## Supporting Information

# Mild and efficient photo-catalytic-coupled alcohol oxidation dehydrogenation and CO<sub>2</sub> reduction driven by visible light

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<sup>b</sup>College of Chemistry and Chemical Engineering, Jishou University, Jishou 416000, Hunan, China 1. Transmission Electron Microscope (TEM) images of 4%Al-DT and TBADT



Figure S1 Transmission Electron Microscope (TEM) images of (a) 4% Al-DT and (b) TBADT.

### 2. Schematic diagram of self-assembled photo-reactor used in this work



Figure S2 The self-assembled photo-reactor used this work.

#### 3. Comparison of two quantitative analyses of HCOOH

Entries 1-2 in Table S1 show that in the two parallel experiments of 4% Al-DT-photocatalyticcoupled reaction of CyHA with CO<sub>2</sub>, the detected CH<sub>3</sub>OH amounts by GC were 89.6 and 85.4 µmol, the measured HCOOH by an acid-base titration were 113.5 and 120 µmol. The data for the total amount of these products between two parallel experiments differed by less than 2%. HCOOH was derived to HCOOCH<sub>3</sub> with CH<sub>3</sub>I and the amount of HCOOCH measured by GC analysis was an almost consistent with the measured HCOOH amount by an acid-base titration, suggesting that the acid-base titration could be used as a simple quantitative method of HCOOH. Entries 3-4 show that the above CH<sub>3</sub>OH and HCOOH could not be generated when the use of N<sub>2</sub> instead of CO<sub>2</sub>, supporting these two products originate from the reduction of CO<sub>2</sub>.

Enters	C	Reductive products (µmol)			
Entry	Gas	CH <sub>3</sub> OH <sup>b</sup>	HCOOH <sup>c</sup>	HCOOCH <sub>3</sub> <sup>d</sup>	
1	$CO_2$	89.6	113.5	113.3	
2	$CO_2$	85.4	120.0	118.9	
3	$N_2$	0.0	0.0	0.0	
4	$N_2$	0.0	0.0	0.0	

Table S1 Data for reduction products in photo-catalytic reaction of CyHA in CO<sub>2</sub> or N<sub>2</sub><sup>a</sup>.

<sup>a</sup> Reaction condition: CyOH (1.0 mmol), 4%Al-DT (1.0 %, 0.01 mmol), CH<sub>3</sub>CN (5 mL), room temperature, 35W of tungsten–bromine lamp, 12 h; <sup>b</sup> CH<sub>3</sub>OH was quantized by GC analysis; <sup>c</sup>HCOOH was quantized by an acid-base titration method after deducting the blank value obtained from the photoreaction under N<sub>2</sub> atmosphere. <sup>d</sup> Reaction condition of CH<sub>3</sub>I and HCOOH: the reaction solution after 12 hours of irradiation is distilled under reduced pressure to remove acetonitrile, then dry DMF (4 mL), Na<sub>2</sub>CO<sub>3</sub> (1.0 mmol), CH<sub>3</sub>I (1.0 mmol) were added, and magnetic stirring overnight at room temperature.

#### 4. Qualitative and quantitative analyses of CO

Fig. S3 illuminates that the chromogenic dots of palladium chloride test paper, as supported in Table S2, are closely related to the photo-catalytic-coupled conversion efficiency of alcohol with CO<sub>2</sub>, which can be used to qualitatively detect the generated CO in the current photo-catalytic –coupled system.



**Figure S3** Qualitative analysis of CO for four representative photocatalytic-coupled reactions by palladium chloride test paper. Reaction condition: Alcohol (1.0 mmol), TBADT or 4%Al-DT (1.0 mol%), MeCN (5 mL), 1atm CO<sub>2</sub>, 35 W of tungsten–bromine lamp, room temperature, 12 h. The chromogenic dots in red circles originated from the reduction of the test paper by CO. (a) TBADT and BA; (b) 4%Al-DT and BA; (c) 4%Al-DT and CyHA, (d) 4%Al-DT and CyHMA.

The quantitative analysis of CO in the storage balloon (0.5 L) of supplying  $CO_2$  for the photo-catalytic-coupled reaction was carried out on the GC equipped with a in-situ catalytic device for CO hydrogenation to methane and a FID detector. Table S2 lists the CO data detected from three representative photo-catalytic-coupled reactions of BA, CyHA and CyHMA with  $CO_2$  under catalysis of 4% A1-DT.

Entry	Alcohol	Amount of CO (µmol)
1	BA	0.13
2	СуНА	0.14
3	СуНМА	13.46

Table S2 Quantitative analysis of CO for three representative photo-catalytic-coupled reactions.<sup>a</sup>

<sup>a</sup>Reaction condition: Alcohol (1.0 mmol), 4%Al-DT (1.0 mol%), MeCN (5 mL), 1atm CO<sub>2</sub>, 35 W of tungstenbromine lamp, room temperature, 12 h.

## 5. Effect of Al<sup>3+</sup> doping levels on the synthesis quality of DT



Figure S4 UV-vis spectra of TBADT and 1%, 2%, 3%, 4%, 5%, 7%, 9% Al-DT samples with concentration  $(4.6 \times 10^{-5} \text{ M})$ .

Entry	Sample	R	Entry	Sample	R
1	TBADT	0.790	5	4%Al-DT	0.789
2	1%Al-DT	0.852	6	5%Al-DT	0.779
3	2%Al-DT	0.846	7	7%Al-DT	0.752
4	3%Al-DT	0.834	8	9%Al-DT	0.713

Table S3 The ratio ( $R = I_{320 \text{ nm}}/I_{265 \text{ nm}}$ ) for the integral areas of both bands at 320 and 265 nm in Fig. S4.





Figure S5 The  $\lambda_{abs}$  of TBADT and 4% Al-DT.

Table S4 Data for the band gap energy ( $E_{\rm g}/eV)$  of pure TBADT and Al-DTs.

Entry	Catalyst	Eg (eV) <sup>a</sup>	Entry	Catalyst	$Eg(eV)^{a}$
1	TBADT	3.00	5	4%Al-DT	3.02
2	1%Al-DT	3.00	6	5%Al-DT	3.03
3	2%Al-DT	3.00	7	7%Al-DT	3.05
4	3%Al-DT	3.02	8	9%Al-DT	3.05

<sup>a</sup>Estimated Eg from the Tauc plots and Tauc's equations.

#### 7. X-ray photoelectron spectroscopy (XPS)



**Figure S6** XPS spectra: (a) Full XPS spectrum of TBADT; (b-c): High resolution XPS spectra of O 1s and W 4f of TBADT; (d) high resolution XPS spectra of Cl 2p of 4%Al-DT.

### 8. Effect of Al<sup>3+</sup> doping levels on transient photocurrent (TPC) of DT



Figure S7 Transient photocurrent (TPC) curves of TBADT and Al-DTs work electrodes prepared in MeCN.

#### 9. Cyclic voltammograms (CVs) of the electrolyte and catalysts

Fig. S8b shows that a pair of redox waves of  $W^{6+}/W^{5+}$  in Al-DTs still maintain a good reversibility and there are no obvious shifts with hoisting the doping amount of  $AI^{3+}$  species. Table S5 shows that there is no significant difference in redox potential ( $E_{1/2}/V$ ) between Al-DTs and TBADT. The differences ( $E_D/V$ ) between the oxidative and reductive potentials for the  $W^{6+}/W^{5+}$  redox waves can reflect the redox cycling capacity and the  $E_D$  potential calculated from Fig. S8b has a negligible difference between Al-DTs and TBADT (Table S5). These findings suggest that the redox performance of DT anion is basically influenced by the doping levels of  $AI^{3+}$  species.



**Figure S8** Cyclic voltammograms (CVs) of tetrabutylammonium hexafluorophosphate (TBAH) (a) and Al-DTs (b,  $2.4 \times 10^{-3}$  M) in MeCN (10 mL) containing 0.1 M TBAH electrolyte under anhydrous anaerobic conditions at a scan rate of 100 mV/s.

Entry Catalyst		F	Б	Oxidative capacity	Redox cycling capacity
Entry	Catalyst	E <sub>red</sub>	E <sub>oxi</sub>	$E_{1/2} (V)^{a}$	$E_D(V)^b$
1	TBADT	-1.785	-1.708	-1.747	0.077
2	1%Al-DT	-1.802	-1.720	-1.761	0.082
3	2%Al-DT	-1.787	-1.716	-1.752	0.071
4	3%Al-DT	-1.785	-1.710	-1.748	0.075
5	4%Al-DT	-1.777	-1.702	-1.740	0.075
6	5% Al-DT	-1.764	-1.693	-1.729	0.071
7	7%Al-DT	-1.774	-1.701	-1.738	0.073
8	9%Al-DT	-1.773	-1.707	-1.740	0.066

Table S5 The oxidative and reductive potentials of TBADT and Al-DTs summarized from Fig. S8b.

<sup>a</sup>  $E_{1/2} = (E_{oxi} + E_{red})/2$ ; <sup>b</sup>  $E_D = E_{oxi} - E_{red}$ .

#### 10. Optimization of reaction conditions

The effect of catalyst concentration and illumination time on the photocatalytic ODH reaction of BA in anhydrous MeCN under CO<sub>2</sub> atmosphere was checked using 4%Al-DT as the catalyst and the obtained data without deducting the photo-auto-conversion data of BA under N<sub>2</sub> atmosphere are shown in Figs.S9 and S10. Fig. S9 shows that the conversion of BA rises slowly with the increase of the catalyst concentration, reaching a maximum 51.3% at 1.0 mol % catalyst concentration. After that, further hoisting the concentration of catalyst results in a slight reduction of BA conversion likely owing to the decrease of its solubility. The use of 1.0 mol % catalyst concentration can achieve the highest BA conversion and ODH product PhCHO yield. Fig.S10 shows that BA conversion and PhCOOH selectivity continuously increase with extending the illumination time from 2 to 18 h, along with a decrease of PhCHO selectivity. After that, further extending the time to 24 h only slightly increases the conversion. The relatively high BA conversion and PhCHO selectivity can be obtained after illuminating 12 h.



**Figure S9** Influence of catalyst concentration (Reaction condition: 4%Al-DT (0.6 -1.8 mol%), benzyl alcohol (1.0 mmol), MeCN (5 mL), CO<sub>2</sub> (1 atm), 35W of tungsten–bromine lamp, room temperature, 12 h)



**Figure S10** Influence of illumination time (Reaction condition: 4%Al-DT (1.0 mol%), benzyl alcohol (1.0 mmol), MeCN (5 mL), CO<sub>2</sub> (1 atm), , 35W of tungsten–bromine lamp, room temperature)

# 11. ODH reaction of methanol and it's competing ODH reaction with BA or $\alpha$ -PEA in photo-catalytic-coupled system

Table S6 shows that under the photo-catalysis of 4%Al-DT, there is about 18% methanol to be consumed under CO<sub>2</sub> atmosphere, 75.8 µmol HCOOH as the same product of methanol oxidation and CO<sub>2</sub> reduction was detected from GC analysis (Entry 1), but the ODH product HCHO was not detected out from the reaction solution likely owing to it strong volatility. The competing ODH reactions in Entries 2 and 3 indicated that in the case of adding 0.4 mmol methanol, the photo-coupled reactions of BA and  $\alpha$ -PEA with CO<sub>2</sub> can still proceeds efficiently and their coupled conversion efficiencies slightly decrease compared to without adding methanol (Entries 4-5). 64 and 35µmol methanol consumptions were found in Entries 2 and 3, respectively. These findings support that in the current photo-catalytic-coupled conversion system, the produced methanol from CO<sub>2</sub> reduction could be re-oxidized by CO<sub>2</sub> but its ODH reactivity is much inferior to that of BA and  $\alpha$ -PEA. On the other hand,  $\alpha$ -PEA can reduce the re-oxidation of the produced CH<sub>3</sub>OH more efficiently than BA, which should be due to its high ODH reactivity, as supported by the significantly reduced methanol consumption in its competing ODH reaction with methanol.

Enters	0.1.4.4	Conv.% -	Content (µmol) of products			
Entry	Substrate		ODH products	CH <sub>3</sub> OH	НСООН	
1	CH <sub>3</sub> OH	18.0	No <sup>b</sup>	180 <sup>f</sup>	75.8	
2	BA+ CH <sub>3</sub> OH <sup>c</sup>	34.6 <sup>e</sup>	174(33.6) <sup>d</sup>	64 <sup>f</sup>	105	
3	$\alpha$ -PEA+ CH <sub>3</sub> OH <sup>c</sup>	45.5 <sup>e</sup>	273	35 <sup>f</sup>	80	
4	$BA^{g}$	35.7	$164(5.1)^{d}$	12	109	
5	$\alpha$ -PEA <sup>g</sup>	47.9	287	46	90	

**Table S6** Data for photo-catalytic reaction of methanol, BA or  $\alpha$ -PEA and mixed alcohols in CO<sub>2</sub><sup>a</sup>.

<sup>a</sup> Reaction condition: Alcohol (1.0 mmol), 4%Al-DT (1.0 %, 0.01 mmol), CH<sub>3</sub>CN (5 mL), room temperature, 35W of tungsten–bromine lamp, 12 h; <sup>b</sup> HCHO as the ODH product of CH<sub>3</sub>OH was not detected out from GC analysis; <sup>c</sup>Using 0.4 mmol CH<sub>3</sub>OH and 0.6 mmol BA/ $\alpha$ -PEA as the mixed substrates; <sup>d</sup> The datum in parentheses indicated the amount of PhCOOH; <sup>e</sup>Indicating the conversion of BA/ $\alpha$ -PEA; <sup>f</sup>Indicating the consumption amount of CH<sub>3</sub>OH; <sup>g</sup>Using 0.6 mmol BA/ $\alpha$ -PEA as the substrate.

#### 12. Photo-catalytic formic acid decomposition

Table S7 shows that the decomposition rate of formic acid photo-catalyzed by 4%Al-DT under  $CO_2$  or  $N_2$  atmosphere only has 0.9% after illuminating 12 h, and there is no CO to be detected out qualitatively from this photo-catalytic decomposition reaction, indicating that the decomposition of formic acid is negligible in the current photo-catalytic system.

Entry	Gas	Decomposition rate (%)	Qualitative detection of CO
3	$CO_2$	0.9	no
4	$N_2$	0.9	no

Table S7 Decompositio of benzoic acid photo-catalyzed by 4% Al-DT <sup>a</sup>.

<sup>a</sup>Reaction conditions: formic acid (1.0 mmol), Catalyst (1.0 mol%),  $CH_3CN$  (5 mL), 1atm  $CO_2$  or  $N_2$ , 35 W of tungsten– bromine lamp, room temperature, illumination 12h

# 13. Color change of three typical photo-catalytic-coupled reaction solutions with illumination time



**Figure S11** Influence of illumination time on the color change of photoreaction solution under CO<sub>2</sub>. Reaction condition: Alcohol (1.0 mmol), 4%Al-DT (1.0 mol%), MeCN (5 mL), 35 W of tungsten–bromine lamp room temperature. (a) Benzyl alcohol (BA), (b) Cyclohexanol (CyHA), (c) *p*-NO<sub>2</sub>-BA.

#### 14. Quality of recovered and regenerated catalysts

The ratio ( $R = I_{320} / I_{265}$ ) for the integral areas of both bands at 320 and 265 nm in Fig. 5b was used to assess the quality of recovered and regenerated catalysts and the obtained R values are listed in Table S8. It is seen from Table S8 that the R value gradually and slowly decreases with the recycling run times of catalyst, which can be indicative of the continuous decline of catalyst quality. When the catalyst after the third recycling run was treated with hydrochloric acid solution (pH=2) at 100 °C for 12 h, the obtained catalyst has an obviously enhanced R value, indicating its quality can be restored well by this regeneration way.

**Table S8** The ratio ( $R = I_{320} / I_{265}$ ) for the integral areas of both bands at 320 and 265 nm in Fig. 5b and the recovery rate of 4%Al-DT catalyst.

Entry	Sample	R value	Recovery rate/%
1	Fresh catalyst	0.789	
2	1 <sup>th</sup> running catalyst <sup>a</sup>	0.710	96,6
3	2 <sup>th</sup> running catalyst <sup>a</sup>	0.708	92.8
4	3 <sup>th</sup> running catalyst <sup>a</sup>	0.691	74.9
5	Regenerated catalyst <sup>b</sup>	0.760	85.5

<sup>a</sup>Recovered condition: the used catalyst was precipitated from the condensed reaction solution with excess ethyl acetate and then washed repeatedly with ethyl acetate to remove the possible organic impurities, finally dried at 60  $\degree$  for 12 h under vacuum; <sup>b</sup>Regenerated condition: Catalyst (134.2 mg) after the third recycling run was added to the pH=2 hydrochloric acid solution (10 mL), reflux at 100  $\degree$  for 12 h and then dried at 60  $\degree$  for 12 h under vacuum.

#### 15. UV-vis spectral change of catalyst



**Figure S12** UV-vis spectral change of 4%Al-DT catalyst in MeCN. Sample concentration is  $4.6 \times 10^{-5}$  M. **Curve 1**: irradiating 5 min; **Curve 2**: irradiating 15 min under CO<sub>2</sub> atmosphere and further placing 30 min after stopping the irradiation; **Curve 3**: exposing in the air for 30 minutes after stopping the irradiation; Curve 4: fresh catalyst.

#### 16. Mass spectra of benzyl formate and benzyl alcohol.



**Figure S13** Mass spectra of benzyl formate (a) and benzyl alcohol (b) obtained from the coupled reaction of benzyl alcohol with  $CO_2$  photo-catalyzed by the <sup>18</sup>O-labeled-4%Al-DT reaction (Using the same reaction conditions as Entry 4 in Table 1).