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Synthesis, structure and enhanced photoluminescence properties of two robust, water stable calcium and magnesium coordination networks

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Two new 3D coordination networks $Ca(cca)\cdot H_2O$ (**1**) and $Mg(cca)\cdot 2H_2O$ (**2**) (H_2cca = 4-carboxycinnamic acid) are synthesized by solvothermal reactions and characterized by Single crystal and powder X-ray diffraction, thermogravimetric analysis, optical diffuse reflection, photoluminescence spectroscopy, and internal quantum yield measurements. Crystal structure analysis reveals that compound **1** is built from edge-sharing chains of seven-coordinated calcium polyhera, which are connected by the cca ligand to form a 2D layered structure. Compoud **2** contains isolated magnesium polyhedra layers. These layers are linked by cca ligands to complete the 3D connectivity. Both compounds **1** and **2** have high thermal stability and remain intact in aqueous solutions of a broad range of pH values ranging from 3 to 11. Both compounds also show significantly enhanced luminescence with respect to the free ligand, giving rise to an increase in qauntum yield by as much as 4-fold.

Introduction

Much attention has been attracted to Metal Organic Frameworks (MOFs) due to their structural diversity and potential applications in gas storage and separation,[1] catalysis,[2] luminescence,[3] magnetism,[4] electronics,[5] sensing,[6] drug delivery,[7] and health science[8] in the past decade. MOFs are commonly constructed from organic ligands and inorganic building units (metal ions or clusters). Intensive studies have been carried out on divalent and trivalent transition metals such as zinc and copper because of their well-known coordination behaviours. However, investigations of MOFs built on s-block metal centers (e.g. M = Ca, Mg) remain sporadic.[9] The use of light weight elements most likely leads to the formation of MOFs of relatively low density. MOFs made of s-block metals usually have stronger bonds between metal (M) and oxygen (O) due to large difference in their electronegativity and therefore more ionic characters. As a result, these compounds are generally more thermally robust compared to those made of transition metals.[9l] Moreover, due to their nontoxicity, s-block metal-containing MOFs are potentially suitable for bioapplications such as biological imaging and drug delivery.

Herein, we report two novel alkaline-earth metal based coordination networks, $Ca(cca)\cdot H_2O$ (**1**) and $Mg(cca)\cdot 2H_2O$ (**2**). We describe the crystal growth and structure determination of the two compounds, as well as their thermal and water stability, optical absorption and emission properties. Both compounds exhibit very high thermal and water stability, and strong photoluminescence, with greatly enhanced quantum yields with respect to the free ligand.

Experimental Section

Materials and Methods

All chemicals were purchased from commercial sources and used as received without further purification. Starting materials include calcium nitrate tetrahydrate ($Ca(NO_3)_2\cdot 4H_2O$, Alfa, 99%), magnesium nitrate hydrate ($Mg(NO_3)_2\cdot 6H_2O$, Alfa, 98%), 4-carboxycinnamic acid (Alfa, 98%), dimethylformamide (Alfa, 99%), ethanol (Pharmco-Aaper, 100%).

Synthesis of $Ca(cca)\cdot H_2O$ （1）

A mixture of $Ca(NO_3)_2\cdot 4H_2O$ (0.2 mmol, 47.2 mg), 4-carboxycinnamic acid (0.1 mmol, 19.2 mg), dimethylformamide (7 ml) and deionized water (3 ml) was sealed in a 20 ml glass vial. The solution was sonicated for 10 min and heated at 100 °C for 48 h. The resultant colourless crystals were filtered, washed 3 times with DMF (10 ml) and dried under air. Yield: 71% based on Ca.

Synthesis of $Mg(cca)\cdot 2H_2O$ （2）

$Mg(NO_3)_2\cdot 6H_2O$ (0.2 mmol, 51.2 mg) and 4-carboxycinnamic acid (0.1 mmol, 19.2 mg) were dissolved in a solution of dimethylformamide (7 ml), ethanol (1 ml) and deionized water (2 ml) in a 20 ml glass vial. The solution was sonicated for 10

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Table 1. Crystallographic data and structural refinement details of compounds **1** and **2**

Parameters	**1**	**2**
Empirical formula	$C_{10}H_8CaO_5$	$C_{10}H_{10}MgO_6$
Formula weight	248.24	250.49
Temperature (K)	100(2)	100(2) K
Wavelength (Å)	0.7749	0.7749
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	11.6947(4)	11.3400(6)
b (Å)	6.8463(3)	6.6324(3)
c (Å)	12.2702(4)	7.1986(3)
β (°)	90.4060(16)	102.313(3)
Volume ($Å^3$)	982.39(6)	528.96
Z	4	2
Calculated Density (mg/m^3)	1.678	1.573
Absorption coefficient (mm^{-1})	0.803	0.224
F(000)	512	260
Crystal size (mm)	0.300 x 0.150 x 0.030	0.200 x 0.060 x 0.030
Theta range of data collection	3.621 to 42.502	3.904 to 40.307
Index range	-20<=h<=20 -11<=k<=11 -19<=l<=19	-18<=h<=18 -11<=k<=11 -11<=l<=12
Total reflection	17010	9473
Independent reflection	4757 [R(int) = 0.0250]	2553 [R(int) = 0.0360]
Goodness of fit	1.055	1.223
Data/ Restraints/parameter	4757 / 88 / 241	2553 / 6 / 108
Final R indices [I>2sigma(I)]	R1 = 0.0276, wR2 = 0.0739	R1 = 0.0495, wR2 = 0.1133
R indices (all data)	R1 = 0.0309, wR2 = 0.0759	R1 = 0.0574, wR2 = 0.1167

min and heated at 100 °C for 48 h. The resultant colourless crystals were filtered, washed 3 times with DMF (10 ml) and dried under air. Yield: 56% based on Mg.

Single Crystal X-ray Diffraction (SXRD) and Powder X-ray Diffraction (PXRD)

SXRD data of compounds **1** and **2** were collected at 100 K on a D8 goniostat equipped with a Bruker PHOTON100 CMOS detector using synchrotron radiation (λ = 0.7749 Å) at the Advanced Light Source (ALS) in Lawrence Berkeley National Laboratory. The structures are solved by direct methods and refined by full-matrix least-squares on F^2 using the Bruker SHELXTL package. CCDC numbers: 1426301, 1426302.

PXRD patterns were recorded on a Ultima Ⅳ with Cu Kα radiation (λ = 1.5406 Å). The data were collected at room temperature in a 2θ range of 3-55° with a scan speed of 2 deg/min and operating power of 40 kV and 40 mA.

Thermogravimetric Analysis (TGA)

Thermogravimetric analyses were carried out on a TA Q5000 analyzer. Crystal samples were loaded onto a platinum pan and heated with a ramp rate of 10 °C/min from room temperature to 600 °C under nitrogen flow.

Water Stability Test

Six as-made samples of each compound produced in the same batch (50 mg) were soaked in pH = 0, 3, 7, 11, 14 aqueous solutions and in 80 °C water for 12 h, respectively. The samples were then collected after filtering and drying in air, followed by PXRD analysis.

UV-Vis Diffuse Reflectance Measurements

Optical diffuse reflectance spectra of both compounds were obtained on a Shimadzu UV-3600 spectrophotometer with a $BaSO_4$ standard as baseline at room temperature. Data were collected with a wavelength range of 300−1000 nm. The reflectance data were converted to Kubelka−Munk function and used to estimate the band gap.

Photoluminescence (PL) Spectroscopy

Photoluminescence measurements were performed on a Varian Cary Eclipse spectrometer at room temperature. Powder samples were uniformly coated on glass slides which have no emission in the visible range.

Internal Quantum Yield (QY) Measurements

Internal QYs of samples are carried on a Hamamatsu C9920-03 absolute quantum yield measurement system with a 150 W xenon monochromatic lamp and 3.3 in. integrating sphere.

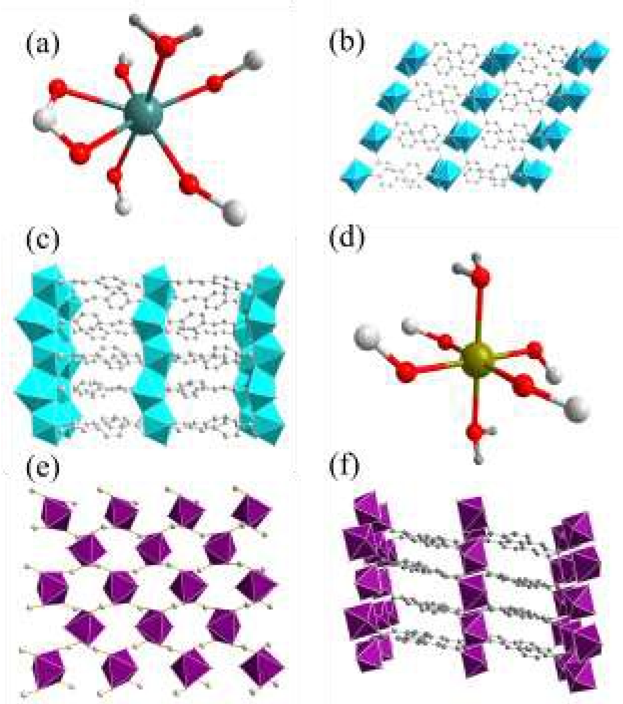

Fig. 1. (a) View of the metal environment and coordination mode for compound **1**; (b) View of compound **1** along the [010] direction; (c) View of compound **1** along the [001] direction; (d) View of the metal environment and coordination mode for compound **2**; (e) View of compound **2** along the [100] direction; (f) View of compound **2** along the [010] direction.

Results and discussion

A solvothermal reaction of metal salt $Ca(NO_3)_2 \cdot 4H_2O$ with the organic linker (H_2cca) led to colourless plate-like crystals of compound **1** (see Experimental Section). Single crystal structure analysis reveals that compound **1** is a three dimensional (3D) network crystallized in the monoclinic crystal system with a space group *P*2$_1$/c (Table 1). The Ca ion coordinates to one water molecule (via O) and six oxygen atoms from five different cca ligands (Fig. 1a), resulting in a distorted pentagonal bipyramidal geometry. The Ca – O distances in compound **1** are in the range of 2.346 – 2.486 Å (av. 2.404 Å). The $CaO_6(H_2O)$ units are linked to form edge-sharing chains running along the [010] direction, which are further linked by cca ligands along the *a* and *c* direction to complete the three dimensional dense architecture (Fig. 1b and 1c).

The reaction of metal salt $Mg(NO_3)_2 \cdot 6H_2O$ with cca under solvothermal conditions resulted in the formation of colourless block crystals of compound **2** (see Experimental Section). Single crystal structure analysis reveals that compound **2** is a 3D structure crystallized in the same space group as Compound **1**, P2$_1$/c (Table 1). The Mg ion coordinates to four oxygen atoms from four individual cca anions and the remaining two coordination sites are occupied by water molecules, giving rise to a distorted octahedral geometry (Fig. 1d). The coordination modes of the two metals clearly follow their relative atomic sizes, thus, 6-coordination for the smaller Mg and 7-coordination for the larger Ca. The Mg-O distances in compound **2** vary from 2.06 to 2.078 Å (av. 2.07 Å) which was shorter than the typical Ca-O bond length. The Mg polyhedra are connected to one another through carboxylic groups in a Mg-O-C-O-Mg fashion to form a two-dimensional layer parallel to the bc plane (Fig. 1e). These layers are further pillared by cca ligands to generate the three dimensional network (Fig. 1f).

Thermogravimetric (TG) analysis was performed on both compounds **1** and **2** to test their thermal stability. TGA curve of compound **1** indicates that the coordination water molecular can be removed below 150 °C (observed 7.2%, calculated 7.25%). The dehydrated network was stable up to 500 °C (Fig. S3). The TG analysis of compound **2** reveals that the coordination water molecules were evolved from the

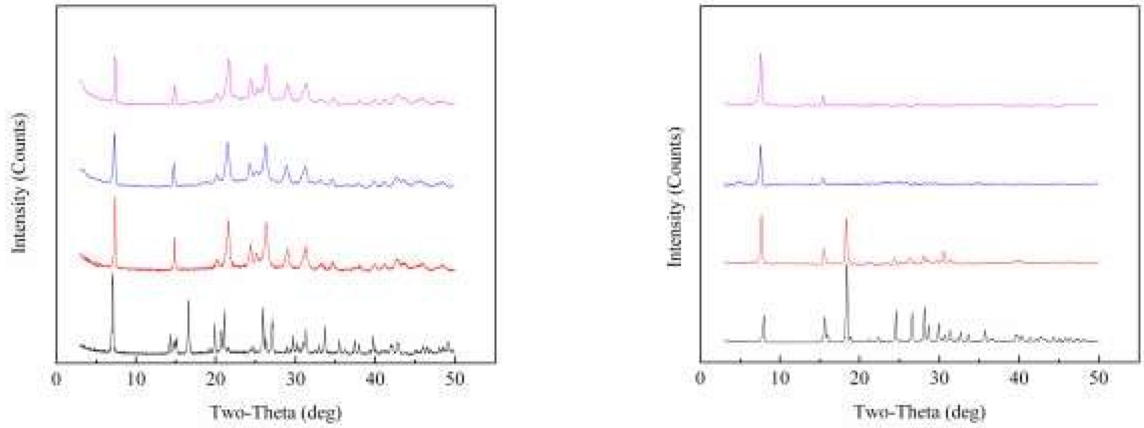

Fig. 2. PXRD patterns of the as-made samples and samples after being heated at variable temperature for 1 hour in N_2. (left) compound **1**, from bottom to top: as made, 200 °C, 300 °C, 400 °C; (right) compound **2**, from bottom to top: as made, 150 °C, 200 °C, 300 °C. In all cases (except as-made samples) coordinated water was removed.

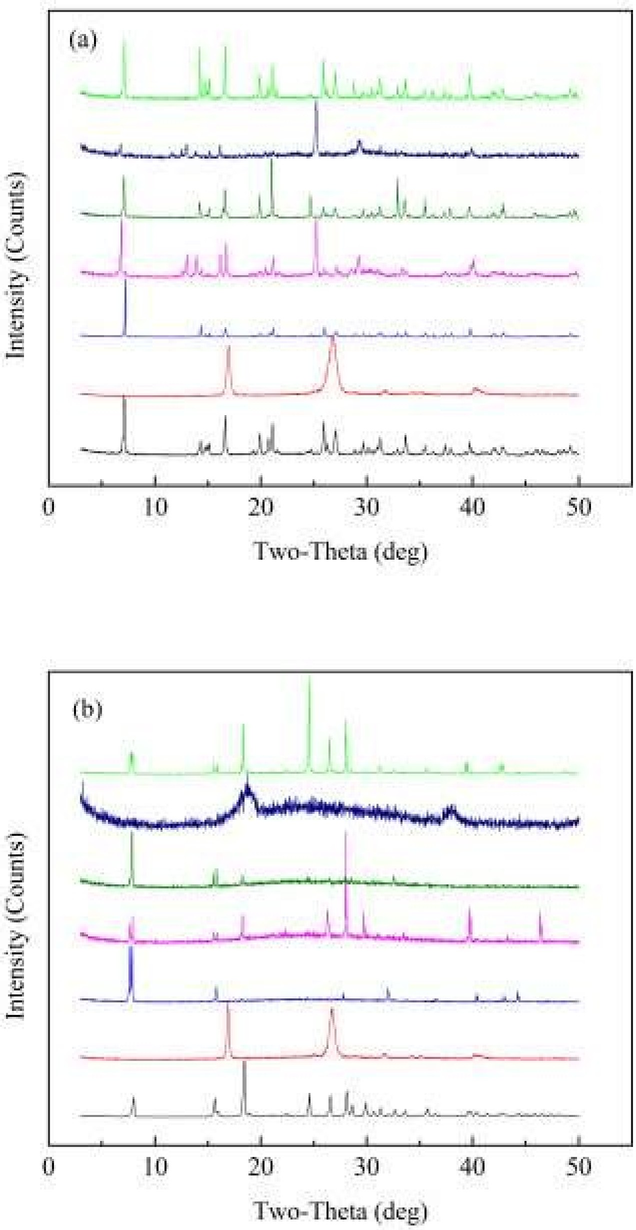

Fig. 3. PXRD patterns (from bottom to top) of as made compound **1** (a, black) or compound **2** (b, black), compound after soaked in pH = 0 (red), 3 (blue), 7 (magenta), 11 (olive) and 14 (navy) aqueous solutions and 80 °C water (green), respectively, for 12 h.

framework before 250 °C (observed 15.5%, calculated 14.4%). The second weight loss at 450 °C corresponds to the decomposition of the compound (Fig. S4). However results from N_2 (77 K) and CO_2 (298 K) adsorption experiments show that solvent-free samples of both compounds are not accessible for these gases, and therefore they are essentially non-porous.

In order to further examine the thermal stability, powder X-ray diffraction (PXRD) measurements were performed on samples after thermal treatments. As shown in Fig. 2, the crystal structures of both compounds **1** and **2** remained intact after being heated up to 400 °C and 300 °C for 1 hour under N_2, respectively. Strikingly, both compounds also exhibit high chemical stability under various acidity and in water. PXRD results suggest that their structures were kept intact after being soaked in water at 80 °C and in aqueous solutions with pH values in the range of 3–11 for a long period of time (12 h, Fig. 3). Changes in their crystal structures were observed at either very low pH (= 0) or high pH (= 14) for both compounds.

The optical absorption and photoluminescence emission spectra of compounds **1** and **2** were investigated at room temperature. Optical absorption spectra of compounds **1** and **2** are plotted in Fig. 4. The estimated energy gaps between filled and empty orbitals of compounds **1** and **2** are ~3.0 and

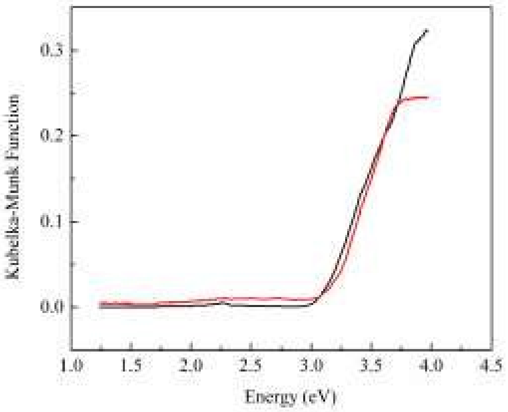

Fig. 4. Optical absorption spectra of compound **1** (black) and compound **2** (red).

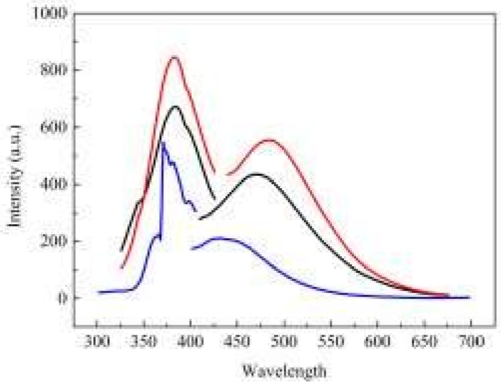

Fig. 5. The photoluminescence spectrum (λ_{ex} = 365 nm) of compounds **1** (black), **2** (red) and free H_2cca ligand (blue).

~3.1 eV, respectively. The room temperature photoluminescence (PL) spectra of these two compounds and the free H_2cca ligand are plotted in Fig. 5. Compounds **1** and **2** exhibit similar behaviour when excited at a wavelength of 365 nm. Compared to the H_2cca ligand (λ_{em} = 431 nm), emissions of the two MOF compounds are both largely enhanced and red-shifted to 471 nm for compound **1** and 484 nm for compound **2**.

The room temperature internal quantum yields (QYs) were measured on a C9920-03 absolute quantum yield measurement system (Hamamatsu Photonics), and the values are given in Table S1. The IQYs of compound **1**, **2** and H_2cca ligand are 15.1%, 16.2%, and 4.2%, respectively, at excitation energy of 365 nm. The significantly enhanced luminescence of **1** and **2** is most likely due to the immobilization of the ligand (cca) in the MOF backbone which efficiently reduces nonradiative decay attributed to molecular vibration and rotation.[3d]

Conclusions

In summary, we have synthesized and characterized two novel calcium and magnesium based coordination frameworks **1** and **2** by using solvothermally method. In both compounds, ligand cca connect to the metal polyhedra to form a 3D framework. Both compounds have high thermal stability and water stability, as a result of strong M-O bonds and high connectivity between the ligand and the metals. The incorporation of luminescent ligand into MOF backbone greatly improves the photoluminescence, giving rise to an increase in quantum yield by as high as 4-fold. The combination of s-block metals and luminescent ligands in forming new and highly stable coordination network structures may be a feasible approach for future synthesis of highly luminescent materials for various applications.

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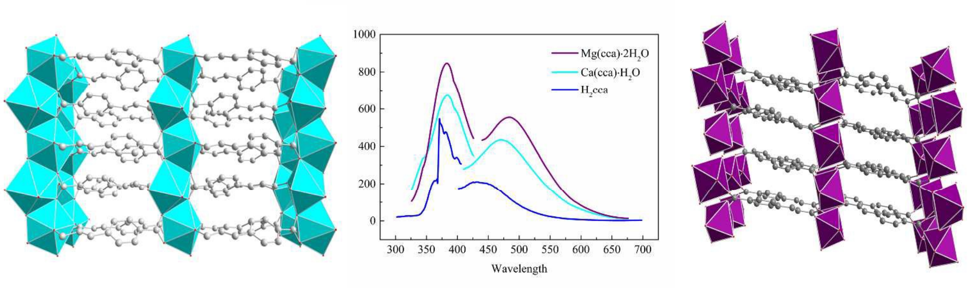

TOC graph
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