Supplementary Information

Photo-Induced Magnetization and First-Principles Calculations of a Two-Dimensional Cyanide-Bridged Co–W Bimetal Assembly

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Table S1. Crystallographic data of $(H_5O_2^+)[Co^{III}(4\text{-bromopyridine})_2[W^{IV}(CN)_8]$ from single crystal XRD analysis.

Formula	C18 Br2 Co N10 O2 W
Crystal size / mm	0.05 × 0.03 × 0.01
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14)
a / Å	13.0471(10)
b / Å	13.5910(10)
c / Å	14.6790(10)
β / °	106.3410(10)
V / Å^3	2497.8(3)
T / K	300(2)
Z	4
Absorption coeff. / cm^{-1}	8.503
Reflection collected	53379
Unique	9651 (R_{int} = 0.0774)
R_1 / wR_2 (all data)	0.0650 / 0.1486
GOF on F^2	1.117

The calculated formula in the cif check is different from the reported formula in Supplementary Information. This discrepancy is due to the presence of disordered cobalt atoms near crystallographic special positions.

Table S2-1. Atomic positions of $(H_5O_2^+)[Co^{III}(4\text{-bromopyridine})_2[W^{IV}(CN)_8]$ from single crystal XRD analysis.

atom	*x*	*y*	*z*	occupancy
Co1A	0.00027(12)	0.99942(10)	0.26956(7)	0.8
W1A	0.09616(2)	0.77375(2)	0.02463(2)	0.8
Br1L	0.5092(7)	1.1219(5)	0.3985(14)	0.6
Br2L	−0.5172(4)	0.9090(2)	0.1608(4)	0.6
C1	0.0446(7)	0.8585(7)	0.1263(7)	0.8
N1	0.0244(5)	0.9041(4)	0.1848(5)	0.8
C2	−0.0771(7)	0.7689(7)	−0.0202(5)	0.8
N2	−0.1691(10)	0.7639(10)	−0.0539(10)	0.6
C3	0.0582(7)	0.6559(5)	−0.0761(7)	0.8
N3	0.0328(4)	0.5946(4)	−0.1316(4)	0.8
C4	0.0473(4)	0.8595(4)	−0.0994(4)	1.0
N4	0.0292(5)	0.9076(5)	−0.1701(5)	0.8
C5	0.0512(5)	0.6541(4)	0.1051(4)	1.0
N5	0.0271(7)	0.5961(5)	0.1460(7)	0.8
C6	0.2294(5)	0.7373(5)	0.1444(5)	0.8
N6	0.3004(9)	0.7037(10)	0.2014(8)	0.4
C7	0.1919(7)	0.9053(7)	0.0600(7)	0.8
N7	0.2433(7)	0.9766(7)	0.0785(7)	0.8
C8	0.2307(8)	0.7473(7)	−0.0311(7)	0.8
N8	0.3062(10)	0.7388(8)	−0.0564(9)	0.8
N1L	0.1528(8)	1.0334(11)	0.3008(13)	0.6
C2L	0.2277(9)	0.9633(8)	0.3204(9)	0.6
C3L	0.3360(11)	0.9882(10)	0.3464(11)	0.6
C4L	0.3693(11)	1.0737(13)	0.3572(13)	0.6
C5L	0.2882(11)	1.1571(10)	0.3407(13)	0.6
C6L	0.1828(9)	1.1295(8)	0.3094(10)	0.6
N8L	−0.1515(16)	0.9637(14)	0.2390(13)	0.6
C9L	−0.1978(8)	0.9481(7)	0.3088(7)	0.6
C10L	−0.3071(10)	0.9289(9)	0.2880(9)	0.6
C11L	−0.3672(13)	0.9277(13)	0.1959(11)	0.6
C12L	−0.3198(11)	0.9418(10)	0.1235(9)	0.6
C13L	−0.2107(8)	0.9570(7)	0.1481(7)	0.6
Co1B	0.0002(5)	0.9977(4)	0.2364(4)	0.2
W1B	0.09645(9)	0.73308(16)	0.02225(8)	0.2
Br1M	0.5160(13)	1.0935(18)	0.417(2)	0.2
Br2M	−0.5161(4)	0.9085(5)	0.0797(7)	0.2
C1B	0.060(2)	0.848(2)	0.108(2)	0.2
N1B	0.035(2)	0.911(2)	0.153(2)	0.2
C2B	−0.079(3)	0.738(3)	−0.016(2)	0.2
N2B	−0.1721(17)	0.7356(18)	−0.041(2)	0.2
N2C	−0.1674(16)	0.7643(18)	−0.0254(17)	0.2
C3B	0.040(2)	0.650(2)	−0.103(2)	0.2
N3B	0.019(2)	0.602(2)	−0.171(2)	0.2

Table S2-2. Atomic positions of $(H_5O_2^+)[Co^{III}(4\text{-bromopyridine})_2[W^{IV}(CN)_8]$ from single crystal XRD analysis.

atom	*x*	*y*	*z*	occupancy
N4B	0.018(2)	0.907(2)	−0.145(2)	0.2
N5B	0.030(2)	0.592(2)	0.171(2)	0.2
C6B	0.194(2)	0.5946(17)	0.0340(17)	0.2
N6B	0.242(2)	0.521(2)	0.044(2)	0.2
N6C	0.3050(10)	0.7417(9)	0.2106(9)	0.4
C7B	0.192(2)	0.910(2)	0.033(3)	0.2
N7B	0.244(2)	0.979(2)	0.039(2)	0.2
C8B	0.2318(17)	0.7722(18)	−0.0316(15)	0.2
N8B	0.305(2)	0.7823(18)	−0.0557(18)	0.2
N1M	0.1501(13)	1.042(3)	0.3139(18)	0.2
C2M	0.2105(18)	1.040(2)	0.2538(14)	0.2
C3M	0.3190(18)	1.065(2)	0.2860(17)	0.2
C4M	0.3613(17)	1.096(3)	0.3674(18)	0.2
C5M	0.306(2)	1.070(2)	0.4436(15)	0.2
C6M	0.1987(18)	1.053(2)	0.4083(15)	0.2
N8M	−0.1521(14)	0.9612(18)	0.1873(16)	0.2
C9M	−0.210(2)	0.956(2)	0.2488(14)	0.2
C10M	−0.320(2)	0.935(4)	0.217(2)	0.2
C11M	−0.3696(18)	0.929(3)	0.132(2)	0.2
C12M	−0.307(2)	0.928(3)	0.0582(16)	0.2
C13M	−0.2000(17)	0.947(2)	0.0932(14)	0.2
O3WM	−0.297(8)	0.740(6)	0.163(7)	0.2
Br1N	0.5085(13)	1.111(2)	0.368(2)	0.2
N1N	0.150(2)	1.039(2)	0.280(2)	0.2
C2N	0.2291(17)	0.9635(16)	0.297(2)	0.2
C3N	0.338(3)	0.986(2)	0.322(3)	0.2
C4N	0.362(2)	1.091(2)	0.329(2)	0.2
C5N	0.291(2)	1.154(2)	0.307(2)	0.2
C6N	0.184(2)	1.128(2)	0.278(2)	0.2
Br2N	−0.5053(9)	0.8743(7)	0.1577(15)	0.2
N8N	−0.152(4)	0.960(4)	0.230(4)	0.2
C9N	−0.232(3)	1.039(2)	0.206(2)	0.2
C10N	−0.338(3)	1.003(3)	0.182(3)	0.2
C11N	−0.367(3)	0.914(3)	0.172(3)	0.2
C12N	−0.295(5)	0.840(5)	0.191(5)	0.2
C13N	−0.185(3)	0.870(3)	0.223(3)	0.2
O1WA	−0.543(2)	0.758(3)	−0.140(2)	0.2
O2WA	−0.3651(9)	0.8480(8)	−0.1192(9)	0.4
O1WB	−0.5611(13)	0.8350(13)	−0.1408(13)	0.3
O1WC	−0.550(4)	0.730(4)	−0.130(4)	0.1
O2WB	−0.3640(11)	0.8485(10)	−0.0805(13)	0.3
O4W	−0.362(3)	0.653(3)	−0.064(3)	0.2
O1WD	−0.548(2)	0.787(2)	−0.1403(18)	0.3

2. Powder XRD pattern of $(H_5O_2^+)[Co^{III}(4\text{-bromopyridine})_2[W^{IV}(CN)_8]$

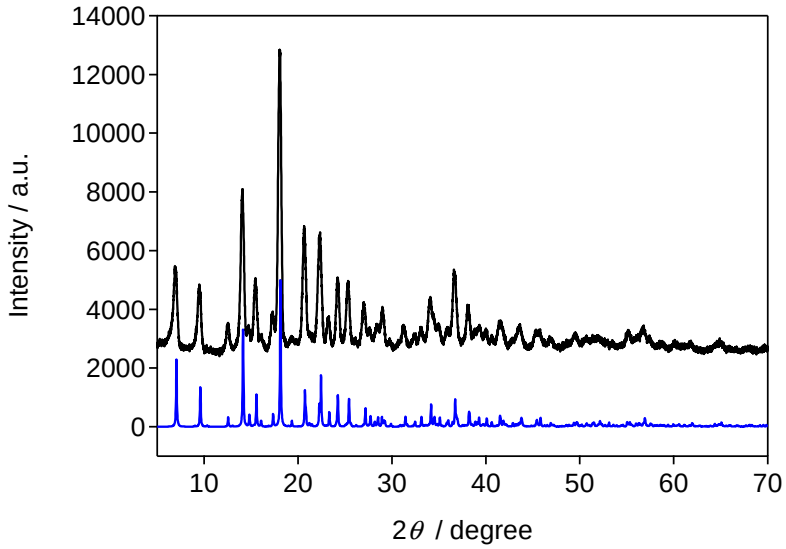

Figure S1. Powder XRD pattern of powder-form sample of $(H_5O_2^+)[Co^{III}_{ls}(4\text{-bromopyridine})_2\{W^{IV}(CN)_8\}]$. Black and blue lines represent powder XRD pattern of powder-form sample and simulation pattern calculated from the crystal structure of single crystal, respectively.

3. IR measurement of $(H_5O_2^+)[Co^{III}(4\text{-bromopyridine})_2[W^{IV}(CN)_8]$

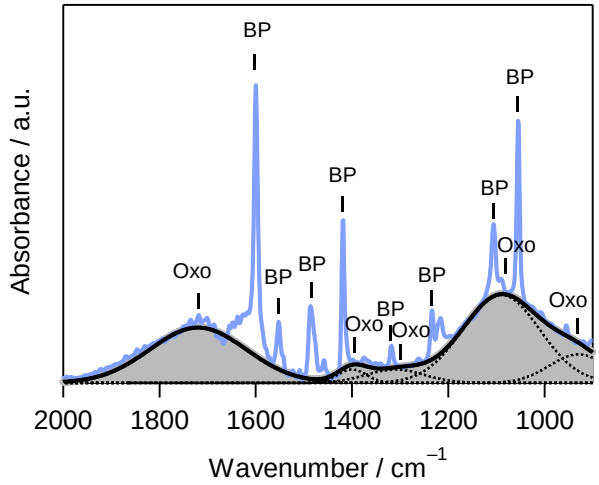

Figure S2. Micro-IR spectrum at room temperature in the range of 2000–900 cm^{-1} (blue line). Black solid line represents the sum of the respective peaks due to the vibration modes of oxonium cation (Oxo) shown by dotted lines. Sharp peaks are due to vibration modes of 4-bromopyridine (BP).

Table S3. Vibration modes of O–H^+–O group of $H_5O_2^+$ cation.

ν / cm^{-1}	vibration mode
930	OHO stretching
1090	OHO stretching
1720	overtone
1310	OHO bending
1400	OHO bending

4. Magnetic measurement of $(H_5O_2^+)[Co^{III}(4\text{-bromopyridine})_2[W^{IV}(CN)_8]$

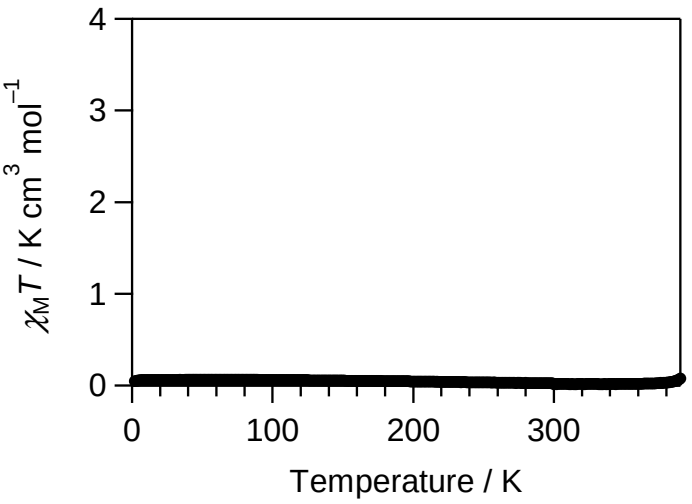

Figure S3. $\chi_M T$-T plots measured in an external magnetic field of 5000 Oe.

5. TG measurement of $(H_5O_2^+)[Co^{III}(4\text{-bromopyridine})_2[W^{IV}(CN)_8]$

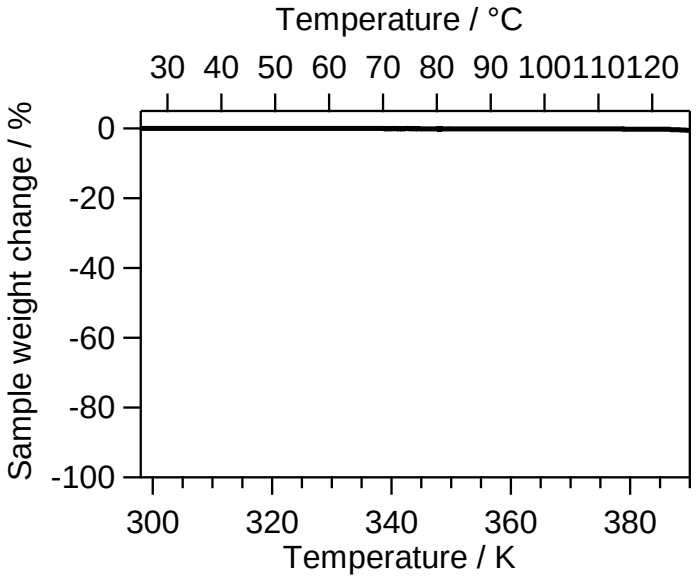

Figure S4. TG analysis under a scan rate of 1 K min^{-1}.

6. pH dependence of oxidation potential of $[W(CN_8\})]^{3-/4-}$

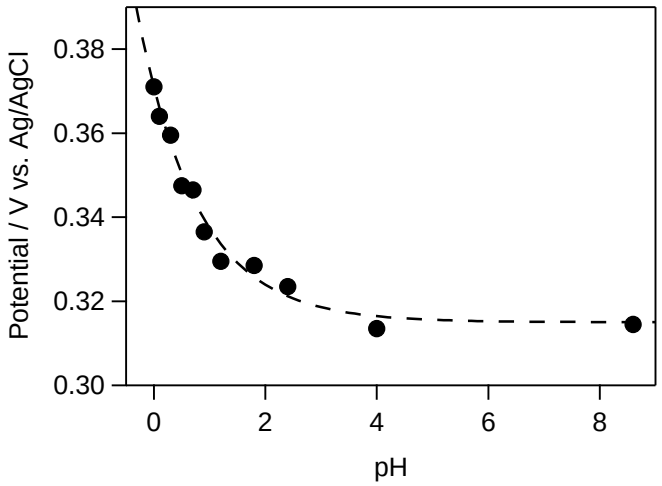

Figure S5. pH dependence of oxidation potential of $[W(CN)_8]^{3-/4-}$. Dotted line is an eye guide.

7. First-principles calculations of $(H_5O_2^+)[Co^{III}(4\text{-bromopyridine})_2[W^{IV}(CN)_8]$

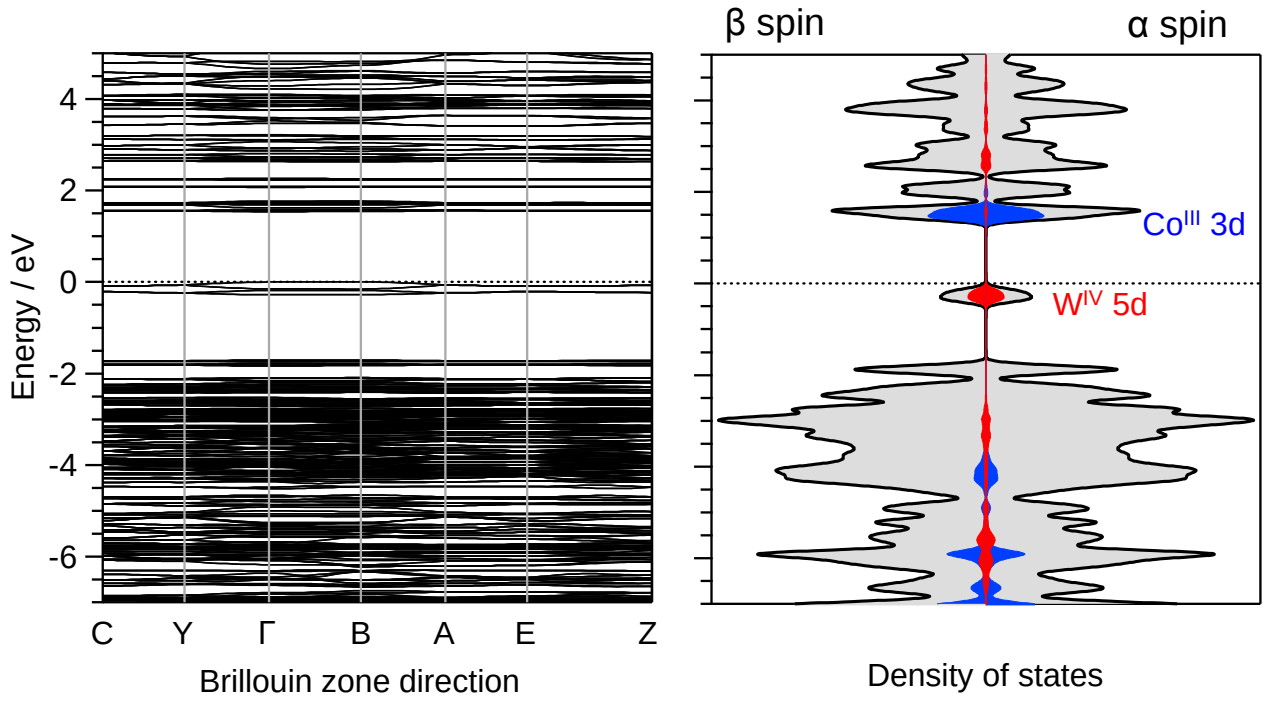

Figure S6. Band structure (left) and density of states (DOS) (right) of **1** from −7 eV to 5 eV. Grey, blue, and red areas represent total DOS and partial DOS for Co^{III} 3d and W^{IV} 5d, respectively.

8. Crystallographic data of the crystal structure of photo-induced phase

Table S4. Crystallographic data of the structure of photo-induced phase.

Formula	C18 Br2 Co N10 O2 W
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14)
a / Å	13.193(10)
b / Å	13.949(11)
c / Å	15.040(12)
β / °	107.35(9)
V / Å^3	2642(4)
T / K	13
Z	4
R_{wp} / R_p	0.0044 / 0.0033
S	1.18

The calculated formula in the cif check is different from the reported formula in Supplementary Information. This discrepancy is due to the presence of cobalt atoms near crystallographic special positions.

Table S5. Atomic position of the structure of photo-induced phase.

atom	*x*	*y*	*z*
W	0.10	0.78	0.02
C1	0.04	0.85	0.13
N1	0.01	0.89	0.18
C2	0.04	0.67	0.10
N2	0.01	0.61	0.14
C3	0.05	0.66	−0.07
N3	0.03	0.60	−0.12
C4	0.04	0.86	−0.10
N4	0.03	0.91	−0.17
C5	−0.08	0.79	−0.01
N5	−0.17	0.79	−0.03
C6	0.21	0.73	0.15
N6	0.27	0.71	0.21
C7	0.19	0.91	0.06
N7	0.24	0.98	0.08
C8	0.21	0.74	−0.05
N8	0.28	0.72	−0.09
Co	0.00	1.00	0.27
N1L	0.16	1.04	0.31
C2L	0.24	0.97	0.32
C3L	0.34	1.00	0.35
C4L	0.37	1.09	0.34
C5L	0.29	1.16	0.33
C6L	0.19	1.13	0.31
Br1L	0.51	1.12	0.37
N8L	−0.16	0.96	0.24
C9L	−0.21	0.95	0.31
C10L	−0.31	0.93	0.29
C11L	−0.37	0.93	0.19
C12L	−0.32	0.94	0.12
C13L	−0.21	0.96	0.15
Br2L	−0.51	0.90	0.16
O1	−0.55	0.78	−0.14
O2	−0.36	0.85	−0.12

9. Crystal structure of photo-induced phase

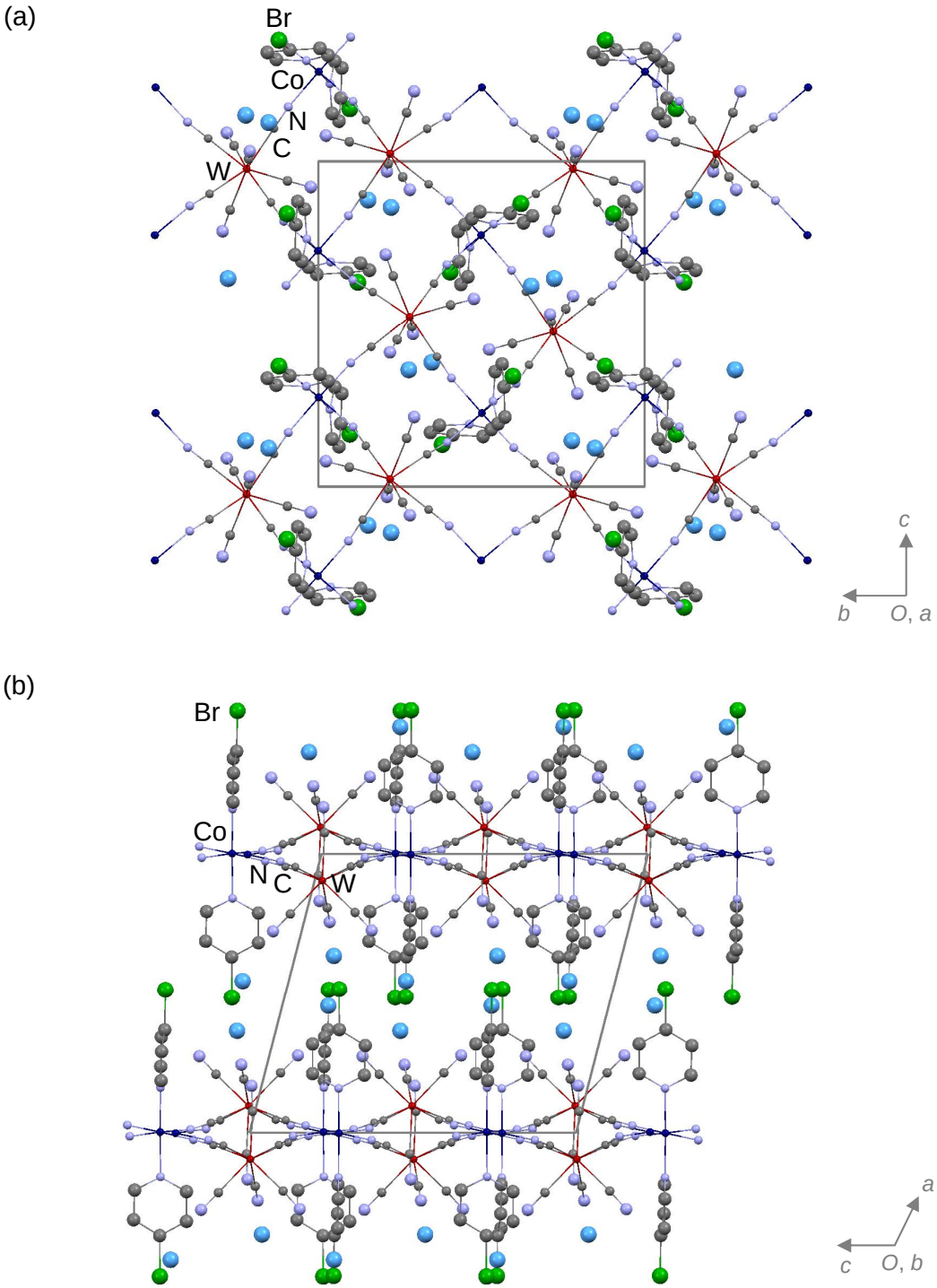

Figure S7. Crystal structure of the photo-induced phase. Views along (a) the *a*-axis and (b) the *b*-axis. Blue, red, grey, purple, light blue, and green balls represent Co, W, C, N, O, and Br, respectively.

10. W–C and Co–N distances before and after light irradiation

Table S6. W–C and Co–N distances of original and photo-induced phases at 13 K.

original phase		photo-induced phase	
W–C distance / Å		W–C distance / Å	
W1A–C1	2.14	W–C1	2.19
W1A–C2	2.17	W–C2	2.18
W1A–C3	2.14	W–C3	2.14
W1A–C4	2.10	W–C4	2.13
W1A–C5	2.18	W–C5	2.17
W1A–C6	2.15	W–C6	2.15
W1A–C7	2.16	W–C7	2.13
W1A–C8	2.17	W–C8	2.22
average	2.15	average	2.16
Co–N distance / Å		Co–N distance / Å	
Co1A–N1	1.88	Co–N1	2.03
Co1A–N3	1.97	Co–N2	2.06
Co1A–N4	1.88	Co–N3	2.05
Co1A–N5	1.88	Co–N4	2.02
Co1A–N1L	1.91	Co–N1L	2.08
Co1A–N8L	1.97	Co–N9L	2.08
average	1.92	average	2.05