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Editorial

Recent Developments in Multifunctional Coordination Polymers

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[†] Regretfully: Professor Ileana Dragutan, an important contributor to the development of the Special Issue of Crystals, "Multifunctional Coordination Polymers: Synthesis, Structure, Properties and Applications" passed away during the progress of this Issue. All of us will miss her greatly.

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This Special Issue of *Crystals* "Multifunctional Coordination Polymers: Synthesis, Structure, Properties and Applications" [1] is dedicated to recent research related to the design, synthesis, structure and properties of these high-value hybrid materials [2,3]. As an attractive class of coordination polymers, metal–organic frameworks (MOFs) have also been considered, with emphasis on their emerging applications in contemporary areas of science and technology [4,5].

The papers published in this Special Issue [1] focus on current investigations into a selected array of metal complexes and related coordination polymers. The synthesis of multifunctional coordination polymers has been developed at a fast rate, covering a broad range of main-group metals, transition metals, rare-earth metals and non-metallic elements as constituents of their basic framework [6]. This large pool of constitutive elements has allowed us to construct coordination polymers with unprecedented structures and topologies and to specifically induce high-value physical and chemical properties in their networks, thus widening their areas of application and making them more environmentally friendly [7]. In this respect, new studies on coordination polymers containing main-group metals and transition metals have been extended to Zn, Cd, Cu and Co mixed with ligands of 1,4-di(1*H*-imidazol-4-yl)benzene and 4-methylphthalic acid [8,9].

The innovative progress of coordination polymers has unveiled interesting features in their structure and morphology. Of interest for their unparalleled physical chemical properties and significant economic effect, novel networks based on Fe(II) MOF systems, displaying ligand-engineered spin crossover, have attracted significant attention [10]. Furthermore, the extension of the incorporation of different transition metals such as Ni and Co into the construction of stable two-dimensional cluster organic layers, suitable for high-performance supercapacitors, has been properly demonstrated [11].

Coordination polymers designed for targeted hepatocellular carcinoma therapy have been delivered on a core–shell nanostructured drug delivery platform based on a biocompatible metal–organic framework containing polyethyleneimine [12]. As an important development, performant synthetic approaches have been revealed in a comprehensive study, and their essential determinant parameters were defined for a variety of applications in energy storage, drug delivery and wastewater treatment [13].

New MOF configurations of high value as therapy agents, drug carriers, imaging agents and biosensors in cancer have been further described in new research [14]. Important advances in the structure and applications of coordination polymers derived from cyclohexane polycarboxylate ligands have recently been reported [15]. Furthermore, in a very interesting study, the quantitative quantum sensing of lithium ions at room temperature was accomplished using an inventively designed radical-embedded metal–organic framework [16].

The fast-growing development of luminescent functional coordination polymers [17–22] is due to their ability to be used in many analytical and biological applications [23], for instance, as physical and chemical sensors for a variety of anions and cations [24–26] of different gases and vapors. The identification of small or complex organic molecules [27–29] and the detection of luminescent polymeric materials [30] have been consistently investigated. Numerous analytical applications have been developed for food components [31] and agricultural products [32], as well as for biomolecules, pharmaceuticals [33,34] and medical investigations [35–38].

In the construction of multifunctional coordination polymers with luminescent properties, assembling various lanthanides as functional constitutive elements has been convincingly outlined as a future trend in the economical utilization of these new materials in optoelectronics [39] and communications [18]. Recent developments in luminescent coordination polymers, and especially in their design strategies, sensing applications and specified theoretical aspects, have also been made [40,41]. Moreover, details on the preparation, structure and spectroscopic properties of a diverse range of luminescent coordination polymers have been fully provided [42].

Important research on luminescence thermometry based on one-dimensional benzoato-bridged coordination polymers containing lanthanide ions has recently been carried out [43]. Additionally, innovative achievements in the synthesis, crystal structure and magnetic properties of new cyanido-bridged heterometallic 3d-4f 1D coordination polymers have been unveiled [44]. It is remarkable that the crystal structures in these studies displayed crenel-like Ln^{III}-M^{III} alternate chains with their Ln^{III} ions connected by two *cis* cyanido groups of the hexacyanido metalloligand. Notably, the field-induced slow relaxation of their magnetization was accurately evidenced for two compounds, one of these being a new attractive example of a polymer chain with the specific features of single-ion magnets. Of much interest, molecule-based magnetic materials constructed from paramagnetic organic ligands and two different metal ions have been comprehensively surveyed [45].

Bifunctional self-penetrating Co(II) polymers containing three-dimensional MOF structures have been carefully developed for high-performance environmental and energy storage applications [46]. Emissive Pt(II) coordination polymers with promising applications in artificial-light-harvesting systems endowed with sequential energy transfer have been effectively synthesized [47]. Of great interest for their specific properties, sulfur-based nodes have been designed for the construction of coordination polymers and MOFs with specific desired functionalities [48]. These sulfur-based coordination polymers are promising materials for use in semiconductors, conductivity applications and photocatalysis.

Studies on metal–organic frameworks for biomass conversion have been reported as well [49]. The current state of the art and future developments of this important promising domain have been fully illustrated. Trifunctional ionic metal–organic frameworks based on imidazolium cation ligands have been employed as efficient catalysts for the CO_2–epoxide cycloaddition into cyclocarbonate without the use of a cocatalyst or solvent [50].

Lanthanide coordination polymers have attracted rich and productive investigations from many research groups around the world [51]. The synthesis, structure and catalytic applications of a considerable number of lanthanide coordination polymers have recently been surveyed [2,52]. These reviews focus on the relevant structural features and coordination environment that modulate these coordination polymers' catalytic properties through their large pool of incorporated lanthanides and organic ligands. Such cutting-edge assemblies have allowed for their application in a diverse range of chemical transformations. In one particular case, functional noncentrosymmetric lanthanide-based MOF materials, exhibiting strong SHG activity and an NIR luminescence of Er^{3+} with the application in nonlinear optical thermometry [53,54], took advantage of their ligand modulation protocol to effectively expand the structural topologies of rare-earth porphyrinic metal–organic frameworks. Furthermore, luminescent lanthanide coordination polymers with transformative energy transfer processes used for physical and chemical sensing applications have also been widely described [25].

A large variety of lanthanide coordination polymers have been designed and manufactured, providing an attractive and useful platform for their successful application in catalysis and photocatalysis. In this respect, well-defined isostructural lanthanide coordination polymers, associated with Tb and Eu through 2,2′-bipyridyl-4,4′-dicarboxylic acid as an organic linker, have been synthesized and applied as catalysts with high activity and selectivity in the Strecker reaction to α-amino nitriles [55]. New heterobimetallic coordination polymers with Pr, Gd and Tb lanthanides have been assembled through the same heteroleptic ligand [56]. In this protocol, a reticular synthesis approach was applied to coordinate the nitrophilic Pd(II) units and oxophilic Ln(III) ions. Their effective applications in Sonogashira, Suzuki–Miyaura and Heck cross-coupling reactions have been illustrated [57]. Using the heteroleptic ligand mentioned above, 2,2′-bipyridine-4,4′-dicarboxylic acid, in Ln/Pd coordination polymers with Nd, Sm, Eu and Dy, new catalysts have been successfully employed in aqueous Heck and Suzuki–Miyaura cross-couplings. An important array of lanthanide coordination polymers featuring Er, Tm and Yb and containing a 1,3-bis(4-carboxyphenyl) imidazolium carboxylate ligand have been prepared, and their utilization as heterogeneous catalysts for the coupling reactions between halogenated propylene oxides and CO_2 and their corresponding cyclic carbonates has been accurately documented [58].

The elaborated synthesis of heterodinuclear Pd-Ln complexes, combining Pd with Sm, Eu, Gd and Tb by means of a 2,2′-bipyridine-5,5′-dicarboxylate linker, has been developed for their use as efficient catalysts in the Suzuki–Miyaura cross-coupling of aryl halides with phenylboronic acid and the Heck reaction of aryl halides with substituted olefins [59]. At the same time, multifunctional lanthanide coordination polymers consisting of 12 connected lanthanide clusters incorporating Yb, Dy and Sm as $[Ln_6(\mu_3\text{-}OH)_8(COO-)_{12}]$ secondary building units have been synthesized as well, using 2-aminobenzenedicarboxylate as an efficient organic linker. These cluster-based metal–organic frameworks have been productively used in CO_2 adsorption and in a tandem deacetalization–Knoevenagel reaction [60]. To substantially improve the performance of catalytic processes, the high hydrolytic robustness of coordination polymers has been elaborated in an innovative procedure using different lanthanides as constituents for their basic framework [61]. Notably, valuable heterobimetallic coordination polymers built using the bifunctional organic ligand 1,1′-di(p-carboxybenzyl)-2,2′-diimidazole and incorporating Sm, Eu, Tb and Dy into their structure, as well as Pd, have been reported as generating almost quantitative yields in the Suzuki–Miyaura cross-coupling reactions of aryl bromides with arylboronic acids [62].

Of particular scientific interest, unusual homochiral lanthanide coordination polymers of Sm, Eu, Gd, Tb, Dy, Ho, Er and Yb, derived using achiral rigid ligand 5-[(pyridin-4-ylmethyl)amino]-isophthalic acid, have been designed and consistently produced [63]. Significantly, and illustrating the versatility of rare-earth metals as constituents of new coordination polymers endowed with attractive physical–chemical properties, a broad range of lanthanides have been embedded into these unusual materials; in particular, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb have been linked using 3,3′,5,5′-azobenzenetetracarboxylic acid [64]. Their utility as excellent catalysts has been demonstrated in CO_2 cycloaddition reactions with epichlorohydrin under ambient CO_2 pressure and solvent-free conditions. Moreover, the effective application of a diverse range of coordination polymers and metal–organic frameworks in many cutting-edge domains of materials science is only continuing to expand [65–80].

In summary, we hope that the numerous emerging trends of development in the area of multifunctional coordination polymers, fully revealed in this account, along with the latest contributions published in this Special Issue of *Crystals*, will bring to light new information on the current state of the field and open new directions for the future advances of this fascinating domain of chemical research.

Conflicts of Interest: The authors declare no conflicts of interest.

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