Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Figure Caption

Fig. S1 The IR spectra of the $(C_{16}TA)_nH_{6-n}P_2W_{18}O_{62}$: (a) $(C_{16}TA)H_5P_2W_{18}O_{62}$; (b) $(C_{16}TA)_2H_4P_2W_{18}O_{62}$; (c) $(C_{16}TA)_3H_3P_2W_{18}O_{62}$; (d) $(C_{16}TA)_4H_2P_2W_{18}O_{62}$; (e) $(C_{16}TA)_5HP_2W_{18}O_{62}$; and (f) $(C_{16}TA)_6P_2W_{18}O_{62}$

Fig. S2 ^{31}P MAS NMR spectra of (a) $(C_{16}TA)H_5P_2W_{18}O_{62}$, (b) $(C_{16}TA)_3H_3P_2W_{18}O_{62}$, (c) $(C_{16}TA)_6P_2W_{18}O_{62}$ and (d) after the reaction.

Fig. S3 XRD patterns of $H_6P_2W_{18}O_{62}$ (a) and $(C_{16}TA)H_5P_2W_{18}O_{62}$ (b).

Fig. S4 The conductivity of $(C_{16}TA)_nH_{6-n}P_2W_{18}O_{62}$ at the room temperature. (a) $(C_{16}TA)H_5P_2W_{18}O_{62}$, (b) $(C_{16}TA)_2H_4P_2W_{18}O_{62}$, (c) $(C_{16}TA)_3H_3P_2W_{18}O_{62}$, (d) $(C_{16}TA)_4H_2P_2W_{18}O_{62}$, (e) $(C_{16}TA)_5HP_2W_{18}O_{62}$, (f) $(C_{16}TA)_6P_2W_{18}O_{62}$.

Fig. S5 The TEM and EDAX of the $(C_{16}TA)H_5P_2W_{18}O_{62}$

Fig. S6 The IR spectra of $(C_{16}TA)H_5P_2W_{18}O_{62}$ adsorbing cellulose(left) and $(C_{16}TA)H_2PW_{12}O_{40}$ absorbing cellulose (right)

Fig. S7 The IR spectra of the $(C_{16}TA)H_5P_2W_{18}O_{62}$ before (a) and after the reaction (b)

Table S1 Hydrolysis of cellulose comparision with recently reported chemical procedures.

Table S2 The elemental analysis of $(C_{16}TA)_nH_{6-n}P_2W_{18}O_{62}$ and acid contents.

Table S3 Voltammetric Data for heteropolytungstates using a wax-Impregnated graphite electrode.

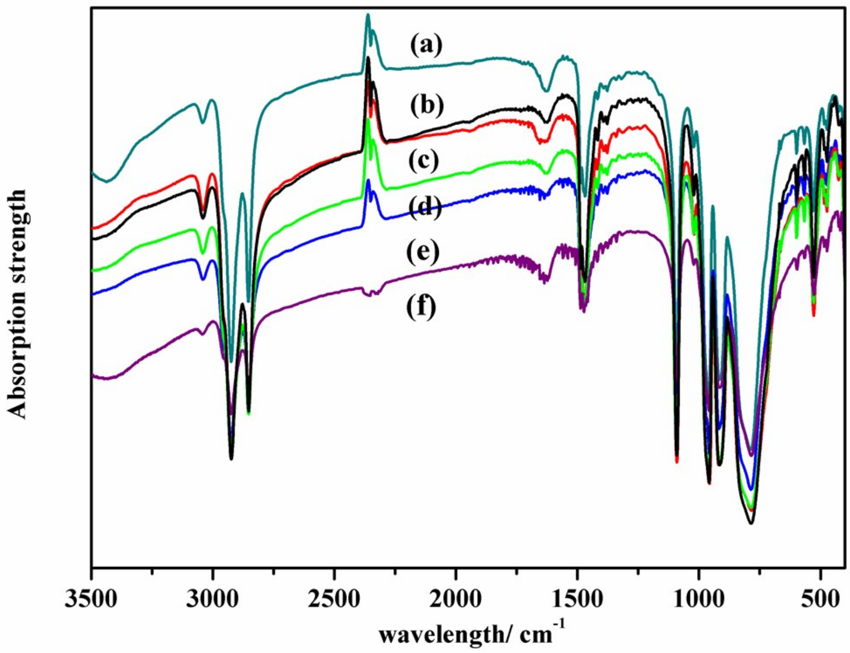

Fig. S1 The IR spectra of the $(C_{16}TA)_nH_{6-n}P_2W_{18}O_{62}$: (a) $(C_{16}TA)H_5P_2W_{18}O_{62}$; (b) $(C_{16}TA)_2H_4P_2W_{18}O_{62}$; (c) $(C_{16}TA)_3H_3P_2W_{18}O_{62}$; (d) $(C_{16}TA)_4H_2P_2W_{18}O_{62}$; (e) $(C_{16}TA)_5HP_2W_{18}O_{62}$; and (f) $(C_{16}TA)_6P_2W_{18}O_{62}$

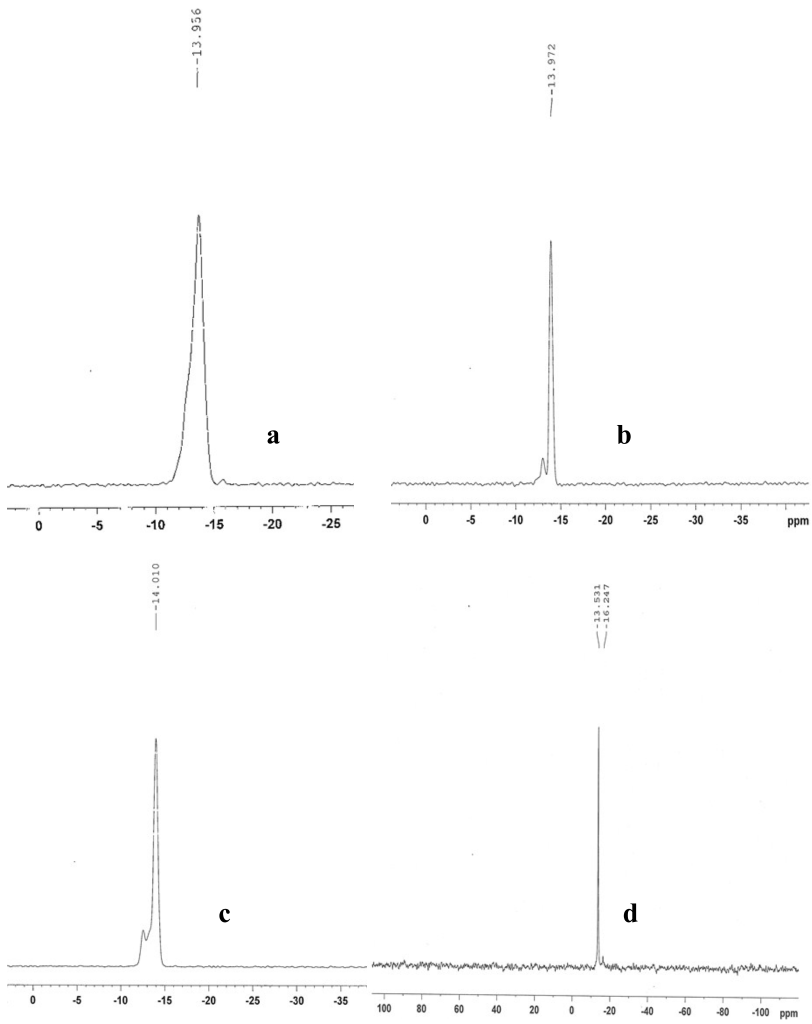

Fig. S2 ^{31}P MAS NMR spectra of (a) $(C_{16}TA)H_5P_2W_{18}O_{62}$, (b) $(C_{16}TA)_3H_3P_2W_{18}O_{62}$, (c) $(C_{16}TA)_6P_2W_{18}O_{62}$ and (d) after the reaction.

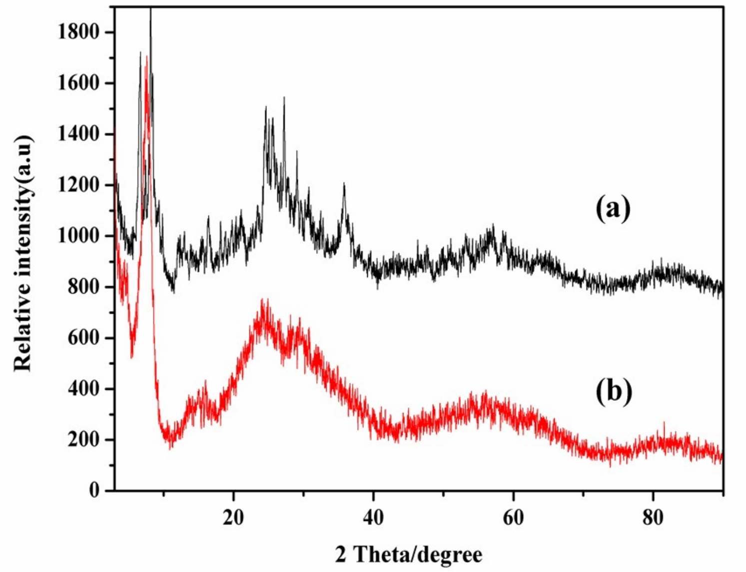

Fig. S3 XRD patterns of $H_6P_2W_{18}O_{62}$ (a) and $(C_{16}TA)H_5P_2W_{18}O_{62}$ (b).

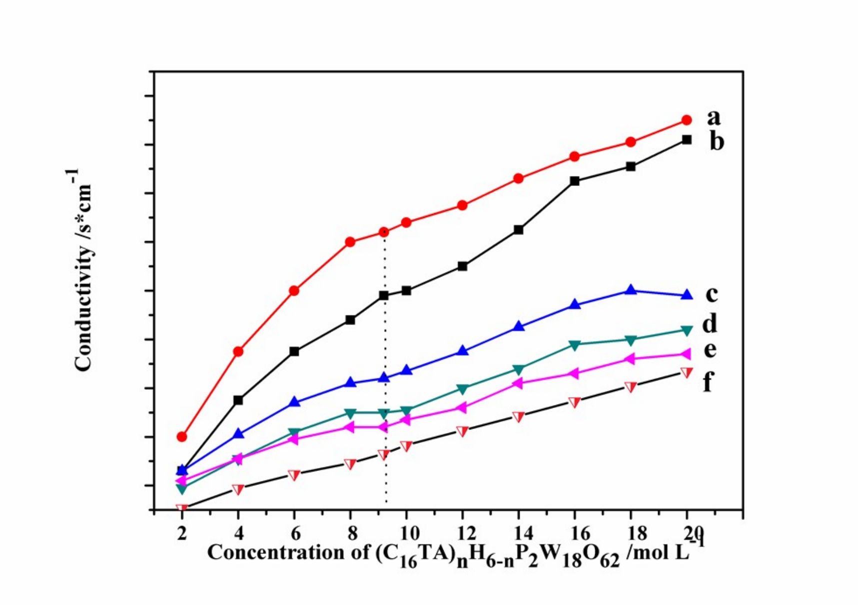

Fig. S4 The conductivity of $(C_{16}TA)_nH_{6-n}P_2W_{18}O_{62}$ at the room temperature. (a) $(C_{16}TA)H_5P_2W_{18}O_{62}$, (b) $(C_{16}TA)_2H_4P_2W_{18}O_{62}$, (c) $(C_{16}TA)_3H_3P_2W_{18}O_{62}$, (d) $(C_{16}TA)_4H_2P_2W_{18}O_{62}$, (e) $(C_{16}TA)_5HP_2W_{18}O_{62}$, (f) $(C_{16}TA)_6P_2W_{18}O_{62}$.

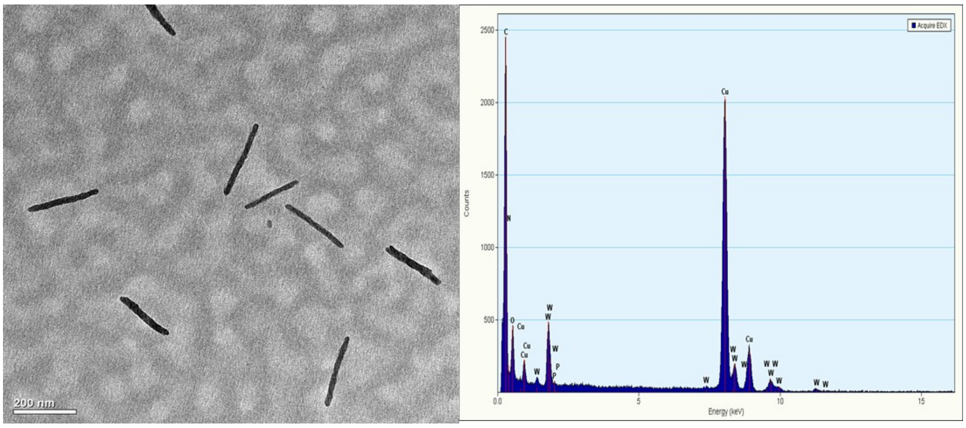

Fig. S5 The TEM and EDX of the $(C_{16}TA)H_5P_2W_{18}O_{62}$

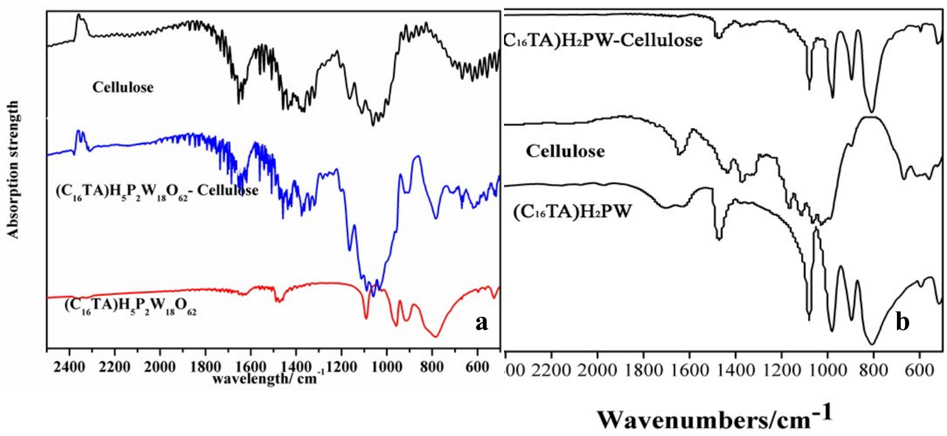

Fig. S6 The IR spectra of $(C_{16}TA)H_5P_2W_{18}O_{62}$ adsorbing cellulose(left) and $(C_{16}TA)\ H_2PW_{12}O_{40}$ absorbing cellulose (right)

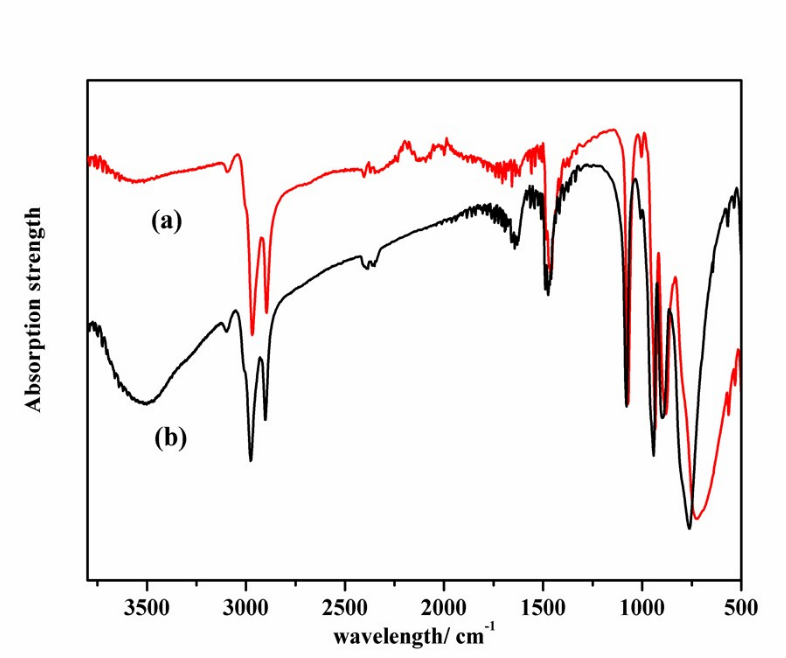

Fig. S7 The IR spectra of the $(C_{16}TA)H_5P_2W_{18}O_{62}$ before (a) and after the reaction (b)

Table S1 Hydrolysis of cellulose comparision with recently reported chemical procedures.

Catalyst	Solvents	Temp. (K)	Time (h)	Glucose yield (%)	Ref.
$HNbMoO_6$	H_2O	403	12	8.5	1
Zn–Ca–Fe	H_2O	433	20	29	2
Amberlyst–15	[BMIm]Cl/H_2O	373	5	11	3
CP–SO_3H	H_2O	393	10	93	4
Nafion NR50	H_2O	403	2	35	5
Nafion SAC50	H_2O	463	24	11	6
PCPs–SO_3H	H_2O	393	3	5.3	7
AC–SO_3H	H_2O	373	3	64	8
BC–SO_3H	H_2O	363(MW)	1	19.8	9
CSA–SO_3H^b	H_2O	403(MW)	1	34.6	10
SC–SO_3H	[BMIm]Cl/H_2O	383	4	63	11
AC–N–SO_3H–250	H_2O	423	24	62.6	12
CMK–3–SO_3H	H_2O	423	24	74.5	12
SimCn–SO_3H	H_2O	423	24	50.4	13
$H_3PW_{12}O_{40}$	H_2O	423	2	18	14
$H_3PW_{12}O_{40}$	H_2O	453	2	50.5	15
$H_5BW_{12}O_{40}$	H_2O	333	6	77	16
$H_3PW_{12}O_{40}$	H_2O	363(MW)	3	75.6	17
Micellar HPA	H_2O	443	8	39.3	18
$[MIMPSH]_nH_{3-n}PW$	H_2O/MIBK	413	5	36	19
$CsH_2PW_{12}O_{40}$	H_2O	433	6	27	20
H-beta	H_2O	423	24	12	21
HY zeolite	$[C_4mim]Cl/H_2O$	373(MW)	0.13	37	22
HY zeolite	[BMIm]Cl/H_2O	403	2	50	23
Fe_3O_4–SBA–SO_3H	H_2O	423	3	26	24
Fe_3O_4–SBA–SO_3H	H_2O	423	3	50	25
MNPs@SiO_2–SO_3H	H_2O	423	3	30.2	26
Ru/CMK–3	H_2O	503	24	34.2	27
$CaFe_2O_4$	H_2O	423	24	36	28
HT–OH_{Ca}	H_2O	423	24	40.7	29
AC-SO_3H	H_2O	423	12	42.5	30
PDVB-SO_3H-[C_3vim]- [SO_3CF_3]	$[C_4mim]Cl/H_2O$	373	5	77.0	31
PVP–HPW	Butanol	433	4	61.6α-BGS	32
PVP–HSiW (1/5 : 3/4)		433	4	60.8α-BGS	
K26, HCl	H_2O	453	1	88	33
K26			1	36	
Cp-SO_3H-1.69	H_2O	443	10	2.1	34
NbP	H_2O	453(MW)	0.25	22	35
(CTA)$H_5P_2W_{18}O_{64}$	H_2O	433	9	69.1	This work
(CTA)$H_5P_2W_{18}O_{64}$	methanol	433	7	58.5MLA	This work

Table S2 The elemental analysis of $(C_{16}TA)_nH_{6-n}P_2W_{18}O_{62}$ and acid contents

Catalysts	Elementary results (experiment value in parenthesis)/%					Acid content [mol·kg^{-1}]
	H	**C**	**N**	**P**	**W**	
$[C_{16}H_{33}N(CH_3)_3]\ H_5P_2W_{18}O_{62}$	1.02(1.10)	4.90(4.81)	0.30(0.29)	1.33(1.21)	71.12(71.45)	3.2
$[C_{16}H_{33}N(CH_3)_3]_2H_4P_2W_{18}O_{62}$	1.80(1.64)	9.25(8.43)	0.57(0.49)	1.26(1.22)	67.04(67.97)	2.8
$[C_{16}H_{33}N(CH_3)_3]_3H_3P_2W_{18}O_{62}$	2.49(2.52)	13.12(14.56)	0.81(0.76)	1.19(1.22)	63.40(62.70)	2.1
$[C_{16}H_{33}N(CH_3)_3]_4H_2P_2W_{18}O_{62}$	3.11(3.28)	16.59(15.44)	1.02(0.83)	1.13(1.31)	60.13(60.68)	1.5
$[C_{16}H_{33}N(CH_3)_3]_5HP_2W_{18}O_{62}$	3.68(3.53)	19.72(18.26)	1.21(1.09)	1.07(1.24)	57.18(59.70)	1.1
$[C_{16}H_{33}N(CH_3)_3]_6P_2W_{18}O_{62}$	4.18(4.10)	22.56(23.50)	1.38(1.29)	1.02(1.17)	54.51(54.69)	0.6

Table S3 Voltammetric data[a] for heteropolytungstates using a wax-impregnated graphite electrode

Anion	Medium	Epa (V)	Epc (V)	Amout (mmol)	P_{O2} (MPa)	Conversion (%)	Yield (%)
$PW_{12}O_{40}^{-3}$	**1** *M* H_2SO_4	-0.04	-0.10	0.07	1.0	41.2	28.2 [b]
		-0.30	-0.36			51.8	29.1[c]
$P_2W_{18}O_{62}^{-6}$	pH=5	0.02	-0.05	0.07	1.0	66.1	29.9 [b]
		-0.16	-0.22			91.2	21.1 [c]
		-0.55	-0.61				
		-0.68	-0.75				

[a]Anion concentration 1.0 mM; sweep rate 0.5 V min^{-1}; all reductions are one-electron processes.

[b] Reaction condition: 100 mg of cellulose, 5 mL water at 160 °C in 3 h and in O_2 for 10 min.

[c] Reaction condition: 100 mg of cellulose, 5 mL water at 160 °C in 3 h and in O_2 for 30 min.

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