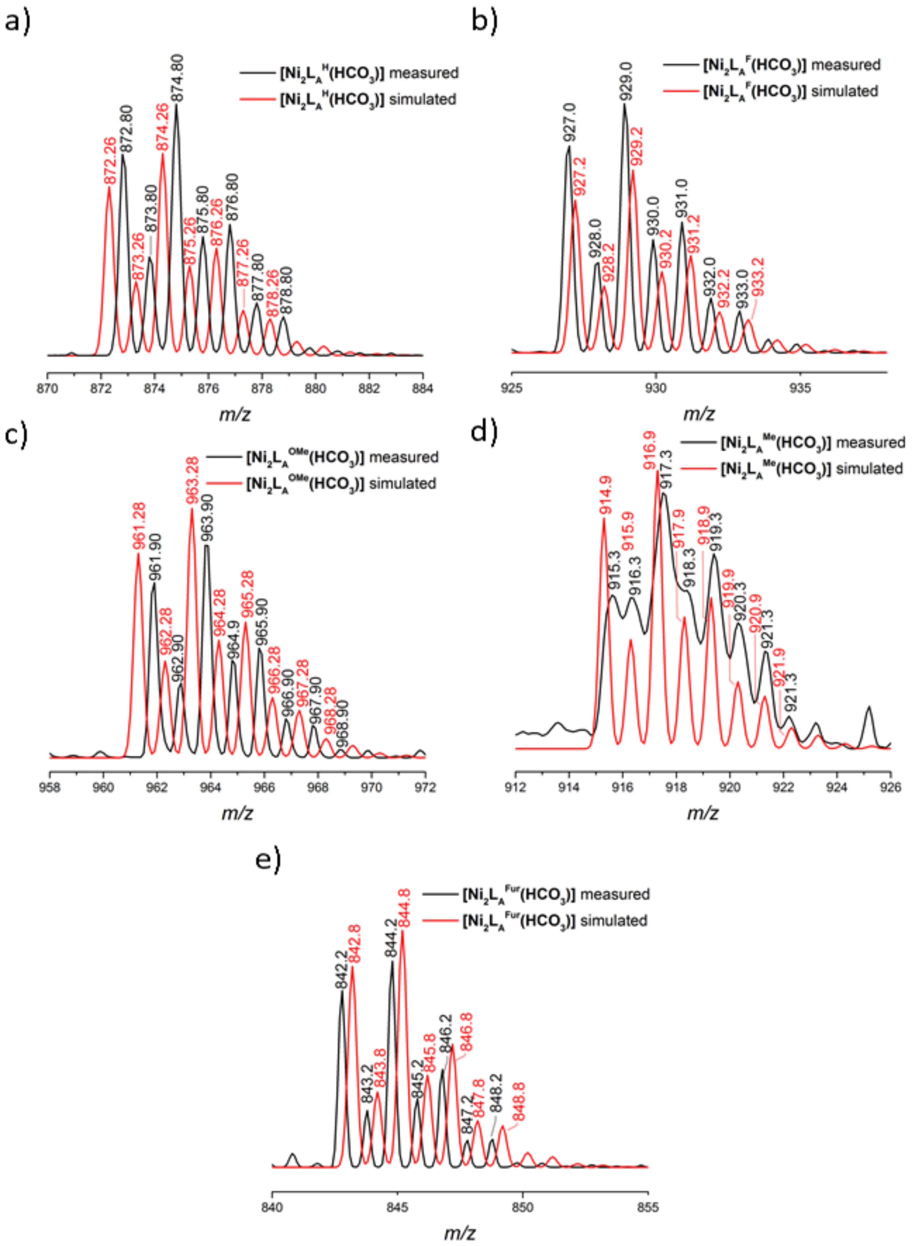

Figure S7. ESI spectra of the mass-peak **$[Ni_2L_A^R(HCO_3)](ClO_4)_2$** (black: measured, red: simulated) of a) **$[Ni_2L_A^H(HCO_3)]$**,[1] b) **$[Ni_2L_A^F(HCO_3)]$**, c) **$[Ni_2L_A^{Me}(HCO_3)]$**, d) **$[Ni_2L_A^{OMe}(HCO_3)]$** and e) **$[Ni_2L_A^{Fur}(HCO_3)]$**.

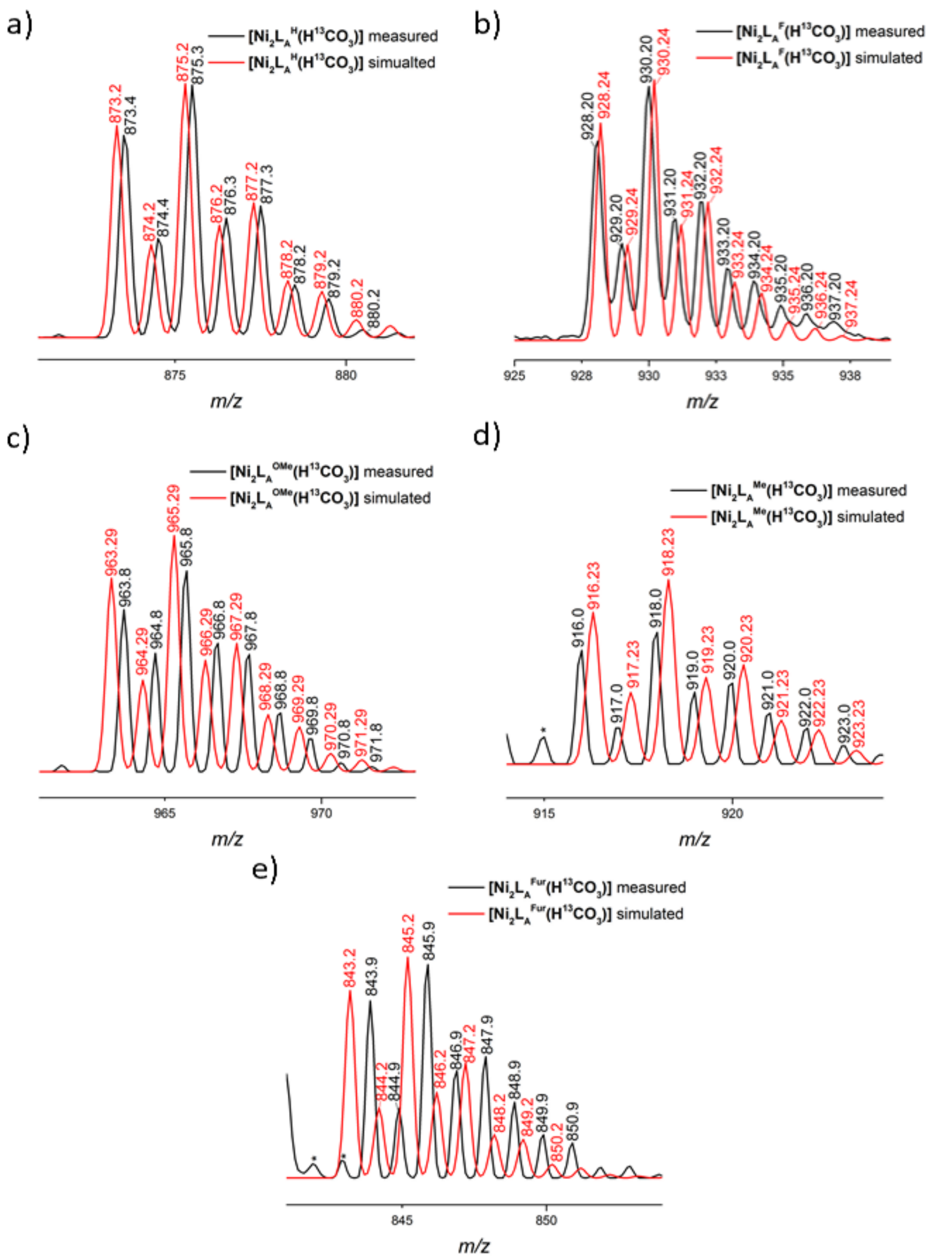

Figure S8. ESI spectra of the mass-peak of **[Ni$_2$L$_A$^{R}(H^{13}CO$_3$)](ClO$_4$)$_2$** (black: measured, red: simulated) of a) **[Ni$_2$L$_A$^{H}(H^{13}CO$_3$)]**,[1] b) **[Ni$_2$L$_A$^{F}(H^{13}CO$_3$)]**, c) **[Ni$_2$L$_A$^{Me}(H^{13}CO$_3$)]**, d) **[Ni$_2$L$_A$^{OMe}(H^{13}CO$_3$)]** and e) **[Ni$_2$L$_A$^{Fur}(H^{13}CO$_3$)]**. (*signal from neighboring mass peak)

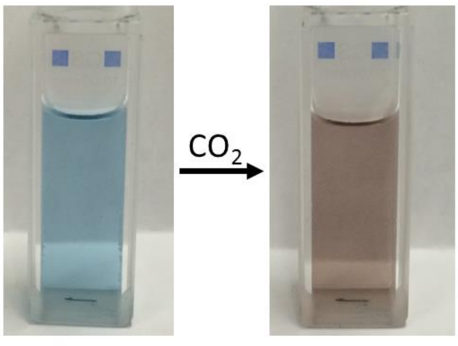

Figure S9. Observed color change during the CO_2-coordination in **[Ni$_2$L$_A$^{F}]**, left: before CO_2 addition, right: after CO_2-purging.

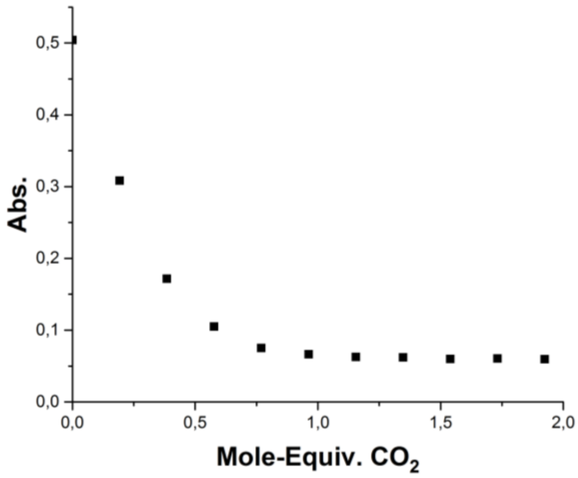

Figure S10. Change in absorption at 475 nm from the coordination of CO_2 in **[$Ni_2L_A{}^F$]**.

Table S1. k_{obs} values obtained from the change in absorption of **L^H** (470 nm), **L^F** (475 nm), **L^{Me}** (550 nm), **L^{OMe}** (550 nm) and **L^{Fur}** (550 nm) from a pseudo 1. order plot at different temperatures, [CO_2] = 280 mM.[2]

	15°C	**20°C**	**25°C**	**30°C**	**35°C**	**40°C**	**45°C**
L^H	$2.379 \cdot 10^{-2}$	*n.a*	$2.766 \cdot 10^{-2}$	*n.a*	$3.443 \cdot 10^{-2}$	*n.a*	$4.449 \cdot 10^{-2}$
L^F	$2.106 \cdot 10^{-4}$	*n.a*	$8.327 \cdot 10^{-3}$	*n.a*	$1.267 \cdot 10^{-2}$	*n.a*	$2.150 \cdot 10^{-2}$
L^{Me}	$4.910 \cdot 10^{-3}$	$5.940 \cdot 10^{-3}$	$6.280 \cdot 10^{-3}$	$9.190 \cdot 10^{-3}$	$1.008 \cdot 10^{-2}$	$1.035 \cdot 10^{-2}$	$1.229 \cdot 10^{-2}$
L^{OMe}	$2.920 \cdot 10^{-3}$	*n.a.*	$5.410 \cdot 10^{-3}$	*n.a.*	$9.850 \cdot 10^{-3}$	*n.a.*	$1.560 \cdot 10^{-2}$
L^{Fur}	$1.646 \cdot 10^{-4}$	$3.459 \cdot 10^{-4}$	$4.215 \cdot 10^{-4}$	$8.248 \cdot 10^{-4}$	*n.a*	$1.509 \cdot 10^{-3}$	$2.329 \cdot 10^{-3}$

(*n.a* = not available/measured)

Table S2. Obtained values from the change in absorption of **L^H** (470 nm), **L^F** (475 nm), **L^{Me}** (550 nm), **L^{OMe}** (550 nm) and **L^{Fur}** (550 nm) at different [CO_2]-concentrations at 298.15 K.

	28mM	**40 mM**	**56mM**	**93 mM**	**140 mM**	**210 mM**	**280 mM**
L^H	*n.a*	$1.106 \cdot 10^{-2}$	n.a	$1.413 \cdot 10^{-2}$	$1.809 \cdot 10^{-2}$	$2.153 \cdot 10^{-2}$	$2.766 \cdot 10^{-2}$
L^F	$3.420 \cdot 10^{-3}$	*n.a*	$4.010 \cdot 10^{-3}$	*n.a*	$6.05 \cdot 10^{-3}$	*n.a*	$8.310 \cdot 10^{-3}$
L^{Me}	*n.a*	*n.a*	*n.a*	$3.230 \cdot 10^{-3}$	$4.06 \cdot 10^{-3}$	$4.900 \cdot 10^{-3}$	$6.280 \cdot 10^{-3}$
L^{OMe}	*n.a*	*n.a*	*n.a*	$1.700 \cdot 10^{-3}$	$2.360 \cdot 10^{-3}$	$3.350 \cdot 10^{-3}$	$5.390 \cdot 10^{-3}$
L^{Fur}	*n.a*	*n.a*	*n.a*	$2.450 \cdot 10^{-3}$	$2.630 \cdot 10^{-3}$	$3.410 \cdot 10^{-3}$	$4.210 \cdot 10^{-3}$

(*n.a* = not available/measured)

Table S3. Obtained values from stopped-flow measurements at different CO_2-concentrations and the resulting $\Delta H^‡$ and $\Delta S^‡$ values, calculated from the Eyring-plot.

	k_2 [$M^{-1}s^{-1}$]	**$\Delta H^‡$ [kJ/mol]**	**$\Delta S^‡$ [J/mol·K]**
L^H	$6.70 \cdot 10^{-2} \pm 5.00 \cdot 10^{-3}$	7.55 ± 1.07	2.64 ± 3.55
L^F	$1.97 \cdot 10^{-2} \pm 3.10 \cdot 10^{-3}$	36.93 ± 1.04	83.93 ± 3.50
L^{Me}	$1.60 \cdot 10^{-2} \pm 1.10 \cdot 10^{-3}$	23.55 ± 2.62	37.64 ± 8.66
L^{OMe}	$1.93 \cdot 10^{-2} \pm 2.70 \cdot 10^{-3}$	43.40 ± 7.28	102.72 ± 23.67
L^{Fur}	$9.75 \cdot 10^{-4} \pm 1.08 \cdot 10^{-4}$	23.539 ± 2.62	37.59 ± 8.65

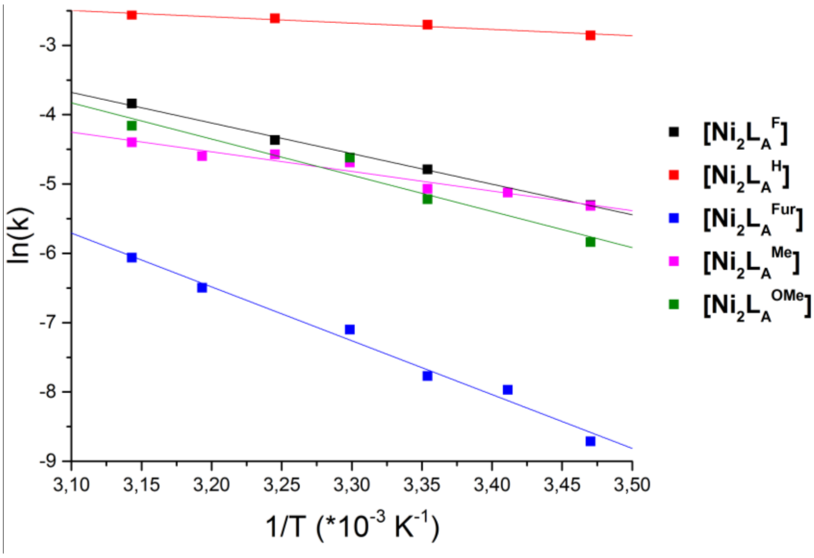

Figure S11. Eyring plot for the CO_2-fixation in **[$Ni_2L_A{}^H$]** (red, 470 nm), **[$Ni_2L_A{}^F$]** (black, 475 nm), **[$Ni_2L_A{}^{Me}$]** (violet, 550 nm) and **[$Ni_2L_A{}^{Fur}$]** (blue, 550 nm) and **[$Ni_2L_A{}^{OMe}$]** (green, 550 nm) in MeCN at different temperatures. [CO_2] = 280 mM.

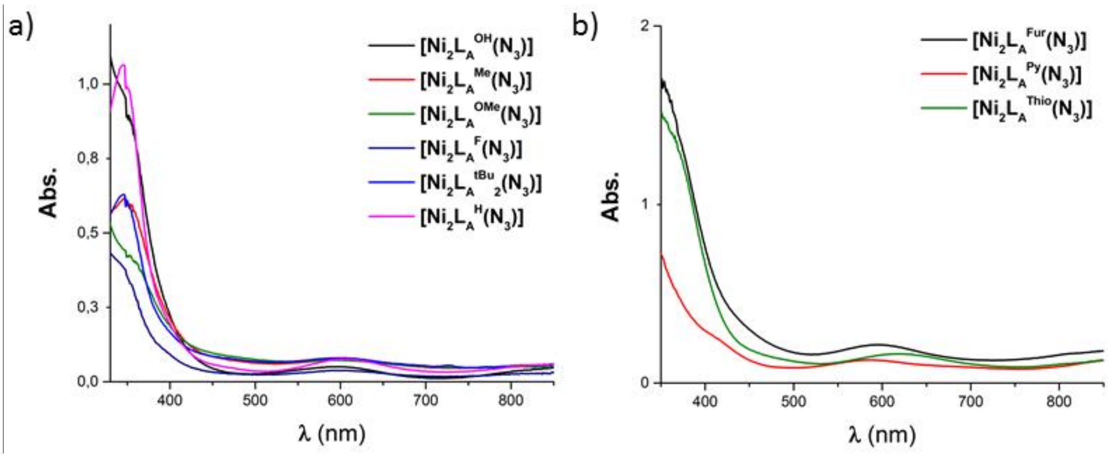

Figure S12. UV-vis spectra (MeCN/MeOH 20%, RT) of **[$Ni_2L_A{}^R(N_3)$]**.

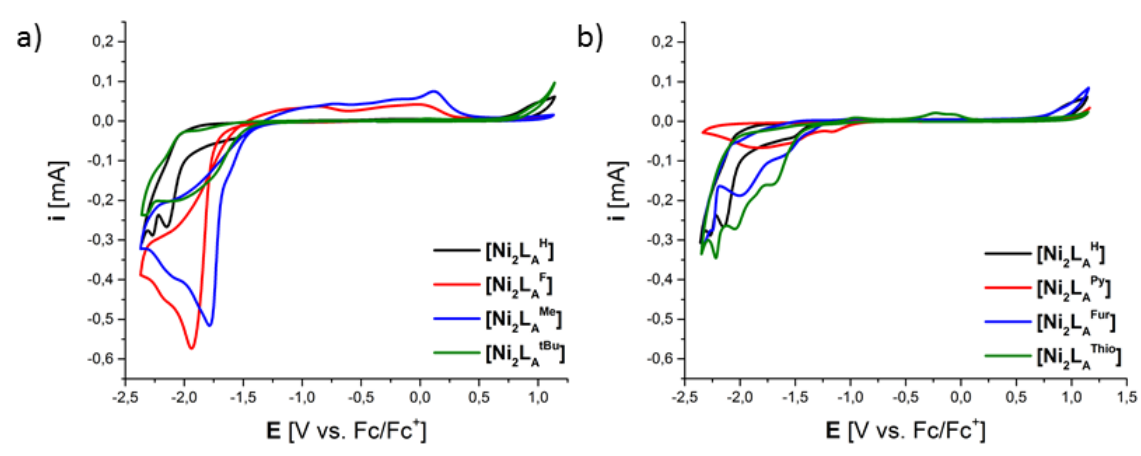

Figure S13. Cyclic voltammograms (100 mV/s) of dinickel compounds **[$Ni_2L_A{}^F$]**, **[$Ni_2L_A{}^{Me}$]** and **[$Ni_2L_A{}^{tBu}$]** a) and **[$Ni_2L_A{}^{Py}$]**, **[$Ni_2L_A{}^{Fur}$]** and **[$Ni_2L_A{}^{Thio}$]**, b) in comparison to **[$Ni_2L_A{}^H$]** in degassed MeCN (100 mM $TBAPF_6$) without CO_2.

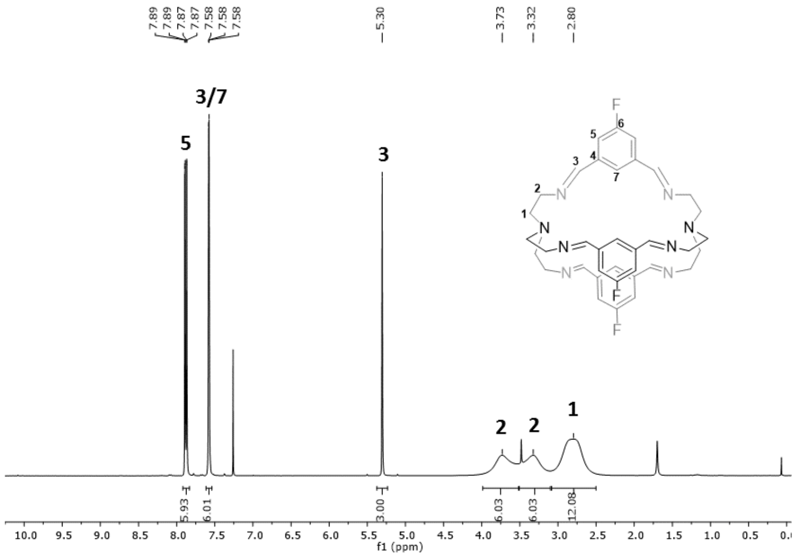

Figure S14. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of $\mathbf{L_I^F}$.

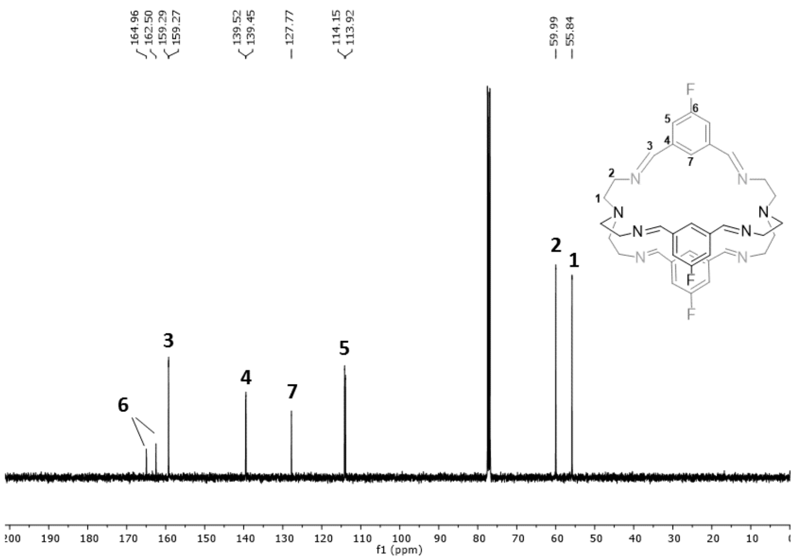

Figure S15. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of $\mathbf{L_I^F}$.

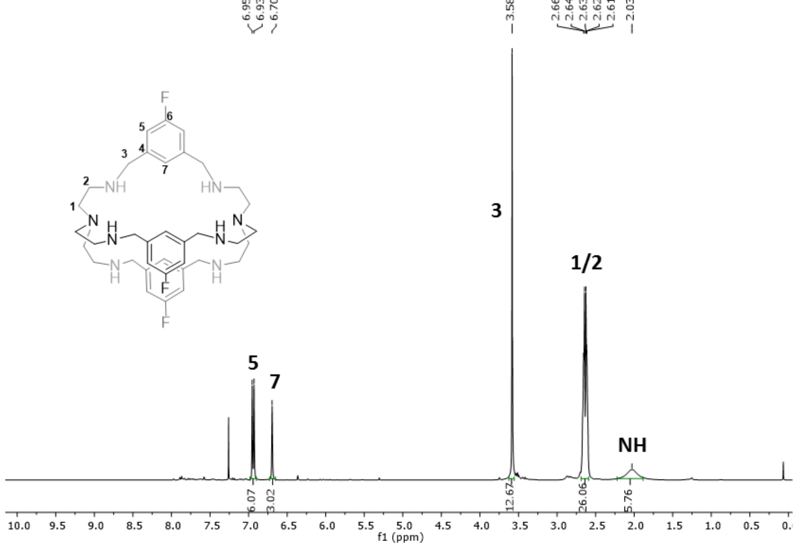

Figure S16. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of $\mathbf{L_A^F}$.

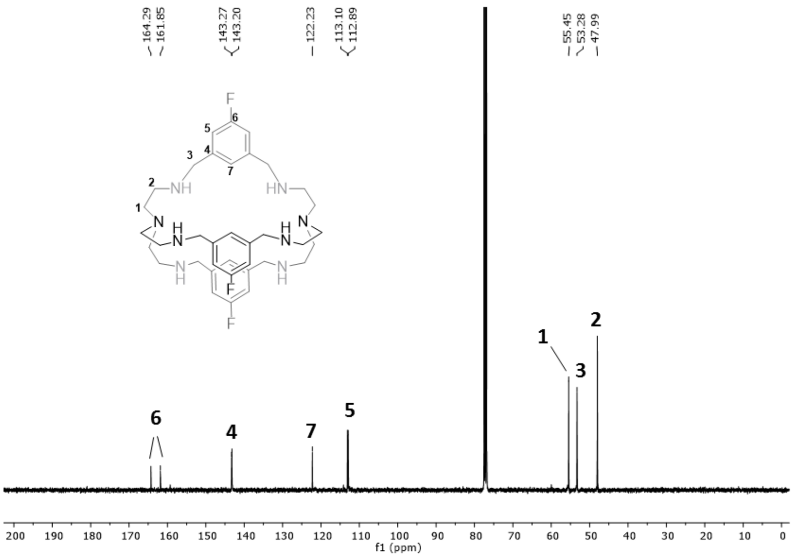

Figure S17. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of $\mathbf{L_A^F}$.

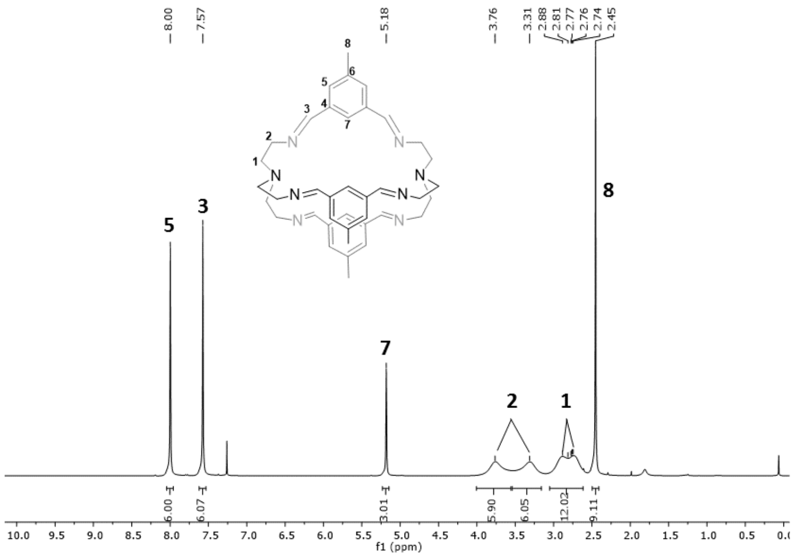

Figure S18. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of $\mathbf{L_I^{Me}}$.

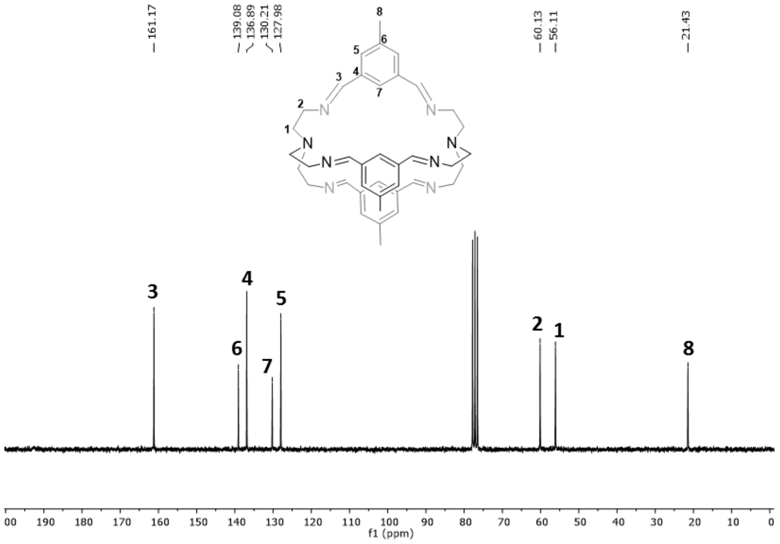

Figure S19. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of $\mathbf{L_I^{Me}}$.

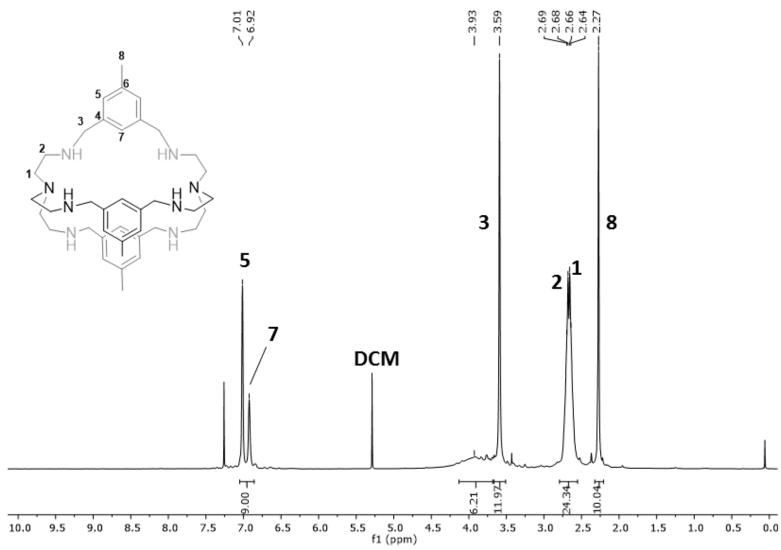

Figure S20. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of $\mathbf{L_A^{Me}}$.

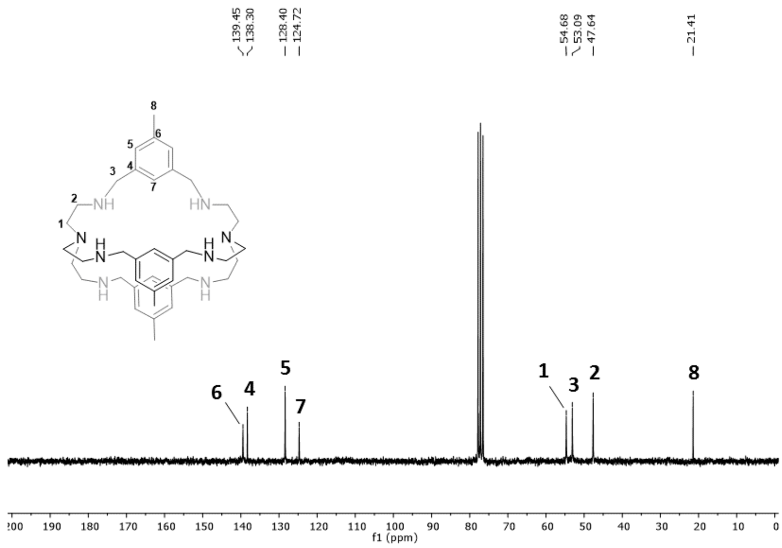

Figure S21. ^{1}H NMR spectrum ($CDCl_3$, 100 MHz) of $\mathbf{L_A^{Me}}$.

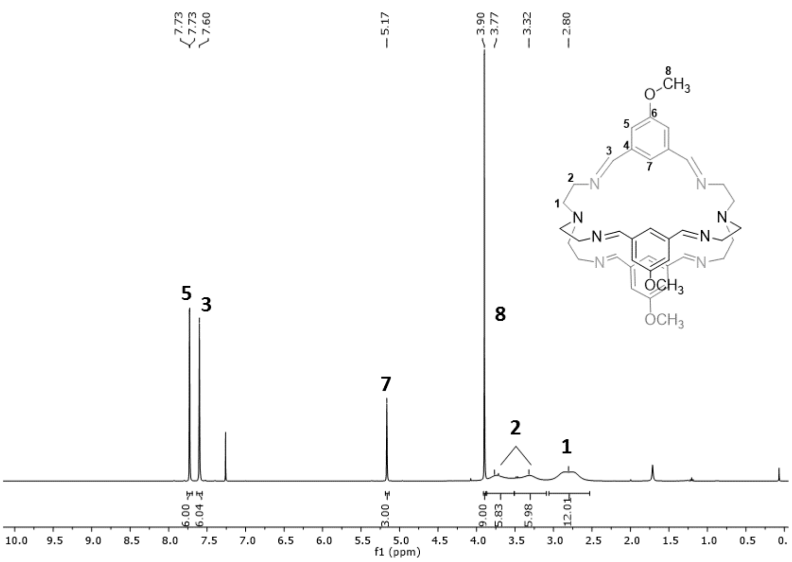

Figure S22. ^{1}H NMR spectrum ($CDCl_3$, 200 MHz) of hexa-imine $\mathbf{L_I^{OMe}}$.

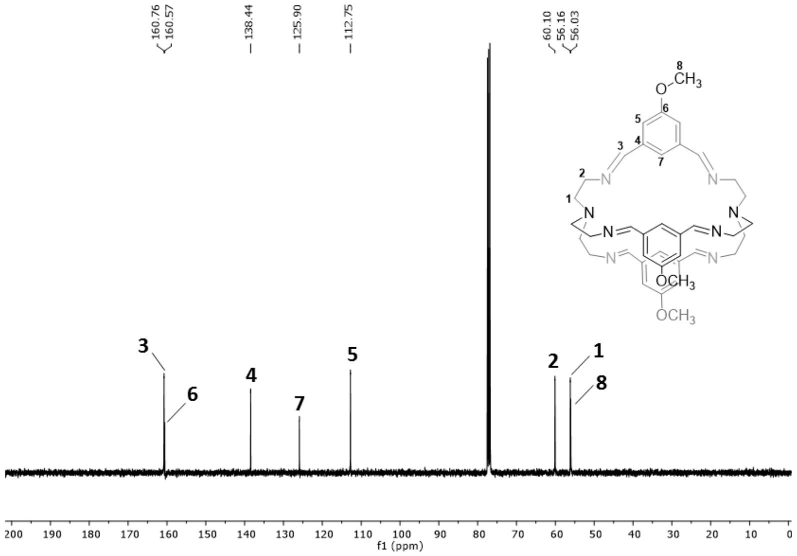

Figure S23. ^{13}C NMR spectrum ($CDCl_3$, 50 MHz) of hexa-imine **L$_I^{OMe}$**.

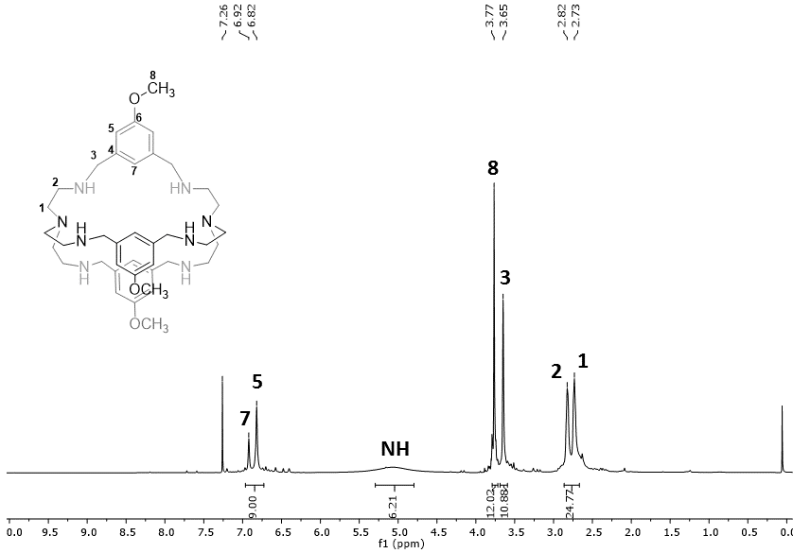

Figure S24. ^{1}H NMR spectrum ($CDCl_3$, 200 MHz) of **L$_A^{OMe}$**.

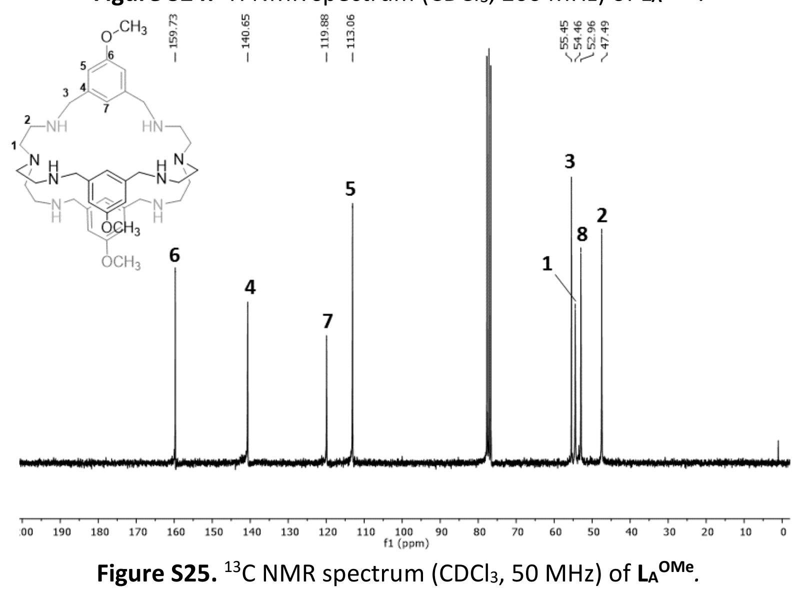

Figure S25. ^{13}C NMR spectrum ($CDCl_3$, 50 MHz) of **L$_A^{OMe}$**.

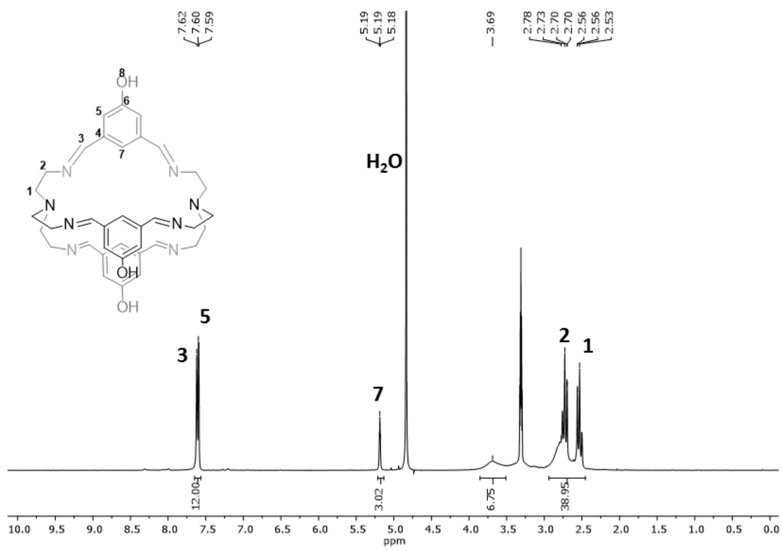

Figure S26. ^1H NMR spectrum (MeOD, 250 MHz) of $\mathbf{L_I^{OH}}$.

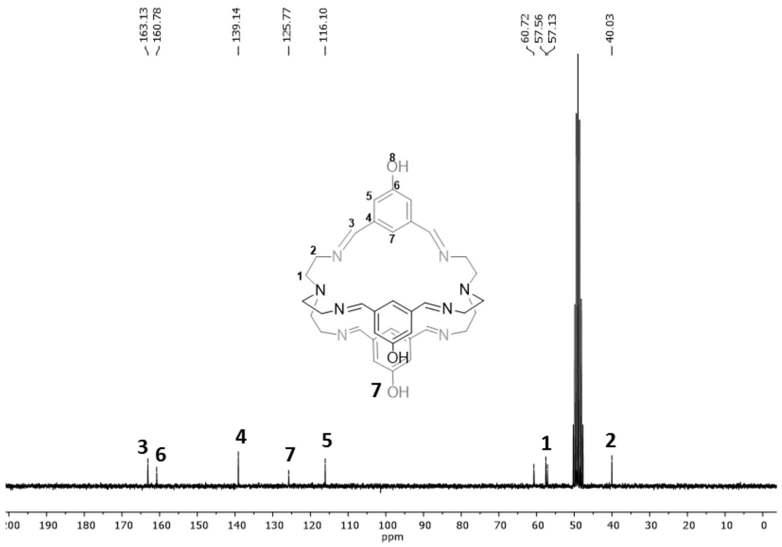

Figure S27. ^{13}C NMR spectrum (MeOD, 50 MHz) of $\mathbf{L_I^{OH}}$.

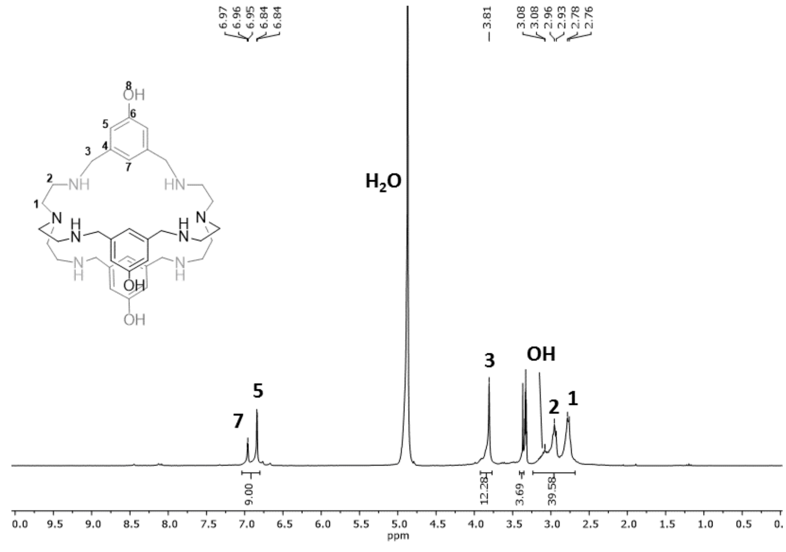

Figure S28. ^1H NMR spectrum (MeOD, 250 MHz) of $\mathbf{L_A^{OH}}$.

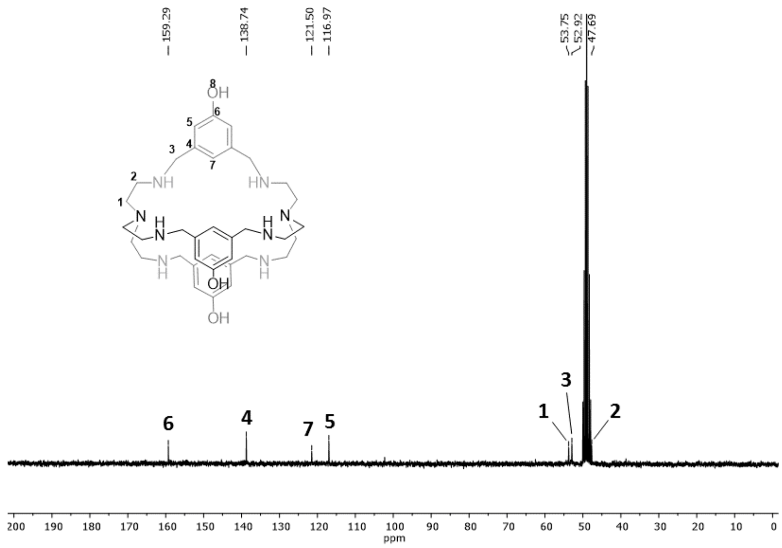

Figure S29. ^{13}C NMR spectrum (MeOD, 50 MHz) of $\mathbf{L_A^{OH}}$.

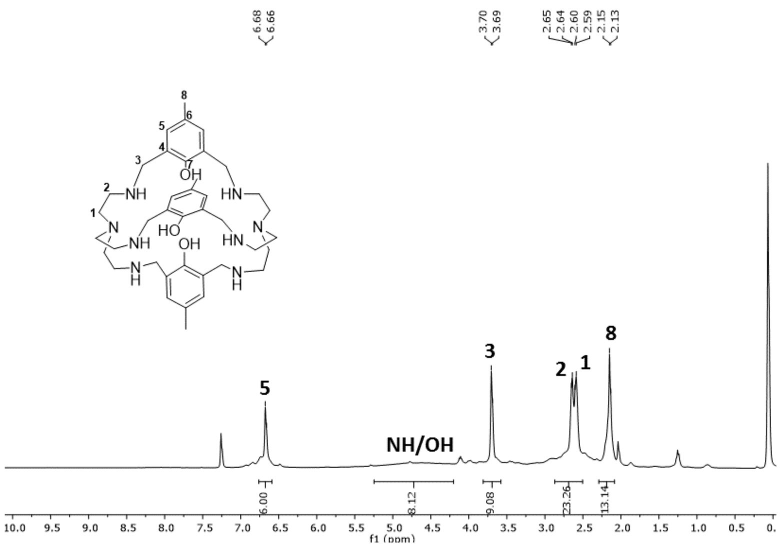

Figure S30. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of $\mathbf{L_A^{OH,Me}}$.

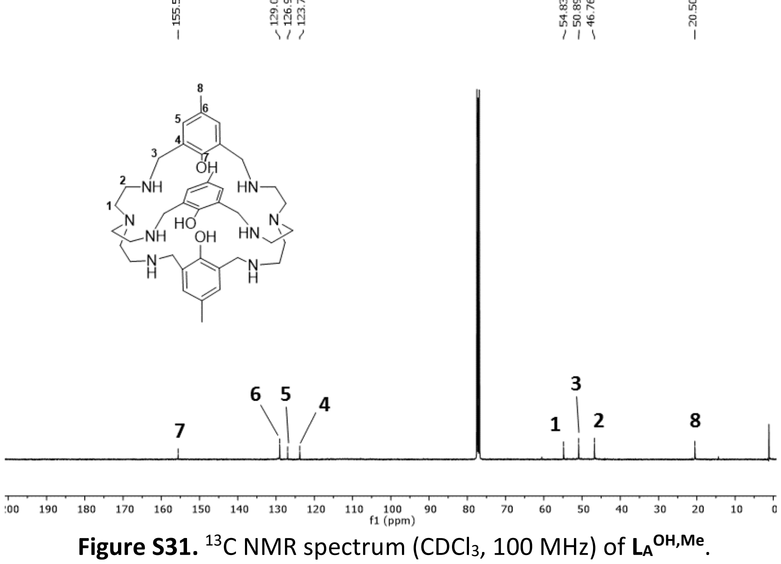

Figure S31. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of $\mathbf{L_A^{OH,Me}}$.

Table S4. Crystallographic data of **[(Tren)Ni(CH_3CN)$_2$](ClO_4)$_2$** and **[$Ni_2L_A^{Thio}$](ClO_4)$_4$.**

	[(Tren)Ni(CH_3CN)$_2$](ClO_4)$_2$	**[$Ni_2L_A^{Thio}$](ClO_4)$_4$**
Empirical formular	$C_{10}H_{24}Cl_2N_6NiO_8$	$C_{38}H_{61}Cl_4N_{12}Ni_2O_{18}S_3$*
Formular weight [g·mol^{-1}]	485.96	1329.35
Temperature [K]	110.15	170(2)
λ [Å]	CuK$_\alpha$, 1.54184	MoK$_\alpha$, 0.71073
Crystal system	Orthorhombic	Triclinic
Space group	Cmc2$_1$	P-1
a [Å]	31.9793(9)	10.180(5)
b [Å]	10.8558(3)	15.292(5)
c [Å]	11.0677(4)	21.793(5)
α [°]	90	101.454(5)
β [°]	90	103.465(5)
γ [°]	90	102.672(5)
V [Å^3]	3842.27(19)	3105.3(5)
Z	8	2
ρ_{ber} [g·cm^{-3}]	1.680	1.422
μ [mm^{-1}]	4.502	0.950
F(000)	2016.0	1278.0
2θ for data collection [deg]	8.602 to 152.378	3.002 to 53.32
Index-ranges	-36 ≤ h ≤ 39, -4 ≤ k ≤ 13, -13 ≤ l ≤ 9	-12 ≤ h ≤ 12, -16 ≤ k ≤ 19, -26 ≤ l ≤ 23
Reflections collected	4184	22448
Independent reflections	2652	10966
R_{int}	0.0308	0.0673
S[a)]	1.184	1.090
R_1 [I ≥ 2σ(I)][b)]	0.0493	0.1246
wR_2 [all data, F^2][c)]	0.1381	0.3811
Residual electron density [e Å^{-3}]	0.95/-0.60	1.434/-1.129
CCDC number	1517786	1517782

a) $S = \{\sum[w(F_0^2 - F_c^2)^2]\}/(n-p)\}^{0.5}$, n = number of reflections, p = number of parameters.

b) $R_1 = \sum|F_0|| \, |F_c|| \, \sum|F_0|$. c) $wR_2 = \{\sum[w(F_0^2 - F_c^2)^2 / \sum[(F_0^2)^s]\}^{0.5}$

*One perchlorate molecule was squeezed.[3]

Table S5. Crystallographic data of **[$Ni_2L_A^F(N_3)$](ClO_4)$_3$**, and **[$Ni_2L_A^{OH,Me}$](ClO_4)$_2$**.

	[$Ni_2L_A^F(N_3)$](ClO_4)$_3$	**[$Ni_2L_A^{OH,Me}$](ClO_4)$_2$**
Empirical formular	$C_{90}H_{137}Cl_6F_6N_{29}Ni_4O_{28}\cdot 1.68\ C_2H_6O$	$C_{43}H_{63}Cl_2N_{10}Ni_2O_{11}$
Formular weight [g·mol^{-1}]	2696.14	1083.81
Temperature [K]	100(2)	170(2)
λ [Å]	CuK$_\alpha$, 1.54184	MoK$_\alpha$, 0.71073
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	P2$_1$/c
a [Å]	67.725(3)	13.2094(10)
b [Å]	12.0716(7)	14.0369(6)
c [Å]	29.6586(15)	25.4984(19)
α [°]	90	90
β [°]	90.888(5)	92.086(9)
γ [°]	90	90
V [Å^3]	24245(2)	4724.8(5)
Z	8	4
ρ_{ber} [g·cm^{-3}]	1.477	1.524
μ [mm^{-1}]	2.696	0.981
F(000)	11261.4	2276.0
2θ for data collection [deg]	6.544 to 152.856	6.02 to 56.26
Index-ranges	-85 ≤ h ≤ 64, -15 ≤ k ≤ 13, -37 ≤ l ≤ 34	-17 ≤ h ≤ 17, -18 ≤ k ≤ 17, -33 ≤ l ≤ 33
Reflections collected	44869	42885
Independent reflections	22018	10314
R*int*	0.1394	0.0441
S[a)]	1.039	1.084
R$_1$ [I ≥ 2σ(I)][b)]	0.1386	0.0686
*w*R$_2$ [all data, F^2][c)]	0.4619	0.1999
Residual electron density [e Å^{-3}]	1.43/-1.13	1.13/-1.29
CCDC number	1517783	1517781

a) $S = \{\sum[w(F_0^2 - F_c^2)^2]\}/(n-p)\}^{0.5}$, n = number of reflections, p = number of parameters.

b) $R_1 = \sum|F_0|| \ |F_c|| \ \sum|F_0|$. c) $wR_2 = \{\sum[w(F_0^2 - F_c^2)^2 / \sum[(F_0^2)^s]\}^{0.5}$

Table S6. Crystallographic data of $\mathbf{L_I^F}$, $\mathbf{L_I^{OMe}}$ and $\mathbf{L_A^{Py}}$.

	$\mathbf{L_I^F}$	$\mathbf{L_I^{OMe}}$	$\mathbf{L_A^{Py}}$
Empirical formular	$C_{36}H_{39}F_3N_8$	$C_{39}H_{51}N_8O_3$	$C_{35}H_{62}Cl_2N_{12}O_3$*
Formular weight [g·mol^{-1}]	640.44	679.88	769.85
Temperature [K]	170(2)	293(2)	170(2)
λ [Å]	MoK$_\alpha$, 0.71073	MoK$_\alpha$, 0.71073	MoK$_\alpha$, 0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	Cc	Pna2$_1$	C2/c
a [Å]	15.888(3)	14.368(2)	16.679(3)
b [Å]	13.4639(18)	20.759(2)	19.9817(18)
c [Å]	16.442(3)	12.3557(9)	14.9744(15)
α [°]	90	90	90
β [°]	102.98(2)	90	120.298(10)
γ [°]	90	90	90
V [Å^3]	3427.3(10)	3685.3(7)	4308.9(10)
Z	4	4	4
ρ_{ber} [g·cm^{-3}]	1.241	1.225	1.187
μ [mm^{-1}]	0.087	0.080	0.206
F(000)	1352.0	1460.0	1528.0
2θ for data collection [deg]	5.054 to 56.44	3.84 to 47.96	5.82 to 73.24
Index-ranges	-21 ≤ h ≤ 21, -17 ≤ k ≤ 17, -21 ≤ l ≤ 21	-16 ≤ h ≤ 16, -23 ≤ k ≤ 23, -13 ≤ l ≤ 14	-27 ≤ h ≤ 25, -26 ≤ k ≤ 27, -24 ≤ l ≤ 24
Reflections collected	17944	24606	39717
Independent reflections	17944	5630	6847
R$_{int}$	0.0748	0.0646	0.0520
S$^{a)}$	0.782	0.873	1.054
R_1 [I ≥ 2σ(I)]$^{b)}$	0.0793	0.0629	0.0845
wR_2 [all data, F^2]$^{c)}$	0.2570	0.1853	0.2812
Residual electron density [e Å^{-3}]	0.38/-0.43	0.19/-0.21	0.58/-0.41
CCDC number	1517784	1517785	1517950

$^{a)}$ $S = \{\sum[w(F_0^2 - F_c^2)^2]\}/(n-p)\}^{0.5}$, n = number of reflections, p = number of parameters.

$^{b)}$ $R_1 = \sum|F_0|| \; |F_c|| \; \sum|F_0|$. $^{c)}$ $wR_2 = \{\sum[w(F_0^2 - F_c^2)^2 / \sum[(F_0^2)^s]\}^{0.5}$

*One water and acetonitrile molecule was squeezed.[3]

Table S7. Crystallographic data of $\mathbf{L_I^{Me}}$ and $\mathbf{L_A^{OH}}$.

	$\mathbf{L_I^{Me}}$	$\mathbf{L_A^{OH}}$
Empirical formular	$C_{39}H_{48}N_8$	$C_{40}H_{75}Cl_6N_{10}O_{16}$
Formular weight [g·mol^{-1}]	628.86	1148.8
Temperature [K]	170(2)	100(2)
λ [Å]	MoK$_\alpha$, 0.71073	CuK$_\alpha$, 1.54184
Crystal system	Orthorhombic	Triclinic
Space group	Pna2$_1$	P-1
a [Å]	14.4185(18)	11.1345(2)
b [Å]	20.046(3)	14.5818(3)
c [Å]	12.574(2)	18.3859(4)
α [°]	90	107.412(2)
β [°]	90	101.170(2)
γ [°]	90	102.173(2)
V [Å^3]	3634.3(9)	2676.69(9)
Z	4	2
ρ_{ber} [g·cm^{-3}]	1.149	1.425
μ [mm^{-1}]	0.070	3.540
F(000)	1160.0	1214.0
2θ for data collection [deg]	5.66 to 56.5	6.64 to 152.72
Index-ranges	-19 ≤ h ≤ 18, -26 ≤ k ≤ 24, -16 ≤ l ≤ 16	-13 ≤ h ≤ 12, -18 ≤ k ≤ 18, -22 ≤ l ≤ 22
Reflections collected	26225	51557
Independent reflections	8835	9971
R_{int}	0.1620	0.0428
S[a)]	0.540	1.062
R_1 [I ≥ 2σ(I)][b)]	0.0595	0.0571
wR_2 [all data, F^2][c)]	0.1933	0.1532
Residual electron density [e Å^{-3}]	0.26/-0.16	1.57/-1.04
CCDC number	1517787	1517780

a) $S = \{\sum[w(F_0^2 - F_c^2)^2]\}/(n-p)\}^{0.5}$, n = number of reflections, p = number of parameters.

b) $R_1 = \sum|F_0|| \, |F_c|| \, \sum|F_0|$. c) $wR_2 = \{\sum[w(F_0^2 - F_c^2)^2 / \sum[(F_0^2)^s]\}^{0.5}$

Cartesian coordinates [Angstrom] of geometry optimized structures (including COSMO) of $\mathbf{Ni_2L_A^R}$.

R=H

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7	-3.540193000	12.394114000	18.903180000
7	1.436327000	5.282269000	19.688733000
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1	-5.131605000	10.941275000	16.231423000
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1	0.140224000	3.912643000	18.749950000
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R=F

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7	1.839295000	5.660543000	16.454057000
1	2.371018000	6.135403000	15.711586000
7	-3.154607000	9.869458000	20.104236000
1	-4.032453000	9.504478000	19.709229000
7	-3.551226000	12.397754000	18.889595000
7	1.432929000	5.279118000	19.678449000
1	1.413356000	5.907910000	20.490750000
7	3.979554000	5.431176000	18.330518000
7	3.795699000	8.093732000	17.274985000
1	3.987592000	8.719477000	18.066684000
7	-0.953612000	12.609532000	17.769941000
1	-0.264990000	12.630946000	18.536224000
6	-1.205449000	6.758038000	20.119280000
1	-0.321412000	7.232826000	20.560297000
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7	-3.167828000	10.398809000	16.913878000
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1	-1.548708000	9.112811000	21.231717000
7	2.793001000	7.773686000	19.954218000
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6	1.249297000	12.068295000	16.694920000
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