Electronic Supporting Information (ESI)

Chromous carbonates containing square-grid layer $Cr_2(CO_3)_4\}_n^{4n-}$ based on dichromium(II,II) paddlewheel core

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Table S1. Crystal data and structural refinement parameters for compound **1**

Compound **1**	
Empirical formula	$C_4H_{21}Na_3Cr_2O_{22}$
Formula weight	594.18
Crystal system	Monoclinic
Space group	*C*2/*c*
a /Å	21.463(16)
b /Å	8.882(7)
c /Å	9.942(8)
α/°	90
β/°	96.899(12)
γ/°	90
V/Å^3	1882(3)
Z	4
ρ_{calc} (g ·cm^{-3})	2.097
μ (mm^{-1})	1.335
F (000)	1208
Reflections collected	4499
Reflections unique	1793
parameters	141
GOF on F^2	1.110
R_{int}	0.108
R_1, $wR_2{}^a$ [$I>2\sigma(I)$]	0.1056, 0.2729
R_1, $wR_2{}^a$ (all data)	0.1213, 0.2840
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ [e/Å^3]	1.550, -0.817

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

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Table S2. Selected bond distances (Å) for compound **1**

Selected bond distances (Å)					
Cr(1)–Cr(1h)	2.268(3)	Na(1)–O(5)	2.357(8)	Na(2)–O(7)	2.342(10)
Cr(1)–O(1)	2.047(7)	Na(1)–O(7)	2.427(10)	Na(2)–O(9)	2.418(10)
Cr(1)–O(4)	2.036(6)	Na(1)–O(8)	2.417(8)	Na(2)–O(10)	2.519(10)
Cr(1)–O(2h)	2.036(7)	Na(1)–O(1c)	2.437(8)	Na(2)–O(7a)	2.342(10)
Cr(1)–O(5h)	2.028(6)	Na(1)–O(4c)	2.520(8)	Na(2)–O(9a)	2.418(10)
Cr(1)–O(6d)	2.294(6)	Na(1)–O(6g)	2.372(7)	Na(2)–O(10a)	2.519(10)
C(1)–O(1)	1.296(12)	C(1)–O(2)	1.308(11)	C(1)–O(3)	1.249(14)
C(2)–O(4)	1.296(11)	C(2)–O(5)	1.291(10)	C(2)–O(6)	1.283(10)

Table S3. Selected angles (˚) for compound **1**

Cr(1h)–Cr(1)–O(1)	88.8(2)	Cr(1)–O(1)–C(1)	120.8(6)
Cr(1h)–Cr(1)–O(4)	91.03(18)	Cr(1h)–O(2)–C(1)	119.1(6)
Cr(1h)–Cr(1)–O(5h)	88.07(18)	Cr(1)–O(4)–C(2)	118.0(5)
Cr(1h)–Cr(1)–O(2h)	90.8(2)	Cr(1h)–O(5)–C(2)	121.6(5)
Cr(1h)–Cr(1)–O(6d)	171.52(17)	Cr(1c)–O(6)–C(2)	126.1(6)
O(1)–Cr(1)–O(4)	90.6(3)	Na(1)–O(5)–C(2)	135.2(6)
O(1)–Cr(1)–O(6d)	90.5(3)	Na(1d)–O(4)–C(2)	111.3(5)
O(1)–Cr(1)–O(2h)	178.5(3)	Na(1d)–O(1)–C(1)	110.1(6)
O(1)–Cr(1)–O(5h)	88.6(3)		
O(4)–Cr(1)–O(6d)	97.4(2)	O(1)–C(1)–O(3)	118.9(9)
O(2h)–Cr(1)–O(4)	88.0(3)	O(2)–C(1)–O(3)	121.2(10)
O(4)–Cr(1)–O(5h)	178.8(3)	O(1)–C(1)–O(2)	119.9(9)
O(2h)–Cr(1)–O(6d)	90.1(3)	O(4)–C(1)–O(6)	120.0(8)
O(5h)–Cr(1)–O(6d)	83.5(2)	O(5)–C(1)–O(6)	120.3(8)
O(2h)–Cr(1)–O(5h)	92.9(3)	O(4)–C(1)–O(5)	119.7(7)
O(5)–Na(1)–O(7)	99.4(3)	O(7)–Na(2)–O(9)	172.6(4)
O(5)–Na(1)–O(8)	156.2(3)	O(7)–Na(2)–O(10)	93.0(3)
O(1c)–Na(1)–O(5)	83.4(2)	O(7)–Na(2)–O(7a)	98.6(4)
O(4c)–Na(1)–O(5)	82.9(2)	O(7)–Na(2)–O(9a)	88.2(3)
O(5)–Na(1)–O(6g)	75.1(2)	O(7)–Na(2)–O(10a)	88.9(3)
O(7)–Na(1)–O(8)	96.9(3)	O(9)–Na(2)–O(10)	90.0(3)
O(1c)–Na(1)–O(7)	79.5(3)	O(7a)–Na(2)–O(9)	88.2(3)
O(4c)–Na(1)–O(7)	150.6(3)	O(9)–Na(2)–O(9a)	85.2(4)
O(6g)–Na(1)–O(7)	95.6(3)	O(9)–Na(2)–O(10a)	87.8(3)
O(1c)–Na(1)–O(8)	116.7(3)	O(7a)–Na(2)–O(10)	88.9(3)
O(4c)–Na(1)–O(8)	91.2(3)	O(9a)–Na(2)–O(10)	87.8(3)

O(6g)–Na(1)–O(8)	86.2(3)	O(10)–Na(2)–O(10a)	177.1(5)
O(1c)–Na(1)–O(4c)	71.6(2)	O(7a)–Na(2)–O(9a)	172.6(4)
O(1c)–Na(1)–O(6g)	156.9(3)	O(7a)–Na(2)–O(10a)	93.0(3)
O(4c)–Na(1)–O(6g)	113.2(3)	O(9a)–Na(2)–O(10a)	90.0(3)

Symmetry codes: a 1-x,y,1/2-z; c x,-y,-1/2+z; d x,-y,1/2+z; g 1/2-x,1/2+y,1/2-z; h 1/2-x,1/2-y,1-z.

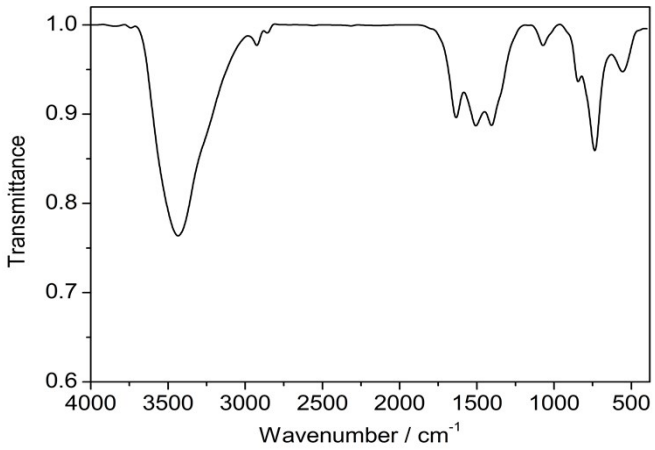

Fig. S1 IR spectrum of compound **1**.

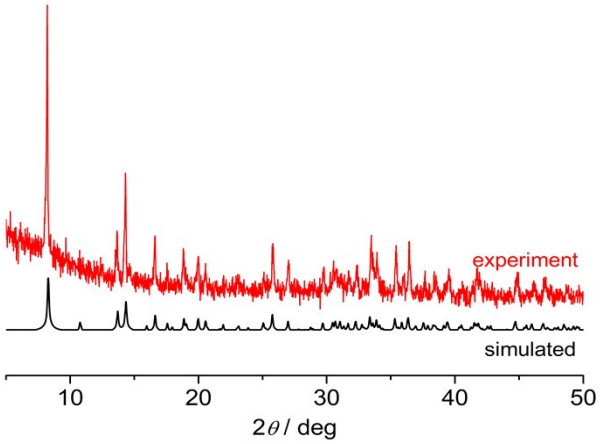

Fig. S2 Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination and the as-synthesized bulk samples of **1.**

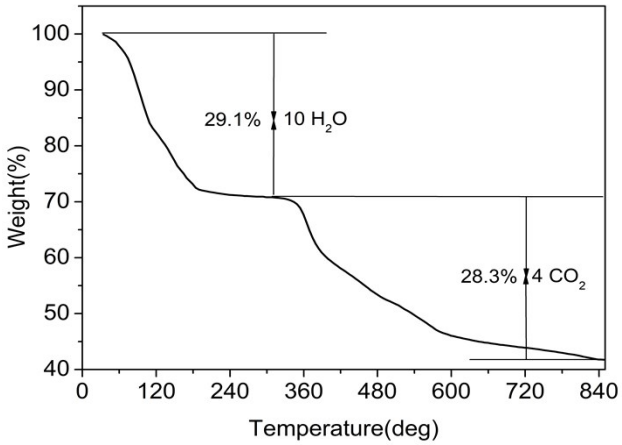

Fig. S3 TG curve of compound **1**.

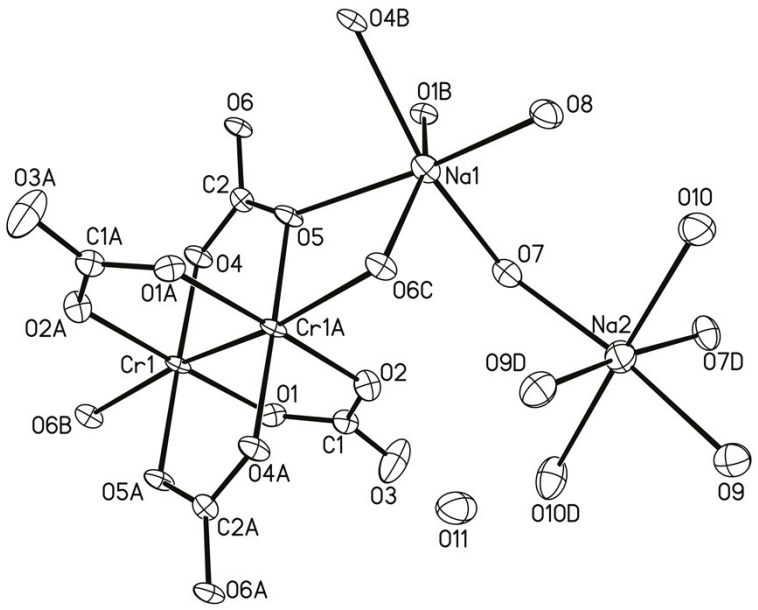

Fig. S4 ORTEP representation (30% thermal probability ellipsoids) of the crystal structure of **1.**

Table S4. Selected bond distances (Å) from the experiment and calculation.

	Exp.	Calc.(close-shell)	Calc.(open-shell)
Cr(1)–Cr(1A)	2.268(3)	1.7626	2.11760
Cr(1)–O(1)	2.047(7)	2.0107	1.87495
Cr(1)–O(4)	2.036(6)	2.0103	1.87330
Cr(1)–O(2A)	2.036(7)	2.0107	1.87495
Cr(1)–O(5A)	2.028(6)	2.0103	1.87330
Cr(1)–O(6B)	2.294(6)	3.1594	2.28620
C(1)–O(1)	1.296(12)	1.3238	1.31556
C(1)–O(2)	1.308(11)	1.3238	1.31556
C(1)–O(3)	1.249(14)	1.2712	1.21613
C(2)–O(4)	1.296(11)	1.3242	1.32311
C(2)–O(5)	1.291(10)	1.3242	1.32311
C(2)–O(6)	1.283(10)	1.2710	1.21613

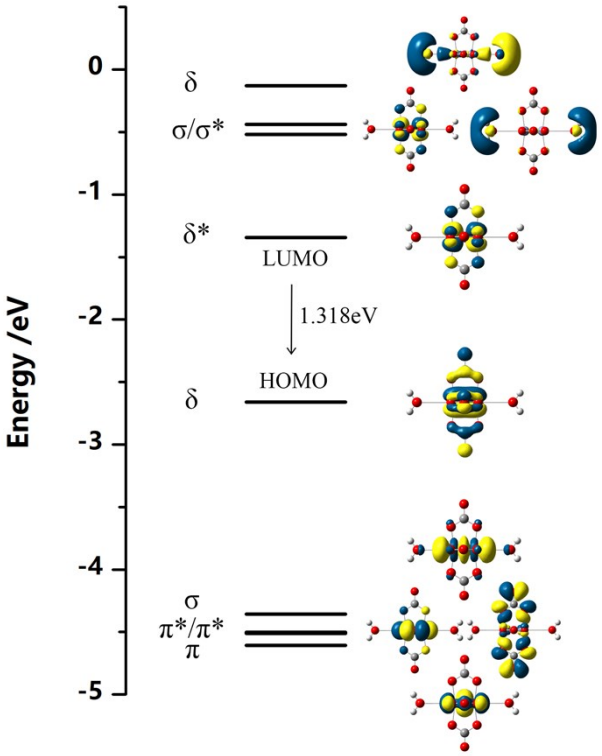

Fig. S5 Selected frontier orbital diagrams for the model anion $[Cr_2(CO_3)_4(H_2O)_2]^{4-}$ in compound **1** derived from the close-shell electronic structure DFT calculation in vacuum.

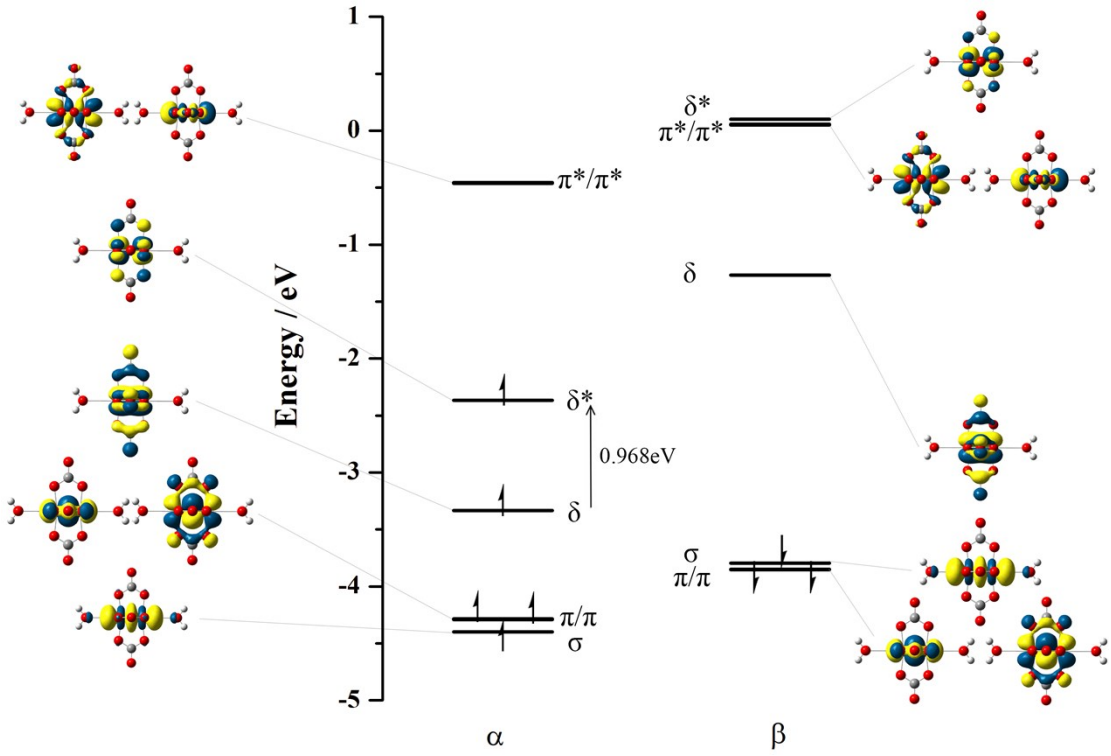

Fig. S6 Selected frontier orbital diagrams for the model anion $[Cr_2(CO_3)_4(H_2O)_2]^{4-}$ in compound **1** derived from the open-shell electronic structure DFT calculation in vacuum.

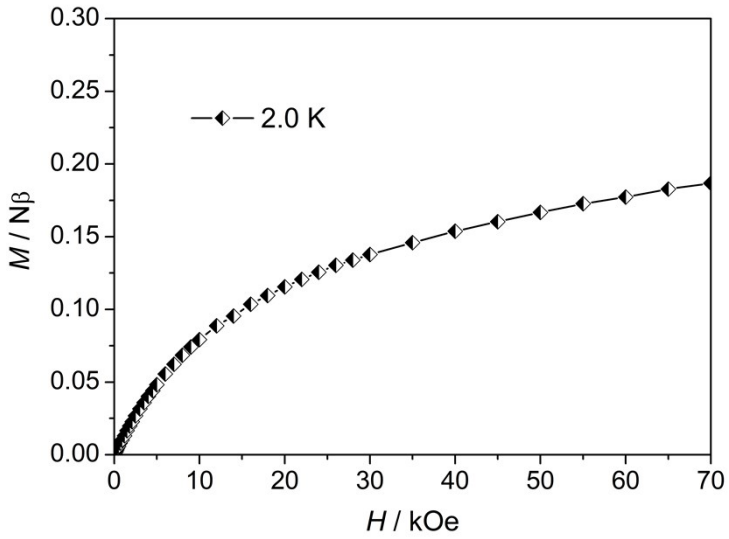

Fig. S7. *M* versus *H* data of compound **1**.

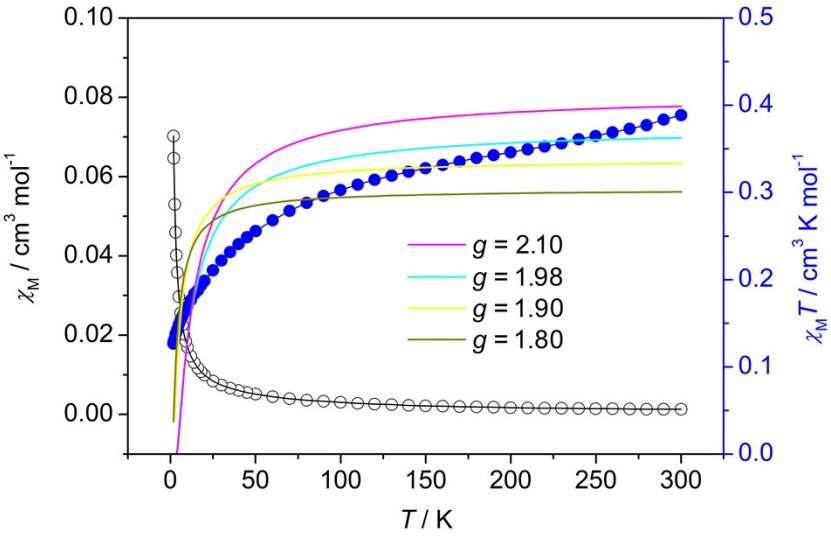

Fig. S8. The susceptibility data of compound **1** fit using the model of Curély with a square-grid 2D symmetry of the Heisenberg exchange interactions $H = \Sigma_{nn} JS_iS_j$. (fixed g). The fits (fixed g) give parameters: $g_{Cr} = 2.10$, $J = -3.7$ cm^{-1}; $g_{Cr} = 1.98$, $J = -3.4$ cm^{-1}; $g_{Cr} = 1.90$, $J = -1.5$ cm^{-1} and $g_{Cr} = 1.80$, $J = -1.1$ cm^{-1}.

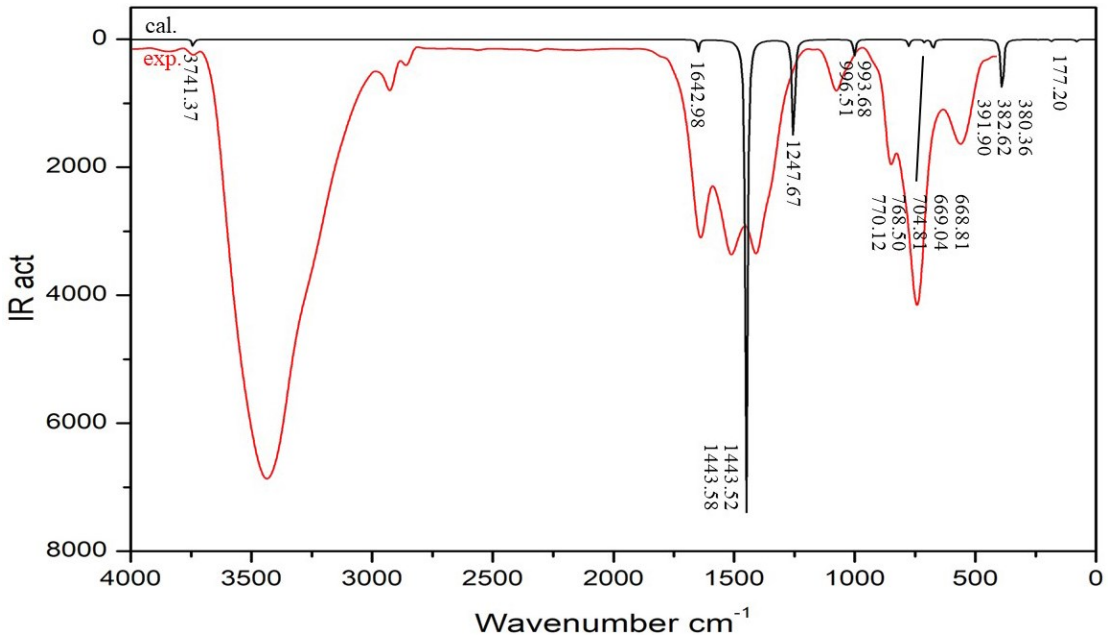

Fig. S9. IR spectrum of compound **1** in solid form and DFT calculated spectrum of model $Cr_2(CO_3)_4(H_2O)_2^{4-}$ for comparison.

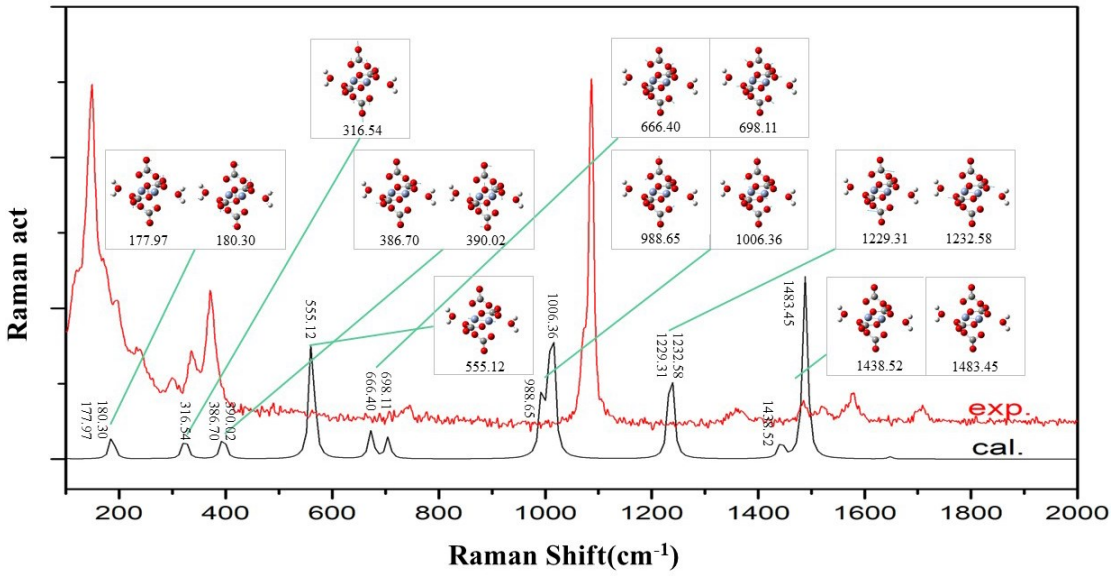

Fig. S10. Raman spectra of compound **1** in solid form recorded at 300 K and with excitation wavelengths of 532 nm. The lowest trace is the calculated Raman spectrum using method UBP86/(SDD for Cr, 6-311+G* for C, H, O) with vibrational wavenumbers scaled by 0.81.

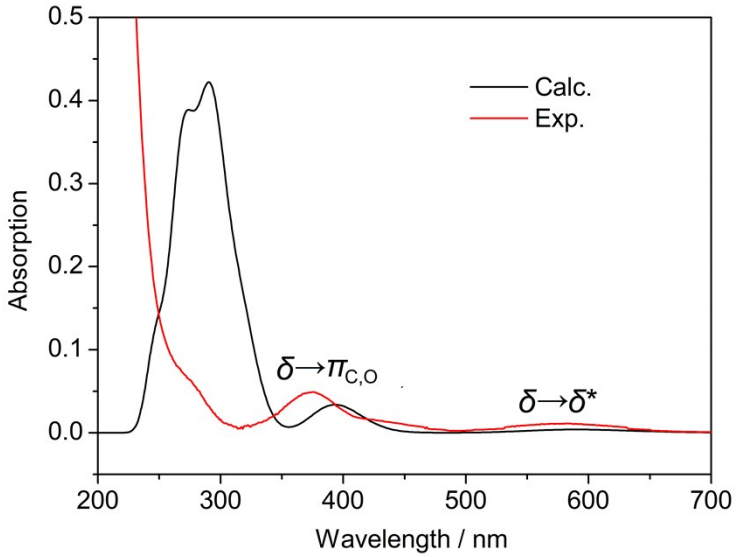

Fig. S11 Experimental UV–vis spectrum of compound **1** in aqueous solution and calculated (TDDFT) spectrum of model $Cr_2(CO_3)_4(H_2O)_2^{4-}$ for comparison.

Table S5. The representative calculated optical transitions for anion $Cr_2(CO_3)_4(H_2O)_2^{4-}$.

λ(nm)	f	assign.	%
589.56	0.0011	$\delta\rightarrow\delta^*$	98
400.24	0.0017	$\delta\rightarrow\pi_{C,O}$	99
397.86	0.0017	$\delta\rightarrow\pi_{C,O}$	99
315.73	0.0372	$\sigma\rightarrow\sigma^*$	99
		$\pi^*\rightarrow\sigma^*$	99
292.14	0.0516	$\delta\rightarrow\pi^*_{C,O}$	97
292.07	0.0479	$\delta\rightarrow\pi^*_{C,O}$	97
273.11	0.0179	$\pi^*_{Cr\text{-}O}\rightarrow\delta^*$	76
271.22	0.0210	$\pi^*_{Cr\text{-}O}\rightarrow\delta^*$	47
266.19	0.0142	$\pi\rightarrow\delta$	78
265.90	0.0264	$\pi\rightarrow\delta$	43