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Supporting Information

Nickel, copper, and zinc dinuclear helicates. How do bulky groups influence their architecture?

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1. Experimental data of Schiff base ligands (3-5)

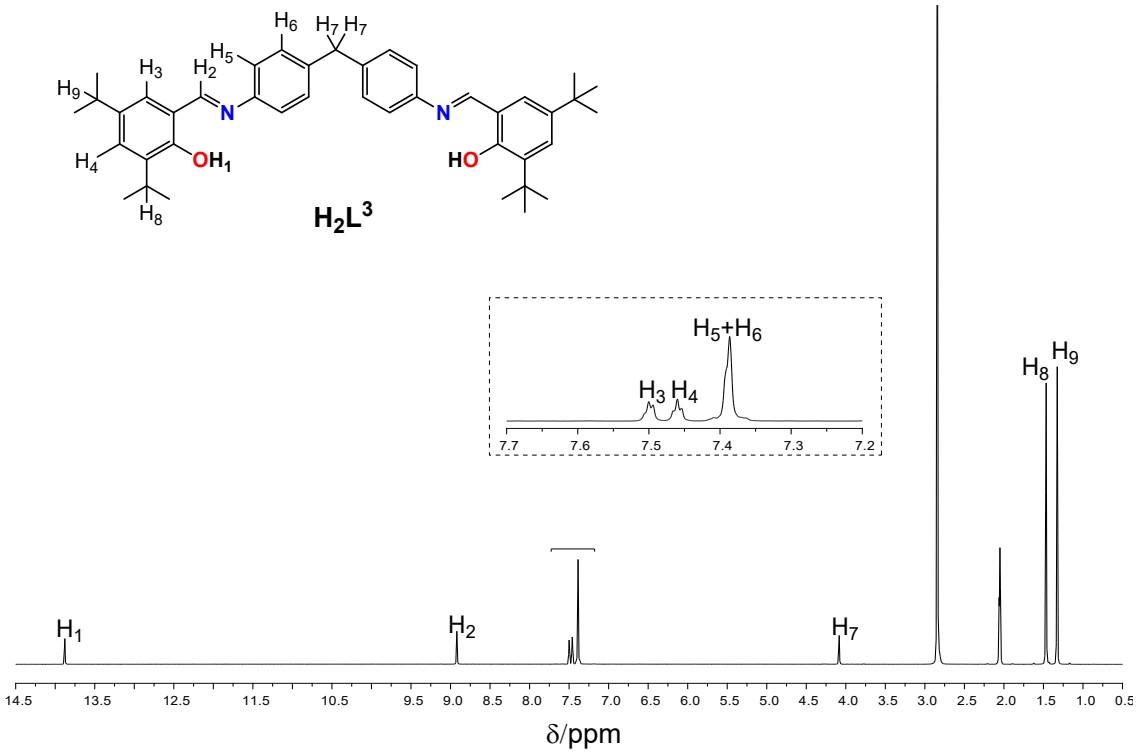

Figure S1. NMR spectrum of the ligand H_2L^3 **3** (400 MHz, acetone-d_6).

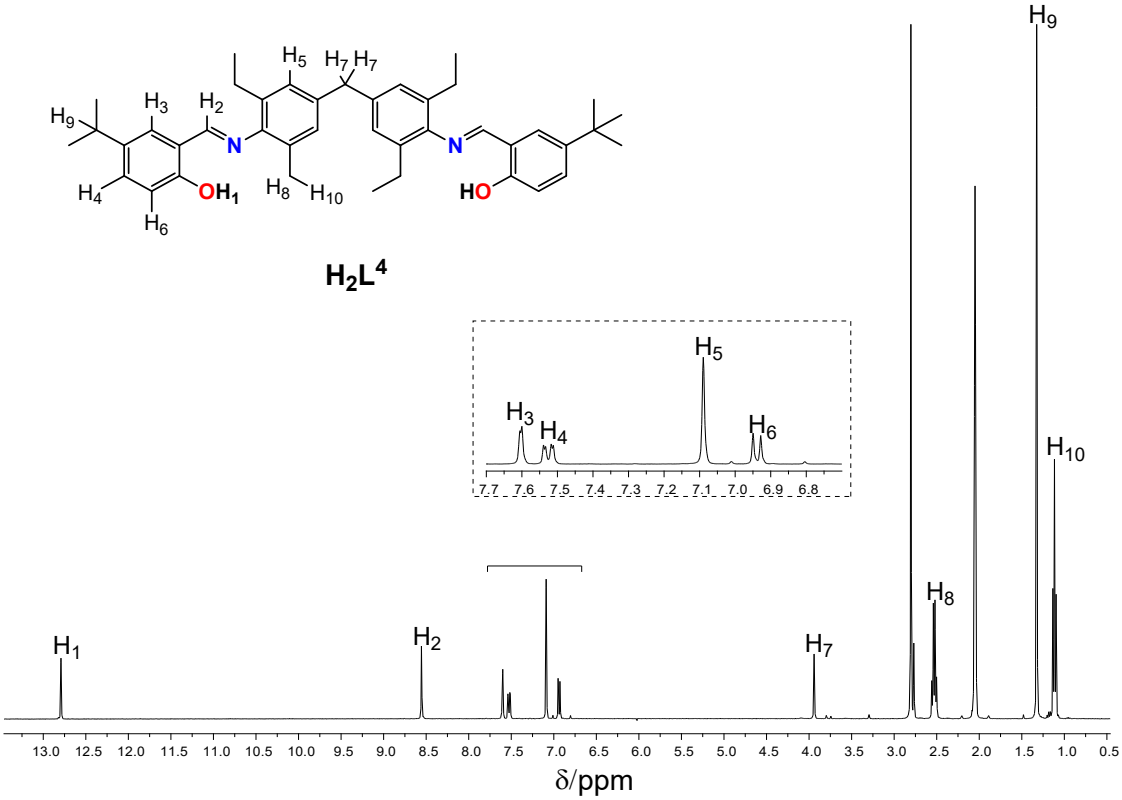

Figure S2. NMR spectrum of the ligand H_2L^4 **4** (400 MHz, acetone-d_6).

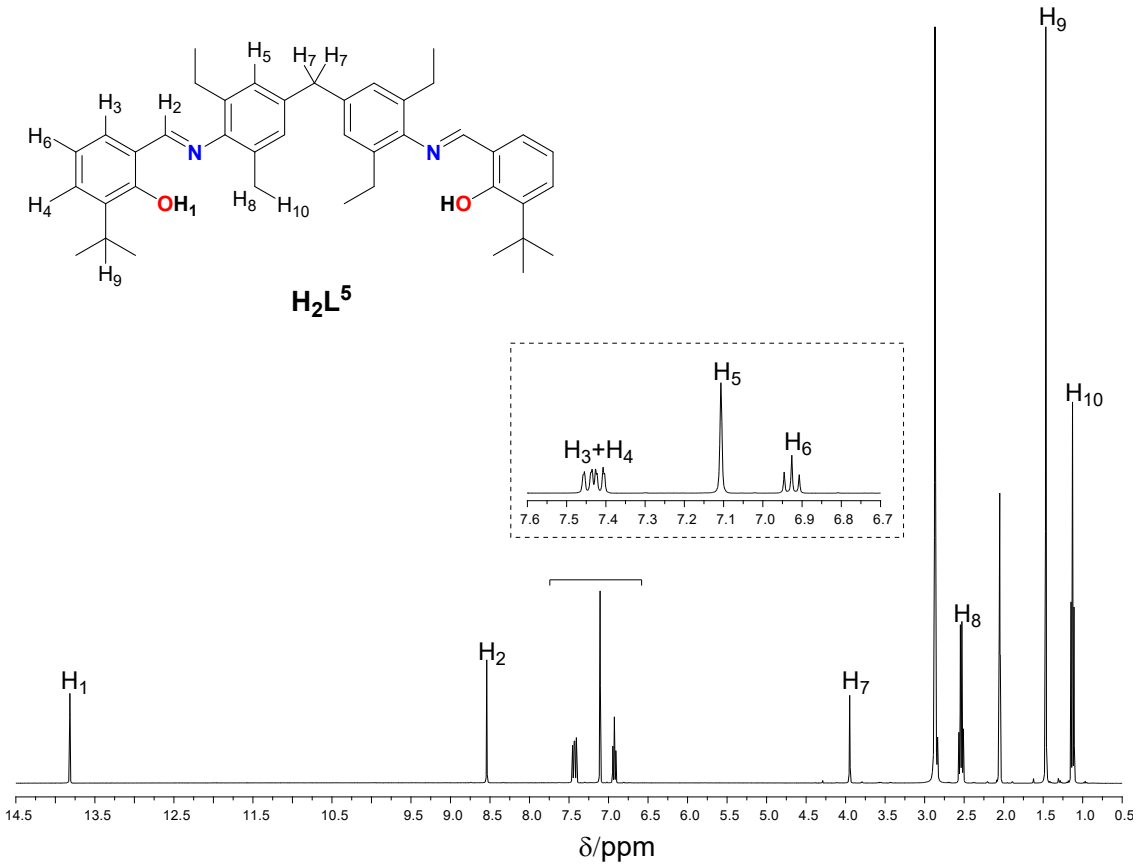

Figure S3. NMR spectrum of the ligand H_2L^5 **5** (400 MHz, acetone-d_6).

2. Crystallographic data of ligands H_2L^4 4* and H_2L^5 5*

H_2L^4 4*: $C_{43}H_{54}N_2O_2$, *Mw* = 630.88 g/mol, crystal dimensions: 0.34 × 0.22 × 0.05 mm^3, triclinic, *P* $\bar{1}$, *a* = 9.0717(8), *b* = 9.9041(7), *c* = 22.0498(19) Å, *α* = 77.049(3), *β* = 78.483(4), *γ* = 79.415(4) º, *V* = 1871.7(3) Å^3, *Z* = 2, *μ* = 0.07 mm^{-1}, radiation *λ*(Mo-K$_\alpha$) = 0.7107 Å, *T* = 100 K, measured/unique reflexions 139133/13629 (R_{int} = 0.068), *R* = 0.049, *wR* = 0.146, *GOF* = 1.032, max/min residual density 0.37/ -0.27 e.Å^{-3}.

H_2L^5 5*: $C_{43}H_{54}N_2O_2$, *Mw* = 630.88 g/mol, crystal dimensions: 0.18 × 0.11 × 0.09 mm^3, triclinic, *P* $\bar{1}$, *a* = 9.9049(12), *b* = 13.1890(19), *c* = 15.798 (2) Å, *α* = = 67.796(5), *β* = 82.499(5), *γ* = 76.969(5) º, *V* = 1859.2 (4) Å^3, *Z* = 2, *μ* = 0.07 mm^{-1}, radiation *λ*(Mo-K$_\alpha$) = 0.7107 Å, *T* = 100 K, measured/unique reflexions 78814/9228 (R_{int} = 0.111), *R* = 0.065, *wR* = 0.135, *GOF* = 1.073, max/min residual density 0.27/ -0.28 e.Å^{-3}.

Table S1. Main bond distances and angles in H_2L^4 **4***.

Bond distances (Å)			
C4—O1	1.3547 (13)	**C23—O2**	1.3509 (12)
C8—N1	1.4339 (13)	**C21—N2**	1.2837 (13)
O1—H1···N1	0.94 (2)	**O2—H2···N2**	0.923 (19)
Bond angles (°)			
O1—C4—C3	119.18 (9)	**O2—C23—C22**	122.02 (9)
O1—C4—C5	121.98 (9)	**O2—C23—C24**	118.89 (9)
C13—C8—N1	119.92 (9)	**C17—C18—N2**	118.62 (9)
C9—C8—N1	118.39 (9)	**C19—C18—N2**	119.65 (9)
N1—C7—C5	121.60 (9)	**N2—C21—C22**	120.80 (9)
C13—C8—N1	119.92 (9)	**C17—C18—N2**	118.62 (9)
C7—N1—C8	119.04 (9)	**C21—N2—C18**	122.22 (9)

Table S2. Main bond distances and angles in H_2L^5 **5***.

Bond distances (Å)			
C18—O1	1.348 (2)	**C4—O2**	1.351 (2)
C6—N1	1.277 (2)	**C16—N2**	1.281 (2)
C7—N1	1.435 (2)	**C15—N2**	1.420 (2)
O1—H1···N2	0.92 (2)	**O2—H2···N1**	0.95 (2)
Bond angles (°)			
O1—C18—C19	119.39 (16)	**O2—C4—C5**	119.49 (17)
O1—C18—C17	119.63 (17)	**O2—C4—C3**	119.32 (17)
N1—C6—C5	122.89 (18)	**C14—C15—N2**	116.82 (16)
C8—C7—N1	120.33 (16)	**C32—C15—N2**	122.59 (16)
C28—C7—N1	118.24 (16)	**N2—C16—C17**	121.88 (17)
C6—N1—C7	120.01 (16)	**C16—N2—C15**	123.51 (16)
O1—C18—C19	119.39 (16)	**O2—C4—C5**	119.49 (17)

3. Experimental data of nickel and zinc helicates

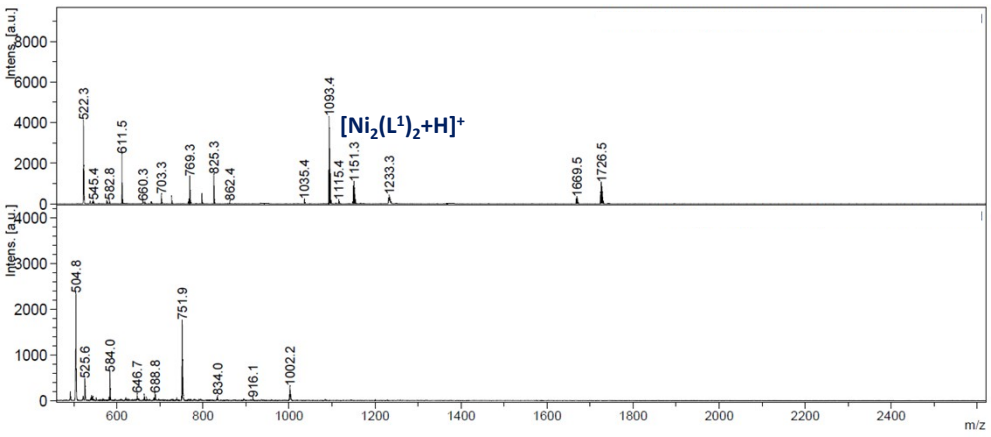

Figure S4. Mass spectrum of $[Ni_2(L^1)_2]$ **6**.

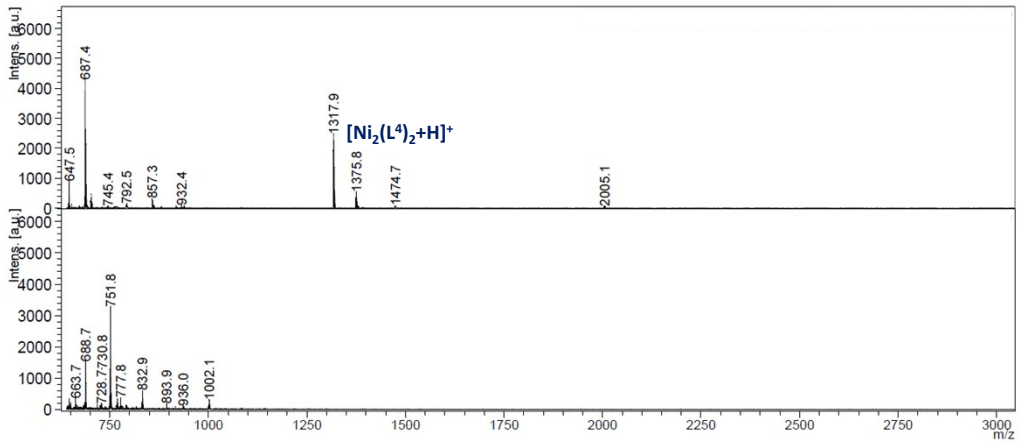

Figure S5. Mass spectrum of $[Ni_2(L^4)_2]$ **9**.

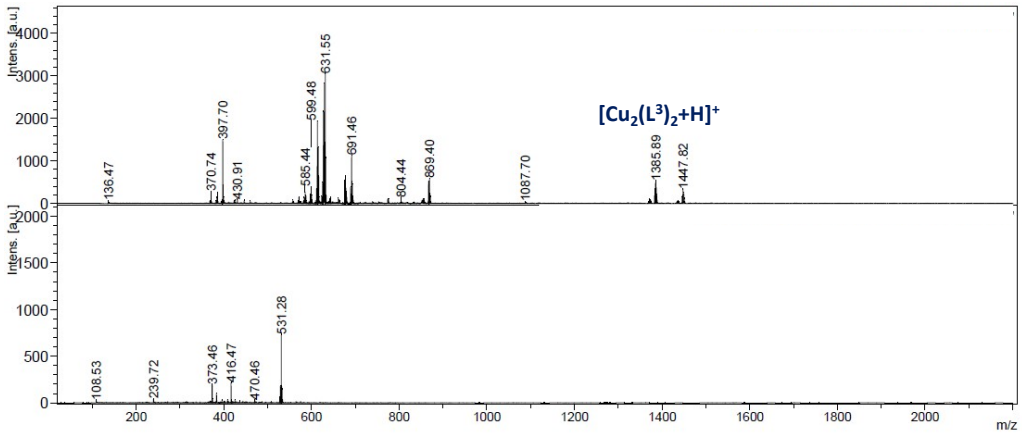

Figure S6. Mass spectrum of $[Cu_2(L^3)_2]$ **11**.

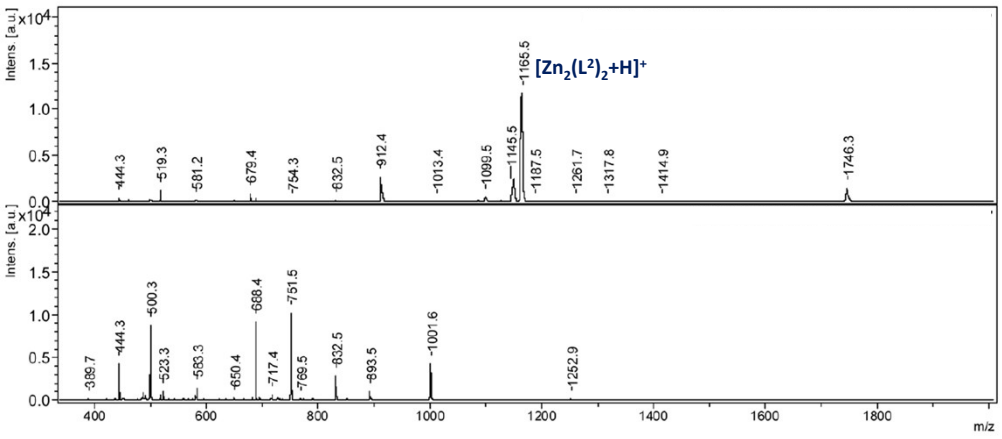

Figure S7. Mass spectrum of $[Zn_2(L^2)_2]$ **12**.

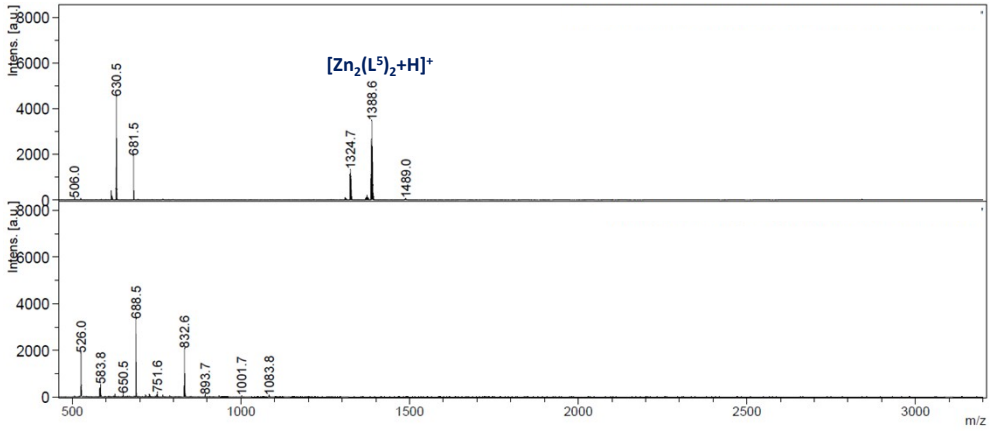

Figure S8. Mass spectrum of $[Zn_2(L^5)_2]$ **15**.

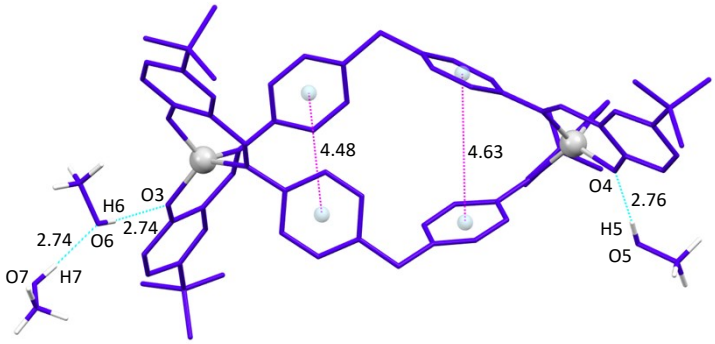

Figure S9. π-π interactions and hydrogen bonds in $[Zn_2(L^1)_2]$ $2.8CH_3OH$ **6***.

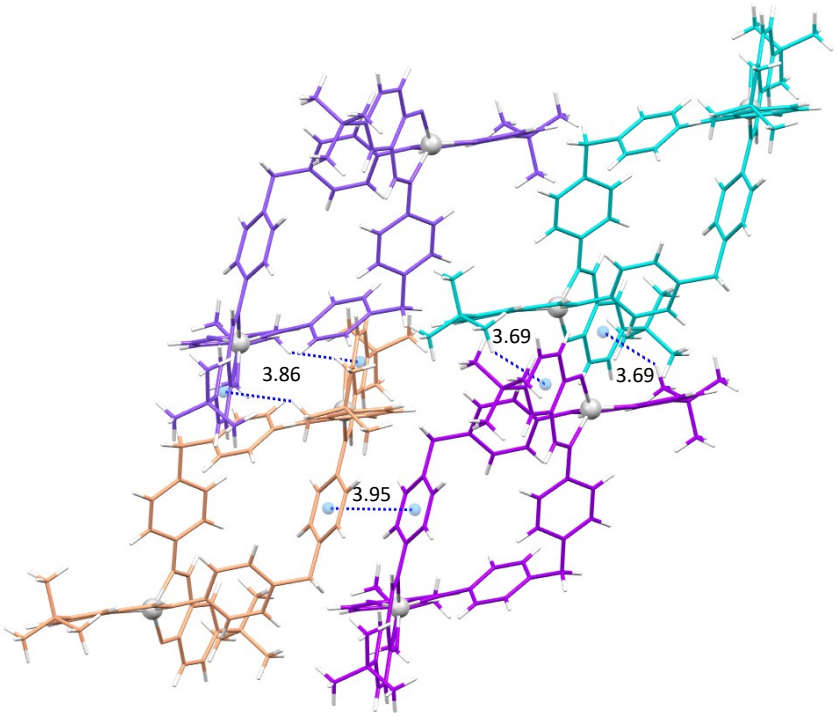

Figure S10. Intermolecular CH···π interactions in the crystal lattice of the $[Zn_2(L^1)_2]$ $2.8CH_3OH$ **6***: C66—H66c···centroid 3.86 Å, C33-H33c···centroid 3.69 Å.

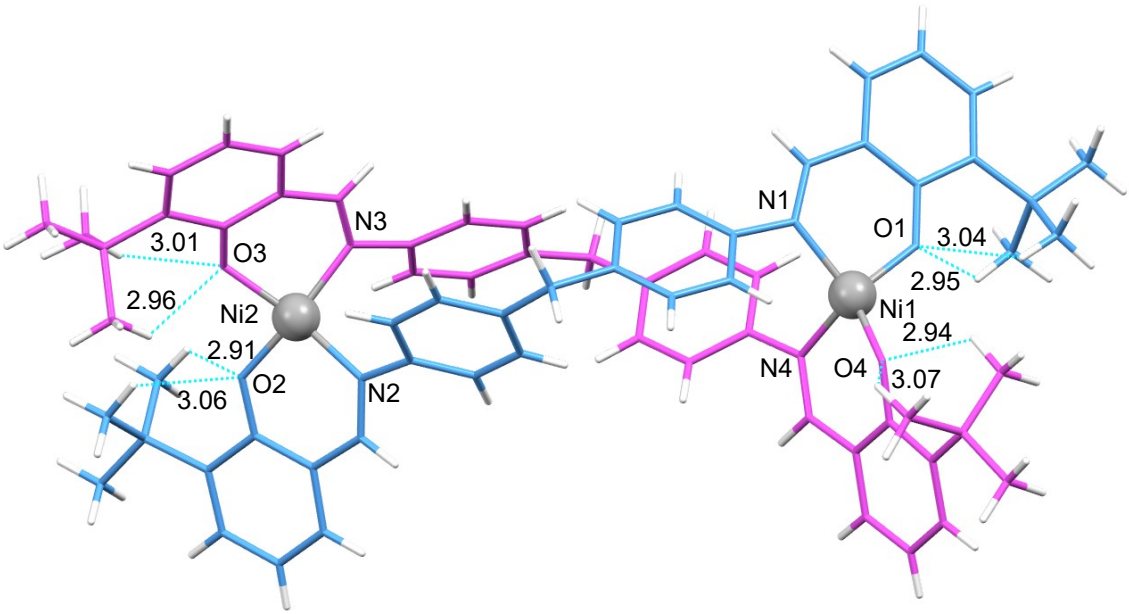

Figure S11. Intramolecular hydrogen bonds in $[Ni_2(L^2)_2]\cdot CH_3CN$ **7***: C33–H33B···O2 3.05 Å, C34–H34C···O2 2.94 Å, C64–H64B···O3 2.91 Å, C65–H65C···O3 2.99 Å, C69–H69B···O4 2.97 Å, C70–H70C···O4 2.99 Å, C29–H29B···O1 2.92 Å, C30–H30B···O1 3.03 Å.

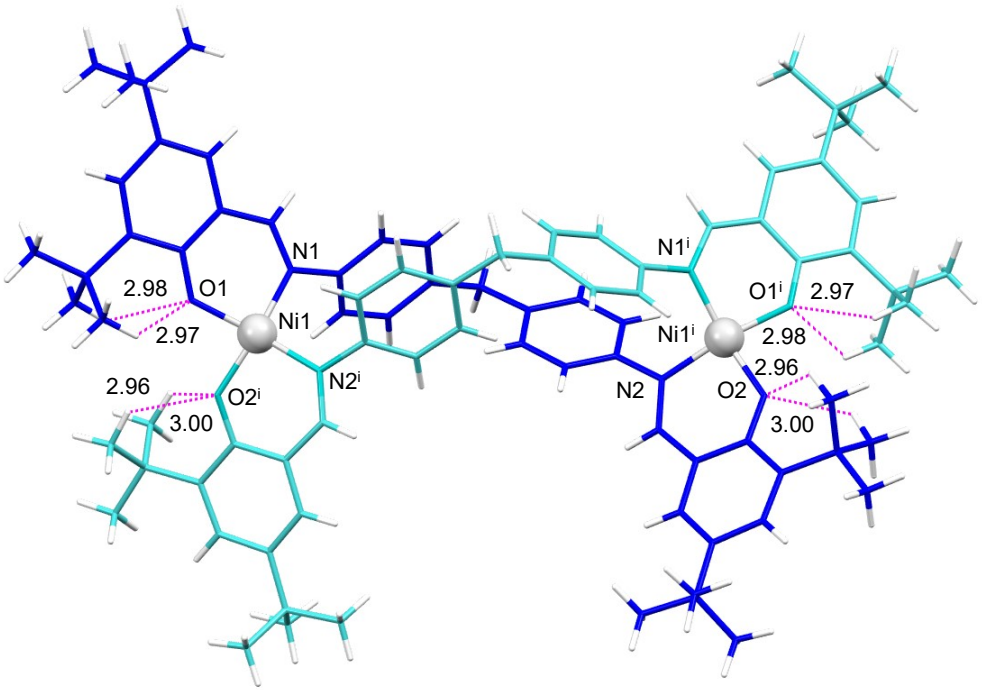

Figure S12. Intramolecular hydrogen bonds in $[Ni_2(L^3)_2]\cdot 2CH_2Cl$ **8***: C29–H29B···O2 2.97 Å, C30–H30B···O1 2.98 Å, C37–H37A···O2 2.96 Å, C38–H38C···O2 3.00 Å.

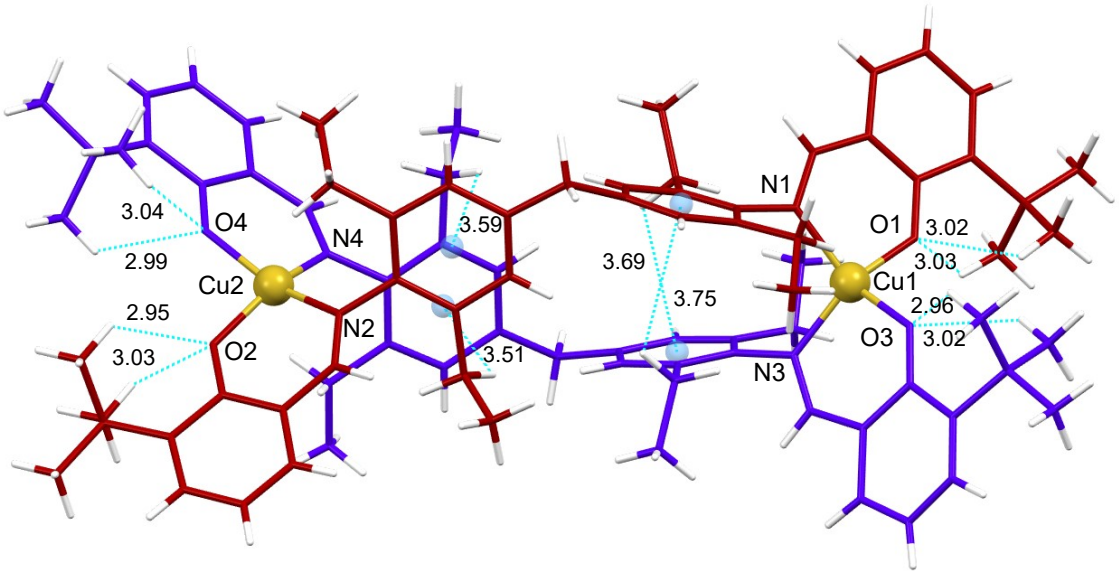

Figure S13. Intramolecular hydrogen bonds in $[Cu_2(L^5)_2]\cdot 3CH_3CN$ **13***: C84–H84C···O4 3.04 Å, C86–H86B···O4 2.99 Å, C41–H41C···O2 3.03 Å, C42–H42B···O2 2.95 Å, C29–H29E···O1 3.02 Å, C30–H30F···O1 3.03 Å, C73–H73B···O3 2.96 Å, C74–H74C···O3 3.02 Å

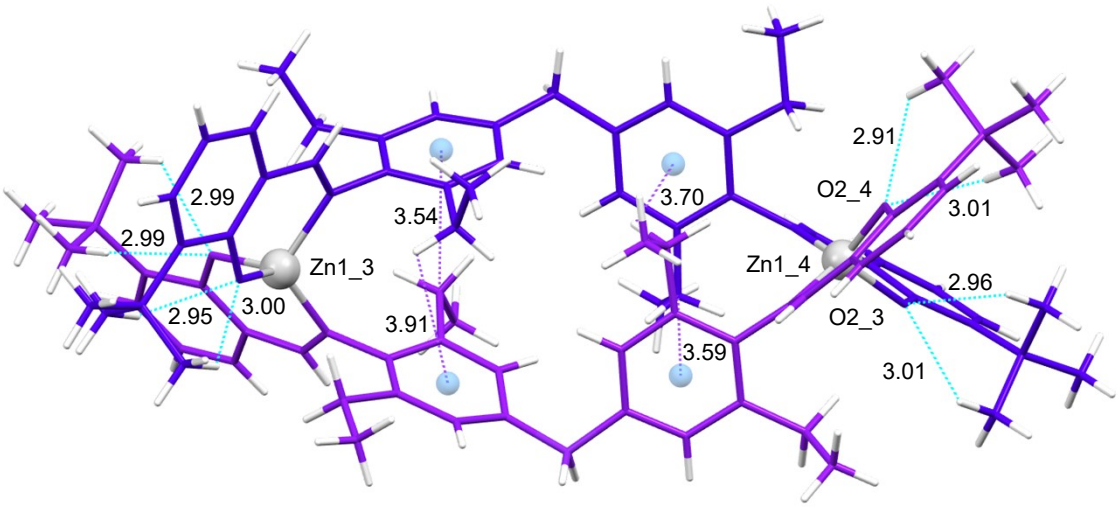

Figure S14. Intramolecular hydrogen bonds in $[Zn_2(L^5)_2]\cdot 2CH_3CN$ **18***: C41–H41C_4···O2_4 2.91 Å, C42–H42B_4···O2_4 3.01 Å, C42–H42C···O2_3 3.01 Å, C43–H43B···O2_3 2.96 Å, C30–H30B···O1_4 2.99 Å, C31–H31C···O1_4 2.99 Å, C29–H29C···O1_3 2.95 Å, C30–H30B···O1_3 3.00 Å.

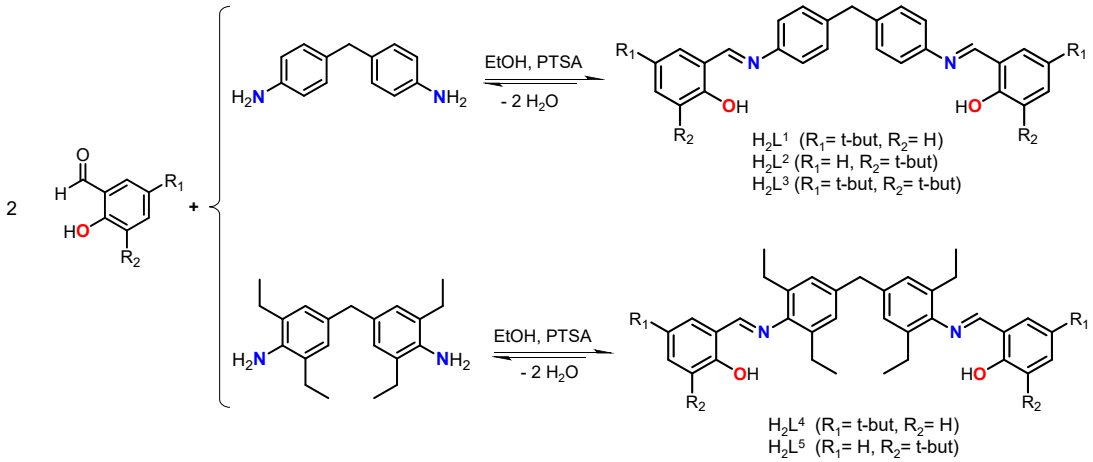

Figure S15. Synthesis of the Schiff base ligands H_2L^n (n= 1-5).

Crystallographic data of helicates

$[Ni_2(L^2)_2]\cdot CH_3CN$ 7*: $C_{72}H_{75}N_5O_4Ni_2$, *Mw* = 1191.79 g/mol, crystal dimensions: 0.18 × 0.16 × 0.04 mm^3, triclinic, $P\bar{1}$, *a* = 11.7230(6), *b* = 13.6632(7), *c* = 19.6313(7) Å, α = 97.023(2), β = 100.791(2), γ = 101.103(2) °, *V* = 2989.8(2) Å^3, *Z* = 2, μ = 0.69 mm^{-1}, Radiation λ(Mo-K$_\alpha$) = 0.7107 Å, *T* = 100 K, measured/unique reflexions 96565/14845 (R_{int} = 0.061), *R* = 0.047, *wR* = 0.123, *GOF* = 1.042, max/min residual density 0.57/ -1.11 e.Å^{-3}.

$[Ni_2(L^3)_2]\cdot 2CH_2Cl_2$ 8*: $C_{90}H_{108}N_4Ni_2O_4Cl_4$, *Mw* = 1375.18 g/mol, crystal dimensions: 0.13 × 0.04 × 0.03 mm^3, monoclinic, *I2/a*, *a* = 19.7738(18), *b* = 17.4199(10), *c* = 23.6472(11) Å, α = 90, β = 100.801(1), γ = 90 °, *V* = 8001.2(9) Å^3, *Z* = 4, μ = 0.59 mm^{-1}, Radiation λ(Mo-K$_\alpha$) = 0.7107 Å, *T* = 100 K, measured/unique reflexions 160186/9930 (R_{int} = 0.065), *R* = 0.093, *wR* = 0.099, *GOF* = 1.02, max/min residual density 0.38/ -0.55 e.Å^{-3}.

$[Cu_2(L^3)_2]\cdot 2CH_3CN$ 11*: $C_{90}H_{110}N_6Cu_2O_4$, *Mw* = 1466.91 g/mol, crystal dimensions: 0.24 × 0.12 × 0.11 mm^3, monoclinic, *I2/a*, *a* = 19.6676(9), *b* = 17.5879(8), *c* = 23.6719(17) Å, α = 90, β = 101.008(2), γ = 90 °, *V* = 8038.7(8) Å^3, *Z* = 4, μ = 0.65 mm^{-1}, Radiation λ(Mo-K$_\alpha$) = 0.7107 Å, *T* = 100 K, measured/unique reflexions 46963/7369 (R_{int} = 0.065), *R* = 0.046, *wR* = 0.123, *GOF* = 1.02, max/min residual density 0.39/ -0.47 e.Å^{-3}.

$[Cu_2(L^5)_2]\cdot 3CH_3CN$ 13*: 2($C_{90}H_{110}N_6Cu_2O_4$)3(C_2H_3N), *Mw* = 2892.84 g/mol, crystal dimensions: 0.17 × 0.15 × 0.05 mm^3, triclinic, $P\bar{1}$, *a* = 13.6211(3), *b* = 16.0269(4), *c* = 18.3522(5) Å, α = 92.519(1), β = 97.528(1), γ = 95.604(1) °, *V* = 3946.30(17) Å^3, *Z* = 1, μ = 0.59 mm^{-1}, Radiation λ(Mo-K$_\alpha$) = 0.7107 Å, *T* = 100 K, measured/unique reflexions 116110/22115 (R_{int} = 0.045), *R* = 0.045, *wR* = 0.121, *GOF* = 1.022, max/min residual density 0.56/ -0.57 e.Å^{-3}.

$[Zn_2(L^1)_2]\cdot 2.8CH_3OH$ 14*: $C_{73}H_{84}N_4O_7Zn_2$, *Mw* = 1260.23 g/mol, crystal dimensions: 0.22 × 0.18 × 0.13 mm^3, triclinic, $P\bar{1}$, *a* = 11.9567(6), *b* = 14.1684(5), *c* = 20.5193(10) Å, α = 88.561(2), β = 74.498(2), γ = 79.166(2) °, *V* = 3288.3(3) Å^3, *Z* = 2, μ = 0.790 mm^{-1}, radiation λ(Mo-K$_\alpha$) = 0.7107 Å, *T* = 100 K, measured/unique reflexions 80891/15651 (R_{int} = 0.046), *R* = 0.045, *wR* = 0.120, *GOF* = 1.055, max/min residual density 1.06/ -0.55 e.Å^{-3}.

$[Zn_2(L^5)_2]\cdot 2CH_3CN$ 18*: $C_{90}H_{110}Zn_2N_6O_4$, *Mw* = 1470.63 g/mol, crystal dimensions: 0.08 × 0.06 × 0.03 mm^3, triclinic, $P\bar{1}$, *a* =16.3465(6), *b* = 19.9440(7), *c* = 25.4842(10) Å, α = 98.5050(10), β = 93.3200(10), γ = 97.5040(10) °, *V* = 8121.2(5) Å^3, *Z* = 4, μ = 0.64 mm^{-1}, Radiation λ(Mo-K$_\alpha$) = 0.7107 Å, *T* = 100 K, measured/unique reflexions 342113/9707 (R_{int} = 0.053), *R* = 0.079, *wR* = 0.121, *GOF* = 1.076, max/min residual density 0.64/ -0.61 e.Å^{-3}.

Table S3. Main bond distances and angles in $[Ni_2(L^2)_2]\cdot CH_3CN$ **7***.

Bond distances (Å)			
N1—Ni1	1.9586 (19)	**O1—Ni1**	1.8878 (16)
N2—Ni2	1.906 (2)	**O2—Ni2**	1.8464 (18)
N3—Ni2	1.905 (2)	**O3—Ni2**	1.8796 (17)
N4—Ni1	1.974 (2)	**O4—Ni1**	1.8873 (16)
Bond angles (°)			
O4—Ni1—O1	116.41 (7)	**O2—Ni2—O3**	87.96 (8)
O4—Ni1—N1	134.68 (8)	**O2—Ni2—N3**	161.01 (9)
O1—Ni1—N1	93.46 (8)	**O3—Ni2—N3**	90.84 (8)
O4—Ni1—N4	92.30 (8)	**O2—Ni2—N2**	93.93 (8)
O1—Ni1—N4	118.27 (8)	**O3—Ni2—N2**	156.50 (8)
N1—Ni1—N4	102.96 (8)	**N3—Ni2—N2**	94.68 (9)
O4—Ni1—O1	116.41 (7)	**O2—Ni2—O3**	87.96 (8)

Table S4. Main bond distances and angles in $[Ni_2(L^3)_2]\cdot 2CH_2Cl_2$ **8***.

Bond distances (Å)			
N1—Ni1	1.905 (2)	**O1—Ni1**	1.8421 (19)
N2—Ni1^i	1.903 (2)	**O2—Ni1^i**	1.8516 (19)
Bond angles (°)			
O1-Ni1-O2^i	84.16 (9)	**O1-Ni1-N1**	93.18 (9)
N2^i-Ni1-N1	97.16 (10)	**O2^i-Ni1-N1**	160.70 (10)
O1-Ni1-N2^i	159.14 (10)	**O2^i-Ni1-N2^i**	91.73 (9)

Table S5. Main bond distances and angles in $[Cu_2(L^3)_2]\cdot 2CH_3CN$ **11***.

Bond distances (Å)			
N1—Cu1	1.9661 (17)	**O1—Cu1**	1.8952 (15)
N2^i—Cu1	1.9640 (17)	**O2—Cu1^i**	1.8829 (15)
Bond angles (°)			
O1-Cu1-O2^i	89.15 (7)	**O1-Cu1-N1**	91.96 (7)
N2^i-Cu1-N1	100.40 (7)	**O2^i-Cu1-N1**	147.51 (8)
O1-Cu1-N2^i	151.84 (7)	**O2^i-Cu1-N2^i**	93.56 (7)

Table S6. Main bond distances and angles in $[Cu_2(L^5)_2]\cdot 3CH_3CN$ **13***.

Bond distances (Å)			
N1—Cu1	1.9552 (16)	**O1—Cu1**	1.8919 (14)
N2—Cu2	1.9798 (15)	**O2—Cu2**	1.8969 (14)
N3—Cu1	1.9613 (15)	**O3—Cu1**	1.9012 (13)
N4—Cu2	1.9558 (16)	**O4—Cu2**	1.9204 (13)
Bond angles (°)			
O1—Cu1—O3	92.11 (6)	**O2—Cu2—O4**	88.25 (6)
O1—Cu1—N1	94.40 (7)	**O2—Cu2—N4**	150.24 (7)
O3—Cu1—N1	141.15 (6)	**O4—Cu2—N4**	92.59 (6)
O1—Cu1—N3	137.23 (7)	**O2—Cu2—N2**	93.59 (6)
O3—Cu1—N3	93.98 (6)	**O4—Cu2—N2**	150.94 (6)
N1—Cu1—N3	106.50 (6)	**N4—Cu2—N2**	99.76 (6)
O1—Cu1—O3	92.11 (6)	**O2—Cu2—O4**	88.25 (6)

Table S7. Main bond distances and angles in $[Zn_2(L^1)_2]\cdot 2.8CH_3OH$ **14***.

Bond distances (Å)			
N1—Zn1	2.0038 (18)	**O1—Zn1**	1.9186 (16)
N2—Zn2	2.003 (2)	**O2—Zn2**	1.9005 (17)
N3—Zn2	2.003 (2)	**O3—Zn2**	1.9164 (16)
N4—Zn1	2.0027 (19)	**O4—Zn1**	1.9185 (17)
Bond angles (°)			
O4—Zn1—O1	116.81 (7)	**O2—Zn2—O3**	110.01 (7)
O4—Zn1—N1	120.48 (7)	**O2—Zn2—N3**	126.14 (8)
O1—Zn1—N1	96.61 (7)	**O3—Zn2—N3**	96.41 (7)
O4—Zn1—N4	96.04 (7)	**O2—Zn2—N2**	96.87 (8)
O1—Zn1—N4	120.26 (7)	**O3—Zn2—N2**	126.54 (8)
N1—Zn1—N4	108.02 (8)	**N3—Zn2—N2**	103.74 (8)
O4—Zn1—O1	116.81 (7)	**O2—Zn2—O3**	110.01 (7)

Table S8. Main bond distances and angles in $[Zn_2(L^5)_2]\cdot 2CH_3CN$ **18***.

Bond distances (Å)			
N1—Zn1	1.998 (2)	**N1^i—Zn1^i**	2.012 (2)
O1—Zn1	1.924 (2)	**O1^i—Zn1**	1.920 (2)
Bond angles (°)			
O1^i—Zn1—O1	105.84 (9)	**O1^i—Zn1—N1^i**	94.25 (9)
O1^i—Zn1—N1	124.79 (10)	**O1—Zn1—N1^i**	118.01 (10)
O1—Zn1—N1	95.57 (9)	**N1—Zn1—N1^i**	119.40 (10)