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Stereochemically Dependent Synthesis of Two Cu(I) Cluster-Based Coordination Polymers with Thermochromic Luminescence

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Supporting Information

ABSTRACT: Two Cu(I) cluster based coordination polymers, $[CuI(cis-bpype)]\cdot CH_3CN$ (1) and $[Cu_4I_4(cis-bpype)_3(trans-bpype)]\cdot 3DMF$ (2), have been synthesized from *cis-* and *trans-1,2-bis*(4-(pyridin-2-yl)phenyl)ethane (*cis-* and *trans-bpype*) ligands and $\{Cu_4I_4(PPh_3)_4\}$ as starting materials. In compound 1, adjacent rhomboid-type $\{Cu_2I_2\}$ units from the decomposition of $\{Cu_4I_4(PPh_3)_4\}$ starting material connect by *cis-bpype* ligands to form a 1D framework. Compound 2 also has a 1D structure, but it has a $\{M_2L_3\}$ -type coordinated cage constructed by three *cis-bpype* ligands and two $\{Cu_4I_4\}$ secondary building units (SBU), and these coordination cages further link by *trans-bpype* to form the final frameworks. Upon cooling from 300 to 80 K, these Cu(I)



cluster based coordination polymers exhibit interesting thermochromic behavior. In particular, compound 2 gives a chromic process from green luminescence at room temperature to red luminescence at 80 K and its corresponding CIE coordinates shift from green (0.34, 0.43) at 300 K to red (0.46, 0.42) at 80 K, respectively. This red shift of 124 nm (516 to 640 nm) is large enough to ensure a color change visible to the naked eye, which can be potentially utilized as a temperature sensor with a wide range.

INTRODUCTION

Luminescent coordination polymers (CPs) or metal-organic frameworks (MOFs) have received immense attention due to their diverse topological structures and potential applications in detection and sensing, bioimaging, displays, and optical devices.¹⁻⁵ One promising strategy for the preparation of such functional materials is based on the inorganic connecting nodes and organic linkers within the coordination polymer framework, since those nodes or linkers could be exploited as luminophores to generate interesting luminescence.^{6–8} As one important subclass of aggregation-induced emission (AIE) molecules, tetraphenylethylene (TPE) based ligands with carboxyl or pyridyl sites have been designed and successfully introduced into coordination polymer frameworks, resulting in intriguing luminescent properties and other potential applications.⁹⁻¹⁷ A new zirconium tetraphenylethylene based MOF with a deep blue fluorescent emission and high quantum yield $(99.9 \pm 0.5\%)$ under Ar has been obtained recently.¹⁸ In addition, a rare earth (RE) free, three-dimensional coordination polymer has been synthesized, and this compound contains a blue-excitable yellow phosphor, which can be used as a promising material for phosphor conversion WLEDs.¹⁹ These successful examples may not only provide us with guidance in designing and synthesizing novel luminescent coordination

polymers but also inspire us exploring new characters in this field.

In the structural chemistry of MOFs, metal cluster based nodes, also known as secondary building units (SBUs), may act as anchors to ensure the overall architectural stability of the MOF.^{20,21} The synthesis of MOFs has mainly relied on a onepot synthetic method, and the existence of metal cluster based SBUs within the final framework is unpredictable. Notably, utilization of these existing metal cluster compounds as starting materials in the synthesis of MOFs represents a feasible strategy to construct metal cluster based structures, and this strategy may also help to predict their structure-property relationship at the crystal engineering level.²²⁻²⁴ Among these existing clusters, cubane-like { $Cu_4I_4L_r$ } (L = ligand) clusters have been extensively studied for their remarkable luminescent performance under external stimulation, such as temperature and pressure.²⁵⁻³² For the synthesis of coordination polymers, some Cu(I) cluster-based coordination polymers containing a $\{Cu_4I_4\}$ SBU or other more complex SBU have already been prepared in one pot,³³⁻⁴² but utilization of $\{Cu_4I_4L_x\}$ clusters as starting materials has been less studied.⁴

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Scheme 1. Synthesis of cis-bpype and trans-bpype



Herein, $\{Cu_4I_4(PPh_3)_4\}^{26}$ has been selected as the starting material due to its external stimuli luminescence feature and the weak coordination bonds between PPh₃ groups and Cu(I) sites. Two organic ligands with a pyridyl function and novel luminescent properties, cis-1,2-bis(4-(pyridin-2-yl)phenyl)ethane and trans-1,2-bis(4-(pyridin-2-yl)phenyl)ethane (cisbpype and trans-bpype), have been synthesized in two steps according to previous works, but with some modification (Scheme 1).^{19,44} The solvothermal reaction of *cis*-bpype and $\{Cu_4I_4(PPh_3)_4\}$ starting material in acetonitrile yields a onedimensional coordination polymer with {Cu₂I₂} nodes, [CuI-(cis-bpype)]·CH₃CN (1). In the reaction of cis-bpype and trans-bpype ligands with $\{Cu_4I_4(PPh_3)_4\}$ starting material in N,N-dimethylformamide (DMF), another one-dimensional coordination polymer with $\{Cu_4I_4\}$ nodes, $[Cu_4I_4(cis-bpy$ $pe_{3}(trans-bpype)]$ ·3DMF (2), has been obtained. The structural and thermochromic luminescence of the assynthesized Cu(I) cluster based coordination polymers have been well studied.

EXPERIMENTAL SECTION

Materials and Methods. The C, H, and N elemental analyses were performed on a Euro vector EA3000 elemental analyzer. FT-IR spectra were obtained on a Mattson Alpha Centauri spectrometer. The thermal analyses were measured using a gravimetric analyzer (Pyris Diamond TGA/DTA) under nitrogen. ¹H NMR spectra were measured in DMSO- d_6 at 20 ± 1 °C by an AV-400 NMR spectrometer from Bruker. The UV–vis diffuse reflectance spectra (DRS) measurements were carried out on a UV-2600 spectrophotometer (Shimadzu) with BaSO₄ as a reference. Powder X-ray diffraction (PXRD) patterns were determined on a Rigaku Dmax 2000 X-ray diffractometer with Cu K α radiation (λ = 0.154 nm). The photoluminescent properties of compounds 1 and 2 were conducted utilizing a PerkinElmer FLSP920 edinburgh fluorescence spectrometer with cooling from 300 to 80 K. Photoluminescence (PL) measurements of 1,2-bis(4-(pyridin-2-yl)phenyl)ethane (bpype) were carried out on a Hitachi F-7000 spectrophotometer.

Synthesis of cis-/trans-1,2-Bis(4-bromophenyl)-1,2-diphenylethene (cis-/trans-bbpe). cis-bbpe and trans-bbpe were prepared via the McMurry coupling of 4-bromobenzophenone, and the product was a mixture with a cis/trans isomer ratio of 44/56, as previously reported.⁴⁴ 4-Bromobenzophenone (5 g, 19.15 mmol) and zinc powder (3.75 g, 57.7 mmol) were placed in a two-necked flask (250 mL) under an argon atmosphere. After the flask was immersed into an ice bath, dry THF (60 mL) was placed in the flask through the branch. Then titanium tetrachloride (3.2 mL, 29.2 mmol) was slowly added with rapid stirring over approximately 30 min. The mixture was refluxed for 16 h at 90 °C. Then, the product was filtered and then vacuum-evaporated. A 50 mL portion of chloroform was added to the black oil and then recrystallized with methanol (400 mL) to give a white powder.

Synthesis of cis-1,2-Bis(4-(pyridin-2-yl)phenyl)ethane and trans-1,2-Bis(4-(pyridin-2-yl)phenyl)ethane (cis-bpype and trans-bpype). The preparation of the ligands cis-bpype and transbpype (Scheme 1 and Figure S1 in the Supporting Information) was modified from the original reported procedure.¹⁹ The cis-/trans-bbpe mixture (0.84 mmol, 0.411 g), pyridine-4-boronic acid (6.72 mmol, 1.209 g), tetrakis(triphenylphosphine)palladium (Pd(PPh₃)₄; 0.0588 mmol, 68 mg), and potassium carbonate (25.2 mmol, 3.48 g) were placed in the 100 mL flask. A 30 mL portion of dimethylformamide (DMF) and 8 mL of water were then also added, and the solution was refluxed at 130 °C for 48 h. After a Schiffs base reaction, the product was first vacuum-evaporated and then extracted three times with dichloromethane. After it was washed with water and dried with anhydrous Na2SO4, the product was recrystallized in petroleum ether to give a pale yellow powder. The final products of *cis*-bpype and *trans*byppe were purified by column chromatography with CH₂Cl₂/MeOH 30/1 mobile phase; the product ratio of these ligands was 1:1. transbpype: ¹H NMR (DMSO-*d*₆, 400 MHz) δ 8.59 (dd, 4H), 7.69–7.62 (m, 8H), 7.23-7.05 (m, 14H). cis-bpype: ¹H NMR (DMSO-d⁶, 400 MHz) δ 8.58 (4H, dd), 7.70–7.64 (m, 8H), 7.21–7.1 (m, 10H), 7.03 (dd, 4H) (Figure S1).

Synthesis of { $Cu_4I_4(PPh_3)_4$ } Starting Material.²⁶ CuI (1.9 g, 10 mmol), triphenylphosphine (2.65 g, 0.1 mmol), and 250 mL of toluene were placed in a 500 mL flask, and the solution was refluxed at 120 °C for 16 h. Then, the product was filtered through double-layered filter paper. The precipitates were dried under vacuum at room temperature, yielding { $Cu_4I_4(PPh_3)_4$ } as a white powder.

Solvothermal Synthesis of 1 and 2. Typically, $\{Cu_4I_4(PPh_3)_4\}$ starting material (19 mg, 0.025 mmol), *cis*-bpype (8 mg, 0.016 mmol), and acetonitrile (6 mL) were sealed in a Teflon reactor (15 mL) and heated at 120 °C for 3 days. Yellow block crystals of 1 were obtained in a 40% yield based on Cu. Anal. Calcd for $C_{38}H_{29}N_3CuI$ ($M_r =$ 718.08): C, 63.56; H, 4.07; N, 5.85. Found: C, 63.51; H, 4.01; N, 5.87. IR data (KBr, cm⁻¹): 3054 (s), 3025 (s), 2994 (s), 2250 (s), 1681 (s), 1605 (w), 1535 (m), 1485 (w), 1441 (w), 1420 (w), 1399 (w), 1326 (m), 1274 (s), 1216 (w), 1182 (s), 1154 (s), 1111 (m), 1069 (m), 1031 (m), 1005 (m), 975 (s), 958 (s), 916 (s), 858 (m), 836 (m), 803 (w), 769 (m), 748 (w), 733 (w), 700 (w), 671 (w), 643 (w), 625 (m), 586 (s), 573 (m), 548 (m), 529 (s), 498 (m), 470 (m), 415 (s).

For 2, { $Cu_4I_4(PPh_3)_4$ } starting material (19 mg, 0.025 mmol), *cis*byppe (4 mg, 0.008 mmol), and *trans*-bpype (4 mg, 0.008 mmol) were dissolved in DMF (6 mL). Then the mixture was heated in a Teflon reactor (15 mL) at 120 °C for 3 days. Dark yellow crystals of **2** were obtained in a 50% yield based on Cu. Anal. Calcd for $C_{153}H_{125}O_3N_{11}Cu_8I_8$ (M_r = 3689.15): C, 49.81; H, 3.42; N, 4.18. Found: C, 49.87; H, 3.45; N, 4.23. IR data (KBr, cm⁻¹): 3641 (s), 3050 (s), 3025 (s), 2923 (s), 1672 (w), 1605 (w), 1533 (m), 1486 (w), 1440 (w), 1421 (w), 1400 (w), 1382 (w), 1254 (m), 1218 (w), 1154 (m), 1112 (m), 1084 (m), 1069 (m), 1032 (m), 1005 (m), 858 (s), 837 (s), 817 (w), 804 (w), 771 (m), 747 (m), 730 (w), 701 (w), 672 (m), 644 (s), 623 (s), 576 (s), 553 (s), 525 (s), 492 (m).

X-ray Crystallography. Crystallographic data of 1 were collected at 193 K on a Bruker APEX CCD area detector using Mo K α radiation ($\lambda = 0.71073$ Å). Single-crystal X-ray data of **2** were measured on an Oxford Diffraction Gemini R Ultra diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å) at 293 K. The starting structural models were solved by direct methods and refined by full-matrix least-squares techniques using SHELXL-2014 within WINGX,⁴⁵ and all nonhydrogen atoms were refined anisotropically. The SQUEEZE function in PLATON was applied to remove residual electron density by disordered solvent molecules.⁴⁶ Further crystallographic details and structure refinements for 1 and 2 are provided in Table 1. Selected bond lengths and angles for 1 and 2 are given in Tables S1 and S2 in the Supporting Information.

Table 1. Crystal Data and Structure Refinement for 1 and 2

	1	2
formula	C38H29N3CuI	$C_{153}H_{125}O_{3}N_{11}Cu_{8}I_{8}$
$M_{ m r}$	718.08	3689.15
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1$
a (Å)	10.1530(7)	16.8555(12)
b (Å)	11.6380(9)	17.5982(12)
c (Å)	26.7750(19)	25.041(2)
α (deg)	90	90
β (deg)	95.8520(14)	99.550(7)
γ (deg)	90	90
V (Å ³)	3147.3(4)	7324.7(9)
Ζ	4	2
$D_{\rm calc}~({\rm g}~{\rm cm}^{-3})$	1.515	1.673
F(000)	1440	3360
$R_{ m int}$	0.0651	0.0816
GOF on F^2	1.092	1.088
Flack factor		0.00(5)
$\mathrm{R1}^a (I > 2\sigma(I))$	0.0650	0.1126
wR2 ^b (all data)	0.1305	0.2951
${}^{t}R1 = \sum_{w(F_{o}^{2})^{2}} F_{o} - \sum_{w(F_{o}^{2})^{2}} F_{o} ^{1/2}.$	$ F_c /\sum F_o $. ^b wR2 =	$= \{\sum [w(F_o^2 - F_c^2)^2]/$

RESULTS AND DISCUSSION

Structural Description of 1 and 2. Compound 1 crystallizes in the monoclinic space group $P2_1/n$ and its asymmetric unit (Figure 1) is composed of one Cu(I) cation, one *cis*-bpype ligand, and one lattice acetonitrile molecule. Cu1 sites are coordinated with two iodine atoms and two N atoms of *cis*-bpype ligands to form an approximate tetrahedron. Average bond lengths of Cu–I and Cu–N are 2.66 and 2.12 Å, respectively, which are close to those in similar reported



Figure 1. Asymmetric unit of compound **1**. Symmetry codes: (#1) -x, -y + 1, -z; (#2) -x - 1, -y, -z.

structures.^{16,47} Two Cu1 sites connect each other by a μ_2 bridging I1 atom to form a rhomboid-like {Cu₂I₂} unit coming from decomposed {Cu₄I₄(PPh₃)₄} starting material, and the Cu–Cu bond distance is about 2.71 Å, within the region of metallophilic interactions. Adjacent {Cu₂I₂} units connect by *cis*-bpype ligands to form a 1D chain (Figure 2a). Moreover, adjacent chains are further interlinked by C–H··· π interactions between a hydrogen of benzene and pyridine into a 3D supramolecular structure (Figure 2b).



Figure 2. (a) View of the 1D chain in compound **1**. (b) View of the 3D supramolecular structure of compound **1**. The CH \cdots π interactions are illustrated by black dotted lines.

Compound 2 crystallized in the space group $P2_1$, and its asymmetric unit includes three *cis*-byppe ligands, one *trans*byppe ligand, eight crystallographically independent Cu(I) ions, and eight crystallographically unique I atoms (Figure 3). Four Cu(I) ions are coordinated to four adjacent μ_3 -bridging iodine ions to build up a cubane-shaped {Cu₄I₄} SBU. Similar to the case for compound 1, all of the Cu(I) sites within the {Cu₄I₄} SBU adopt a distorted-tetrahedral coordination mode but can be divided into two types according to the coordinated N

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Figure 3. Asymmetric unit of compound **2**. Symmetry codes: (#1) x - 2, *y*, z - 1; (#2) x + 2, *y*, z + 1.

atoms from the cis-bpype ligand or trans-bpype ligand. The average bond lengths of Cu-I, Cu-N, Cu-Cu, and I-I in the {Cu₄I₄} SBUs are 2.69, 2.03, 2.70, and 4.49 Å, respectively, which are in agreement with those in isolated $\{Cu_4I_4\}$ SBUs. Notably, the Cu–Cu distances all fall in the range 2.63–2.78 Å, shorter than the sum of the van der Waals radii of Cu atoms (2.80 Å),⁴⁸ suggesting effective metallophilic interactions in the $\{Cu_4I_4\}$ SBU of 2. Two $\{Cu_4I_4\}$ SBUs (simplified as M) and *cis*-bpype ligands (simplified as L) within the $\{Cu_4I_4\}_2\{cis$ bpype}, coordination cage connect with each other to form a ${M_2L_3}$ -type cage (Figure S2 in the Supporting Information). These coordination cages link with *trans*-bpype ligands to construct a 1D chain with a "candied gourd" shape. Adjacent chains are joined together by $\pi \cdots \pi$ stacking between pyridine and pyridine groups, resulting in a 3D supramolecular architecture (Figures 4 and 5). PLATON calculations reveal that the solvent-accessible volume for 2 is 17.8%,⁴⁶ which is occupied by three DMF molecules on the basis of elemental and thermogravimetric analysis (Figure S3 in the Supporting Information).

Characterizations of 1 and 2. The crystal structure and photophysical properties of compounds 1 and 2 have been well characterized by various measurements at room temperature. Powder XRD patterns for samples 1 and 2 are nearly identical to their simulated patterns, which confirmed the phase purity of as-synthesized samples (Figure S4 in the Supporting Information). Compounds 1 and 2 show similar characteristic frequencies within all measured regions in infrared spectra (Figure S5 in the Supporting Information). The UV absorption bands (Figure S6 in the Supporting Information) of samples 1 and 2 range from 225 to 650 cm^{-1} and from 225 to 550 cm^{-1} respectively. Upon excitation at 372 nm, the emission peak of bpype is blue-shifted from 485 nm at 298 K to 457 nm at 77 K, which could be attributed to the nature of the AIE ligands at low temperature (Figure 6a). At 298 K, compound 1, which is composed of rhombic {Cu₂I₂} units, gives light green emission centered at 500 nm on excitation at 340 nm (Figure 6b). For compound 2 with cubane-type $\{Cu_4I_4\}$ cores as SBUs, its



Figure 4. Structural presentation and illustration of as-synthesized compound 2. $\{M_2L_3\}$ -type coordination cages formed by $\{Cu_4I_4\}$ SBUs and three *cis*-bpype ligands are drawn with balls for clarity. *trans*-bpype is simplified as a "gold stick" for clarity.



Figure 5. View of the $\pi \cdots \pi$ stacking mode of compound 2.

room-temperature solid-state emission spectrum (Figure 6c) also shows a green emission at 516 nm (λ_{ex} 380 nm). In contrast to the emission of the free byppe ligand at 485 nm, both emissions of compounds 1 and 2 exhibit slight red shifts, giving approximate wavelengths of 15 and 31 nm, respectively. This phenomenon may be assigned to ligand to metal charge transfer (LMCT) from the byppe ligands to the Cu(I) centers. The excited-state lifetimes (τ) (Figure S7 and Table S3 in the Supporting Information) of the as-synthesized samples are 0.88 ns for 1 and 0.45 ns for 2, respectively.

Thermochromic Luminescence Properties. One of the interesting features for Cu(I) cluster-based coordination polymers is their novel emission shifts and color changes under external stimuli.^{36–38} Hence, the significant structural diversity of compounds 1 and 2 may lead to different thermochromic behavior. To further study the thermochromic

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Figure 6. Solid-state emission spectra of byppe at 298 and 77 K (a) and of 1 (b) and 2 (c) at room temperature.



Figure 7. Emission changes and the commission internacionaled eclairage (CIE) color space chromaticity diagram of samples 1 (a) and 2 (b) from 80 to 300 K. The excitation wavelength for samples 1 and 2 are 340 and 380 nm, respectively.

properties of 1 and 2, their solid-state emission spectra have been monitored from 300 to 80 K by dipping those samples into liquid nitrogen. For compound 1, emission intensities are gradually enhanced upon cooling, and its emission maximum blue-shifts by about 12 nm when the temperature is lowered to 80 K (Figure 7a). This slight color change can hardly be distinguished by the naked eye, which is in agreement with the result of the 1931 Commission Internationale d'Eclairage (CIE) chromaticity from (0.331, 0.44) at 300 K to (0.294, 0.485) at 80 K. This result is similar to the observed phenomenon of the ligand at 298 and 77 K, essentially belonging to ligand-dominated luminescence.^{51,52}

However, compound **2** exhibits a chromic process from green luminescence at room temperature to red luminescence at 80 K at an excitation wavelength of 380 nm. At 298 K, it also has ligand-dominated luminescence. As shown in Figure 7b, in addition to the existence of green luminescence at 516 nm, a

new red luminescence with a maximum wavelength of around 640 nm at low energy (LE) appears during the temperature decrease from 300 K to about 240 K. Under further continual cooling to 80 K, the continuing enhancement of emission intensities and the blue shift of maximum wavelengths for both green and red luminescence have been observed, but the emission intensity of red luminescence increases more rapidly and the LE band plays a dominant role. Its corresponding CIE coordinates shift from green (0.34, 0.43) at 300 K to red (0.46, 0.42) at 80 K, respectively. This red shift of 124 nm (516 to 640 nm) is large enough to ensure a color change visible to the naked eye. Unlike those reported $\{Cu_{4}I_{4}\}$ cluster-based frameworks with a new band at high energy (HE) at low temperature coming from a halide to ligand charge-transfer (³XLCT) excited state,³⁶ the probable explanation for compound 2 may be ascribed to the structure composition and coordination mode of the $\{Cu_4I_4\}$ SBU and the two types

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of byype ligands, which may lead to more complex charge transfer processes among Cu(I) sites, I atoms, and *cis*- or *trans*-byype, such as halide to metal charge transfer and coppercentered d \rightarrow s, p transitions.^{25,48} Moreover, these results also demonstrate that the existence of higher nuclearity Cu(I) clusters is essential for the design and synthesis of functional coordination polymers with stimuli-responsive properties.

CONCLUSION

In summary, two Cu(I) cluster based coordination polymers with cis-bpype and trans-bpype ligands have been successfully prepared. Compound 1 exhibits a classical 1D chain with a single cis-bpype ligand, while 2 shows a 1D chain with a {M₂L₃}-type coordination cage containing both *cis*-bpype and trans-bpype ligands. Remarkably, compound 2 exhibits interesting thermochromic behavior during cooling from 300 to 80 K, giving a large 124 nm red shift and a visible color change from green (0.34, 0.43) at 300 K to red (0.46, 0.42) at 80 K, respectively. It could be potentially applied in temperature sensor devices with a wide range. The successful synthesis of those coordination polymers by using the metal clusters as starting materials supply a feasible route for the design and preparation of smart cluster based coordination polymers with stimuli-responsive properties, and this strategy could also be used to prepare other types of hybrid frameworks.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b02123.

¹H NMR spectra of *trans*-bpype and *cis*-bpype, selected bond lengths and angles, structural views, TGA analysis, powder X-ray diffraction patterns, FT-IR spectra, solid state UV–vis spectra, and lifetimes of compounds 1 and 2 (PDF)

Accession Codes

CCDC 1563659–1563660 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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