Supporting Information for

Amino and Triazole-Containing Metal–Organic Framework: Cellobiose Sensing and Its Catalytic Conversion under Mild Conditions

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Materials and Methods.

Reagents and chemicals: All reagents and solvents were of AR grade and used without further purification unless otherwise noted. 4,4',4''-nitrilotribenzoic acid was synthesized according to the literature methods.[S1] 3,5-di(pyridin-4-yl)-4H-1,2,4-triazol-4-amine (dpta) was purchased from Jinan Henghua Technology Co., Ltd. $Zn(NO_3)_2{\cdot}6H_2O$ was purchased from Shanghai Fourth Chemical Reagent Company (China). All of the sugars (Xylose (Xyl), Mannose (Man), Glucose (Glu), Ribose (Rib), Fructose (Fru), Maltose (Mal), Lactose (Lac), Sucrose (Suc), Trehalose (Tre), Melibiose (Mel), Raffinose (Raf), Cellotriose (CelT), Cellobiose(CelB)) were purchased from Beijing Innochem Science & Technology Co., Ltd. Stock solution (2×10^{-2} M) of the aqueous sugars of Xyl, Man, Glu, Rib, Fru, Mal, Lac, Suc, Tre, Mel, Raf, CelT and CelB were prepared for further experiments.

Instruments and spectroscopic measurements: The elemental analyses of C, H and N were performed on a Vario EL III elemental analyzer. $^{1}H/^{13}C$ NMR spectra were measured on a Bruker-400 spectrometer with Me_4Si as an internal standard. X-Ray powder diffraction (XRD) patterns of the Zn-TDA was recorded on a Rigaku D/max-2400 X−ray powder diffractometer (Japan) using Cu-*K*α (λ = 1.5405 Å) radiation. FT−IR spectra were recorded as KBr pellets on JASCO FT/IR−430. Fluorescence spectra of the solution were obtained using the F−4600 spectrometer (Hitachi).

Synthesis of Zn–TDA: 4,4',4''-nitrilotribenzoic acid (H_3tca) (3.8 mg, 10 mM), 3,5-di(pyridin-4-yl)-4H-1,2,4-triazol-4-amine (dpta) (4.0 mg, 17 mM), and

$Zn(NO_3)_2 \cdot 6H_2O$ (10 mg, 34 mM) were dissolved in N, N-Dimethylacetamide/water (2/1, 1 mL) in a screw-capped vial. The resulting mixture was placed in an oven at 90°C for 3 days; upon cooling, light yellow block crystals were collected by filtration. Yield: 73%. Anal calc. for $[Zn_3(tca)_2(dpta)] \cdot (DMA)_3(H_2O)$: C 54.28, H 4.21, N 10.55%; Found: C 54.19, H 4.19, N 10.52%.

Fluorescent Spectra Detection: For carbohydrate sensing, the high-concentration stock solutions of related carbohydrates (2×10^{-2} M) were directly prepared in water, and 1 mg Zn-TDA powder was introduced into a 3.0 mL HEPES buffer (pH = 7.4) for preparing the Zn-TDA emulsion. Both excitation and emission slit widths were 5 nm. Fluorescence measurements were performed in a 1 cm quartz cuvette with stirring the suspension of Zn-TDA.

Typical procedure for the catalytic reaction of cellobiose conversion: The sample was prepared by dispersing 4.8 mg cellobiose in 2 mL water, and then 5 mg Zn-TDA was added as catalyst. The catalytic reaction was conducted in a 10 mL glass reactor. The vessel was set in a heater with frequent stirring 300 rpm at 353 K for a given time. At the end of the reaction, the reactor was placed in a water bath for 10 min to stop the reaction. A small aliquot of the supernatant reaction mixture was diluted ten-fold, filtered, and determined by HPLC to calculate the concentration of 5-HMF.

The recycle experiment was carried by separating the material from the after-reaction solution, and the recycled catalyst was filtered, washed using deionized water for 5 times, and then dried in an oven under 50 ℃.

The yield of 5-HMF calculation: Certain amount of 5-HMF was prepared into a specific concentration of 5-HMF aqueous solution to obtain a series of specific concentration range standard solutions. The standard solution were performed on liquid chromatography detection to obtain the corresponding chromatographic absorption peak signal intensity. The standard curve was obtained through linear fitting of the standard solution concentration and the specific absorption peak area.

5-HMF concentration was determined using high-performance liquid chromatography (HPLC, Agilent 1200) using a column (Zorbax SB-C18) with a UV detector to analyze 5-HMF yield and the column was maintained at a column temperature of 35 ℃, using water-methanol ($V_{methanol}$: V_{water}=40: 60) as the mobile phase at a flow rate of 0.6 mL·min^{-1}. The injection volume was 20 μL.

The yield of 5-HMF was calculated according the equation below:

$$y_p = [(C_{p\text{-}t} - C_{p\text{-}0})/C_{g\text{-}0}]*100\% \quad (1)$$

Where C_g and C_p corresponds to the molar concentration of cellobiose and product (5-HMF), and the subscripts 0 and t correspond to t=0 and reaction time t, respectively.

MS determination method:

Mass spectrometry parameters: The ESI source worked in full scan modes under the following conditions: nebulizer temperature and gas flow were set at 500 ℃ and 12.0 L/min, respectively; Nebulizer gas was set at 35 psi; and electrospray capillary voltage was set at 3500 V with a range of m/z 50-1000. The scanning mode was set as positive and negative ion mode.

Figure S1 The ^{1}H NMR spectra of Zn-TDA decomposed by DCl.

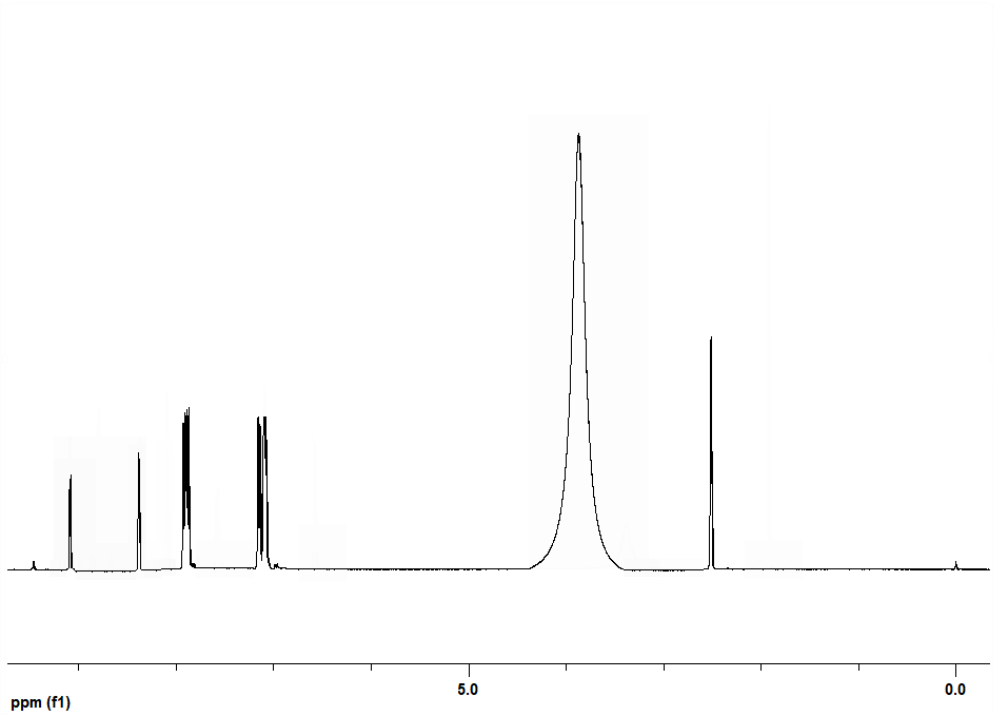


Figure S2 The ^{13}C NMR spectra of Zn-TDA decomposed by DCl.

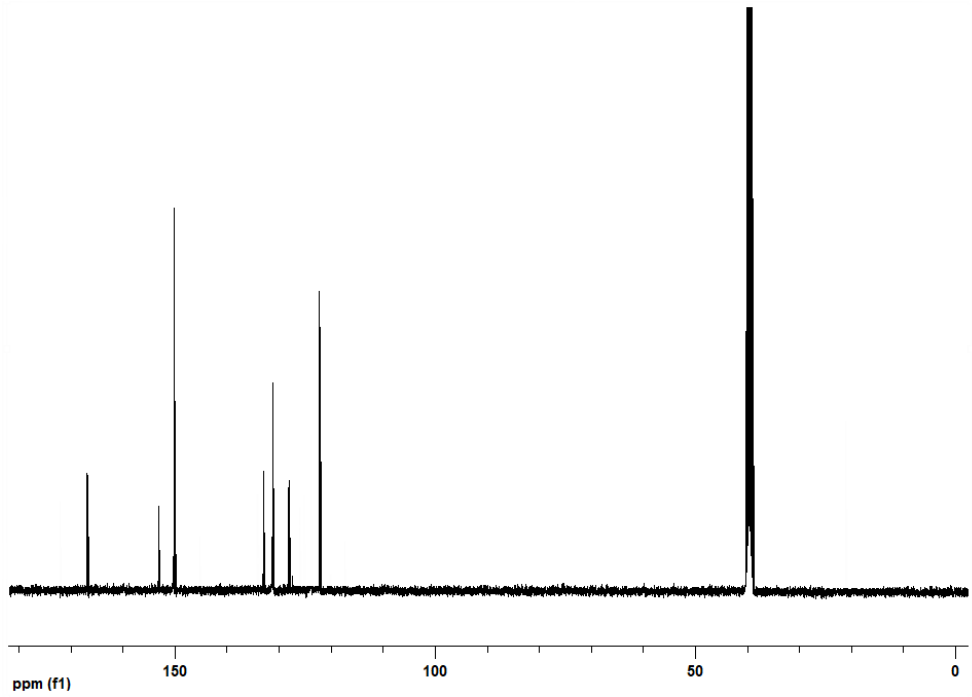


Figure S3 The structure and coordination mode of tca^{3-} ligands in Zn-TDA.

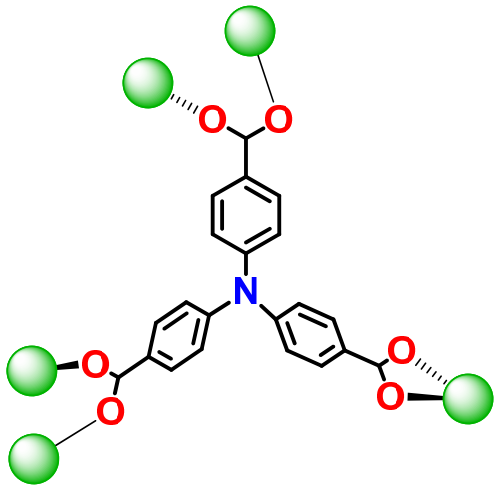


Figure S4 An extended three-dimensional coordination framework consolidated by tca^{3-}, and dpta ligands.

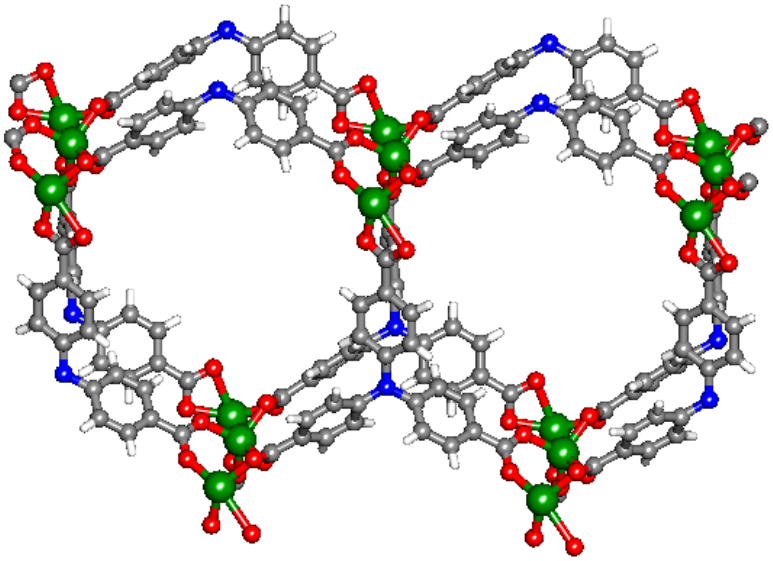
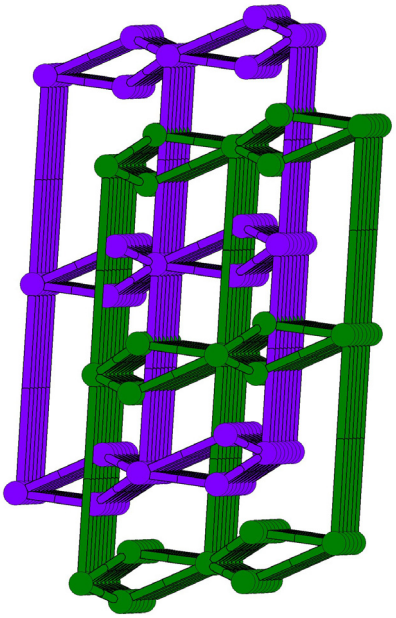
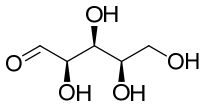


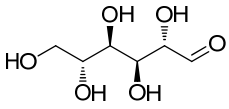
Figure S5 The structure of Zn-TDA can be viewed as a new 3,8-c topology with an schlafli symbol of $\{4^3.6^2 4.8\}\{4^3\}^2$.



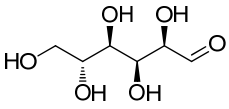
Molecular structure of selected sugars



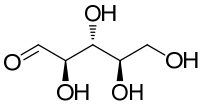
Xylose



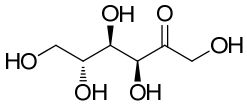
Mannose



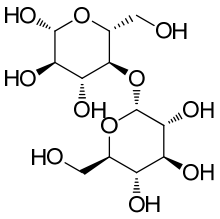
Glucose



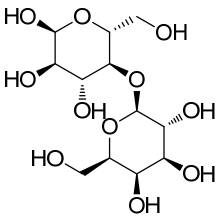
Ribose



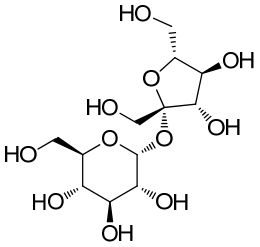
Fructose



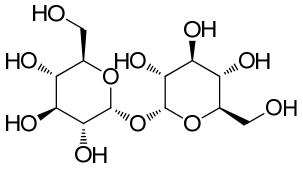
Maltose



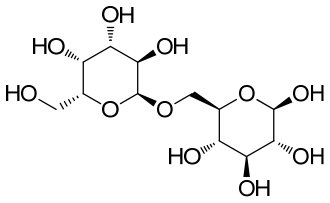
Lactose



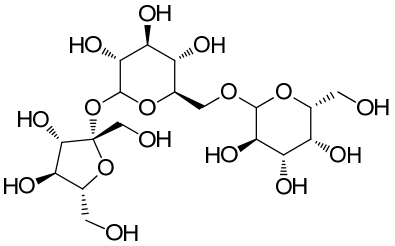
Sucrose



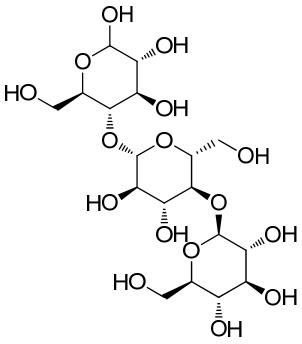
Trehalose



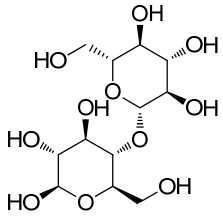
Melibiose



Raffinose



Cellotriose



Cellobiose

Figure S6 The Stern−Volmer plot of Zn-TDA quenched by Cellobiose aqueous solution, where I_0 and I are the fluorescence intensity ratio before and after metal ion incorporation, respectively.

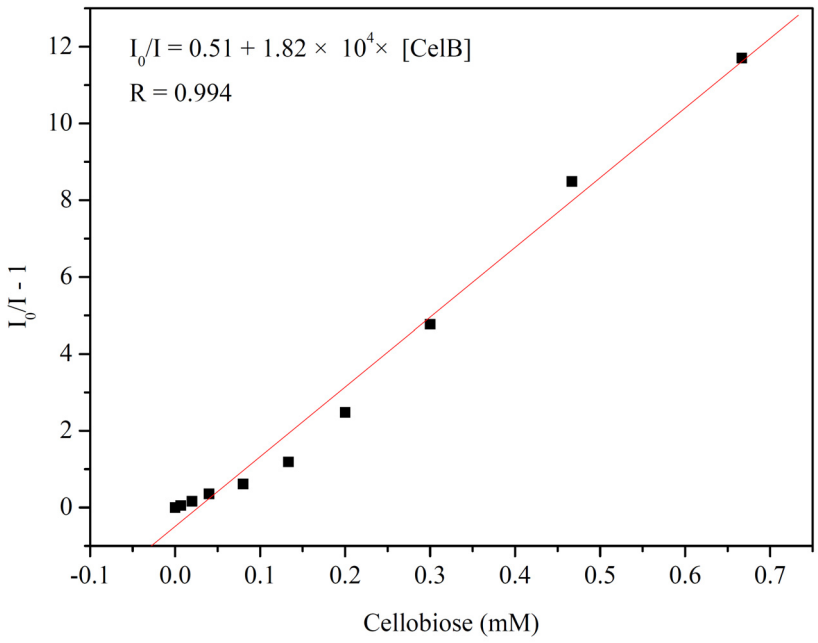
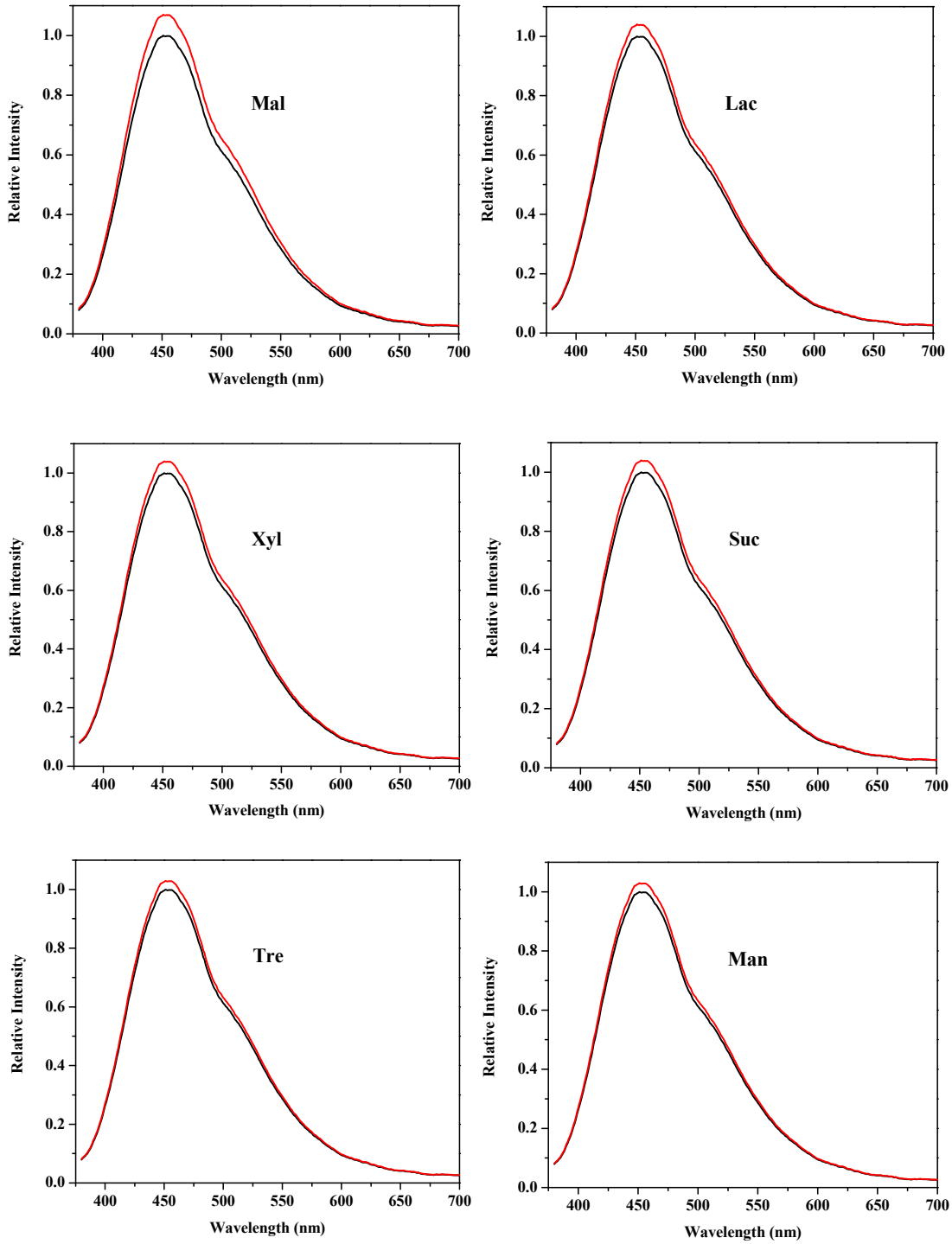


Figure S7 The fluorescence spectra of Zn-TDA in HEPES buffer solution upon the addition of 0.67 mM of varioussugars.



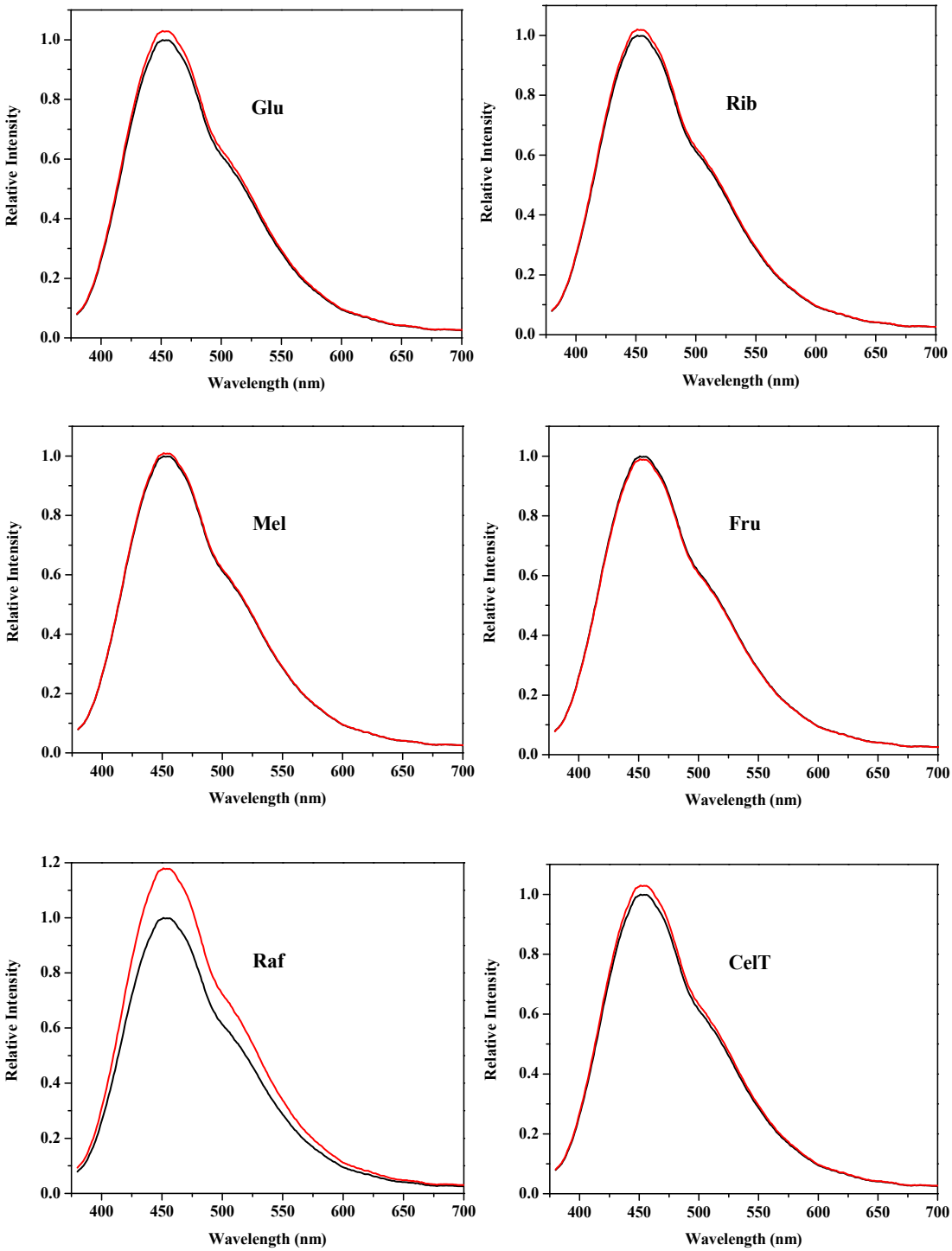
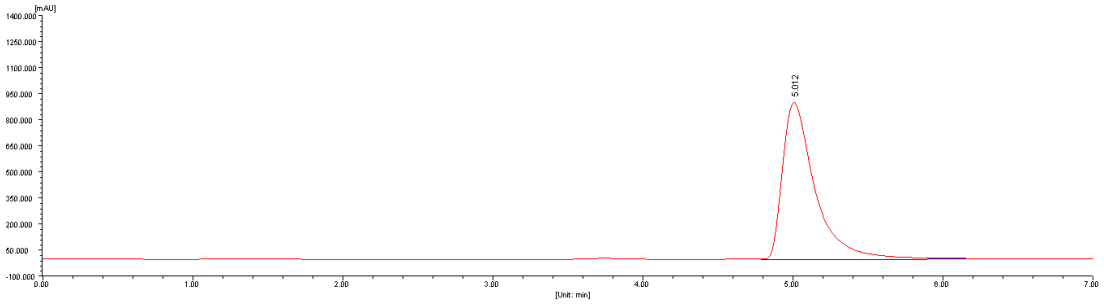
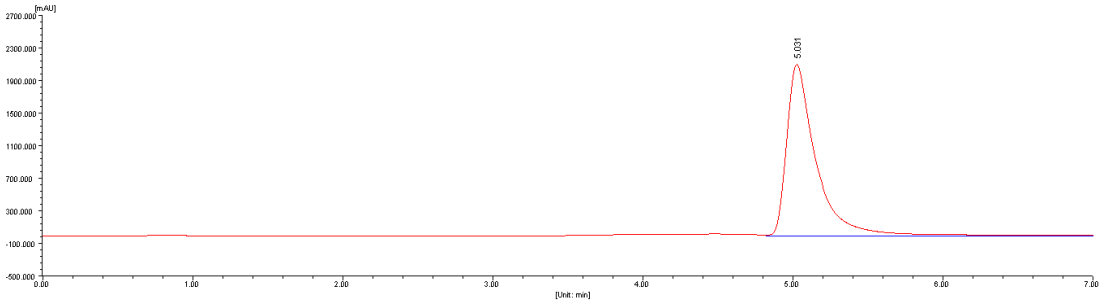

Glu
Rib
Mel
Fru
Raf
CelT
Relative Intensity
Wavelength (nm)
400
450
500
550
600
650
700
0.0
0.2
0.4
0.6
0.8
1.0
1.2

Figure S8 HPLC determination spectra for samples treated for 60 min (a) and 90 min (b).



(a)



(b)

Figure S9 MS determination spectrum for 5-HMF in 90 min treated sample.

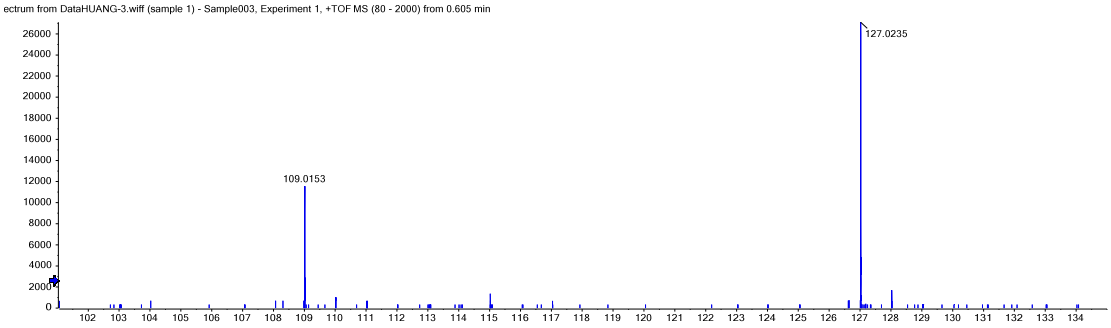
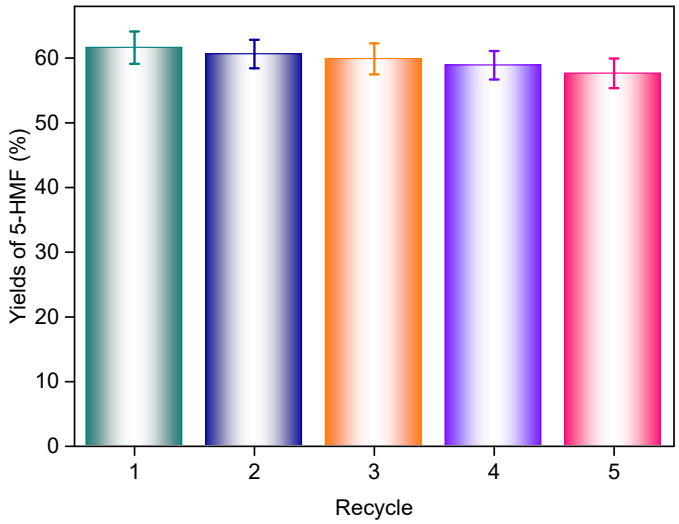


Figure S10 The recycle experiments for CelB conversion were conducted under the following conditions:.temperature of 80 ℃, atmospheric pressure, water as solvent, catalyst dosage of 2.5 g/L, CelB dosage of 2.4 g/L, and agitation speed at 300 rpm.



Supplementary Reference:

[S1] J. Wang, C. He, P. Wu, J. Wang and C. Duan, *J. Am. Chem. Soc.*, 2011, **132**, 12402–12405.