RIGIDITY *VERSUS* FLEXIBILITY OF THE LIGAND UPON THE POROSITY DEGREE OF NEW METAL-ORGANIC POLYMERIC MATERIALS

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In the context of the adsorption gas property, four metal-organic polymeric materials based on cobalt(II), palladium(II), nickel(II) and zinc(II) with the rigid 4,4′-bipyrazole (labeled as Co-bpz, Pd-bpz, Ni-bpz and Zn-bpz), and four polymeric materials based on cobalt(II) nitrate, cobalt(II) acetate, nickel(II) nitrate and copper(II) acetate with the flexible bis(1,2,4-triazolyl)methane (labeled as Co1-btm, Co2-btm, Ni-btm and Cu-btm) have been investigated toward N_2 adsorption at 77 K. Their porous nature is manifested by the following values of the Langmuir surface area: 1057 m^2/g, 1035 m^2/g, 962 m^2/g and 866 m^2/g for Co-bpz, Pd-bpz, Ni-bpz and Zn-bpz, respectively, whereas the values of the surface area for the *btm*-based materials are all null. These results show that the rigid 4,4′-bipyrazolyl ligand induces the formation of porous polymeric structures, whereas the flexible bis(1,2,4-triazolyl)methane ligand induces the formation of nonporous structures.

INTRODUCTION

Porous coordination polymers (PCPs), including metal-organic frameworks (MOFs), are highly crystalline structures with nanometer-sized pores that allow them to store hydrogen and other high-energy gases.[1] The larger specific surface area and high porosity on the nanometer scale enable MOFs to hold relatively large amounts of gas.[2] The pores are adjustable in terms of size and polarity and so can be fine-tuned for specific applications. For these reasons, MOFs open up new opportunities for alternative propulsion systems, in catalysis, as nanoreactors, in drug delivery, gas sensors and many others.[3-7]

There are many cases reported in the literature about MOFs in which the porosity degree is given by long and rigid organic linkers (*e.g.,* polycarboxylates and/or polyazolates), and cases about MOFs in which the porosity degree is given by flexible organic linkers.[8] In our case, the bridging N-donor ligands used within the metal-organic polymeric materials investigated in this work, are the rigid 4,4′-bipyrazole (*H₂bpz*)[9] and the flexible bis(1,2,4-triazolyl)methane (*Btm*)[10] (Fig. 1).
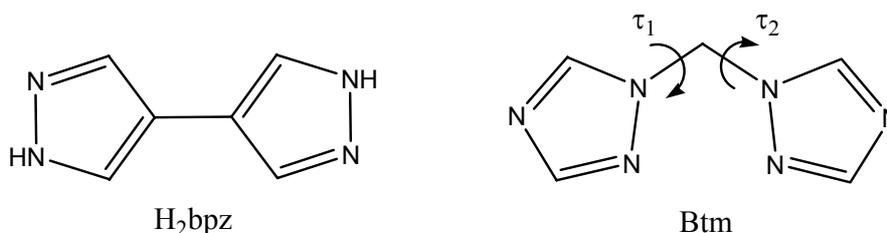

Fig. 1 – Schematic drawing of the rigid *H₂bpz* and flexible *Btm* ligands.

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The *Btm* ligand, which acts as a bis(monodentate) bridging ligand, is mainly characterized by the presence of a methylenic spacer between two imidazolyl groups that can rotate around the torsion angles τ_1 and τ_2, respectively, which may lead to an increased flexibility and coordination versatility. This flexible bitopic spacer can readily coordinate toward transition metals in an *exo bidentate* fashion, and can construct coordination polymeric materials with different dimensionalities and topologies.[10] Contrary to *Btm*, *H2bpz* ligand features rigidity due to the strong 4,4′ carbon–carbon bond (1.111 Å) by which the two pyrazolic moieties are connected, thus rendering it planar and possessing a torsion angle $\varphi \approx 0°$ of the pyrazolic planes with respect to one another.[11] On the other hand, the pyrazolic moieties can be readily deprotonated to form the corresponding diazolate anion, in which each individual nitrogen atom is a very strong *N*-ligating donor for a d-metal, and thus, it can act as a useful bridging ligand. After deprotonation, the coordination ability of the resultant diazolate ligand further increases from the gain of negative charge and higher basicity, leading thus to 1D, 2D or 3D coordination polymers, the latter featuring porous structures with potential adsorptive capacity.

In the context of the gas storage application, adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature.[12]

Herein we focus on the adsorption measurements with gaseous nitrogen at low temperature (77 K) upon four new metal-organic coordination polymers based on cobalt, palladium, nickel and zinc with the *H2bpz* ligand (labeled as **Co-bpz, Pd-bpz, Ni-bpz** and **Zn-bpz**), and four polymeric materials based on cobalt nitrate, cobalt acetate, nickel nitrate and copper acetate with the *Btm* ligand (labeled as **Co1-btm, Co2-btm, Ni-btm** and **Cu-btm**). An assessment of their adsorptive capacities is performed taking into account the values of their Langmuir surface areas along with the influence of the rigidity and the flexibility of each ligand used toward the formation of polymeric materials.

RESULTS AND DISCUSSION

The presence of cavities inside the polymeric structures of the synthesized compounds was preliminary essayed toward N_2 at 77 K in the range of relative pressures of 0 – 1 bar. Their porous nature is manifested by their specific surface areas, as obtained by the Langmuir method (Table 1).

From the results reported in Table 1 it can be observed that the species based on cobalt(II), palladium(II), nickel(II) and zinc(II) with the rigid ligand *H2bpz* indicate adsorption capacity. On the contrary, the *Btm*-based species do not show any adsorption capacity. As indicated by the X-ray powder diffraction analysis, Co1-btm and Ni-btm are isostructural and feature 2-D layers, whereas Co2-btm and Cu-btm seem to feature just a 1-D polymeric chain, and thus, there is no chance for them to display any porosity. In this respect, the *Btm* linker, due to its flexible nature, was not able to construct 3-D polymeric networks (as a sufficient condition for displaying inner cavities for gas adsorption property).

The porous nature of the M-bpz polymers (M = Co, Pd, Ni, Zn), indicated by the X-ray analysis as well, show that Co-bpz and Zn-bpz are isostructural possessing a 3-D network that feature uniform square channels, whereas Ni-bpz and Pd-bpz are also isostructural possessing a 3-D network featuring uniform rhombic channels. In this respect, the *H2bpz* linker, due to its rigid nature and strong bridging character in a tetradentate fashion, was able to lead to the construction of porous networks as suitable candidates for gas adsorption property.

Table 1

Values of Langmuir surface area and maximum volume of N_2 adsorbed on the polymeric materials

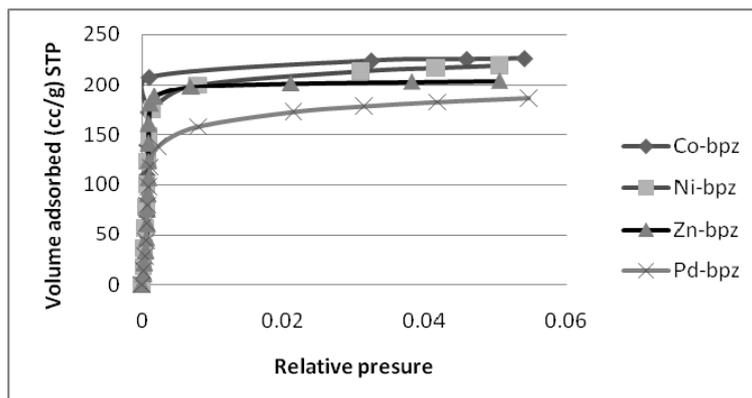| Material	Co-bpz	Pd-bpz	Ni-bpz	Zn-bpz	Co1-btm	Co2-btm	Ni-btm	Cu-btm
Langmuir surface area (m^2/g)	1057	1035	962	866	0	0	0	0
Volume of adsorbed N_2 (cm^3/g)	243	238	221	199	0	0	0	0

Fig. 2 – Adsorption isotherms with N_2 at 77 K by Langmuir equation.

Table 2

Values of the Langmuir surface area and maximum volume
of adsorbed N_2 at 77 K for Zn-bpz based MOF at three different outgas temperatures

Outgas temperature (°C)	Langmuir surface area (m^2/g)	Volume of adsorbed N_2 (cm^3/g)
150	776	178
200	866	199
250	893	204

The MOFs based on Co(II), Pd(II), Ni(II), and Zn(II), respectively, with the 4,4′-bipyrazolyl ligand, after being degassed at 200°C, demonstrated to display the Langmuir isotherms in the range of relative pressure of 0 – 0.05 bar as shown in Fig. 2, giving a first indication about their porous nature. The reasonable porosity degree of these materials, manifested by their specific surface areas, is highlighted by the values of ca. 1057, 1035, 962 and 866 m^2/g for Co-bpz, Pd-bpz, Ni-bpz and Zn-bpz, respectively, as obtained by the Langmuir method (Table 1). These values may be comparable with those of the already reported coordination polymers such as, *e.g.*, 846 m^2/g for $[Cu_2(pzdc)_2(4,4′-bpy)]_n$ (pzdc = pyrazine-2,3-dicarboxylate, 4,4′-bpy = 4,4′-bipyridine) and 1013 m^2/g for $[Cu_2(pzdc)_2(pia)]_n$ (pia = *N*-pyridylisonicotinamide).[8a,13]

The Co-bpz and Pd-bpz materials exhibit a larger gas storage capacity with respect to Ni-bpz and Zn-bpz, amounting to 10.84 mmol/g (for Co-bpz) and 10.61 mmol/g (for Pd-bpz) of N_2 at 77 K, which is indicative of a higher accessibility of their microporous structure.

In the case of the Zn-bpz based MOF we can speak also about some *flexibility of the porous structure*, that is, higher is the outgas temperature, higher will be the surface area, and thus, more the porous structure will open. As a consequence, the Zn-bpz based MOF presents three different values of the Langmuir surface area and maximum volume adsorbed of N_2 at three different outgas temperatures, which are given in Table 2. We considered, however, the thermal stability of this MOF by thermal gravimetric analysis in which it appears to be stable till 450°C, in order for the polymeric structure not to collapse even at 250°C.

The N_2 adsorption at low temperature (77 K) is generally used for the evaluation of the porosity degree through adsorption/desorption isotherms. Fig. 3 shows the adsorption/desorption isotherms of N_2 at 77 K for the M-bpz based materials, which display the typical behavior of microporous crystalline MOFs. Indeed, all of them exhibit type I adsorption isotherms by the IUPAC classification with a sharp knee at low relative pressures ($p/p_0 \sim$ 0.01) corresponding to the filling of the porous structure, followed by a *plateau*, suggesting that the permanent porosity of the samples is mainly composed of micropores, of quite uniform size. In addition, the presence of a hysteresis loop in the N_2 isotherms at relative pressures above 0.8 bar is indicative of textural mesoporosity arising from interparticle mesopores (voids).[14] This is indeed in line with the apparent average particle sizes (approximated by the coherent scattering domains) determined by diffraction methods, typically lying in the 50-200 nm. As a matter of fact, the hysteresis loops, in the case of Co-bpz, Pd-bpz and Zn-bpz, are quite thin, indicating a facile release of the nitrogen during the desorption process at higher relative pressure. In the case of Ni-bpz, instead, the hysteresis loop seems a little larger in comparison to the others, suggesting that the removal of the nitrogen trapped into more tight mesopores by capillary condensation, is somewhat delayed while passing from higher to lower relative pressure.
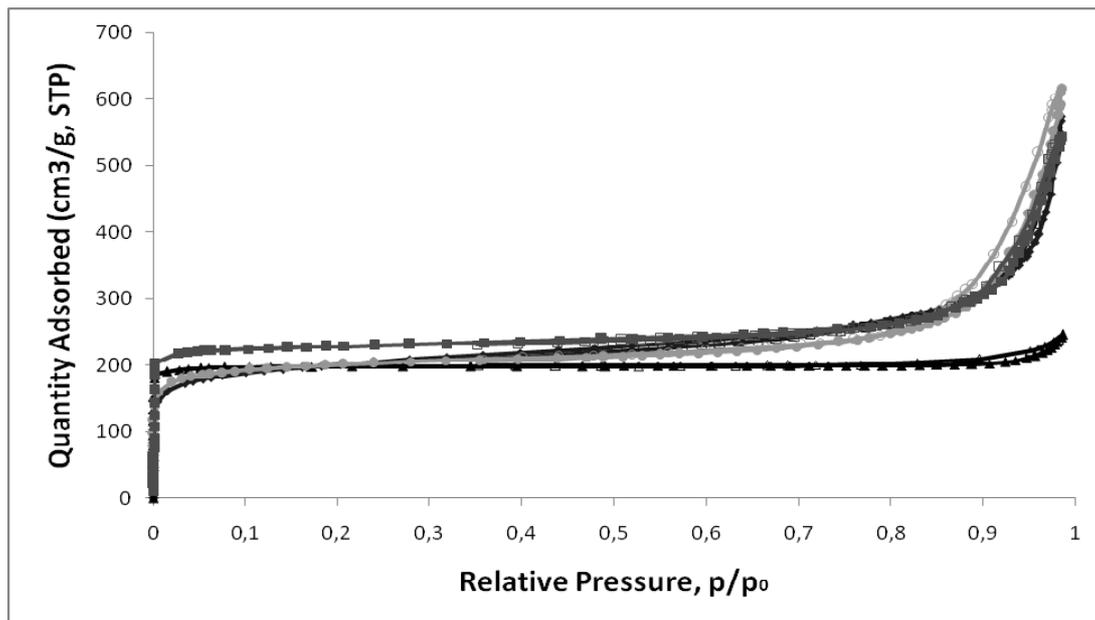
Fig. 3 – N_2 adsorption/desorption isotherms at 77 K of Co-bpz (red squares),
Pd-bpz (green circles), Ni-bpz (blue rhombi) and Zn-bpz (black triangles). The empty symbols denote the desorption branches.

EXPERIMENTAL

The polymeric materials **Co-bpz, Pd-bpz, Ni-bpz** and **Zn-bpz** have been synthesized solvothermally at 120 °C by simply mixing together M(II) acetate (M = Co, Pd, Ni and Zn) and the *H₂bpz* ligand in dimethylformamide for 24 h.[15] Instead, the polymeric materials **Co1-btm, Co2-btm, Ni-btm** and **Cu-btm** have been synthesized according to the procedure reported in literature.[16] All these compounds have been taken further under the adsorption study with N_2 at 77 K.

Gas sorption isotherms for pressures in the range of 0-1 bar were measured by the volumetric method using a Beckman Coulter SA 3100 Surface Area & Pore Size Analyzer instrument, adopting the following procedure. A sample of *ca.* 50 mg of as-synthesized material was introduced into a pre-weighed analysis tube (9-mm diameter, 9 cm³ bulb), capped with a gas-tight transeal to prevent intrusion of oxygen and atmosphere moisture during transfer and weighing. The samples were evacuated under dynamic vacuum (*ca.* 10^{-5} bar) at 200 °C, till a constant weight was achieved. The analysis tube was then transferred to an electronic balance and weighed again to determine the mass of the sample. Finally, it was transferred to the analysis port of the gas sorption instrument. For all isotherms, warm and cold free space correction measurements were performed using ultra high purity He gas (UHP grade 5.0, 99.999% purity); N_2 isotherms at 77 K were measured in a liquid nitrogen bath—using UHP-grade gas sources.

CONCLUSIONS

An assessment of the rigidity *versus* flexibility of two bitopic nitrogen donor ligands upon the porosity degree has been performed toward new metal-organic polymeric materials based on late transition metals such as cobalt, nickel, zinc, copper and palladium. The flexible bis(1,2,4-triazolyl)methane ligand did not lead to the formation of porous materials, and therefore, null values of the surface area were obtained. On the contrary, the rigid 4,4′-bipyrazole manifested a very good ability for leading to the formation of uniform porous structures. Their adsorptive capacity, investigated toward N_2 adsorption at 77 K, highlighted the highest values of Langmuir surface areas in the case of Co-bpz and Pd-bpz, confirming the presence within their porous systems of highly accessible channels. The case of Zn-bpz is interesting to be noted, taking into account its network flexibility, that is, it opens as the outgas temperature increases.

Future outcome will be focused on the assessment of the adsorptive capacity upon the M-bpz materials toward H_2 and CO_2 adsorption at high pressures, which would be of interest for practical applications such as gas storage and transport along with molecular separations.

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