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2018

Pei, W.-B., Jing, Z.-Y., Ren, L.-T., Wang, Y., Wu, J., Huang, L., . . . Huang, W. (2018). Nearly pure red color upconversion luminescence of Ln-doped Sc₂O₃ with unexpected RE-MOFs molecular alloys as precursor. *Inorganic Chemistry*, 57(17), 10511–10517.
doi:10.1021/acs.inorgchem.7b02255

<https://hdl.handle.net/10356/138997>

<https://doi.org/10.1021/acs.inorgchem.7b02255>

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Nearly Pure Red Color Upconversion Luminescence of Ln-doped Sc_2O_3 with Unexpected RE-MOFs Molecular Alloys as Precursor

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KEYWORDS upconversion, molecular alloy, RE-MOFs

Supporting Information Placeholder

ABSTRACT: Unexpected Sc/Ln co-doped rare earth metal-organic frameworks (RE-MOFs) molecular alloys (MAs) based on oxalic acid ligand were obtained. Calcination of the RE-MOFs MAs gave the corresponding co-doped rare earth oxides a strong and nearly pure red color upconversion luminescence. It allows the resulting lanthanide ion (Ln^{3+}) doped upconversion materials (LDUMs) a wide range of applications from optical communications to disease diagnosis. Moreover, the pyrolysis RE-MOFs MAs precursor has demonstrated to be an effective preparation method for uniform Ln-doped Sc_2O_3 system.

INTRODUCTION

Photon upconversion (UC) materials have drawn great scientific interests due to a wide range of applications from high-resolution displays, integrated optical systems, solid-state lasers, to biological labels and imaging, as well as optical communication.¹⁻⁹ Among the UC materials found, lanthanide ion (Ln^{3+}) doped upconversion materials (LDUMs) show excellent near-infrared to visible UC efficiency,¹⁰⁻¹² and other superior characteristics including narrow emission band widths, long luminescence lifetime, low autofluorescence background, high resistance to photobleaching, photoblinking, photochemical degradation and low toxicity.¹³⁻¹⁵ The aforementioned characteristics make LDUMs a good substitution for conventional organic dyes and quantum dots as highly promising optical materials.¹⁶⁻²⁰

Inorganic fluorides and oxides are extensively researched as host materials for effective UC process in combination with Yb^{3+} as the sensitizer and $\text{Er}^{3+}/\text{Tm}^{3+}/\text{Ho}^{3+}$ as emitter.²¹⁻²³ RE-MOFs are potential host materials, but they are rarely studied because of the presence of multiphonon relaxation and

decreased UC efficiency.²⁴⁻²⁶ Zheng and coworkers synthesized Ln-doped RE-Na heterometallic complex, but no visible UC luminescence was observed owing to the quenching effect by water molecules.²⁷ However, RE-MOFs are still attractive to be used as host materials due to distinctive advantages, such as simple synthetic approach, easily tailored molecular structure and functional properties. Nonetheless, there are still great challenges to develop designed molecules for efficient UC luminescence.

Scandium (Sc) is a unique rare earth element that has distinct electron configuration and much smaller ion radius than other Ln^{3+} ions. It received less attention in both LDUMs and coordination chemistry fields.²⁸⁻³⁴ The main reason is that phase separation may occur in Ln-doped Sc-based systems because of the aforementioned differences between Sc^{3+} and Ln^{3+} ions.³⁵ However, our recent work demonstrated for the first time that the $\text{Na}_x\text{ScF}_{3+x}\cdot\text{Yb}/\text{Er}$ nanocrystals prepared gave strong UC emission with a large red to green ratio, which was different from other widely researched UC systems.³⁶ Encouraged by our previous work to develop highly promising Sc-based UC systems, we are exploring Sc-based MOFs systems and the corresponding Ln-doped Sc_2O_3 systems prepared by calcination of the RE-MOFs MAs.

MOFs are well-known functional materials in many research fields, such as gas absorption, sensors and catalysis, etc. Recent reports indicated that MOFs could be used as sacrificial precursors to synthesize useful derivant with high effectiveness and unique properties. Kennedy and co-authors reported Ru-impregnated Zr-MOF-derived highly active catalyst for CO_2 methanation. Yamauchi et al. obtained ZIF-8 derived nanoporous carbons for supercapacitor applications.^{37,38} It is found that some derivants have unique properties that can only be achieved using the MOFs templating strategy. In

addition, the composition of the derivant can be precisely controlled.³⁸

As for LDUMs, there are few reports on RE-MOFs materials and the corresponding derivant²⁷. Considering the possible phase separation phenomenon by inorganic synthesis method, we synthesized and studied the Ln-doped Sc₂O₃ systems using RE-MOFs MAs as precursor.

Unexpected RE-MOFs MAs were serendipitously obtained, though Sc-based and Ln-based MOFs showed two different structural types (named as S_{Sc} and S_{Yb}). Moreover, the main crystalline lattice structure changes from S_{Yb} to S_{Sc} at a specific Sc:Ln mole ratio (Scheme 1). The co-doped rare earth oxides (REO) prepared by calcination of RE-MOFs MAs as precursor show relatively strong and nearly pure red color emission. It provides wide range of applications of LDUMs from optical communications to disease diagnosis.

Scheme 1. Schematic illustration of the unexpected MAs formation based on RE-MOFs and the evolution at various Sc/Ln mole ratio.

EXPERIMENTAL SECTION

Synthesis of RE-MOFs and co-doped MAs. A mixture of oxalic acid (1 mmol), RECl₃·6H₂O (1 mL, 0.1 M·L⁻¹, RE = Sc, Yb and Er respectively, or a mixture of REs at specific mole ratio instead of 100% RECl₃·6H₂O) and H₂O (8 mL) were stirred for half an hour and then sealed in a 23 mL Teflon-lined autoclave before heating under autogenous pressure to 130 °C for 72 h. After cooling to room temperature, microcrystals were obtained by filtration, followed by DI water rinse and finally dried naturally. The product yields were 69 ± 5 % (based on RECl₃·6H₂O) for each sample.

Synthesis of co-doped REO. The RE-MOFs MAs with different mole ratio were prepared following the synthesis procedure mentioned above. The obtained MAs samples were subsequently calcinated at 800 °C for 2 h at air atmosphere in the furnace and then cooled down to room temperature. The obtained powders were collected and used for further measurement.

Instrumentation. The crystallographic information of the samples was obtained by using XRD measurements, on a Bruker D2 Phaser X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å) from 5° to 50° at a step of 0.01°/s. The UC luminescence spectra were recorded on Horiba Jobin Yvon FluoroMax-4 system and an external MDL/MDL-H-980 nm

CW laser system was used as the excitation source. The elemental concentrations (Sc, Yb and Er) were determined using inductively-coupled plasma atomic emission spectroscopy (ICP-AES) (Teledyne Leeman, Prodigy Prism High Dispersion ICP, USA). High resolution TEM (HRTEM) images were collected at an accelerating voltage of 200 kV on a JEOL JEM-2100F field emission electron microscope. Energy-dispersive X-ray spectroscopy (EDS) measurement was collected by using JEOL JSM-7800F electron microscope operating at 20 kV. Elemental analyses (C, H and N) were performed with an Elementar Vario EL III analytical instrument. IR spectra were recorded on a Bruker Vector 22 fourier transform infrared (FTIR) spectrometer (170SX) (KBr disc). Thermogravimetric analysis (TGA) experiment was performed with a simultaneous SDT 2960 thermal analyzer in the range of 20–800 °C at a warming rate of 10 °C/min under air environment.

RESULTS AND DISCUSSION

The crystalline structure analysis. XRD results shown in Figure 1a indicate that there are two different crystalline structural types. Microcrystals based on RE = Yb and Er, show reasonably similar diffraction patterns, demonstrating a universal isomorphous structure (denoted as S_{Yb}). On the other hand, Sc-based sample shows obviously different XRD patterns that correspond to a distinct structural type (labelled as S_{Sc}). S_{Yb} structure was confirmed by a perfect match between the diffraction patterns and the calculated pattern (Simu of S_{Yb}) based on the triclinic Yb₂(C₂O₄)₃(H₂O)₄·2H₂O reported at CCDC database³⁹ as shown in Figure 1. The RE ion adopts an eight coordination mode. Each RE is coordinated by eight oxygen ions, six of which come from the three ox ions bonded as chelates, and the other two come from two water molecules. Each ox ion acts as a bridge between two RE ions and each RE ion is shared by three rings. This way, rings formed in six RE and six ox ions in each unit further connect into two-dimensional (2D) networks parallel to the -ac plane. The non-coordinated water molecules are situated in the cavities formed. IR spectra and elemental analyses (EA) for C, H shown in Figure S1 and Table S1 also prove the S_{Yb} structure indirectly. S_{Sc} structure confirmation was failed because there was a lack of sufficiently large single crystal needed for X-ray diffraction analysis and there is no matching XRD data for the reported oxalate complexes. In order to obtain the structural information of S_{Sc}, alternative conventional analytical techniques such as IR, EDS measurement and EA were carried out. IR spectrum shows similar absorption peak at 3320, 1651, 1371, 813 cm⁻¹ as those of S_{Yb}, proving the presence of ox ligand and H₂O molecules. EDS result for composition analysis shown in Figure S2 indicates that the compound is mainly composed of C, O and Sc element (H element cannot be detected). Though accurate C, H contents are confirmed by EA tests (Table S1), it is still difficult to obtain the crystal structure of S_{Sc}. However, it is possible to exclude the soluble starting chemicals of ScCl₃·6H₂O and oxalic acid ligand. Considering that Sc³⁺ ion typically possesses a low coordination number (6–8) in complexes, it is reasonable to assume the structure as a seven coordination mode with a conjectural formula of Sc₂(C₂O₄)₃(H₂O)₂·2H₂O. Each Sc ion is coordinated by seven oxygen ions, six of which are from three ox ions bonded as chelates, and the other one is from water molecule. Similar to other known compounds, there are also non-coordinated water molecules situated in the cavities

formed. Works on proving the conjecture is ongoing in the lab.

Figure 1. The XRD patterns for the simulated data of crystal $Yb_2(C_2O_4)_3(H_2O)_4 \cdot 2H_2O$ (S_{Yb}) and the experimental results for the microcrystals based on RE = Sc, Yb, Er, Yb/Er (a); The asymmetric unit (b) and packing structures (c and d) of $Yb_2(C_2O_4)_3(H_2O)_4 \cdot 2H_2O$ (S_{Yb})³⁹

The isomorphous structures in Yb- and Er-based compounds and similar RE ion radius ensure a successful doping to form uniform MAs. The similar XRD pattern for the Yb/Er co-doped sample (equal mole ratio added) to the calculated one of S_{Yb} in Figure 1a proves the conjecture clearly. Unexpectedly, uniform MAs were also formed within the Sc/Yb/Er co-doped sample (equal mole ratio added, labelled as Er-1). The XRD pattern shown in Figure 2a indicates analogous diffraction pattern to that of S_{Yb} , but not in mixture of both S_{Sc} and S_{Yb} phases. This finding is obviously contradicting the common rule that isomorphous structures and similar ion radius are required for the host and doping ion-based coordination compound body. It is believed that the approach of doping other elements into the main compound body, which is a classical method in pure inorganic luminescent materials, cannot be simply redirected into MOFs. The additional component usually perturbs the coordination equilibrium, preventing the crystal formation or resulting in a different framework⁴⁰.

Figure 2. The XRD patterns for the simulated data of crystal $Yb_2(C_2O_4)_3(H_2O)_4 \cdot 2H_2O$ (S_{Yb}) and the experimental results for the microcrystals of Er-1 to Er-4 samples (a) and the partly magnified images (b-d, data for RE = Yb and Er were also added), which shows the regular shifts of the Bragg reflections

Figure 3. The XRD patterns for the experimental results for the microcrystals based on RE = Sc and Er-5 to Er-7 (a) and the partly magnified images (b-d), which shows the regular shifts of the Bragg reflections

To prove the phenomenon more adequately, verified experiments were performed and a series of MAs with different Sc/Ln mole fractions were obtained (Table 1). As shown in Figure 2a and 3a, Er-1 to Er-4 show similar XRD patterns to the calculated pattern of S_{Yb} , while Er-5 to Er-7 show similar XRD patterns to that based on S_{Sc} structure. It is obvious that two kinds of MAs systems with the structure of S_{Yb} or S_{Sc} as the main crystalline lattice were serendipitously obtained at specific Sc:Ln mole ratios. MAs having S_{Yb} structure are obtained when Sc:Ln mole ratio added is less than 9:1 (mole fraction less than 0.9:0.1); while MAs having main crystalline lattice of S_{Sc} can be collected at a Sc:Ln mole ratio no less than 9:1 (mole fraction no less than 0.9:0.1). For MAs of S_{Yb} system, the partially magnified XRD patterns shown in Figure 2b-2d indicate distinct shifts of the Bragg reflections to higher degrees accompanied with an increase in the Sc content added. Meanwhile, all the peaks for MAs shift to higher degrees than those of un-doped compounds of RE = Yb and Er. The shift is originating from the decreased lattice parameter because more Sc^{3+} ions of smaller ionic radius substitute the Ln^{3+} ions of the larger ionic radii. Therefore, it gives clear evidence of MAs formation. Similarly, as shown in Figure 3b-3d, the shifts of the Bragg reflections to lower degrees than that of S_{Sc} were found along with an increase in Ln^{3+} ions doping concentration within the S_{Sc} structure MAs system. It indicates an increased cell volume because Ln^{3+} ions replace

the Sc^{3+} ions and form MAs. The regular shifts of the Bragg reflections to higher or lower degrees in the XRD patterns strongly prove the formation of the two MAs systems as it reflects the crystalline structure information in the molecular level. In addition, EDS data shown in Figure S3 for Er-1 to Er-7 indicates the composition of C, O, Sc, Ln elements varies in a similar trend as Sc:Ln content and it demonstrates the formation of the MAs indirectly.

It is anticipated that synergistic effects from many aspects, such as versatile coordination structures for RE-MOFs, smaller ion radius for favorable low coordination mode for RE of Sc, Yb and Er, as well as structure inducing effect for molecules with different energies, are responsible for the unexpected MAs forming. Samples with co-doped RE of Yb/Er/Ln (Ln = Nd, Sm, Eu, Gd, Tb, Ho, Tm and Lu) and each individual RE compound were also prepared. Those with larger ionic radii (larger than Ho^{3+}) formed nine-coordinated structure and mixed phases for the co-doped samples (Figure S4). Only RE with smaller ion radius can form the MAs under the structure inducing effect though they show different structural types.

Table 1. The element mole fractions found, Yb:Er ratio in the ICP results, and the main crystal lattice type for the resulting MAs systems as well as the R/G ratio for the resulting REO for Er-1 to Er-11.

Sample	RE (Sc:Yb:Er) mole fractions added	RE (Sc:Yb:Er) mole fractions found	Yb:Er ratio	Structure	R/G ratio of REO
Er-1	0.34:0.33:0.33	0.09:0.43:0.48	1.10	S_{Yb}	5.01
Er-2	0.60:0.20:0.20	0.24:0.37:0.39	1.05	S_{Yb}	9.01
Er-3	0.75:0.125:0.125	0.37:0.32:0.31	0.98	S_{Yb}	15.93
Er-4	0.80:0.10:0.10	0.47:0.27:0.26	0.94	S_{Yb}	14.30
Er-5	0.90:0.05:0.05	0.65:0.18:0.17	0.96	S_{Sc}	13.66
Er-6	0.92:0.07:0.01	0.70:0.26:0.04	0.16	S_{Sc}	19.17
Er-7	0.96:0.03:0.01	0.82:0.13:0.05	0.35	S_{Sc}	7.35
Er-8	0.90:0.067:0.033	0.65:0.23:0.12	0.51	S_{Sc}	17.25
Er-9	0.90:0.08:0.02	0.66:0.27:0.07	0.25	S_{Sc}	18.84
Er-10	0.90:0.09:0.01	0.64:0.32:0.04	0.11	S_{Sc}	38.26
Er-11	0.78:0.20:0.02	0.41:0.53:0.06	0.10	S_{Yb}	13.75

Elements concentration. ICP measurement was performed to evaluate the actual element concentration in the resulting MAs. It can be found that the actual Sc:Ln element concentration is different from the values added in the starting chemicals (Table 1). Sc element possesses quite a low value, which is $21 \pm 3\%$ of those added for $ScCl_3 \cdot 6H_2O$, while Ln elements show approximately identical concentration as those added. It is reasonable as S_{Yb} and S_{Sc} structure cannot co-doped easily because of the diverse structural type. The determination of the actual element concentration in the resulting MAs gives a reasonable explanation for the phenomenon of main crystal lattice changing from S_{Yb} to S_{Sc} structure. As the Sc:Yb:Er mole fraction added increases from 0.34:0.33:0.33 to 0.80:0.10:0.10, the actual element mole fraction in the as-prepared MAs increases from 0.09:0.43:0.48 to 0.47:0.27:0.26. The total amount of Ln elements is significantly larger than that of Sc element, leading to the formation of S_{Yb} structure. When Sc element gradually becomes the dominant composition and the mole fraction added is 0.90:0.05:0.05 or above, S_{Sc} structure is observed accordingly.

Photo-luminescence property of RE-MOFs MAs. UC luminescence was investigated for the as-prepared MAs under 980 nm laser excitation. Weak green color emission could be observed with a power of 1.5 W (Figure S5). As it is known

that there are less high-energy bonds in the designed MA systems, but still coordinating water and lattice water molecules within the structure, the O-H oscillator is apt to quench the emission greatly. Therefore, the series MAs gave weak emission. MAs with improved UC luminescence could be expected from structures with no high-energy bonds.

Elemental distribution in co-doped REO. Controlled pyrolysis of MOFs sacrificial precursor under controlled atmospheres yields metal oxides in high effectiveness and low cost, which is regarded as the most attractive method currently.⁴¹ Calcination of the as-prepared MAs systems at 800 °C under air environment was performed and the corresponding REO were obtained. TGA data shown in Figure S6 demonstrates the thermal decomposition behavior and stable REO were obtained in the final samples. The XRD patterns indicate a cubic structure, corresponding to the standard pattern of Yb₂O₃ or Sc₂O₃ (JCPDS: 43-1037 and 05-0629) and no impurity peak is observed (Figure S7). Moreover, regular shifts of the Bragg reflections in the XRD patterns are also observed, demonstrating the uniform co-doped REO system. The observed elemental distribution from EDS mapping shown in Figure 4 infers that the Sc, Yb and Er ions are homogeneously dispersed within the REO particles. Meanwhile, controlled experiments were also conducted. It is found that calcination of the physical mixed RE-MOFs at the same mole ratios gives the corresponding REO mixtures. As can be seen in Figure S7, the peak intensity of Sc₂O₃ gradually increases while that of Yb₂O₃ decreases as Sc:Yb:Er mole fraction changes from 0.34:0.33:0.33 to 0.92:0.07:0.01. In addition, no shift of the Bragg reflections is found. Such REO mixtures give quite poor UC emissions as there are no efficient host crystalline materials and sensitizer available for the emitted Er³⁺ ion (Figure S8). It is clear that by using the RE-MOFs MAs as the precursor, Sc/Ln co-doped inorganic REO system is realized, which is otherwise difficult to prepare by direct inorganic synthesis method. The significant difference of electron configuration and ionic radius between Sc³⁺ and Ln³⁺ could lead to crystallization separately and mixture of phases in the inorganic compound body. The proposed method of pyrolysing the RE-MOFs MAs precursor demonstrates an effective way to prepare uniform inorganic Ln-doped Sc₂O₃ system. It is, to the best of our knowledge, rarely studied for UC luminescence except a few reports in ceramics fields.⁴²

Figure 4 Microscopy images including backscattered electrons (BSE) and EDS elemental mapping of Sc, Yb and Er for the corresponding REO derived from Er-1 (a) and Er-10 (b).

Photo-luminescence property of co-doped REO. The resulting co-doped REO shows significantly improved UC luminescence. Furthermore, nearly pure red color emission is

observed for all samples at different doping level. As shown in Figure 5a, all samples show reasonably strong characteristic peaks at red color region centered at 654 nm and weak emission at green color region centered at 541 nm, which can be ascribed to the corresponding $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition as well as $^2H_{11/2} \rightarrow ^4I_{15/2}$ and $^4S_{3/2} \rightarrow ^4I_{15/2}$ transitions respectively.⁴³ It is noticed that all the red to green (R/G) ratio are above 5 (integral area), and Er-6 sample shows R/G ratio as high as 19.17. All samples emit nearly pure red color output observed by naked eyes. Such remarkable red color UC output is rarely found in other inorganic systems, such as doped NaLnF₄ and LnF₃ nanocrystals. It is believed to be attributed to the remarkable enhancement of the cross-relaxation effect and the particular Sc₂O₃ host material. It is known that Ln³⁺ ions possess a high doping level for all REO samples because low Sc³⁺ concentration is found in the resulting MAs precursor. The shorter distance between Ln³⁺ ions in the resulting REO could enhance the cross-relaxation greatly between them, leading to diminished population in the $^2H_{11/2}$ and $^4S_{3/2}$ levels and enhanced population in the $^4F_{9/2}$ energy level of Er³⁺.^{36, 44} Therefore, strong and nearly pure red color output is obtained, which broadens the applications of LDUMs ranging from optical communications to disease diagnosis.

Figure 5. The UC luminescence spectra for co-doped REO (a) (b) and the optimized sample of Er-10 and the corresponding digital photos for the solid sample (inset of (b)) under the 980 nm laser excitation with power of 1.5 W.

Further observation reveals that Er-5 has the strongest emission, but smaller R/G ratio of 13.66 than that of Er-6 (19.17). Higher Yb/Er doping level samples of Er-1 to Er-4 show poor

UC efficiency because of concentration quenching phenomenon. Lower Yb/Er content in Er-6 and Er-7 leads to decreased UC intensity. However, it is found that increase in Yb³⁺ and reduction in Er³⁺ ion concentration in the Sc₂O₃ host gives much higher R/G ratio in Er-6. Therefore, optimized samples of Er-8, Er-9 and Er-10 with added mole fraction of 0.90:0.067:0.033, 0.90:0.08:0.02 and 0.90:0.09:0.01 were prepared. As expected, they show S_{8c} structure (Figure S9) and reasonable RE element concentration as compared to Er-1 to Er-7 samples. More importantly, they show improved UC efficiency and much larger R/G ratio (17.25, 18.84 and 38.26 respectively) than that of Er-5 (Figure 5b). It is believed that more Yb³⁺ and less Er³⁺ ion could increase the absorption cross section greatly and enhance the population in the ⁴F_{9/2} energy level of Er³⁺. In addition, Er-11, with added mole fraction of 0.78:0.20:0.02, which is a classical added mole ratio in the inorganic LDUMs, was prepared as well for comparison. However, it shows poorer UC efficiency. Thus, the optimal sample is Er-10, which possesses a Sc:Yb:Er added mole fraction of 0.90:0.09:0.01, shows the strongest UC intensity as well as nearly pure red color UC emission with a high R/G ratio of 38.26. Its spectra and the corresponding digital photo for the solid sample under the 980 nm laser excitation are shown in the inset of Figure 5b.

CONCLUSIONS

In summary, series of unexpected MAs based on Sc/Ln co-doped RE-MOFs at different Sc:Ln mole fraction (Ln = Yb/Er) were serendipitously obtained though they show different crystalline structural types. Using the RE-MOFs MAs as the precursor, uniform co-doped REO were prepared by pyrolysis. It demonstrates an effective method to prepare uniform Ln-doped Sc₂O₃ system. The resulting co-doped REO shows strong and nearly pure red color UC luminescence. Efforts on improving new co-doped RE-MOFs MAs to get better UC luminescence are still going on in our lab.

Supporting Information

IR and EA for RE-MOFs (RE=Yb, Er, Sc), EDS, XRD profiles and TGA data are included. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

Authors thank the National Nature Science Foundation of China for financial support (grant no. 21601084). R. L. thanks the financial support from NEA ETRP Grant (Ref No. 1102 108). It is also supported by Natural Science Foundation of Jiangsu Province (grant no. BK20130918). Authors thank Prof. Xiao-Ming Ren at Nanjing Tech University for discussions on the crystal structures of the MOF compounds.

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