

# HOMO- AND HETEROMETALLIC Zn(II) AND Cd(II) COORDINATION POLYMERS CAPABLE OF RETAINING GUEST MOLECULES



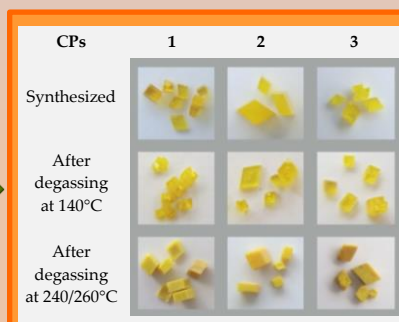
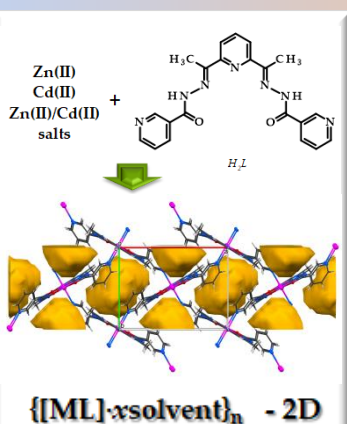
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Coordination polymers (CPs) are an attractive area of research in coordination chemistry and crystal engineering due to their intriguing topological architectures and various applications. Schiff bases derived from 2,6-diacetylpyridine are suitable candidates for the development of magnetic homo- and/or heterometallic CPs.

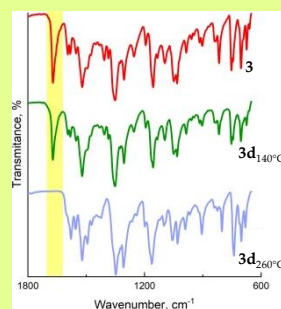
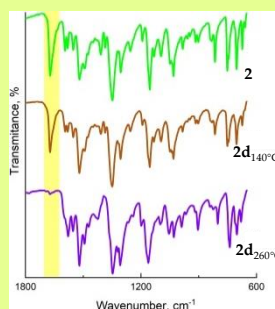
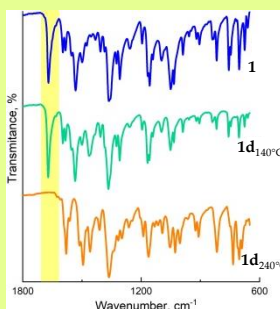
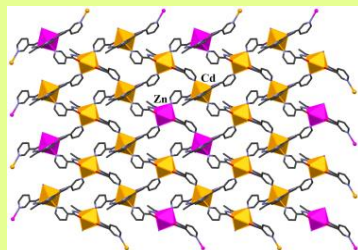
Herein, we present our method for the synthesis of Zn(II) and Cd(II) CPs based on the 2,6-diacetylpyridine bis(nicotinoylhydrazone) Schiff base ligand (H<sub>2</sub>L), which led to the obtention of two homo-  $\{[ZnL] \cdot 0.5dmf \cdot 1.5H_2O\}_n$  (1) and  $\{[CdL] \cdot 0.5dmf \cdot H_2O\}_n$  (2) and as well as one heterometallic  $\{[Zn_{0.75}Cd_{1.25}L_2] \cdot dmf \cdot 0.5H_2O\}_n$  (3) 2D isostructural and isomorphous coordination layers, where dmf = N,N-dimethylformamide.



Thermal analysis of the CPs 1-3 indicated that the solvent molecules were removed at a surprisingly high temperature (240-260°C), when the ligand thermal degradation began. These observations indicate that water and dmf molecules accommodated in their compartments, and being heated these spaces get free. Thus, to prove this assumption, N<sub>2</sub> adsorption isotherms were measured at 77K on degassed samples at 140 °C to remove molecules adsorbed from the air and 240/260°C to eliminate the solvent guest molecules.

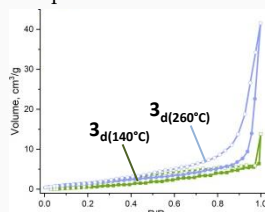
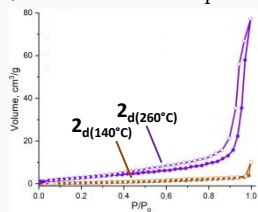
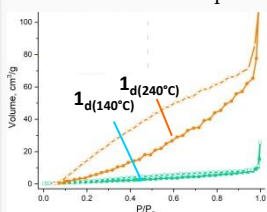
All degassing crystals kept their shape and crystallinity after heating at 140°C, becoming brighter, but lost their lustre after degassing at higher temperatures.

The Monte Carlo generator of Special Quasirandom Structures code was used to generate the Special Quasirandom Structure (SQS) to find the sequence of metals in the CP 3 in a ratio of 0.75:1.25.



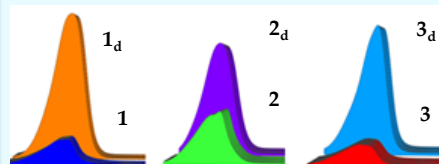
Comparable IR spectra for CPs 1-3 and desolvated samples with the coloration of the  $\nu(C=O)$  band which corresponds to  $\sim 1670$   $cm^{-1}$

The obtained results clearly show that there is a significant increase of volume pores and specific surface area. At the same time, the appearance of hysteresis rings for degassed samples at 240/260°C indicates the presence of mesopores.



Adsorption-desorption isotherms of N<sub>2</sub> at 77K for degassed crystals

The degassing crystals reveal a significant increase of volume pores and specific surface area, as well as PL emission with respect to synthesized ones.



Comparable solid-state emission plots ( $\lambda_{exc} = 337$  nm) for 1-3, and degassed samples.

These results show that obtained materials have sensitivity to the guest-molecules removal and can be recommended as sensors, thus extending the Zn(II)/Cd(II) family of coordination polymers with impressive sorption-luminescent properties.