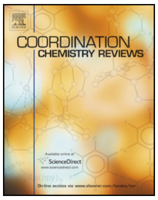
Coordination Chemistry Reviews 307 (2016) 1–31

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

Coordination polymers and metal–organic frameworks based on poly(pyrazole)-containing ligands

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Contents

ARTICLE INFO

Article history:
Received 18 June 2015
Accepted 20 August 2015
Available online 2 September 2015

ABSTRACT

In the past two decades, the vast classes of coordination polymers (CPs) and metal–organic frameworks (MOFs) have received deep attention in both the academic and industrial realms, as they can possess different functional properties of economic, technological and/or environmental interest, such as luminescence, electric conductivity, magnetism, catalytic activity, gas storage or separation, drug delivery – to mention only a few.

Abbreviations: Boc, *tert*-butoxycarbonyl; bpe, 1,2-bis(4-pyridyl)ethylene; CP, coordination polymer; DEF, *N*,*N*-diethylformamide; DMAc, *N*,*N*-dimethylacetamide; DMF, *N*,*N*-dimethylformamide; F_6dmpz, hexafluoromethyl-pyrazole; F-pymo, 5-fluoro-pyrimidinolate; FTIR, Fourier transform infrared; H_2BDC, 1,4-benzenedicarboxylic acid; H_2BDMPX, 1,4-bis((3,5-dimethyl-1*H*-pyrazol-4-yl)methyl)benzene; $H_2BDP\text{-}NH_2$, 2-amino(1,4-bis(1*H*-pyrazol-4-yl)benzene); $H_2BDP\text{-}NO_2$, 2-nitro(1,4-bis(1*H*-pyrazol-4-yl)benzene); $H_2BDP\text{-}OH$, 2-hydroxo(1,4-bis(1*H*-pyrazol-4-yl)benzene); $H_2BDP\text{-}SO_3H$, 2,5-di(1*H*-pyrazol-4-yl)benzenesulfonic acid; H_2BDT, 5,5′-(1,4-phenylene)bis(1*H*-tetrazole); H_2BPE, 4,4′-buta-1,3-diyne-1,4-diylbis(3,5-dimethyl-1*H*-pyrazole); H_2BPEB, 4,4′-(benzene-1,4-diyldiethyne-2,1-diyl)bis(1*H*-pyrazole); $H_2BPEB\text{-}R$, (R = methyltrifluoromethyl); H_2BPZ, 4,4′-bipyrazole; H_2DMPMB, 4,4′-bis((3,5-dimethyl-1*H*-pyrazol-4-yl)methyl)biphenyl; H_2Et_4BPZ, 3,3′,5,5′-tetraethyl-4,4′-bipyrazole; H_2Me_4BPZ, 3,3′,5,5′-tetramethyl-4,4′-bipyrazole; $H_2NDI\text{-}H$, bis(*N*-(3,5-dimethyl-1*H*-pyrazol-4-yl))naphtalenetetracarboxylicdianhydride; 4,4′-bpy, 4,4′-bipyridine; H_2PBP, 4,4′-bis(1*H*-pyrazol-4-yl)biphenyl; H_2TET, 2,6-bis(1*H*-pyrazol-4-yl)pyrrolo[3,4-*f*]isoindole-1,3,5,7(2*H*,6*H*)-tetrone; H_3BTP, 1,3,5-tris(1*H*-pyrazol-4-yl)benzene; H_3BTPP, 1,3,5-tris((1*H*-pyrazol-4-yl)phenyl)benzene; H_3BTT, 1,3,5-tris(tetrazol-5-yl)benzene; H_3BTTri, 1,3,5-tris(1*H*-1,2,3-triazol-5-yl)benzene; $H_3TPB\text{-}3tz$, 1,3,5-tri-*p*-(tetrazol-5-yl)phenylbenzene; HPz, pyrazole; IR, infrared; KDP, potassium dihydrogenophosphate; MOF, metal–organic framework; NHPI, *N*-hydroxyphthalimide; NIR, near infrared; NLO, non linear optics; OAc, acetate; PCP, porous coordination polymer; PTA, 1,3,5-triaza-7-phospha-adamantane; PXRD, powder X-ray diffraction; py, pyridine; RH, relative humidity; SBU, secondary building unit; SHG, second harmonic generation; STA, simultaneous thermal analysis; TED, triethylenediamine; TGA, thermogravimetric analysis; tmttf, tetrakis(methylsulfanyl)tetrathiafulvalene; UV–Vis, ultraviolet–visible; VT-PXRD, variable-temperature powder X-ray diffraction; 1,3-H_2BDP, 1,3-bis(4-pyrazolyl)benzene; 1,4-H_2BDP, 1,4-bis(4-pyrazolyl)benzene; 1,4-H_2BDPB, 1,4-bis[(3,5-dimethyl)-pyrazol-4-yl]benzene; 3,5-$(CF_3)_2Pz$, 3,5-bis(trifluoromethyl)pyrazole; 3,5-Me_2Pz, 3,5-dimethylpyrazole.

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http://dx.doi.org/10.1016/j.ccr.2015.08.005

Keywords:
Poly(pyrazole)-based ligand
Block *d* metals
Coordination polymer
Metal–organic framework
Crystal structure
Functional properties

Within this vast landscape, this review proposes a survey on those transition metal containing CPs and MOFs built up with poly(pyrazole)- and poly(pyrazolate)-based ligands, in which up to three *N*-donor heterocyclic rings are organized on rigid or flexible cores. The overview has been restricted to the most recurrent transition metals, namely copper, zinc, cobalt, nickel, cadmium, silver and iron. For each material, mentioning of the synthetic method(s) yielding to its isolation is complemented by a description of its thermal behaviour, of the main structural aspects and, whenever investigated, of its functional properties.

1. Introduction

One of the most exciting challenges of modern chemistry and material science is the design and preparation of tailored hybrid inorganic/organic polymeric materials, the structural features and functional properties of which make them appealing in key applications involving different fields of technological, economic and/or environmental relevance. Engineering and isolating these materials are based on a rational choice of building units [1], followed by a careful control of their self-assembly processes [2–4]. As a matter of fact, thanks to the knowledge accumulated in the past decades mainly in the fields of organic and coordination chemistry, chemists and material scientists, above all, are presently able to engineer and prepare different classes of functional polymeric materials. A great impulse, in this respect, has been the development and diffusion of modern solid state techniques for the spectral and structural characterization of “real” materials.

Among functional polymeric materials, the class of coordination polymers (CPs) [5], along with that of metal–organic frameworks (MOFs) [6–10], has recorded a massive expansion in the past two decades, especially due to the promising functionalities they may possess, ranging from magnetism [11–13], to conductivity [14], catalytic activity [15–18], luminescence [19–21], as well as, when permanent porosity is present, gas storage [22–27] or separation [25–30], drug delivery [31], biomedical properties [32,33], chemical sensing [34,35], optoelectronics [36]. The huge importance of these materials is manifested by the great interest they have raised even at the industrial level [37–39].

Coordination polymers (CPs) are generally defined as coordination compounds in which the building blocks – metal ions or metal-containing clusters, acting as nodes, and organic ligands, acting as spacers – are reciprocally linked by means of coordination bonds and develop repetitively into one, two or three dimensions [40]. When (permanent) porosity is present, they are referred to as either metal–organic frameworks (MOFs) or porous coordination polymers (PCPs). There exists a long-lasting debate in the scientific literature [41,42] with respect to the use of different terms, within the crystal engineering community, to describe polymeric structures built up by combining metal ions or metal clusters and spacers. Either entering into or detailing upon such a debate is out of the scope of this work. In the following, we will refer to CPs when dealing with non-porous coordination polymers, to MOFs in all of the cases in which the polymeric network is porous.

The enormous library of experimental data accumulated on the synthesis and characterization of CPs and MOFs has been conveniently rationalized on the basis of self-assembly criteria. Due to the possibility of tuning the stereochemistry at the metal ions, along with the hapticity, size, shape and functionality of the spacers, ultimately influencing the metal centre through steric and electronic effects, CPs and MOFs may offer substantial advantages, with respect to inorganic polymeric materials, in terms of versatility of the architectural topologies that can be engineered and constructed [43] – hence of the functional properties which can be achieved. In this respect, the assessment of synthetic strategies such as the net-based [44], reticular synthesis [45–47], supermolecular building block and supermolecular building layer [48], template-directed [49] approaches have been proposed and successfully applied. As a complementary investigation, the topological classification of the networks [50,51] has been highly beneficial.

Numerous are the organic molecules containing donor atoms, especially oxygen, nitrogen [52], and phosphorous [53], that have been intensively exploited in the construction of functional CPs and MOFs, coupling them to a variety of (transition) metal ions [54].

Within this vast landscape, this review aims to overview those poly(pyrazole)- and poly(pyrazolate)-based CPs and MOFs, built up with the most recurrent transition metals – namely copper, zinc, cobalt, cadmium, nickel, silver and iron - that have been prepared and characterized in the past years. For each compound, mentioning of the synthetic method(s) yielding to its isolation is complemented by a description of its thermal behaviour, of the main structural aspects and, whenever investigated, of its functional properties. For the sake of legibility, all of the materials described in the following are collected in Table 1.

2. Overview of pyrazole-based ligands

One of the pioneering examples of nitrogen-donor ligands is represented by 4,4′-bipyridine, a very attractive building block for constructing structural architectures with different dimensionality, such as one-dimensional chains and ladders [55,56], two-dimensional grids [57–59], and three-dimensional networks [60–62].

Azoles and poly(azoles), in their neutral or anionic forms, have emerged as promising ligands more than forty years ago [63] and, due to the versatility they have demonstrated, they still play a crucial role in coordination chemistry. As representative examples, the reader is referred to the recent surveys dedicated to the coordination chemistry of azoles [64], azolates (with a specific focus on MOFs) [52], imidazoles and benzazoles [65], triazoles [66], tetrazoles [67], triazoles and tetrazoles [68].

Pyrazole has been and still is one of the most studied heterocyclic compounds in coordination chemistry [69], both as it is [70], and incorporated in polydentate (chelating) ligands [70,71], such as poly(pyrazolyl)borates or ‘scorpionates’ [72–74], acylpyrazolones [75,76], poly(pyrazolyl)alkanes [72,77,78]. Pyrazoles are widely used as core tectons in the preparation of coordination compounds for diverse application as catalysis [79], magnetism [80], medicine [81], biomimetism [82]. Remarkable are the advances accomplished, in the past decade, in the synthesis of pyrazole derivatives [83].

Deprotonation of pyrazole increases, concomitantly, its hapticity and basicity. The position of the two donor atoms makes pyrazolate an *exo*-bidentate ligand; compared to its isomer imidazolate, pyrazolate possesses a rather small bridging angle (*ca.* 70°), which allows it to hold two metal centres at a rather short distance (*ca.* 3.5–4.7 Å, depending on the ionic radius of the metal ion). As a matter of fact, twenty different terminal or bridging coordination modes have been identified so far for pyrazolates [84]. With these attractive features, it is not surprising that pyrazolates have received and still receive a massive