Site-selective ligands deficiency opens up Zr-oxo clusters' electron transfer pathway for CO₂ photoreduction

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Section 5. References

Section 1. Materials and synthesis

Materials

Zirconium(IV) chloride (98%, ZrCl₄, Acros/thermo Scientific), cerium(III) chloride heptahydrate (99.5%, CeCl₃·7H₂O, Energy Chemical), 2-Aminoterephthalic acid (99%, Alfa Aesar/thermo Scientific), N, N-dimethylformamide (DMF, China National Medicines Corporation Ltd.), methanol (General-reagent), Dimethyl sulfoxide-d6 ((D, 99.8% and TMS, 0.03%), Energy Chemical), cesium fluoride (99.5%, 3A), deuterium oxide (99.8%, Energy Chemical), and deuterium chloride ((D, 99.5%) DCl 20 wt.% in D₂O, Energy Chemical)

Synthesis of UiO-66(Ce/Zr)-NH₂

UiO-66(Ce/Zr)-NH₂ (short for UN-*x*, "*x*" represents the mole percentage of Ce, x = 0.17, 0.25, 0.28, 0.30, etc.) was synthesized according to a reported solvothermal route with some modifications.^[1] Typically, total 6 mmol metal salts (ZrCl₄ and CeCl₃·7H₂O) with different Ce/Zr mole ratio were mixed in 40 mL DMF and 1.086 g (6 mmol) 2-Aminoterephthalic acid is dissolved in 20 mL DMF. Those solvents were separately stirring for one hour, followed by mixing up and stirring for another hour. After stirring, the mixed solvent was transferred to a 100 mL Teflon-lined stainless-steel autoclave for a solvothermal treatment at 120 °C for 24 h. Then the autoclave was cooled down naturally in air and milk white products were collected through centrifugation, washed with DMF and methanol for 4 times. Products were dried in oven at 80 °C overnight. UiO-66(Zr)-NH₂ (short for UN(Zr)) was synthesized as mentioned above without adding CeCl₃·7H₂O.

Synthesis of Defective UiO-66(Ce/Zr)-NH₂

D-UN-x, short for defective UiO-66(Ce/Zr)-NH₂, were prepared by heating-treat. About 2g UN-x was added to a porcelain boat covered by a perforated aluminized paper. Then it was placed in a tube furnace. The samples were heated with a constant ramp (5 °C·min⁻¹) up to 250°C and kept at this temperature for 2h. During the period, the system was purged with Argon at temperature-rise process. At last, the system was allowed to cool down naturally.

Synthesis of modulator induced defective UiO-66-NH₂ (D-UiO-66-NH₂-x)

Typically, 132.2mg (0.73mmol) amino terephthalate is dissolved in 30mL mixture of DMF and x ml acetic acid (x = 2, 4, 6). Then 169mg (0.73mmol) ZrCl4 is poured into above solution and stir for 10 minutes. Then the solution is transferred to a 50mL Teflon-lined stainless-steel autoclave for a solvothermal treatment at 120 °C for 24 h. All samples are washed with DMF and ethanol for 3 times. Products

were dried in oven at 80 °C overnight.

Synthesis of mixed linkers (ML) induced selective linker defect UiO-66 (D-ML-UiO-66(y))

D-ML-UiO-66(y) was synthesized as previous report.^[2] Typically, total 0.73mmol terephthalate and amino terephthalate are added into 30mL DMF. The proportion of amino terephthalate is 10%, 30%, 70%, 90%. Then 169mg (0.73mmol) ZrCl4 is poured into above solution and stir for 10 minutes. Then the solution is transferred to a 50mL Teflon-lined stainless-steel autoclave for a solvothermal treatment at 120 °C for 24 h. All samples are washed with DMF and ethanol for 3 times. Products were dried in oven at 80 °C overnight. Finally, all products are heated to 300 °C with a constant ramp (10 °C·min⁻¹) in air and kept for 2hours.

Section 2. Instruments and characterization

Structure characterization

The XRD data of the as-synthesized product were obtained at a step of 0.02° in the range from $3^{\circ}-40^{\circ}$ performed in Rigaku D/MAX-2550 with Cu K α radiation, accelerating voltage and applied current were 40 kV and 30 mA, respectively. The morphologies of the as-obtained product were characterized via a JEOL JSM-6700 SEM with a low accelerating voltage of 5 kV. TEM and EDS mapping exams were

performed on a FEI Tecnai G2 S-Twin F20 and Talos F200s TEM at 200 kV. XPS data were recorded via an Thermo Scientific ESCALAB 250X with an excitation source of Mg Ka radiation, adventitious carbon was used as a reference. XPS data was fitting on the Thermo Avantage (auto fitting). UV-vis DRS were carried out through PerkinElmer Lambda 850, with the BaSO₄ as reference. The range is 200nm – 800nm, scan speed is 266.75 nm/min and lighter switch wavelength is 319.20 nm. Number of scan is 1. Fluorescence emission spectra and fluorescence lifetime of the as-prepared samples were detected with an Edinburgh Instruments FLS 1000. Emission spectra was gotten from 400 - 600 nm, excitation wavelength is 375 nm and step is 1. Number of scan is 1. FT-IR spectra and in situ FT-IR spectra were collected in IFS-66 V/S (Bruker). FT-IR spectra was gotten from 400 - 4000 cm⁻¹ and resolution is 4 cm⁻¹. In-situ FT-IR was gotten from 1000 - 2200 cm⁻¹ and resolution is 4 cm⁻¹. Baseline correction and steam compensation were conducted. The EPR spectra were obtained on a JES-FA 200 EPR spectrometer at room temperature and micro frequency is 9441.564 µFMHz. ¹³C labeling exam was carried on GC-MS, Agilent, 5977B GC/MSD. ICP-OES was carried on Agilent, Agilent 725. 10 mg samples and 2 mL HNO₃ was added in a 25 mL teflon autoclave and heated in a 100°C oven. Then the clear liquid was diluted to 100 mL, so the concentration is 100ppm. TGA-

DSC was carried on TA Q500, rate of temperature increase is 10° C/min. Atmosphere is N₂ and air, flow speed is 60 mL/min.

XAS data was gotten from Shanghai Synchrotron Radiation Facility (SSRF) beamline BL13SSW, BL17B1 and BL11B.

The XAS data was analyzed with Demeter software package.^[3]

Photocatalytic CO₂ Reduction

As shown in **Figure S1**, the photocatalysis experiment was carried on Perfectlight Labsolar 6A system with a circulating water system to avoid the photothermal effect. Typically, 10 mg catalyst was pressed in nickel foam placed on an upholder and the whole was placed on the bottom of a sealed glass reactor. 3 mL water was also injected into the reactor as reactant. The system was vacuumized and purged with pure CO_2 . A 300 W Xe lamp with an AM 1.5G filter was used as the simulated sunlight. After every 5h of reaction, the products were quantified with SHIMADAZU GC 2014C online by the comparison of the peak areas with that of pure standards. In this work, the products were detected by a flame ionization detector (FID) (CO was transferred into CH₄ by a methanation reactor before detected).

Electrochemical Characterization

Electrochemical measurements were carried out in a three standard electrode system (BioLogic, France). The working electrodes were obtained via spin-coating 2 mL slurry to the surface of fluoride-tin oxide glass plate of which the effective area was $\approx 1 \text{ cm}^2$. The slurry was prepared via mixing 2 mL ethanol with the 0.01g as-prepared samples and ultrasonicated for 10 min. Platinum mesh was used as counter electrode, and a saturated calomel electrode as a reference electrode. The experiment was performed in 0.1 M Na₂SO₄ as electrolyte at room temperature.

¹H-NMR characterization

Method for digestion of MOFs is from a previous report.^[4] 5-10mg samples were digested by mixture of 30mg CsF and 20 μ L 30% DCl plus 180 μ L D₂O, then the digestive liquid was mixed with 500 μ L DMSO-d₆.

Calibration was performed using external standard solutions of $H_2BDC-NH_2$. Typically, 2 – 10 mg $H_2BDC-NH_2$ is dissolved in the mixture of digestive liquid and DMSO-d₆. And the concentration of four external standard solutions is 0.0158 mM, 0.0356mM, 0.0573mM and 0.111mM. All measurements were carried on Bruker AVANCE III 400MHz. Gain and relaxation delay was set by software automatically. Number of scans is 16.

For D-UiO-66-NH₂-x and D-ML-UiO-66-NH₂(y), specially, 100μ L CH₃CN was added into digestive liquid as interior label.

Fs-TAS Characterization

In the ultrafast transient absorption spectroscopy system (Ultrafast

System LLC, Helios Fire), a titanium-sapphire laser amplifier (Coherent Inc., Astrella) was utilized to emit femtosecond pulses at a central wavelength of 800 nm, a pulse width of 100 fs, and a repetition rate of 1 kHz. The oscillator (Coherent Inc., Vitara-S) and the amplifier pump source (Coherent Inc., REVOLUTION 38 SYSTEM) are integrated components of the system. The tunable optical parametric amplifier (Coherent Inc., TOPAS Prime) provided output light serving as the pump light (350 nm/380 nm), while the femtosecond beam at 800 nm generated by the sapphire crystal produced a supercontinuum white light for use as the probe light (420 - 760 nm). The time delay between the pump and probe pulses was precisely controlled using a motorized optical delay line. Both spectral and kinetic analyses were performed using Surface Xplore.

Ex-situ XPS

Ex-situ XPS was carried out on Thermo SCIENTIFIC ESCALAB 250Xi with an excitation source of Al K α radiation. Typically, the sample was swept with N₂ to removed impurity on the surface in darkness and the test before illumination was conducted. Then the 300W Xe lamp was turned on for 10 minutes to excite the sample and the test after illumination was conducted. Data was fit in Thermo Avantage.

Computational details

The first-principles calculations are performed in the framework of the density functional theory with the projector augmented planewave method, as implemented in the Vienna ab initio simulation package.^[5] The generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE) functional is employed for the exchangecorrelation potential.^[6] The long range van der Waals interaction is described by the DFT-D3 approach.^[7] The plane-wave basis with a kinetic energy cutoff of 450 eV and the Monkhorst-Pack^[8] scheme with a k-point grid spacing of $2\pi \times 0.04$ Å⁻¹, were employed to ensure convergence of the total energy. The converged conditions for ionic and electronic optimizations were chosen as 0.02 eV/Å and 1×10^{-5} eV, respectively. The adsorption energy E ads is defined as: E ads = E ad/sub – (E ad + E sub), where E ad/sub, E ad, and E sub are the total energies of the adsorbate/substrate system, the adsorbate in the structure, and the clean substrate, respectively. The free energy was calculated by G = E ads + ZPE - TS, where G, E ads, ZPE, and TS are the free energy, total energy from DFT calculations, zero-point energy, and entropic contributions, respectively. The entropic contribution to the free energy was conducted by using the VASPKIT package.^[9]





 $Figure \ S1. Scheme \ of \ photocatalytic \ reaction \ process$



Figure S2.PXRD patterns of UN-x



Figure S3. PXRD of D-UN-x



Figure S4. XRD patterns of D-UiO-66-NH₂(ZrCe_{0.33}), D-UiO-66-NH₂(ZrCe_{0.5}) and D D-UiO-66-NH₂(ZrCe_{0.67})



Figure S5. FTIR of UN-x





Figure S7. SEM and TEM pictures of (a, c) UN-0.25 and (b, d) D-UN-0.25



Figure S8. ¹H NMR patterns of standard NH₂-H₂BDC (The mass of NH₂-H₂BDC increase from (a) to (d))



Figure S9. ¹H NMR patterns of digested (a) UN(Zr), (b) UN-0.25, (c) D-UN-0.167, (d) D-UN-0.25, (e) D-UN-0.28 and (f) D-UN-0.3



Figure S10. UV-Vis DRS of UN-x



Figure S11. UV-Vis DRS of D-UN-x



Figure S12. Tauc plots of UN-x



Figure S13. Tauc plots of D-UN-x



Figure S14. 3D contour WTEXAFS maps with 2D projection of Ce L₃-edge of D-UN-0.25



Figure S15. 3D contour WTEXAFS maps with 2D projection of Zr K-edge of D-UN-0.25



Figure S16. 3D contour WTEXAFS maps with 2D projection of Zr K-edge of UN(Zr)



Figure S17. Ce L₃-edge EXAFS (points) and curve-fit (line) for D-UN-0.25 in k^2 weighted k space



Figure S18. Zr K-edge EXAFS (points) and curve-fit (line) for D-UN-0.25 in k² weighted k space



Figure S19. Zr K-edge EXAFS (points) and curve-fit (line) for UN(Zr) in k² weighted k space



Figure S20. Structure of (a) pristine and (b) optimized D-ZrCe-oxo-clusters



Figure S21. Structure of optimized ZrCe-oxo-clusters, a ligand is removed for charge compensation. This model was only applied for COHP calculation



Figure S22. Structure of optimized Zr-oxo-clusters



Figure S23. Photoreduction rates of all samples and contrast



Figure S24. ¹H NMR patterns water after 10 hours' photocatalysis (Pyridine as internal standard)



Figure S25. ¹H NMR patterns of digested (a) D-UiO-66-NH₂-2, (b) D-UiO-66-NH₂-4, (c) D-UiO-66-NH₂-6, (d) D-ML-UiO-66-NH₂(0.1), (e) D-ML-UiO-66-NH₂(0.3), (f) D-ML-UiO-66-NH₂(0.7), (g) D-ML-UiO-66-NH₂(0.9), (h) D-UiO-66-NH₂ (Zr/Ce_{0.25}) after 12 hours' photocatalysis



Figure S26. XRD patterns of D-UiO-66-NH₂-x



Figure S27. XRD patterns of D-ML-UiO-66(y)



Figure S28. Photoreduction rates of UiO-66 with other defective engineering strategies



Figure S29. TEM photographs of D-UN-0.25 after 12 hours' photocatalysis



Figure S30. XRD patterns of D-UN-0.25 after 12 hours' photocatalysis



Figure S31. Mott-Schottky plots of UN-0.25



Figure S32. Mott-Schottky plots of D-UN-0.25



Figure S33. Mott-Schottky plots of UN(Zr)



Figure S34. Density of state plots of D-CeZr-oxo clusters (upper) and Zr-oxo-clusters (under)



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Figure S36. XPS fine spectroscopy of Zr 3d get from UiO-66-NH₂ (Zr/Ce_{0.25}) and D-UiO-66-NH₂ (Zr/Ce_{0.25})



Figure S37. XPS fine spectroscopy of Ce 3d get from UiO-66-NH₂ (Zr/Ce_{0.25}) and D-UiO-66-NH₂ (Zr/Ce_{0.25})



Figure S38. Ce L3 edge XAS for D-UiO-66-NH2 (Zr/Ce0.25), UiO-66-NH₂ (Zr/Ce_{0.25}) and CeCl₃





Figure S40. Mechanism scheme of photocatalytic CO₂ reduction and H₂O oxidation on ZrCe-oxo cluster



Figure S41. Charge density difference plots of Zr-oxo cluster with adsorbed (a, b) CO₂; (c, d) COOH; (e, f) CO



Figure S42. Charge density difference plots of ZrCe-oxo cluster with absorbed (a, b) CO₂; (c, d) COOH; (e, f) CO

Section 4. Tables

Sample	Concentration (Zr)/ppm	Concentration (Ce)/ppm	Molar percentage of
			$Ce(n_{Ce}/n_{Ce}+n_{Zr})$
D-UiO-66-NH ₂	17.2	1.385	4.97%
$(Zr/Ce_{0.30})$			
D-UiO-66-NH ₂	16.95	1.227	4.49%
$(Zr/Ce_{0.28})$			
D-UiO-66-NH ₂	17.82	0.795	2.82%
$(Zr/Ce_{0.25})$			
D-UiO-66-NH ₂	26.08	0.5708	1.4%
$(Zr/Ce_{0.167})$			
D-UiO-66-NH ₂ -2	23.46		
D-UiO-66-NH ₂ -4	22.94		
D-UiO-66-NH ₂ -6	24.73		
D-ML-UiO-66-	25.19		
NH ₂ (0.1)			
D-ML-UiO-66-	26.25		
NH ₂ (0.3)			
D-ML-UiO-66-	24.86		
NH ₂ (0.7)			
D-ML-UiO-66-	25.97		
NH ₂ (0.9)			

Table S1. ICP-OES elements content analysis ^a

^a Sample concentration is 100ppm

Sample	Sample mass/mg	Calculated formula	Amount of clusters/m ol ^a	Amount of ligands/mol	Ligands/clu sters
D-UiO-66- NH ₂ (Zr/Ce _{0.30})	5.09	Ce _{0.298} Zr _{5.702} O ₆ (NH ₂ - BDC) x	1.68733E- 6	4.75644E-6	2.82
D-UiO-66- NH ₂ (Zr/Ce _{0.28})	6.08	Ce _{0.269} Zr _{5.731} O ₆ (NH ₂ -BDC) _x	1.97628E- 6	5.66974e-6	2.87
D-UiO-66- NH ₂ (Zr/Ce _{0.25})	3.81	Ce _{0.169} Zr _{5.831} O ₆ (NH ₂ -BDC) _x	1.27951E- 6	5.72038e-6	4.47
D-UiO-66- NH ₂ (Zr/Ce _{0.167})	8.30	Ce _{0.084} Zr _{5.916} O ₆ (NH ₂ -BDC) _x	4.02093E- 6	1.91508E-5	4.76
UiO-66-NH ₂	6.74	$Zr_6O_6(NH_2-BDC)_x$	2.81944E- 6	1.641E-5	5.82
D-UiO-66- NH ₂ -2	5.04	Zr ₆ O ₆ (NH ₂ -BDC) _x	2.16554E- 6	9.55943E-6	4.41
D-UiO-66- NH ₂ -4	7.02	Zr ₆ O ₆ (NH ₂ -BDC) _x	2.94943E- 6	1.12449E-5	3.81
D-UiO-66- NH ₂ -6	7.17	Zr ₆ O ₆ (NH ₂ -BDC) _x	3.24751E- 6	1.16048E-5	3.57
D-ML-UiO- 66-NH ₂ (0.1)	6.1	Zr ₆ O ₆ (NH ₂ -BDC) _x (BDC) _y	2.81427E- 6	1.26691E-5	4.50
D-ML-UiO- 66-NH ₂ (0.3)	7.6	Zr ₆ O ₆ (NH ₂ -BDC) _x (BDC) _y	3.65385E- 6	1.23458E-5	3.38
D-ML-UiO- 66-NH ₂ (0.7)	6.0	Zr ₆ O ₆ (NH ₂ -BDC) _x (BDC) _y	2.73187E- 6	6.16083E-6	2.26
D-ML-UiO- 66-NH ₂ (0.9)	6.14	Zr ₆ O ₆ (NH ₂ -BDC) _x (BDC) _y	2.92044E- 6	3.41656E-6	1.17
D-UiO-66- NH ₂ (Zr/Ce _{0.25}) after 12hours' photocatalysis	3.42	Ce _{0.169} Zr _{5.831} O ₆ (NH ₂ -BDC) _x	1.4914E-6	3.69085E-6	4.33

Table S2. Ligands/clusters (L/C) ratio analysis

^a According to ICP-OES, we got the mass percentages of metal elements and it's assumed that every six Zr or Ce atoms form a cluster.

Path	Ν	R/ Å	$\sigma^2/\text{ Å}^2$	ΔR
Ce-O	2.63(±0.49)	2.55	0.015(±0.006)	0.16(±0.023)
Ce-Zr	4 ^b	3.60	0.017(±0.006)	0.06(±0.039)

Table S3. Curve-fit Parameters ^a for Ce L3-edge EXAFS for D-UiO-66-NH₂ (Zr/Ce_{0.25})

^a S_0^2 was fixed as 0.7 to reduce variable parameters. ΔE_0 was refined as a global fit parameter, returning a value of (2.61±1.02) eV. Data ranges: 2.000≤k≤6.481 Å⁻¹, 1.0≤R≤3.8 Å. The number of variable parameters is 6, out of a total of 7.734 independent data points. R factor for this fit is 1.0%. ^b The coordination number was constrained as N(Ce-Zr)-4 for the assumption that the CeZr5O clusters wouldn't lose Zr.

		0		2 (0.25)
Path	Ν	R/ Å	$\sigma^{2/}$ Å ²	ΔR
Zr-O _{COO}	3.36(±0.41)	2.12	0.005(±0.001)	-0.024(±0.015)
Zr-O _{µ3}	3.68(±0.38)	2.28	0.003(±0.002)	-0.026(±0.015)
Zr-Zr	4 ^b	3.53	0.011(±0.001)	0.011(±0.012)

Table S4. Curve-fit Parameters ^a for Zr K-edge EXAFS for D-UiO-66-NH₂ (Zr/Ce_{0.25})

^a S_0^2 was fixed as 1.12, which was gotten from fitting Zr-K edge EXAFS of UiO-66-NH₂ with fixed coordination number. ΔE_0 was refined as a global fit parameter, returning a value of (0.070±1.123) eV. Data ranges: $3.000 \le k \le 12.327$ Å⁻¹, $1.0 \le R \le 3.6$ Å. The number of variable parameters is 8, out of a total of 15.18 independent data points. R factor for this fit is 1.46%. ^b This coordination number was constrained as *N*(Zr-Zr)-4 based on the assumption that Zr-O cluster wouldn't be broken in D-UN-0.25.

Path	Ν	R/ Å	$\sigma^2/\text{ Å}^2$	ΔR
Zr-O _{COO}	4 ^a	2.13	0.005(±0.002)	-0.010(±0.012)
Zr-O _{µ3}	4 ^a	2.28	0.004(±0.002)	-0.018(±0.013)
Zr-Zr	4 ^a	3.52	0.006(±0.001)	0.010(±0.008)

Table S5. Curve-fit Parameters ^a for Zr K-edge EXAFS for UiO-66-NH₂ standard

^a S_0^2 was calculated as 1.12 when coordination number were constrained as N(Zr-O_{COO})-4, N(Zr-O_{µ3})-4 and N(Zr-Zr)-4. ΔE_0 was refined as a global fit parameter, returning a value of (0.58±1.11) eV. Data ranges: 3.000≤k≤12.327 Å⁻¹, 1.0≤R≤3.5 Å. The number of variable parameters is 8, out of a total of 14.633 independent data points. R factor for this fit is 1.2%.

Defective MOFs	Defective type	Application	Photocatalytic conditions	Performance	References
Ni-MOF- 74	Ligand deficiency	CO ₂ to CO	Photosensitizer and sacrificial agents,λ>400nm	1380µmol/g/h	[10]
Cu-BTC	Ligand deficiency	H ₂ evolution	Photosensitizer and sacrificial agents, λ >420nm	15107µmol/g/h	[11]
ZIF-67	Ligand deficiency	O ₂ evolution	Photosensitizer and sacrificial agents,λ>420nm	TOF = 0.079s-	[12]
NH ₂ -MIL- 125(Ti)	Ligand deficiency	H ₂ evolution	Sacrificial agents,λ>420nm 500W Xe lamp	337µmol/g/h	[13]
ZIF-67	Ligand deficiency	H ₂ evolution	Photosensitizer and sacrificial agents, λ >420nm	6.14 mmol/g/h	[14]
UiO-67	Ligand deficiency	CO ₂ to HCOOH	Photosensitizer and sacrificial agents, λ >420nm	14.7μmol/g/h	[15]
D-UiO- 66(Zr/Ce _x)- NH ₂	Ligand deficiency	CO ₂ to CO	No photosensitizer and sacrificial agents, AM 1.5G	4.42µmol/g/h	This work

Table S6. Summary of defect containing MOFs-based photocatalytic performance

Sample	Band	V _{EB} VS	V _{FR} VS	Fermi	E _{VB} /eV	E _{CB} /eV	V _{VB} VS	V _{CB} VS
	gan	SCE/V	NHE/V	level/eV		-CD	NHE/V	NHE/V
	sup (aV)	JCL/ V		b				
	(ev)			-				
UiO-66-	2.831	-1.100	-0.856	-3.644	-6.275	-3.444	1.775	-1.056
NH ₂								
(Zr/Ce _{0.25})								
D-UiO-66-	2.487	-1.267	-1.023	-3.477	-5.764	-3.277	1.264	-1.223
NH ₂								
(Zr/Ce _{0.25})								
UiO-66-	2.899	-1.177	-0.933	-3.567	-6.266	-3.367	1.766	-1.133
NH ₂								

Table S7. Flat band potential (V_{FB}) and band structure calculation ^a

^a Band gap energy was gotten from UV-vis DRS and Tauc-plot. According to the Mott-Schottky curves, flat band potential (V_{FB}) was accessed. Then V_{FB} plus 0.244V can get (V_{FB} vs NHE). All samples are n-type semiconductor, the bottom of conduction band is 0.1-0.3 eV minus V_{FB}. So V_{FB} minus 0.2eV can get V_{CB}. All statistics is listed at table S5. ^b Fermi level was calculated according to the following function: $E_F = -4.5eV + (-e) * V_f$

sample	τ_1/ns	τ_2/ns	А	B ₁	B_2	χ^2	τ*/ns
UiO-66-	0.2117	2.189	0.8549	7967.9819	91.6532	1.0189	0.422
NH ₂							
(Zr/Ce _{0.25})							
D-UiO-66-	0.1731		0.7086	4854.3901		1.0358	0.173
NH ₂							
(Zr/Ce _{0.25})							
UiO-66-	0.2366		0.8552	3856.8665		1.2428	0.237
NH ₂							

Table S8. TRPL lifetime of D-UN-0.25, UN-0.25 and UN(Zr)

sample	element	Spin-orbit	BE	sample	element	Spin-	BE
		doublet	(eV)			orbit	(eV)
						doublet	
		Ce 3d _{5/2}	881.88			Ce 3d _{5/2}	882.46
		Ce 3d _{5/2}	886.20			Ce 3d _{5/2}	886.74
UiO-66-	Ce(III)	Ce 3d _{3/2}	900.60	D-UiO-66-	Ce(III)	Ce 3d _{3/2}	901.10
NH_2		Ce 3d _{3/2}	904.94	NH ₂ (Zr/Ce _{0.25})		Ce 3d _{3/2}	905.41
$(Zr/Ce_{0.25})$	Zr(IV)	Zr 3d _{5/2}	183.08		Zr(IV)	Zr 3d _{5/2}	182.47
		Zr 3d _{3/2}	185.48			Zr 3d _{3/2}	184.88

Table S9. Assignment of the Ce $3d_{3/2}$, $3d_{5/2}$ components from XPS spectra collected for UN-0.25 and D-UN-0.25

	element	Spin-orbit	BE		element	Spin-	BE
		doublet	(eV)			orbit	(eV)
						doublet	
		Ce 3d _{5/2}	882.25			Ce 3d _{5/2}	882.73
		Ce 3d _{5/2}	885.98			Ce 3d _{5/2}	886.37
Before	Ce(III)	Ce 3d _{3/2}	900.94	After	Ce(III)	Ce 3d _{3/2}	901.79
illumination		Ce 3d _{3/2}	904.79	illumination		Ce 3d _{3/2}	905.30
	Zr(IV)	Zr 3d _{5/2}	182.96		Zr(IV)	Zr 3d _{5/2}	182.87
		Zr 3d _{3/2}	185.31			Zr 3d _{3/2}	185.22

Table S 10. Assignment of the Ce $3d_{3/2},\,3d_{5/2}$ components from ex-situ XPS spectra collected for D-UiO-66-NH_2(CeZr_{0.25})

sample		μ3-Ο	M-0-C	μ3-ОН	0-C=0
D-UiO-66-	BE (eV)	530.55	532.02	532.77	
NH ₂	% Area	18.1	58.5	23.4	
(Zr/Ce _{0.25})					
UiO-66-NH ₂	BE (eV)	530.76	532.00	532.64	533.87
(Zr/Ce _{0.25})	% Area	64.1	18.6	12.2	5.13

Table S11. O species proportion from XPS spectra collected for D-UN-0.25 and UN-0.25

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