Supplementary Materials

[2 × 2] Molecular Grids of Ni(II) and Zn(II) with Redox-Active 1,4-Pyrazine-Bis(thiosemicarbazone) Ligands

Natalia Arefyeva, Aaron Sandleben, Alexander Krest, Ulrich Baumann, Mathias Schäfer, Maxim Kempf, Axel Klein*

Contents:

A) Experimental Section

Materials. Thiosemicarbazine was purchased from Acros Organics. All commercially available reagents were used without further purification. Solvents (THF, toluene, diethyl ether and CH_3CN) were dried using a MBRAUN MB SPS-800 solvent purification system.

Synthesis of the pyrazine-2,5-carbaldehydes (R = Me, Et, *i*Pr, Ph) - General procedure: Derived from a literature procedure,[1] *we* prepared an ice-cooled solution of 0.8 g (10 mmol) 1,4-pyrazine and the corresponding aldehyde (60 mmol) in 15 mL water and added 15 mL acetic acid and 3 mL of conc. sulfuric acid. To this mixture, 3.87 mL of a solution of *t*-butyl hydroperoxide (70% solution in H_2O) (40 mmol) and a solution of 5.56 g iron(II)sulfate (20 mmol) in 20 mL water were added simultaneously and dropwise. After stirring for 1 h the dark brown reaction mixture was filtered and the thus obtained yellow products were recrystallized from ethanol. **Important:** These syntheses require a lot of experience concerning the temperature, the sequence of adding the reagents, and even the polarity of the reaction mixture.

2,5-diacetylpyrazine: Yellow solid. Yield: 0.56 g (34%). Anal. Calc. for $C_8H_8N_2O_2$: C, 58.53; H, 4.91; N, 17.06. Found: C, 58.63; H, 4.70; N, 17.02%. MS (EI+ 20eV, *m/z*): 164$[M]^+$, 149. ^{1}H NMR, (300 MHz, DMSO-d_6): 9.3 (s, 2H, H_{pz}), 2.8 (s, 6H, H_{Me}) ppm.

2,5-dipropionylpyrazine: Yellow solid. Yield: 0.59 g (35 %). Anal. Calc. for $C_{10}H_{12}N_2O_2$: C, 62.49; H, 6.29; N, 14.57. Found: C, 62.58; H, 8.62; N, 14.55%. MS (EI$^+$ 20eV, *m/z*): 192$[M]^+$. ^{1}H NMR, (300 MHz, DMSO-d_6): 9.19 (s, 2H, H_{pz}), 3.24-3.17 (q, 4H, H_{CH2}), 1.14-1.09 (t, 6H, H_{Me}) ppm.

2,5-diisobutanylpyrazin: Yellow solid. Yield: 0.77 g (35%). Anal. Calc. for $C_{12}H_{16}N_2O_2$: C, 65.43; H, 7.32; N, 12.72; Found: C, 64.38; H, 6.67; N, 12.61%. MS (EI+ 20eV, *m/z*): 220$[M]^+$. ^{1}H NMR, (300 MHz, acetone-d_6): 9.19 (s, 2H, H_{pz}), 4.05-3.96 (m, 2H, H_{CH}), 1.20-1.18 (d, 12H, H_{Me}) ppm.

2,5-dibenzoylpyrazin: Yellow solid. Yield: 1.30 g (45%). Anal. Calc. for $C_{18}H_{12}N_2O_2$: C, 74.99; H, 4.20; N, 9.72; Found: N, C, 74.97; H, 4.04; 9.64%. MS (EI+ 20eV, *m/z*): 288$[M]^+$. ^{1}H NMR, (300 MHz,

DMSO-d_6): 9.26 (s, 2H, H_{pz}), 8.06-8.03 (d, 4H, $H_{Ph1/Ph5}$), 7.78-7.73 (t, 2H, H_{Ph3}), 7.63-7.58 (t, 4H, $H_{Ph2/Ph4}$) ppm.

Synthesis of the bis(thiosemicarbazone) ligands - General procedure: A solution of the pyrazine-2,5-carbaldehyde (1.0 mmol) in toluene was heated to 105 °C. To this solution was added 0.21 g (2.3 mmol) thiosemicarbazide dissolved in hot water and the reaction mixture was acidified with glacial acetic acid. The mixture was stirred at 105 °C for 5-24 h and the product precipitated as a yellow solid. The solid was vacuum filtered and washed with hot water, ethanol and then dried.

H_2L^{Me}: Yellow solid. Yield: 0.28 g (90%). Anal. Calc. for $C_{10}H_{14}N_8S_2$: C, 38.69; H, 4.55; N, 36.10; S, 20.66. Found: C, 39.03; H, 4.35; N, 36.47; S, 19.55%. MS (EI+ 20eV, *m/z*): 310$[M]^+$. ^{1}H NMR, (600 MHz, DMSO-d_6): 10.50 (s, 2H, -N*H*), 9.60 (s, 2H, H_{pz}), 8.47 (s, 2H, -NH_a), 8.30 (s, 2H, -NH_b), 2.39 (s, 6H, H4) ppm. ^{13}C NMR (150.9 MHz, DMSO-d_6) δ [ppm]: 179.2 (C4), 148.9 (C2), 146.1(C3), 141.2 (C1), 11.9 (C_{Me}). ^{15}N NMR (60.83 MHz, DMSO-d_6) δ [ppm]: 325 (N1), 319 (N2) 168 (N3), 113 (N4); FT-IR: [cm^{-1}] = 3404 m, 3282 m, 3168 m, 2965 w, 1597 s, 1504 m, 1477 m, 1455 s, 1368 s, 1294 m, 1277 s, 1201 m, 1180 m, 1128 w, 1094 s, 1050 w, 1029 s, 960 m, 908 s, 850 s, 722 s, 613 s, 577 w, 494 s. UV-Vis (THF) λ_{max} [nm]: 389sh, 372, 277, 253.

H_2L^{Et}: Yellow solid. Yield: 0.21 g (63%). Anal. Calc. for $C_{12}H_{18}N_8S_2$: C, 42.58; H, 5.36; N, 33.11; S, 18.95. Found: C, 43.26; H, 5.59; N, 33.59; S, 18.91%. MS(EI+ 20eV, *m/z*): 338$[M]^+$, ^{1}H NMR (600 MHz, DMSO-d_6) δ [ppm]: 10.66 (s, 2H, NH), 9.57 (s, 2H, H_{pz}), 8.43 (s, 2H, NH_{2b}), 8.26 (s, 2H, NH_{2a}), 3.07-3.00 (q, 4H, H_{CH2}), 1.04-1.00 (t, 6H, H_{Me}). ^{15}N NMR (60.83 MHz, DMSO-d_6) δ [ppm]: 325 (N1), 315 (N2) 167 (N3), 112 (N4); FT-IR: [cm^{-1}] = 3418 m, 3225 m, 3145 m, 2980 w, 2938 w, 2871 w, 1597 s, 1500 s, 1448 s, 1372 m, 1278 s, 1243 m, 1183 m, 1095 s, 1052 s, 1025 m, 922 s, 858 s, 786 m, 708 m, 666 w, 579 s, 470 s. UV-Vis (THF) λ_{max} [nm]: 372, 277, 230sh.

H_2L^{iPr}: Yellow solid. Yield: 0.23 g (69%); Anal. Calc. for $C_{14}H_{22}N_8S_2$: C, 45.88; H, 6.05; N, 30.57; S, 17.50. Found: C, 46.25; H, 6.34; N, 29.80; S, 18.28%; MS(EI+ 20eV, *m/z*): 366$[M]^+$, ^{1}H NMR (600 MHz, DMSO-d_6) δ [ppm]: 12.56 (s, 2H, NH), 9.17 (s, 2H, H_{pz}), 8.59 (s, 2H, NH_{2b}), 7.87 (s, 2H, NH_{2a}), 3.40-3.35 (m, 4H, H_{CH}), 1.21-1.20 (d, 12H, H_{Me});); FT-IR: 3410 m, 3232 m, 3145 m, 2963 w, 2925 w, 2864 w, 1600 s, 1576 m, 1435 s, 1386 w, 1322 s, 1259 w, 1200 w, 1175 m, 1120 s, 1055 s, 1006 s, 911 m, 874 w, 838 s, 731 m, 656 m, 619 s, 568 s, 521 s, 499 s, 418 s cm^{-1}. UV-Vis (THF) λ_{max} [nm]: 421, 311, 258.

H_2L^{Ph}: Brown solid. Yield: 0.36 g (83%); Anal. Calc. for $C_{20}H_{18}N_8O_2$: C, 55.28; H, 4.18; N, 25.79; S, 14.76. Found: C, 54.65; H, 3.66; N, 25.49; S, 14.84%; MS(EI+ 20eV, *m/z*): 434$[M]^+$, ^{1}H NMR (600 MHz, DMSO-d_6) δ [ppm]: 11.37 (s, 2H, NH), 8.88 (s, 2H, H_{pz}), 8.56 (s, 2H, NH_{2b}), 8.25 (s, 2H, NH_{2a}), 7.79 (m, 4H, H_{Ph}), 7.47 (m, 6H, H_{Ph}); FT-IR: [cm^{-1}] = 1596 s, 1551 w, 1456 s, 1328 m, 1265 m, 1220 m, 1172 m, 1094 s, 1050 s, 1023 s, 943 m, 912 m, 845 s, 773 s, 734 m, 703 s, 689 w, 661 m, 637 w, 619 m, 532 s, 493 m, 426 s, 412 s. UV-Vis (THF) λ_{max} [nm]: 422sh, 406, 363, 289, 251.

(1) T. Caronna and G. Fronza, *J. Chem. Soc.* **1972**, 2035–3038.

B) Supporting Figures (Figures S1–S37)

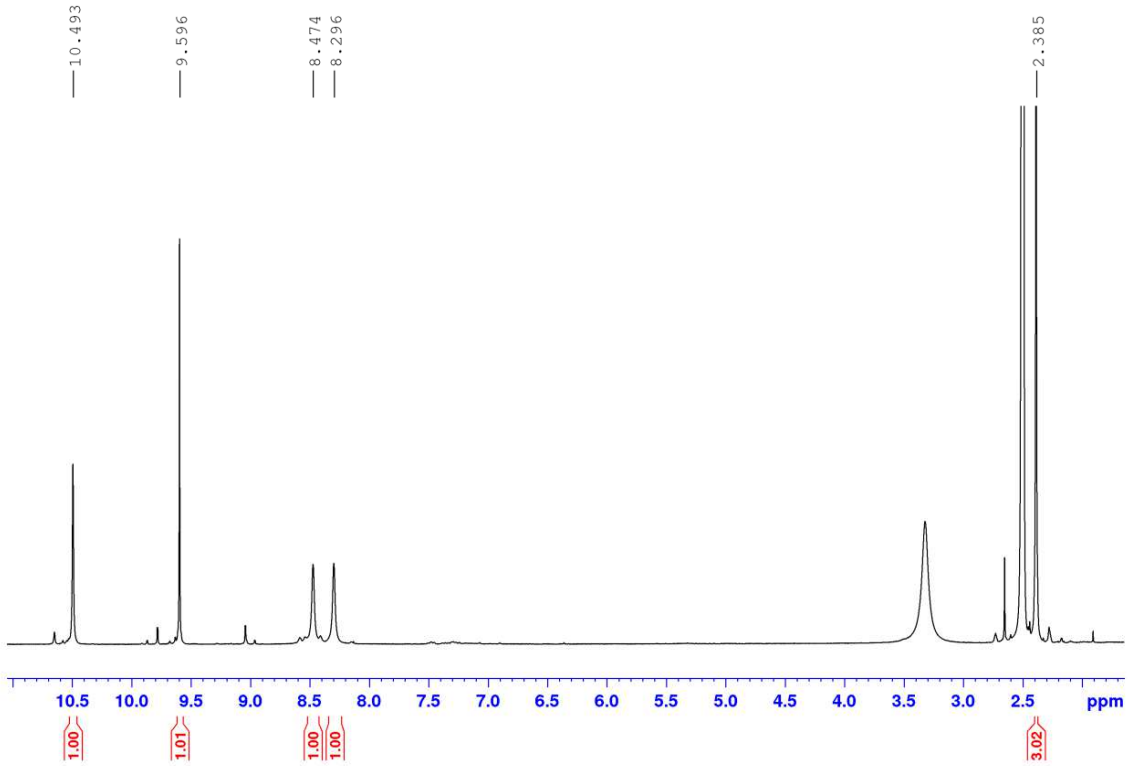

Figure S1. ^{1}H NMR spectrum of H_2L^{Me} in DMSO-d_6.

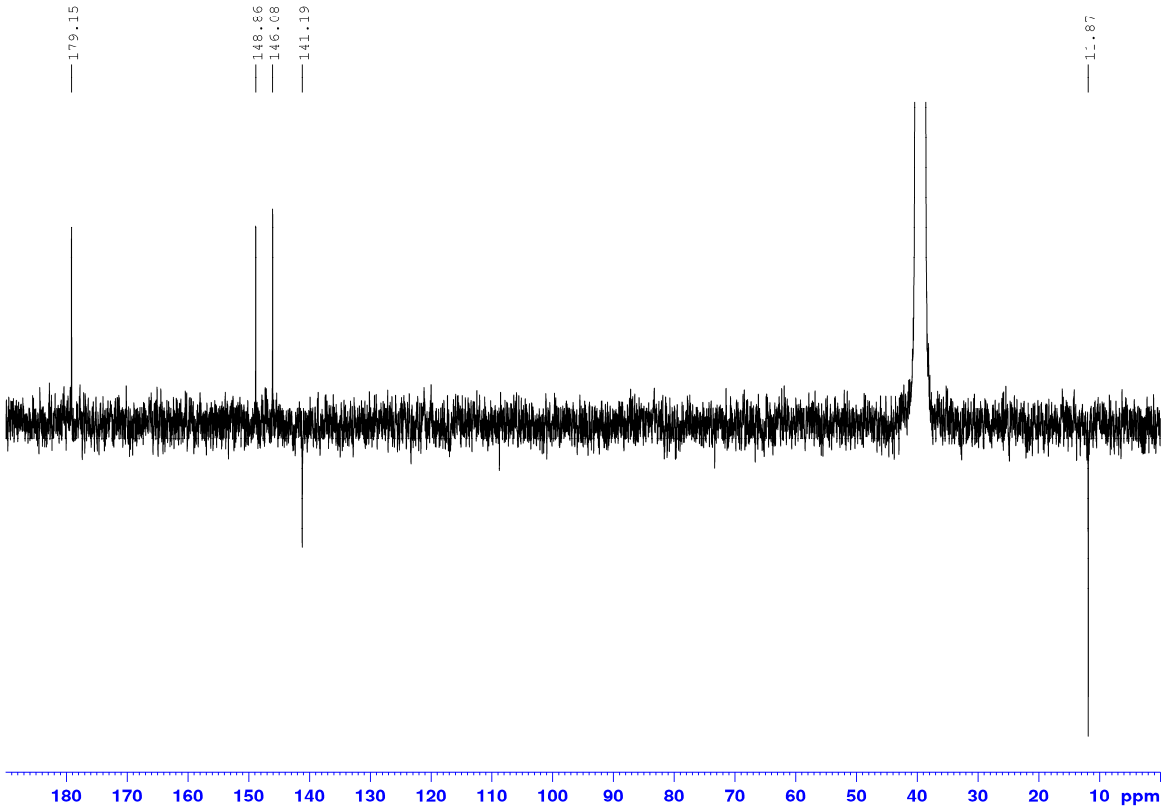

Figure S2. ^{13}C NMR APT spectrum of H_2L^{Me} in DMSO-d_6.

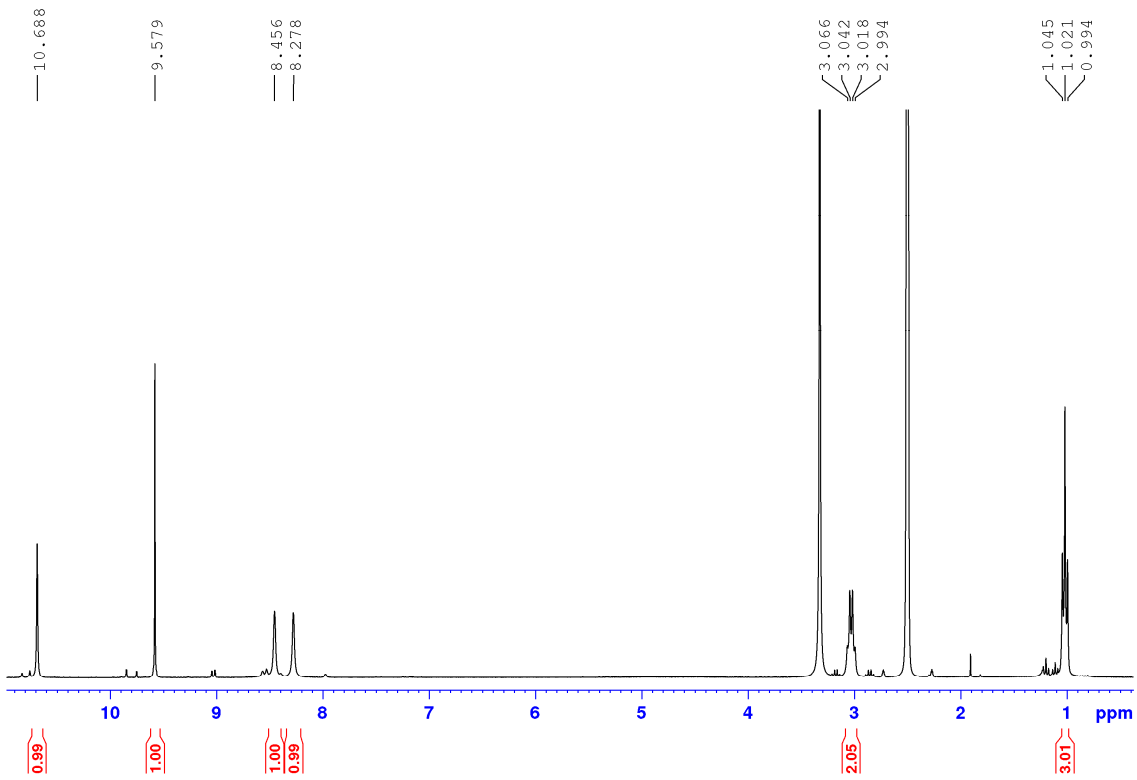

Figure S3. ^{1}H NMR spectrum of H_2L^{Et} in DMSO-d_6.

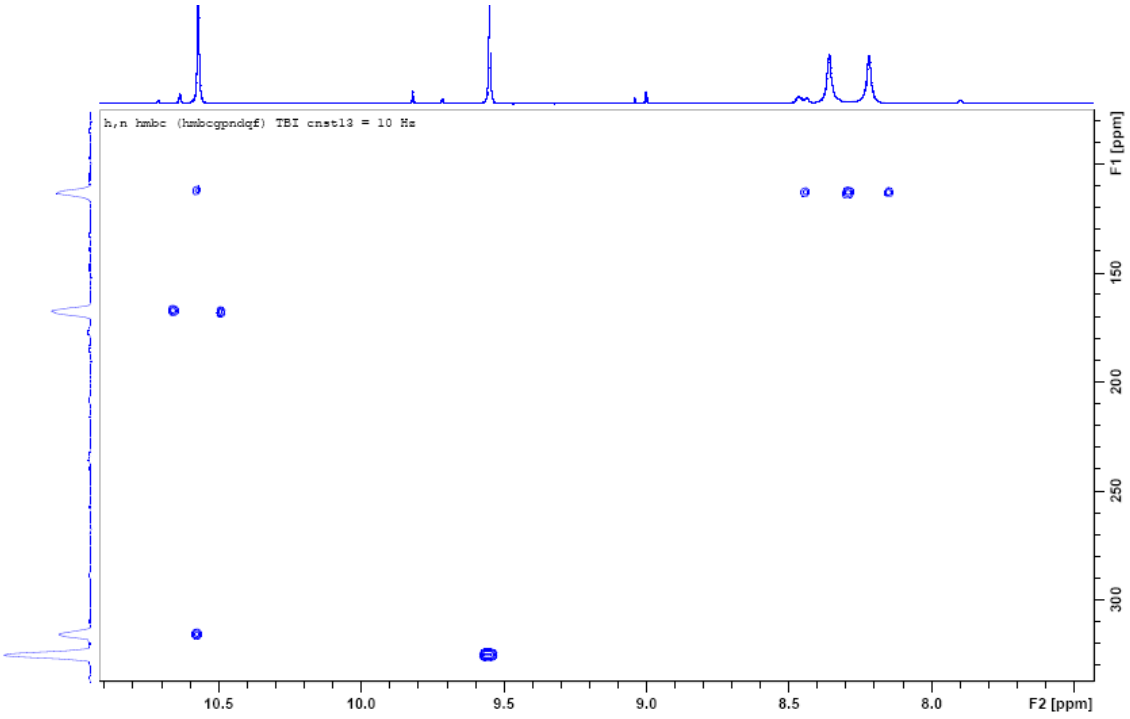

Figure S4. ^{15}N NMR HMBC spectrum of H_2L^{Et} in DMSO-d_6 (cnst13 = 10Hz).

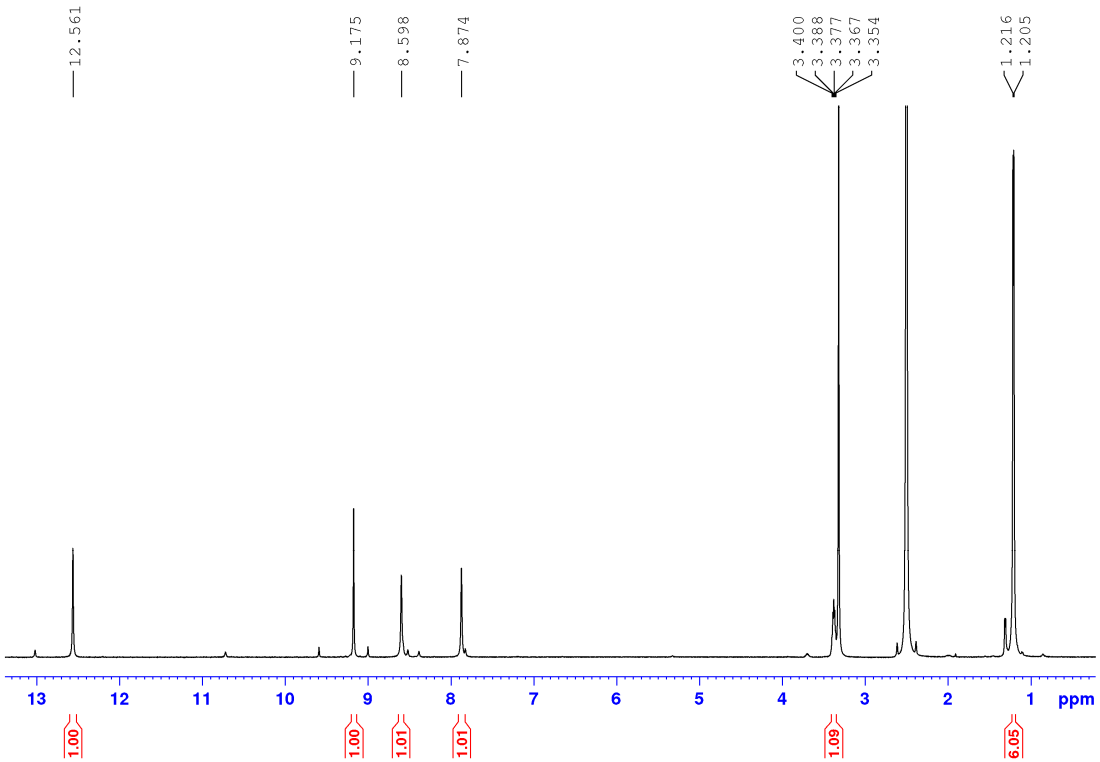

Figure S5. ^{1}H NMR spectrum of H_2L^{iPr} in DMSO-d_6.

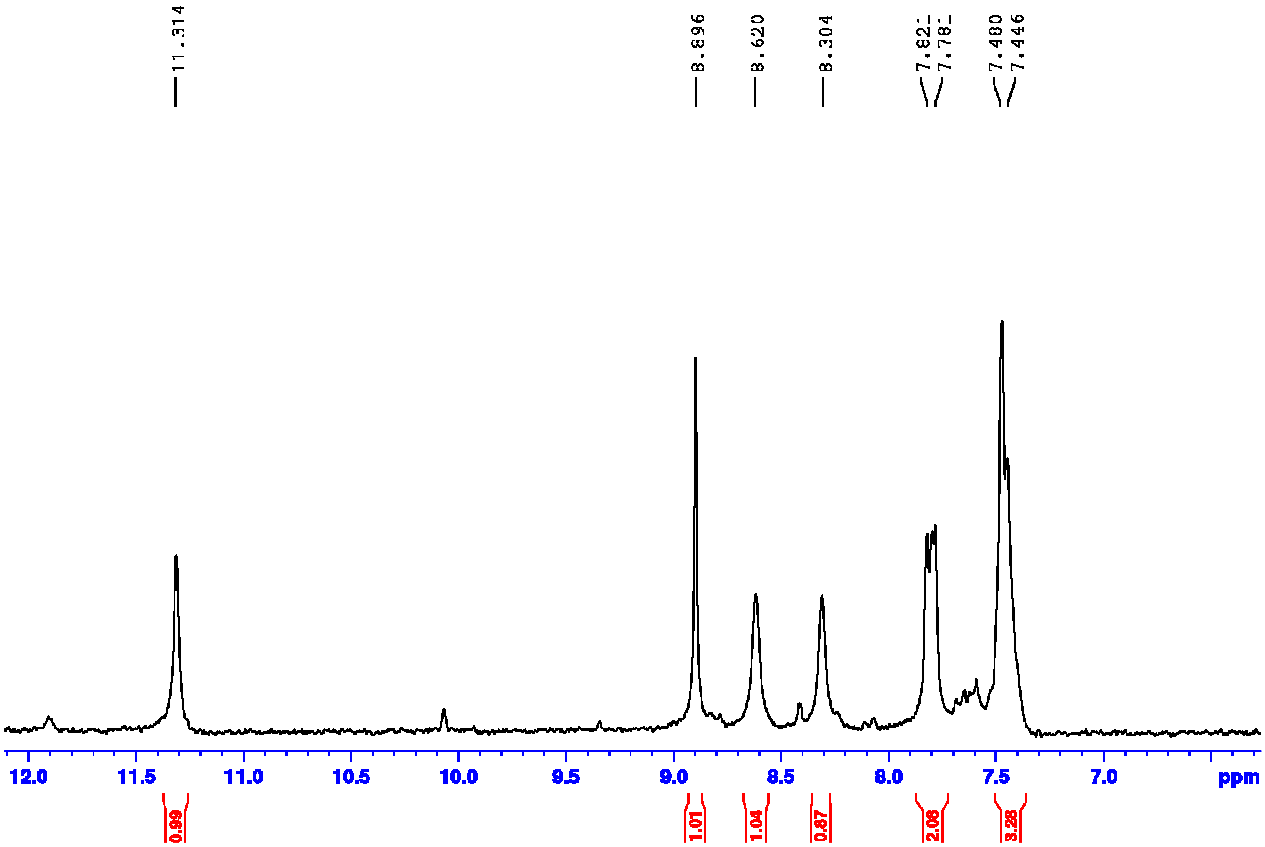

Figure S6. ^{1}H NMR spectrum of H_2L^{Ph} in DMSO-d_6.

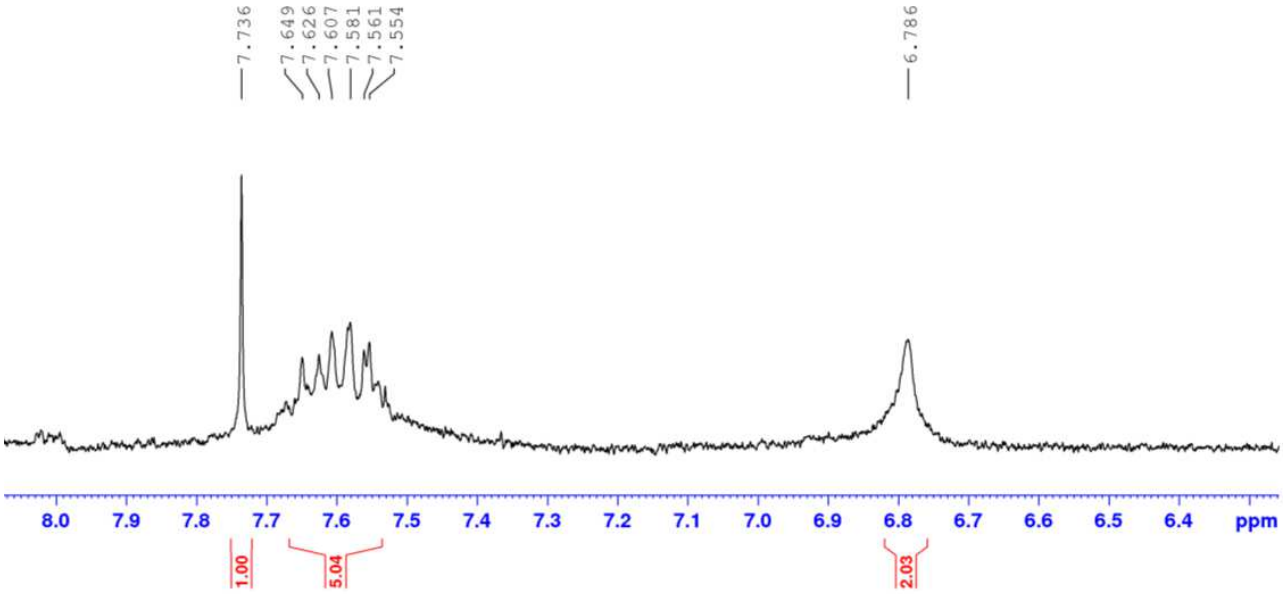

Figure S7. ^{1}H NMR spectrum of $[Zn_4(L^{Ph})_4]$ in acetone-d_6 with NS = 1024 und D_1 = 2 s.

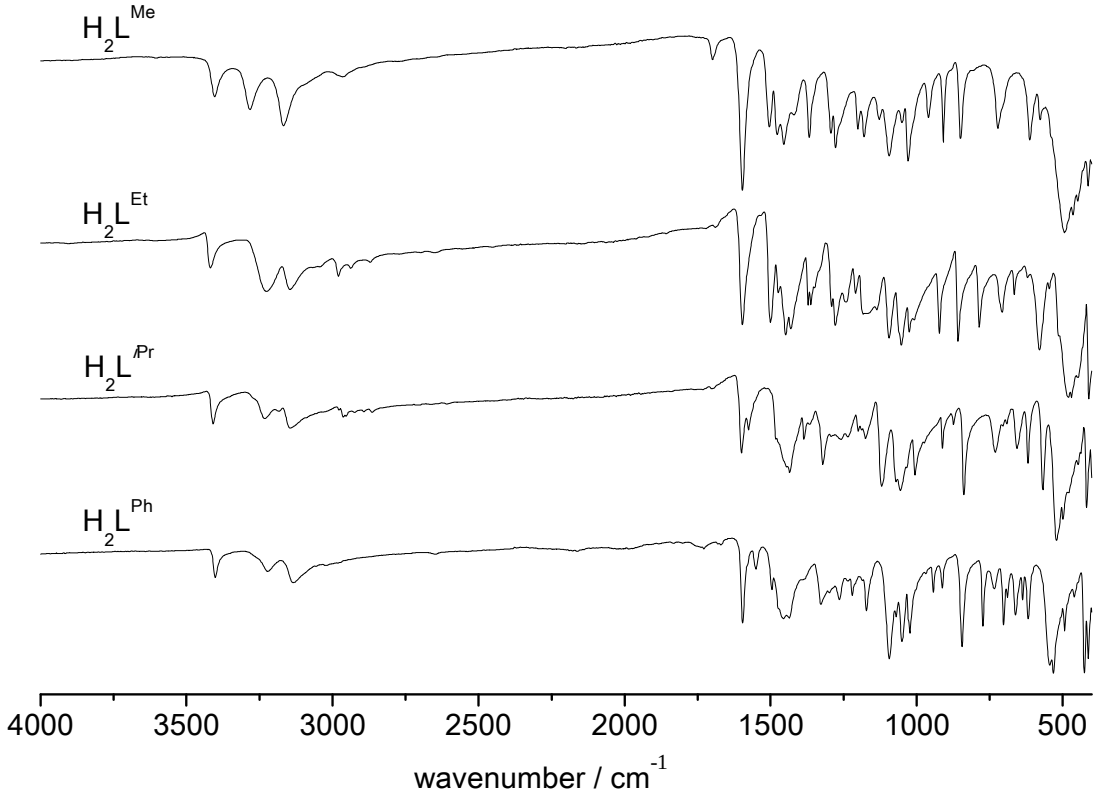

Figure S8. IR spectra of H_2L^R (neat).

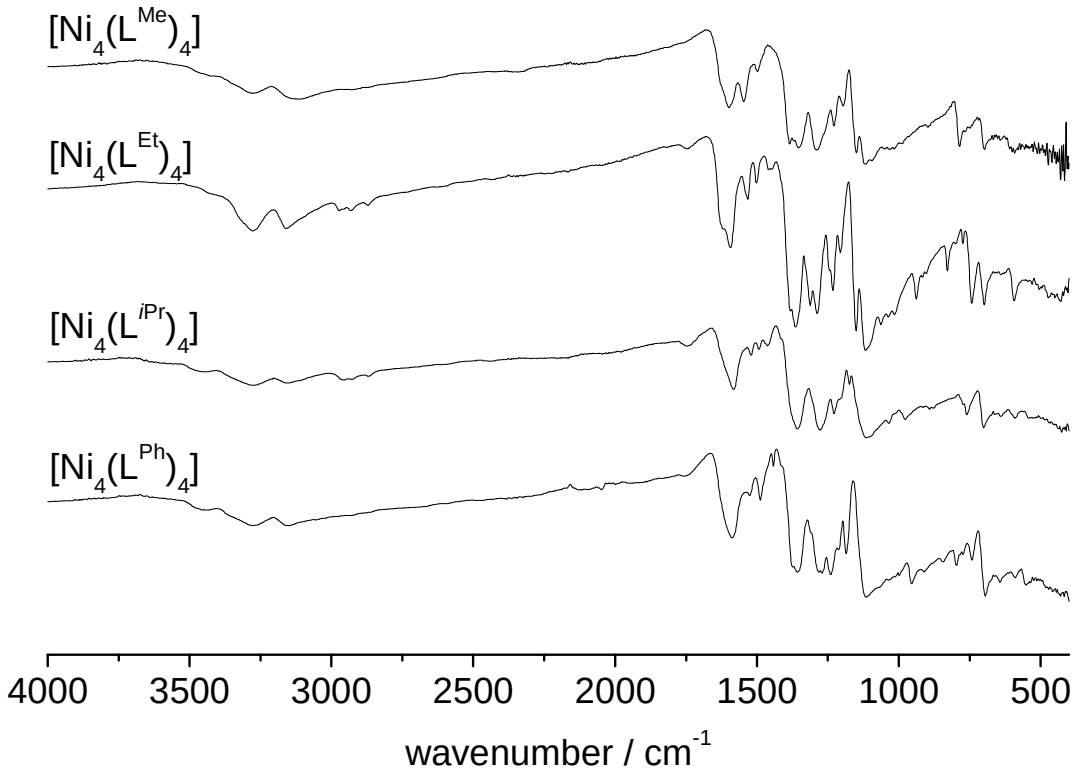

Figure S9. IR spectra of $[Ni_4(L^R)_4]$ (neat).

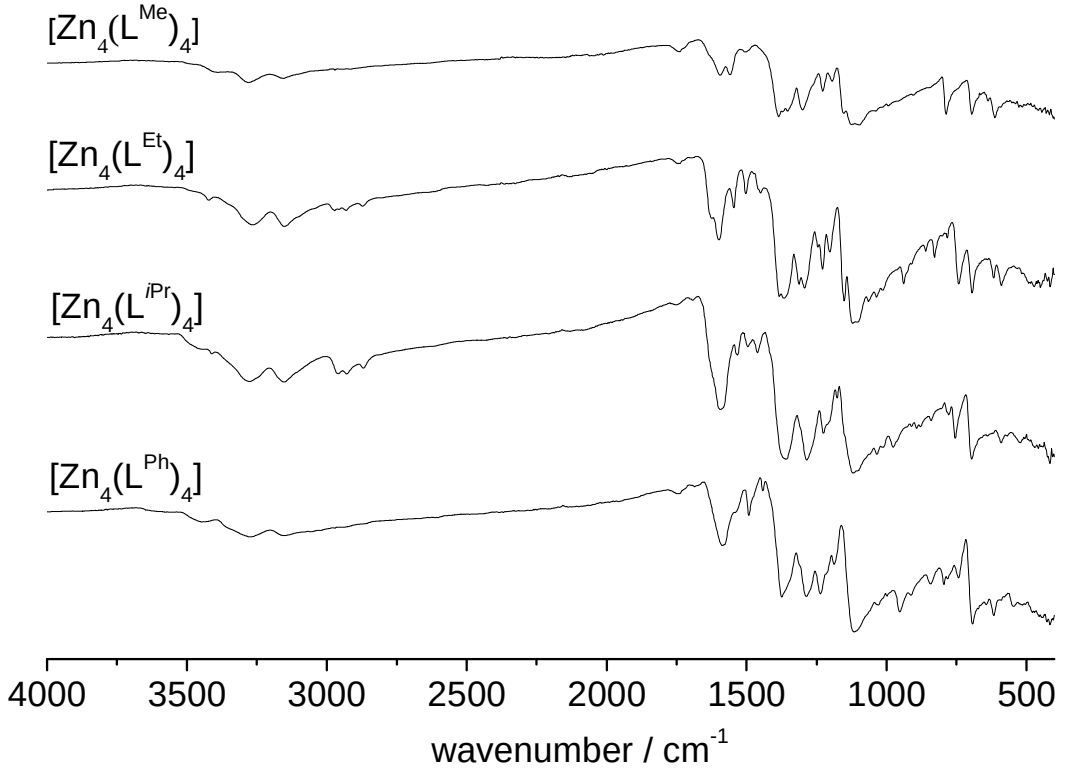

Figure S10. IR spectra of $[Zn_4(L^R)_4]$ (neat).

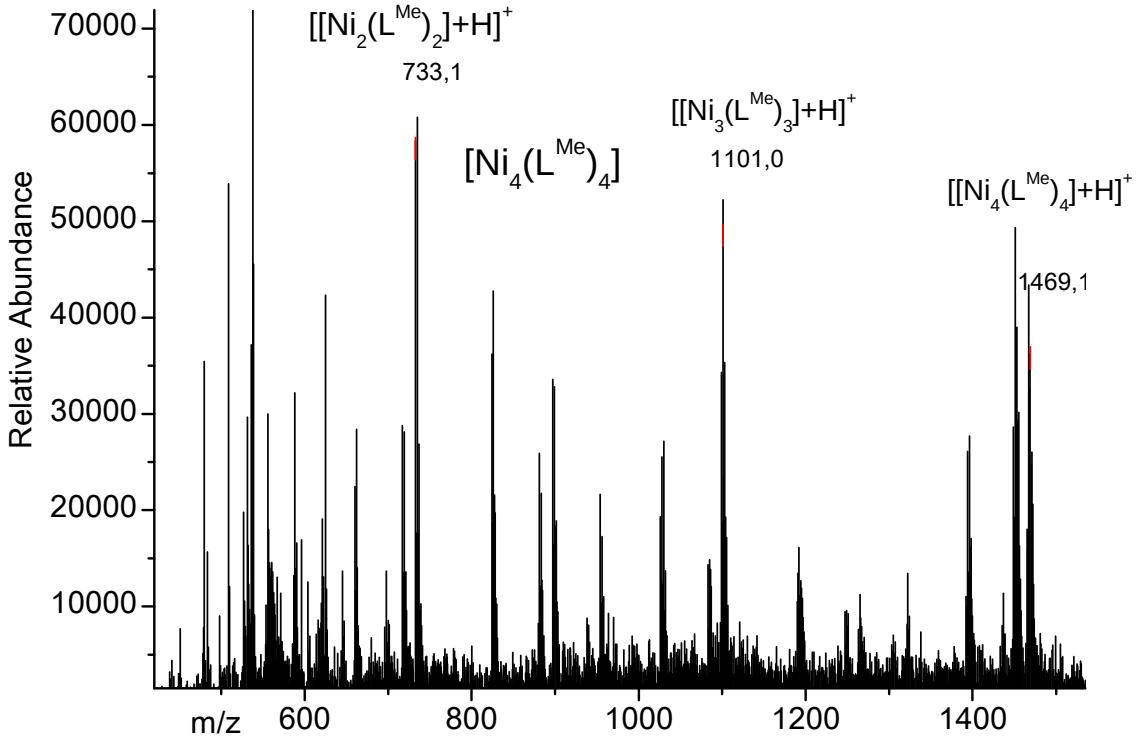

Figure S11. ESI MS(+) of $[Ni_4(L^{Me})_4]$.

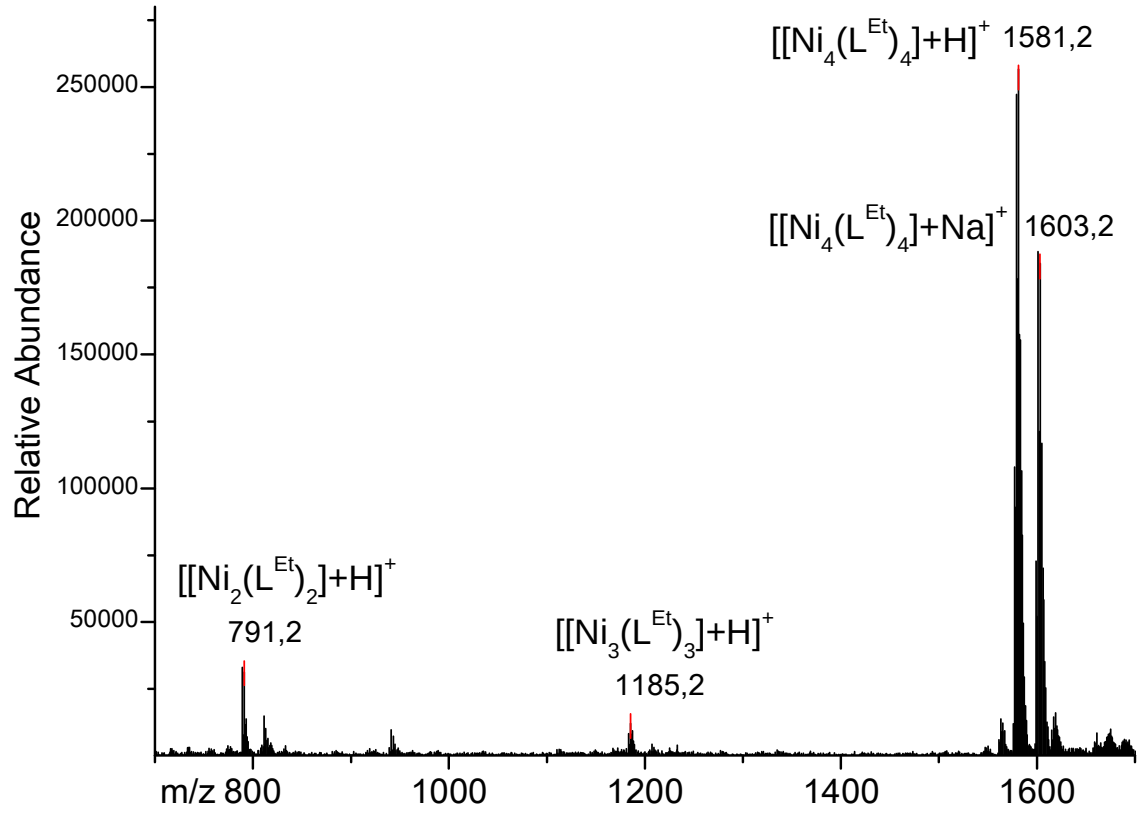

Figure S12. ESI MS(+) of $[Ni_4(L^{Et})_4]$.

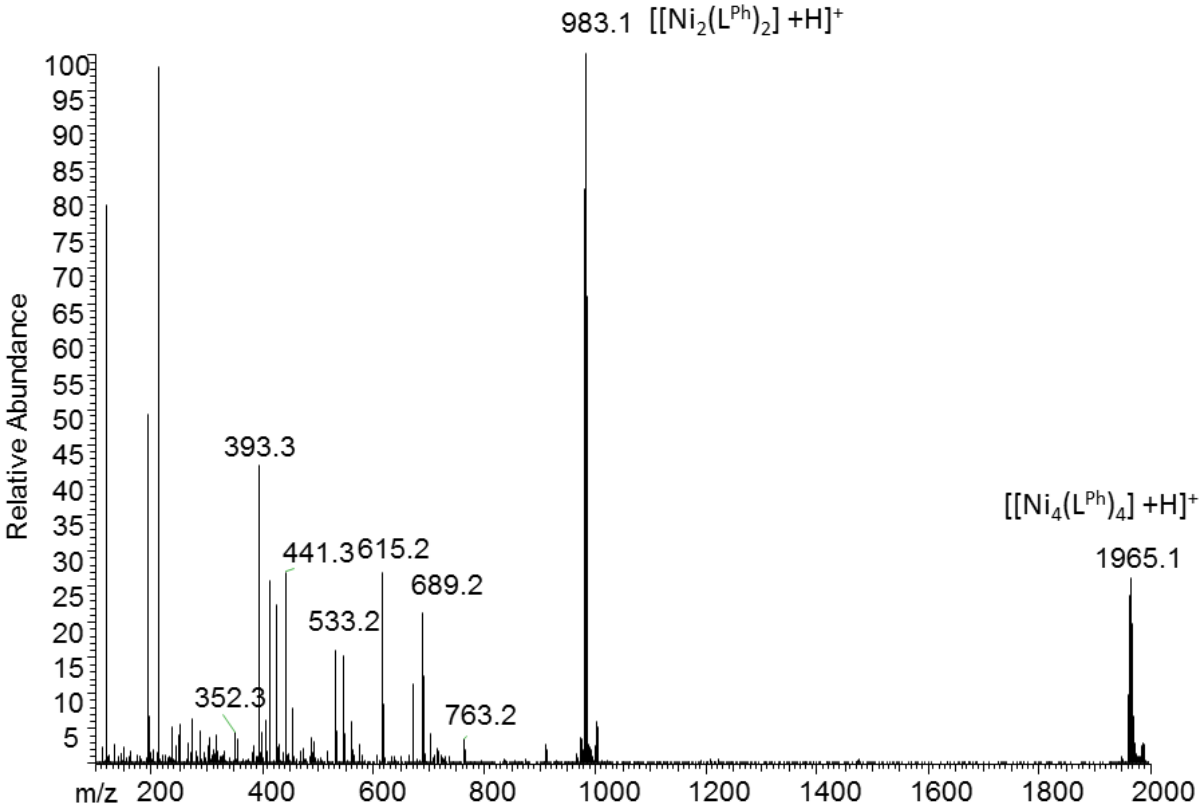

Figure S13. ESI MS(+) of $[Ni_4(L^{Ph})_4]$.

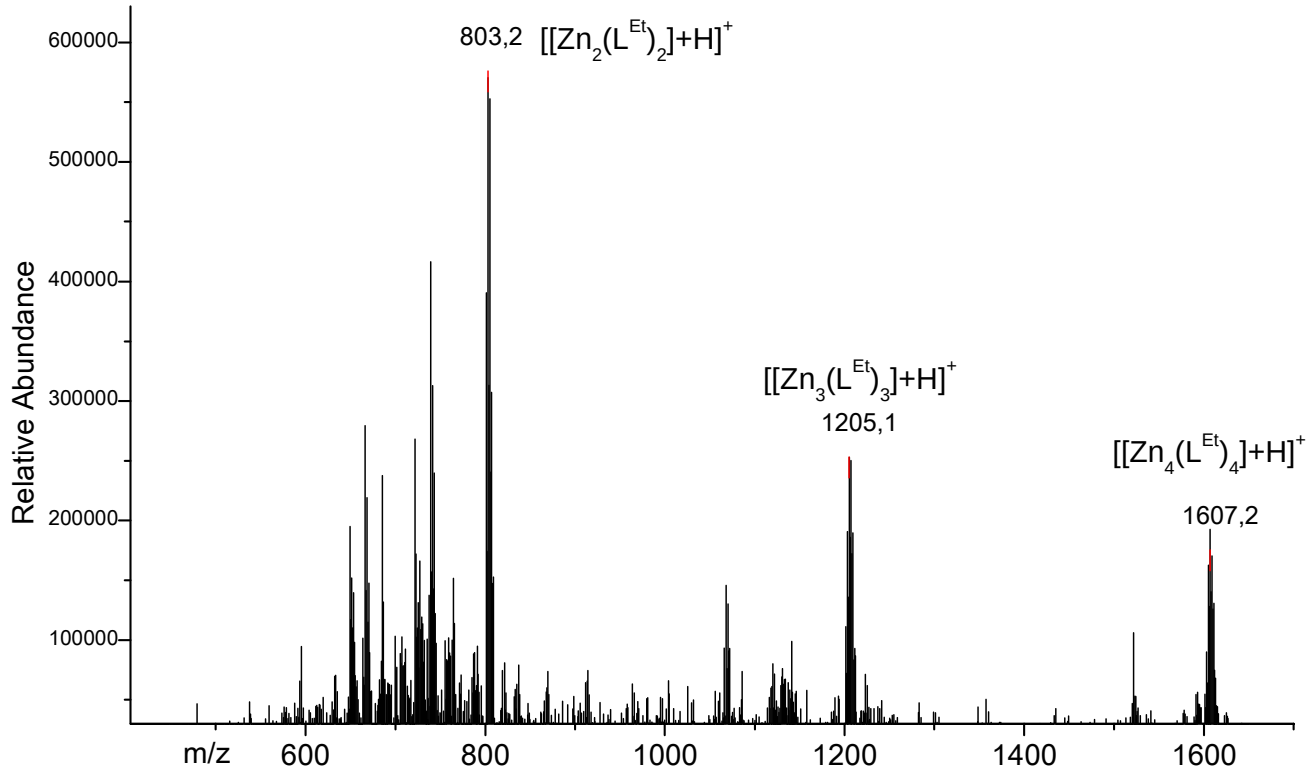

Figure S14. ESI MS(+) of $[Zn_4(L^{Et})_4]$.

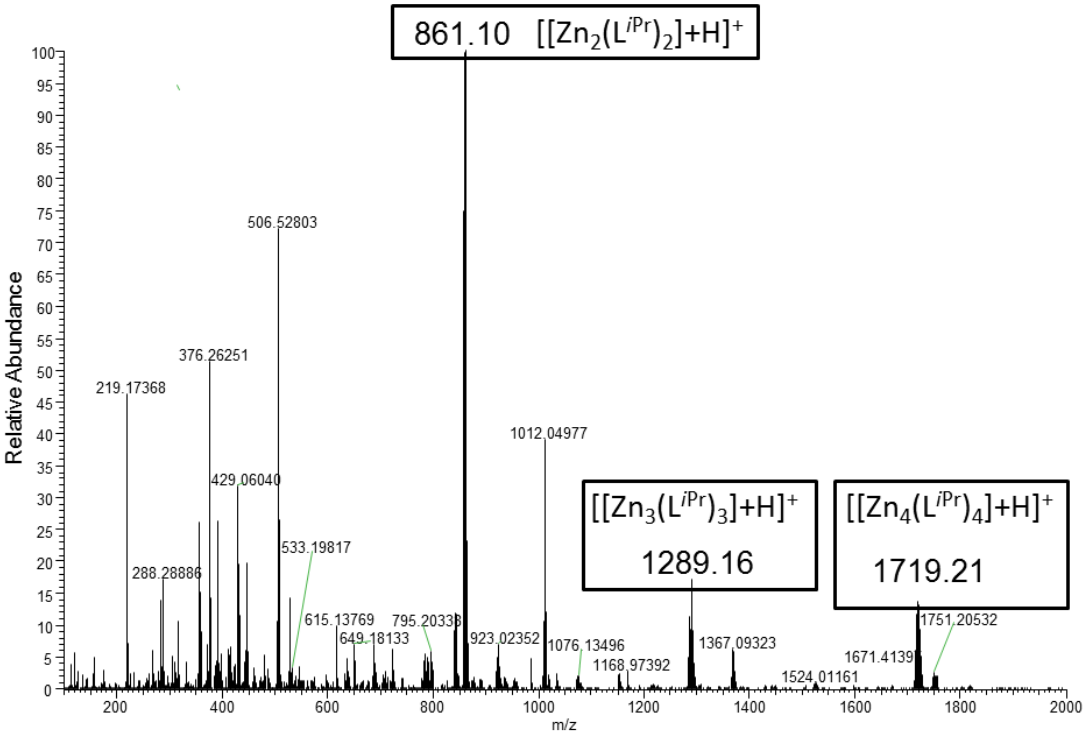

Figure S15. ESI MS(+) of $[Zn_4(L^{iPr})_4]$.

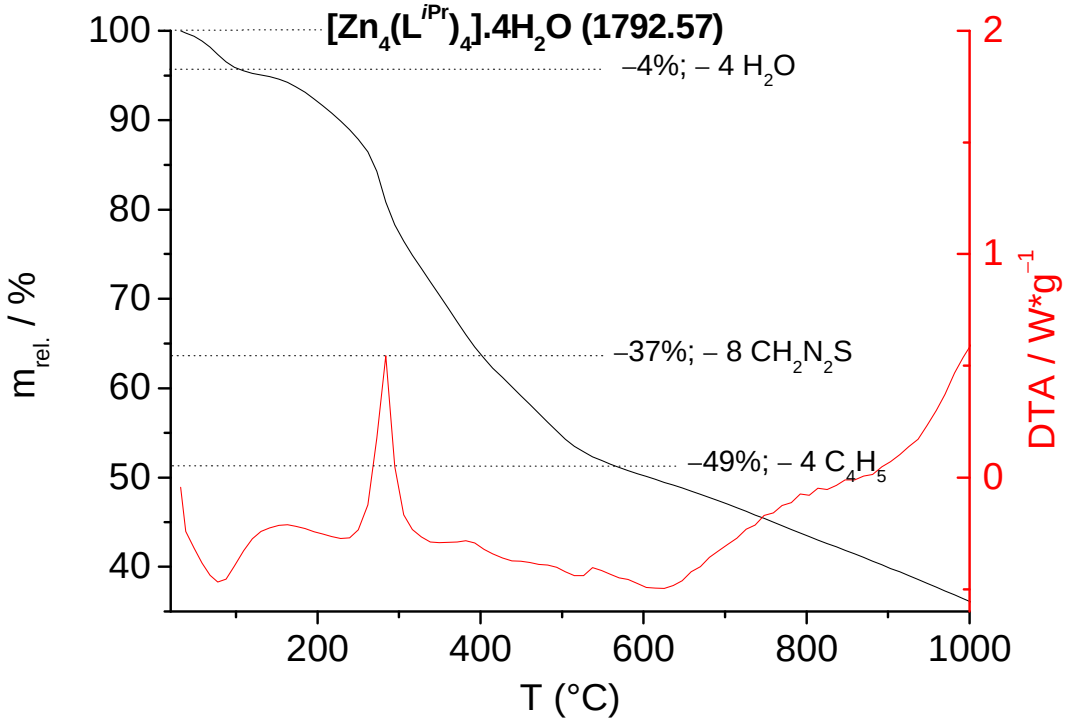

Figure S16. TG-DTA of $[Zn_4(L^{iPr})_4]\cdot 4H_2O$.

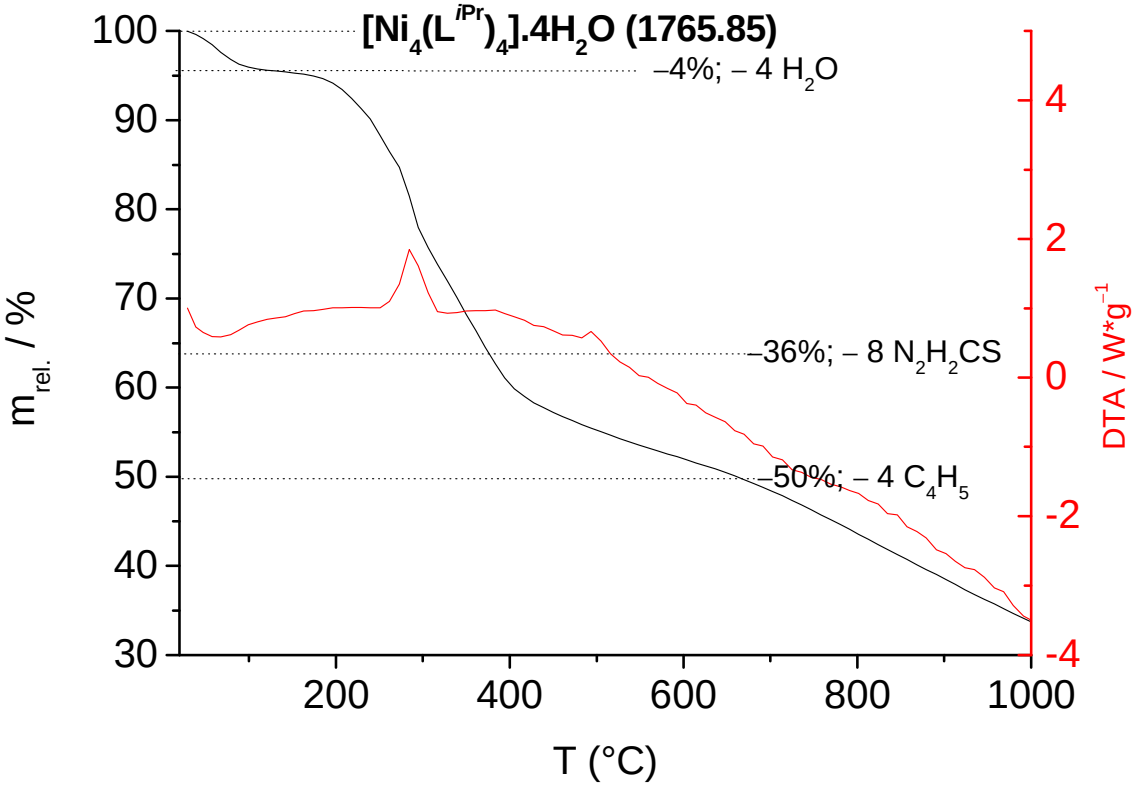

Figure S17. TG-DTA of $[Ni_4(L^{iPr})_4]\cdot 4H_2O$.

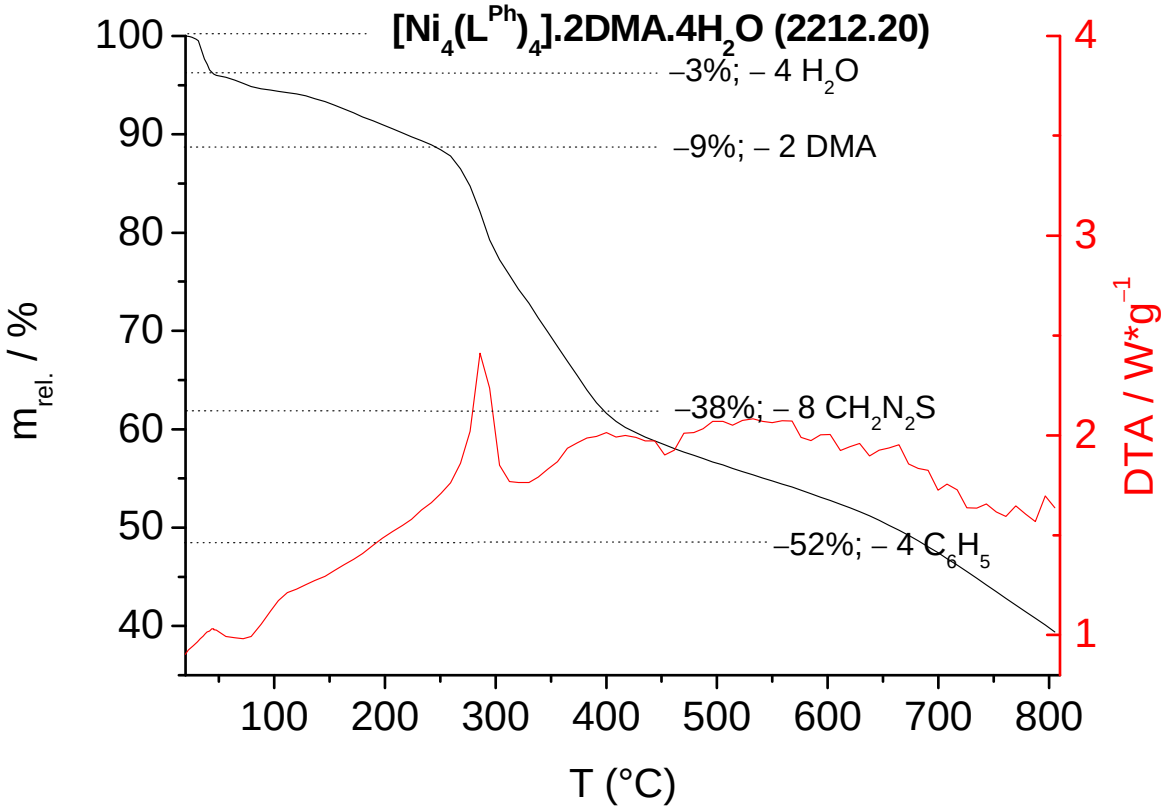

Figure S18. TG-DTA of $[Ni_4(L^{Ph})_4]\cdot 2DMA\cdot 4H_2O$.

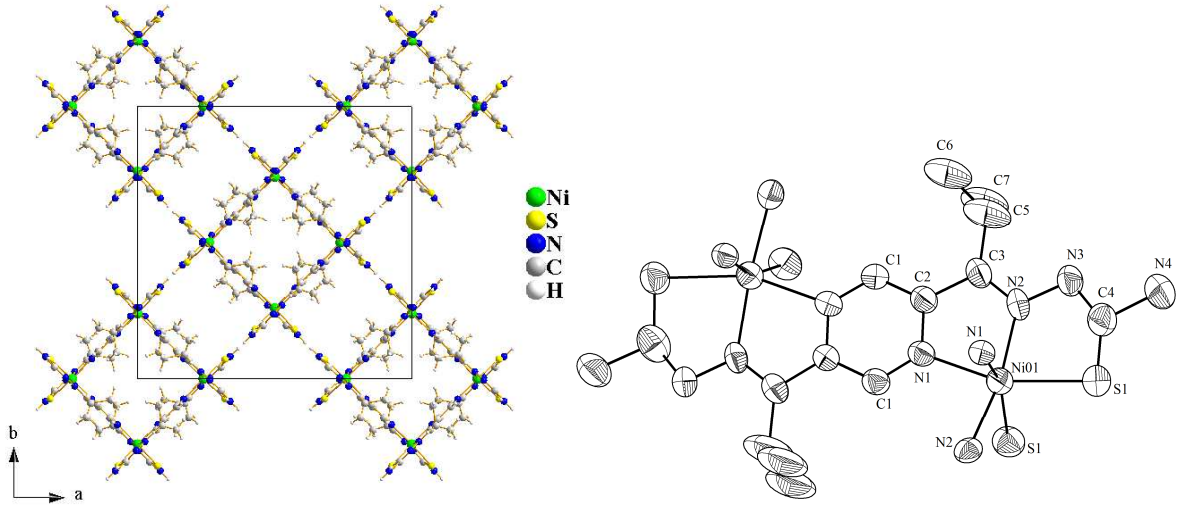

Figure S19. Crystal structure of $[Ni_4(L^{iPr})_4]$ at 293(2) K (left) viewed along the crystallographic *c* axis and an ORTEP plot of the binuclear coordination unit (right) shown at 50% probability level; protons were omitted for clarity.

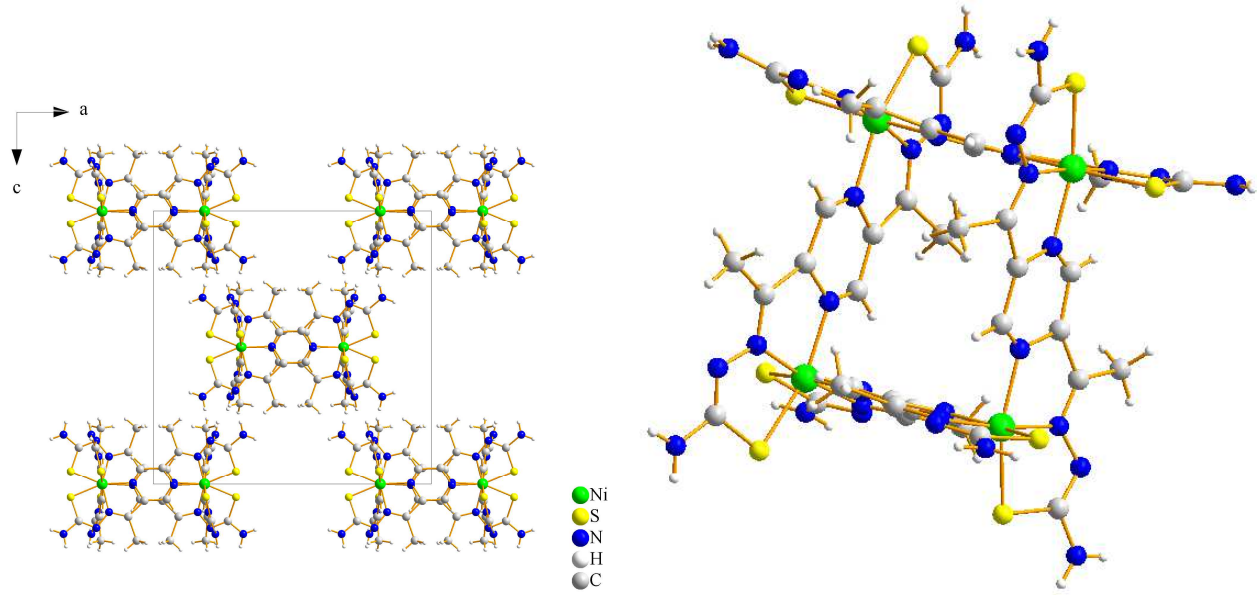

Figure S20. Crystal structure of $[Ni_4(L^{Me})_4]$ at 293(2) K, solved in *I*422 (left) viewed along the crystallographic *b* axis and a molecular view on the complex (right).

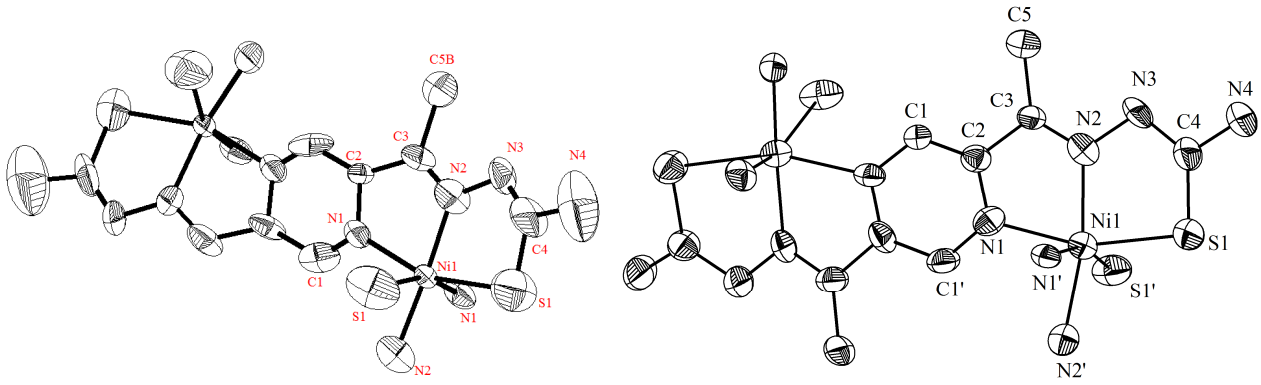

Figure S21. ORTEP plots of the binuclear coordination unit of $[Ni_4(L^{Me})_4]$ at 293(2) K, solved in *I*422 (left) and $[Ni_4(L^{Me})_4]\cdot H_2O$ at 170(2) K, solved in *P*4nc (right) with numbering shown at 50% probability level; protons were omitted for clarity.

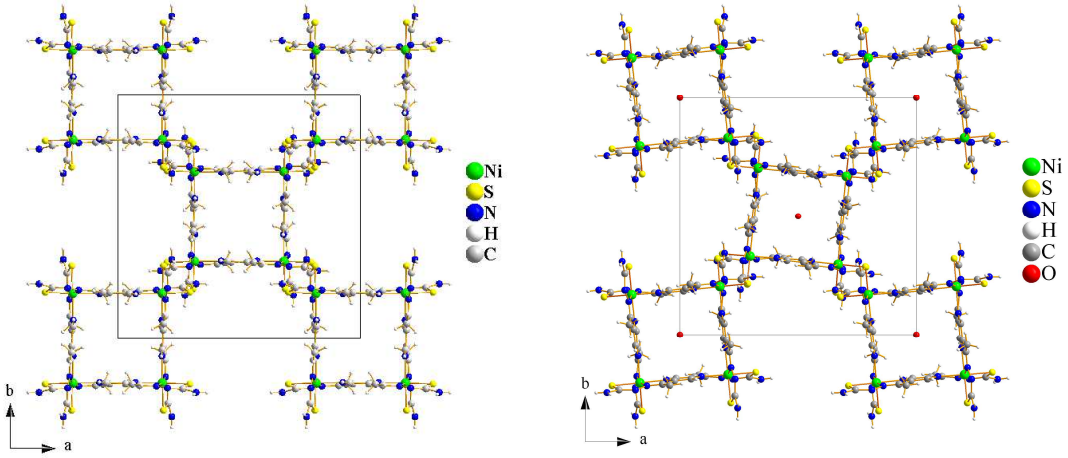

Figure 22. Crystal structures of $[Ni_4(L^{Me})_4]$ at 293(2) K in *I*422 (left) and $[Ni_4(L^{Me})_4]\cdot H_2O$ at 170(2) K in *P*4nc (right) both viewed along the crystallographic *c* axis.

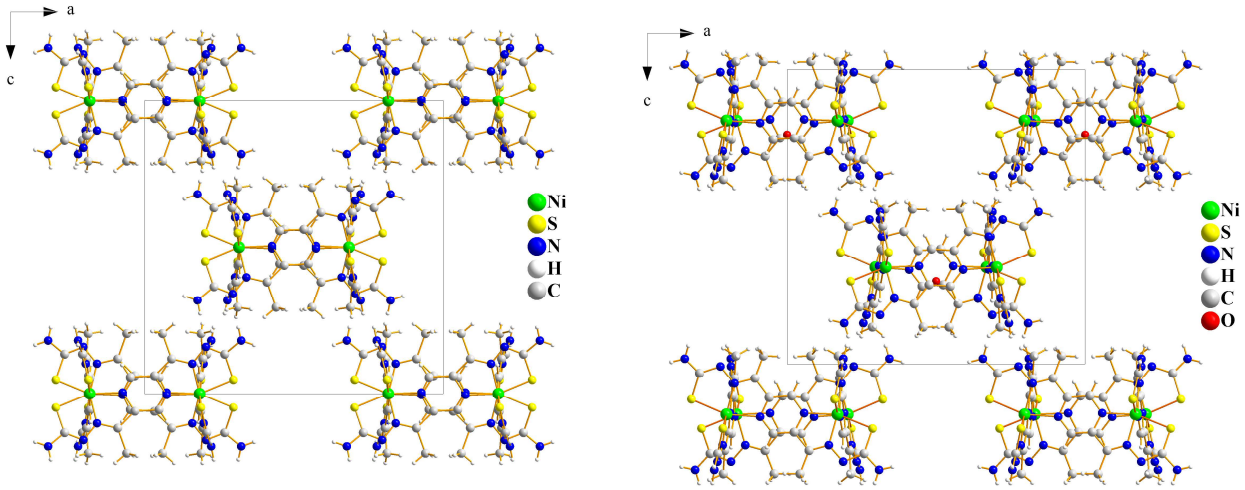

Figure S23. Crystal structures of $[Ni_4(L^{Me})_4]\cdot H_2O$ at 293(2) K in *I*422 (left) and $[Ni_4(L^{Me})_4]\cdot H_2O$ at 170(2) K in *P*4nc (right) both viewed along the crystallographic *b* axis.

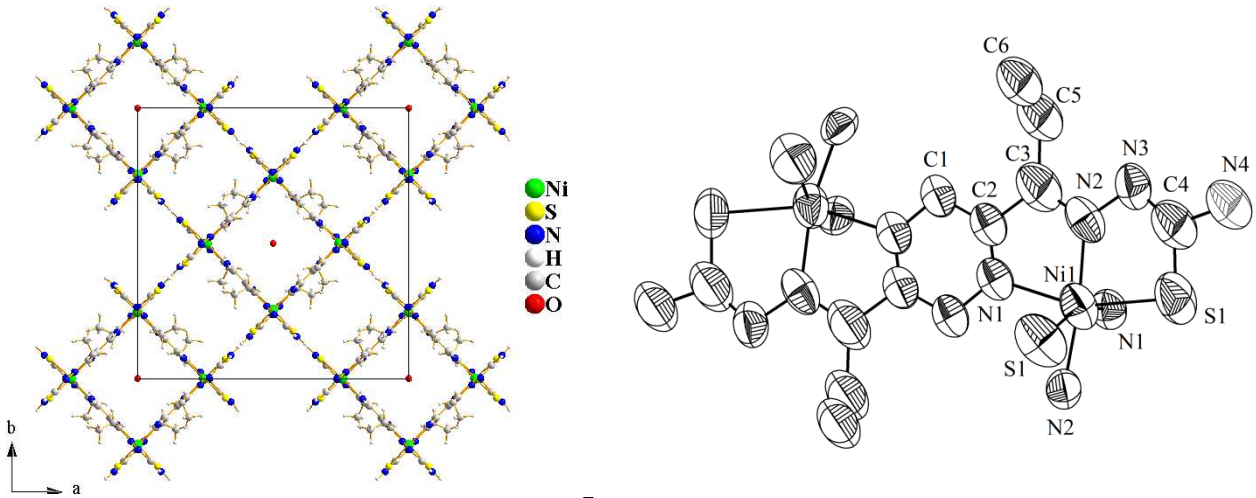

Figure S24. Crystal structure of $[Ni_4(L^{Et})_4]\cdot H_2O$ at 293(2) K (left) viewed along the crystallographic *c* axis and an ORTEP plot of the binuclear coordination unit (right) shown at 50% probability level; protons were omitted for clarity.

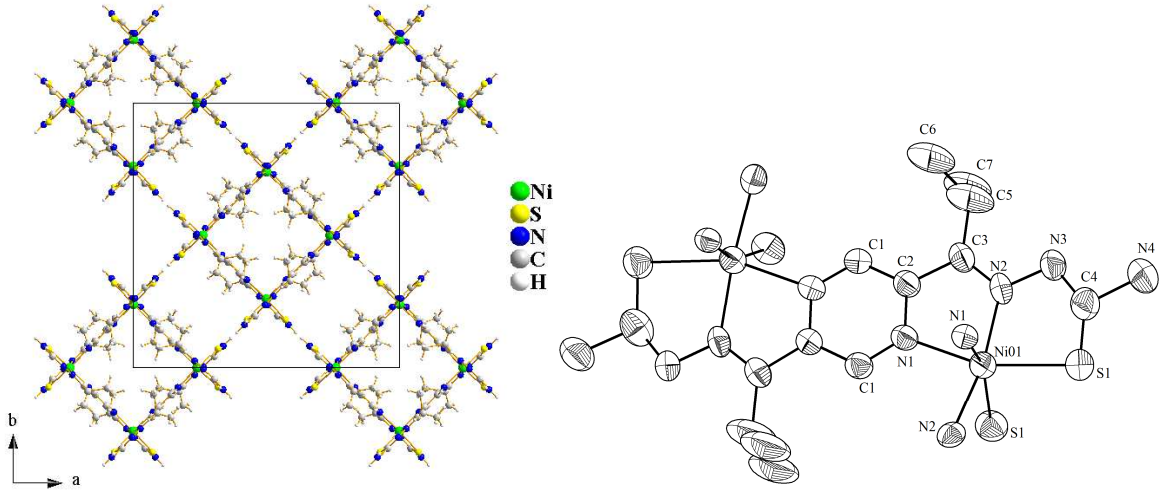

Figure S25. Crystal structure of $[Ni_4(L^{iPr})_4]$ at 293(2) K (left) viewed along the crystallographic *c* axis and an ORTEP plot of the binuclear coordination unit (right) shown at 50% probability level; protons were omitted for clarity.

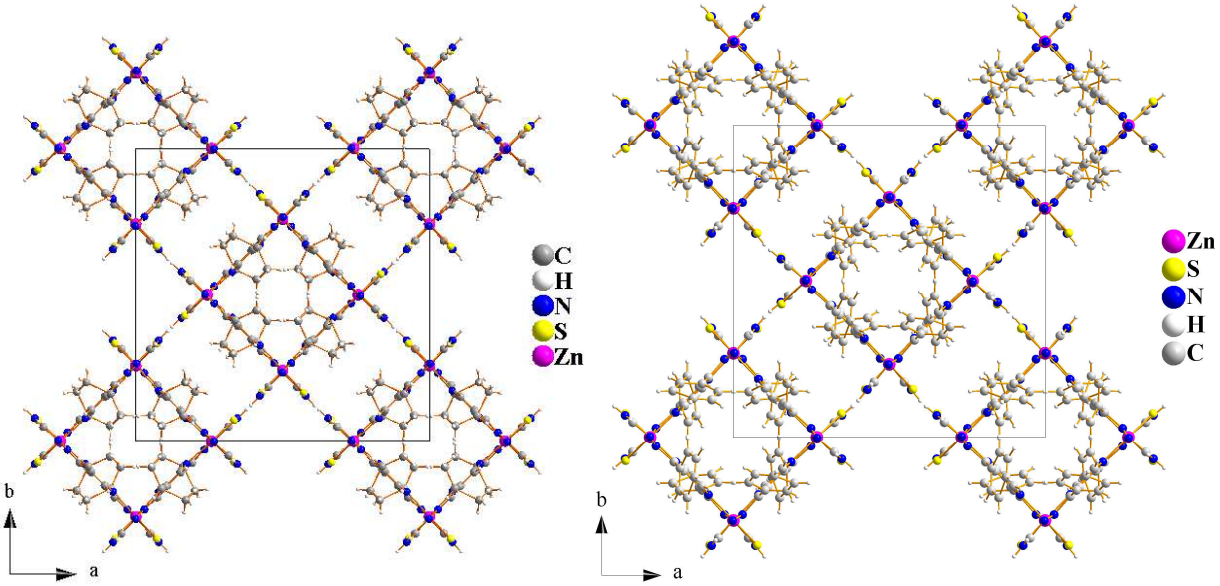

Figure S26. Crystal structures of $[Zn_4(L^{iPr})_4]$ at 170(2) K in *I*422 (left) and $[Zn_4(L^{Ph})_4]$ (right) at 293(2) K in *I*422 both viewed along the crystallographic *c* axis.

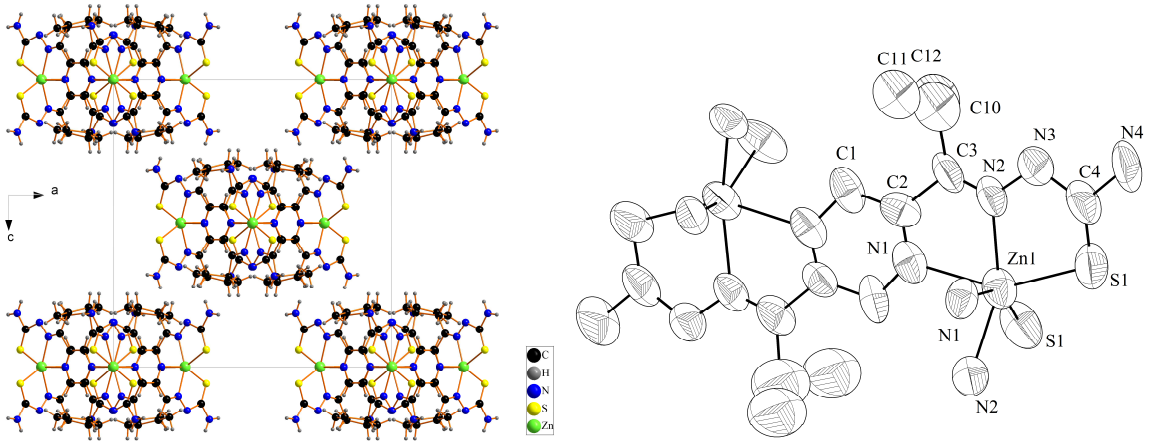

Figure S27. Crystal structure of $[Zn_4(L^{iPr})_4]$ at 170(2) K (left) viewed along the crystallographic *b* axis and an ORTEP plot of the binuclear coordination unit (right) shown at 30% probability level; protons were omitted for clarity.

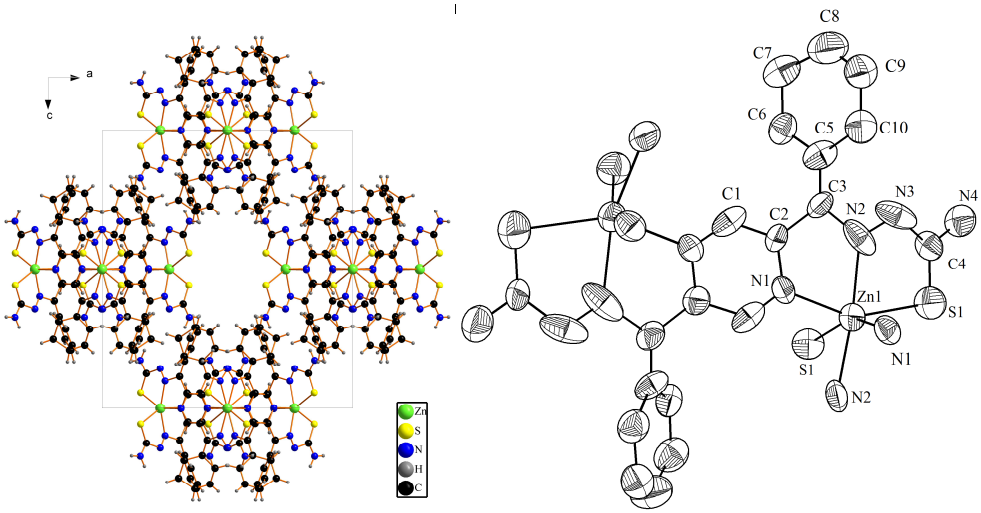

Figure S28. Crystal structure of $[Zn_4(L^{Ph})_4]$ at 170(2) K (left) viewed along the crystallographic *b* axis and an ORTEP plot of the binuclear coordination unit (right) shown at 30% probability level; protons were omitted for clarity.

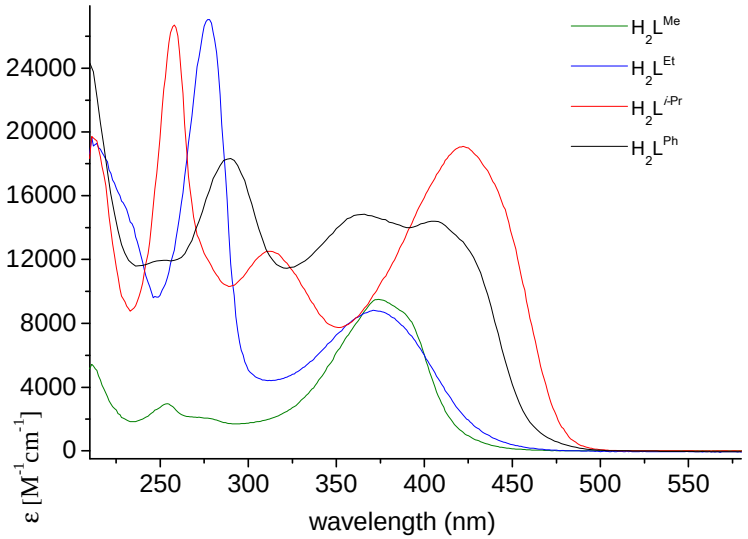

Figure S29. UV-vis absorption spectra of ligands H_2L^R in THF.

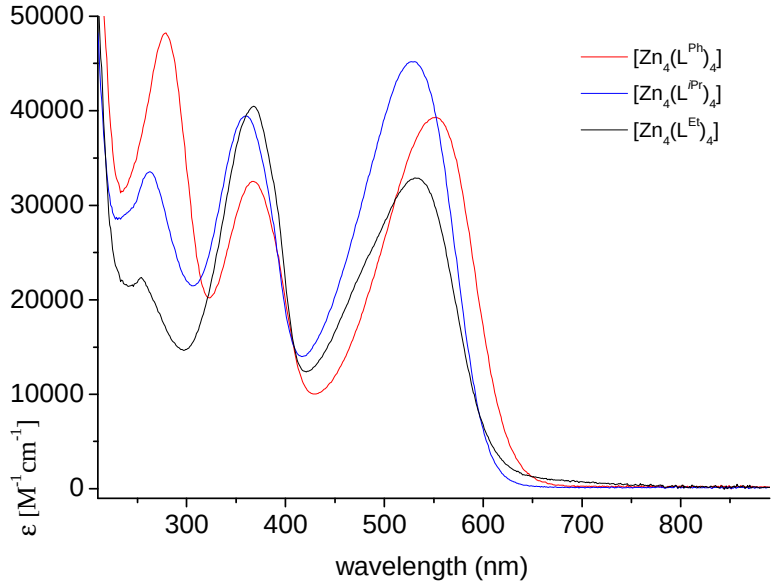

Figure S30. UV-vis absorption spectra of $[Zn_4(L^R)_4]$ in THF.

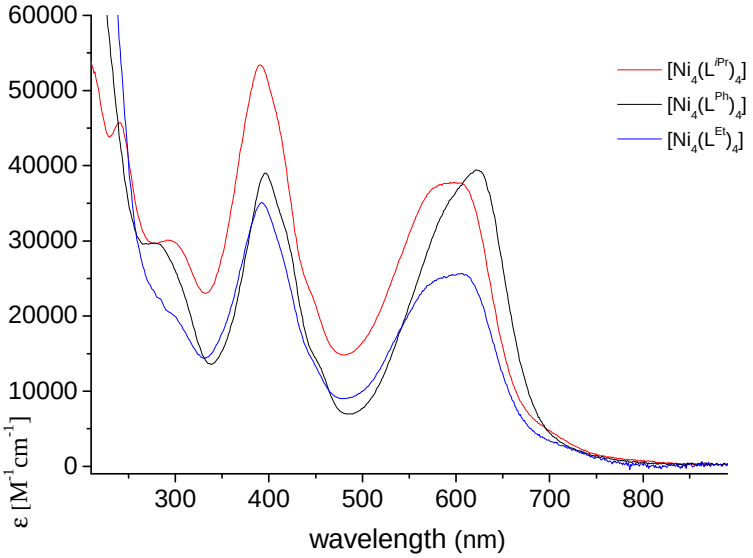

Figure S31. UV-vis absorption spectra of $[Ni_4(L^R)_4]$ in THF.

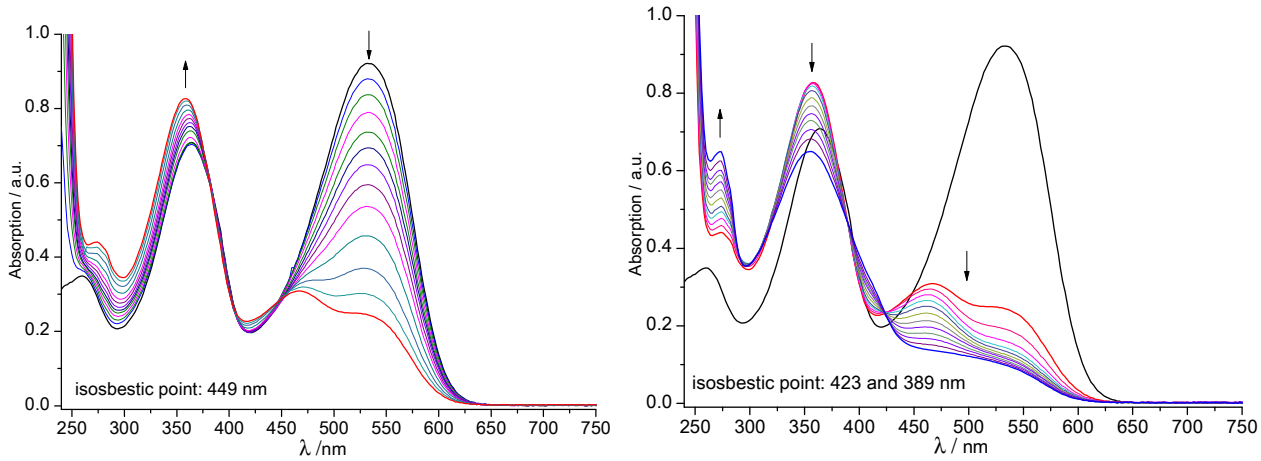

Figure S32. UV-vis absorption spectra of $[Zn_4(L^{iPr})_4]$ (4.1×10^{-5} mol in 2 mL = 20.5 mmol) in THF after the addition of 0–120 µL (left), 120–230 µL of glacial acetic acid (right). 120 µL represents 0.21 mol.

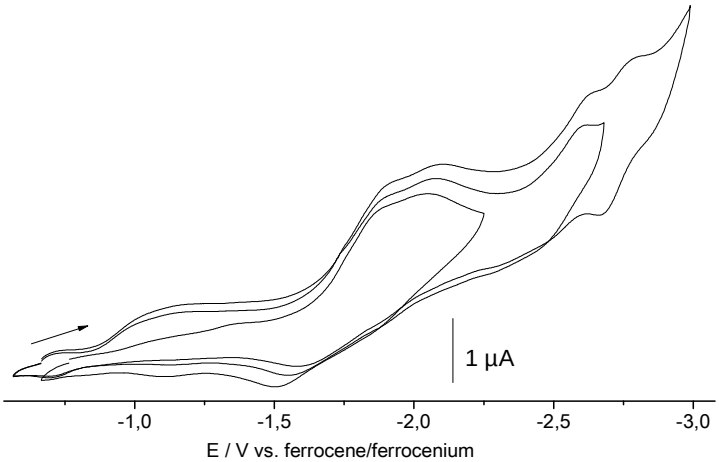

Figure S33. Cyclic voltammograms of H_2L^{Me} in 0.1 M nBu$_4$NPF$_6$/THF solution at 298 K (scan rate 20 mV/s).

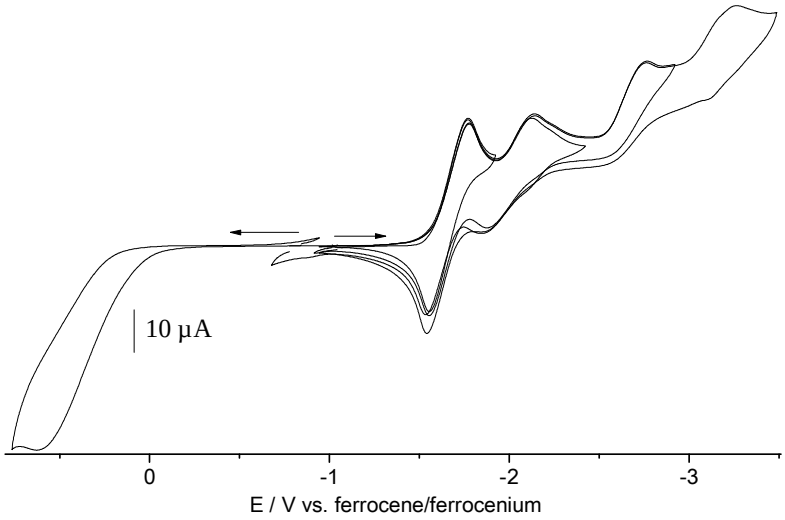

Figure S34. Cyclic voltammograms of H_2L^{Et} in 0.1 M nBu$_4$NPF$_6$/THF solution at 298 K (scan rate 20 mV/s).

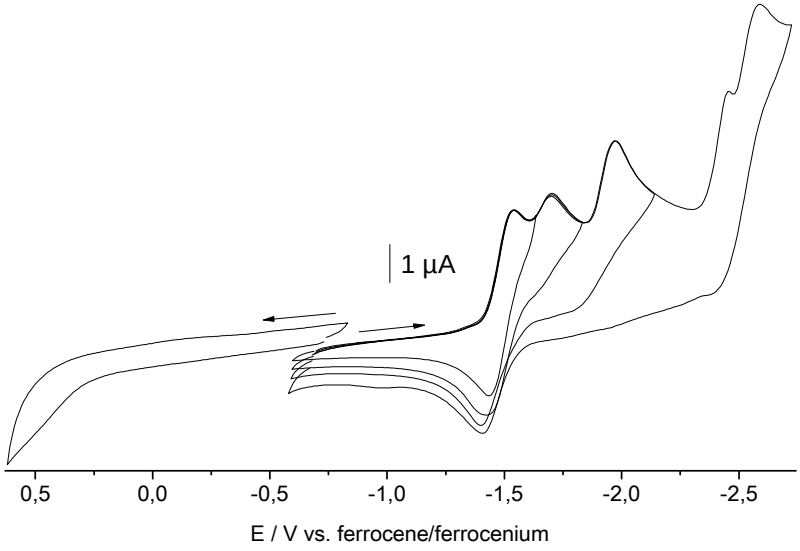

Figure S35. Cyclic voltammograms of H_2L^{Ph} in 0.1 M nBu$_4$NPF$_6$/THF solution.

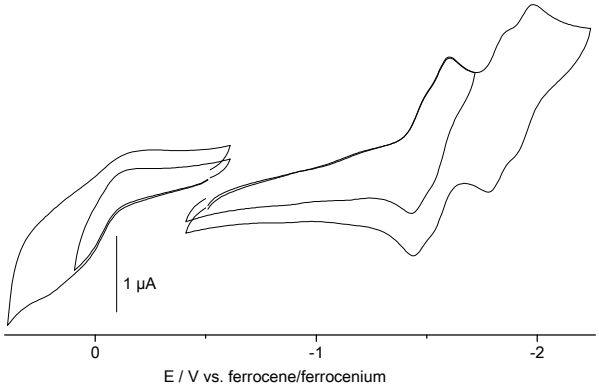

Figure S36. Cyclic voltammograms of [Ni$_4$(L^{Et})$_4$] in 0.1 M nBu$_4$NPF$_6$/THF solution (scan rate 20 mV/s).

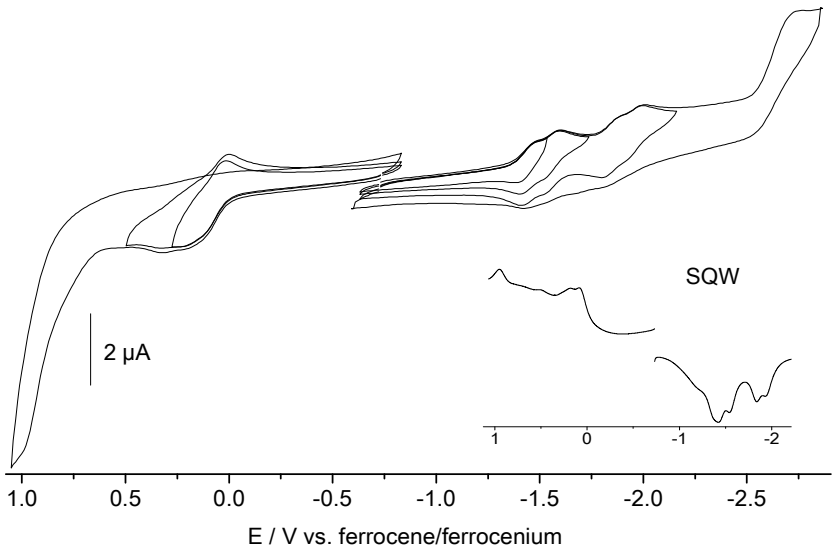

Figure S37. Cyclic voltammograms of $[Ni_4(L^{Ph})_4]$ in 0.1 M nBu$_4$NPF$_6$/THF solution (top) with square-wave voltammogramms (SQW; bottom).

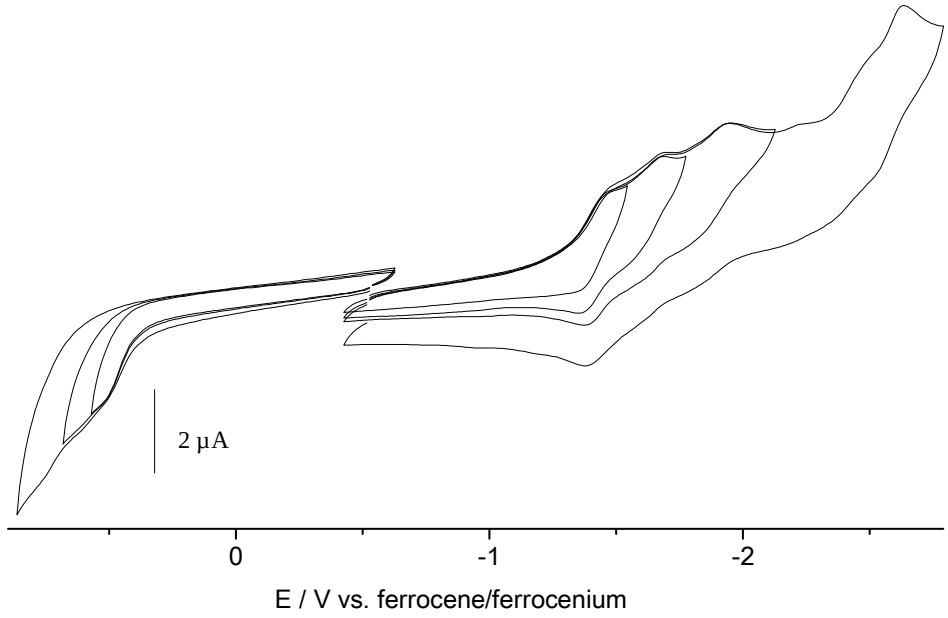

Figure S38. Cyclic voltammograms of $[Zn_4(L^{Ph})_4]$ in 0.1 M of nBu$_4$NPF$_6$/THF solution.

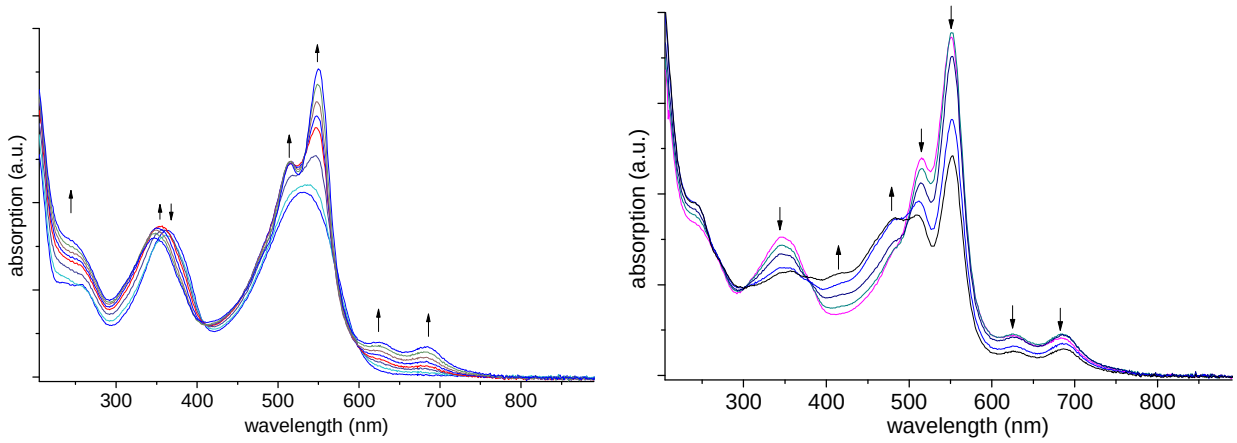

Figure S39. UV-vis absorption spectra recorded during cathodic reduction of $[Zn_4(L^{iPr})_4]$ in THF/$^{n}Bu_4NPF_6$ solutions, spectra were recorded at E = 0, and –1.3 to –1.9 V (left) and from E = –1.9 to –2.3 V (right).

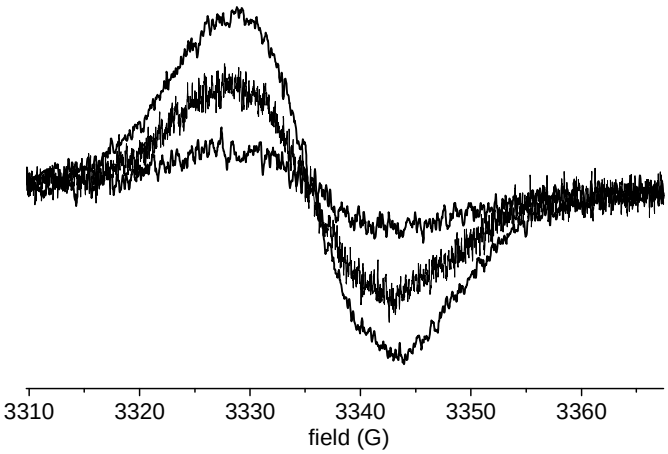

Figure S40. X-band EPR spectrum during cathodic reduction of $[Ni_4(L^{iPr})_4]$ in THF/$^{n}Bu_4NPF_6$ solution. Spectra recorded at –1.5, –1.7 and –1.9 V with a signal at g = 2.016.

C) Supporting Tables

Table S1. Selected crystallographic and structure refinement data for $[M_4(L^R)_4]$ (M = Ni or Zn)

	$[Ni_4(L^{iPr})_4]$	$[Ni_4(L^{Et})_4]\cdot H_2O$	$[Ni_4(L^{Me})_4]$	$[Ni_4(L^{Me})_4]\cdot H_2O$	$[Zn_4(L^{iPr})_4]$	$[Zn_4(L^{Ph})_4]$
formula	$C_{56}H_{80}N_{32}S_8Ni_4$	$C_{48}H_{64}N_{32}Ni_4OS_8$	$C_{40}H_{48}N_{32}Ni_4S_8$	$C_{40}H_{48}N_{32}Ni_4OS_8$	$C_{56}H_{80}N_{32}S_8Zn_4$	$C_{80}H_{64}N_{32}S_8Zn_4$
weight / $g\cdot mol^{-1}$	1693.74	1596.53	1468.32	1484.32	1719.60	1991.73
T /K	293(2)	170(2)	293(2)	170(2)	170(2)	293(2)
crystal system	tetragonal	tetragonal	tetragonal	tetragonal	tetragonal	tetragonal
space group	*I*422	*I*422	*I*422	*P*4nc	*I*422	*I*422
cell: a /Å	20.434(2)	20.065(2)	18.8863(9)	18.4946(9)	19.780(1)	19.095(1)
b /Å	20.434(2)	20.065(2)	18.8863(9)	18.4946(9)	19.780(1)	19.095(1)
c /Å	19.356(2)	19.137(2)	18.481(1)	18.1930(9)	20.291(1)	21.311(1)
V /Å^3; Z	8082(1); 2	7705(5); 2	6592.1(7); 2	6222.9(7); 2	7938.8(9); 2	7770(1); 2
ρ_{calc} /Mg·m^3	0.696	0.688	0.740	0.792	0.719	0.851
F (000)	1760	1648	1504	1520	1776	2032
Total; unique reflections	64478; 4581	27427; 3261	31910; 3526	41383; 5129	41764; 4242	41805; 4143
R_{int}	0.0937	0.3155	0.2731	0.1826	0.1391	0.1862
Goof on F^2	1.224	1.102	0.989	1.230	1.145	1.189
R_1; wR_2 [I_0>2σ(I)]	0.1087; 0.3048	0.1743; 0.4296	0.1191; 0.3035	0.1235; 0.3323	0.1616; 0.3933	0.1635; 0.3885
R_1; wR_2 [all data]	0.1611; 0.3617	0.3209; 0.4928	0.2531; 0.3937	0.1782; 0.3646	0.2583; 0.4359	0.2697; 0.4430
Residual / e·Å^{-3}	1.833/–0.570	0.919/–0.423	2.441/–0.681	1.923/–0.717	1.038/–0.517	2.266/–0.731
CCDC	1484517	1484516	1484515	1484512	1435303	1435304

Table S2. Selected bond lengths /Å and bond angles /° of Ni complexes.

bond lengths	$[Ni_4(L^{Me})_4]\cdot H_2O$	$[Ni_4(L^{Me})_4]$	$[Ni_4(L^{Et})_4]\cdot H_2O$	$[Ni_4(L^{iPr})_4]$
Ni1–N2’	2.00(2)	1.96(2)	2.01(2)	2.023(8)
Ni1–N2	2.00(2)	1.96(2)	2.01(2)	2.023(8)
Ni1–N1	2.09(2)	2.09(1)	2.12(2)	2.115(6)
Ni1–N1'	2.10(1)	2.09(1)	2.12(2)	2.115(6)
Ni1–S1	2.356(6)	2.313(7)	2.377(8)	2.381(3)
Ni1–S1'	2.373(6)	2.313(7)	2.378(8)	2.381(3)
S1–C4	1.68(2)	1.73(2)	1.70(4)	1.60(1)
S1'–C4'	1.73(2)			
N(4)–C(4)	1.39(3)	1.38(3)	1.40(4)	1.57(2)
N(4')–C(4')	1.30(3)			
N(3)–C(4)	1.38(3)	1.28(3)	1.32(4)	1.29(2)
N(3')–C(4')	1.37(3)			
N(3)–N(2)	1.39(2)	1.37(2)	1.40(2)	1.38(1)
N(2')–N(3')	1.38(3)			
N(2)–C(3)	1.28(3)	1.34(2)	1.39(4)	1.28(1)
N(2')–C(3')	1.30(3)			
angles				
N(2')–Ni(1)–N(2)	168.4(6)	171.0(8)	166(1)	168.7(4)
N(2')–Ni(1)–N(1)	93.3(7)	95.0(6)	92.6(8)	93.7(2)
N(2)–Ni(1)–N(1)	77.1(8)	78.5(6)	77.3(10)	78.4(3)
N(2')–Ni(1)–N(1')	79.1(7)	78.5(6)	77.3(10)	78.4(3)
N(2)–Ni(1)–N(1')	93.8(7)	95.0(6)	92.6(8)	93.7(2)
N(1)–Ni(1)–N(1')	88.0(5)	88.7(8)	91.4(9)	91.9(3)
N(2')–Ni(1)–S(1)	105.8(5)	105.0(5)	108.9(6)	106.3(2)
N(2)–Ni(1)–S(1)	83.3(5)	81.2(5)	81.0(7)	81.6(2)
N(1)–Ni(1)–S(1)	160.2(6)	159.7(5)	158.3(7)	159.9(2)
N(1')–Ni(1)–S(1)	90.2(4)	91.8(5)	90.8(6)	90.3(2)
N(2')–Ni(1)–S(1')	82.0(5)	81.2(5)	81.0(7)	81.6(2)
N(2)–Ni(1)–S(1')	104.4(5)	105.0(5)	108.9(6)	106.3(2)
N(1)–Ni(1)–S(1')	90.4(4)	91.8(5)	90.8(6)	90.3(2)
N(1')–Ni(1)–S(1')	160.9(5)	159.7(5)	158.3(7)	159.9(2)
S(1)–Ni(1)–S(1')	97.6(2)	94.6(4)	95.0(5)	94.5(2)

Table S3. Selected bond lengths /Å and bond angles /° of Zn complexes.

bond lengths	$[Zn_4(L^{iPr})_4]$	$[Zn_4(L^{Ph})_4]$
Zn(1)–N(2)	2.21(2)	2.20(3)
Zn(1)–N(1)	2.28(1)	2.20(2)
Zn(1)–S(1)	2.380(5)	2.415(7)
C(4)–S(1)	1.54(2)	1.62(3)
C(4)–N(4)	1.42(2)	1.19(3)
C(4)–N(3)	1.44(3)	1.42(3)
N(2)–N(3)	1.35(2)	1.18(3)
C(3)–N(2)	1.22(2)	1.52(3)

angles		
N(2')–Zn(1)–N(2)	154.6(7)	161(1)
N(2)–Zn(1)–N(1')	90.0(6)	92.4(7)
N(1)–Zn(1)–N(1')	84.7(6)	88.4(9)
N(1)–Zn(1)–S(1')	93.6(4)	91.0(5)
S(1)–Zn(1)–S(1')	101.3(3)	103.1(4)
N(2')–Zn(1)–S(1)	117.0(4)	115.2(5)
N(2)–Zn(1)–S(1)	79.9(4)	77.1(7)
N(1)–Zn(1)–S(1)	150.9(5)	151.0(5)
N(2)–Zn(1)–N(1)	71.1(6)	74.0(8)

Table S4. Absorption maxima of the H_2L^R ligands and the Zn and Ni complexes.[a]

compound	λ_1 (ε)	λ_2 (ε)	λ_3 (ε)	λ_4 (ε)	λ_5 (ε)	λ_6 (ε)
H_2L^{Me}	253 (3.0)	277 (2.0)	372 (9.5)	389sh (8.6)		
H_2L^{Et}	230sh (14.9)	277 (27)	372 (8.9)			
H_2L^{iPr}	258 (26.7)	311 (12.7)	422 (19.2)	439sh (16.9)		
H_2L^{Ph}	251 (11.9)	289 (18.3)	364 (14.9)	406 (14.6)	422sh (13.2)	
$[Zn_4(L^{Me})_4]$	354	472	531sh			
$[Zn_4(L^{Et})_4]$	254 (22.8)	368 (40.8)	532 (33.3)			
$[Zn_4(L^{iPr})_4]$	261 (33.8)	360 (39.6)	528 (45.3)			
$[Zn_4(L^{Ph})_4]$	277 (48.5)	367 (32.5)	550 (39.3)			
$[Ni_4(L^{Me})_4]$	295	385	578		600	
$[Ni_4(L^{Et})_4]$	283 (22.3)	392 (35.5)	579sh (24.7)		602 (25.6)	703sh (3.1)
$[Ni_4(L^{iPr})_4]$	241 (46.4)	293 (30.3)	390 (53.7)	579sh (37.3)	601 (38.0)	702sh (4.1)
$[Ni_4(L^{Ph})_4]$	277 (29.9)	396 (39.3)	450sh (15.2)	585sh (33.9)	623 (39.4)	720sh (2.6)

[a] Measured in THF, wavelengths λ in nm (extinction coefficients ε in 1000 $M^{-1}cm^{-1}$)

Table S5. Selected DFT-calculated and experimental bond lengths /Å and bond angles /° of Zn complexes.

	$[Zn_4(L^{Me})_4]$ def2-TZVP	$[Zn_4(L^{Et})_4]$ def2-TZVP	$[Zn_4(L^{iPr})_4]$ def-SV(P)	$[Zn_4(L^{iPr})_4]$	$[Zn_4(L^{Ph})_4]$ def-SV(P)	$[Zn_4(L^{Ph})_4]$
bond lengths	calc.	calc.	calc.	exp.	calc.	exp.
M–N2’	2.178	2.169	2.177		2.178	
M–N2	2.178	2.169	2.177	2.21(2)	2.176	2.19(2)
M–N1	2.310	2.311	2.249	2.28(1)	2.252	2.20(2)
M–N1'	2.310	2.312	2.249		2.253	
M–S1	2.449	2.453	2.477	2.380(5)	2.481	2.42(1)
M–S1'	2.449	2.453	2.477		2.482	
S1–C4	1.717	1.716	1.724	1.54(2)	1.723	1.62(3)
S1'–C4'	1.717	1.716	1.724		1.723	
N(4)–C(4)	1.364	1.364	1.365	1.42(2)	1.367	1.19(3)
N(4')–C(4')	1.364	1.364	1.365		1.367	

N(3)–C(4)	1.352	1.353	1.357	1.44(3)	1.359	1.42(4)
N(3')–C(4')	1.352	1.353	1.357		1.359	
N(3)–N(2)	1.335	1.336	1.329	1.35(2)	1.325	1.18(3)
N(2')–N(3')	1.335	1.336	1.329		1.325	
N(2)–C(3)	1.320	1.320	1.332	1.22(2)	1.333	1.52(3)
N(2')–C(3')	1.320	1.320	1.332		1.333	
angles						
N(2')–M–N(2)	157.3	157.8	167.1	154.6(7)	163.2	161.2(9)
N(2')–M–N(1)	90.2	90.7	96.8	90.0(6)	93.5	92.4(8)
N(2)–M–N(1)	73.3	73.2	74.1	71.1(6)	74.4	74.0(8)
N(2')–M–N(1')	73.3	73.2	74.1		74.4	
N(2)–M–N(1')	90.3	90.7	96.8		93.4	
N(1)–M–N(1')	88.2	88.2	89.6	84.7(6)	89.8	88.4(6)
N(2')–M–S(1)	114.8	114.4	107.8	117.0(4)	110.9	115.2(6)
N(2)–M–S(1)	80.5	80.5	80.5	79.9(4)	80.2	77.1(6)
N(1)–M–S(1)	153.8	153.7	154.4	150.9(5)	154.7	151.0(5)
N(1')–M–S(1)	91.5	91.7	90.2		90.6	
N(2')–M–S(1')	80.5	80.5	80.5		80.2	
N(2)–M–S(1')	114.7	114.4	107.8		111.1	
N(1)–M–S(1')	91.5	91.7	90.2	93.6(4)	90.6	91.0(5)
N(1')–M–S(1')	153.8	153.7	154.4		154.6	
S(1)–M–S(1')	99.9	99.7	100.7	101.3(3)	99.6	103.0(3)

Table S6. Selected DFT-calculated and experimental bond lengths /Å and bond angles /° of Ni complexes.

	$[Ni_4(L^{Me})_4]$ def-SV(P)	$[Ni_4(L^{Me})_4]$	$[Ni_4(L^{Me})_4]$	$[Ni_4(L^{Et})_4]$def-SV(P)	$Ni_4(L^{Et})_4]$	$[Ni_4(L^{iPr})_4]$	$[Ni_4(L^{Ph})_4]$def-SV(P)
bond lengths	calc.	exp. (RT)	exp. (TT)	calc.	exp.	exp.	calc.
M–N2’	1.881		2.00(2)	1.883	2.01(2)		1.886
M–N2	2.013	1.96(1)	1.99(2)	2.006	2.01(2)	2.02(3)	2.007
M–N1	2.688	2.09(1)	2.10(1)	2.689	2.12(2)	2.11(3)	2.690
M–N1'	1.903		2.09(1)	1.903	2.12(2)		1.900
M–S1	2.385	2.312(8)	2.373(6)	2.393	2.377(8)	2.38(2)	2.389
M–S1'	2.225		2.357(8)	2.236	2.378(8)		2.234
S1–C4	1.727	1.73(2)	1.73(2)	1.730	1.70(4)	1.60(4)	1.729
S1'–C4'	1.750		1.68(2)	1.750			1.750
N(4)–C(4)	1.372	1.38(4)	1.30(3)	1.371	1.40(4)	1.57(4)	1.372
N(4')–C(4')	1.369		1.39(3)	1.368			1.370
N(3)–C(4)	1.341	1.28(3)	1.37(3)	1.340	1.32(4)	1.28(4)	1.339
N(3')–C(4')	1.331		1.39(3)	1.330			1.329
N(3)–N(2)	1.348	1.37(2)	1.38(3)	1.347	1.40(2)	1.38(4)	1.342
N(2')–N(3')	1.348		1.39(3)	1.349			1.345
N(2)–C(3)	1.337	1.34(3)	1.30(3)	1.337	1.39(4)	1.28(4)	1.339
N(2')–C(3')	1.349		1.28(2)	1.349			1.357
angles							
N(2')–M–N(2)	154.3	171.0(6)	168.4(7)	155.1	166(1)	168.7(9)	156.6

N(2')–M–N(1)	82.7	95.0(6)	93.8(7)	83.0	92.6(8)	93.7(9)	84.3
N(2)–M–N(1)	71.6	78.5.(6)	79.1(6)	72.2	77.3(10)	78.4(9)	72.3
N(2')–M–N(1')	83.7		77.1(7)	83.8	77.3(10)		84.0
N(2)–M–N(1')	95.0		93.3(7)	95.7	92.6(8)		96.2
N(1)–M–N(1')	88.2	88.7(5)	88.0(6)	86.0	91.4(9)	92(1)	87.6
N(2')–M–S(1)	120.4	105.0(5)	104.4(5)	119.6	108.9(6)	106.2(9)	118.1
N(2)–M–S(1)	85.3	81.2(5)	82.0(5)	85.2	81.0(7)	81.6(8)	85.3
N(1)–M–S(1)	156.9	159.7(4)	160.9(4)	157.2	158.3(7)	159.9(8)	157.6
N(1')–M–S(1)	94.3	91.8(5)	90.3(5)	93.7	90.8(6)	90.3(7)	93.5
N(2')–M–S(1')	83.7		77.1(7)	85.5	81.0(7)		85.8
N(2)–M–S(1')	93.6		105.7(5)	92.7	108.9(6)		91.9
N(1)–M–S(1')	87.6		90.2(4)	89.5	90.8(6)		88.3
N(1')–M–S(1')	168.8		160.2(4)	168.8	158.3(7)		169.4
S(1)–M–S(1')	93.7	94.6(3)	97.6(2)	94.4	95.0(5)	94.5(9)	94.0

Table S7. Atom coordinates of the geometry optimized molecular structure of $[Ni_4(L^{Me})_4]$ on DFT BP86/def-SV(P) level.

	X	y	z		x	y	z
S	−5.16284	−4.53517	0.41199	C	−4.62181	4.98306	2.15046
Ni	−2.99413	−4.21768	0.02753	C	−1.09874	3.54096	−0.81977
C	−4.98306	−4.62181	2.15046	C	−0.78830	3.57477	1.47841
S	−2.76737	−6.22854	−1.23388	N	−4.08940	3.31758	−2.86719
N	−3.41909	−1.59747	0.44793	C	−2.02107	3.47536	−1.95301
N	−3.30964	−3.33209	−1.75225	C	5.40515	−3.10652	−2.71391
N	−1.12539	−3.86000	0.06107	C	4.62181	−4.98306	2.15046
N	−2.81177	−4.24252	1.89938	C	3.74521	−0.29585	−0.98492
N	−6.09512	−4.82922	2.92066	C	3.82597	−0.60788	1.34847
N	−3.81376	−4.47768	2.77053	N	4.47768	−3.81376	2.77053
C	−3.10652	−5.40515	−2.71391	C	4.05711	−1.56562	2.38194
C	−3.54096	−1.09874	−0.81977	N	−6.12889	3.13635	−3.87880
C	−3.57477	−0.78830	1.47841	N	−4.82922	6.09512	2.92066
N	−3.31758	−4.08940	−2.86719	C	0.29585	3.74521	−0.98492
C	−3.47536	−2.02107	−1.95301	H	−1.24622	3.49777	2.48245
C	−0.29585	−3.74521	−0.98492	C	0.60788	3.82597	1.34847
C	−0.60788	−3.82597	1.34847	C	−1.53759	3.63692	−3.37386
C	−1.56562	−4.05711	2.38194	N	6.12889	−3.13635	−3.87880
H	−5.95151	−5.06335	3.90602	N	4.82922	−6.09512	2.92066
H	−6.95765	−5.13835	2.47069	C	3.54096	1.09874	−0.81977
N	−3.13635	−6.12889	−3.87880	H	3.82036	−0.77232	−1.97163
C	−3.74521	0.29585	−0.98492	C	3.57477	0.78830	1.47841
H	−3.49777	−1.24622	2.48245	C	4.10902	−1.28235	3.85432
C	−3.82597	0.60788	1.34847	H	−5.66837	3.51015	−4.71385
C	−3.63692	−1.53759	−3.37386	H	−7.14725	3.17121	−3.81583
C	1.09874	−3.54096	−0.81977	H	−5.06335	5.95151	3.90602
H	−0.77232	−3.82036	−1.97163	H	−5.13835	6.95765	2.47069
C	0.78830	−3.57477	1.47841	N	1.12539	3.86000	0.06107
C	−1.28235	−4.10902	3.85432	H	0.77232	3.82036	−1.97163

H	–3.51015	–5.66837	–4.71385	C	1.56562	4.05711	2.38194
H	–3.17121	–7.14725	–3.81583	H	–0.44459	3.78483	–3.45249
N	–3.86000	1.12539	0.06107	H	–1.82599	2.75090	–3.98109
H	–3.82036	0.77232	–1.97163	H	–2.05044	4.50181	–3.84900
C	–4.05711	1.56562	2.38194	H	5.66837	–3.51015	–4.71385
H	–3.78483	–0.44459	–3.45249	H	7.14725	–3.17121	–3.81583
H	–2.75090	–1.82599	–3.98109	H	5.06335	–5.95151	3.90602
H	–4.50181	–2.05044	–3.84900	H	5.13835	–6.95765	2.47069
N	1.59747	–3.41909	0.44793	N	3.41909	1.59747	0.44793
C	2.02107	–3.47536	–1.95301	C	3.47536	2.02107	–1.95301
H	1.24622	–3.49777	2.48245	H	3.49777	1.24622	2.48245
H	–0.20899	–3.93931	4.07339	H	3.93931	–0.20899	4.07339
H	–1.88293	–3.34822	4.40165	H	3.34822	–1.88293	4.40165
H	–1.57929	–5.09587	4.27458	H	5.09587	–1.57929	4.27458
Ni	–4.21768	2.99413	0.02753	Ni	2.99413	4.21768	0.02753
N	–4.24252	2.81177	1.89938	N	2.81177	4.24252	1.89938
C	–4.10902	1.28235	3.85432	C	1.28235	4.10902	3.85432
Ni	4.21768	–2.99413	0.02753	N	3.30964	3.33209	–1.75225
N	3.33209	–3.30964	–1.75225	C	3.63692	1.53759	–3.37386
C	1.53759	–3.63692	–3.37386	S	2.76737	6.22854	–1.23388
S	–6.22854	2.76737	–1.23388	S	5.16284	4.53517	0.41199
S	–4.53517	5.16284	0.41199	N	3.81376	4.47768	2.77053
N	–1.59747	3.41909	0.44793	H	0.20899	3.93931	4.07339
N	–3.33209	3.30964	–1.75225	H	1.88293	3.34822	4.40165
N	–4.47768	3.81376	2.77053	H	1.57929	5.09587	4.27458
H	–3.93931	0.20899	4.07339	N	3.31758	4.08940	–2.86719
H	–3.34822	1.88293	4.40165	H	3.78483	0.44459	–3.45249
H	–5.09587	1.57929	4.27458	H	2.75090	1.82599	–3.98109
S	6.22854	–2.76737	–1.23388	H	4.50181	2.05044	–3.84900
S	4.53517	–5.16284	0.41199	C	3.10652	5.40515	–2.71391
N	3.86000	–1.12539	0.06107	C	4.98306	4.62181	2.15046
N	4.24252	–2.81177	1.89938	N	3.13635	6.12889	–3.87880
N	4.08940	–3.31758	–2.86719	N	6.09512	4.82922	2.92066
H	0.44459	–3.78483	–3.45249	H	3.51015	5.66837	–4.71385
H	1.82599	–2.75090	–3.98109	H	3.17121	7.14725	–3.81583
H	2.05044	–4.50181	–3.84900	H	5.95151	5.06335	3.90602
C	–5.40515	3.10652	–2.71391	H	6.95765	5.13835	2.47069

Table S8. Atom coordinates of the geometry optimized molecular structure of $[Ni_4(L^{Et})_4]$ on DFT BP86/def-SV(P) level.

	X	y	z		x	y	z
S	–5.12745	–4.61348	0.40014	N	–4.97376	6.07224	2.82609
Ni	–2.96896	–4.24033	0.01779	C	0.28485	3.69000	–0.99245
C	–4.93834	–4.74835	2.13439	H	–1.25154	3.44978	2.47765
S	–2.66148	–6.24219	–1.25620	C	0.59571	3.78832	1.33794
N	–3.36696	–1.61741	0.45641	C	–1.46388	3.54628	–3.37563
N	–3.33540	–3.37068	–1.75223	N	6.14186	–3.31533	–3.90665
N	–1.11141	–3.82819	0.04888	N	4.97732	–6.07555	2.81937

N	–2.78022	–4.28998	1.89086
N	–6.04197	–5.00951	2.89977
N	–3.77277	–4.58654	2.75511
C	–3.20758	–5.45638	–2.69692
C	–3.48669	–1.13233	–0.81602
C	–3.53919	–0.79621	1.47624
N	–3.45815	–4.14835	–2.84556
C	–3.43314	–2.05239	–1.95111
C	–0.28379	–3.69504	–0.99562
C	–0.59465	–3.78694	1.33509
C	–1.54274	–4.04861	2.37167
H	–5.89207	–5.25400	3.88160
H	–6.89582	–5.33380	2.44416
N	–3.37431	–6.20685	–3.83209
C	–3.70838	0.25774	–1.00009
H	–3.47118	–1.24016	2.48704
C	–3.80099	0.59593	1.32679
C	–3.60179	–1.52135	–3.36218
C	1.10609	–3.46003	–0.82768
H	–0.75161	–3.79646	–1.98409
C	0.79693	–3.51416	1.46827
C	–1.22828	–4.11400	3.84369
H	–3.85001	–5.77067	–4.62730
H	–3.38201	–7.22377	–3.74382
N	–3.83573	1.09814	0.03475
H	–3.80295	0.71548	–1.99397
C	–4.05676	1.55805	2.35180
H	–3.12773	–0.52072	–3.45166
H	–3.05733	–2.20584	–4.04400
C	–5.07801	–1.44587	–3.80542
N	1.60481	–3.33530	0.43895
C	2.01233	–3.39629	–1.97329
H	1.25206	–3.44264	2.47386
H	–0.33677	–3.48559	4.05968
H	–2.08540	–3.67114	4.39581
C	–0.99469	–5.55049	4.35669
Ni	–4.22671	2.95937	–0.01877
N	–4.28538	2.79211	1.85617
C	–4.12792	1.26135	3.82725
Ni	4.22814	–2.96100	–0.02305
N	3.33282	–3.30011	–1.78933
C	1.46413	–3.55154	–3.37937
S	–6.21703	2.66168	–1.31068
S	–4.58271	5.12503	0.33775
N	–1.60430	3.33691	0.44308
N	–3.33243	3.29852	–1.78489
N	–4.57301	3.79747	2.70841
H	–3.51027	0.36511	4.05452
C	3.48493	1.13061	–0.81700
H	3.80636	–0.71531	–1.99654
C	3.53320	0.79185	1.47498
C	4.12152	–1.26700	3.82461
H	–5.69219	3.77275	–4.69994
H	–7.16019	3.33579	–3.82559
H	–5.22204	5.93633	3.80899
H	–5.28694	6.92457	2.35998
N	1.11267	3.82476	0.05166
H	0.75277	3.78804	–1.98122
C	1.54388	4.05251	2.37383
H	–0.45967	3.07667	–3.44616
H	–2.13655	2.98891	–4.05889
C	–1.39148	5.01695	–3.83745
H	5.69176	–3.77142	–4.70562
H	7.15975	–3.33338	–3.83178
H	5.22409	–5.94046	3.80275
H	5.29166	–6.92714	2.35270
N	3.36144	1.61394	0.45577
C	3.43235	2.05185	–1.95108
H	3.46204	1.23434	2.48618
H	3.49906	–0.37414	4.05215
H	3.67326	–2.12801	4.36622
C	5.55966	–1.04930	4.33992
Ni	2.97076	4.23575	0.01987
N	2.78171	4.29113	1.89262
C	1.22914	4.12329	3.84554
N	3.33545	3.37001	–1.75061
C	3.60150	1.52259	–3.36273
S	2.66311	6.24103	–1.24992
S	5.13036	4.60361	0.40184
N	3.77404	4.59101	2.75599
H	0.33670	3.49683	4.06336
H	2.08550	3.68105	4.39936
C	0.99740	5.56178	4.35377
N	3.45885	4.14930	–2.84265
H	3.12753	0.52203	–3.45354
H	3.05715	2.20790	–4.04384
C	5.07783	1.44786	–3.80576
C	3.20919	5.45733	–2.69172
C	4.94018	4.74825	2.13522
N	3.37683	6.20957	–3.82556
N	6.04366	5.01213	2.89993
H	3.85217	5.77449	–4.62157
H	3.38450	7.22635	–3.73573
H	5.89335	5.26176	3.88040
H	6.89783	5.33394	2.44313
H	5.55803	–0.85574	5.43591

H	–3.67588	2.11945	4.37040
C	–5.56776	1.05050	4.34068
S	6.21715	–2.66101	–1.31622
S	4.58629	–5.12646	0.33175
N	3.83596	–1.10020	0.03180
N	4.28503	–2.79552	1.85215
N	4.09601	–3.40586	–2.89472
H	0.45890	–3.08413	–3.44979
H	2.13534	–2.99308	–4.06320
C	1.39471	–5.02260	–3.84039
C	–5.40774	3.16865	–2.75273
C	–4.72201	4.95740	2.07403
C	–1.10539	3.45755	–0.82390
C	–0.79624	3.51774	1.47189
N	–4.09592	3.40487	–2.88999
C	–2.01184	3.39295	–1.96925
C	5.40763	–3.16838	–2.75804
C	4.72442	–4.96036	2.06830
C	3.70918	–0.25889	–1.00231
C	3.79797	–0.59957	1.32435
N	4.57334	–3.80125	2.70369
C	4.05346	–1.56240	2.34874
N	–6.14236	3.31681	–3.90093
H	0.78955	5.56220	5.44714
H	–0.78802	–5.54718	5.45028
H	1.89962	6.18335	4.17209
H	–0.13225	–6.02915	3.84354
H	6.17728	–1.95221	4.14828
H	0.71234	–5.62200	–3.19845
H	–5.54693	–2.45117	–3.74663
H	–5.15104	–1.08790	–4.85643
H	–0.70692	5.61507	–3.19665
H	–5.56843	0.85611	5.43653
H	6.04403	–0.18403	3.83697
H	5.15108	1.09138	–4.85725
H	2.40471	–5.48339	–3.80195
H	5.54664	2.45312	–3.74548
H	–6.18048	1.95671	4.14897
H	0.13630	6.04027	3.83820
H	–1.89566	–6.17415	4.17599
H	–6.05588	0.18808	3.83647
H	–1.02022	5.07836	–4.88459
H	5.66295	0.75008	–3.16723
H	–2.40033	5.48019	–3.79800
H	1.02227	–5.08539	–4.88702
H	–5.66320	–0.74892	–3.16603

Table S9. Atom coordinates of the geometry optimized molecular structure of $[Ni_4(L^{Ph})_4]$ on DFT BP86/def-SV(P) level.

	X	y	z
S	–5.21009	–4.49136	0.36981
Ni	–3.03591	–4.18355	0.02092
C	–5.03390	–4.70228	2.09757
S	–2.78681	–6.19164	–1.24823
N	–3.41452	–1.55826	0.47433
N	–3.37594	–3.30177	–1.74944
N	–1.16749	–3.84158	0.06557
N	–2.86148	–4.28840	1.89604
N	–6.14773	–4.96863	2.84951
N	–3.87023	–4.59411	2.73118
C	–3.26789	–5.38256	–2.69904
C	–3.54208	–1.06558	–0.79374
C	–3.58487	–0.74058	1.49772
N	–3.49576	–4.07095	–2.84289
C	–3.52387	–1.98400	–1.93144
C	–0.33636	–3.69404	–0.97545
C	–0.64872	–3.87060	1.35004
C	–1.60031	–4.16388	2.38159
H	–5.99483	–5.28341	3.81138
H	–6.99495	–5.28293	2.37370
N	3.40921	6.11706	–3.84818
N	6.14816	4.96771	2.85001
H	3.84367	5.65164	–4.65103
H	3.46919	7.13333	–3.77014
H	5.99542	5.28215	3.81201
H	6.99530	5.28216	2.37418
C	4.34501	–1.24030	3.80807
C	5.18832	–0.16034	4.16814
C	5.35751	0.20486	5.51365
C	4.68878	–0.50237	6.52700
C	3.85269	–1.58024	6.18314
C	3.68519	–1.95012	4.84106
H	5.73873	0.38427	3.38364
H	6.02647	1.04336	5.76995
H	4.82135	–0.21734	7.58411
H	3.32034	–2.13968	6.97036
H	3.03190	–2.79634	4.58358
C	1.23973	4.33866	3.81010
C	1.95130	3.68009	4.84269
C	1.58029	3.84489	6.18479

N	–3.40981	–6.11591	–3.84939
C	–3.69672	0.33311	–0.97454
H	–3.47873	–1.17024	2.51006
C	–3.87486	0.64671	1.35064
C	1.06200	–3.53588	–0.79527
H	–0.79475	–3.70648	–1.97427
C	0.73774	–3.57622	1.49635
H	–3.84441	–5.65026	–4.65204
H	–3.46980	–7.13220	–3.77163
N	–3.84320	1.16497	0.06604
H	–3.70695	0.79117	–1.97355
C	–4.16637	1.59945	2.38164
N	1.55465	–3.40491	0.47250
C	1.98013	–3.51778	–1.93316
H	1.16727	–3.46713	2.50843
Ni	–4.18022	3.03436	0.02060
N	–4.28689	2.86082	1.89567
Ni	4.18018	–3.03431	0.01912
N	3.29805	–3.37099	–1.75136
S	–6.18957	2.78946	–1.24759
S	–4.48135	5.20962	0.36866
N	–1.55461	3.40482	0.47370
N	–3.29835	3.37153	–1.74991
N	–4.59053	3.87067	2.73025
S	6.18934	–2.78906	–1.24930
S	4.48136	–5.20967	0.36652
N	3.84316	–1.16493	0.06512
N	4.28713	–2.86130	1.89421
N	4.06687	–3.49021	–2.84512
C	–5.37943	3.26618	–2.69923
C	–4.69456	5.03449	2.09628
C	–1.06216	3.53619	–0.79410
C	–0.73754	3.57582	1.49748
N	–4.06732	3.49103	–2.84353
C	–1.98046	3.51841	–1.93185
C	5.37900	–3.26541	–2.70094
C	4.69483	–5.03502	2.09416
C	3.69654	–0.33278	–0.97520
C	3.87503	–0.64703	1.34987
N	4.59090	–3.87138	2.72847
C	4.16669	–1.60005	2.38056
N	–6.11247	3.40774	–3.84980
N	–4.95823	6.14934	2.84767
C	0.33617	3.69442	–0.97445
H	–1.16691	3.46640	2.50959
C	0.64889	3.87024	1.35104
N	6.11188	–3.40669	–3.85166
N	4.95860	–6.15008	2.84521
C	0.49949	4.67699	6.52910
C	–0.20954	5.34446	5.51617
C	0.15680	5.17797	4.17064
H	2.79982	3.02994	4.58487
H	2.14117	3.31355	6.97166
H	0.21356	4.80746	7.58624
H	–1.05037	6.01036	5.77282
H	–0.38932	5.72743	3.38652
C	–4.34448	1.23930	3.80909
C	–3.68451	1.94883	4.84217
C	–3.85181	1.57858	6.18418
C	–4.68785	0.50061	6.52785
C	–5.35672	–0.20634	5.51441
C	–5.18773	0.15923	4.16898
H	–3.03126	2.79513	4.58483
H	–3.31935	2.13780	6.97147
H	–4.82027	0.21529	7.58491
H	–6.02564	–1.04492	5.77057
H	–5.73825	–0.38516	3.38441
C	–1.23915	–4.33986	3.80903
C	–0.15614	–5.17925	4.16910
C	0.21042	–5.34622	5.51451
C	–0.49847	–4.67914	6.52780
C	–1.57936	–3.84695	6.18396
C	–1.95059	–3.68169	4.84197
H	0.38989	–5.72842	3.38471
H	1.05133	–6.01217	5.77079
H	–0.21238	–4.80997	7.58484
H	–2.14014	–3.31593	6.97110
H	–2.79917	–3.03148	4.58451
C	3.74032	1.44330	–3.31171
C	2.73590	1.55411	–4.30042
C	2.94474	1.03995	–5.58881
C	4.16055	0.40999	–5.91428
C	5.16461	0.29469	–4.93949
C	4.95691	0.80847	–3.64780
H	1.78185	2.04884	–4.05832
H	2.14931	1.13675	–6.34649
H	4.32224	0.00649	–6.92794
H	6.11636	–0.20749	–5.17736
H	5.75003	0.71207	–2.88836
C	1.43818	–3.73390	–3.31331
C	1.54734	–2.72841	–4.30108
C	1.03269	–2.93656	–5.58940
C	0.40377	–4.15271	–5.91564
C	0.29010	–5.15783	–4.94174
C	0.80450	–4.95087	–3.65018
H	2.04125	–1.77410	–4.05830

C	3.54194	1.06586	–0.79399	H	1.12826	–2.14034	–6.34640
H	3.70660	–0.79056	–1.97434	H	–0.00017	–4.31385	–6.92921
C	3.58507	0.74023	1.49737	H	–0.21127	–6.10985	–5.18021
H	–5.64592	3.83982	–4.65327	H	0.70944	–5.74483	–2.89146
H	–7.12865	3.46963	–3.77226	C	–3.74079	–1.44231	–3.31154
H	–5.27445	5.99762	3.80926	C	–4.95744	–0.80744	–3.64733
H	–5.26967	6.99731	2.37133	C	–5.16529	–0.29329	–4.93884
N	1.16746	3.84165	0.06649	C	–4.16132	–0.40825	–5.91376
H	0.79440	3.70720	–1.97334	C	–2.94544	–1.03823	–5.58859
C	1.60065	4.16317	2.38254	C	–2.73645	–1.55277	–4.30037
H	5.64521	–3.83857	–4.65517	H	–5.75049	–0.71131	–2.88778
H	7.12807	–3.46861	–3.77427	H	–6.11709	0.20890	–5.17648
H	5.27497	–5.99863	3.80679	H	–4.32312	–0.00446	–6.92729
H	5.26997	–6.99792	2.36858	H	–2.15008	–1.13477	–6.34637
N	3.41457	1.55819	0.47424	H	–1.78235	–2.04752	–4.05851
C	3.52357	1.98461	–1.93143	C	–1.43872	3.73495	–3.31202
H	3.47909	1.16960	2.50985	C	–0.80520	4.95207	–3.64864
Ni	3.03588	4.18361	0.02164	C	–0.29099	5.15943	–4.94021
N	2.86175	4.28784	1.89683	C	–0.40470	4.15456	–5.91437
N	3.37565	3.30232	–1.74903	C	–1.03345	2.93827	–5.58838
S	2.78659	6.19205	–1.24690	C	–1.54791	2.72972	–4.30005
S	5.21011	4.49133	0.37029	H	–0.71011	5.74583	–2.88971
N	3.87064	4.59326	2.73191	H	0.21025	6.11157	–5.17850
N	3.49530	4.07181	–2.84227	H	–0.00090	4.31602	–6.92795
C	3.26745	5.38338	–2.69802	H	–1.12904	2.14225	–6.34558
C	5.03420	4.70163	2.09816	H	–2.04170	1.77529	–4.05747

Table S10. Atom coordinates of the geometry optimized molecular structure of $[Zn_4(L^{Me})_4]$ on DFT BP86/def2-TZPV level.

	X	y	z		x	y	z
C	3.50664	–1.97529	–3.65285	H	–1.43369	–4.13363	–4.38828
C	3.88040	–1.51420	–2.27347	H	0.94557	–6.91157	–4.71243
H	4.15207	–1.48385	–4.38731	H	1.99003	–7.85129	–3.66841
C	6.40088	0.84705	–2.72891	H	–0.86689	–6.92633	4.72344
N	7.04561	1.37050	–3.81117	H	–1.90879	–7.86513	3.67598
N	5.47395	–0.07815	–3.06615	H	1.49355	4.08822	–4.38921
S	6.82080	1.43607	–1.17202	N	0.08811	5.41261	–3.07059
C	2.19762	–3.04221	–1.18256	N	–1.57592	3.53104	–0.10147
N	1.64143	–3.57745	–0.10446	N	–0.57513	4.76430	2.05928
C	3.21598	–2.06461	–1.10301	S	–1.42594	6.76353	–1.17922
H	1.82786	–3.39859	–2.14594	S	1.47607	6.76890	1.19338
N	3.59111	–1.62316	0.12617	C	–3.42690	–1.98690	3.68048
N	4.82067	–0.62041	–2.03576	N	–4.74789	–0.63338	2.06797
C	3.05807	–2.18150	1.20425	Zn	–5.18085	–0.02939	0.02038
Zn	5.24653	–0.01704	0.01356	C	–0.83670	6.34056	–2.73521
H	6.92999	0.89731	–4.70231	C	–2.13347	2.99601	–1.17897
H	7.86698	1.94072	–3.65475	C	–2.01587	3.15555	1.12813
N	4.81621	0.58639	2.06187	C	–1.46654	3.82200	2.29795

N	3.58526	1.58333	–0.10211
S	6.82380	–1.46460	1.20215
C	2.08291	–3.20219	1.12466
Zn	0.03951	–5.23695	0.00813
H	3.41428	–1.81160	2.16764
C	3.87336	1.47793	2.29785
N	5.47005	0.04702	3.09344
C	3.05104	2.13872	–1.18113
C	3.20841	2.02541	1.12631
C	6.40013	–0.87565	2.75806
C	1.53507	–3.86886	2.29505
N	–1.56486	–3.57972	0.12634
N	–0.56663	–4.80657	–2.03936
N	0.64343	–4.81118	2.05732
S	1.49005	–6.80971	–1.18283
S	–1.40873	–6.81576	1.19366
C	3.49721	1.93939	3.67645
H	3.40862	1.76851	–2.14389
C	2.07309	3.15688	–1.10334
C	2.18788	3.00088	1.20413
N	7.04507	–1.39636	3.84154
C	1.99628	–3.49499	3.67435
C	–2.12069	–3.04766	1.20621
C	–2.00884	–3.20302	–1.10144
C	–1.46067	–3.86574	–2.27391
N	–0.02647	–5.45829	–3.07186
N	0.10362	–5.46660	3.08763
C	0.89879	–6.38632	–2.73793
C	–0.81952	–6.39557	2.75040
H	4.14274	1.44973	4.41202
C	1.52338	3.81988	–2.27493
N	1.63066	3.53321	0.12511
H	1.81726	3.35802	2.16690
H	6.92697	–0.92273	4.73213
H	7.86852	–1.96399	3.68655
H	1.75401	–2.44692	3.91006
H	–1.74883	–3.40504	2.16841
C	–3.14130	–2.07215	1.12996
C	–2.98684	–2.18481	–1.17771
C	–1.92427	–3.48979	–3.65185
N	1.42023	–7.02915	–3.82232
N	–1.34049	–7.04246	3.83258
C	1.98510	3.44421	–3.65358
N	0.62962	4.76063	–2.03897
Zn	0.02616	5.19048	0.00941
C	–3.80474	–1.52499	2.30250
N	–3.51969	–1.62971	–0.09786
H	–3.34562	–1.81432	–2.13991
N	–0.03398	5.41949	3.08903
C	0.88882	6.34846	2.75080
H	–4.07153	–1.49748	4.41700
N	–5.40039	–0.09428	3.10054
N	–3.52534	1.57672	0.13122
N	–4.75763	0.57443	–2.02935
S	–6.75664	–1.48224	–1.16350
S	–6.75662	1.41783	1.21142
N	–1.35954	6.98370	–3.81874
H	–1.76491	3.35257	–2.14275
C	–3.15174	2.01841	–1.09834
C	–2.99094	2.13485	1.20875
C	–1.92608	3.44794	3.67776
N	1.41124	6.99508	3.83243
C	–6.33091	0.82848	2.76662
C	–3.81763	1.46823	–2.26807
N	–5.41222	0.03239	–3.05902
C	–6.33872	–0.89287	–2.72079
H	–0.88604	6.86635	–4.70950
H	–1.92912	7.80581	–3.66387
H	–3.34596	1.76478	2.17252
H	–1.43594	4.09507	4.41161
H	0.93878	6.87881	4.72389
H	1.97940	7.81774	3.67527
N	–6.97445	1.34890	3.85108
C	–3.44557	1.92956	–3.64783
N	–6.98484	–1.41608	–3.80233
H	–6.85520	0.87501	4.74138
H	–7.79810	1.91655	3.69731
H	–4.09193	1.43828	–4.38158
H	–6.87036	–0.94271	–4.69352
H	–7.80601	–1.98635	–3.64499
H	–2.39702	1.68974	–3.88390
H	3.07533	3.55720	–3.75233
H	2.44853	1.69783	3.91017
H	1.50703	–4.14222	4.40870
H	–3.01658	3.55780	3.77707
H	–3.53718	–3.07747	3.77846
H	–1.68546	–2.44037	–3.88507
H	3.61917	–3.06554	–3.75175
H	–2.37793	–1.74539	3.91298
H	3.08690	–3.60487	3.77232
H	3.60764	3.02994	3.77464
H	1.74594	2.39485	–3.88670
H	2.45778	–1.73546	–3.88758
H	–3.55819	3.01984	–3.74640
H	–1.68351	2.39984	3.91305
H	–3.01462	–3.60281	–3.74916

Table S11. Atom coordinates of the geometry optimized molecular structure of $[Zn_4(L^{Et})_4]$ on DFT BP86/def2-TZPV level.

	X	y	z
C	3.50890	−1.91946	−3.67728
C	4.36882	−3.10483	−4.15592
C	3.85464	−1.47402	−2.28080
H	2.44302	−2.18306	−3.73715
H	4.22919	−3.98882	−3.51833
H	5.43308	−2.83572	−4.14011
H	4.09948	−3.38368	−5.18442
C	6.38801	0.86703	−2.74467
N	7.04631	1.36538	−3.82974
N	5.46889	−0.07064	−3.07218
S	6.78329	1.49265	−1.19604
C	2.18522	−3.02148	−1.17795
N	1.63718	−3.55328	−0.09459
C	3.19140	−2.02997	−1.11152
H	1.82009	−3.39878	−2.13478
N	3.56959	−1.58480	0.11665
N	4.80336	−0.58901	−2.03630
C	3.04378	−2.13841	1.20009
Zn	5.21493	0.03442	0.00018
H	6.93498	0.87925	−4.71431
H	7.86060	1.94682	−3.67865
N	4.79178	0.65057	2.03651
N	3.53919	1.62236	−0.11665
S	6.81046	−1.39377	1.19687
C	2.07088	−3.16260	1.13378
Zn	0.04859	−5.22849	0.02231
H	3.41085	−1.76298	2.15691
C	3.82678	1.51786	2.28082
N	5.46706	0.14524	3.07252
C	3.00307	2.16585	−1.20017
C	3.15319	2.06099	1.11145
C	6.40361	−0.77510	2.74530
C	1.52284	−3.83155	2.30354
N	−1.57101	−3.58275	0.12500
N	−0.56598	−4.82538	−2.01851
N	0.65626	−4.79725	2.05947
S	1.51210	−6.80165	−1.16094
S	−1.38502	−6.81887	1.21937
C	3.47314	1.95735	3.67720
H	3.37673	1.79686	−2.15695
C	2.01161	3.17209	−1.13401
C	2.12908	3.03398	1.17775
N	7.07131	−1.26051	3.83048
C	1.95690	−3.47272	3.70029
H	−1.82849	−7.89471	3.70452
H	2.15465	2.41289	−3.75711
C	3.07449	4.33711	−4.18727
N	0.04418	5.44105	−3.09646
N	−1.63700	3.52477	−0.12507
N	−0.65558	4.78662	2.01823
S	−1.51134	6.76372	−1.21966
S	1.38568	6.80083	1.16057
C	−3.47406	−1.95510	3.69385
N	−4.79153	−0.66126	2.04199
Zn	−5.21424	−0.06232	0.00048
H	3.96093	4.20024	−3.55249
H	2.80526	5.40139	−4.17479
H	3.34946	4.06362	−5.21572
C	−0.89215	6.36157	−2.76912
C	−2.18526	2.98394	−1.20384
C	−2.07024	3.14417	1.10662
C	−1.52197	3.82290	2.27062
N	−0.14562	5.46647	3.04897
C	0.77356	6.40124	2.71350
H	−2.40369	−2.19916	3.75623
C	−4.31298	−3.15184	4.18139
N	−5.46696	−0.14705	3.07354
N	−3.56887	1.55767	0.10302
N	−4.80294	0.54371	−2.04126
S	−6.78247	−1.53097	−1.18294
S	−6.80928	1.37670	1.18466
N	−1.39505	7.01506	−3.85501
H	−1.82050	3.35344	−2.16385
C	−3.19116	1.99276	−1.12891
C	−3.04289	2.12036	1.18169
C	−1.95550	3.47559	3.67044
N	1.26384	7.07375	3.79351
H	−4.15716	−4.03818	3.55085
H	−5.38187	−2.90191	4.16292
H	−4.03938	−3.41772	5.21219
C	−6.40302	0.77091	2.73834
C	−3.85458	1.42698	−2.29336
N	−5.46858	0.01646	−3.07257
C	−6.38743	−0.91859	−2.73693
H	−0.91253	6.89988	−4.74106
H	−1.97578	7.83007	−3.70507
H	−3.40964	1.75281	2.14169
H	−2.19960	2.40543	3.73622

C	–2.12921	–3.05244	1.20388
C	–2.01102	–3.20975	–1.10661
C	–1.45005	–3.87781	–2.27075
N	–0.04304	–5.49513	–3.04935
N	0.14654	–5.46837	3.09603
C	0.89327	–6.41279	–2.71394
C	–0.77270	–6.40596	2.76872
H	3.65427	1.10508	4.34683
C	4.31156	3.15818	4.15544
C	1.45098	3.83038	–2.30385
N	1.57116	3.55526	0.09432
H	1.75733	3.40492	2.13451
H	6.95089	–0.77627	4.71489
H	7.89636	–1.82663	3.67954
H	2.20119	–2.40209	3.75713
H	–1.75782	–3.41550	2.16381
C	–3.15314	–2.07987	1.12918
C	–3.00234	–2.20398	–1.18145
C	–1.88957	–3.53795	–3.67054
N	1.39647	–7.07547	–3.79408
N	–1.26284	–7.06917	3.85454
H	4.15584	4.03937	3.51771
H	5.38050	2.90835	4.13950
H	4.03741	3.43231	5.18394
C	1.89110	3.47897	–3.70059
N	0.56676	4.77997	–2.05985
Zn	–0.04824	5.20048	–0.02265
C	–3.82697	–1.52689	2.29379
N	–3.53869	–1.65141	–0.10264
H	–3.37569	–1.84294	–2.14137
H	–1.03113	–3.70620	–4.33562
H	0.91427	–6.96779	–4.68125
H	1.97732	–7.88907	–3.63710
H	–0.78224	–6.94535	4.74046
C	–3.15424	4.31624	4.15001
H	0.78345	6.95745	4.68057
H	1.82955	7.89792	3.63638
N	–7.07074	1.26577	3.81925
C	–3.50947	1.86107	–3.69356
N	–7.04569	–1.42641	–3.81762
H	–4.03814	4.15770	3.51674
H	–2.90444	5.38509	4.12819
H	–3.42401	4.04674	5.18089
H	–6.95069	0.78897	4.70774
H	–7.89557	1.83087	3.66334
H	–3.67506	0.99999	–4.35591
H	–6.93452	–0.94788	–4.70634
H	–7.85989	–2.00664	–3.66147
C	3.15568	–4.30956	4.18637
C	–3.07278	–4.40003	–4.15065
C	–4.36994	3.04224	–4.18153
H	2.90571	–5.37852	4.17346
H	3.42585	–4.03161	5.21489
H	4.03939	–4.15640	3.55150
H	–2.80360	–5.46418	–4.12928
H	–3.34729	–4.13501	–5.18144
H	–3.95950	–4.25789	–3.51741
H	–5.43412	2.77295	–4.16314
H	–4.10107	3.31279	–5.21237
H	–4.23035	3.93143	–3.55122
H	–2.44369	2.12449	–3.75598
H	1.03293	3.64169	–4.36741
H	2.40269	2.20165	3.73711
H	1.10197	–3.65116	4.36725
H	–1.10037	3.65967	4.33561
H	–3.65529	–1.09739	4.35647
H	–2.15306	–2.47236	–3.73596
H	3.67450	–1.06388	–4.34671

Table S12. Atom coordinates of the geometry optimized molecular structure of $[Zn_4(L^{iPr})_4]$ on DFT BP86/def-SV(P) level.

	X	y	z
C	4.01625	17.38829	16.64545
C	2.68595	17.56314	15.88030
C	4.07351	18.07117	18.00856
C	4.46463	15.91055	16.71505
H	4.78710	17.93443	16.06257
H	2.35205	18.62409	15.88549
H	1.85920	16.93784	16.28312
H	2.82517	17.26094	14.81778
H	5.46723	15.82196	17.18797
H	4.53576	15.48856	15.68698
	x	y	z
C	1.56086	21.82601	16.01393
N	–0.00293	25.13450	17.21027
N	–1.62646	23.30762	20.22454
N	–0.55461	24.46152	22.36883
S	–1.47738	26.48841	19.14189
S	1.47780	26.48827	21.44024
C	–4.01636	17.38849	23.93651
N	–4.93667	19.05617	22.33032
Zn	–5.17611	19.78015	20.29109
H	–0.48118	17.95399	16.16364

H	3.76145	15.26722	17.28900
C	6.56480	20.50662	17.60853
N	7.33301	20.92970	16.56268
N	5.71996	19.49896	17.27435
S	6.75664	21.29294	19.13103
C	2.23158	16.69315	19.12676
N	1.62647	16.25236	20.22441
C	3.28593	17.64820	19.16740
H	1.86636	16.27683	18.17596
N	3.57950	18.19828	20.38245
N	4.93662	19.05591	18.25166
C	2.99672	17.73423	21.48320
Zn	5.17611	19.77984	20.29089
H	7.27821	20.41835	15.67748
H	8.06822	21.61858	16.72282
N	4.93674	20.50377	22.33014
N	3.57957	21.36147	20.19941
S	6.75664	18.26668	21.45069
C	2.03298	16.68666	21.45336
Zn	–0.00015	14.69337	20.29095
H	3.30891	18.20829	22.42605
C	4.07367	21.48854	22.57329
N	5.72010	20.06069	23.30742
C	2.99677	21.82555	19.09869
C	3.28607	21.91155	21.41447
C	6.56489	19.05300	22.97320
C	1.46319	16.03385	22.63376
N	–1.62667	16.25247	20.35752
N	–0.55495	15.09851	18.21319
N	0.55468	15.09843	22.36871
S	1.47734	13.07160	19.14171
S	–1.47774	13.07168	21.44016
C	4.01646	22.17138	23.93642
H	3.30889	21.35148	18.15582
C	2.03309	22.87318	19.12856
C	2.23178	22.86667	21.45516
N	7.33314	18.62989	24.01902
C	1.91628	16.31898	24.06185
C	–2.23176	16.69326	21.45517
C	–2.03316	16.68681	19.12857
C	–1.46341	16.03399	17.94816
N	0.00283	14.42556	17.21016
N	–0.00315	14.42550	23.37174
C	0.91511	13.48643	17.56586
C	–0.91549	13.48644	23.01602
H	4.78737	21.62526	24.51922
C	2.68622	21.99643	24.70166
C	1.46332	23.52604	17.94818
H	–2.14228	18.54093	16.51164
H	–1.77080	17.80680	14.92313
H	0.48120	21.60618	16.16346
H	2.14229	21.01924	16.51147
H	1.77086	21.75350	14.92301
C	–0.91520	26.07362	17.56601
C	–2.23161	22.86685	19.12691
C	–2.03293	22.87330	21.45350
C	–1.46311	23.52610	22.63389
N	0.00325	25.13444	23.37184
C	0.91559	26.07349	23.01611
H	–4.78718	17.93466	24.51939
C	–2.68604	17.56328	24.70164
N	–5.71999	19.49924	23.30764
N	–3.57949	21.36170	20.38262
N	–4.93670	20.50411	18.25186
S	–6.75671	18.26709	19.13126
S	–6.75658	21.29330	21.45098
N	–1.43992	26.74225	16.49676
H	–1.86640	23.28315	18.17610
C	–3.28597	21.91180	19.16757
C	–2.99667	21.82572	21.48335
C	–1.91623	23.24103	24.06198
N	1.44036	26.74206	24.08539
H	–2.35210	18.62421	24.69645
H	–1.85932	16.93795	24.29880
H	–2.82526	17.26108	25.76416
C	–6.56478	20.50694	22.97347
C	–4.07359	21.48886	18.00875
N	–5.72009	20.06110	17.27457
C	–6.56492	19.05344	17.60877
H	–1.03624	26.57477	15.57087
H	–2.06262	27.53458	16.65643
H	–3.30883	21.35166	22.42621
H	–1.31157	23.94992	24.66521
C	–1.56078	21.82599	24.56807
H	1.03667	26.57460	25.01127
H	2.06312	27.53435	23.92573
N	–7.33298	20.93004	24.01933
C	–4.01635	22.17174	16.64563
N	–7.33318	18.63039	16.56294
H	–0.48114	21.60607	24.41852
H	–2.14230	21.01930	24.07050
H	–1.77077	21.75346	25.65899
H	–7.27820	20.41867	24.90451
H	–8.06816	21.61894	23.85919
H	–4.78723	21.62561	16.06279
C	–2.68607	21.99685	15.88045

N	1.62665	23.30750	20.35753
H	1.86661	23.28299	22.40597
H	7.27839	19.14124	24.90422
H	8.06832	17.94100	23.85884
H	1.31164	15.61008	24.66509
C	1.56077	17.73402	24.56790
H	−1.86659	16.27689	22.40596
C	−3.28605	17.64839	21.41455
C	−2.99684	17.73444	19.09876
C	−1.91646	16.31918	16.52008
N	1.43980	12.81783	16.49657
N	−1.44022	12.81785	24.08530
H	2.35237	20.93547	24.69644
H	1.85941	22.62172	24.29893
H	2.82551	22.29859	25.76419
C	1.91643	23.24099	16.52009
N	0.55488	24.46153	18.21327
Zn	0.00015	24.86662	20.29105
H	0.48112	17.95390	24.41832
H	2.14227	18.54072	24.07032
H	1.77074	17.80659	25.65882
C	−4.07360	18.07138	22.57340
N	−3.57958	18.19851	20.19951
H	−3.30900	18.20852	18.15591
H	−1.31188	15.61024	15.91683
C	−1.56084	17.73419	16.01405
H	1.03608	12.98532	15.57070
H	2.06250	12.02549	16.65621
H	−1.03650	12.98531	25.01117
H	−2.06298	12.02556	23.92565
H	1.31186	23.94997	15.91688
H	−3.76148	24.29280	17.28917
H	−7.27841	19.14175	15.67775
H	−8.06839	17.94152	16.72310
H	−2.35220	20.93589	15.88564
H	−1.85930	22.62213	16.28325
H	−2.82532	22.29905	14.81793
C	4.46477	23.64914	23.86684
C	3.39873	15.95092	24.29970
C	−3.39894	15.95123	16.28221
C	3.39891	23.60898	16.28231
C	−4.46480	15.91077	23.86690
C	−3.39867	23.60915	24.29980
C	−4.46469	23.64948	16.71525
H	5.46733	23.73779	23.39385
H	4.53594	24.07110	24.89492
H	3.76152	24.29245	23.29295
H	3.59568	14.89698	24.00449
H	3.64303	16.05098	25.38144
H	4.11076	16.59453	23.73809
H	−3.59598	14.89730	16.57739
H	−3.64323	16.05133	15.20046
H	−4.11093	16.59488	16.84383
H	3.59592	24.66288	16.57759
H	3.64324	23.50898	15.20056
H	4.11089	22.96529	16.84390
H	−5.46741	15.82222	23.39398
H	−4.53593	15.48877	24.89496
H	−3.76165	15.26742	23.29294
H	−3.59558	24.66309	24.00457
H	−3.64299	23.50913	25.38155
H	−4.11072	22.96556	23.73820
H	−5.46728	23.73810	17.18820
H	−4.53584	24.07148	15.68718

Table S13. Atom coordinates of the geometry optimized molecular structure of $[Zn_4(L^{Ph})_4]$ on DFT BP86/def-SV(P) level.

	X	y	z
C	3.91556	−1.58187	−2.32198
C	6.45593	0.79994	−2.72403
N	7.18926	1.24634	−3.78779
N	5.55445	−0.15529	−3.07196
S	6.74743	1.49442	−1.17420
C	2.13231	−3.02108	−1.20050
N	1.60545	−3.55429	−0.10240
C	3.19763	−2.07972	−1.14816
H	1.70336	−3.34550	−2.16284
N	3.55716	−1.60125	0.07852
N	4.82498	−0.63865	−2.07665
C	3.03072	−2.13487	1.17662
H	−0.74613	7.10554	−4.61284
H	−1.85576	7.99028	−3.54889
H	−3.30565	1.67595	2.18752
H	0.78022	7.08549	4.66813
H	1.88985	7.97526	3.60837
N	−7.14879	1.22454	3.81990
N	−7.18990	−1.25983	−3.71389
H	−7.06185	0.70812	4.70076
H	−7.95716	1.82576	3.65412
H	−7.11252	−0.74493	−4.59653
H	−7.99641	−1.86077	−3.53832
C	−2.10586	3.64097	3.69277

Zn	5.15194	–0.01381	–0.01825
H	7.10408	0.73434	–4.67139
H	7.99709	1.84706	–3.61761
N	4.84498	0.60908	2.04397
N	3.55682	1.57334	–0.09810
S	6.75861	–1.52276	1.12046
C	2.09039	–3.20106	1.12358
Zn	0.01885	–5.14979	–0.00559
H	3.36005	–1.71096	2.13953
C	3.93744	1.55153	2.29895
N	5.58396	0.12464	3.03168
C	3.02006	2.10792	–1.19071
C	3.20831	2.05018	1.13240
C	6.48206	–0.83018	2.67388
C	1.60012	–3.92626	2.29608
N	–1.56824	–3.55470	0.10179
N	–0.62159	–4.82439	–2.05945
N	0.65721	–4.83600	2.05080
S	1.51667	–6.74796	–1.17179
S	–1.47917	–6.75533	1.14972
H	3.34078	1.68527	–2.15704
C	2.07960	3.17346	–1.12778
C	2.14279	2.99064	1.19562
N	7.22548	–1.27788	3.73006
C	–2.09393	–3.02727	1.20324
C	–2.05480	–3.19533	–1.12175
C	–1.56547	–3.91403	–2.29862
N	–0.14592	–5.55457	–3.05794
N	0.18052	–5.57177	3.04466
C	0.81101	–6.45675	–2.71659
C	–0.77563	–6.47243	2.69703
C	1.57811	3.89982	–2.29486
N	1.60560	3.52478	0.10301
H	1.72238	3.31358	2.16218
H	7.14897	–0.76666	4.61490
H	8.03154	–1.87854	3.55149
H	–1.66375	–3.35651	2.16342
C	–3.15959	–2.08596	1.15705
C	–2.99584	–2.12944	–1.16816
N	1.24874	–7.19118	–3.78316
N	–1.21447	–7.21286	3.75899
N	0.63595	4.80765	–2.03982
Zn	0.01808	5.11961	0.02318
C	–3.87591	–1.59417	2.33437
N	–3.52106	–1.60154	–0.06672
H	–3.32672	–1.70095	–2.12853
H	0.73055	–7.10582	–4.66314
H	1.85011	–7.99937	–3.61701
C	–3.50447	3.68151	3.90532
C	–4.04568	3.45526	5.18140
C	–3.19812	3.18674	6.26907
C	–1.80572	3.14836	6.07144
C	–1.26234	3.37779	4.79868
H	–4.18193	3.90434	3.06421
H	–5.13899	3.48468	5.31892
H	–3.62127	3.00879	7.27191
H	–1.13219	2.93812	6.91898
H	–0.17219	3.34957	4.65599
C	2.14082	3.65686	–3.65355
C	3.53939	3.69808	–3.86631
C	4.08026	3.47685	–5.14341
C	3.23236	3.21282	–6.23193
C	1.84001	3.17390	–6.03410
C	1.29697	3.39831	–4.76030
H	4.21709	3.91746	–3.02448
H	5.17354	3.50665	–5.28108
H	3.65523	3.03879	–7.23558
H	1.16622	2.96715	–6.88230
H	0.20685	3.36966	–4.61746
C	3.69729	2.11711	3.65695
C	3.73888	3.51612	3.86664
C	3.52024	4.05968	5.14304
C	3.25848	3.21408	6.23389
C	3.21922	1.82131	6.03910
C	3.44104	1.27559	4.76600
H	3.95648	4.19202	3.02291
H	3.55026	5.15326	5.27833
H	3.08647	3.63908	7.23700
H	3.01422	1.14931	6.88915
H	3.41211	0.18517	4.62553
C	3.66336	–2.14913	–3.67710
C	3.70453	–3.54828	–3.88581
C	3.47529	–4.09325	–5.15975
C	3.20300	–3.24899	–6.24904
C	3.16384	–1.85608	–6.05520
C	3.39629	–1.30895	–4.78460
H	3.93026	–4.22316	–3.04341
H	3.50538	–5.18691	–5.29432
H	3.02271	–3.67511	–7.25021
H	2.95064	–1.18511	–6.90404
H	3.36749	–0.21843	–4.64486
C	2.17396	–3.68026	3.64958
C	3.57420	–3.72078	3.85098
C	4.12535	–3.49702	5.12324
C	3.28627	–3.23099	6.21810
C	1.89235	–3.19261	6.03151

H	–0.69720	–7.13236	4.63996
H	–1.81544	–8.02026	3.58765
N	0.14915	5.54434	–3.02809
N	–1.56918	3.52455	–0.06413
N	–0.60042	4.79852	2.08451
S	–1.49428	6.72288	–1.11583
S	1.52973	6.71832	1.16975
N	–4.78616	–0.65018	2.09519
Zn	–5.11607	–0.01437	0.04066
C	–0.80509	6.44300	–2.67017
C	–2.10594	2.99498	–1.15917
C	–2.04376	3.16817	1.16498
C	–1.54268	3.88958	2.33530
N	–0.11412	5.53099	3.07616
C	0.84000	6.43146	2.72258
N	–5.51425	–0.17232	3.09418
N	–3.52081	1.57256	0.12802
N	–4.80884	0.61814	–2.01857
S	–6.72429	–1.51648	–1.10522
S	–6.71092	1.48683	1.20706
N	–1.25536	7.18393	–3.72701
H	–1.68507	3.32186	–2.12423
C	–3.17163	2.05443	–1.10034
C	–2.98444	2.10254	1.22307
N	1.28965	7.16794	3.78278
C	–6.41675	0.78426	2.75272
C	–3.90035	1.56083	–2.26926
N	–5.54753	0.13829	–3.00872
C	–6.44654	–0.81737	–2.65547
H	–3.89024	–4.23879	3.04329
H	–3.46214	–5.21332	5.28901
H	–2.97567	–3.71092	7.25119
H	–2.90295	–1.21934	6.91655
H	–3.32306	–0.24194	4.66260
C	1.33908	–3.41959	4.76260
H	4.24501	–3.94161	3.00406
H	5.21972	–3.52642	5.25211
H	3.71727	–3.05499	7.21796
H	1.22541	–2.98427	6.88471
H	0.24783	–3.39131	4.62856
C	–2.14135	–3.66160	–3.65008
C	–3.54178	–3.70281	–3.84991
C	–4.09478	–3.47350	–5.12038
C	–3.25741	–3.20102	–6.21495
C	–1.86330	–3.16176	–6.02989
C	–1.30819	–3.39431	–4.76280
H	–4.21124	–3.92863	–3.00325
H	–5.18926	–3.50366	–5.24806
H	–3.68986	–3.02068	–7.21340
H	–1.19769	–2.94841	–6.88290
H	–0.21682	–3.36536	–4.62992
C	–3.65883	2.13127	–3.62500
C	–3.70013	3.53101	–3.82975
C	–3.48032	4.07906	–5.10403
C	–3.21759	3.23730	–6.19763
C	–3.17855	1.84384	–6.00772
C	–3.40157	1.29367	–4.73676
H	–3.91842	4.20391	–2.98381
H	–3.51019	5.17310	–5.23550
H	–3.04468	3.66583	–7.19908
H	–2.97278	1.17482	–6.85991
H	–3.37279	0.20275	–4.60014
C	–3.62145	–2.16794	3.68634
C	–3.66285	–3.56803	3.88851
C	–3.43179	–4.11905	5.15951
C	–3.15736	–3.28002	6.25232
C	–3.11785	–1.88623	6.06494
C	–3.35215	–1.33308	4.79730