

**Electronic Supplementary Material (ESI) for New Journal of Chemistry**

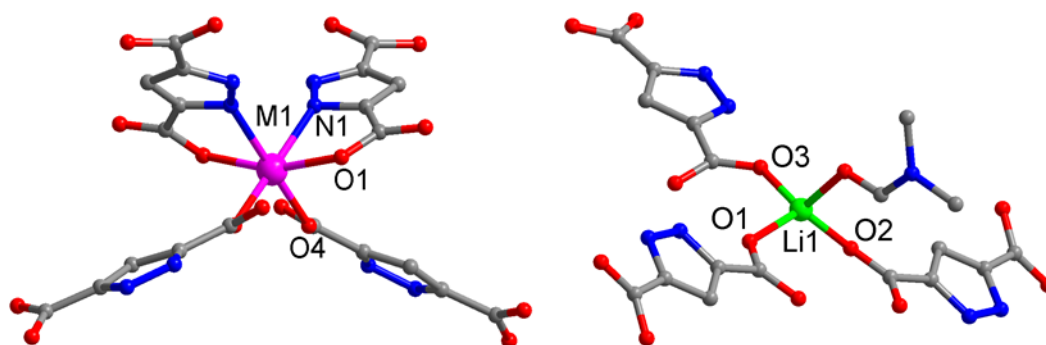
**Mg<sub>1-x</sub>Co<sub>x</sub>Li<sub>2</sub>(3,5-pdcH)<sub>2</sub>(DMF)<sub>2</sub> (x = 0, 0.285, 0.575, 1): A Series of  
Heterometallic Coordination Polymers upon Doping Magnetic Co<sup>2+</sup>  
Ions**

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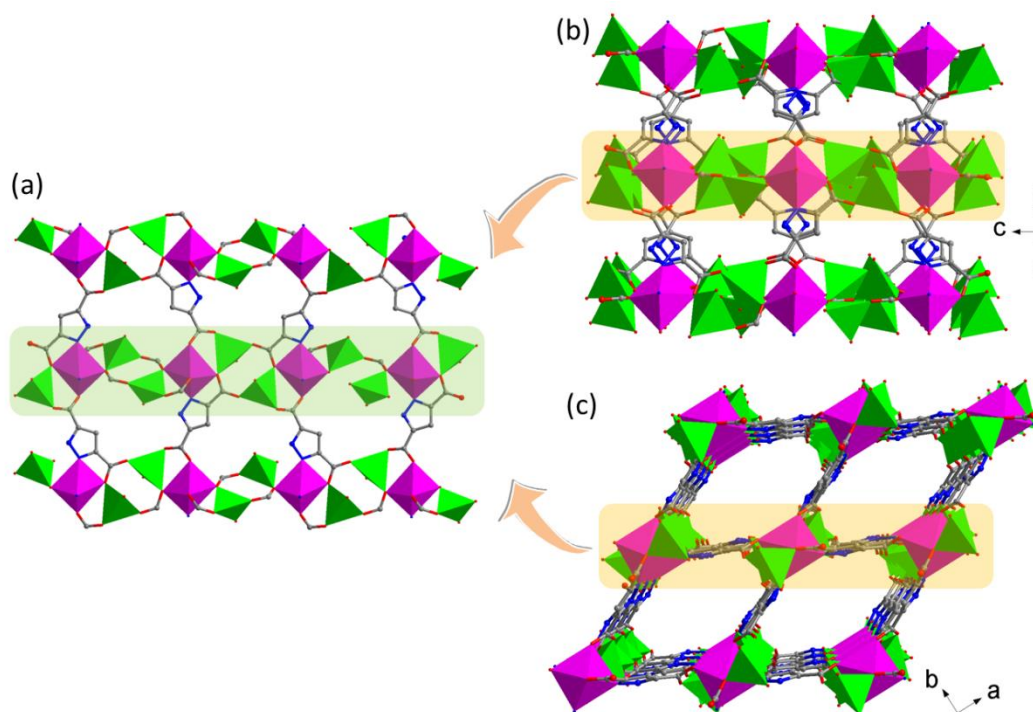
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## More structural details

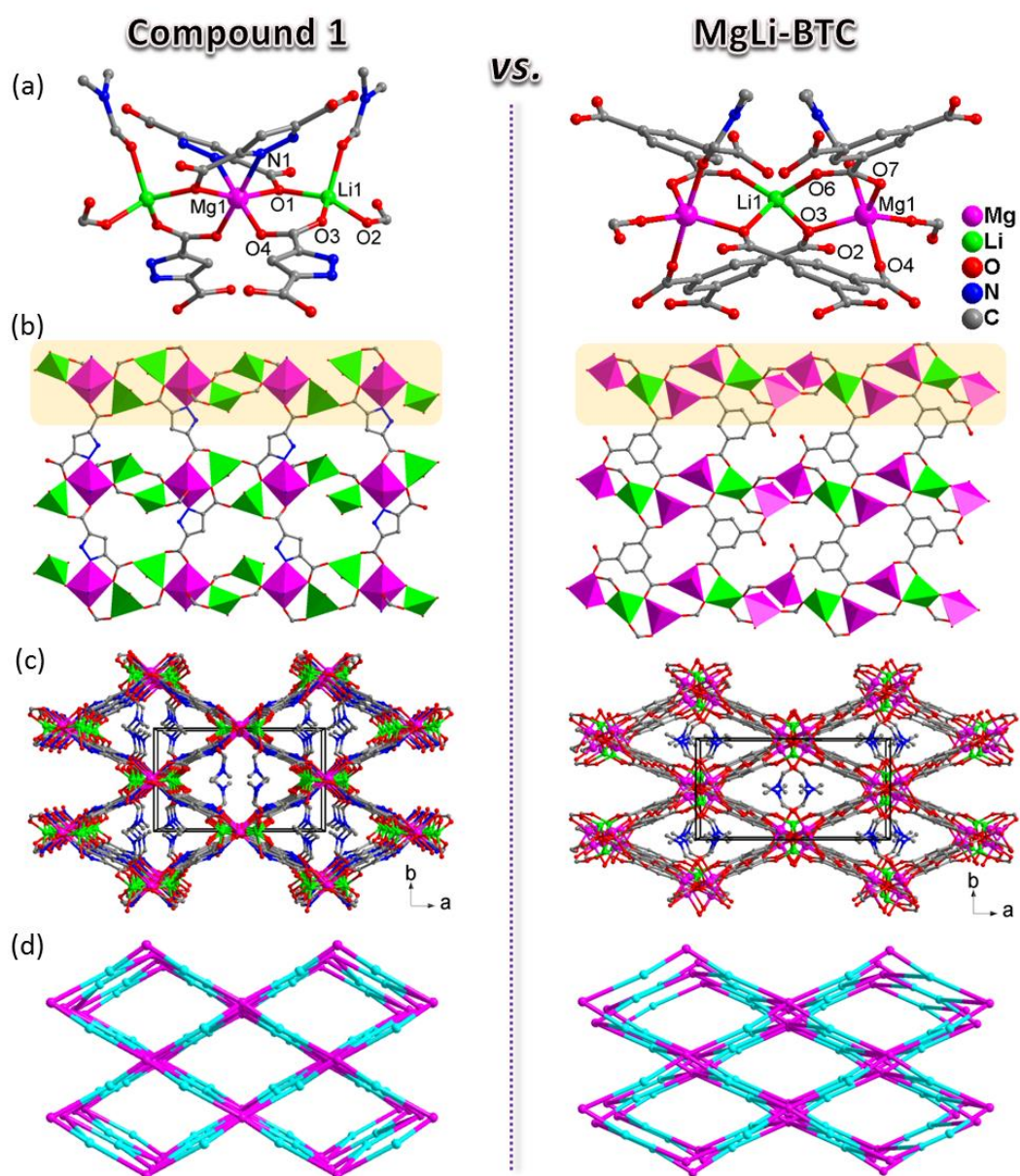


**Fig. S1** The coordination environments of  $M^{2+}$  ions ( $M = \text{Mg}$  (**1**),  $\text{Co}_{0.285}\text{Mg}_{0.715}$  (**2**),  $\text{Co}_{0.575}\text{Mg}_{0.425}$  (**3**),  $\text{Co}$  (**4**)) and  $\text{Li}^+$  ions in title compounds.

The fabrication mode from the chain-like SBUs to the 3D framework of **1** could be described in the following manner. As shown in Fig. S2a, the neighboring 1D chains are interlinked by 3,5-pd $\text{CH}_2^{2-}$  ligands to form a 2D layer, then, the 3D network is formed by 3,5-pd $\text{CH}_2^{2-}$  ligands interlinking the chains in the adjacent layer, Figs. S2b-c.

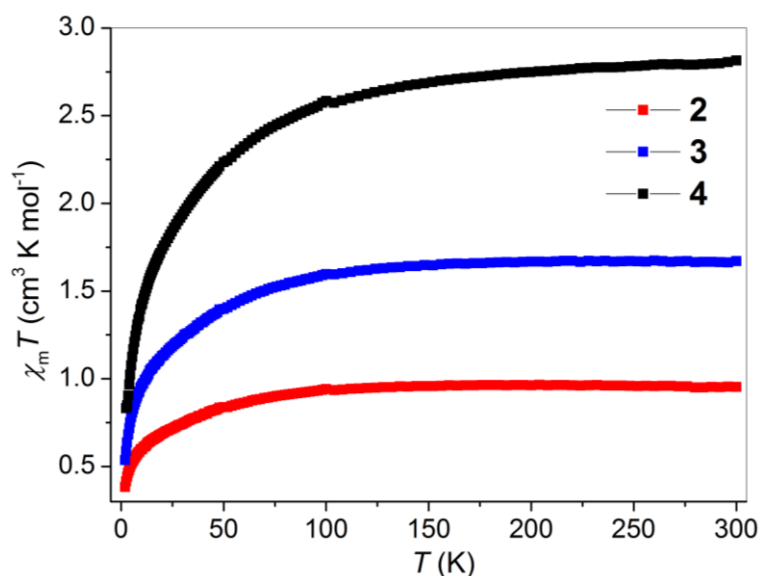


**Fig. S2** Illustrations of the fabrication mode from chain-like SBUs to 3D frameworks of title compounds. (a) The 2D layer, in which one of the chains is highlighted in green. (b-c) View of the 3D frameworks along different directions. The coordinated DMF molecules and hydrogen atoms are omitted for clarity.



**Fig. S3** Illustration of the comparison between the structures of compound **1** and the reported MgLi-BTC. (a) Tri-nuclear monomers; (b) 2D layers constructed from chain-like SBUs interconnected by ligands, in which one of the chains is highlighted in orange; (c) 3D representative structures along the *c* axis; (d) topologies. Hydrogen atoms are omitted for clarity.

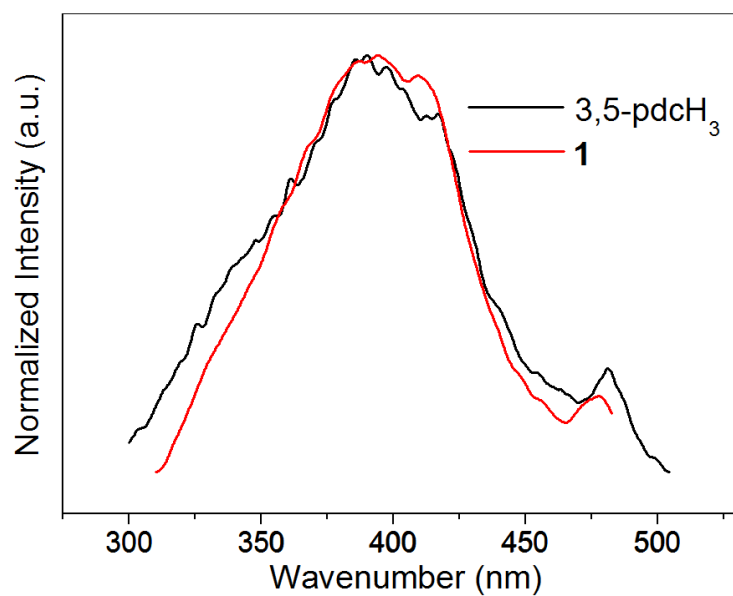
## Magnetic susceptibility curves



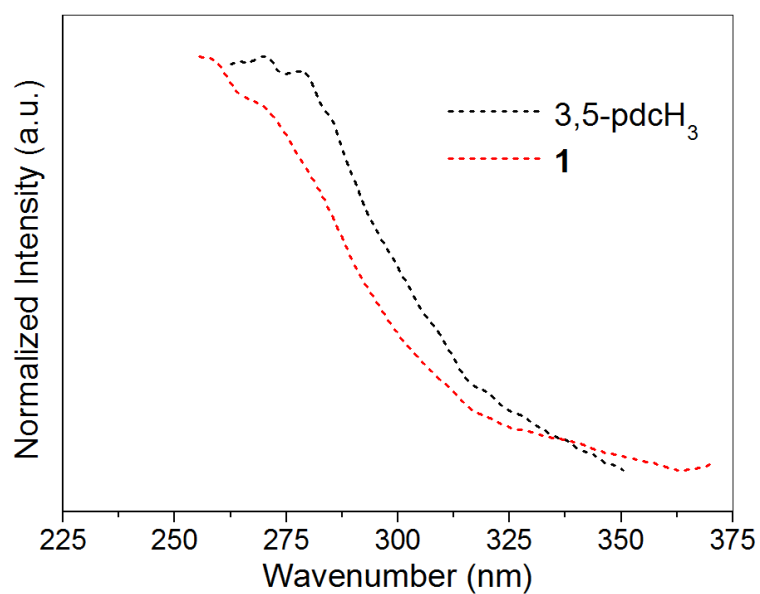
**Fig. S4** Temperature dependence of  $\chi_m T$  vs.  $T$  curves for **2–4** under an applied field of 1000 Oe in the temperature range of 2–300 K, respectively.

## Luminescent properties

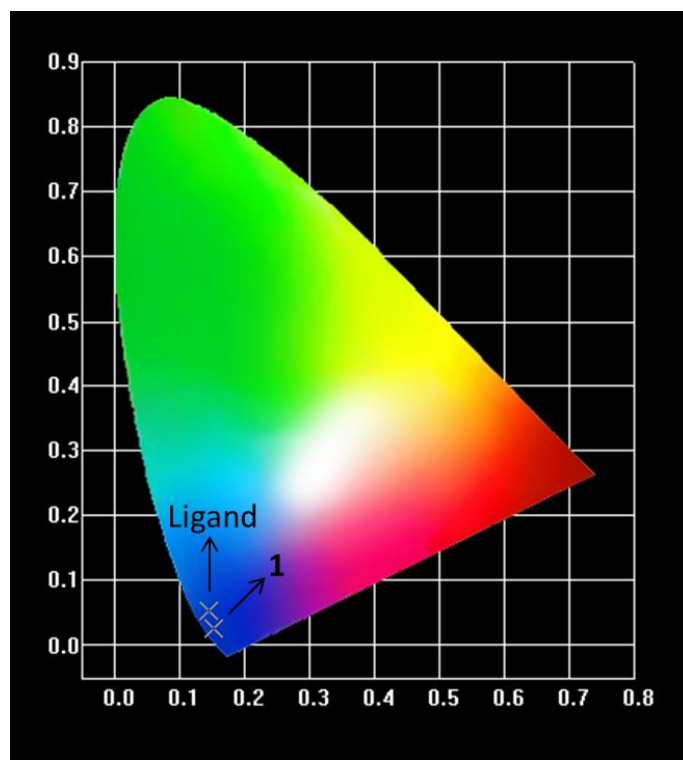
The photoluminescence (PL) properties of the colorless compound **1** in the solid state were investigated on a PerkinElmer LS55 luminescence spectrometer. As shown in Fig. S5, the emission of compound **1** is centered at 395 nm when excited by 270 nm wavelength. As a comparison, the free 3,5-pdcH<sub>3</sub> ligand showed very similar PL behaviour with the emission centered at 390 nm. Both of the emissions are located in the blue light region, as convinced by the CIE chromaticity diagram (Fig. S7). Considering that the s-block Mg<sup>2+</sup>/Li<sup>+</sup> ions are difficult to be oxidized or reduced, the PLs of **1** are neither based on metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT). Instead, the highly similar PL spectra of **1** with free ligand indicates a ligand-centered (intraligand,  $\pi \rightarrow \pi^*$ ) emission<sup>1-2</sup>. With the increasing of Co<sup>2+</sup> contents from compounds **2** to **4**, the crystal colors become darken gradually which makes the photoluminescence emission negligible.



**Fig. S5** Solid-state PL emission spectra of **1** and 3,5-pdcH<sub>3</sub> ligand at the excitation wavenumber of 270 nm at room temperature.



**Fig. S6** Solid-state PL excitation spectra of compound **1** and 3,5-pdcH<sub>3</sub> ligand at room temperature.



**Fig. S7** The photograph of the CIE chromaticity diagram for compound **1** and 3,5-pdcH<sub>3</sub> ligand.

## References

- 1 J. D. Furman, A. Y. Warner, S. J. Teat, A. A. Mikhailovsky and A. K. Cheetham, *Chem. Mater.*, 2010, **22**, 2255.
- 2 Q. F. Zhang, H. G. Hao, H. N. Zhang, S. N. Wang, J. Jin and D. Z. Sun, *Eur. J. Inorg. Chem.*, 2013, 1123.