Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Hydrated Metal Ions as Weak Bronsted Acids Show the Promoting Effects in Proton Conduction

Xia-Lu Huang,[a] Yi-Qing Chen,[a] Ge-Hua Wen,[a] Song-Song Bao,[*a] and Li-Min Zheng[a]

[a]State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China

Contents

Table S1. Crystallographic data for **1·2H$_2$O, 1·3H$_2$O,** and **1·5H$_2$O**. 5
Table S2. Selected bond lengths (Å) for **1·2H$_2$O** and **1·3H$_2$O**. 6
Table S3. Selected bond angles (°) for **1·2H$_2$O** and **1·3H$_2$O**. 7
Table S4. Selected bond lengths (Å) and angles (°) for **1·5H$_2$O**. 8
Table S5. Selected bond lengths (Å) and angles (°) for **2**. 10
Table S6. Selected bond lengths (Å) and angles (°) for **3**. 11
Table S7. Selected bond lengths (Å) and angles (°) for **4**. 12
Table S8. Hydrogen bonds present in compound **1·2H$_2$O**. 13
Table S9. Hydrogen bonds present in compound **1·3H$_2$O**. 14
Table S10. Hydrogen bonds present in compound **1·5H$_2$O**. 15
Table S11. Hydrogen bonds present in compound **2**. 16
Table S12. Hydrogen bonds present in compound **3**. 17
Table S13. Hydrogen bonds present in compound **4**. 18

Figure S1. (a) The PXRD patterns for pure products of **1**, **2**, **3**, and **4**. (b) The PXRD patterns for the products with different starting reactants ratios after 24h reactions at 110 °C. (c) The PXRD patterns for the time-dependent products at 90 or 110 °C (the molar ratio of [Co(notpH$_3$)] / Co(NO$_3$)$_2$ kept at 1 : 1). 18
Figure S2. The PXRD patterns for products of **4** under various conditions.. 19
Figure S3. IR spectra of **1**, **2**, **3**, and **4** (KBr pellets). 20
Figure S4. Packing diagram of **1·2H$_2$O**. 21
Figure S5. Packing diagram of **1·5H$_2$O**. 21
Figure S6. Crystal structure of **4**. 22
Figure S7. The H-bonding network of **1·2H$_2$O**. 23
Figure S8. The H-bonding network of **1·3H$_2$O**. 23
Figure S9. The H-bonding network of **2**. 24
Figure S10. The H-bonding network of **3**. 25
Figure S11. The H-bonding network of **4**. 26
Figure S12. Water adsorption (filled circle) and desorption (open circle) isotherms of **1** at 25 °C. 27
Figure S13. Water adsorption (filled circle) and desorption (open circle) isotherms of **2** at 25 °C. 27
Figure S14. Water adsorption (filled circle) and desorption (open circle) isotherms of **3** at 25 °C. 28
Figure S15. Water adsorption (filled circle) and desorption (open circle) isotherms of **4** at 25 °C. 28
Figure S16. PXRD patterns for **1 - 4** after desorption. 29
Figure S17. IR spectra of **3** and **4** after desorption. 29
Figure S18. Water adsorption (filled circle) and desorption (open circle) isotherms of **3** (without thermal pretreatment) at 25 °C. 30
Figure S19. Water adsorption (filled circle) and desorption (open circle) isotherms of **4** (without thermal pretreatment) at 25 °C. 30
Figure S20. PXRD patterns for **3** and **4** after desorption without thermal pretreatment. 31
Figure S21. Nyquist plots for the pellet of **1** at 25 °C and various RH. Up: RH increases from 40 to 95%. 32
Figure S22. Nyquist plots for the pellet of compound **1** at 25 °C and various RH. Up: RH decreases from 95 to 60%. 33
Figure S23. Nyquist plots for the pellet of compound **2** at 25 °C and various RH. Up: RH increases from 40 to 95%. 34
Figure S24. Nyquist plots for the pellet of compound **2** at 25 °C and various RH. Up: RH decreases from 95 to 60%. 35

Figure S25. Nyquist plots for the pellet of compound **3** at 25 °C and various RH. Up: RH increases from 40 to 95%. 36
Figure S26. Nyquist plots for the pellet of compound **3** at 25 °C and various RH. Up: RH decreases from 95 to 60%.37
Figure S27. Nyquist plots for the pellet of compound **4** at 25 °C and various RH. Up: RH increases from 40 to 95%. 38
Figure S28. Nyquist plots for the pellet of compound **4** at 25 °C and various RH (from 95 to 60%).....39
Figure S29. Nyquist plots for the pellet of **1** at 95% RH and various temperatures (from 70 to 20 °C). 40
Figure S30. Nyquist plots for the pellet of **2** at 95% RH and various temperatures (from 70 to 20 °C). 40
Figure S31. Nyquist plots for the pellet of **3** at 95% RH and various temperatures. Up: temperature decreases from 70 to 20 °C.. 41
Figure S32. Nyquist plots for the pellet of **4** at 95% RH and various temperatures. Up: temperature decreases from 70 to 20 °C. 42
Figure S33. PXRD patterns for **1 - 4** after AC impedance measurements.....43
Figure S34. Nyquist plots for a single crystal of **3** at 95% RH and various temperatures (50 to 20 °C).....44
Figure S35. Nyquist plots for a single crystal of **4** at 95% RH and various temperatures. Up: temperature decreases from 50 to 20 °C.. 45

Table S1. Crystallographic data for **1·2H$_2$O**, **1·3H$_2$O**, and **1·5H$_2$O**.

	1·2H$_2$O	**1·3H$_2$O**	**1·5H$_2$O**
Temperature (K)	190(2)	296(2)	190(2)
Formula	$C_9H_{29}Co_2N_3O_{14}P_3$	$C_9H_{31}Co_2N_3O_{15}P_3$	$C_{18}H_{70}Co_4N_6O_{34}P_6$
M	614.12	632.14	1336.34
Crystal size (mm)	0.15×0.10×0.03	0.15×0.05×0.03	0.20×0.05×0.04
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	*P*-1	*C*2/*c*	*P*-1
a (Å)	7.812(3)	23.971(4)	12.790(16)
b (Å)	10.859(4)	7.8678(13)	14.685(18)
c (Å)	12.709(5)	22.429(4)	15.514(19)
α (deg)	89.402(15)	90	103.49(5)
β (deg)	72.201(9)	93.589(8)	108.36(5)
γ (deg)	79.402(11)	90	103.32(6)
V (Å^3)	1007.7(7)	4221.7(13)	2539(6)
Z	2	8	2
D_c (g cm^{-3})	2.024	1.989	1.748
μ (mm^{-1})	1.962	1.880	1.573
F(000)	630	2600	1380
R_{int}	0.0485	0.0552	0.0411
GOF	1.049	1.018	1.038
R_1, wR_2 [$I > 2\sigma(I)$]	0.0633, 0.1329	0.0467, 0.0944	0.0739, 0.1942
R_1, wR_2 (all data)	0.0994, 0.1454	0.0776, 0.1090	0.0956, 0.2099
$\triangle\rho_{max}$, $\triangle\rho_{min}$ (e Å^{-3})	1.828, -1.011	0.828, -0.838	3.076, -0.994
CCDC	2158580	2158581	2158582

Table S2. Selected bond lengths (Å) for **1·2H$_2$O** and **1·3H$_2$O**.

	1·2H$_2$O	**1·3H$_2$O**
Co(1)-O(1)	1.925(4)	1.926(3)
Co(1)-O(4)	1.948(4)	1.949(3)
Co(1)-O(7)	1.940(4)	1.929(3)
Co(1)-N(1)	1.945(5)	1.933(3)
Co(1)-N(2)	1.955(5)	1.949(3)
Co(1)-N(3)	1.961(5)	1.960(4)
Co(2)-O(2)	2.060(4)	2.051(3)
Co(2)-O(2A)	2.223(5)	2.184(3)
Co(2)-O(5B)	2.030(4)	2.063(3)
Co(2)-O(1W)	2.203(5)	2.145(3)
Co(2)-O(2W)	2.069(4)	2.048(3)
Co(2)-O(3W)	2.118(5)	2.163(3)

Symmetry transformations used to generate equivalent atoms: For **1·2H$_2$O**, A: 2-x, 1-y, 2-z ; B: 1-x, 1-y, 2-z; for **1·3H$_2$O**, A: 1-x, 1-y, 1-z ; B: 1-x, -y, 1-z.

Table S3. Selected bond angles (°) for **1·2H$_2$O** and **1·3H$_2$O**.

	1·2H$_2$O	**1·3H$_2$O**
O(1)-Co(1)-O(4)	92.83(18)	92.81(12)
O(1)-Co(1)-O(7)	88.92(17)	88.84(11)
O(1)-Co(1)-N(1)	87.99(19)	88.13(12)
O(1)-Co(1)-N(2)	176.1(2)	176.41(13)
O(1)-Co(1)-N(3)	90.4(2)	90.90(13)
O(4)-Co(1)-O(7)	90.21(18)	90.73(12)
O(4)-Co(1)-N(1)	92.7(2)	91.54(13)
O(4)-Co(1)-N(2)	89.3(2)	88.72(13)
O(4)-Co(1)-N(3)	176.7(2)	176.28(12)
O(7)-Co(1)-N(1)	175.9(2)	176.30(13)
O(7)-Co(1)-N(2)	94.40(19)	94.39(12)
O(7)-Co(1)-N(3)	89.51(19)	89.48(13)
N(1)-Co(1)-N(2)	88.6(2)	88.58(14)
N(1)-Co(1)-N(3)	87.8(2)	88.44(14)
N(2)-Co(1)-N(3)	87.5(2)	87.56(14)
O(2)-Co(2)-O(2A)	80.07(19)	80.00(12)
O(2)-Co(2)-O(5B)	95.93(16)	95.97(10)
O(2)-Co(2)-O(1W)	94.16(18)	93.36(11)
O(2)-Co(2)-O(2W)	173.79(16)	171.03(11)
O(2)-Co(2)-O(3W)	88.44(18)	84.23(10)
O(2A)-Co(2)-O(5B)	94.73(17)	89.79(11)
O(2A)-Co(2)-O(1W)	173.83(16)	172.52(11)
O(2A)-Co(2)-O(2W)	97.40(16)	99.46(11)
O(2A)-Co(2)-O(3W)	85.3(2)	82.55(11)
O(5B)-Co(2)-O(1W)	83.65(18)	87.46(11)
O(5B)-Co(2)-O(2W)	89.91(16)	92.97(11)
O(5B)-Co(2)-O(3W)	175.56(18)	172.19(12)
O(1W)-Co(2)-O(2W)	88.56(17)	87.64(12)
O(1W)-Co(2)-O(3W)	96.8(2)	100.33(11)
O(2W)-Co(2)-O(3W)	85.69(18)	86.83(11)

Symmetry transformations used to generate equivalent atoms: For **1·2H$_2$O**, A: 2-x, 1-y, 2-z ; B: 1-x, 1-y, 2-z; for **1·3H$_2$O**, A: 1-x, 1-y, 1-z ; B: 1-x, -y, 1-z.

Table S4. Selected bond lengths (Å) and angles (°) for **1·5H$_2$O**.

Co(1)-O(1)	1.943(5)	Co(3)-O(11)	1.921(5)
Co(1)-O(4)	1.918(5)	Co(3)-O(13)	1.948(5)
Co(1)-O(7)	1.930(6)	Co(3)-O(16)	1.932(6)
Co(1)-N(1)	1.933(6)	Co(3)-N(4)	1.945(7)
Co(1)-N(2)	1.944(7)	Co(3)-N(5)	1.930(6)
Co(1)-N(3)	1.941(6)	Co(3)-N(6)	1.946(6)
Co(2)-O(2)	2.071(5)	Co(4)-O(6B)	2.270(6)
Co(2)-O(6A)	2.083(5)	Co(4)-O(10C)	2.078(5)
Co(2)-O(10)	2.140(6)	Co(4)-O(14)	2.022(5)
Co(2)-O(1W)	2.139(6)	Co(4)-O(4W)	2.167(6)
Co(2)-O(2W)	2.094(5)	Co(4)-O(5W)	2.060(5)
Co(2)-O(3W)	2.099(5)	Co(4)-O(6W)	2.110(5)
O(1)-Co(1)-O(4)	92.7(2)	O(11)-Co(3)-O(13)	92.7(2)
O(1)-Co(1)-O(7)	90.0(2)	O(11)-Co(3)-O(16)	89.1(2)
O(1)-Co(1)-N(1)	88.3(2)	O(11)-Co(3)-N(4)	88.5(2)
O(1)-Co(1)-N(2)	91.5(2)	O(11)-Co(3)-N(5)	176.8(2)
O(1)-Co(1)-N(3)	176.6(2)	O(11)-Co(3)-N(6)	89.9(2)
O(4)-Co(1)-O(7)	88.9(2)	O(13)-Co(3)-O(16)	90.3(2)
O(4)-Co(1)-N(1)	177.8(2)	O(13)-Co(3)-N(4)	92.1(3)
O(4)-Co(1)-N(2)	88.3(2)	O(13)-Co(3)-N(5)	89.0(2)
O(4)-Co(1)-N(3)	90.7(2)	O(13)-Co(3)-N(6)	177.4(2)
O(7)-Co(1)-N(1)	93.1(2)	O(16)-Co(3)-N(4)	176.7(2)
O(7)-Co(1)-N(2)	176.8(2)	O(16)-Co(3)-N(5)	93.6(2)
O(7)-Co(1)-N(3)	89.7(2)	O(16)-Co(3)-N(6)	89.3(2)
N(1)-Co(1)-N(2)	89.7(3)	N(4)-Co(3)-N(5)	88.7(3)
N(1)-Co(1)-N(3)	88.3(2)	N(4)-Co(3)-N(6)	88.3(3)
N(2)-Co(1)-N(3)	88.9(3)	N(5)-Co(3)-N(6)	88.4(3)
O(2)-Co(2)-O(6A)	93.18(19)	O(6B)-Co(4)-O(10C)	76.66(19)
O(2)-Co(2)-O(10)	87.5(2)	O(6B)-Co(4)-O(14)	104.8(2)
O(2)-Co(2)-O(1W)	86.2(2)	O(6B)-Co(4)-O(4W)	158.4(2)
O(2)-Co(2)-O(2W)	88.22(19)	O(6B)-Co(4)-O(5W)	101.3(2)
O(2)-Co(2)-O(3W)	171.5(2)	O(6B)-Co(4)-O(6W)	79.4(2)
O(6A)-Co(2)-O(10)	79.5(2)	O(10C)-Co(4)-O(14)	88.4(2)
O(6A)-Co(2)-O(1W)	94.3(2)	O(10C)-Co(4)-O(4W)	93.4(2)
O(6A)-Co(2)-O(2W)	178.35(19)	O(10C)-Co(4)-O(5W)	177.24(19)
O(6A)-Co(2)-O(3W)	93.2(2)	O(10C)-Co(4)-O(6W)	91.60(19)
O(10)-Co(2)-O(1W)	170.9(2)	O(14)-Co(4)-O(4W)	93.8(2)
O(10)-Co(2)-O(2W)	99.7(2)	O(14)-Co(4)-O(5W)	90.4(2)
O(10)-Co(2)-O(3W)	88.2(2)	O(14)-Co(4)-O(6W)	175.7(2)
O(1W)-Co(2)-O(2W)	86.6(2)	O(4W)-Co(4)-O(5W)	89.2(2)
O(1W)-Co(2)-O(3W)	98.9(2)	O(4W)-Co(4)-O(6W)	81.9(2)
O(2W)-Co(2)-O(3W)	85.3(2)	O(5W)-Co(4)-O(6W)	89.78(19)

Symmetry transformations used to generate equivalent atoms: A: 1-x,1-y,2-z; B: x,y,-1+z; C: 1-x,1-y,1-z.

Table S5. Selected bond lengths (Å) and angles (°) for **2**.

Co(1)-O(1)	1.926(5)	Co(1)-N(3)	1.946(6)
Co(1)-O(4)	1.934(6)	Co(2)-O(2)	1.936(6)
Co(1)-O(7)	1.937(6)	Co(2)-O(3A)	1.980(6)
Co(1)-N(1)	1.932(7)	Co(2)-O(8B)	1.932(6)
Co(1)-N(2)	1.952(7)	Co(2)-O(1W)	1.975(6)
O(1)-Co(1)-O(4)	90.8(2)	O(7)-Co(1)-N(3)	89.4(3)
O(1)-Co(1)-O(7)	91.5(3)	N(1)-Co(1)-N(2)	88.5(3)
O(1)-Co(1)-N(1)	88.2(3)	N(1)-Co(1)-N(3)	88.8(3)
O(1)-Co(1)-N(2)	91.1(3)	N(2)-Co(1)-N(3)	88.0(3)
O(1)-Co(1)-N(3)	176.9(3)	O(2)-Co(2)-O(3A)	109.9(3)
O(4)-Co(1)-O(7)	90.3(3)	O(2)-Co(2)-O(8B)	113.0(3)
O(4)-Co(1)-N(1)	177.4(3)	O(2)-Co(2)-O(1W)	104.2(3)
O(4)-Co(1)-N(2)	89.2(3)	O(3A)-Co(2)-O(8B)	108.4(3)
O(4)-Co(1)-N(3)	92.2(3)	O(3A)-Co(2)-O(1W)	108.5(3)
O(7)-Co(1)-N(1)	92.1(3)	O(8B)-Co(2)-O(1W)	112.8(3)
O(7)-Co(1)-N(2)	177.3(3)		

Symmetry transformations used to generate equivalent atoms: A: 1.5-x, y, 0.5+z; B: 1.5-x, -1+y, 0.5+z.

Table S6. Selected bond lengths (Å) and angles (°) for **3**.

Co(1)-O(1)	1.9323(13)	Co(2)-O(4W)	2.1129(15)
Co(1)-O(4)	1.9375(13)	Co(2)-O(5W)	2.1221(14)
Co(1)-O(7)	1.9553(14)	Co(2)-O(6W)	2.1423(16)
Co(1)-N(1)	1.9531(16)	Co(3)-O(5)	2.0631(13)
Co(1)-N(2)	1.9497(17)	Co(3)-O(5A)	2.0631(13)
Co(1)-N(3)	1.9376(16)	Co(3)-O(9B)	2.1192(14)
Co(2)-O(2)	2.0635(14)	Co(3)-O(9C)	2.1192(14)
Co(2)-O(2W)	2.0588(15)	Co(3)-O(1W)	2.1992(14)
Co(2)-O(3W)	2.1040(14)	Co(3)-O(1WA)	2.1991(14)
O(1)-Co(1)-O(4)	89.49(6)	O(2W)-Co(2)-O(6W)	91.19(6)
O(1)-Co(1)-O(7)	91.55(6)	O(3W)-Co(2)-O(4W)	88.25(6)
O(1)-Co(1)-N(1)	88.64(6)	O(3W)-Co(2)-O(5W)	86.63(5)
O(1)-Co(1)-N(2)	92.43(7)	O(3W)-Co(2)-O(6W)	88.68(6)
O(1)-Co(1)-N(3)	177.40(6)	O(4W)-Co(2)-O(5W)	88.04(6)
O(4)-Co(1)-O(7)	91.93(6)	O(4W)-Co(2)-O(6W)	176.90(6)
O(4)-Co(1)-N(1)	175.98(7)	O(5W)-Co(2)-O(6W)	92.15(6)
O(4)-Co(1)-N(2)	88.76(6)	O(5)-Co(3)-O(5A)	180.0
O(4)-Co(1)-N(3)	93.07(6)	O(5)-Co(3)-O(9B)	88.85(6)
O(7)-Co(1)-N(1)	91.68(6)	O(5)-Co(3)-O(9C)	91.15(6)
O(7)-Co(1)-N(2)	175.96(6)	O(5)-Co(3)-O(1W)	91.41(5)
O(7)-Co(1)-N(3)	87.92(6)	O(5)-Co(3)-O(1WA)	88.59(5)
N(1)-Co(1)-N(2)	87.76(7)	O(5A)-Co(3)-O(9B)	91.15(6)
N(1)-Co(1)-N(3)	88.83(7)	O(5A)-Co(3)-O(9C)	88.85(6)
N(2)-Co(1)-N(3)	88.07(7)	O(5A)-Co(3)-O(1W)	88.59(5)
O(2)-Co(2)-O(2W)	93.56(7)	O(5A)-Co(3)-O(1WA)	91.41(5)
O(2)-Co(2)-O(3W)	171.88(6)	O(9B)-Co(3)-O(9C)	180.00(7)
O(2)-Co(2)-O(4W)	89.75(6)	O(9B)-Co(3)-O(1W)	90.88(6)
O(2)-Co(2)-O(5W)	85.43(6)	O(9B)-Co(3)-O(1WA)	89.12(6)
O(2)-Co(2)-O(6W)	93.35(6)	O(9C)-Co(3)-O(1W)	89.12(6)
O(2W)-Co(2)-O(3W)	94.27(6)	O(9C)-Co(3)-O(1WA)	90.88(6)
O(2W)-Co(2)-O(4W)	88.67(6)	O(1W)-Co(3)-O(1WA)	180.0
O(2W)-Co(2)-O(5W)	176.56(7)		

Symmetry transformations used to generate equivalent atoms: A: 2-x, 1-y, 2-z; B: x, 1.5-y, 0.5+z; C: 2-x, -0.5+y, 1.5-z.

Table S7. Selected bond lengths (Å) and angles (°) for **4**.

Co(1)-O(1)	1.9306(14)	Ni(1)-O(4W)	2.0594(16)
Co(1)-O(4)	1.9377(14)	Ni(1)-O(5W)	2.0676(14)
Co(1)-O(7)	1.9571(14)	Ni(1)-O(6W)	2.0883(15)
Co(1)-N(1)	1.9530(17)	Ni(2)-O(5)	2.0526(13)
Co(1)-N(2)	1.9495(17)	Ni(2)-O(5A)	2.0526(13)
Co(1)-N(3)	1.9341(17)	Ni(2)-O(9B)	2.0992(14)
Ni(1)-O(2)	2.0497(14)	Ni(2)-O(9C)	2.0992(14)
Ni(1)-O(2W)	2.0462(16)	Ni(2)-O(1W)	2.1315(15)
Ni(1)-O(3W)	2.0744(14)	Ni(2)-O(1WA)	2.1315(15)
O(1)-Co(1)-O(4)	89.36(6)	O(2W)-Ni(1)-O(6W)	90.05(6)
O(1)-Co(1)-O(7)	91.29(6)	O(3W)-Ni(1)-O(4W)	89.13(6)
O(1)-Co(1)-N(1)	88.82(6)	O(3W)-Ni(1)-O(5W)	88.04(6)
O(1)-Co(1)-N(2)	92.65(6)	O(3W)-Ni(1)-O(6W)	88.52(6)
O(1)-Co(1)-N(3)	177.45(6)	O(4W)-Ni(1)-O(5W)	88.80(6)
O(4)-Co(1)-O(7)	92.05(6)	O(4W)-Ni(1)-O(6W)	177.39(6)
O(4)-Co(1)-N(1)	175.91(7)	O(5W)-Ni(1)-O(6W)	92.24(6)
O(4)-Co(1)-N(2)	88.69(6)	O(5)-Ni(2)-O(5A)	180.0
O(4)-Co(1)-N(3)	93.07(7)	O(5)-Ni(2)-O(9B)	89.01(6)
O(7)-Co(1)-N(1)	91.66(6)	O(5)-Ni(2)-O(9C)	90.99(6)
O(7)-Co(1)-N(2)	176.01(6)	O(5)-Ni(2)-O(1W)	92.19(5)
O(7)-Co(1)-N(3)	87.85(6)	O(5)-Ni(2)-O(1WA)	87.81(5)
N(1)-Co(1)-N(2)	87.73(7)	O(5A)-Ni(2)-O(9B)	89.01(6)
N(1)-Co(1)-N(3)	88.80(7)	O(5A)-Ni(2)-O(9C)	90.99(6)
N(2)-Co(1)-N(3)	88.19(7)	O(5A)-Ni(2)-O(1W)	87.81(5)
O(2)-Ni(1)-O(2W)	93.22(7)	O(5A)-Ni(2)-O(1WA)	92.19(5)
O(2)-Ni(1)-O(3W)	173.70(6)	O(9B)-Ni(2)-O(9C)	180.00(7)
O(2)-Ni(1)-O(4W)	88.56(6)	O(9B)-Ni(2)-O(1W)	90.23(6)
O(2)-Ni(1)-O(5W)	86.05(6)	O(9B)-Ni(2)-O(1WA)	89.78(6)
O(2)-Ni(1)-O(6W)	93.90(6)	O(9C)-Ni(2)-O(1W)	89.77(6)
O(2W)-Ni(1)-O(3W)	92.60(6)	O(9C)-Ni(2)-O(1WA)	90.22(6)
O(2W)-Ni(1)-O(4W)	88.92(6)	O(1W)-Ni(2)-O(1WA)	180.0
O(2W)-Ni(1)-O(5W)	177.63(7)		

Symmetry transformations used to generate equivalent atoms: A: 2-x, 1-y, 2-z; B: x, 1.5-y, 0.5+z; C: 2-x, -0.5+y, 1.5-z.

Table S8. Hydrogen bonds present in compound **1·2H$_2$O**.

D-H···A	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠ DHA (°)
O8-H8C···O6(i)	0.84	1.67	2.495(5)	165.7
O1W-H1WA···O5W(ii)	0.90	1.99	2.877(7)	167.1
O1W-H1WB···O6(iii)	0.90	1.87	2.768(6)	172.1
O2W-H2WA···O1(iv)	0.90	1.96	2.789(6)	153.2
O2W-H2WB···O9(ii)	0.90	1.78	2.676(6)	171.3
O3W-H3WA···O4(iv)	0.90	1.92	2.820(7)	178.9
O3W-H3WB···O4W(v)	0.90	2.31	3.093(8)	145.6
O4W-H4WA···O3(v)	0.90	1.88	2.768(6)	167.3
O4W-H4WB···O3	0.90	1.83	2.729(7)	173.1
O5W-H5WA···O9	0.90	1.76	2.641(7)	165.2
O5W-H5WB···O4W(vi)	0.90	1.86	2.682(7)	150.1

Symmetry transformations used to generate equivalent atoms: i: 2-x, 1-y, 1-z; ii: x, y, 1+z; iii: 1-x, 1-y, 2-z; iv: 2-x, 1-y, 2-z; v: 2-x, 2-y, 2-z; vi: 2-x, 2-y, 1-z.

Table S9. Hydrogen bonds present in compound **1·3H$_2$O**.

D-H···A	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠ DHA (°)
O8-H8C···O6(i)	0.82	1.75	2.556(4)	167.0
O1W-H1WA···O5W(ii)	0.90	1.95	2.847(5)	175.5
O1W-H1WB···O6(iii)	0.90	1.87	2.754(4)	167.5
O2W-H2WA···O1(iv)	0.90	1.98	2.766(4)	144.6
O2W-H2WB···O9(ii)	0.90	1.77	2.670(4)	178.6
O3W-H3WA···O5(v)	0.90	2.18	3.059(4)	164.9
O3W-H3WB···O4(iv)	0.90	1.92	2.814(4)	175.4
O4W-H4WA···O6W(i)	0.90	2.37	3.087(5)	136.3
O4W-H4WB···O6	0.90	2.00	2.876(5)	164.6
O5W-H5WA···O6W	0.90	1.88	2.707(5)	152.1
O5W-H5WB···O9	0.90	1.85	2.698(5)	156.9
O6W-H6WA···O3(vi)	0.90	1.83	2.717(4)	167.7
O6W-H6WB···O3(vii)	0.90	1.91	2.792(5)	167.4

Symmetry transformations used to generate equivalent atoms: i: 1.5-x, 0.5-y, 1-z; ii: -0.5+x, 0.5+y, z; iii: 1-x, -y, 1-z; iv: 1-x, 1-y, 1-z; v: x, 1+y, z; vi: 0.5+x, -0.5+y, z; vii: 1.5-x, -0.5+y, 0.5-z.

Table S10. Hydrogen bonds present in compound **1·5H$_2$O**.

D-H···A	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠ DHA (°)
O8-H8C···O15(i)	0.84	1.66	2.474(8)	163.8
O17-H17C···O3(i)	0.84	1.74	2.556(7)	164.7
O1W-H1WA···O3	0.91	1.98	2.822(8)	153.5
O1W-H1WB···O16W	0.90	2.03	2.697(18)	129.5
O2W-H2WA···O11	0.90	1.99	2.773(8)	144.3
O2W-H2WB···O9(i)	0.90	1.85	2.712(7)	161.0
O3W-H3WA···O10W(ii)	0.90	1.96	2.785(13)	151.4
O3W-H3WB···O13	0.90	1.91	2.811(7)	175.3
O4W-H4WA···O12(ii)	0.90	1.75	2.632(8)	165.8
O4W-H4WB···O13W(ii)	0.90	1.97	2.852(8)	165.3
O5W-H5WA···O7(iii)	0.90	2.20	2.973(7)	143.6
O5W-H5WB···O18(iv)	0.90	1.79	2.688(8)	172.0
O6W-H6WA···O1(iii)	0.90	1.79	2.662(7)	160.3
O6W-H6WB···O2(ii)	0.90	1.83	2.703(8)	162.2

Symmetry transformations used to generate equivalent atoms: i: 2-x, 1-y, 2-z; ii: 1-x, 1-y, 1-z; iii: x, y, -1+z; iv: 2-x, 1-y, 1-z.

Table S11. Hydrogen bonds are present in compound **2**.

D-H···A	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠ DHA (°)
O5-H5C···O2W(i)	0.82	1.67	2.458(9)	159.8
O1W-H1WA···O6(ii)	0.90	1.79	2.624(7)	153.3
O1W-H1WB···O7(iii)	0.90	2.06	2.840(6)	144.4
O2W-H2WA···O9(iv)	0.90	1.73	2.444(9)	133.8
O2W-H2WB···O3W(v)	0.90	1.88	2.649(10)	141.7
O3W-H3WA···O3	0.90	1.97	2.816(8)	156.2
O3W-H3WB···O6(ii)	0.90	1.93	2.802(8)	163.8

Symmetry transformations used to generate equivalent atoms: i: 2-x, 1-y, -0.5+z; ii: -0.5+x, 1-y, z; iii: 1.5-x, y, 0.5+z; iv: x, y, 1+z; v: 1.5-x, 1+y, 0.5+z.

Table S12. Hydrogen bonds are present in compound **3**.

D-H···A	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠ DHA (°)
O1W-H1WA···O8(i)	0.90	1.86	2.757(2)	169.6
O1W-H1WB···O6	0.90	1.93	2.790(2)	158.3
O2W-H2WA···O7W(ii)	0.90	1.81	2.677(2)	160.1
O2W-H2WB···O1W(iii)	0.90	1.89	2.764(2)	162.1
O3W-H3WA···O8(iv)	0.90	1.91	2.768(2)	157.7
O3W-H3WB···O4(iv)	0.90	1.84	2.727(2)	166.3
O4W-H4WA···O1(iv)	0.90	1.79	2.6802(19)	165.9
O4W-H4WB···O6(iv)	0.90	2.05	2.888(2)	152.6
O5W-H5WA···O7(iv)	0.90	1.84	2.7269(19)	167.4
O5W-H5WB···O2(iv)	0.90	1.90	2.750(2)	156.0
O6W-H6WA···O8(v)	0.90	2.01	2.897(2)	168.2
O6W-H6WB···O3	0.90	1.76	2.651(2)	169.9
O7W-H7WA···O6(iii)	0.90	1.95	2.755(2)	148.2
O7W-H7WB···O3	0.90	1.81	2.647(2)	153.7

Symmetry transformations used to generate equivalent atoms: i: 2-x, -0.5+y, 1.5-z; ii: x, 1.5-y, -0.5+z; iii: 1-x, 0.5+y, 1.5-z; iv: 1-x, 1-y, 1-z; v: -1+x, y, z.

Table S13. Hydrogen bonds are present in compound **4**.

D-H···A	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠ DHA (°)
O1W-H1WA···O8(i)	0.90	1.85	2.731(2)	165.5
O1W-H1WB···O6	0.90	1.90	2.778(2)	164.7
O2W-H2WA···O7W(ii)	0.90	1.80	2.678(2)	165.6
O2W-H2WB···O1W(iii)	0.90	1.94	2.799(2)	159.6
O3W-H3WA···O8(iv)	0.90	1.93	2.780(2)	157.7
O3W-H3WB···O4(iv)	0.90	1.84	2.726(2)	167.0
O4W-H4WA···O1(iv)	0.90	1.77	2.664(2)	170.0
O4W-H4WB···O6(iv)	0.90	2.15	2.932(2)	145.3
O5W-H5WA···O7(iv)	0.90	1.84	2.7164(19)	165.0
O5W-H5WB···O2(iv)	0.90	1.89	2.750(2)	158.2
O6W-H6WA···O8(v)	0.90	2.05	2.918(2)	163.2
O6W-H6WB···O3	0.90	1.74	2.627(2)	166.3
O7W-H7WA···O6(iii)	0.90	1.94	2.731(2)	145.8
O7W-H7WB···O3	0.90	1.86	2.646(2)	145.3

Symmetry transformations used to generate equivalent atoms: i: 2-x, -0.5+y, 1.5-z; ii: x, 1.5-y, -0.5+z; iii: 1-x, 0.5+y, 1.5-z; iv: 1-x, 1-y, 1-z; v: -1+x, y, z.

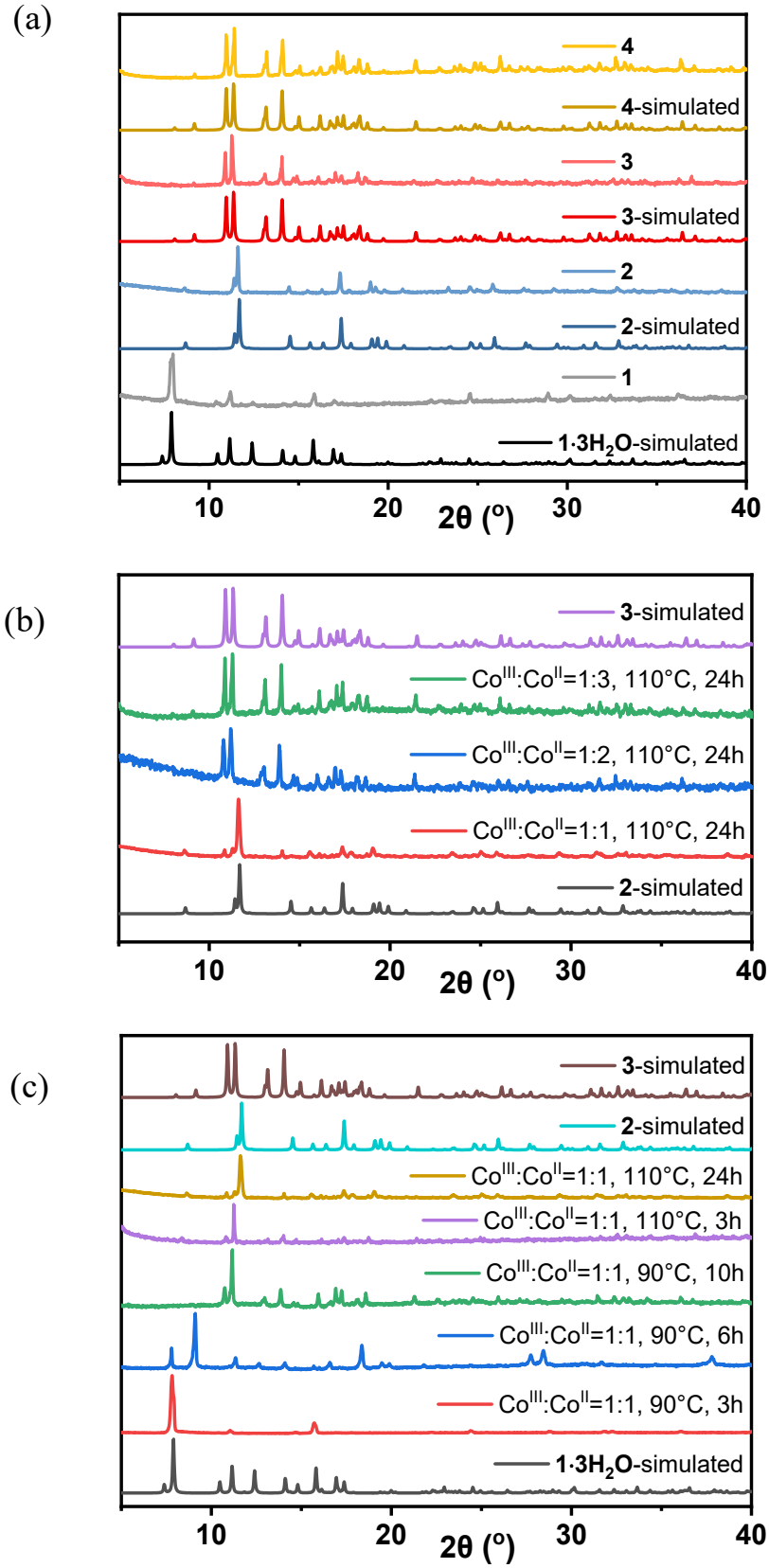

Figure S1. (a) The PXRD patterns for pure products of **1**, **2**, **3**, and **4**. (b) The PXRD patterns for the products with different starting reactants ratios after 24 h reactions at 110 °C. (c) The PXRD patterns for the time-dependent products at 90 or 110 °C (the molar ratio of $Co(notpH_3)$ / $Co(NO_3)_2$ kept at 1 : 1).

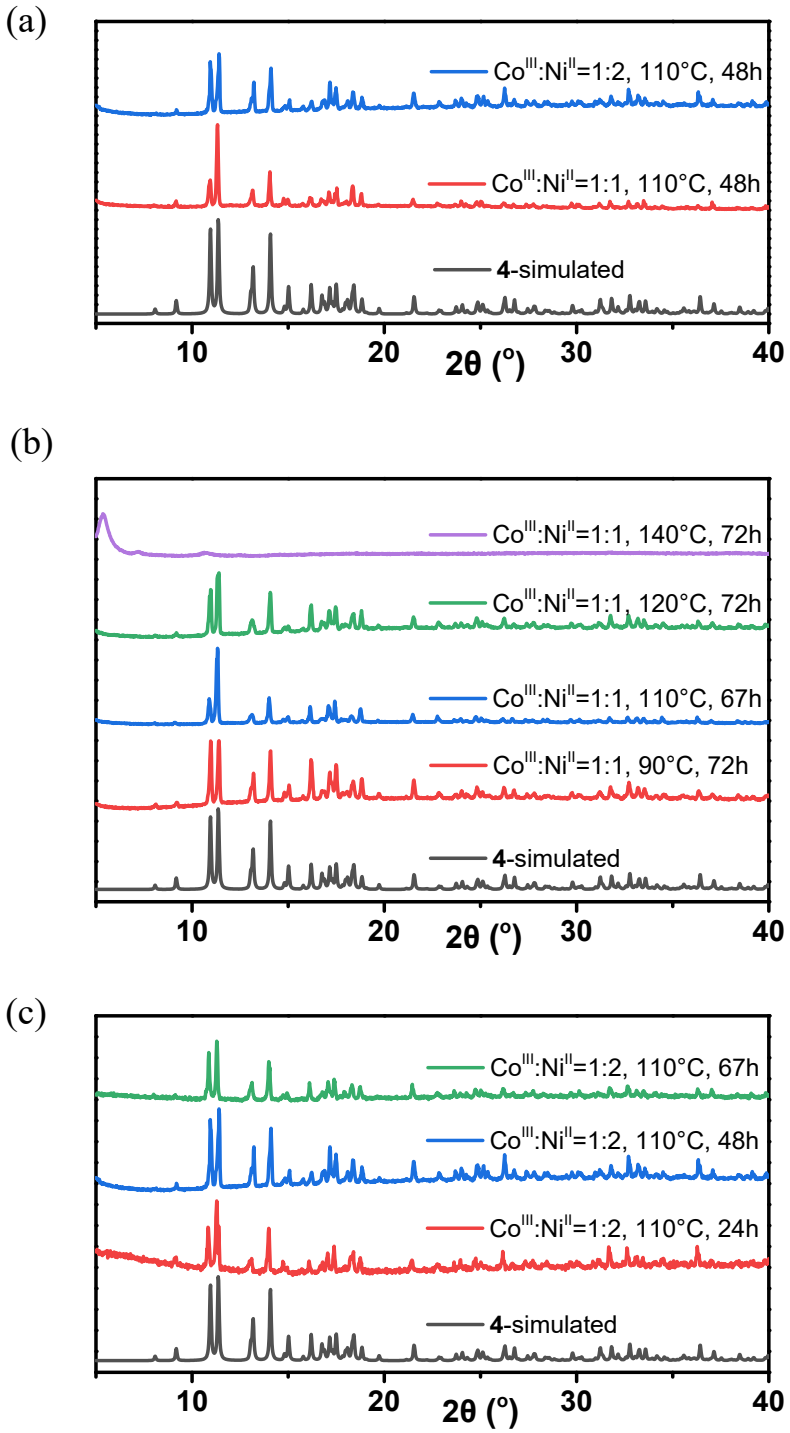

Figure S2. The PXRD patterns for products of **4** under various conditions: (a) the different molar ratio of [Co(notpH$_3$)] / NiCl$_2$; (b) the different reaction temperature; (c) the different reaction time.

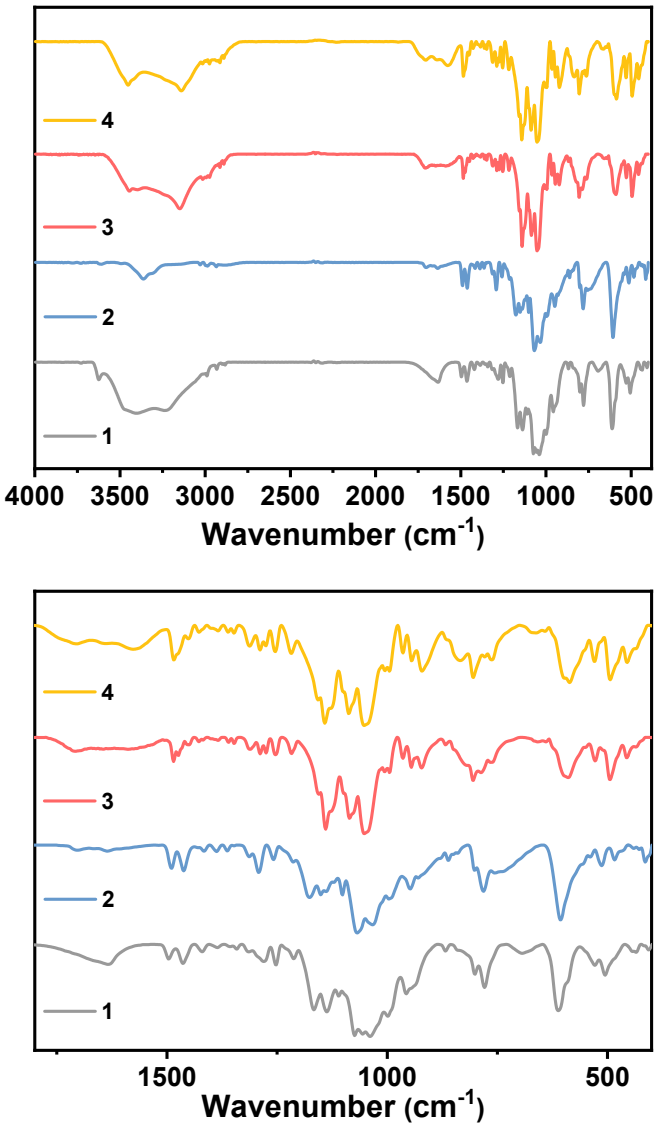

Figure S3. IR spectra of **1**, **2**, **3**, and **4** (KBr pellets). [Peaks (cm^{-1}). **1·nH$_2$O**: 3727(w), 3624(w), 3404(m), 3239(m), 2990(w), 2932(w), 2883(w), 2311(w), 1633(w), 1496(w), 1464(w), 1420(w), 1386(w), 1342(w), 1315(w), 1281(w), 1253(w), 1212(w), 1167(m), 1137(m), 1110(m), 1074(s), 1056(s), 1039(s), 999(s), 957(m), 868(w), 801(m), 779(m), 694(w), 612(m), 529(w), 506(w), 435(w), 407(w). **2**: 3362(w), 3029(w), 2986(w), 2935(w), 1703(w), 1635(w), 1490(w), 1462(w), 1416(w), 1387(w), 1363(w), 1313(w), 1292(w), 1258(w), 1213(w), 1177(m), 1151(m), 1139(m), 1102(m), 1068(s), 1033(s), 996(m), 948(m), 930(m), 861(w), 802(w), 782(m), 756(w), 607(s), 539(w), 513(w), 484(w), 440(w), 428(w), 414(w). **3**: 3444(m), 3397(m), 3148(m), 3015(w), 2975(w), 2913(w), 2890(w), 1707(w), 1645(w), 1588(w), 1485(w), 1474(w), 1450(w), 1428(w), 1384(w), 1360(w), 1347(w), 1288(w), 1275(w), 1254(w), 1217(w), 1155(m), 1140(s), 1086(s), 1052(s), 1006(m), 995(m), 965(w), 945(m), 922(m), 868(w), 805(m), 787(m), 765(w), 658(w), 640(w), 589(m), 528(w), 495(m), 456(w). **4**: 3449(m), 3142(m), 3016(w), 2976(w), 2927(w), 2914(w), 2891(w), 1704(w), 1580(w), 1485(w), 1474(w), 1454(w), 1427(w), 1383(w), 1360(w), 1348(w), 1311(w), 1288(w), 1275(w), 1253(w), 1217(w), 1156(m), 1142(s), 1128(s), 1087(s), 1053(s), 1005(m), 995(m), 964(w), 945(m), 922(m), 835(m), 806(m), 779(w), 766(w), 670(w), 639(w), 600(m), 587(m), 531(w), 496(m), 457(w).]

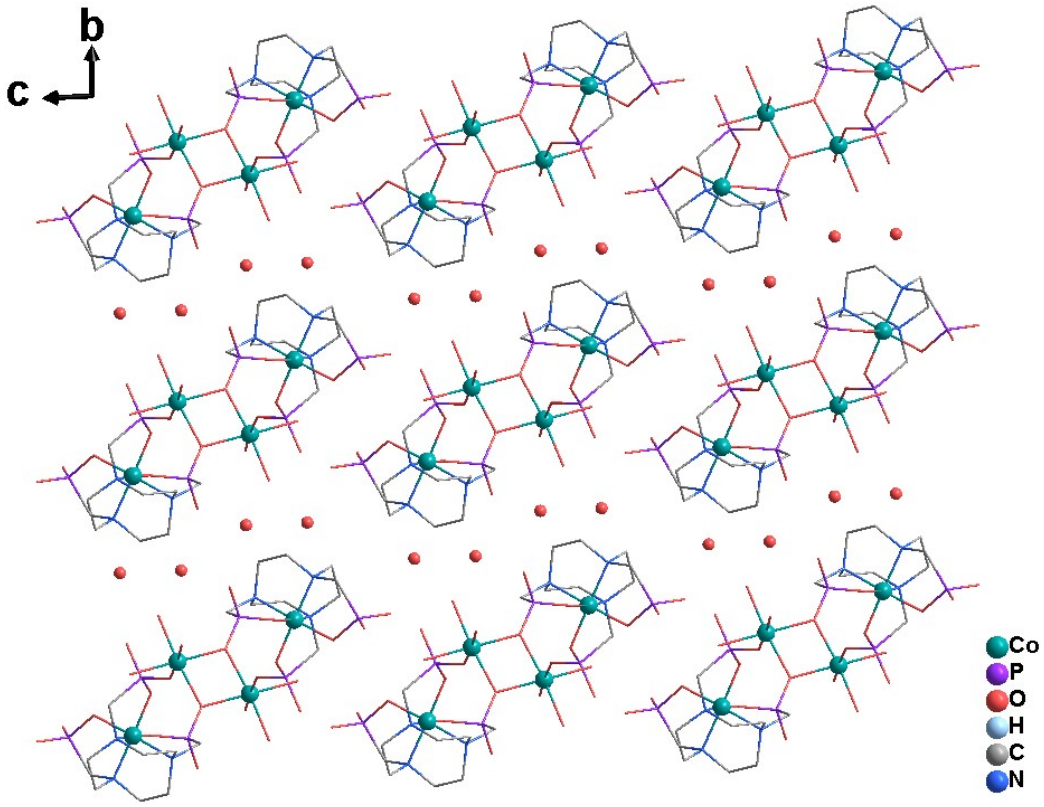

Figure S4. Packing diagram of **1·2H$_2$O**.

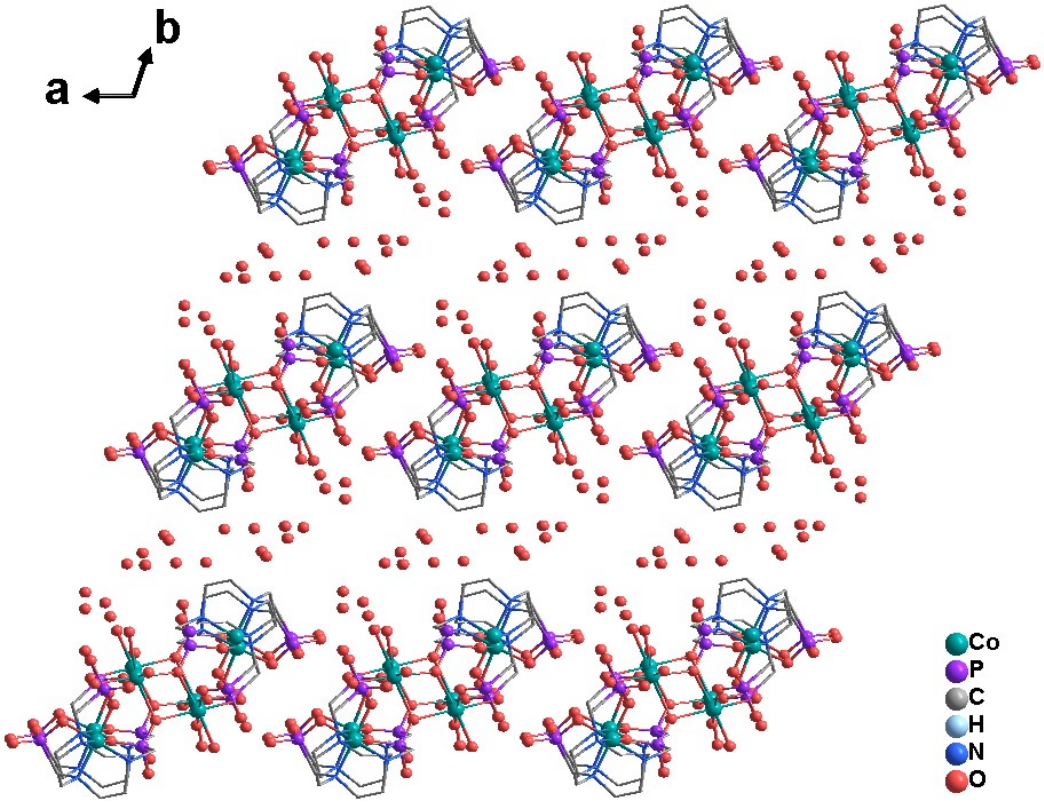

Figure S5. Packing diagram of **1·5H$_2$O**.

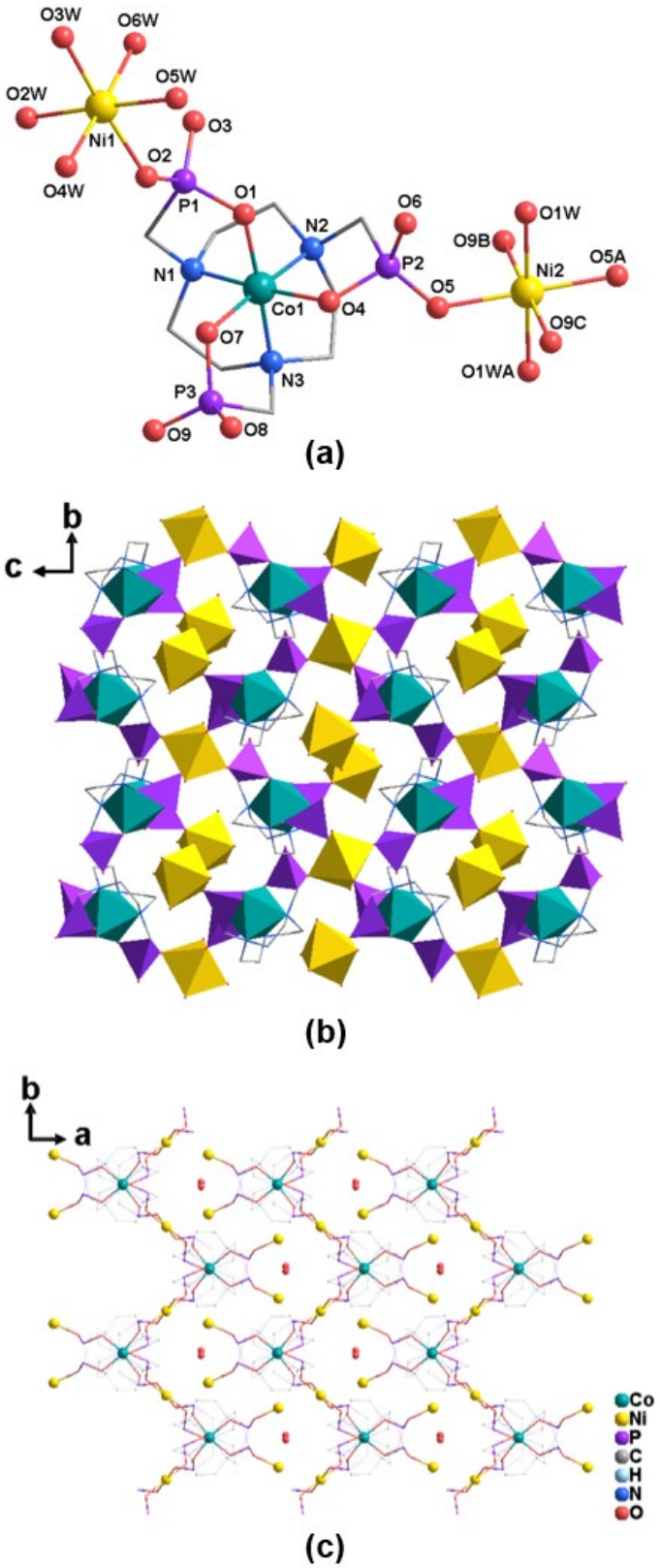

Figure S6. Crystal structure of **4**: (a) building unit, (b) one layer, and (c) packing diagram. Color codes for polyhedral: $\{NiO_6\}$ yellow, $\{CoO_3N_3\}$ cyan, and $\{PO_3C\}$ purple. All hydrogen atoms and coordinated water are omitted for clarity.

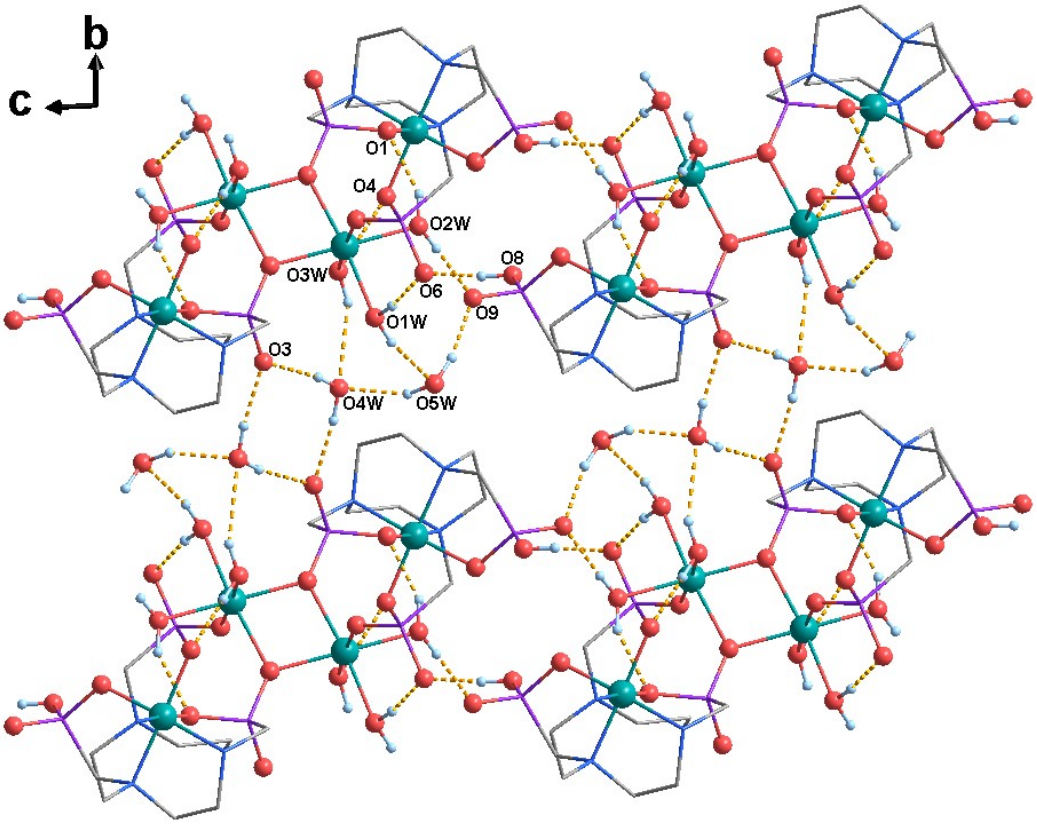

Figure S7. The H-bonding network of **1·2H$_2$O**.

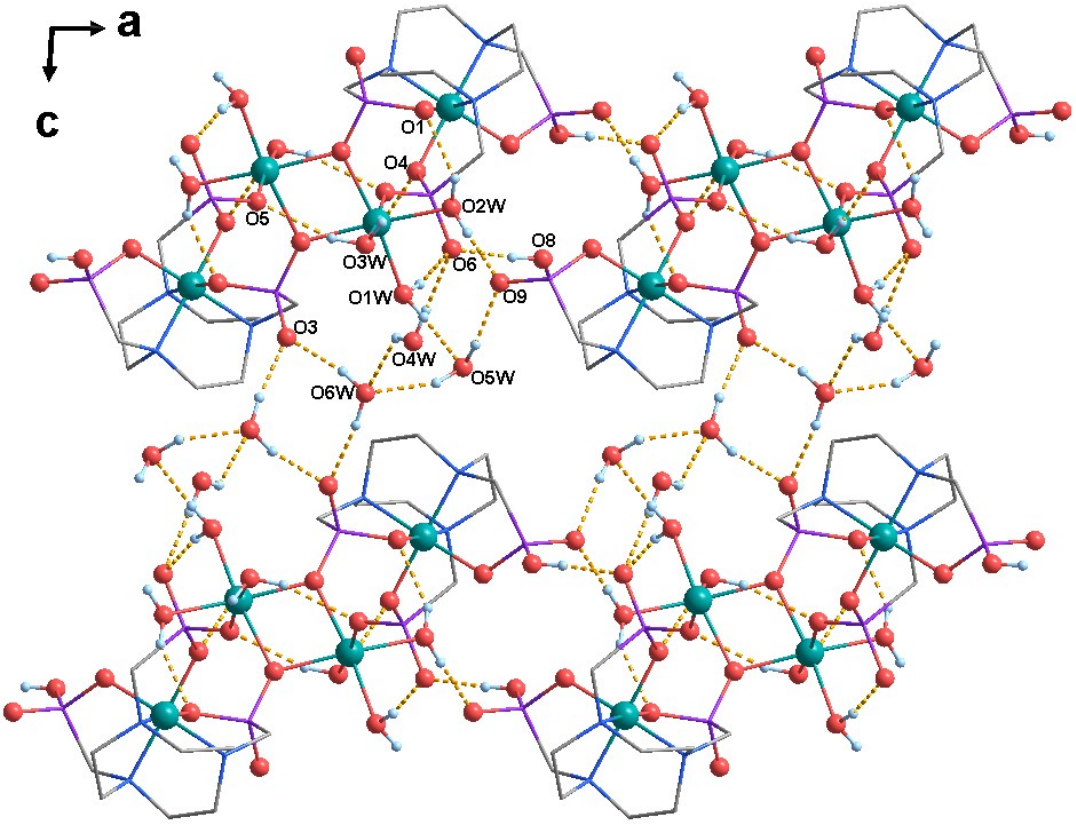

Figure S8. The H-bonding network of **1·3H$_2$O**.

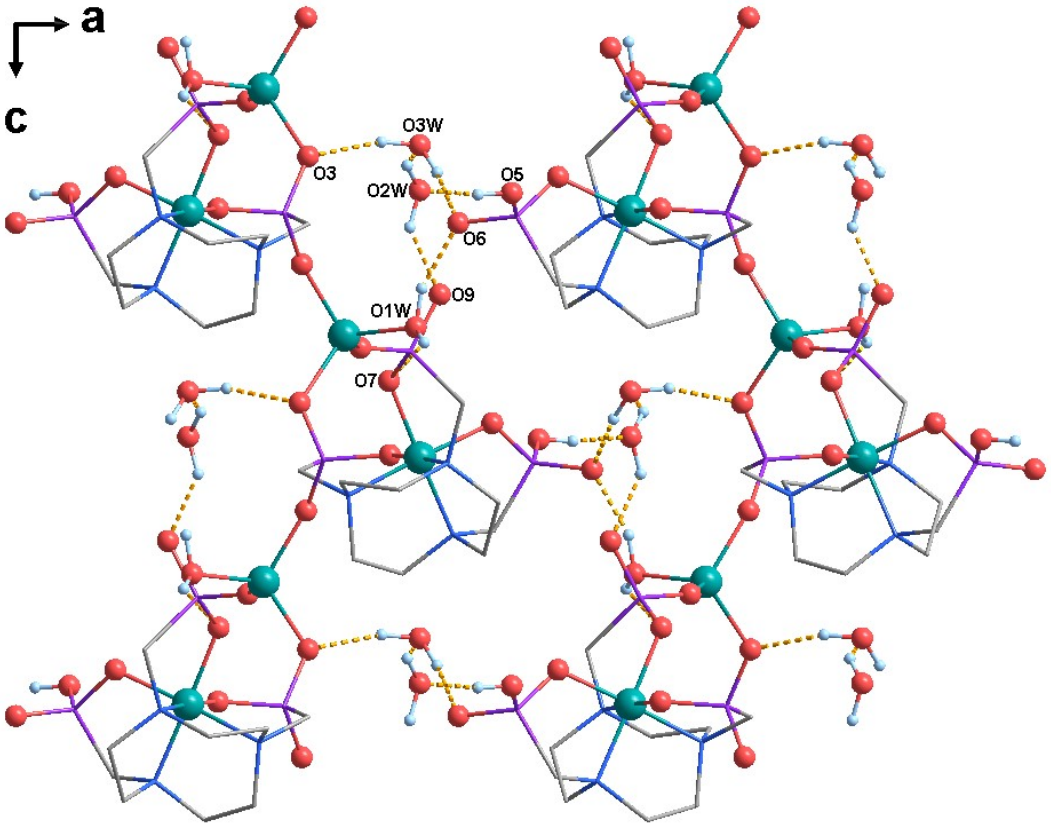

Figure S9. The H-bonding network of **2**.

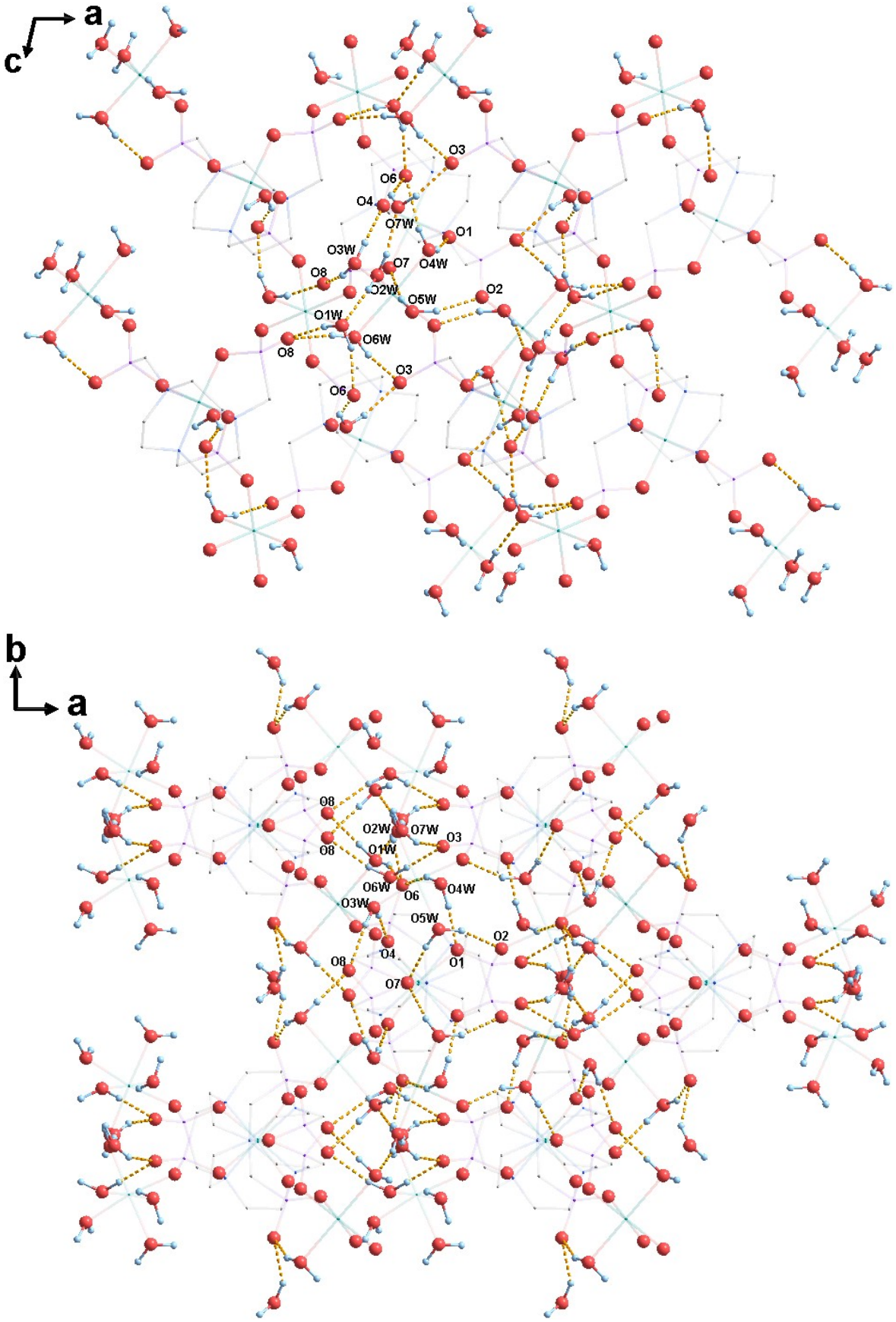

Figure S10. The H-bonding network of **3**.

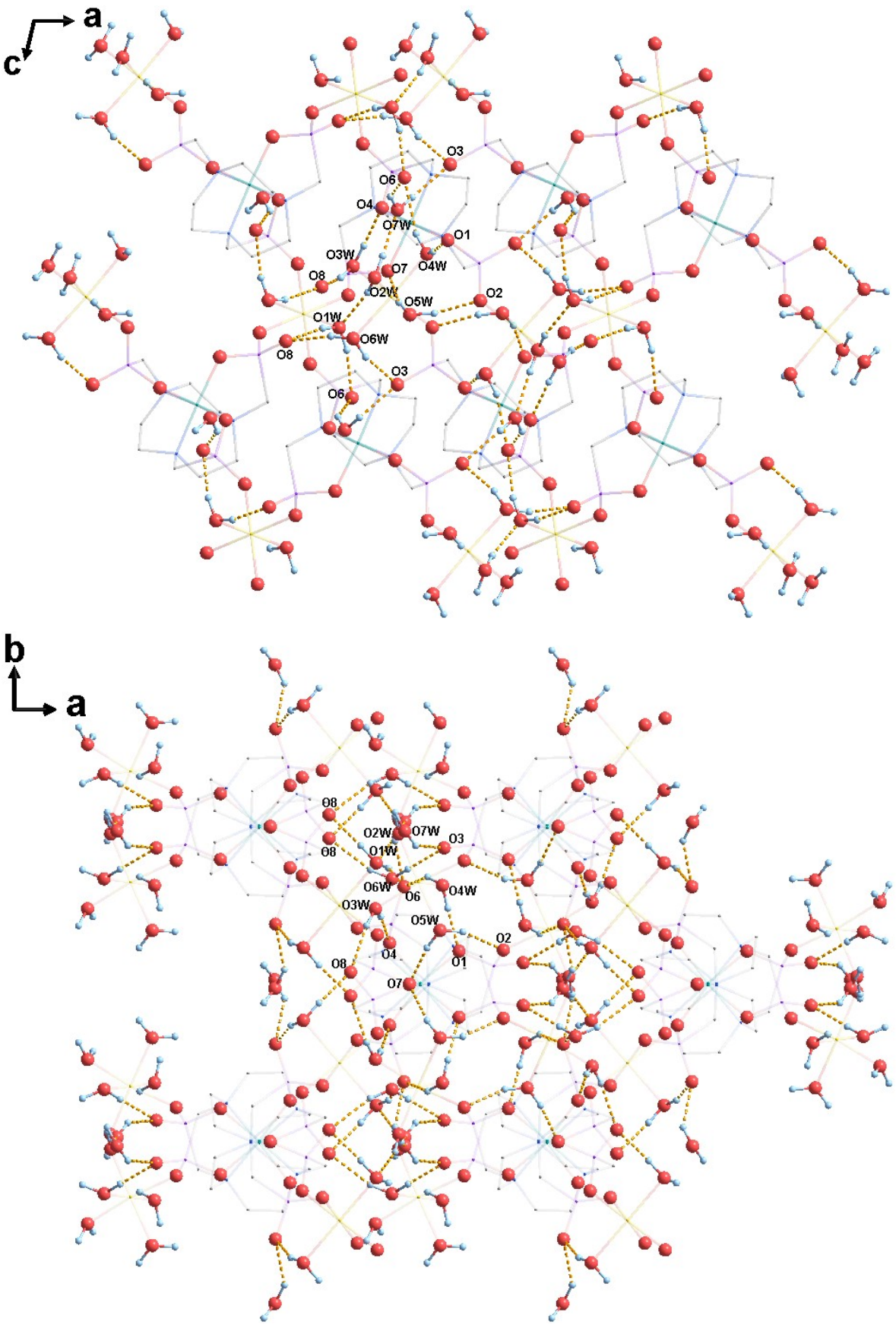

Figure S11. The H-bonding network of **4**.

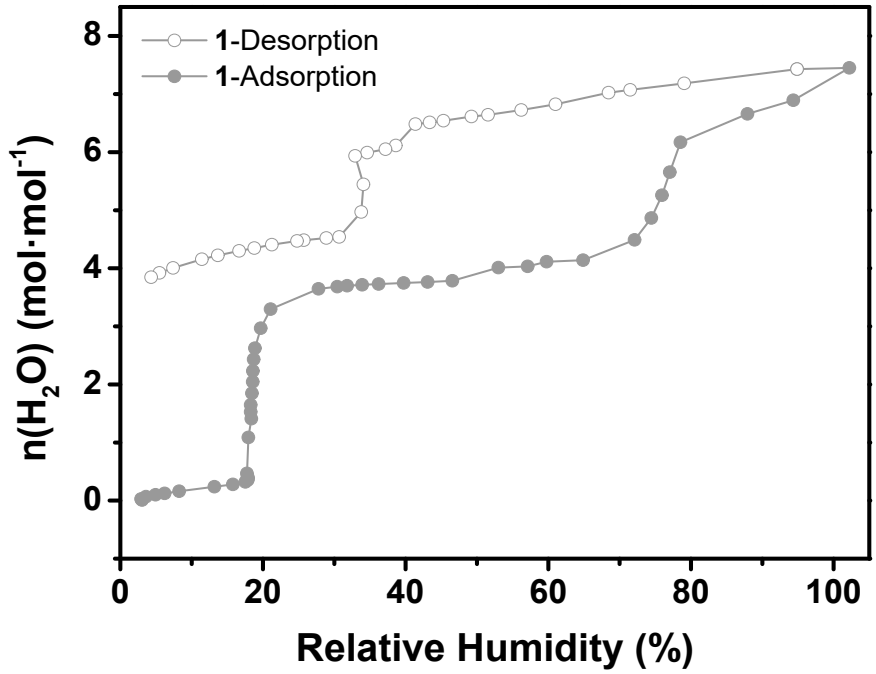

Figure S12. Water adsorption (filled circle) and desorption (open circle) isotherms of **1** at 25 °C.

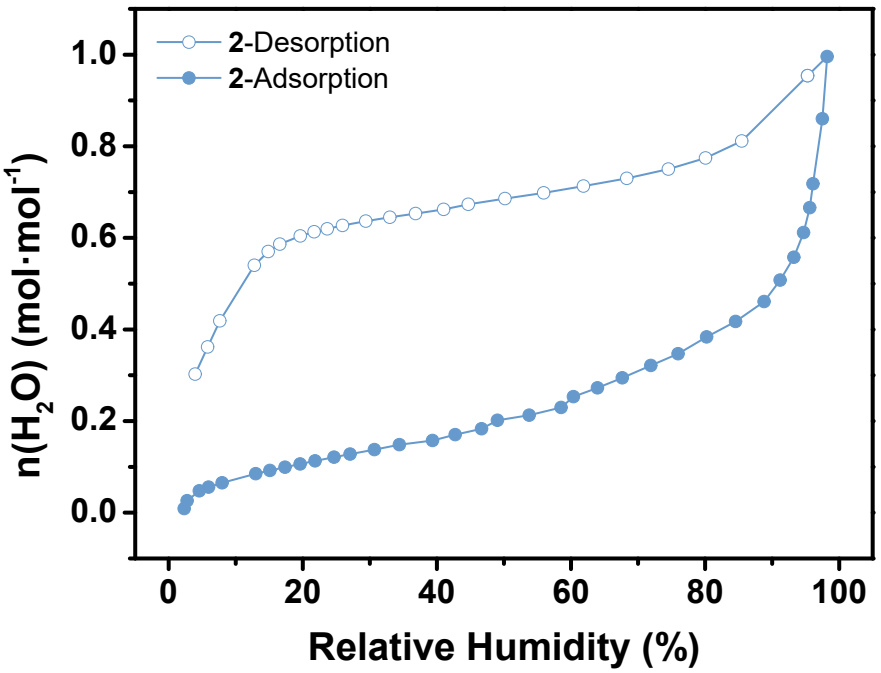

Figure S13. Water adsorption (filled circle) and desorption (open circle) isotherms of **2** at 25 °C.

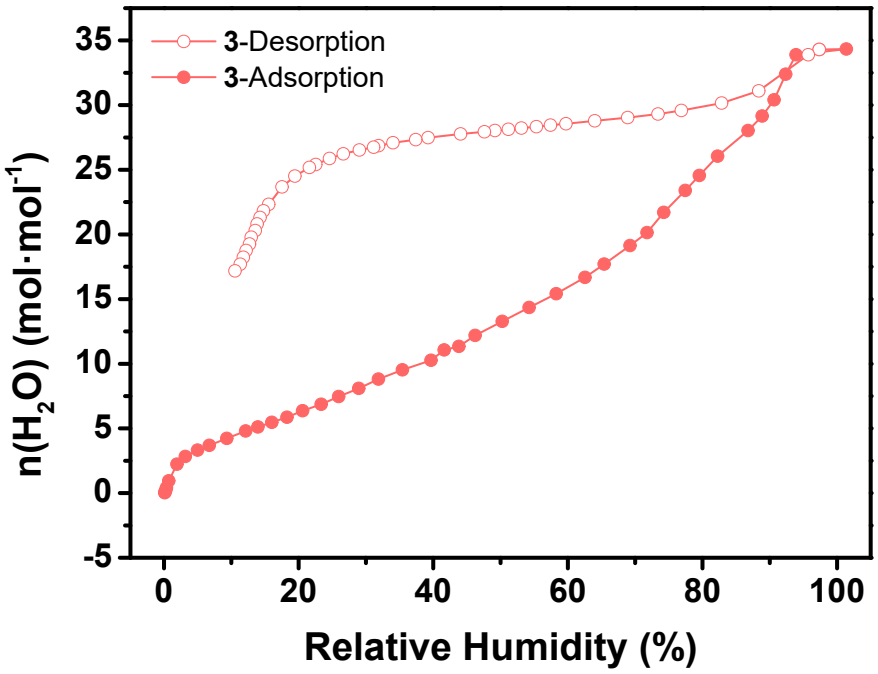

Figure S14. Water adsorption (filled circle) and desorption (open circle) isotherms of **3** at 25 °C.

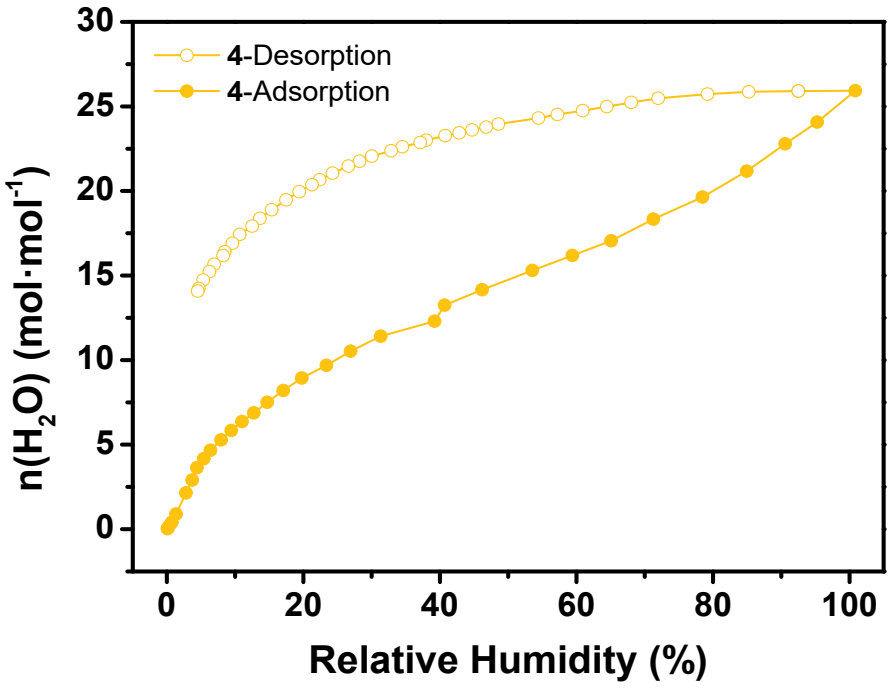

Figure S15. Water adsorption (filled circle) and desorption (open circle) isotherms of **4** at 25 °C.

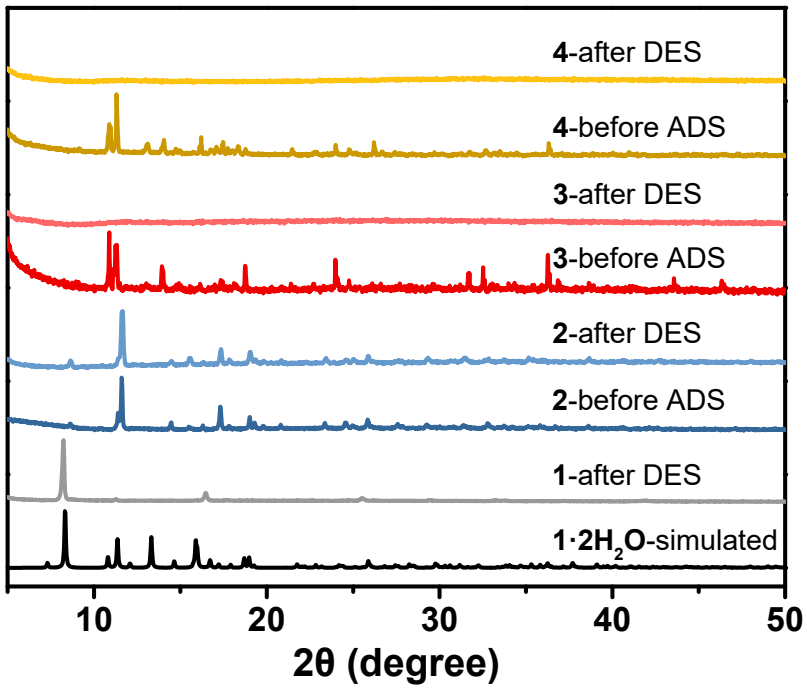

Figure S16. PXRD patterns for **1 - 4** after desorption.

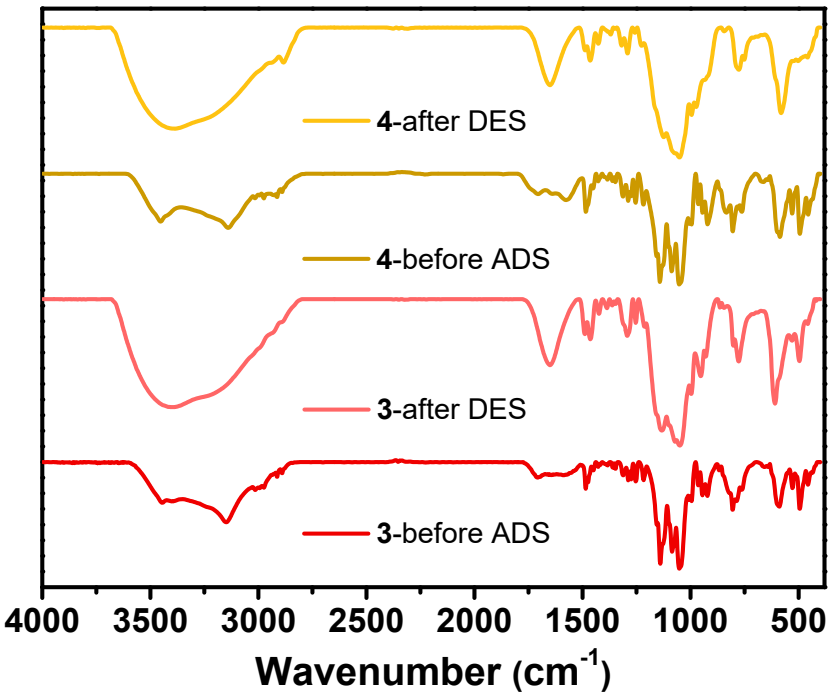

Figure S17. IR spectra of **3** and **4** after desorption.

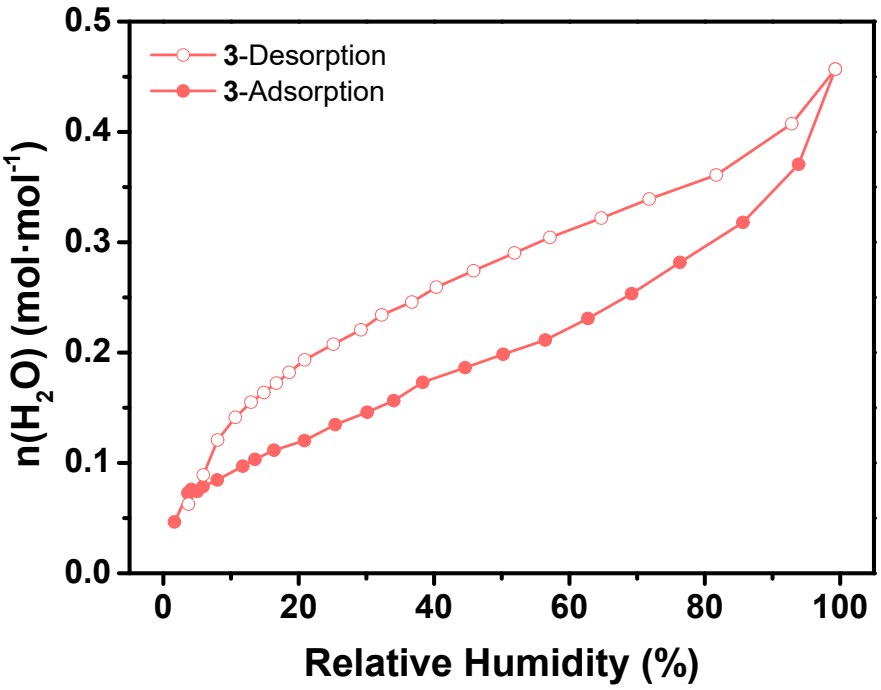

Figure S18. Water adsorption (filled circle) and desorption (open circle) isotherms of **3** (without thermal pretreatment) at 25 °C.

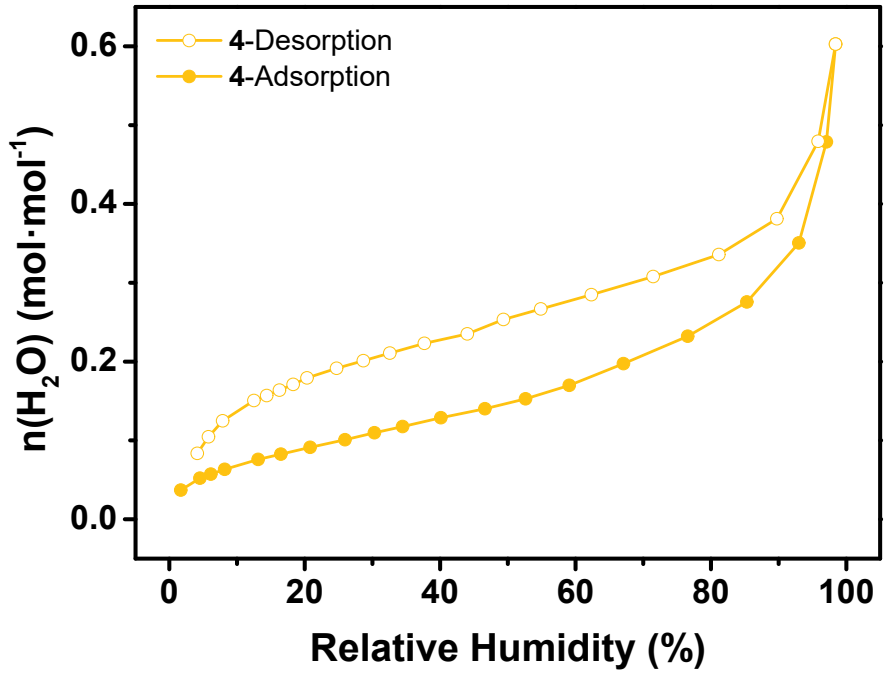

Figure S19. Water adsorption (filled circle) and desorption (open circle) isotherms of **4** (without thermal pretreatment) at 25 °C.

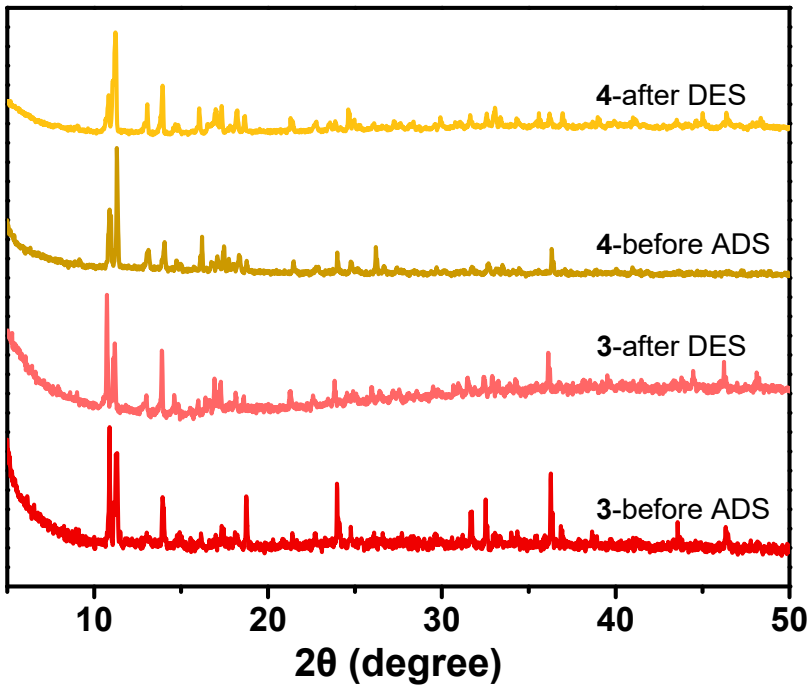

Figure S20. PXRD patterns for **3** and **4** after desorption without thermal pretreatment.

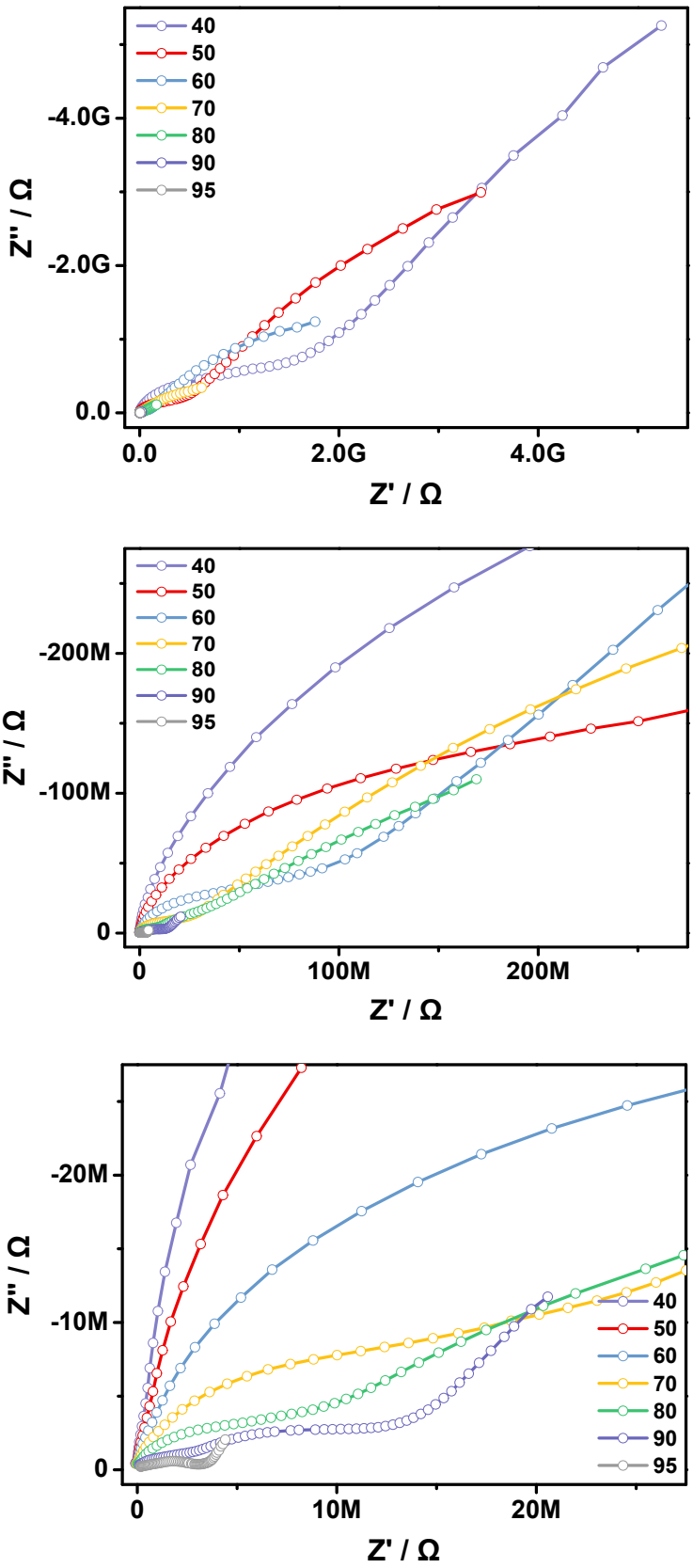

Figure S21. Nyquist plots for the pellet of **1** at 25 °C and various RH. Up: RH increases from 40 to 95%; Middle and Bottom: the enlarged view of the graph.

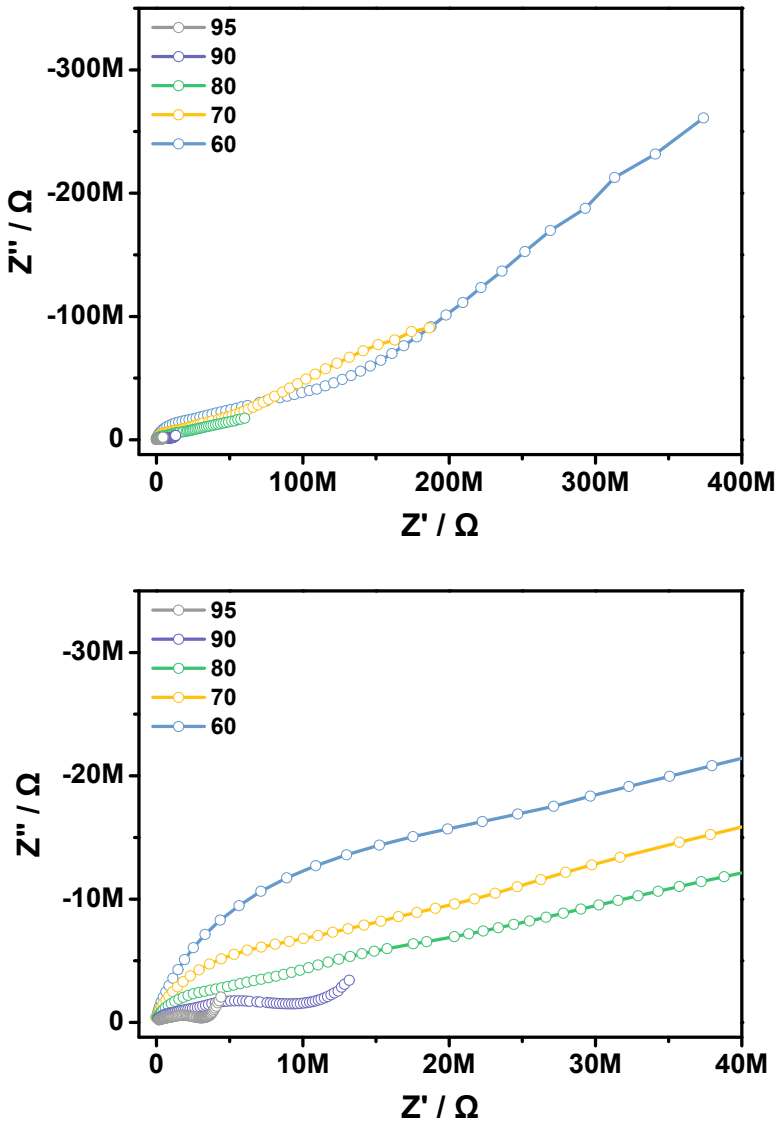

Figure S22. Nyquist plots for the pellet of compound **1** at 25 °C and various RH. Up: RH decreases from 95 to 60%; Bottom: the enlarged view of the graph.

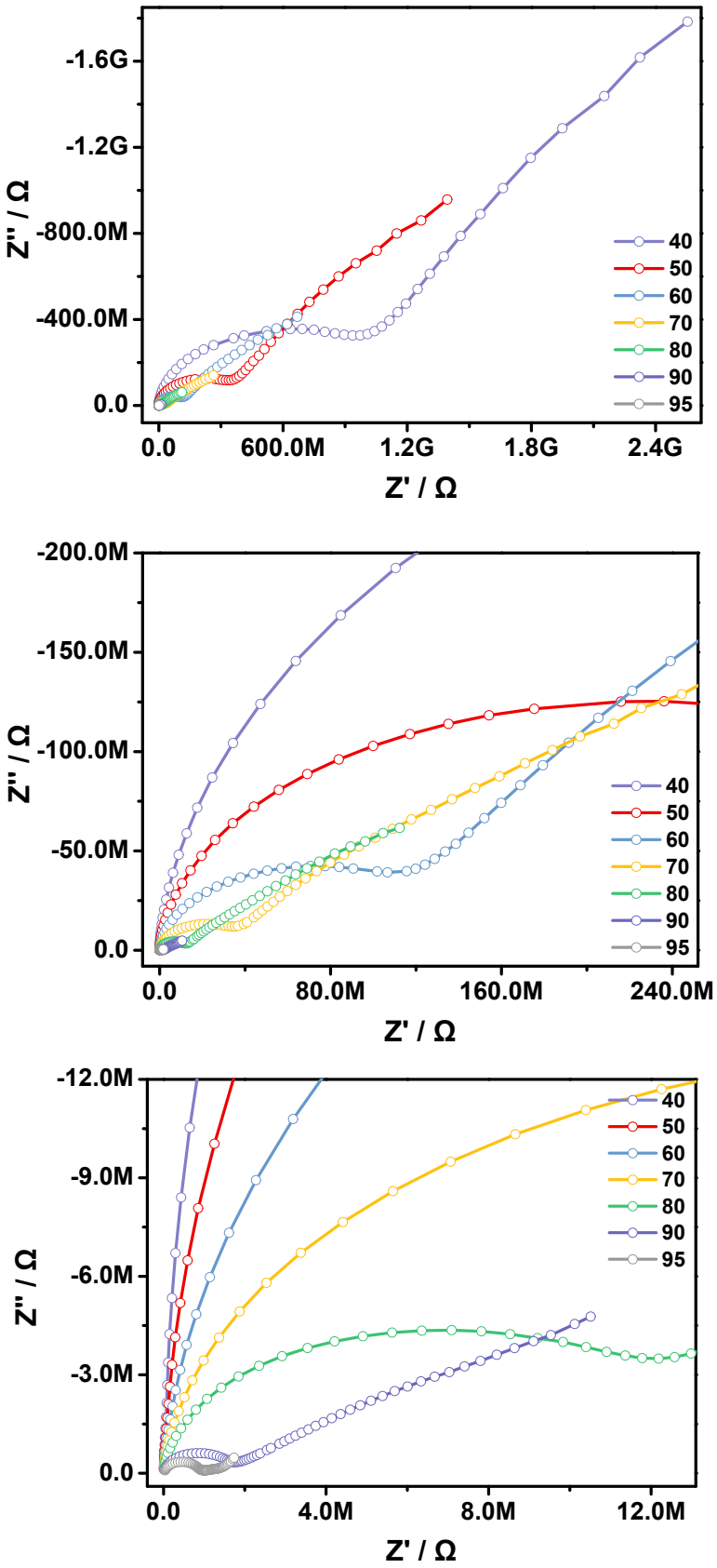

Figure S23. Nyquist plots for the pellet of compound **2** at 25 °C and various RH. Up: RH increases from 40 to 95%; Middle and Bottom: the enlarged view of the graph.

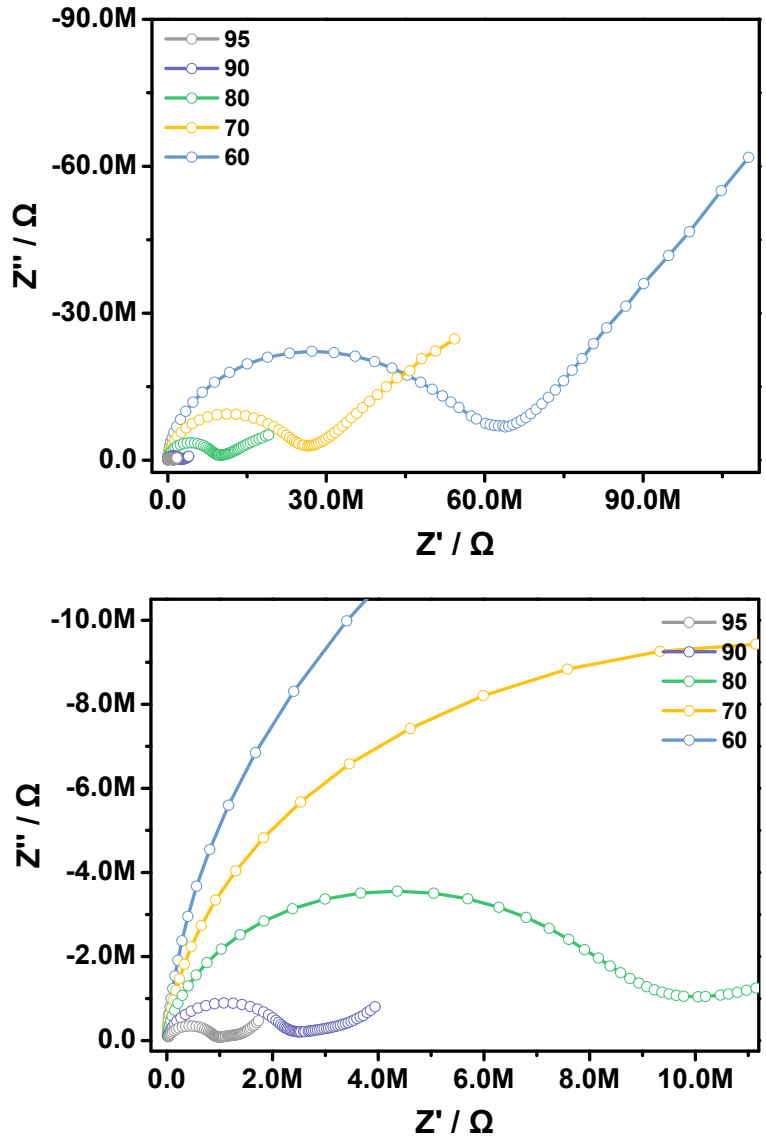

Figure S24. Nyquist plots for the pellet of compound **2** at 25 °C and various RH. Up: RH decreases from 95 to 60%; Bottom: the enlarged view of the graph.

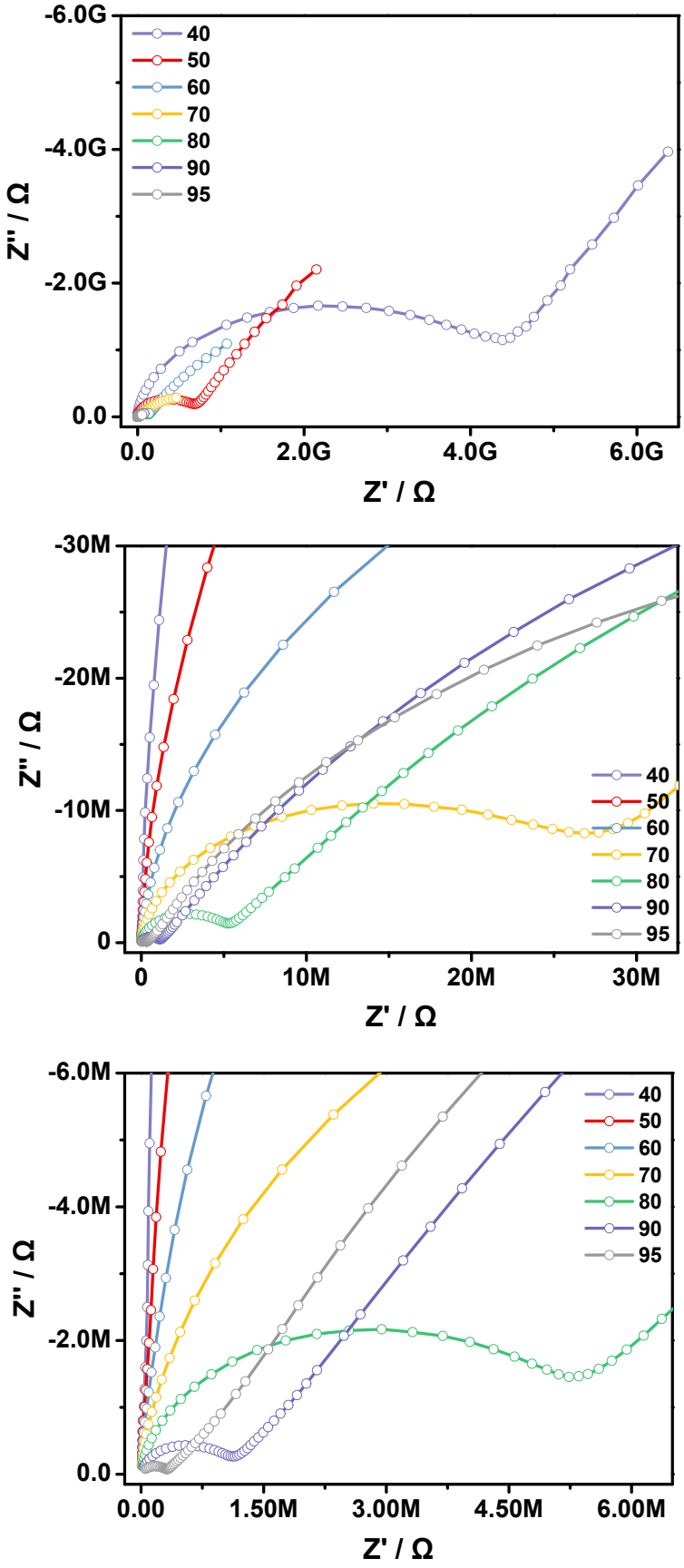

Figure S25. Nyquist plots for the pellet of compound **3** at 25 °C and various RH. Up: RH increases from 40 to 95%; Middle and Bottom: the enlarged view of the graph.

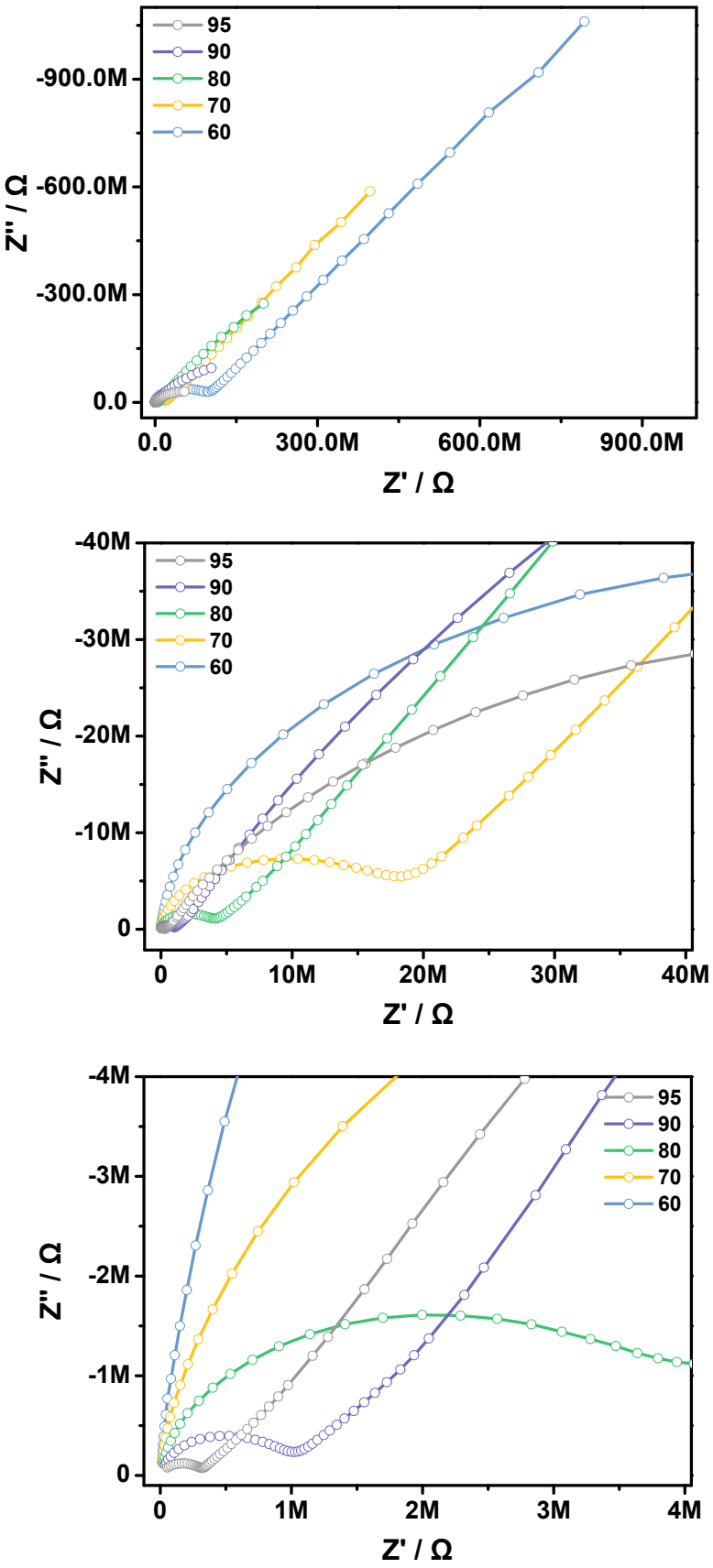

Figure S26. Nyquist plots for the pellet of compound **3** at 25 °C and various RH. Up: RH decreases from 95 to 60%; Middle and Bottom: the enlarged view of the graph.

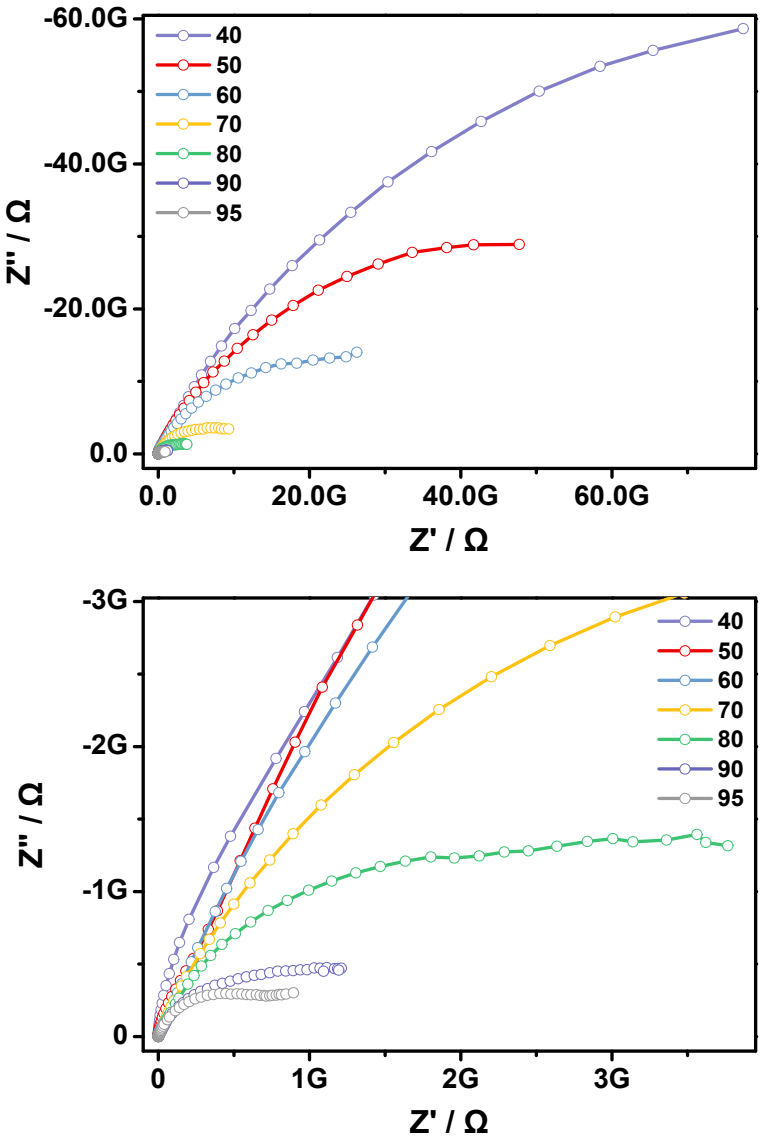

Figure S27. Nyquist plots for the pellet of compound **4** at 25 °C and various RH. Up: RH increases from 40 to 95%; Bottom: the enlarged view of the graph.

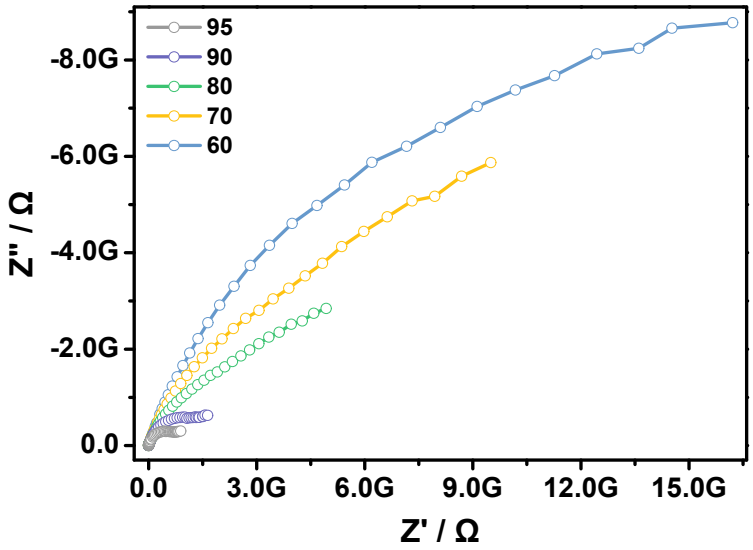

Figure S28. Nyquist plots for the pellet of compound **4** at 25 °C and various RH (from 95 to 60%).

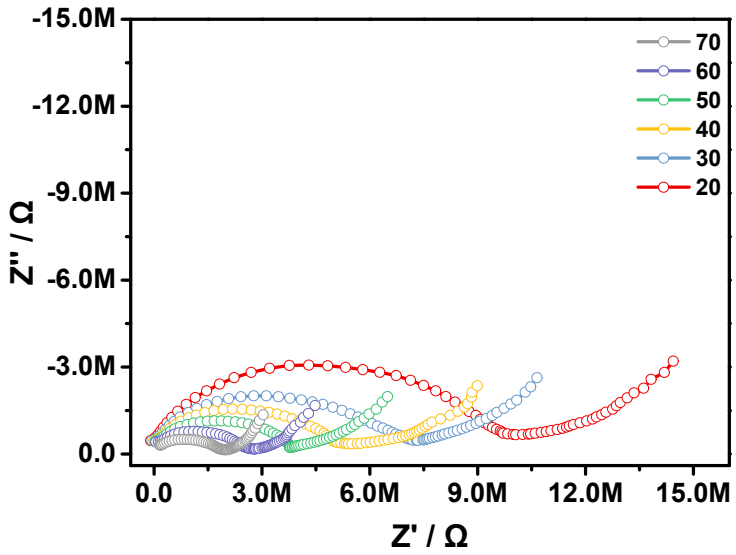

Figure S29. Nyquist plots for the pellet of **1** at 95% RH and various temperatures (from 70 to 20 °C).

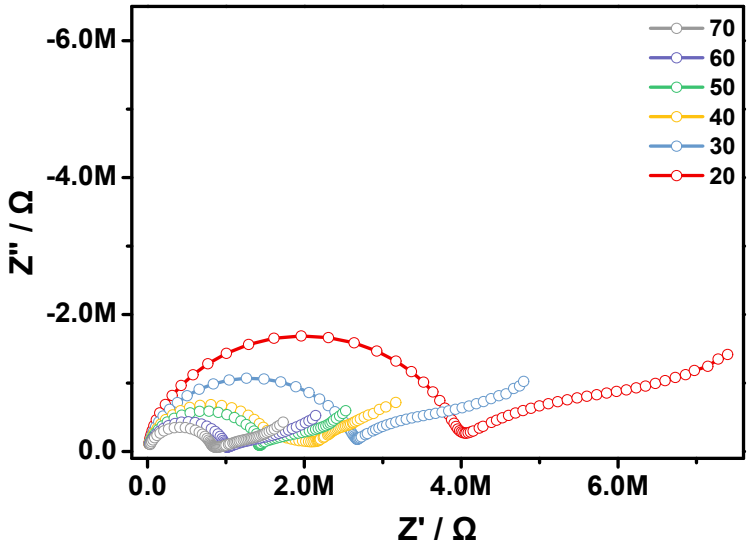

Figure S30. Nyquist plots for the pellet of **2** at 95% RH and various temperatures (from 70 to 20 °C).

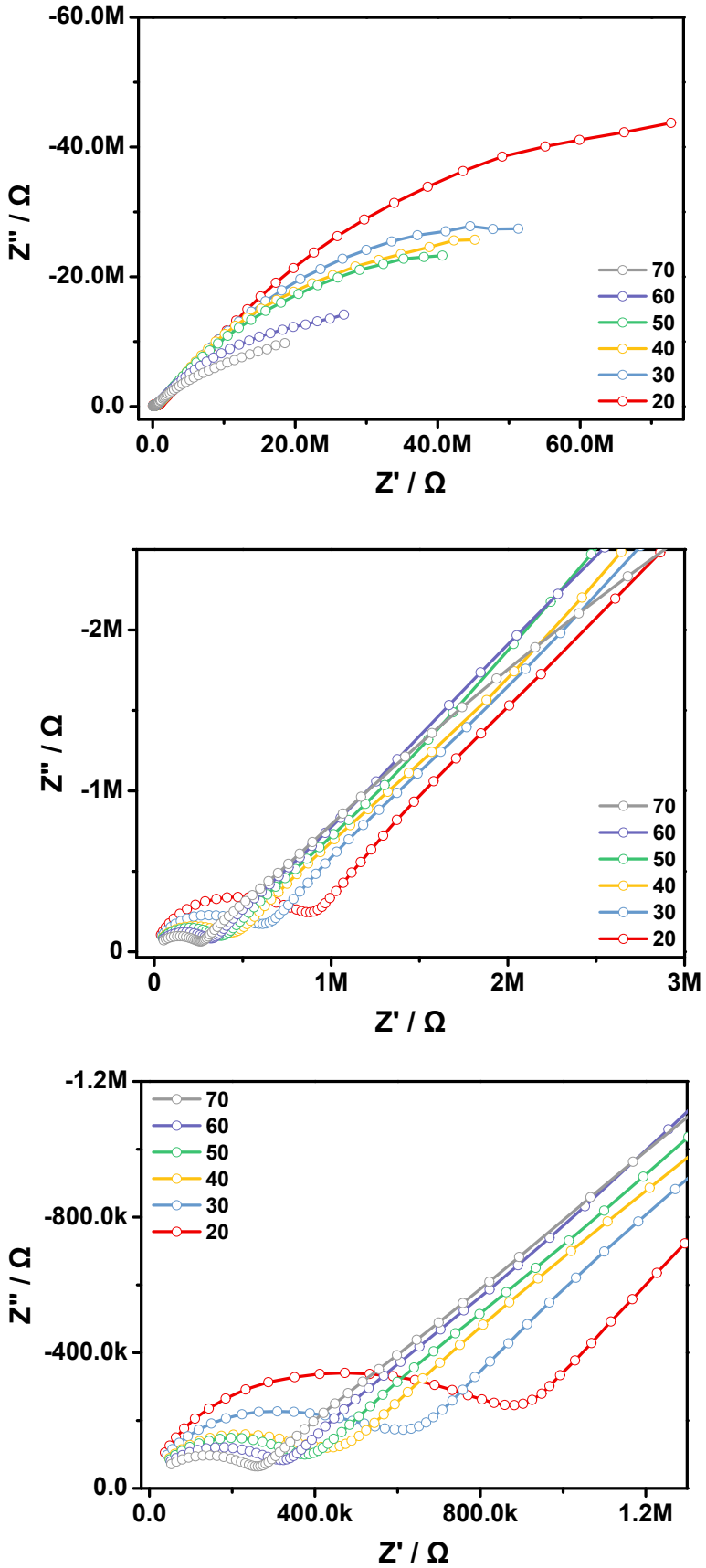

Figure S31. Nyquist plots for the pellet of **3** at 95% RH and various temperatures. Up: temperature decreases from 70 to 20 °C; Middle and Bottom: the enlarged view of the graph.

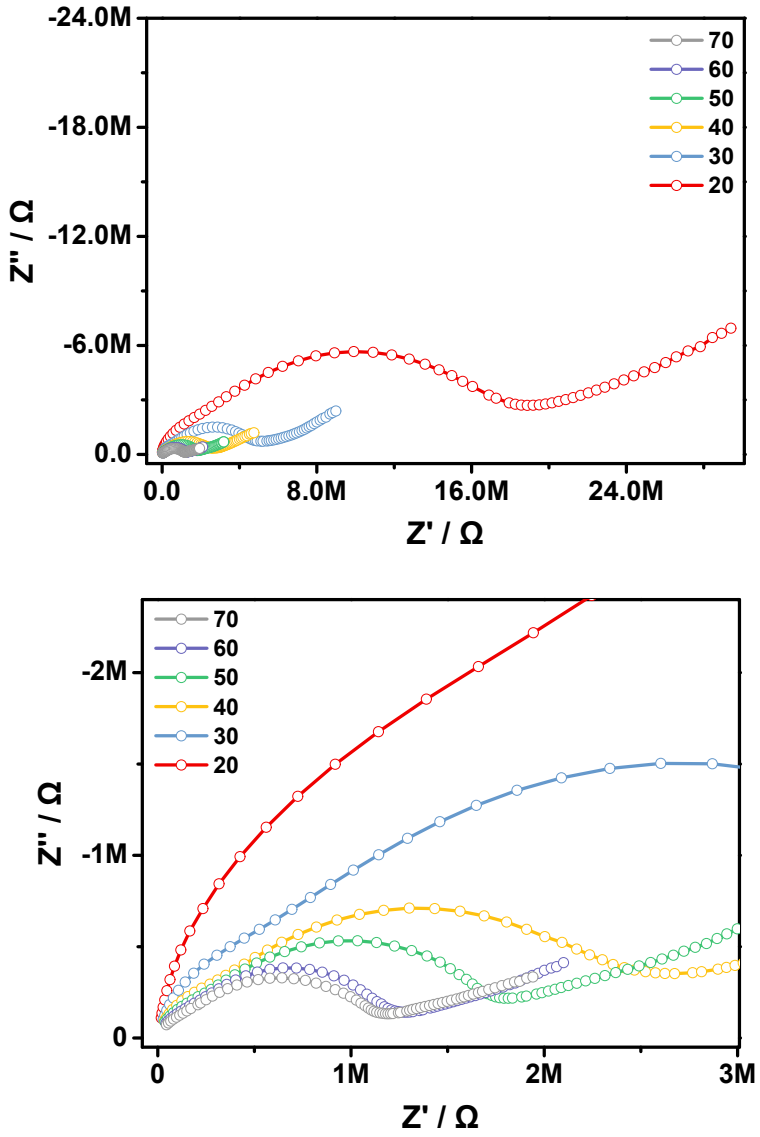

Figure S32. Nyquist plots for the pellet of **4** at 95% RH and various temperatures. Up: temperature decreases from 70 to 20 °C; Bottom: the enlarged view of the graph.

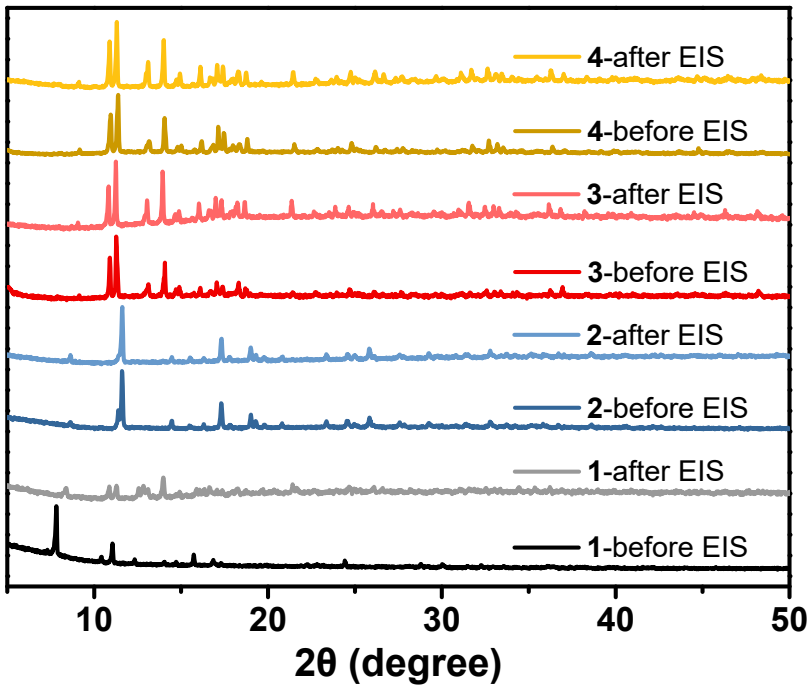

Figure S33. PXRD patterns for **1 - 4** after AC impedance measurements.

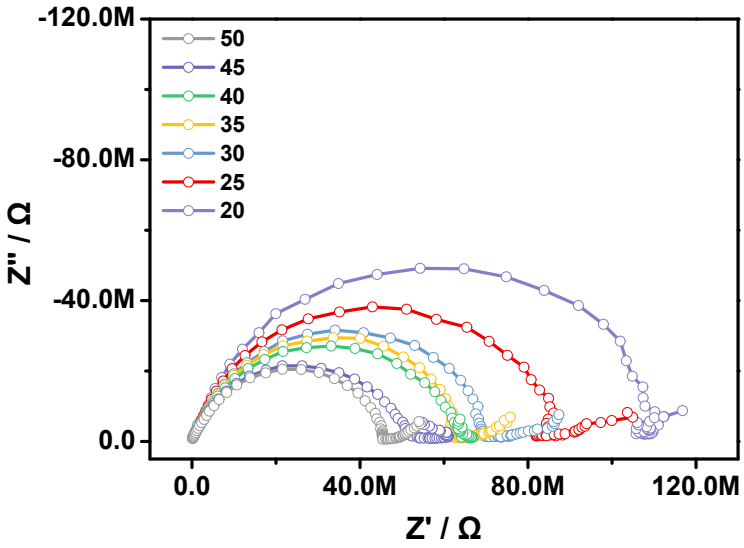

Figure S34. Nyquist plots for a single crystal of **3** at 95% RH and various temperatures (from 50 to 20 °C).

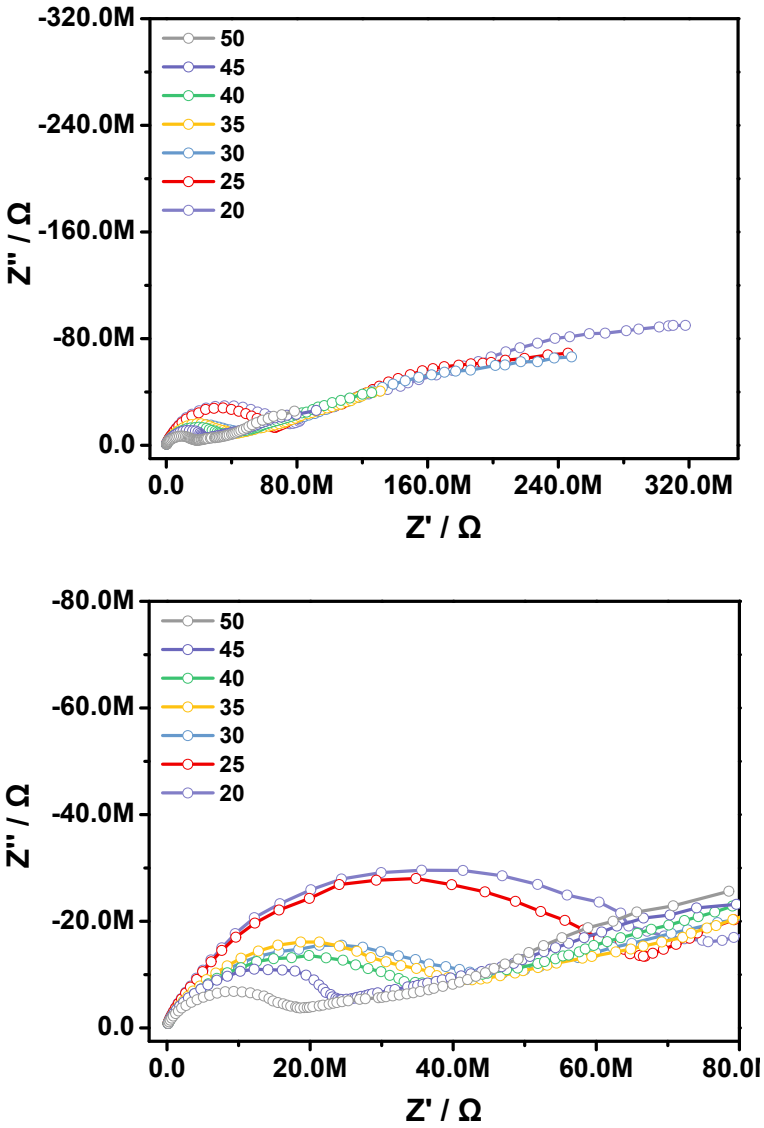

Figure S35. Nyquist plots for a single crystal of **4** at 95% RH and various temperatures. Up: temperature decreases from 50 to 20 °C; Bottom: the enlarged view of the graph.