

Supplementary information:

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**Synthesis, structures and properties of two-dimensional honeycomb and stepwise networks from self-assembly of tripodal ligand 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene with metal salts**

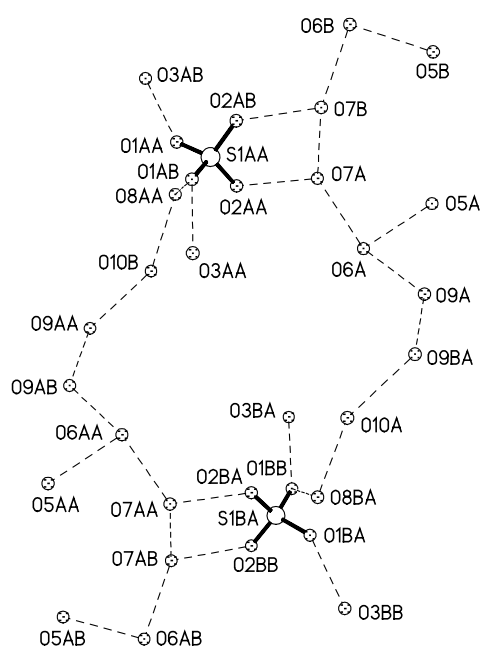
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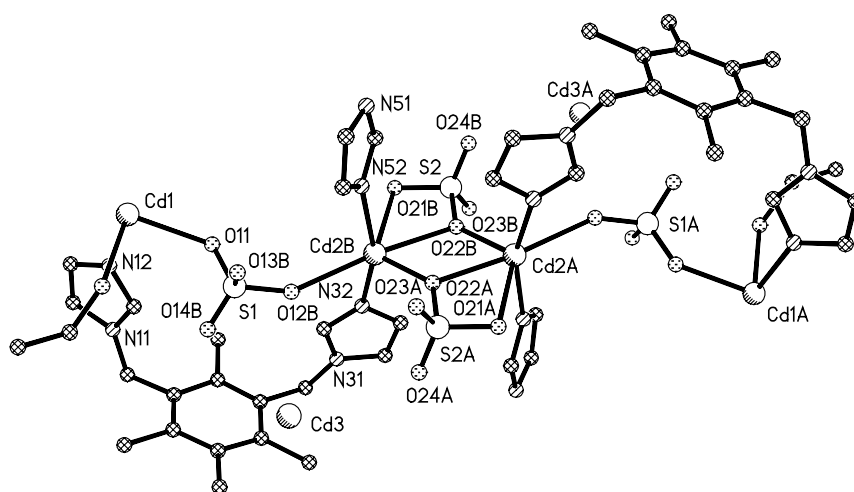
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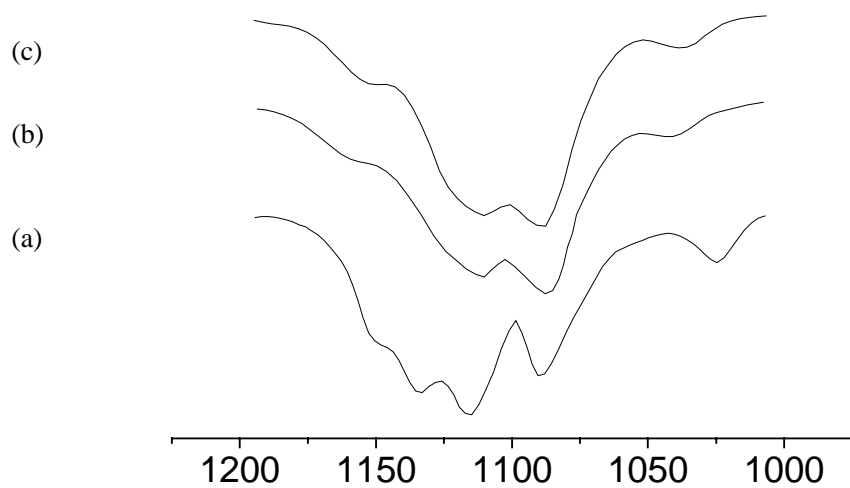
1. Hydrogen bonds network in complex **2**.
2. Coordination environment of Cd<sup>2+</sup> in minor component of complex **3**.
3. FT-IR spectra of anion exchange.
4. Excitation and emission spectra of **2**.



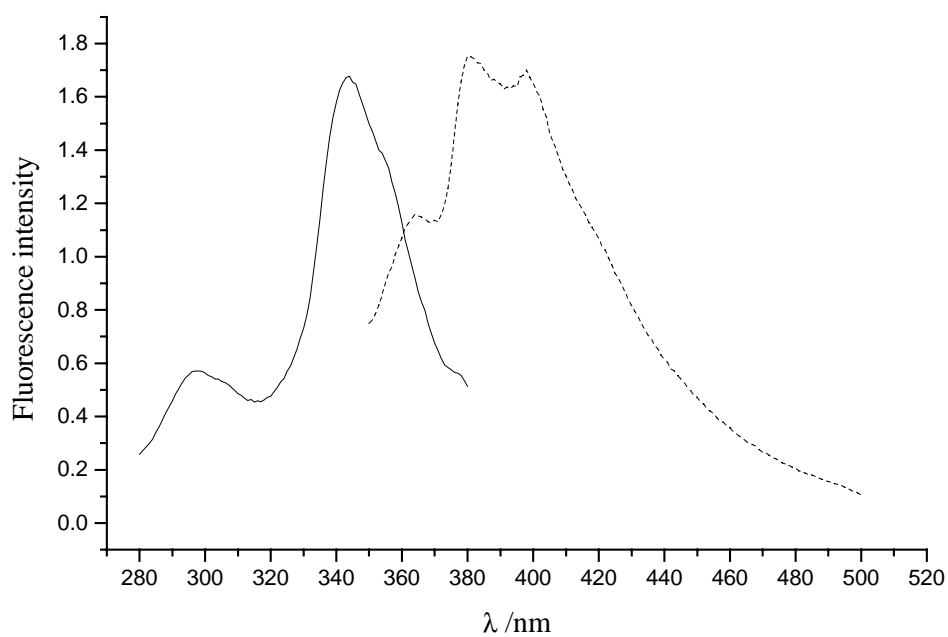
**Figure S1.** Hydrogen bonds network indicated by dashed lines in **2**. Distance between two O atoms ( $\text{\AA}$ ):  $\text{O1AB-O3AA} = 2.75$ ,  $\text{O1AB-O8AA} = 2.93$ ,  $\text{O8AA-O10B} = 2.90$ ,  $\text{O10B-O9AA} = 2.87$ ,  $\text{O9AA-O9AB} = 2.82$ ,  $\text{O9AB-O6AA} = 2.89$ ,  $\text{O6AA-O5AA} = 2.83$ ,  $\text{O6AA-O7AA} = 2.78$ ,  $\text{O7AA-O7AB} = 2.77$ ,  $\text{O7AA-O2BA} = 2.75$ .



**Figure S2.** Coordination environment of Cd2b (minor component).



**Figure S3.** FT-IR spectra of (a) complex **2**; (b)  $[\text{Mn}(\text{L})_2](\text{ClO}_4)_2$  and (c) product of **2** exchanged with  $\text{NaClO}_4$ .



**Figure S4.** Excitation and emission spectra of **2** in solution ( $4 \text{ mg ml}^{-1}$ ,  $\text{CH}_3\text{OH}/\text{DMF}$  1 : 1) at ambient temperature. Excitation = solid line, emission = dashed line.