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meso-Tetrakis(4-*N*-benzylpyridyl)porphyrin and its supramolecular complexes formed with anionic metal–oxo cluster: spectroscopy and electrocatalytic reduction of dioxygen

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Abstract

The research results show that MTBPyP (*meso*-tetrakis(4-*N*-benzylpyridyl)porphyrin, $M = H_2$, Zn) bearing quadruply positive charges associates with an anionic metal-oxo cluster (SiW₁₂O₄₀⁴⁻) to form a supramolecular complex in aqueous solution. The spectral evolution and Job's plots reveal that the aggregates contain equal numbers of the cationic porphyrins and the anionic SiW₁₂O₄₀⁴⁻. The association is accompanied by significant changes in the Soret band of the individual porphyrins. The 1:1 supramolecular complex [CoTBPyP][SiW₁₂O₄₀] may serve as an electrocatalyst for electrocatalytic reduction of O₂, and more of O₂ is reduced to H₂O at potential where the SiW₁₂O₄₀⁴⁻ is in reduced state. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Interest in fuel cell technology has motivated the search for an inexpensive electrode material that can accomplish the direct four-electron reduction of dioxygen to water at or near the reversible thermodynamic potential (+1.23 V vs. NHE at pH 0). Many transition metal complexes with macrocyclic ligands have been examined as dioxygen reduction catalyst [1]. Most of these electrocatalysts reduce dioxygen (via the two-electron pathway) to hydrogen peroxide at relatively negative potentials. For an oxygen-reducing electrode to operate at or near the thermodynamic equilibrium potential, hydrogen peroxide cannot be a free intermediate [2]. Thus, in order to achieve high efficiency, the catalysts should reduce dioxygen to water directly without the production of hydrogen peroxide. To date, only a few molecular electrocatalysts have been used to achieve the four-electron direct reduction of dioxygen to water. The catalysts include bis(cobalt) cofacial

diporphyrins and the related systems [2-4], cobalt tetrakisbis(4-pyridyl)porphyrin with three or four [Ru(NH₃)₅]²⁺ groups appended to the porphyrin periphery [5], some iridium porphyrin systems [6], (5,15,15,20-tetramethylporphyrinato) cobalt (II) [7] and the simplest systems of the cobalt porphyrins [8]. Recently, D'Souza reported an electrocatalyst formed by an ion-pair cobalt porphyrin dimer that reduced dioxygen to water by four electrons [9]. We report here the novel properties of the several supramolecular complexes formed by spontaneous association of the cationic porphyrins and the anionic metal-oxo clusters 1), including (Scheme spectral properties $[ZnTBPyP][SiW_{12}O_{40}]$ and $[H_2TBPyP][SiW_{12}O_{40}]$ systems in aqueous solution and electrocatalytic activity reducing O₂ to H₂O of [CoTBPyP][SiW₁₂O₄₀].

2. Experimental

2.1. Materials

Pyrolle was distilled at atmospheric pressure before use. 4-Pyridine aldehyde, benzyl bromide, N,N-

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dimethylformamide (DMF), sodium perchlorate and tungstosilicic acid ($H_4SiW_{12}O_{40}$) were used as received from commercial sources. The *meso*-tetrakis(4-pyridyl)porphyrin (H_2TPyP) was prepared according to the literature method [10].

2.2. Instruments

UV–Vis absorption spectral measurements were performed on a UV-3100 (Shimadzu, Japan) or a UV-922 (Kontron, Italy) spectrometer. FTIR spectra were determined on a Nicolet Impact 410 spectrophotometer. The proton magnetic resonance (¹H NMR) spectrum was carried out on a Varian Unity-400 NMR system. Elemental analyses were obtained on a Perkin–Elmer 240C elemental analyzer. And MALDI-TOF-MS (matrix-assisted laser desorption/ionization, time of flight, mass spectrometry) determination was carried out on an LDI-1700 mass spectrometer (Linear Scientific Inc., USA).

2.3. Syntheses

2.3.1. $[H_2TBPyP](ClO_4)_4$

H₂TPyP (0.200 g, 0.324 mmol) was dissolved in 100 ml of hot ($\sim 80^{\circ}$ C) N,N-dimethylformamide (DMF), then excess of benzyl bromide (about 10 ml, 80 mmol) was added to the solution. The unreacted H₂TPyP was monitored by thin-layer chromatography (TLC, Silica, $CHCl_3-C_2H_5OH$) during the reaction process. The reaction was completed after refluxing for about an hour. The mixture was then allowed to cool to room temperature (r.t.) and was poured into 50 ml of ethyl ether, crude product [H₂TBPyP]Br₄ precipitated instantly out of the solution. The precipitate was isolated by filtration and dissolved in 250 ml of distilled water, excess of sodium perchlorate (10.0 g, 80 mmol) was added (it would be best to pay attention to the explosion hazard associated with organic perchlorate salts). The solution was stirred until its color changed from red to light

yellow, which showed that the product [H₂TBPyP]-(ClO₄)₄ precipitated completely. Then the precipitate was isolated by centrifugation and washed for several times with cold distilled water to remove excess sodium perchlorate. Deep-red product $[H_2TBPyP](ClO_4)_4$ (0.357 g) was obtained by drying over P₂O₅ under vacuum. The yield, based on H₂TPyP, was 80%, m.p. > 250°C. Anal. Calc. for $[H_2TBPyP](ClO_4)_4 \cdot 3H_2O$ $(C_{68}H_{60}N_8O_{19}Cl_4)$ ($F_w = 1435$): C, 56.86; H, 3.97; N, 7.80. Found: C, 57.10; H, 3.91; N, 7.60%. ¹H NMR (DMSO-d₆): δ (ppm) 9.68(d, J = 10.24Hz, H_{*m*-pyridyl}), 9.23 (br, S, $H_{pyrrole}$), 9.05 (d, J = 10.4Hz, $H_{o-pyridyl}$), 7.59–7.91 (m, H_{phenyl}), 6.24 (S, H_{CH_2}), – 3.12 (S, NH). Visable absorption: λ nm (in DMSO) ($\varepsilon \times 10^{-3}$ l mol⁻¹ cm^{-1}) 428.8(210), 518.4(16.6), 554.2(6.91), 589.2(6.49), 645.0(2.28). FTIR spectral data: 3320.0 (v_{N-H}), 3114.2 (v_{Ar-H}) , 1634.0 (C=N⁺, C=C), 1086.9 (Cl=O), 971.5 (π_{p}), 801.1 cm⁻¹ ($\delta_{\text{phenyl-H}}$). MALDI-TOF-MS: M = $[H_2TBPyP](ClO_4)_4$, $[M - 4ClO_4]^+$ (m/z = 983.8), $[M - 4ClO_4]^+$ $3ClO_4$]⁺ (*m*/*z* = 1082.3).

2.3.2. $[CoTBPyP](ClO_4)_4$

[H₂TBPyP](ClO₄)₄ (0.060 g, 0.046 mmol) was dissolved in 100 ml of boiling distilled water. Excess of $Co(OAc)_2$ ·4H₂O (0.060 g, 0.24 mmol) was added to the solution under refluxing. The process of the reaction was monitored by UV-Vis spectroscopy. It is observed that the formation of cobalt porphyrin causes a red shift of the Soret band and reduction of the number of Q bands. The reaction was completed after refluxing for 2 h. The mixture was allowed to cool to r.t. and excess of sodium perchlorate (1.0 g, 8.0 mmol) was added. The solution was stirred until its color changed from red to light yellow, which also showed that the product $[CoTBPyP](ClO_4)_4$ precipitated completely. Then the precipitate was isolated by centrifugation and washed for several times with cold distilled water to remove excess of sodium perchlorate. Brownish black product $[CoTBPyP](ClO_4)_4$ (0.06 g) was obtained with yield



 $M = H_2, Zn, Co$



95%, m.p. > 250°C. Visable absorption: λ nm (in DMSO) ($\varepsilon \times 10^{-3}$ l mol⁻¹ cm⁻¹) 435.8(59.2), 540.2(7.07). FTIR spectral data: 3114.1 (ν_{Ar-H}), 1632.6 (C=N⁺, C=C), 1087.5 (Cl=O), 1002.2 (π_{p}), 798.4 cm⁻¹ ($\delta_{phenyl-H}$).

2.3.3. $[ZnTBPyP](ClO_4)_4$

[H₂TBPyP](ClO₄)₄ (0.096 g, 0.070 mmol) was dissolved in 100 ml of boiling distilled water. Then excess of Zn(OAc)₂·2H₂O (0.120 g, 0.55 mmol) was added to the solution under refluxing. Other procedures were the same as those of [CoTBPyP](ClO₄)₄. The violet product of [ZnTBPyP](ClO₄)₄ was obtained (yield 0.071 g, 71%). Visable absorption: λ (in H₂O) 440.0, 566.5, 606.5 nm.

2.3.4. $[CoTBPyP][SiW_{12}O_{40}]$

A precipitate appeared immediately when 5 ml of aqueous solution of $H_4SiW_{12}O_{40}$ (0.019 g, 0.007 mmol) was added into 5 ml of aqueous solution of [CoTBPyP](ClO₄)₄ (0.010 g, 0.007 mmol). After stirring for 1/2 h, the solution was centrifuged and the obtained precipitate was washed for several times with water. A brownish powder was obtained by drying over P_2O_5 under vacuum (yield 0.020 g, 70%). Elemental analysis and FTIR spectrum of [CoTBPyP][SiW₁₂O₄₀] indicated the presence of a number of water molecules. Anal. Calc. for $[CoTBPyP][SiW_{12}O_{40}]$ ($CoC_{68}H_{52}N_8SiW_{12}O_{40}$) $(F_{\rm w} = 3913)$: C, 20.85; H, 1.33; N, 2.86; C–N, 7.29. Found: C, 17.02; H, 1.50; N, 2.50; C-N, 6.81%. Visible absorption: λ (in DMSO) 440.2, 539.0 nm. FTIR spectrum: 3435 cm⁻¹ (broad and strong) attibuted to H₂O, 1630.3, 1550.4, 1453.0, 1384.4, 1208.1, 1012.2 cm⁻¹ attributed to [CoTBPyP], 970.0, 920.1, 883.2, 791.6 cm^{-1} attributed to [SiW₁₂O₄₀].

2.4. Spectroscopic methods

Spectroscopic measurements were performed at r.t. in quartz cell (1 cm optical pathlength). Titration were achieved by adding, with a micropipette, directly into the quartz cell, small aliquots (typical 1 μ l) of a 10⁻³ M solution of SiW₁₂O₄₀⁴⁻ to 3 ml of a ca. 10⁻⁵ M solution of porphyrin. Dilution effects were thus negligible. The added volumes were nevertheless take into account in the construction of Job's diagrams.

2.5. Electrochemical experiments

Cyclic, rotating disk, rotating ring-disk voltammetries and stability of electrocatalytic current were carried out with a Model HPD-IA potentiostat (Yanbian, China) associated with a Type $3086A_4 X-Y_1-Y_2$ (Sichuan, China) recorder using a three-electrode system. A rotating platinum ring-glassy carbon (GC) disk electrode (EG&G, Model 636) was used as working electrode, Ag–AgCl (sta's KCl) was used as the reference electrode, and platinum wire was used as the counterelectrode. The collection coefficient of platinum ring electrode $N = 0.22 \pm 0.01$ and the area of glassy carbon disk electrode ($A = 0.159 \pm 0.05$ cm²) were determined using the ferrocyanide–ferricyanide couple.

Sonication and warming were required for dissolving the porphyrin-cluster compound in dimethyl sulfoxide (DMSO). 5.0 μ l of solution (0.1 mM) of the porphyrin and porphyrin-cluster was transferred, respectively, to the surface of the glassy carbon disk electrode. Then the surface of the electrode was pumped to dry at r.t. Most of the porphyrin sample modified on the electrode was lost when the electrode was subsequently dipped to acidic aqueous solutions. But the porphyrin-cluster sample was strongly bound to the surface of the glassy carbon electrode due to its insolubility in acidic aqueous solution.

To calculate the Levich limiting currents at rotating disk electrodes, the following parameters were used: kinematic viscosity of water, $0.01 \text{ cm}^2 \text{ s}^{-1}$; diffusion coefficient for dioxygen, $1.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$; concentration of O₂ in air-saturated solutions, 0.28 mM at $20 \pm 2^{\circ}$ C.

3. Results and discussion

3.1. The spectra of $[MTBPyP][SiW_{12}O_{40}]$ $(M = H_2, Zn)$

There are numerous examples of supramolecular assemblies bound by ion-pair attraction in solution [11]. In most cases, the properties of such complexes differ notably from those of the parent compounds. It is well known that charged porphyrins can bind oppositely charged molecules through electrostatic interaction [9,11b, 12], and the heteroaggregation between them can be conveniently studied by spectroscopic methods. In this paper, we studied the interaction between MTBPyP⁴⁺ (M = H₂, Zn) and SiW₁₂O⁴⁻₄₀ in aqueous solution using UV-Vis absorption spectroscopy. Fig. 1a gives the spectral evolution of a solution of the ZnTBPyP⁴⁺ in H₂O upon titration with a solution of anionic metal-oxo cluster $SiW_{12}O_{40}^{4-}$. Similarly, the spectral evolution of a solution of H_2TBPyP^{4+} in H_2O upon addition of $SiW_{12}O_{40}^{4-}$ is shown in Fig. 1(b). In above-mentioned both cases, the reaction proceeds with an isosbestic point (at 454, 436 nm in Fig. 1(a) and (b), respectively, at number equivalents of $SiW_{12}O_{40}^{4-}$: MTBPyP < 1) and linear hypochromophores effect in the Soret band of porphyrins (insert chart of Fig. 1(a) and (b)), which is completed when the (1:1) stoichiometry is nearly reached. At the 1:1 stoichiometric point, the resulting spectrum of the solution differs markedly from the sum of those of the reactants (the Soret bands of porphyrin shift from 440, 423 to 455, 438 nm,



Fig. 1. (a) Spectral evolution of a solution of 4.8×10^{-6} M ZnTBPyP in H₂O upon addition of small aliquots of 10^{-3} M SiW₁₂O₄₀⁴⁻ (insert chart is the plot of $A_{440 \text{ nm}}$ versus increasing concentration of SiW₁₂O₄₀⁴⁻; (b) Spectral evolution of a solution of 6.1×10^{-6} M H₂TBPyP in H₂O upon addition of small aliquots of 10^{-3} M SiW₁₂O₄₀⁴⁻ (insert chart is the plot of $A_{423 \text{ nm}}$ versus increasing concentration of SiW₁₂O₄₀⁴⁻.

respectively), revealing the formation of at least one new species, in which the porphyrin chromophores interact strongly with the metal-oxo clusters. Similar results, observed by Lipskier [11b] and others [13], were interpreted as evidence of the formation of 1:1 heteroaggregates held by electrostatic attraction, in equilibrium with the starting monomers. Over the 1:1 stoichiometry, an isosbestic point disappears and the absorbance at the Soret of the porphyrins decreases slightly but no new break point occurs (insert chart of Fig. 1), which probably suggests the formation of higher unstable aggregates with the stoichiometry other than 1:1.

The data from the spectroscopic titration experiments were treated using Job's method, which is constructed to ascertain the stoichiometries of the aggregates [14]. This method relies on the fact that the optical absorbance of a mixture of chromophores that do not react on each other is the sum of the absorptions due to each chromophore separately. Correlatively, departures from additivity as the composition of the solution is continuously varied can be interpreted as evidence of the formation of a complex. By using Job's method, the stoichiometry of a complex can be deduced from the mole ratio of parent compounds in solution, at which the deviation from additivity has a maximum. In practice, the absorption measured at a given wavelength for mixtures with various mole ratios of the porphyrin and $SiW_{12}O_{40}^{4-}$ has been used to calculate by Eq. (1):

$$\Delta A_{(x)} = A_{(x)} - \varepsilon_{\rm p} c x - \varepsilon_{\rm w} c (1 - x) \tag{1}$$

where $c = [\text{porphyrin}] + [\text{SiW}_{12}\text{O}_{40}]$ is the total concentration, x = [porphyrin]/c is the mole fraction of porphyrin, ε_{p} and ε_{w} are the molar absorptivities of the porphyrin and the $\text{SiW}_{12}\text{O}_{40}^{4-}$ respectively, and $A_{(x)}$ is the measured optical absorbance of the solution. Thus, $\Delta A_{(x)}$ represents a deviation of the absorbance of the

solution from the additivity of absorbance for the porphyrin and the metal-oxo cluster. Because $SiW_{12}O_{40}^{4-}$ has no absorption at the wavelength of the Soret band of porphyrin, Eq. (1) may change to Eq. (2):

$$\Delta A_{(x)} = A_{(x)} - \varepsilon_{\rm p} cx \tag{2}$$

Job's diagrams were obtained by plotting $\Delta A_{(x)}$ against x. Fig. 2 displays the Job's plots examined at the wavelength of the Soret band of porphyrins, and it the formation of suggests a 1:1 complex, $[ZnTBPyP][SiW_{12}O_{40}]$ and $[H_2TBPyP][SiW_{12}O_{40}]$, respectively. However, the existence of higher order aggregates containing equal numbers of the porphyrins and the metal-oxo clusters $SiW_{12}O_{40}^{4-}$ can not be ruled out because the dimers of porphyrins can be formed owing to their $\pi - \pi$ interaction and van der Walls force. The observed similarity in the $[ZnTBPyP][SiW_{12}O_{40}]$ and [H₂TBPyP][SiW₁₂O₄₀] systems in aqueous solution suggests that the interaction between the porphyrin cations and the metal-oxo cluster anions is primarily electrostatic while the central ions do not play an important role in determining the nature of the interaction. Similarly, CoTBPyP⁴⁺ and SiW₁₂O₄₀⁴⁻ may also form 1:1 complex by electrostatic interaction (Although we failed to get perfect spectral evolution and Job's plot because the absorption of the Soret band of CoTBPyP is weak and only a little absorption change occurs upon addition with a solution of anionic metal-oxo cluster $SiW_{12}O_{40}^{4-}$).

Job's plots do not show the formation of higher aggregates with the stoichiometry other than 1:1, which indicate that the further aggregations at higher anion concentrations is too weak to observe by this method.

3.2. Electrocatalytic reduction of dioxygen

A strategy to achieve rapid, multiple-electron transfers (simultaneously avoiding undesired intermediates formation) has been tested with a variety of substrates, in which the syntheses of catalysts containing multiple metal centers and serving as electron donors or acceptors are involved [5]. In order to search for highly efficient electrocatalysts reducing O₂ to H₂O through a four-electron transfer pathway, we designed and synthesized the cationic cobalt porphyrin-anionic metaloxo cluster supramolecular complex. It is well known that cobalt porphyrins have electrocatalytic activity reducing dioxygen [9,15] and metal-oxo clusters can accept or donate multielectrons but their cluster skeletons are not destroyed [16]. Our research results show that the [CoTBPyP][SiW₁₂O₄₀] complex possesses good electrocatalytic activity reducing O_2 to H_2O .

A rotation platinum ring-glassy carbon disk electrode (RRDE) was used to determine the amount of H_2O_2 produced during the reduction of O_2 . The glassy carbon (GC) disk was coated with [CoTBPyP](ClO₄)₄ or [CoTBPyP][SiW₁₂O₄₀] and the platinum ring was maintained at 1.0 V to oxidize H_2O_2 generated at the GC electrode due to the reduction of O_2 . The product of reduction of O_2 is essentially H_2O_2 when using GC disk electrode coated with [CoTBPyP](ClO₄)₄ (see Fig. 3(a)). The plateau current for the first step is generated by reduction of O_2 electrocatalyzed probably by face-to-face cobalt porphyrin formed through $\pi - \pi$ interaction and van der Waals force, while one for the second step is produced through reduction of O_2 electrocatalyzed by monoric cobalt porphyrin. By contrast, when the



Fig. 2. (a) Job's plot for the [ZnTBPyP][SiW₁₂O₄₀] system in H₂O, $\lambda = 440$ nm; (b) Job's plot for the [H₂TBPyP][SiW₁₂O₄₀] system in H₂O, $\lambda = 423$ nm.



Fig. 3. Reduction of O₂ at a rotating platinum ring-glassy carbon disk (0.164 cm²) electrode (RRDE) having a collection efficiency of 23%. The potential of the ring electrode was maintained at 1.0 V versus Ag–AgCl (sat's KCl). $S_1 = 5$, $S_2 = 1.25 \mu$ A. The supporting electrolyte, 0.5 M H₂SO₄ was saturated with air. Rotation rate: 100 rpm, scan rate: 2 mV s⁻¹. (a) The RRDE of the GC disk electrode coated with [CoTBPyP](ClO₄)₄; (b) The RRDE of the GC disk electrode coated with [CoTBPyP][SiW₁₂O₄₀]. The dashed line shows the cyclic voltammogram obtained for [CoTBPyP][SiW₁₂O₄₀] in argon-saturated 0.5 M H₂SO₄ solution, $S_3 = 5 \mu$ A, scan rate is 10 mV s⁻¹.

GC disk was coated with $[CoTBPyP][SiW_{12}O_{40}]$, the ring current became smaller while the disk current became larger, especially for the plateau current of the second step (Fig. 3(b)). For the first step, the main product of reduction of O_2 is H_2O_2 . For the second step, the ratio of the ring current to that of disk is 22% and it corresponds to 78% of the disk current resulting in the four-electron reduction of O_2 to H_2O , i.e. 64% of the O_2 molecules were reduced to H_2O and 36% to H_2O_2 . In addition, the behavior shown in Fig. 3(b) can be understood by comparison with the current-potential curve for the adsorbed catalyst of [CoTBPyP]- $[SiW_{12}O_{40}]$ in the absence of O_2 , shown by the dashed curve in Fig. 3(b). Although the second step of the catalyzed reduction of O2 at the GC disk begins before the $SiW_{12}O_{40}^{4-}$ in electrocatalyst [CoTBPyP][SiW_{12}O_{40}] is reduced, the more of O_2 is reduced to H_2O_2 at this situation than that after $SiW_{12}O_{40}^{4-}$ reduction. That is, the more of O₂ is reduced to H₂O at more negative disk

potentials where the $SiW_{12}O_{40}^{4-}$ is in reduced state that is the most active for catalyzing the four-electron reduction of O₂.

In Fig. 4(a), the current-potential curve is a tendency for the second step plateau currents to become less and less plat as the electrode rotation rate is increased. This pattern of behavior is a very common feature for the steady state current-potential curves recorded at rotating disk electrodes for electrode reactions [17]. The *n*-value, electrons involved in the reduction of O₂, calculated from the slope of Fig. 4(c), is 3.8 per O₂ molecule, essentially corresponding to the result of RRDE at the same potential of -0.45 V (n = 3.5, according to $n = 4 - 2i_{\rm R}/(Ni_{\rm D})$, N = 0.22).



Fig. 4. Reduction of O₂ at a rotating glassy carbon disk electrode coated with [CoTBPyP][SiW₁₂O₄₀]. (a) Current-potential curves at electrode rotation rates (from bottom to top) of 100, 144, 225, 400, 625, 900 and 1600 rpm. For clarity, the base line for each successive curve was adjusted upward. Scan rate = 2 mV s⁻¹, $S = 5 \mu$ A; (b) Levich plot of the plateau currents at potential of -0.45 V from (a) for the second step; (c) Koutecky-Levich plot of the data from (b). The n = 2 and 4 lines are the calculated responses for the diffusionconvection-limited reduction of O₂ by two or four electrons. Supporting electrolyte is 0.5 M H₂SO₄ aqueous saturated with air.



Fig. 5. The stability of the catalytic activity of electrocatalyzing reduction of O_2 at GC electrode coated with [CoTBPyP][SiW₁₂O₄₀] in air-saturated 0.5 M H₂SO₄. Potential was maintained at -0.45 V versus Ag–AgCl (sat's KCl), rotation rate = 1600 rpm.

The stability of catalytic activity of [CoTBPyP]-[SiW₁₂O₄₀] coated at the GC disk electrode for reduction of dioxygen was examined at -0.45 V. It can be seen from Fig. 5 that catalytic current increases gradually in first 5 h then decreases slightly, and about 8 h later becomes stable. It seems that a desirable catalyst for electrocatalyzing reduction of O₂ to H₂O will likely be found from metal porphyrin-metal-oxo cluster supramolecular complexes.

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