Journal Name



ARTICLE

Supporting Information

Experimental details

1. Materials and measurements

All reagents were purchased from commercial sources and used without any further purification. Diffraction data sufficient for unit cell determination for compound **1** was determined on a Bruker Apex CCD diffractometer. The structures were solved using the direct methods, completed by subsequent difference Fourier syntheses, and refined by full matrix least-squares procedures on F² with WinGX (1.70) program package (L. J. J. Farrugia, Appl. Crystallogr. 32, 837 (1999)). The CCDC data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. CCDC number 1429061 for **1**, Elemental analyses (C, H and N) were performed on Flash EA 112 CHN Elemental Analyzer; metal elemental analyses were determined by a Leaman inductively coupled plasma (ICP) spectrometer and SpectrAA-220FS atomic absorption spectrophotometer. Infrared spectra of solid samples were obtained on a BRUKER Vertex 70 FTIR spectrometer in the 400–4000 cm⁻¹ region with a KBr pellet. UV electronic spectra were obtained on a Varian Cary 50 Conc UV-vis spectrophotometer.

2. Synthesis

The materials $Na_9[SbW_9O_{33}] \cdot 19.5H_2O$, $Na_{12}[Sb_2W_{22}O_{74}(OH)_2] \cdot 27H_2O$, $Na_8[Sb_2W_{20}Fe^{III}_2O_{70}(H_2O)_6]$ and $Na_9[BiW_9O_{33}] \cdot 19.5H_2O$ were prepared according to the literature¹⁻³ and confirmed by IR spectroscopy.

Compound $Na_2H_4[C_3H_5N_2]_4[Sb_2W_{20}Fe^{II}_2(H_2O)_6O_{70}]\cdot 12H_2O$ (1) was synthesized by a conventional reaction method. $Na_{12}[Sb_2W_{22}O_{74}(OH)_2]\cdot 27H_2O$ (0.3420g, 0.05mmol) was dissolved in 20 ml of 0.5M NaAc/HAc buffer solution containing 0.4mmol hydrazine, the pH value of the solution was adjusted to 3.50 with 6M HCl, 0.03g Fe was added to the solution, after the mixture was stirred 15min, the colour of solution was changed from blue to light brown. 0.1g imidazole and 0.125g sodium sulphite were added to the solution respectively, than the pH value was adjusted to

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	Journal Name		ARTICLE		
3.50. The resulting react	ion mixture was hea	ted to 77 °C for	1 h and t	then filtered v	vhile hot.
Finally, the solution was	slowly evaporated a	at room temper	ature and	brown crystal	s formed
after a few days. (Yield: ().1619g, 0.027 mmol,	53% based on a	antimony.)	Elemental and	alysis (%):
calcd for $C_{12}H_{60}N_8O_{88}Na_3$	Fe ₂ Sb ₂ W ₂₀ C,2.48; H,	1.04; N,1.93; Na	,0.79; Fe,	1.92; Sb,4.19;	W,63.36;
Found: C,2.53; H,1.02; N,	2.12; Na,1.39; Fe, 1.9	9; Sb,4.36; W,63	.03.		

If the $Na_{12}[Sb_2W_{22}O_{74}(OH)_2]\cdot 27H_2O$ was replaced by $Na_9[SbW_9O_{33}]\cdot 19.5H_2O$ or $Na_9[BiW_9O_{33}]\cdot 19.5H_2O$, the reaction solutions were heated to 70 °C and 90 °C. We can acquire two compounds. The IR spectra confirmed that the complexes are isomorphic.

3. Titrimetric analysis of compound 1 with potassium permanganate

The molar concentration of potassium permanganate was 0.350mmol/L, which was calibrated by using the standard solution of sodium oxalate. Solution A: 0.4272g compound 1 was disolved in 0.2M H₂SO₄, and then the solution was transfered to 10 ml volumetric flask. 1.00 ml solution A,1.00 ml 2M H₂SO₄ and 20 ml water were transfered to erlenmeyer flask, then titrated with standard potassium permanganate solution. In the parallel titrimetric experiments of three times, the consumed volume of potassium permanganate solution was 8.68 ml, 8.65 ml, and 8.67 ml, respectively, which corresponds to the ammount of Fe²⁺ at 0.0148 mmol, 0.0148 mmol, and 0.0147 mmol. Thus, the mean of [Fe²⁺]_{found} is 0.0148 mmol, which is in agreement with the [Fe²⁺]_{calc} (0.0148 mmol).

4. (GC/CNTs/Chitosan/POM) modified electrode

The modified electrode was prepared as follow: The GCE was polished before each experiment with 1.0, 0.3 and 0.05 μ m α -Al₂O₃ powder, respectively, and rinsed with water between each polishing step. Then, washed successively with 1:1 nitric acid, acetone and water in ultrasonic bath and dried in air. 10 mg chitosan was dissolved in 10 ml 0.1 M acetic acid with magnetic stirring for some time and 5 mg oxidized CNTs were dispersed in 10 ml 0.1 M acetic acid with ultrasonication for 15 min. The CNTs–chitosan composites were prepared by mixing the above two solutions by ultrasonic agitation over 30 min. Then, 6 μ l of the resulting homogeneous solution was cast on the surface of cleaned GCE, dried at room temperature for 10 h. In order to form a uniform CNTs–chitosan composite film at the GCE surface, a beaker was

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	Journal Name	AR	TICLE	
covered over the elect	rode so that water ca	in evaporate slowly. I	Before every measu	rement, the
CNTs-chitosan modifie	ed electrode was a	ctivated in 0.25 M	NaAc/HAc buffer	solution by
successive cyclic swee	ps between 0.0 and	1.2 V until the volta	mmetric curve was	s stable. The
activation treatments	made the CNTs-chit	osan modified GCE	possess not only s	ensitive and
stable electrochemical	response, but also	low memory effect.	After that, the CN	NTs-chitosan
coated electrode was	dipped in 1 mM com	pound 1 (pH 3.85 Na	aAc/HAc buffer sol	ution) for 20
min. Then, the electroo	de was rinsed and im	mersed in doubly dis	tilled water for and	other 20 min
to remove excess physi	cal adsorbed compou	ınd 1 .		

The limit of detection (LOD) is calculated by Eq: $LOD=3*S_{bl}/m$ (S_{bl} : blank signal standard deviation, m: slope of the calibration curve).



Fig. S1 Comparison of IR spectra. a, compound 1 (red); b, {Bi₂W₁₉Fe₃} (black); c, {Sb₂W₁₉Fe₃} (blue).

The IR spectra of three compounds are shown in Fig. S1. Four characteristic vibration sharp peaks resulting from the polyoxoanions namely v(W-Od), v(Sb/Bi-Oa), v(W-Ob), and v(W-Oc) appear at 943, 879, 773, 728 cm⁻¹ for compound **1**; 941, 876, 779, 734 cm⁻¹ for {Sb₂W₁₉Fe₃} and 945, 880, 790, 725 cm⁻¹ for {Bi₂W₁₉Fe₃}, respectively.

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Fig. S2 (a) Powder XRD pattern of compound **1** (red) and simulated pattern of **1** (green). (b) Powder XRD pattern of compound **1** (red); $\{Sb_2W_{19}Fe_3\}$ (blue) and $\{Bi_2W_{19}Fe_3\}$ (black).

The powder XRD pattern of **1** is in good agreement with the simulated XRD patterns, emonstrating the good phase purity for **1**. In the Fig. S2 (b) we can see that compound **1**, $\{Sb_2W_{19}Fe_3\}$ and $\{Bi_2W_{19}Fe_3\}$ have similar powder XRD patterns. Combining the infrared spectra and XRD patterns of these three compounds, we can conclude that they are isomorphic. Furthermore, similar synthetic method and crystal parameters can also prove that they have similar structures (Table S1).



Fig. S3 The XPS pattern for $W4f_{7/2}$ and $W4f_{5/2}$ in compound 1.

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J. Name., 2015, 00, 1-3 | 4



Fig. S4 The TGA and DTA curve of compound 1.

The TGA curve of Compound **1** exhibits two steps of weight loss in the range of 30-600 $^{\circ}$ C. The first weight loss of 5.55% from 30-125 $^{\circ}$ C corresponds to 18 molecules of water (calc. 5.58%). The second weigh loss is from 126 to 510 $^{\circ}$ C with a value of 4.79%, which is assigned to the loss of 4 molecules of Imidazole ligands (calc. 4.76%), accompanied with the decomposition of the main structure.



Fig. S5 Decolorization rates of MO. Initial concentrations: 0.015g compound 1, MO (10 mg/L, 30 ml, pH=3.5) within 1 ml 30% H_2O_2 .



ARTICLE



Fig. S6 Current–time responses for three (GC/CNTs/Chitosan/POM) modified electrodes at 0.3 V with the addition of 0.7 to 19.8 μ M ascorbic acid. (a, compound **1**; b, [Sb₂W₂₀Fe^{III}₂O₇₀]⁸⁻; c, Na₁₂Sb₂W₂₂O₇₄)

Three modified electrodes have different responses for the same ascorbic acid. The modified electrode with compound **1** and $[Sb_2W_{20}Fe^{III}_2O_{70}]^{8-}$ has a good and well-defined amperometric response than $Na_{12}Sb_2W_{22}O_{74}$. So the introduction of transition metal iron is beneficial for detection of ascorbic acid. The modified electrode with compound **1** have a higher amperometric response than $[Sb_2W_{20}Fe^{III}_2O_{70}]^{8-}$. So the modified electrode with compound **1** have a higher amperometric response than $[Sb_2W_{20}Fe^{III}_2O_{70}]^{8-}$. So the modified electrode with compound **1** may have high sensitivity.



Fig. S7 Diffuse reflectance UV-vis spectra of K-M function versus E (eV). (a) The E_g value assessed from the steep absorption edge is 2.2 eV for compound **1**, (b) the E_g value is 2.1 eV for {Sb₂W₁₉Fe₃} and (c) the E_g value is 1.6 eV for {Bi₂W₁₉Fe₃}.

Journal Name	ARTICLE
The plot of transformed Kubelka-Munk function v	ersus the energy of light affords band gap energies

of 2.2, 2.1 and 1.6 eV for compound 1, {Sb₂W₁₉Fe₃} and {Bi₂W₁₉Fe₃}, respectively. Here, UV-Vis diffuse

reflectance spectra are used to obtain the band gap energies of Krebs-type polyoxometalates.



Fig. S8 The CVs of the (GC/CNTs/Chitosan/compound **1**) modified electrode in 0.25 M NaAc/HAc buffer solution at different time.

The quasi-reversible redox peaks located at +0.163 V (I-I') and 0.001 V (II-II') are assigned to oneelectron Fe^{III}/Fe^{II} redox process. The redox peaks of Fe^{III}/Fe^{II} could be maintained after an hour, which proves that the ferrous ions in the modified electrode are stable during the ascorbic acid sensing experiment.



Fig. S9 Current–time responses for the (GC/CNTs/Chitosan/compound 1) modified electrode at 0.3 V with the addition of 0.7 to 19.8 μ M ascorbic acid.

The Fig. S9 shows that reused modified electrode has almost the same amperometric response in the ascorbic acid solution with lower concentration. With the increase of the usage frequency, the modified electrode has a worse linear response, especially for high concentration ascorbic acid solution.



Fig. S10 pH stability test of compound 1.

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J. Name., 2015, 00, 1-3 | 8

	Journal Name	ARTICLE	
The compound 1 is st	able at pH 3 to 7. If the co	mpound 1 is dissolved in solution	with pH less than 3,
it will slowly decompose	e into isopolyacid. The abs	sorbance at 200nm will be rising.	With increasing pH
from 4 to 8, the absor	bance at 275nm decrease	gradually. Compound 1 gradually	v decomposes. Two
absorption bands at 20	5 nm and 275 nm is attrib	uted to the charge transfer transit	tion of $O_t \rightarrow W$ and
$O_{b,c} \rightarrow W$ in compound	1.		



Fig. S11 Response of modified electrode for 100 µl ascorbic acid in solution. (GC/CNTs/Chitosan/POM) modified electrode has a good response compared with the electrode without POM.

Table ST	The crystal	data for	Compound 1	., {BI2VV ₁₉ Fe ₃ }	$and {SD}_2 vv_{19} Fe_3$.	

	a/Å	b/Å	c/Å	α/ °	в/ °	γ/ °	V/ų	space group
Compound 1	13.017	13.539	17.702	68.517	79.923	62.222	2568.4	triclinic, P-1
${Bi_2W_{19}Fe_3}$	13.173	13.503	17.593	68.467	79.468	61.639	2561.42	triclinic, P-1
$\{Sb_2W_{19}Fe_3\}$	13.262	13.551	17.677	68.030	79.199	61.050	2577.88	triclinic, P-1

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Notes and references

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J. Name., 2015, 00, 1-3 | 9