

Editorial

Editorial for Special Issue “Functional Coordination Polymers and Metal–Organic Frameworks”

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Metal–Organic Frameworks (MOFs) and Coordination Polymers (CPs) are at the forefront of contemporary coordination chemistry research, as witnessed by the impressive (and ever-growing) number of publications appearing in the literature on this topic in the last 20 years (Figure 1), reaching almost 4000 papers in 2020. Among them, several recent review articles and books clearly illustrate the huge potential of this class of compounds [1–6].

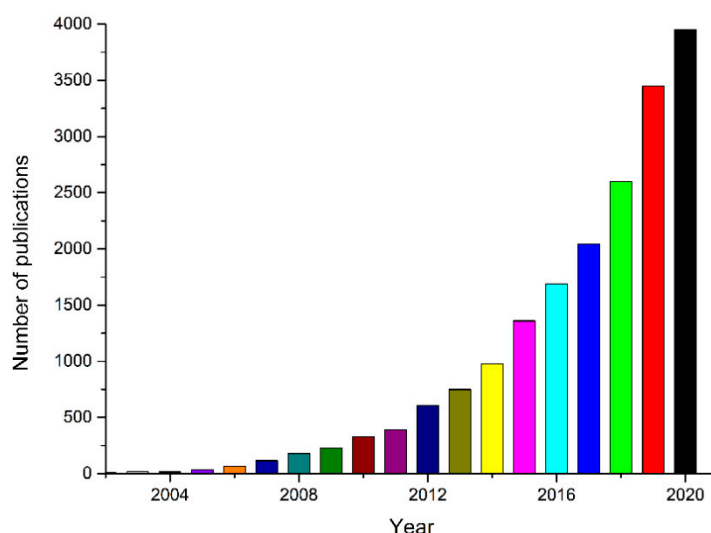


Figure 1. The number of publications in the 2002–2020 time period whose titles or keywords contain “MOF”. Data from Web of Science.

The virtually infinite combination of tailored organic linkers and inorganic metal nodes (in the form of isolated ions or more complex cluster structures) generates a wide variety of functional materials for assorted applications. With a specific application in mind, chemists and materials scientists devoted to MOFs synthesis “play LEGO[®]” [7] every day in their laboratories to reach their targets, choosing the most suitable pairs to create valuable MOFs.

The present Special Issue collects a total number of 10 papers: 8 original articles and 2 review articles covering multiple aspects of MOFs and CPs chemistry.

Two fundamental synthetic studies are part of this collection. Armelao et al. (Padova, Italy) [8] examined the solvent effects in the structures of Cu^{II}-4,4'-bipyridyl CPs coupled to different coordinating solvents, such as DMA, DMF and DMSO. The CP dimensionality (either 2D sheet or 1D chain) strongly depends on the solvent of choice. Thus, the coordinating solvent approach (CSA) can be used as an effective tool to modulate and control the dimensionality, composition and network of CPs. Galli and co-workers (Como,



Citation: Rossin, A. Editorial for Special Issue “Functional Coordination Polymers and Metal–Organic Frameworks”. *Inorganics* **2021**, *9*, 33. <https://doi.org/10.3390/inorganics9050033>

Received: 12 April 2021

Accepted: 28 April 2021

Published: 3 May 2021

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Italy) [9] proved the versatility of the 1,3-bis(1,2,4-triazol-4-yl)adamantane (tr₂ad) linker in the synthesis of new Cd^{II}, Cu^{II} and Zn^{II} CPs of assorted dimensionality (ranging from 1D to 2D) and featured by excellent thermal stability. The high thermal robustness is quite common in MOFs and CPs built with N-donors like pyrazolates, triazolates and imidazolates, and it stems from the strength of the metal-nitrogen coordination bond.

This Special Issue though is focused on applications, collecting contributions covering many different applicative contexts. In the field of heterogeneous catalysis, an excellent and comprehensive review article by Zhou et al. (College Station, TX, USA) [10] summarizes the most recent advances in organometallic functionalization of MOFs from both linker-centric and metal-cluster-centric perspectives. MOFs can function as a tailorable platform for traditional organometallic transformations, including reaction of alkenes, cross-coupling reactions and C–H activations.

The timely CO₂ adsorption topic [at the core of contemporary Carbon Capture and Sequestration (CCS) technology to reduce carbon dioxide levels in the Earth's atmosphere and concomitant greenhouse effect] is developed by Bonino and co-workers (Torino, Italy) [11]. The research team in Torino reports on the synthesis, spectroscopic characterization and adsorption properties of the Ce^{III} MOF Ce₅(BDC)_{7,5}(DMF)₄, containing the simple terephthalic acid (H₂BDC) as linker. The coordinated DMF solvent can be removed from the metal nodes generating open metal sites, as confirmed by FTIR spectroscopy. The interaction of the desolvated material with CO₂ was characterized by volumetric and calorimetric measurements, finding a relevant heat of adsorption (Q_{st}) for the very first dose, typical of MOFs with open metal sites. Another contribution focused on the same topic comes from Taddei et al. (Swansea, Wales, UK) [12]. The team reported a systematic approach aimed at identifying the optimal conditions for the compaction (i.e., pellets preparation) of MOF-801, a small-pore zirconium-based MOF containing fumaric acid as linker. The MOF pellets (prepared under different experimental pressure conditions and in the presence of assorted binders) were tested in CO₂ adsorption, retaining as much as 90% of the CO₂ working capacity of the powder, while displaying unaffected sorption kinetics. This work provides a starting point for future exploration of shaping of MOF powders, which is becoming a progressively more important aspect as MOFs move towards commercialization and employment in industrial applications.

Another application of growing interest for MOFs and CPs is luminescence. As chemical sensors, luminescent MOFs possess a number of advantages over other luminescent materials. Analyte adsorption within MOF pores allows for its pre-concentration, increasing sensor sensitivity. Selectivity in MOFs can be achieved by tuning pore dimensionality and/or by proper functionalization of the linkers. Porosity allows for adsorption of chromophores which can be luminescent themselves or act as antennas, this enlarging the number of mechanisms beyond luminescence. Given my long-lasting interest in the design and synthesis of thiazole-containing linkers and related MOFs/CPs in Firenze (Italy) [13–20], I have personally contributed to this Special Issue with a mini-review article describing the luminescent features of thiazole- and thiadiazole-based MOFs and CPs [21]. Thiazoles are intrinsically fluorescent heterocycles, and their exploitation in the construction of MOFs is still at its infancy. Within this Special Issue, there are two additional contributions on the luminescence topic. Cepeda, Rodríguez-Diéguez et al. (País Vasco/Granada, Spain) published two new Zn^{II} and Cd^{II} CPs based on 1H-indazole-6-carboxylic acid, along with their photoluminescence (PL) properties [22]. Both CPs present emission spectra similar to the free ligand, confirming that the electronic transitions of the polymers are ligand-centered (of π - π^* type). This kind of emission is typical of MOFs and CPs built with an electronically inert metal ion (like Zn^{II} or Cd^{II}, with a d¹⁰ closed-shell electronic configuration). The Russian team of Artem'ev and colleagues (Novosibirsk, Russian Federation) has synthesized a 1D Ag^I-based CP with 4,6-bis(diphenylphosphino)pyrimidine [23]. The material exhibits pronounced thermochromic luminescence, expressed by reversible changing of the emission chromaticity from yellow (at ambient temperature) to orange (at the liquid nitrogen temperature). The detailed temperature-dependent photophysical study has shown

that the ambient temperature photoluminescence may be tentatively ascribed to thermally activated delayed fluorescence (TADF) caused by formation of (M + L')LCT excited states. This class of materials find promising application in luminescent thermometry.

The water tolerance of MOFs is an essential feature for many practical applications when operating under ordinary humid atmosphere. Resistance toward hydrolysis in such environment is not common, given the intrinsically reactive metal-ligand coordination bond. The most important MOF family that is resistant to hydrolysis is that of the zirconium based "UiOs". Water stability opens greener synthetic routes, and aqueous synthesis of MOFs at room temperature offers many advantages such as reduction in the generation of toxic byproducts and operation costs, as well as increased safety in the material's production. The American team of Islamoglu and Farha (Chicago, US) has reported an aqueous solution-based synthesis of the robust zirconium MOF UiO-66-NO₂ at room temperature [24]. Water vapor sorption isotherms at room temperature indicated high uptake, suggesting the potential of this MOF for adsorption-based cooling applications or water harvesting systems. Water can also be considered a substrate for heterogeneous catalysis. In this regard, the team of Macchioni and Costantino (Perugia, Italy) has functionalized UiO-66 post-synthetically with the organometallic Ir^{III} complex [Ir(HEDTA)Cl]Na, placing it on the defective MOF sites occupied by formate linkers [25]. Anchoring of the complex occurs through an exchange of formate with the free HEDTA carboxylate group. The modified material was tested as a heterogeneous catalyst for the water chemical oxidation reaction (water splitting with concomitant O₂ production) by using cerium ammonium nitrate as sacrificial agent.

In conclusion, I hope that these open-access contributions will serve as guiding lights for future MOFs and CPs development in still undiscovered applications. I thank the authors for their original contributions for the Special Issue, and I thank the reviewers for their tireless enthusiasm, insightful comments and revisions. Last but not least, my warmest acknowledgments go to the *Inorganics* Editorial Staff for its constant dedication, support and patience in collecting so many excellent papers over a time period of two years.

Conflicts of Interest: The author declares no conflict of interest.

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