

*Electronic Supplementary Information for*

## Efficient TADF-based aerobic photocatalysts for sulfide oxidation in water by increasing hydrophobic crosslinking

Gaobo Hong,<sup>a</sup> Wenlong Chen,<sup>a</sup> Jianjun Du,<sup>a</sup> Fengling Song<sup>\*ab</sup> and Xiaojun Peng<sup>a</sup>

<sup>a</sup>*State Key Laboratory of Fine Chemicals, Frontiers Science Center for Smart Materials Oriented Chemical Engineering, Dalian University of Technology, Dalian 116024, P. R. China.*

<sup>b</sup>*Institute of Frontier Chemistry, School of Chemistry and Chemical Engineering, Shandong University, Qingdao 266237, P. R. China.*

\*Corresponding author.

E-mail: [songfl@dlut.edu.cn](mailto:songfl@dlut.edu.cn), [songfl@sdu.edu.cn](mailto:songfl@sdu.edu.cn).

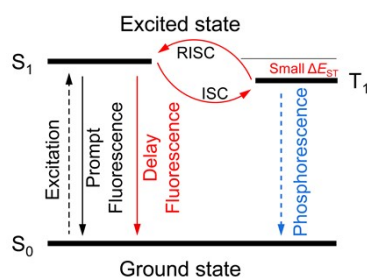
### Contents

1 General methods.....	1
2 Experimental procedures .....	1
2.1 Preparation of Photocatalysts .....	2
2.2 FTIR measurements.....	2
2.3 PXRD measurements .....	3
2.4 SEM measurements .....	4
2.5 TG measurements .....	4
2.6 Absorption and fluorescence spectra.....	4
2.7 FL content determination.....	5
2.8 WCA measurements.....	6
2.9 Fluorescence lifetime measurements .....	6
2.10 ROS generation.....	8
2.11 Photooxidation experiments.....	10
3 NMR data .....	15
4 References.....	18

## 1 General methods

Unless otherwise noted, all chemicals were commercially available and used as received without further purification. Powder X-ray diffraction (PXRD) profiles were recorded on a Bruker D8 Advance diffractometer (40 Kv, 40 mA, Cu-K $\alpha$ ,  $\lambda = 1.5418 \text{ \AA}$ ) from 5 - 40° with a step of 0.01° at a scan speed of 6° min<sup>-1</sup>. Fourier Transform Infrared (FTIR) spectra were recorded with a Nicolet IS50 FT-IR spectrophotometer of Thermo Scientific in the range of 400 to 4000 cm<sup>-1</sup>. Scanning electron microscopy (SEM) images were recorded on a Nova NanoSEM 450 field emission scanning electron microscope of FEI and a gold layer was sputtered on the surface of each sample before the measurement. Thermogravimetric analysis (TGA) profiles were recorded on a SDT-Q600 simultaneous DSC-TGA instrument of TA from 25 °C to 800 °C with a temperature increasing rate of 10 °C • min<sup>-1</sup>. Water droplet contact angle (WCA) values were obtained by an OCA50 optical contact angle measuring and contour analysis system of DataPhysics. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Bruker Avance II 400 and Vaian DLG400 spectrometer using CDCl<sub>3</sub> or 90% H<sub>2</sub>O+10% D<sub>2</sub>O as solvents. The chemical shift was internally referenced to tetramethylsilane signal (TMS:  $\delta \text{ } ^1\text{H} = 0$ ) or residual solvent signals (CDCl<sub>3</sub>:  $\delta \text{ } ^{13}\text{C} = 77.06$ ). <sup>1</sup>H NMR are recorded as follows: chemical shift ( $\delta$ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). <sup>13</sup>C NMR are reported in terms of chemical shift ( $\delta$ , ppm).

## 2 Experimental procedures

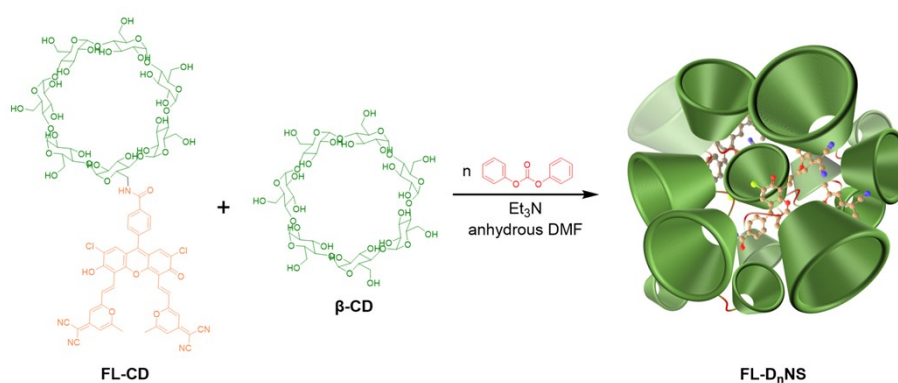


**Scheme S1** Simplified Jablonski diagram for TADF compounds.

## 2.1 Preparation of Photocatalysts

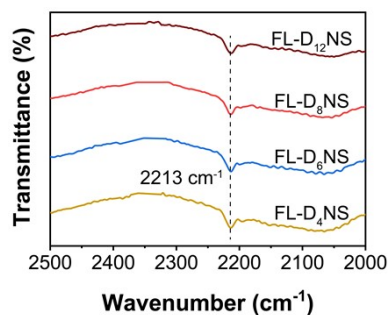
FL-CD was synthesized according to the previously reported method<sup>1</sup>.

FL-CD (5.64 mg, 0.003 mmol) and  $\beta$ -CD (337 mg, 0.297 mmol) were dissolved in anhydrous DMF (5.0 mL) and heated to 80 °C. DPC (257 mg, 1.2 mmol for n=4; 386 mg, 1.8 mmol for n=6; 514 mg, 2.4 mmol for n=8; 772 mg, 3.6 mmol for n=12) and Et<sub>3</sub>N (150  $\mu$ L) were added in sequence and the reaction mixture was stirred at 80 °C for 12 h. After the completion of crosslinking, the reaction mixture was cooled to room temperature and distilled water (30 mL) was added. The precipitation was centrifuged and washed alternately with distilled water and ethanol to remove unreacted reagents and byproducts. Finally, the precipitation was washed with distilled water many times to remove ethanol and dispersed in distilled water (30 mL) again, obtaining the stock solution of FL-D<sub>n</sub>NS. For PXRD, FTIR, SEM, TGA, and WCA measurements, the precipitation was dried by lyophilization, and traces of water was completely removed by vacuum drying to obtain the powder.



**Scheme S2** Preparation of FL-D<sub>n</sub>NS.

## 2.2 FTIR measurements



**Figure S1** Magnified FTIR spectra of FL-D<sub>n</sub>NS.

**Table S1** FTIR absorption peaks and their assignment<sup>2</sup>.

Wavelength/cm <sup>-1</sup>	Associated vibration	Origin
3420	O-H stretching	β-cyclodextrin
2934	C-H stretching	β-cyclodextrin
1156	Glycosidic bond C–O–C stretching	β-cyclodextrin
1031	Glycosidic bond C-O-C blending	β-cyclodextrin
950	“Breathing” of cyclodextrin ring	β-cyclodextrin
1757	C=O carbonyl group	carbonate bonds
1274	O–C–O–O ester group	carbonate bonds
2213	C≡N group	FL
1633	H-O-H bending	H <sub>2</sub> O in the macrocyclic cavity

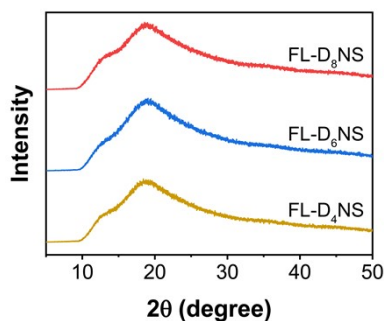
The degree of substitution (DS) was calculated by Eq. S1, where  $A_{1757}$  is the absorbance of carbonyl groups (C=O) at 1757 cm<sup>-1</sup> and  $A_{1156}$  is the absorbance of glycosidic bonds at 1156 cm<sup>-1</sup> in the carbonate-based cyclodextrin polymer.

$$\text{Degree of substitution} = A_{1757}/A_{1156} \quad \text{Eq. S1}$$

**Table S2** DS of FL-D<sub>n</sub>NS

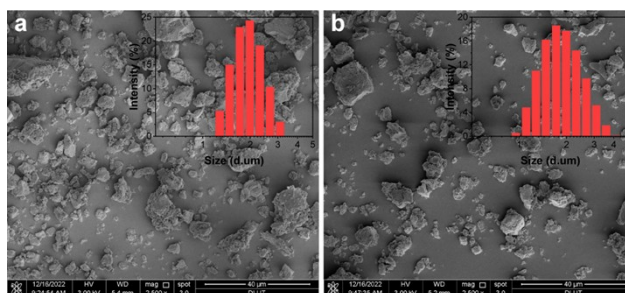
Photocatalysts	$A_{1757}$	$A_{1156}$	DS
FL-D <sub>4</sub> NS	0.497	0.551	0.90
FL-D <sub>6</sub> NS	0.584	0.543	1.08
FL-D <sub>8</sub> NS	0.634	0.525	1.21
FL-D <sub>12</sub> NS	0.639	0.522	1.22

### 2.3 PXRD measurements



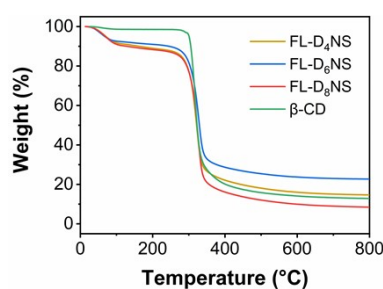
**Figure S2** PXRD profiles of FL-D<sub>n</sub>NS.

## 2.4 SEM measurements



**Figure S3** SEM images of a) FL-D<sub>4</sub>NS and b) FL-D<sub>6</sub>NS. Scale bar = 40 μm. Insert: particle size distribution of the sample in water.

## 2.5 TG measurements



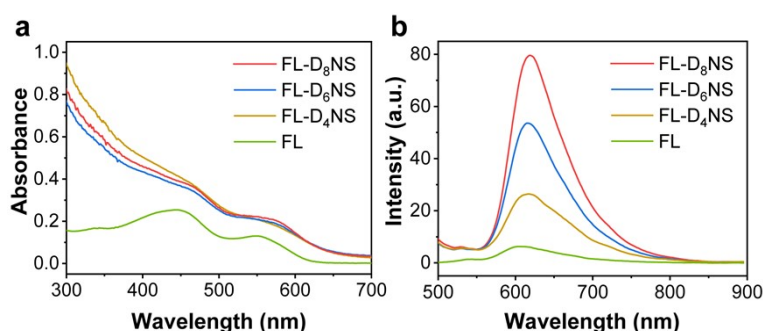
**Figure S4** TG curves of FL-D<sub>4</sub>NS, FL-D<sub>6</sub>NS, FL-D<sub>8</sub>NS, and β-CD.

## 2.6 Absorption and fluorescence spectra

Absorption spectra were recorded on a Carry 60 UV-vis spectrophotometer of Agilent with a sample concentration of 5 μM (calculated by FL content) in a quartz cuvette (1 cm×1 cm) at room temperature in air atmosphere.

Fluorescence spectra were recorded on a Cary Eclipse fluorescence spectrophotometer of Agilent with a sample concentration of 5 μM (calculated by FL content) and an excitation wavelength of 460 nm at room temperature in air atmosphere. Both the excitation and emission slits are 5 nm and PMT detector voltage was 600 V.

Time-resolved fluorescence spectra were recorded with a sample concentration of 5 μM (calculated by FL content) and an excitation wavelength of 460 nm at room temperature in argon atmosphere. In the phosphorescence mode, the total decay time, delay time, and gate time were 5.0 ms, 0.1 ms, and 1.0 ms, respectively. Both the excitation and emission slits were 20 nm and PMT detector voltage was 600 V.

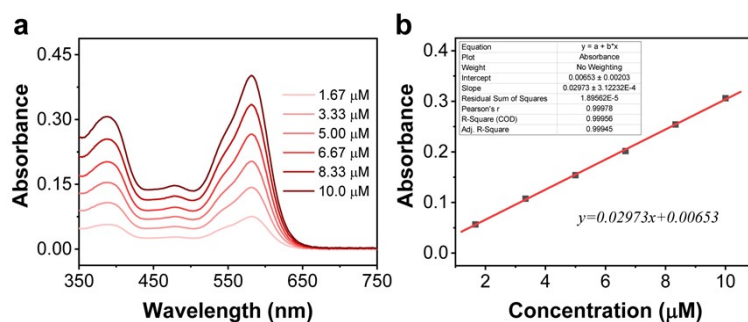


**Figure S5** a) Absorption and b) fluorescence spectra of FL-D<sub>n</sub>NS and FL in water.

## 2.7 FL content determination

The content of FL in FL-D<sub>n</sub>NS was determined by standard curve. FL-CD was dissolved in a mixed solvent of DMF, H<sub>2</sub>O and NH<sub>3</sub>•H<sub>2</sub>O (2.5 : 0.4 : 0.1, V/V) to prepare a stock solution with a concentration of 1 mmol/L (1 mM). Taking 5, 10, 15, 20, 25, 30 μL of the stock solution, respectively, and diluting to 3 mL with the above mentioned mixed solution to test the absorption spectra. Plotting the absorbance at 390 nm versus corresponding concentration to obtain the standard curve with the concentration range of 0 - 10 μM.

Mixing the stock solution of FL-D<sub>n</sub>NS (0.4 mL) and NH<sub>3</sub>•H<sub>2</sub>O (0.1 mL), and sonicating the resulting suspension for 0.5 h to get a clear solution. Diluting the clear solution to 3 mL with DMF to test the absorption spectra. The content of FL in FL-D<sub>n</sub>NS was calculated by the absorbance at 390 nm according to the standard curve.



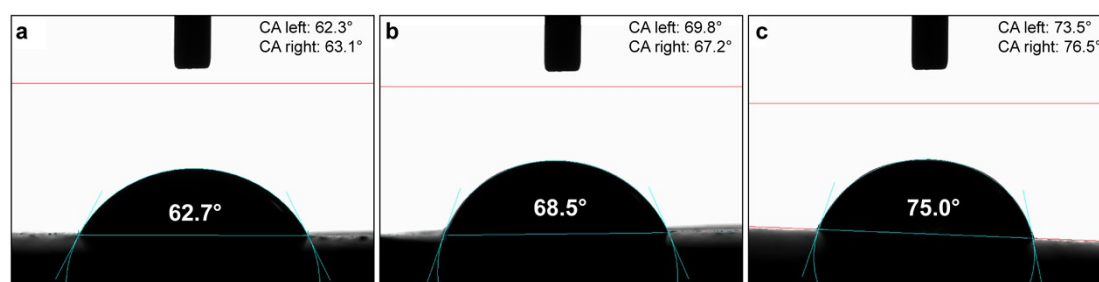
**Figure S6** a) Absorption spectra of FL-CD in the mixed solvent with different concentrations.

b) The standard curve obtained by plotting the absorbance at 390 nm versus corresponding concentration.

**Table S3** FL contents in FL-D<sub>n</sub>NS

Photocatalyst s	Absorbance at 390 nm			Mean	Content μmol/mL
	1	2	3		
FL-D <sub>4</sub> NS	0.4259	0.4316	0.4232	0.4269	0.1060
FL-D <sub>6</sub> NS	0.4215	0.4184	0.4188	0.4196	0.1042
FL-D <sub>8</sub> NS	0.4249	0.4244	0.4300	0.4264	0.1059

## 2.8 WCA measurements

**Figure S7** WCA measurements of a) FL-D<sub>4</sub>NS, b) FL-D<sub>6</sub>NS, and c) FL-D<sub>8</sub>NS.

## 2.9 Fluorescence lifetime measurements

For prompt fluorescence lifetime measurements, FL-D<sub>n</sub>NS was dispersed in H<sub>2</sub>O with a concentration of 5 μM. FL was dissolved in H<sub>2</sub>O with the same concentration. Taking 3 mL of the sample into a quartz cuvette (1 cm×1 cm) to acquire the fluorescence lifetime decay curve by a photo counting fluorescence system of HORIBA at room temperature in air atmosphere. Silicon spheres dispersed in H<sub>2</sub>O was used as a blank sample to test the IRF of the excitation source. The excitation and emission wavelengths were 460 nm and 620 nm, respectively. And the measurement range of data acquisition was 100 ns (TCSPC). To study the effect of sulfide on prompt fluorescence lifetime, the sample of FL-D<sub>8</sub>NS (5 μM) mixing with or without 3-(methylthio)propionic acid (2.5 mM) in a quartz cuvette was bubbled with argon at a flow of 20 mL/min<sup>-1</sup> for 20 min to remove O<sub>2</sub>. Then the cuvette was sealed and taken for the prompt fluorescence lifetime measurement.

For delay fluorescence lifetime measurements, the FL-D<sub>n</sub>NS was dispersed in H<sub>2</sub>O with a concentration of 5 μM. FL was dissolved in H<sub>2</sub>O with the same concentration. Taking 3 mL of the sample into a quartz cuvette (1 cm×1 cm) to acquire the fluorescence lifetime decay curve by a photo counting fluorescence system of HORIBA at room temperature in an air or argon atmosphere (argon bubbling at a flow of 20 mL/min<sup>-1</sup> for 20 min). The excitation and emission wavelengths were 460 nm and 620 nm, respectively. For all samples in air atmosphere, the measurement range of data acquisition was 340 μs (Phos). For the sample in argon atmosphere, the measurement range of data acquisition of FL and FL-D<sub>n</sub>S were 340 μs (Phos) and 11 ms (Phos), respectively. To study the effect of sulfide on delay fluorescence lifetime, the sample of FL-D<sub>8</sub>NS (5 μM) mixing with 3-(methylthio)propionic acid (2.5 mM) in a quartz cuvette was bubbled with argon at a flow of 20 mL/min<sup>-1</sup> for 20 min to remove O<sub>2</sub>. Then the cuvette was sealed and taken for the delay fluorescence lifetime measurement.

The obtained data file was opened directly with DAS6 of HORIBA to analyze fluorescence lifetime. After fitting the data according to the built-in exponential functions,

$$\tau = A + B_n \times e^{(-i/\tau_n)}$$

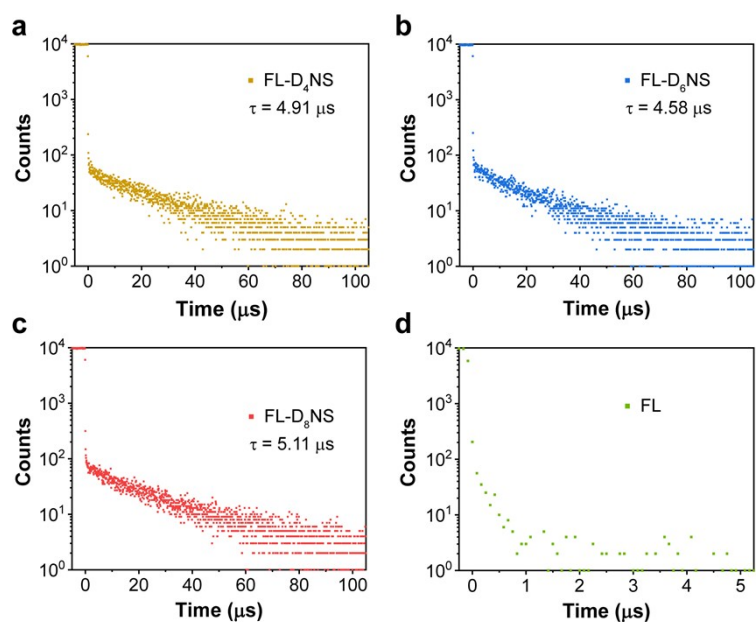
where *n* is the number of exponentials used for fitting, the fluorescence lifetime value was obtained.

**Table S4** Prompt fluorescence lifetimes of FL-D<sub>n</sub>NS in H<sub>2</sub>O.

Photocatalysts	$\tau_1/\text{ns}$	$B_1$	$\tau/\text{ns}$	$\chi^2$
FL	1.01	1	1.01	1.03
FL-D <sub>4</sub> NS	2.03	1	2.03	1.04
FL-D <sub>6</sub> NS	2.19	1	2.19	1.16
FL-D <sub>8</sub> NS	2.33	1	2.33	1.06
FL-D <sub>8</sub> NS <sup>a</sup>	2.32	1	2.32	1.13
FL-D <sub>8</sub> NS <sup>b</sup>	2.21	1	2.21	0.99

<sup>a</sup>In argon atmosphere. <sup>b</sup>In argon atmosphere with the presence of sulfide.





**Figure S8** Delay fluorescence lifetime curves of a) FL-D<sub>4</sub>NS, b) FL-D<sub>6</sub>NS, c) FL-D<sub>8</sub>NS, and d) FL in H<sub>2</sub>O in air atmosphere.

**Table S5** Delay fluorescence lifetimes of FL-D<sub>n</sub>NS in H<sub>2</sub>O

Photocatalysts	Conditions	$\tau_1/\mu\text{s}$	$B_1$	$\tau_2/\mu\text{s}$	$B_2$	$\tau/\mu\text{s}$	$\chi^2$
FL	Air	/		/		/	
	Ar	77.56	1			77.56	1.04
FL-D <sub>4</sub> NS	Air	0.10	0.79	22.99	0.21	4.91	1.02
	Ar	237.03	0.58	631.20	0.42	402.58	0.99
FL-D <sub>6</sub> NS	Air	0.10	0.78	20.49	0.22	4.58	0.98
	Ar	284.50	0.63	727.69	0.37	448.48	1.00
FL-D <sub>8</sub> NS	Air	0.12	0.77	21.83	0.23	5.11	1.00
	Ar	290.52	0.63	746.78	0.37	459.34	1.03
	Ar <sup>a</sup>	158.93	0.33	391.05	0.67	314.45	1.00
	Ar <sup>b</sup>	273.71	0.66	716.16	0.34	424.14	1.01
	O <sub>2</sub> <sup>b</sup>	0.11	0.91	3.06	0.09	0.38	0.98

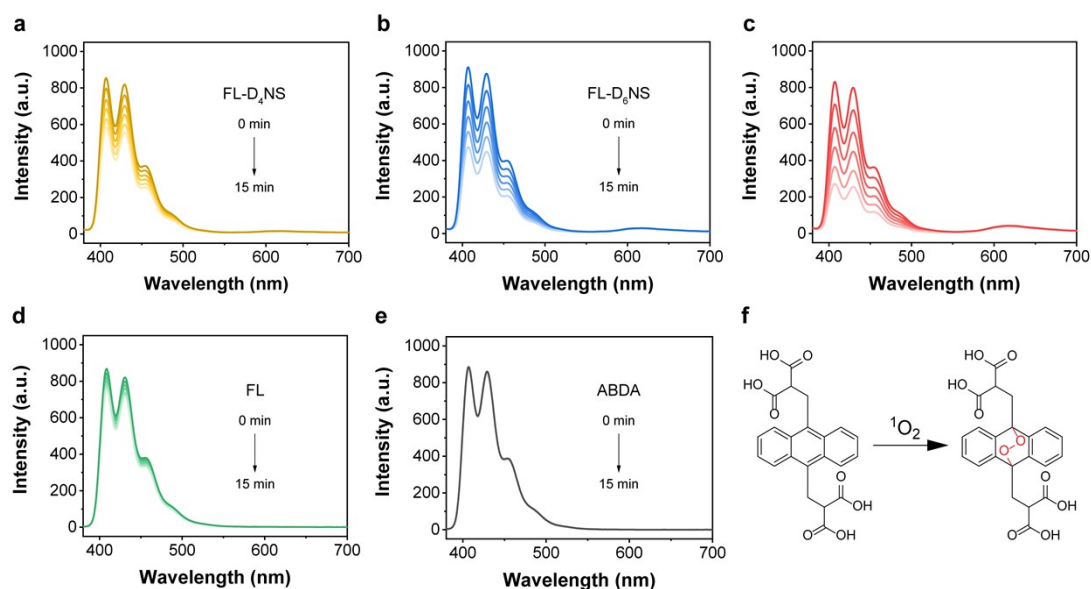
<sup>a</sup>With the presence of 3-(methylthio)propionic acid (2.5 mM). <sup>b</sup>The delay fluorescence lifetime of FL-D<sub>8</sub>NS after the tenth cycle.

## 2.10 ROS generation

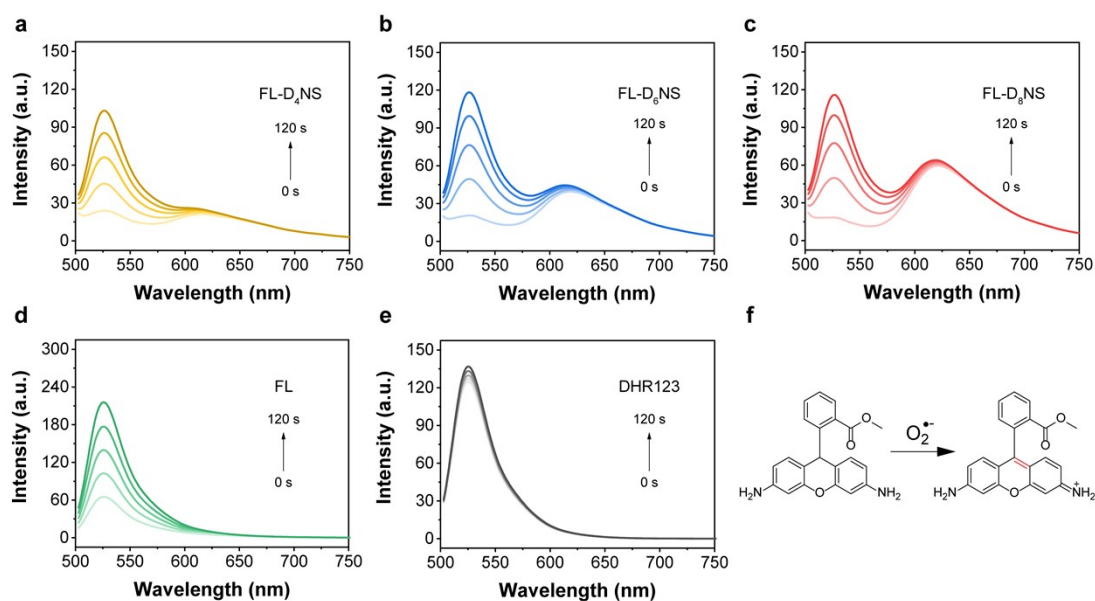
To test the generation of <sup>1</sup>O<sub>2</sub>, FL-D<sub>n</sub>NS was dispersed in H<sub>2</sub>O (2 mL) with a concentration of 5  $\mu\text{M}$ . FL was dissolved in H<sub>2</sub>O (2 mL) with the same concentration.

Then 1  $\mu\text{L}$  ABDA (10 mM in DMSO) was added and the mixture was irradiated with a white-light LED ( $20 \text{ mW}\cdot\text{cm}^{-2}$ ) under stirring (1000 r/min). The emission spectrum of the mixture was recorded every 5 min with an excitation wavelength of 360 nm. The fluorescence intensity change of ABDA was defined as  $(I_t - I_0)/I_0$ , where  $I_t$  and  $I_0$  referred to the fluorescence intensity at 407 nm after irradiation for  $t$  min and before irradiation, respectively. Plotting the fluorescence intensity change of ABDA versus the irradiation time to reveal the ability of FL-DnNS or FL to generate  $^1\text{O}_2$ .

To test the generation of  $\text{O}_2^{\bullet-}$ , FL-D<sub>n</sub>NS was dispersed in  $\text{H}_2\text{O}$  (2 mL) with a concentration of 5  $\mu\text{M}$ . FL was dissolved in  $\text{H}_2\text{O}$  (2 mL) with the same concentration. Then 8  $\mu\text{L}$  of DHR 123 (2.5 mM in DMSO) was added and the mixture was irradiated with a white-light LED ( $20 \text{ mW}\cdot\text{cm}^{-2}$ ) under stirring. The emission spectrum of the mixture was recorded every 30 s with an excitation wavelength of 488 nm. The fluorescence intensity change of Rhodamine 123 was defined as  $(I_t - I_0)/I_0$ , where  $I_t$  and  $I_0$  referred to the fluorescence intensity at 528 nm after irradiation for  $t$  s and before irradiation, respectively. Plotting the fluorescence intensity change of Rhodamine 123 versus the irradiation time to reveal the ability of FL-D<sub>n</sub>NS or FL to generate  $\text{O}_2^{\bullet-}$ .



**Figure S9** Time-course fluorescence intensity of a) FL-D<sub>4</sub>NS and ABDA, b) FL-D<sub>6</sub>NS and ABDA, c) FL-D<sub>8</sub>NS and ABDA, d) FL and ABDA, and e) ABDA alone after photoirradiation. f) The reaction between ABDA and  $^1\text{O}_2$ .



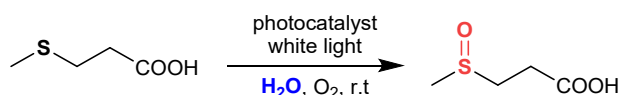
**Figure S10** Time-course fluorescence intensity of a) FL-D<sub>4</sub>NS and DHR 123, b) FL-D<sub>6</sub>NS and DHR 123, c) FL-D<sub>8</sub>NS and DHR 123, d) FL and DHR 123, and e) DHR 123 alone after photoirradiation. f)

The reaction between DHR 123 and O<sub>2</sub><sup>•-</sup>.

## 2.11 Photooxidation experiments

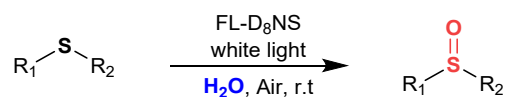
### 2.11.1 General procedure

#### General procedure A



3-(methylthio)propionic acid (0.1 mmol, 10.4  $\mu\text{L}$ ) and photocatalyst (0.2 mol%) were dispersed in O<sub>2</sub>-saturated H<sub>2</sub>O (5.0 mL) in a 25 mL glass vessel (25×95 mm) equipped with an O<sub>2</sub> balloon. Then the reaction vessel was irradiated with a white-light LED (20 mW•cm<sup>-2</sup>) under stirring (400 r/min) at room temperature for 60 min. 0.4 mL of the suspension was poured out from the reaction vessel and mixed well with additional 0.1 mL of D<sub>2</sub>O. After filtering out of the photocatalyst, the filtrate was characterized by <sup>1</sup>H NMR to determine the conversion and selectivity.

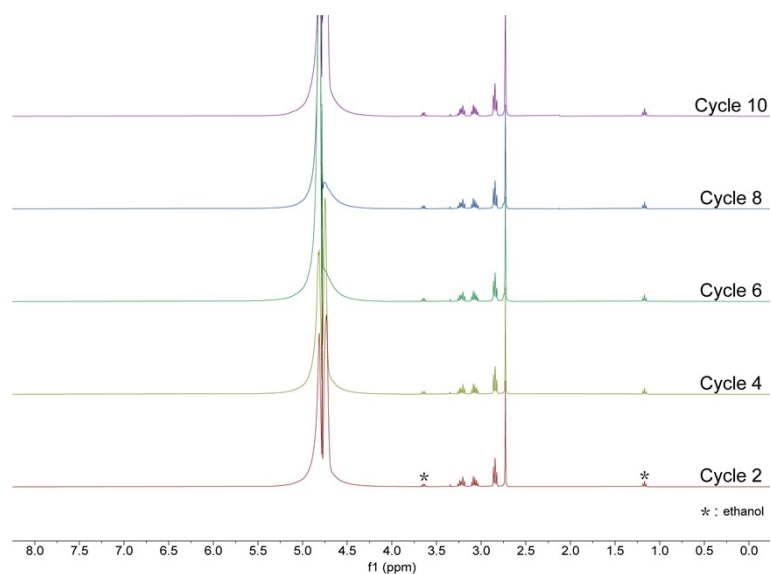
#### General procedure B



Sulfides (0.1 mmol) and FL-D<sub>8</sub>NS (0.2 mol%) were dispersed in H<sub>2</sub>O (5.0 mL) in a 25 mL glass vessel (25×95 mm). Then the reaction vessel was irradiated with a white-light LED (20 mW•cm<sup>-2</sup>) under stirring (1250 r/min) at room temperature in air atmosphere. After complete transformation of the substrate as determined by thin-layer chromatography, the suspension was extracted with CH<sub>2</sub>Cl<sub>2</sub> (5×3 mL), and the organic phases were combined, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and filtered under reduced pressure. The product was obtained after removing the solvent from the filtrate.

### 2.11.2 Recycling experiments

For the recovery and reuse of FL-D<sub>8</sub>NS, 3-(methylthio)propionic acid (0.1 mmol, 10.4 μL) and FL-D<sub>8</sub>NS (0.2 mol%) were suspended in O<sub>2</sub>-saturated H<sub>2</sub>O (5.0 mL) in a 25 mL glass vessel (25×95 mm) equipped with an O<sub>2</sub> balloon. Then the reaction vessel was irradiated with a white-light LED (20 mW•cm<sup>-2</sup>) for 60 min under stirring (400 r/min). After recovering by centrifugation and washing three times with H<sub>2</sub>O, FL-D<sub>8</sub>NS was reused in the next cycle. The yield of 3-(methylsulfinyl)propanoic acid for each cycle was determined by <sup>1</sup>H NMR.



**Figure S11** <sup>1</sup>H NMR spectra of the reaction solutions of the second, fourth, sixth, eighth, and tenth cycles.

**Table S6** Performances of visible-light-driven oxidation of thioanisole using various photocatalysts

Entry	Photocatalyst	Light source	Oxygen source / ROS	Solvent	Time/h	Conv./%	Sel./%	TOF/h <sup>-1a</sup>	TOF/ mmol g <sup>-1</sup> h <sup>-1b</sup>
1	3%-C <sub>60</sub> @PCN-222 <sup>3</sup>	LED lamp (50 mW/cm <sup>2</sup> , λ > 400 nm)	Air / O <sub>2</sub> <sup>•-</sup> ; <sup>1</sup> O <sub>2</sub>	CH <sub>3</sub> OH	3	>99	100	80	3.3
2	NNU-45 <sup>4</sup>	300 W Xe lamp (λ > 420 nm)	Air, H <sub>2</sub> O <sub>2</sub> / O <sub>2</sub> <sup>•-</sup>	CH <sub>3</sub> OH/CHCl <sub>3</sub> = 1/4	4	99	95	16.7	23.5
3	3D-PdPor-COF <sup>5</sup>	3 W blue LEDs	Air / O <sub>2</sub> <sup>•-</sup>	CF <sub>3</sub> CH <sub>2</sub> OH	0.4	98	/	49	/
4	h-LZU1 <sup>6</sup>	300 W Xe lamp (λ > 380 nm)	Air / O <sub>2</sub> <sup>•-</sup>	CH <sub>3</sub> CN	22	100	92.6	/	1.3
5	AQ-COF <sup>7</sup>	300 W Xe lamp (λ = 400–780 nm)	O <sub>2</sub> / O <sub>2</sub> <sup>•-</sup> ; <sup>1</sup> O <sub>2</sub>	CH <sub>3</sub> CN	3	>99	97	/	3.2
6	C <sub>3</sub> N <sub>4</sub> NSs-5 h <sup>8</sup>	Xe lamp (λ > 400 nm)	O <sub>2</sub> / O <sub>2</sub> <sup>•-</sup> ; <sup>1</sup> O <sub>2</sub>	CH <sub>3</sub> OH	1	99	99	/	50
7	DhaTph-Zn <sup>9</sup>	300 W Xe lamp (λ > 400 nm)	O <sub>2</sub> / O <sub>2</sub> <sup>•-</sup> ; <sup>1</sup> O <sub>2</sub>	CH <sub>3</sub> CN	10	82	>99	/	0.4
8	ARS-Nb <sub>2</sub> O <sub>5</sub> <sup>10</sup>	green LEDs (520 ± 15 nm, 3W × 4)	Air / O <sub>2</sub> <sup>•-</sup>	CH <sub>3</sub> OH	1.3	94	99	/	7.2

9	Zr <sub>12</sub> -NBC <sup>11</sup>	24 W blue LED	Air / O <sub>2</sub> <sup>•-</sup>	CH <sub>3</sub> OH	10	100	100	5	/
10	CCNU-16 <sup>12</sup>	6 W white LED	Air / O <sub>2</sub> <sup>•-}; <sup>1</sup>O<sub>2</sub></sup>	CH <sub>3</sub> OH/CHCl <sub>3</sub> = 1/1	0.67	99	96	190.7	95
11	Por-sp <sup>2</sup> c-COF <sup>13</sup>	red LEDs (λ = 623 nm, 3W × 4)	Air / O <sub>2</sub> <sup>•-</sup>	CH <sub>3</sub> OH	0.6	92	98	150.3	/
12	TTO-COF <sup>14</sup>	blue LEDs (3 W × 4)	O <sub>2</sub> / O <sub>2</sub> <sup>•-}; <sup>1</sup>O<sub>2</sub></sup>	CH <sub>3</sub> OH	2	90	98	/	26.5
13	paper-supported TPP <sup>15</sup>	white LED	Air / O <sub>2</sub> <sup>•-}; <sup>1</sup>O<sub>2</sub></sup>	/	3	92	72	220.8	/
14	2-AA-TiO <sub>2</sub> <sup>16</sup>	Violet LEDs (410 nm, 3 W × 4)	Air / O <sub>2</sub> <sup>•-</sup>	CH <sub>3</sub> OH	0.83	85	88	261.8	7.9
15	4-NA-Cu <sub>2</sub> O RDs <sup>17</sup>	40 W blue LED	O <sub>2</sub> / O <sub>2</sub> <sup>•-</sup>	CH <sub>3</sub> OH/ H <sub>2</sub> O = 1/2	12	/	96	/	2.8
16	nanoAmbSO <sub>3</sub> @ H <sub>2</sub> TMPyP(HCOOH) <sub>2</sub> <sup>18</sup>	20W white LED	Air / <sup>1</sup> O <sub>2</sub>	H <sub>2</sub> O	5	93	100	558	/
17	Zr <sub>6</sub> -Irphen <sup>19</sup>	100 W blue LED (λ = 460 nm)	O <sub>2</sub> / O <sub>2</sub> <sup>•-</sup>	H <sub>2</sub> O	6	98	100	4.1	/

18	AQ-COF <sup>7</sup>	300 W Xe lamp ( $\lambda = 400\text{--}780\text{ nm}$ )	$\text{O}_2 / \text{O}_2^{\bullet-}; {}^1\text{O}_2$	$\text{H}_2\text{O}$	3	89	>99	/	3.0
19	$\text{Bi}_4\text{O}_5\text{Br}_2$ <sup>20</sup>	30 W blue LED (Kessil PR160-456 nm)	$\text{O}_2 / \text{O}_2^{\bullet-}$	$\text{H}_2\text{O}$	6	99	98	/	1.6
20	FL-D <sub>8</sub> NS <sup>this work</sup>	white LED (20 mW•cm <sup>-2</sup> )	Air / $\text{O}_2^{\bullet-}; {}^1\text{O}_2$	$\text{H}_2\text{O}$	0.67	99	99	686.6	/

<sup>a</sup>TOF = mmol product/(mmol catalyst × reaction time). <sup>b</sup>TOF = mmol product/(g catalyst × reaction time).

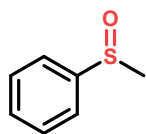
### 2.11.3 Controlled and quenching experiments

**Table S7** Controlled and quenching experiments<sup>a</sup>

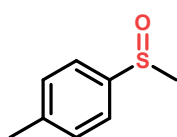
Entry	FL-D <sub>8</sub> NS	Light	O <sub>2</sub>	Scavengers <sup>b</sup>	Inhibited species	Yield/% <sup>c</sup>
1	–	+	+	/	/	n.d.
2	+	–	+	/	/	n.d.
3 <sup>d</sup>	+	+	–	/	/	3
4	+	+	+	1,4-benzoquinone	$\text{O}_2^{\bullet-}$	2
5	+	+	+	$\text{NaN}_3$	${}^1\text{O}_2$	44
6	+	+	+	isopropanol	$\bullet\text{OH}$	99
7	+	+	+	catalase	$\text{H}_2\text{O}_2$	99
8	+	+	+	1,4-dimethoxybenzene	sulfur radical cation	46

<sup>a</sup>Reaction conditions: 3-(methylthio)propionic acid (0.1 mmol), FL-D<sub>8</sub>NS (0.2 mol %), O<sub>2</sub>-saturated H<sub>2</sub>O (5.0 mL), white light (20mW•cm<sup>-2</sup>), 400 r/min, room temperature. <sup>b</sup>The amount of Scavenger was 0.1 mmol, except for catalase (50 mg, 2000-5000 unit/mg). <sup>c</sup>Determined by <sup>1</sup>H NMR, n.d. = not detected. <sup>d</sup>Using argon to bubble for 20 min with a flow rate of 20 mL/min<sup>-1</sup>.

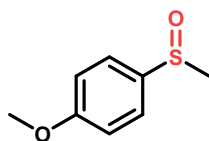
### 3 NMR data



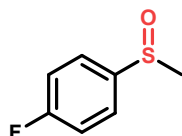
(Methylsulfinyl)benzene (**1b**):  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.68 – 7.63 (m, 2H), 7.57 – 7.49 (m, 3H), 2.73 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  145.7, 131.1, 129.4, 123.5, 44.0.



1-methyl-4-(methylsulfinyl)benzene (**2b**):  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.54 (dd,  $J = 7.7, 2.1$  Hz, 2H), 7.33 (d,  $J = 7.8$  Hz, 2H), 2.71 (s, 3H), 2.42 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  142.5, 141.5, 130.0, 123.5, 44.0, 21.4.

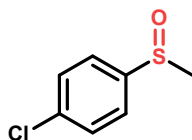


1-methoxy-4-(methylsulfinyl)benzene (**3b**):  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.63 – 7.57 (m, 2H), 7.07 – 7.01 (m, 2H), 3.86 (s, 3H), 2.71 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  162.1, 136.7, 125.5, 114.9, 55.6, 44.0.

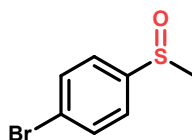


1-fluoro-4-(methylsulfinyl)benzene (**4b**):  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.71 – 7.62 (m, 2H), 7.24 (td,  $J = 8.5, 1.6$  Hz, 2H), 2.73 (d,  $J = 1.5$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  164.4 (d,  $J = 251.3$  Hz), 141.2, 125.9, 125.8, 116.9, 116.7, 77.1, 44.2 (d,  $J = 1.4$  Hz).

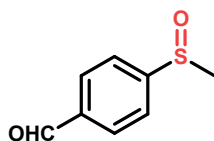




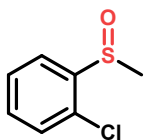
1-chloro-4-(methylsulfinyl)benzene (**5b**):  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.62 – 7.56 (m, 2H), 7.56 – 7.49 (m, 2H), 2.72 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  144.3, 137.3, 129.7, 125.0, 44.1.



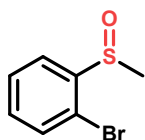
1-bromo-4-(methylsulfinyl)benzene (**6b**):  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.69 – 7.65 (m, 2H), 7.54 – 7.50 (m, 2H), 2.72 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  145.0, 132.7, 125.5, 125.2, 44.1.



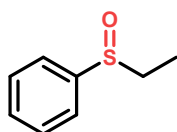
4-(methylsulfinyl)benzaldehyde (**7b**):  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  10.09 (s, 1H), 8.08 – 8.02 (m, 2H), 7.87 – 7.79 (m, 2H), 2.78 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  191.1, 152.6, 138.2, 130.4, 124.2, 43.8.



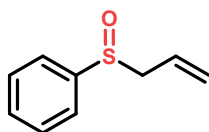
1-chloro-2-(methylsulfinyl)benzene (**8b**):  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.96 (dd,  $J = 7.8, 1.6$  Hz, 1H), 7.54 (td,  $J = 7.5, 1.3$  Hz, 1H), 7.45 (td,  $J = 7.6, 1.7$  Hz, 1H), 7.39 (dd,  $J = 7.9, 1.4$  Hz, 1H), 2.82 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  143.8, 132.1, 129.9, 129.9, 128.2, 125.4, 41.8.



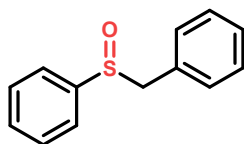
1-bromo-2-(methylsulfinyl)benzene (**9b**):  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.95 (dd,  $J = 7.8, 1.7$  Hz, 1H), 7.61 – 7.54 (m, 2H), 7.37 (td,  $J = 7.8, 1.7$  Hz, 1H), 2.82 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  145.5, 133.0, 132.3, 128.8, 125.8, 118.5, 42.0.



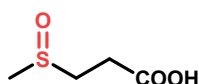
(Ethylsulfinyl)benzene (**10b**):  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.64 – 7.59 (m, 2H), 7.56 – 7.47 (m, 3H), 2.84 (ddq,  $J = 55.4, 13.2, 7.4$  Hz, 2H), 1.20 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  143.4, 130.9, 129.2, 124.2, 50.3, 6.0.



(Allylsulfinyl)benzene (**11b**):  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.61 (dq,  $J = 8.6, 2.8, 2.3$  Hz, 2H), 7.55 – 7.48 (m, 3H), 5.65 (ddt,  $J = 17.5, 10.1, 7.5$  Hz, 1H), 5.37 – 5.16 (m, 2H), 3.62 – 3.47 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  143.0, 131.2, 129.1, 125.3, 124.4, 123.9, 61.0.



(Benzylsulfinyl)benzene (**12b**):  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.49 – 7.34 (m, 5H), 7.31 – 7.20 (m, 3H), 7.01 – 6.94 (m, 2H), 4.13 – 3.94 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  142.8, 131.2, 130.4, 129.1, 128.8, 128.4, 128.2, 124.4, 63.6.



3-(methylsulfinyl)propanoic acid (**13b**):  $^1\text{H}$  NMR (400 MHz, 90% $\text{H}_2\text{O}$ +10% $\text{D}_2\text{O}$ )  $\delta$  3.24 (dt,  $J = 13.5, 7.6$  Hz, 1H), 3.09 (dt,  $J = 13.5, 6.7$  Hz, 1H), 2.87 (t,  $J = 7.2$  Hz, 2H), 2.75 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz, 90% $\text{H}_2\text{O}$ +10% $\text{D}_2\text{O}$ )  $\delta$  175.2, 47.5, 36.7, 27.0.

## 4 References

1. G. Hong, Y. Wu, J. An, et al., *Sustain. Energ. Fuels*, 2023, **7**, 3447-3453.
2. a) B. Garrido, S. González, J. Hermosilla, et al., *J. Soil Sci. Plant Nutr.*, 2019, **19**, 620-630; b) I. Kritskiy, T. Volkova, T. Sapozhnikova, et al., *Mater. Sci. Eng. C*, 2020, **111**, 110774.
3. D. Zheng, E. Chen, C. Ye, et al., *J. Mater. Chem. A*, 2019, **7**, 22084-22091.
4. H. Wei, Z. Guo, X. Liang, et al., *ACS Appl. Mater. Interfaces*, 2019, **11**, 3016-3023.
5. Y. Meng, Y. Luo, J.-L. Shi, et al., *Angew. Chem.-Int. Edit.*, 2020, **59**, 3624-3629.
6. L. Liu, B. Zhang, X. Tan, et al., *Chem. Commun.*, 2020, **56**, 4567-4570.
7. Q. Li, X. Lan, G. An, et al., *ACS Catal.*, 2020, **10**, 6664-6675.
8. J. Li, Y. Chen, X. Yang, et al., *J. Catal.*, 2020, **381**, 579-589.
9. Y. Qian, D. Li, Y. Han, et al., *J. Am. Chem. Soc.*, 2020, **142**, 20763-20771.
10. X. Ma, H. Hao, W. Sheng, et al., *J. Mater. Chem. A*, 2021, **9**, 2214-2222.
11. X.-N. Zou, D. Zhang, T.-X. Luan, et al., *ACS Appl. Mater. Interfaces*, 2021, **13**, 20137-20144.
12. S.-D. Wang, C.-L. Lai, Y.-X. Zhang, et al., *J. Mater. Chem. A*, 2022, **10**, 20975-20983.
13. J.-L. Shi, K. Feng, H. Hao, et al., *Sol. RRL*, 2022, **6**, 2100608.
14. F. Zhang, H. Hao, X. Dong, et al., *Appl. Catal. B-Environ.*, 2022, **305**, 121027.
15. E. Oheix, E. Gravel and E. Doris, *Catal. Sci. Technol.*, 2022, **12**, 1751-1755.
16. H. Li, X. Li, J. Zhou, et al., *Chin. Chem. Lett.*, 2022, **33**, 3733-3738.
17. M.-H. Hsieh, Z.-H. Su, E.-T. Wu, et al., *ACS Appl. Mater. Interfaces*, 2023, **15**, 11662-11669.
18. A. Heydari-turkmani and S. Zakavi, *J. Catal.*, 2018, **364**, 394-405.
19. L.-Q. Wei and B.-H. Ye, *ACS Appl. Mater. Interfaces*, 2019, **11**, 41448-41457.
20. W. Zhao, C. Yang, J. Huang, et al., *Green Chem.*, 2020, **22**, 4884-4889.