

Electronic Supplementary Information

Synthesis, structures and electrocatalytic properties of coordination polymers of 4,4',4'',4'''-tetrakis(carboxyphenyl)silane and 1,3,5-tris(2-methyl-1*H*-imidazol-1-yl)benzene

Tingting Cao^a, Yang Li^a, Tinghui Xie^a, Xinfang Wang^a, Zuogang
Huang^{a,b,*}, Huaguang Yu^{a,b,*}

^a*Key Laboratory of Optoelectronic Chemical Materials and Devices, Ministry of
Education, College of Optoelectronic Materials and Technology, Jiangnan University,
Wuhan 430056, P. R. China*

^b*State Key Laboratory of Fine Blasting, Jiangnan University, Wuhan 430056, P. R.
China*

*Corresponding author. Tel.: +86-27-84225508; fax: +86-27-84225508.

Email addresses: hzg19@jhun.edu.cn (Zuogang Huang), hgyu@jhun.edu.cn
(Huaguang Yu)

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1. General

Nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and *N,N'*-dimethylformamide (DMF) were used as received from Sinopharm Chemical Reagent Corporation. The ligand 4,4',4'',4'''-tetrakis(carboxyphenyl)silane (H_4tcps) (Fig. S1(a)) was prepared according to the literature [1]. The ligand 1,3,5-tris(2-methyl-1*H*-imidazol-1-yl)benzene (tmib) (Fig. S1(b)) was synthesized according to the literature [2]. Phase purity of the CPs was confirmed using a Panalytical X'pert powder X-ray diffractometer (PXRD) with Cu $K\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$), and the data were collected in the range of $5 - 60^\circ$. Fourier transform infrared spectroscopy (FT-IR) was performed using a Bruker Tensor 27 FTIR spectrometer. Thermal gravimetric analyses (TGA) were carried out using a TA Instruments SDT Q600 thermal analyzer under a constant stream of dry nitrogen gas (flow rate 20 mL min^{-1}) over the temperature range of $40 - 800^\circ\text{C}$ and at a heating rate of 20 K min^{-1} . Elemental analyses (C, H, and N) were carried out on an Elementar vario EL cube elemental analyzer. A Renishaw *InVia* Raman spectrometer was used to record Raman spectra. The morphologies of the materials were investigated by a Hitachi SU8010 scanning electron microscope (SEM). A Shimadzu Kratos Analytical AXIS SUPRA⁺ X-ray photoelectron spectrometer equipped with a micro-focus Al $K\alpha$ X-ray source was employed to perform X-ray photoelectron spectroscopy (XPS) measurements.

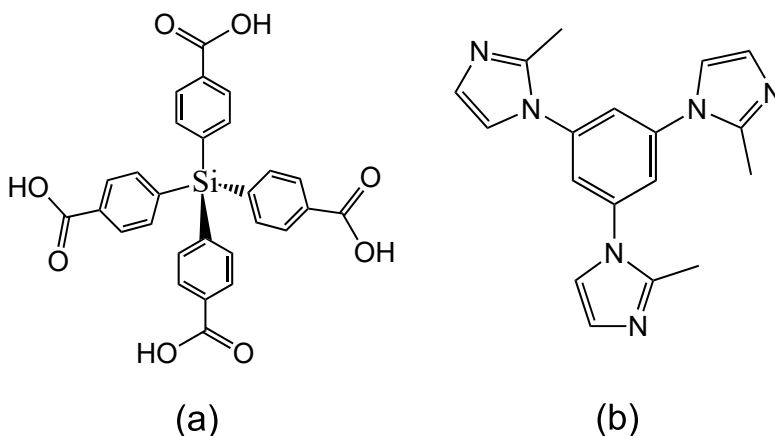


Figure S1: The chemical structures of (a) 4,4',4'',4'''-tetrakis(carboxyphenyl)silane (H_4tcps) and (b) 1,3,5-tris(2-methyl-1*H*-imidazol-1-yl)benzene (tmib).

2. Synthesis of coordination polymers

Synthesis of $[\text{Ni}_6(\text{tcps})_3(\text{tmib})_4(\text{H}_2\text{O})_2]$ (**1**). A mixture containing $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (58.0 mg, 0.2 mmol), H_4tcps (30.7 mg, 0.06 mmol), and tmib (23.8 mg, 0.075 mmol) in a mixed-solvent of 4 mL H_2O and 1 mL DMF was sealed in a 25 mL Teflon reactor, and was heated at 120°C for 3 days. After being cooled to room temperature, green crystals of **1** were collected in about 21 % yield (based on tmib). Elemental anal. Found: C, 57.31; H, 4.62; N, 10.23 %. Calc. for $\text{C}_{156}\text{H}_{126}\text{Ni}_6\text{N}_{24}\text{O}_{27}\text{Si}_3$: C, 58.46; H, 3.96; N, 10.49 %. FT-IR (KBr pellet, cm^{-1}): 3420 (m), 3130 (w), 3013 (w), 2926 (w), 1659 (s), 1609 (s), 1579 (s), 1526 (s), 1503 (s), 1413 (s), 1387 (s), 1311 (m), 1283 (m), 1254 (w), 1172 (w), 1145 (w), 1099 (m), 1017 (w), 887 (w), 862 (m), 831 (w), 775 (m), 731 (m), 707 (m), 673 (m), 636 (w), 557 (w), 481 (w), 413 (w).

Synthesis of $[\text{Co}_6(\text{tcps})_3(\text{tmib})_4]$ (**2**). A mixture containing $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (58.2 mg, 0.2 mmol), H_4tcps (25.6 mg, 0.05 mmol), and tmib (15.9 mg, 0.05 mmol) in a mixed-solvent of 3 mL H_2O and 2 mL DMF was sealed in a 25 mL Teflon reactor, and was heated at 120°C for 3 days. After being cooled to room temperature, purple crystals of **2** were collected in about 24 % yield (based on tmib). Elemental anal. Found: C, 58.18; H, 4.53; N, 10.31 %. Calc. for $\text{C}_{156}\text{H}_{120}\text{Co}_6\text{N}_{24}\text{O}_{24}\text{Si}_3$: C, 59.43; H, 3.84; N, 10.66 %. FT-IR (KBr pellet, cm^{-1}): 3430 (m), 3129 (w), 3016 (w), 1660 (m), 1609 (s), 1535 (m), 1501 (m), 1479 (w), 1397 (s), 1312 (w), 1284 (w), 1253 (w), 1171 (w), 1144 (w), 1099 (m), 1017 (w), 887 (w), 858 (w), 774 (w), 731 (s), 706 (w), 673 (w), 636 (w), 552 (w), 481 (w), 415 (w).

Synthesis of $[\text{Cu}_2(\text{tcps})(\text{tmib})(\text{H}_2\text{O})]$ (**3**). A mixture containing $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (4.8 mg, 0.02 mmol), H_4tcps (6.4 mg, 0.0124 mmol), and tmib (5.3 mg, 0.0167 mmol) in a mixed-solvent of 2.5 mL H_2O and 2.5 mL DMF with 1 drop of 1 M HNO_3 solution was sealed in a 25 mL Teflon reactor, and was heated at 120°C for 3 days. After being cooled to room temperature, blue crystals of **3** were collected in about 29 % yield (based on tmib). Elemental anal. Found: C, 55.89; H, 4.28; N, 8.36 %. Calc. for $\text{C}_{46}\text{H}_{36}\text{Cu}_2\text{N}_6\text{O}_9\text{Si}$: C, 56.84; H, 3.73; N, 8.65 %. FT-IR (KBr pellet, cm^{-1}): 3418 (m), 3034 (w), 2968 (w), 2928 (w), 1608 (m), 1543 (m), 1503 (m), 1479 (m), 1414 (m), 1373 (s), 1313 (w), 1284 (w), 1186 (w), 1168 (w), 1151 (w), 1103 (m), 1039 (w), 1016 (w), 943 (w), 887 (w), 854 (w), 773 (m), 731 (s), 708 (m), 671 (w), 640 (w), 543 (w), 488 (w), 440 (w), 416 (w).

Synthesis of $[\text{Zn}_2(\text{tcps})(\text{tmib})]$ (**4**). A mixture containing $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (5.9 mg, 0.02 mmol), H_4tcps (6.5 mg, 0.0129 mmol), and tmib (6.4 mg, 0.02

mmol) in a mixed-solvent of 3 mL H₂O and 3 mL DMF with 2 drops of 1 M HNO₃ solution was sealed in a 25 mL Teflon reactor, and was heated at 120°C for 3 days. After being cooled to room temperature, colorless bipyramid crystals of **4** were collected in about 27 % yield (based on tmib). Elemental anal. Found: C, 56.52; H, 4.45; N, 8.39 %. Calc. for C₄₆H₃₄Zn₂N₆O₈Si: C, 57.69; H, 3.58; N, 8.78 %. FT-IR (KBr pellet, cm⁻¹): 3431 (m), 3128 (w), 3063 (w), 3019 (w), 2968 (w), 2926 (w), 2387 (m), 2287 (w), 1663 (s), 1611 (s), 1543 (s), 1501 (m), 1481 (m), 1410 (s), 1389 (s), 1369 (s), 1317 (m), 1284 (m), 1254 (m), 1171 (m), 1149 (m), 1099 (s), 1062 (w), 1041 (w), 1016 (m), 885 (w), 847 (m), 773 (m), 729 (s), 704 (m), 673 (m), 636 (w), 586 (w), 543 (m), 482 (m), 416 (m).

3. Structure determination of single crystals

Suitable single crystals of the coordination polymers **1**, **2**, **3** and **4** were selected for single crystal X-ray diffraction analyses. Crystallographic data were collected on a Bruker AXS D8 QUEST single crystal X-ray diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) or Cu K α radiation ($\lambda = 1.54178$ Å). The APEX 3 program was used to collect the frames of data, index the reflections and determine the lattice parameters; SAINT [3] was used for the integration of the intensities of the reflections and scaling; SADABS [4] was used for the absorption correction; and SHELXTL [5, 6] was used for the space-group determination. The structures were solved by direct method or Patterson method with SHELXT program [7] and refined by the full matrix least-square method on the basis of F^2 using SHELXL-2014 program [8, 9] contained in OLEX2 suite graphical user interface [10]. The contribution of the disordered solvent molecules to the diffraction pattern could not be rigorously included in the model and were consequently removed with the SQUEEZE routine [11] of PLATON [12] or with the mask tool implemented in OLEX2. All non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. All hydrogen atoms of the organic molecule were placed by geometrical considerations and were added to the structure factor calculation. The crystallographic information files (CIFs) were compiled with OLEX2. The program PLATON enabled checking for additional symmetry elements. The overall structures of the coordination polymers were analyzed by TOPOS software [13]. The formula for **1**, **2**, **3** and **4** were determined by single crystal structure. Crystallographic figures were generated with the Diamond 3.1e software [14]. The

detailed bond lengths and bond angles for these compounds were tabulated in Tables S1 – S8.

3.1. The crystal structure of compound **1**

Table S1: Selected bond lengths (Å) of compound **1**

bond	length (Å)	bond	length (Å)
Ni1–O2	2.1826(17)	C5–C4	1.383(4)
Ni1–O3	2.0857(18)	N7–C48	1.308(3)
Ni1–N1	2.103(2)	N7–C50	1.376(3)
Ni1–N5#1 ¹	2.058(2)	C21–C16	1.391(3)
Ni1–O8#2 ¹	2.0587(17)	C46–C45	1.384(4)
Ni1–O1	2.128(2)	C46–C41	1.387(3)
Ni2–O6	2.1006(18)	C30–C29	1.478(4)
Ni2–O4#3 ¹	2.0908(18)	C45–C44	1.387(4)
Ni2–N3#4 ¹	2.040(2)	C15–C16	1.492(3)
Ni2–O7	2.1291(18)	C17–C16	1.387(4)
Ni2–O5#3 ¹	2.1367(19)	C17–C18	1.385(4)
Ni2–N7	2.026(2)	C38–C37	1.480(4)
Si1–C19	1.875(2)	C38–N5	1.317(3)
Si1–C5	1.877(2)	C42–C41	1.386(3)
Si1–C12	1.874(3)	C42–C43	1.390(4)
Si1–C26	1.869(3)	C11–C10	1.388(4)
O2–C1	1.256(3)	C11–C12	1.392(3)
O6–C15	1.267(3)	C2–C1	1.502(3)
O3–C1	1.255(3)	C2–C3	1.383(4)
O4–Ni2#5 ¹	2.0908(18)	C14–C13	1.385(4)
O4–C8	1.262(3)	C44–C43	1.369(4)
N2–C30	1.354(3)	N8–C49	1.379(4)
N2–C43	1.433(3)	N8–C48	1.358(4)
N2–C31	1.376(3)	N8–C51	1.430(3)
C19–C20	1.386(3)	C49–C50	1.334(4)
C19–C18	1.394(4)	C48–C47	1.486(4)
N3–Ni2#6 ¹	2.040(2)	C13–C12	1.390(4)
N3–C34	1.315(3)	C3–C4	1.385(4)
N3–C36	1.370(3)	C34–C33	1.483(4)

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Table S1 – continued from previous page

bond	length (Å)	bond	length (Å)
O7–C15	1.253(3)	C40–C39	1.327(4)
N1–C30	1.324(3)	C40–N5	1.380(3)
N1–C32	1.383(3)	C32–C31	1.347(4)
N6–C38	1.360(3)	C52–C51#7 ¹	1.369(4)
N6–C41	1.429(3)	C52–C51	1.386(4)
N6–C39	1.385(3)	C35–C36	1.333(4)
N4–C45	1.430(3)	C51–C52#8 ¹	1.369(4)
N4–C34	1.363(3)	N5–Ni1#9 ¹	2.057(2)
N4–C35	1.370(3)	O8–Ni1#10 ¹	2.0588(17)
O5–Ni2#5 ¹	2.1365(19)	O8–C22	1.232(4)
O5–C8	1.267(3)	C26–C27	1.356(4)
C7–C6	1.389(3)	C26–C25	1.372(4)
C7–C2	1.369(3)	C23–C28	1.365(4)
C6–C5	1.388(4)	C23–C24	1.367(5)
C20–C21	1.380(3)	C23–C22	1.506(4)
C9–C14	1.379(4)	C28–C27	1.384(4)
C9–C8	1.490(4)	C24–C25	1.377(5)
C9–C10	1.373(4)	C22–O9	1.244(4)

¹ #1: $4/3 + y - x$, $2/3 - x$, $-1/3 + z$; #2: $1 - y$, $+x - y$, $+z$;
#3: $1/3 - y$, $-1/3 + x - y$, $-1/3 + z$; #4: $-y$, $-1 + x - y$, $+z$;
#5: $2/3 + y - x$, $1/3 - x$, $1/3 + z$; #6: $1 + y - x$, $-x$, $+z$;
#7: $+y - x$, $-x$, $+z$; #8: $-y$, $+x - y$, $+z$;
#9: $2/3 - y$, $-2/3 + x - y$, $1/3 + z$; #10: $1 + y - x$, $1 - x$, $+z$.

Table S2: Selected angles (°) of compound **1**

angle	(°)	angle	(°)
O3–Ni1–O2	61.57(7)	C46–C45–C44	120.9(2)
O3–Ni1–N1	90.48(8)	C44–C45–N4	117.9(2)
O3–Ni1–O1	90.24(9)	O6–C15–C16	120.3(2)
N1–Ni1–O2	91.08(7)	O7–C15–O6	120.5(2)
N1–Ni1–O1	173.85(8)	O7–C15–C16	119.2(2)
N5#1–Ni1–O2 ¹	110.71(8)	C18–C17–C16	120.5(2)

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Table S2 – continued from previous page

angle	(°)	angle	(°)
N5#1–Ni1–O3 ¹	172.26(8)	N6–C38–C37	125.2(2)
N5#1–Ni1–N1 ¹	90.10(8)	N5–C38–N6	109.9(2)
N5#1–Ni1–O8#2 ¹	92.92(8)	N5–C38–C37	124.8(2)
N5#1–Ni1–O1 ¹	88.37(9)	C41–C42–C43	118.4(2)
O8#2–Ni1–O2 ¹	155.01(7)	C10–C11–C12	120.9(2)
O8#2–Ni1–O3 ¹	94.66(7)	C7–C2–C1	122.1(2)
O8#2–Ni1–N1 ¹	97.10(8)	C7–C2–C3	118.7(2)
O8#2–Ni1–O1 ¹	88.92(8)	C3–C2–C1	119.2(2)
O1–Ni1–O2	83.90(8)	O2–C1–C2	120.4(2)
O6–Ni2–O7	62.28(7)	O3–C1–O2	121.0(2)
O6–Ni2–O5#3 ¹	95.12(8)	O3–C1–C2	118.5(2)
O4#3–Ni2–O6 ¹	149.83(7)	C9–C14–C13	120.0(2)
O4#3–Ni2–O7#3 ¹	94.12(7)	C46–C41–N6	120.3(2)
O4#3–Ni2–O5#3 ¹	62.67(7)	C42–C41–N6	117.9(2)
N3#4–Ni2–O6 ¹	106.18(8)	C42–C41–C46	121.5(2)
N3#4–Ni2–O4#3 ¹	96.29(8)	C43–C44–C45	119.5(2)
N3#4–Ni2–O7 ¹	168.40(8)	C49–N8–C51	124.5(3)
N3#4–Ni2–O5#3 ¹	94.60(8)	C48–N8–C49	107.9(2)
O7–Ni2–O5#3 ¹	85.67(8)	C48–N8–C51	127.6(3)
N7–Ni2–O6	99.88(8)	C21–C16–C15	120.2(2)
N7–Ni2–O4#3 ¹	99.73(8)	C17–C16–C21	119.0(2)
N7–Ni2–N3#4 ¹	90.64(9)	C17–C16–C15	120.7(2)
N7–Ni2–O7	92.61(8)	C50–C49–N8	105.9(3)
N7–Ni2–O5#3 ¹	162.06(8)	O4–C8–O5	120.8(2)
C19–Si1–C5	109.09(11)	O4–C8–C9	119.7(2)
C12–Si1–C19	109.57(11)	O5–C8–C9	119.4(2)
C12–Si1–C5	111.25(11)	C42–C43–N2	119.8(2)
C26–Si1–C19	113.08(12)	C44–C43–N2	119.0(2)
C26–Si1–C5	106.98(11)	C44–C43–C42	121.2(2)
C26–Si1–C12	106.86(11)	N7–C48–N8	109.4(2)
C1–O2–Ni1	86.32(14)	N7–C48–C47	125.8(3)
C15–O6–Ni2	88.91(15)	N8–C48–C47	124.8(2)
C1–O3–Ni1	90.70(15)	C14–C13–C12	121.5(2)
C8–O4–Ni2#5 ¹	88.85(15)	C2–C3–C4	120.7(2)
C30–N2–C43	124.6(2)	C17–C18–C19	120.9(2)

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Table S2 – continued from previous page

angle	(°)	angle	(°)
C30–N2–C31	107.7(2)	C9–C10–C11	120.4(2)
C31–N2–C43	127.6(2)	N3–C34–N4	109.8(2)
C20–C19–Si1	118.88(18)	N3–C34–C33	126.0(3)
C20–C19–C18	117.7(2)	N4–C34–C33	124.2(3)
C18–C19–Si1	123.37(19)	C39–C40–N5	110.1(2)
C34–N3–Ni2#6 ¹	132.08(18)	C31–C32–N1	109.9(2)
C34–N3–C36	106.5(2)	C51#7–C52–C51 ¹	118.4(3)
C36–N3–Ni2#6 ¹	121.33(17)	C40–C39–N6	106.4(2)
C15–O7–Ni2	87.98(15)	C36–C35–N4	106.5(2)
C30–N1–Ni1	133.89(18)	C35–C36–N3	110.1(2)
C30–N1–C32	105.9(2)	C5–C4–C3	121.2(3)
C32–N1–Ni1	120.16(16)	C49–C50–N7	109.7(3)
C38–N6–C41	129.4(2)	C32–C31–N2	106.0(3)
C38–N6–C39	107.2(2)	C52#8–C51–N8 ¹	119.9(3)
C39–N6–C41	123.4(2)	C52–C51–N8	118.4(3)
C34–N4–C45	128.0(2)	C52#8–C51–C52 ¹	121.6(3)
C34–N4–C35	107.2(2)	C38–N5–Ni1#9 ¹	134.64(17)
C35–N4–C45	124.3(2)	C38–N5–C40	106.4(2)
C8–O5–Ni2#5 ¹	86.72(16)	C40–N5–Ni1#9 ¹	118.29(17)
C2–C7–C6	120.4(2)	C22–O8–Ni1#10 ¹	131.96(19)
C5–C6–C7	121.6(2)	C11–C12–Si1	122.72(19)
C21–C20–C19	121.9(2)	C13–C12–Si1	119.70(19)
C14–C9–C8	119.9(2)	C13–C12–C11	117.6(2)
C10–C9–C14	119.6(2)	C27–C26–Si1	120.7(2)
C10–C9–C8	120.4(2)	C27–C26–C25	116.6(3)
C6–C5–Si1	120.92(18)	C25–C26–Si1	122.1(2)
C4–C5–Si1	121.30(19)	C28–C23–C24	116.7(3)
C4–C5–C6	117.2(2)	C28–C23–C22	121.4(3)
C48–N7–Ni2	128.08(19)	C24–C23–C22	121.8(3)
C48–N7–C50	107.2(2)	C23–C28–C27	120.9(3)
C50–N7–Ni2	124.56(18)	C26–C27–C28	122.4(3)
C20–C21–C16	119.8(2)	C23–C24–C25(3)	122.2(3)
C45–C46–C41	118.5(2)	O8–C22–C23	117.9(3)
N2–C30–C29	122.7(2)	O8–C22–O9	125.0(3)
N1–C30–N2	110.4(2)	O9–C22–C23	117.1(3)

Continued on next page

Table S2 – continued from previous page

angle	(°)	angle	(°)
N1–C30–C29	126.8(2)	C26–C25–C24	121.0(3)
C46–C45–N4	121.2(2)		

¹ #1: $4/3 + y - x$, $2/3 - x$, $-1/3 + z$; #2: $1 - y$, $+x - y$, $+z$;
#3: $1/3 - y$, $-1/3 + x - y$, $-1/3 + z$; #4: $-y$, $-1 + x - y$, $+z$;
#5: $2/3 + y - x$, $1/3 - x$, $1/3 + z$; #6: $1 + y - x$, $-x$, $+z$;
#7: $+y - x$, $-x$, $+z$; #8: $-y$, $+x - y$, $+z$;
#9: $2/3 - y$, $-2/3 + x - y$, $1/3 + z$; #10: $1 + y - x$, $1 - x$, $+z$.

3.2. The crystal structure of compound **2**

Table S3: Selected bond lengths (Å) of compound **2**

bond	length (Å)	bond	length (Å)
Co2–O3	2.066(3)	C26–C27	1.402(5)
Co2–O4	2.284(3)	C26–C25	1.381(5)
Co2–O5#1 ¹	2.170(3)	C44–C43	1.482(5)
Co2–O6#1 ¹	2.185(3)	C5–C4	1.385(5)
Co2–N5#2 ¹	2.092(3)	C5–C6	1.385(6)
Co2–N7	2.075(3)	O1–C1	1.220(9)
Co1–O7#3 ¹	2.029(2)	N2–C30	1.326(5)
Co1–O8#3 ¹	2.293(3)	N2–C33	1.436(6)
Co1–N3#4 ¹	2.123(4)	N2–C32	1.360(6)
Co1–O1	1.956(3)	C13–C14	1.392(5)
Co1–N1	2.041(3)	N4–C35	1.436(5)
Si1–C19	1.867(3)	N4–C40	1.322(6)
Si1–C12	1.870(3)	N4–C42	1.401(6)
Si1–C26	1.867(3)	N1–C30	1.327(5)
Si1–C5	1.864(3)	N1–C31	1.364(6)
O3–C8	1.271(4)	C23–C22	1.504(4)
O7–Co1#5 ¹	2.029(2)	C23–C28	1.385(5)
O7–C22	1.261(5)	C23–C24	1.377(5)
O4–C8	1.245(5)	C27–C28	1.383(5)
O5–Co2#6 ¹	2.170(3)	C16–C17	1.367(6)

Continued on next page

Table S3 – continued from previous page

bond	length (Å)	bond	length (Å)
O5–C15	1.252(6)	C16–C15	1.504(5)
N6–C44	1.361(4)	C16–C21	1.386(6)
N6–C37	1.426(5)	C10–C11	1.378(5)
N6–C46	1.375(6)	C20–C21	1.382(6)
O6–Co2#6 ¹	2.185(3)	C37–C38	1.390(6)
O6–C15	1.259(6)	C37–C36	1.396(5)
O8–Co1#5 ¹	2.293(3)	C4–C3	1.384(5)
O8–C22	1.240(5)	C51–C52	1.381(6)
N5–Co2#7 ¹	2.092(3)	C51–C52#9 ¹	1.383(6)
N5–C44	1.320(5)	C30–C29	1.494(6)
N5–C45	1.373(5)	C52–C51#10 ¹	1.383(6)
N8–C51	1.431(5)	C25–C24	1.390(5)
N8–C48	1.358(6)	C35–C36	1.397(6)
N8–C50	1.371(6)	C35–C34	1.393(7)
N7–C49	1.377(5)	C38–C33	1.381(6)
N7–C48	1.314(6)	C49–C50	1.343(7)
N3–Co1#8 ¹	2.123(4)	C33–C34	1.403(6)
N3–C41	1.345(6)	C1–C2	1.535(6)
N3–C40	1.308(5)	C1–O2	1.229(9)
C9–C8	1.496(4)	C3–C2	1.369(7)
C9–C14	1.383(4)	C46–C45	1.351(6)
C9–C10	1.377(5)	C48–C47	1.482(7)
C19–C18	1.395(5)	C2–C7	1.372(9)
C19–C20	1.391(5)	C6–C7	1.403(8)
C12–C13	1.396(4)	C41–C42	1.358(7)
C12–C11	1.394(4)	C40–C39	1.499(7)
C18–C17	1.388(5)	C32–C31	1.337(7)

¹ #1: $2/3 + y - x$, $4/3 - x$, $1/3 + z$; #2: $1/3 + x$, $-1/3 + y$, $-1/3 + z$;
#3: $1 - y$, $1 + x - y$, $+ z$; #4: $1/3 + y - x$, $5/3 - x$, $-1/3 + z$;
#5: $+ y - x$, $1 - x$, $+ z$; #6: $4/3 - y$, $2/3 + x - y$, $-1/3 + z$;
#7: $-1/3 + x$, $1/3 + y$, $1/3 + z$; #8: $5/3 - x$, $4/3 + x - y$, $1/3 + z$;
#9: $1 + y - x$, $2 - x$, $+ z$; #10: $2 - y$, $1 + x - y$, $+ z$.

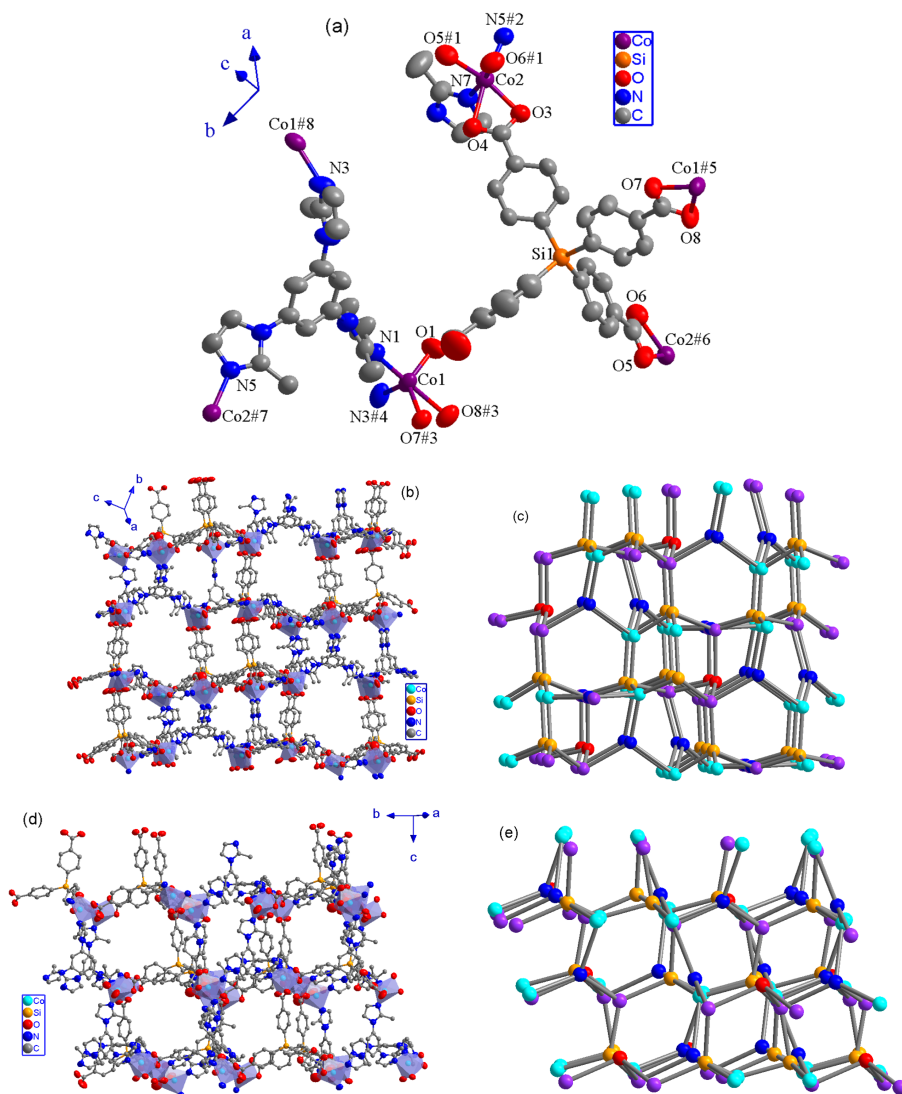


Figure S2: (a) Coordination environments (at 50 % probability level) of Co1 and Co2 centers in compound **2**. The hydrogen atoms and crystal water molecules were omitted for clarity. Symmetry codes for the generated atoms: #1: $2/3 + y - x, 4/3 - x, 1/3 + z$; #2: $1/3 + x, -1/3 + y, -1/3 + z$; #3: $1 - y, 1 + x - y, + z$; #4: $1/3 + y - x, 5/3 - x, -1/3 + z$; #5: $+ y - x, 1 - x, + z$; #6: $4/3 - y, 2/3 + x - y, -1/3 + z$; #7: $-1/3 + x, 1/3 + y, 1/3 + z$; #8: $5/3 - x, 4/3 + x - y, 1/3 + z$; #9: $1 + y - x, 2 - x, + z$; #10: $2 - y, 1 + x - y, + z$. (b) and (d) Perspective view of the 3D framework in compound **2**. The Co1 and Co2 centers were bridged by tcps⁴⁻ anions and tmib ligands to form the 3D network. (c) and (e) Schematic view of the 3D (3,4)-connected framework with the point symbol of $(6^3)_4(6^6)_9$ topology in compound **2**. Color code: purple ball, 4-connected Co1 node; sky blue ball, 4-connected Co2 node; yellow ball, 4-connected tcps⁴⁻ node; blue ball, 3-connected tmib (tmib-1) node; red ball, 3-connected tmib (tmib-2) node.

Table S4: Selected angles (°) of compound **2**

angle	(°)	angle	(°)
O3–Co2–O4	60.32(9)	C30–N2–C33	127.8(3)
O3–Co2–O5#1 ¹	141.51(12)	C30–N2–C32	106.9(4)
O3–Co2–O6#1 ¹	89.79(11)	C32–N2–C33	125.2(4)
O3–Co2–N5#2 ¹	111.64(11)	C14–C13–C12	121.2(3)
O3–Co2–N7	96.17(12)	C40–N4–C35	126.7(4)
O5#1–Co2–O4 ¹	92.09(11)	C40–N4–C42	106.6(4)
O5#1–Co2–O6#1 ¹	59.97(12)	C42–N4–C35	126.1(4)
O6#1–Co2–O4 ¹	86.04(12)	C30–N1–Co1	135.0(3)
N5#2–Co2–O4 ¹	171.16(11)	C30–N1–C31	105.5(4)
N5#2–Co2–O5#1 ¹	93.13(12)	C31–N1–Co1	118.1(3)
N5#2–Co2–O6#1 ¹	90.40(13)	C28–C23–C22	120.2(3)
N7–Co2–O4	87.24(12)	C24–C23–C22	120.7(3)
N7–Co2–O5#1 ¹	109.64(13)	C24–C23–C28	119.0(3)
N7–Co2–O6#1 ¹	167.35(14)	C28–C27–C26	120.9(3)
N7–Co2–N5#2 ¹	97.70(13)	C9–C14–C13	120.4(3)
O7#3–Co1–O8#3 ¹	60.16(10)	C17–C16–C15	119.2(4)
O7#3–Co1–N3#4 ¹	115.13(14)	C17–C16–C21	119.8(3)
O7#3–Co1–N1 ¹	112.70(12)	C21–C16–C15	121.0(4)
N3#4–Co1–O8#3 ¹	89.92(13)	C9–C10–C11	120.9(3)
O1–Co1–O7#3 ¹	129.37(18)	C21–C20–C19	122.2(4)
O1–Co1–O8#3 ¹	85.52(15)	C10–C11–C12	121.5(3)
O1–Co1–N3#4 ¹	99.5(2)	C16–C17–C18	120.3(3)
O1–Co1–N1	97.15(15)	O5–C15–O6	120.2(4)
N1–Co1–O8#3 ¹	171.67(13)	O5–C15–C16	121.3(4)
N1–Co1–N3#4 ¹	97.40(15)	O6–C15–C16	118.5(4)
C19–Si1–C12	109.68(14)	O7–C22–C23	119.7(3)
C19–Si1–C26	109.71(14)	O8–C22–O7	121.2(3)
C26–Si1–C12	106.40(13)	O8–C22–C23	119.1(3)
C5–Si1–C19	110.01(15)	C27–C28–C23	120.8(3)
C5–Si1–C12	110.56(14)	C38–C37–N6	120.2(3)
C5–Si1–C26	110.41(15)	C38–C37–C36	120.7(4)
C8–O3–Co2	93.7(2)	C36–C37–N6	118.8(3)
C22–O7–Co1#5 ¹	95.0(2)	C3–C4–C5	122.4(4)
C8–O4–Co2	84.5(2)	C52#9–C51–N8 ¹	119.3(3)

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Table S4 – continued from previous page

angle	(°)	angle	(°)
C15–O5–Co2#6 ¹	90.3(3)	C52–C51–N8	119.4(3)
C44–N6–C37	127.2(3)	C52–C51–C52#9 ¹	121.2(4)
C44–N6–C46	108.5(3)	C20–C21–C16	119.4(4)
C46–N6–C37	124.2(3)	N2–C30–N1	111.2(3)
C15–O6–Co2#6 ¹	89.4(3)	N2–C30–C29	125.0(4)
C22–O8–Co1#5 ¹	83.5(2)	N1–C30–C29	123.8(4)
C44–N5–Co2#7 ¹	129.2(2)	C51–C52–C51#10 ¹	118.8(4)
C44–N5–C45	107.2(3)	C26–C25–C24	121.9(3)
C45–N5–Co2#7 ¹	123.6(3)	C36–C35–N4	117.7(4)
C48–N8–C51	124.6(4)	C34–C35–N4	120.7(4)
C48–N8–C50	107.5(3)	C34–C35–C36	121.3(4)
C50–N8–C51	127.4(4)	C33–C38–C37	119.8(3)
C49–N7–Co2	123.6(3)	C23–C24–C25	120.1(3)
C48–N7–Co2	129.2(3)	C50–C49–N7	109.5(4)
C48–N7–C49	106.6(3)	C37–C36–C35	118.7(4)
C41–N3–Co1#8 ¹	125.2(3)	C38–C33–N2	119.5(4)
C40–N3–Co1#8 ¹	124.7(3)	C38–C33–C34	120.9(4)
C40–N3–C41	106.5(4)	C34–C33–N2	119.6(4)
C14–C9–C8	121.5(3)	O1–C1–C2	117.6(5)
C10–C9–C8	119.6(3)	O1–C1–O2	124.8(6)
C10–C9–C14	118.9(3)	O2–C1–C2	117.6(7)
C18–C19–Si1	121.0(2)	C2–C3–C4	120.7(4)
C20–C19–Si1	122.2(3)	C35–C34–C33	118.4(4)
C20–C19–C18	116.8(3)	C45–C46–N6	105.4(3)
C13–C12–Si1	123.5(2)	N8–C48–C47	125.1(4)
C11–C12–Si1	119.3(2)	N7–C48–N8	110.0(4)
C11–C12–C13	117.2(3)	N7–C48–C47	124.9(4)
C17–C18–C19	121.4(3)	C3–C2–C1	118.7(5)
C27–C26–Si1	123.0(2)	C3–C2–C7	118.1(4)
C25–C26–Si1	119.7(2)	C7–C2–C1	123.2(5)
C25–C26–C27	117.3(3)	C49–C50–N8	106.4(4)
N6–C44–C43	125.5(3)	C5–C6–C7	120.6(5)
N5–C44–N6	109.0(3)	N3–C41–C42	110.0(4)
N5–C44–C43	125.5(3)	C46–C45–N5	109.8(4)
O3–C8–C9	118.6(3)	N3–C40–N4	111.6(4)

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Table S4 – continued from previous page

angle	(°)	angle	(°)
O4–C8–O3	121.3(3)	N3–C40–C39	126.4(4)
O4–C8–C9	120.1(3)	N4–C40–C39	121.9(4)
C4–C5–Si1	119.9(3)	C2–C7–C6	121.5(4)
C4–C5–C6	116.7(4)	C31–C32–N2	107.3(4)
C6–C5–Si1	123.3(3)	C32–C31–N1	109.1(4)
C1–O1–Co1	111.6(4)	C41–C42–N4	104.6(4)

¹ #1: $2/3 + y - x$, $4/3 - x$, $1/3 + z$; #2: $1/3 + x$, $-1/3 + y$, $-1/3 + z$;
#3: $1 - y$, $1 + x - y$, $+ z$; #4: $1/3 + y - x$, $5/3 - x$, $-1/3 + z$;
#5: $+ y - x$, $1 - x$, $+ z$; #6: $4/3 - y$, $2/3 + x - y$, $-1/3 + z$;
#7: $-1/3 + x$, $1/3 + y$, $1/3 + z$; #8: $5/3 - x$, $4/3 + x - y$, $1/3 + z$;
#9: $1 + y - x$, $2 - x$, $+ z$; #10: $2 - y$, $1 + x - y$, $+ z$.

3.3. The crystal structure of compound **3**

Table S5: Selected bond lengths (Å) of compound **3**

bond	length (Å)	bond	length (Å)
C1–C2	1.478(10)	C29–C30	1.342(11)
C1–O1	1.231(8)	C29–N1	1.368(9)
C1–O2	1.290(8)	C30–N2	1.377(9)
C2–C3	1.399(9)	C31–C32	1.487(10)
C2–C7	1.384(9)	C31–N2	1.352(9)
C3–C4	1.369(10)	C31–N1	1.321(9)
C4–C5	1.387(10)	C35–C34	1.379(9)
C5–C6	1.410(10)	C35–C36	1.396(9)
C5–Si1	1.858(7)	C35–N4	1.441(8)
C6–C7	1.369(10)	C34–C33	1.384(9)
C8–C9	1.384(9)	C33–C38	1.380(9)
C8–C13	1.378(10)	C33–N2	1.422(9)
C8–Si1	1.874(7)	C38–C37	1.370(10)
C9–C10	1.391(10)	C37–C36	1.394(9)
C10–C11	1.382(10)	C37–N6	1.432(8)
C11–C12	1.381(10)	C40–C39	1.335(10)

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Table S5 – continued from previous page

bond	length (Å)	bond	length (Å)
C11–C14	1.499(10)	C40–N3	1.386(9)
C12–C13	1.387(10)	C39–N4	1.355(9)
C14–O3	1.278(9)	C41–C42	1.485(10)
C14–O4	1.242(9)	C41–N4	1.360(8)
C15–C16	1.389(10)	C41–N3	1.327(9)
C15–C20	1.358(10)	C43–C44	1.352(10)
C15–Si1	1.848(8)	C43–N6	1.325(9)
C16–C17	1.383(10)	C44–N5	1.368(9)
C17–C18	1.374(11)	C45–C46	1.502(10)
C18–C19	1.391(11)	C45–N5	1.327(9)
C18–C21	1.485(11)	C45–N6	1.373(9)
C19–C20	1.392(10)	Cu1–N1	1.963(6)
C21–O5	1.278(11)	Cu1–O2	1.948(5)
C21–O6	1.234(11)	Cu1–O3#1 ¹	1.940(5)
C22–C23	1.383(10)	Cu1–O9	1.963(5)
C22–C27	1.389(10)	Cu2–N5#1 ¹	1.963(6)
C22–Si1	1.859(7)	Cu2–N3#2 ¹	1.993(5)
C23–C24	1.382(11)	Cu2–O8	1.920(6)
C24–C25	1.376(11)	Cu2–O5#3 ¹	1.905(6)
C25–C26	1.373(11)	N5–Cu2#4 ¹	1.963(6)
C25–C28	1.488(11)	N3–Cu2#5 ¹	1.993(5)
C26–C27	1.379(10)	O3–Cu1#4 ¹	1.940(5)
C28–O7	1.235(11)	O5–Cu2#6 ¹	1.905(6)
C28–O8	1.262(10)		

¹ #1: $-1/2 + x, 3/2 - y, -1/2 + z$; #2: $1/2 + x, 3/2 - y, -1/2 + z$;
#3: $1/2 + x, 5/2 - y, -1/2 + z$; #4: $1/2 + x, 3/2 - y, 1/2 + z$;
#5: $-1/2 + x, 3/2 - y, 1/2 + z$; #6: $-1/2 + x, 5/2 - y, 1/2 + z$.

Table S6: Selected angles (°) of compound **3**

angle	(°)	angle	(°)
O1–C1–C2	122.7(7)	C35–C34–C33	120.0(6)
O1–C1–O2	122.5(7)	C34–C33–N2	122.2(6)

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Table S6 – continued from previous page

angle	(°)	angle	(°)
O2–C1–C2	114.7(7)	C38–C33–C34	120.3(7)
C3–C2–C1	119.5(7)	C38–C33–N2	117.5(6)
C7–C2–C1	121.8(7)	C37–C38–C33	119.6(7)
C7–C2–C3	118.7(7)	C38–C37–C36	121.2(6)
C4–C3–C2	119.6(7)	C38–C37–N6	121.1(6)
C3–C4–C5	122.8(7)	C36–C37–N6	117.7(6)
C4–C5–C6	116.8(6)	C37–C36–C35	118.5(7)
C4–C5–Si1	124.7(6)	C39–C40–N3	108.8(7)
C6–C5–Si1	118.4(5)	C40–C39–N4	107.4(7)
C7–C6–C5	120.9(7)	N4–C41–C42	126.7(7)
C6–C7–C2	121.2(7)	N3–C41–C42	124.4(6)
C9–C8–Si1	120.4(6)	N3–C41–N4	108.9(6)
C13–C8–C9	117.0(7)	N6–C43–C44	107.1(7)
C13–C8–Si1	122.7(6)	C43–C44–N5	108.7(7)
C8–C9–C10	121.9(7)	N5–C45–C46	125.9(7)
C11–C10–C9	119.7(7)	N5–C45–N6	107.8(6)
C10–C11–C14	120.4(7)	N6–C45–C46	126.2(7)
C12–C11–C10	119.2(7)	O2–Cu1–N1	91.3(2)
C12–C11–C14	120.4(7)	O2–Cu1–O9	166.5(2)
C11–C12–C13	119.9(7)	O3#1–Cu1–N1 ¹	169.9(2)
C8–C13–C12	122.1(7)	O3#1–Cu1–O2 ¹	91.1(2)
O3–C14–C11	116.1(7)	O3#1–Cu1–O9 ¹	88.9(2)
O4–C14–C11	121.1(7)	O9–Cu1–N1	91.0(3)
O4–C14–O3	122.8(7)	N5#1–Cu2–N3#2 ¹	168.4(3)
C16–C15–Si1	118.7(6)	O8–Cu2–N5#1 ¹	93.7(2)
C20–C15–C16	117.2(7)	O8–Cu2–N3#2 ¹	89.1(2)
C20–C15–Si1	123.0(6)	O5#3–Cu2–N5#1 ¹	88.0(3)
C17–C16–C15	121.9(8)	O5#3–Cu2–N3#2 ¹	89.7(2)
C18–C17–C16	119.2(8)	O5#3–Cu2–O8 ¹	176.9(3)
C17–C18–C19	119.6(7)	C44–N5–Cu2#4 ¹	124.7(5)
C17–C18–C21	119.8(9)	C45–N5–C44	107.3(6)
C19–C18–C21	120.0(9)	C45–N5–Cu2#4 ¹	127.8(5)
C18–C19–C20	118.9(8)	C43–N6–C37	125.6(6)
C15–C20–C19	122.2(8)	C43–N6–C45	109.0(6)
O5–C21–C18	115.8(10)	C45–N6–C37	125.4(6)

Continued on next page

Table S6 – continued from previous page

angle	(°)	angle	(°)
O6–C21–C18	119.3(10)	C39–N4–C35	125.1(6)
O6–C21–O5	124.8(9)	C39–N4–C41	108.2(6)
C23–C22–C27	116.2(7)	C41–N4–C35	126.7(6)
C23–C22–Si1	121.6(6)	C40–N3–Cu2#5 ¹	125.5(5)
C27–C22–Si1	121.5(6)	C41–N3–C40	106.7(6)
C24–C23–C22	121.3(7)	C41–N3–Cu2#5 ¹	127.8(5)
C25–C24–C23	121.3(8)	C30–N2–C33	124.0(6)
C24–C25–C28	120.5(8)	C31–N2–C30	108.4(6)
C26–C25–C24	118.5(7)	C31–N2–C33	126.2(6)
C26–C25–C28	121.0(8)	C29–N1–Cu1	124.1(6)
C25–C26–C27	119.8(8)	C31–N1–C29	106.8(6)
C26–C27–C22	122.9(7)	C31–N1–Cu1	128.6(5)
O7–C28–C25	120.2(9)	C1–O2–Cu1	105.4(5)
O7–C28–O8	124.9(9)	C14–O3–Cu1#4 ¹	104.0(5)
O8–C28–C25	114.8(9)	C28–O8–Cu2	128.8(6)
C30–C29–N1	110.3(7)	C21–O5–Cu2#6 ¹	117.5(6)
C29–C30–N2	105.3(7)	C5–Si1–C8	111.3(3)
N2–C31–C32	125.7(7)	C5–Si1–C22	112.1(3)
N1–C31–C32	125.1(7)	C15–Si1–C5	111.5(3)
N1–C31–N2	109.2(6)	C15–Si1–C8	104.5(3)
C34–C35–C36	120.2(6)	C15–Si1–C22	107.5(3)
C34–C35–N4	121.1(6)	C22–Si1–C8	109.6(3)
C36–C35–N4	118.6(6)		

¹ #1: $-1/2 + x, 3/2 - y, -1/2 + z$; #2: $1/2 + x, 3/2 - y, -1/2 + z$;
#3: $1/2 + x, 5/2 - y, -1/2 + z$; #4: $1/2 + x, 3/2 - y, 1/2 + z$;
#5: $-1/2 + x, 3/2 - y, 1/2 + z$; #6: $-1/2 + x, 5/2 - y, 1/2 + z$.

3.4. The crystal structure of compound **4**

Table S7: Selected bond lengths (Å) of compound **4**

bond	length (Å)	bond	length (Å)
Zn2–O2	1.994(3)	C44–C43	1.392(6)

Continued on next page

Table S7 – continued from previous page

bond	length (Å)	bond	length (Å)
Zn2–O3#1 ¹	1.930(3)	C45–C46	1.374(6)
Zn2–N5#2 ¹	2.021(4)	C2–C7	1.379(6)
Zn2–O6#3 ¹	1.902(4)	C43–C42	1.369(6)
Zn1–O1	1.987(3)	C34–N3	1.317(5)
Zn1–N1	2.015(4)	C34–C33	1.467(6)
Zn1–O8#4 ¹	2.012(3)	C17–C16	1.392(7)
Zn1–N3#5 ¹	2.023(4)	C41–C46	1.394(6)
Si1–C26	1.871(4)	C41–C42	1.379(6)
Si1–C5	1.860(5)	C23–C24	1.391(6)
Si1–C19	1.864(5)	C23–C28	1.363(7)
Si1–C12	1.863(4)	C23–C22	1.488(7)
O2–C1	1.242(5)	C6–C7	1.400(6)
O1–C1	1.271(5)	C20–C21	1.377(7)
N1–C32	1.370(6)	C16–C21	1.379(7)
N1–C30	1.320(6)	C16–C15	1.510(8)
C18–C19	1.377(6)	C24–C25	1.396(7)
C18–C17	1.384(7)	C28–C27	1.378(6)
C1–C2	1.488(6)	C40–C39	1.307(7)
N4–C45	1.441(5)	C40–N5	1.397(6)
N4–C34	1.355(5)	C35–C36	1.318(7)
N4–C35	1.394(6)	O8–Zn1#6 ¹	2.012(3)
C26–C25	1.384(6)	O8–C22	1.256(6)
C26–C27	1.396(6)	O3–Zn2#2 ¹	1.930(3)
C5–C6	1.382(6)	O3–C8	1.270(6)
C5–C4	1.401(7)	N3–Zn1#5 ¹	2.023(4)
N6–C38	1.348(6)	N3–C36	1.385(6)
N6–C41	1.428(6)	N5–Zn2#1 ¹	2.021(4)
N6–C39	1.402(6)	C12–C11	1.398(6)
C19–C20	1.423(6)	C12–C13	1.381(6)
C31–N2	1.390(6)	O6–Zn2#7 ¹	1.902(4)
C31–C32	1.340(6)	O6–C15	1.267(7)
N2–C30	1.359(5)	O5–C15	1.220(7)
N2–C43	1.421(5)	O4–C8	1.231(6)
C30–C29	1.500(7)	C11–C10	1.371(7)
C3–C2	1.386(6)	C8–C9	1.520(7)

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Table S7 – continued from previous page

bond	length (Å)	bond	length (Å)
C3–C4	1.385(7)	C9–C10	1.378(7)
C38–N5	1.316(6)	C9–C14	1.358(7)
C38–C37	1.488(7)	C22–O7	1.225(6)
C44–C45	1.381(6)	C13–C14	1.393(7)

¹ #1: 1 – x, –1/2 + y, 1/2 – z; #2: 1 – x, 1/2 + y, 1/2 – z;
#3: –1 + x, + y, + z; #4: 1 – x, –1/2 + y, –1/2 – z;
#5: – x, 1 – y, – z; #6: 1 – x, 1/2 + y, –1/2 – z;
#7: 1 + x, + y, + z.

Table S8: Selected angles (°) of compound 4

angle	(°)	angle	(°)
O2–Zn2–N5#1 ¹	108.93(14)	C7–C2–C3	118.1(4)
O3#2–Zn2–O2 ¹	110.19(14)	C44–C43–N2	120.6(4)
O3#2–Zn2–N5#1 ¹	93.85(15)	C42–C43–N2	118.1(4)
O6#3–Zn2–O2 ¹	113.28(16)	C42–C43–C44	121.2(4)
O6#3–Zn2–O3#2 ¹	108.39(17)	N4–C34–C33	123.7(4)
O6#3–Zn2–N5#1 ¹	120.29(17)	N3–C34–N4	109.8(4)
O1–Zn1–N1	111.34(14)	N3–C34–C33	125.9(4)
O1–Zn1–O8#4 ¹	95.99(13)	C18–C17–C16	120.0(5)
O1–Zn1–N3#5 ¹	106.97(15)	C46–C41–N6	118.0(4)
N1–Zn1–N3#5 ¹	116.49(15)	C42–C41–N6	120.2(4)
O8#4–Zn1–N1 ¹	124.21(14)	C42–C41–C46	121.8(4)
O8#4–Zn1–N3#5 ¹	98.97(14)	C24–C23–C22	122.9(5)
C5–Si1–C26	108.20(19)	C28–C23–C24	118.4(4)
C5–Si1–C19	108.7(2)	C28–C23–C22	118.7(5)
C5–Si1–C12	109.42(19)	C5–C6–C7	121.9(4)
C19–Si1–C26	106.37(19)	C45–C46–C41	117.0(4)
C12–Si1–C26	115.1(2)	C21–C20–C19	122.4(5)
C12–Si1–C19	108.9(2)	C2–C7–C6	120.9(4)
C1–O2–Zn2	149.3(3)	C17–C16–C15	120.3(5)
C1–O1–Zn1	121.7(3)	C21–C16–C17	119.2(5)
C32–N1–Zn1	123.2(3)	C21–C16–C15	120.5(5)

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Table S8 – continued from previous page

angle	(°)	angle	(°)
C30–N1–Zn1	129.9(3)	C23–C24–C25	120.3(5)
C30–N1–C32	106.7(4)	C26–C25–C24	122.0(4)
C19–C18–C17	122.8(5)	C23–C28–C27	121.0(5)
O2–C1–O1	121.9(4)	C39–C40–N5	109.9(4)
O2–C1–C2	121.2(4)	C43–C42–C41	118.9(4)
O1–C1–C2	116.8(4)	C3–C4–C5	122.3(5)
C34–N4–C45	127.3(4)	C40–C39–N6	106.8(4)
C34–N4–C35	107.4(4)	C20–C21–C16	119.9(5)
C35–N4–C45	125.1(4)	C36–C35–N4	106.1(4)
C25–C26–Si1	125.1(3)	C28–C27–C26	122.5(5)
C25–C26–C27	115.9(4)	C22–O8–Zn1#6 ¹	105.4(3)
C27–C26–Si1	118.6(3)	C8–O3–Zn2#1 ¹	126.0(3)
C6–C5–Si1	123.2(3)	C34–N3–Zn1#5 ¹	129.3(3)
C6–C5–C4	116.2(4)	C34–N3–C36	106.4(4)
C4–C5–Si1	120.2(3)	C36–N3–Zn1#5 ¹	121.6(3)
C38–N6–C41	127.5(4)	C38–N5–Zn2#2 ¹	132.9(3)
C38–N6–C39	106.7(4)	C38–N5–C40	106.1(4)
C39–N6–C41	125.7(4)	C40–N5–Zn2#2 ¹	120.2(3)
C18–C19–Si1	124.0(4)	C11–C12–Si1	122.0(3)
C18–C19–C20	115.7(4)	C13–C12–Si1	122.7(4)
C20–C19–Si1	120.3(3)	C13–C12–C11	115.2(4)
C32–C31–N2	106.7(4)	C15–O6–Zn2#7 ¹	117.8(4)
C31–N2–C43	123.7(4)	C10–C11–C12	122.6(4)
C30–N2–C31	106.4(4)	O3–C8–C9	114.1(5)
C30–N2–C43	129.9(4)	O4–C8–O3	127.2(5)
C31–C32–N1	109.7(4)	O4–C8–C9	118.7(5)
N1–C30–N2	110.5(4)	C10–C9–C8	119.9(5)
N1–C30–C29	126.5(4)	C14–C9–C8	122.2(5)
N2–C30–C29	122.9(4)	C14–C9–C10	117.8(4)
C4–C3–C2	120.6(4)	O6–C15–C16	114.9(5)
N6–C38–C37	124.5(4)	O5–C15–C16	119.5(6)
N5–C38–N6	110.5(4)	O5–C15–O6	125.5(6)
N5–C38–C37	124.9(4)	C11–C10–C9	120.9(5)
C45–C44–C43	117.8(4)	C35–C36–N3	110.3(4)
C44–C45–N4	118.5(4)	O8–C22–C23	120.2(5)

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Table S8 – continued from previous page

angle	(°)	angle	(°)
C46–C45–N4	118.6(4)	O7–C22–C23	118.4(5)
C46–C45–C44	122.8(4)	O7–C22–O8	121.2(5)
C3–C2–C1	120.5(4)	C12–C13–C14	122.0(5)
C7–C2–C1	121.4(4)	C9–C14–C13	121.4(5)

¹ #1: $1 - x, 1/2 + y, 1/2 - z$; #2: $1 - x, -1/2 + y, 1/2 - z$;
#3: $-1 + x, + y, + z$; #4: $1 - x, -1/2 + y, -1/2 - z$;
#5: $-x, 1 - y, -z$; #6: $1 - x, 1/2 + y, -1/2 - z$;
#7: $1 + x, + y, + z$.

4. Characterization of the CPs and their thermal derivation composites

The PXRD patterns of compound **3**, compound **4**, Ni-700, Ni-800, Ni-900, Co-700, Co-800 and Co-900 were shown in Fig. S3.

The FT-IR and Raman spectra of compounds **1**, **2**, **3** and **4** (Figs. S4 and S5(a)) exhibited related features with the bands at 1700–1300 cm^{-1} ascribed to the asymmetric and symmetric carboxyl groups in H_4tcps ligand, and the stretching vibrations of $\nu_{\text{as}}(\text{C}=\text{C})$ and $\nu_{\text{as}}(\text{C}=\text{N})$ in tmib ligand. Vibrational absorption of $\text{C}=\text{N}$ in tmib ligand appeared near 730 cm^{-1} . The broad absorption peaks near 3400 cm^{-1} should be attributed to the vibration of $\nu(\text{OH})$ of water molecules. In the Raman spectra of the compounds **1**, **2** and **3**, the bands at 862 and 626 cm^{-1} were assigned to the C–H stretching region, and the two peaks at 1601 and 1404 cm^{-1} corresponded to the in- and out-of-phase stretching region of the carboxylate group, respectively.

TGA curves of compounds **1**, **2**, **3** and **4** (Fig. S6) showed that the first step of weight loss occurred at about 100 °C, which can be attributed to the loss of lattice water molecules. Further loss weight of the compounds in the range of 130 – 300 °C corresponded to the evaporation of coordination water molecules. The weight losses after 300 °C, were mainly due to the collapse of the coordination skeleton and the decomposition of the organic ligands.

The morphologies of compounds **1** and **2** were characterized by SEM as depicted in Figs. S7 and S8. The irregular crystals of compounds **1** and **2** presented mulit-layer morphology.

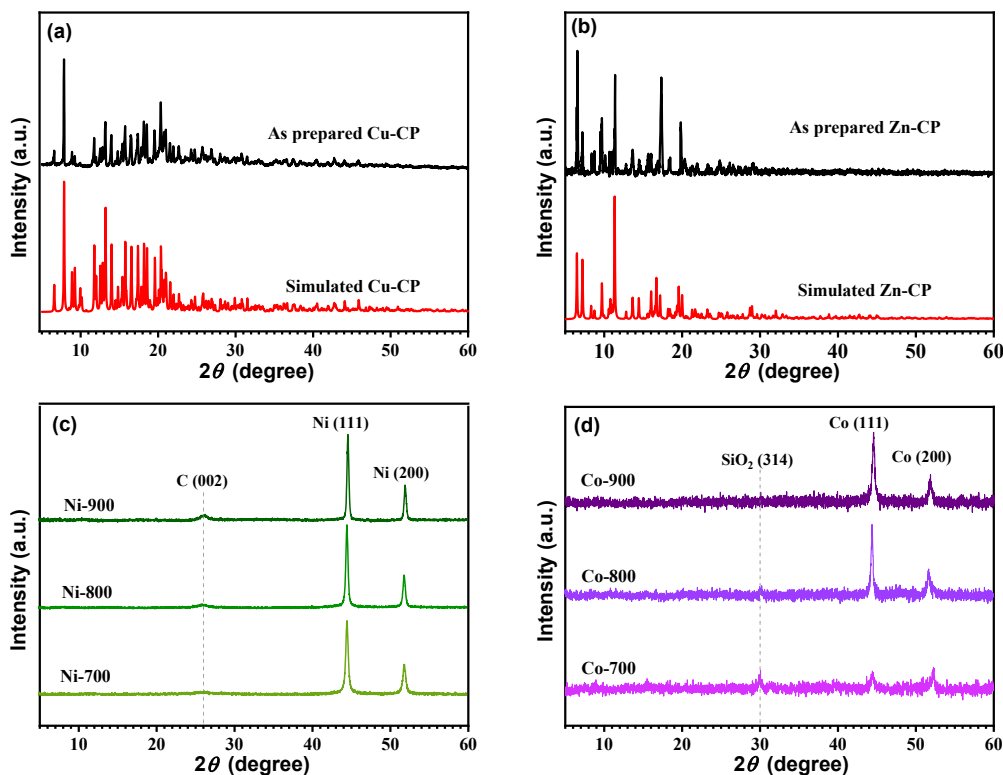


Figure S3: Powder X-ray diffraction patterns of (a) compound **3**, (b) compound **4**, (c) Ni-700, Ni-800 and Ni-900, and (d) Co-700, Co-800 and Co-900.

The domination of the amorphous carbon in Ni-700/800/900 and Co-700/800/900 can be confirmed by comparing the intensities of the D-band peak at 1318 cm^{-1} and the G-band peak at 1596 cm^{-1} from the graphitic carbon in the Raman spectra (Fig. S5(b)(c)). The intensity ratios of D-band and G-band (I_D/I_G) corresponded to the graphitization degree of carbon-based materials. The I_D/I_G of Ni-700/800/900 varied from 1.20 to 1.26, and the I_D/I_G of Co-700/800/900 increased from 1.35 to 1.48, which indicated that high carbonization temperature tended to expedite a large degree of graphitization [15].

XPS measurements were implemented to determine the chemical identity and detailed chemical and electronic states of Ni 2p, C 1s, N 1s, O 1s and Si 2p species in the as-prepared Ni-CP and Ni-700. The XPS survey spectrum of Ni-CP (Fig. S9(a)) displayed five peaks, which were ascribed to C 1s, N 1s, O 1s, Si 2p and Ni 2p, respectively. The Ni 2p spectrum of Ni-CP

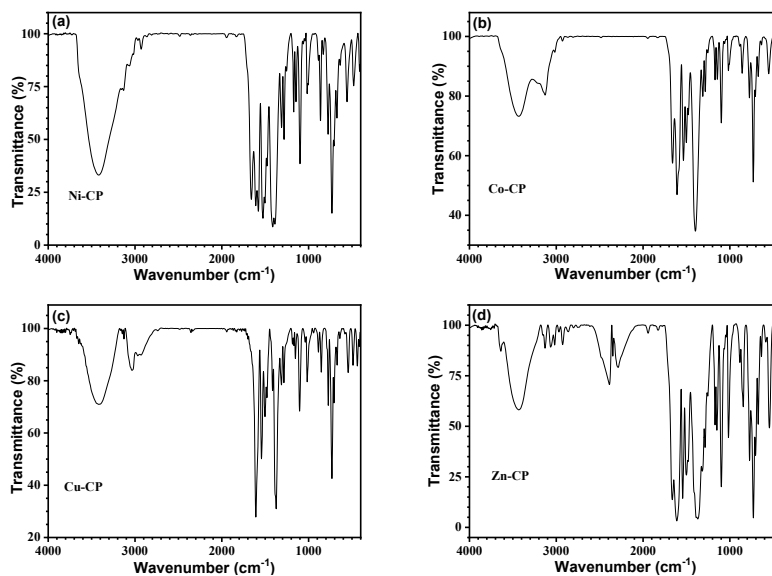


Figure S4: FT-IR spectra of compounds (a) **1**, (b) **2**, (c) **3** and (d) **4**.

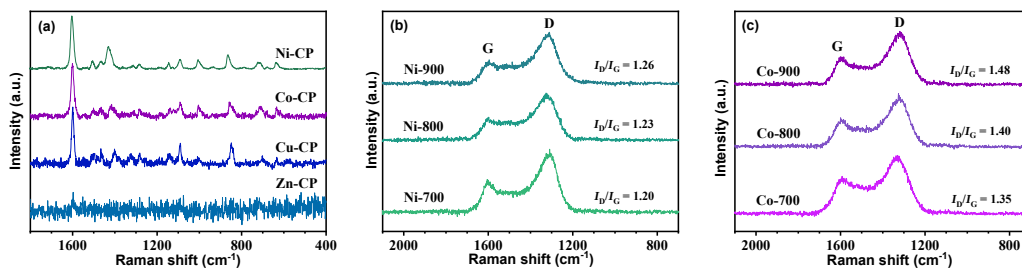


Figure S5: Raman spectra of (a) compounds **1**, **2**, **3** and **4**, (b) Ni-700, Ni-800 and Ni-900, (c) Co-700, Co-800 and Co-900.

(Fig. S9(b)) can be divided into two spin-orbit doublets. The signal peaks at 855.6/856.9 eV of Ni 2p_{3/2} and 873.2/874.7 eV of Ni 2p_{1/2} were assigned to Ni1 and Ni2 of Ni-CP, with their satellite peaks (identified as “Sat.”). The O 1s spectrum (Fig. S9(c)) of both physisorbed H₂O (532.3 eV) and carboxylate groups (531.3 eV) existed on the surface of Ni-CP [16]. Fig. S9(d) displayed the C 1s spectrum, which can be deconvoluted into three surface carbon components at around 284.8 eV (non-oxygenated carbon C–C/C=C), 285.7 eV (C–N/C=N), and 287.2 eV (carboxyl carbon O=C–O) [17]. The three peaks at 398.9, 399.6 and 401.3 eV in the N 1s spectrum (Fig. S9(e)) can be assigned to N–Ni2, N–Ni1 and N–benzene, respectively, on the

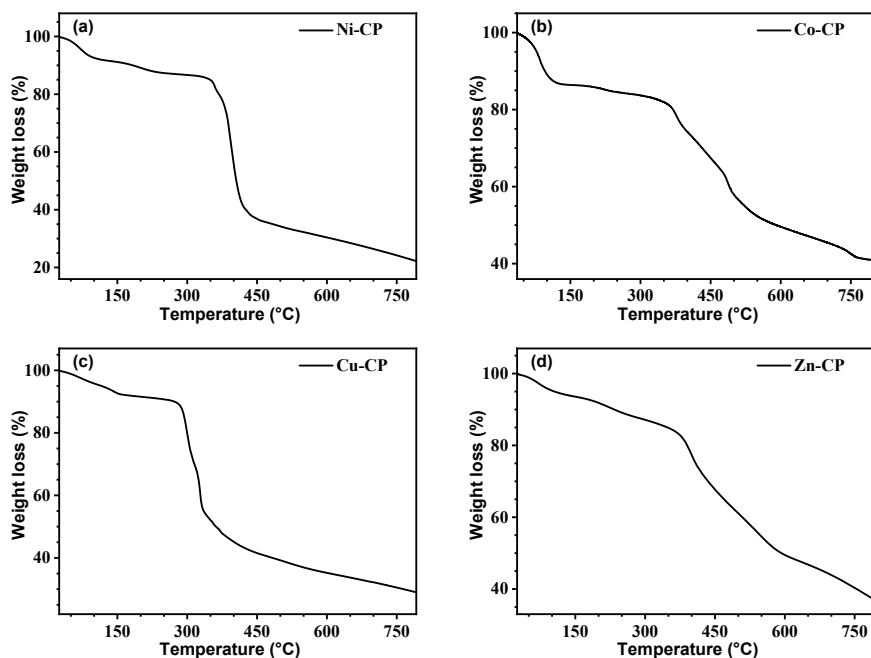


Figure S6: TG curves of compounds (a) **1**, (b) **2**, (c) **3** and (d) **4**.

basis of the relative ratio. The Si 2p spectrum (Fig. S9(f)) at the binding energies of 100.6 and 101.2 eV represented Si–C [18]. The binding energies of 852.9/855.2/856.9 eV of Ni 2p_{3/2} and 871.2/873.1/873.1 eV of Ni 2p_{1/2} were assigned to Ni⁰ (nickel metal), NiO_x and NiN_y [19], in the Ni 2p spectrum of Ni-700 (Fig. S9(b)). The amorphous NiO_x and NiN_y were not found in the PXRD pattern of Ni-700, in virtue of PXRD only can characterize crystalline materials (e.g. crystalline Ni). Amorphous structures and particles with crystalline size below 2 nm do not produce discernible diffraction patterns in conventional PXRD [20]. The O 1s spectrum of Ni-700 (Fig. S9(c)) can be deconvoluted into three peaks, corresponding to oxycarbide O=C–O (533.9 eV) [21], and the one at 532.1 eV attributed to the adsorbed H₂O molecules, as well as the one in NiO_x (530.4 eV) [22], respectively. The N 1s spectrum of Ni-700 revealed the presence of four types for the nitrogen species (Fig. S9(e)), pyridinic–N at 398.2 eV, NiN_y at 399.1 eV, pyrrolic–N at 400.7 eV and graphitic–N at 401.6 eV [23].

A full XPS spectrum of Co-CP was shown in Fig. S10(a), unambiguously indicating the existence of C, N, O, Si and Co elements. The two core-level signals of Co-CP located at 781.3/783.4 eV of Co 2p_{3/2} and 796.9/798.0 eV

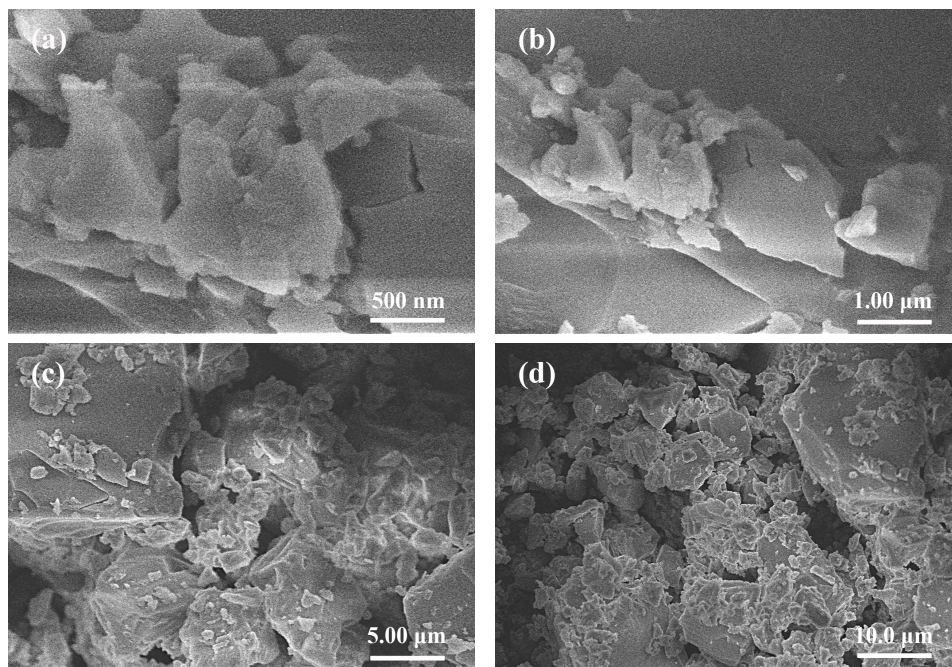


Figure S7: SEM images of compound 1.

of Co 2p_{1/2} (Fig. S10(b)) were attributed to Co⁰ and Co²⁺, which was further confirmed by the Co 2p satellite peaks. Both the physisorption H₂O (532.7 eV) and the carboxylate group (531.5 eV) existed on the surface of Co-CP as proved in O 1s spectrum (Fig. S10(c)) [16]. The C 1s and N 1s spectra of Co-CP shown in Fig. S10(d) and (e). For Co-800 (Fig. S10(b)), the binding energies at 778.9/781.2/783.0 eV of Co 2p_{3/2} and 795.6/796.9/798.2 eV of Co 2p_{1/2} corresponded to Co⁰, CoO_x and CoN_y, along with their shake-up satellites [16, 23, 24]. There were crystalline Co metal, but the amorphous CoO_x and CoN_y were not found in the PXRD pattern of Co-800. The O 1s spectrum of Co-800 (Fig. S10(c)) could be fitted by three components, corresponding to oxygen atoms of oxycarbide O=C-O (533.7 eV) [21], the absorbed water (532.5 eV), and the peak at 529.8 eV due to CoO_x. The N 1s spectrum of Co-800 (Fig. S10(e)) exhibited four types of the nitrogen species, pyridinic-N (398.1 eV), CoN_y (399.2 eV), pyrrolic-N (401.0 eV) and graphitic-N (401.8 eV) [23].

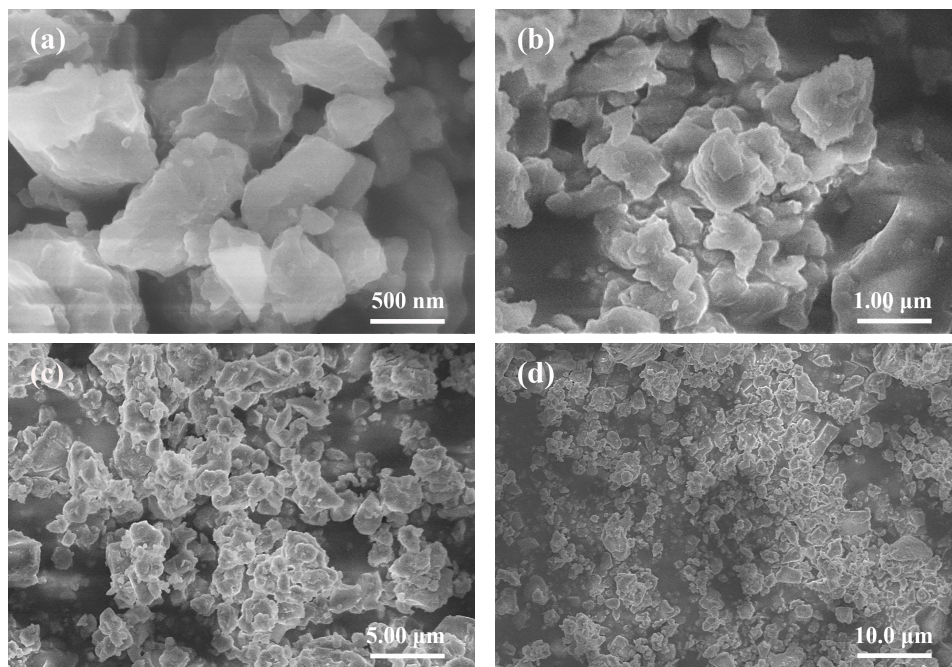


Figure S8: SEM images of compound **2**.

5. Electrochemical properties of the Ni and Co materials

5.1. Preparation of working electrodes

The modified graphite electrodes were used as the working electrodes. The working electrodes were prepared according to the following process. After being polished with 0.3 and 0.05 μm Al_2O_3 particles, the graphite substrate electrode (1 cm $\times$ 1 cm $\times$ 0.5 cm) was cleaned with ultrapure H_2O . $m_{\text{CP}}: m_{\text{PVDF}}: m_{\text{carbonblack}} = 7: 1.5: 1.5$ (where m_{CP} , m_{PVDF} , $m_{\text{carbonblack}}$ denoting the mass ratio of CP or its thermal derivations, the mass ratio of polyvinylidene fluoride (PVDF), and the mass ratio of carbon black, respectively), were mixed in 1 mL *N*-methyl-2-pyrrolidone (NMP), and the ink-like slurry was obtained. The obtained slurry was homogenized by ultrasonication, and 100 μL of the slurry was dropped onto the graphite electrode to form thin film on the electrodes, and then dried under an infrared lamp. The other surfaces of the graphite electrodes were covered by polytetrafluoroethylene (PTFE) thin film (the photograph of the working electrode was depicted in Fig. S11), and the surface area of the electrode, $A = 1 \text{ cm}^2$. All of the working electrodes were kept in a desiccator before electrochemical

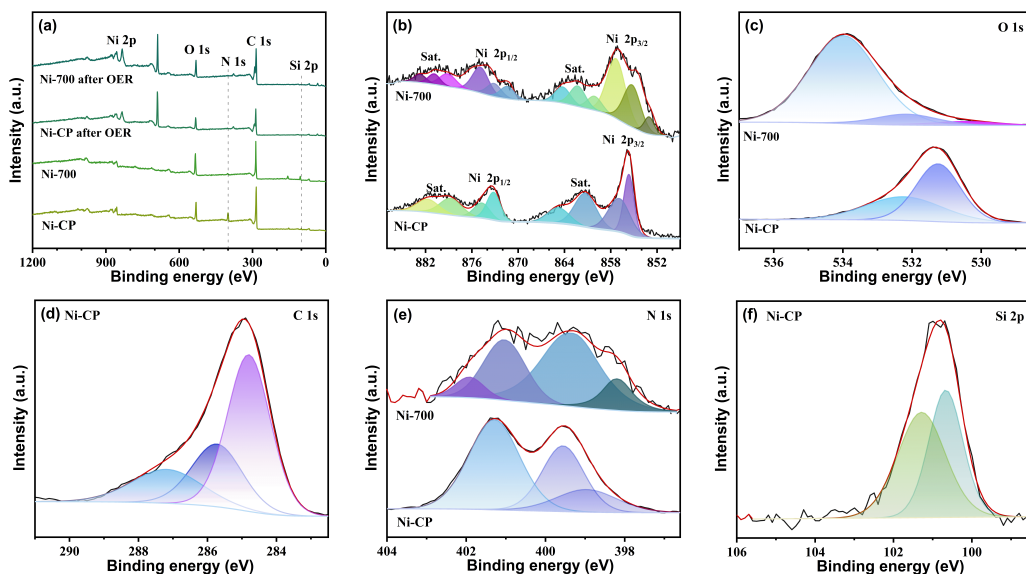


Figure S9: (a) XPS spectra of Ni-CP, Ni-700 before and after OER. (b) Ni 2p XPS spectra of Ni-CP and Ni-700. (c) O 1s XPS spectra of Ni-CP and Ni-700. (d) C 1s XPS spectrum of Ni-CP. (e) N 1s XPS spectrum of Ni-CP and Ni-700. (f) Si 2p XPS spectrum of Ni-CP.

measurements.

5.2. Electrochemical measurements

The electrochemical measurements were carried out using an electrochemical workstation (CHI 660E, CH Instruments) using the conventional three-electrode system. A saturated calomel electrode (SCE) and a platinum wire electrode were used as the reference electrode and the counter electrode, respectively. The electrochemical measurements were recorded in 1 M KOH solution, which was bubbled with high purity nitrogen gas for at least 30 min before the electrochemical tests. All potentials in this study referred to the reversible hydrogen electrode (RHE), $E_{\text{RHE}} = E_{\text{SCE}} + 0.059 \text{ pH} + 0.2415 \text{ V}$. The electrodes were activated by the cyclic voltammetry (CV) at least 20 – 40 cycles with a potential cycling window ranging from -0.1 to 0.8 V (*vs.* SCE) and a sweep speed of 10 mV s^{-1} , until a stable cyclic voltammogram was reached. The CV experiments at different scan rates ($10, 20, 30, 40, 50, 60, 70, 80, 90$ and 100 mV s^{-1}), and the linear scanning voltammetry (LSV) were recorded with the potential windows of -0.1 to 0.8 V (*vs.* SCE) and the sweep speed of 5 mV s^{-1} . The electrochemical impedance spectroscopy

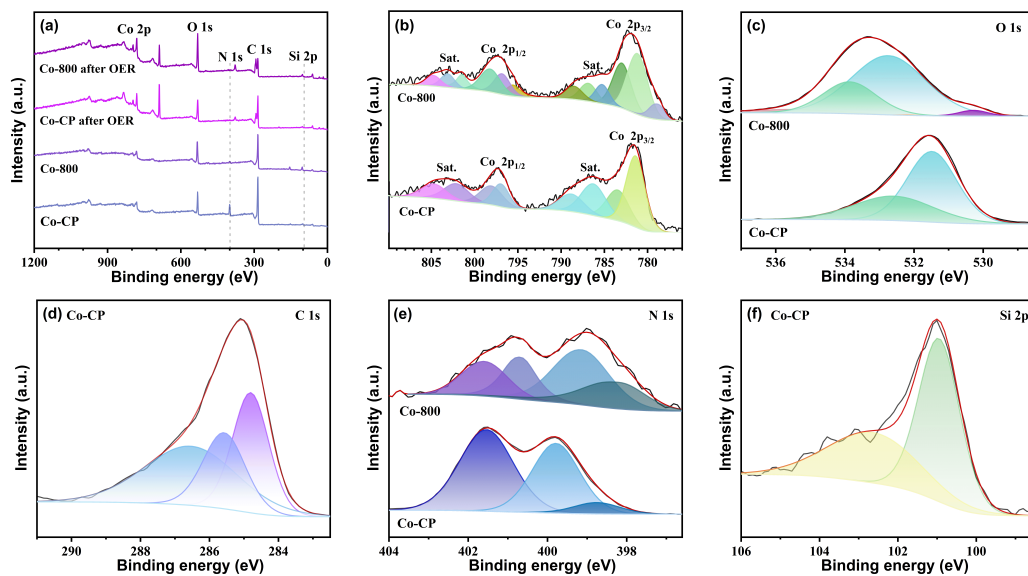


Figure S10: (a) XPS spectra of Co-CP, Co-800 before and after OER. (b) Co 2p XPS spectra of Co-CP and Co-800. (c) O 1s XPS spectra of Co-CP and Co-800. (d) C 1s XPS spectrum of Co-CP. (e) N 1s XPS spectrum of Co-CP and Co-800. (f) Si 2p XPS spectrum of Co-CP.



Figure S11: Photograph of the working electrode.

(EIS) were performed with the frequencies of 10^5 to 10^{-2} Hz and an amplitude of 5 mV. The chronoamperometric ($i-t$) experiments were applied with a potential at a current density of 10 mA cm^{-2} continuously for 12 hours.

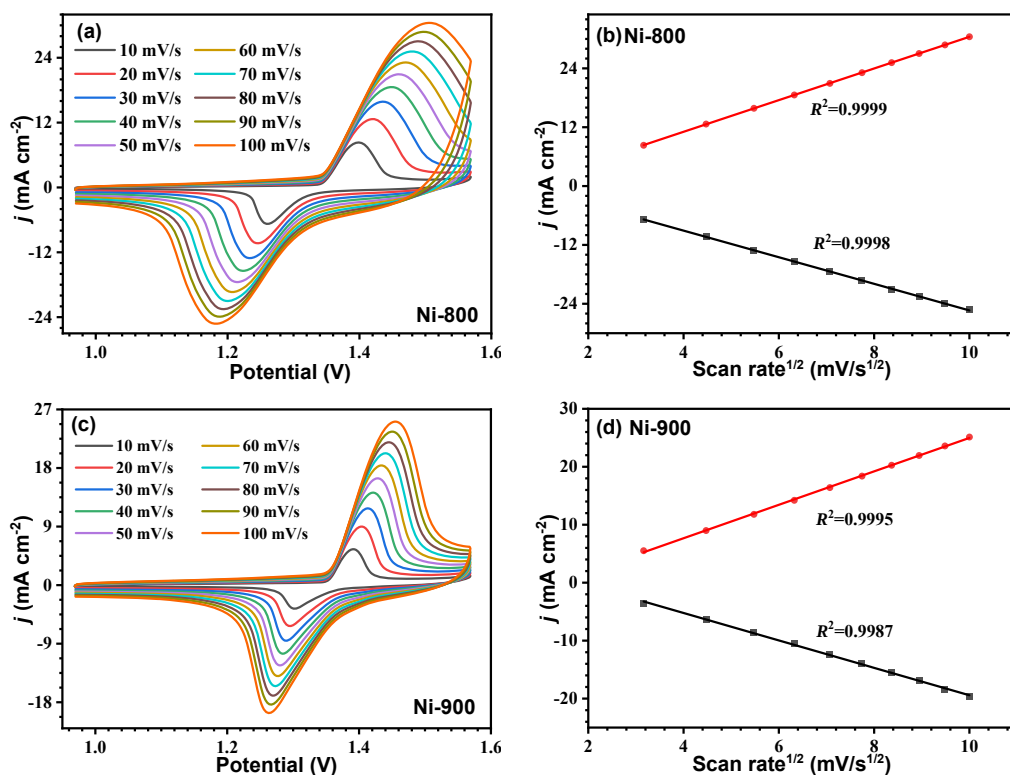


Figure S12: CV curves of (a) Ni-800 and (c) Ni-900 at different scan rates (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mV s⁻¹) with -0.1 to 0.5 V (*vs.* SCE). The linear relationship between the anode (red) and cathode (black) CV current densities with different half of the square of the scan rates of (b) Ni-800 and (d) Ni-900.

Table S9: $E_{1/2}$ and ΔE_p data of the Ni materials

Sample	Scan rate (mV s ⁻¹)	E_{pc} (V)	E_{pa} (V)	$E_{1/2}$ (V)	ΔE_p (mV)
Ni-CP	10	1.3079	1.3889	1.3484	81
	20	1.3049	1.4019	1.3534	97
	30	1.3029	1.4099	1.3564	107
	40	1.3099	1.4169	1.3589	116
	50	1.2999	1.4229	1.3614	123
	60	1.2989	1.4289	1.3639	130
	70	1.2969	1.4359	1.3664	139

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Table S9 – continued from previous page

Sample	Scan rate	E_{pc}	E_{pa}	$E_{1/2}$	ΔE_p
	(mV s ⁻¹)	(V)	(V)	(V)	(mV)
	80	1.2959	1.4409	1.3684	145
	90	1.2949	1.4469	1.3709	152
	100	1.2939	1.4519	1.3729	158
Ni-700	10	1.2559	1.4059	1.3309	150
	20	1.2389	1.4319	1.3354	193
	30	1.2269	1.4499	1.3384	223
	40	1.2169	1.4659	1.3414	249
	50	1.2079	1.4799	1.3439	272
	60	1.2009	1.4919	1.3464	291
	70	1.1939	1.5049	1.3494	311
	80	1.1869	1.5139	1.3504	327
	90	1.1819	1.5239	1.3529	342
	100	1.1759	1.5339	1.3549	358
Ni-800	10	1.2609	1.3989	1.3299	138
	20	1.2449	1.4199	1.3324	175
	30	1.2329	1.4349	1.3339	202
	40	1.2229	1.4479	1.3354	225
	50	1.2139	1.4589	1.3364	245
	60	1.2059	1.4699	1.3379	264
	70	1.1989	1.4789	1.3389	280
	80	1.1929	1.4869	1.3399	294
	90	1.1879	1.4969	1.3424	309
	100	1.1819	1.5049	1.3434	323
Ni-900	10	1.3019	1.3909	1.3464	89
	20	1.2949	1.4039	1.3494	109
	30	1.2899	1.4129	1.3514	123
	40	1.2839	1.4209	1.3524	137
	50	1.2799	1.4269	1.3534	147
	60	1.2759	1.4329	1.3544	157
	70	1.2729	1.4389	1.3559	166
	80	1.2699	1.4449	1.3574	175
	90	1.2659	1.4499	1.3579	184
	100	1.2629	1.4549	1.3589	192

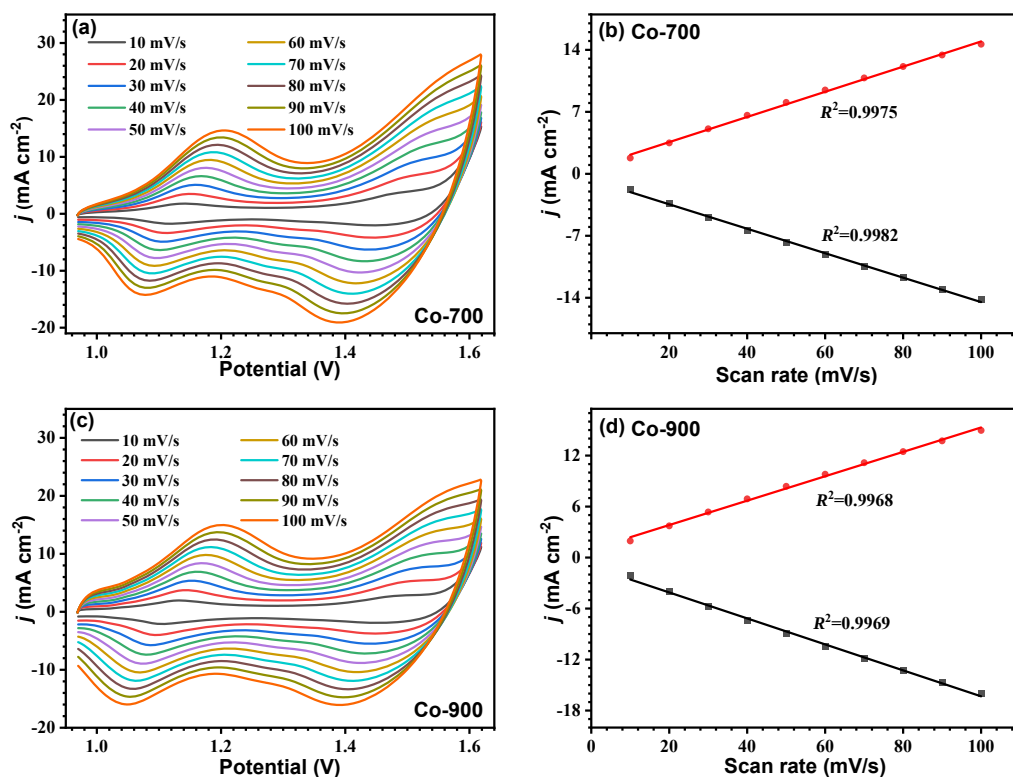


Figure S13: CV curves of (a) Co-700 and (c) Co-900 at different scan rates (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mV s^{-1}) with -0.1 to 0.55 V (*vs.* SCE). The linear relationship between the anode (red) and cathode (black) CV current densities with different scan rates of (b) Co-700 and (d) Co-900.

Table S10: $E_{1/2}$ and ΔE_p data of the Co materials

Sample	Scan rate (mV s^{-1})	E_{pc} (V)	E_{pa} (V)	$E_{1/2}$ (V)	ΔE_p (mV)
Co-CP	10	1.1129	1.1289	1.1209	16
	20	1.1079	1.1449	1.1264	37
	30	1.1079	1.1529	1.1304	45
	40	1.1079	1.1579	1.1329	50
	50	1.1079	1.1649	1.1364	57
	60	1.1079	1.1689	1.1384	61
	70	1.1079	1.1719	1.1399	64

Continued on next page

Table S10 – continued from previous page

Sample	Scan rate	E_{pc}	E_{pa}	$E_{1/2}$	ΔE_p
	(mV s ⁻¹)	(V)	(V)	(V)	(mV)
	80	1.1049	1.1769	1.1409	72
	90	1.1049	1.1799	1.1424	75
	100	1.1039	1.1849	1.1444	81
Co-700	10	1.1179	1.1399	1.1289	22
	20	1.1109	1.1509	1.1309	40
	30	1.1059	1.1599	1.1329	54
	40	1.1009	1.1669	1.1339	66
	50	1.0959	1.1739	1.1349	78
	60	1.0919	1.1819	1.1369	90
	70	1.0869	1.1869	1.1369	100
	80	1.0849	1.1929	1.1389	108
	90	1.0809	1.1979	1.1394	117
	100	1.0779	1.2029	1.1404	125
Co-800	10	1.1159	1.1529	1.1344	37
	20	1.1059	1.1739	1.1399	68
	30	1.0979	1.1899	1.1439	92
	40	1.0889	1.2019	1.1454	113
	50	1.0819	1.2139	1.1479	132
	60	1.0769	1.2249	1.1509	148
	70	1.0719	1.2349	1.1534	163
	80	1.0659	1.2439	1.1549	178
	90	1.0619	1.2539	1.1579	192
	100	1.0579	1.2619	1.1599	204
Co-900	10	1.1049	1.1319	1.1184	27
	20	1.0949	1.1429	1.1189	48
	30	1.0869	1.1529	1.1199	66
	40	1.0799	1.1609	1.1204	81
	50	1.0739	1.1689	1.1214	95
	60	1.0669	1.1769	1.1219	110
	70	1.0619	1.1799	1.1209	118
	80	1.0579	1.1869	1.1224	129
	90	1.0519	1.1939	1.1229	142
	100	1.0479	1.1989	1.1234	151

Table S11: Comparison of overpotentials of the thermal derivation composites with other studies

Catalyst	Electrolyte	j (mA cm ⁻²)	Overpotential (mV)	Ref.
Co-800	1 M KOH	10	338	this work
CoP/rGO-400	1 M KOH	10	340	[25]
Co@N-CNTF	1 M KOH	10	350	[26]
CoSe ₂ /CFC	1 M KOH	10	356	[27]
Fe ₂ O ₃ @Ni-450	1 M KOH	10	370	[28]
rGO/Co ₂ P-800	1 M KOH	10	378	[29]
Ni-700	1 M KOH	10	388	this work
MoS ₂ /Co-N-CN ₂	1 M KOH	10	398	[30]
Fe ₃ C@C/CNT	1 M KOH	10	407	[31]
UTSA-16	1 M KOH	10	408	[32]
FeP/Fe ₃ C@NPC	1 M KOH	10	440	[33]

Table S12: Atomic ratios of surface species determined by the XPS survey spectra and the relative ratios

Sample	O (at.%)	N (at.%)	Si (at.%)	M ^a (at.%)	N/M ^a	N/O
Ni-CP	9.34	7.36	4.26	2.05	3.59	0.79
Ni-700	14.89	1.73	21.68	1.42	1.22	0.12
Ni-CP after OER	9.86	0.57	1.33	1.15	0.49	0.06
Ni-700 after OER	8.97	0.51	2.79	2.57	0.20	0.06
Co-CP	9.01	7.35	5.88	1.47	5.00	0.82
Co-800	12.87	2.24	20.43	1.64	1.37	0.17
Co-CP after OER	12.62	0.42	5.50	2.69	0.16	0.03
Co-800 after OER	18.02	0.47	11.95	4.06	0.12	0.03

^a M = Ni or Co.

Table S13: XPS binding energies for samples. All peaks were referenced to C 1s at 284.8 eV.

Sample	M ^a 2p _{3/2} (eV)	M ^a 2p _{1/2} (eV)	O 1s (eV)
Ni-CP	855.6/856.9	873.2/874.7	531.3/532.3
Ni-700	852.9/855.2/856.9	871.2/873.1/875.0	530.4/532.1/533.9
Ni-CP after OER	852.7/855.6/858.7	872.5/873.8/876.4	531.6/532.3/533.7
Ni-700 after OER			
Co-CP	781.3/783.4	796.9/798.0	531.5/532.7
Co-800	778.9/781.2/783.0	795.6/796.9/798.2	529.8/532.5/533.7
Co-CP after OER	780.2/781.2	795.3/796.7	529.6/531.2/532.2
Co-800 after OER			

^a M = Ni or Co.

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