Supplementary Information

Self-assembly of a nonanuclear Ni^{II} cluster *via* atmospheric CO_2 fixation: synthesis, structure, collision-induced dissociation mass spectrometry and magnetic property

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Experimental details

All reagents were used as received from commercial suppliers without further purification. C, H, and N analyses were performed on an EA1110 CHNS-0 CE 65 elemental analyzer. IR spectra were recorded on a PerkinElmer Spectrum Two in the frequency range of 500-4000 cm^{-1}. Thermogravimetic analysis (TGA) was performed with a TA SDT Q600 thermal analyzer at a scanning rate of 20 °C/min under N_2, from 20 to 800 °C. The variable-temperature magnetic susceptibilities were measured using a Magnetic Property Measurement System (MPMS) and a SQUID-VSM (superconducting quantum interference device-vibrating sample magnetometer) (Quantum Design, USA). UV-Vis diffuse reflectance spectra (DRS) were recorded on a Thermo Scientific Evolution 220 UV-visible spectrophotometer equipped with a 60 mm integrating sphere and SPECTRALON® was used as the reference. High-resolution mass spectra (HR-MS) were recorded on a Bruker impact II high definition mass spectrometer, quadrupole and time-of-flight (Q/TOF) modules in the positive ion mode. Typical measurement conditions are as follows: end plate offset = 500 V; dry gas = 4 L/min, nebulizer = 0.3 bar, capillary voltage = 4500 V, sample flow rate = 4 μL/min. Collision-induced dissociation (CID) mass spectrometry studies were performed by selecting one parent ion using a quadrupole mass filter and then colliding the ions with N_2 in the trap chamber. Samples were analyzed at four different collision voltage: 5, 10, 15 and 20 eV. The data analyses of mass spectra were performed based on the isotope distribution patterns using Compass Data Analysis software (Version 4.4). The reported *m/z* values represent the monoisotopic mass of the most abundant peak within the isotope pattern. Photocurrent measurements were carried out using the CHI-660E electrochemical workstation in a three-electrode system. Generally: the samples (5 mg) of **SD/Ni9a** and naphthol (0.5 wt. %, 10 μL) were dispersed in 0.5 mL ethanol, and the mixture was sonicated for about 30 min. Then a 100 μL solution was transferred by pipet dropped on the cleaned ITO glass and the coated film was obtained after evaporation under ambient atmosphere. The prepared ITO glass film was used as working electrode, a Pt wire as the counter electrode, and an Ag/AgCl electrode as the reference electrode. A Na_2SO_4 aqueous solution (0.2 M) was used as the medium. A 50 W LED lamp was used as the light source with 420 nm fixed wavelength.

Synthesis of SD/Ni9a

$Ni(NO_3)_2 \cdot 6H_2O$ (58 mg, 0.2 mmol), 3,5-dimethylpyrazole (20 mg, 0.2 mmol) and benzoic acid (12 mg, 0.1 mmol) were dissolved in 6 mL EtOH/DMF (v/v = 4/2), then 50 μL Et_3N (0.36 mmol) was added to above mixture. After stirring for 2h, a clear green solution with few precipitates was obtained. Thereafter, the solution was filtered and the filtrate was allowed to evaporate at room temperature undisturbed. Green block crystals of **SD/Ni9a** were obtained for about one week with the yield of about 55% (based on Ni). Calcd (found) for $C_{102}H_{128}N_{16}Ni_9O_{33}$ (**SD/Ni9a**), calcd (found): C, 46.50 (46.46); H, 4.89 (4.92); N, 8.51 (8.48) %; IR: 3670 (w), 3230 (w), 2982 (m), 1606 (s), 1566 (s), 1393 (vs), 1033 (s), 810 (m), 723 (s), 670 (s) cm^{-1}.

X-ray Crystallography

Single crystal of **SD/Ni9a** with appropriate dimensions was chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) to prevent decomposition. Crystal was mounted on CryoLoop™ loop and the cell parameters and intensity data were recorded on a Rigaku Oxford Diffraction XtaLAB Synergy-S diffractometer equipped with a HyPix-6000HE Hybrid Photon Counting (HPC) detector operating in shutterless mode and an Oxford Cryosystems Cryostream 800 Plus at 173 K using CuKα (λ = 1.54184Å) PhotonJet micro-focus X-ray Source. Data were processed using the *CrystAlis*^{Pro} software suite.[1] The structure was solved using the charge-flipping algorithm, as implemented in the program *SUPERFLIP*[2] and refined by full-matrix least-squares techniques against F_o^2 using the SHELXL program[3] through the OLEX2 interface.[4] Hydrogen atoms at carbon were placed in calculated positions and refined isotropically by using a riding model. Appropriate restraints or constraints were applied to the geometry and the atomic displacement parameters of the atoms in the cluster. The structure was examined using the Addsym subroutine of PLATON[5] to ensure that no additional symmetry could be applied to the models. Pertinent crystallographic data collection and refinement parameters are collated in Table S1 Selected bond lengths and angles are collated in Table S2.

Table S1 Crystal Data of **SD/Ni9a**.

Compound	**SD/Ni9a**
Formula	$C_{102}H_{128}N_{16}Ni_9O_{33}$
Formula weight	2634.59
Temperature/K	173.00(10)
Crystal system	Triclinic
Space group	*P*-1
a/Å	14.8190(3)
b/Å	15.4014(3)
c/Å	28.1536(3)
α/°	103.9220(10)
β/°	90.0550(10)
γ/°	112.649(2)
Volume/Å^3	5724.34(19)
Z	2
ρ_{calc}, g/cm^3	1.529
μ/mm^{-1}	2.267
F(000)	2736.0
Radiation	Cu*K*α (λ = 1.54184)
2θ range for data collection/°	6.414 to 134.146
Index ranges	-17 ≤ h ≤ 17, -18 ≤ k ≤ 18, -33 ≤ l ≤ 32
Reflections collected	56053
Independent reflections	20035 R_{int} = 0.0490, R_{sigma} = 0.0511
Data/restraints/parameters	20035/3/1477
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0520, wR_2 = 0.1365
Final R indexes [all data]	R_1 = 0.0691, wR_2 = 0.1535
Largest diff. peak, hole / e Å^{-3}	1.04, -0.73

Table S2 The selected bond lengths [Å] and angles [°] for **SD/Ni9a**.

Ni—O1	2.191 (2)	Ni5—O9	2.282 (2)
Ni—O6	1.986 (2)	Ni5—O19	2.065 (2)
Ni—O9	2.154 (2)	Ni5—O22	2.022 (3)
Ni—O11	1.998 (2)	Ni5—N2	2.074 (3)
Ni—O15	2.047 (3)	Ni6—O2	2.145 (2)
Ni—O20	2.039 (3)	Ni6—O3	1.986 (2)
Ni2—Ni9	2.9946 (8)	Ni6—O7	2.174 (2)
Ni2—O2	2.266 (2)	Ni6—O14	1.989 (3)
Ni2—O3	2.039 (2)	Ni6—O17	2.054 (3)
Ni2—O12	2.065 (3)	Ni6—O21	2.029 (3)
Ni2—O13	2.008 (3)	Ni7—O1	2.148 (2)
Ni2—O16	2.039 (3)	Ni7—O11	2.058 (3)
Ni2—N5	2.066 (3)	Ni7—O14	2.021 (3)
Ni3—Ni5	2.9813 (8)	Ni7—O27	2.035 (3)
Ni3—O4	2.226 (2)	Ni7—O29	2.102 (3)
Ni3—O6	2.042 (2)	Ni7—N7	2.064 (3)
Ni3—O8	2.038 (3)	Ni8—O7	2.160 (3)
Ni3—O10	2.047 (2)	Ni8—O11	2.031 (3)
Ni3—O25	2.054 (3)	Ni8—O14	2.062 (3)
Ni3—N1	2.055 (3)	Ni8—O26	2.043 (3)
Ni4—O4	2.172 (2)	Ni8—O30	2.108 (3)
Ni4—O5	2.171 (2)	Ni8—N8	2.076 (3)
Ni4—O8	1.980 (2)	Ni9—O3	2.025 (2)
Ni4—O13	1.970 (3)	Ni9—O5	2.226 (3)
Ni4—O24	2.033 (3)	Ni9—O13	2.034 (3)
Ni4—O28	2.030 (3)	Ni9—O18	2.059 (3)
Ni5—O6	2.037 (2)	Ni9—O23	2.034 (3)
Ni5—O8	2.018 (3)	Ni9—N4	2.064 (3)
O6—Ni1—O1	92.91 (9)	O19—Ni5—O9	170.18 (10)
O6—Ni1—O9	81.85 (9)	O19—Ni5—N2	96.39 (12)
O6—Ni1—O11	173.59 (10)	O22—Ni5—O6	95.12 (11)
O6—Ni1—O15	89.49 (10)	O22—Ni5—O9	90.78 (10)
O6—Ni1—O20	96.85 (10)	O22—Ni5—O19	90.90 (11)
O9—Ni1—O1	89.32 (9)	O22—Ni5—N2	88.39 (13)
O11—Ni1—O1	81.00 (9)	N2—Ni5—Ni3	135.25 (10)
O11—Ni1—O9	96.00 (10)	N2—Ni5—O9	93.32 (11)
O11—Ni1—O15	92.96 (11)	O2—Ni6—O7	90.61 (9)
O11—Ni1—O20	89.21 (10)	O3—Ni6—O2	81.86 (9)
O15—Ni1—O1	94.49 (10)	O3—Ni6—O7	94.93 (10)
O15—Ni1—O9	170.72 (10)	O3—Ni6—O14	175.41 (11)
O20—Ni1—O1	170.16 (10)	O3—Ni6—O17	91.54 (10)

O20—Ni1—O9	90.78 (10)	O3—Ni6—O21	88.44 (11)
O20—Ni1—O15	86.91 (11)	O14—Ni6—O2	96.47 (10)
O3—Ni2—O2	77.82 (9)	O14—Ni6—O7	80.78 (11)
O3—Ni2—O12	91.55 (10)	O14—Ni6—O17	92.83 (11)
O3—Ni2—O16	94.62 (10)	O14—Ni6—O21	93.46 (12)
O12—Ni2—O2	169.33 (10)	O17—Ni6—O2	93.31 (10)
O12—Ni2—N5	96.59 (11)	O17—Ni6—O7	172.86 (10)
O13—Ni2—O2	89.80 (10)	O21—Ni6—O2	169.70 (11)
O13—Ni2—O3	82.95 (10)	O21—Ni6—O7	93.68 (10)
O13—Ni2—O12	87.96 (11)	O21—Ni6—O17	83.46 (11)
O13—Ni2—O16	176.67 (11)	O11—Ni7—O1	80.70 (9)
O13—Ni2—N5	93.95 (11)	O11—Ni7—O29	93.08 (12)
O16—Ni2—Ni9	134.52 (8)	O11—Ni7—N7	174.89 (12)
O16—Ni2—O2	91.91 (10)	O14—Ni7—O1	93.97 (10)
O16—Ni2—O12	89.84 (11)	O14—Ni7—O11	80.78 (11)
O16—Ni2—N5	88.78 (11)	O14—Ni7—O27	173.72 (12)
N5—Ni2—O2	93.98 (10)	O14—Ni7—O29	88.55 (12)
O6—Ni3—O4	90.98 (9)	O14—Ni7—N7	96.50 (12)
O6—Ni3—O10	88.59 (10)	O27—Ni7—O1	89.56 (10)
O6—Ni3—O25	173.84 (11)	O27—Ni7—O11	94.69 (11)
O6—Ni3—N1	94.24 (11)	O27—Ni7—O29	87.35 (12)
O8—Ni3—O4	78.72 (9)	O27—Ni7—N7	88.34 (12)
O8—Ni3—O6	83.22 (10)	O29—Ni7—O1	172.81 (12)
O8—Ni3—O10	91.22 (10)	N7—Ni7—O1	95.24 (11)
O8—Ni3—O25	92.34 (11)	N7—Ni7—O29	91.16 (13)
O8—Ni3—N1	172.36 (11)	O11—Ni8—O7	92.94 (10)
O10—Ni3—O4	169.91 (10)	O11—Ni8—O14	80.44 (11)
O10—Ni3—O25	87.23 (11)	O11—Ni8—O26	171.59 (11)
O10—Ni3—N1	95.93 (11)	O11—Ni8—O30	90.02 (12)
O25—Ni3—O4	92.34 (10)	O11—Ni8—N8	97.76 (12)
O25—Ni3—N1	90.69 (12)	O14—Ni8—O7	79.53 (10)
N1—Ni3—O4	94.16 (10)	O14—Ni8—O30	96.69 (13)
O5—Ni4—O4	91.86 (9)	O14—Ni8—N8	172.85 (13)
O8—Ni4—O4	81.27 (10)	O26—Ni8—O7	91.28 (11)
O8—Ni4—O5	95.69 (10)	O26—Ni8—O14	93.20 (11)
O8—Ni4—O24	89.81 (11)	O26—Ni8—O30	85.24 (13)
O8—Ni4—O28	93.87 (11)	O26—Ni8—N8	89.22 (13)
O13—Ni4—O4	95.34 (10)	O30—Ni8—O7	174.73 (11)
O13—Ni4—O5	81.48 (10)	N8—Ni8—O7	93.70 (12)
O13—Ni4—O8	175.55 (11)	N8—Ni8—O30	90.21 (14)
O13—Ni4—O24	93.73 (11)	O3—Ni9—O5	91.71 (9)
O13—Ni4—O28	89.11 (11)	O3—Ni9—O13	82.64 (10)
O24—Ni4—O4	170.50 (10)	O3—Ni9—O18	87.90 (10)

O24—Ni4—O5	92.28 (11)	O3—Ni9—O23	176.49 (12)
O28—Ni4—O4	91.83 (11)	O3—Ni9—N4	93.82 (11)
O28—Ni4—O5	170.17 (10)	O13—Ni9—O5	78.78 (10)
O28—Ni4—O24	85.48 (13)	O13—Ni9—O18	90.99 (11)
O6—Ni5—O9	77.70 (9)	O13—Ni9—O23	94.74 (11)
O6—Ni5—O19	92.51 (10)	O13—Ni9—N4	172.50 (13)
O6—Ni5—N2	170.38 (11)	O18—Ni9—O5	169.73 (10)
O8—Ni5—O6	83.84 (10)	O18—Ni9—N4	95.49 (13)
O8—Ni5—O9	89.42 (9)	O23—Ni9—O5	90.07 (11)
O8—Ni5—O19	88.72 (10)	O23—Ni9—O18	89.81 (12)
O8—Ni5—O22	178.88 (11)	O23—Ni9—N4	89.05 (12)
O8—Ni5—N2	92.70 (12)	N4—Ni9—O5	94.78 (12)

Figure S1 IR spectrum of **SD/Ni9a**.

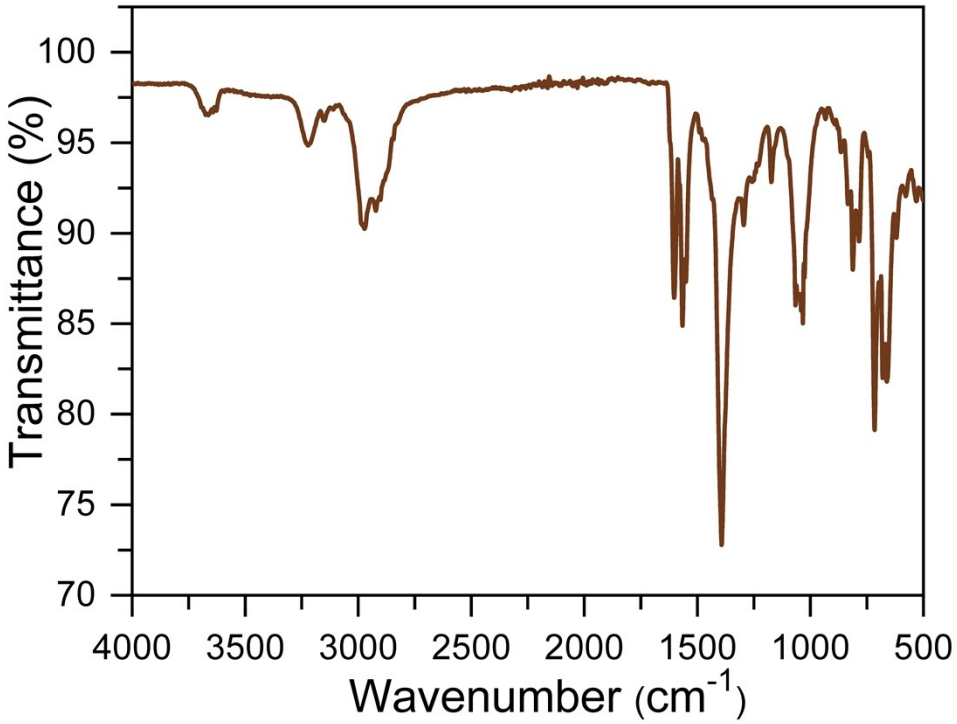


Figure S2 The TGA of **SD/Ni9a**.

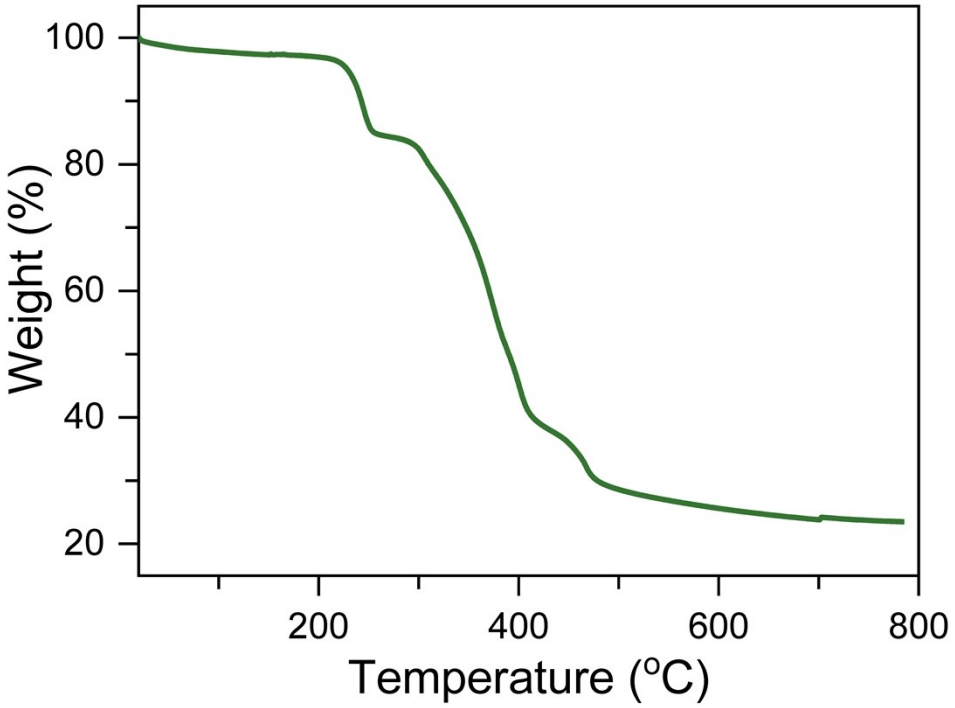


Figure S3 (a) Three layered arrangement of the nine Ni atoms in the structure: Ni2-Ni3-Ni7-(CO_3), Ni1-Ni4-Ni6, and Ni5-Ni8-Ni9-(CO_3) planes. (b) The carbonates are separated by 2.87 Å. Ni: green, O: red, C: grey.

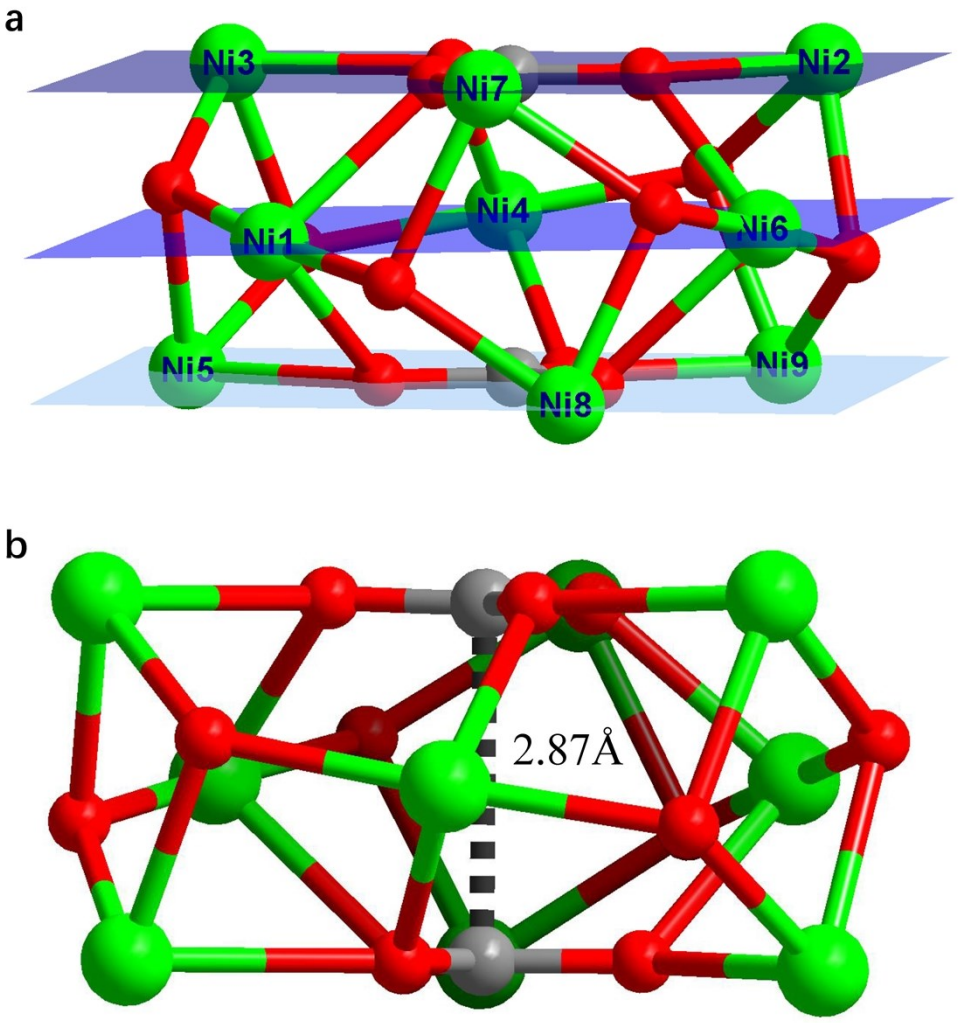


Figure S4 The coordination mode of carbonate anion within the cluster ([$6.2_{17}2_{26}2_{34}$] and [$6.2_{15}2_{49}2_{68}$]). Ni: green, O: red, C: grey.

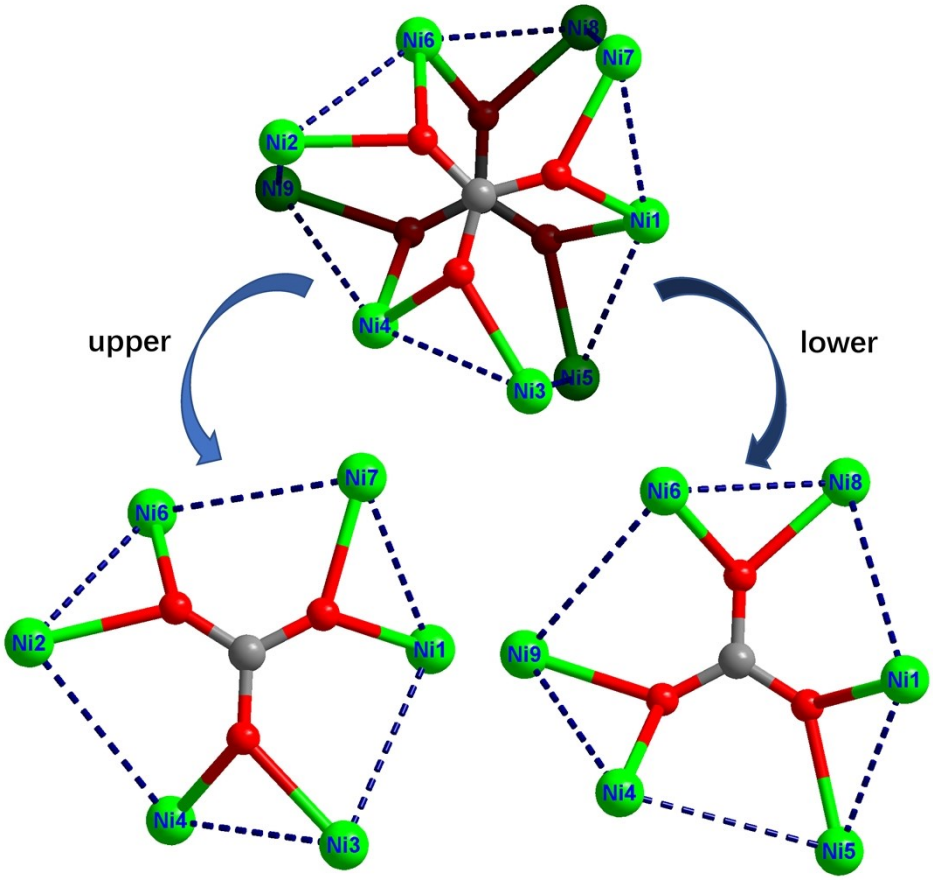


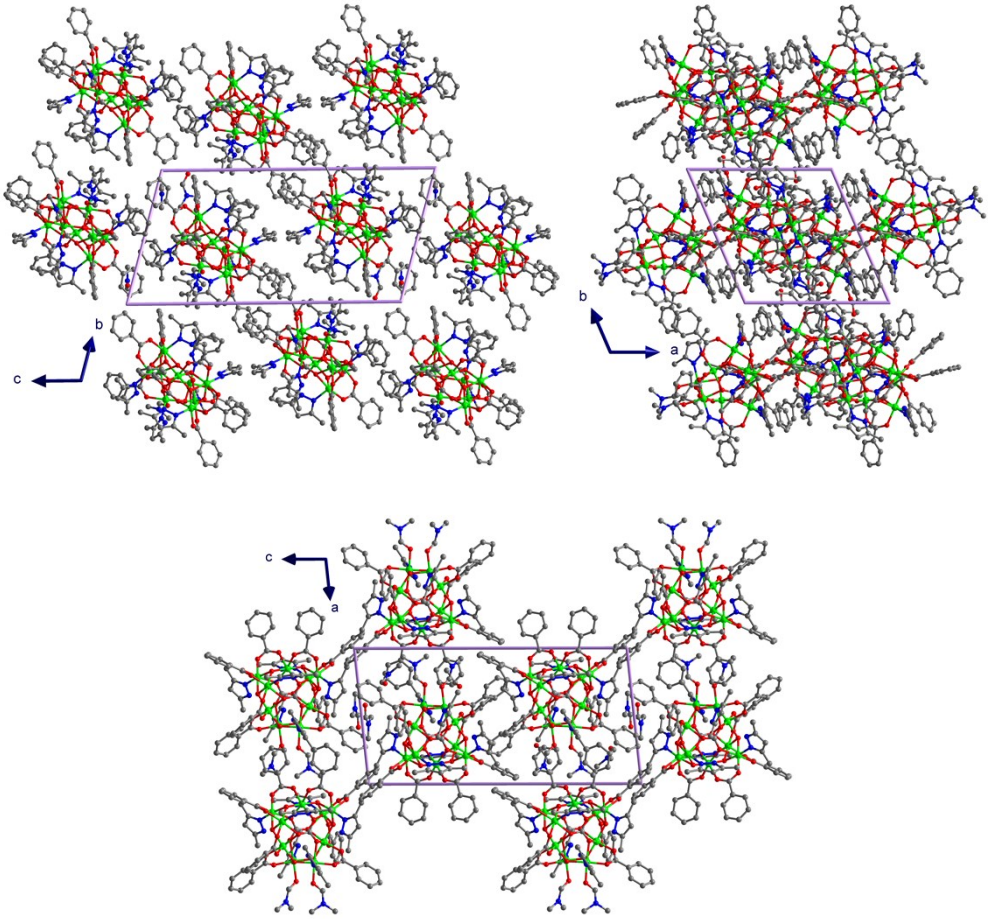
Table S3 The intramolecular hydrogen bond lengths [Å] and angles [°] in **SD/Ni9a** (D and A represent donor and acceptor, respectively).

D−H···*A*	D−H	H···*A*	D···*A*	D−H···*A*
N3−H3··O1	0.86	2.13	2.944(4)	158.2
N6−H6···O4	0.86	2.06	2.885(4)	161.1
N9−H9···O5	0.86	2.07	2.910(3)	164.8
N10−H10···O7	0.86	2.12	2.942(4)	160.4
N11−H11··· O2	0.86	2.12	2.929(3)	156.0
N12−H12···O9	0.86	2.09	2.906(5)	159.2

Table S4 Identification of the key species in ESI-MS of **SD/Ni9a**.

Species	Molecular formula	Exp. *m*/*z*	Sim. *m*/*z*
1a	$[Ni_9(OH)_8(ba)_9(Hdmpz)_2]^+$	1944.865	1944.828
1b	$[Ni_9(OH)_7(CO_3)(ba)_8(Hdmpz)_3]^+$	1962.878	1962.850
1c	$[Ni_9(OH)_6(CO_3)_2(ba)_7(Hdmpz)_4]^+$	1980.889	1980.871
1d	$[Ni_9(OH)_5(CO_3)_3(ba)_6(Hdmpz)_5]^+$	1998.919	1998.893
1e	$[Ni_9(OH)_6(CO_3)_2(ba)_7(Hdmpz)_5]^+$	2076.979	2076.940
1f	$[Ni_9(OH)_5(CO_3)_2(ba)_8(Hdmpz)_3(EtOH)_2(MeOH)_2]^+$	2144.969	2144.965
1g	$[Ni_9(OH)_6(CO_3)_2(ba)_7(Hdmpz)_6]^+$	2172.998	2173.009
1h	$[Ni_9(OH)_3(CO_3)(ba)_{12}(Hdmpz)_2]^+$	2282.865	2282.887
1i	$[Ni_9(OH)_7(CO_3)_2(ba)_6(Hdmpz)_8(EtOH)(MeOH)]^+$	2339.151	2339.189
1j	$[Ni_9(OH)_6(CO_3)_2(ba)_7(Hdmpz)_7(DMF)(H_2O)]^+$	2360.224	2360.142
1k	$[Ni_9(OH)_3(CO_3)(ba)_{12}(Hdmpz)_3]^+$	2378.945	2378.956
1l	$[Ni_9(OH)_5(CO_3)_2(ba)_8(Hdmpz)_6(EtOH)(DMF)]^+$	2396.157	2396.131
1m	$[Ni_9(OH)_3(CO_3)(ba)_{12}(Hdmpz)_4]^+$	2475.005	2475.025

Figure S5 The crystal packing structure of **SD/Ni9a**. Ni: green, O: red, N: blue, C: grey. All the solvent molecules and H atoms are omitted for clarity.



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