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COMMUNICATION

Tunable photoluminescence and direct white-light emission in Mg-based coordination networks

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The bpy, dpe and dppe were introduced as auxiliary ligands, respectively, to construct three magnesium-1,4-NDC coordination polymers (Mg-CPs) that exhibited tunable photoluminescence (PL) and direct white-light emission by varying the excitation light.

White light emitting materials have received continuous attention for their applications in light-emitting devices (LEDs), chemical sensing and so on.¹ As a new type of single-component materials, luminescent coordination polymers (L-CPs) have recently undergone tremendous development.² There are various ways towards white light emission in L-CPs. For instances, it can be realized by appropriately incorporating various lanthanide ions based on primary colors of red–green–blue (RGB) in the 4f and 3d-4f metal-L-CPs arising from lanthanide-centred emission,³ constructing Ag⁺/Pb²⁺-L-CPs based on MLCT or LMCT mechanism⁴ or changing the guest molecules of L-CPs.⁵

On the other hand, the L-CPs with tunable photoluminescence (PL) are desirable for some applications.^{4b,5c} An effective method for PL tuning is to introduce different organic chromophores in one structure so that the PL can simply be tuned by exciting different luminophores at different excitation energies.⁶ This way has rarely been utilized to explore tunable L-CPs, exemplified only by some Zn-CPs in which the emissions could be tuned from blue to yellow gradually.⁷ To the best of our knowledge, however, direct white emission has never been realized in L-CPs via this method until now.

As a low-cost, non-toxic and abundant metal ion, Mg²⁺ ion has been rarely exploited compared to the 3d and 4f-metal ions for constructing L-CPs.^{3c} Recently, it has been found that some Mg-CPs exhibited benign luminescent properties.⁸ Furthermore, due to the electronic configuration of Mg²⁺, it shall be favorable to build up the Mg-L-CPs with tunable PL via the abovementioned method.

Herein, the pyridine derivatives, namely 4,4'-dipyridyl (bpy), 1,2-di-4-pyridylethane (dpe) and 1,3-di(4-pyridyl)propane (dppe), together with 1,4-naphthalene dicarboxylic acid (1,4-NDCH₂), were chosen to construct three Mg-CPs, namely [Mg₃(OH)₂(1,4-NDC)₂(bpy)(H₂O)] 0.5H₂O (**1**), [Mg₃(OH)₂(1,4-

NDC)₂(dpe)(CH₃OH)₂] H₂O (**2**) and [Mg₃(OH)₂(1,4-NDC)₂(dppe)(H₂O)] (**3**). The title compounds exhibited finely tunable PL properties by simply varying the excitation light, and white light emission could be achieved in compounds **1** and **3**. Of particular interest is the unusual persistence of white light emitting in **3** through the whole irradiation wavelength varying process.

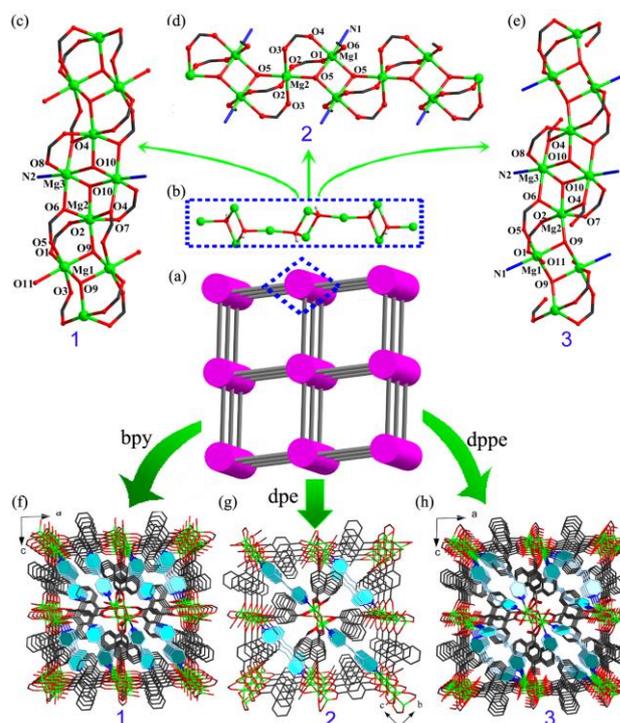


Figure 1 (a) The schematic presentation of the network of compounds **1**, **2** and **3** formed by interlinking the Mg-OH chains (simplified as purple rods) through the 1,4-NDC ligands (grey rods); (b) the common [Mg₃(OH)₂]_n chain in **1**, **2** and **3**; (c), (d) and (e) show the infinite [Mg-OH/COO]_n chains and the coordination environments of the Mg²⁺ ions in **1**, **2** and **3**, respectively; (f), (g) and (h) show the 3D frameworks of **1**, **2** and **3**, respectively.

The title compounds were obtained by heating a closed bomb containing a mixture of 1,4-NDCH₂, Mg(NO₃)₂·6H₂O, NaOH, the auxiliary ligand (bpy for **1**, dpe for **2** and dppe for **3**), H₂O and CH₃OH at 433 K for 6 days, as detailed in ESI. The structures of the title compounds were determined via single-crystal X-ray diffraction analyses. Compounds **1**, **2** and **3** feature a similar neutral three-dimensional (3D) network (Figure 1a) that is constructed by interlinking the same parallel rod-like [Mg₃(OH)₂]_n chains⁹ (Figure 1b) through the 1,4-NDC ligands. The detailed descriptions for the crystallographically asymmetric units, metal ion coordination modes, and connecting modes of the ligands are given in ESI. As depicted in Figure 1b, the OH⁻ groups act as tridentate ligands to bridge the Mg²⁺ ions to form a similar 1D chain of [-Mg₂-OH-(Mg₁)₂-OH-Mg₂-OH-(Mg₃)₂-OH-Mg₂-] in **1** and **3**, and a 1D chain of [-Mg₂-OH-(Mg₁)₂-OH-Mg₂-] in **2**. Then the 1D chains were further connected to the same four neighboring chains through the COO⁻ groups of the bridging 1,4-NDC ligands with different coordination modes (Figure S2) to give rise to a 3D framework. It is interesting to note that there exist parallel [Mg-OH/COO]_n chains in compounds **1-3** which are similar but somewhat different from each other, Figures 1c-e and Figure S3. For the [Mg-OH/COO]_n chains in **1** and **3**, the only difference lies in the coordination environment of Mg1 atom, that is, in **3** the N donor from a dppe ligand replaces the O donor of a COO⁻ group (O3) in **1** that coordinates to the Mg1, so that the O3 in **3** becomes dangling without connecting to any Mg²⁺ ion. While the difference of the [Mg-OH/COO]_n chains between compounds **2** and **3** is that one of the four coplanar COO⁻ groups that is mono-coordinated to Mg2 atom in **2** further connects the neighboring Mg3 atom at the same chain in **3**. The auxiliary N-containing ligands take different part in constructing the structures due to their different molecular length and steric configuration, that is, the bpy acts as a terminal ligand in **1** while the dpe and dppe act as bridging ligands in **2** and **3**, Figures 1f-1h.

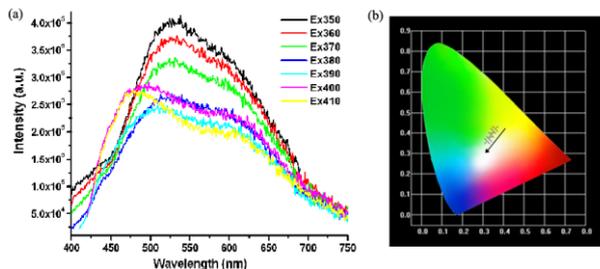


Figure 2 (a) Solid-state PL spectra of **1** by varying excitation lights; (b) the photograph of the CIE chromaticity diagram for **1**.

Photoluminescence of the compounds in solid state were studied in detail. As shown in Figure 2a, compound **1** exhibited two emission bands when varying the excitation wavelengths from 350 to 410 nm. Changing the excitation wavelengths from 350 to 380 nm, **1** showed a maximum emission at ~525 nm with a broad shoulder at 600 nm, and the overall emission was always in yellow region, as illustrated the CIE chromaticity coordinates of the emission spectra in Figure 2b. When the excitation wavelengths were varied from 390 nm to 410 nm, the green emission band around 525 nm blue-shifted to 475 nm with enhanced intensities, while the emission band at 600 nm within yellow region was almost unchanged but the emission intensities reduced. As a result, the overall emissions evolved from yellow to white-light region little by little. When being excited by

410 nm, the optimized chromaticity coordinate was tuned to (0.28, 0.28) that was well located at the value of white-light region, Figure 2b.

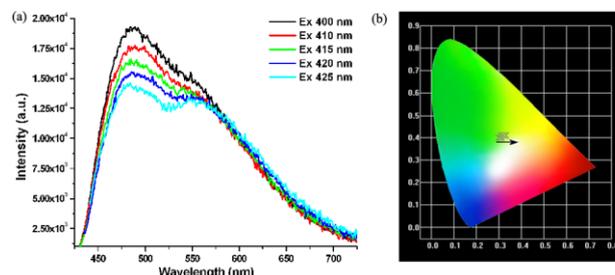


Figure 3 (a) Solid-state PL spectra of **2** by varying excitation lights; (b) the photograph of the CIE chromaticity diagram for **2**.

As depicted in Figure 3a, compound **2** featured a dominant emission band at 475 nm with a shoulder emission at 560 nm. Similar to that of compound **1**, compound **2** also featured tunable emission properties. When changing the excitation wavelengths from 400 to 425 nm, the intensities of 475 nm emission decreased while the 560 nm emission increased relatively. From the chromaticity diagram (Figure 3b), the overall emissions of **2** began to change from green light to fall within the yellowish green region gradually. The chromaticity coordinates for **2** were (0.30, 0.40), (0.31, 0.40), (0.31, 0.41), (0.32, 0.41) and (0.33, 0.41) corresponding to the different excitation lights, respectively.

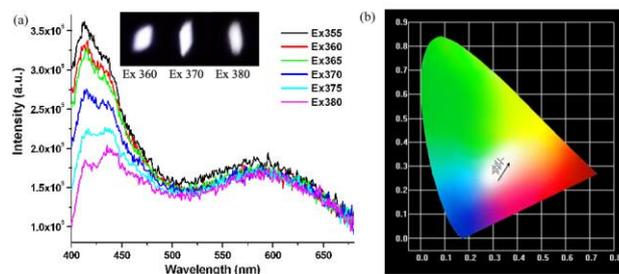


Figure 4 (a) Solid-state PL spectra of **3** by varying excitation lights; the inset are the PL images of **3** excited by 360, 370 and 380 nm light respectively; (b) the photograph of the CIE chromaticity diagram for **3**.

Compound **3** showed two obvious emission maxima at 410 and 580 nm when varying the excitation wavelengths from 355 to 380 nm, which were located in the blue and yellow light region, respectively, Figure 4a. As increasing the excitation wavelength, the intensities of the blue light emission reduced while the yellow upshot was enhanced. From the CIE chromaticity diagram (Figure 4b), it was obvious that the PLs of **3** were all located at the white light region throughout changing the excitation wavelengths. The chromaticity coordinate for compound **3** was (0.30, 0.30) when irradiated by 370 nm light, which nearly reached the value for ideal white-light (0.33, 0.33). Along with the increasing in the excited wavelength, the quantum yields (Φ) of **3** were 2.42% at 360 nm, 2.35% at 370 nm and 2.36% at 380 nm, respectively, which were comparable to those of the Pb, Zn-Ln and Cd-Ln-CPs.^{3c, 3d, 4b} The CRI of 89.41, 92.97, 93.12 and the CCT of 6622, 6106, 5606 K were monitored at 370 nm, 375 nm and 380 nm, respectively. Noticeably, for most of the compounds such as **1** and **2**, the PLs changed

gradually when varying the excitation wavelengths,^{4a, 4b} while for compound **3**, the overall emissions remained well within the white domain of the chromaticity diagram though the irradiation wavelengths were varied from 355 to 380 nm (the inset of Figure 4b). Such remarkable persistence of the white light feature is rare,^{4b} which makes **3** advantageous in lighting applications. The thermal stabilities of PL response are important for white-light emissive materials. The PLs of compound **3** in varied temperatures monitored at 360 nm excitation wavelength were further measured (Figure S7), indicating sound thermal-stable emissions up to 528K.

The two emission bands in the PL spectra of the title compounds shall arise from different origins. The emission bands around 500 nm could be assigned to ligand-centered emission features of the auxiliary ligands compared with the emissions of the free ligands (Figure S12).^{4a, 10} While the low energy emission beyond 550 nm has a red-shift compared with the emissions of Mg/Cd-CPs based on 1,4-NDC ligand¹¹ and the emission of 1,4-NDC ligand (Figure S12), possibly due to the LLCT process between 1,4-NDC and auxiliary N-donor ligands in compounds **1-3**.^{10b, 12} The PL spectra tunability of the title compounds could be presumably ascribed to the difference of the adsorption bands of the 1,4-NDC and N-donor ligands, which results in the tuning of the ratio of the two emission bands with varied excitation energies.⁷ For instance, for compound **1**, the absorption spectrum of NDC shows a good overlap with bpy, which indicates an efficient energy transfer from bpy to 1,4-NDC, Figure S13b.

To deeply understand the luminescent properties of the title compounds from a theoretical aspect, the molecular orbital calculations were implemented by the density functional theory (DFT) at the B3LYP level.¹³ As shown in Figure S14a, in compound **1**, the highest occupied molecular orbital (HOMO) is mainly associated with the π -bonding orbitals from pyridine group of bpy ligand, whereas the lowest unoccupied molecular orbital (LUMO) is on the π^* -antibonding orbitals of corresponding naphthalene rings of NDC ligand. Thus, the origin of the long-wave emission of **1** might be mainly attributed to the intraligand $\pi^*-\pi$ transitions, confirming the LLCT from the auxiliary ligands of bpy to the NDC ligand. The origin of the different emission of **2** might also be due to the similar mechanism, Figure S13b and Figure S14b. The PLs of the title compounds responded differently to the variation of excitation wavelength, which might be due to the different conjugated abilities of the auxiliary ligands causing the different LLCT process.¹⁴ The DFT calculations of compound **3** could also confirm this conclusion (Figure S14c), the LUMO and HOMO of which were located on dppe and NDC ligands which are different from **1** and **2**.¹⁵ Compared to the CPs that constructed from the same ligands without tunable emission property, the specific 3D structures of the title compounds might be one of the main factors as well.¹⁶

In summary, the bpy, dpe and dppe were introduced as auxiliary ligands to synthesize three 3D Mg-CPs with the 1,4-NDCH₂ ligand. The photoluminescence of the title compounds could be finely tunable by varying the excitation wavelength and direct white-light emission can be achieved. Future work will be focused on constructing more L-Mg-CPs based on mixed ligands. Our work would shed light on exploring L-CPs based on low-cost, non-toxic, and abundant Mg²⁺ ion, thus encourage people to pay more attention to constructing useful CPs based on environmentally and abundant metals.

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† Electronic Supplementary Information (ESI) available: Crystallographic data in CIF format, detailed synthetic procedures, more structural details, PXRD, TGA curves, elemental analyses results, more PL spectra, absorption spectra and more DFT calculation details. CCDC nos. 1025192-1025194. See DOI: 10.1039/b000000x/.

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