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From biomass to C4 chemicals: selective transformation of bio-based furans to succinic anhydride in the presence of oxygen

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Supplementary Information

1. Experimental section

1.1 Reagents and apparatus

All reagents and chemicals used were of analytical grade unless otherwise specified. The furfuryl alcohol (FAL), succinic anhydride (SAN), maleic anhydride (MAN), 5-hydroxy-2(5H)-furanone (5-HFO), tetraphenyl porphyrin zinc (ZnTPP), tetra (p-chlorophenyl) porphyrin manganese (MnTClPP), tetraphenyl porphyrin cobalt (CoTPP), tetraphenyl porphyrin copper (CuTPP), tetraphenyl porphyrin nickel (NiTPP), tetra (p-chlorophenyl) porphyrin iron (FeTClPP), zinc phthalocyanine (PcZn), copper phthalocyanine (PcCu), manganese phthalocyanine (PcMn), iron phtalocyanine (PcFe), cobalt phthalocyanine (PcCo), nickel phthalocyanine (PcNi), gamma-butyrolactone, gammavalerolactone, dimethyl sulfoxide (DMSO), diethyl succinate, tetramethylene sulfone, ethyl formate, β-carotene, p-benzoquinone, t- butanol, 2, 2, 6, 6 -tetramethyl piperidine oxide (TEMPO), acetonitrile, toluene, acetone, ethyl acetate, ethanol and deionized water are all purchased from the Shanghai Alading Co., Ltd., and these are of analytical grade, which are used without any further purification treatment.

The equipment for valuation of catalytic reaction was a 120 mL stainless -steel autoclave with a glass window and magnetic stirring. The CEL-HXF300 Xe lamp was employed as the light supply. The quantitative analysis of the products was carried out on the Agilent 8860 gas chromatograph (GC) equipped with HP-5 column and flame ion detector (FID). The conversion of the substrate and selectivity of products were calculated with the internal standard method. The Agilent 6890/5973 gas chromatography-mass spectrometry (GC-MS) and nuclear mangetic respondence spectroscopy(NMR, 500 MHz) was used to detect the structure of product.

1.2 The general procedure for the photocatalytic transformation of furans

The photocatalytic transformation of furans was performed in the autoclave with a glass window and mangetic stirring. The typical step for the conversion of furfuryl alcohol is as follows: 0.1 g of furfuryl alcohol, 0.001 g of metalloporphyrin-based catalyst and 10 mL solvent are added to the steel high-pressure reactor. After the autoclave being sealed, pure oxygen is charged to replace the inner air of the reactor. Then, the oxygen pressure is kept at about 0.3 MPa after the gas inside being exchanged for three times; in the following, the autoclave is placed under the irradiation of Xe lamp light supply. When the reaction is completed, the solution is transferred to the volumetric flask and the obtained products are examined by the HPLC, the GC and GC-MS instruments, respectively

1.3 The detailed quantitative analysis method

The obtained reaction mixture is diluted by the acetonitrile solvent. The conversion of FAL is quantitatively analyzed using HPLC equipped with Eclipse XDB-C18 liquid chromatography column and an ultraviolet detector. The mobile phase was the mixed solution of acetonitrile : 0.1wt.% acetic acid (5 : 95, v/v), and flow rate was 0.4 mL/min. The column temperature was set at 20 °C and the injection volume was 20 uL. The yield of SAN is quantitatively analyzed by gas chromatogram with the flame ion detector (FID) and HP-5(30m×0.32mm×0.25µm) chromatography column.

The reactant conversion (α), the yield (Y), and the selectivity of product (S) are calculated by the following formula, respectively.

 $\frac{\text{The amount of added reactant - the amount of left reactant after reaction}}{\text{The amount of added reacant}} \times 100\%$

 $Y = \frac{The \ mol \ amount \ of \ obtained \ product}{The \ total \ mol \ amount \ of \ reactant} \times 100\%$

 $\frac{The \ product \ yield}{S=The \ conversion \ of \ reactant} \times 100\%$

1.4 The detailed EPR experiment for detecting the active oxygen species

In this study, a Bruker EMXplus-6/1 electron EPR was used to detect the active oxygen species including the superoxide anion and singlet oxygen in the photocatalytic conversion of FAL with ZnTPP as photosensitizer in ethyl acetate solvent. The generated superoxide anion was characterized by adding the trapping agent 5, 5-dimethyl-1-pyrrolin-n-oxide (DMPO), and the formed singlet oxygen was investigated by adding the trapping agent 2,2,6, 6-tetramethylpiperidine (TEMP) during the experiment. In a typical EPR detection process, the substrate FAL, ZnTPP, the trapping agent and ethyl acetate solvent were respectively added to the autoclave; then, the obtained mixture was irradiated under 400mW Xe lamp. The concentration of FAL is 1×10^{-2} mol/L, the concentration of ZnTPP is about 1.5×10^{-4} mol/L, and the concentration of trapping agent DMPO and TEMP is about 2×10^{-2} mol/L. The two groups of experiments were as follows: 1) DMPO/ZnTPP/ furfuryl alcohol/ethyl acetate. The detection of EPR technique was performed before and after the visible light irradiation, respectively.

2. The effects of reaction medium and different light sources

Entry	Solvent	Conv.(%) ^b	Product distribution (%) ^b				
Lifti y			MAN	5-HFO	SAN	Others	
1	Ethyl acetate	>99	11.7	5.9	79.4	3.0	
2	γ-Valerolactone	>99	9.5	26.1	32.3	32.1	
3	γ-Butyrolactone	>99	6.8	16.4	35.8	41.0	
4	DMSO	>99	1.0	5.0	2.2	91.8	
5	Tetramethylene sulfone	>99	6.9	-	-	93.1	
6	Diethyl succinate	>99	10.3	-	-	89.7	

Table S1. The oxidation of furfuryl alcohol with different solvents ^a

7	Methyl acetate	>99	10.5	4.2	62.8	22.5
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^{*a*} Reaction condition:0.1 g of FAL, 0.001 g of Zinc tetraphenylporphyrin, in 10ml solvent, with 0.3MPa of O_2 pressure, irradiate under a 400 mW xenon lamp for 6h.

^b The conversion were attained by HPLC and selectivity of product were attained by GC using the internal standard method.



Figure S1. The conversion of FAL under different light sources (Reaction conditions: 0.1 g of FAL, 0.001 g of ZnTPP, in 10 mL ethyl acetate solvent, with 0.3MPa pressure of O_2 , under the different light irradiations; The reaction time of Xe lamp is 6 h and others are 40h)

Entry	Light	Time (h)	Conv. (%) ^b	Product	distribution (%) ^b		
	C .			MAN	SAN	others	
1	LED blue (455 nm)	20	70.6	0.7	94.9	4.4	
2	LED yellow (590 nm)	20	8.9	10.5	14.8	74.7	

Table S2. The selective transformation of 5-HFO with the different light sources ^a

3	LED yellow (590 nm)	40	11.5	6.2	16.4	77.4
4	LED red (620 nm)	20	3.1	10.7	9.8	79.5

^{*a*} Reaction conditions: 0.02 g of 5-HFO, in 10 mL ethyl acetate, under 0.3MPa of O_2 pressure, with the different light irradiations.

^b The results were attained by the GC using the internal standard method.

3. Proposed reaction mechanism for the generation of succinic anhydride

The reaction mechanism for the transformation of FAL to SAN under the visible light is proposed. As shown in the Scheme S1, two possible reaction routes are given according to the experiment results and catalytic principle. 1) The O₂ is firstly activated to the ${}^{1}O_{2}$ in the presence of ZnTPP photocatalyst; next, the cycloaddition reaction of FAL with ${}^{1}O_{2}$ occurs and the endoperoxide as intermediate I is generated. Further, the intermediate I is transformed to the 5-HFO through the cleavage of C-C bond and the ring-opening cracking of -O-O- bond under the visible light. Finally, the 5-HFO as intermediate II can be isomerized to produce the SAN with assistance of the high intensity light. 2) The FAL is firstly oxidized to generate the furoic acid (FAC) under the visible light. Then, the ${}^{1}O_{2}$ reacts with FAC through the cycloaddition reaction where the coresponding endoperoxide (intermediate III) is produced. Next, the intermediated III is further converted to the 5-HFO based on the decarbonylation and the ring-opening cleavage of -O-O- bond. Finally, the SAN is achieved through the isomerization of 5-HFO under the high intensity light. On the other hand, it needs to be mentioned that another competitive route is the conversion of 5-HFO to generate the byproduct MAN in the presence of O₂.



Scheme S1. Proposed mechanism for the transformation of FAL to product SAN under the visible light

4. GC, GC-MS and ¹HNMR spectra for the transformation of furfuryl alcohol



Figure S2. GC spectrum for photocatalytic oxygenation of furfuryl alcohol (Reaction conditions: 0.1 g of reactant, in 10 mL ethyl acetate, under 0.3 Mpa of O_2 , at the light intensity of 400 mW of Xe lamp, for 0.5 h)



Figure S3. GC spectrum for photocatalytic oxygenation of furfuryl alcohol (Reaction conditions: 0.1 g of reactant, 0.001 g of ZnTPP, in 10 mL ethyl acetate, under 0.3 Mpa of O₂, at the light intensity of 400 mW of Xe lamp, for 0.5 h)



Figure S4. GC spectrum for photocatalytic oxygenation of furfuryl alcohol (Reaction conditions: 0.1 g of reactant, 0.001 g of ZnTPP, in 10 mL ethyl acetate, under 0.3 Mpa of O_2 , at the light intensity of 400 mW of Xe lamp, for 6 h)



Figure S5. GC-MS spectra for the SAN obtained from the photocatalytic oxygenation of furfuryl alcohol



Figure S6. GC-MS spectra for the 5-HFO generated from the photocatalytic oxygenation of furfuryl alcohol



Figure S7. GC-MS spectra for the isotope labeling experiment of the furfuryl alcohol transformation (Reaction conditions: 0.1 g of reactant, 0.001 g of ZnTPP, in 10 mL ethyl acetate, under 0.3 Mpa of ¹⁸O₂, at the light intensity of 400 mW of Xe lamp)



Figure S8. The ¹H NMR spectra of product in the photocatalytic oxygenation of furfuryl alcohol with O₂