

Supplementary Material

Enhanced Hydroxyl Bridge-Mediated Microalgal Lipid Conversion via Mixed-Valence Zr/Ce-MOF-808 Catalysts at Reduced Temperatures

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S1. Materials

The marine microalgae *Nannochloropsis oceanica* were provided by Yantai Hearol Biotechnology Co., Ltd. (Shandong, China). Zirconium oxychloride octahydrate (99.9%, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$), cerium(III) chloride heptahydrate (99%, $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$), and benzene-1,3,5-tricarboxylic acid (99%, H_3BTC) were purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). *N,N*-dimethyl formamide (99%, DMF), formic acid (99%), methanol (99.9%), chloroform (99%), sulfuric acid (96%), and *n*-hexane (98%) were obtained from Aladdin Industrial Inc. (Shanghai, China). All chemicals were of reagent-grade quality and used as received without any further purification.

S2. Analytical techniques

X-ray diffraction (XRD) was conducted on an X'Pert³ PRO diffractometer (Malvern Panalytical, UK, the Netherlands) operated at 40 kV with Cu $K\alpha$ radiation using a scanning speed of 2° min^{-1} . Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were performed on a SU8010 instrument (Hitachi, Japan) equipped with an EDS system. Thermogravimetric analysis (TGA) was conducted with a Q500 TGA instrument (TA Instruments, USA) under nitrogen atmosphere. Fourier transform infrared (FT-IR) spectra were collected using a Nicolet iS5 FT-IR spectrometer (Thermo Fisher Scientific, USA) for additional studies of the composition and chemical valence of the catalysts. X-ray photoelectron spectroscopy (XPS) was performed on an Escalab 250XI instrument (Thermo Fisher Scientific, USA) using Al $K\alpha$ radiation. Nitrogen adsorption-desorption experiments were performed with a Quantachrome Autosorb-iQ3 instrument (Micromeritics, USA) at -196°C to determine Brunauer–Emmett–Teller (BET) surface areas and pore size distributions. Prior to the measurement, all samples of about 200 mg were dried at 150°C under vacuum. The acid and base properties of catalysts were determined by temperature-programmed desorption of ammonia (NH_3 -TPD) and carbon dioxide (CO_2 -TPD), outlined briefly as follows. First, the samples (60 mg) were pretreated at 200°C under helium atmosphere for 2 h, then subjected to a helium gas flow (40 mL min^{-1}) for 2 h, and cooled to 50°C . Adsorption of NH_3 or CO_2 (40 mL min^{-1}) was performed at 50°C for 1 h, which was followed by desorption from room temperature to 800°C at a heating rate of $10^\circ \text{C min}^{-1}$ under helium atmosphere. The bonding mode of methanol on Zr/Ce(1:1)-MOF-808 was probed by

in situ IR techniques (Fig. 8). The samples were immersed in methanol and dried overnight at 50 °C in a vacuum oven prior to testing. During testing, samples were activated at 50 °C under a helium atmosphere until the spectra were stable. IR spectra were recorded in the range of 550-4000 cm⁻¹ at intervals of 10 °C during ramping up from room temperature to 200 °C at 2 °C min⁻¹ after holding for 5 min at each temperature before scanning. The composition of the catalyst was determined by gas analysis during programmed temperature pyrolysis. Briefly, a 60 mg sample was weighed in a reaction tube and purged under a helium gas flow (40 mL min⁻¹), heated to 200 °C for drying and pretreatment, then cooled to 50 °C, and finally heated to 800 °C at a rate of 10 °C min⁻¹, and the pyrolysis gas was analyzed by mass spectrometry (MS). Inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed using a PerkinElmer Optima 5300 DV instrument.

S3. FAME production

Optimized Bligh and Dyer protocol

Briefly, 100 mg of dried microalgal biomass was fully ground and extracted with a mixture of chloroform (3 mL) and methanol (5 mL). After ultrasonic treatment for 3 min and centrifugation (8000 r·min⁻¹, 3 min), the chloroform phase containing microalgal lipids was isolated, transferred to a glass bottle, and kept at 60 °C for 24 h to evaporate the solvent and obtain microalgal oil.

The relative contents of fatty acids in the extracted microalgal oil are C16:0 (21.9%), C16:1 (1.7%), C18:0 (3.3%), C18:1 (18.2%), and C18:2 (54.9%). The water content is 1.2%, the unsaponifiable matter content is 5.67%, and the acid value is 11.34 mg KOH/g lipid.

One-step conversion method

The microalgal lipids were mixed with methanol (2 mL) and transferred into a 5-mL autoclave. After adding the catalyst, the autoclave was heated to 160 °C and kept at this temperature for 120 min. The reactor was cooled to room temperature, and the FAME reaction mixture was extracted with a mixture of 6 ml *n*-hexane and 4 ml deionized water by shaking for 3 min. Then, the resulting liquid was centrifuged (8000 r min⁻¹, 3 min). The phases were separated, and the FAME-containing *n*-hexane layer was transferred to a glass bottle and kept in an oven at 60 °C overnight to evaporate the solvent. The catalyst was separated from the water phase and

recovered for the next reaction cycle. The effects of reaction temperature (60, 70, 80, 90, 100, 120, 140, 160, 180, and 200 °C), reaction time (30, 60, 90, 120, 150, and 180 min), and catalyst concentration (1, 2, 3, 5, and 7 wt.%) on the conversion efficiency of Zr/Ce(1:1)-MOF-808 catalyst were investigated by this method.

Two-step method

The lipids were saponified with 4 ml of a saturated methanolic sodium hydroxide solution at 60 °C for 30 min and then methanolated with 8 ml methanol containing 5% H₂SO₄ at 90 °C for 60 min. FAME was extracted from the product with *n*-hexane, and the yield and composition of FAME were determined by gas chromatography with a 7890A instrument (Agilent, USA).

Catalytic efficiency was calculated according to

$$\text{Catalytic efficiency} = \frac{\text{mass of FAME produced by catalyst (mg)}}{\text{mass of total lipid (mg)}}$$

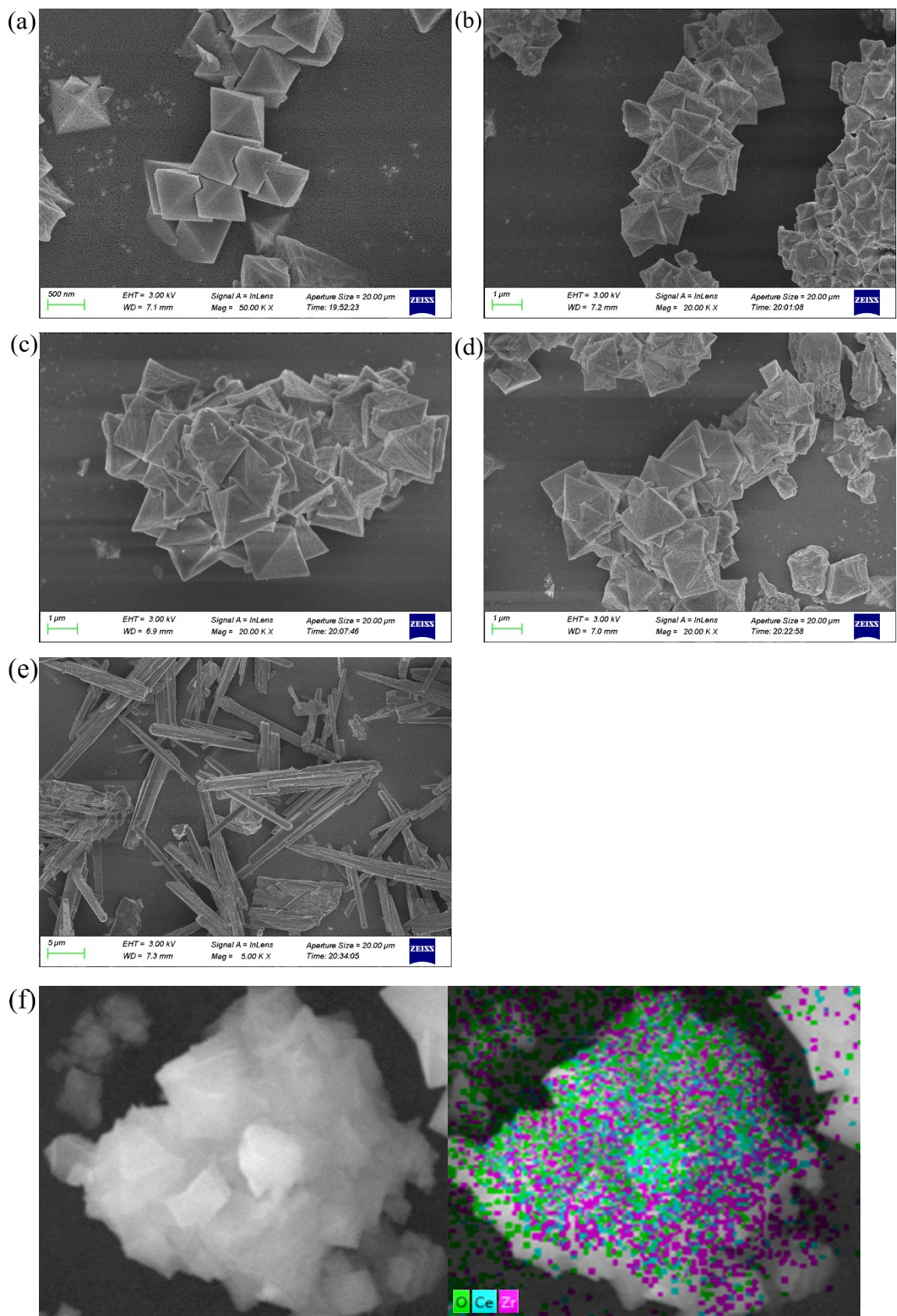


Fig.S1 SEM images of (a) MOF-808 (b) Zr/Ce(2:1)-MOF-808 (c) Zr/Ce(1:1)-MOF-808 (d) Zr/Ce(1:2)-MOF-808 (e) Ce(III)-MOF-808 (f) EDS images of Zr/Ce(1:1)-MOF-808

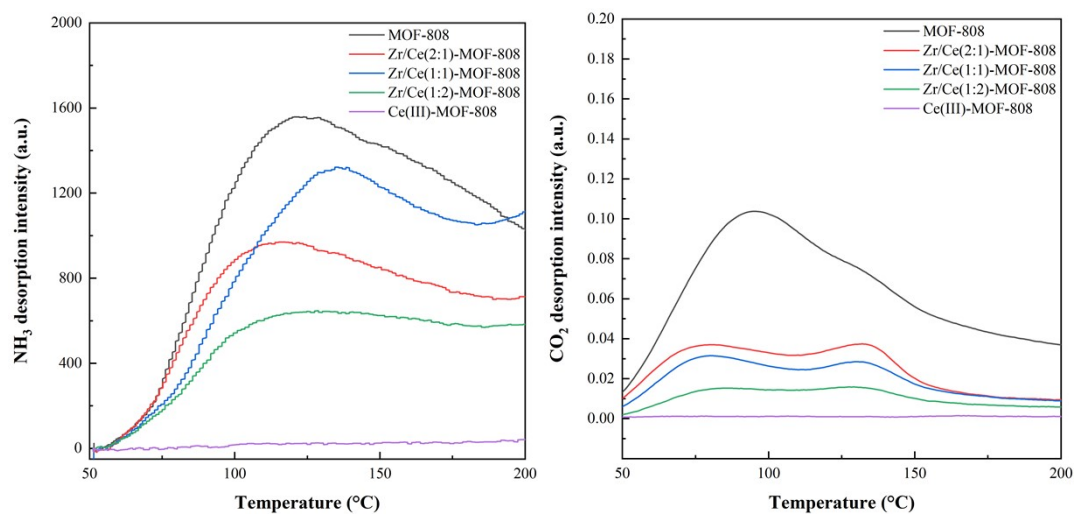


Fig. S2 (a) NH₃-TPD and (b) CO₂-TPD profiles of catalysts

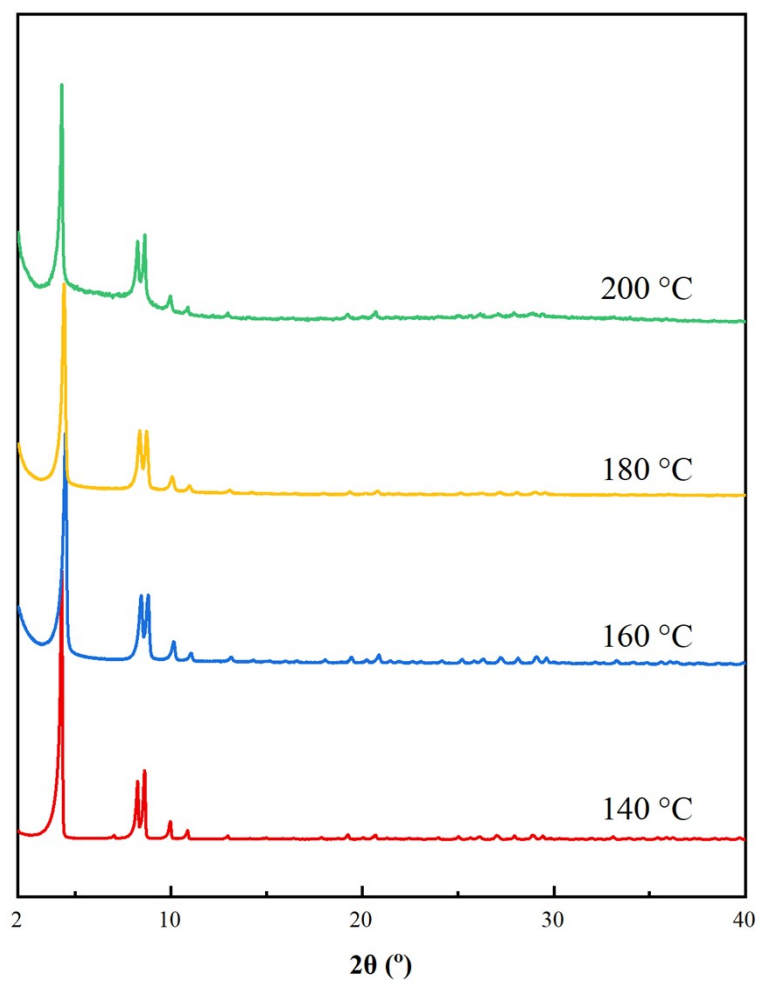


Fig. S3 XRD analysis of Zr/Ce(1:1)-MOF-808 catalyst post-reaction at a catalyst loading of 2 wt.% and a reaction time of 2 hours

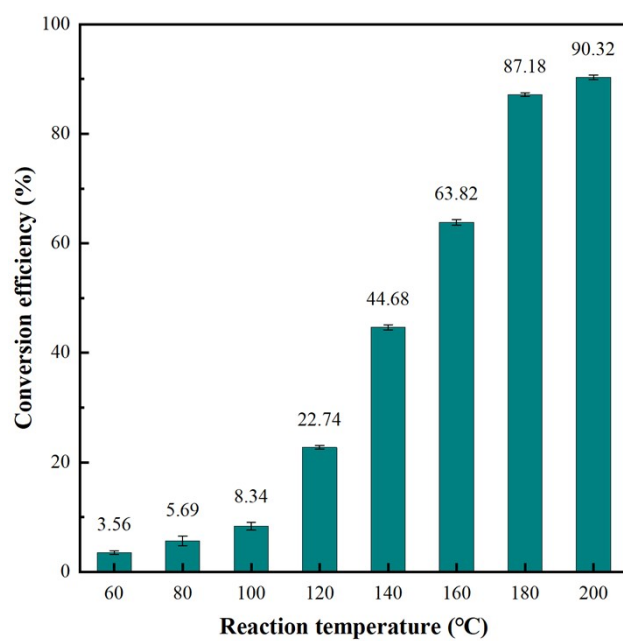


Fig. S4 Conversion efficiency with temperature for the catalyst MOF-808 at a catalyst loading of 2 wt.% and a reaction time of 2 hours

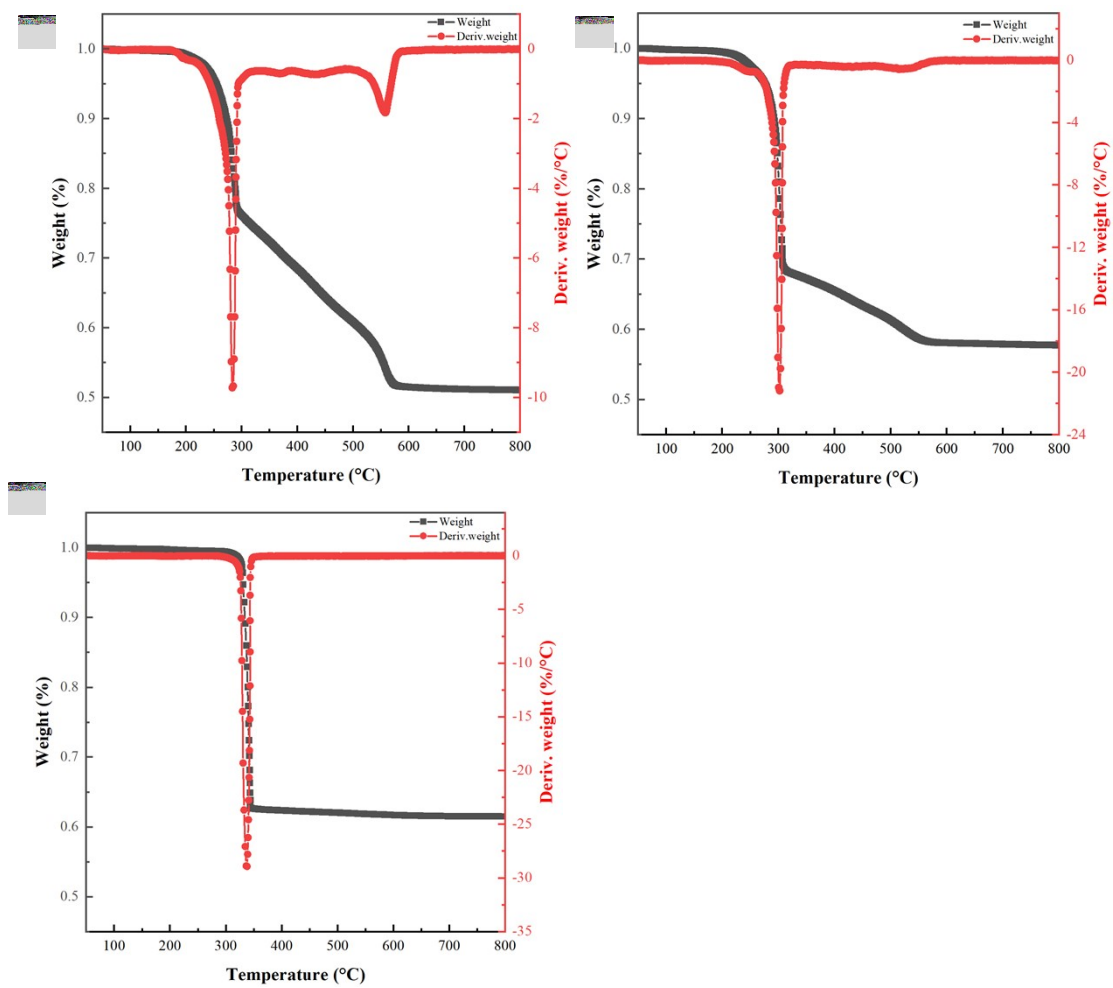


Fig. S5 TGA (black curves) and DTG (red curves) profiles of (a) Zr/Ce(2:1)-MOF-808, (b) Zr/Ce(1:2)-MOF-808, (b) Ce(III)-MOF-808.

Table S1 Synthesis a series of Zr/Ce-MOF-808s

Catalyst	ZrCl ₂ O·8H ₂ O		CeCl ₃ ·7H ₂ O		H ₃ BTC	DMF	Formic acid
MOF-808	9 mmol	2.9 g	0 mmol	0 g			
Zr/Ce(2:1)-MOF-808	6 mmol	1.93 g	3 mmol	1.12 g	3 mmol 0.63 g	150 ml	150 ml
Zr/Ce(1:1)-MOF-808	4.5 mmol	1.45 g	4.5 mmol	1.68 g			
Zr/Ce(1:2)-MOF-808	3 mmol	0.97 g	6 mmol	2.24 g			
Ce(III)-MOF-808	0 mmol	0 g	9 mmol	3.35 g			

Table S2 Atomic compositions (at.%) from XPS analysis

Catalyst	Atomic%				
	Zr 3d	Ce 3d	N 1s	O 1s	C 1s
MOF-808	8.12	0	2.37	34.87	54.65
Zr/Ce(2:1)-MOF-808	6.01	1.73	2.45	35.28	54.53
Zr/Ce(1:1)-MOF-808	3.98	3.8	1.83	35.38	55.01
Zr/Ce(1:2)-MOF-808	2.79	5.15	2.3	36.04	53.72
Ce(III)-MOF-808	0	4.99	0	37.28	57.73

Table S3 Full width at half maximum (FWHM), peak position and peak area

Catalyst	Name of fitted peaks	Binding energies (eV)	FWHM (eV)	Peak area (cps·eV)
MOF-808	C1s C-C	284.8	1.45	168213.67
	C1s O-C=O	288.74	1.34	32572.03
	C1s C-O	286.6	1.42	11376.89
	O1s COOMe	531.63	1.81	269362.79
	O1s metal oxide	530.06	1.53	99910.77
	Zr3d5	182.56	1.43	193120.18
	Zr3d3	184.94	1.43	132914.85
Zr/Ce(2:1)-MOF-808	C1s C-C	284.8	1.4	157455.52
	C1s C-O	286.65	1.38	11669.08
	C1s O-C=O	288.77	1.37	32635.51
	Ce3d3 u	898	3.49	13063.92
	Ce3d3 U	900.56	2.17	46752.43
	Ce3d3 u'	903.47	3.67	27126.44
	Ce3d3 U'	907.37	1.88	8167.19
	Ce3d3 U''	916.31	1.88	29702.59
	Ce3d5 v	880.4	3.49	18866.17
	Ce3d5 V	882.11	2.17	67519.84
	Ce3d5 v'	885	3.67	39176.42
	Ce3d5 V'	888.47	1.88	11794.48
	Ce3d5 V''	897.94	1.88	42894.36
	O1s electron-rich hydroxyl group	529.18	1.06	28210.69
	O1s COOMe	531.72	1.7	217979.62
	O1s metal oxide	530.24	1.98	95256.59
	Zr3d3	185.06	1.4	92805.02
Zr3d5	182.68	1.4	134842.14	
Zr/Ce(1:1)-MOF-808	C1s C-C	284.8	1.43	134970.08
	C1s C-O	286.74	1.28	4455.63
	C1s O-C=O	288.79	1.48	25234.69
	Ce3d3 u	898	2.48	17988.26
	Ce3d3 U	900.53	1.94	70689.15
	Ce3d3 u'	903.14	3.9	74041.15
	Ce3d3 U'	907.37	1.88	14190.4
	Ce3d3 U''	916.27	1.92	54247.25
	Ce3d5 v	880.4	2.48	25977.37
	Ce3d5 V	882.11	1.94	102086.04
	Ce3d5 v'	884.64	3.9	106928.8
	Ce3d5 V'	888.47	1.88	20492.76
	Ce3d5 V''	897.94	1.92	78865.85
	O1s electron-rich	529.19	1.1	73682.56

	hydroxyl group			
	O1s COOMe	531.73	1.76	159383.21
	O1s metal oxide	530.49	1.97	60737.07
	Zr3d3	185.12	1.4	52034.29
	Zr3d5	182.73	1.4	75603.82
	C1s C-C	284.8	1.42	132447.77
	C1s C-O	286.76	1.43	6890.5
	C1s O-C=O	288.75	1.54	24459.59
	Ce3d3 u	898	5.44	67829.84
	Ce3d3 U	900.58	1.85	82863.59
	Ce3d3 u'	903.48	2.57	70725.23
	Ce3d3 U'	907.13	1.89	33892.17
	Ce3d3 U''	916.32	1.87	73148.69
	Ce3d5 v	880.4	5.44	98275.84
Zr/Ce(1:2)-MOF-808	Ce3d5 V	882.11	1.85	119665.69
	Ce3d5 v'	885.1	2.57	102133.42
	Ce3d5 V'	888.47	1.89	48944.5
	Ce3d5 V''	897.94	1.87	105636.13
	O1s electron-rich	529.16	1.06	88066.49
	hydroxyl group			
	O1s COOMe	531.69	1.65	105253.54
	O1s metal oxide	530.65	2.71	111916.24
	Zr3d3	185.12	1.46	36906.82
	Zr3d5	182.73	1.46	53624.2
	C1s C-C	284.8	1.49	96543.01
	C1s C-O	286.64	1.89	6430.87
	C1s O-C=O	288.68	1.38	60194.67
	Ce3d3 u	900.27	3.97	136626.23
	Ce3d3 u'	904.39	3.35	169019.26
	Ce3d5 v	882.11	3.97	197903.83
	Ce3d5 v'	885.93	3.35	244490.13
Ce(III)-MOF-808	O1s COOMe	531.82	1.59	307331.64