Electronic Supplementary Information for

Hydrolysis of Cellobiose to Monosaccharide Catalyzed by Functional Lanthanum (Ⅲ) Metallomicelle

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Contents

1. cmc of surfactant

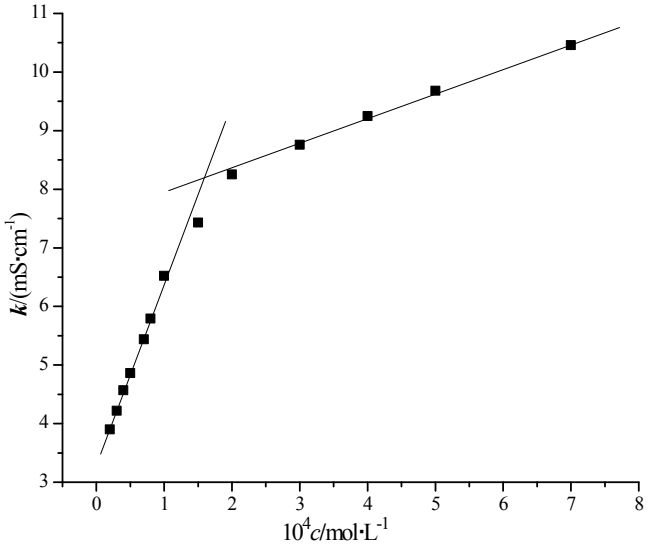


Fig.S1 Variation of electric conductivity with concentration of surfactant DMBO, 25°C

2 Determination of chelating ratio of La^{3+} to ligand

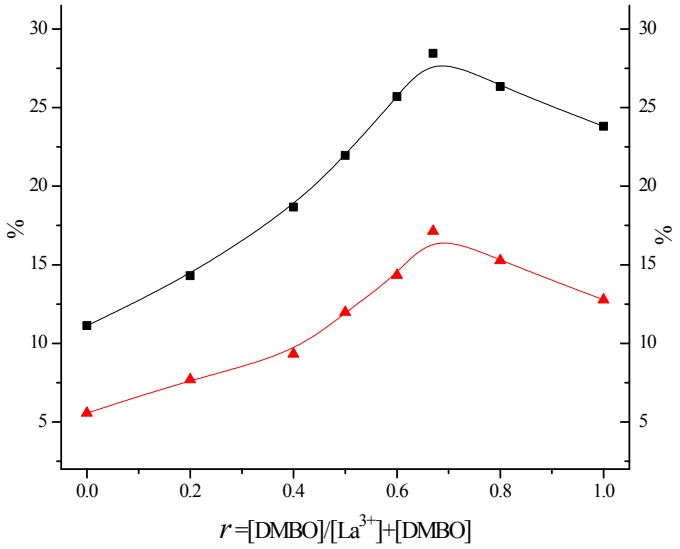


Fig.S2 Job plots for the ligand (DMBO) and La^{3+} ion complexation as measured by conversion of cellobiose (■) and yield of monosaccharide (▲)
$[Cellobiose]_0$ =0.02 mol·L^{-1}, [DMBO]+$[La^{3+}]$=0.002 mol·L^{-1} , pH9.0, 90°C, 10h

3. Effect of pH

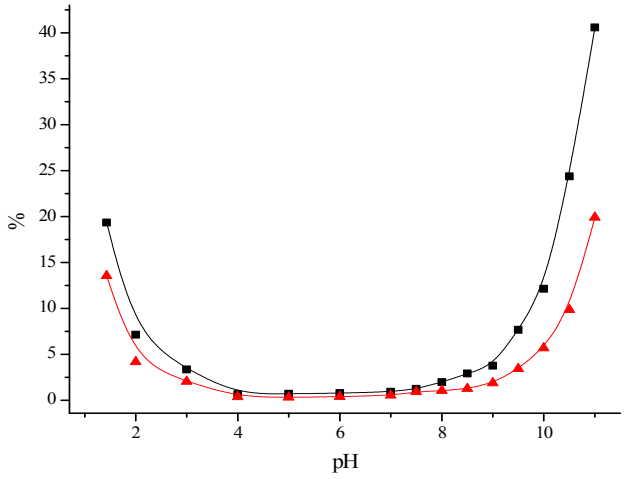


Fig.S3 Plots of conversion of cellobiose (■) and yield of monosaccharide (▲) with pH
$[Cellobiose]_0$=0.02mol·L^{-1}, 90°C, 10h

Fig.S3 showed the effect of pH on conversion of cellobiose and yield of monosaccharide in the absence of catalyst in aqueous solution.

4. Comparison with other metal complexes

To understand the effect of structure of metal complex on reaction activity, several metal complexes were employed as catalysts to catalyze cellobiose hydrolysis. The structures of these metal complexes were shown in Fig.S4 and the results were listed in table S1.

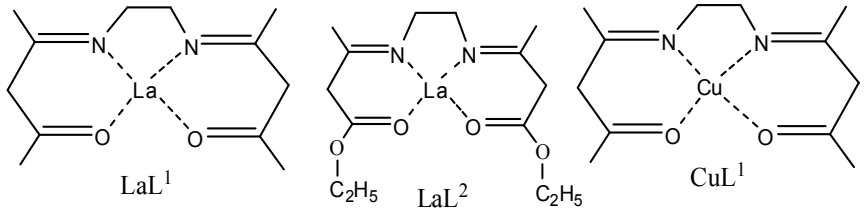


Fig.S4 Structures of metal complexes

Table S1 Conversion of cellobiose, yield of monosaccharide and selectivity of monosaccharide catalyzed by different metal complexes*

Systems	Conversion of cellobiose /%	Yield of monosaccharide/%	Selectivity of monosaccharide/%
LaL^1	9.8	4.8	49.0
LaL^2	10.4	5.5	52.9
CuL^1	8.5	4.4	51.8

*[Cellobiose]=0.02mol·L^{-1}, [Catalyst]=0.002mol·L^{-1}, pH9.0, 10h

5. PAD-MS (E+) spectrum of reaction solution

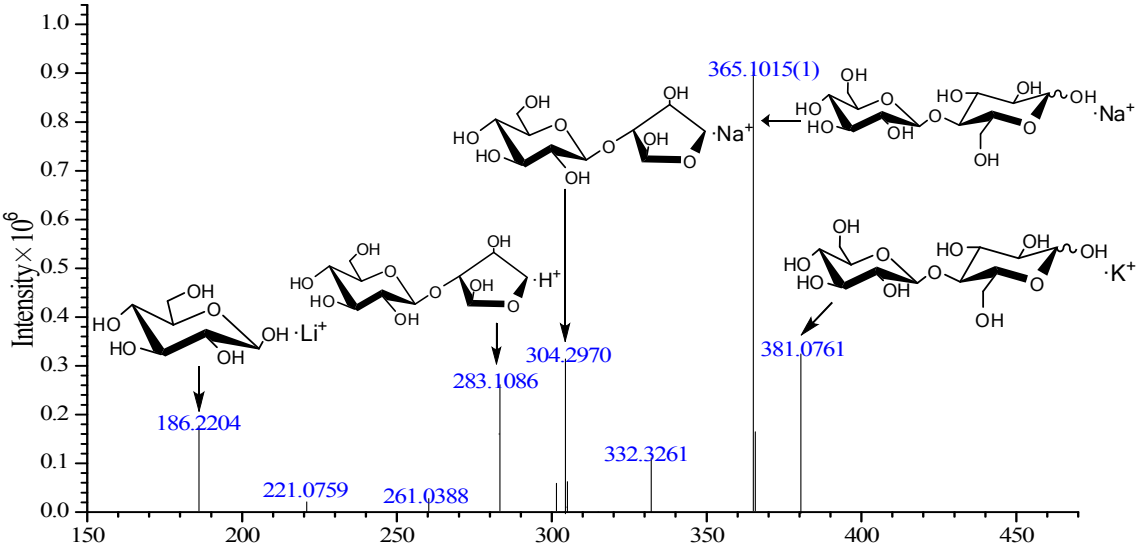


Fig.S5 PAD-MS (E+) spectrum of reaction solution of cellobiose hydrolysis catalyzed by metallomicelle $La(DMBO)_2$

$[Cellobiose]_0$ =0.02 mol·L^{-1}, [DMBO]=0.002 mol·L^{-1} pH9.0, 10h

6 Reaction kinetics

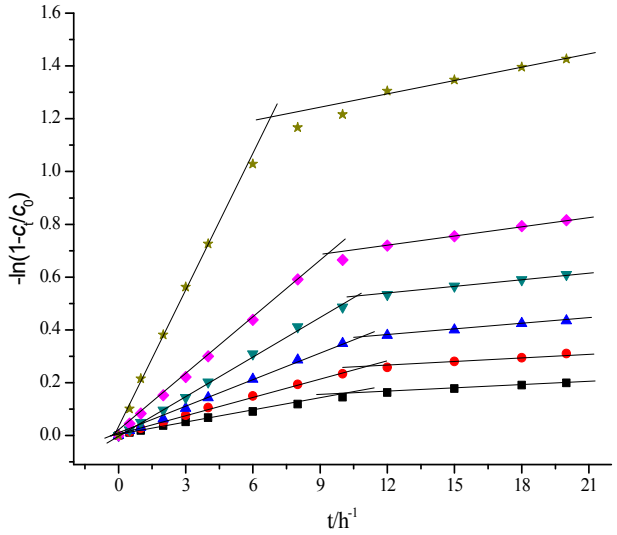
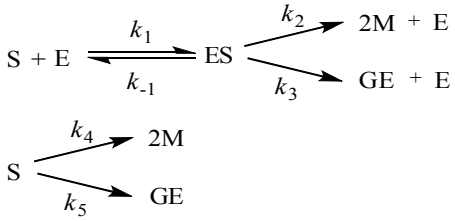


Fig.S6 Plots of $-\ln(1-c_t/c_0)$ vs reaction time t at different temperature
$[\text{Cellobiose}]_0$=0.02mol·L^{-1}, $[\text{La(DMBO)}_2]$=0.002mol·L^{-1}, pH9.0
(■)80 °C, (●)85°C , (▲)90°C, (▼) 95°C, (◆)100°C, (★)110℃

According to our experimental results a more detailed reaction pathway for cellobiose hydrolysis reaction was proposed as shown in scheme S1: firstly cellobiose S combined with surfactant E to form an intermediate compound ES, and then ES further reacted to monosaccharide M and glucosyl-erythrose GE. In the first step, the surfactant E combined with substrate S reversibly with rate constants k_1 and k_{-1}, then followed the rate-determining steps with rate constants k_2 and k_3($k_{cat}=k_2+k_3$). k_4 and k_5 are the rate constant of cellobiose hydrolysis to M and GE in bulk solution, respectively($k_0=k_4+k_5$).



Scheme S1 The reaction pathway proposed for catalysis reaction

The cellobiose hydrolysis reaction rate equation is described as

$$r=\frac{d[\mathrm{S}]}{d_t}=k_{-1}[ES]-k_1[\mathrm{S}][\mathrm{E}]-k_0[\mathrm{S}] \qquad \text{S(1)}$$

And the production of monosaccharide rate equation could be desribed as

$$\frac{d[\mathrm{M}]}{dt}=k_2[\mathrm{ES}]+k_4[\mathrm{S}] \qquad \text{S(2)}$$

According to Steady State Approximation,

$$\frac{\mathrm{d[ES]}}{\mathrm{dt}}=k_1[\mathrm{S}][\mathrm{E}]-(k_2+k_3+k_{-1})[\mathrm{ES}]=0 \qquad \text{S(3)}$$

Thus $$[ES]=\frac{k_1[E][S]}{k_2+k_3+k_{-1}}=\frac{[S][E]}{K_m} \quad S(4)$$

Where $K_m=\frac{k_2+k_3+k_{-1}}{k_1}$, is the Michaelis constant. Due to total concentration E_T of surfactant keeps constant, E_T=[E]+[ES],

Hence $$[E]=\frac{K_m * E_T}{K_m+[S]} \quad S(5)$$

Thus the equation S(1) and S(2) are transformed as equation S(6) and S(7).

$$r=\frac{d[S]}{d_t}=-\frac{k_{cat}E_T[S]}{K_m+[S]}-k_0[S] \quad S(6)$$

$$\frac{d[M]}{dt}=k_2[ES]+k_4[S]=(\frac{k_2}{K_m}[E]+k_4)[S]=(\frac{k_2E_T}{K_m+[S]}+k_4)[S] \quad S(7)$$

And after integrating equation S(6) and rearrangement, the following equation S(8) is obtained.

$$K_mk_0\ln\frac{c_t}{c_0}+k_{cat}E_T\ln\frac{k_{cat}E_T+K_mk_0+k_0c_t}{k_{cat}E_T+K_mk_0+k_0c_0}=-(k_{cat}E_T+K_mk_0)*k_0t \quad S(8)$$

Thus equation S(9) is obtained through transferring equation S(8).

$$t=\frac{K_mk_0}{(k_{cat}E_T+K_mk_0)k_0}\ln\frac{c_0}{c_t}+\frac{k_{cat}E_T}{(k_{cat}E_T+K_mk_0)k_0}\ln\frac{k_{cat}E_T+K_mk_0+k_0c_0}{k_{cat}E_T+K_mk_0+k_0c_t} \quad S(9)$$

Based on equation S(9), K_m and k_{cat} can be obtained by nonlinear fitting, as illustrated in Fig. S(7). All of the nonlinear correlation coefficients are above 0.97, this indicated that the kinetic model (Scheme S1 and equation S(9)) was reasonable.

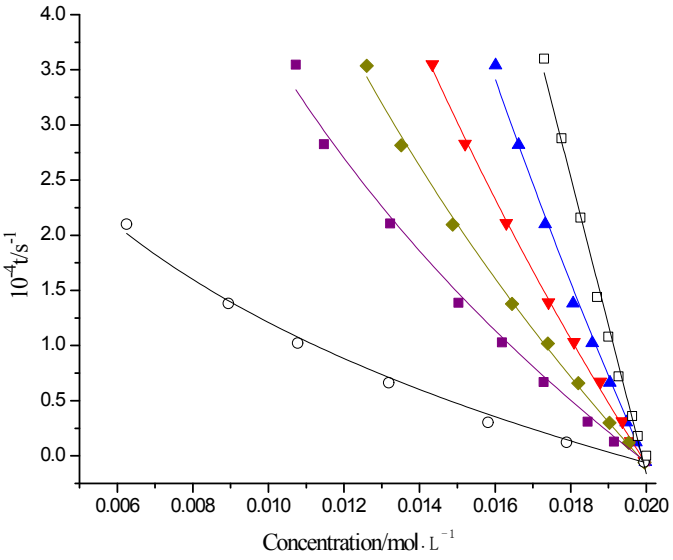


Fig.S7 Plots of reaction time *vs.* concentration of cellobiose
[Cellobiose]$_0$=0.02mol·L^{-1}, [La(DMBO)$_2$]=0.002mol·L^{-1}, pH9.0
(□)80 °C, (▲)85°C , (▼)90°C, (◆) 95°C, (■)100°C, (○)110°C

Base on the equation S(10):

$$\frac{d[\mathrm{M}]}{d[\mathrm{S}]}=\frac{d[\mathrm{M}]/dt}{d[\mathrm{S}]/dt}=\frac{\frac{k_2E_{\mathrm{T}}}{K_m+[\mathrm{S}]}+k_4}{-\frac{k_{cat}E_T}{K_m+[\mathrm{S}]}-k_0}=-\frac{k_2E_{\mathrm{T}}+k_4(K_m+[\mathrm{S}])}{k_{cat}E_T+k_0(K_m+[\mathrm{S}])} \qquad \mathrm{S(10)}$$

Hence the equation S(11) is obtained,

$$\int_0^{[\mathrm{M}]}[\mathrm{M}]=[\mathrm{M}]=-\int_{[\mathrm{S}]_0}^{[\mathrm{S}]}\frac{k_2E_{\mathrm{T}}+k_4(K_m+[\mathrm{S}])}{k_{cat}E_T+k_0(K_m+[\mathrm{S}])}d[\mathrm{S}] \qquad \mathrm{S(11)}$$

And from equation S(11) the following equation is obtained.

$$[\mathrm{M}]=\frac{k_2E_{\mathrm{T}}+k_4K_m}{k_0}\ln\frac{k_{cat}E_T+K_mk_0+k_0c_0}{k_{cat}E_T+K_mk_0+k_0[\mathrm{S}]}+\frac{k_4}{k_0}(c_0-[\mathrm{S}])-\frac{k_4(k_{cat}E_T+K_mk_0)}{k_0{*}k_0}\ln\frac{k_{cat}E_T+K_mk_0+k_0c_0}{k_{cat}E_T+K_mk_0+k_0[\mathrm{S}]}$$

……S(12)

Therefore equation S(13) is obtained through transferring equation S(12).

$$k_0[\mathrm{M}]-k_4(c_0-[\mathrm{S}])+\frac{k_4(k_{cat}E_T+K_mk_0)}{k_0}\ln\frac{k_{cat}E_T+K_mk_0+k_0c_0}{k_{cat}E_T+K_mk_0+k_0[\mathrm{S}]}=(k_2E_{\mathrm{T}}+k_4K_m)\ln\frac{k_{cat}E_T+K_mk_0+k_0c_0}{k_{cat}E_T+K_mk_0+k_0[\mathrm{S}]}$$

……S(13)

Let $$\mathrm{Y}=k_0[\mathrm{M}]-k_4(c_0-[\mathrm{S}])+\frac{k_4(k_{cat}E_T+K_mk_0)}{k_0}\ln\frac{k_{cat}E_T+K_mk_0+k_0c_0}{k_{cat}E_T+K_mk_0+k_0[\mathrm{S}]} \qquad \mathrm{S(14)}$$

$$\mathrm{X}=\ln\frac{k_{cat}E_T+K_mk_0+k_0c_0}{k_{cat}E_T+K_mk_0+k_0[\mathrm{S}]} \qquad \mathrm{S(15)}$$

Thus

$$\mathrm{Y}=(k_2E_{\mathrm{T}}+k_4K_m)\,\mathrm{X} \qquad \mathrm{S(16)}$$

Therefore according to the equation S(16), k_2 can be calculated from the slope of straight line Y *vs.* X (see Fig.S8). All of the linear correlation coefficients are above 0.95.

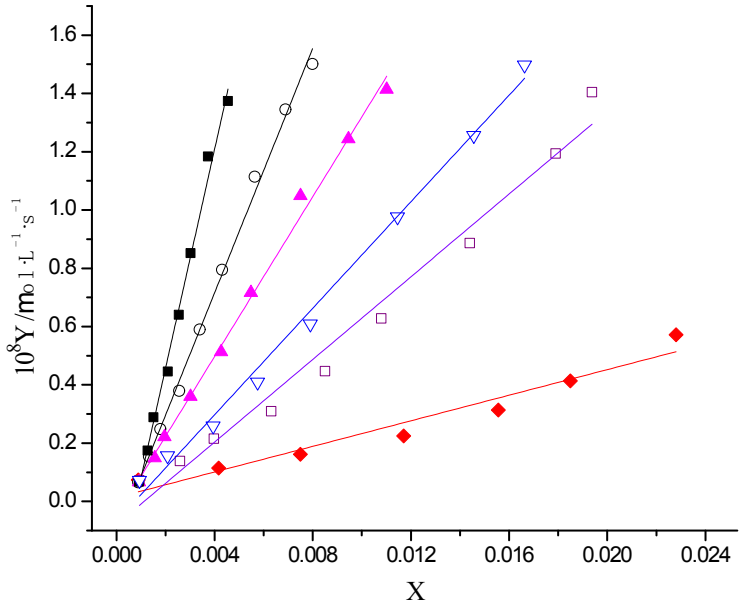


Fig.S8 Plots of Y *vs.* X

$[Cellobiose]_0$=0.02mol·L^{-1}, $[La(DMBO)_2]$=0.002mol·L^{-1}, pH9.0

(■)80 °C, (○)85°C , (▲)90°C, (▽) 95°C, (□)100°C, (◆)110°C