Surpporting Information

Water-Controlled Synthesis and Single-Crystal Structural Transformations of Cyanide-Bridged W(IV)−Ni(II) Molecular Wheel Complex and 3D Networks

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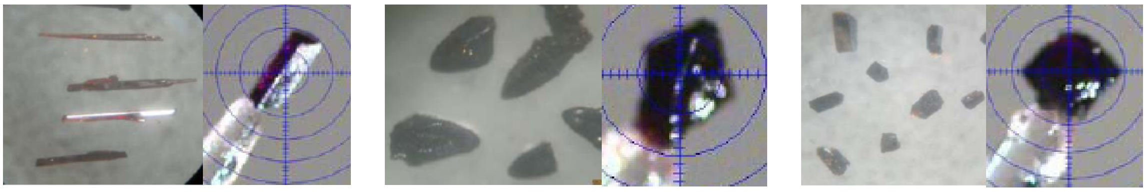
Experimental Section

Syntheses of complexes 1-3

Complex 1: A solution containing $K_4[W^{IV}(CN)_8]$ (0.1 mmol, 54.8 mg) with or without 18-Crown-6 (0.4 mmol, 105.6 mg) dissolved in a mixture solvent distilled water and DMF (5 mL, V:V = 1:1) was laid in the bottom of a tube, upon which a mixture solvent of water and CH_3CN with a ratio of 1:2 was carefully added. Then, a solution of $[Ni(L)(H_2O)_2][ClO_4]_2$ (L = 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene) (0.2 mmol, 103.4 mg) in 5 mL CH_3CN was carefully added to the top of the solvent layer above formed. The tube was undisturbed in the dark and needle-like single crystals suitable for X-ray diffraction were obtained about one week later, which were then collected by filtration and dried in air. Yield: 47.6 mg (ca. 52%). Anal Calc. for $C_{228}H_{352}N_{96}Ni_{12}O_{42}W_6$: C, 39.59; H, 5.12; N, 19.44. Found: C, 39.41; H, 5.16; N, 19.38. Selected IR frequencies (KBr disk, cm^{-1}): 2105 (vs, $\nu C\equiv N$), 2144 (w, $\nu C\equiv N$).

Complex 2: In a single tube, a solution containing $K_4[W(CN)_8]$ (0.1 mmol, 54.8 mg) and 18-Crown-6 (0.4 mmol, 105.6 mg) dissolved in a mixed solvent CH_3CN and DMF (5 mL, V:V = 1:1) was laid on the bottom and solvent anhydrous CH_3CN as a separate layer was laid carefully on the top. Then, a solution of $[Ni(L)(H_2O)_2][ClO_4]_2$ (0.2 mmol, 103.4 mg) in 5 mL CH_3CN was added the above formed system. The tube was undisturbed in the dark and flower-like crystals with diamond-like leaves suitable for X-ray diffraction were obtained about one week later, which were then collected by filtration and dried in air. Yield: 6.5 mg (ca. 6%). Anal Calc. for $C_{38}H_{44}N_{16}Ni_2W$: C, 44.48; H, 4.32; N, 21.84. Found: C, 44.30; H, 4.41; N, 21.69. Selected IR frequencies (KBr disk, cm^{-1}): 2105 (vs, νC≡N).

Complex 3: In a single tube, a solution containing $K_4[W^{IV}(CN)_8]$ (0.1 mmol, 54.8 mg) with 18-Crown-6 (0.2 mmol, 105.6 mg) dissolved in a mixture solvent of CH_3CN (5 mL) and water (0.5 mL) was laid in the bottom of a tube, upon which solvent CH_3CN was carefully added. Then, a solution of $[Ni(L)(H_2O)_2][ClO_4]_2$ (0.2 mmol, 103.4 mg) in 5 mL CH_3CN was carefully added to the top of the solvent layer above formed. The tube was undisturbed in the dark and block single crystals suitable for X-ray diffraction were obtained about several days later, which were then manually collected immediately for the crystal structural analysis. The single crystals of this complex are not stable and can transform to complex **1** after several days. Even so, the repeated single X-ray diffraction analysis evidenced that the formation of complex **3** is undoubtedly.



Complex **1** Complex **2** Complex **3**

Figure S1. Single crystals of complexes **1-3** with very different shapes synthesized by water-controlled synthesis (the pictures were obtained by common camera under microscope (right) and by instrument of single X-ray diffraction (left)).

Water-controlled two-steps single-crystal transformations

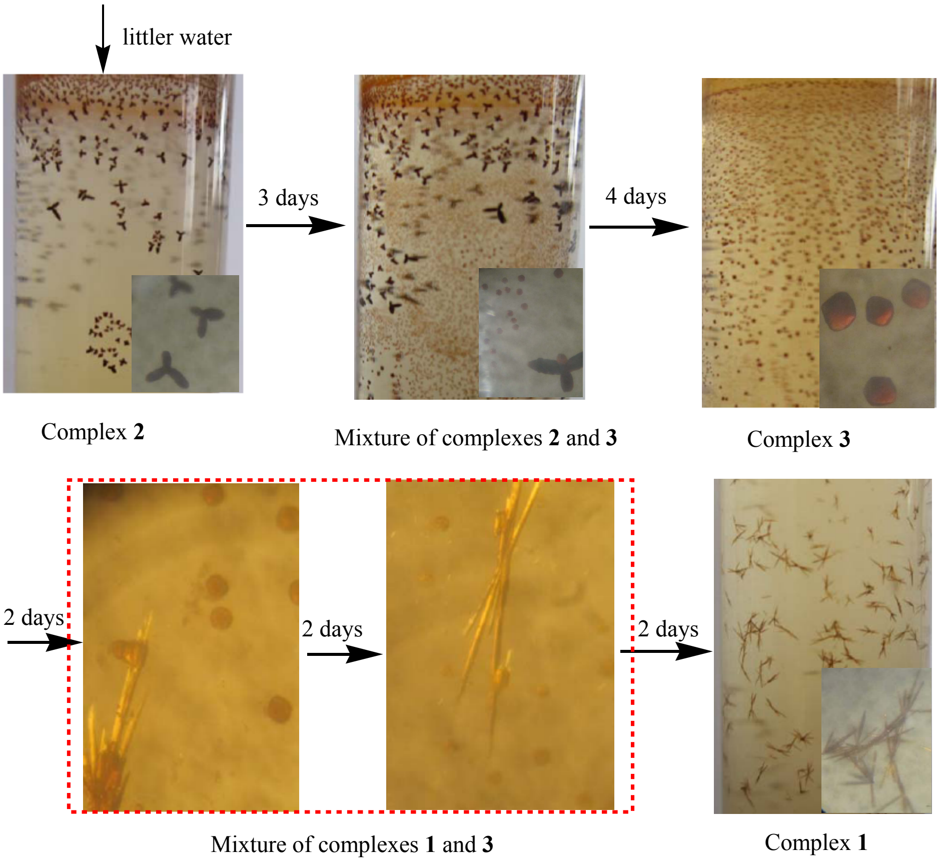
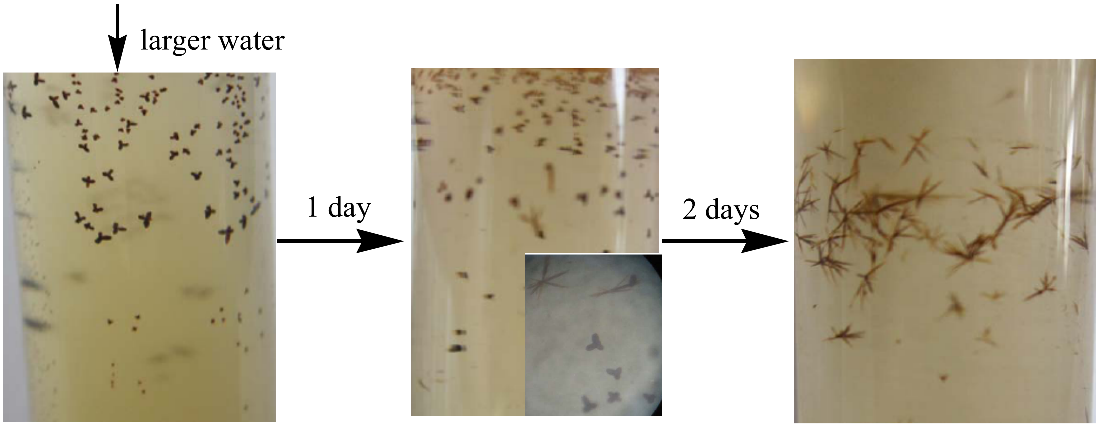


Figure S2. Water-controlled single-crystal transformation by two-steps (the pictures were obtained in the single tube by camera under common condition or microscope (right bottom)).

Following the procedure for the preparation of complex **2**, very little water (ca. 0.5 mL) was slowly added into the single tube. Firstly, there were only some flower-like with diamond-like leaves brown single crystals of complex **2**, then the single crystals of complex **2** became small and some block brown single crystals of complex **3** started to deposit on the tube wall after several days, which were then manually collected immediately for the structural analysis. The single crystals of complex **3** can keep about several days after which they transformed to needle-like single crystals of complex **1** completely (Figure S2). The procedure of two-steps single-crystal transformation from complex **2** to complex **1** to complex **3** can be judged easily by the change of their crystal shape and the process also was traced by the determination of cell parameters again and again by single X-ray diffraction analysis as well as the powder XRD analysis. It is note that it is difficult to separate fully pure sample of this complex because there is still have some complex **1** and/or complex **2** as reflected by XRD pattern even though the sample have been separated by manually under microscope before analysis.

Water-controlled one-step single-crystal transformation

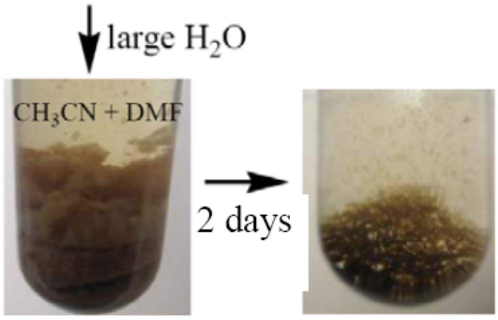


Complex **2** Mixture of complexes **1** and **2** Complex **1**

Figure S3. Water-controlled one step single-crystal transformation (the pictures were obtained in the single tube by camera under common condition or microscope (right bottom)).

The procedure is similar to the above described two-steps single-crystal transformation, the added amount of water was about 5 mL. After one day, diamond-like single crystals of complex **2** began becoming bad the needle-like micro single crystal of complex **1** deposited. After about seven days the there are no obvious single crystals of complex **2** and nearly uniform needle-like single crystals of complexes **1** (Figure S3). There are no obvious block single crystals of complexes **3** during this process in several repeated experiments.

Water-controlled quick amorphous to single-crystal transformation



Amouphous product by mixing $K_4[W(CN)_8]$ and $[Ni(L)(H_2O)_2](ClO_4)_2$

single crystals of complex **1**

Figure S4. Water-controlled quick amorphous to single-crystal transformation.

Amorphous sample was obtained easily by mixing the two building blocks of $K_4[W(CN)_8]$ (0.1 mmol, 54.8 mg) and 18-Crown-6 (0.4 mmol, 105.6 mg) dissolved in anhydrous CH_3CN and DMF (5 mL, V:V = 1:1) and a solution of $[Ni(L)(H_2O)_2][ClO_4]_2$ (0.2 mmol, 103.4 mg) in 5 mL CH_3CN. Then, about 5 mL of water was added into the mixture, uniform needle-like crystals complex **1** were obtained after about two days (Figure S4). It is noteworthy that structure of the amorphous sample is uncertain, which may be complex **2** or other compounds even mixture of different compounds. The structure of the final crystal was determined by the cell parameters by single X-ray diffraction analysis and XRD analysis.

Water-controlled slow amorphous to single-crystal transformation

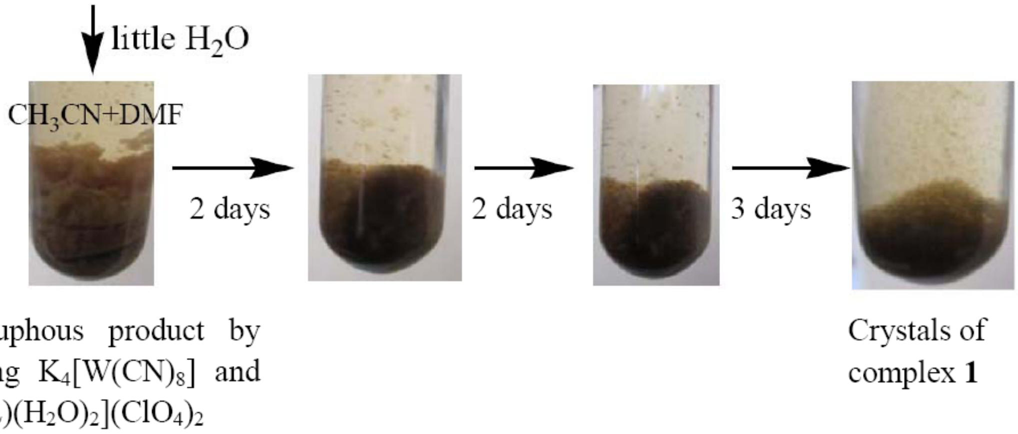


Figure S5. Water-controlled slow amorphous to single-crystal transformation.

Amorphous samples were obtained easily by mixing the two building blocks of $K_4[W(CN)_8]$ (0.1 mmol, 54.8 mg) and 18-Crown-6 (0.4 mmol, 105.6 mg) dissolved in anhydrous CH_3CN and DMF (5 mL, V:V = 1:1) and a solution of $[Ni(L)(H_2O)_2][ClO_4]_2$ (0.2 mmol, 103.4 mg) in 5 mL CH_3CN. Then, about 0.5 mL of water was added into the mixture, very small single crystals started to deposit after about four days. Uniform small needle-like crystals complex **1** accompanying small quantity of amorphous unknown samples were obtained after one week (Figure S5). It is worthy noting it is difficult to determine the structure of the small crystal during the intermediate course. The structure of the final needle-like crystal was determined by the cell parameters by single X-ray diffraction analysis.

Description of the single crystal structures of complexes 1-3

Complex **1** is characterized structurally as octadecanuclear cluster containing a 36-membered macrocycle. Each $[W^{IV}(CN)_8]^{4-}$ module presenting a bicapped trigonal prism conformation link three $[Ni(L)]^{2+}$ units, in which two are bridged by $[W^{IV}(CN)_8]^{4-}$ in the macrocycle and the other one hung out of the ring is terminal with the additional axial position occupied by a O atom of H_2O. Both of the two types of Ni(II) ions are six coordinated, and the bond parameters around them can prove their slightly distorted octahedron geometry. The Ni-N_{CN} bond lengths on the ring are 2.108(5) and 2.105(5) Å, respectively, slightly longer than that in the terminal one with the value 2.054(5) Å. The angles between the bridging cyanide groups on the ring around the W atom is 79.7(2) °, while the angles of C1-W1-C2 and C1-W1-C3 are 144.2(2) and 124.1(2) °, respectively.

Complex **2** structurally characterized as three-dimensional network with the highest symmetry space group *Ia-3d*. Two pairs of cyanide groups in the two vertical tetragonal pyramid around the W atom with a almost *trans* position are employed to link four $[Ni(L)]^{2+}$ units, which can be further linked to another $[W^{IV}(CN)_8]^{4-}$ to form 3D structure. The Ni-N_{CN} bond length is 2.05(2) Å, slightly shorter than those corresponding distances found in complex 1. The angles between the bridging cyanide groups are 96.1(5) and 141.9(15)°, respectively, obviously different from those angles in complex **1**.

Complex **3** can also be structurally described as three-dimensional network, but crystallizes in monoclinic space group *Cc*. Each $[W^{IV}(CN)_8]^{4-}$ ion also connect four $[Ni(L)]^{2+}$ units through four bridging cyanide groups. However, inspection carefully the linkage conformation of complexes **2** and **3** can find the difference for the cyanide bridges used. In complex **2**, two pairs of cyanide groups in the two vertical tetragonal pyramid are used as bridges, which can give comparative higher symmetric structure. Different from that in complex **2**, three and one cyanide group(s) in the two vertical tetragonal pyramid acting as bridges link four $[Ni(L)]^{2+}$ units in complex **3**, respectively, therefore forming an other type of three-dimensional structure. The bond parameters around the Ni atom and W atom are almost same to those in complex **2**, except the $C_{bridging\text{-}CN}$-W-$C_{bridging\text{-}CN}$ angles, for which in complex **3** are 74.2(10), 71.2(10), 114.8(10), 144.8(9), 80.4(9) and 143.0(10) °, respectively.

Table 1. Selected bond distances (Å) and angles (°) of complex **1**.

W(1)–C(1)	2.157(6)	W(1)–C(8)	2.166(6)	Ni(2) –N(2)	2.155(5)
W(1)–C(2)	2.155(6)	Ni(1) –N(1)	2.054(5)	Ni(2) –N(3)	2.108(5)
W(1)–C(3)	2.173(6)	Ni(1) –N(9)	1.949(5)	Ni(2) –N(13)	1.955(5)
W(1)–C(4)	2.181(6)	Ni(1) –N(10)	2.037(5)	Ni(2) –N(14)	2.040(5)
W(1)–C(5)	2.168(6)	Ni(1) –N(11)	2.006(5)	Ni(2) –N(15)	2.024(5)
W(1)–C(6)	2.166(7)	Ni(1) –N(12)	2.058(5)	Ni(2) –N(16)	2.052(5)
W(1)–C(7)	2.154(6)	Ni(1) –O(1)	2.214(4)		
W(1)–C(1) –N(1)	179.6(7)	W(1)–C(1) –N(5)	178.0(5)	Ni(1) –N(1)–C(1)	165.2(5)
W(1)–C(2) –N(2)	174.9(5)	W(1)–C(2) –N(6)	179.2(6)	Ni(2) –N(2)–C(2)	145.1(4)
W(1)–C(2) –N(3)	178.9(5)	W(1)–C(2) –N(7)	177.3(5)	Ni(2) –N(3)–C(3)	165.4(5)
W(1)–C(2) –N(4)	179.0(6)	W(1)–C(2) –N(8)	177.1(6)		

Table 2. Selected bond distances (Å) and angles (°) of complex **2**.

W(1)–C(1)	2.14(3)	Ni(1) –N(1)	2.05(2)	Ni(1) –N(4)	2.27(3)
W(1)–C(2)	2.18(3)	Ni(1) –N(3)	2.22(4)	Ni(1) –N(5)	2.07(5)
W(1)–C(1) –N(1)	169(3)	W(1)–C(2) –N(2)	176(3)	Ni(1) –N(1)–C(1)	160(3)

Table 3. Selected bond distances (Å) and angles (°) of complex **3**.

W(1)–C(1)	2.18(3)	W(1)–C(8)	2.21(3)	Ni(2) –N(2)	2.13(2)
W(1)–C(2)	2.18(3)	Ni(1) –N(1)	2.155(19)	Ni(2) –N(3)	2.10(2)
W(1)–C(3)	2.17(3)	Ni(1) –N(4)	2.12(2)	Ni(2) –N(13)	1.95(3)
W(1)–C(4)	2.18(2)	Ni(1) –N(9)	1.94(3)	Ni(2) –N(14)	2.00(4)
W(1)–C(5)	2.24(3)	Ni(1) –N(10)	2.05(2)	Ni(2) –N(15)	2.07(4)
W(1)–C(6)	2.11(3)	Ni(1) –N(11)	1.99(3)	Ni(2) –N(16)	2.09(5)
W(1)–C(7)	2.20(3)	Ni(1) –N(12)	2.04(2)		
W(1)–C(1) –N(1)	172(2)	W(1)–C(1) –N(5)	176(2)	Ni(1) –N(1)–C(1)	149(2)
W(1)–C(2) –N(2)	178(2)	W(1)–C(2) –N(6)	175(2)	Ni(1) –N(4)–C(4)	153(2)
W(1)–C(2) –N(3)	176(3)	W(1)–C(2) –N(7)	173(3)	Ni(2) –N(2)–C(2)	155(2)
W(1)–C(2) –N(4)	174(2)	W(1)–C(2) –N(8)	176(3)	Ni(2) –N(3)–C(3)	169(3)

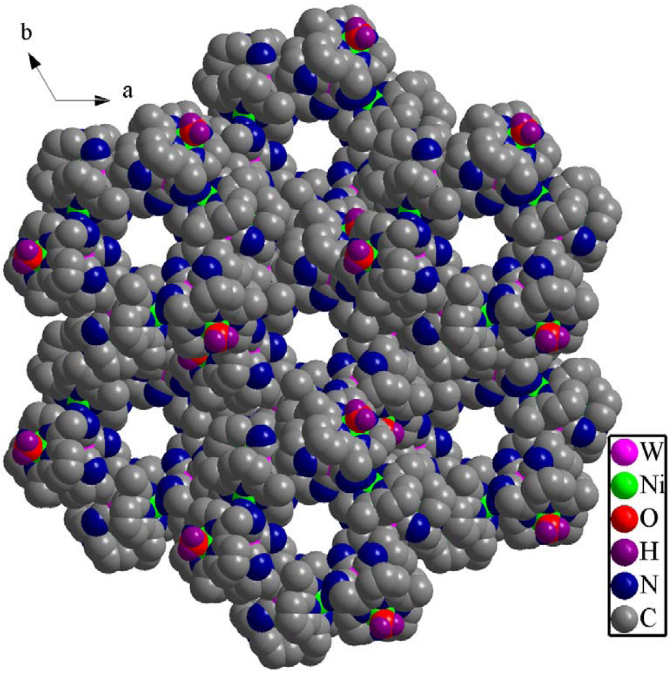
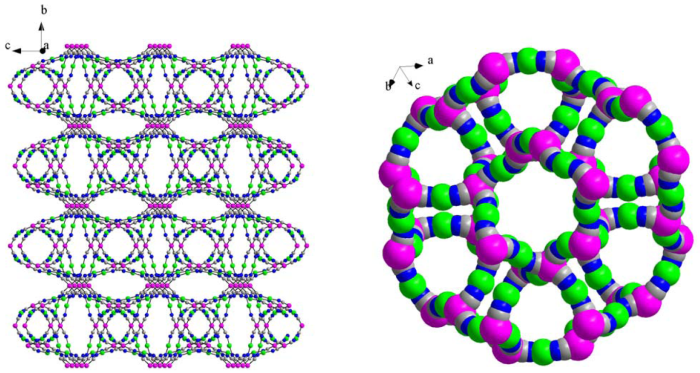
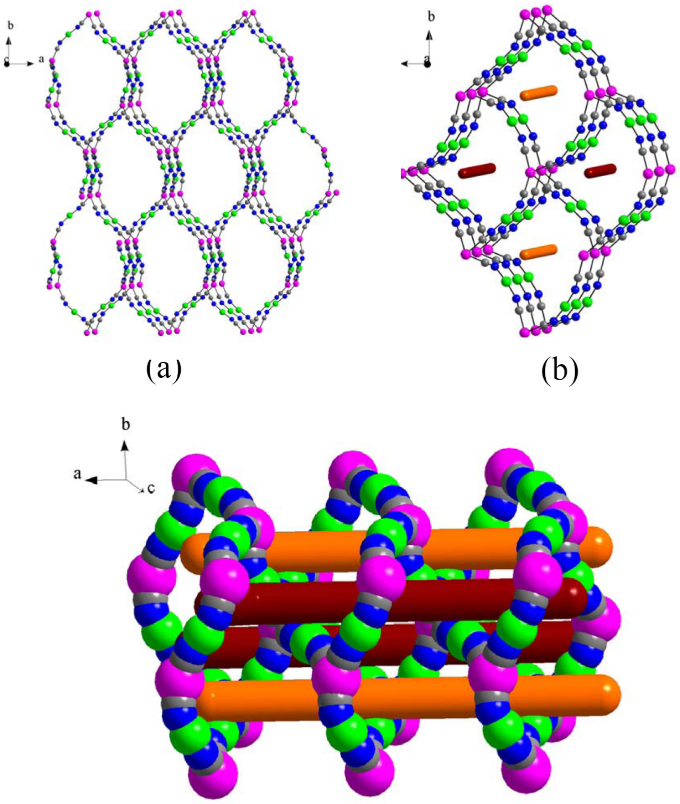


Figure S6. Cell packing diagram of complex **1** along the *c* axis (free waters were omitted for clarity).



(a) (b)

Figure S7. Cell packing diagram of complex **2** (only bridging cyanide and metals are presented for clarity).



(a) (b)

(c)

Figure S8. Cell packing diagram of complex **3** (only bridging cyanides and metals are presented for clarity).

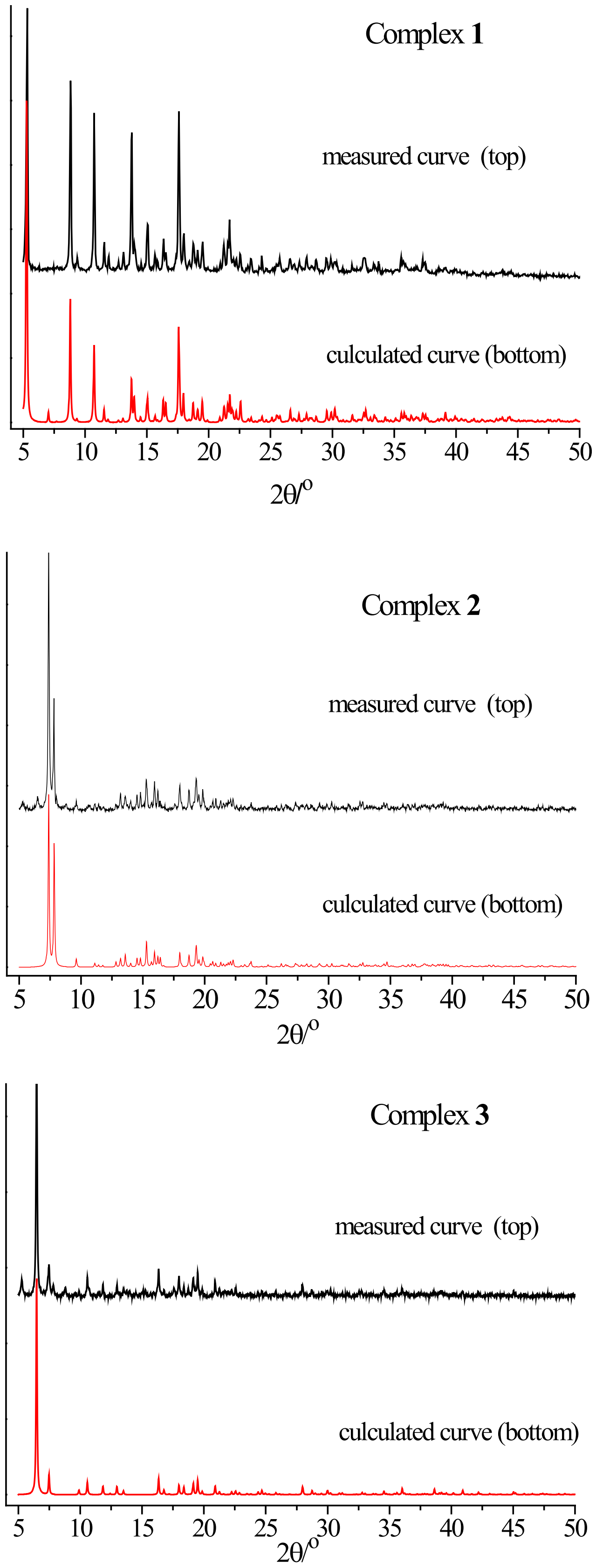


Figure S9. Powder XRD analysis of complexes **1**-**3**.