

Supporting Information for Cryst. Growth Des.

Chiral Metallocycles Templated Novel Chiral Water Frameworks

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1. Materials and Methods

Commercially available reagents were used as received without further purification. Element analyses were performed with a Carlo-Erba 1106 elemental analyzer. IR spectra were recorded on a Bruker VECTOR22 spectrophotometer with KBr pellets in 400–4000 cm^{-1} region. Thermal analysis curves were scanned in a range of 30–680 °C with air atmosphere on a STA 409 PC thermal analyzer. Specific rotation was measured on a Perkin Elmer 341 with the wavelength of 589 nm in methanol solution at a temperature of 20 °C. Electronic absorption spectra were recorded on a Unico-2102 UV-vis spectrometer. The solid-state CD spectra were recorded on a MOS-450 spectrometer. Powered X-ray diffraction (PXRD) patterns of the samples were recorded by a RIGAKU-DMAX2500 X-ray diffractometer with Cu K α radiation.

2. X-ray Crystallography

Single crystal X-ray data of **1** and **2** were collected on an Oxford diffractometer equipped with a CCD detector and graphite-monochromated MoK α radiation from a sealed tube at 288(2) K. Raw data collection and reduction were done using CrysAlisPro software. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Structures were solved by direct method and refined by full-matrix least-squares on F^2 using *SHELXTL*.¹ Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Organic hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to $1.2 \times U_{\text{eq}}$ of the attached atom. Water H atoms were located in a difference map and their positions were fixed during the refinement such that they remained in chemically meaningful positions.

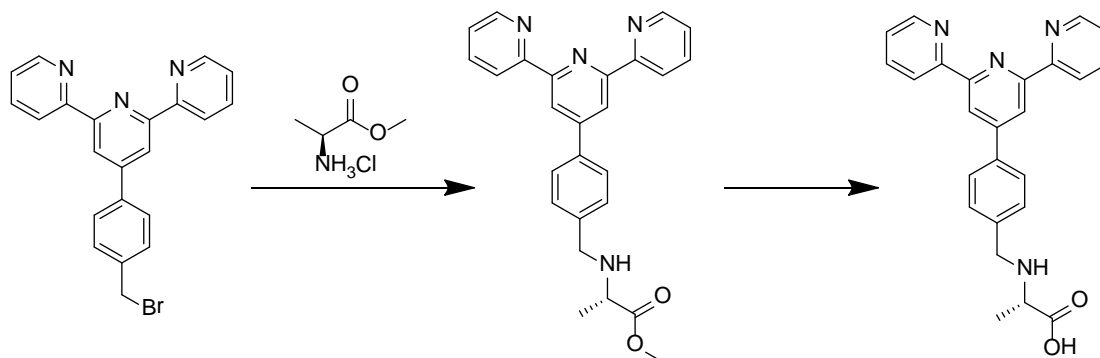
Crystal data for **1**: $\text{C}_{50}\text{H}_{82}\text{N}_{14}\text{Ni}_2\text{O}_{24}$, $M = 1380.72$, brown block, $0.17 \times 0.15 \times 0.13 \text{ mm}^3$, monoclinic, space group *C2* (No. 5), $a = 32.703(11)$, $b = 14.7164(12)$, $c = 13.4949(13) \text{ \AA}$, $\beta = 91.808(18)^\circ$, $V = 6491(2) \text{ \AA}^3$, $Z = 4$, $D_c = 1.413 \text{ g/cm}^3$, $F_{000} = 2912$, Xcalibur, Eos, Gemini, MoK α radiation, $\lambda = 0.71073 \text{ \AA}$, $T = 288(2)\text{K}$, $2\theta_{\text{max}} = 52.7^\circ$, 13073 reflections collected, 10821 unique ($R_{\text{int}} = 0.0170$). Final $GooF = 1.042$, $R1 = 0.0490$, $wR2 = 0.1217$, R indices based on 8543 reflections with $I > 2\sigma(I)$ (refinement on F^2), 814 parameters, 44 restraints. Lp and absorption corrections

applied, $\mu = 0.667 \text{ mm}^{-1}$. Absolute structure parameter = 0.36(3) (Flack, H. D. *Acta Cryst.* **1983**, A39, 876-881). CCDC-842495.

Crystal data for **2**: $\text{C}_{50}\text{H}_{56}\text{N}_{14}\text{Ni}_2\text{O}_{11}$, $M = 1146.51$, brown block, $0.15 \times 0.13 \times 0.12 \text{ mm}^3$, triclinic, space group $P1$ (No. 1), $a = 8.0276(7)$, $b = 10.9031(8)$, $c = 16.9025(13) \text{ \AA}$, $\alpha = 71.996(7)$, $\beta = 82.528(6)$, $\gamma = 87.128(6)^\circ$, $V = 1394.94(19) \text{ \AA}^3$, $Z = 1$, $D_c = 1.365 \text{ g/cm}^3$, $F_{000} = 598$, Xcalibur, Eos, Gemini, $\text{MoK}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$, $T = 296(2) \text{ K}$, $2\theta_{\text{max}} = 51.0^\circ$, 10883 reflections collected, 8650 unique ($R_{\text{int}} = 0.0272$). Final $\text{Goof} = 1.037$, $RI = 0.0650$, $wR2 = 0.1823$, R indices based on 7363 reflections with $I > 2\sigma(I)$ (refinement on F^2), 696 parameters, 25 restraints. Lp and absorption corrections applied, $\mu = 0.744 \text{ mm}^{-1}$. Absolute structure parameter = 0.039(17). CCDC-842496.

3. Syntheses, Reactions, and Characterizations

3.1 Synthesis of *S*-2-(4-(2,6-di(pyridin-2-yl)pyridin-4-yl)-benzylamino)propanoic acid (**H₂L**)



4'-(Phenyl-*p*-bromomethyl)-2,2':6',2''-terpyridine was prepared by previous literature.² A mixture of *L*- α -alanine methyl ester hydrochloride (3.12 g, 22.44 mmol) and anhydrous Na_2CO_3 (3.18 g, 30.00 mmol) in dry DMF (40 mL) were stirring at room temperature for 1 h, then was added dropwise a solution of 4'-(phenyl-*p*-bromomethyl)-2,2':6',2''-terpyridine (3.00 g, 7.48 mmol) and DMF (80 mL). With stirring the resulting yellow solution was heated to 45°C and kept for 18 h. All above processes were under nitrogen atmosphere. Cooled to room temperature, the red

mixture was filtered to remove any solids. Red oil was obtained as removed solvent in vacuo. The red oil was redissolved by dichloromethanol and washed with distilled water several times. After complete evaporation of the solvent the pure red oil of (S)-methyl 2-(4-(2,6-di(pyridin-2-yl)pyridin-4-yl)benzylamino)propanoate was obtained. Yield: 2.58 g (81%). Selected IR (KBr, cm^{-1}): 3055(w), 2987(w), 1735(s), 1584(s), 1566(m), 1468(m), 1388(s), 1200(m), 791(s). Then a mixture of (S)-methyl 2-(4-(2,6-di(pyridin-2-yl)pyridin-4-yl)benzylamino)propanoate (2.58 g, 6.08 mmol), methanol (40 mL) and aqueous solution of NaOH (10 mL, 5%) was heated at 40 °C for 48 h with stirring. Then pale-yellow powder was obtained by adjusting the pH value of the reaction solution to 6–7, washed with DMF and dried in air, and white powder of H_2L was obtained. Yield: 1.91 g (77%). M.p. 264 °C. Elemental analysis (%) calcd for $\text{C}_{25}\text{H}_{21}\text{N}_4\text{O}_2$: C 73.32, H 5.17, N 13.69; found: C 72.86, H 5.24, N 13.55. Selected IR (KBr, cm^{-1}): 3425 (w), 3049 (w), 2978 (w), 1603 (m), 1585 (s), 1567 (m), 1466 (m), 1391 (m), 789 (m). Specific rotation $[\alpha]_{\text{D}}^{20} = +3.5$ for Na(Hptpy) (*c* 0.02, CH_3OH).

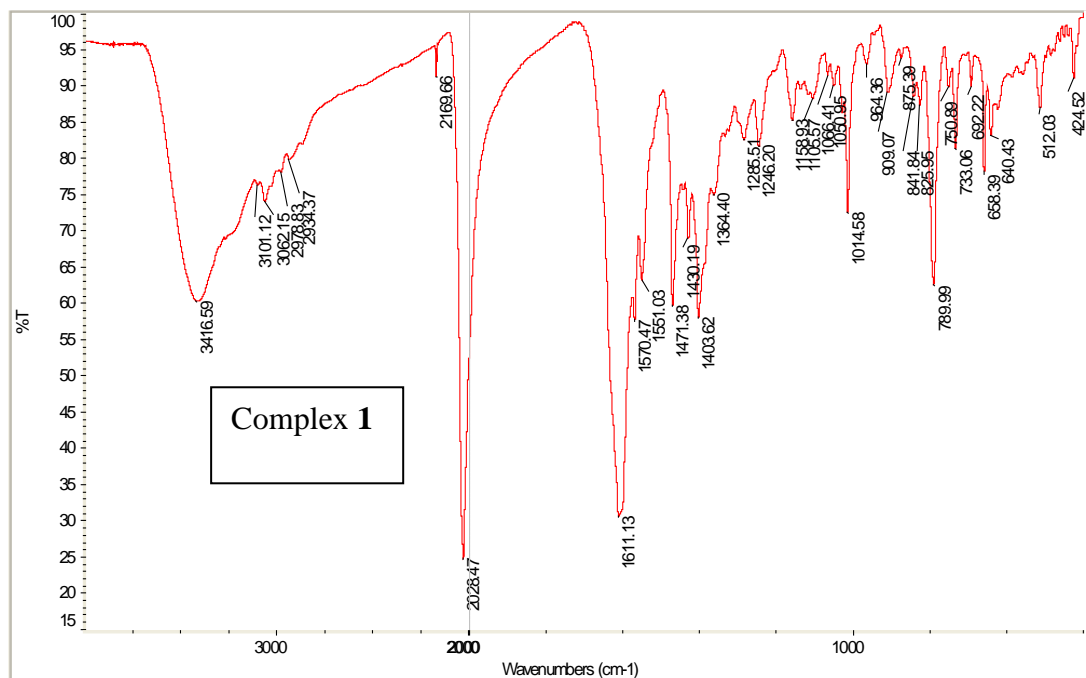
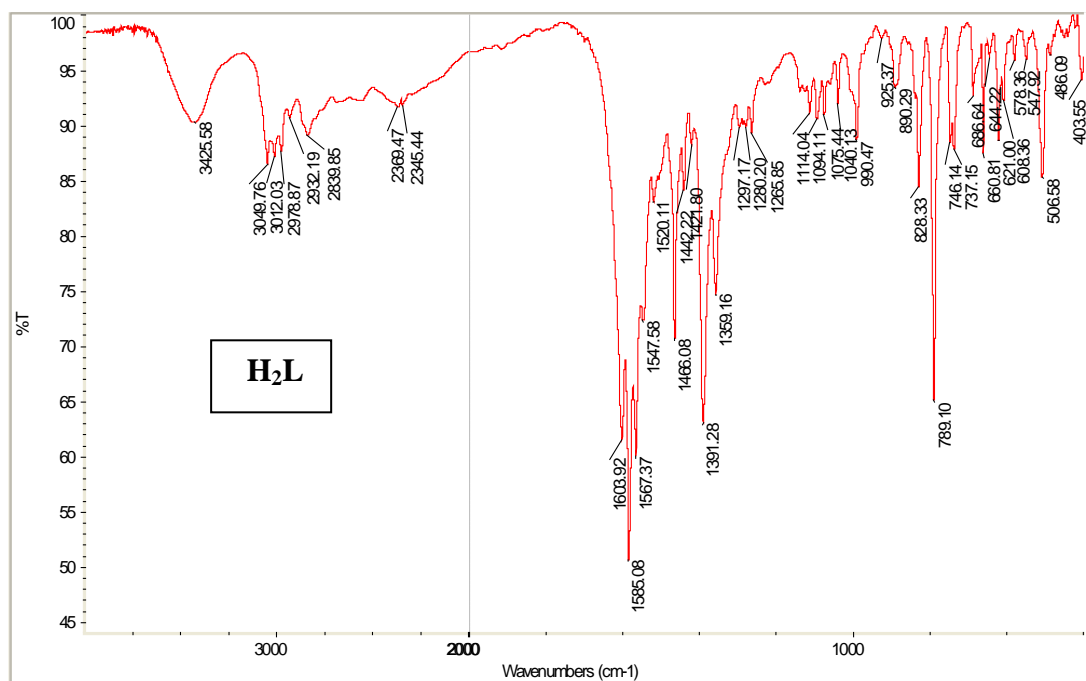
3.2 Synthesis of **1**

Hydrothermal reaction of H_2L (41.0 mg, 0.1 mmol), NaOH (4.0 mg, 0.1 mmol), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (23.8 mg, 0.1 mmol), NaN_3 (13.0 mg, 0.2 mmol) and H_2O (8 mL) in 25 mL Parr Teflon-lined stainless steel vessels at 130 °C for 72 h, and allowed the filtrate to evaporate at ambient temperature for two weeks resulted in brown block crystals suitable for single-crystal X-ray diffraction studies. Yield: 38.7 mg (56%). Elemental analysis (%) calcd for $\text{C}_{50}\text{H}_{82}\text{N}_{14}\text{Ni}_2\text{O}_{24}$: C 43.53, H 6.00, N 14.22; found: C 43.79, H 6.13, N 14.01. Selected IR (KBr, cm^{-1}): 3416(m), 3233(m), 3062(w), 2978(w), 2028(vs), 1611(s), 1570(m), 1471(m), 1403(s), 1014(m), 789 (m). Specific rotation $[\alpha]_{\text{D}}^{20} = -30.4$ for **1** (*c* 0.01, CH_3OH)

3.3 Synthesis of **2**

As the hydrothermal temperature was set at 90 °C for the same reaction system of **1**, brown needle crystals suitable for single-crystal X-ray diffraction studies were directly obtained. Yield: 24.6 mg (43%). Elemental analysis (%) calcd for $\text{C}_{50}\text{H}_{56}\text{N}_{14}\text{Ni}_2\text{O}_{11}$: C 52.43, H 4.93, N 17.13; found: C 52.10, H 5.15, N 16.92. Selected IR (KBr, cm^{-1}): 3415(m), 3237(m), 3067(w), 2985(w), 2021(vs), 1600(s), 1551(w), 1469(m), 1401(s), 1384(m), 1366(m), 1013(m), 787(s). Specific rotation $[\alpha]_{\text{D}}^{20} = -34.1$ for **2** (*c* 0.01, CH_3OH)

4. Infrared spectra (IR)



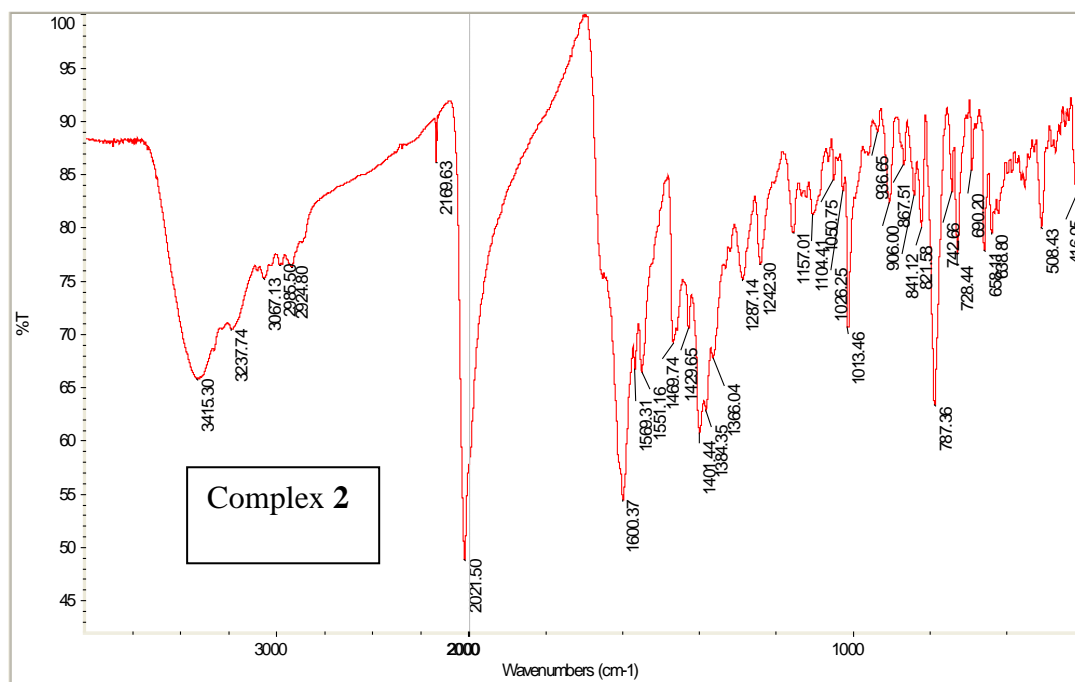


Figure S1. IR spectra of H₂L and **1** and **2**.

5. Thermogravimetric Analysis (TGA)

6. Electronic Absorption Spectra (UV-vis)

All operations were performed at room temperature (ca. 24 °C) using the UV-vis spectrometer described above. The solutions used to record UV-vis spectra were prepared through completely dissolving certain amount of Na(Hptpy) and complexes **1–2** in methanol in volumetric flasks. The results are presented in **Fig. S9**.

7. Solid-state Circular Dichroism Spectra (CD)

The solid-state CD spectra were recorded on a MOS-450 spectrometer.

8. Powder X-ray Diffraction (PXRD)

Powered X-ray diffraction (PXRD) patterns of the samples were recorded by a RIGAKU-DMAX2500 X-ray diffractometer with Cu K α radiation. The results are presented in **Fig. S10**.

9. Additional Figures

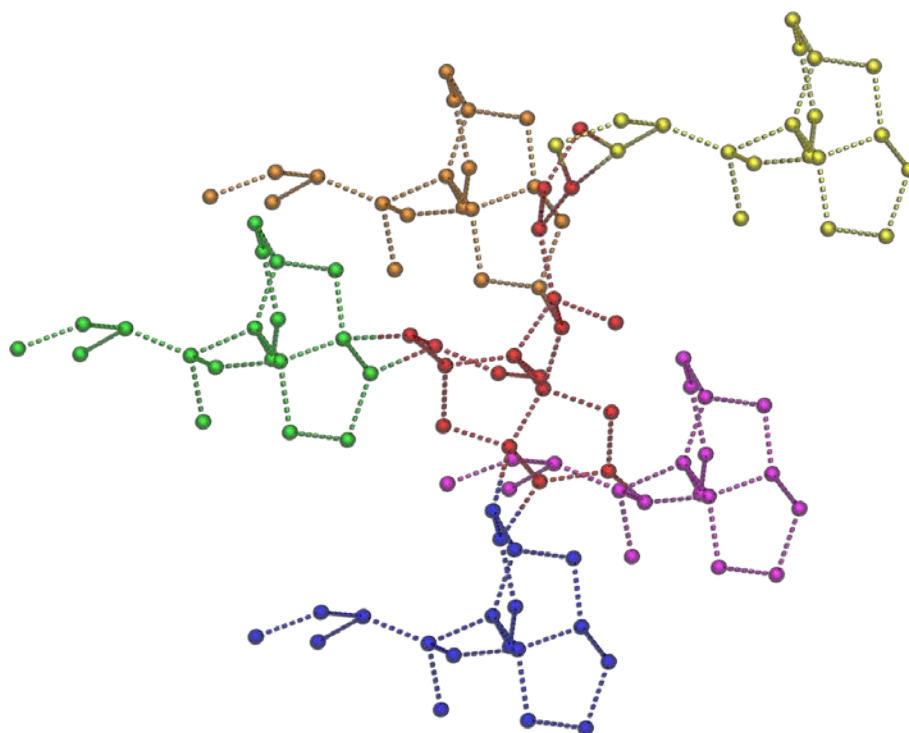


Figure S2. The hydrogen-bonding water cluster subunit of 19 water molecules fused with five the same water cluster subunits (red) through sharing the edges by doubly hydrogen-bonding interactions.

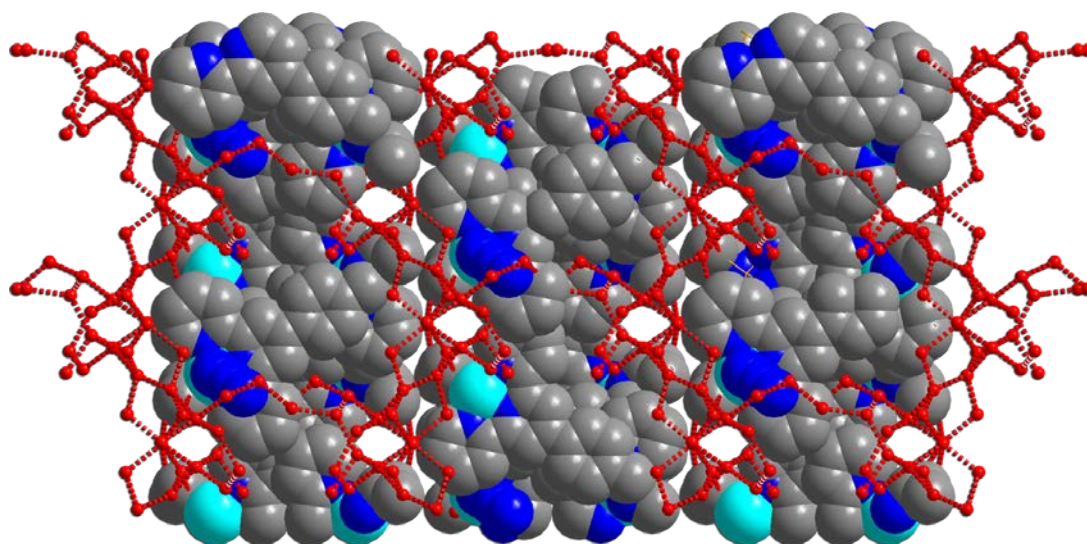


Figure S3. A chiral 3D zeolite-like water network encapsulates the chiral metallocycle cations in its nanocages.

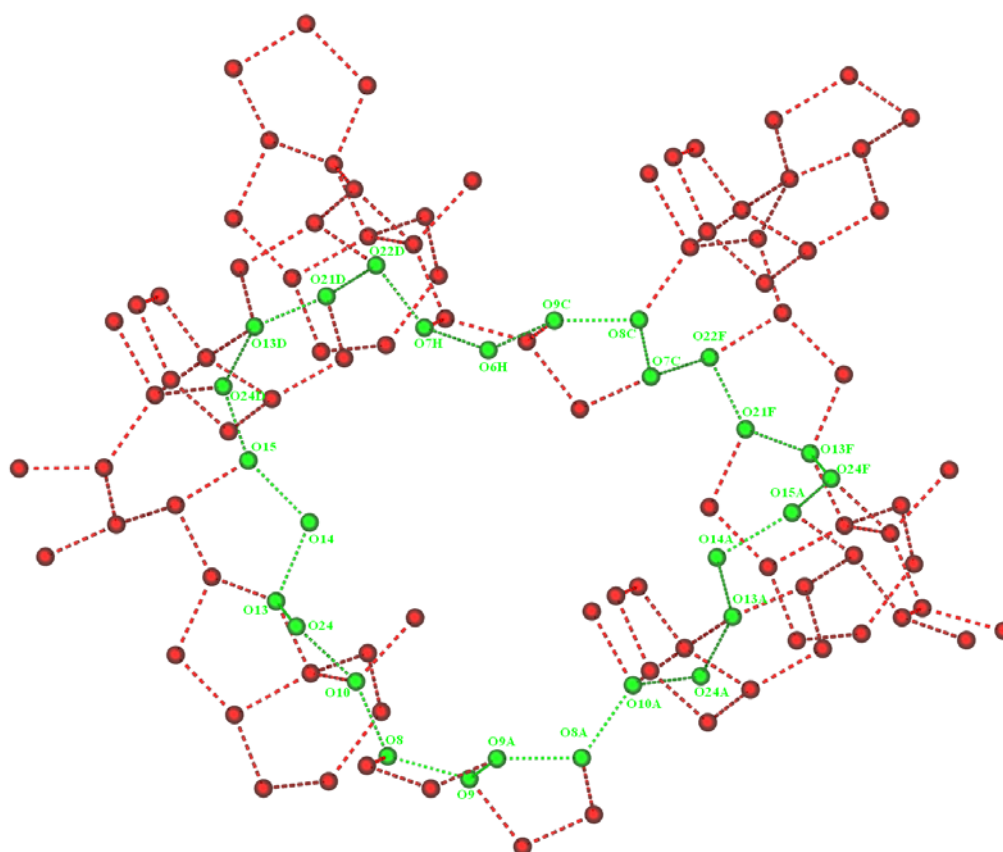


Figure S4. Larger 27-membered water opening (green) with centroid-to-centroid distances of O6H...O9A and O14...O24F being 13.283 and 16.763 Å, respectively.

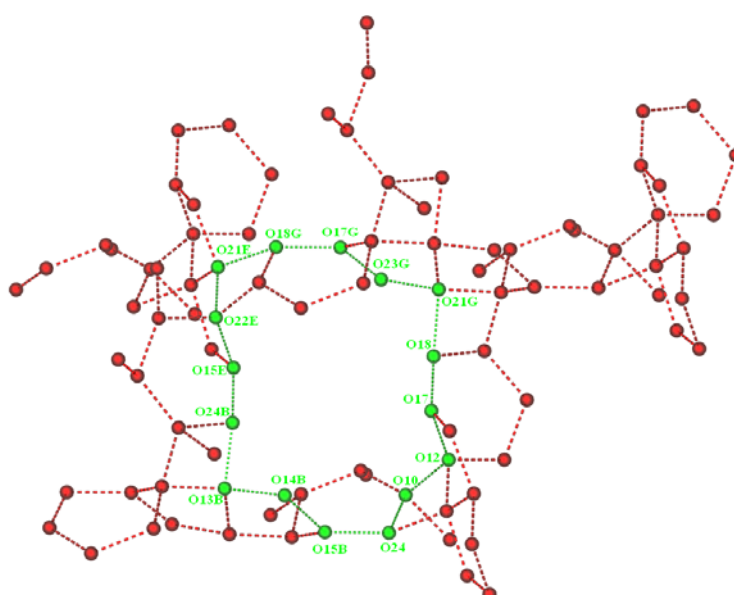


Figure S5. Smaller 16-membered water opening (green) centroid-to-centroid distances of O13B...O21E and O13B...O12 being 9.334 and 9.595 Å, respectively.

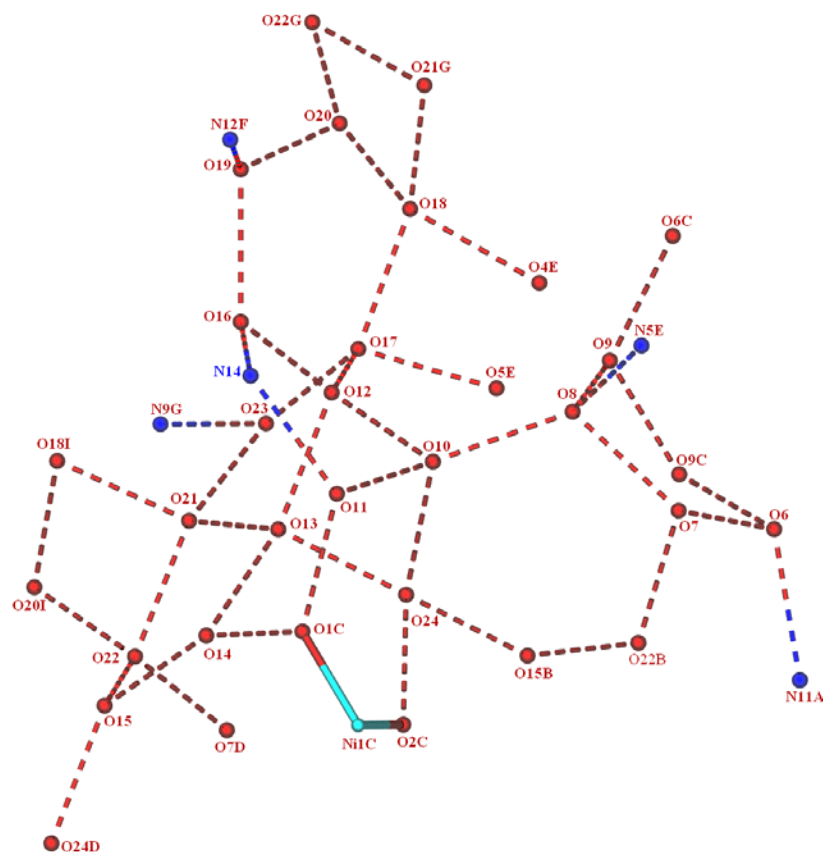


Figure S6. View of various water rings, coordination modes of every water in the asymmetric unit of twenty H₂O molecules and simple representation of multiple hydrogen-bonding occurrences between the host and guest systems. Distances [Å]: O6...O7 2.764(10), O7...O8 2.726(11), O8...O9 2.759(11), O8...O10 2.845(11), O10...O11 2.804(13), O10...O24 2.854(11), O11...N14 2.763(11), O12...O10 2.839(12), O12...O17 2.811(13), O13...O12 2.738(13), O14...O13 2.893(13), O14...O15 2.695(12), O16...O12 2.690(12), O16...N14 2.761(10), O17...O18 2.753(11), O18...O20 2.782(11), O19...O16 2.821(10), O20...O19 2.811(11), O21...O23 2.756(14), O22...O15 2.836(11), O22...O21 2.808(13), O23...O17 2.832(11), O24...O13 2.796(10), O6...N11A 2.799(10), O7...O22B 2.752(12), 2.832(11), O24...O13 2.796(10), O6...N11A 2.799(10), O7...O22B 2.752(12), O9...O9C 2.765(17), O24...O2C 2.777(8), O9...O6C 2.843(11), O1...O14C 2.695(11), O1...O11C 2.742(9), O15...O24D 2.769(9), O17...O5E 2.672(9), O18...O4E 2.852(9), O19...N12F 2.798(11), N1...O19F 3.154(11), O20...O22G 2.835(11), O23...N9G 2.696(10), O21...O18I 2.833(12), N5...O8J 3.123(10). Angles [°]: O6...O9C...O9 104.40, O9C...O9...O8 105.02, O9...O8...O7 99.21, O8...O7...O6 116.93, O7...O6...O9C 95.22, O7...O8...O10 114.39, O8...O10...O24 124.31, O10...O24...O15B 114.83, O24...O15B...O22B 104.72, O15B...O22B...O7 122.51, O22B...O7...O8 115.31, O10...O11...O1C 95.53, O11...O1C...O14 114.27,

O1C...O14...O13 91.03, O14...O13...O24 87.32, O13...O24...O10 85.19,
 O24...O10...O11 94.77, O10...O12...O13 86.58, O12...O13...O24 92.38,
 O13...O24...O10 85.19, O24...O10...O12 89.09, O12...O16...O19 118.64,
 O16...O19...O20 109.33, O19...O20...O18 126.91, O20...O18...O17 116.34,
 O18...O17...O12 104.45, O17...O12...O16 121.76, O12...O17...O23 105.56,
 O17...O23...O21 107.60, O23...O21...O13 100.82, O21...O13...O12 109.01,
 O13...O12...O17 99.09, O13...O14...O15 109.62, O14...O15...O22 106.76,
 O15...O22...O21 98.54, O22...O21...O13 109.66, O21...O13...O14 98.76. Symmetry
 codes: A = x, y+1, z-1; B = 3/2-x, y+1/2, -z; C = 2-x, y, -z; D = 3/2-x, y-1/2, -z; E = x,
 y+1, z; F = 2-x, y, 1-z; G = 3/2-x, y+1/2, 1-z; H = 3/2-x, y, 1-z; I = 3/2-x, y-1/2, 1-z; J
 = x, y-1, z.

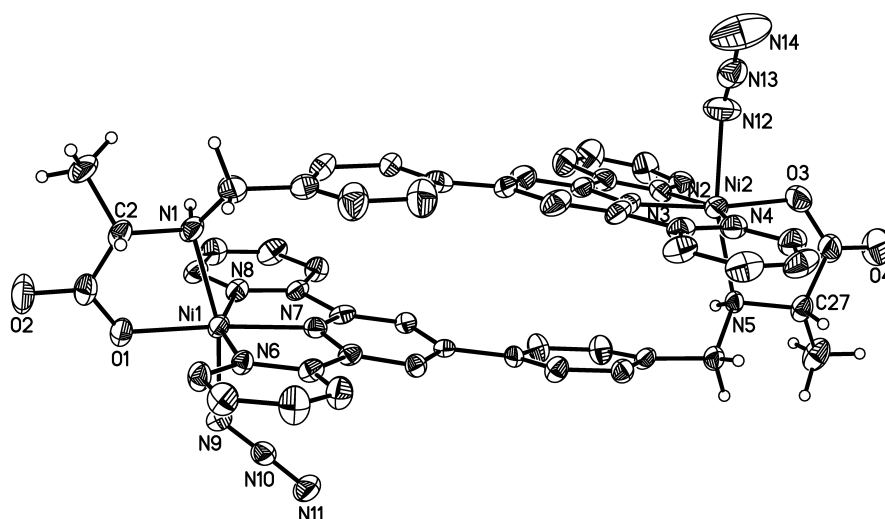


Figure S7. View of chiral neutral metalocycle $[\text{Ni}_2(\text{HL})_2(\text{N}_3)_2]$, showing permanent chiral carbon atoms C2 and C27, and labile chiral nitrogen atoms N1 and N5 all in *S*-configuration.

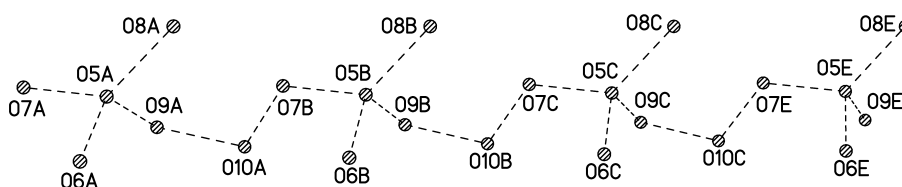


Figure S8. Interesting chiral water chain consisting of tetrahedral water cluster units in **2**.

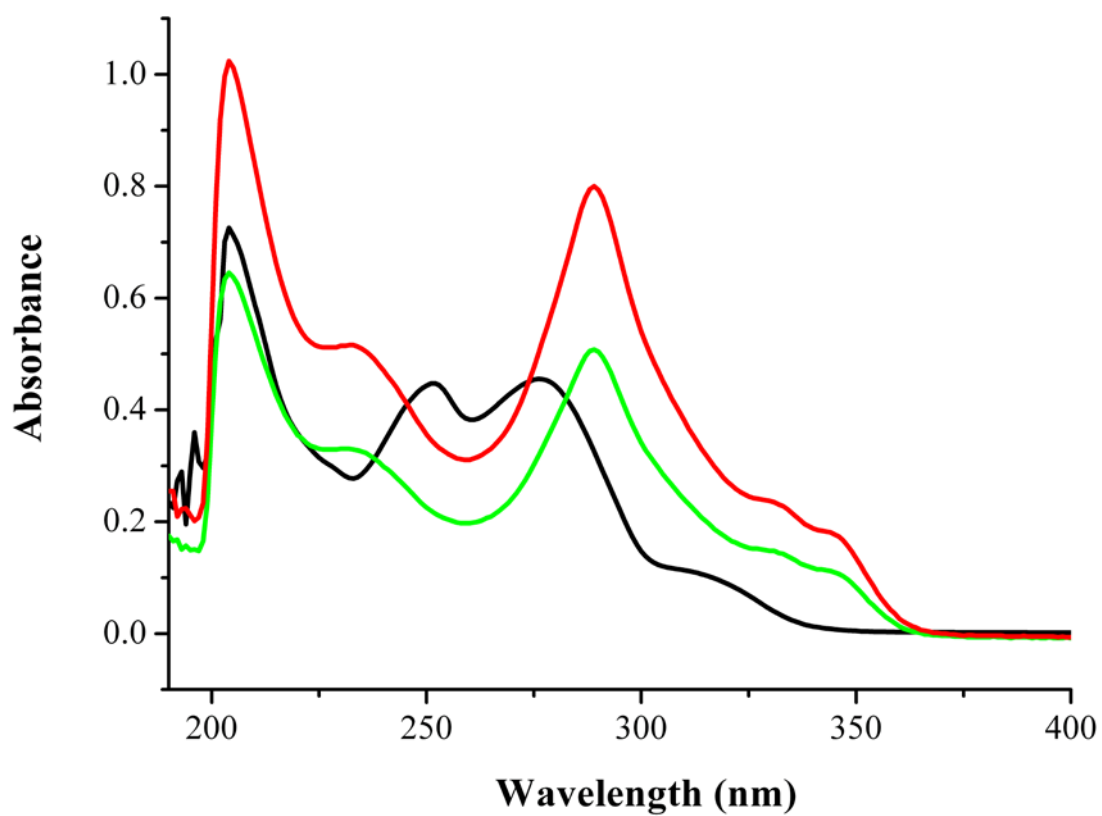


Figure S9. UV-vis spectra of free anion (HL)⁻ (black), **1** (red) and **2** (green).

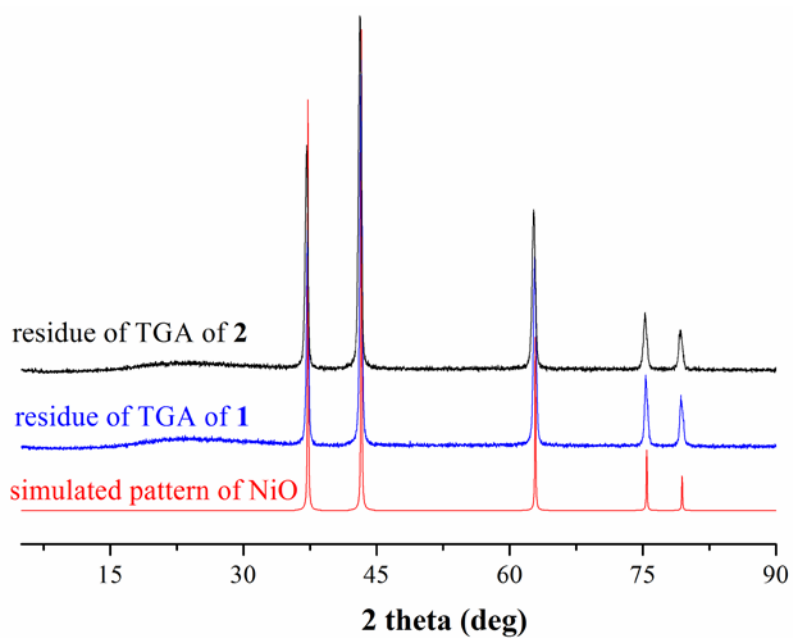


Figure S10. Simulated X-ray diffraction pattern of NiO, and experimental X-ray diffraction patterns of the residues of TGA of compounds **1** and **2**.

10. References

- (1) Sheldrick, G. M. *SHELXTL*, 6.14, Structure Determination Software Suite, Bruker AXS, Madison, WI, **2003**.
- [2] Tessore, F.; Roberto, D.; Ugo, R.; Pizzotti, M. *Inorg. Chem.* **2005**, *44*, 8967.