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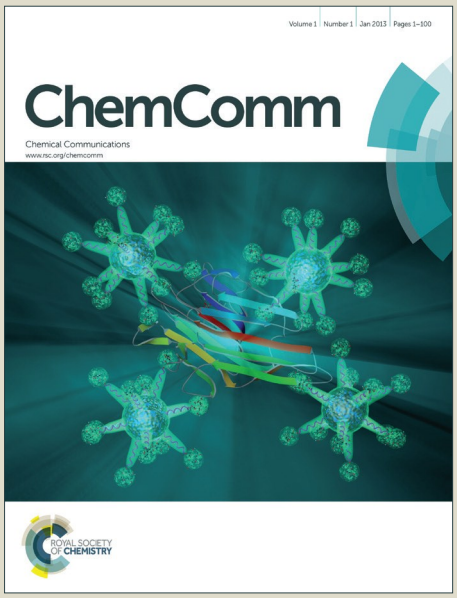

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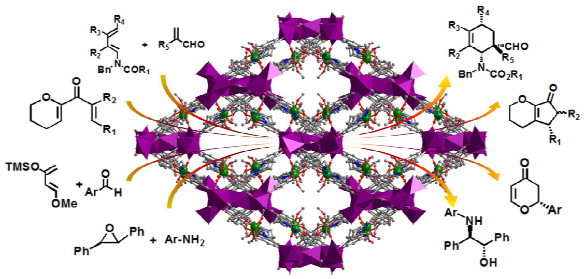

A novel Cr(salen)-based metal-organic framework (MOF) is constructed, which is shown to be a versatile heterogeneous catalyst for a series of important asymmetric transformations including Nazarov cyclization reaction, aminolysis reaction, Diels-Alder and hetero Diels-Alder reactions with the highest ee up to 99%.

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DOI: 10.1039/C6CC06019F

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COMMUNICATION

A Cr(salen)-Based Metal-Organic Framework as Versatile Catalyst for Efficient Asymmetric Transformations†

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Qingchun Xia,[a] Yan Liu,*[a] Zijian Li,[a] Wei Gong[a] and Yong Cui*[a,b]

A porous Cr(salen)-MOF can serve as an efficient and effective heterogeneous catalyst for a series of important asymmetric transformations including Nazarov cyclization, aminolysis reaction, Diels-Alder and hetero Diels-Alder reactions, resulting in comparable or supreior diastereo- or enantioselectivity with respect to the corresponding homogeneous systems.

The search for novel catalyst that can efficiently catalyze various asymmetric transformations with high stereoselectivity has long been of great interest in both academia and industry particularly pharmaceutical industry.[1,2] Albeit tremendous progresses have been made in asymmetric catalysis under homogeneous systems,[2] the development of heterogeneous asymmetric catalysts that are reusable and can facilitate the products separation is still at the infancy stage.[3] Recently, crystalline porous metal-organic frameworks (MOFs),[4] have emerged as a new class of functional materials with potential for applications in gas adsorption,[5] sensing,[6] catalysis,[7] separation,[8] and others.[9] MOFs have provided particularly new opportunities for heterogeneous asymmetric catalysis since the local chiral environments can be readily created within MOFs through either constructing helical porous structures[10,11] or directly utilizing chiral ligands as the linkers.[11-13] MOF catalysts functionalized with Binol, Biphenol and metallosalen catalytic struts have been reported,[12,13] whereas it remains a challenge to achieve great performances on meaningful asymmetric reactions, probably due to the difficulty in exerting precise control over the physical and chemical properties of the framework to improve catalytic activity and selectivity.[11] Moreover, the effective and efficient catalysis of various asymmetric organic reactions by one single MOF-based catalyst has not yet been achieved. Herein, we report such a MOF that is constructed from a custom-designed salen-ligand that can catalyze a series of important asymmetric transformations including Nazarov cyclization reaction, aminolysis reaction, Diels-Alder (DA) and hetero Diels-Alder (HDA) reactions.

It's been documented that metallosalen complexes are one of the best catalysts and privileged ligands for asymmetric synthesis,[14] and MOFs based on M(salen) have been explored as catalysts for asymmetric transformations, where M is Mn/Ru/Co/Fe/VO.[13] Cr(salen) complexes have also been found significant applications in asymmetric catalysis;[15] however, the direct incorporation of Cr(salen) into MOFs as heterogeneous asymmetric catalysts has not been reported despite our recent attempt to introduce Cr(salen) into MOFs *via* post-synthetic solvent-assisted linker exchange approach, which afforded only [Cr/VO(salen)] mixed framework with 40% Cr(salen) moieties.[12f] Indeed, the construction of Cr(salen)-based MOF largely relies on the custom-design of the Cr(salen)-ligand as reported in this work. The resultant Cr(salen)-MOF can serve as a versatile heterogeneous catalyst for efficient asymmetric transformations in Nazarov cyclization reaction, aminolysis reaction, DA and hetero DA reactions.

Heating a mixture of Cr(H_2**L**)Cl, CdI_2 and NaOAc in a mixed solvents containing DMF and MeOH at 100 °C afforded red crystals of $[Na_5Cd_2(Cr\mathbf{L})_4(OH)_2(O_2CCH_3)(O_2CH)_2(H_2O)_7(CH_3OH)_3]\cdot 12H_2O$ (**1**). Single-crystal X-ray diffraction revealed that **1** crystallizes in the chiral orthorhombic space group *F*222, with one whole formula unit in the asymmetric unit. The basic building blocks are two heptanuclear $[Cd_2Na_5(CO_2)_9]$ clusters, which have the same composition but some different connectivity. Two crystallographically distinct Na atoms and one Cd are held together by four bridging carboxylate groups into a $[CdNa_2(CO_2)_4]$ motif, and two of such C_2-symmetry-related units are connected to a Na atom through five carboxylate bridges into a Cd_2Na_5 cluster (Fig. 1a). The Cr in the Cr**L** ligand adopts an octahedral geometry with the equatorial plane occupied by the N_2O_2 donors of one **L** and two apical positions by MeOH and H_2O, OH^- or $HCOO^-$. As a result, each Cr**L** ligand binds to two different Cd_2Na_5 clusters *via* two carboxylate groups, whereas each Cd_2Na_5 connects four pairs of eight Cr**L** ligands to form a 3D network with diamond topology, upon considering a pair of parallel Cr**L** ligands as one linear linker and Cd_2Na_5 clusters as four-connected nodes. A pair of such independent networks is interwoven to form a 2-

[a] *School of Chemistry and Chemical Engineering and State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, China. E-mail: yongcui@sjtu.edu.cn, liuy@sjtu.edu.cn; Fax: (+86) 21-5474-1297*
[b] *Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, China*
† *Electronic Supplementary Information (ESI) available: Experimental details, crystallographic data and spectroscopic data. CCDC 1449027. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/*

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fold interpenetrated 3D framework with 1D channels of ~12.8 × 7.7 Å^2 along the *a*-axis (Fig. 1b).

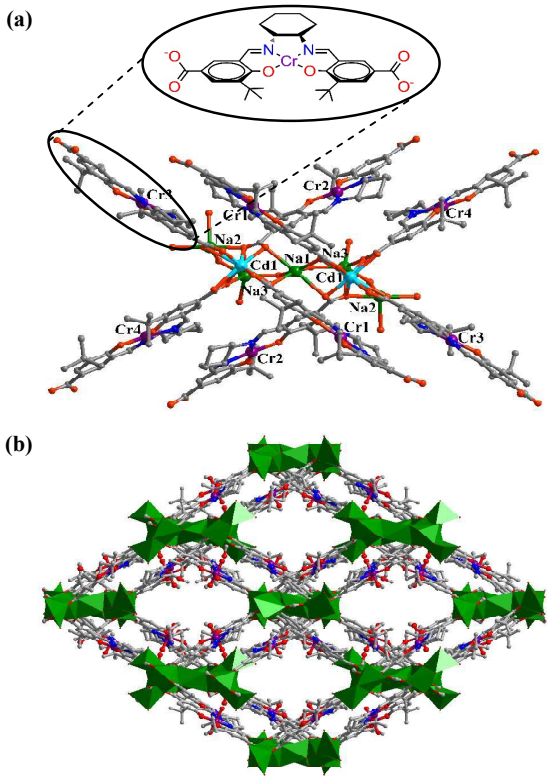
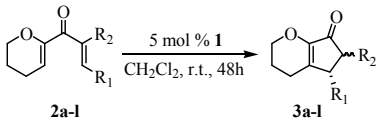


Fig 1. (a) Coordination environment of one [Cd_2Na_5] cluster (the two oxygen atoms of MeOH and H_2O/or OH- at the apical position of Cr**L** were omitted for clarity). (b) View of the interpenetrated 3D framework of **1** along the *a*-axis (violet Cr, green Na, sky blue Cd, red O, blue N, gray C; the metal centers are shown as polyhedra).

1 has ~ 44% solvent accessible volume as calculated from PLATON.[16] The solid-state circular dichroism (CD) spectra of **1** made from *R* and *S* enantiomers of Cr(H_2**L**)Cl showed the mirror images of each other, indicating their enantiomeric nature (Fig. S7). TGA revealed that the guest molecules could be readily removed in the temperature range 80-150 °C, and it is stable up to 400 °C after guest loss (Fig. S6). **1** can be activated under dynamic vacuum at 100 °C with the retention of both crystallinity and structural integrity as proved by powder X-ray diffraction (PXRD) studies (Fig. S5). The chromium ion in **1** is in the +3 oxidation state, as suggested by the Cr $2p_{3/2}$ and $2p_{1/2}$ peaks around 577.3 and 586.7 eV, respectively, in X-ray photoelectron spectroscopy (XPS) spectrum (Fig. S8).[17] The permanent porosity of **1** was evaluated by CO_2 adsorption experiment at 273K, and the Type-I isotherm yielded a BET (Brunauer-Emmett-Teller) surface area of 155 $m^2 \cdot g^{-1}$. Dye uptake measurement showed that **1** could adsorb 2.3 methyl orange (MO, ca. 1.47 × 0.53 × 0.53 nm^3 in size) and 1.7 Rhodamine 6G molecules (R6G, ca. 1.4 × 1.6 nm^2 in size) per formula unit in solution, respectively, indicating the retention of the framework structure in solution.

We first investigated the performances of **1** in catalyzing asymmetric Nazarov cyclization reaction, which is one of the most versatile methods for the synthesis of functionalized cyclopentenones that are the key structural elements of numerous natural products.[15c,18] Cyclization of alkoxydienone substrate **2a** was selected as a model reaction. After screening a series of solvents and different temperature conditions, the asymmetric cyclization was conducted with 5.0 mol% **1** (based on Cr(salen)) in CH_2Cl_2 at room temperature. The reaction was favorably influenced by the addition of 4Å molecular sieves, which may lead to increased conversions and enantioselectivities, and (*R*)-**1** catalyzed cyclization of **2a** afforded corresponding cyclopentenone **3a** as a 5.1:1 mixture of *trans/cis* diastereomers with 81% (*trans*) and 84% (*cis*) ee's after 48 h in the presence of 4 Å molecular sieves.

Table 1. Asymmetric Nazarov Cyclization Catalyzed by **1**.[a]



Entry	R_1	R_2	**3**/Conv (%)[b]	dr[b]	ee_{trans} (%)[c]	ee_{cis} (%)[c]
1	Ph	Me	**a**/86(95)	5.1(3.3)	81(86)	84(92)
2[d]	Ph	Me	**a**/89	4.8	80	75
3	*p*-MeC_6H_4	Me	**b**/82	4	75	75
4	*o*-MeC_6H_4	Me	**c**/83	4.2	77	77
5	*p*-$MeOC_6H_4$	Me	**d**/79	3.7	81	83
6	*p*-FC_6H_4	Me	**e**/84(93)	4.8(3.6)	72(75)	95(87)
7	*p*-ClC_6H_4	Me	**f**/85	4.8	78	86
8	*p*-BrC_6H_4	Me	**g**/89	4.8	81	70
9	Thiophene	Me	**h**/86	4.8	70	73
10	Furan	Me	**i**/86	2	90	91
11	Ph	Et	**j**/72	2.7	80	72
12	Ph	Pr	**k**/80	1.2	79	76
13	*p*-BrC_6H_4	Et	**l**/94(94)	3.3(2.6)	84(80)	90(92)

[a]For reaction details see Experimental section in SI; the data in parentheses are results catalyzed by Cr(Me_2**L**)Cl. [b]Calculated by ^{1}H NMR. [c]Determined by HPLC. [d]Catalyzed by 1 mol% (S)-**1**, the configuration of products is opposite to above.

We then examined different dienones under the optimal reaction condition to evaluate the scope of the MOF catalyzed Nazarov reaction. Various aryl-substituted dienones bearing either electron-withdrawing or electron-donating groups, as well as substituents at *para* or *ortho* positions, could be successfully cyclized to the desired products in good conversions (79-89%) with moderate to high enantioselectivities (70-95% ee, Table 1, entries 3-8). Dienones bearing heterocyclic groups such as thiophene and furan at the *β*-position could also afford the corresponding cyclopentenone derivatives in 86% conversion with 70-91% enantioselectivities (Table 1, entries 9 and 10). When the methyl group at the *α*-position of **2a** was replaced with ethyl and propyl groups, there is almost no loss in either conversion or enantioselectivity, however, the diastereoselectivity decreased sharply to 2.7 and 1.2 for **3j-k**, respectively (Table 1, entries 11 and 12). Similar result could be obtained in cyclization of bromo-substituted **2l** (Table 1, entry 13). (*S*)-**1** catalyzed Nazarov reaction afforded desired cyclopentenone with opposite configuration in both *trans* and *cis* products, indicating that the enantiocontrol of products is directed by the handedness of the catalyst (Table 1, entry 2).

To investigate the confinement of the MOF catalyst, we compared the catalytic activities of **1** and the homogeneous Cr(Me_2**L**)Cl monomer. As shown in Table 1, 5 mol% Cr(Me_2**L**)Cl afforded slightly higher conversions (95%, 93% and 94%) and comparable enantioselectivities (86/92%, 75/87% and 80/92%) of **3a**, **3e** and **3l** under identical conditions. However, the framework-confined catalyst displayed significantly higher diastereoselectivity than the homogeneous counterpart, probably due to the steric restrictions imposed by the inner side of the confined network. The supernatant from the Nazarov reaction after filtration could not afford any

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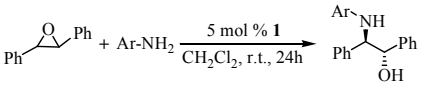
additional product. The inductively coupled plasma-atomic mass spectrometry (ICP-AMS) of the product solution after removal of **1** particles indicated 0.0061% and 0.0010% loss of Cr and Cd ions, respectively, from the structure, which also confirms the heterogeneous nature of the catalytic system. To the best of our knowledge, the MOF catalyst **1** represents the first heterogenized catalyst over framework that is prone to efficiently catalyze the asymmetric Nazarov reaction, although various Brønsted acids and Lewis acids catalyzed processes have been developed in homogeneous systems.[18]

Table 2. Asymmetric Aminolysis Catalyzed by **1**.[a]



4a-i **5a-i**

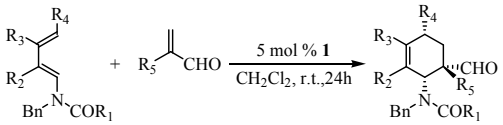
Entry	Ar	**5**/Conv (%)[b]	ee (%)[c]
1	Ph	**a**/92(97)	82(74)
2	*o*-MeC_6H_4	**b**/93	94
3	*m*-MeC_6H_4	**c**/88	93
4	*p*-MeC_6H_4	**d**/97	93
5	*o*-$MeOC_6H_4$	**e**/93(97)	84(72)
6	*p*-$EtOC_6H_4$	**f**/93	91
7	*p*-IC_6H_4	**g**/91(96)	99(89)
8	(2,4-$(OMe)_2$)C_6H_4	**h**/92	92
9	(2-Et-6-Me)C_6H_4	**i**/76(97)	99(17)

[a]For reaction details see Experimental section in SI; the data in parentheses are results catalyzed by Cr(Me_2**L**)Cl. [b]The conversions were determined by ^{1}H NMR analysis based on anilines **4a-i** (0.5 equiv). [c]Determined by HPLC.

To examine the applicability of MOF **1** as heterogeneous catalyst in other types of asymmetric reactions, we investigated its performances in the aminolysis of *trans*-stilbene oxide with anilines, which constitutes a useful method to synthesize enantioenriched anti-*β*-amino alcohols that are core structures of various natural products and biologically active compounds.[15d,19] The combination of *trans*-stilbene oxide, aniline (0.5 equiv), **1** (5 mol%), CH_2Cl_2 and room temperature was crucial to obtain the best result with 92% conversion and 82% ee of desired amino alcohol after 24h (Table 2, entry 1). We next turned our attention to the scope of the reaction with respect to diverse anilines. Toluidines, either *ortho*-, *meta*- or *para*-substituted, were well tolerated, providing the corresponding products **5b-d** with good reactivity (88-97% conv.) and very promising asymmetric induction (93-94% ee), respectively (Table 2, entries 2-4). Methoxy- and ethoxy-substituted anilines also underwent the aminolysis reaction smoothly, affording **5e-f** with satisfying conversions and enantioselectivities (Table 2, entries 5 and 6). When electron-deficient *p*-iodoaniline was employed, 91% conversion together with up to 99% ee was obtained (Table 2, entry 7). Dialkyl- and dialkoxy-substituted anilines such as 2,4-dimethoxyaniline **4h** and 2-ethyl-6-methylaniline **4i** also proved to engage in this reaction in excellent enantioselectivity, despite a little lower conversion for the latter (Table 2, entries 8-9). Remarkably, the MOF catalyst **1** gave 8%, 12%, 10% even 82% higher enantioselectivity compared to its homogeneous analogue for the aminolysis of *trans*-stilbene oxide with aniline, *o*-methoxyaniline, *p*-iodoaniline and 2-ethyl-6-methylaniline, respectivily. These results showed clearly that the reaction in framework, in comparison with that in the homogeneous system, can improve the enantioselectivity, and the significant enhancement may be attributed to restricted movement of the substrates in combination with multiple chiral induction in the confined system.

Besides Nazarov cyclization and asymmetric aminolysis, we have also demonstrated the versatility of **1** in other important asymmetric processes, such as Diels-Alder (DA) and Hetero-Diels-Alder (HDA) reactions, which provide versatile building blocks for(**6a**) reacted with methacrolein (**7a**) in the presence of 5 mol%

Table 3. Asymmetric Diels-Alder Reactions Catalyzed by **1**.[a]



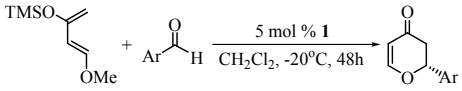
6a-g **7a-c** **8a-g**

Entry	Diene	R_1	R_2	R_3	R_4	R_5	**8**/Conv (%)[b]	ee (%)[c]
1	**6a**	MeO	H	H	H	**7a**/Me	**a**/90(98)	87(70)
2	**6b**	MeO	Me	H	H	**7a**/Me	**b**/32	86
3	**6c**	MeO	H	Me	H	**7a**/Me	**c**/79(98)	91(86)
4	**6d**	MeO	H	H	Me	**7a**/Me	**d**/30	87
5	**6e**	Me	H	H	H	**7a**/Me	**e**/81(85)	81(58)
6	**6f**	MeO	H	H	H	**7b**/H	**f**/88	84
7	**6g**	MeO	H	H	H	**7c**/Et	**g**/81	83

[a]For reaction details see Experimental section in SI; the data in parentheses are results catalyzed by Cr(Me_2**L**)Cl. [b]Calculated by ^{1}H NMR. [c]Determined by HPLC.

chromium catalyst **1** and 4 Å molecular sieves in CH_2Cl_2 to give cycloadduct **8a** in 90% conversion with 87% ee in 24 h at r.t. (Table 3, entry 1). The DA reaction was then extended, and a range of methyl-substituted dienes reacted smoothly with methacrolein under the same reaction condition, affording corresponding products in moderate conversions with ee up to 91% (Table 3, entries 2-4). When the methoxy group at $\mathbf{R_1}$ was replaced by methyl group, the diene **6e** could be transformed to the corresponding product in 81% conversion and 81% ee (Table 3, entry 5). The DA reaction with different aldehydes such as acrolein **7b** and ethacrolein **7c** gave products **8f** and **8g** in 88% conversion with 84% ee and 81% conversion with 83% ee, respectively (Table 3, entries 6 and 7).

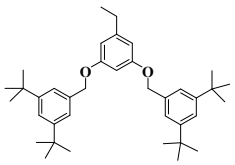
Table 4. Asymmetric Hetero-Diels-Alder Reactions Catalyzed by **1**.[a]



9a-h **10a-h**

Entry	Ar	**10**/Conv (%)[b]	ee (%)[c]
1	Ph	**a**/87(92)	78(66)
2	(2-F)Ph	**b**/89	78
3	(4-F)Ph	**c**/84(95)	79(64)
4	(4-Br)Ph	**e**/86	72
5	(3-NO_2)Ph	**f**/83	75
6	(4-NO_2)Ph	**g**/77(89)	75(70)
7	(3-G_0)Ph	**h**/<5(88)	n.d.(n.d.)

G_0:



[a]For reaction details see Experimental section in SI; the data in parentheses are results catalyzed by Cr(Me_2**L**)Cl. [b]Calculated by ^{1}H NMR. [c]Determined by HPLC.

The heterogeneous hetero Diels-Alder (HDA) reactions were also performed with 5% catalyst **1** and 4 Å molecular sieves at -20°C in CH_2Cl_2. It was found that the desired products, from various benzaldehydes and Danishefsky diene, could be obtained in 77-89%

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conversions after 48h with 72-79% enantioselectivity (Table 4). The electronic nature of benzaldehyde substrates is crucial to the reaction obviously, and only species bearing electron-withdrawing groups (-F, -Cl, -Br, $-NO_2$) could be transferred efficiently, but substituent at different positions of the phenyl groups had little influence on the conversion and selectivity. The benzaldehyde with large steric hindrance, such as G_0 group, could not be a suitable substrate for HDA transformation, and only a very small amount of product (<5% conversion) was detected (Table 4, entry 7). Meanwhile, the corresponding homogeneous catalyst still afforded 88% conversion, indicating that the bulky substrate could not diffuse into the MOF catalyst efficiently and the heterogeneous catalysis indeed occurred inside the pores of MOF.

MOF **1** displayed obviously higher enantioselectivity than the homogeneous analogue in both DA and HDA reaction, further highlighting the unique confinement effect of MOF catalysis, which can optimize the environment around the active sites in asymmetric chemical processes. In addition, the turnover number (TON) values for all the above four reactions are about 3.1-4 times of those in homogeneous cases. The MOF catalyst can be recycled and reused with negligible loss of efficiency and enantioselectivity. For instance, the conversion/ee's of aminolysis of benzaldehyde for four consecutive runs are 92/81%, 90/81%, 90/77%, 87/77%, respectively. PXRD showed the recovered solid remained crystalline and structurally intact. XPS measurement showed the recovered chromium catalyst retained +3 oxidation state.

In summary, we have demonstrated the construction of a porous Cr(salen)-MOF and explored its universality in a series of important asymmetric organic reactions. Our work not only advances MOFs as a new type of versatile catalyst for general application in asymmetric catalysis, but also provides a new perspective for heterogeneous asymmetric catalysis in industry. Moreover, our work also expands the scope of diverse and tailored porous framework materials, promising potential breakthrough in practical application of MOF-based catalysts in heterogeneous access to optical active chemicals.

This work was supported by NSFC-21371119, 21431004, 21401128 and 21522104, "973" Program (2014CB932102 and 2012CB8217), Shanghai "Eastern Scholar" Program and SSTC-14YF1401300.

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