Porous coordination polymers (PCPs) represent a consolidated research line for numerous disciplines, from chemistry to physics, materials science, biology and even pharmacology. As a matter of fact, the clever combination of tailored structural features and key functional properties renders PCPs potentially suitable for technologically advanced applications. As shown also by our work [1-4], polyazolato-based PCPs are particularly promising in this respect, because they typically juxtapose, to interesting structures and functions, high thermal and chemical stability. Along this research line, the present contribution focuses upon the family of bipyrazolato-based PCPs isolated by reacting the ditopic ligand 1,4-bis(4-acetylydopyrazolyl) benzene (H2L) with a number of transition metal ions. Special concern is dedicated to structural aspects, retrieved by state-of-the-art XRPD methods applied to laboratory data, thermal and chemical robustness, adsorption properties. All the materials possess 3-D networks: while NiL and Fe2L3 feature non interpenetrated architectures, interpenetration is found in ZnL. Despite this, all show 1-D pervious channels, the shape of which depends on the stereochemistry of the metal ions: square, rhombic, or triangular channels are observed for ZnL, NiL, or Fe2L3, accounting for 49, 75 or 64% of the total volume. Coupling DSC to in situ variable temperature XRPD allowed to demonstrate i) the remarkable thermal robustness of the materials, stable in air up to 310 °C; ii) their stability along consecutive cycles of thermal activation; iii) the existence of permanent porosity; iv) the response of the unit cell parameters to temperature increase. Solution-phase tests allowed to assess the chemical stability toward a number of common solvents at room temperature for a few days. Finally, N2 adsorption measurements at 77 K allowed to estimate promising BET specific surface areas above 1000 m2/g.

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