Electronic Supplementary Information (ESI) for

Hyperstable Chromium(III)/Manganese(II) Bimetallic Wheel Cluster with Visible Photoactivity

Table S1. Crystal data and structure refinement summary for cluster of **1** and **2**.

Complex Name	**1**	**2**
CCDC No.	1889241	1818720
Formulae	$C_{112}H_{88}O_{40}Cr_7Mn$	$C_{92}H_{72}O_{28}Cr_4Mn_4$
Mol. wt.	2492.76	2164.05
Crystal system	Tetragonal	Triclinic
Space group	P 4/n n c	*P -1*
Temperature (K)	293	293
Wavelength (Å)	0.71073	0.71073
a, b, c /Å	a 16.8255(9) b 16.8255(9) c 23.4167(14)	a 14.682(2) b 15.378(3) c 24.143(4)
α, β, γ/°	90, 90, 90	74.940(5), 89.845(5), 65.801(5)
V/ Å^3	6629.2(8)	4768.0 (14)
Z	2	2
Density / g.cm^{-3}	1.249	1.507
Abs. Coeff. /mm^{-1}	0.716	1.031
F(000)	2546	2203
Total no. of reflections	3365	21666
Reflections, $I > 2\sigma(I)$	1365	14925
Max. 2θ/°	27.517	27.513
Ranges (h, k, l)	-21 ≤ h ≤21 -21 ≤ k ≤17 -30 ≤ l ≤ 30	-19 ≤ h ≤19 -19 ≤ k ≤19 -31 ≤ l ≤ 31
Complete to 2θ (%)	0.876	98.9
Restraints	381	76
Parameters	189	1270
Goof (F^2)	1.067	1.015
Rindices [$I > 2\sigma(I)$]	0.0876	0.0451
Rindices (all data)	0.1996	0.0795
WR_2 [$I > 2\sigma(I)$]	0.1867	0.1082
WR_2 (all data)	0.2496	0.1230

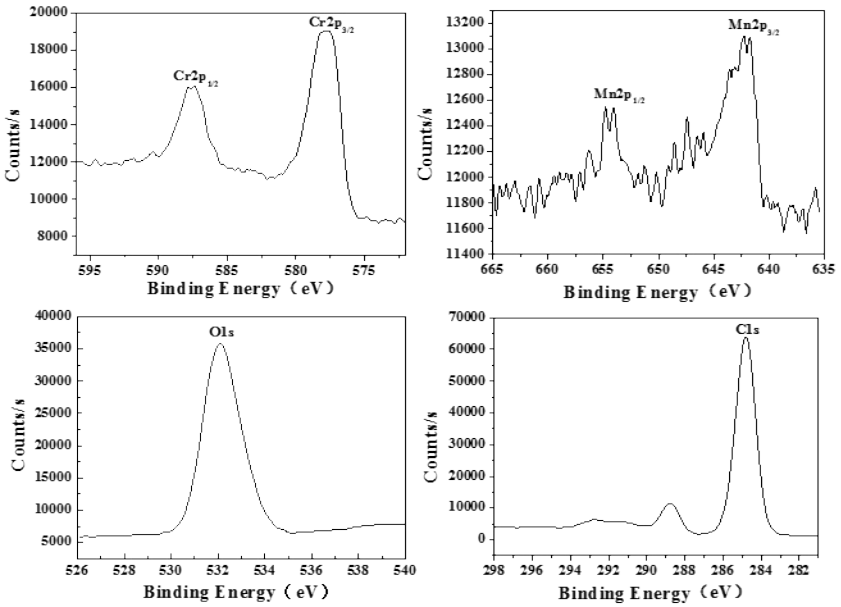

Figure S1. XPS high-resolution spectra of Cr 2p, Mn 2p, O 1s and C 1s core levels for cluster **1** indicates the existence oxidation state of (a) Cr^{3+} (577.8 eV for $2p_{3/2}$ and 587.7 eV for $2p_{1/2}$), (b) Mn^{2+} (642.3 eV for $2p_{3/2}$ and 654.3 eV for $2p_{1/2}$), (c) O 1s (532.1 eV), (d) C 1s (284.8 eV and 288.8 eV).

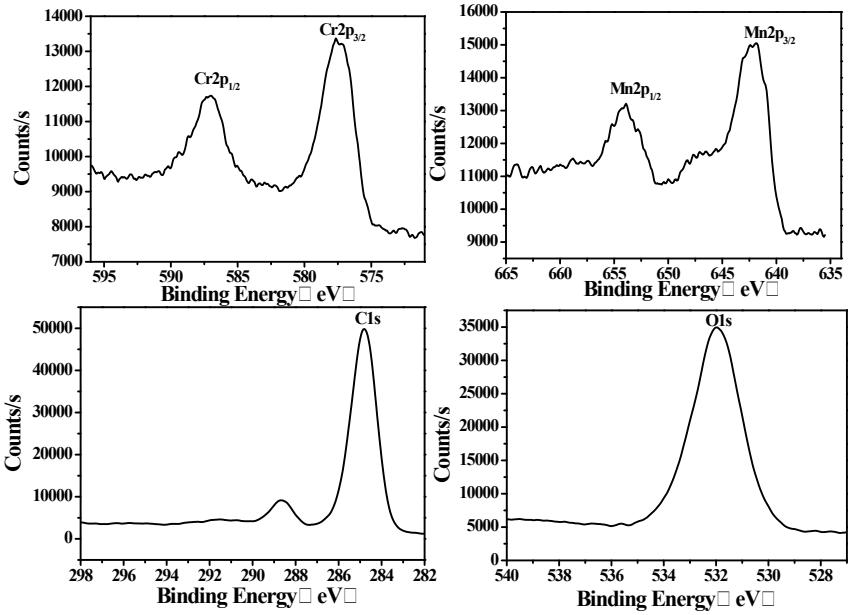

Figure S2. XPS high-resolution spectra of Cr 2p, Mn 2p, O 1s and C 1s core levels for cluster **2** indicates the existence oxidation state of (a) Cr^{3+} (577.4 eV for $2p_{3/2}$ and 587.2 eV for $2p_{1/2}$), (b) Mn^{2+} (642.1 eV for $2p_{3/2}$ and 653.9 eV for $2p_{1/2}$), (c) C 1s (284.8 eV and 288.7 eV). (d) O 1s (531.9 eV).

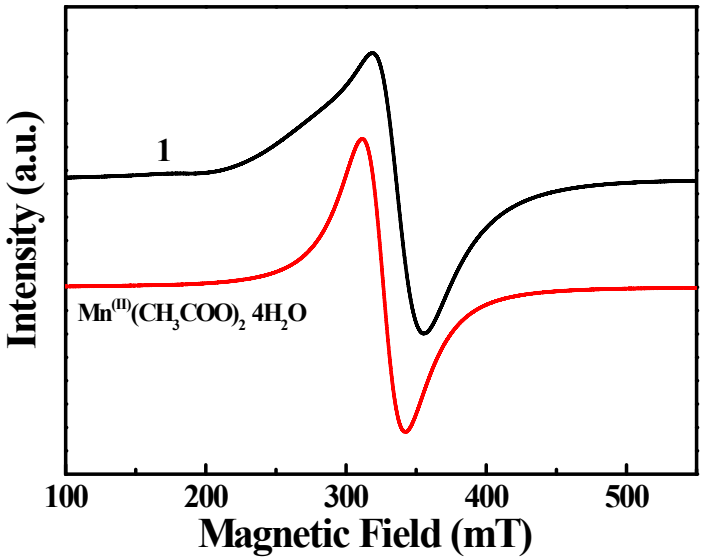

Figure S3. The ESR spectrum of **1** (black line) and maganese acetate terahydrate (red line).

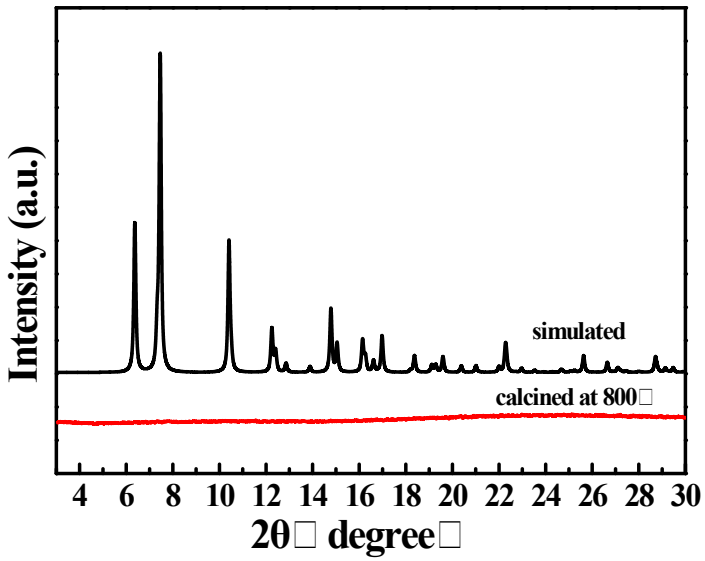

Figure S4 Simulated XRD patterns of 1 from single-crystal X-ray diffraction data (black line) and PXRD pattern of 1 after calcined at 800 ℃ in Ar flow using tube furnace.

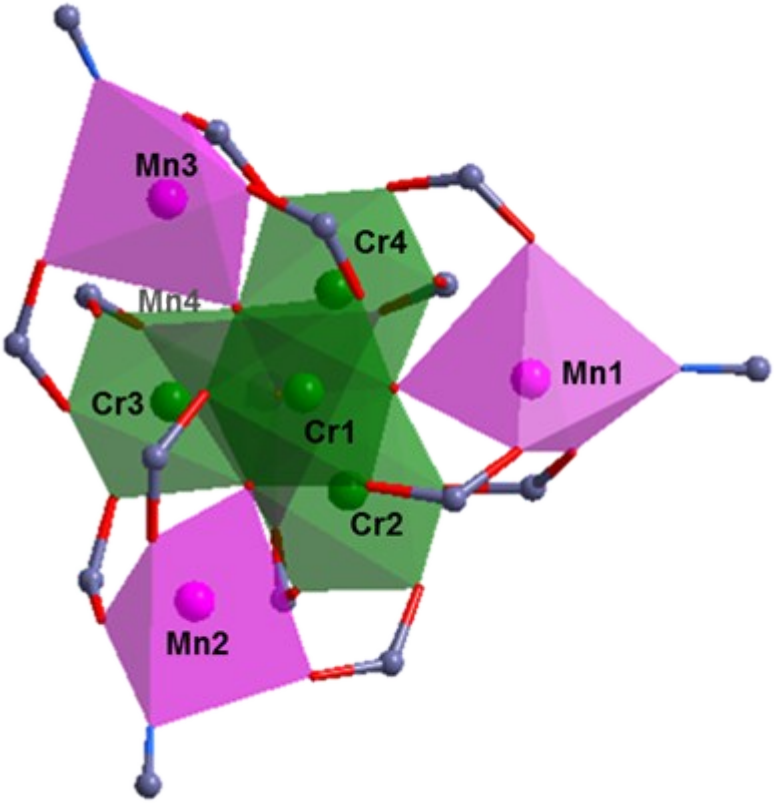

Figure S5. Polyhedral and ball-and-stick representations of **2.**

Table S2. Selected bond lengths (Å) and angles (°) for **2.**.

Lengths			
Cr1-O1	1.959	Mn4-O1	2.059
Cr1-O2	1.967	Mn4-O2	2.135
Cr1-O3	1.966	Mn4-O3	2.102
Cr1-O4	1.988	Mn4-O4	2.100
Cr1-O5	1.988	Mn4-O5	2.198
Cr1-O6	2.004	Mn1-O1	2.064
Cr2-O1	1.9568	Mn1-O2	2.073
Cr2-O2	1.965	Mn1-O3	2.088
Cr2-O3	1.963	Mn1-O4	2.070
Cr2-O4	1.999	Mn1-N	2.275
Cr2-O5	1.985	Mn2-O1	2.059
Cr2-O6	1.993	Mn2-O2	2.080
Cr3-O1	1.958	Mn2-O3	2.086
Cr3-O2	1.967	Mn2-O4	2.087
Cr3-O3	1.968	Mn2-N	2.224
Cr3-O4	1.997	Mn3-O1	2.061
Cr3-O5	2.010	Mn3-O2	2.095
Cr3-O6	1.998	Mn3-O3	2.093

Cr4-O1	1.970	Mn3-O4	2.097
Cr4-O2	1.970	Mn3-N	2.231
Cr4-O3	1.964		
Cr4-O4	1.987		
Cr4-O5	1.989		
Cr4-O6	2.003		
Angles			
O1-Cr1-O2	83.21	O1-Mn2-O2	96.48
O1-Cr1-O3	83.26	O1-Mn2-O3	93.63
O1-Cr1-O4	95.38	O1-Mn2-O4	94.10
O1-Cr1-O5	175.72	O1-Mn2-O5	174.14
O1-Cr1-O6	94.26	O2-Mn2-O5	87.9
O2-Cr1-O3	82.14	O2-Mn2-O3	118.05
O2-Cr1-O4	93.96	O2-Mn2-O4	118.70
O2-Cr1-O5	94.42	O3-Mn2-O4	121.24
O2-Cr1-O6	176.95	O3-Mn2-O5	87.7
O3-Cr1-O4	175.98	O4-Mn2-O5	80.3
O3-Cr1-O5	92.89	O1-Mn4-O2	92.71
O3-Cr1-O6	95.89	O1-Mn4-O3	94.77
O4-Cr1-O5	88.34	O1-Mn4-O4	93.88
O4-Cr1-O6	87.97	O1-Mn4-N2	175.3
O5-Cr1-O6	87.99	O12-Mn4-O3	116.1
O1-Cr2-O2	82.69	O12-Mn4-O4	118.6
O1-Cr2-O3	83.14	O2-Mn4-N2	91.4
O1-Cr2-O4	94.8	O3-Mn4-O4	123.9
O1-Cr2-O5	175.05	O3-Mn4-N2	81.3
O1-Cr2-O6	92.61	O4-Mn4-N2	86.2
O2-Cr2-O3	82.14	O1-Mn3-O2	93.78
O2-Cr2-O4	176.92	O1-Mn3-O3	93.96
O2-Cr2-O5	92.75	O1-Mn3-O4	94.65
O2-Cr2-O6	95.80	O1-Mn3-N1	174.6
O3-Cr2-O4	95.74	O2-Mn3-O3	114.6
O3-Cr2-O5	94.35	O2-Mn3-O4	118.4
O3-Cr2-O6	175.47	O2-Mn3-N1	91.3
O4-Cr2-O5	89.62	O3-Mn3-O4	125.4
O4-Cr2-O6	86.16	O3-Mn3-N1	82.2
O5-Cr2-O6	89.77	O3-Mn3-N1	84.5
O1-Cr3-O2	82.91	O1-Mn1-O2	93.75
O1-Cr3-O3	82.34	O1-Mn1-O3	94.23
O1-Cr3-O4	95.49	O1-Mn1-O4	96.38
O1-Cr3-O5	178.85	O1-Mn1-N3	177.3
O1-Cr3-O6	94.76	O2-Mn1-O3	121.6
O2-Cr3-O3	81.98	O2-Mn1-O4	115.4
O2-Cr3-O4	95.81	O2-Mn1-N3	83.8

O2-Cr3-O5	96.10	O3-Mn1-O4	120.9
O2-Cr3-O6	177.20	O3-Mn1-N3	86.1
O3-Cr3-O4	177.06	O4-Mn1-N3	85.7
O3-Cr3-O5	96.95		
O3-Cr3-O6	96.19		
O4-Cr3-O5	85.18		
O4-Cr3-O6	85.95		
O5-Cr3-O6	86.22		
O1-Cr4-O2	82.85		
O1-Cr4-O3	82.67		
O1-Cr4-O4	94.90		
O1-Cr4-O5	175.86		
O1-Cr4-O6	94.62		
O2-Cr4-O3	82.68		
O2-Cr4-O4	95.21		
O2-Cr4-O5	93.71		
O2-Cr4-O6	177.17		
O3-Cr4-O4	176.95		
O3-Cr4-O5	94.63		
O3-Cr4-O6	95.77		
O4-Cr4-O5	87.68		
O4-Cr4-O6	86.25		
O5-Cr4-O6	88.77		

Table S3. Summary of stability test of cluster **1** and **2** in different solvent for at least 24 h.

	1	**2**
methanol	no	yes
ethanol	no	yes
$CHCl_3$	no	yes
CCl_4	no	no
CH_2Cl_2	no	no
acetone	no	yes
isopropanol	no	yes
propylene oxide	no	yes
cyclohexanol	no	yes
nitrobenzene	no	no
cyclohexane	no	no
DMSO	no	yes
DMF	yes	yes

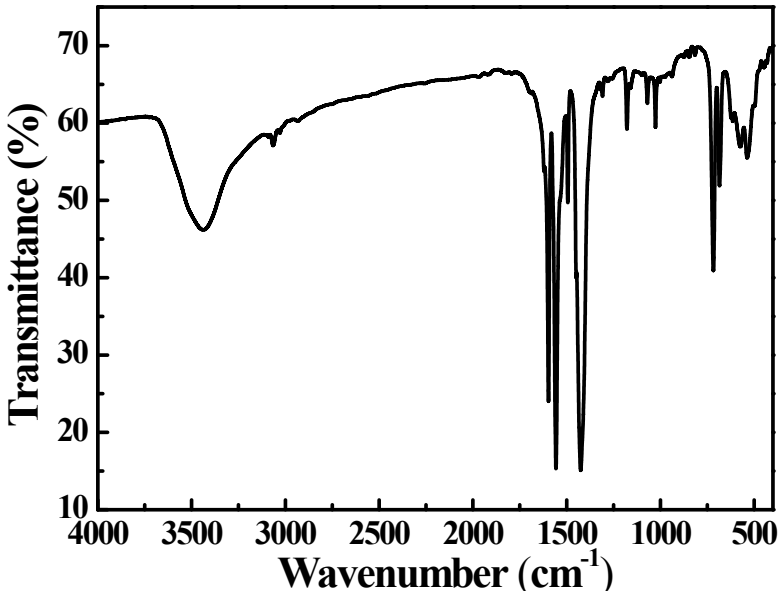

Figure S6. Infrared spectra of **1**: characteristic bands of the coordinated carboxylate in 1400 - 1600 cm $^{-1}$ as well as M - O (M = Cr, Mn) vibrations in 400 - 800 cm $^{-1}$, but no free carboxyl group vibrations in 1650 - 1750cm $^{-1}$. The broad vibration around 3400 cm $^{-1}$ arises from water molecules.

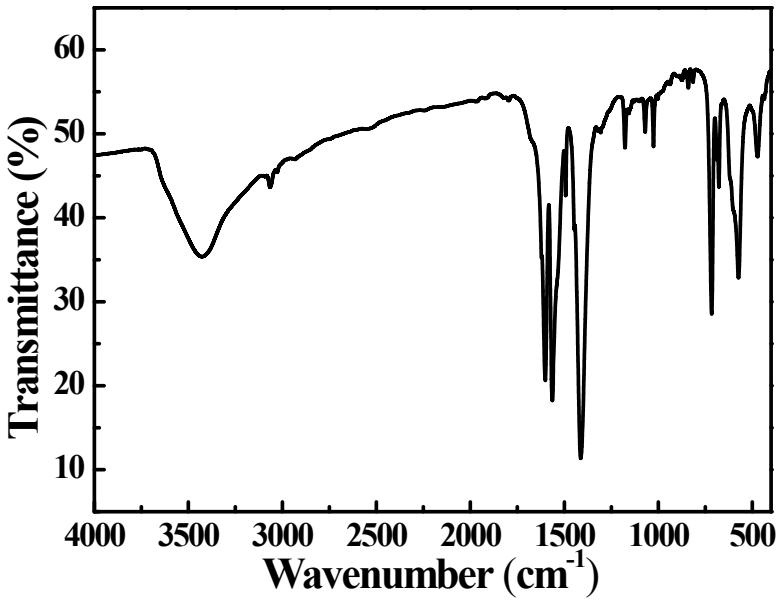

Figure S7. Infrared spectra of **2**: characteristic bands of the coordinated carboxylate in 1400 - 1600 cm $^{-1}$ as well as M - O (M = Cr, Mn) vibrations in 400 - 800 cm $^{-1}$, but no free carboxyl group vibrations in 1650 - 1750cm $^{-1}$. The broad vibration around 3400 cm $^{-1}$ arises from water molecules.

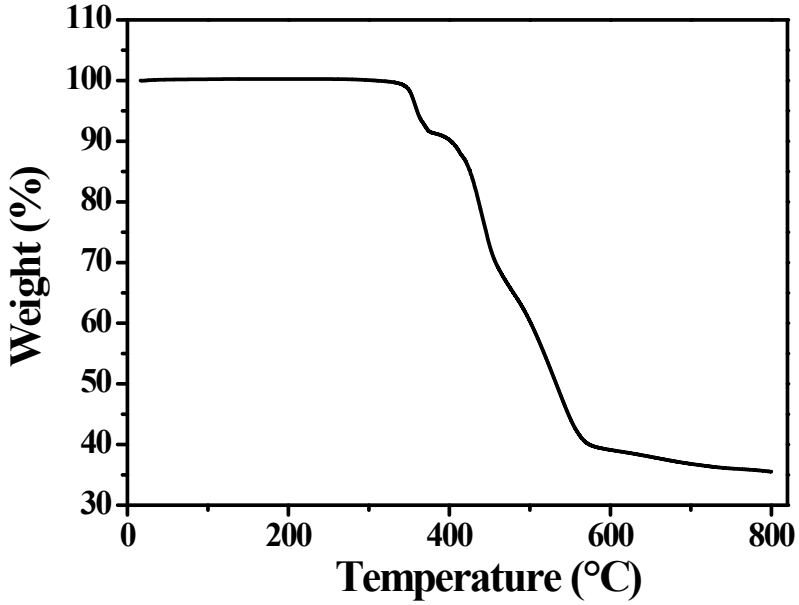

Figure S8. TG curve of cluster **1**. The cluster can keep intact above 300 °C, following by decomposition of **1**.

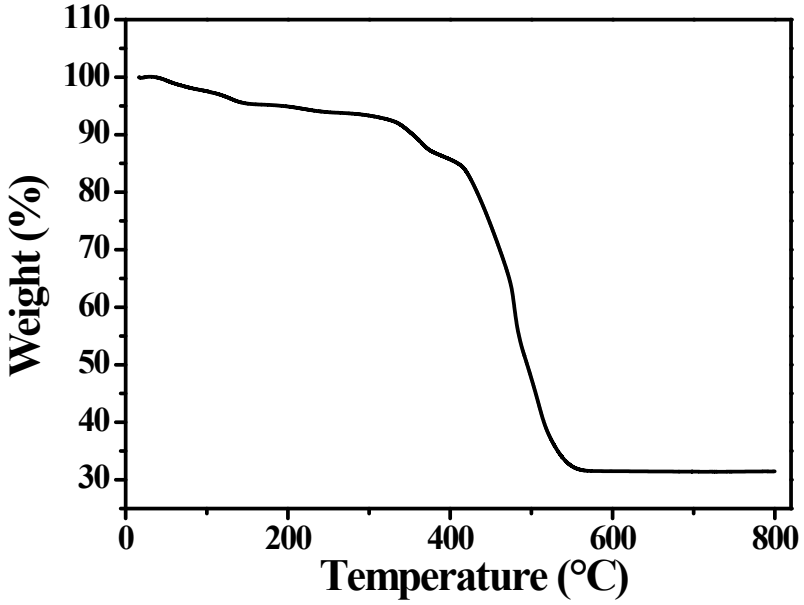

Figure S9. TG curve of cluster **2**. The cluster can keep intact above 200 °C, following by decomposition of **2**.

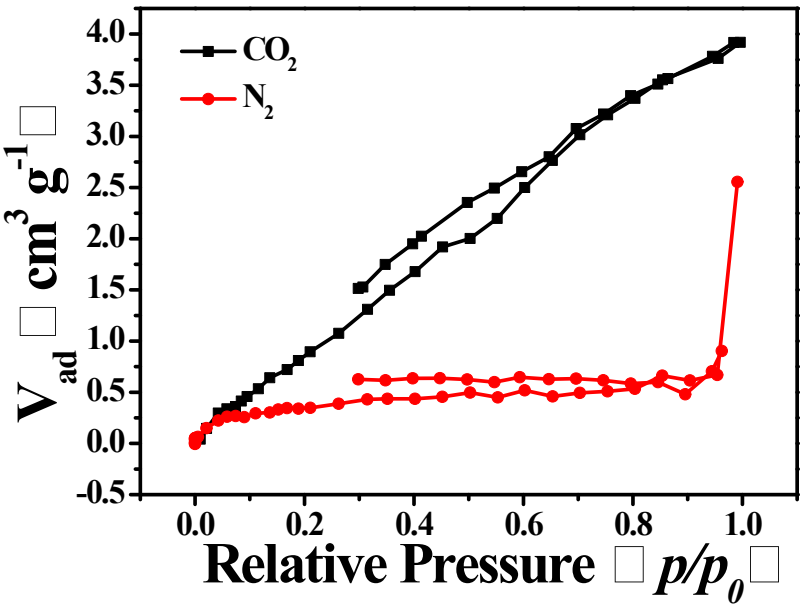

Figure S10. CO_2 sorption isotherms at 298 K and N_2 sorption isotherm at 77 K over evacuated **1**.

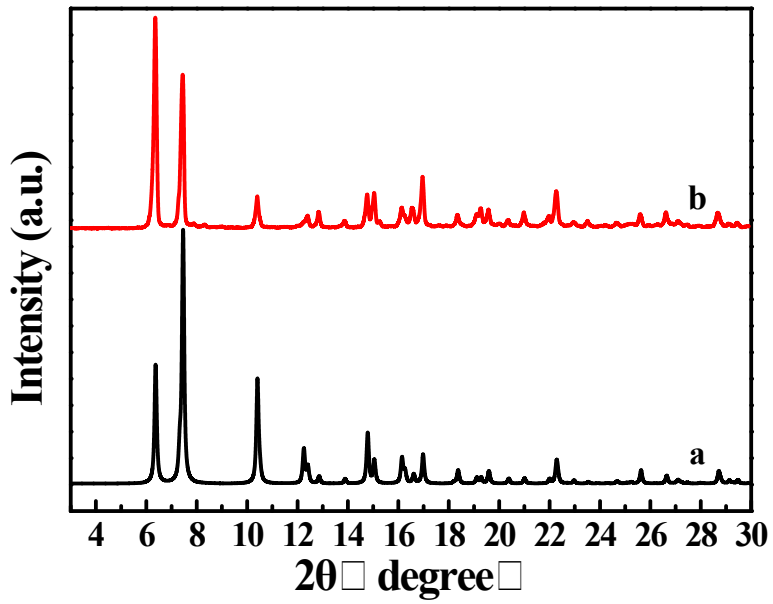

Figure S11. (a) Simulated XRD patterns of **1** nanocluster and (b) PXRD of $Cr_8(OH)_8(OOCPh)_{16}$.

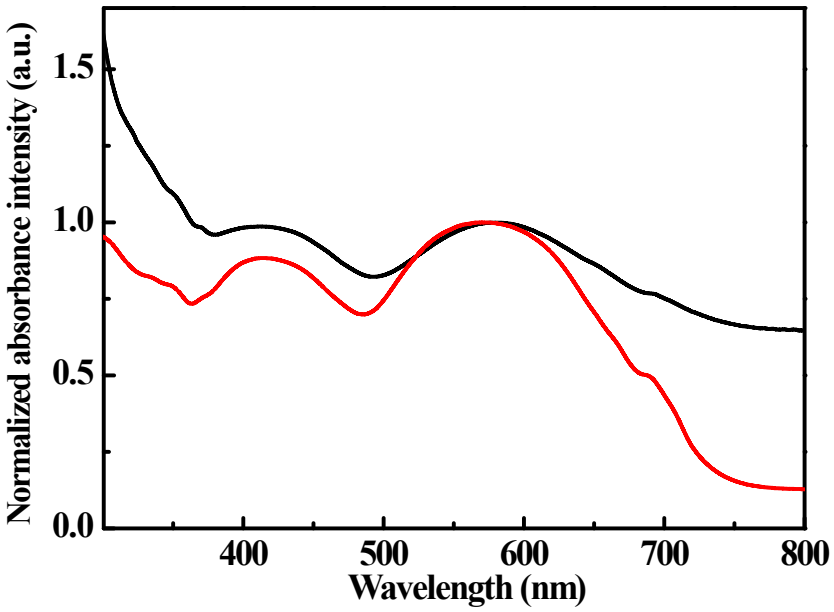

Figure S12. Normalized UV-Vis absorption spectrum of $Cr_8(OH)_8(OOCPh)_{16}$ (black line) and crystalline **1** sample (λ_{max}= 571 nm, red line).