Electronic Supporting Information (ESI) for

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

Zhao-Feng Wu,^{*a,b*} Bin Tan,^{*a,b*} Jin-Yun Wang,^{*a*} Cheng-Feng Du,^{*a,b*} Zhong-Hua Deng^{*a,b*} and Xiao-Ying Huang^{*a*,*}

^a State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, the Chinese Academy of Sciences, Fuzhou, Fujian 350002, P.R. China. E-mail: xyhuang@fjirsm.ac.cn; Fax: +86 591-83793727; Tel: +86-591 83793727.
 ^b University of the Chinese Academy of Sciences, Beijing 100049, P.R. China.

1. Syntheses

All reagents and chemicals were purchased from commercial sources and used without further purification.

Synthesis of 1: A mixture of Mg(NO₃)₂·6H₂O (0.256 g, 1 mmol), 1,4-NDCH₂ (0.216 g, 1 mmol), bpy (0.156 g, 1 mmol), NaOH (0.080 g, 2 mmol) in CH₃OH (2 mL) and H₂O (2 mL) was sealed in a 20 mL Teflon-lined stainless-steel autoclave at 433K for 6 days. Brown block crystals of **1** (0.036 g, yield: 16% based on magnesium) were obtained. Anal. Calc. for **1**: C 53.98%, H 3.53%, N 2.13%. Found: C, C 53.75%, H 3.49%, N 2.27%.

Synthesis of 2: Brown block crystals were obtained by the same procedure of 1 except that dpe (0.182 g, 1 mmol) was used instead of bpy (0.030 g, yield: 11.3% based on magnesium). Anal. Calc. for 2: C, 57.08%; H, 4.29%; N, 3.50%. Found: C, 56.88%; H, 4.18%; N, 3.47%.

Synthesis of 3: Brown block crystals were obtained by the same procedure of 1 except that dppe (0.198 g, 1 mmol) was used instead of bpy (0.050 g, yield: 19.9% based on magnesium). Anal. Calc. for 3: C, 58.99%; H, 3.93%; N, 3.57%. Found: C, 59.13%; H, 4.02%; N, 3.73%.

2. Single-crystal X-ray crystallography and more structure details

Single–crystal X-ray diffraction data of compounds **1**, **2** and **3** were collected on a Xcalibur E Oxford diffractometer with graphite monochrochromated Mo*K* α radiation ($\lambda = 0.71073$ Å) at room temperature. The absorption corrections were applied using multi-scan technique. The structures of the compounds were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX-97 program.¹ The non-hydrogen atoms were refined with anisotropic displacement parameters. While the hydrogen atoms bonded to C and O atoms were positioned with idealized geometry and located from D-F maps, respectively, and were refined with isotropic displacement parameters using a riding model. In

compound **1** the lattice water molecule was half-occupied. In compound **2**, the S.O.Fs of the disordered C18/C18 were refined to 0.346(12) and 0.654(12), respectively; while the O1W was half-occupied. The empirical formulae were confirmed by thermogravimetric analyses (TGA) and element analyses (EA) results. The relevant crystallographic data and structure refinement details for compounds **1**, **2** and **3** are depicted in Table S1.

As shown in Figure S1a, the crystallographically asymmetric unit of compound 1 consists of three Mg(II) atoms, two 1,4-NDC ligands, one bpy ligand, two hydroxide groups, one coordinated water molecule and half of a free water molecule. In compound 1, the Mg(2) atom was octahedrally coordinated by four COO⁻ groups in the equatorial plane and two OH⁻ ions that occupied the vertexes, Figure S2a. While the Mg(1) and Mg(3) ions were six-coordinated with three COO⁻ groups and two OH⁻ groups, with the last coordination site occupied by an oxygen atom from a H₂O and a nitrogen atom from a bpy ligand, respectively, Figure S2a. The asymmetric unit of 2 contains one and a half of Mg²⁺ ion, one 1,4-NDC, half of a dpe ligand, one coordinated methanol and half of a free water molecular, Figure S1b. As depicted in Figure S2b, the Mg(1) was six-coordinated by two carboxylate oxygen atoms from two different 1,4-NDC ligands, the other four coordination sites were occupied by a N atom from dpe ligand, a O atom from a methanol and two OH⁻ ions. While the Mg(2) was six-coordinated by four carboxylate groups in coplanar positions and two hydroxyl groups that occupied the axial positions. The asymmetric unit of **3** consists three crystallographic independent Mg²⁺ ions, two 1,4-NDC ligands, one dppe ligand, two OH- ions and one coordinated water molecule, Figure S1c. The Mg(2) was bonded to four carboxylate oxygen atoms from four 1,4-NDC ligands and the axial positions are occupied by two hydroxyl groups, forming a little distorted octahedron. While the Mg(1) was surrounded by two oxygen from two COO⁻ groups, two OH⁻ groups, one oxygen from a water molecule and one N atom from a dppe ligand, forming a octahedral geometry. The Mg(3) was six-coordinated with two OH⁻ ions, one N atom from dppe ligand and three carboxylate oxygen atoms from three 1,4-NDC ligands, Figure S2c. The 1,4-NDC ligand exhibits three different coordination modes in compounds 1-3, as shown in Figure S3. In the three compounds, the OH group acts as a tridentate ligand (μ_3 -O) to bridge Mg(II) ions to form the same 1D $[Mg_3(OH)_2]_n$ chains shown in Figure 1b in the text. The neighboring 1D chains are further interlinked by the 1,4-NDC ligands to form the three-dimensional networks of 1-3. It is evident that $[Mg_3(OH)_2]_n$ chains are interconnected by the L1 or L2 ligands to form the 2D layers of the title compounds, Figure S4. The pH values of the reaction systems for synthesizing 1, 2 and 3 were around 6.0 before heating, while that for the similar reaction in the absence of N-containing ligands was about 3.5. The N-containing ligands should increase the pH values of the reaction systems for 1, 2 and 3, leading to the presence of OH⁻ groups which participated in the Mg coordination to form rod-like $[Mg_3(OH)_2]_n$ chains in compounds 1-3. Furthermore, due to their different molecular lengths and steric configurations, the bpy acts as a

terminal ligand in 1 while the dpe and dppe act as bridging ligands in 2 and 3, as shown in Figures 1f-1h in the text, which also further increases the thermal stabilities of the title compounds (Figure S6).

Reference

[1] G. M. Sheldrick, SHELXS97 and SHELXL97, University of Göttingen, Germany, 1997.

Empirical formula	$C_{34}H_{25}Mg_3N_2O_{11.50}$	$C_{38}H_{34}Mg_{3}N_{2}O_{13}$	$C_{37}H_{30}Mg_{3}N_{2}O_{11} \\$
Crystal Size (mm)	0.35 x 0.28 x 0.22	0.21 x 0.21 x 0.20	0.35 x 0.27 x 0.24
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_{1}/c$	$P2_{1}/c$	$P2_{1}/c$
a (Å)	11.5486(2)	6.75674(18)	11.5400(3)
<i>b</i> (Å)	11.3339(2)	16.2310(5)	12.0576(4)
<i>c</i> (Å)	23.0576(4)	16.3562(5)	22.8377(5)
eta (°)	90.649(2)	97.495(3)	92.783(2)
$V(Å^3)$	3017.83(9)	1778.44(8)	3174.00(15)
Z	4	2	4
$\mu(\mathrm{mm}^{-1})$	0.174	0.159	0.168
λ (MoK α) (Å)	0.71073	0.71073	0.71073
<i>F</i> (000)	1484	832	1560
θ range (°)	2.48 to 26.75	2.51 to 27.09	2.63 to 26.50
Reflections measured	13603	7904	13818
Independent reflections	6384	3857	6548
Temperature (K)	293(2)	293(2)	293(2)
$ ho_{ m calc}/ m g~cm^{-3}$	1.581	1.493	1.573
Parameter	466	273	478
$R_{\rm int}$	0.0228	0.0231	0.0202
R_1 , $wR_2 [I > 2\sigma(I)]^a$	0.0583, 0.1672	0.0456,0.1086	0.0322, 0.0715
R_{1} , wR_2 [all data]	0.0708, 0.1710	0.0594,0.1172	0.0450, 0.0739
GOF	1.043	1.008	1.013
Largest diff. Peak and hole/e Å ⁻³	0.369 and -0.453	0.347 and -0.518	0.254 and -0.261

Table S1 Crystallographic data and refinement details for compounds 1, 2 and 3.



Figure S1. The asymmetric units of compounds **1** (a), **2** (b) and **3** (c). Thermal ellipsoids are given at the 30% probability level.



Figure S2. The coordination environments of the Mg^{2+} ions in compounds 1 (a), 2 (b) and 3 (c). Hydrogen atoms are omitted for clarity.



Figure S3. The 1,4-NDC ligand coordination modes in compounds 1 (a), 2 (b) and 3 (c). Hydrogen atoms are omitted for clarity.



Figure S4. The 2D layers constructed from Mg-OH chains interconnected by 1,4-NDCH₂ ligands (L1 and L2) in compounds **1** (a), **2** (b) and **3** (c). Hydrogen atoms are omitted for clarity.

3. Physical measurements

Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku Miniflex II diffractometer using a CuK α radiation. Microprobe elemental analyses were performed by using a field-emission scanning electron microscope (FESEM, JSM6700F) equipped with an energy-dispersive X-ray spectroscope (EDXS, Oxford INCA). Elemental analyses for C, H, and O were performed on a German Elementary Vario EL III instrument. Thermogravimetric analyses were carried out with a NETZSCH STA 449F3 unit at a heating rate of 5 °C/min under nitrogen atmosphere. The UV/Vis diffuse reflectance spectra were measured at room temperature using a PE Lambda 950 UV/Vis spectrophotometer. The spectrophotometer was calibrated against the surface of BaSO₄ for 100% reflectance over the wavelength range under consideration in the UV/Vis diffuse reflectance spectra measurents. The absorption spectrum was calculated from reflectance spectrum by using the function: $\alpha/S = (1-R^2)/2R$, ² where α is the absorption coefficient, *S* is the scattering coefficient, and *R* is the reflectance.

3a). PXRD



Figure S5. The PXRD patterns of 1 (a), 2 (b) and 3 (c) are comparable to the simulated from the single crystal X-ray data.

3b). TGA



Figure S6. TGA curves for compounds 1, 2 and 3.

4. Fluorescence measurements

Emission and excitation spectra of the compounds, and the photoluminescence lifetime measurements were carried out using laser pulses at 378 nm as the excitation source and determined by a Varian Cary Eclipse and an Edinburgh FLS980 fluorescence spectrometer at room temperature.



Figure S7. The PL spectra of compound 3 under different temperatures monitored at $\lambda_{ex} = 360$ nm.







Figure S9. Fluorescence decay profiles of compound 1 monitored at 500 and 525 nm.



Figure S10. Fluorescence decay profiles of compound 2 monitored at 475 and 560 nm.



Figure S11. Fluorescence decay profiles of compound 3 monitored at 410 and 580 nm.



Figure S12. The luminescent spectra of bpy, dpe, dppe and 1,4-NDCH₂ ligands in the solid state.





Figure. S13 Absorption spectra of the compounds (a), bpy, dpe, dppe and 1,4-NDCH₂ ligands (b) in the solid state.



Figure S14. Plots for the frontier molecular orbitals HOMO and LUMO (isovalue = 0.02) for the investigated models of **1** (a), **2** (b) and **3** (c) calculated by DFT method at the B3LYP level, combined with the corresponding orbital composition (%).