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Note

A novel supramolecular compound 2,2′-bipyridyl-phosphotungstic acid: synthesis and catalysis

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ABSTRACT

A new supramolecular compound $(C_{10}H_8N_2)_{3.2}\cdot H_3PW_{12}O_{40}\cdot 25.6H_2O$ (Bipy–PW_{12}) was synthesized by self-assembly design, and characterized by elemental analysis, Fourier-transform infrared spectra (FTIR), and ^{31}P NMR spectra. Bipy–PW_{12} can effectively catalyze oxidative degradation of chitosan with H_2O_2 in heterogeneous phase. To obtain water-soluble chitosan with an average molecular weight of 5000, the optimum reaction conditions were determined as follows: reaction temperature, 80 °C; reaction time, 13 min; H_2O_2 concentration, 2.7 mol/L; and mass ratio of Bipy–PW_{12} to chitosan, 0.01.

Chitosan and its derivatives have a special set of interesting properties: nontoxicity, biocompatibility, controllable biodegradability, and nonantigenicity.[1,2] These properties make chitosan an attractive biopolymer for applications in wide areas such as biotechnology, pharmaceuticals, wastewater treatment, cosmetics, agriculture, food science, and textiles.[3] Generally, chitosan obtained from the deacetylation of chitin has high molecular weight and low solubility in most solvents, which limit its applications, especially in medicine and in the food industry. However, the solubility of chitosan can be improved through its degradation. Furthermore, chitosan oligomers obtained from chitosan were shown to possess improved biological, chemical, and physical properties compared to chitosan.[4,5] Various processes for degrading chitosan have been carried out in order to obtain the oligomers with a required molecular weight range.[6–16] Recently, oxidative degradation with hydrogen peroxide has been studied.[7,17–21] The technique is based on the formation of a reactive hydroxyl radical by the disassociation of hydrogen peroxide. Hydroxyl radicals, which are powerful oxidizing species, can attack the β-D-(1→4) glucosidic linkages of chitosan. However, the disassociation of hydrogen peroxide is inefficient when hydrogen peroxide is used alone. Therefore, the preparation and selection of an appropriate catalyst to accelerate the efficiency of oxidative degradation of chitosan with hydrogen peroxide is of great significance.[22,23]

Heteropoly acid and its derivatives can be used as acidic, oxidative or bifunctional catalysts due to their advantages of high catalytic activity, excellent selectivity, and mild condition.[11] Based on the fact that heteropoly acid, which has strong electron receptivity, can act as an acceptor molecule, many supramolecular architectures based on heteropoly acid have been self-assembled through electrostatic attraction, hydrogen bonding or covalent bonds.[24,25] These supramolecular compounds not only exhibit special optical, electrical, and magnetic properties, but also have application in catalysis, functional materials, and medicine. Thus, in this article, a new supramolecular compound $(C_{10}H_8N_2)_{3.2}\cdot H_3PW_{12}O_{40}\cdot 25.6H_2O$ (Bipy–PW_{12}) was synthesized by self-assembling and its catalytic property of oxidative degradation of chitosan with H_2O_2 was investigated.

Bipy–PW_{12} was synthesized starting from 2,2′-bipyridyl (Bipy) and phosphotungstic acid ($H_3[PW_{12}O_{40}]\cdot nH_2O$) in ethanol (Fig. 1). FT-IR spectra of Bipy, $H_3[PW_{12}O_{40}]\cdot nH_2O$, and Bipy–$PW_{12}$ were shown in Figure 2. Curves a, b, and c in Figure 2 show the four characteristic absorption peaks of $[PW_{12}O_{40}]^{3-}$ in Bipy–PW_{12}, indicating that Bipy–PW_{12} kept Keggin structure. Compared with the parent phosphotungstic acid, the characteristic absorption peaks show the shifts in different extent. The vibration band of W=O_t blue shifted from 982 to 984 cm^{-1}, and the bands of W–O_b–W and W–O_c–W shifted, respectively, from 887 and 897 cm^{-1} to 799 and 804 cm^{-1} (O_t terminal oxygen, O_b bridged oxygen of two octahedral sharing a corner, O_c bridged oxygen of two octahedral sharing an edge). These shifts appeared as a result of the new con-

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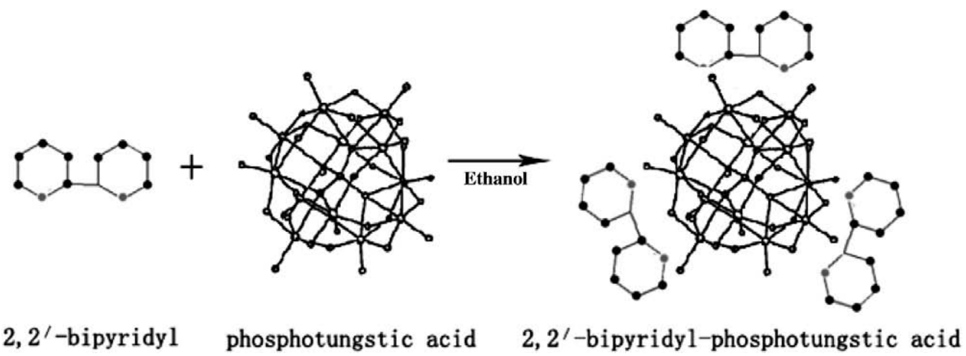

Figure 1. Scheme of the synthesis of 2,2′-bipyridyl-phosphotungstic acid.

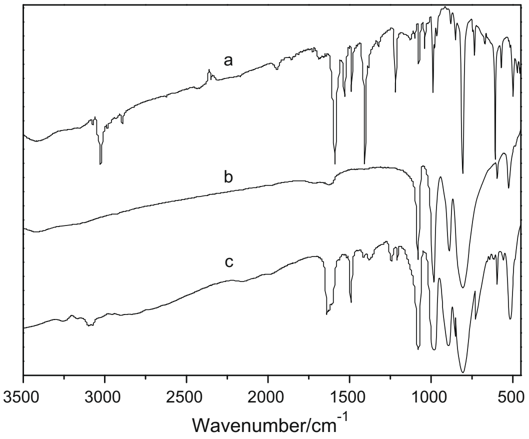

Figure 2. FTIR spectra of (a) Bipy, (b) $H_3PW_{12}O_{40}$ and (c) Bipy–PW_{12}.

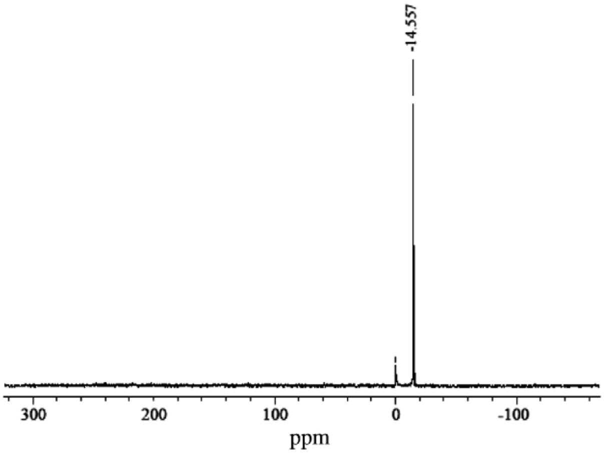

Figure 3. ^{31}P NMR spectra of Bipy–PW_{12} in DMF solution.

jugation of $[PW_{12}O_{40}]^{3-}$ with Bipy. $[PW_{12}O_{40}]^{3-}$ shares electrons with Bipy, which changed the electron density of $[PW_{12}O_{40}]^{3-}$ anion and affected the force constant of W with terminal oxygen and bridged oxygen. Moreover, compared with Bipy , the stretching vibrations of C=C and C=N in Bipy obviously shifted, respectively, from 1410 and 1590 cm^{-1} to 1490 and 1630 cm^{-1}. The above results demonstrated that Bipy interacted with phosphotungstic acid and formed Bipy–PW_{12}. ^{31}P NMR spectrum analysis is shown in Figure 3. A peak of Bipy–PW_{12} in DMF solution appeared at −14.56 ppm, which showed a slight displacement compared with parent $H_3PW_{12}O_{40}$ (−14.9 ppm).[25] The displacement indicated that the electron density of the whole $[PW_{12}O_{40}]^{3-}$ anions increased to some extent,[26] owing to the charge transition from Bipy to $[PW_{12}O_{40}]^{3-}$. This result further demonstrated that Bipy and phosphotungstic acid were not just mixed physically, but also interacted with each other chemically.

The optimal conditions for Bipy–PW_{12} degrading chitosan with H_2O_2 were studied by an orthogonal test. Three controllable variables, reaction temperature, concentration of hydrogen peroxide, and the mass ratio of Bipy–PW_{12} to chitosan were selected, each at three levels (Table 1). According to the experimental design theory, the orthogonal array $L_9(3^3)$ was selected to arrange the test program. The test results are listed in Table 2. It was seen through analyzing the extreme difference (R) of intrinsic viscosity of the degraded chitosan solution that the reaction temperature had the highest influence, the mass ratio of Bipy–PW_{12} to chitosan had the lowest influence and the concentration of hydrogen peroxide had in-between influence. In the degradation experiment of chitosan, the degradation product is desired to have high water-solubility and a lighter color. Through comprehensively analyzing the intrinsic viscosity, reaction time, and the color of degraded chitosan solution in the Table 2, the optimum reaction conditions were determined as follows: reaction temperature, 80 °C; reaction time, 13 min; $H_2O_{2,}$ concentration, 2.7 mol/L; and mass ratio of Bipy–PW_{12} to chitosan, 0.01. Under these conditions, the dissolution of chitosan was 100%, and the viscosity–average molecular weight of degraded chitosan was around 5000 in all parallel experiments.

The IR spectra of chitosan and degraded chitosan are shown in Figure 4. Both the N–H and O–H stretching vibrations of chitosan can be characterized by a strong, broad band centered at 3440 cm^{-1}. The bands at 1602 and 599 cm^{-1} correspond to the binding vibrations of the amido groups of chitosan, the bands in the range 1158–895 cm^{-1} are assigned to the characteristics of chitosan polysaccharide structure.[27] The IR spectra of degraded chitosan exhibited most of the characteristic adsorption peaks of chitosan but with some differences. The vibration band at 1100 cm^{-1} corresponding to the other bond in the pyranose ring was weakened, which indicates that the rupture of the β-glycosidic bonds possibly influenced the amount and distribution of glycosidic bonds in the molecular chains of chitosan. The bands at 1602 and 599 cm^{-1} became stronger, and the peak at 599 cm^{-1} moved toward the higher wavenumbers. In addition, the N–H stretching vibration moved toward lower wavenumbers, which indicates that the intermolecular and intramolecular hydrogen bonds of chitosan were weakened.

In conclusion, Bipy–PW_{12}, as catalyst, not only effectively degraded chitosan with H_2O_2 in heterogeneous phase, but was also easily prepared, separated from reaction system, and repetitively used. Compared with the oxidative degradation occurred in homogeneous phase,[22] the method not only overcame the disadvantages of the low concentration of chitosan, large consumption of subse-

Table 1
The variables investigated and their levels

Variables investigated	Levels of each variable		
	1	2	3
A: reaction temperature (°C)	60	70	80
B: concentration of hydrogen peroxide(mol/L)	0.9	1.8	2.7
C: mass ratio of Bipy–PW_{12} to chitosan	7.0×10^{-3}	1.0×10^{-2}	1.3×10^{-2}

Table 2
Experimental arrangement and test results

Experiment number	A	B	C	Entire solution time (min)	Degradation solution color	Intrinsic viscosity (mL/g)
1	1	1	1	143	Faint red	6.97
2	1	2	2	75	Faint red	6.44
3	1	3	3	45	Yellow	6.62
4	2	1	2	75	Faint red	6.80
5	2	2	3	32	Yellow	5.89
6	2	3	1	30	Yellow	5.80
7	3	1	3	37	Yellow	6.07
8	3	2	1	23	Faint yellow	6.07
9	3	3	2	13	Faint yellow	4.95
K_1	20.03	19.84	18.84			
K_2	18.49	18.4	18.19			
K_3	17.09	17.37	18.58			
R	2.94	2.47	0.65			

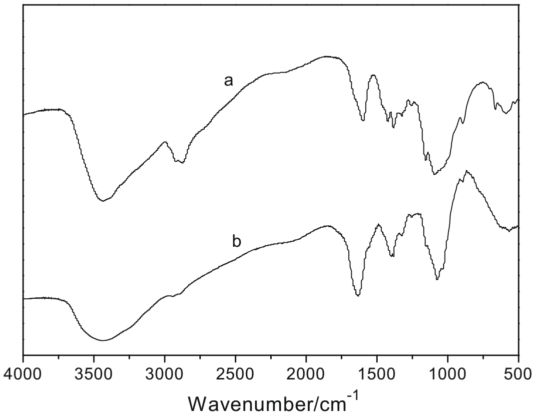

Figure 4. FTIR spectra of chitosan (a) and degraded chitosan (b).

quent sedimentation, and separation, but also made the precipitation process of a water-soluble low-molecular weight chitosan convenient, which may have potential applications.

1. Experimental

1.1. General methods

The starting materials included $H_3[PW_{12}O_{40}]\cdot nH_2O$, 2,2′-bipyridyl (Bipy), 30% (wt %) hydrogen peroxide, and chitosan. The viscosity-average molecular weight (M_v) of chitosan, which was obtained from Yuhuan Biology Engineering (Zhejiang, China), and whose degree of acetylation is 95.54%, is about 750,000. Other reagents were analytical grade materials without further purification. The IR spectra were recorded on a Nicolet Nexus 670 FTIR spectrometer using KBr pellets. Elemental analyses were carried out using a Vario EL III Elemental Analyzers and a Philips Magix pw 2424 X-ray fluorescence spectroscopy (XRF). ^{31}P NMR spectra were recorded using a UNITY—500 NMR Spectrometer. The intrinsic viscosities of chitosan and degraded chitosan solution were determined using an Ubbelodhe viscosimeter by capillary viscometry.

1.2. Synthesis of Bipy–PW_{12}

A solution of 2,2′-bipyridyl (1.5 mmol) in ethanol(10 mL) was added dropwise to a stirred solution of phosphotungstic acid (0.67 mmol) in ethanol (40 mL).After the mixture was stirred under room temperature for 30 min, the milky pulverous solid (Bipy–PW_{12}) was obtained through filtering and washing with distilled water and ethanol successively. The contents of C, H, N of Bipy–PW_{12} were recorded on Vario EL III Elemental Analyzers, and P, W on Philips Magix pw 2424 X-ray fluorescence spectroscopy. The formula of Bipy–PW_{12} is $(C_{10}H_8N_2)_{3.2}\cdot H_3PW_{12}O_{40}\cdot 25.6H_2O$, based on elemental contents (%) of C, 10.8; H, 2.09; N, 2.34; P, 0.80; W, 56.9; which are close to the theoretical contents (%) of C, 10.0; H, 2.07; N, 2.33; P, 0.81; W, 57.3.

1.3. Bipy–PW_{12} catalytic property of oxidative degradation of chitosan with H_2O_2

One gram of chitosan was put into 50 mL cone bottle with plug, then 14.5 mL of water, 5.5 mL of hydrogen peroxide (30%), and 0.01 g of Bipy–PW_{12} were sequentially added. The mixture was stirred at 80 °C for 13 min. The intrinsic viscosities of degraded chitosan solutions were determined using an Ubbelodhe viscosimeter by capillary viscometry at 30 °C. Prior to measurement of flow times, chitosan solutions were dissolved in 0.1 mol/L CH_3COONa–0.2 mol/L CH_3COOH solution.[21] The intrinsic viscosities $[\eta]$ were calculated according to the following equation:[28]

$$[\eta] = \frac{\eta_{sp} + 3\ln\eta_r}{4c} \tag{1}$$

Here, η_r, η_{sp} refer to the relative viscosity and the incremental viscosity, respectively, and c is the concentration of chitosan (mg/L). The viscosity average molecular weight (M_v) was calculated according to the following equation:[29]

$$[\eta] = 1.81 \times 10^{-3} M_v^{0.93} \tag{2}$$

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