SUPPORTING INFORMATION

Fast Capture, Separation and Luminescent Probe of Pollutant Chromate, and Slow Magnetic Relaxation Behavior: A Promising Multifunctional Cationic Heterometal-Organic Framework[†]

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Materials and General Characterizations

All of chemicals are analytically grade and purchased without further purification. Elemental analyses for C, H, and N were obtained at the Institute of Elemental Organic Chemistry, Nankai University. The FT-IR spectra were measured with a Bruker Tensor 27 Spectrophoto meter on KBr disks. TGA experiment was performed on a NETZSCH TG 209 instrument with a heating rate of 10 °C min⁻¹. Powder X-ray diffraction measurements were recorded on a D/Max-2500 X-ray diffractometer using Cu-K α radiation. UV-vis spectroscopic studies were collected on a HITACHI U-3900 spectrophotometer to monitor the exchange progress. The pH measurements were performed with a pH-3C model pH-meter. The fluorescent spectra were measured on an F-4500 FL Spectrophotometer. The magnetic properties were measured on a Quantum Design MPMS-XL7 and a PPMS-9 ACMS magnetometer. Diamagnetic correction was made with Pascal's constants for all the constituent atoms.

Synthesis of {[Dy₂Zn(BPDC)₃(H₂O)₄](ClO₄)₂·10H₂O}_n (1-ClO₄)

A mixture of H₂BPDC (0.0488 g, 0.2 mmol), Zn(ClO₄)₂· 6H₂O (0.0186 g, 0.05 mmol), Dy(NO₃)₃· 6H₂O (0.0456 g, 0.1 mmol), 4 mL distilled water and 4 mL anhydrous alcohol were sealed in a Teflon-lined stainless vessel (25 mL) and heated at 130°C for 72 h under autogenous pressure. The vessel was then cooled slowly down to room temperature at 1.5 °C h. Colorless needlelike crystals were obtained. The yield was 68% (based on Dy(NO₃)₃·6H₂O). Elemental anal (%) Calcd: C, 27.57; H, 2.96; N: 5.36. Found: C, 27.26; H, 2.88; N: 5.65.

Crystallographic Studies

Crystallographic data of **1-ClO₄** was collected on a SuperNova Single Crystal Diffractometer equipped with graphite-monochromatic MoK α radiation ($\lambda = 0.71073$ Å). The data integration and empirical absorption corrections were carried out by SAINT programs. The structure was solved by direct methods (SHELXS 97). All the non-hydrogen atoms were refined anisotropically on F² by full-matrix least-squares techniques (SHELXL 97). All the hydrogen atoms except for those of the uncoordinated water molecules in these coordination polymers were generated geometrically and refined isotropically using the riding model. Additionally, ClO₄⁻ is disorder and refined with a disorder model of two overlapping configurations with occupancies of 0.673 and 0.327, and some Cl-O bonds were restrained.

Structures of 1-ClO₄



Fig. S1. The coordinated environments of Dy^{3+} , Zn^{2+} and $BPDC^{2-}$ ligand.



Fig. S2. The structure along the a direction, the green pillar acts as the channel of c direction.



Fig. S3. (a) $[Dy_2]$ unit; (b) $[Zn(BPDC)_3]$ unit; (c) Topology of **1**, the red acts as the $[Dy_2]$ unit, and the blue acts as $[Zn(BPDC)_3]$ unit.

Anion Exchange of 1-ClO₄

(a) Molar ratio 1:1 (1-ClO₄ and K₂CrO₄)

78 mg **1-ClO₄** (0.05 mmol) solid was placed into 10 mL containing 0.05 mmol K_2CrO_4 aqueous solution, slowly stirring for 8 hours at room temperature. The process was monitored at 373 nm of CrO_4^{2-} typical absorption by liquid UV-vis spectroscopy at intervals. 0.2 mL of K_2CrO_4 solution was pipetted from the exchanging solution for each time and diluted to 2.5 mL with deionized water to measure the change of UV-vis adsorption intensity. The adsorption intensity of

solution decreases from 1.83 to 0.28 with continuously exchanging, and keep unchanged after exchanging 6 h. The case means 85% CrO_4^{2-} were exchanged into the channels of **1-ClO**₄, and thus the molar ratio of Cr/Zn in **1-ClO**₄ after exchanged is 0.85:1. It should be noted that the exchange speed is dramatically fast within first 30 minutes. After exchange, the solid samples were centrifuged, rinsed with water and dried in the air, namely **1-ClO**₄-**A**. ICP data of **1-CrO**₄-**A** was listed in Table S1, and the result with Cr/Zn molar ratio of 0.89:1 is consistent with liquid UV-vis analysis. Compared with other CrO_4^{2-} sorbents,² **1-ClO**₄ presents more fast and high capacity to exchange CrO_4^{2-} .

 Table S1. ICP data of compounds

Compounds	Zn (%)	Cr (%)	Cr/Zn (molar ratio)
1-CrO ₄ -A	3.060	2.18	0.89:1
1-CrO ₄	3.11	2.41	0.97:1
1-CrO ₄ (selective)	3.18	2.59	1.02:1
1-CO ₃	2.92	1.00	0.43:1
1-SO ₄	2.77	1.65	0.75:1

Table S2. Capture capacity and time of CrO_4^{2-} in different compounds

Compounds	Capacity (mol/mol)	Capacity (mg/g)	Exchange Time (h)
Uncalcined LDHs ¹	0.03	5.80	48
Calcined LDHs ¹	0.09	17.39	48
SLUG-21 ¹	0.41	60.10	48
1-ClO ₄ (in this work)	0.85	62.88	6

(b) Molar ratio 1:2 (1-ClO₄ and K₂CrO₄)

78 mg 1-ClO₄ (0.05 mmol) solid was placed into 10 mL containing 0.1 mmol K₂CrO₄ aqueous solution, stirring for 10 hours at room temperature. The process was also monitored by liquid UV-vis spectroscopy at intervals (Fig. S4). 0.1 mL of K₂CrO₄ solution was pipetted from the exchanging solution for each time and diluted to 2.5 mL with deionized water to measure the change of UV-vis adsorption intensity. With the exchange experiment went on, the intensity of the main characteristic adsorption peak of CrO_4^{2-} in solution at 373 nm promptly decreased within 1 hour, indicating the $CrO_4^{2^2}$ in solution entered into the channels in **1-ClO**₄. After exchanging for 8 hours, the UV-vis adsorption intensity almost kept constant, and the corresponding CrO_4^{2-} concentration in solution decreased by 50%, indicative of Zn/Cr molar ratio of 1:1 in solid sample. Simultaneously, the color of the solid in solution changed from colorless to yellow, which was similar to that of the equimolar exchange. After exchange, the samples were centrifuged, rinsed with water and dried in the air, marking 1-CrO₄. ICP test for 1-CrO₄ revealed the molar ratio of Cr/Zn was 0.97:1, well consistent with the ratio of the 1:1 mentioned above (Table S1). ICP and UV-vis studies suggested that all of ClO_4^- in the channels of **1-ClO₄** may be completely exchanged under excess K₂CrO₄ and enter into the solution. The entire exchange process was also repeated for several times.



Fig. S4. UV-vis spectra of the K_2CrO_4 solution during anion exchange with **1-ClO₄** (molar ratio 1:2), slowly stirring for 10 hours.

(c) Extremely low concentration CrO₄²⁻

2 mg **1-ClO₄** (1.2×10^{-3} mmol) solid and 2.5 mL of 5×10^{-5} mol/L (9.5 ppm) K₂CrO₄ aqueous solution were placed into a 3 mL cuvette, which was always accompanied with UV-vis spectrophotometer, and statically stayed for 24 hours at room temperature. The process was monitored by liquid UV-vis spectroscopy at intervals. As the exchanging experiment progressed, the intensity of the main characteristic adsorption peak of CrO_4^{2-} at 373 nm gradually dropped, and after 24 hours, no adsorption peaks were observed, suggesting CrO_4^{2-} in solution completely entered into the channels of **1-ClO**₄ (Fig. S5).



Fig. S5. UV-vis spectra of the K₂CrO₄ solution during anion exchange under extremely low concentration (9.5 ppm) K₂CrO₄, statically for 24 hours.

(d) Selective capture of CrO₄²⁻

78 mg **1-ClO₄** (0.05 mmol) solid was placed into 10 mL mixed anions aqueous solution containing 0.1 mmol K₂CrO₄, 0.1 mmol KCl, 0.1 mmol KBr, 0.1 mmol KI and 0.1 mmol KNO₃, statically for 30 hours at room temperature. The process was monitored by liquid UV/Vis spectroscopy at intervals. 0.1 mL solution containing mixed anions ($CrO_4^{2^-}$, NO_3^- , Cl^- , Br^- , Γ) was pipetted from the exchanging solution for

each time and diluted to 2.5 mL with deionized water to measure the change of UV-vis adsorption intensity. As the exchanging experiment proceeded, the intensity of the main characteristic adsorption peak of CrO_4^{2-} at 373 nm decreased gradually and down to 50%, which was similar to the exchange experiments only with K_2CrO_4 solution, indicating the CrO_4^{2-} in the solution could be exchanged by ClO_4^{-} and enter into the channels of 1-ClO₄. After that, the solid sample in the solution was centrifuged, rinsed with water and dried in the air, named 1-CrO₄. XPS measurement of **1-CrO₄** shows the peak of Cr $2p_{3/2}$ at 574 ev and the disappearance of the Cl (ClO₄⁻) 2p_{3/2} peak at 207ev, as well as does not emerge the K, Cl, Br, I (Cl⁻, Br⁻, I⁻) peaks² (Fig. S6). No adsorption peak of NO_3^{-1} (~1330 cm⁻¹) was observed in FT-IR spectra of **1-CrO₄** (Fig. S7). The all results indicated that only the CrO_4^{2-} entered into the channels by exchanging ClO_4^- , while other anions including NO_3^- , Cl^- , Br^- , I^- , did not exchange ClO_4^- . The case clearly confirmed **1-ClO₄** may separate CrO_4^{2-} from mixed anions solution. ICP analyses of 1-CrO₄ revealed the molar ratio of Cr/Zn was 1.02:1 (Table S1), suggesting ClO_4^- in solid sample was thoroughly exchanged by CrO_4^{-2-} .



Fig. S6. XPS for **1-ClO₄** (black), **1-CrO₄** (formed by the experiment with 1:2 molar ratio, red), **1-CrO₄** (produced by selective capture, green).



Fig. S7. FT-IR of 1-ClO₄, 1-CrO₄ and 1-CrO₄ (selective capture)

(e) Release of CrO₄²⁻ in 1-CrO₄

10 mg **1-CrO₄** was placed into 5mL 0.002 mol/L K_2CO_3 or 5mL of 0.002 mol/L Na_2SO_4 aqueous solution, and statically stayed for 36 hours. The process was also monitored by liquid UV-vis spectroscopy at intervals. 2.5 mL of 0.002 mol/L K_2CO_3 or Na_2SO_4 solution was pipetted from the exchanging solution for each time to measure the change of UV-vis adsorption intensity. After measured for each time, the 2.5 mL solution was then returned to the original solution for continuously exchanging. With the exchange experiment went on, the main characteristic

adsorption peak of $\text{CrO}_4^{2^-}$ in solution at 373 nm emerged and the intensity increased gradually, indicating the $\text{CrO}_4^{2^-}$ was released in the solution (Fig. S9). After exchanging for 36 hours, the UV-vis adsorption intensity almost kept constant, and the release rate was faster in K₂CO₃ than that in Na₂SO₄ solution. Simultaneously, the color of the soild samples faded in some extent (Fig. S8). After that, the samples were centrifuged, rinsed with water and dried in the air, marking **1-CO**₃ and **1-SO**₄, respectively. ICP test revealed the molar ratio of Cr/Zn in **1-CO**₃ and **1-SO**₄ was 0.43 and 0.75, respectively, implying 57% and 25% CrO₄²⁻ was released into solution of K₂CO₃ and Na₂SO₄, respectively (Table S1). Comparably, 10 mg **1-CrO**₄ was immersed 5mL of 0.1 mol/L NaClO₄, and KX solution (X= NO₃, Cl, Br, I) solution for 36 h, respectively, and the process was monitored by liquid UV-vis spectroscopy. The results indicated that the no typical peaks of CrO₄²⁻ were observed (Fig. S10-S14), meaning no CrO₄²⁻ were released from **1-CrO**₄ by NO₃⁻, Cl, Br⁻, Γ and ClO₄⁻ exchanging.



Fig. S8. (a) The color of the solid-state **1-ClO₄**, **1-CrO₄**, and **1-CO₃**. (b) The change of solution color during the release process of $\text{CrO}_4^{2^-}$ by exchanging $\text{CO}_3^{2^-}$.



Fig. S9. The release of CrO_4^{2-} in Na_2SO_4 solution.



Fig. S10. UV-vis spectra of the KNO₃ solution after anion exchange with **1-CrO₄** statically for 36 hours.

Fig. S12. UV-vis spectra of the KBr solution after anion exchange with **1-CrO₄** statically for 36 hours.

Fig. S14. UV-vis spectra of the NaClO₄ solution after anion exchange with 1-CrO₄ statically for 36 hours.

Effect of CrO₄²⁻ on the luminescence of 1-ClO₄

The solid-state photoluminescent spectrum of 1-ClO₄ was firstly measured at room temperature, which displayed the typical bands of Dy³⁺ upon excitation at 300 nm with two main bands 479 and 573 nm, being ascribed to ${}^{4}F_{5/2} \rightarrow {}^{6}H_{15/2}$, ${}^{4}F_{5/2} \rightarrow {}^{6}H_{13/2}$ transition.³ Then 0.025 mmol 1-ClO₄ (39 mg) samples were placed into 5 mL of 0.02 mol/L K₂CrO₄ solution. At various time intervals (5 minutes, 30 minutes, 1 hour and 8 hours), the samples were centrifuged, rinsed with water and dried in the air, respectively. The photoluminescent spectra of the solid sample given at different exchange time were measured under the same experimental conditions. The results displayed the luminescent intensity of Dy^{3+} will gradually decrease with CrO_4^{2-} entering into the channels in 1-ClO₄. The luminescent intensity of the sample after exchanging for 8 h decreases to minimum. Then the exchanged sample was centrifuged, rinsed with water and dried in the air, and further immersed into 0.002 mol/L K₂CO₃ or 0.002 mol/L Na₂SO₄ aqueous solution. The solid-state photoluminescent spectra were measured at the same experimental conditions as above. With the release of $CrO_4^{2^2}$, the luminescent intensity rebound gradually (Fig. S15). Therefore, **1-ClO₄** may be considered as the luminescent probe of CrO_4^{2-} .

Fig. S15. Photoluminescent spectra of **1-CrO₄** upon excited at 300 nm during exchange with CO_3^{2-} (solid line) and SO_4^{2-} (dash line).

Magnetic Properties

Variable-temperature magnetic susceptibility was measured at 2-300K and 1000Oe. The $\chi_M T$ value decreases very slowly from 300 to 50 K and more rapidly below 50K. (Fig. S16), indicating an antiferromagnetic coupling between adjacent Dy³⁺ and/or a progressive depopulation of excited Stark sublevels.

Fig. S16. The plot of $\chi_m T$ versus *T* for **1-ClO**₄.

The magnetization of 1-ClO₄ vs field was measured at 2 K. Below 10000 Oe, the magnetization increases sharply. Above this field, it increases slowly, and it has not reached a saturation value until 80000 Oe, suggesting the existence of magnetic anisotropy and/or low-lying excited states (Fig. S17).

Fig. S17. Field dependence of magnetization for 1-ClO₄ at 2 K.

Fig. S18. Temperature dependence of the in-phase (χ'_{M}) and out-of-phase (χ''_{M}) signals of the ac susceptibility for **1-ClO**₄ at $H_{ac} = 3$ Oe, $H_{dc} = 0$.

Fig. S19. Temperature dependence of the in-phase (χ'_m) and out-of-phase (χ''_m) signals of the ac susceptibility for **1-ClO₄** at $H_{ac} = 3$ Oe, $H_{dc} = 1000$ Oe.

Thermogravimetric Analysis (TGA) and Powder X-Ray Diffraction (PXRD)

TGA curve of **1-ClO₄** exhibits two steps of weight loss. The first weight loss of 15.78% between 100 and 200°C arises from the loss of ten free water molecules and four coordinated water molecules, which is well consistent with the calculated 16.07%. During the range of 200-370°C, it mainly stays in a plateau, indicating the higher thermal stability for **1-ClO₄**. The second weight loss above 370°C stems from the decomposition of 3D framework in **1-ClO₄** (Fig. S20).

The PXRD patterns for 1-ClO₄, 1-CrO₄-A, 1-CrO₄, 1-CrO₄ (Selective capture), 1-CO₃ and 1-SO₄ are in conformity with the simulated, which are indicative of the high purity of the samples and the 3D framework remained intact during all of the exchange process. Importantly, when the samples were immersed in NaOH (pH=9 and pH=11) for two days, PXRD studies demonstrated the 3D framework also remained intact (Fig. S21). These results exhibit **1-ClO₄** have higher thermal stability and stronger alkali resistance, providing a favorable foundation to exchange CrO_4^{2-} in practical application.

Fig. S20. The TGA curve of 1-ClO₄.

Fig. S21. The PXRD for 1-ClO₄, 1-CrO₄-A, 1-CrO₄, 1-CrO₄ (selective capture), 1-SO₄, 1-CO₃, 1-ClO₄ in pH=9 and 11 NaOH solution for two days.

Crystallographic Parameters and selected bond lengths and angles for 1-ClO₄

Table S3 Crystal data and structure refinement for $1-ClO_4$

Empirical formula	C36 H46 Cl2 Dy2	N6 O34 Zn
Formula weight	1568.06	
Temperature	293(2) K	
Wavelength	0.71073 A	
Crystal system, space group	Monoclinic, C2/c	
Unit cell dimensions	a = 17.3797(4) Å	alpha = 90 deg.
	b = 16.6989(3) Å	beta = 107.578(2) deg.
	c = 21.4272(5) Å	gamma = 90 deg.
Volume	5928.3(2) Å ^3`	
Z, Calculated density	4, 1.734 Mg/m^3	
Absorption coefficient	3.081 mm^-1	

F(000)	3088
Crystal size	0.30 x 0.20 x 0.20 mm
Theta range for data collection	2.46 to 25.01 deg.
Limiting indices	-13<=h<=20, -15<=k<=19, -25<=l<=24
Reflections collected / unique	11712 / 5235 [R(int) = 0.0302]
Completeness to theta $= 25.01$	99.90%
Max. and min. transmission	0.5777 and 0.5130
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5235 / 16 / 397
Goodness-of-fit on F^2	1.176
Final R indices [I>2sigma(I)]	R1 = 0.0421, $wR2 = 0.1309$
R indices (all data)	R1 = 0.0532, $wR2 = 0.1343$

Table S4 Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103)for 1-ClO4. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	Х	У	Z	U(eq)	
C(1)	574(4)	4333(4)	8491(3)	15(2)	
C(3)	2599(4)	5785(5)	8646(4)	23(2)	
C(5)	2689(4)	5150(5)	9076(3)	17(2)	
C(6)	2022(4)	4677(4)	9034(4)	17(2)	
C(7)	-90(4)	-1314(4)	9226(3)	15(2)	
C(8)	-807(4)	3507(4)	8388(4)	19(2)	
C(9)	-6(4)	-1999(4)	8196(3)	14(2)	
C(10)	-141(4)	-2048(4)	8811(3)	14(2)	
C(11)	-818(5)	4250(4)	8116(4)	20(2)	
C(12)	326(5)	6549(5)	6367(3)	20(2)	
C(13)	-65(4)	3148(4)	8703(3)	14(2)	
C(14)	-58(4)	-2684(4)	7835(3)	12(2)	
C(15)	-12(4)	2299(4)	8955(3)	16(2)	
C(17)	1299(4)	4835(4)	8554(3)	14(2)	
C(18)	-303(5)	-2788(4)	9026(3)	21(2)	
C(19)	1838(4)	5915(5)	8191(4)	19(2)	
C(20)	620(4)	3569(5)	8759(3)	18(2)	
C(1A)	1536(4)	59(5)	10405(3)	17(2)	
Cl(1)	2624(4)	3010(4)	8016(3)	41(1)	
Cl(1')	3132(2)	3987(2)	7208(2)	41(1)	
Dy(1)	217(1)	677(1)	9309(1)	10(1)	
N(3)	210(3)	6595(3)	6951(3)	12(1)	
N(4)	1214(4)	5450(4)	8138(3)	14(1)	
N(7)	-144(3)	4659(4)	8155(3)	14(1)	
O(1)	303(3)	1384(3)	10268(2)	20(1)	

O(2)	1574(3)	548(4)	9977(3)	27(1)
O(3)	897(3)	-269(3)	10414(2)	20(1)
O(4)	-628(3)	1939(3)	8990(2)	20(1)
O(5)	672(3)	1975(3)	9116(3)	26(1)
O(6)	153(3)	-676(3)	9028(2)	20(1)
O(7)	-639(4)	608(3)	8216(3)	41(2)
O(8)	1127(4)	557(4)	8645(3)	44(2)
O(9)	859(6)	1799(4)	7684(3)	64(2)
O(10)	2896(9)	930(10)	9226(9)	188(8)
O(12)	880(9)	5248(12)	120(7)	178(7)
O(13)	8409(11)	2178(17)	9845(11)	111(10)
O(14)	1941(5)	2483(6)	330(4)	83(3)
O(15)	2880(11)	2206(7)	7988(10)	71(3)
O(16)	1861(6)	3009(11)	8115(8)	77(4)
O(17)	3175(7)	3413(8)	8565(5)	22(2)
O(18)	2616(10)	3424(13)	7435(6)	102(6)
O(13')	8568(10)	3021(18)	9753(8)	99(9)
O(15')	3165(7)	3132(7)	7062(6)	71(3)
O(16')	2900(9)	4089(8)	7780(6)	77(4)
O(17')	3922(5)	4369(5)	7303(4)	22(2)
O(18')	2575(7)	4355(10)	6642(7)	102(6)
Zn(2)	0	5610(1)	7500	10(1)

Table S5. Bond lengths [Å] and angles [°] for $1\text{-}ClO_4$

$Dy(1)-O(3)#2$ $2.293(5)$ $Dy(1)-O(6)$ $2.333(5)$ $Dy(1)-O(1)$ $2.335(5)$ $Dy(1)-O(7)$ $2.368(5)$ $Dy(1)-O(2)$ $2.371(5)$ $D_{2}(1)-O(5)$ $2.296(5)$
$Dy(1)-O(6)$ 2.333(5) $Dy(1)-O(1)$ 2.335(5) $Dy(1)-O(7)$ 2.368(5) $Dy(1)-O(2)$ 2.371(5) $D_{1}(1)-O(5)$ 2.295(5)
Dy(1)-O(1) 2.335(5) Dy(1)-O(7) 2.368(5) Dy(1)-O(2) 2.371(5) D (1) O(5)
Dy(1)-O(7) 2.368(5) Dy(1)-O(2) 2.371(5) D (1) O(5)
Dy(1)-O(2) 2.371(5)
Dy(1)-O(5) 2.386(5)
Dy(1)-O(8) 2.434(6)
Dy(1)-O(4) 2.541(5)
Dy(1)-O(3) 2.794(5)
Dy(1)-Dy(1)#2 3.9742(6)
N(3)-Zn(2) 2.116(6)
N(4)-Zn(2) 2.156(6)
N(7)-Zn(2) 2.184(6)
O(3)-Dy(1)#2 2.293(5)
Zn(2)-N(3)#5 2.116(6)
Zn(2)-N(4)#5 2.156(6)
Zn(2)-N(7)#5 2.184(6)
O(3)-C(1A)-Dy(1) 71.4(4)

O(2)-C(1A)-Dv(1)	51.8(4)
C(5)#1-C(1A)-Dv(1)	169.2(5)
C(12)-N(3)-Zn(2)	125.4(5)
C(14)#3-N(3)-Zn(2)	115.1(4)
C(19)-N(4)-Zn(2)	127.4(5)
C(17)-N(4)-Zn(2)	114.0(5)
C(11)-N(7)-Zn(2)	126.9(5)
C(1)-N(7)-Zn(2)	111.6(5)
C(7)#2-O(1)-Dv(1)	139.2(5)
C(1A)-O(2)-Dv(1)	103.9(4)
C(1A)-O(3)-Dy(1)#2	164.3(5)
C(1A)-O(3)-Dv(1)	83.7(4)
Dy(1)#2-O(3)-Dy(1)	102.32(17)
C(15)-O(4)-Dy(1)	88.8(4)
C(15)-O(5)-Dy(1)	95.9(4)
C(7)-O(6)-Dy(1)	136.4(5)
N(3)#5-Zn(2)-N(3)	78.0(3)
N(3)#5-Zn(2)-N(4)#5	98.6(2)
N(3)-Zn(2)-N(4)#5	92.5(2)
N(3)#5-Zn(2)-N(4)	92.5(2)
N(3)-Zn(2)-N(4)	98.6(2)
N(4)#5-Zn(2)-N(4)	165.8(3)
N(3)#5-Zn(2)-N(7)	97.8(2)
N(3)-Zn(2)-N(7)	174.2(2)
N(4)#5-Zn(2)-N(7)	92.1(2)
N(4)-Zn(2)-N(7)	77.4(2)
N(3)#5-Zn(2)-N(7)#5	174.2(2)
N(3)-Zn(2)-N(7)#5	97.8(2)
N(4)#5-Zn(2)-N(7)#5	77.4(2)
N(4)-Zn(2)-N(7)#5	92.1(2)
N(7)-Zn(2)-N(7)#5	86.6(3)
O(3)#2-Dy(1)-O(6)	78.53(19)
O(3)#2-Dy(1)-O(1)	75.95(18)
O(6)-Dy(1)-O(1)	134.62(17)
O(3)#2-Dy(1)-O(7)	85.1(2)
O(6)-Dy(1)-O(7)	74.38(19)
O(1)-Dy(1)-O(7)	138.5(2)
O(3)#2-Dy(1)-O(2)	125.49(18)
O(6)-Dy(1)-O(2)	91.6(2)
O(1)-Dy(1)-O(2)	74.1(2)
O(7)-Dy(1)-O(2)	143.7(2)
O(3)#2-Dy(1)-O(5)	131.70(18)
O(6)-Dy(1)-O(5)	145.83(18)
O(1)-Dy(1)-O(5)	75.94(18)

$O(7)$ $D_{rr}(1)$ $O(5)$	00.0(2)	
O(7)-Dy(1)-O(5)	90.9(2) 82.26(10)	
O(2)+Dy(1)+O(3)	82.20(19)	
O(3)#2-Dy(1)-O(8)	76.0(2)	
O(0)-Dy(1)-O(8)	122 5(2)	
O(1)-Dy(1)-O(8)	75 1(2)	
O(7) - Dy(1) - O(8)	73.1(3) 60.0(2)	
O(2)-Dy(1)-O(8)	70.4(2)	
O(3)-Dy(1)-O(6)	70.4(2) 81 46(17)	
O(3)#2-Dy(1)-O(4)	61.40(17) 120.04(17)	
O(0)-Dy(1)-O(4) O(1) Dy(1) $O(4)$	$72 \ 30(17)$	
O(1)-Dy(1)-O(4) O(7) Dy(1) $O(4)$	(12.30(17) 68 58(10)	
O(7) - Dy(1) - O(4) O(2) Dy(1) O(4)	128 81(18)	
O(2)-Dy(1)-O(4) O(5) Dy(1) $O(4)$	52 81(16)	
O(3)-Dy(1)-O(4)	100 6(2)	
O(8)-Dy(1)-O(4) O(2)+2 Dy(1) O(2)	77.68(17)	
O(3)#2-Dy(1)-O(3)	(7.08(17))	
O(0)-Dy(1)-O(3)	69.20(10)	
O(1)-Dy(1)-O(3)	142.00(18)	
O(7) - Dy(1) - O(3)	40 21(17)	
O(2)-Dy(1)-O(3) O(5) Dy(1) $O(3)$	49.31(17)	
O(3) - Dy(1) - O(3)	125.07(17) 105 4(2)	
O(8) - Dy(1) - O(3)	103.4(2) 120.28(15)	
O(4) - Dy(1) - O(3) O(2) + 2 Dy(1) - O(15)	107.1(2)	
O(3)#2-Dy(1)-C(13)	107.1(2)	
O(0)-Dy(1)-C(13) O(1) Dy(1) C(15)	72 51(18)	
O(1)-Dy(1)-C(15)	77.6(2)	
O(7)-Dy(1)-C(15)	106 5(2)	
O(2)-Dy(1)-C(13) O(5) Dy(1) C(15)	26.44(10)	
O(3) - Dy(1) - C(15)	20.44(19)	
O(8)-Dy(1)-C(15) O(4) Dy(1) C(15)	89.2(2)	
O(4)-Dy(1)-C(15)	20.42(18)	
O(3)-Dy(1)-C(13)	101 8(2)	
O(3)#2-Dy(1)-C(1A)	80.21(10)	
O(0)-Dy(1)-C(1A) O(1) Dy(1) C(1A)	60.22(19)	
O(1)-Dy(1)-C(1A) O(7) Dy(1) C(1A)	09.28(19)	
O(7) - Dy(1) - C(1A)	24.36(10)	
O(2)-Dy(1)-C(1A)	24.30(19)	
O(3)-Dy(1)-C(1A)	24.06(18)	
O(3) - Dy(1) - O(1A) O(15) Dy(1) - O(1A)	24.70(10)	
U(13)-Uy(1)-U(1A) O(3)#2 Dy(1) Dy(1)#2	124.7(2)	
O(3) # 2 - Dy(1) - Dy(1) # 2	(13)	
O(0) - Dy(1) - Dy(1) + 2 O(1) Dy(1) - Dy(1) + 2	00.07(12)	
O(1) - Dy(1) - Dy(1) = 2	00.94(12)	
O(7)-Dy(1)-Dy(1)#2	120.34(17)	

O(2)-Dy(1)-Dy(1)#2	82.91(13)	
O(5)-Dy(1)-Dy(1)#2	142.53(14)	
O(8)-Dy(1)-Dy(1)#2	133.74(16)	
O(4)-Dy(1)-Dy(1)#2	116.61(11)	
C(1A)-Dy(1)-Dy(1)#2	58.74(13)	
Symmetry transformations used to generate equivalent atoms:		

#1 -x+1/2,-y+1/2,-z-	+2 #2 -x,-y,-z+2
#3 -x,y+1,-z+3/2	#4 -x,y-1,-z+3/2
#5 -x, y, -z+3/2	

Reference

1 H. Fei, M. R. Bresler, S. R. J. Oliver, J. Am. Chem. Soc. 2011, 133, 11110.

2 J. F. Moulder, W. F. Stickle, P. E. Sobol, K. D. Bomben, Handbook of x-ray photoelectron

spectroscopy, PE Corporation, USA, 1992.

3 N. Arnaud, E. Vaquer, J. Georges, Analyst. 1998, 123, 261.