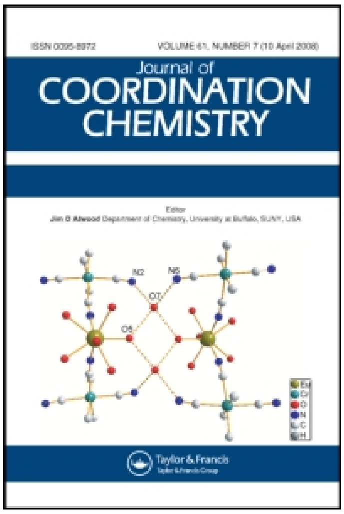

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Ionothermal synthesis and characterization of two new heteropolytungstates with 1-ethyl-3-methylimidazolium bromide ionic liquid as solvent

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Ionothermal synthesis and characterization of two new heteropolytungstates with 1-ethyl-3-methylimidazolium bromide ionic liquid as solvent

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In this article, we have synthesized two new heteropolytungstate-based compounds $[EMIM]_4[SiW_{12}O_{40}]$ (**1**) and $[EMIM]_6[P_2W_{18}O_{62}] \cdot 4H_2O$ (**2**) using the ionic liquid (IL) [EMIM]Br (EMIM = 1-ethyl-3-methylimidazolium) as a solvent and characterized them by infrared (IR) and ultraviolet (UV) spectra, thermogravimetric (TG) and elemental analyses, electrochemistry, and single-crystal X-ray analyses. Compound **1** is constructed from one $[SiW_{12}O_{40}]^{4-}$ and four $[EMIM]^+$. In the structure, $[SiW_{12}O_{40}]^{4-}$ and $[EMIM]^+$ are connected by hydrogen bonds with the surface oxygens of the polyoxoanion to form a 3-D supramolecular framework. The heteropolyanion of **2** is a classical Dawson-type structure $[P_2W_{18}O_{62}]^{6-}$ and connected with six cations through hydrogen bonds. The structures of these two heteropolyanions are consistent with those synthesized by traditional methods, indicating that ionothermal synthesis is an effective method for the preparation of heteropolyoxometalates. The photocatalytic properties of these compounds have also been investigated.

Keywords: Polyoxometalates; Ionothermal synthesis; Photocatalysis; Crystal structure

1. Introduction

Ionothermal synthesis is a new material synthesis method in which ionic liquids (ILs) act as reaction media, templates, or charge-compensating groups [1]. ILs are salts which are liquid at low temperature, usually composed of large organic cations, such as imidazolium, pyridinium, pyrrolidinium, quaternary ammonium, or phosphonium ions, and counter anions including inorganic or organic species. The irregularly shaped organic cations do not allow close packing of the ionic species into solids, thereby lowering the melting points to ambient temperature [2]. As a result, they have the characters of high fluidity, low melting temperature, high boiling temperature, high thermal stability, non-flammability, and very low vapor pressure [3]. With these attributes, ionothermal synthesis is considered to be more environment friendly and safer than conventional solution synthesis and hydro(solvo)thermal synthesis.

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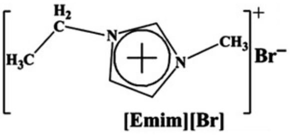
Polyoxometalates (POMs) have attracted large interest because of their compositional diversity and series of potential applications in catalysis, photochemistry, magnetism, and electrochemistry [4]. Evolution of POM chemistry is dependent upon exploring suitable methods for synthesis. Conventional solution synthesis and hydro(solvo)thermal synthesis are the two main ways of synthesizing POMs. The solvents of these systems have been largely restricted to water and a few organic solvents. However, the temperature of these systems may not reach too high, because the boiling points of most used solvents are lower than 100°C. Therefore, it is necessary to explore new synthetic methods to synthesize POMs. Recently, change of the solvent to ILs has been reported in the synthesis of zeotypes [5, 6], molecular sieves [7], and metal–organic frameworks (MOFs) [8, 9]. As an extension of our study of synthetic POM chemistry, we focus on the ionothermal synthesis of POMs.

We have synthesized two POMs: $[EMIM]_4(W_{10}O_{32})$ and $[EMIM]_4(W_6O_{19})(BF_4)_2$, indicating that ionothermal synthesis is effective for the preparations of isopolyoxometalates [10]. As a continuation, in this article, we isolated two heteropolyoxometalates $[EMIM]_4[SiW_{12}O_{40}]$ (**1**) and $[EMIM]_6[P_2W_{18}O_{62}] \cdot 4H_2O$ (**2**) by ionothermal synthesis using [EMIM]Br (scheme 1) as a solvent. Compound **1** is constructed from one $[SiW_{12}O_{40}]^{4-}$ and four $[EMIM]^+$. Heteropolyanion **2** is a classical Dawson-type structure $[P_2W_{18}O_{62}]^{6-}$, connected with six $[EMIM]^+$ through hydrogen bonds. The structures of heteropolyanions are consistent with those synthesized conventionally, indicating that the ionothermal synthesis method is effective for the preparation of heteropolyoxometalates.

2. Experimental

2.1. *Materials and methods*

All reagents were purchased commercially and used without purification. The IL, [EMIM]Br, was synthesized according to procedures in the literature [11]. Elemental analyses (C, H, and N) were obtained with a Perkin Elmer 2400 CHN elemental analyzer; W was analyzed on a PLASMA-SPE (I) ICP atomic emission spectrometer. Infrared (IR) spectra were recorded from 4000 to 400 cm^{-1} on an Alpha Centauti Fourier transform (FT)-IR spectrophotometer using KBr pellets. Ultraviolet visible (UV-Vis) absorption spectra were recorded on a 756 CRT UV-Vis spectrophotometer. Diffuse reflectance UV-Vis spectra (BaSO4 pellet) were obtained with a Varian Cary 500 UV-Vis NIR spectrometer. Thermogravimetric (TG) analyses were performed on a Perkin Elmer TGA7 in flowing N_2 with a heating rate of 10°C min^{-1}. Electrochemical experiments were carried out on a BAS Epsilon Analyzer in a three-electrode cell: glassy



Scheme 1. The structure of the IL [Emim]Br.

carbon electron (GCE, diameter 3 mm) as a working electrode, platinum wire as a counter electrode, and Ag/AgCl/KCl (3 mol L^{-1}) as a reference electrode.

2.2. *Synthesis of 1*

Compound **1** was prepared by mixing $Na_2WO_4 \cdot 2H_2O$ (1 g, 3.0 mmol L^{-1}) and $Na_2SiO_3 \cdot 9H_2O$ (0.42 g, 1.5 mmol L^{-1}) in 2.0 g of [EMIM]Br and 0.5 mL of glacial acetic acid, then heating in a Teflon-lined autoclave (20 cm^3) for 3 days at 150°C, followed by slowly cooling to ambient temperature resulting in yellow crystals in 48% yield based on W. Elemental analysis for $C_{24}N_8H_{44}SiW_{12}O_{40}$ (3318.8), Calcd (%): W, 66.47; N, 3.37; C, 8.69; and H, 1.34. Found (%): W, 66.15; N, 3.52; C, 8.28; and H, 1.13.

2.3. *Synthesis of 2*

Compound **2** was prepared by mixing $Na_2WO_4 \cdot 2H_2O$ (1 g, 3.0 mmol) and $Na_2HPO_4 \cdot 12H_2O$ (0.358 g, 1 mmol) in 2.0 g of [EMIM]Br and 0.5 mL of glacial acetic acid, then heating in a Teflon-lined autoclave (20 cm^3) for 3 days at 150°C followed by slowly cooling to ambient temperature, resulting in blue crystals in 36% yield based on W. Elemental analysis for $C_{36}N_{12}H_{74}P_2W_{18}O_{66}$ (5094.3), Calcd (%): W, 64.86; N, 3.29; C, 8.47; and H, 1.46. Found (%): W, 64.52; N, 3.57; C, 8.13; and H, 1.23.

2.4. *X-ray crystallography*

Measurements for **1** and **2** were performed on a Rigaku R-AXIS RAPID IP diffractometer. The data were collected at 150(2) K and graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) was used. The structures were solved by direct methods and refined by full matrix least-squares on F^2 using *SHELXL-97* [12]. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogens on their parent *C* and *N* atoms were fixed in geometrically calculated positions. Crystal data and structure refinement for **1** and **2** are summarized in table 1. Selected bond lengths and angles for **1** and **2** are listed in tables S1 and S2.

2.5. *Photocatalysis experiments*

To study the photocatalytic properties of **1** and **2**, we added 13.3 mg of **1** to 200 mL of rhodamine B(RhB) solutions (2.0×10^{-5} mol L^{-1}), and then magnetically stirred them in the dark for 30 min. The solution was then exposed to UV irradiation from a 125 W Hg lamp at a distance of 4–5 cm between the liquid surface and the lamp. The solution was stirred during irradiation. At 60 min intervals, 3 mL of samples were taken from the beaker and subsequently analyzed by UV-Vis spectroscopy. An identical procedure was followed for **2**, except that 13.3 mg was replaced with 20.4 mg. The photocatalytic performance of **1** and **2** were investigated for the photodegradation of RhB.

Table 1. Crystal data and structure refinement for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{24}N_8H_{44}SiW_{12}O_{40}$	$C_{66}N_{12}H_{74}P_2W_{18}O_{74}$
Formula weight	3318.7	5590.3
Temperature (K)	150(2)	150(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P\ 2_1/c$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	13.149(3)	15.387(3)
b	13.581(3)	16.713(3)
c	20.287(6)	22.763(5)
α	90	71.25(3)
β	127.29(2)	90.00(3)
γ	90	62.59(3)
Volume (Å^3), Z	2882.2(13), 2	4844.1(17), 2
Reflections collected	21,350	36,969
Reflections unique	4940	16,557
Data/restraints/parameters	4940/150/379	16,557/249/1182
Goodness-of-fit on F^2	1.114	0.910
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0757$, $wR_2 = 0.1627$	$R_1 = 0.0639$, $wR_2 = 0.1353$
R indices (all data)	$R_1 = 0.0947$, $wR_2 = 0.1753$	$R_1 = 0.1354$, $wR_2 = 0.1637$

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

3. Results and discussion

3.1. *Syntheses*

There are some main impact factors in the ionothermal synthesis, such as the amount of ILs, the molar ratio of the reactants and ILs, the amount of acid added to the reaction mixture, reaction time and temperature, crystallization time, etc. A series of parallel experiments indicate that two key factors are important in the ionothermal synthesis of **1** and **2**. First, the amount of acid added to the reaction mixture. During the reactions, only by adding 0.5 mL glacial acetic acid can we successfully obtain crystals **1** and **2**. Also, no analogous compound was obtained by replacing glacial acetic acid by hydrochloric acid. Second, the reaction temperature plays an important role in the synthesis of **1** and **2**. If the reaction temperature is lower than 150°C, no crystals were obtained.

3.2. *Structure description*

The molecule structure of **1** is constructed from one $[SiW_{12}O_{40}]^{4-}$ and four $[EMIM]^+$ cations (figure 1). $[SiW_{12}O_{40}]^{4-}$ shows a typical α-Keggin structure. Si–O bonds range from 1.44(9) to 1.70(8) Å. All tungstens have $\{WO_6\}$ octahedral environments and are disposed in four groups $\{W_3O_{13}\}$ of three edge-sharing octahedra, each joined to adjacent groups and to the central tetrahedron-sharing corners. Tungstens are not at the center of the octahedron, but located toward the terminal oxygen giving the following distribution of distances: W–O_a (center oxygen atom), 2.279(9)–2.495(9) Å; W–$O_{b/c}$ (bridging oxygen atom), 1.65(3)–2.49(8) Å; and W–O_d (terminal oxygen atom), 1.644(4)–1.71(2) Å. These bond distances agree with those previously reported for

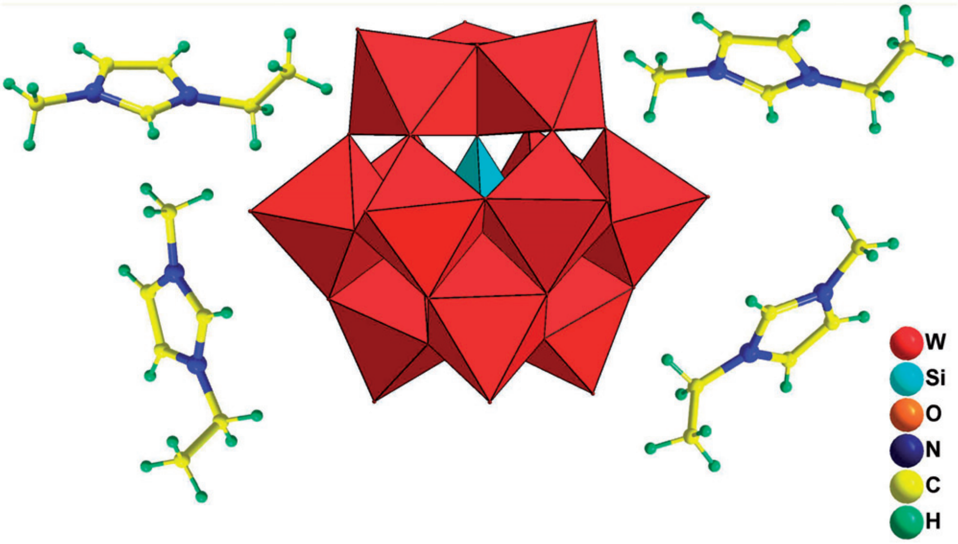


Figure 1. Polyhedral and ball-and-stick representation of **1**.

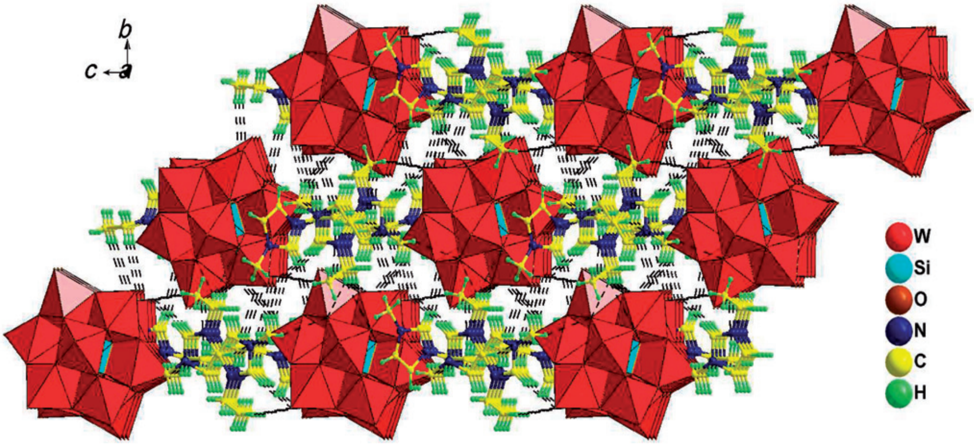


Figure 2. The 3-D hydrogen-bonded supramolecular framework of **1**.

α-Keggin anions. Each $[EMIM]^+$ is surrounded by four polyoxoanions and connected by surface oxygens forming a 3-D supramolecular framework (figure 2 and table S3).

X-ray structural analysis reveals that **2** consists of one α-$[P_2W_{18}O_{62}]^{6-}$ unit, four water molecules, and six $[EMIM]^+$. As shown in figure 3, the heteropolyanion maintains a classical α-Dawson-type structure, containing two $[\alpha\text{-A-}PW_9O_{34}]^{9-}$ units derived from an α-Keggin anion by the removal of a set of three corner-shared WO_6 octahedra [13]. The polyanion which is close to D_{3h} point symmetry contains two types of tungstens, 6 at "polar" positions and 12 at "equator" positions. The two tetrahedrally coordinated phosphoruses are surrounded by four oxygens with P–O distances from 1.514(16) to 1.565(17) Å (mean value, 1.5365 Å). The W–O distances

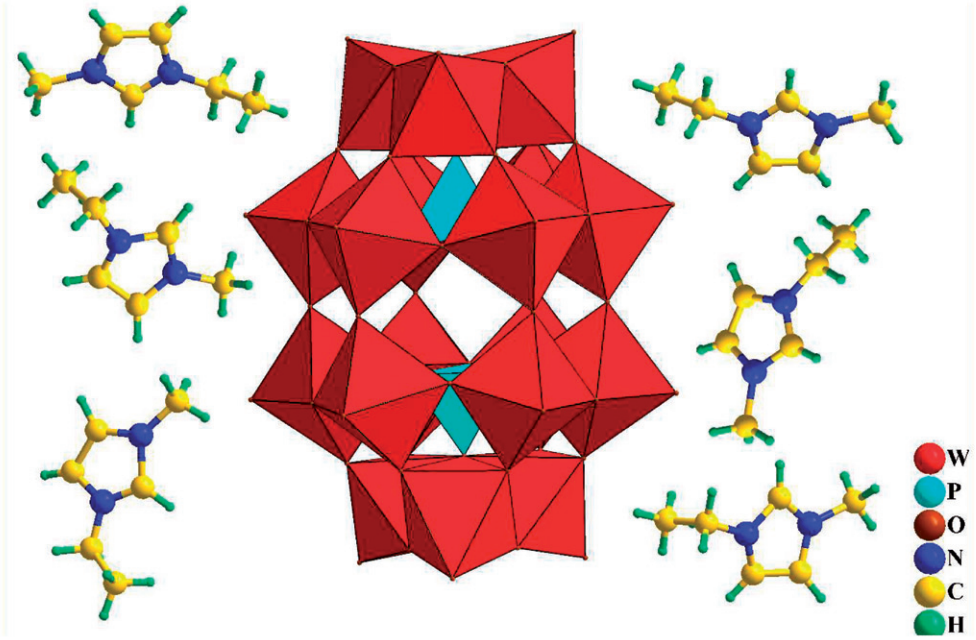


Figure 3. Polyhedral and ball-and-stick representation of **2**.

vary over a wide range of 1.66(2)–2.394(19) Å and can be divided into three groups: (1) The W–O_d (O_d terminal oxygen) bonds are in the usual range of 1.66(2)–1.733(19) Å; (2) W–$O_{b/c}$ ($O_{b/c}$ bridging oxygen) distances vary from 1.67(1) to 2.394(19) Å; and (3) the longest W–O_a (O_a oxygen coordinated with *P* atom) bonds are in the range of 2.25(18)–2.94(19) Å. These bond distances are in accord with those previously reported for α-Dawson anions. Around the polyoxoanion, there are six $[EMIM]^+$ to balance the charge. Each anion is surrounded by six $[EMIM]^+$ cations and are water hydrogen bonded to form a 3-D supramolecular framework (figure 4 and table S4).

3.3. *Electrochemistry*

Before electrochemical research, the stability of **1** and **2** (figures S5 and S6) in aqueous solution was evaluated by monitoring their UV-Vis spectrum and cyclic voltammograms (CV) over a period of 42 h. Figure 5 shows typical cyclic voltammetric behavior of **1** in 40 mL of 0.5 mol L^{-1} H_2SO_4 aqueous solution at different scan rates. In the potential range of 600−800 mV, three redox peaks appear and $E_{1/2} = (E_{pa} + E_{pc})/2$ are −561(I), −411(II), and 200(III) mV (scan rate: 100 mV s^{-1}). The three peaks I–I′, II–II′, and III–III′ correspond to the redox of the W^{VI} in the polyoxoanion framework. The electrochemical properties of **2** were detected in 40 mL of 1 mol L^{-1} H_2SO_4 at different scan rates (figure 6). Three peaks in the potential range of 800−800 mV have mean peak potentials, and $E_{1/2} = (E_{pa} + E_{pc})/2$ are −612(I), −353(II), and −128(III) mV at a scan rate of 100 mV s^{-1} [13].

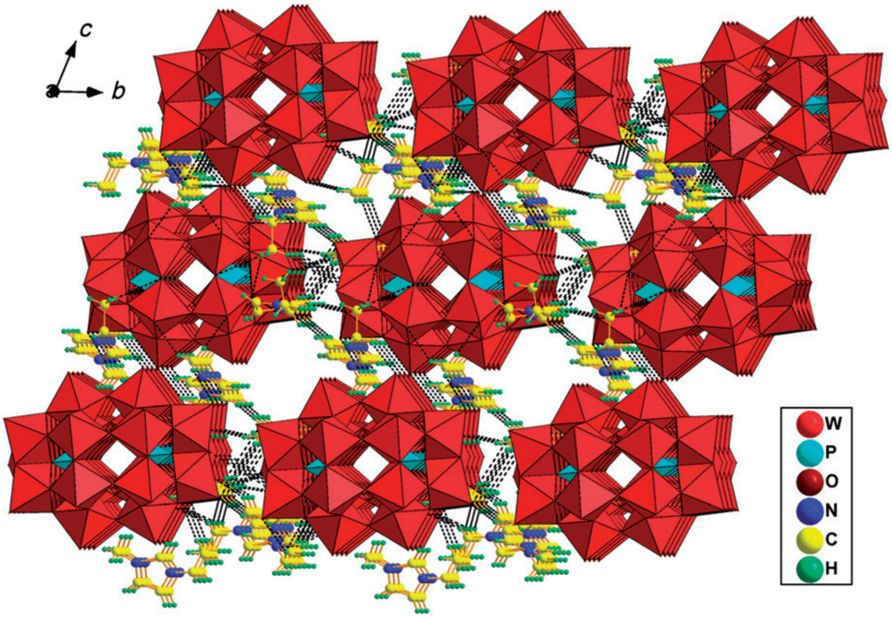


Figure 4. The 3-D hydrogen-bonded supramolecular framework of **2**.

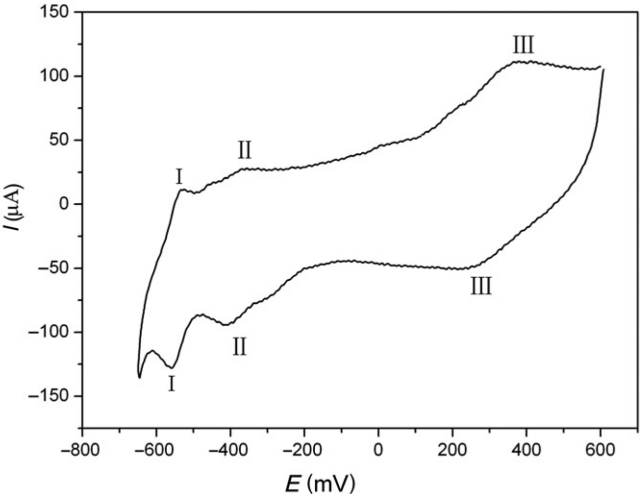


Figure 5. The electrochemistry of **1**.

3.4. *Photocatalysis property*

UV-Vis diffuse reflectance spectra of **1** and **2** are shown in figure 7. The absorptions of **1** and **2** are mostly in the UV region. With $\lambda_g(\text{nm}) = 1240/E_g(\text{eV})$ we can calculate an effective band gap, where $\lambda_g(\text{nm})$ is the corresponding long-wave absorption edge

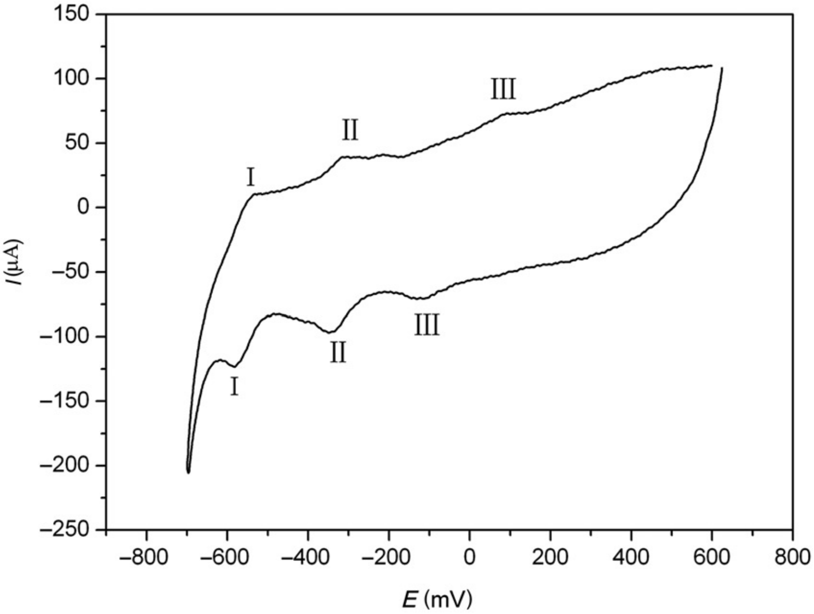


Figure 6. The electrochemistry of **2**.

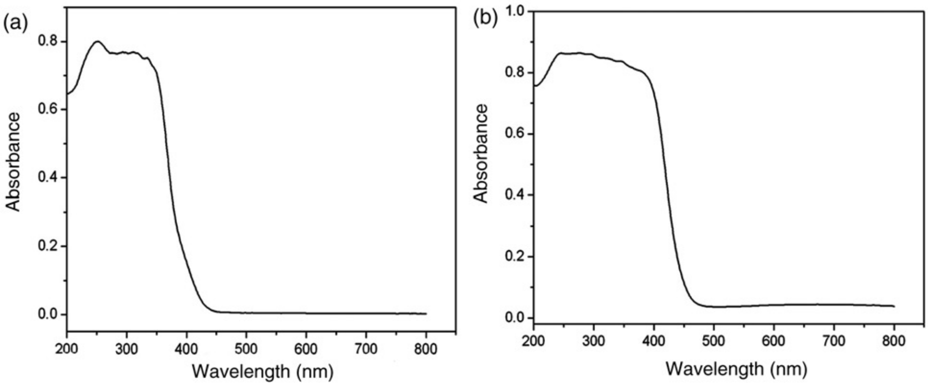


Figure 7. (a) UV-Vis diffuse reflectance spectra of **1**. (b) UV-Vis diffuse reflectance spectra of **2**.

wavelength λ_{max} (350 nm for **1** and 394 nm for **2**). After calculation, the effective band gap of **1** is 3.54 eV and 3.15 eV for **2**, showing some photocatalytic activity. The changes in UV-Vis absorption spectra of RhB solutions with different photocatalysts are shown in figure 8. For **1**, the UV-Vis absorption of RhB decreased from 1.23 to 0.62 in the irradiation time 0 – 300 min ($\lambda = 554$ nm). For **2**, the UV-Vis absorption of RhB decreased from 1.45 to 0.91 in the irradiation time of 0 – 300 min ($\lambda = 554$ nm). The absorption intensity decreased upon irradiation, indicating that the title compounds have good photocatalytic properties for the photocatalytic degradation of RhB.

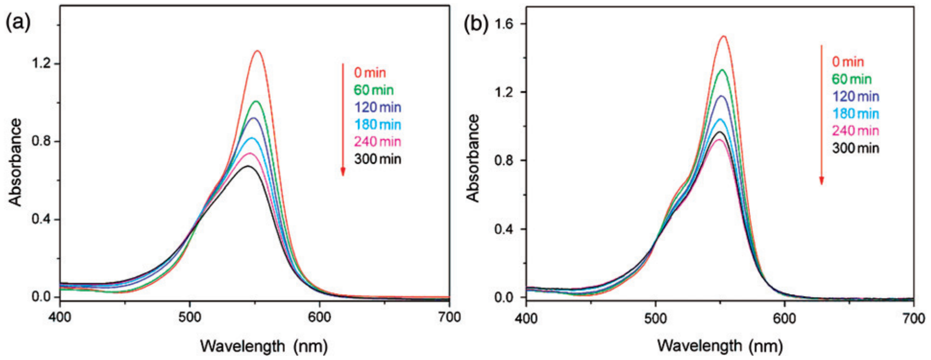


Figure 8. Changes in UV-Vis absorption spectra of RhB solutions ($2 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$) in the presence of (a) 13.3 mg of **1** and (b) 20.4 mg of **2**.

3.5. *IR spectrum*

IR spectrum of **1** has four characteristic vibrational bands resulting from the α-Keggin-type heteropolyanion, ν(P–O_a), ν(W–O_a), ν(W–O_b–W), and ν(W–O_c–W) appearing at 1168, 973, 919, and 786 $\mathrm{cm^{-1}}$, respectively (O_d-terminal oxygen, O_b-bridged oxygen of two octahedral sharing a corner, and O_c-bridged oxygen of two octahedral sharing an edge). Bands at 1375, 1512, 1627, and 1694 $\mathrm{cm^{-1}}$ are attributed to characteristic vibrations of $[\mathrm{EMIM}]^+$ (figure S3). In the IR spectrum of **2**, four characteristic vibrational bands from the α-Dawson-type heteropolyanion, ν(P–O_a), ν(W–O_d), ν(W–O_b–W), and ν(W–O_c–W) appear at 1089, 958, 906, and 779 $\mathrm{cm^{-1}}$, respectively. Peaks at 522, 1564, 1456, 1376, and 1382 $\mathrm{cm^{-1}}$ are characteristic vibrations of $[\mathrm{EMIM}]^+$ (figure S4).

3.6. *TG analyses*

The thermal behavior of **1** and **2** have been investigated between 30°C and 600°C. Thermal analysis of **1** gives a loss of 13.83% in the range of 380–400°C, which agrees with the calculated weight loss of 13.69% corresponding to the loss of $[\mathrm{EMIM}]^+$ (figure S7). The thermal analysis of **2** exhibits two steps of weight loss. Weight loss (30–150°C) is attributed to the dehydration of **2** (crystallization water molecules) (found: 1.35%; Calcd: 1.43%). A second weight loss (280–430°C) is assigned to the loss of six $[\mathrm{EMIM}]^+$, and 13.42% loss agrees with the calculated value of 13.31% (figure S8). The TG analysis is in agreement with the structure determination.

4. Conclusion

We have synthesized two new heteropolyoxometalates using ionothermal synthesis, in which IL acts as both solvent and charge compensating species. The structures of these two POMs are consistent with those synthesized by traditional methods, indicating that ionothermal synthesis is effective for the preparation of POMs, opening up a new possibility in the synthesis of POMs. We are particularly interested in applying this methodology to synthesize new POM-based aggregates where new chemistry could lead to exciting solids.

Supplementary materials

The IR spectra, UV spectra, and TG curves of **1** and **2** and the additional tables are available. Crystallographic data have been deposited with the Cambridge Crystallography Data Centre (CCDC) as deposition numbers CCDC-751482 for **1** and CCDC-751481 for **2**. The data can be obtained, free of charge, from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK *via* (Fax +44 1223 336033 or Email deposit@ccdc.cam.ac.uk).

Acknowledgments

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References

[1] L. Xu, E.Y. Choi, Y.U. Kwon. *Inorg. Chem.*, **46**, 10670 (2007).
[2] L. Xu, E.Y. Choi, Y.U. Kwon. *J. Solid State Chem.*, **181**, 3185 (2008).
[3] (a) P. Wasserscheid, W. Keim. *Angew. Chem. Int. Ed.*, **39**, 3926 (2000); (b) N.E. Leadbeater, H.M. Torenius. *J. Org. Chem.*, **67**, 3145 (2002); (c) Y.J. Zhu, W.W. Wang, R.J. Qi, X.L. Hu. *Angew. Chem. Int. Ed.*, **43**, 1410 (2004); (d) J. Dupont, R.F. de Souza, P.A.Z. Suarez. *Chem. Rev.*, **102**, 3667 (2002).
[4] (a) M.T. Pope. *Heteropoly and Isopoly Oxometalates*, Springer Verlag, Berlin (1983); (b) D.L. Long, E. Burkholder, L. Cronin. *Chem. Soc. Rev.*, **36**, 105 (2007); (c) A. Müller, F. Peters, M.T. Pope, D. Gatteschi. *Chem. Rev.*, **98**, 239 (1998); (d) M.T. Pope, A. Müller. *Angew. Chem. Int. Ed.*, **30**, 34 (1991); (e) A. Müller. *Nature*, **352**, 115 (1991); (f) H.T. Evans. *J. Am. Chem. Soc.*, **70**, 1291 (1948); (g) P. Gouzerh, M. Che. *Actual. Chim.*, **298**, 1 (2006); (h) J.S. Anderson. *Nature*, **140**, 850 (1937).
[5] E.R. Cooper, C.D. Andrews, P.S. Wheatley, P.B. Webb, P. Wormald, R.E. Morris. *Nature*, **430**, 1012 (2004).
[6] (a) E.R. Parnham, R.E. Morris. *Chem. Mater.*, **18**, 4882 (2006); (b) J. Ranke, S. Stolte, R. Störmann, J. Arning, B. Jastorff. *Chem. Rev.*, **107**, 2183 (2007); (c) E.R. Parnham, R.E. Morris. *J. Am. Chem. Soc.*, **128**, 2204 (2006); (d) R.E. Morris. *Angew. Chem. Int. Ed.*, **47**, 442 (2008); (e) E.R. Parnham, P.S. Wheatley, R.E. Morris. *Chem. Commun.*, 380 (2006).
[7] (a) H.J. Ma, Z.J. Tian, R.S. Xu, B.C. Wang, Y. Wei, L. Wang, Y.P. Xu, W.P. Zhang, L.W. Lin. *J. Am. Chem. Soc.*, **130**, 8120 (2008); (b) E.A. Drylie, D.S. Wragg, E.R. Parnham, P.S. Wheatley, A.M.Z. Slawin, J.E. Warren, R.E. Morris. *Angew. Chem. Int. Ed.*, **46**, 7839 (2007).

[8] (a) Z.J. Lin, A.M.Z. Slawin, R.E. Morris. *J. Am. Chem. Soc.*, **129**, 4880 (2007); (b) K. Jin, X.Y. Huang, L. Pang, J. Li, A. Appel, S. Wherland. *Chem. Commun.*, 2872 (2002); (c) Z.J. Lin, D.S. Wragg, J.E. Warren, R.E. Morris. *J. Am. Chem. Soc.*, **129**, 10334 (2007).

[9] (a) E.R. Parnham, R.E. Morris. *Acc. Chem. Res.*, **40**, 1005 (2007); (b) L. Xu, E.Y. Choi, Y.U. Kwon. *Inorg. Chem.*, **47**, 1907 (2008); (c) L. Xu, E.Y. Choi, Y.U. Kwon. *Inorg. Chem. Commun.*, **11**, 150 (2008); (d) S.M. Chen, J. Zhang, X.H. Bu. *Inorg. Chem.*, **47**, 5567 (2008); (e) C.P. Tsao, C.Y. Sheu, N.K. Nguyen, K.H. Lii. *Inorg. Chem.*, **45**, 6361 (2006); (f) Z.J. Lin, D.S. Wragg, R.E. Morris. *Chem. Commun.*, 2021 (2006); (g) D.N. Dybtsev, H. Chun, S.H. Yoon, D. Kim, K. Kim. *J. Am. Chem. Soc.*, **126**, 32 (2004).

[10] N. Zou, W.L. Chen, Y.G. Li, W.L. Liu, E.B. Wang. *Inorg. Chem. Commun.*, **11**, 1367 (2008).

[11] S.V. Dzyuba, R.A. Bartsch. *J. Heterocycl. Chem.*, **38**, 265 (2001).

[12] G.M. Sheldrick. *SHELXL97*, *Program for Crystal Structure Refinement*, University of Gottingen, Gottingen, Germany (1997); G.M. Sheldrick. *SHELXS97*, *Program for Crystal Structure Solution*, University of Gottingen, Gottingen, Germany (1997).

[13] (a) J.P. Wang, J.W. Zhao, J.Y. Niu. *J. Mol. Struct.*, **697**, 191 (2004); (b) Y. Lu, Y. Xu, Y.G. Li, E.B. Wang, X.X. Xu, Y. Ma. *Inorg. Chem.*, **45**, 2055 (2006); (c) A.X. Tian, Z.G. Han, J. Peng, J.L. Zhai, Y.L. Zhao. *Z. Anorg. Allg. Chem.*, **633**, 495 (2007).