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PAPER

Assembly of a phospho-molybdc Wells–Dawson-based silver coordination polymer derived from Keggin polyoxoanion cluster†

Dong-Bin Dang, Bing An, Yan Bai* and Jing-Yang Niu*

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A 2D Wells–Dawson-based silver(I) coordination polymer was achieved based on silver-Schiff base building blocks and $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ clusters using AgNO_3 , *N,N'*-bis(furan-2-ylmethylene)hydrazine and Keggin $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ as original materials at room temperature. It is structurally characterized by IR spectroscopy, ^{31}P NMR, XRPD, thermogravimetric (TG) analyses and X-ray crystallography. The structure of **1** exhibits a novel crystalline 2D coordination polymer constructed by the coordination interaction between the Wells–Dawson polyoxoanion $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ and Ag–L species. The luminescent property of **1** in the solid state is investigated.

Introduction

Polyoxometalates (POMs) are an attractive and vast class of inorganic materials with a virtually unmatched range of physical and chemical properties applicable to diverse areas of research such as catalysis, photochemistry, electrochromism, sorption, biology and medicine.^{1–4} POMs are structures that contain arrays of corner- and edge-sharing pseudo-octahedrally coordinated MO_6 ($\text{M} = \text{Mo}, \text{W}, \text{V}, \text{Nb}$ etc.) units, with which different numbers and array modes can self-assemble to form various POM clusters, such as Keggin, Wells–Dawson and Anderson.⁵ Because of the large number of potential coordination sites and the relatively weak coordination ability of POMs, embedding them into the framework of the Werner-type solids might be an efficient approach to creating POM-based coordination polymers with novel structures and interesting properties.^{6,7} Although plenty of high-dimensional polymers combining Keggin-type POMs with transition-metal complexes (TMCs) have been reported,^{8–10} only a few examples of high-dimensional POM/TMCs based on Wells–Dawson type anions were reported up to now,^{11,12} especially on $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ anions.⁵ On the other hand, the synthesis of Wells–Dawson phosphomolybdc acid salts is a complicated process: in sequence, refluxing, crystalline precipitating, dissolving, crystallizing, redissolving and recrystallizing. The crux of the matter is that it is quite easy to produce by-products $[\text{PMo}_{12}\text{O}_{40}]^{3-}$.^{13,14} Yet the construction of high-dimensional TMCs modified $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ is still a challenging issue.

Among the transition metal cations adopted to construct POM/TMCs compounds, Ag(I) is an excellent candidate and

employed for its ability to form from 2 up to 8 bonds with various donors in a wide range of observed coordination geometries, such as linear, T-type, seesaw, square pyramidal, trigonal-bipyramidal, octahedral and other geometries.^{15,16} Besides, the argentophilicity of Ag(I) may form a $[\text{Ag}–\text{Ag}]^{2+}$ dimer, which provides smart opportunities to extend dimensions of structures.^{17,18} Furthermore, the probable synergistic effect between silver ions and POMs may strongly improve their catalytic selectivity when utilized as catalysts for the oxidation of numerous organic molecules.^{19,20}

Theoretically there are all possible complexes in a solution of molybdate and phosphoric acid, and the equilibrium can be displaced in one direction or another under different conditions.^{13,21} That is to say, in the solution of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ acid, there must exist an equilibrium between Keggin $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ and Wells–Dawson $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ anions. So it provides an opportunity to prepare Wells–Dawson compounds using Keggin species as starting materials through the control of the reaction conditions. On the basis of the aforementioned points, we adopt a strategy that uses transition metal, organic bridging ligand and Keggin $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ acid as starting materials to construct phospho-molybdc Wells–Dawson-based compounds. Herein, using Schiff-base *N,N'*-bis(furan-2-ylmethylene)hydrazine **L** as the ligand, we exploited this convenient method and obtained a 2D Wells–Dawson-based coordination polymer $\text{H}_{0.5}[\{\text{Ag}_3\text{L}_2(\text{DMF})_3\}\{\text{Ag}_2\text{L}(\text{DMF})_{1.5}\}\{\text{Ag}_{0.5}(\text{DMF})(\text{H}_2\text{O})_{0.25}\}(\text{P}_2\text{Mo}_{18}\text{O}_{62})\cdot 1.25\text{H}_2\text{O}$ **1** in a DMF/MeOH environment. To the best of our knowledge, **1** is the first 2D silver polymer containing $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ building blocks synthesized from Keggin species at room temperature.

Experimental

Materials and methods

All the chemicals were of reagent grade quality obtained from commercial sources. Ligand **L** was synthesized by a previously

Institute of Molecular and Crystal Engineering, School of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, P.R. China. E-mail: baiyan@henu.edu.cn, dangdb@henu.edu.cn; Fax: (+86)-378-3881589; Tel: (+86)-378-3881589

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reported procedure and well characterized.^{22,23} $\text{H}_3\text{PMo}_{12}\cdot x\text{H}_2\text{O}$ was synthesized as described in the literature.²⁴ Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 240C analytical instrument. Elemental analyses (P, Mo and Ag) were determined by a Perkin Elmer Optima 2100DV inductively coupled plasma-optical emission spectrometer. IR spectra were recorded in KBr pellets with a Nicolet 170 SXFT-IR spectrophotometer in the 4000–400 cm^{-1} region. X-ray powder diffraction patterns were recorded on a D/max- γ A rotating anode X-ray diffractometer with graphite-monochromatic Cu-K α (mean λ ca. 1.542 Å) radiation at the temperature of 296 K. Thermogravimetric analysis was carried out on a Perkin-Elmer-7 thermal analyzer at a heating rate of 10 °C min^{-1} from 22 to 700 °C, and the luminescent spectra were performed on a Hitachi F-7000 fluorescence spectrophotometer. ³¹P NMR spectra[‡] (162.13 MHz) were measured on a Varian INOVA 400 spectrometer.

Syntheses

$\text{H}_{0.5}[\{\text{Ag}_3\text{L}_2(\text{DMF})_3\}\{\text{Ag}_2\text{L}(\text{DMF})_{1.5}\}\{\text{Ag}_{0.5}(\text{DMF})(\text{H}_2\text{O})_{0.25}\}\text{-}(\text{P}_2\text{Mo}_{18}\text{O}_{62})\cdot 1.25\text{H}_2\text{O}$ **1**. A 3 mL methanol solution of **L** (18.8 mg, 0.1 mmol) was layered onto a mixed solution of AgNO_3 (0.051 g, 0.3 mmol) and $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$ (0.18 g) in DMF (3 mL). The solution was left for one month at ambient temperature in darkness and red crystals were obtained. Yield: 52%. Anal. calcd (found) for $(\text{C}_{46.5}\text{H}_{66}\text{Ag}_{5.5}\text{Mo}_{18}\text{N}_{11.5}\text{O}_{75}\text{P}_2)$: C, 12.79 (12.71); H, 1.52 (1.66); N, 3.69 (3.85); P 1.42 (1.54); Mo 39.54 (40.28); Ag 13.58 (13.91). IR (cm^{-1} , KBr pellet): 3448 (m), 1637 (vs), 1561 (w), 1458 (m), 1390 (w), 1301 (w), 1215 (w), 1145 (w), 1076 (s), 1025 (w), 937 (vs), 904 (s), 823 (s), 781 (vs), 590 (w), 524 (w).

X-ray crystal structure determination

X-ray single crystal diffraction data for polymers **1** was collected on a Siemens SMART-CCD diffractometer with graphite-monochromatic Mo-K α radiation ($\lambda = 0.71073$ Å) using SMART and SAINT programs. The structure was solved by direct method of SHELXS-97²⁵ and refined by full-matrix least-squares methods using the SHELXL-97 program package.²⁶ Anisotropic thermal parameters were refined for all non-hydrogen atoms. The positions of the hydrogen atoms were generated geometrically refined using the riding model.

Polymer **1** crystallizes in the space group $P\bar{1}$. The asymmetric unit consists of one $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ anion, 5.5 Ag(I) centers, 3 ligands, 5.5 coordinated DMF molecules, 0.25 coordination H_2O , 1.25 water molecules of crystallization and 0.5 proton based on charge balance. To assist the refinement, the thermal parameters on adjacent atoms were restrained to be similar for the DMF molecule containing O(70). For the half DMF molecule containing O(73), all bonds were restrained and the thermal parameters on adjacent atoms were restrained to be similar. The DMF molecule coordinated to Ag(6) is rotationally disordered

[‡] The solutions for ³¹P NMR spectra measurements are prepared as follows: first, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, $\text{H}_2\text{P}_2\text{Mo}_{18}\text{O}_{62}$ or the mixed reactants were dissolved in DMF solvent, respectively. Second, the pH value of each solution was adjusted to a specified value by 1 M HNO_3 or 1 M NaOH .

Table 1 Crystal data for polymer **1**

Chemical formula	$\text{C}_{46.5}\text{H}_{66}\text{Ag}_{5.5}\text{Mo}_{18}\text{N}_{11.5}\text{O}_{75}\text{P}_2$
Formula mass	4368.25
Temperature/K	296(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
$a/\text{Å}$	14.677(10)
$b/\text{Å}$	16.798(11)
$c/\text{Å}$	25.188(17)
$\alpha/^\circ$	88.157(14)
$\beta/^\circ$	83.527(16)
$\gamma/^\circ$	67.799(13)
$V/\text{Å}^3$	5713(7)
Z	2
$D_c/\text{g cm}^{-3}$	2.539
Measured reflections	29 426
Independent reflections	19 975
Data/restraints/parameters	19 975/75/1432
μ/mm^{-1}	2.949
Goodness of fit on S	1.022
R_{int}	0.0477
Final R indices [$I > 2\sigma(I)$] ^a	$R_1 = 0.0698$, $wR_2 = 0.1039$
R indices (all data)	$R_1 = 0.1881$, $wR_2 = 0.1713$
Largest residuals/e Å^{-3}	1.560/−2.490
^a $R_1 = \sum F_o - F_c /\sum F_o $, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.	

over two orientations in the refined ratio 0.4028 : 0.5972. The bonds of N(12)–C(46), N(12)–C(47), N(12)–C(48) and O(74)–C(46) were restrained and the thermal parameters on adjacent atoms were restrained to be similar. N(7), C(32), C(33) and C(36) were refined with restraints for the anisotropic displacement parameters. Crystallographic data, data collection parameters and refinement statistics for **1** are listed in Table 1. Relevant interatomic bond distances and bond angles for **1** are given in Table S1.†

Results and discussion

X-Ray crystal structures

Single-crystal X-ray diffraction analysis reveals that the structure of **1** exhibits a novel crystalline 2D coordination polymer constructed by the coordination interaction between the Wells–Dawson polyoxoanion $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ and Ag–L species. The asymmetric unit consists of one $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ anion, 5.5 Ag(I) centers, 3 ligands, 5.5 coordinated DMF molecules, 0.25 coordination H_2O , 1.25 water molecules of crystallization and 0.5 proton based on charge balance (Fig. 1). The polyoxoanion $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ in **1** retains a classical Wells–Dawson structure, which may be described as two $[\text{PMo}_9\text{O}_{34}]^{9-}$ units fused into a cluster of virtual D_{3h} symmetry. The PO_4 tetrahedrons and the MoO_6 octahedra of $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ are distorted to different extents for the sake of the influence of the outer coordination cations.

A significant aspect in the structure of polymer **1** is that, there are 5.5 crystallographically independent silver(I) centers and each has a different coordination environment. Such multi-silver atoms with polytopic coordinating configuration construct an intriguing structure. As shown in Fig. 2, Ag(I) atom is bound to two terminal oxygen atoms O(11), O(16) of two symmetric $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ cores, O(69), O(70) from two DMF molecules and one silver atom Ag(2). The average Ag(I)–O distance is

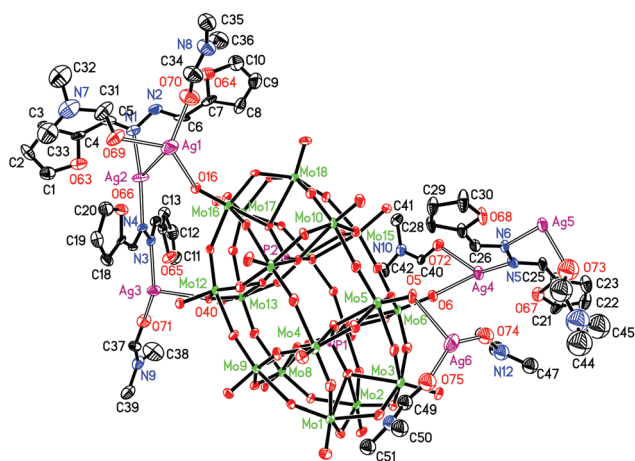


Fig. 1 ORTEP view of polymer **1** with atom labelling (30% probability displacement ellipsoids). All the H atoms and non-coordinated H₂O molecules are omitted for clarity.

2.33 Å. Ag(2) atom is surrounded by Ag(1) and two furanyl-imine units from two ligands with the average Ag(2)–N bond of 2.18 Å and Ag(2)–O bond of 2.73 Å. One of the keys to the framework assembly is the ability of Ag(1) and Ag(2) atoms to connect the particular units by self-organizing into a [Ag₂] dimer with short Ag(1)–Ag(2) separation of 3.286(3) Å which is stabilized by argentophilic metal–metal interactions. Ag(3) exhibits a distorted square pyramidal geometry surrounded with O(12), O(40) of two [P₂Mo₁₈O₆₂]⁶⁻ clusters, O(65), N(3) of one furanyl-imine unit and O(71) from a DMF molecule ($\tau = 0.35$).²⁷ The axial site is situated by bridging oxygen atom O(40) and the planar sites are defined by four other donors with RMS deviation of the contributing atoms of 0.091 Å. Ag(2) and Ag(3) centers are coupled through the two nitrogen atoms of single –N(3)–N(4)– bridge with a Ag...Ag separation of 5.38 Å. Ag(4) is coordinated by two terminal oxygen atoms O(6), O(7) of one [P₂Mo₁₈O₆₂]⁶⁻, O(72) of DMF and N(5) of bridging ligand, exhibiting a seesaw coordination environment ($\tau = 0.63$). There is a weak coordination interaction between Ag(4) and O(67) of the furan ring with a Ag...O distance of 2.88 Å. Ag(5) atom is bound to N(6), O(15), O(68), O(72) and O(73) and shows an intermediate structure between square pyramidal and trigonal bipyramidal with τ approximately 0.5. In the Ag(5) coordination environment, N(6) and O(68) are chelated with Ag(5), whilst O(72) is one shared coordinated atom by Ag(4) and Ag(5) atoms. Simultaneously, Ag(4) and Ag(5) are bridged by one twisted ligand with the Ag...Ag distance of 5.46 Å. And then, a 10-membered four-silver loop is formed through above coordination effects of Ag(4) and Ag(5). The polyoxoanion-supported Ag(6) with the occupancy rate of 0.5 is linked together through a terminal oxygen atom O(5) from the polyoxoanion, while the other coordination sites are occupied by three O donors from two DMF molecules and one water to obtain a seesaw environment ($\tau = 0.75$). The bond distances of Ag–O are in the range of 2.16(3)–2.61(6) Å.

It is worthwhile noticing that the whole structure of polymer **1** shows a 2D microporous layer formed by the connections between [Ag(1)–Ag(2)⋯Ag(3)] coordination segments or 10-member-loop units and [P₂Mo₁₈O₆₂]⁶⁻ polyanions (Fig. 3).

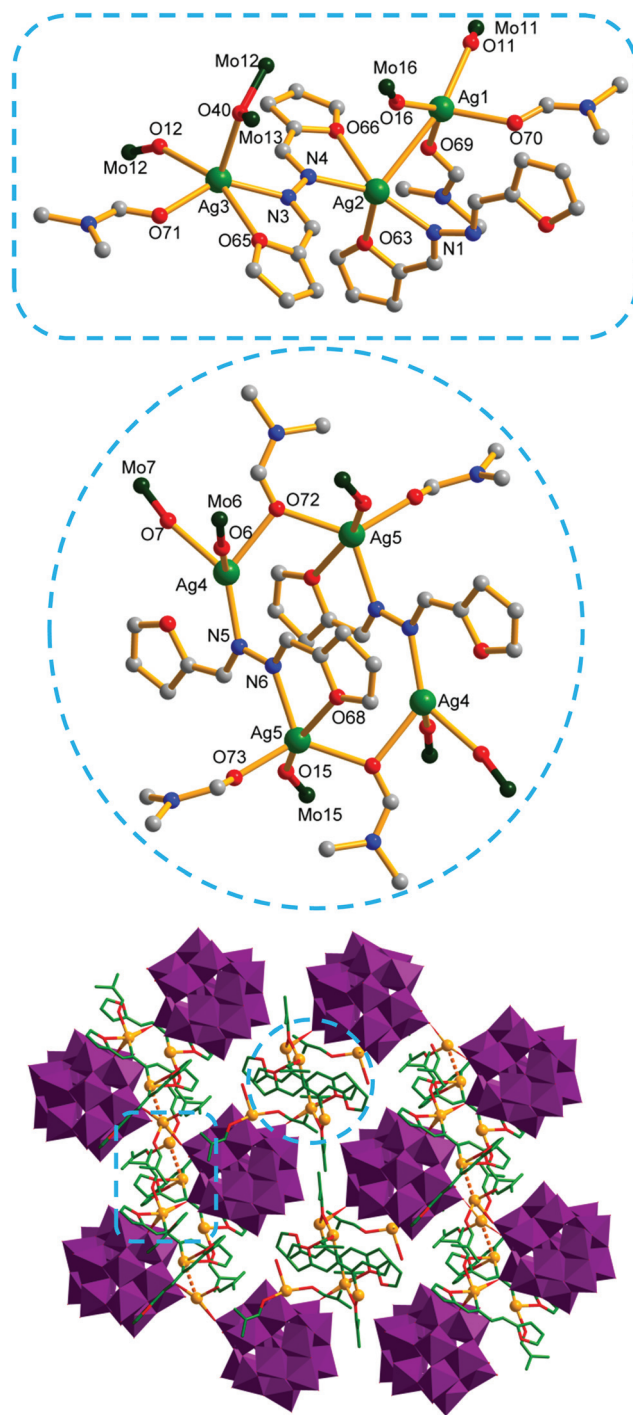


Fig. 2 View of the coordination environments for Ag(1), Ag(2) and Ag(3) (top); view of the coordination environments for Ag(4) and Ag(5) containing a 10-membered four-silver loop (middle); view of a 2D layer in polymer **1** (bottom).

The former segment, [Ag(1)–Ag(2)⋯Ag(3)], links three polyoxoanions by four Ag–O bonds for both Ag(1) and Ag(3) have two arms to couple two polyoxoanions; while four polyoxoanions respectively occupying four vertexes of parallelogram are linked by two symmetric [Ag(1)–Ag(2)⋯Ag(3)] segments. The latter connector, 10-member-loop, is just like claws of octopus to catch hold of four [P₂Mo₁₈O₆₂]⁶⁻ anions *via* six Ag–O bonds. In

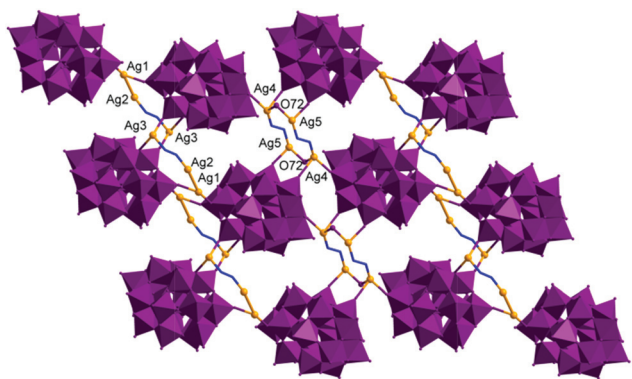


Fig. 3 Linking view of construction of the 2D network in polymer **1** with part atoms of the ligands and solvent molecules omitted for clarity.

terms of polyoxoanions, each $[P_2Mo_{18}O_{62}]^{6-}$ acts as a heptadentate linker coordinating with seven Ag(I) ions through six terminal and one bridge oxygen atoms. Owing to the presence of nanoscale POMs as bridges which allows the existence of inter-space, polymer **1** exhibits a 2D network of micropores which propagates along the crystallographic *a* and *c* axes. Through the intermolecular π - π stacking interactions between the furan rings, the 2D networks further assemble to form a 3D supramolecular structure (Fig. S3[†]). Otherwise, multiform hydrogen bonds and C-H \cdots π interactions are found in the network.

Thermogravimetric analysis

Thermal gravimetric (TG) curve of **1** exhibits a total weight loss of 25.75% from 40 °C to 600 °C, which corresponds to the loss of all water molecules, DMF molecules and organic ligands, accompanying the sublimation of P_2O_5 (Fig. S5[†]).

X-ray powder diffraction

The stability of this network was studied by X-ray powder diffraction (XRPD). As shown in Fig. S6,[†] the experimental XRPD pattern is quite similar to that calculated from the single crystal data, indicating that the bulk product of **1** is pure phase.

Luminescent properties

The solid state luminescent properties of **1** were investigated at room temperature (Fig. 4). Polymer **1** shows the main emission peaks at 400, 448 and 468 nm upon excitation at 290 nm. In comparison with the free ligand,²² two new emission bands at 448 and 468 nm were found. According to literature, the existence of Ag-Ag interactions may play a role in the solid state for the origin of the fluorescence.^{22,28,29} Therefore, the nature of polymer **1** may be attributed to the cooperativity of the intra-ligand π^* - π charge transfer, the coupling of a metal-ligand charge transfer and a metal-centered transition disturbed by argentophilic interactions.

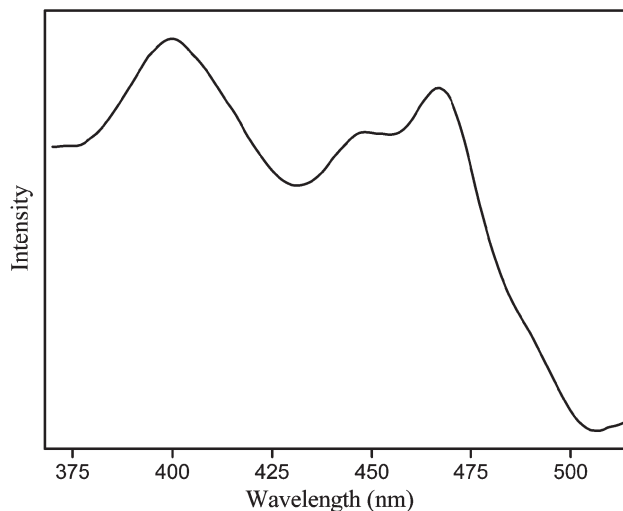


Fig. 4 Photoinduced emission spectrum of **1** in the solid state at room temperature ($\lambda_{ex} = 290$ nm).

Study of synthetic conditions

Polymer **1** was obtained by diffusing a methanol solution of **L** into a DMF solution of $H_3PMo_{12}O_{40} \cdot xH_2O$ and $AgNO_3$. But when the solvent DMF was replaced by H_2O , the obtained product was a Keggin-based compound which was proven by IR spectrum. As we know, POMs are sensitive to the pH value of the studied media. The synthesis of Wells-Dawson polyoxoanion requires the range of pH values of 3–5, while that of Keggin type anion is 1–2.³⁰ In order to confirm the pH range where polymer **1** was generated, a detailed investigation of the synthesis was performed. In our initial synthesis process, the pH value of the under layered DMF solution was 2.8. When the solution of methanol and DMF mixed uniformly to form the crystals, the pH value of the whole miscible liquid was 3.7, which matches with the condition of Wells-Dawson polyoxoanion formation. In the subsequent experiments, all the conditions were kept the same as those mentioned above, except that the pH value of the solution of $H_3PMo_{12}O_{40} \cdot xH_2O$ and $AgNO_3$ was adjusted to 1.8, 2.2 by 1 M HNO_3 and 3.4, 3.8 using 1 M NaOH, respectively. When the pH value was beyond 3.8, the synthesis could not be continued because the under layered solution becomes turbid. IR spectra of the final products indicated that the latter two agree well with **1** to form Wells-Dawson-based polymers, while the other two still exhibit the characteristic bands of Keggin anion without conversion (Fig. S7[†]).^{31,32} The transformation of the polyoxoanions from Keggin to Dawson in DMF solution was also confirmed by ^{31}P NMR spectra (Fig. 5). As shown in Fig. S8 and S9,[†] both the signals corresponding to $[P_2Mo_{18}O_{62}]^{6-}$ and $[PMo_{12}O_{40}]^{3-}$ could be observed when the pH value of the solution containing mixed reactants is 2.8, 3.4 and 3.8, respectively. But when the pH value of the solution is lower than 2.8, there is only a single signal of $[PMo_{12}O_{40}]^{3-}$ that can be observed in the spectrum. Such a result further authenticates the existence of an observable equilibrium between Keggin and Wells-Dawson anions in the DMF solution with the pH value no less than 2.8. In addition, when DMF solution was replaced by aqueous solution, no Wells-Dawson-based polymer was achieved in spite of the pH value of

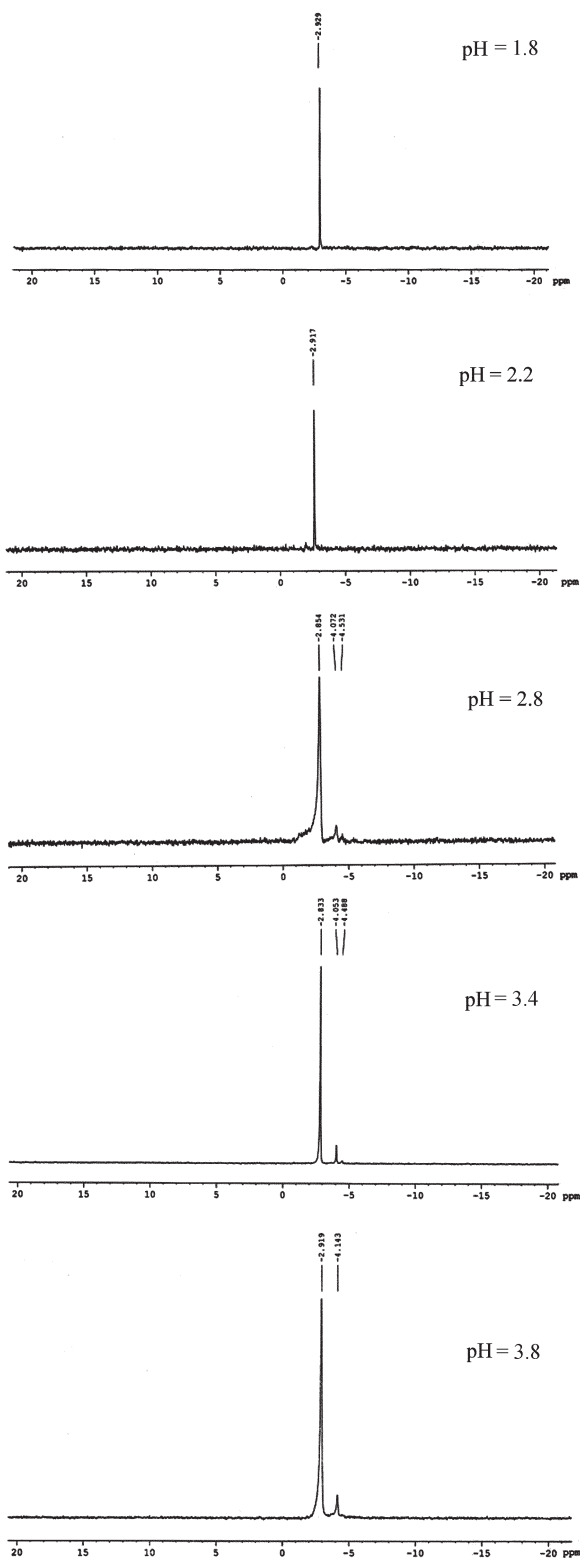


Fig. 5 ^{31}P NMR spectra for the solutions containing mixed reactants at different pH values.

solution being adjusted gradually from 1.8 to 3.8 with other experimental conditions remaining unchanged (Fig. S10†). To sum up, the polyoxoanion transition from $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ to $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ is not only influenced by the pH value of the

media but also the participate in the solvent species in the assembly process.

Conclusions

In summary, we have developed a convenient approach to the synthesis of phospho-molybdc Wells–Dawson-based polymer using Keggin polyoxoanion as the starting material. And a 2D polymer **1** based on silver-Schiff-base building blocks and $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ clusters was obtained by the aforementioned method. Studies on the self-assembly process of **1** revealed that the Keggin anion can self-transform to a Wells–Dawson anion at appropriate pH value in appropriate solvent species. Studies of this strategy involving other types of metal-Schiff-base systems containing Wells–Dawson polyoxoanion are currently underway.

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