Supplementary Information

Cerium-oxo clusters for photocatalytic aerobic oxygenation of sulfides to sulfoxides

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1. Materials

(NH₄)₂Ce(NO₃)₆ and isonicotinic acid were purchased from Adamas, NH₄I was purchased from Rhawn, 2-thiophenecarboxylic acid was purchased from Bide Pharmatech Ltd., acetonitrile and pyridine were purchased from General Reagent, methanol was purchased from Acros. All reagents were of A.R. grade and used without further purification.

2. Instrumentation

Crystallography: The crystallographic data of compounds were collected using synchrotron radiation ($\lambda = 0.67011$ Å) on beamline 17B1 at the National Facility for Protein Science Shanghai (NFPS) in the Shanghai Synchrotron Radiation Facility, People's Republic of China. Then the diffraction data reduction and integration were performed by the APEX3 program after converting the format into sfrm. The empirical absorption correction was conducted using the SADABS program.¹ The structure was solved by Intrinsic Phasing with ShelXT² and refined with a full-matrix least-squares technique of ShelXL³ interpreted by Olex2⁴. Anisotropic thermal parameters were applied to all non-hydrogen atoms except the isolated water molecules. The hydrogen atoms were generated by the riding mode. For compound 1, DFIX, SIMU, RIGU and ISOR were used to obtain more reasonable parameters. For compound 2, almost all the thiophene rings have been split into two parts due to its large anisotropic parameters. The restrains such as DFIX, SADI, SIMU, RIGU, FLAT, ISOR, etc have been used to obtain more reasonable parameters. Solvent molecules of the two clusters, are highly disordered and cannot be modeled for refinement. Contributions to the scattering from these species were removed using the Solvent Mask of Olex2.4 Structures were then refined again using the data generated. Crystal data and details of the data collection are given in Table S1. CCDC-2159759 (1), 2159760 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data request/cif.

Element Analyses: Element analyses C, N and H content were determined by VARIDEL III Elemental Analyzer.

Thermogravimetric Analysis (TGA): Thermogravimetric analysis was performed on a METTLER TOLEDO TG8000 Thermogravimetric Analyzer under nitrogen flow at a typical heating rate of 10 °C·min⁻¹.

Powder X-ray Diffraction (PXRD): Powder XRD was recorded on a Haoyuan DX-2700B diffractometer equipped with monochromatized Cu-K α ($\lambda = 1.5418$ Å) radiation in the range of $3^{\circ} \le 2\theta \le 40^{\circ}$, with a scanning rate of 0.02° s⁻¹.

Fourier-transform infrared (FT-IR) spectroscopy: The samples were prepared as a KBr pellet and the FT-IR spectrum was collected in transmission mode in the range of $600-4000 \text{ cm}^{-1}$ using a NEXUS-670 spectrometer. Wavenumbers are given in cm⁻¹. Intensities are denoted as w = weak, m = medium, s = strong, vs = very strong, br = broad.

Solid-state UV-Vis absorption spectroscopy: All compounds were prepared into powders, which were tested in wavelength mode by integrating sphere attachment in UV3600 UV-Vis spectrometer.

GC-Mass spectra: GC-Mass analysis was carried out on Agilent 8860 GC system and 5977B GC/MSD system with EI mode.

Cyclic voltammetry measurements.: Cyclic voltammetry was performed with a CH Instrument model 760E potentiostat.

3. Synthesis

Synthesis of $[Ce_{16}^{IV}(IN)_{24}O_{17}(OH)_6(H_2O)_4] \cdot 4py \cdot 6MeCN \cdot 12H_2O$ (1, IN = isonicotinate, py = pyridine).

 $(NH_4)_2Ce(NO_3)_6$ (0.2 mmol, 0.11 g), isonicotinic acid (0.8 mmol, 0.0985 g) and NH₄I (0.2 mmol, 0.03 g) were dissolved in the solution of aqueous pyridine (2.2 mL, 10:1 v/v). The

solution was stirred for 30 minutes, followed by the addition of 4 mL of acetonitrile. Then the mixture was kept in 10 mL glass vial undisturbed for 1 week. The resulting yellow square crystals were collected and dried in air (yield 12.71 mg, 18.10 % based on Ce). Elemental analysis, calc.: C, 33.02 %; H, 2.69 %; N, 7.44 %; found: C, 33.05 %; H, 2.71 %; N, 7.49 %. IR (KBr pellet, 4000-400 cm⁻¹): 3126(br), 1584(s), 1538(s), 1494(w), 1391(vs), 1223(w), 1061(w), 1003(w), 863(w), 766(s), 709(m), 675(s), 568(s), 511(m), 443(m).

Synthesis of $[Ce_{22}^{IV}Ce_{2}^{III}O_{28}(py)_4(TPC)_{30}(OH)_8]$ ·16py·6MeCN·5H₂O (2, TPC = thiophene-2-carboxylate, py = pyridine).

 $(NH_4)_2Ce(NO_3)_6$ (0.1 mmol, 0.055 g), 2-thiophenecarboxylic acid (0.4 mmol, 0.0513 g) and NH_4I (0.1 mmol, 0.015 g) were dissolved in the solution of aqueous pyridine (2.1 mL, 20:1 v/v). The solution was stirred for 30 minutes, followed by the addition of 2 mL of acetonitrile. Then the mixture was kept in 10 mL glass vial undisturbed for 2 weeks. The resulting yellow hexagon crystals were collected and dried in air (yield 3.86 mg, 11.47 % based on Ce). Elemental analysis, calc.: C, 33.23 %; H, 2.38 %; N, 3.47 %; found: C, 33.21 %; H, 2.33 %; N, 3.50 %. IR (KBr pellet, 4000-400 cm⁻¹): 3092(w), 1511(s), 1417(vs), 1382(vs), 1337(s), 1225(w), 1121(m), 1035(w), 858(m), 808(w), 768(m), 708(m), 653(m), 527(vs), 480(s).

4. Crystallographic data and crystal structures of 1-2

1 461		
Compound	1	2
Empirical formula	Ce ₁₆ C ₃₀₄ H ₄₁₄ O ₁₃₅ N ₇₄	$Ce_{24}S_{30}C_{241}H_{250}O_{124}N_{26}$
Formula weight	9506.99	9819.33
Crystal system	Cubic	Trigonal
Space group	<i>P-43m</i>	<i>R-3</i>
a /Å	18.9003(8)	40.8409(18)
b /Å	18.9003(8)	40.8409(18)
c /Å	18.9003(8)	51.871(4)
α/°	90	90
β/°	90	90
$\gamma/^{\circ}$	90	120
V /Å ³	6751.6(9)	74928(8)
Z	1	9
ρ calc /g·cm ⁻³	2.338	1.959
μ (MoK α) /mm ⁻¹	2.383	2.988
F(000)	4764	42678
2θ range /°	1.760 to 24.756	0.940 to 23.244
	-23<=h<=23	-48<=h=48
Index ranges	-23<=k<=23	-47<=k=47
	-23<=1<=23	-61<=l<=61
Reflections collected	86270	285392
Data / restraints / parameters	2625 / 342 / 166	28337 / 6297 / 2024
$R_1/wR_2 (I \ge 2\sigma(I))^a$	0.0397/0.1155	0.0920/0.2542
R_1/wR_2 (all data)	0.0407/0.1163	0.1099/0.2705
GooF (all data) ^b	1.064	1.037
Data completeness	99.5%	99.4%

 Table S1 Crystallographic Details for 1-2.

 $\frac{1}{{}^{a}R_{1} = \sum ||Fo|-|Fc||/\sum |Fo|; wR_{2} = \{\sum w[(Fo)^{2}-(Fc)^{2}]^{2}/\sum w[(Fo)^{2}]^{2}\}^{1/2}}$ ${}^{b}GooF = \{\sum w[(Fo)^{2}-(Fc)^{2}]^{2}/(n-p)\}^{1/2}$

1				2			
Atom	CN	Ce ^{III}	Ce ^{IV}	Atom	CN	Ce ^{III}	Ce ^{IV}
Cel	8	4.866	4.127	Ce1	9	4.727	4.008
Ce2	9	4.447	3.771	Ce2	8	4.766	4.042
				Ce3	8	4.622	3.919
				Ce4	9	4.845	4.109
				Ce5	9	4.659	3.951
				Ce6	8	4.910	4.164
				Ce7	9	4.547	3.856
				Ce8	10	3.239	2.746
				Ce9	8	4.877	4.135
				Ce10	9	4.856	4.109
				Cell	8	4.437	3.763
				Ce12	9	4.768	4.043

Table S2 Bond Valence Sums and Coordination Numbers (CN) for Ce Atoms in 1 and 2.^{a, b}

^aThe bold values are the ones closest to the charge for which they were calculated; the oxidation state is thus the nearest integer to the bold value. ${}^{b}CN = coordination$ number.

Table S3 Bond Valence Sums and Assignments for the non-Carboxylate O Atoms in 1.ª

1		
Atom	BVS	Assignment
01	1.96	O ²⁻
02	1.595	O ²⁻ /OH-
03	0.33	H ₂ O
04	2.05	O ²⁻
05	1.83	O ²⁻

^aAn oxygen BVS in the \sim 1.8-2.0, \sim 0.9-1.2 and \sim 0.2-0.4 ranges is indicative of non-, single- and double- protonation, respectively.

2		
Atom	BVS	Assignment
01	0.72	μ4 - OH ^{- b, c}
O2	2.07	O ²⁻
O6	2.26	O ²⁻
O8	1.96	O ²⁻
O9	2.21	O ²⁻
O10	2.06	O ²⁻
O14	0.69	μ_4 -OH ^{- b, c}
015	2.28	O ²⁻
O17	2.22	O ²⁻
O18	1.23	<i>µ</i> 3 - ОН ^{- ь}
O19	2.22	O ²⁻
O20	2.22	O ²⁻
O21	2.02	O ²⁻
O24	1.25	<i>µ</i> 3 - ОН ^{- b}
O40	1.96	O ²⁻
O41	2.04	O ²⁻
O47	1.93	O ²⁻
O49	2.01	O ²⁻

Table S4 Bond Valence Sums and Assignments for the non-Carboxylate O Atoms in 2.ª

^aAn oxygen BVS in the ~1.8-2.0, ~0.9-1.2 and ~0.2-0.4 ranges is indicative of non-, single- and double- protonation, respectively. ^b Two by symmetry. ^c Square pyramidal O geometry.

Table S5 Selected bond lengths (Å) for 1.ª			
Bond	Length	Bond	Length
Ce(1)-O(1)	2.3549(13)	Ce(2)-O(2)#4	2.329(8)
Ce(1)-O(2)#2	2.279(13)	Ce(2)-O(2)#6	2.329(8)
Ce(1)-O(2)	2.279(13)	Ce(2)-O(4)	2.349(10)
Ce(1)-O(2)#4	2.279(13)	Ce(2)-O(5)	2.281(10)
Ce(1)-O(3)	2.50(2)	Ce(2)-O(6)	2.621(8)
Ce(1)-O(4)#5	2.327(10)	Ce(2)-O(6)#3	2.621(8)
Ce(1)-O(4)	2.327(10)	Ce(2)-O(7)#7	2.579(17)
Ce(1)-O(4)#4	2.327(10)	Ce(2)-O(8)#8	2.411(12)
		Ce(2)-O(8)	2.411(12)

^aSymmetry transformations used to generate equivalent atoms: #2 -z+1,x,-y+1; #3 -x+1,y+1,z; #4 y,-z+1,-x+1; #5 -z+1,-x+1,y; #6 z,-x+1,-y+1; #7 y,x,z; #8 -y+1,-x+1,z

Length 2.245(9) 2.288(9) 2.731(11) 1 2.412(10)
2.245(9) 2.288(9) 2.731(11) 1 2.412(10)
2.288(9) 2.731(11) 1 2.412(10)
2.731(11) 1 2.412(10)
1 2.412(10)
2.548(13)
2.699(10)
1 2.465(10)
1 2.218(11)
2.812(10)
2.526(13)
2.421(9)
2.516(11)
2.661(12)
2.854(10)
2.438(9)
2.488(10)
2.514(11)

Table S6 Selected bond lengths (Å) for 2.^a

Ce(3)-O(2)	2.290(10)	Ce(8)-O(43)	2.696(11)
Ce(3)-O(19)#1	2.388(9)	Ce(9)-O(6)	2.332(9)
Ce(3)-O(20)	2.351(9)	Ce(9)-O(9)#1	2.311(8)
Ce(3)-O(21)	2.325(9)	Ce(9)-O(15)	2.312(9)
Ce(3)-O(40)#1	2.307(10)	Ce(9)-O(17)	2.297(9)
Ce(3)-O(41)	2.292(9)	Ce(9)-O(19)#1	2.337(9)
Ce(3)-O(47)	2.358(9)	Ce(9)-O(20)#1	2.314(9)
Ce(3)-N(1)	2.684(13)	Ce(9)-O(21)#1	2.365(9)
Ce(4)-O(8)	2.207(10)	Ce(9)-O(21)	2.387(9)
Ce(4)-O(9)	2.274(9)	Ce(10)-O(1)	2.672(10)
Ce(4)-O(14)#1	2.812(10)	Ce(10)-O(7)	2.603(11)
Ce(4)-O(19)	2.249(9)	Ce(10)-O(10)	2.185(10)
Ce(4)-O(35)	2.491(12)	Ce(10)-O(15)	2.240(10)
Ce(4)-O(37)	2.614(10)	Ce(10)-O(16)	2.559(10)
Ce(4)-O(40)	2.215(9)	Ce(10)-O(17)	2.279(9)
Ce(4)-O(42)	2.562(10)	Ce(10)-O(18)	2.404(11)
Ce(4)-O(48)	2.400(10)	Ce(10)-O(39)	2.316(11)
Ce(5)-O(1)	2.865(10)	Ce(10)-O(44)	2.418(10)
Ce(5)-O(4)	2.394(11)	Ce(11)-O(8)	2.330(10)
Ce(5)-O(8)	2.214(10)	Ce(11)-O(9)	2.369(10)
Ce(5)-O(17)	2.283(9)	Ce(11)-O(10)	2.328(10)
Ce(5)-O(20)#1	2.259(8)	Ce(11)-O(17)	2.377(9)
Ce(5)-O(26)#1	2.477(10)	Ce(11)-O(21)	2.296(9)
Ce(5)-O(40)	2.219(10)	Ce(11)-O(47)	2.417(10)
Ce(5)-O(44)	2.612(10)	Ce(11)-O(49)	2.309(9)
Ce(5)-O(46)	2.548(9)	Ce(11)-N(2)	2.640(13)
Ce(6)-O(2)	2.193(10)	Ce(12)-O(2)	2.199(10)
Ce(6)-O(10)	2.185(10)	Ce(12)-O(11)	2.390(11)
Ce(6)-O(13)	2.457(11)	Ce(12)-O(12)	2.447(12)
Ce(6)-O(18)	2.422(10)	Ce(12)-O(14)	2.632(11)
Ce(6)-O(25)	2.490(13)	Ce(12)-O(15)	2.270(9)
Ce(6)-O(29)	2.354(13)	Ce(12)-O(18)	2.404(10)
Ce(6)-O(36)	2.418(14)	Ce(12)-O(19)#1	2.264(9)
Ce(6)-O(47)	2.337(9)	Ce(12)-O(22)#1	2.549(12)
Ce(7)-O(3)#1	2.410(11)	Ce(12)-O(35)#1	2.556(9)

^aSymmetry transformations used to generate equivalent atoms: #1 - x + 1/3, -y + 2/3, -z + 2/3



Fig. S1 Ball-and-stick view of 1 with H atoms removed for clarity. Colour codes (the same in the following pictures): Ce^{IV} gold, O red, N blue, C grey.



Fig. S2 ORTEP representation of 1 with thermal ellipsoids drawn at the 30%

probability level. H atoms have been omitted for clarity.



Fig. S3 The two coordination modes of Ce^{IV} in 1.



Fig. S4 The coordination modes of the isonicotinate in 1.



Fig. S5 Ball-and-stick view of **2** with H atoms removed for clarity. Colour codes (the same in the following pictures): Ce^{IV} gold, Ce^{III} sky blue, O red, S purple, N blue, C



Fig. S6 ORTEP representation of **2** with thermal ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity.



Fig. S7 The three types of eight-coordinated Ce^{IV} in 2.

grey.



Fig. S8 a) Nine-coordinated Ce^{IV} in 2. b) Ten-coordinated Ce^{III} in 2.



Fig. S9 The coordination modes of the 2-thiophenecarboxylates in 2.



Fig. S10 Space-filling view of 1. Colour codes: Ce^{IV} gold, H_2O green, other O atoms red, N blue, C grey.



Fig. S11 Space-filling view of **2**. Colour codes: Ce^{IV} gold, Ce^{III} sky blue, O red, S purple, N blue, C grey.



Fig. S12 TGA curve for 1.



Fig. S13 TGA curve for 2.

6. PXRD spectra of 1-2



Fig. S14 Experimental and simulated PXRD patterns of 1.



Fig. S15 Experimental and simulated PXRD patterns of 2.





Fig. S16 The FT-IR spectrum of 1.



Fig. S17 The FT-IR spectrum of 2.

8. UV-Vis spectra and band gap results of 1 and 2



Fig. S18 The UV-Vis spectrum of 1.



Fig. S19 The UV-Vis spectrum of 2.



Fig. S20 The band gap result of 1.



Fig. S21 The band gap result of 2.

9. General procedures for photocatalytic oxidation of sulphides to sulfoxides.

All manipulations were conducted under aerobic condition. Into a test tube (φ 20 mm × 170 mm) equipped with an O₂ balloon (1 atm) were successively placed compound **1** (0.2 mol%), sulfides (0.1 mmol), internal standard (mesitylene 0.1 mmol) and solvent (4 mL). A Teflon-coated magnetic stir bar was added, and was irradiated with light sources with stirring at room temperature. When performing quenching experiments, 5 eq. scavenger was added to the above reactants. The products were confirmed by comparison of their GC-Mass spectra with those of authentic data. The yield was calculated with respect to the internal standard. Thioanisole was taken as a model compound. Similarly, we use the above procedure to screen light sources, solvents and the amount of photocatalyst. After the reaction, methanol was evaporated, followed by addition of diethyl ether to precipitate the catalyst. The retrieved catalyst was washed with diethyl ether, and then air-dried prior to being used for the cycle experiment.

S 3a	1 MeOH, O ₂ (1 atm) light sources, r.t., 12h	O S 4a	+ 5a
		Yi	elds (%) ^b
Entry	Light sources	4 a	5a
1	365 nm	98	trace
2	385 nm	19	n.d.
3	405 nm	n.d.	n.d.
4	Blue LEDs	n.d.	n.d.

Table S7 Screening the light sources for photocatalytic oxidation of sulfides^a.

^aReaction conditions: **3a** (0.1 mmol), **1** (0.2 mol%), O₂(1 atm), r.t., methanol (4 mL), 12 h. ^bYields were determined by GC-MS using mesitylene as an internal standard.

S 3a	1 Solvent, O ₂ (1 atm) 365nm, r.t., 12h	$\rightarrow \qquad \qquad$	+ 0, 0 5a
		Yiel	ds (%) ^b
Entry	Solvent	4a	5a
1	Methanol	98	trace
2	Ethanol	70	trace
3	Acetonitrile	42	n.d.
4	Acetone	34	n.d.
5	1,4-Dioxane	24	n.d.
6	Tetrahydrofuran	27	n.d.
7	Dichloromethane	68	n.d.
8	Dimethyl Sulfoxide	61	n.d.

Table S8 Screening the solvents for photocatalytic oxidation of sulfides^a.

^aReaction conditions: **3a** (0.1 mmol), **1** (0.2 mol%), 365 nm, O_2 (1 atm), r.t., 12 h. ^bYields were determined by GC-MS using mesitylene as an internal standard.

 Table S9 Screening the amount of photocatalyst for photocatalytic oxidation of

sulfides^a.

Ĺ	S 1 MeOH, O ₂ (1 atm) 365nm, r.t., 12h	\rightarrow $4a$	s S S S S S S S S S S S S S S S S S S S
		Yield	ds (%) ^b
Entry	Amount of photocatalyst (mol%)	4a	5a
1	0.1	73	n.d.
2	0.2	98	trace
3	0.4	89	5

^aReaction conditions: **3a** (0.1 mmol), 365 nm, $O_2(1 \text{ atm})$, r.t., methanol (4 mL), 12 h. ^bYields were determined by GC-MS using mesitylene as an internal standard.

Table S10 Quenching experiments to determine the reactive oxygen species (ROS)for photocatalytic oxidation of sulfidesª.

	S 1 MeOH, O ₂ (1 atm) 365nm, r.t., 12h	\rightarrow $4a$	0 5a	0
			Yield (‰) ^b
Entry	Scavenger (eq.)	Roles	4a	5a
1	Standard	-	98	trace
2	p-BQ	O_2^{-} scavenger	37	n.d.
3	AgNO ₃	e _{cb} ⁻ scavenger	n.d.	n.d.
4	1,4-dimethoxybenzene	$R_1S^{\bullet+}$ scavenger	n.d.	n.d.
5	9,10-Diphenylanthracene	¹ O ₂ scavenger	92	6

^aReaction conditions: **3a** (0.1 mmol), **1** (0.2 mol%), 365 nm, O₂ (1 atm), r.t., methanol (4 mL), scavenger (5 eq.), 12 h. ^bYields were determined by GC-MS using mesitylene as an internal standard.

10. Recycling experiments.



Fig. S22 Recycling experiments for the photocatalytic oxidation of thioanisole.



Fig. S23 IR spectra of 1 before and after photocatalytic oxidation of thioanisole.

11. Cyclic voltammetry measurements.

All cyclic voltammetry (CV) measurements were performed on a CH Instruments 760E potentiostat. Clusters **1** and **2** (c = 0.0625 mM) were dissolved in a 0.1 M methanol solution of LiClO₄, which was used as the supporting electrolyte with a glassy carbon working electrode, a carbon rod auxiliary electrode, a silver wire reference electrode. The cylic voltammograms was carried out at a scan rate of 100 mV s⁻¹. All experiments were carried out under inert atmosphere after N₂ bubbling.



Fig. S24 The cyclic voltammetry curves of 1 and 2 (c = 0.0625 mM) in methanol with LiClO₄ (0.1 M) using GC electrode with scan rate 100 mV s⁻¹ (working electrode: 3 mm diameter glassy carbon electrode).

12. References

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