Electronic Supplementary Information (ESI) for

$Mg(H_2O)_6[(IO_2(OH))_2(IO_3)]_2$: a new iodate with very large ultraviolet cutoff edge and optical anisotropy

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Table S1. Crystallographic data and structure refinement for $Mg(H_2O)_6[(IO_2(OH))_2(IO_3)]_2$.

Formula	$Mg(H_2O)_6[(IO_2(OH))_2(IO_3)]_2$
Formula weight	1185.84
Temperature/K	300.0
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	7.1697(2)
b/Å	21.3401(5)
c/Å	7.6048(2)
α/°	90
β/°	107.1430(10)
γ/°	90
Volume/Å^3	1111.86(5)
Z	2
ρ_{calc} g/cm^3	3.542
μ/mm^{-1}	8.515
F(000)	1076.0
Crystal size/mm^3	0.24 × 0.193 × 0.16
Radiation	MoKα (λ = 0.71073)
2ϑ range for data collection/°	5.922 to 56.614
Index ranges	$-9 \le h \le 9$, $-28 \le k \le 28$, $-10 \le l \le 10$
Reflections collected	27316
Independent reflections	2770 [R_{int} = 0.0279, R_{sigma} = 0.0137]
Data/restraints/parameters	2770/4/148
Goodness-of-fit on F^2	1.166
Final R indexes [$I \ge 2\sigma(I)$][a]	R_1 = 0.0149, wR_2 = 0.0269
Final R indexes [all data]	R_1 = 0.0174, wR_2 = 0.0274
Largest diff. peak/hole / e Å^{-3}	0.57/-0.41

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ and $wR_2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$

Table S2. Atomic coordinates (×10^4), equivalent isotropic displacement parameters (Å^2 × 10^3) and bond valence sum calculations for $Mg(H_2O)_6[(IO_2(OH))_2(IO_3)]_2$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Atoms	*x*	*y*	*z*	U_{eq}	BVS
Mg1	0	5000	5000	23.2(3)	2.14
I1	5317.4(2)	7932.6(2)	9670.8(2)	15.61(4)	5.12
I2	5679.9(2)	6125.1(2)	9976.8(2)	16.64(4)	5.23
I3	1015.4(2)	6779.8(2)	277.4(2)	17.26(5)	5.22
O1	5428(3)	8823.4(9)	9970(3)	27.4(5)	-1.28
O2	2838(3)	4757.0(10)	6623(3)	30.9(5)	-0.32
O3	9269(3)	7427.0(10)	467(3)	29.2(5)	-1.34
O4	5841(3)	5612.0(9)	8132(3)	23.8(4)	-1.68
O5	9808(3)	6181.8(10)	1157(3)	29.5(5)	-1.83
O6	2716(3)	7873.6(9)	9139(3)	25.0(4)	-1.76
O7	5192(3)	6841.9(9)	8625(3)	24.3(4)	-1.94
O8	877(3)	4999.8(11)	2625(3)	36.2(5)	-0.35
O9	5594(3)	8025.7(9)	7424(3)	23.0(4)	-1.98
O10	649(3)	5929.7(10)	5322(3)	35.7(5)	-0.39
O11	3237(3)	5932.1(9)	9996(3)	27.5(4)	-2.01
O12	9842(3)	6694.1(9)	7861(3)	24.6(4)	-1.77

Table S3. Selected bond lengths (Å) for $Mg(H_2O)_6[(IO_2(OH))_2(IO_3)]_2$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I1	O1	1.9133(19)	I3	O11	2.461(2)
I1	O6	1.7928(19)	I3	O12	1.7909(19)
I1	O7	2.4529(19)	Mg1	O2	2.110(2)
I1	O9	1.7883(18)	Mg1	O2[1]	2.110(2)
I2	O4	1.8102(18)	Mg1	O8	2.080(2)
I2	O7	1.8187(18)	Mg1	O8[1]	2.080(2)
I2	O11	1.8037(19)	Mg1	O10	2.036(2)
I3	O3	1.898(2)	Mg1	O10[1]	2.036(2)
I3	O5	1.7796(19)			

[1]-X,1-Y,1-Z

Table S4. Bond Angles for $Mg(H_2O)_6[(IO_2(OH))_2(IO_3)]_2$.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O1	I1	O7	167.84(7)	$O8^1$	Mg1	$O2^1$	91.25(9)
O6	I1	O1	95.78(9)	$O8^1$	Mg1	O2	88.75(9)
O6	I1	O7	85.64(8)	O8	Mg1	$O2^1$	88.75(9)
O9	I1	O1	89.47(9)	O8	Mg1	O2	91.25(9)
O9	I1	O6	101.13(9)	$O8^1$	Mg1	O8	180.00(13)
O9	I1	O7	78.42(8)	O10	Mg1	$O2^1$	88.72(9)
O4	I2	O7	96.66(9)	$O10^1$	Mg1	$O2^1$	91.28(9)
O11	I2	O4	98.76(9)	$O10^1$	Mg1	O2	88.72(9)
O11	I2	O7	99.87(9)	O10	Mg1	O2	91.28(9)
O3	I3	O11	179.10(8)	$O10^1$	Mg1	O8	90.71(9)
O5	I3	O3	95.07(10)	O10	Mg1	O8	89.29(9)
O5	I3	O11	84.53(8)	O10	Mg1	$O8^1$	90.71(9)
O5	I3	O12	100.32(10)	$O10^1$	Mg1	$O8^1$	89.29(9)
O12	I3	O3	91.80(9)	O10	Mg1	$O10^1$	180.0
O12	I3	O11	87.48(8)	O2	Mg1	$O2^1$	180.0

^{1}-X,1-Y,1-Z

Table S5. Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for $Mg(H_2O)_6[(IO_2(OH))_2(IO_3)]_2$.

Atom	*x*	*y*	*z*	U_{eq}
H1	5525.72	8925.27	970.54	56(13)
H2A	3381.08	4483.57	6136.72	63(14)
H2B	3532.18	5025.17	6942.32	61(15)
H3	9870.41	7699.62	1166.96	44
H8A	1673.63	4825.69	2299.3	69(15)
H8B	656.73	5291.29	2031.4	67(15)
H10A	969.11	6129.64	4544.23	54
H10B	568.81	6123.34	6216.53	54

Table S6. Hydrogen bonds in $Mg(H_2O)_6[(IO_2(OH))_2(IO_3)]_2$.

D-H	*d*(D-H)/Å	*d*(H···A)/Å	<D-H···A/°	*d*(D···A)/Å	A
O3-H3	0.820	1.830	147.77	2.561	O12
O10-H10A	0.815	2.465	134.53	3.092	O5
O10-H10A	0.815	2.533	141.52	3.211	O6
O10-H10B	0.812	1.924	164.95	2.717	O12
O1-H1	0.775	1.873	164.32	2.627	O4
O8-H8A	0.781	2.121	170.20	2.894	O4
O8-H8B	0.758	2.046	161.13	2.774	O5
O2-H2A	0.845	1.961	177.67	2.805	O1
O2-H2B	0.750	2.060	167.49	2.797	O4

Table S7. List of reported birefringence compounds in alkali, alkaline earth, and rare earth metal cations-containing iodates/fluoroiodates system.

compound	Δn (@1064 nm)	refs.
KIO_3	0.1442	[1]
KIO_2F_2	0.043	[2]
$RbIO_3$	0.063	[3]
$RbIO_2F_2$	0.058	[3]
NaI_3O_8	0.213*	[4]
$CsIO_3$	0.19	[5]
$CsIO_2F_2$	0.046	[5]
$Cs_3(IO_2F_2)_3 \cdot H_2O$	0.093	[5]
$Cs(IO_2F_2)_2 \cdot H_5O_2$	0.086	[5]
$Ba(IO_2F_2)_2$	0.092	[6]
$SrI_2O_5F_2$	0.18	[6]
$Sr(IO_3)_2$	0.093	[6]
$K_2Na(IO_3)_2(I_3O_8)$	0.055	[7]
α-$LiIO_3$	0.1399 (@ 1100 nm)	[8]
α-HIO_3	0.1372 (@ 1100 nm)	[8]
NH_4IO_3	0.082 (@589 nm)	[9]
YI_5O_{14}	0.091	[10]
GdI_5O_{14}	0.092	[10]
$Ce(IO_3)_4$	0.039	[11]
$Mg(H_2O)_6[(IO_2(OH))_2(IO_3)]_2$	0.230	this work

* Calculate this time.

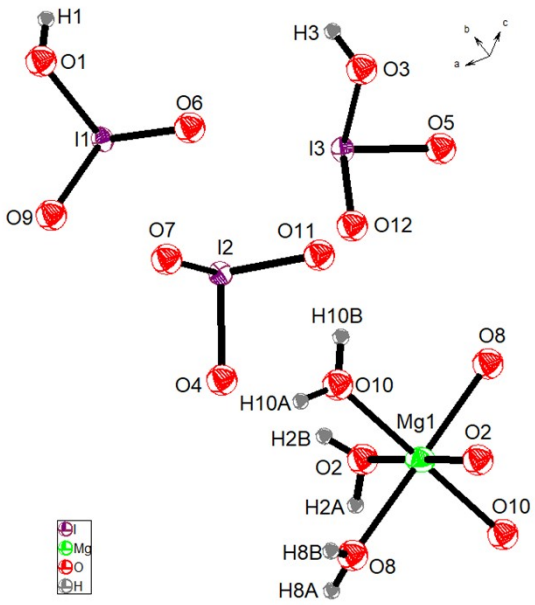

Fig. S1. Asymmetric unit of $Mg(H_2O)_6[(IO_2(OH))_2(IO_3)]_2$. The ellipsoids are drawn at 50% probability level.

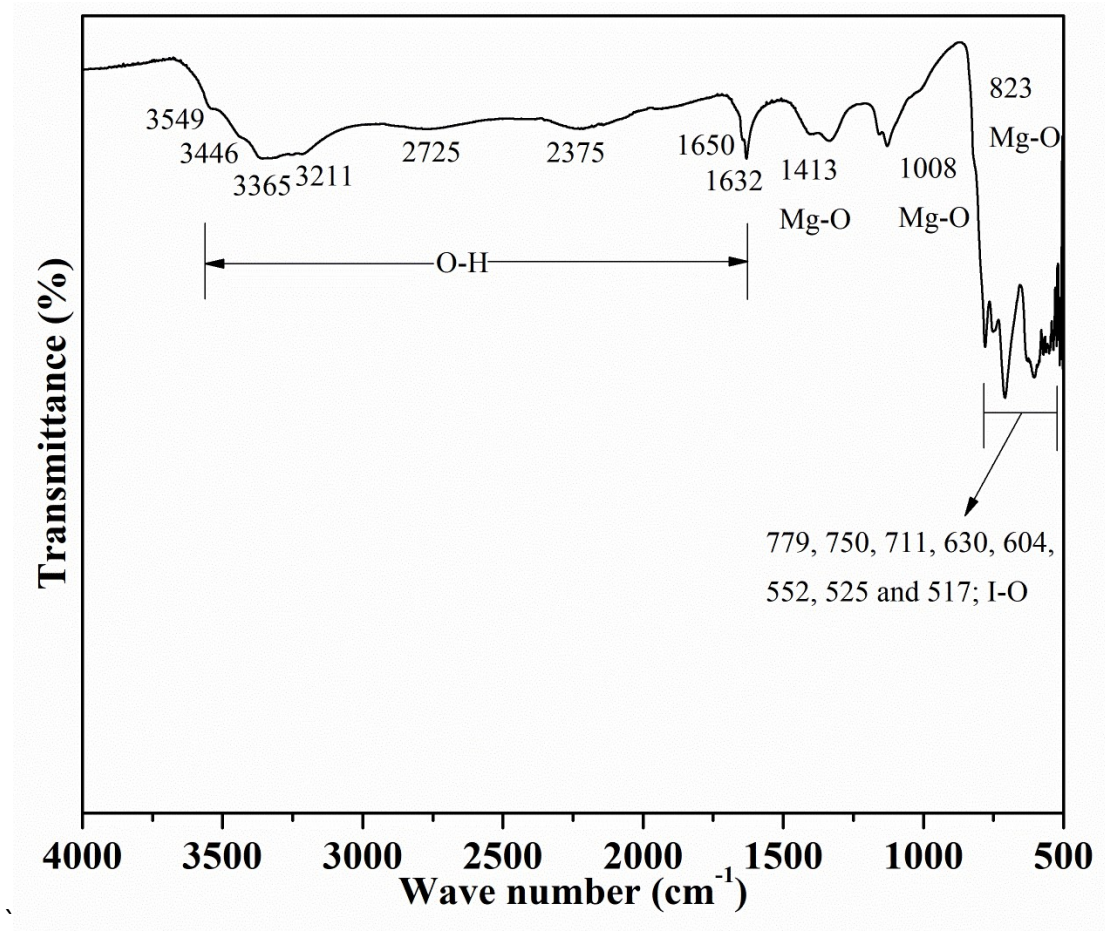

Fig. S2. IR spectrum of $Mg(H_2O)_6[(IO_2(OH))_2(IO_3)]_2$.

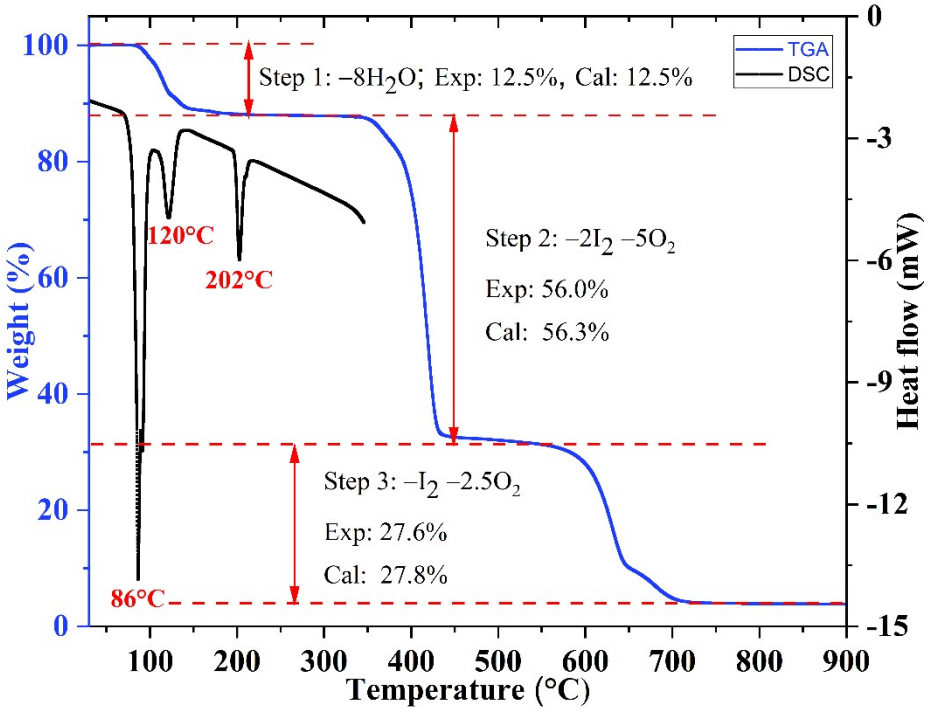

Fig. S3. TGA and DSC diagrams of $Mg(H_2O)_6[(IO_2(OH))_2(IO_3)]_2$.

In $Mg(H_2O)_6[(IO_2(OH))_2(IO_3)]_2$, six H_2O, four $IO_2(OH)$, and two IO_3 groups exist. The H_2O and OH units from the $IO_2(OH)$ group are easily released in step 1 as observed from other similar reported compounds.[12] The observation is in agreement with the endothermic peaks at 86 to 204 °C in the DSC diagram.

Step 1: $Mg(H_2O)_6[(IO_2(OH))_2(IO_3)]_2 \rightarrow MgO + 3\ I_2O_5 + 6\ H_2O \uparrow$

In steps 2 and 3, the rest of I_2O_5 group was decomposed. It also could be found in many other iodates, such as $HBa_{2.5}(IO_3)_6(I_2O_5)$ and $HBa(IO_3)(I_4O_{11})$.[13]

Step 2: $2\ I_2O_5 \rightarrow 2\ I_2 \uparrow + 5\ O_2 \uparrow$

Step 3: $I_2O_5 \rightarrow\ I_2 \uparrow + 5/2\ O_2 \uparrow$

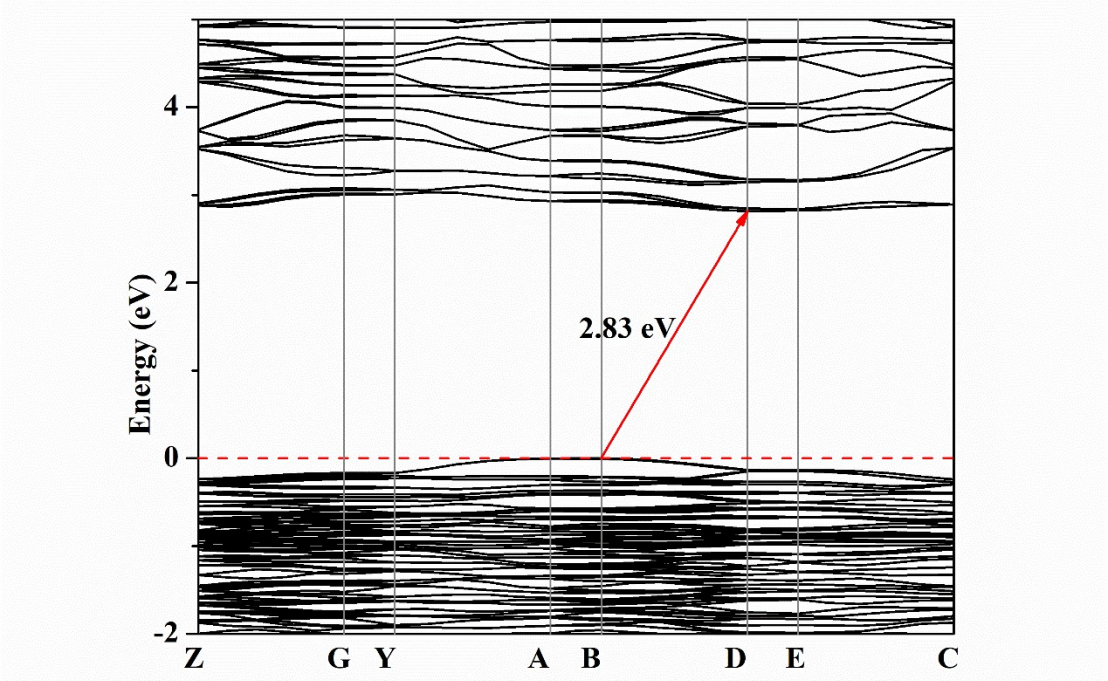

Fig. S4. Band structure for $Mg(H_2O)_6[(IO_2(OH))_2(IO_3)]_2$.

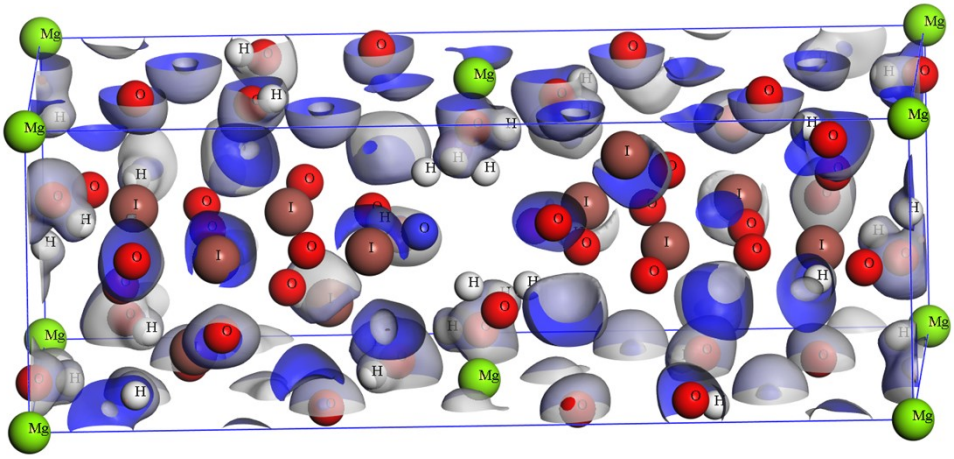

Fig. S5. The electron density difference map of $Mg(H_2O)_6[(IO_2(OH))_2(IO_3)]_2$.

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