Supplementary Information

A rod-like hexanuclear nickel cluster based on bi(pyrazolyl-alcohol) ligand: Structure, electrospray ionization mass spectrometry, magnetism and photocurrent response

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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). The solid-state UV-Vis diffuse reflectance spectrum was recorded on a UV/Vis spectrophotometer (Evolution 220, ISA-220 accessory, Thermo Scientific) using a built-in 10 mm silicon photodiode with a 60 mm Spectralon sphere. 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. 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. The samples (5 mg) of **SD/Ni6a** 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 and 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/Ni6a

$Ni(OAc)_2 \cdot 4H_2O$ (50 mg, 0.2 mmol), H_2bdped (25 mg, 0.1mmol) were dissolved in 5 mL EtOH. 50 μL Et_3N were added to the above solution. The mixture was then stired for 2 hours at room temperature and a dark green solution with few precipitate was finally obtained. After filtration, the filtrate was allowed to evaporate at ambient temperature undisturbed. Green block crystals were obtained in about 3 days with the yield 63% (based on Ni). Calcd. (found) for $C_{52}H_{100}N_8Ni_6O_{30}$ (**SD/Ni6a**), calcd. (found): C, 37.41 (37.39); H, 6.04 (6.01); N, 6.71 (6.73) %. IR: ν = 3253 (w), 2948 (s), 1555 (w), 1404 (w), 1047 (m), 868 (m), 790 (s), 730 (m), 670 (m) cm^{-1}.

X-ray Crystallography

Single crystal of **SD/Ni6a** with appropriate dimensions was chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) to prevent decomposition. Intensity data and cell parameters were recorded at 173 K on a Bruker Apex II single crystal diffractometer, employing a Mo K_α radiation (λ = 0.71073 Å) and a CCD area detector. The raw frame data were processed using SAINT and SADABS to yield the reflection data file.[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/Ni6a**.

Empirical formula	$C_{52}H_{100}N_8Ni_6O_{30}$
Formula weight	1669.55
Temperature/K	173(2)
Crystal system	monoclinic
Space group	*C*2/*c*
a/Å	29.039(3)
b/Å	12.0094(11)
c/Å	22.276(2)
α/°	90
β/°	111.4801(10)
γ/°	90
Volume/Å^3	7229.0(11)
Z	4
ρcalcg/cm^3	1.532
μ/mm^{-1}	1.616
F(000)	3496.0
Radiation	Mo*K*α (λ = 0.71073)
2Θ range for data collection/°	3.712 to 55.108
Index ranges	$-37 \leq h \leq 29$, $-15 \leq k \leq 10$, $-28 \leq l \leq 28$
Reflections collected	25420
Independent reflections	8325 [R_{int} = 0.0499, R_{sigma} = 0.0661]
Data/restraints/parameters	8325/0/448
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0475, wR_2 = 0.0908
Final R indexes [all data]	R_1 = 0.0822, wR_2 = 0.1046
Largest diff. peak/hole / e Å^{-3}	0.75/-0.50

Table S2 The selected bond lengths [Å] and angles [°] for **SD/Ni6a**.

Ni1—O3^{i}	2.029 (2)	Ni2—O6	2.059 (2)
Ni1—O5	2.057 (2)	Ni2—O9	2.054 (2)
Ni1—O9	2.042 (2)	Ni2—O10	2.046 (2)
Ni1—O9^{i}	2.090 (2)	Ni3—O2	2.036 (3)
Ni1—N2	2.062 (3)	Ni3—O4	2.136 (2)
Ni1—N3	2.088 (3)	Ni3—O7	2.060 (2)
Ni2—O1	2.011 (2)	Ni3—O10	2.067 (2)
Ni2—O4	2.078 (2)	Ni3—O11	2.068 (2)
Ni2—O5^{i}	2.092 (2)	Ni3—O12	2.070 (3)
O3i—Ni1—O5	88.32 (9)	O9—Ni2—O4	90.46 (9)
O3i—Ni1—O9^{i}	93.38 (9)	O9—Ni2—O5^{i}	80.21 (8)
O3i—Ni1—O9	170.04 (10)	O9—Ni2—O6	97.24 (9)
O3i—Ni1—N2	93.47 (11)	O10—Ni2—O4	82.08 (9)
O3i—Ni1—N3	99.49 (10)	O10—Ni2—O5^{i}	161.50 (9)
O5—Ni1—O9^{i}	80.18 (9)	O10—Ni2—O6	99.61 (9)
O5—Ni1—N2	177.74 (11)	O10—Ni2—O9	82.50 (8)
O5—Ni1—N3	91.31 (10)	O2—Ni3—O4	90.16 (9)
O9—Ni1—O5	98.25 (9)	O2—Ni3—O7	90.32 (10)
O9—Ni1—O9^{i}	80.48 (8)	O2—Ni3—O10	90.30 (10)
O9—Ni1—N2	79.79 (10)	O2—Ni3—O11	86.63 (10)
O9—Ni1—N3	87.89 (10)	O2—Ni3—O12	171.94 (10)
N2—Ni1—O9^{i}	98.33 (10)	O7—Ni3—O4	172.31 (9)
N2—Ni1—N3	89.76 (11)	O7—Ni3—O10	92.11 (9)
N3—Ni1—O9^{i}	164.38 (10)	O7—Ni3—O11	89.92 (9)
O1—Ni2—O4	87.86 (10)	O7—Ni3—O12	90.24 (10)
O1—Ni2—O5^{i}	97.92 (9)	O10—Ni3—O4	80.22 (8)
O1—Ni2—O6	84.43 (10)	O10—Ni3—O11	176.34 (10)
O1—Ni2—O9	177.45 (10)	O10—Ni3—O12	97.71 (10)
O1—Ni2—O10	99.15 (9)	O11—Ni3—O4	97.77 (9)
O4—Ni2—O5^{i}	91.50 (9)	O11—Ni3—O12	85.33 (10)
O6—Ni2—O4	172.27 (10)	O12—Ni3—O4	90.36 (9)
O6—Ni2—O5^{i}	89.09 (9)		
Symmetry code: (*i*) −*x*+1, *y*, −*z*+1/2.			

Figure S1 The inter- and intra-cluster hydrogen bonds (green dashed lines) in **SD/Ni6a**. The Hirshfeld surface of **SD/Ni6a** was generated by CrystalExplorer 17.5.[6] In all cases red represents the closest contacts, and blue the most distant contacts. Color legend: Ni, green; N, blue; O, red; C, grey; H, white.

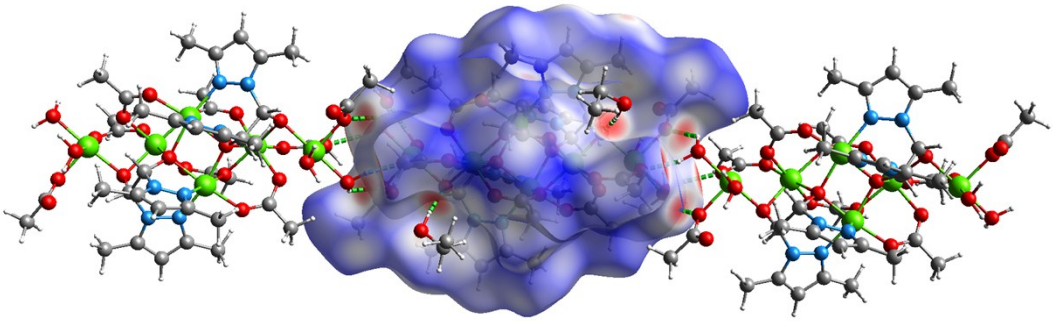

Table S3 Hydrogen bond length [Å] and angles [°] in **SD/Ni6a** (D and A represent hydrogen bonding donor and acceptor, respectively).

D−H···*A*	D−H	H···*A*	D···*A*	D−H···*A*
O11−H11A···O2	0.85	1.90	2.734(4)	165.8
O11−H11B···O7	0.85	2.07	2.690(4)	129.5
O12−H12B···O8	0.89	1.82	2.6177(5)	148.8
O12−H12A··O15	0.88	1.84	2.717(4)	173.9
O13−H13··· O14	0.84	2.00	2.665(4)	135.7
O14−H14···O10	0.84	2.01	2.823(4)	162.2
O15−H15···O13	0.84	1.90	2.782(5)	172.4

Table S4 Identification of the key species in ESI-MS of **SD/Ni6a**.

Species	Molecular formula	Exp. *m*/*z*	Sim. *m*/*z*
1*a*	$[Ni_4(OAc)_7(H_2O)_4(EtOH)_2]^+$	810.959	810.956
1*b*	$[Ni_4(OAc)_7(H_2O)_6(EtOH)_2]^+$	846.966	846.977
1*c*	$[Ni_4(OAc)_7(H_2O)_3(EtOH)_3(MeOH)]^+$	870.939	871.013
1*d*	$[Ni_4(bdped)_2(OAc)_3]^+$	907.028	907.031
1*e*	$[Ni_5(CH_3COO)_9(H_2O)_2(EtOH)_2(MeOH)_3]^+$	1046.945	1046.975
1*f*	$[Ni_5(bdped)_2(OAc)_5]^+$	1082.990	1082.993
1*g*	$[Ni_5(bdped)(OAc)_7(H_2O)_8(EtOH)]^+$	1142.960	1143.019
1*h*	$[Ni_5(bdped)_2(OAc)_5(H_2O)_2(EtOH)]^+$	1165.023	1165.056
1*i*	$[Ni_5(bdped)(OAc)_7(H_2O)_5(EtOH)_3]^+$	1180.998	1181.071
1*j*	$[Ni_6(bdped)_2(OAc)_7]^+$	1260.952	1260.951
1*k*	$[Ni_6(bdped)_2(OAc)_7(H_2O)_2(EtOH)]^+$	1342.990	1343.015
1*l*	$[Ni_6(bdped)(OAc)_9(H_2O)_5(EtOH)_3]^+$	1358.989	1359.029

Figure S2 The TGA of **SD/Ni6a**.

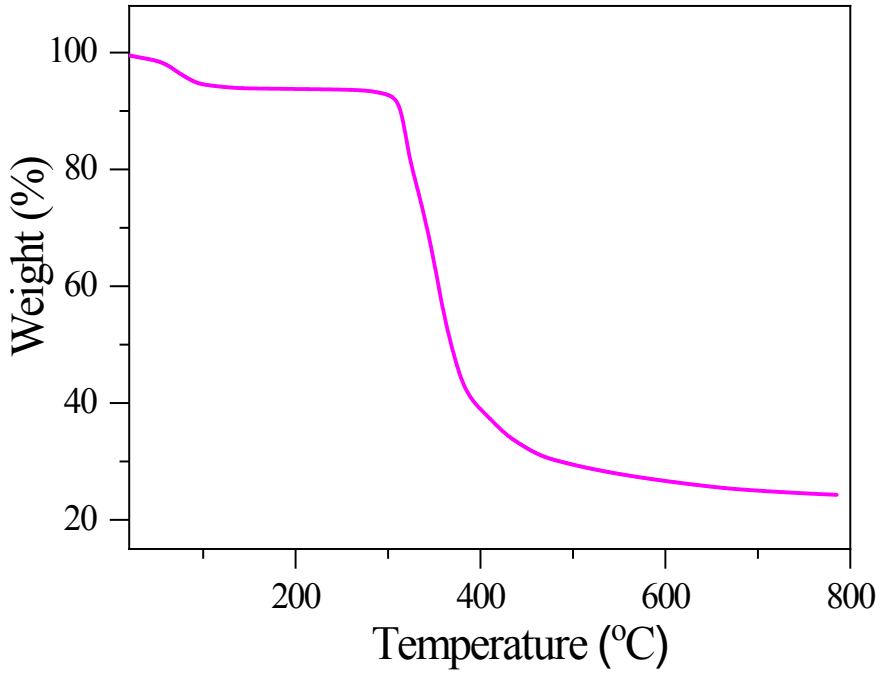

Figure S3 IR spectrum of **SD/Ni6a**.

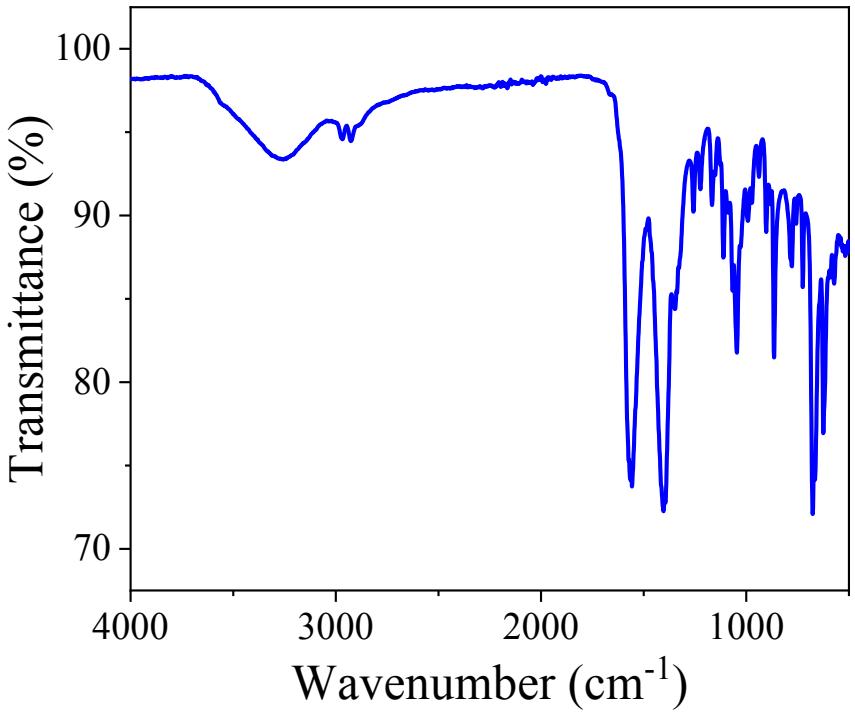

Figure S4 The picture of bulky sample of **SD/Ni6a**.

References

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