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Giant Hollow Heterometallic Polyoxoniobates with Sodalite-Type Lanthanide–Tungsten–Oxide Cages: Discrete Nanoclusters and Extended Frameworks

*Lu Jin, Xin-Xiong Li, Yan-Jie Qi, Ping-Ping Niu, and Shou-Tian Zheng**

Abstract: *The first series of niobium–tungsten–lanthanide (Nb-W-Ln) heterometallic polyoxometalates $\{Ln_{12}W_{12}O_{36}(H_2O)_{24}(Nb_6O_{19})_{12}\}$ (Ln = Y, La, Sm, Eu, Yb) have been obtained, which are comprised of giant cluster-in-cluster-like ($\{Ln_{12}W_{12}\}$-in-$\{Nb_{72}\}$) structures built from 12 hexaniobate $\{Nb_6O_{19}\}$ clusters gathered together by a rare 24-nuclearity sodalite-type heterometal–oxide cage $\{Ln_{12}W_{12}O_{36}(H_2O)_{24}\}$. The Nb-W-Ln clusters present the largest multi-metal polyoxoniobates and a series of rare high-nuclearity 4d-5d-4f multicomponent clusters. Furthermore, the giant Nb-W-Ln clusters may be isolated as discrete inorganic alkali salts and can be used as building blocks to form high-dimensional inorganic–organic hybrid frameworks.*

Polyoxometalates (POMs) of V, Mo, and W have been developed over the past two decades, in pursuit of unique structural characteristics (for example, high negative charge, oxygen-rich surface, and rich redox properties) and wide potential applications.[1,2] Moreover, new discoveries are becoming more and more frequent and abundant. In contrast, the development of polyoxoniobate (PONb) chemistry is still at a nascent stage because of some major limiting factors, including the lack of soluble niobate oxoanion precursors, low activity and the narrow working pH region of niobate species.[3] For a long time, PONb chemistry was dominated by the isopolyniobates $\{Nb_6O_{19}\}$ and $\{Nb_{10}O_{28}\}$. Some new isopolyniobates were obtained in recent years, including $\{Nb_{20}O_{54}\}$,[4a] $\{H_9Nb_{24}O_{72}\}$,[4b] $\{HNb_{27}O_{76}\}$, $\{H_{10}Nb_{31}O_{93}(CO_3)\}$,[4c] and the largest, $\{Nb_{32}O_{96}H_{28}\}$.[4d] Therefore, the exploration of elusive PONb chemistry is of great interest.

The introduction of metals (for example, transition metals and lanthanides) into POMs is an effective strategy for construction of POMs with diverse chemical compositions, structures, and functionalities. For instance, this strategy has achieved great success in creating transition-metal-substituted polyoxotungstates.[5] Especially, this strategy can allow access to a greater level of self-assembly to form surprising giant high-nuclearity heterometallic POMs,[6–8] such as the recently reported examples $[H_{22}\{Ag_{12}Cl(Te_3W_{38}O_{134})_2\}]^{23-}$, $[Zr_{24}O_{22}(OH)_{10}(H_2O)_2(W_2O_{10}H)_2(GeW_9O_{34})_4(GeW_8O_{31})_2]^{32-}$, $[Ni_{25}(H_2O)_2OH)_{18}(CO_3)_2(PO_4)_6(SiW_9O_{34})_6]^{50-}$, and also $[Dy_{30}Co_8Ge_{12}W_{108}O_{408}(OH)_{42}(OH_2)_{30}]^{56-}$.[8a,b,c,d]

Since the first heteropolyoxoniobate $[SiNb_{12}O_{40}]^{16-}$ was reported by Nyman et al. in 2002,[9] intensive efforts have been invested into development of novel heterometallic PONbs by the introduction of metals. Nevertheless, the integration of metals into PONbs remains largely undeveloped to date because the working pH region (ca. 10.5–12.5) of PONbs is incompatible with the solubility of most metal cations (acidic nature). Among known heterometallic PONbs (except for some new types of structures)[10,11] the major structure types are derived from isopolyniobates $\{Nb_6O_{19}\}$, $\{Nb_{10}O_{28}\}$, or heteropolyniobates $\{XNb_{12}O_{40}\}$ (X = Si, Ge, P, and V) by the attachment of a few addendum metals or by the substitution of one or several Nb metals with addendum metals.[12–15] Especially, compared with giant high-nuclearity heterometallic POMs of Mo and W, the majority of known heterometallic PONbs are low-nuclearity (< 20) structures. Based on the current research status of PONbs and their promising applications in fields such as nuclear-waste treatment, virology, and photochemistry,[4] the synthesis of whole new types of heterometallic PONbs (especially with giant high-nuclearity structures) is challenging and scientifically interesting.

Herein, we report a series of unprecedented giant high-nuclearity heterometallic PONbs $\{Ln_{12}W_{12}O_{36}(H_2O)_{24}(Nb_6O_{19})_{12}\}$ (**$Ln_{12}W_{12}Nb_{72}$**) (Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb), which possess the following remarkable features: 1) **$Ln_{12}W_{12}Nb_{72}$** is the first series of Nb-W-Ln heterometallic POMs, and of rare 4d-5d-4f composite clusters; 2) **$Ln_{12}W_{12}Nb_{72}$** PONbs are by far the largest multi-metal PONbs reported thus far; 3) the incorporated 12 W^{6+} and 12 Ln^{3+} ions in **$Ln_{12}W_{12}Nb_{72}$** form novel nanoscale 24-nuclearity hollow sodalite-type heterometal-oxide cages $\{Ln_{12}W_{12}O_{36}(H_2O)_{24}\}$; 4) **$Ln_{12}W_{12}Nb_{72}$** acts as a giant building block for three-dimensional inorganic–organic hybrid framework $Na_6K_{10}[Cu(en)_2]_4[Ln_{12}W_{12}O_{36}(H_2O)_{24}(H_3Nb_6O_{19})_{12}]\cdot$solv (**1Ln**, en = ethylenediamine, solv = solvents) that can be isolated as discrete inorganic sodium–potassium salts, as shown by isolation of a Y-based PONb $Na_8K_{16}[Y_{12}W_{12}O_{36}(H_2O)_{24}(H_3Nb_6O_{19})_{12}]\cdot 34\,en\cdot 29\,H_2O$ (**2**). The overall structures of **1Ln** can be viewed as a multi-layered self-assembly.

Solid **1Eu** was first obtained and employed for single-crystal X-ray diffraction analyses. The results show that **1Eu** is a really interesting composite material based on various kinds of metals. Specifically, **1Eu** exhibits an anionic 3D inorganic–organic hybrid framework built by 4d-5d-4f heterometallic clusters **$Eu_{12}W_{12}Nb_{72}$** bridged together by 3d Cu-complexes $[Cu(en)_2]^{2+}$, which is charge-balanced by s-block metals Na^+

[*] L. Jin, Dr. X.-X. Li, Y.-J. Qi, P.-P. Niu, Prof. Dr. S.-T. Zheng
State Key Laboratory of Photocatalysis on Energy and Environment
College of Chemistry, Fuzhou University
Fuzhou, Fujian 350108 (China)
E-mail: stzheng@fzu.edu.cn

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and K^+. The giant $\mathbf{Eu_{12}W_{12}Nb_{72}}$ consists of $12\,Eu^{3+}$, $12\,W^{6+}$, and $72\,Nb^{5+}$ (12 $\{Nb_6O_{19}\}$) metal ions, forming the first Nb-W-Ln heterometallic PONb with an intriguing cluster-in-cluster-like ($\{Eu_{12}W_{12}\}$-in-$\{Nb_{72}\}$) structure.

As shown in Figure 1a, $12\,Eu^{3+}$ and $12\,W^{6+}$ ions are alternately linked by 36 μ_2-O bridges to form a centrosymmetric hollow 24-nucelarity heterometal-oxide cluster $\{Eu_{12}W_{12}O_{36}\}$ with nanosized dimensions of $1.2\times1.2\times1.2$ nm (atom-to-atom distance), in which each Eu^{3+} ion is connected to three W^{6+} ions, and vice versa. The hollow $\{Eu_{12}W_{12}O_{36}\}$ cluster, containing eight large hexagon rings $\{Eu_3W_3O_6\}$ and four small rhombus rings $\{Eu_2W_2O_4\}$, can be described as a zeolite-type sodalite cage (also called a truncated octahedral cage) based on simplifying Eu^{3+} and W^{6+} as three-connected nodes and μ_2-O as linkers. The face-centered site of each large hexagon ring of the sodalite-type cage $\{Eu_{12}W_{12}O_{36}\}$ is occupied by one alkali metal ion K^+ (Supporting Information, Figure S1), forming a closed cage. The free diameter of the largest sphere that can fit into the cage is approximately 0.7 nm (after consideration of the van der Waals radii of Eu and W). In the cage, some disordered water molecules are found to serve as the pore-filling species (Supporting Information, Figure S1).

Besides the three μ_2-O atoms shared with three Eu^{3+} ions, each W^{6+} ion of the $\{Eu_{12}W_{12}O_{36}\}$ cage also bonds to three edge oxygen atoms of one hexaniobate polyoxoanion $[Nb_6O_{19}]^{8-}$ (Supporting Information, Figure S2), forming a WO_6 octahedron (W–O bonds: 1.779(7)–2.152(7) Å). As a result, a total of 12 polyoxoanions $[Nb_6O_{19}]^{8-}$ are attached to the external surface of the $\{Eu_{12}W_{12}O_{36}\}$ cage. In contrast to the W^{6+} ions, each Eu^{3+} ion of $\{Eu_{12}W_{12}O_{36}\}$ cage further coordinates with three vertex oxygen atoms from three adjacent $[Nb_6O_{19}]^{8-}$ polyoxoanions (Figure 1b) and two water molecules, forming an eight-coordinate bicapped trigonal prism configuration (Eu–O bonds: 2.315(10)–2.384(7) Å; Eu-H_2O bonds: 2.586(8)–2.628(8) Å; Supporting Information, Figure S3). With the W^{6+} and Eu^{3+} ion linkers, the 12 polyoxoanions $[Nb_6O_{19}]^{8-}$ are gathered together by the nanosized $\{Eu_{12}W_{12}O_{36}\}$ cage to generate the largest multimetal PONbs $\mathbf{Eu_{12}W_{12}Nb_{72}}$ thus far, with the dimensions $2.5\times2.5\times2.5$ nm (Figure 1c); the Nb, W, and Eu contents were further confirmed by energy dispersive X-ray spectroscopy (EDS) element analyses (Supporting Information, Table S1). Interestingly, if every three adjacent $[Nb_6O_{19}]^{8-}$ polyoxoanions held together by one Eu^{3+} ion is simplified as a triangle, the geometric arrangement of the 12 $[Nb_6O_{19}]^{8-}$ polyoxoanions can be viewed as an icosahedron with $[Nb_6O_{19}]^{8-}$ as vertices. Thus, the complicated giant $\mathbf{Eu_{12}W_{12}Nb_{72}}$ can be regarded as a sodalite cage in an icosahedron cage, that is a ($\{Eu_{12}W_{12}O_{36}(H_2O)_{24}\}$-in-$\{(Nb_6O_{19})_{12}\}$) configuration.

Except for the 4f Eu^{3+}, 4d Nb^{5+}, and 5d W^{6+} metal ions, the 3d Cu^{2+} metal ions are also integrated into the structure of **1Eu** to act as linkers. As shown in Figure 2, each $\mathbf{Eu_{12}W_{12}Nb_{72}}$ is linked to eight adjacent units by eight Cu-complex cations $[Cu(en)_2]^{2+}$ to give a three-dimensional eight-connected uninodal network with bcu-type topology, in which each six-coordinate Cu^{2+} ion is defined by four N atoms from two chelating en ligands (Cu–N bonds: 2.006(14)–2.029(14) Å) and two terminal oxo atoms from two polyanions $[Nb_6O_{19}]^{8-}$ (Cu–O bonds: 2.449(1)–2.756(2) Å). On the basis of valence sum (Σ_s) calculations,[16] in **1Eu** the oxidation states of all Nb, W, Eu, and Cu atoms is +5 (Σ_s = 4.89–5.08), +6 (Σ_s = 5.80–5.96), +3 (Σ_s = 2.97–3.21), and +2 (Σ_s = 1.60), respectively.

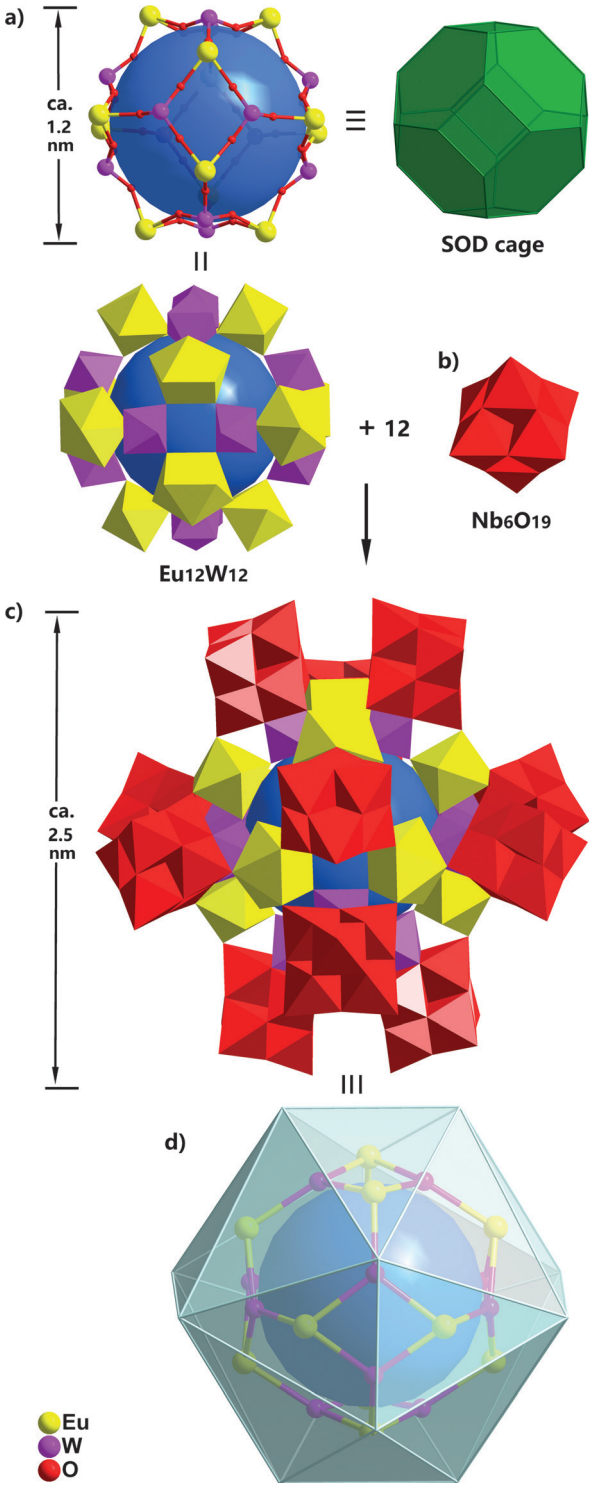

Figure 1. a)–d) Structures of sodalite-type cage $\{Eu_{12}W_{12}O_{36}\}$, hexaniobate anion $[Nb_6O_{19}]^{8-}$, heterometallic PONb $\mathbf{Eu_{12}W_{12}Nb_{72}}$, and cluster-in-cluster-like configurations, respectively. Polyhedra key: WO_6, purple; LnO_8, yellow; NbO_6, red.

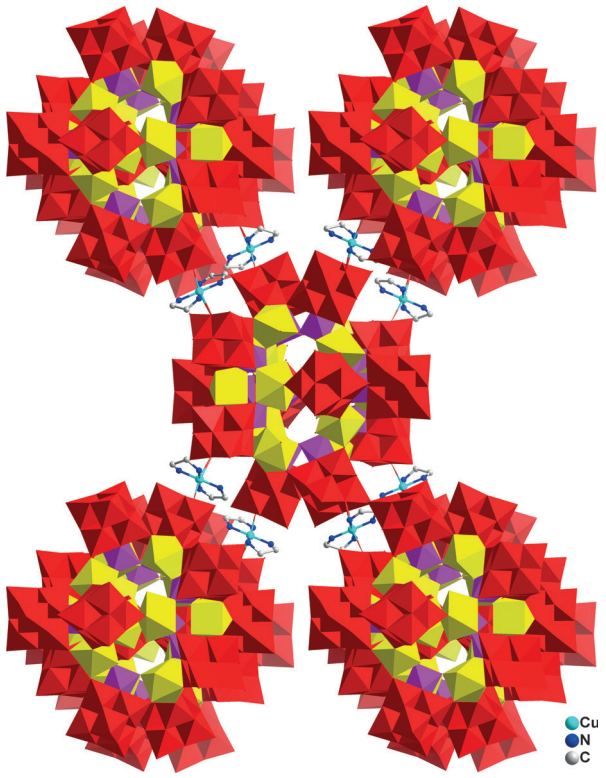

Figure 2. View of an extended structure of **1Eu**, showing the bonding mode between $\mathbf{Eu_{12}W_{12}Nb_{72}}$ and $[Cu(en)_2]^{2+}$. Polyhedra key: WO_6, purple; LnO_8, yellow; NbO_6, red.

Notably, the overall structure of **1Eu** can be regarded as an intriguing multi-layered self-assembly. The innermost species are some neutral water molecules, which are enclosed into a cationic cage $[Eu_{12}W_{12}O_{36}]^{24+}$. Twelve anionic $[Nb_6O_{19}]^{8-}$ PONbs centered around the cationic cage give a larger anionic $\mathbf{Eu_{12}W_{12}Nb_{72}}$ cluster. Finally, the anionic $\mathbf{Eu_{12}W_{12}Nb_{72}}$ cluster is further surrounded by eight Cu^{2+} cations (Supporting Information, Figure S4).

The structure of **1Eu** is quite flexible in chemical compositions, and a series of isomorphic compounds (**1Ln**) with other Ln ions, such as lighter Y^{3+}, light La^{3+}, heavy Sm^{3+}, and heavier Yb^{3+}, have also been obtained (Supporting Information, Figures S5–9, Table S2). Additionally, the giant $\mathbf{Ln_{12}W_{12}Nb_{72}}$ can also be isolated as discrete PONbs, as shown in a Y-based PONb (**2**) composed of a discrete $[Y_{12}W_{12}O_{36}(H_2O)_{24}(H_3Nb_6O_{19})_{12}]^{24-}$ polyoxoanion charge-balanced by alkali metal ions Na^+ and K^+ (Supporting Information, Figure S10). Single crystal X-ray diffraction reveals that the discrete $[Y_{12}W_{12}O_{36}(H_2O)_{24}(H_3Nb_6O_{19})_{12}]^{24-}$ polyanion in **2** is isostructural with $\mathbf{Ln_{12}W_{12}Nb_{72}}$ in **1Ln**.

Notably, Su and Wang et al. reported a 96-Nb-containing PONb $K_{12}[Nb_{24}O_{72}H_{21}]_4{\cdot}107\,H_2O$ in 2012,[4d] which is constructed from three isopolyoxoniobate clusters $[H_{21}Nb_{24}O_{72}]^{3-}$ linked together by eight alkali metal ions (K^+). Generally, alkali metal ions are regarded as extra-cluster charge-balancing cations in POM chemistry. Without regard to the linkage of alkali metals, the $\mathbf{Ln_{12}W_{12}Nb_{72}}$ series is the largest among heterometallic PONbs reported thus far, and contains the largest number of Nb centers in a discrete POM. Additionally, almost all known Nb-W-based POMs allow adaptation of niobate chemistry to tungstate chemistry, forming tungsten-rich structures. The $\mathbf{Ln_{12}W_{12}Nb_{72}}$ series is a rare example in which tungstate chemistry has been adapted to niobate chemistry.

Solid **1Sm** is taken as a representative example for the investigation of solid-state photoluminescent properties. The phase purity of as-synthesized **1Sm** was confirmed by PXRD (Supporting Information, Figure S6). The temperature-dependent photoluminescent properties of the powder sample **1Sm** are displayed in Figure 3. Under 336 nm UV

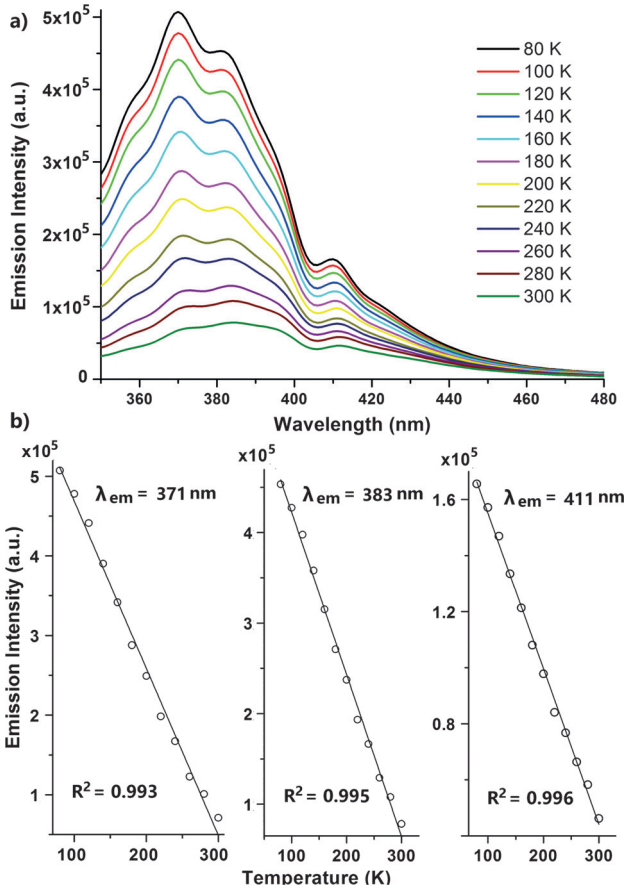

Figure 3. a) Emission spectra of **1Sm** recorded between 80 and 300 K (excited at 336 nm). b) Temperature-dependent intensity of emissions at 371, 383, and 411 nm, and the fitted curves for **1Sm**.

light excitation at 300 K, **1Sm** exhibits a broad emission band in the range of 350–450 nm, which is attributed to O→Nb charge transfer.[15c,d] When sample **1Sm** is cooled, its luminescence intensity gradually increases with decreasing temperature from 300 to 80 K. A series of emission peaks at 371, 383, and 411 nm become more and more clear with increased luminescence intensity, which is attributed to the existence of different NbO_6 octahedral environments. Interestingly, the luminescence intensity of the series of emissions at 371, 383, and 411 nm increases linearly with decreasing temperature in the range of 80–300 K (Figure 3b), which can be fitted as a function of $I = aT + b$ with very good correlation

coefficients $R^2 = 0.993$, 0.995, and 0.996 for the respective emissions intensities (luminescence intensity (I), temperature (T)). Furthermore, the luminescence of **1Sm** has good reversibility without an obvious loss of emission intensity for at least three cycles (Supporting Information, Figure S11), suggesting that compound **1Sm** is a potential sensor as a luminescent thermometer in a broad temperature range of 80–300 K.

In summary, we have successfully integrated mixed metals W and Ln into PONb chemistry to prepare a series of the largest multi-metal composite PONbs $\{Ln_{12}W_{12}O_{36}(H_2O)_{24}(Nb_6O_{19})_{12}\}$ reported to date, which are also the first family of Nb-W-Ln heterometallic POMs. The PONbs $\{Ln_{12}W_{12}O_{36}(H_2O)_{24}(Nb_6O_{19})_{12}\}$ present intriguing high-nuclearity and multi-layered structures and also contain 24-nuclearity sodalite-type W-Ln-O cages $\{Ln_{12}W_{12}O_{36}\}$. The giant PONbs, either alone or in combination with metal–organic complexes, are capable of generating discrete alkaline salts or high-dimensional hybrid framework materials. Among these new materials, **1Sm** exhibited a very good linear relationship between luminescence intensity and temperature. This work reveals the potential of introducing mixed metals into PONb chemistry for the synthesis of diverse composite PONb materials, especially for exciting giant PONbs with useful applications. The possibility of integrating s, 3d, 4d, 5d, and 4f metals into composite structures, as demonstrated by this work, showcases the interesting structural chemistry of different metals and offers promising routes to novel multi-component materials.

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Keywords: heterometals · high-nuclearity · lanthanides · polyoxoniobates · tungsten

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