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Ligation of the quinolone antibacterial agent pipemidic acid to Keggin polyoxotungstates

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ABSTRACT

Three new drug molecules modifying Keggin polyoxometallate compounds have been synthesized under hydrothermal conditions and structurally characterized by routine techniques. Single-crystal X-ray diffraction analysis shows that compound **1** is constructed by a Keggin cluster and two $[Cu(PPA)_2]$ drug complexes, formulated as $[Cu(PPA)_2]_2{\cdot}[PW_{12}O_{40}]{\cdot}6H_2O$. Compound **2** consists of a Cd substituted Keggin cluster $[PW_{11}CdO_{39}]$ and five isolated HPPA drug molecules, formulated as $[HPPA]_5{\cdot}[PW_{11}CdO_{39}]{\cdot}2H_2O$. Compound **3** consists of a full oxidised Keggin $[PW_{12}O_{40}]$ cluster and three isolated HPPA drug molecules, formulated as $[HPPA]_3{\cdot}[PW_{12}O_{40}]{\cdot}2H_2O$. Additionally, the antitumor activity of the three new compounds and their parent components *in vitro* were studied by a MTT experiment. The results show that introduction of TM-PPA/PPA into the polyoxoanion surface could increase their antitumor activity and make the compounds penetrate into the cells easily. Furthermore, the antitumor activity of the compounds can be modulated by their different structures.

1. Introduction

Polyoxometallates (POMs) are early transition metal oxygen anion clusters, and they are oligomeric aggregates of metal cations (usually the d^0 species V(V), Nb(V), Ta(V), Mo(VI) and W(VI)) bridged by oxygen atoms by self-assembly processes [1–4]. As a unique class of metal–oxide clusters, they have many properties that make them attractive for applications in catalysis, biology, magnetism, optics and medicine [5–10]. Recently, an important advance in POMs chemistry is modifying the polyoxoanions with transition metal complexes (TMCs), because the introduction of TMCs can not only enrich the structures of POMs but also enhance their electronic and magnetic properties [11–15]. For example, Hill and Pope have reported that grafting organic and organometallic groups onto the POM surface can significantly increase their catalytic or medical applications [16,17], particularly with the introduction of some medicine molecules into the POM surface.

Quinolones, with the term quinolonecarboxylic acids or 4-quinolones, are a group of synthetic antibacterial agents containing a 4-oxo-1,4-dihydroquinoline skeleton (Scheme 1a). Pipemidic acid (HPPA) (Scheme 1b), a 4-quinolone product, is an antibacterial agent used to treat gram-negative urinary tract infections [18] and severely damages DNA in the absence of an exogenous metabolizing system [19]. Due to the quinolone oxygen and one carboxylate oxygen atom, PPA may act as an excellent multidentate ligand to coordinate with metal ions and further to modify POMs. In the reported literature, TM and rare earth complexes based on HPPA molecules have been reported [20–22], and the results suggest that metal ion coordination might be involved in the antibacterial activity of HPPA [23]. However, no compounds based on HPPA/HPPA-TM complexes modifying POMs have been reported yet. Therefore, it is still a great challenge to obtain new functional POMs modified by medicinal molecules.

Additionally, POMs, as anti-tumor, -viral and -bacterial inorganic medical agents, are rendered attractive for applications in medicine. Unfortunately POMs are too toxic to be effective in clinical trials [24,25], which has lead to a decline in the study of POMs as inorganic drugs. Nevertheless, researchers familiar with POMs have been investigating the possibility of their anti-tumor, -viral and -bacterial activity for the following reasons. The first is nearly every molecular property, such as polarity, redox, surface charge distribution, shape and acidity, that impacts the recognition and reactivity of POMs with target biological macromolecules can be altered easily. The second is that the surface of POMs can be modified to enable the design of multifunctional compounds by the covalent attachment of organic groups. To date a plentiful amount of multifunctional compounds based on POMs and various complexes have been reported [26–30]. These researches, including our own [11,31], have indicated that POMs, organic ligands and TM ions all play important roles in the self-assembly processes.

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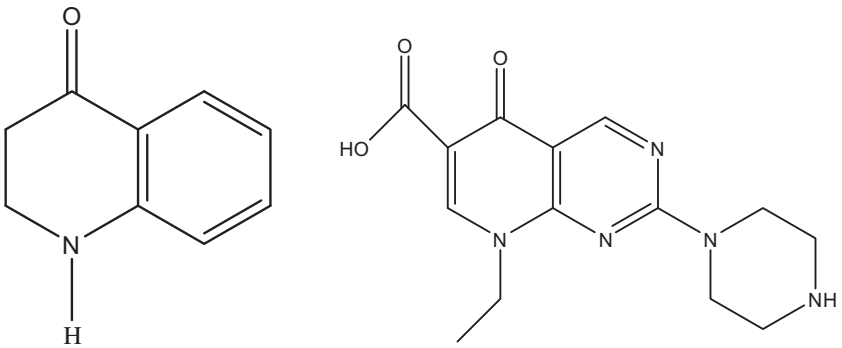

Scheme 1. (a) The 4-oxo-1,4-dihydroquinoline skeleton. (b) Pipedimic acid (8-ethyl-5,8-dihydro-5-oxo-2-(1-piperazinyl)pyrido(2,3-d)pyrimidine-6-carboxylic acid = HPPA).

On the basis of the aforementioned points, in this work we have chosen Keggin POMs as modules and M-PPA/PPA as modifiers to constitute the drug molecule HPPA modifying POM based compounds. Also we hope that the isolated HPPA drug and pendent PPA drug groups could be used to modulate the POMs' bioavailabilities and increase recognition of key substructures in the target biomacromolecules. Herein we report a compound based on the Keggin cluster $[PW_{12}O_{40}]$ modified by two $[Cu(PPA)_2]$ drug complexes, formulated as $[Cu(PPA)_2]_2{\cdot}[PW_{12}O_{40}]{\cdot}6H_2O$ (**1**), and a Cd substituted Keggin cluster $[PW_{11}CdO_{39}]$ modified by five HPPA drug molecules, formulated as $[HPPA]_5{\cdot}[PW_{11}CdO_{39}]{\cdot}2H_2O$ (**2**), and a fully oxidised Keggin cluster $[PW_{12}O_{40}]$ modified by three HPPA drug molecules, formulated as $[HPPA]_3{\cdot}[PW_{12}O_{40}]{\cdot}2H_2O$ (**3**). The results of antitumor activity studies show that introduction of M-PPA/PPA into the polyoxoanion surface can modulate their antitumor activity and enable the compounds to penetrate into the cells easily.

2. Experimental

2.1. Materials and methods

All reagents were purchased commercially and used without further purification. Elemental analyses were performed on a Perkin–Elmer 2400 CHN Elemental Analyzer (C, H and N), and on a Leaman inductively coupled plasma spectrometer (Cu and Cd). The IR spectra were obtained on an Alpha Centaurt FT/IR spectrometer with KBr pellets in the 400–4000 cm^{-1} region. XPS analyses were performed on a VG ESCALAB MkII spectrometer with a Mg Kα (1253.6 eV) achromatic X-ray source. The vacuum inside the analysis chamber was maintained at 6.2×10^{-6} Pa during the analysis.

2.2. Syntheses

2.2.1. $[Cu(PPA)_2]_2{\cdot}[PW_{12}O_{40}]{\cdot}6H_2O$ (**1**)

A mixture of $H_3PW_{12}O_{40}$ (288 mg), $Cu(CH_3COO)_2{\cdot}2H_2O$ (50 mg), HPPA (60 mg), $NaHCO_3$ (20 mg) and H_2O (10 mL) was stirred for 1 h in air. The pH was then adjusted to 4.3 with 1 M CH_3COOH, and the mixture was transferred to an 18 ml Teflon-lined reactor. After 6 days of heating at 155 °C, the reactor was slowly cooled to room temperature over a period of 16 h. Green block crystals of **1** were filtered, washed with water and dried at room temperature. *Anal.* Calc. for $C_{56}H_{76}PCu_2W_{12}N_{20}O_{58}$ (4321.58): C, 15.55; H, 1.76; N, 6.48; Cu, 2.96. Found: C, 15.59; H, 1.81; N, 6.45; Cu, 2.94%.

2.2.2. $[HPPA]_5{\cdot}[PW_{11}CdO_{39}]{\cdot}2H_2O$ (**2**)

Compound **2** was prepared in a manner similar to that described for **1**, except $Cd(CH_3COO)_2$ replaced $Cu(CH_3COO)_2$. Light

Table 1
Crystal data and structure refinements for **1**–**3**.

Compounds	**1**	**2**	**3**
Empirical formula	$C_{56}H_{76}PCu_2W_{12}N_{20}O_{58}$	$C_{70}H_{89}PW_{11}CdN_{25}O_{56}$	$C_{42}H_{55}PW_{12}N_{15}O_{51}$
CCDC	796344	796142	796146
Formula weight	4321.58	4341.57	3822.87
Wavelength (Å)	0.71069	0.71069	0.71069
Crystal system	triclinic	triclinic	hexagonal
Space group	$P\bar{1}$	$P\bar{1}$	$R\bar{3}c$
a (Å)	12.061(5)	12.317(5)	20.024(5)
b (Å)	12.711(5)	17.203(5)	20.024(5)
c (Å)	17.346(5)	26.810(5)	65.234(5)
α (°)	91.948(5)	73.447(5)	90.000(5)
β (°)	105.011(5)	79.258(5)	90.000(5)
γ (°)	110.290(5)	77.754(5)	120.000(5)
V (Å^3)	2386.5(15)	5273(3)	22652(8)
Z	1	2	12
Reflections collected/unique	4517/10594[R_{int} = 0.0343]	28216/19869[R_{int} = 0.0577]	45543/6200[R_{int} = 0.0717]
D_{calc} (mg/m^3)	3.046	3.899	3.359
Absorption coefficient (mm^{-1})	14.962	26.897	18.334
F(0 0 0)	2001	5304	20627
Goodness-of-fit on F^2	0.992	0.946	1.019
Final R_1[a], WR_2[b] indices [$I > 2\sigma(I)$]	R_1 = 0.0674, wR_2 = 0.1557	R_1 = 0.0833, wR_2 = 0.2108	R_1 = 0.0343, wR_2 = 0.0760
R_1[a], WR_2[b] indices (all data)	R_1 = 0.1227, wR_2 = 0.1855	R_1 = 0.1557, wR_2 = 0.2666	R_1 = 0.0646, wR_2 = 0.0963

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

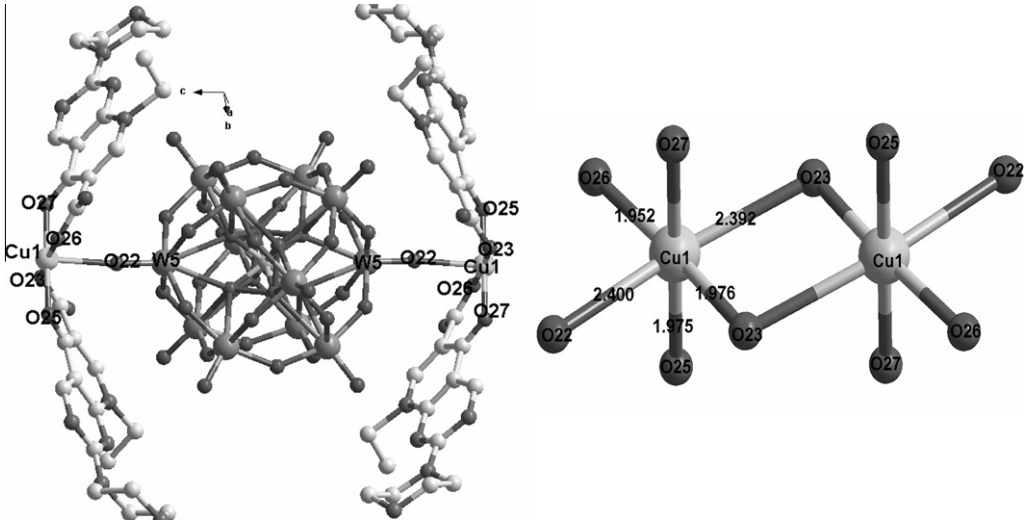

Fig. 1. Left: Ball/stick representation of the molecular structure unit of **1**. All the hydrogen atoms and water molecules have been omitted for clarity. Right: Simplified view of the binuclear copper cluster.

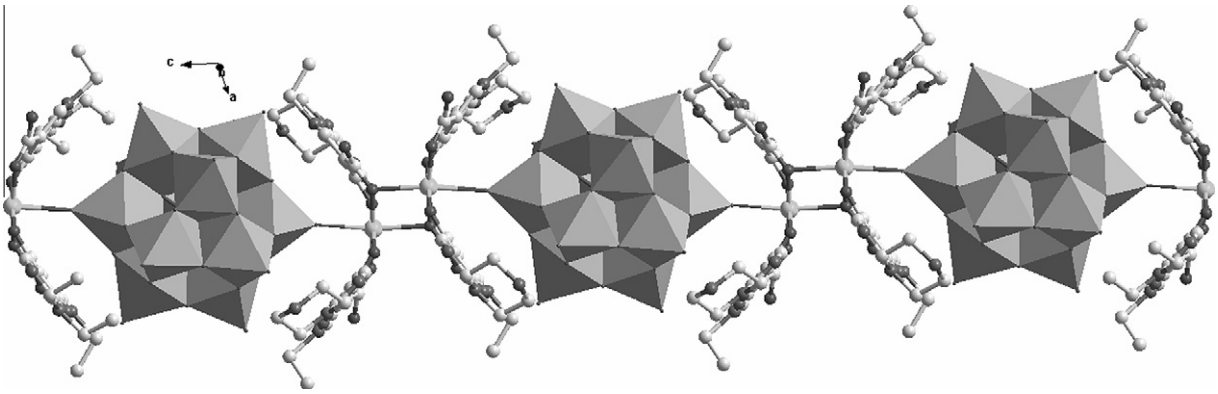

Fig. 2. Polyhedral/stick representation of the 1D chain structure of **1** constructed by POMs and Cu-PPA binuclear clusters.

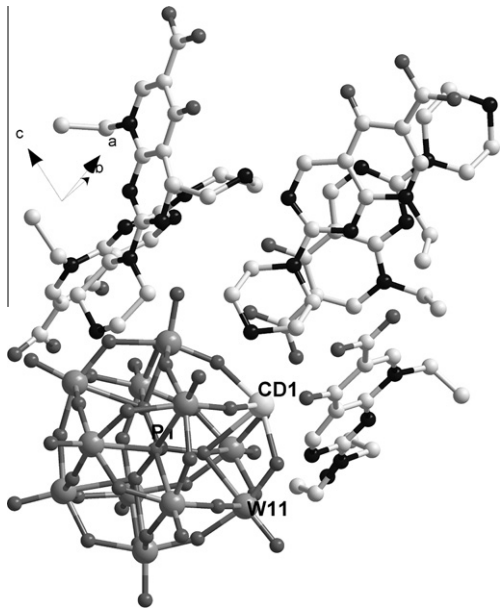

Fig. 3. Ball/stick representation of the molecular structure unit of **2**. All the hydrogen atoms and water molecules have been omitted for clarity.

grey block crystals were obtained. *Anal.* Calc. for $C_{70}H_{89}PW_{11}CdN_{25}O_{56}$ (4341.57): C, 19.35; H, 2.05; N, 8.06; Cd, 2.58. Found: C, 19.39; H, 2.17; N, 8.04; Cd, 2.54%.

2.2.3. $[HPPA]_3{\cdot}[PW_{12}O_{40}]{\cdot}2H_2O$ (**3**)

Compound **3** was prepared in a manner similar to that described for **1**, except $Zn(CH_3COO)_2$ replaced $Cu(CH_3COO)_2$. Light yellow block crystals were obtained. *Anal.* Calc. for $C_{42}H_{55}PW_{12}N_{15}O_{51}$ (3822.87): C, 13.18; H, 1.44; N, 5.50. Found: C, 13.19; H, 1.53; N, 5.48%.

2.3. X-ray crystallographic study

Crystal data for compounds **1**–**3** were collected on a Bruker SMART-CCD diffractometer, with Mo Kα monochromatic radiation (λ = 0.71069 Å) at 293 K. All the structures were solved by direct methods and refined by full matrix least-squares on F^2 using the SHELXTL crystallographic software package [32,33]. All the non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms on carbon atoms were calculated theoretically. The crystal data and structure refinements of compounds **1**–**3** are summarized in Table 1. Selected bond lengths and angles for compounds **1**–**3** are listed in Tables S1–S3.

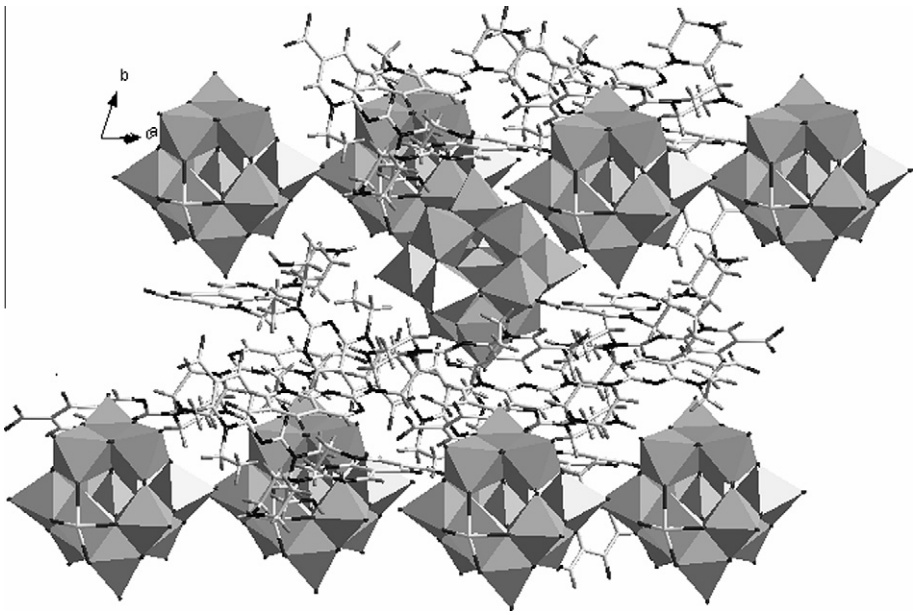

Fig. 4. The 3D packing drawing of compound **2**. In the structure, the PPA drug molecules layer and the POMs layer array alternately.

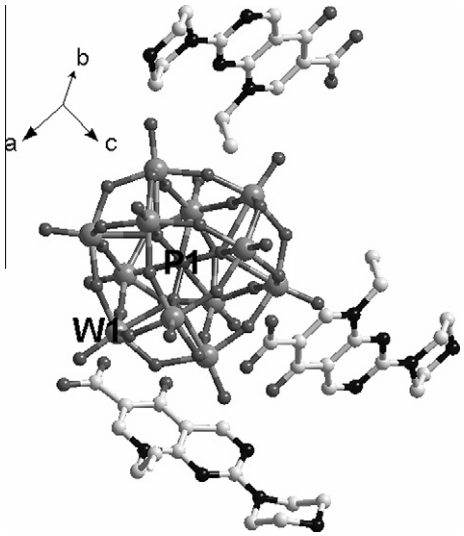

Fig. 5. Ball/stick representation of the molecular structure unit of **1**. All the hydrogen atoms and water molecules have been omitted for clarity.

2.4. Antitumor activity studies

The antitumor activity of compounds **1**–**3** and their parent anion on PC-3, Hela and HepG2 cells was tested by the MTT experiment [34]. MTT, 3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyltetrazolium bromide, also known as thiazolyl blue, is a dye which can accept a hydrogen atom. Surviving tumor cells are able to reduce the yellow MTT to the insoluble blue formazan in water, whereas dead tumor cells do not possess this capability. The formazan product is dissolved in DMSO and then determined colorimetrically with a Microplate Reader (490 nm).

Subcultured PC-3, Hela and HepG2 cells were suspended in 0.25% trypsin. The cell suspension (*ca.* 10^5–10^6 cells mL) was added to a 96 well plate (100 μL per well) and incubated at 37 °C in a 5% CO_2 incubator for 24 h (100 μL). Samples containing the compounds were then added. After 72 h, 20 μL MTT solution (5 mg mL^{-1} in 0.01 M PBS (phosphate buffer solution)) was added, and the mixture allowed to incubate for 4 h. The supernatant was removed and DMSO (150 μL) added. The resulting mixture was shaken for 10 min at room temperature, and colorimetric analysis was used to examine the cell survival rate. These samples containing the title compounds and parent compound ($H_3PW_{12}O_{40}$) were obtained by dissolving the title compounds in DMSO, autoclaving and diluting by a RPMI 1640 medium to a final concentration of 50, 25, 12.5, 6.25 or 3.125 μg mL^{-1}.

3. Results and discussion

The $[PW_{12}O_{40}]^{n-}$ (abbreviated to PW_{12}) anions are the inorganic building blocks in compounds **1**–**3**, which possess classic Keggin structures and contain four W_3O_{13} units derived from the α-Keggin anion by removal of a set of three corner-shared WO_6 octahedrons. The P–O and W–O lengths are in the normal ranges. Bond valence sum calculations [35] show that all tungsten atoms are in the +VI oxidation states in **2** and **3**, while one out of twelve tungsten atoms is in the +5 oxidation state in compound **1**, and the copper and cadmium atoms are in the +II oxidation state, which is consistent with the elemental analysis, coordination geometries, crystal color and charge balance.

3.1. Crystal structures

3.1.1. Structure description of compound *1*

Single-crystal X-ray diffraction analysis reveals that compound **1** is constructed from one PW_{12} cluster, two $Cu(PPA)_2$ cations and six water molecules. The PW_{12} clusters as bridging bi-dentate inorganic ligands and PPA as chelating bidentate organic ligands coordinate to copper ions together, so that the copper atoms adopt hexacoordinated octahedral geometries achieved by six O atoms (O23, O25, O26,O27, O22 and O23) of three PPA and a PW_{12} cluster (shown in Fig. 1). Note, there are two crystallographically unique PPA drug molecules, which covalently link to the same copper ions to form binuclear copper clusters, and the bond distances around the Cu(II) ions are 1.952–2.400 Å (Cu–O). Furthermore, these binuclear copper clusters connect the POM clusters to form a 1D chain architecture *via* Cu–O bonds, as shown in Fig. 2.

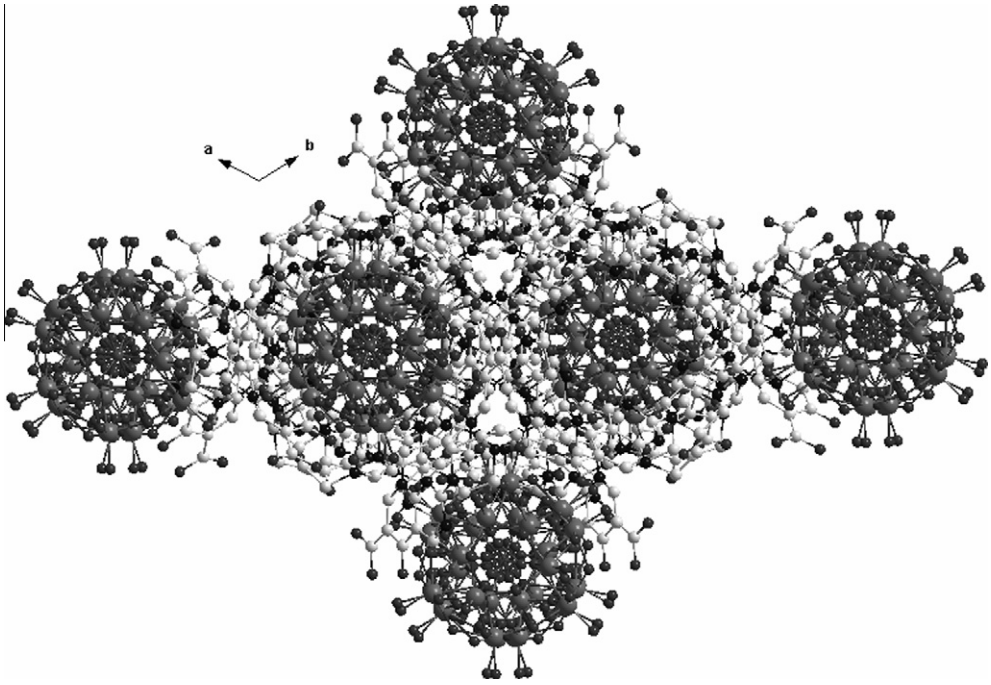

Fig. 6. The 3D packing drawing of compound **3** along the *c*-axis.

*3.1.2. Structure description of compound **2***

Single-crystal X-ray diffraction analysis reveals that compound **2** is constructed from one mono-substituted Keggin cluster $[PW_{11}CdO_{39}]^{5-}$, five HPPA drug molecules and two water molecules, as shown in Fig. 3. The Cd atom is coordinated by five oxygen atoms from the vacancy of the PW_{11} fragment, with Cd–O bond lengths in the range 2.101(1)–2.670 Å. The crystallographic data show that no Cd ion is present as a counter-cation. The elemental analysis, XPS and the electron densities of Cd indicate that the Cd atom is incorporated into the vacancy of the genuine PW_{11} cluster. Furthermore, these subunits are fused together *via* a short interaction to form a 3D supramolecular compound, as shown in Fig. 4.

*3.1.3. Structure description of compound **3***

Single-crystal X-ray diffraction analysis reveals that the compound **3** is constructed by one fully oxidised Keggin cluster, $[PW_{12}O_{40}]^{3-}$, three HPPA drug molecules and two water molecules, as shown in Fig. 5. It is interesting that 12 terminal oxygen atoms and 9 bridging oxygen atoms of the Keggin POM are linked with 12 PPA drug molecules *via* supramolecular interactions to form a 3D supramolecular structure, that is to say, all the terminal oxygen atoms of the Keggin POMs serve to stabilize the whole structure. Seen from the *c*-axis direction, these drug HPPA molecules give rise to regular chambers, and inorganic POMs are located in the chambers to stabilize the whole structure (Fig. 6).

3.2. IR and XPS spectra

In the IR spectra (Figs. S1–S3), characteristic vibration modes of the Keggin polyoxoanions are observed for ν(P–O), ν(W–Od), ν(W–Ob–W) and ν(W–Oc–W) at 1060, 956, 883 and 808 cm^{-1} for **1**, and 1074, 975, 883 and 804 cm^{-1} for **3**, and for ν(P–O) at 1071 and 1047 cm^{-1}, ν(W–Od), ν(W–Ob–W) and ν(W–Oc–W) at 954, 883 and 806 cm^{-1} for **2**, (where O_d = terminal oxygen, O_b = bridged

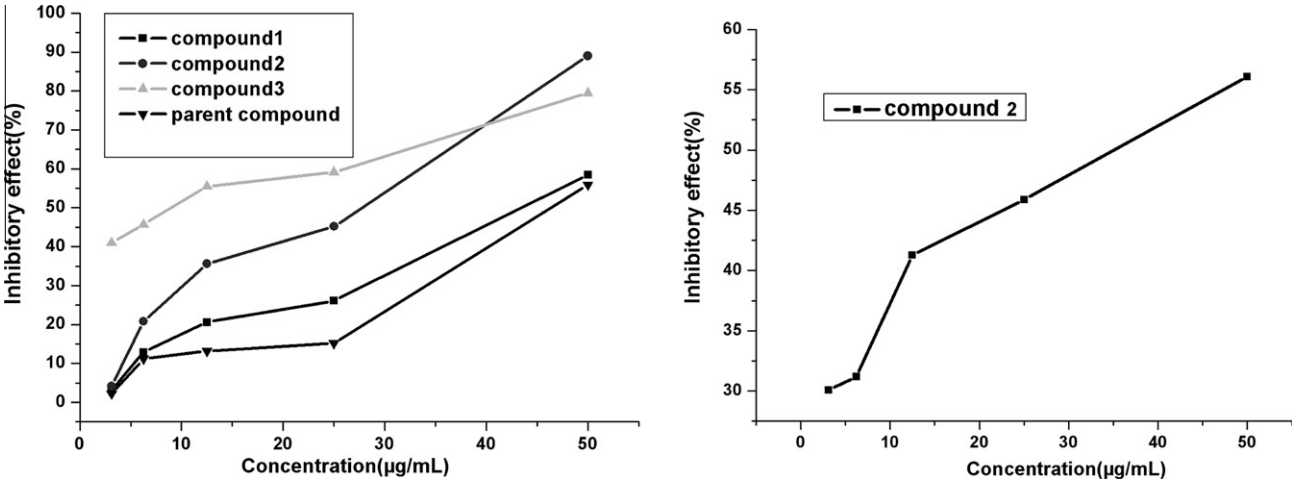

Fig. 7. Left: The anti-tumor activity against PC-3 for compounds **1**–**3** and the parent compound. Right: The anti-tumor activity against Hela for compound **2**.

oxygen of two octahedral sharing a corner, O_c = bridged oxygen of two octahedral sharing edge), respectively. Compared to a typical value of approximately 1067 cm^{-1} for the Keggin anion [36], the P–O stretch of vibrations in compound **2** splits, but the basic Keggin POM skeleton is maintained. The characteristic absorption bands of the HPPA group are in the 3450–1200 cm^{-1} range. Additionally, in compound **2**, direct evidence of the Cd substituted inorganic Keggin polyoxoanion is provided by XPS measurement. The XPS spectrum of compound **2** (Fig. S4) exhibit two peaks at 404.7 and 411.5 eV, attributed to $Cd^{2+}{}_{3d5/2}$ and $Cd^{2+}{}_{3d3/2}$, respectively [37], consistent with the elemental analysis, coordination geometries, crystal color and charge balance.

3.3. Antitumor activity studies

A comparison of the antitumor activity of compounds **1**–**3** and their parent compound was made. The inhibitory effect against PC-3 human cancer cell lines shows that the compounds **1**–**3** and the parent compound all exhibit high antitumor activity to PC-3, and the inhibitory effect of compounds **1–3** is higher than the parent compound (shown in Fig. 7 left). Firstly, comparing the three new compounds with the parent compound, while they are based on PW_{12} polyoxoanions, they show significant differences in antitumor activity. The differences can be reasonably explained by the modified chemistry of the POMs. The introduction of PPA-TM/PPA onto the POMs surface can ameliorate the POMs' electronic distribution, polarity and redox potentials, so that the recognition and reactivity of POMs with target biological macromolecules can be altered, which results in enforcement of their antitumor activity. Secondly, in the three new compounds, their different antitumor activity may be explained by the differences in their structures. In compounds **1** and **3**, the POMs are surrounded by PPA drug molecules (shown in Figs. 2 and 6), which hinder the interactions with tumor cells and result in the relatively feeble antitumor activity. However, the PPA drug molecules layer and POMs layer array alternately in compound **2** (shown in Fig. 4), which results in the modifying POMs interacting with tumor cells more easy. Thus compound **2** exhibits higher antitumor activity than **1** and **3**. So the antitumor activity comes from the synergism of POMs and PPA or M-PPA.

Furthermore, the above mentioned conclusions are also proved to be reasonable by the inhibitory effect against Hela and HepG2 human cancer cell lines. As shown in Fig. 7 (right), compound **2** exhibits good anti-hela activity, while compounds **1**, **3** and the parent are without anti-hela activities. This fact shows that drug molecules modifying POMs can ameliorate the parent POMs' properties to alter their biological activity. Additionally, the anti-HepG2 activity of the three new compounds and their parent anion was also studied, and the results show the four compounds exhibit no anti-HepG2 activity, which indicates the POMs and the derivatives possess a selectivity of antitumor activity.

4. Conclusions

In this paper, three PW_{12}-HPPA/M-PPA compounds were synthesized under hydrothermal conditions and were structurally characterized. The MTT investigations found that these three new compounds possess stronger antitumor activity than the parent compound, which may be due to changes of their properties. Additionally, the antitumor activity of the three compounds can be modulated by synthesizing compounds with different structures. This work implies that the introduction of M-PPA/HPPA onto the POM surface could enforce their antitumor activity and make the compounds penetrate into the cells easily. Additionally, more effort will be focused on TM-drugs-POMs systems so as to explore the possible effect of drug molecules modifying POM clusters and their multi-functionalities.

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Appendix A. Supplementary data

CCDC 796344, 796142 and 796146 contains the supplementary crystallographic data for compounds **1**–**3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2011.03.044.

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