

## ***Supporting information***

### **Highly efficient and tunable visible-light-catalytic synthesis of 2, 5-diformylfuran via HBr and molecular oxygen**

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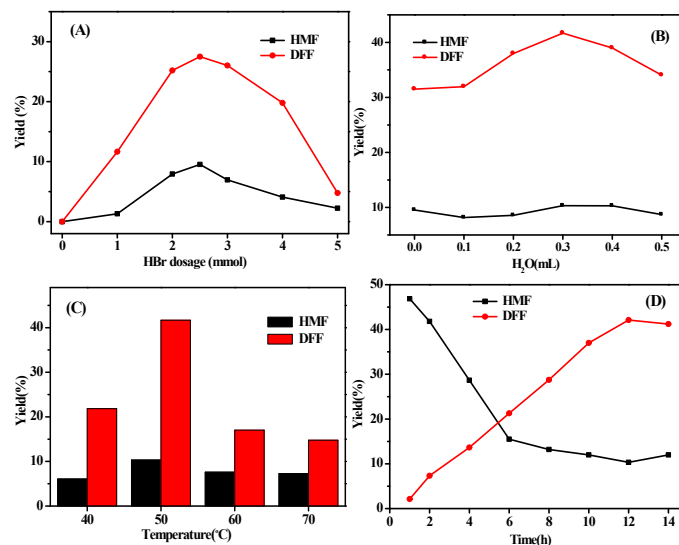
#### **1. Effect of various variables on the HBr-photocatalyzed fructose to DFF in MeCN**

The reaction parameters were optimized to enhance the HBr-photocatalyzed fructose to DFF in MeCN and the results are shown in Figure S1. Figure S1A shows that when the amount of HBr increased from 0 to 2.5 mmol, HMF and DFF yields were gradually and drastically enhanced. When HBr dosage exceeded 2.5 mmol, the yields of DFF and HMF did not increase and the black polymers produced by HMF polymerization could be observed. In order to improve the solubility of fructose, we added different amounts of water in the reaction. When the addition of water was 0.3 mL, the highest 42.1% DFF yield could be obtained, as shown in Figure S1B. In addition, we also examined the effect of temperature and time on the current photoreaction. As shown in Figures S1C and S1D, the optimal temperature and time were 50°C and 12 h, respectively accelerating polymerization of HMF would reduce DFF yield. Under optimized conditions (2.5 mmol HBr, 0.3 mL water, 50°C and 12 h), 10.3% HMF and 42.1% DFF yields could be obtained.

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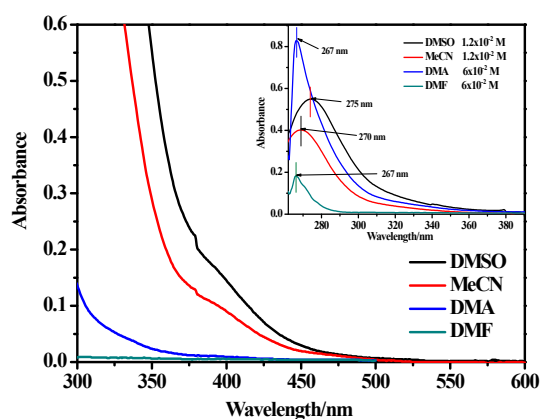
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**Figure S1.** Influence of HBr (A), H<sub>2</sub>O dosage (B), reaction temperature (C) and reaction time (D) on the HBr-photocatalyzed fructose to DFF in MeCN.

## 2. UV-Vis spectrum of HBr in different solvents

Figure S2 gives the UV-Vis spectra of HBr in different solvents. It is seen from Figure S2 that HBr had a weak visible absorption about at 400-550 nm and its visible absorption ability presented an increasing sequence of DMSO>MeCN>DMA>DMF.



**Figure S2.** UV-vis spectra (300 nm-600 nm) of HBr in same concentration ( $6 \times 10^{-2}$  M) in different solvents (Inset is the absorption of HBr at different concentrations).

## 3. Synthesis of HMF from fructose using HBr in MeCN

As shown in Table S1, HBr in MeCN shows a very high acid-catalytic activity for this dehydration at room temperature (25°C), providing 65.9% conversion and 60.7% HMF yield. With temperature from 25 to 40°C, fructose conversion continuously increased from 65.9 to 78.1% and HMF yield underwent a change that slightly increased and then decreased. 62.1% HMF yield could be obtained at the optimized temperature (30°C).

**Table S1** Synthesis of HMF from fructose using HBr in different solvents

Entry	Solvent	Temperature(°C)	Conversion of fructose (%)	Yield of HMF (%)
1	MeCN	25	65.9	60.7
2	MeCN	30	67.0	62.1
3	MeCN	40	78.1	58.9

Reaction condition: fructose, 0.1 mmol; HBr, 1.0mmol; Time, 12 h; Solvent, 5 mL.

#### 4. Effect of Br-ions on DFF synthesis from HMF

**Table S2** Synthesis of DFF from HMF in DMSO using HBr

Entry	Catalyst (mmol)	Conversion of HMF (%)	Yield of DFF (%)
1	-	37.4	0
2	NaBr (0.3)	16.0	<1
3	HBr (0.3)	92.2	86.7
4	HBr (0.6)	81.4	73.5
5	HBr (0.3) + NaBr (0.3)	64.3	56.4

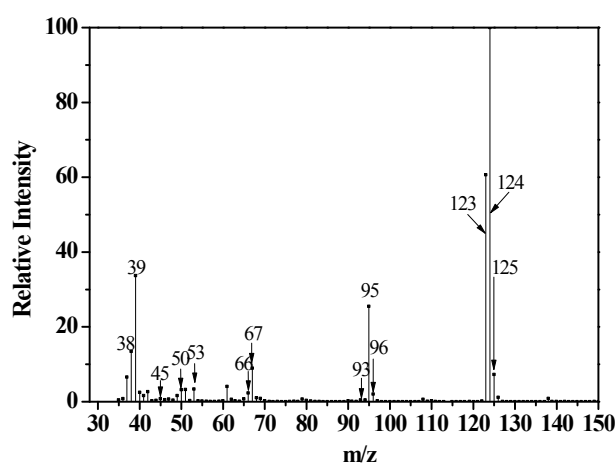
Reaction condition: HMF, 0.3 mmol; temperature, 80 °C; time, 8 h; DMSO, 5 mL; O<sub>2</sub>, 1 atm.

As shown in Table S2, HMF polymerization in DMSO easily occurred in the absence of HBr (Entry 1) but was obviously restrained in presence of 0.3 mmol NaBr (Entries 2 vs 1). Obviously, HMF conversion was reduced from 92.2 to 81.4% with the increasing amount of HBr from 0.3 to 0.6 mmol, along with decreasing of DFF yield from 86.7 to 73.5% (see Entries 3 and 4). Furthermore, the addition of 0.3 mmol NaBr in Entry 3 resulted in a more significant reduction in

the photocatalytic efficiency of HBr (Entries 5 vs 4), supporting that the introduction of excessive Br-ions plays an inhibiting role in the photo-oxidation of HMF to DFF.

### 5. Isotope tracing test of heavy oxygen water ( $\text{H}_2^{18}\text{O}$ )

The test of adding  $\text{H}_2^{18}\text{O}$  ( $^{18}\text{O}$  content, 97%) in HBr photo-catalytic system were carried out using dry HBr gas dissolved in anhydrous DMSO under  $\text{N}_2$  and the photoreaction conditions and results were the same as the standard conditions in Table 2. GC-MS analysis of the only oxidative product DFF was conducted on GC/MS-QP2010 and the obtained MS spectrum is shown in Figure S3. It can be seen from Figure S3 that there are not the  $^{18}\text{O}$ -labelled fragment peaks to be detected out in the mass spectrum of DFF except for the  $^{16}\text{O}$ -labelled fragment peaks. This indicates that under pure  $\text{N}_2$ , the introduced water likely participates in HBr-photocatalyzed HMF oxidation in the form of its derived HBrO instead of the  $\text{O}_2$  form generated by further decomposition of HBrO under visible light.



**Figure S3.** Mass spectra of DFF obtained from HBr-photocatalyzed HMF oxidation in anhydrous DMSO with dry HBr (0.3 mmol) in the presence of 0.05 mL  $\text{H}_2^{18}\text{O}$  under visible light irradiation (Condition: HMF (0.1 mmol), DMSO (5 mL),  $\text{N}_2$  (1 atm), 80°C, 8 h).